



TARTU STATE UNIVERSITY

ORGANIC REACTIVITY

English Edition
of

Реакционная способность
органических соединений

Vol. XII
ISSUE 1(43)
November 1975

TARTU

TARTU STATE UNIVERSITY

ORGANIC REACTIVITY

English Edition
of

Реакционная способность
органических соединений

Vol. XII
ISSUE 1(43)
November 1975

TARTU

The Editorial Board:

V. Palm, Editor-in-Chief

Ü. Haldna

I. Koppel

CONTENTS

S.M. Shein and P.P. Rodionov, Nucleophilic Substitution in Polyfluoroaromatic Series. VIII. Solvent Effects in Reaction of Hexafluorobenzene and p-Nitrofluorobenzene with Piperidine.....	7
O.P. Sheremet, P.P. Rodionov and S.M. Shein, Nucleophilic Substitution in Polyfluoroaromatic Series. X. Kinetics of Reaction of Pentafluorobenzenes with p-Toluidine.....	17
E.A. Ponomareva and N.I. Kulik, Ionization Kinetics of t-BuX in Methylene Chloride, Dichloroethane and Dibromoethane.....	27
A.G. Bazanov, M.F. Kozlova, I.V. Tselinsky, B.V. Ghidasov, and S.M. Dzubenko, α -Halonitroalkane Reactivity. V. Thermodynamic and Kinetic Acidity of Aryl Chloronitromethanes.....	35
V.P. Chernykh, T.S. Jan-Temirova, and V.I. Makurina, Ionization Constants of Some Derivatives of Sulfonic Acid in Aqueous Methanol and Dioxane.....	45
L.N. Bykova, S.I. Petrov, L.A. Karaseva, E.M. Gorynina, and A.D. Galitsyn, Potentiometric and Polarographic Investigation of Substituted Benzoic Acids in Dimethylsulphoxide Medium.....	53
B.I. Istomin, V.A. Baransky, A.D. Lobanov, E.F. Grechkin, The Polylinarity Principle and Relationships Between Structure and Properties of Organophosphorus Compounds 1. Analysis of σ^p Constants. Inductive and Steric Contributions.....	67
V.A. Baransky and B.I. Istomin, The Polylinearity Principle and Relationships Between Structure and Properties of Organophosphorus Compounds 2. Analysis of Constants σ^p . The Resonance Contribution.....	83

V.F. Andrianov, A. Ya. Kaminsky, S.S. Ghitis, A.V. Ivanov, T.M. Bere- govykh, N.I. Faingold, Infrared Spectra and Electronic Effects. IV. Influence of Substi- tuent on the Frequencies of the Stretching Band and the Basicity of Amino Group in Diphenyl Sys- tems with Heterobridges.....	91
I.A. Kuzovnicova, L.A. Badovskaya, Ya.I. Turyan, and V.G. Kulnevich, The Polarographic Study of Equilibrium of Levulinic Acid Hydrazone Formation and its Acid-Base Prop- erties.....	103
O.M. Polumbrik, O.I. Zaika, B.M. Yarmol- yuk, Triphenyl Verdazyl Reactivity, when Influenced by n-Donating Solvents in Reaction with Lauroyl Peroxide.....	113
T.J. Jürjado and V.A. Palm, Dissociation Con- stants of Substituted Acetic Acids and Inductive Attenuation Factors of Some Alicyclic Systems in Aqueous Methanol.....	125
A. Talvik, A. Pihl, H. Timotheus, A. Osa, J. Viira, and V. Timotheus, Interpretation of Acidity of Carbon Acids Using Ψ -Constants of Substituents. III Malononitriles..	135
V.M. Nummert, Estimation of "Ortho-Effect" and Inductive Transmittancy of Aromatic Cycles.....	143
U. Haldna, An Estimation of the Degree of Disso- ciation of Ion-Pairs in Water.....	159
O.M. Polumbrik, V.I. Staninets, B.M. Yarmolyuk, On the Effect of Carboxy- inversion on Triphenyl Verdazyl Reaction with sub- stituted Benzoyl Peroxides.....	163
N.N. Zatssepina, I.F. Tupitsyn, A.I. Belyaschova, and G.N. Sudakova, The Kinetic CH-Acidity of the IV-VII Group Methyl Derivatives.....	169

N.N. Z a t s e p i n a, A.A. K a n e, and I.F. T u p i t s y n, A Quantum-Chemical Study of the CH Acidity of Substituted Alkanes.....	179
N.N. Z a t s e p i n a, I.F. T u p i t s y n, A.I. B e l y a s h o v a, A.A. K a n e, and A.V. K i r o v a, The Base-Catalyzed Deuterium Exchange in Five-Membered Saturated Heterocycles.....	195
N.N. Z a t s e p i n a, I.F. T u p i t s y n, and A.I. B e l y a s h o v a, The Isotopic Hydrogen Exchange in Heteroaromatic Trans-Stilbene Derivatives and Similar Compounds.....	207
N.N. Z a t s e p i n a, I.F. T u p i t s y n, A.I. B e l y a s h o v a, E.A. M e d j a n t s e v a, I.M. A n d r e e v a, and V.I. M i n k i n, The Isotopic Hydrogen Exchange in Aromatic Nitrones....	223
I.F. T u p i t s y n, N.N. Z a t s e p i n a, N.S. K o l o d i n a, and A.I. B e l y a s h o v a, Infrared Study of Electronic Interactions in Saturated Heterocycles.....	235
N.N. Z a t s e p i n a, I.F. T u p i t s y n, A.I. B e l y a s h o v a, and N.S. K o l o d i n a, On the Mechanism of Transfer of Electronic Effects Through a Nitrogen or Oxygen Bridge in $[(CH_3)_m M]_n X$ Compounds. Ir and PMR Spectroscopic Parameters and the Kinetic CH-Acidity of Methyl Groups.....	245
A.M. K u l i e v, M.A. A l l a k h v e r d i e v, E.Ya. B o r i s o v a, V.M. F a r z a l i e v, and E.M. C h e r k a s o v a, Ionization Constants of Some I-Amino-3-Alkoxy-(Alkylthio)-2-Propanols.....	263
S.V. B o g a t k o v, N.A. B e l o v a, and S.S. M e d v e d, Tertiary Amines in Reactions of Isocyanates and Their Steric Characteristics.....	267
G.J. D i e n y s, L.J.J. K u n s k a i t é, A.K. V a i t k e v i č i u s, A.V. K l i m a v i č i u s, Kinetics of Nucleophilic Addition of Aliphatic Amines to the Activated Ethylenic Bond.....	275

NUCLEOPHILIC SUBSTITUTION IN POLYFLUOROAROMATIC SERIES.
VIII. SOLVENT EFFECTS IN REACTION OF HEXAFLUOROBENZENE AND
p-NITROFLUOROBENZENE WITH PIPERIDINE.

S.M.Shein and P.P.Rodionov

Novosibirsk Institute of Organic Chemistry, Siberian
Division, Ac. Sc. U.S.S.R., Novosibirsk 90, U.S.S.R.

Received April 10, 1975

The kinetics of reaction of hexafluorobenzene and p-nitrofluorobenzene with piperidine in different solvents has been investigated. The solvent effects on reaction rate constant of nucleophilic substitution of fluorine in both compounds has been compared. In polar and aprotic dipolar solvents p-nitrofluorobenzene is more reactive than hexafluorobenzene and has the same or lower reactivity in nonpolar solvents. The reaction of hexafluorobenzene with piperidine is less sensitive to change of solvent polarity and solvent catalysis than that of p-nitrofluorobenzene.

The study of solvent effects on nucleophilic reactivity of aromatic fluoro compounds is of great interest.¹ In this paper the solvent effects on reactivity of hexafluorobenzene and p-nitrofluorobenzene with piperidine (Tables 1,2) have been studied.

From Table 1 and other data³ one could see the peculiarities of solvent effects in reaction of hexafluorobenzene with piperidine. The reaction rate constant increased 5000 times when passing from n-hexane to DMSO in range of solvents: n-hexane < benzene < N-n-amyloxy-piperidine < t-butanol < hexafluorobenzene < n-propanol < n-butanol < n-heptanol < anisole < methanol < ethanol < chlorobenzene < N,N-dimethylaniline < dioxane < 1,2-dimethoxy-ethane < ethylene-

glycol < tetrahydrofuran < nitrobenzene < acetonitrile < piperidine < acetone < acetophenone < triethylene glycol < aniline < nitromethane < benzonitrile < pyridine < sulpholane < DMF < DMSO.

The influence of each solvent was caused by polarity, polarizability, proton acceptor and donor ability and structure. The proton acceptor ability rouse the base catalysis. Ethers (dioxane, THF, 1,2-dimethoxy-ethane, anisole), ketons (acetone, acetophenone), tertiary amines (N,N-dimethylaniline, pyridine, N-n-amympiperidine), amide (DMF), sulfone (sulpholane), sulphoxide (DMSO), were solvents of this type. The proton donor ability caused the general acid catalysis and both protic donor and acceptor ability the bifunctional catalysis. Alcohols, glycols, primary and secondary amines were solvents of this type.

The rate constants of the reaction of hexafluorobenzene with piperidine in benzene or hexafluorobenzene were in 4-5 times higher than in n-hexane in spite of approximately the same polarity of these solvents. That can be explained by the polarizability of both benzene and hexafluorobenzene and their ability to specific solvation of base catalysis nature.

The specific solvation of solvents is based on acid-base catalysis in transition state.⁴ In connection with this one could propose a correlation between logarithm of the reaction rate constant and pK of amines as solvents. However the analysis of kinetic data showed the absence of such correlation that can be explained by steric hindrance of solvation

of transition state in nucleophilic substitution and by neutralization of amine with acid in determination of its basicity. The proton of NH-group of amines in intermediate σ^- -complexes that interacted with solvent by the mechanism of base catalysis was sterically more hindranced than the proton of amine in interaction with acid in determination of the amine basicity.

The group of solvents with different polarity but close in nature is that of alcohols. The influence of alcohols on

the rate constant of the reaction of hexafluorobenzene with piperidine decreased in series: triethylene glycol > ethylene glycol > ethanol > methanol > n-heptanol > n-butanol > n-propanol > t-butanol. Such sequence with exception of methanol and ethanol was in agreement with the decrease in basicity of alcohols. In addition to that the reactivity of hexafluorobenzene in alcohols had to be higher than we have obtained. Earlier we have shown ⁵ that the low reactivity in alcohols have been related to solvation by alcohols of ortho-fluorine atoms in hexafluorobenzene.

Not only the polarity and steric factors but the chemical structure of solvents affect the solvation. It is important whether the solvent is an aliphatic or aromatic compound. The both groups of solvent, aliphatic and aromatic series, were of close polarity but they led to different reactivity. Thus the reactivity of hexafluorobenzene increased by 4, 1.4, 3.5, and 2.8 times when passing from n-hexane to benzene, from acetone to acetophenone, from acetonitrile to benzonitrile, and from piperidine to pyridine. That was evidently dependent on the possibility of aromatic solvents to specific solvation at the expense of π -electronic system of benzenes and electron pairs of heteroatoms.

The kinetics p-nitrofluorobenzene with piperidine was studied earlier.^{2,6} But in those works the reaction rate constant were measured in catalytic region of concentrations of piperidine that led to overrated values of reaction rate constant. In present study we made the measurements with low values of the piperidine concentration (Table 2).

The reactivity of p-nitrofluorobenzene increased by 10^6 times in the series of solvents from n-hexane to DMSO: n-hexane < benzene < dioxane < ethylene glycol < THF < t-butanol < acetone < nitrobenzene < ethanol < benzonitrile < methanol < nitromethane < triethylene glycol < aniline < acetonitrile < piperidine < pyridine < DMF < DMSO.² One can see the difference between the solvent sequence for the reaction of p-nitrofluorobenzene and that of hexafluorobenzene

Table 1

Kinetics of Reaction of Hexafluorobenzene with Piperidine

Solvent	Temperature °C	Reaction rate constant $k \cdot 10^5$ $l \cdot mol^{-1} s^{-1}$	E kcal/mol	lg A	Dielectric constant at 25°C ¹¹
1	2	3	4	5	6
n-Hexane	120	0.33 ± 0.03	10.4	0.3	1.9
	140	0.63 ± 0.06			
Hexafluoro- benzene	100	0.77 ± 0.17			
	120	1.4 ± 0.2	9.4 ± 0.2	0.4 ± 0.1	1.55
	140	2.6 ± 0.4			
	150	3.4 ± 0.2			
N,N-di- methyl- aniline	130	13 ± 2	11.6	2.4	5.0
	140	18 ± 2			
Chloro- benzene	100	2.4 ± 0.3	8.8	0.6	5.6
	140 ^a	7.6 ± 0.2			
N-n-Amyl- piperi- dine	140	4.3 ± 0.2			
	150	6.3 ± 0.6	14.9 ± 1.0	3.5 ± 0.5	-
	160	10			
Aniline	100	31			
	130	100 ± 20	11.7 ± 0.1	3.3 ± 0.1	7.0
	140	140 ± 30			
	150	200			
THF	90	8.0 ± 0.5			
	120	21 ± 2	9.3 ± 0.1	1.5 ± 0.1	7.4
	140 ^a	38 ± 3			
t-Butanol	120	2.3 ± 0.3	17.5	5.1	10.9
	140	6.8 ± 0.6			

1	2	3	4	5	6
n-Heptanol	120	3.4 ± 0.3	14.9	3.8	11.8
	140 ^a	8.6 ± 0.8			
Pyridine	100	65 ± 6	11.7 ± 0.3	3.7 ± 0.2	12.3
	110	100 ± 20			
	120	150			
	130	210			
n-Butanol	120	3.3 ± 0.3	13.7	3.1	17.7
	140	7.7 ± 0.3			
n-Propanol	120	3.5 ± 0.2	19.8	6.6	20
	140 ^a	12 ± 1			
Acetone	110	30 ± 4			
	120	39 ± 4	9.6 ± 0.6	2.0 ± 0.3	20.7
	130	53 ± 3			
	140	75 ± 5			
Ethanol	120	4.9 ± 0.5	13.0	2.9	25.2
	140	11 ± 1			
Triethylene glycol ^b	100	25			
	110	40	12.6 ± 0.1	3.8 ± 0.1	26.5
	120	60			
	130	90			
	140	130			
DMF ^b	90	150			
	120	520	10.8 ± 0.7	3.7 ± 0.4	37.6
	140	910			
Ethylene glycol ^b	90	7			
	120	16	8.0 ± 0.2	0.7 ± 0.1	38.7
	140 ^a	27			

a) Data from a previous paper.³

b) The data were obtained by extrapolation to zero time.³

Table 2

Kinetics of Reaction of p-Nitrofluorobenzene with Piperidine

Solvent	Temperature °C	Reaction rate constant $k \cdot 10^4$ $l \cdot mol^{-1} s^{-1}$	E kcal/mol	lg A
n-Hexane	120	0.006 ± 0.0006	22.3 ± 0.5	6.2 ± 0.3
	140	0.024 ± 0.008		
Benzene	110	0.1 ± 0.01	12.7 ± 0.2	2.3 ± 0.1
	120	0.16 ± 0.01		
	130	0.23 ± 0.03		
Dioxane	120	2.5 ± 0.2	7.6 ± 0.2	0.6 ± 0.1
	130	3.3 ± 0.2		
	140	4.0 ± 0.1		
Piperidine ^a	22	1.8 ± 0.06	-	-
Aniline	70	33 ± 3	6.1 ± 0.2	1.4 ± 0.1
	100	69 ± 6		
	120	100 ± 5		
Pyridine ^b	90	190	5.4	1.6
	130	400		
Methanol	100	27 ± 1	10.5 ± 0.3	3.6 ± 0.1
	120	60 ± 4		
	130	80 ± 3		
Nitrobenzene	90	11 ± 0.5	7.8	1.7
	110	18 ± 2		
	130	32 ± 1		

a) The measurement was carried out in spectrophotometric cell.

b) The data were obtained by extrapolation to zero time.³

The comparison of reaction rate constants for hexafluorobenzene and p-nitrofluorobenzene show that the former is less reactive than the latter in ethers, ketones, nitriles, amines, nitro compounds, DMF and DMSO. Only in nonpolar medium (n-hexane) hexafluorobenzene is more reactive (Table 3).

Table 3

Solvent	Relative rate constant at 100°C		Rate constant ratio for re- actions of p-O ₂ NC ₆ H ₄ F and C ₆ F ₆ with C ₅ H ₁₀ NH at 100°C
	C ₆ F ₆	p-O ₂ NC ₆ H ₄ F ²	
1	2	3	4
n-Hexane	1	1	0.075
Benzene	3.8	50	1.1
N-n-Amylpiperidine	4.0	-	-
t-Butanol	4.1	3.6·10 ³	67
Hexafluorobenzene	4.8	-	-
n-Propanol	6.2	-	-
n-Butanol	7.4	-	-
n-Heptanol	7.9	-	-
Anisole	11	-	-
Methanol	11	2.1·10 ⁴	140
Ethanol	12	1.4·10 ⁴	88
Chlorobenzene	15	-	-
N,N-Dimethylaniline	24	-	-
Dioxane	28	1.2·10 ³	3
1,2-Dimethoxyethane	38	2.0·10 ³	4
Ethylene glycol	64	-	-
THF	73	2.8·10 ³	3
Nitrobenzene	110	1.1·10 ⁴	8
Acetonitrile	110	6.0·10 ⁴	41
Piperidine	140	5.5·10 ⁵ ^a	300 ^a
Acetone	150	1.1·10 ⁴	6

1	2	3	4
Acetophenone	160	-	-
Triethylene glycol	160	$3.0 \cdot 10^3$ ^b	14 ^b
Aniline	190	$5.6 \cdot 10^4$	22
Nitromethane	320	$4.2 \cdot 10^4$	10
Benzonitrile	380	$1.9 \cdot 10^4$	4
Pyridine	400	$1.8 \cdot 10^5$	34
Sulfolane	750	-	-
DMF	1300	$4.4 \cdot 10^5$	26
DMSO	4900	$1.4 \cdot 10^6$	21

a) at 22°, b) at 194° after Liotta.¹²

In contrast to p-nitrofluorobenzene hexafluorobenzene has two fluorine atoms in ortho-position with respect to reaction site that stipulated the ortho-effect (steric effects and built-in solvation) in aromatic nucleophilic substitution.⁷

Steric effects were more effective in alcohols ⁵ where p-nitrofluorobenzene was more reactive than hexafluorobenzene. The existance of built-in-solvation of ortho-fluorine atoms in hexafluorobenzene was shown in reaction with alcoxides. ^{5,8} In reaction of hexafluorobenzene with piperidine less charged reagents than alkoxides built-in-solvation was effective only in nonpolar solvents (n-hexane).

Therefore hexafluorobenzene was in n-hexane 12 times more reactive than p-nitrofluorobenzene.

Experimental

The purification of hexafluorobenzene was described previously.³ p-Nitrofluorobenzene was obtained by interaction of p-nitrochlorobenzene with KF in DMSO ⁹, B.p. 205°, n_D^{20} 1.5340, contents by g.l. c. 99.7%. Solvents were purified by known procedure. ¹⁰

The procedure of kinetic measurements of reaction of 0.002-0.05 M p-nitrofluorobenzene with 0.01-0.1 M piperi-

dine was carried out spectrophotometrically at 395 nm and is described earlier.² The upper values of concentration were used at low reaction rate (n-hexane) or for almost negligible catalysis (dioxane). The procedure of kinetic measurements of reaction of 0.02-0.1 M hexafluorobenzene with 0.1-0.5 M piperidine was described earlier.⁵ The reaction in N-n-amylo-piperidine was monitored spectrophotometrically and by titration of fluorine-ion by $\text{Th}(\text{NO}_3)_4$. In solvents that prevented the UV-spectroscopy procedure⁴ (benzenes, ketones, DMF) the kinetic measurements were carried out by titration of piperidine.

References

1. R.Parker, Progress in Fluorine Chemistry (Russian Translation), *Chimia*, vol., 3-4, 210(1970).
2. H.Suhr, *Ber. Bunsenges. phys. chem.*, 67, 893(1963); 70, 544(1966).
3. S.M.Shein and P.P.Rodionov, *Kinetica i Catalis (USSR)*, 11, 1378(1970); P.P.Rodionov and S.M.Shein, *Reakts.sposobn. organ. soedin.*, 7, 1150, 1168(1970).
4. S.M.Shein, N.K.Danilova, and N.I.Kuznetsova, *Reakts. sposobn. organ. soedin.*, 7, 458(1970); F.Pietra, *Quart. Revs.*, 23, 504(1969); S.D.Ross, *Reaction of Aromatic Compounds Comprehensive Chemical Kinetics*, Amsterdam, 13, 407 (1972); S.M.Shein, N.K.Danilova, and M.V.Shternshis, First IUPAC Conference on Physical Organic Chemistry, Switzerland 1972, p. 58.
5. S.M.Shein and P.P.Rodionov, *Kinetica i Catalis (USSR)*, 13, 1129 (1973).
6. N.B.Chapman, R.E.Parker, and P.W.Soanes, *J.Chem.Soc.*, 1954, 2109; F.Pietra and F.DelCima, *Tetrah. Lett.*, 1967, 4573; J.D.Reinheimer and J.F.Bunnnett, *J.Amer. Chem.Soc.*, 81, 315(1959).
7. P.B.De La Mar, *Progress in Stereochemistry (Russian Translation)*, 1961; G.S.Hammond and M.E.Hauthorn, *Steric Effects in Organic Chemistry (Russian Translation)*, 1960.

8. S.M.Shein and P.P.Rodionov, *Kinetika i Catalis (USSR)*, 15, 1131(1974).
9. G.S.Finger and C.W.Kruse, *J.Amer.Chem.Soc.*, 78, 6034 (1956).
10. A.Weissberger, E.S.Proskauer, J.Riddick, and E.E.Toops *Organic Solvents (Russian Translation)*, 1958.
11. *Spravochnik chimika (Russian Eddition)*, 1, 950(1962).
12. L.Liotta and D.F.Pinholster, *Chem.Comm.*, 1969, 1245.

NUCLEOPHILIC SUBSTITUTION IN POLYFLUOROAROMATIC SERIES.
X. KINETICS OF REACTION OF PENTAFLUOROBENZENES WITH p-TOLUIDINE.

O.P.Sheremet, P.P.Rodionov, and S.M.Shein

Novosibirsk Institute of Organic Chemistry, Siberian
Division, Ac. Sc. U.S.S.R., Novosibirsk 90, U.S.S.R.

Received April 10, 1975

The rate of reaction of octafluorotoluene, octafluoroacetophenone, pentafluoroacetophenone and pentafluoronitrobenzene with p-toluidine have been measured. The absence of correlation between reaction rate constants and Hammett ρ -constant has been shown. The reaction rate constant of polyfluoro compounds by para-substitution increased in a range of solvents: n-hexane, benzene < nitrobenzene < acetonitrile < dioxane < methanol < DMF < DMSO, by ortho-substitution in pentafluoroacetophenone, n-hexane, benzene < nitrobenzene < dioxan, methanol, DMF, DMSO.

Recently ¹ the reaction of substituted pentafluorobenzenes with p-toluidine in different solvents was studied. Octafluorotoluene and octafluoroacetophenone formed only products of para-substitution, pentafluoroacetophenone and pentafluoronitrobenzene in nonpolar solvent led to ortho-substitution, in polar solvents to para-substitution.¹ Taking into account these data we obtained the reaction rate constant and discussed the effects of structure and medium on reactivity (Tables 1-5). In comparison with analogous investigation of the interaction of pentafluorobenzenes with piperidine ² we used parent compounds with strong electron-withdrawing groups. The carrying out of kinetic measurements of reaction with piperidine was difficult because of the

necessity of measurement at low temperature.

Earlier ³ was shown the existence of correlation between reaction rate constant and Hammett σ -constant for substitution in para-position of pentafluorobenzene in reaction with methoxide, pentafluorothiophenoxide and piperidine. From these data one could expect an increase in the rate constant of reaction of substituted pentafluorobenzenes with p-toluidine in range: $\text{CF}_3 < \text{COCH}_3 < \text{COCF}_3 < \text{NO}_2$ that coincided with σ -constants of these substituents. But as it followed from table 1 the sequence of substituents did not follow the indicated one but depended on the solvent nature.

Table 1

Effect of Structure on the Rate Constants for Reaction of Substituted Pentafluorobenzenes with p-Toluidine

Solvent	k_{rel} at 100°					
	para-substitution				ortho-substitution	
	COCF_3	CF_3	COCH_3	NO_2	COCH_3	NO_2
n-Hexane	-	-	-	-	I	8
Benzene	-	-	-	-	I	5
Nitrobenzene	-	I	-	50	I	20
Dioxane	-	I	-	18	I	11
Methanol	I	2	5	1200	I	15
DMF	I	0.6	0.2	50	I	240
DMSO	-	I	0.5	-		

Thus, in methanol the reactivity of para-fluorine leaving atom increased in a range: $\text{COCF}_3 < \text{CF}_3 < \text{COCH}_3 < \text{NO}_2$; in DMF: $\text{COCH}_3 < \text{CF}_3 < \text{COCF}_3 < \text{NO}_2$ and in DMSO: $\text{COCH}_3 < \text{CF}_3$. The lack of correlation by Hammett equation is due to disturbance of conjugation of substituents with reaction centre in result of steric and electronic interaction with ortho-fluorine atoms in pentafluorobenzenes. The solvation by sol-

vents, especially of methanol, was of importance. Methanol was known as a specific solvating agent for fluorine compounds.² The lack of correlation in the case of aromatic amine as reagent may be due to its low nucleophilicity comparing with other studied reagents.⁵ If the data for compounds with strong electron- withdrawing groups were included in correlation there would be a breakdown of correlation also in the case of reaction with piperidine.

There is no correlation between the logarithm of reaction rate constant and the Kirkwood function. The reaction rate constant depended not only on polarity of solvent but on specific solvation too. One could see the essential role of the latter from the relationship $\lg k$ vs molar fraction of binare solvent (Fig.). All relationships were not linear. That showed the main contribution of catalysis is due solvation.

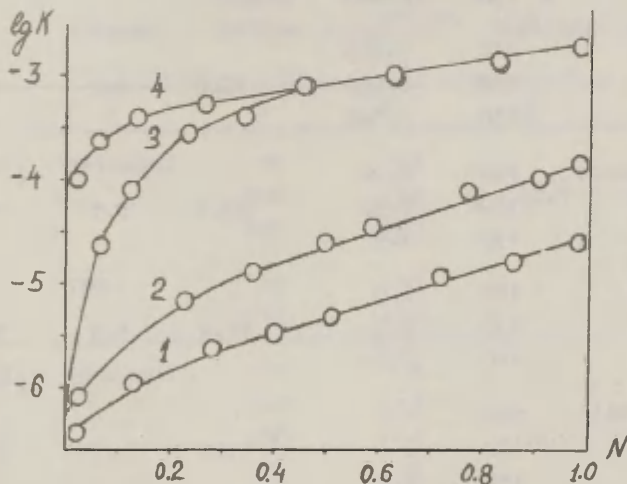


Fig. Kinetics of reaction of octafluorotoluene with p-toluidine in binary mixture of solvents: n-hexane-dioxane, 120° (1); benzene-methanol, 130° (2); benzene-DMF, 120° (3); methanol-DMSO, 120° (4).

The role of polarity and specific solvation can also be seen from the reaction rate constant in case of solvents (Tables 2,3). One could see the main contribution of base (dioxane) and bifunctional (methanol) catalysis.

Table 2

Kinetics of Reaction of Octafluorotoluene with p-Toluidine

Solvent	Temperature °C	Reaction rate constant $k \cdot 10^5$ $\text{l} \cdot \text{mol}^{-1} \text{s}^{-1}$	E kcal/mol	lg A	k_{rel} at 100°
1	2	3	4	5	6
n-Hexane	110	0.021			
	120	0.037	13.2	0.85	1
	130	0.049			
Benzene	110	0.025			
	120	0.050	18.8	4.2	1
	130	0.085			
Nitrobenzene	110	0.28			
	120	0.52	23.9	8.1	9
	130	1.3			
Dioxane	120	2.9			
	130	3.5	14.2	3.3	77
	140	7.0			
Acetonitrile	100	1.1			
	123	2.6	11.4	1.7	85
	131	3.6			
Methanol	110	6.2			
	120	9.9	16.4	5.1	260
	130	18			

1	2	3	4	5	6
DMF	60	20			
	70	28			
	80	49	10.6	3.2	8500
	90	72			
DMSO	60	92			
	70	140			
	80	200	8.5	2.6	30000
	90	290			

Table 3

Kinetics of para-Substitution in Reaction of RC_6F_5 with p-Toluidine

R	Solvent	Temperature	$k \cdot 10^5$ $\text{l} \cdot \text{mol}^{-1} \text{s}^{-1}$	E kcal/mol	lg A	k_{rel} at 100°
1	2	3	4	5	6	7
COCF_3	Methanol	90	41			
		100	59	13.1	3.5	
		120	160			
	DMF	40	48			
		50	70			
COCH_3	Methanol	100	7			
		110	13			
		120	18	15.6	5.0	1
		130	36			
	DMF	70	10			
		80	15	10.5	2.7	5
		90	24			
		98	31			

1	2	3	4	5	6	7
	DMSO	60	39			
		70	63	9.3	2.7	25
		80	82			
		90	130			
	Nitrobenzene	100	6			1
NO ₂	Dioxane	110	28			
		120	34	8.2	1.1	3
		130	48			
	Methanol	30	160			
		40	250	7.7	2.8	300
		50	360			
		60	500			
	DMF	30	1100			
		40	1700	7.2	3.2	1800
		50	2300			

Table 4

Kinetics of ortho-Substitution in Reaction of RC_6F_5 with p-Toluidine

R	Solvent	Tempe- rature °C	$k \cdot 10^5$ $\text{l} \cdot \text{mol}^{-1} \text{s}^{-1}$	E kcal/mol	k_{rel} lg A at 100°	
1	2	3	4	5	6	7
COCH ₃	n-Hexane	100	1.4			
		120	3.6	15.6	4.4	1.2
		130	7.0			
	Benzene	110	2.8			
		120	3.7	14.4	3.5	1
		130	5.3			

1	2	3	4	5	6	7
	Nitrobenzene	110	3.2			
		120	4.3			
		130	6.0	12.7	2.7	1.5
		140	11			
		150	15			
	DMF	100	5.0*			
	Dioxane	110	10			
		120	14	12.4	3.0	4.8
		130	22			
		140	32			
	Methanol	100	7			
		110	13			
		120	16	13.6	3.9	5.2
		130	30			
	DMSO	100	9*			
NO ₂	Benzene	100	9			
		120	16	16.3	5.3	1
		130	27			
	n-Hexane	110	11			
		120	19	15.2	4.7	1.1
		130	29			
	Nitrobenzene	110	48			
		120	58	7.8	1.1	6.7
		130	80			
	Dioxane	110	120			
		120	150	11.1	3.4	15
		130	260			
	Methanol	30	100			
		40	150			

1	2	3	4	5	6	7
		50	220	7.8	2.6	200
		60	310			
	DMF	100	1300*			230

* Approximate value.

The role of polarity was less essential (nitrobenzene). Particularly strong was the influence of dipolar aprotic solvents (DMF, DMSO).

The solvents effected on the reaction rate constant by substitution of para-fluorine atom in series : n-hexane, benzene < nitrobenzene < acetonitrile < dioxane < methanol < DMF < DMSO. In the case of ortho-substitution the influence of solvents: benzene, n-hexane < nitrobenzene < dioxane, methanol, DMF, DMSO (Table 4) was essentially different from that observed for para-substitution. The contrast consisted in another range of influence of solvents and the intensity of influence. The maximum of enhancement of reaction rate constant when passing from benzene to DMSO in the case of para-substitution, is greater (10^4 times) than in that of ortho-substitution (10^2 times). Such influence of solvents is mostly due to the ortho-effect of NO_2 , COCH_3 , COCF_3 groups.¹ It was interesting that in nonpolar solvents where the ortho-orientation took place¹ the difference in reactivity of pentafluoroacetophenone and pentafluoronitrobenzene was small (3-4 times). But it came up to 10^2 times in polar solvents that confirmed the large ortho-effect of the COCH_3 group.

EXPERIMENTAL

The purification of solvents, polyfluoro compounds and reagents was described previously.¹ The kinetic measurements were carried out by measuring of the decrease in the p-toluidine concentration⁴ caused by adding of 15-20 ml HCl (1:1),

Table 2

Kinetics of Reaction of 0.2 M Octafluorotoluene with 0.05 M p-Toluidine in Binary Mixture of Solvents

$C_6H_6 - CH_3OH$		$CH_3OH - DMF$		$C_6H_6 - DMF$		$n-C_6H_{14} - \text{dioxan}$	
molar fraction of CH_3OH	k at 130° $l \cdot mol^{-1} s^{-1}$	molar fraction of DMF	k at 120° $l \cdot mol^{-1} s^{-1}$	molar fraction of DMF	k at 120° $l \cdot mol^{-1} s^{-1}$	molar fraction of dioxane	k at 120° $l \cdot mol^{-1} s^{-1}$
0	$8.5 \cdot 10^{-7}$	0	$9.9 \cdot 10^{-5}$	0	$8.5 \cdot 10^{-7}$	0	$3.7 \cdot 10^{-7}$
0.21	$7.2 \cdot 10^{-6}$	0.05	$2.6 \cdot 10^{-4}$	0.05	$2.7 \cdot 10^{-5}$	0.28	$2.3 \cdot 10^{-6}$
0.36	$1.4 \cdot 10^{-5}$	0.12	$4.2 \cdot 10^{-4}$	0.11	$7.6 \cdot 10^{-5}$	0.40	$3.5 \cdot 10^{-6}$
0.49	$2.6 \cdot 10^{-5}$	0.26	$5.5 \cdot 10^{-4}$	0.22	$3.2 \cdot 10^{-4}$	0.51	$5.0 \cdot 10^{-6}$
0.59	$3.4 \cdot 10^{-5}$	0.44	$8.1 \cdot 10^{-4}$	0.33	$4.4 \cdot 10^{-4}$	0.70	$1.3 \cdot 10^{-5}$
0.77	$7.7 \cdot 10^{-5}$	0.63	$1.2 \cdot 10^{-3}$	0.43	$7.4 \cdot 10^{-4}$	0.86	$1.7 \cdot 10^{-5}$
0.90	$1.2 \cdot 10^{-4}$	0.83	$1.7 \cdot 10^{-3}$	0.63	$1.2 \cdot 10^{-3}$	1.00	$2.9 \cdot 10^{-5}$
1.00	$1.8 \cdot 10^{-4}$	1.00	$2.3 \cdot 10^{-3}$	0.82	$2.2 \cdot 10^{-3}$		
				1.00	$2.3 \cdot 10^{-3}$		

5 ml benzene, 2 ml DMF, 2 g KBr and monitored by potentiometric titrations with 0.02 M NaNO_2 (platine and chloroargentum electrodes). The kinetic procedure and calculations were described earlier.² The reaction kinetics was of the second order. We have not taken into account the second mole of p-toluidine because we found that $\text{p-CH}_3\text{C}_6\text{H}_4\text{NH}_2 \cdot \text{HF}$ was unstable.

The calculated reaction rate constants were divided in the ortho-para ratio.¹ The precision of reaction rate constant was 15% (relative). The results obtained in solvent mixtures are given in Table 5.

REFERENCES

1. O.P.Sheremet, P.P.Rodionov, and S.M.Shein, *Isv. Siberian Division Ac. Sci.U.S.S.R., ser. chim.*, 1975, issue 6.
2. S.M.Shein and P.P.Rodionov, *Kinetika i Catalys*, 11, 1378 (1970); 14, 1129 (1973).
3. S.M.Shein and P.P.Rodionov, *Reakts.sposobn.organ.soedin.*, 8, 961 (1971).
4. L.M.Litvinenko and A.P.Grekov, *Anal.Chem. U.S.S.R.*, 10, 164(1955); L.M.Litvinenko and D.M.Alexandrov, *Ukrain. Chem.J. (U.S.S.R.)*, 25, 81 (1959).

IONIZATION KINETICS OF t-BuX IN METHYLENE
CHLORIDE, DICHLOROETHANE AND DIBROMOETHANE

E.A. Ponomareva and N.I. Kulik

Kiev Polytechnic Institute

39, Brest-Litovsky Avenue, Kiev-56

Received April 23, 1975

Decomposition kinetics of t-BuI in methylene chloride, 1,2-dichloro- and 1,2-dibromoethane, of t-BuBr in CH₂Cl₂ and CH₂Cl-CH₂Cl and of t-BuCl in CH₂Cl₂ has been studied spectroscopically by the change in the concentration of triphenylverdazyl within a temperature range of 21 - 42°C with $v = k[t-BuX]$. At 25°C in CH₂Cl₂ the ratio between the ionization rates of t-BuCl, t-BuBr and t-BuI is 1 : 213 : 2650, respectively. The reaction rate depends little on the dielectric constant of the solvent; for the given series of solvents the ionization rate of t-BuI increases 9 times.

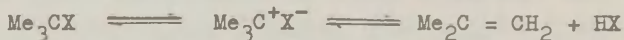
¹H n.m.r. spectroscopy has shown that in the basic state the molecules of t-BuX are characterized by a low solvation level. It is discussed the influence of the solvation of an activated complex by molecules of a halogen-containing solvent through formation of H-bonds upon the activation parameters of t-BuX ionization.

Practically, the ionization kinetics of t-butylhalogenides in halogen-organic solvents (except for phenyl halides^{1,2}) has not been studied. Literature³ provides data on the decomposition kinetics of liquid t-BuCl ($k_{25} = 2.37 \times 10^{-14} \text{ s}^{-1}$, $\Delta H^\ddagger = 34.5 \text{ kcal/mol}$, $\Delta S^\ddagger = -6.0 \text{ e.u.}$,

Also the value of the ionization rate constant has been calculated for t-BuCl at 120°C in perfluorooctane ($k_{120} = 6.3 \times 10^{-10} \text{ s}^{-1}$)⁴.

To study the influence of the specific solvation of halogen-containing organic compounds on the ionization rate of t-BuX, we have chosen such solvents as methylene chloride, 1,2-dichloro- and 1,2 dibromoethane. These solvents have sufficiently polar C-H bonds and must ensure an effective solvation of ion pair t-Bu⁺X⁻ (which is supposedly the transition state in the decomposition process of t-BuX).

The decomposition rate of t-BuX was controlled spectroscopically by the change in the concentration of triphenylverdazyl (in CH₂Cl₂ $\lambda_{\text{max}} = 720$, lg $\epsilon = 3.65$) which reacts fast and quantitatively eliminating the halogen hydride^{5,6}. Under these conditions the decomposition rate of t-BuX is determined by the ionization stage of butylhalogenide.^{2,6}



The solvents were purified⁷ as well as t-BuX (Ref. 6). Special tests showed that under the conditions of kinetic measurements the solvents used by us did not react with triphenylverdazyl. In our tests the concentration of t-BuX was 0.05 - 1.1 mol/l, that of the radical $(2-5) \times 10^{-4}$ mol/l. The decomposition degree of t-BuX in the kinetic tests was 0.2 - 0.01%. ¹H n.m.r. spectra of t-BuI in the solvents under study were taken as before^{2,8}.

Results and Discussion

Data obtained on the ionization kinetics of t-BuI and t-BuBr in CH₂Cl₂, CH₂Cl-CH₂Cl and CH₂Br-CH₂Br are shown in Table. The first column of the table also presents the values of dielectric constants of the solvents at 25°C (ϵ)⁹ and chemical shifts of t-BuI in the solvents under

Table
Kinetic Parameters of Ionization of t-BuI
and t-BuBr in Halogen-Organic Solvents

Solvent	t, °C	kx10 ⁷ , s ⁻¹	ΔH [‡] kcal/mol	-ΔS [‡] e.u.	ΔG [‡] (298°K) kcal/mol
1	2	3	4	5	6
t-BuI					
CH ₂ Cl ₂ ε=8.93 δ=1.95	25.0	7.62±0.05	17.4±1.0 r=0.990	28.1±3.4	25.8±1.0
	29.2	13.4±0.3			
	35.2	23.1±0.7			
	38.0	36.3±0.8			
	40.5 [±]	43.8±1.4			
CH ₂ Cl-CH ₂ Cl ε=10.38 δ=1.95	21.0	3.88±0.08	19.8±0.6 r=0.995	20.4±1.8	25.9±0.6
	25.0	7.08 ^{± ±}			
	25.5	7.18±0.14			
	30.5	11.1±0.3			
	33.5	17.2±0.1			
	38.9	27.0±0.5			
CH ₂ Br-CH ₂ Br ε=4.76 δ=1.98	25.0	0.822±0.033	22.0±1.0 r=0.990	17.1±3.9	27.1±1.0
	29.5	1.57±0.02			
	34.2	2.76±0.14			
	37.0	4.05±0.15			
	41.2	6.10±0.02			
t-BuBr					
CH ₂ Cl ₂	25.0	0.611±0.009	16.6±0.3 r=0.998	35.7±1.0	27.3±0.3
	25.5	0.633±0.006			
	34.9	1.77±0.05			
	39.5	2.23±0.02			
	41.5 [±]	2.78±0.03			

Table (continued)

1	2	3	4	5	6
CH ₂ Cl-CH ₂ Cl	25.0	0.179 \pm 0.004			
	30.2	0.334 \pm 0.001			
	34.7	0.534 \pm 0.007	18.4 \pm 1.0	32.2 \pm 3.4	28.0 \pm 0.1
	39.5	0.862 \pm 0.007	r=0.990		
	42.5	1.21 \pm 0.01			

*) By $\sim 0.5^\circ\text{C}$ lower than the boiling temperatures of t-BuX solutions in CH₂Cl₂ (boiling temperature of CH₂Cl₂ is 40.8°C).

**) Calculated according to temperature equation of k.

study. In all cases the reaction rate can well be expressed by equation $v=k[t\text{-BuX}]$. For t-BuCl in CH₂Cl₂ at 25°C $k = 2.87 \pm 0.01 \times 10^{-10} \text{ s}^{-1}$.

¹H n.m.r. data show that the value of chemical shift of t-BuI in the solvents under study is practically the same as in CCl₄ ($\delta = 1.94 \text{ p.p.m.}$). This would indicate that halogen-containing molecules of solvents cause only a limited solvation of t-BuI in its basic state.¹⁰

The ionization rate of t-BuX in CH₂Cl₂ is less dependent on the nature of the halogen than in other aprotic solvents. Thus, the ratio between the ionization rates of t-BuCl, t-BuBr and t-BuI in CH₂Cl₂ at 25°C is 1:216:2650, respectively. In acetonitrile this ratio is 1:545:23010 (25°C)⁶, in acetone 1:300:25120 (for t-BuCl $k_{25}=2.47 \cdot 10^{-10}$, for t-BuBr $k_{25}=7.41 \cdot 10^{-8}$, for t-BuI $k_{25}=6.2 \times 10^{-6} \text{ s}^{-1}$)¹¹ and for nitrobenzene 1:610:16480 (for t-BuCl $k_{25}=1.82 \times 10^{-10}$, for t-BuBr $k_{25} = 1.11 \times 10^{-7}$, for t-BuI $k_{25} = 3.00 \times 10^{-6} \text{ s}^{-1}$)^{2,12}.

The fact that the ionization rate of t-BuX in CH₂Cl₂ is less dependent on the nature of the halogen can be explained by the peculiarities of specific solvation in this solvent. In methylene chloride an activated complex is solvated through the formation of H-bonds while the strength

of the hydrogen bond grows as the electronegativity of the halogen in t-BuX becomes higher ($I < Br < Cl$) which partially offsets the decrease of the reaction rate within the series $t\text{-BuI} > t\text{-BuBr} > t\text{-BuCl}$. It is known that in proton-donating solvents the ionization rate of t-BuX is much less dependent on the nature of the halogen than in aprotic ones. Thus, the ratio between the ionization rates of t-BuCl, t-BuBr and t-BuI in CH_3OH is 1:40:143 and in water 1:26:53 (25°C)¹³. When passing from t-BuCl to t-BuBr in acetic acid the reaction rate increases only 15 times.¹⁴

Comparison between the ionization constants for t-BuX in nitrobenzene, acetone and CH_2Cl_2 shows that the reaction rate is little dependent on the nature of the solvent despite the fact that the dielectric constants of these solvents vary within quite a wide range (34.6, 20.5 and 8.9, respectively). It is worth noting that the reaction rate of every butylhalogenide in these solvents shows its own dependence on the nature of the solvent (relative values of k_{25} are given).

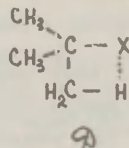
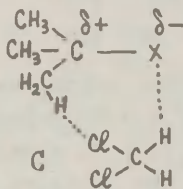
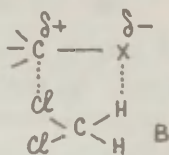
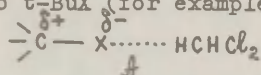
PhNO_2	$\text{CH}_3\overset{\text{O}}{\underset{\parallel}{\text{C}}}\text{CH}_3$	CH_2Cl_2
4	7.2	1 (t-BuI)
1.8	1.2	1 (t-BuBr)
1	1.4	1.6 (t-BuCl)

As ϵ increases, the ionization rate of t-BuBr rises slightly while that of t-BuCl falls. For t-BuI the maximum value of the reaction rate is observed in acetone. These comparisons show that the decisive contribution towards changing the reaction rate in the solvents under study is made by the effects of the specific solvation.

The ionization rates of t-BuI and t-BuBr in CH_2Cl_2 are higher than in dichloroethane though the dielectric constant of the latter is noticeably higher (see Table). It is interesting that when passing from t-BuI to t-BuCl both ΔH^\ddagger and ΔS^\ddagger values decrease for both the solvents. At the same time

the data available in literature show that lower reaction rates in both proton-donating and aprotic solvents in the series $t\text{-BuI} > t\text{-BuBr} > t\text{-BuCl}$ are, as a rule, associated with a rise in the ΔH^\ddagger value.^{2,6,13} In CH_2Cl_2 and $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$ we observe an altogether different effect - the decrease in the reaction rate when passing from $t\text{-BuI}$ to $t\text{-BuBr}$, is attributed to lower entropy of activation, i.e. higher space requirements to be met by the transition state. Here it should be noted that the increase in activation free energy (ΔG^\ddagger) as a result of a decrease in ΔS^\ddagger is partially offset by the reduction in ΔH^\ddagger . In contrast to this, the decrease of the ionization rate of $t\text{-BuI}$ in the series of solvents $\text{CH}_2\text{Cl}_2 > \text{CH}_2\text{Cl}-\text{CH}_2\text{Cl} > \text{CH}_2\text{Br}-\text{CH}_2\text{Br}$ is chiefly connected with a rise in the ΔH^\ddagger value.

The relations we have observed between the activation parameters of $t\text{-BuX}$ ionization and the nature of the solvent and the halogen in the reagent can be explained supposing that during the solvation of an activated complex the formation of linear solvates (A) is accompanied also by stricter orientation of the solvent molecule in relation to $t\text{-BuX}$ (for example, the formation of B or C).



The data obtained show that a rise in the polarity of the C-H bond of the solvent (δ value for CH_2Cl_2 , $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$ and $\text{CH}_2\text{Br}-\text{CH}_2\text{Br}$ in CCl_4 is 5.33, 3.69 and 3.63 p.p.m., respectively¹⁵) and in the electronegativity of the halogen in $t\text{-BuX}$, i.e. in the strength of the H-bond, leads to a decrease in the ΔS^\ddagger value. Therefore, we may conclude that the increase in the transition state solvation energy through the formation of a hydrogen bond increases

the probability of formation of B- or C-type activated complexes. This may be caused by the fact that in nonpolar solvents ionization of the C-X bond in the transition state may be accompanied by formation of four-member complex D (intramolecular H-bond)¹⁶. As the solvation energy increases as a result of the formation of intermolecular H-bond (A, B, C), the probability of the formation of transition state D must decrease. Formation of the transition state of C-type is postulated for the case of ionization of t-BuCl in aniline.¹⁷ This is based on the fact that the ionization rate of t-BuCl ($k_{25} = 7.4 \times 10^{-7} \text{ s}^{-1}$) in aniline which has a rather low dielectric constant (6.99), is practically the same as in methanol.

The strict orientation of the solvents in relation to the reagent in the transition state results, in the long run, in more considerable reduction in the free energy of activation than could be expected in accordance with relationship of $\lg k$ vs $(\delta - 1)/(2\delta + 1)$.⁸ True, the ionization rate of t-BuCl in CH_2Cl_2 is higher than in acetone or PhNO_2 .

From this point of view it is interesting to compare data on the ionization kinetics of liquid t-BuCl³ and t-BuCl in the solution of CH_2Cl_2 . Though the dielectric constant of t-BuCl (9.57) is slightly higher than that of CH_2Cl_2 , the ionization rate in the former case is four orders lower than in the latter case. This must be due to weak solvation of ion pair $\text{t-Bu}^+\text{Cl}^-$ by molecules of t-BuCl, which leads to a rapid decrease in the reaction rate as a result of the increase in ΔH^\ddagger (34.5 kcal/mol). Thus we see what a considerable contribution is made by specific solvation of t-BuX even at comparatively low values of ϵ .

R e f e r e n c e s

1. I. A. Koppel and V.A.Palm, Reakts.sposobn.organ. soedin., 4, 2(12), 381 (1967).
2. G.F. Dvorko, N.I. Kulik, and E.A.Ponomareva, Reakts.sposobn.organ. soedin., 11, 3/4 (41), (1974).
3. E.S. Rudakov, G.P. Valuyeva, and V.P.Tretyakov, Reakts.sposobn.organ. soedin., 4, 1 (11), 150 (1967).
4. I.A. Koppel and V.A.Palm, Reakts.sposobn.organ. soedin., 4, 4 (14), 862 (1967).
5. F.A. Neugebauer, Angew. Chem., 85, 485 (1973).
6. E.A. Ponomareva, N.I. Kulik, and G.F.Dvorko, Reakts.Sposobn.organ. soedin., 11, ~~12~~ (40), 333 (1974).
7. A. Weisberger et al., "Organic Solvents", FL Publ., Moscow, 1958.
8. N.I. Kulik, E.A. Ponomareva, and G.F.Dvorko, Reakts. sposobn.organ. soedin., 12, (1975).
9. R.Yu. Akhadov, "Dielectric Properties of Pure Liquids", Izdatelstvo Standartov, Moscow, 1972.
10. R.S. Armstrong, M.J. Aroney, R.K. Duffin, and H.J.Stootman, J.C.S. Perkin II, 1973, 1272.
11. N.I. Kulik and E.A.Ponomareva, Dop.Akad.Nauk Ukr. SSR, 1975, 329.
12. I.A. Koppel and V.A.Palm, Reakts.sposobn.organ. soedin. 1 (1), 170 (1964).
13. J. Biordi and A.E.Moelwyn-Hughes, J.Chem.Soc., 1962, 4301.
14. M.H. Abraham, J.C.S. Perkin II, 1972, 1343.
15. J. Emsley, J. Faney, and I. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy", Mir, Moscow, Vol. 2, p. 415.
16. M.H. Abraham and R.J.Abraham, J.C.S. Perkin II, 1974, 47.
17. G.P. Valuyeva and E.S.Rudakov, Reakts.sposobn.organ. soedin., 2, 291 (1965).

α -HALONITROALKANE REACTIVITY. V. THERMODYNAMIC AND KINETIC
ACIDITY OF ARYL CHLORONITROMETHANES.

A.G. Bazanov, M.P. Kozlova, I.V. Tselinsky, B.V. Ghidaspov, and
S.M. Dzubenko

Leningrad Lenseviet Institute of Technology,
26, Moskovsky Prospekt, Leningrad, L-13.

Received May 4, 1975

Ionization constants and rates of acetic acid and its anion catalyzed protolytic reactions have been measured spectrophotometrically for a series of aryl chloronitromethanes in aqueous buffer solutions at 25°. The pK_a values of aryl chloronitromethanes excellently correlate with Taft's σ° constants of substituents in the benzene ring, the ρ° value being -1.13 ± 0.05 .

The Brönsted correlation between rates of protolytic reactions and pK_a values of the substrates gives a negative α value and β exceeding unity ($\alpha = -0.23$; $\beta = 1.23$). This anomaly of Brönsted coefficients is shown to be due to specific solvation effects in chloronitrocarbanions.

It was shown earlier [1] that specific solvation of oxygen atoms of α -chloronitrocarbanions in aqueous solution results in a relatively weak dependence of pK_a values of conjugated CH-acids on polar σ^π constants of the substituents and gives rise to anomalous Brönsted coefficients for a series of aliphatic α -halonitrocompounds. The studied chloronitroalkanes [1], however, contained diversified substituents in which both inductive and steric effects varied. This would likely cause some distortion of the Taft and Brönsted correlations. Hence it seemed appropriate to investigate the influence of polar effect on thermodynamic and kinetic acidity in a series of α -chloronitrocompounds with a strictly constant steric factor. With this objective in mind we have studied rates and equilibria of protolytic reactions in a series of meta- and para-substituted aryl chloronitromethanes. The mea-

measurements were performed spectrophotometrically at the wavelengths of chloronitrocarbanions absorption maxima (see Table I). The acidity constants at 25° were calculated from ionization ratios measured in aqueous buffer solutions with pH values in the range of $pK_a \pm 0.7$ and ionic strength 0.10. The pK_a values of aryl chloronitromethanes together with ultraviolet absorption characteristics of the carbanions and σ° constants of substituents in the benzene ring are given in Table I.

Table I. Thermodynamic pK_a Values of Aryl Chloronitromethanes, Ultraviolet Absorption Spectra of the Carbanions, and σ° Constants of Substituents.

No's	$RC_6H_4CH(Cl)NO_2$ R =	pK_a	λ_{max} , nm	$\log \epsilon$	σ°
1	p-CH ₃	6.07 ± 0.02	295	4.10	-0.15
2	p-CH ₃ O	6.01 ± 0.01	297	4.16	-0.12
3	H	5.99 ± 0.01	294	4.08	0
4	p-Br	5.64 ± 0.02	303	4.16	0.26
5	m-Cl	5.57 ± 0.02	303	4.05	0.37
6	m-NO ₂	5.09 ± 0.03	295	4.14	0.70
7	p-NO ₂	5.00 ± 0.04	380	3.80	0.82

The dependence of pK_a values of aryl chloronitromethanes on polar σ° constants of the substituents is plotted in Fig. 1.

The observed bathochromic shift of absorption maxima of aryl chloronitromethide ions ($\lambda_{max} = 294-380$ nm) as compared to those of aliphatic α -chloronitrocarbanions ($\lambda_{max} = 220-245$ nm [1]) is indicative of some conjugation between the carbanion moiety and benzene ring. Hence it may be concluded that steric requirements of a planar chloronitrocarbanion fragment are smaller than those of the dinitrocarbanion grouping. After our views [2] the latter is not conjugated with the benzene ring in aryl dinitromethide ions due to steric crowding. Nevertheless, a treatment of aryl chloronitromethanes pK_a values according to the Yukawa-Tsuno equation

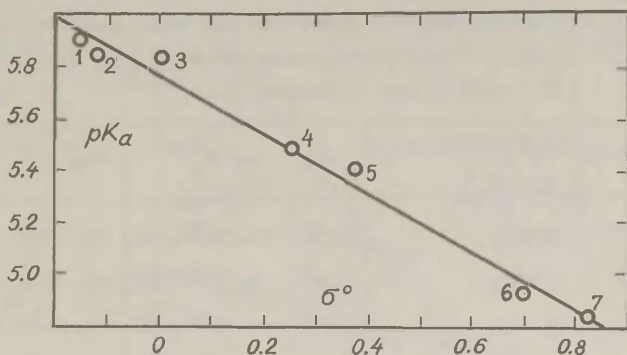


Figure 1. The dependence of pK_a values of aryl chloronitro-methanes on polar σ° constants of the substituents. Numbers of points correspond to Table I.

[3] gives the r value, a sensitivity parameter towards polar conjugation, which differs insignificantly from zero. This implies that conjugation operates mainly in the excited state whereas its contribution to stabilization of the ground state is negligible as compared to polar influence. Thus the use of a simple Hammett equation seems justified.

The estimation of correlation parameters led to Equation I (Table 3). Comparing the value of $\rho^\circ = -1.13 \pm 0.05$ obtained in this series with $\rho^\pi = -1.68 \pm 0.12$ for aliphatic α -chloronitro compounds [1] one can see their significant variance caused by different mechanisms of the polar effect transition in aliphatic and aromatic series [4]. The ratio $\rho^\pi/\rho^\circ = 1.49$ obtained in the series of α -chloronitro compounds lies within usual limits for other series [4], contrary to gem-dinitro compounds where this ratio amounts to 2.15 [2].

The rates of proton abstraction from aryl chloronitro-methanes by acetate ion as well as the rates of protonation of corresponding carbanions by acetic acid were measured as described earlier [6]. The results for 25° and ionic strength 0.10 are presented in Table 2.

The logarithms of dissociation and protonation rates are

Table 2. pK_a Values and Logarithms of Rate Constants of Aryl Chloronitromethanes Dissociation Catalyzed by Acetate Ion ($k_D^{AcO^-}$) and of the Carbanions Protonation by Acetic Acid (k_R^{AcOH}) at 25° and Ionic Strength 0.10.^{a)}

No's	$RC_6H_4CH(Cl)NO_2$, R =	pK_a	$\log k_D^{AcO^-}$	$\log k_R^{AcOH}$
1	p-CH ₃	5.91	-1.91 \pm 0.02	-0.76 \pm 0.03
2	p-CH ₃ O	5.85	-1.71 \pm 0.02	-0.61 \pm 0.02
3	H	5.83	-1.73 \pm 0.02	-0.66 \pm 0.01
4	p-Br	5.48	-1.38 \pm 0.01	-0.64 \pm 0.02
5	m-Cl	5.41	-1.30 \pm 0.02	-0.63 \pm 0.02
6	m-NO ₂	4.93	-0.61 \pm 0.02	-0.44 \pm 0.02
7	p-NO ₂	4.84	-0.56 \pm 0.02	-0.47 \pm 0.02

a) Rate constants in $l \cdot mol^{-1} \cdot s^{-1}$.

plotted against pK_a values of the substrates in Fig. 2. The corresponding Brønsted equations are given in Table 3 (Eqs. (2) and (3)).

As is seen from Fig. 2 and Table 3, the Brønsted coefficients ($\alpha = -0.23$; $\beta = 1.23$) lie beyond the limiting values of 0 and 1 just as it was observed earlier in the series of aliphatic α -chloronitro compounds ($\alpha = -0.20 \pm 0.11$; $\beta = 1.23 \pm 0.11$ [1]). Though the latter values were regarded as approximate due to lack of a strict constancy of the reaction center in the aliphatic series [1] their plausibility is supported by the present study. A similar anomaly of the Brønsted coefficients was noted [9] for the series of 1-aryl-1-nitroethanes and 1-aryl-2-nitropropanes (see Table 4).

It was shown [10] that the "extent of anomaly" of Brønsted β (i.e., the difference between β for a series with variable nitroalkane-substrate and β for a series with variable catalysts) can serve as a measure of relative contributions of

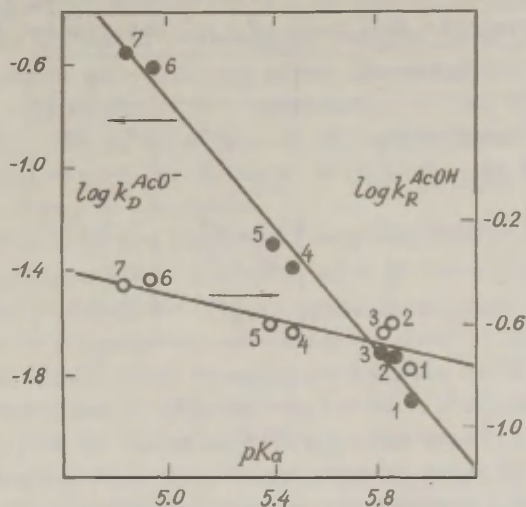


Figure 2. Brønsted correlations of the dissociation rate constants of aryl chloronitromethanes (solid circles) and the protonation rate constants of corresponding carbanions (open circles) with pK_a values of the substrates. Numbers of points correspond to those in Table 2.

Table 3. Correlation Equations for Protolytic Reactions of Aryl Chloronitromethanes.

No's	Correlation Equation	r	s	n
1	$pK_a = (5.77 \pm 0.02) - (1.13 \pm 0.05) \log k_D^{\text{AcO}^-}$	0.995	0.04	7
2	$\log k_D^{\text{AcO}^-} = (5.38 \pm 0.29) - (1.23 \pm 0.05) pK_a$	0.996	0.05	7
3	$\log k_R^{\text{AcOH}} = (0.64 \pm 0.28) - (0.23 \pm 0.05) pK_a$	0.896	0.05	7

effects other than inductive in stabilization of the transition and final states of ionization reactions of CH-acids. In the present case this additional effect can be identified as specific solvation of oxygen atoms of the nitrocarbanions

Table 4. The Values of ρ° (in eq. $pK_a = pK_{a0} + \rho^\circ \sigma^\circ$) and β for Protolytic Reactions of Aryl Substituted Nitroalkanes.

Substrate	ρ°	β
$\text{ArCH}(\text{NO}_2)_2$	-1.53 ^a	0.75 ^b
$\text{ArCH}(\text{NO}_2)\text{Cl}$	-1.13	1.23
$\text{ArCH}(\text{NO}_2)\text{CH}_3$	-1.07 ^c (-1.03 ^d)	1.37 ^{c,e}
$\text{ArCH}_2\text{CH}(\text{NO}_2)\text{CH}_3$	-1.02 ^{c,f}	1.61 ^{c,e}

^a) Data from Ref. [2] in water at 20°; ^b) Data from Ref. [5] in water at 20°; ^c) Data from Ref. [9] in 50% aqueous methanol at 25°; ^d) Data from Ref. [13] in water at 25°; ^e) β determined from the rates of deprotonation by hydroxide ions; the values of β , however, are almost independent of the bases used in a wide range of their basicity; ^f) Estimated from $\rho^\circ = -0.395$ [9] for the reaction center, $\text{CH}_2\text{CH}(\text{NO}_2)\text{CH}_3$, by dividing it by the transmission coefficient of the CH_2 group.

which strengthens with the attenuation of an electron-accepting power of the substituent. This situation can be further illustrated by comparing reaction constants, the Hammett ρ° values for the ionization equilibrium, and Brønsted β for the deprotonation of CH-acids (with a variable substrate), for aryl substituted nitroalkanes containing different substituents at the reaction center (Table 4).

It follows from the data in Table 4 that as the electron-accepting power of substituents at the reaction center (C-H bond) lowers and, accordingly, a negative charge on the oxygen atoms of the nitrocarbanion grows, the absolute value of ρ° reduces whereas that of Brønsted β increases.

The β value for the series of aryl dinitromethanes does not yet exceed the range of "normal" values but upon substitution of one of the nitro groups by the methyl group or a halogen atom the β passes over to anomalous values

exceeding unity. Apparently, the increasing electron density on oxygen atoms of the nitrocarbanion results in strengthening of its specific solvation by water. As was noted [7,11], this results in lowering of the sensitivity of pK_a values of CH-acids towards the polar effect of the substituent and in a corresponding rise of the Brønsted β in excess of unity in series with a variable substrate.

Consequently, both the Hammett ρ° and Brønsted β testify to a considerable specific solvation of α -chloronitrocarbanions in aqueous solution. The solvation characteristics of chloronitrocarbanions seem to be close to those of mononitrocarbanions and differ significantly from solvation behavior of dinitrocarbanions. Apparently, in spite of a highly electronegative nature of chlorine atom its α -effect (or, in other words, a p-electron repulsion effect) prevails, thus resulting in pushing the negative charge off the carbon towards oxygen atoms of the carbanion and favoring their specific solvation. In the transition state, however, the negative charge of the incipient (close to sp^3 -hybridized) carbanion is still localized mainly on the carbon and specific solvation of oxygens develops to a considerably lesser extent. The removal of charge off the substituent attached to the carbon on passing along the reaction coordinate from the transition state to the carbanion final state is responsible for the observed anomaly of Brønsted coefficients.

Experimental Section

The aryl chloronitromethanes used in the study were prepared via chlorination of sodium salts of corresponding nitro compounds in aqueous solution. Aryl nitromethanes were synthesized according to Ref.[12]. The chlorination was performed via simultaneous addition of gaseous chlorine and a sodium salt solution into a flask, the excess of chlorine being maintained in order to avoid ionization of the chloronitro compound and subsequent double chlorination. After the addition was complete, the product was separated and purified by means of vacuum distillation or recrystallization from

appropriate solvents. According to GLC data the purity of the aryl chloronitromethanes amounted to 96-98%.

Characteristics of the products are listed in Table 5.

Table 5. Physical Properties and Elemental Analyses of Aryl Chloronitromethanes.

Compound (Formula)	B.p./torr (M.p.)	n_D^{20}	Found, %		Calcd, %	
			N	Cl	N	Cl
$C_6H_5CH(Cl)NO_2$ ($C_7H_6ClNO_2$)	72/I	1.5415	8.03	19.61	8.16	20.70
$p-CH_3C_6H_4CH(Cl)NO_2$ ($C_8H_8ClNO_2$)	81-2/I	1.5320	7.93	19.15	7.55	18.70
$p-CH_3OC_6H_4CH(Cl)NO_2$ ($C_8H_8ClNO_3$)	125-7/I	1.5380	6.80	17.10	6.95	17.23
$m-NO_2C_6H_4CH(Cl)NO_2$ ($C_7H_5ClN_2O_4$)	115-116	-	12.98	16.29	12.95	16.41
$p-BrC_6H_4CH(Cl)NO_2$ ($C_7H_5BrClNO_2$)	101/I	1.5422	5.60	-	5.59	14.18
$m-ClC_6H_4CH(Cl)NO_2$ ($C_7H_5Cl_2NO_2$)	80/I	1.5590	6.95	34.10	6.80	34.50
$p-NO_2C_6H_4CH(Cl)NO_2$ ($C_7H_5ClN_2O_4$)	72-74	-	13.02	16.34	12.95	16.41

Formic, acetic, succinic, phosphoric, and boric acids of "chemically pure" grade, "pure" sodium hydroxide, and doubly distilled water were used to prepare buffer solutions. The ionic strength was brought to necessary values with potassium chloride of "pure for analysis" grade. Extrapolation of pK_a values to zero ionic strength was made using the Debye-Hückel equation [8]. The estimated value of $\log f_{\pm}$ equals -0.16 for $\mu = 0.10$.

The details of kinetic and equilibrium experiments have been described elsewhere [1,6,7].

R e f e r e n c e s

1. A.G.Bazanov, I.V.Tselinsky, N.B.Nikolskaya, M.P.Kozlova, and B.V.Ghidasov, *Reakts.Sposobn.Org.Soed.*, 10, 817 (1973).
2. G.I.Kolesetskaya, I.V.Tselinsky, and L.I.Bagal, *Reakts. Sposobn.Org.Soed.*, 6, 387 (1969).
3. M.Yoshicka, K.Hamamoto, and T.Kubota, *Bull.Chem.Soc. Japan*, 35, 1723 (1962).
4. V.A.Palm, *Osnovy Kolichestvennoi Teorii Organicheskikh Reaktsii* (Foundations of the Quantitative Theory of Organic Reactions), "Khimiya", Leningrad, 1967, p.143.
5. V.N.Dronov, I.V.Tselinsky, and I.N.Shokhor, *Reakts. Sposobn.Org.Soed.*, 6, 948 (1969).
6. A.G.Bazanov, S.V.Alekseyeva, I.V.Tselinsky, and B.V.Ghidasov, *Reakts.Sposobn.Org.Soed.*, 9, 367 (1972).
7. A.G.Bazanov, M.V.Chistyakova, M.F.Kozlova, I.V.Tselinsky, and B.V.Ghidasov, *Reakts.Sposobn.Org.Soed.*, 10, 807 (1973).
8. R.A.Robinson and R.H.Stokes, *Electrolyte Solutions*, Second Ed., Butterworths, London, 1959.
9. F.G.Bordwell, W.J.Boyle, Jr., and K.C.Yee, *J.Am.Chem.Soc.*, 92, 5026 (1970).
10. I.V.Tselinsky, *Doctoral Thesis*, Leningrad Lensoviet Institute of Technology, 1974.
11. I.V.Tselinsky and V.N.Dronov, *Reakts.Sposobn.Org.Soed.*, 10, 797 (1973).
12. L.P.Zalukaev, *Izvestiya Vysshikh Uchebnykh Zavedenii, Khimiya i Khim.Technol.*, 13, 1764 (1970); N.Kornblum, *J.Am.Chem.Soc.*, 86, 2681 (1964); *Organic Reactions*, ed. by R.Adams, 12, 149 (1965) (Russian Edition).
13. F.G.Bordwell and W.J.Boyle, Jr., *J.Am.Chem.Soc.*, 94, 3907 (1972).

IONIZATION CONSTANTS OF SOME DERIVATIVES OF SULFONIC ACID IN AQUEOUS METHANOL AND DIOXANE

V.P.Chernyk, T.S.Jan-Temirova, and V.I.Makurina

Kharkov Pharmacy Institute, Kharkov, Ukr. S.S.R.

Received April 29, 1975

By the method of potentiometric titration in 50% aqueous methanol and 60% aqueous dioxane at 25°C ionization constants of ethane-(benzene)-sulfonyl oxamides, substituted amides of ethane-(benzene)-sulfonylhydrazides of the oxalic acid and N-arylamides of the ethane-(benzene)-sulfonic acids were determined. The pKa values for the compounds studies were correlated with Hammett's σ -constants. Attenuation factors of the NHCOCONH and NH group for electronic influences in 50% aqueous methanol have been calculated by the " ρ - ρ " method.

Going on with studying the reactivity of the derivatives of oxalic acid [1-7] and with the purpose to select titration conditions for the kinetic study of the acylation reaction of sulfamides [1-2] and sulfohydrazides [4] with the ethers of oxamic acids, the constants of ionization of ethanesulfonyloxamides (series A), the substituted

Table 1

IONIZATION CONSTANTS OF THE $\text{RSO}_2\text{NHR}'$ COMPOUNDS

Compound No	Series	R	R'	pKa** in 50% aqueous methanol
I	2	3	4	5
I	A	C_2H_5	$\text{COCONHC}_6\text{H}_4\text{OCH}_3\text{-P}$	4.78
2			$\text{COCONHC}_6\text{H}_4\text{CH}_3\text{-P}$	4.72
3			$\text{COCONHC}_6\text{H}_5$	4.63
4			$\text{COCONHC}_6\text{H}_4\text{NO}_2\text{-P}$	4.17
5	B	C_2H_5	$\text{NHCOCONHC}_6\text{H}_4\text{OCH}_3\text{-P}$	8.27
6			$\text{NHCOCONHC}_6\text{H}_4\text{CH}_3\text{-P}$	8.18
7			$\text{NHCOCONHC}_6\text{H}_5$	8.14
8			$\text{NHCOCONHC}_6\text{H}_4\text{OCH}_3\text{-m}$	8.08
9			$\text{NHCOCONHC}_6\text{H}_4\text{Cl-P}$	8.05
10			$\text{NHCOCONHC}_6\text{H}_4\text{Br-P}$	8.02
11	C*	C_2H_5	$\text{NHCOCONHC}_6\text{H}_4\text{NO}_2\text{-P}$	7.80
12			$\text{C}_6\text{H}_4\text{OCH}_3\text{-P}$	10.52
13			$\text{C}_6\text{H}_4\text{CH}_3\text{-P}$	10.85
14			C_6H_5	9.87
15			$\text{C}_6\text{H}_4\text{Br-P}$	9.30
16			$\text{C}_6\text{H}_4\text{NO}_2\text{-P}$	7.62
17			$\text{COCONHC}_6\text{H}_4\text{OCH}_3\text{-P}$	4.11

I	2	3	4	5
18	D	C_6H_5	$COCONHC_6H_4CH_3-P$	4.06
19			$COCONHC_6H_5$	3.95
20			$COCONHC_6H_4NO_2-P$	3.56
21	E	C_6H_5	$NHCOCONHC_6H_4OCH_3-P$	7.66
22			$NHCOCONHC_6H_4CH_3-m$	7.58
23			$NHCOCONHC_6H_4Cl-P$	7.45
24			$NHCOCONHC_6H_4Cl-m$	7.41
25			$NHCOCONHC_6H_4NO_2-P$	7.19
26	F	C_6H_5	$C_6H_4OCH_3-P$	9.83
27			$C_6H_4CH_3-P$	9.59
28			C_6H_5	9.28
29			C_6H_4Br-P	8.47
30			$C_6H_4NO_2-P$	7.02

* For the compounds 12,13,14,15 and 16 pKa values in aqueous dioxane (60%) are respectively equal to 11.22; 10.98; 10.68; 10.02; 8.45.

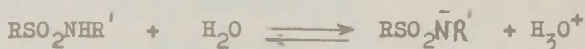
** Average deviation of the pKa values - $\pm 0.01-0.03$.

*** pKa values were determined by our earlier method [6] .

The solvents are shown in per cent by weight.

amides of the oxalic acid ethanesulfohydrazides (series B) and N-arylamides of ethanesulfonic acids (series C), benzene-sulfonyloxamides (series D), substituted amides of benzenesulfohydrazides of oxamic acid (series E) and N-arylamides of benzenesulfonic acid (series F) were measured.

The process of acidic ionization of the above-mentioned groups of substances proceeds in accordance with the following general scheme:



From the data in Table 1 it is evident that the ionization constants of sulfamides depend upon the nature of the radicals connected with the sulfonyl and amide groups. For example, substitution of the alkyl radical (series A,B,C) for the aromatic one in the series D,E,F results in reduction of acidity in the compounds ($\Delta \text{pK}_a \simeq 0.61\text{--}0.70$ units).

Acidity of sulfamides changes more tangibly when the radicals at amide nitrogen are substituted. When passing from arylamides of ethane-(benzene)-sulfonic acids (series C,F) to ethane-(benzene)-sulfonyloxamides, (series A,D) acidity of the latter increases approximately 2 times as compared with the former. Substitution of the oxamide group (series B,E) for hydrogen results almost in two-fold reduction of acidity in the compounds. Such an increase in the values of ionization constants is,

probably, explained by considerable increase of electronic density at nitrogen of the sulfamide group at the expense of the next neighbouring nitrogen.

The pK_a values in 50% aqueous methanol are almost by a unity less than the ionization constants of these substances in 60% aqueous dioxane, which may be due to different dielectric constants of these solvents [8].

The pK_a values found for 50% aqueous methanol for the series A,B,D and E allowed us to determine selection of indicators for the kinetic study of interaction of aryl-(alkane-) sulfamides and aryl-(alkane-) sulfohydrazides with the ethers of oxamic acids.

When the kinetic study of the reaction of acylation of sodium salts of the alkane- and aryl-sulfamides by the ethers of oxamic acids is carried out, used as an indicator for determination of the per cent content of the reaction products may be methyl red one and in the case of acylation of sodium salts of the alkane- and aryl-sulfohydrazides by the above-mentioned ethers used with equal success may be phenol red, bromothymol blue indicator, cresol red one as well as phenolphthalein.

With the purpose of studying the quantitative influence of substituents upon deprotonization of the sulfamide and sulfohydrazide groups, reaction constants were calculated for the series (A-F, Table 2).

Table 2

CORRELATION PARAMETERS OF THE DEPENDENCE OF pKa
VALUES OF COMPOUNDS UPON HAMMETT'S ρ -CONSTANT

Series and Nos of compounds involved	Correlation equation	Equation No.	r**	S
1	2	3	4	5
A (1-4)	$pK_a = (4.62 \pm 0.01) - (0.581 \pm 0.006) \cdot \rho$	1	0.999	0.012
B (5-11)	$pK_a = (8.13 \pm 0.01) - (0.429 \pm 0.021) \cdot \rho$	2	0.994	0.018
C (12-16)	$pK_a = (9.85 \pm 0.03) - (2.794 \pm 0.095) \cdot \rho$	3	0.998	0.018
C* (12-16)	$pK_a = (10.57 \pm 0.03) - (2.656 \pm 0.107) \cdot \rho$	4	0.998	0.138
D (17-20)	$pK_a = (3.96 \pm 0.01) - (0.522 \pm 0.014) \cdot \rho$	5	0.999	0.029
E (21-25)	$pK_a = (7.53 \pm 0.01) - (0.420 \pm 0.032) \cdot \rho$	6	0.992	0.027
F (26-30)	$pK_a = (9.15 \pm 0.03) - (2.719 \pm 0.105) \cdot \rho$	7	0.998	0.135

*Equation (4) has been calculated on the basis of pKa values in 60% aqueous dioxane.

** Values of reaction constants (ρ), correlation coefficients (r) and standard deviation(s) were calculated using the method of the least squares [9] at Nairi-2 computer.

The values of ρ from Table 2 clearly charac-

terize sensitivity of the reaction series to splitting off the proton under the action of substituents in the amide part of the molecule. The values of ρ for the B and E series equal to 0.429 and 0.420 respectively show that the studied series display low sensitivity to structural changes, which is explained by considerable distance of substituents from the reaction center. Approach of these substituents to the sulfamide group increases sensitivity to structural changes in the molecule (ρ in series $C > A > B$; $F > D > E$).

The ρ values of the studied series give possibility of calculating electronic transmission factors of oxamide (NHCOCONH) and NH groups. Given in Table 3 are the values of electronic influence transmission constants (Z) of the above-mentioned groups, calculated using two independent ratios of reaction constants for different series.

Table 3

ELECTRONIC ATTENUATION FACTORS OF THE NHCOCONH
AND NH GROUPS

Group	Ratio of the values of ρ of reaction series	Z
NHCOCONH	B/C	0.15
	E/F	0.16
NH	B/A	0.74
	E/D	0.80

After other works [3,6] Z of NHCOCONH is equal to 0.19; Z of NH - to 0.73 (0.81).

REFERENCE

1. P.A. Petiunin and V.P. Chernykh, J.Org.Chem., 3, 1832 (1967).
2. P.A. Petiunin, V.P. Chernykh, and I.P. Banny, Reakts. sposebn. organ. soedin., 7, 162 (1970).
3. V.P. Chernykh, V.I. Makurina, and P.A. Petiunin, Ukr. chem. j., 40, 414 (1974).
4. V.P. Chernykh, V.I. Makurina, V.I. Gridasov, and P.A. Petiunin, Organ. Reactivity, 11, 7 (1974).
5. V.P. Chernykh, V.I. Makurina, and P.A. Petiunin, Organ. Reactivity, 11, 13, 1974.
6. P.A. Petiunin, V.P. Chernykh, and V.I. Makurina, Reakts. sposobn. organ. soedin., 9, 153 (1972).
7. P.A. Petiunin, V.P. Chernykh, and V.I. Makurina, J.Org.Chem., 10, 2584 (1974).
8. Chemist's ref. book. "Khimia", 4, 418 (1967).
9. L.M. Batuner and M.E. Pozin, Mathematical Methods in Chemical Engineering, L., "Khimia", 1971.
10. V.A. Palm, Usp. Khim., 30, 1069 (1961).

POTENTIOMETRIC AND POLAROGRAPHIC INVESTIGATION OF
SUBSTITUTED BENZOIC ACIDS IN DIMETHYLSULPHOXIDE
MEDIUM

L.N.Bykova, S.I.Petrov, L.A.Karaseva, E.M.Gorynina, and
A.D. Galitsyn

Moscow Textile Institute, Moscow

Moscow Institute of Food Industry Technology, Moscow

Received May 4, 1975

Half-neutralization potentials and reduction half wave potentials on a mercury drop electrode were measured for the purpose of investigating the differentiating action of dimethylsulphoxide (DMSO) on the potentiometric and polarographic behavior of substituted benzoic acids. 34 acids with halogeno-, oxy-, nitro- and some other substituents in m-, p- and o-positions were investigated by potentiometric techniques; 26 acids were investigated by polarographic techniques. Comparison of potentiometric $E_{1/2}$ to σ -constants of substituents and to $pK_A(H_2O)$ demonstrated that benzoic acids can be divided into three subseries: those containing only m- and p-substituents; those containing o-substituents or o-, m- and p-substituents in one molecule; and those containing 2-OH substituents. Comparison of polarographic constants $E_{1/2}$ to σ -constants and $pK_A(H_2O)$ demonstrated that benzoic acids can be divided into three subseries each distinguished by m-, p- or o-substituents, respectively. A large differentiating effect of DMSO on the potentiometric and polarographic behavior of substituted benzoic acids is established.

Differentiating action of non-aqueous solvents with respect to the substituted benzoic acids was investigated by a number of authors ¹⁻⁹. An analysis of data reported by various authors on the investigation of the differentiating action of non-aqueous solvents on the strength of benzoic acids is given in Ref.1 both on the basis of measured dissociation constants and half-neutralization potentials and on the basis of the Hammett equation. The differentiating action was investigated thoroughly by means of measuring half-neutralization potentials of benzoic acids in alcohols, ketons, acetonitrile, methyl pyrrolidone, propylene carbonate, dimethylformamide and dimethylsulphoxide. It is unambiguously established that benzoic acids form two subseries: acids containing m- and p-substituents and acids containing o-substituents and also o-, m- and p-substituents in one molecule. 2-OH-substituted acids show deviations owing to anionic stabilization in non-aqueous solvent media, caused by the intramolecular hydrogen bond. The differentiating action of DMSO on the strength of benzoic acids has been investigated in sufficient detail ^{1,4,6-8}. However, the polarographic behavior of benzoic acids in DMSO has not been investigated at all.

The purpose of the present paper is the potentiometric and polarographic investigation in the DMSO medium of benzoic acids containing various substituents in m-, p- and o-positions with respect to carboxy group. This paper is a follow-up on the potentiometric and polarographic investigation of benzoic acids in the dimethylformamide medium, carried out earlier by three of the authors of the present paper. DMSO is an aprotic dipolar solvent with high differentiating effect; therefore, the investigation of acids' behavior in this medium has both theoretical and practical significance with the view of developing the methods of acids' analysis.

The potentiometric method of investigation was applied to 34 benzoic acids containing halogeno-, nitro-, oxy-, methyl-, ethyl- and methoxy-substituents; some of the acids had several substituents in one molecule. For each of the

acids the half-neutralization potential was determined at least three times by means of potentiometric titration curves and by measuring emf of half-neutralized acid solutions². A 0.1 N solution of tetramethyl ammonium hydroxide, prepared from the 10% aqueous solution in a DMSO medium, was used as titration reagent. Water content in the half-neutralization point, with that in the initial DMSO taken into account, did not exceed 1.5 wt.%. Water content in DMSO, determined by titration with the Fisher reagent, was 0.7 wt.%. Half-neutralization potentials of substituted benzoic acids were corrected for the half-neutralization potential of benzoic acid in order to reduce the effect of oscillations in the junction potential. The rms error of a single measurement of half-neutralization potential, calculated for the number of degrees of freedom $f=64$, was found to be 10 mV.

Reduction halfwave potentials on mercury drop electrode were measured for benzoic acids by means of a LP-60 polarograph. Capillary characteristics: $m = 1.24 \text{ mg/s}$; $\tau = 5.4 \text{ s}$; $m^{2/3} \tau^{1/6} = 1.531 \text{ mg}^{2/3} \text{ s}^{-1/2}$, for background solution with no voltage applied. A 0.05 N solution of tetraethyl ammonium iodide in DMSO was used as a background solution. Solutions of at least three concentrations, with at least two curves taken for each of them, were used for determining halfwave potentials in all the acids. Bottom mercury served as anode, and halfwave potentials were determined relative to a saturated calomel cell, by measuring the potential of bottom mercury with respect to this cell.

26 benzoic acids were investigated by polarographic techniques. In comparison to the potentiometric method, the acids containing nitro-substituents and that with 3,5- Cl_2 -2,4- $(\text{OH})_2$ substituents, for which a polarogram has a complicated character, were not investigated. The rms error of a single measurement of halfwave potential, calculated for the number of degrees of freedom $f=185$, was found to be 5 mV.

The majority of benzoic acids in DMSO yield well-pro-

nounced polarographic waves which are completely suppressed by adding tetraalkyl ammonium hydroxide to the polarographed solution.

Table 1 lists the values of exponents of acid dissociation constants in water¹⁰, those of σ -constants of the substituents¹¹, half-neutralization potentials of acids in DMSO, acid reduction halfwave potentials on a mercury drop electrode with respect to s.c.e. In order to eliminate the effect of the junction potential on the interface between the investigated non-aqueous solution and the reference electrode salt bridge the values of halfwave potentials were reduced to that of benzoic acid ($\Delta E_{1/2}$). The curves $\lg(i/(i_d-i))$ vs. E yielded the slopes of straight lines, corresponding to the values $0.058/n$, and from these slopes - the values of α (charge transfer coefficient) for $n=1$.

Table 1

Potentiometric and Polarographic Characteristics of Substituted Benzoic Acids in the Dimethylsulphoxide Medium, σ -Constants of Substituents and $pK_A(H_2O)$ of the Acids

No.	Substituent	$pK_A(H_2O)$	$\Sigma \sigma$	Potent.	Polarographic		
				$\Delta E_{1/2}$, mV	$E_{1/2}$, V, relative to s.c.e.	$\Delta E_{1/2}$ V	α
1	2	3	4	5	6	7	8
1	H	4.20	0.00	0	-2.13	0	0.644
2	4-F	4.14	+0.06	-39	-2.15	-0.02	0.610
3	3-F	3.87	+0.34	-60	-2.02	+0.11	0.580
4	2-F	3.27	+0.93	-11	-2.08	+0.05	0.552
5	4-Cl	4.03	+0.23	-14	-1.94	+0.19	0.610
6	3-Cl	3.81	+0.37	-74	-1.98	+0.15	0.504
7	2-Cl	2.89	+1.28	-47	-1.93	+0.20	0.483
8	2,4-Cl ₂	2.76	+1.51	-121	-1.77	+0.36	0.483
9	4-Br	3.97	+0.23	-7	-1.84	+0.29	0.483
10	3-Br	3.81	+0.39	-30	-1.88	+0.25	0.725
11	2-Br	2.85	+1.35	-56	-1.85	+0.28	0.414

1	2	3	4	5	6	7	8
12	4-C ₂ H ₅	4.35	-0.15	+8	-2.22	-0.09	0.580
13	2-C ₂ H ₅	3.79	+0.41	+29	-2.20	-0.07	0.580
14	4-CH ₃	4.37	-0.17	+1	-2.23	-0.10	0.610
15	3-CH ₃	4.25	-0.07	+37	-2.17	-0.04	0.644
16	4-CH ₃ O	4.50	-0.27	+23	-2.31	-0.18	0.504
17	4-NH ₂	4.92	-0.66	+101	-2.48	-0.35	0.483
18	3-NH ₂	4.74	-0.16	+60	-2.24	-0.11	0.483
19	2-NH ₂	4.97	-	+10	-2.28	-0.15	0.483
20	4-OH	4.54	-0.36	+67	-2.17	-0.04	0.580
21	3-OH	4.08	-0.00	+39	-2.17	-0.04	0.610
22	2-OH	2.99	+1.22	-235	-1.98	+0.15	0.414
23	2,4-(OH) ₂	3.29	+0.86	-140	-2.03	+0.10	0.446
24	3,4-(OH) ₂	4.48	-0.36	+93	-2.34	-0.21	0.400
25	2,3,4-(OH) ₃	-	+0.86	-155	-2.01	+0.12	0.464
26	3,4,5-(OH) ₃	4.40	-0.36	-	-2.29	-0.16	0.387
27	3,5-Cl ₂ -2,4- -(OH) ₂	-	+1.60	-346	-	-	-
28	4-NO ₂	3.40	+0.78	-144	-	-	-
29	3-NO ₂	3.46	+0.71	-139	-	-	-
30	2-NO ₂	2.20	+1.99	-169	-	-	-
31	2,4-(NO ₂) ₂	1.43	+2.77	-265	-	-	-
32	3,5-(NO ₂) ₂	2.80	+1.42	-215	-	-	-
33	2-Cl-3-NO ₂	2.06	+1.99	-198	-	-	-
34	2-Cl-4-NO ₂	2.00	+2.06	-188	-	-	-
35	2-Cl-5-NO ₂	2.21	+1.99	-183	-	-	-

A comparison of half-neutralization potentials of substituted benzoic acids in the DMSO medium to σ -constants of substituents demonstrated that three types of dependences

△ $E_{1/2}$ (potentiometric) vs. σ take place (Fig. 1a). One dependence corresponds to benzoic acids containing only m- and p-substituents, the second - to acids containing only o-substituents or o-substituents together with m- and p-substituents, and the third - to acids containing an oxygroup in o-position. The hypothesis about a separate dependence for o-oxy-substituted acids is supported by a high correla-

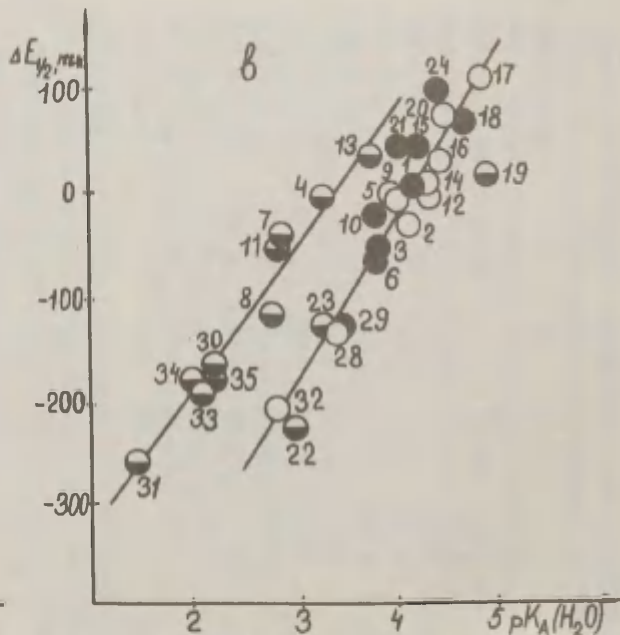
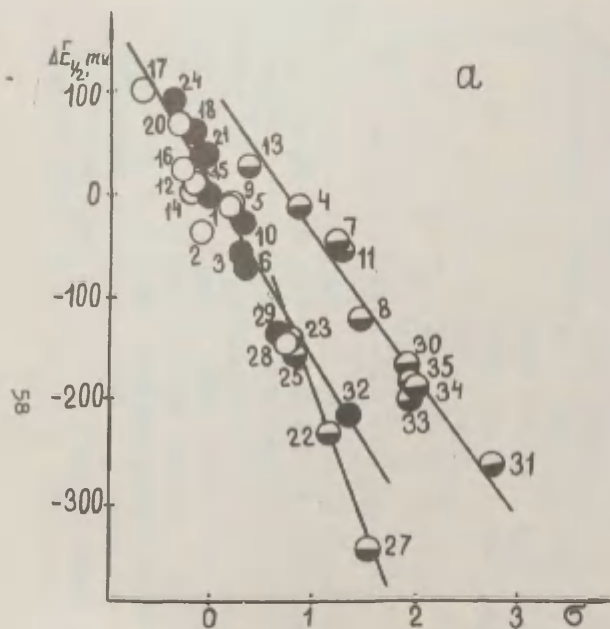


Fig. 1. Half-neutralization potentials of benzoic acids as functions of
a) σ -constants of substituents, b) $pK_A(H_2O)$.

●, m-substituted, ○, n-substituted, ◐, o-substituted acids. Numbers at the points correspond to the numbers of compounds in Table 1.

tion coefficient ($r = 0.997$).

Comparison of half-neutralization potentials of benzoic acids with the exponents of dissociation constants of acids in water also demonstrated the existence of separate dependences: one for m- and p-substituted acids and another for acids containing o-substituents, respectively (Fig.1b). As can be seen from Fig.1b, o-substituted acids behave as weaker acids in comparison with m- and p-substituted ones, characterized in aqueous solutions by the same values of $pK_A(H_2O)$. Just as in the case of comparison with σ -constants of substituents, o-substituted acids are an exception. Unfortunately, the values of $pK_A(H_2O)$ are not known for two out of four o-substituted acids, so that a correlation equation for these acids could not be derived. 2-Aminobenzoic acid, which acts as a stronger acid than would follow from the corresponding value of $pK_A(H_2O)$, exhibits an anomalous behavior. Presumably, by analogy to the case of 2-oxy-substituted acids, this is due to the additional stabilization of anions, caused by the intramolecular hydrogen bond.

The results of potentiometric investigation of benzoic acids in DMSO perfectly agree with the earlier reported potentiometric behavior of these acids in the media of various non-aqueous solvents². Equations, characterizing the dependences of half-neutralization potentials of benzoic acids on the values of σ -constants and $pK_A(H_2O)$, were obtained by the least-squares method. These equations as well as correlation coefficients (r) and standard deviations (s), are presented in Table 2.

Table 2

Correlation Equations for Half-neutralization Potentials of Benzoic Acids as Functions of σ -Constants and $pK_A(H_2O)$

No. Acid	n	Equation	r	s, mV
1 2	3	4	5	6
1 m- and p-substituted	19	$\Delta E_{1/2} = -164.3\sigma$	0.957	25

1	2	3	4	5	6
2	o-substituted	10	$\Delta E_{1/2} = -138.8 \Sigma \sigma + 105$	0.980	20
3	o-oxy-substituted	4	$\Delta E_{1/2} = -266.2 \Sigma \sigma + 83$	0.997	9
4	m- and p-substituted	19	$\Delta E_{1/2} = 155.7 pK - 652$	0.946	28
5	o-substituted	10	$\Delta E_{1/2} = 134.4 pK - 463$	0.981	20

The data of Table 2 indicate that, similarly to other non-aqueous solvents, DMSO exerts a higher differentiating action on m- and p-substituted acids than on those containing o-substituents. However, the differentiating action of DMSO is maximum with respect to 2-OH-substituted acids.

Comparison of differentiating effects of DMSO and other non-aqueous solvents on the strength of benzoic acids demonstrates that DMSO produces the effect as high as that for acetonitrile and dimethylformamide^{1,2,4}. Fig.2 plots polarographic halfwave potentials as a function of σ -constants of substituents, and Fig.3 as a function of $pK_A(H_2O)$. We can see from these plots that halfwave potentials $E_{1/2}$ of benzoic acids and σ -constants of substituents, on one hand, and $pK_A(H_2O)$, on the other hand, are related by linear relationships.

Correlation equations were obtained for the dependence of polarographic halfwave potentials on σ -constants of substituents and $pK_A(H_2O)$. Correlation coefficients for the equations, corresponding to m- and p-substituted acids proved to be low (0.892 and 0.874, respectively). At the same time the equations derived separately for m-substituted and for p-substituted acids are characterized by higher values of correlation coefficients, presented in Table 3. This enables to hypothesize that m- and p-substituted acids form two separate reaction subseries.

o-Substituted acids, containing m- and p-substituents fall in the same class of dependences with o-substituted

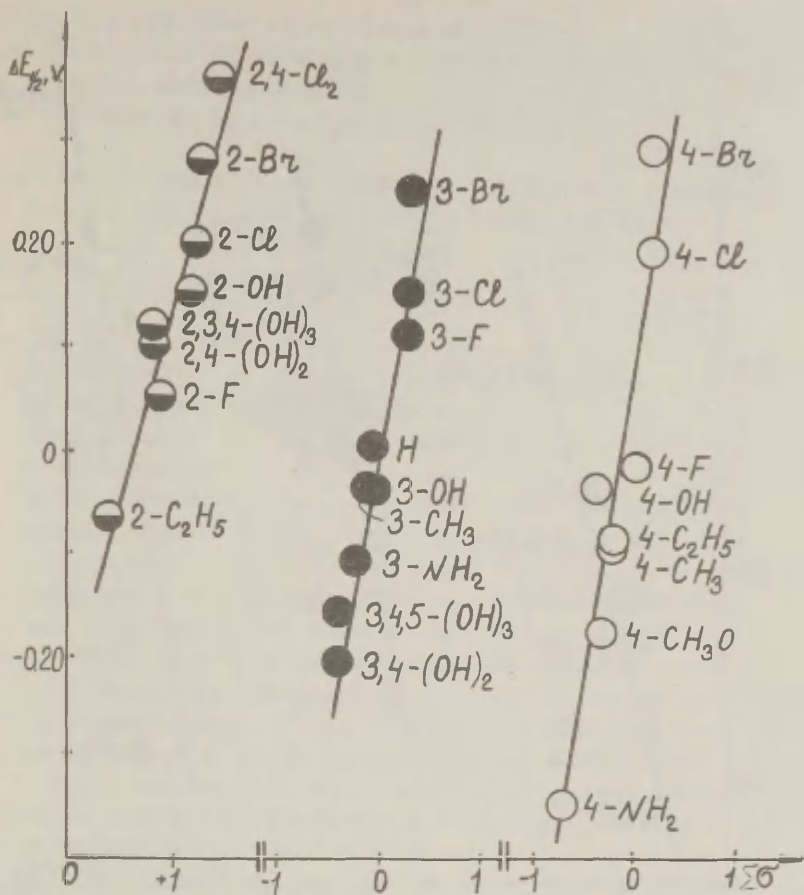


Fig.2. Halfwave potentials of benzoic acids as function of σ -constants of substituents. For symbols see Fig. 1.

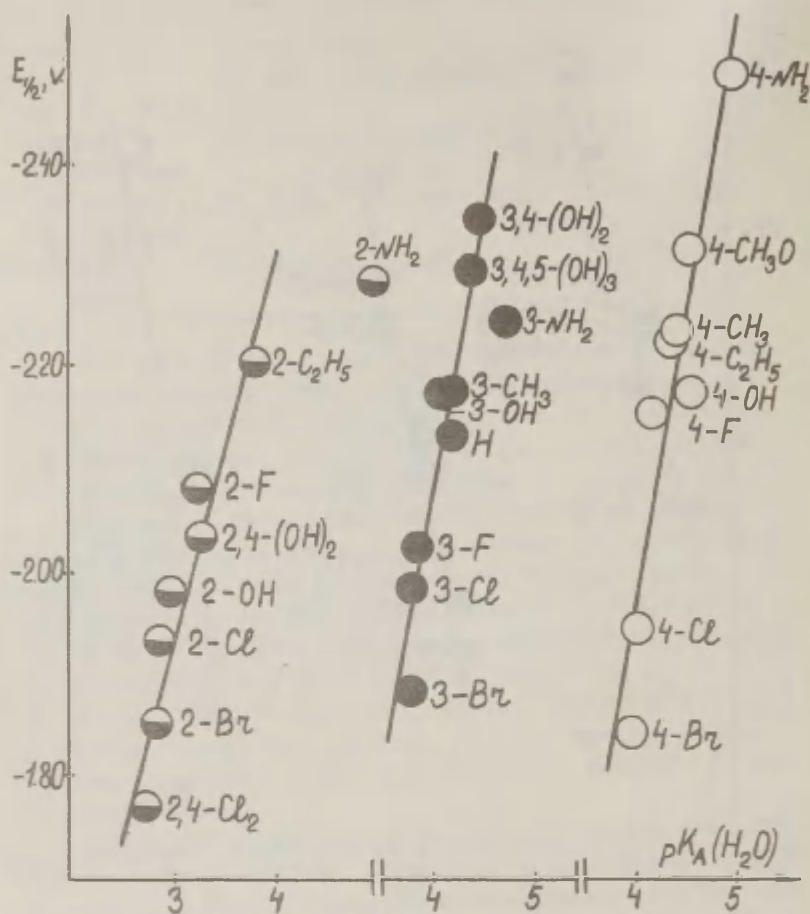


Fig.3. Halfwave potentials of benzoic acids as functions of $pK_A(H_2O)$.

For symbols see Fig. 1.

acids; m-substituted acids, containing also p-substituents, fall in the same class with m-substituted acids. The value of $E_{1/2}$ for m-aminobenzoic acid deviates from the correlation straight line $E_{1/2} = f(pK_A)$ by more than 2s (Fig.3).

Table 3

Correlation Equations for Dependence of Halfwave Potentials of Benzoic Acids' Reduction on σ -Constants and $pK_A(H_2O)$

No.	Acid	n	Equation	r	s, V
1	2	3	4	5	6
1	m-substituted	9	$\Delta E_{1/2} = 0.585\sigma$	0.947	0.05
2	p-substituted	8	$\Delta E_{1/2} = 0.604 \sigma$	0.914	0.09
3	o-substituted	8	$\Delta E_{1/2} = 0.368\sigma - 0.24$	0.957	0.04
4	m-substituted	8	$E_{1/2} = -0.565pK + 0.20$	0.957	0.05
5	p-substituted	8	$E_{1/2} = -0.569pK + 0.43$	0.919	0.09
6	o-substituted	7	$E_{1/2} = -0.379pK - 0.79$	0.946	0.05

For this reason the corresponding equation for m-substituted acids in Table 3 was derived neglecting this acid. Presumably, this is due to the effect of 'zwitter-ion' formation in the aqueous medium. Just as it did in the potentiometric investigation, o-aminobenzoic acid also displays anomalous behaviour in the polarographic investigation.

Fig.3 demonstrates that o-substituted benzoic acids, if judged from the standpoint of polarographic behavior, are weaker acids in comparison with m- and p-substituted acids, characterized by the same values of $pK_A(H_2O)$ in aqueous solutions. This is in good agreement with the described above potentiometric behavior of these acids, and at the same time differs significantly from the potentiometric behavior in the case of acids containing an oxygroup in the o-position. The polarographic halfwave potentials for these acids fall on the straight line drawn for o-substituted benzoic acids. The conditions of the polarographic investigation of acids differ from those of the potentiometric investigation. It appears that interaction between I^- and OH-substituents affects polarographic measurements in

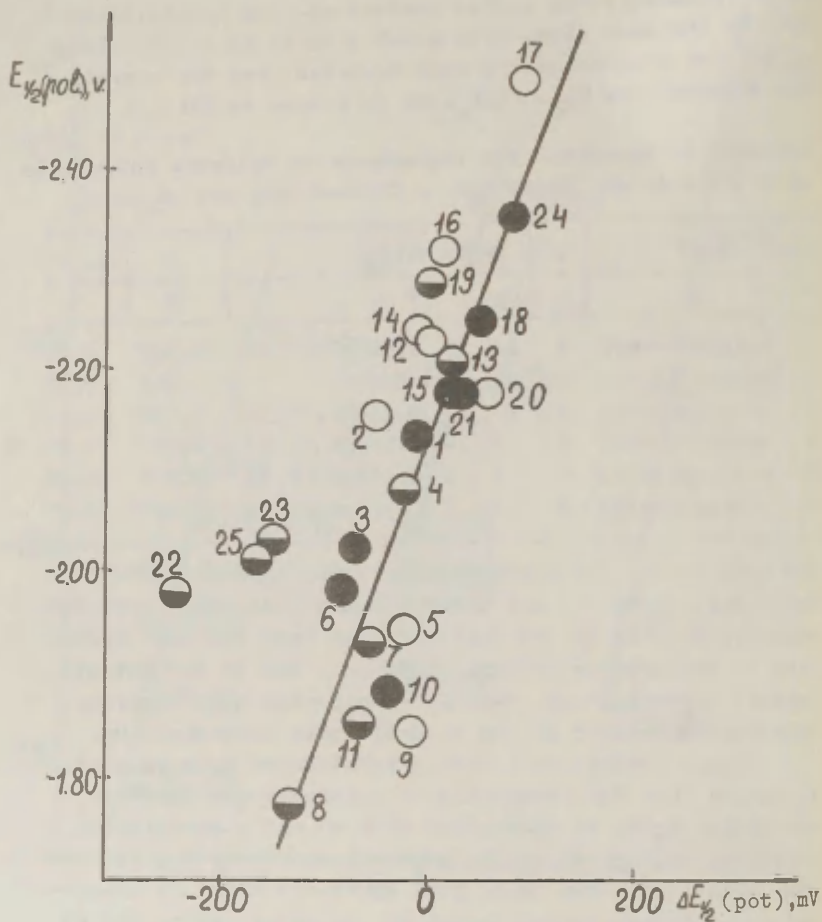


Fig.4. $E_{1/2}$ of polarographic reduction as function of $E_{1/2}$ of potentiometric titration of benzoic acids in the DMSO medium.

Symbols identical to those of Fig.1.

sufficiently concentrated (0.05 N) background solutions of $(C_2H_5)_4NJ$, which results in breaking the intramolecular hydrogen bond.

Comparison of half-neutralization potentials to the halfwave potentials of benzoic acids' reduction is shown in Fig.4. Correlation coefficient for these data is only 0.865. The approximate character of correlation may be explained by differences in conditions under which measurement of polarographic and potentiometric values of $E_{1/2}$ is conducted, and in particular by the influence of the background electrolyte, water admixtures, as well as by variability of the value of α (charge transfer coefficients) for various acids.

A feature that must be emphasized in the comparison between the polarographic and potentiometric behaviour of benzoic acids is a higher differentiating effect of DMSO on $E_{1/2}$ (polar) than on $E_{1/2}$ (potent). For example, the difference between $E_{1/2}$ (potent) of o-ethylbenzoic and 2,4-dichlorobenzoic acids is 150 mV, and that for $E_{1/2}$ (polar) is 430 mV.

REFERENCES

1. L.N.Bykova and S.I.Petrov, Usp.Khim., 32, 1631, (1970).
2. L.N.Bykova, S.I.Petrov, V.D.Ardashnikova, and E.S.Rubtsova, ZhOKh, 40, 2301 (1970).
3. L.N.Bykova and S.I.Petrov, Reakts.sposobn.organ.soedin., 7, issue 2, 403 (1970).
4. I.M.Kolthoff and M.K.Chantooni, J.Amer.Chem.Soc., 93, 3843 (1971).
5. G.M.Galpern, Ya.A.Gurvich, and N.R.Kryuchkova, ZhACh, 25, 1819 (1970).
6. T.Jasinski and A.Stefanik, Chem.Analit.(Polska), 10 211 (1968).
7. R.Morales, Anal.Chim.Acta, 48, 309 (1969).
8. K.Kalfus and M.Vecera, Coll.Czech.Chem.Comm., 37, 3607 2333 (1972).
9. N.A.Baranov, N.A.Vlasov, and L.P.Potekhina, ZhAKh, 27, (1972).
10. G.Kortüm, W.Vogel, and K.Andrussov, Dissociation Constants

for Organic Acids in Aqueous Solution, Butterworths, London, 1961.

11. Yu.A.Zhdanov and V.I.Minkin, Correlation Analysis in Organic Chemistry, Rostov University Publishing House, 1966, p.85.

THE POLYLINEARITY PRINCIPLE AND RELATION-
SHIPS BETWEEN STRUCTURE AND PROPERTIES OF
ORGANOPHOSPHORUS COMPOUNDS

1. Analysis of σ^p Constants. Inductive
and Steric Contributions

B.I. Istomin, V.A. Baransky, A.D. Lobanov,
E.F. Grechkin

Chemistry Department, The State University,
Irkutsk, 664003, USSR

Received April 20, 1975

Constants σ^p for various alkyls and those elect-
ronegative substituents which do not have α, β - π -
-bonds or the α - lone-pair electrons are shown to
consist of the inductive and steric terms. These ones
are described adequately by the mathematical models
which have been accepted for those interaction types
in the correlational analysis. The models are based
on the use of substituent constants σ^x and E_s . Thus,
the special scales of constants are not required to be
introduced for the case when above substituents are at-
tached to the phosphorus atom.

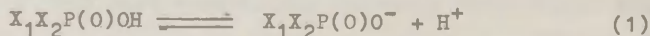
The present series purpose is to attempt successive
application of axiomatics and methods of the correla-
tion analysis (mainly, the successive use of PPL¹⁻³) to
the analysis of relationships between various properties
of organophosphorus compounds and their structure. In orga-
nophosphorus chemistry, the correlation analysis ideas ha-
ve been widely utilized for a long time (e.g., see Refs.4-
-17). However, different correlation equations as well as
different substituent constant scales have been used by
various authors.

The greatest number of the organophosphorus series have

been described¹² in the framework of Hammett-Kabachnick equation. It makes use of the special scale⁵, σ^p , of constants for the substituents attached to phosphorus atom which is out of a reaction center. The scale is assumed to reflect the unique character of a P-atom. On the other hand, constants σ^p , as well as σ , σ^- , or σ^+ ones (e.g., see Refs. 3, 10, 11, 18, 20) appear to consist of the contributions of different interactions between the substituent and P-atom. The attempts to analyse the nature of σ^p -constants have been undertaken by Palm²⁰ and Charton¹¹. In 1969, separation of constants σ^p into inductive σ_I^p and conjugative σ_R^p were made²¹. It allows to describe satisfactorily some reaction series (see Ref. 12) containing P-atom in a reaction center by two-parameter equations. However, the thorough analysis of the σ_I^p and σ_R^p values for a number of substituents (mainly, CH_2X , CHX_2 , and CX_3 where X is a halogen) shows inadequacy of the separation procedure²¹. Therefore, the additivity principle²² as well as PPL¹⁻³, are utilized here in case of ionization of acids $\text{X}_1\text{X}_2\text{P}(\text{O})\text{OH}$ where X_1 and X_2 are any alkyl or/and electronegative substituents. The latter was used as the standard series in evaluating the σ^p constant numerical values. The aim of the present paper is to analyze in depth the nature of σ^p constants and to separate them into the components.

A. Application of the Principle of Additivity of Different Types of Interactions and PPL to pK_a of Acids $\text{X}_1\text{X}_2\text{P}(\text{O})\text{OH}$

From point of view of the additivity²² of different interactions between structural units in an organic molecule, the change, $\Delta\Delta F^0$, of free energy, ΔF^0 , of ionization process



at the substitution of X_1 and X_2 for any standard substituents X_0 is regarded to be as follows:

$$\begin{aligned}\Delta\Delta F^0 &= \Delta F^0(1,2) - \Delta F^0(0,0) = \Delta F_f^0 - \Delta F_{in}^0 = \\ &= \Delta\Delta F_{ind}^0 + \Delta\Delta F_{st}^0 + \Delta\Delta F_R^0\end{aligned}\quad (2)$$

where $\Delta F^0(1,2)$ and $\Delta F^0(0,0)$ are free energies of ionization of $X_1X_2P(O)OH$ and $X_0X_0P(O)OH$; ΔF_f^0 and ΔF_{in}^0 are free energy changes for final and initial states of system at the substitution of X_1 and X_2 for X_0 ; $\Delta\Delta F_{ind}^0 = \Delta F_{ind}^0(1,2) - \Delta F_{ind}^0(0,0)$, $\Delta\Delta F_{st}^0 = \Delta F_{st}^0(1,2) - \Delta F_{st}^0(0,0)$, and $\Delta\Delta F_R^0 = \Delta F_R^0(1,2) - \Delta F_R^0(0,0)$ are relative contributions of inductive, steric and conjugative interactions between the substituents and the reaction center in its final ($P(O)O^-$) and initial ($P(O)OH$) states as well as between X_1 and X_2 themselves. It is convenient to choose as X_0 the substituent CH_3 which is the origin for the scales of constants σ^* and $E_s(E_B^0)$.

According to PPL¹⁻³ and the concept of homogeneity of the inductive interaction, the contribution $\Delta\Delta F_{ind}^0$ should be represented as follows:

$$\begin{aligned}\Delta\Delta F_{ind}^0 &= \Delta F_{ind}^0(1,2) = -\alpha^* \Delta\sigma^* \sum_1 \sigma_1^* - \\ &- \alpha^* \Delta Z^* \sigma_1^* \sigma_2^*\end{aligned}\quad (3)$$

α^* is the inductive interaction type constant; $\Delta\sigma^* = \sigma^*/CH_3P(O)OH/ - \sigma^*/CH_3P(O)O^-/$; $\Delta Z^* = Z^*\{P(O)OH\} - Z^*\{P(O)O^-\}$; $\sigma^*/CH_3P(O)OH/$ and $\sigma^*/CH_3P(O)O^-/$ are the constants for the initial and final states of the reaction center; $Z^*\{P(O)OH\}$ and $Z^*\{P(O)O^-\}$ are the factors of attenuation of inductive interaction between X_1 and X_2 by P-atom in the acid and its anion; σ_1^* and σ_2^* are the polar constants for X_1 and X_2 ; and $i = 1, 2$.

The first term of Eq.(3) is the contribution of the interaction of the substituents with the reaction center; the second one is the contribution of the interaction between X_1 and X_2 through P-atom as an insulating bridge.

Assuming tetrahedral symmetry (see Refs.25-27) for $X_1X_2P(O)OH$ and its anion, it follows that the steric interaction contribution $\Delta\Delta F_{st}^0$ should be described as follows:

$$\begin{aligned}\Delta\Delta F_{st}^{\circ} &= \Delta F_{st}^{\circ}(1,2) = \Delta F_{st,f}^{\circ} - \Delta F_{st,in}^{\circ} = \\ &= -\Delta a \sum_1 E_{s,i}\end{aligned}\quad (4)$$

where $\Delta F_{st,f}^{\circ}$ and $\Delta F_{st,in}^{\circ}$ are the contributions of steric interactions in the final and initial states of the system in question; $\Delta a = a_{in} - a_f$; a_{in} and a_f are the susceptibilities to steric interactions of the substituents with the reaction center in its initial and final states; E_s is a steric constant; $i = 1, 2$.

Eq.(4) indicates that in the acid and its anion steric interactions between X_1 and X_2 are close or approximately equal to each other. If the above assumption had been incorrect, Eq.(4) should contain the term $\Delta S = S_f - S_{in}$ where S_f and S_{in} are relative contributions of steric interactions between X_1 and X_2 in the anion and the acid. The interaction described by $E_s(E_s^{\circ})$ -constants is inhomogeneous one²⁸. However, one may assume $\Delta S \simeq \Delta b E_{s,1} E_{s,2}$ where Δb is a susceptibility factor.

The substitution of Eqs. (2) and (4) to Eq.(2) gives the following equation

$$\begin{aligned}pK_a(X_1X_2P(O)OH) &= pK_a((CH_3)_2P(O)OH) - \rho^{\pm} \sum_1 \sigma_1^{\pm} - \\ &- \gamma \sigma_1^{\pm} \sigma_2^{\pm} - \delta \sum_1 E_{s,i} - R\end{aligned}\quad (5)$$

where $\rho^{\pm} = \alpha^{\pm} \Delta \sigma^{\pm} / 2.303RT$, $\gamma = \alpha^{\pm} \Delta z^{\pm} / 2.303RT$, $\delta = \Delta a / 2.303RT$, and $R = -\Delta\Delta F_R^{\circ} / 2.303RT$.

Hence, pK_a -values for the acids of interest will be described satisfactorily by Eq.(5), if all the postulates used above are correct.

B. The σ^{ϕ} -Constants for the Substituents

Without α , β - π - Bonds and/or the
Lone-pair Electrons

Ionization (H_2O , $25^{\circ}C$) of acids $X_1X_2P(O)OH$ had been used^{5,12} as the standard series for the evaluating of numerical σ^{ϕ} -values, and substituent H has been chosen as the standard one, i.e.

$$pK_a(X_1X_2P(O)OH) = pK_a(H_2P(O)OH) - \sum_1 \sigma_1^{\phi} \quad (6)$$

since the condition $\rho^b \approx 1.0$ had been accepted⁵.

According to Eqs. (5) and (6), the σ^b -constants for the substituents, not conjugated* with the reaction center, should be described by the equation

$$\sigma_X^b = \sigma_{CH_3}^b + \rho^* \sigma_X^* + 0.5 \rho \sigma_X^{*2} + \delta E_{B,X} \quad (7)$$

Table 1
The Results of Treatment of σ^b -Values with
the Aid of Eq.(8)

No	a ₀	a ₁	a ₂	a ₃	n	R	S ₀
1	-0.908 ±0.080	1.087 ±0.130	-0.177 ±0.044	0.167 ±0.075	14 ^a	0.982	0.11
2	-0.938 ±0.036	1.151 ±0.076	-0.199 ±0.030	0.149 ±0.034	25 ^b	0.987	0.11
3	-1.052 ±0.035	1.308 ±0.091	-0.270 ±0.034	---	25 ^c	0.975	0.15
4	-0.818 ±0.055	0.668 ±0.043	---	0.271 ±0.049	25 ^d	0.985	0.19
5	-0.943 ±0.040	1.160 ±0.060	-0.191 ±0.025	0.126 ±0.034	24 ^e	0.992	0.09

^aOnly for the electronegative substituents listed in Table

2. ^bFor all the substituents from Table 2. Deviations $\Delta = \sigma_{exp}^b - \sigma_{calc}^b$ are in Table 2. The paired correlation co-

efficients of σ^b -values with σ^* , σ^{*2} and E_B are respectively 0.897, 0.694 and 0.186. ^cWithout the variable E_B .

^dWithout variable σ^{*2} . ^eThe steric constants E_B^0 are here used instead of the constants E_B . Without the point for H, it deviates significantly.

*As well as for the substituents whose conjugation with the reaction center in its final and initial states is nearly the same.

Table 2

The Deviations, $\Delta = \sigma_{\text{exp}}^b - \sigma_{\text{calc}}^b$, of the Original¹² σ^b - Constants from Those Calculated According to Correlation 2 of Table 1 for the Substituents Which Have No α, β - π - Bonds and/or α - Lone-Pair Electrons

Substituent	Δ	Substituent	Δ
H	+0.238	CH ₂ I	+0.049
CH ₃	-0.022	CHCl ₂	-0.046
C ₂ H ₅	-0.342	CCl ₃	-0.114
n-C ₃ H ₇	-0.053	CF ₃	+0.147
i-C ₃ H ₇	-0.066	CH ₂ OH	-0.127
n-C ₄ H ₉	-0.071	CH ₂ OC ₆ H ₅	-0.047
i-C ₄ H ₉	-0.077	CH ₂ C ₆ H ₅	+0.067
s-C ₄ H ₉	-0.003	(CH ₂) ₂ C ₆ H ₅	-0.157
t-C ₄ H ₉	-0.020	(CH ₂) ₂ Br	-0.051
CH ₂ C(CH ₃) ₃	-0.053	(CH ₂) ₂ OC ₂ H ₅	+0.112
C ₂ H ₅ (CH ₃) ₂ C	+0.230	(CH ₂) ₂ CN	-0.002
CH ₂ Cl	-0.065	(CH ₂) ₃ Cl	+0.143
CH ₂ Br	+0.023		

In Table 1 there are the results of treatment according to Eq.(8) of the original¹² σ^b -values for 25 substituents (see Table 2) which do not have α, β - π - bonds and/or α - lone-pair electrons. The computing has been

$$\sigma_X^b = a_0 + a_1 \sigma_X^{\pi} + a_2 \sigma_X^{\pi^2} + a_3 E_{\text{S},X} \quad (8)$$

fulfilled on the basis of the multiple regression analysis program REGRAN-1 with the computer BESM-4. For statistical tests, the risk level of 5% anywhere are used. Any σ^b value is assumed to be the chance result of an individual measuring. The numerical values of constants σ^{π} and $E_{\text{S}}(E_{\text{S}}^0)$ taken from a compilations^{23,29,30}. Adopting $Z_{\text{C}}^{\pi} = 0.35$ (see Ref.23), the σ^{π} constants for (CH₂)_nX at n = 2,3 are estimated here.

The σ^b -constants of 14 electronegative substituents (see Table 2) are described satisfactorily (see Table 1;

Corr.1) by Eq.(8). The calculated value of a_0 coincides satisfactorily with σ^b -constant for CH_3 , as it is required by Eq.(7). The inclusion of alkyls and H leads to the correlation (see Table 1, Corr.2) whose coefficients a_0 -- a_3 do not differ significantly from those evaluated for the electronegative substituents only. The exclusion² of either the variable σ^{*2} or variable E_s worsens the correlation (see Table 1, Corrs.3,4)

According to Table 2, the maximum but insignificant deviations from Corr.2 of Table 1 are for the substituents H and $\text{C}(\text{CH}_3)_2\text{C}_2\text{H}_5$. The deviation for the latter appears to be related with the unreliable E_s -estimate (see Ref.29) used here. The best one from the correlations of Table 2 is Corr. 5 based on the E_s^0 -scale of steric constants. The point for H deviates significantly from that hypersurface although some grounds for its exclusion are lacking a priori. Therefore, Corr.2 of Table 1 is preferred here in spite of its slightly poorer indices.

According to Refs. 31,32, the real accuracy of a measuring of pK_a -values for organophosphorus acids is ± 0.4 - ± 0.5 units of pK_a . Therefore, on the basis of the law³³ of error accumulation, one can estimate the uncertainty of σ^b -quantities evaluated from pK_a -values to be ± 0.07 units of σ^b -scale or even more. Hence, Corrs.1,2 of Table 1 are not so far from adequacy, and one must conclude the σ^b -constants for all the substituents here considered to consist mainly of the inductive and steric components. Also the alkyls and electronegative substituents give the united totality ad hoc.

When the constants σ^b had been splitted²¹ into the inductive, σ_I^b , and resonance, σ_R^b , terms, non-zero σ_R^b -

²²The inclusion of the contribution $\Delta b E_{s,1} E_{s,2}$ (see above) in Eq.(8) has no real influence on the correlation indices. Hence, the steric interactions between X_1 and X_2 in the acid and its anion appear to be equal.

σ -values²² were ascribed (see refs.21,22) to all the electro-negative substituents satisfying Corr. 2 of Table 1. The σ_R^δ -quantities were evaluated²¹ as $\sigma_R^\delta = \sigma^\delta - \sigma_I^\delta$ where $\sigma_I^\delta = -0.96 + 1.99\sigma^\delta$. Having in mind Correlation 2 of Table 1, one will expect a good correlation between the resonance constants σ_R^δ and the constants σ^δ and E_s for all the substituents collected in Table 2. Such a correlation, indeed, exists

$$\sigma_R^\delta = (+0.050 \pm 0.042) + (-1.087 \pm 0.067)\sigma^\delta + (-0.012 \pm 0.022)\sigma^{\delta 2} + (0.204 \pm 0.038)E_s \quad (9)$$

* $n = 24^{***}$ $R = 0.9924$ $S_0 = 0.14$

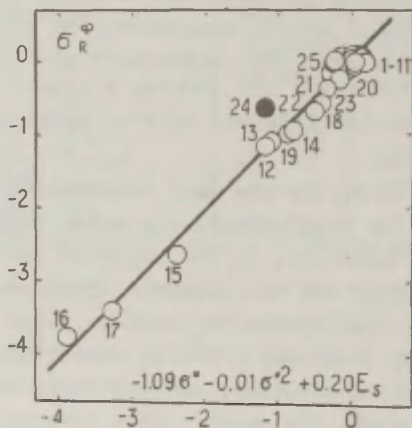


Fig.1 Linear relationship between the constants σ_R^δ and the values of $(-1.09\sigma^\delta - 0.01\sigma^{\delta 2} + 0.20E_s)$ for substituents listed in Table 2.

²²E.g., for CHCl_2 , CCl_3 and CF_3 , the σ_R^δ -constants are¹² -2.63, -3.9 and -3.3 respectively.

^{***}Without the point for $\text{CH}_2\text{CH}_2\text{CN}$ which deviates significantly for unknown reasons.

Fig. 1 illustrates Corr.(9). Hence, for electronegative substituents listed in Table 2, the resonance term σ_R^p is, mainly, the sum of inductive and steric components, i.e. it has no concern in reality to the resonance interaction.

Subtraction of Corr.2 of Table 1 from the equation $\sigma_I^p = -0.96 + 1.99\sigma^{\pm}$ leads to the following equation

$$\sigma_R^p = (+0.022 \pm 0.036) + (-0.84 \pm 0.076) \sigma^{\pm} + (-0.199 \pm 0.030) \sigma^{\pm 2} + (0.149 \pm 0.034) E_s \quad (10)$$

All its parameters, but the intercept, differ significantly from the corresponding parameters of Corr.(9). Such distinction is the result of the biasing of the estimates of the parameters relative their true values. The biasing arises by reason of non-orthogonality[±] of the values σ^{\pm} and $\sigma^{\pm 2}$ for here considered substituents. Therefore, one must accept with care the estimates of the parameters a_1 and a_2 for all the correlations of Table 1 as well as for Corr. (9). At the same time, the reality of corresponding terms (contributions) is clearly demonstrated by the deterioration of correlation (S_0 increases and R decreases) observed in the case when anyone of Eq.(8) variables has been ruled out (e.g., see Table 1).

One can also note great intercorrelation between constants σ_I^p and σ_R^p for the substituents collected in Table 2. Thus, as a rule, the parameters of the corresponding two-parameter correlations rather should be biased.

C. The Hyperconjugation Problem

If hyperconjugation interaction of the reaction center in its final state (e.g., in the anion) with the α -C-H-bonds of the substituents X_1 and X_2 differs significantly from the same one for the reaction center in the initial state of ionization process (e.g., in the acid), one will find a statistically significant contribution of hypercon-

[±]The intercorrelation between σ^{\pm} and $\sigma^{\pm 2}$ is rather strong; $r = 0.872$.

jugative interaction in Eq.(8).

In such a case, the contempt for the hyperconjugation may be assumed to be the possible reason of distinction between the standard error S_0 for Corr.2 of Table 1 and the error of the evaluating of σ^p -constants (± 0.07 ; vide supra). Utilizing the α -hydrogen-atom model³⁶⁻³⁸ for the hyperconjugation interaction, the correlation (11) have been obtained.

$$\sigma^p = (-1.041 \pm 0.050) + (1.207 \pm 0.070) \sigma^{\pi} + \\ + (-0.232 \pm 0.029) \sigma^{\pi 2} + (0.158 \pm 0.030) E_s + \\ + (-0.079 \pm 0.029) \Delta n \quad (11)$$

$$n = 25 \quad R = 0.9904 \quad S_0 = 0.09$$

where $\Delta n = n - 3$; n is the number of α -H-atoms in the substituents.

The maximum deviation from the hypersurface of Corr.2 of Table 1 is observed for the substituents H and $C(CH_3)_2C_2H_5$. When those are ruled out, the correlation becomes as follows

$$\sigma^p = (-0.963 \pm 0.033) + (1.173 \pm 0.059) \sigma^{\pi} + \\ + (-0.203 \pm 0.023) \sigma^{\pi 2} + (0.153 \pm 0.038) E_s \quad (12)$$

$$n = 23 \quad R = 0.9920 \quad S_0 = 0.08$$

This correlation is adequate to Correl. (11) and describes the σ^p -constants with the accuracy practically equal to the accuracy of the evaluating of the original σ^p -quantities from pK_a -values.

Thus, the addition of the hyperconjugative term to Eq. (8) has no justification from the point of view of statistics, since it decreases the deviations for two points only. Hence, if hyperconjugative interaction at the expense of α -C-H-bonds in the substituent actually exists, it should be the same both for the initial and final states of ionization process, e.g., it has no real influence on pK_a values of the acids $X_1X_2P(O)OH$. Ruling out the substituents H and $C(CH_3)_2C_2H_5$, one, indeed, has at once the

insignificance of hyperconjugative interaction described by α -H-model:

$$\begin{aligned} \sigma^{\beta} = & (-0.975 \pm 0.051) + (1.180 \pm 0.064) \sigma^{\pi} + (-0.207 \pm \\ & \pm 0.028) \sigma^{\pi 2} + (0.158 \pm 0.043) E_{\beta} + (-0.013 \pm 0.041) \Delta n \quad (11a) \\ n = 23 \quad R = 0.992 \quad S_0 = 0.09 \end{aligned}$$

Thus, the contempt of hyperconjugative effect is not the reason for the maximum deviation of points for H and $C(CH_3)_2C_2H_5$ from Corr.2 of Table 1. But we are unable to account for the deviation of the former point unlike that of the latter.

D. The Problem of Non-orthogonality of Variables σ^{π} and $\sigma^{\pi 2}$ of Eq.(8)

The Eq.(8) variables σ^{π} and $\sigma^{\pi 2}$ are considerably non-orthogonal. Hence, the estimates of parameters a_1 and a_2 for Corrs.1 and 2 of Table 1 can be biased³⁴ with respect to their true values. To verify the possibility of the biasing, the model calculations have been realized. According to equation³⁵

$$Y = -2.00 + 1.70 \sigma^{\pi} - 0.10 \sigma^{\pi 2} + 0.50 E_{\beta} \quad (13)$$

25 Y-values accurate to ± 0.01 have been calculated to make use of the constants σ^{π} and E_{β} for the substituents listed in Table 2. Then those have been treated by least-squares technique to evaluate the parameters a_0 -- a_3 for Eq.(8). The results are presented in Table 3.

As it is seen, the estimates of the parameters of Corrs. 1 and 2 of Table 3 do not differ significantly. Moreover, a_3 estimate for Corr.2 does not differ from its true value. However, the estimates for the parameters a_0 , a_1 and a_2 differ significantly from their true (expected) values. Hence, the high non-orthogonality of the variables σ^{π} and $\sigma^{\pi 2}$ causes the effect of the 'pumping' of the absolute values of

³⁵The absolute values of Eq.(13) parameters are quite accidental ones; their signs are put in agreement with those for Corrs. of Table 1.

Table 3

The Results of Treatment, According to Eq.(8), of the Y-Values Which Have Been Calculated From Eq. (13) for the Substituents Collected in Table 1

No	a_0	a_1	a_2	a_3	R	S_0
1 ^a	-1.859 ± 0.034	1.448 ± 0.049	-0.009 ± 0.012	0.575 ± 0.047	0.998	0.08
2 ^b	-1.942 ± 0.022	1.501 ± 0.036	-0.016 ± 0.012	0.556 ± 0.020	0.999	0.08

^aFor 14 electronegative substituents only. ^bFor all the substituents listed in Table 2.

a_0 and a_1 to a_2 . As the result of the 'pumping', the estimate of a_1 is obtained to be artificially lowered whereas the estimates for a_0 and a_2 are overstated.

One must, therefore, assume that the estimates of parameters a_1 and a_2 for Corrs.1 and 2 of Table 1 also are biased with respect to their true values; the former appears to be slightly understated whereas the latter is somewhat overstated. Because of its comparatively great uncertainty, the a_0 estimate for Corr.2 of Table 1 is in good agreement with its true value. The estimate of parameter a_3 of this correlation is believed to be non-biased.

The non-orthogonality between the scales of the constants describing the capacity of substituents (or solvents) to interact by different types is a general weak point of the multidimensional correlation analysis (i.e., of multiple linear free energy relationship correlations). The most researchers do not usually pay due attention to that. But because of such non-orthogonalities, the absolute values of the parameters evaluated by least-squares routine for corresponding equations lose their initial physical significance. Hence, it is impossible to compare qualitatively such absolute values of parameters within the same correlation as well as with the corresponding parameters of analogous cor-

relations for other processes.

Two ways out of that difficulty, (i) the refusing the handy least-squares technique, and (ii) the preliminary factorization³⁵ of the variables, appears to be possible, both of which are hardly attractive for the correlation analyses. When the latter procedure used widely in the experiment design is accepted, the remainder variables lose their initial significance (physical or quasi-physical). Moreover, this procedure is non-universal i. e., it is impossible to construct in its framework any invariant scale of constants for substituents or solvents. Hence, at present, the only acceptable way out, in our view, is the preliminary construction of different equations making use of some a priori considerations (ideas, concepts, postulates or hypotheses), and the following logical analysis of the parameters of the corresponding correlations in the framework of the significance which has been attributed to those parameters a priori.

R E F E R E N C E S

1. Palm V.A., Reakts.sposobn.organ.soedin., 1, 7 (1964).
2. Palm V.A., in 'Correlation Equations in Organic Chemistry'; (in Russian), Vol.1, pp 3-66, Tartu State University, Tartu, 1962
3. Palm V.A., Foundations of Quantitative Theory of Organic Reactions (in Russian), Khimiya, Leningrad, 1967
4. Jaffe H.H., Freedman L.D, and Doak G.O., J.Amer.Chem.Soc., 75, 2209 (1953)
5. Kabachnik M.I., Proceedings of Academy of Sciences of USSR, 110, 393 (1956)
6. Henderson W.A. and Buckler S.A., J.Amer.Chem.Soc., 82, 5794 (1960)
7. Henderson W.A. and Streuli C.A., J.Amer.Chem.Soc., 82, 5791 (1960)
8. Neymysheva A.A., Palm V.A., Semin G.K., Loshadkin N.A., and Knunyants I.L., J.General Chem. (in Russian), 32,

2255 (1967)

9. Palm V.A., Neymusheva A.A., and Knunyants I.L., Reakts. sposobn.organ.soedin., 4, 38 (1967)
10. Rakshys J.W., Taft R.W., and Sheppard W.A., J.Amer.Chem. Soc., 90, 5236 (1968).
11. Charton M., J.Org.Chem., 34, 1877 (1969)
12. Mastryukova T.A. and Kabachnik M.I., Usp. Khim., (in Russian), 38, 1751 (1969); see also the references cited by those authors.
13. Neymysheva A.A., Palm V.A., Semin G.K., and Knunyants I.L., Chemistry and Applications of Organophosphorus Compounds, (in Russian), Nauka, pp.189-98, Moscow, 1972
14. Mastrukova T.A., Spivak L.L., Grigoreva A.A., Urjunzeva E.K., and Kabachnik M.I., J.General Chem. (in Russian) 41, 1938 (1971)
15. Spivak L.L., Grigoreva A.A., Mast'yukova T.A., and Kabachnik M.I., J.Gen.Chem., (in Russian), 44, 870 (1974)
16. Tsvetkov E.N. and Kabachnik M.I., Progress in Chemistry, (in Russian), 40, 177 (1971).
17. Tsvetkov E.N. and Malevannaya R.A., J.General Chem. (in Russian), 44, 1225 (1974)
18. Zdanov Yu.A. and Minkin V.I., Correlation Analysis in Organic Chemistry (in Russian), Rostov-na-Donu, 1966.
19. Ehrenson S., Brownlee R.T.C., and Taft R.W., Prog.Phys. (1961)
20. Palm V.A., Usp. Khim. (in Russian), 30 1069 1069 (1961)
21. Mastryukova T.A., Chemistry and Applications of Organophosphorus Compounds (in Russian), p. 76 Nauka, Moscow, 1972
22. Taft R.W., Chap.13 in "Steric Effects in Organic Chemistry", Ed.M. Newman (Russian Translation), Moscow, 1960
23. Koppel I.A., Karelson M.M., and Palm V.A., Reakts. sposobn.organ.soedin., 10, 497 (1973).

24. Istomin B.I. and Palm V.A., Reakts. sposobn. organ. soedin., 10, 583 (1973)
25. Van Vazer, The Phosphorus and its Compounds, (Russian Translation), Moscow, 1962
26. Corbridge D.E.C., Topics on Phosphorus, Vol. 6, pp 235-266 (1969)
27. Kirby A.J. and Warren S.G., The Organic Chemistry of Phosphorus, (Russian Translation), Mir, Moscow, 1971
28. Istomin B.I. and Baransky V.A., Org.Reactivity 11, 4(42), 963 (1975)
29. Handbook of Chemist, Vol.3 (in Russian), Khimia, Moscow-Leningrad, 1965
30. Palm V.A. and Talvik T.V., Reakts. sposobn. organ. soedin., 8, 445 (1971)
31. Demchenko P.O. and Yaroshenko N.A., Ukrainian Chem.J. (in Russian), 36, 359 (1972)
32. Guseva N.N., Sklenskaya E.V., and Karapetiants M.Kch., Radiochemistry (in Russian), 16, 273 (1974)
33. Spiridonov V.P. and Lopatkin A.A., The Mathematical Treatment of Physico-Chemical Data, (in Russian), Moscow, University, 1970
34. Ayvazyan S.A., Statistical Investigation of Relationships (in Russian), Metallurgia, Moscow, 1968
35. Okón Ya., The Factor Analysis, (Russian Translation) "Statistika", Moscow, 1964
36. Kreevoy M.M. and Taft R.M., J.Amer.Chem.Soc., 77 5590 (1955)
37. Taft R.W. and Kreevoy M.M., J.Amer.Chem.Soc., 79, 4011 (1957)
38. Kreevoy M.M. and Eyring H., J.Amer.Chem.Soc., 79, 5121 (1957)

THE POLYLINEARITY PRINCIPLE AND RELATION-
SHIPS BETWEEN STRUCTURE AND PROPERTIES OF
ORGANOPHOSPHORUS COMPOUNDS

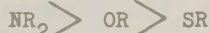
2. Analysis of Constants σ^b . The Reso-
nance Contribution

V.A. Baransky and B.I. Istomin

Chemistry Department, The State University,
Irkutsk, 664003

Received April 20, 1975

The resonance contributions, $\Delta\sigma^b$, are separated from the "phosphorus" substituent constants σ^b for 45 various substituents which have α, β - π -bonds as well as the α -lone-pair electrons. The $\Delta\sigma^b$ value is found to be constant within the same structural type of substituents, it does not depend on R and X for the substituents RO, RS, R₂N and m,p-XC₆H₄. The propensity of the substituents at phosphorus atom to the resonance interaction with that are established to fall progressively in the series



It is in full agreement with generally accepted view on the ability of substituents to go into the resonance interaction

According to Ref.1, the constants σ^b for the substituents which have no α, β - π -bonds as well as the α -lone-pair electrons, are described, almost adequately, by the following equation

$$\begin{aligned} \sigma^b = & (-0.938 \pm 0.036) + (1.151 \pm 0.076) \sigma^{\pi} + \\ & + (0.199 \pm 0.030) \sigma^{\pi 2} + (0.149 \pm 0.034) E_s \end{aligned} \quad (1)$$

$$n = 25 \quad R = 0.987 \quad S_0 = 0.11$$

However, for the substituents which have α, β π -bonds and/or the α -lone-pair electrons, the $\sigma_{\text{calc}}^{\beta}$ values, estimated according to Eq. (1), are more positive, as a rule, than the corresponding "experimental" $\sigma_{\text{exp}}^{\beta}$ = values calculated from pK_a . It should be caused only by the resonance interaction between those substituents and the reaction center. By this mechanism, the substituent "pumps" its electron density to the reaction center, decreasing the acidity of the compounds of standard series. Hence, one can regard the difference $\Delta\sigma^{\beta} = \sigma_{\text{exp}}^{\beta} - \sigma_{\text{calc}}^{\beta}$ as the resonance contribution to the "phosphorus" constant σ^{β} for the substituents in question. In table 1, the quantities $\sigma_{\text{calc}}^{\beta}$ and $\Delta\sigma^{\beta}$ are collected for 45 various substituents which seem to be able to go into the resonance interaction.

The $\Delta\sigma^{\beta}$ -values are positive only for 7 of the substituents. For 6 of them, i.e. for m, p-substituted phenyls, the evaluated $\Delta\sigma^{\beta}$ -values are exceeded completely by the rated uncertainties of the $\sigma_{\text{exp}}^{\beta}$ = values (± 0.07 , see Ref.1) and the $\sigma_{\text{calc}}^{\beta}$ -values (± 0.11 , vide supra). Moreover, for the last substituents, the estimated values of σ^{π} and E_s (see comments to Table 1) are used here. The great positive $\Delta\sigma^{\beta}$ -value for Cl should formally be accounted for, if one had assumed it to be an acceptor in resonance interaction. However, the more probable cause appears to be the erroneous $\sigma_{\text{exp}}^{\beta}$ = value².

From Table 1, one can reveal that within the substituents of the same structural type the difference between various $\Delta\sigma^{\beta}$ -values is smaller than the correlation (1) error, but approximately equal to the error of evaluating of σ^{β} -constants. In other words, the ability, for instance, of the substituents OR, SR or NR₂, in a first approximation, does not depend on the substituent R. Moreover,

²The $\sigma_{\text{exp}}^{\beta}$ -value for Cl had been evaluated² indirectly. It may, therefore, have significant error.

Table 1

The Values of $\Delta\sigma^{\delta} = \sigma_{\text{exp}}^{\delta} - \sigma_{\text{calc}}^{\delta}$ for the Substituents being Able to Go into Resonance Interaction

Substituent	$\sigma_{\text{calc}}^{\delta}$	$\Delta\sigma^{\delta}$	Substituent	$\sigma_{\text{calc}}^{\delta}$	$\Delta\sigma^{\delta}$
CH ₃ O	+0.45	-0.57	p-NO ₂ C ₆ H ₄	0.12	+0.01
C ₂ H ₅ O	0.36	-0.57	m-NO ₂ C ₆ H ₄	0.08	+0.02
n-C ₃ H ₇ O	0.32	-0.64	p-CNC ₆ H ₄	0.05	-0.09
i-C ₃ H ₇ O	0.21	-0.50	p-BrC ₆ H ₄	0.20	-0.05
n-C ₄ H ₉ O	0.31	-0.72	m-CH ₃ OC ₆ H ₄	0.27	-0.18
i-C ₄ H ₉ O	0.30	-0.60	m-CH ₃ C ₆ H ₄	0.43	-0.12
n-C ₅ H ₁₁ O	0.29	-0.68	p-C ₂ H ₅ O ₂ CC ₆ H ₄	-0.06	-0.18
i-C ₅ H ₁₁ O	0.29	-0.67	p-CH ₃ OC ₆ H ₄	-0.55	-0.04
neo-C ₅ H ₁₁ O	0.30	-0.59	p-CH ₃ C ₆ H ₄	-0.45	-0.15
OH	0.24	-0.63	m-ClC ₆ H ₄	-0.10	-0.12
CH ₃ S	0.31	-0.16	p-ClC ₆ H ₄	-0.19	-0.10
C ₂ H ₅ S	0.25	-0.16	p-(CH ₃) ₂ NC ₆ H ₄	-0.76	+0.08
n-C ₃ H ₇ S	0.21	-0.27	p-C ₂ H ₅ OC ₆ H ₄	-0.50	-0.16
i-C ₃ H ₇ S	0.19	-0.13	m-OHC ₆ H ₄	-0.26	-0.08
(CH ₃) ₂ N	-0.37	-0.85	p-HOC ₆ H ₄	-0.60	-0.05
(C ₂ H ₅) ₂ N	-0.81	-0.73	p-HOCC ₆ H ₄	-0.17	+0.03
CH ₂ =CH	-0.33	-0.35	m-HOCC ₆ H ₄	-0.11	-0.07
C ₆ H ₅ C≡C	0.40	-0.12	m-H ₂ NC ₆ H ₄	-0.39	-0.17
C ₆ H ₅ CH=CH	-0.56	-0.02	p-H ₂ NC ₆ H ₄	-0.84	+0.06
F	0.84	-0.28	m-C ₂ H ₅ NHC ₆ H ₄	-0.55	-0.07
Cl	0.76	+0.17	m-CH ₃ NHC ₆ H ₄	-0.55	-0.10
C ₆ H ₅ O	0.59	-0.65	p-CH ₃ NHC ₆ H ₄	-0.91	+0.10
C ₆ H ₅	-0.30	-0.18			

^aThe $\sigma_{\text{calc}}^{\delta}$ -values are evaluated with help of Eq.(1). The constants $\sigma_{\text{exp}}^{\delta}$ are from Ref.2. The constants $\sigma_{\text{R}}^{\delta}$ for the substituents RO and RS are from Ref.2. The $\sigma_{\text{X}}^{\delta}$ values for substituents m,p-substituted XC₆H₄ are estimated from the equation³ $\sigma_{\text{X}}^{\delta}(\text{XC}_6\text{H}_4) = 0.72 \sigma_{\text{X}} + 0.58$. The steric constants E_{S} for RO and RS and R₂N are estimated according to the Isostericity Principle⁴. (P.T.O.)

the resonance component $\Delta\sigma^p$ for m,p-substituted phenyls, XC_6H_4 , has no real dependence on the nature of X, although it may be either a donor or an acceptor.

Therefore, one can regard the $\Delta\sigma^p$ -values (see Table 2) averaged within each of the structural types of substituents as the estimates of the resonance contributions of corresponding substituents to the σ^p -values. The great difference of the σ^p -values for two $\text{XCH}=\text{CH}$ -type substituents appears to be related with rather rough estimation (see the comments to Table 1) of the corresponding steric constants.

Table 2

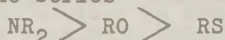
The Averaged $\Delta\bar{\sigma}^p$ -values for Some Structural Types of Substituents

Structural Type of Substituent	n^a	$\Delta\bar{\sigma}^p^b$
RO (R = Alk., H, C_6H_5)	11	-0.62 ± 0.02
RS (R = Alk.)	4	-0.18 ± 0.03
R_2N (R = Alk.)	2	-0.79 ± 0.06
m,p- XC_6H_4 (X = H, Alk., or any electroneg. subst.)	24	-0.07 ± 0.01

^a n = the number of substituents of that type (see Table 1).

^bWith the error of the mean.

Thus, according to Tables 1 and 2, the ability of the substituents at the phosphorus atom to go into the resonance interaction with that (i.e., with the substituents $\text{P}(\text{O})\text{O}^-$ and $\text{P}(\text{O})\text{OH}$, as one should say more accurately) falls progressively in the series



The E_s -values for F and Cl are estimated on the basis of the correlation with van der Waals' radii (see Ref.5). It is accepted that $E_s(\text{C}_6\text{H}_5 \text{ or } \text{XC}_6\text{H}_4) \approx E_s(\text{CH}_2=\text{CH}) \approx E_s(\text{CH}_3) = 0$.

The E_s -values for $\text{C}_6\text{H}_5\text{CH}=\text{CH}$ and $\text{C}_6\text{H}_5\text{C}\equiv\text{C}$ are assumed to be equal approximately to $E_s(\text{C}_6\text{H}_5\text{CH}_2) = -0.38$.

It is in contradiction to certain conceptions^{2,8}, but in full agreement with generally accepted view⁶ on the ability of the substituents of different structural types to go into resonance interaction. Moreover, there exists an obvious correlations between the ΔG^ϕ -values and the G_R^+ -constants reflecting mainly the substituents propensity to the resonance interaction with an electron-deficient reaction center. It should be regarded as quite satisfactory having in mind the possible calculation uncertainties of the G_{exp}^ϕ -quantities and the correlation (1) standard deviation.

Table 3

The Results of Statistic Analysis of the $G_{\text{exp}}^\phi =$
Values According to Eq. (2)

No	a_0	a_1	a_2	a_3	a_4	n	R
1	-0.962 ± 0.035	1.122 ± 0.035	-0.184 ± 0.013	0.162 ± 0.015	0.915 ± 0.050	47 ^a	0.993
2	-0.956 ± 0.015	1.129 ± 0.030	-0.187 ± 0.011	0.166 ± 0.014	0.925 ± 0.044	71 ^b	0.992

^a $S_0 = 0.076$. For 25 substituents from Ref.1 plus the substituents $n\text{-C}_5\text{H}_{11}$, $n\text{-C}_6\text{H}_{13}$, $n\text{-C}_8\text{H}_{17}$, $n\text{-C}_{12}\text{H}_{25}$, cyclo- C_6H_{11} , cyclo- C_5H_9 , $\text{CH}_2\text{CH}=\text{CH}_2$ and plus 16 substituents from Table 1 (without the m,p-substituted phenyls and unsubstituted phenyl itself). The points for $\text{C}_6\text{H}_5\text{C}\equiv\text{C}$ and H are excluded by the reason of significant deviations. ^bFor all the substituents enumerated above plus phenyl and substituted phenyls (see Table 1). $S_0 = 0.073$. The substituents $\text{CH}_2=\text{CH}$, $i\text{-C}_5\text{H}_{11}\text{O}$, $\text{neo-C}_5\text{H}_{11}\text{O}$, $\text{C}_6\text{H}_5\text{C}=\text{C}$, $p\text{-CH}_3\text{NHC}_6\text{H}_4$ and H are excluded by the reason of their significant deviations from the regression hypersurface.

In Table 3 are listed the results of treatment of the $\sigma^{\delta} =$ values² for 74 substituents according to equation

$$\sigma^{\delta} = a_0 + a_1 \sigma^{\pi} + a_2 \sigma^{\pi 2} + a_3 B_s + a_4 \Delta \sigma^{\delta} \quad (2)$$

For the substituents RO, RS, R₂N and XC₆H₄, the corresponding values of $\Delta \sigma^{\delta}$ collected in Table 2 are used; for the substituents C₆H₅CH=CH, C₆H₅C≡C and CH₂=CH the averaged value from those listed in Table 1 is also used. The multiple regression analysis program REGRAN-1 for computer BESM-4 is used for the calculating procedure. For the statistic tests, the 5% risk level is accepted. All the $\sigma^{\delta} =$ values are presumed to be the accidental results of a single measuring.

For all the uncharged substituents collected in Ref. 2, the estimates (see Corr.2 of Table 3) of Eq. (2) parameters do not differ significantly from those obtained without m,p-substituted phenyls and C₆H₅ (see Corr. 1 of Table 3) as well as from the corresponding parameters of Eq.(1). There is $a_4 = 1.0$ in limits of its uncertainty. Hence, the hypothesis of the constancy of the substituent constant σ^{δ} resonance component $\Delta \sigma^{\delta}$ within the substituents of the same structural types does not contradict the reality. Corr.2 of Table 3 adequately describes the σ^{δ} -constants both for the substituents being unable to go into the resonance interaction with reaction center and those which can conjugate with that. The point for H significantly deviates for incomprehensible reasons from that hypersurface.

The intercorrelation of Eq.(2) variables σ^{π} and $\sigma^{\pi 2}$ is close to that for Eq.(1) (see Ref.1). Therefore, the estimates of Table 3 for parameters a_1 and a_2 appear to be slightly biased from their true values.

Keeping in mind the constancy of the $\Delta \sigma^{\delta}$ -values for the substituents of one and the same structural type, one can estimate those values of interest to treat the original constants σ^{δ} with the aid of equation

$$\sigma^{\phi} = a_0 + a_1\sigma^{\pi} + a_2\sigma^{\pi 2} + a_3E_s + \sum_j \Delta\sigma^{\phi}(Y_j)n(Y_j) \quad (3)$$

where the parameters a_0 -- a_3 are such as above;

$\Delta\sigma^{\phi}(Y_j)$ is the resonance contribution to the corresponding constants σ^{ϕ} for the substituent of the structural type Y_j ; $n(Y_1) = 1$ when a substituent belongs to the structural type Y_1 , and $n(Y_1) = 0$ for the substituents of different types $Y_{j \neq 1}$.

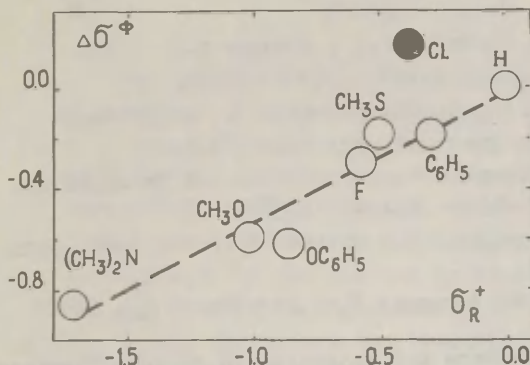


Fig.1. The plot of $\Delta\sigma^{\phi} = \sigma^{\phi}_{\text{exp}} - \sigma^{\phi}_{\text{calc}}$ vs σ_R^+ (see Ref.7). For SCH_3 , σ_R^+ is assumed to be the average one from those estimated on the basis of pK_a for Ar_3COH and $\text{Ar}(\text{C}_6\text{H}_5)\text{COH}$ (see Ref. 7). The radii of the circles are equal to the uncertainty only of $\sigma^{\phi}_{\text{exp}}$ - values (± 0.07 , see Ref.1). The quantities $\Delta\sigma^{\phi}$ are from Table 1.

The constants² σ^{ϕ} for 24 substituents being unable to conjugate (i.e., for those considered by us in Ref.1, with the exception of H), for 11 $\text{RO}(Y_1)$ -type substituents, for 4 $\text{RS}(Y_2)$ -type substituents as well as for 24 substituents of the $\text{C}_6\text{H}_4\text{X}(Y_3)$ -type are treated according to Eq.(3). Then the adequate correlation (4) is found

$$\sigma^{\phi} = (-0.930 \pm 0.019) + (1.133 \pm 0.040)\sigma^{\pi} + (-0.183 \pm 0.016)\sigma^{\pi 2} + (0.198 \pm 0.017)E_s + (-0.592 \pm 0.040)n(\text{RO}) +$$

$$+(-0.205 \pm 0.049)n(RS) + (-0.089 \pm 0.029)n(C_6H_4X) \quad (4)$$

$$n = 63 \quad R = 0.989 \quad S_0 = 0.078$$

As seen, the present estimates of the parameters a_0 :- a_3 are equal to those for correlation (1) and equation (2). The resonance contribution estimates for the substituents of the structural types RO, RS and XC_6H_4 are in full agreement with those listed in Table 2.

REFERENCES

1. Istomin B.I., Baransky V.A., Lobanov A.D., and Grechkin E.F., Org.React. 12, 67 (1975).
2. Mastryukova T.A. and Kabachnik M.I., Progress in Chemistry, (in Russian), 38, 1751 (1969)
3. Nagai Yo., Matsumoto H., Nakano T., and Watanabe H., Bull.Chem.Soc.Japan, 45, 2560 (1972)
4. Talvik I.V. and Palm V.A., Reakts.sposobn.organ.soedin., 8, 445 (1971).
5. Istomin B.I. and Baransky V.A., Org.React., 11, 4(42) 963 (1975)
6. Ingold C., Structure and Mechanism in Organic Chemistry Second Edn., (Russian Translation), MIR, Moscow, 1973
7. Ehrenson S., Brownlee R.T.C., and Taft R.W., Prog.Phys. Org.Chem., 10, 13 (1973)
8. Kabachnik M.I., Chemistry and Applications of Organophosphorus Compounds (in Russian), p.254, NAUKA, Moscow, 1974

Infrared Spectra and Electronic Effects. IV.
Influence of Substituent on the Frequencies
of the Stretching Band and the Basicity of
Amino Group in Diphenyl Systems with Heterobridges

V.F.Andrianov, A.Ya.Kaminsky, S.S.Ghitis,
A.V.Ivanov, T.M.Beregovyyh, N.I.Faingold

Institute of Monomers, Tula

Received May 22, 1975

The influence of substituent on the IR-frequencies (ν_{NH_2}) and the basicity (pKa) of amino group in 4'-X-substituted 4-amino diphenyl sulfides, diphenyl sulfones and benzophenones has been studied. The correlation analysis data for reaction constants ρ (Table 2) were used for comparing the electronic conductivity of the studied systems between themselves and that of anilines and amino diphenyls (Table 3). It was shown that the transmission of the electronic effect in the reaction state (pKa) is two to three times higher than in the ground state (ν_{NH_2}). In diphenyl sulfides the positive bridge effect occurs only in the reaction state. Experimental data are compared with the results of quantum-chemical calculations by the PPP method.

Earlier we have studied the transmission of electronic effects in substituted benzenes, diphenyls and diphenyl oxides with carboxy¹, carbomethoxy², and amino³ groups acting as reaction centres. It was shown, that for the benzene and diphenyl systems there is a direct polar conjugation between the substituent and the reaction center, whilst with the diphenyloxides the interaction occurs by an inductive mechanism.

Here, we have investigated the transmission of the substituent's influence from one ring to the reaction center,

the amino group of the other ring, for the diphenyl sulfide (I), diphenyl sulfone (II) and benzophenone (III) series. The data⁴⁻¹⁴ on conductivity for these systems, most fully presented for diphenyl sulfides⁴⁻⁷ are quite confusing. Thus, according to Litvinenko and co-workers^{4,6} the S-bridging atom enhances the transmission of the electronic effect, while Frankovsky^{8,11} and Zahradnik⁹ show on the contrary that it weakens this effect.

Regardless the available data⁵⁻⁷ for pKa and NH_2 values, we have repeated the measurements of the basicities and frequencies of amino-diphenyl sulfides, using a wider range of compounds, in order to make a more detailed correlation analysis. This is also an opportunity for making a more reliable comparison of our present and previous results. As a measure of the substituent's influence, the acid-base properties (pKa), the symmetric ($\nu_s\text{NH}_2$) and asymmetric ($\nu_{as}\text{NH}_2$) stretching frequencies of amino groups were chosen. The ionization constants values and IR-frequencies (Table 1) change with increase of electron-withdrawing properties of the substituent (X). For 4-amino-4'-diphenyl sulfides (I) the correlation coefficient is higher when using Hammetts σ^- constants, than with σ^- or σ^+ constants (Table 2). The same is observed for other series under consideration. Therefore in the studied systems, as in diphenyloxides³, there is no direct polar conjugation between the substituent (X) and the reaction centre. The difference in the behavior of sulfur and oxygen atoms when transmitting electronic effects (oxygen bridge systems correlate better with σ^+ constants³) is confirmed by electronic spectra, which show a greater capacity of sulfur to conjugate with benzene rings as a result of d-orbitals contribution.¹⁵

For quantitative determinations of the transmission factors¹⁶ (\overline{W}') two series were chosen as standards: the 4-X-anilines¹⁷⁻¹⁹ (\overline{W}'_1) and 4-amino-4-X-diphenyls³ (\overline{W}'_2). Data in Table 3 indicate that this factor for all the three systems is higher when considering pKa values, than the frequencies νNH_2 . In the case of sulfide bridge, it is even

Table 1.

The Values of pK_a , ν_{sNH_2} and ν_{asNH_2} of 4-NH₂-4-X-Diphenylsulfides (I), 4-NH₂-4'-Diphenylsulfones (II) and 4-NH₂-4'-X-Benzophenones (III)

No	X	I			II			III		
		pK_a	ν_{sNH_2}	ν_{asNH_2}	pK_a	ν_{sNH_2}	ν_{asNH_2}	pK_a	ν_{sNH_2}	ν_{asNH_2}
1	NH ₂	4.23	3391.5	3479.5	1.87	3401.5	3497.0	2.75	3399.5	3494.0
2	OCH ₃	-	-	-	-	-	-	2.52	3400.5	3495.5
3	CH ₃	3.89	3394.5	3484.5	1.62	3402.5	3498.5	-	-	-
4	H	3.80	3395.5	3485.5	1.48	3403.0	3499.0	2.32	3401.0	3497.0
5	Cl	3.60	3396.0	3484.5	1.44	3403.0	3499.5	2.30	3401.0	3497.0
6	COOH	-	-	-	-	-	-	2.03	3401.0	-
7	COOCH ₃	3.28	3397.0	3488.0	-	-	-	-	-	-
8	NO ₂	3.15	3398.5	3490.5	1.17	3404.0	3500.5	1.83	3402.5	3499.0

Table 2.

The Correlation Parameters of Equation $Y=Y_0+\rho\sigma$.

Correlation	$Y_0 \pm \Delta Y_0$	$\rho \pm \Delta \rho$	r	s	n
4-amino-4'-X-diphenylsulfide (I)					
pK_a, σ	3.73 ± 0.03	-0.79 ± 0.06	0.986	0.02	6
pK_a, σ^-	3.78 ± 0.03	-0.58 ± 0.06	0.977	0.03	6
pK_a, σ^0	3.81 ± 0.03	-0.85 ± 0.07	0.974	0.03	6
$\log s, \sigma$	3395.2 ± 0.1	4.7 ± 0.3	0.990	0.1	6
$\log s, \sigma^-$	3394.8 ± 0.2	3.0 ± 0.2	0.955	0.3	6
$\log s, \sigma^0$	3394.6 ± 0.2	4.9 ± 0.4	0.947	0.4	6
$\log a_s, \sigma$	3485.0 ± 0.2	7.4 ± 0.3	0.989	0.2	6
$\log a_s, \sigma^-$	3484.6 ± 0.2	5.3 ± 0.2	0.961	0.4	6
$\log a_s, \sigma^0$	3484.3 ± 0.2	7.7 ± 0.3	0.947	0.5	6
4-amino-4'-X-diphenylsulfone (II)					
pK_a, σ	1.53 ± 0.03	-0.48 ± 0.06	0.993	0.02	5
pK_a, σ^0	1.58 ± 0.03	-0.50 ± 0.07	0.957	0.05	5
$\log s, \sigma$	3402.7 ± 0.2	1.7 ± 0.3	0.984	0.1	5
$\log s, \sigma^0$	3402.6 ± 0.2	1.7 ± 0.3	0.937	0.2	5
$\log a_s, \sigma$	3498.8 ± 0.2	2.4 ± 0.3	0.989	0.1	5
$\log a_s, \sigma^0$	3498.6 ± 0.2	2.5 ± 0.3	0.937	0.3	5
4-amino-4'-benzophenone (III)					
pK_a, σ	2.34 ± 0.03	-0.60 ± 0.06	0.981	0.02	6
pK_a, σ^0	2.43 ± 0.03	-0.54 ± 0.07	0.979	0.05	5
$\log s, \sigma$	3400.9 ± 0.2	2.0 ± 0.2	0.975	0.1	6
$\log s, \sigma^0$	3400.7 ± 0.2	2.2 ± 0.3	0.969	0.2	6
$\log a_s, \sigma$	3496.6 ± 0.2	3.5 ± 0.2	0.987	0.2	5
$\log a_s, \sigma^0$	3496.1 ± 0.2	3.7 ± 0.3	0.945	0.4	5

Y_0 =value of Y for $\sigma=0$, r= the correlation coefficient, s= the standard deviation, n=the number of points involved in the correlation. For the values of σ^- , σ^- and σ^0 -constants see ref ¹⁷.

somewhat higher, than for the diphenyls ($\rho'_2=1.19$ which agrees with the value 1.16 found earlier⁶). A comparison of systems I and II shows, that when passing from the S bridge to the SO₂ bridge, the transmission of effects decreases almost two times for the protolytic reaction (pKa) and three times for \downarrow NH₂ values. Probably, this may be explained in the first case, by the existence of a ρ, \overline{W} -conjugation due to the presence of an unshared electron pair on the sulfur atom. The contrary was observed by Frankovsky and co-workers¹⁰⁻²⁰, who, when studying the ionisation constants of 4-hydroxy-diphenyl sulfides and sulfones, have shown that the transmission factor is higher for the SO₂ bridge. This, apparently may be due to a difference in the electronic character of the reaction centres of hydroxy and amino groups, and once more stresses the importance of this factor. A somewhat higher conductivity of benzophenone compared with that of diphenyl sulfone, as found both by spectroscopic (\downarrow NH₂) and thermodynamic parameters (pKa) (Table 3), may be rationalized by the fact that in benzophenone the two phenyl rings deviate only slightly from the molecular plane^{21,22}, while in diphenyl sulfones they do much more.¹⁵

Table 3.

The $\overline{W}'_1, \overline{W}'_2$ (correlation with σ^- constants) and \overline{W}'_3 -Values (correlation with σ°)

Series, M	pKa			\downarrow, NH_2			$\downarrow \text{asNH}_2$		
	\overline{W}'_1	\overline{W}'_2	\overline{W}'_3	\overline{W}'_1	\overline{W}'_2	\overline{W}'_3	\overline{W}'_1	\overline{W}'_2	\overline{W}'_3
- S -	0.21	1.19	1.52	0.18	0.69	0.84	0.20	0.75	0.92
- SO ₂ -	0.13	0.73	0.89	0.06	0.22	0.34	0.07	0.27	0.31
- CO -	0.16	0.91	0.96	0.08	0.29	0.39	0.09	0.35	0.45

It seemed interesting to compare the experimental data with the results of quantum-chemical calculations by the Pariser-Parr-Pople method, since the simple Hückel method is not sensitive enough to structural changes in diphenyl systems.²³ In Table 4 are presented the calculated values for \overline{W} -electronic charge ($q_{\overline{W}}$) on the amino group nitro-

gen, the bridging M group and carbon atoms of the phenyl ring situated between NH_2 and M. It is known that the basicity of the amines increases with increasing electronic density on the nitrogen²⁴ of the amino group. For the studied systems, there is also a linear relationship (Fig.) between the \bar{W} = charge on the nitrogen (q_N) and the basicity of the amino group (pKa).

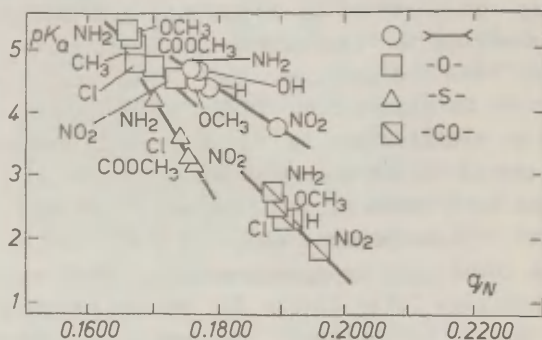


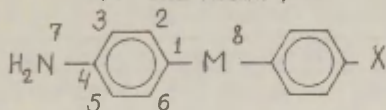
Fig. Relationship between the basicity of the amino group and \bar{W} -electronic charge q_N . The pKa -values for @4'-substituted 4-aminodiphenyls and diphenyloxides, are adapted from Ref.3.

The fact, that the points for the studied series do not fall on a common line, is primarily due to the difference in solvation effect's contribution²⁵ to the total basicity of the studied diphenyls. Moreover, the q_N -value reflects only \bar{W} -charge on the nitrogen atom, whereas its \bar{G} -electron density, which influences the density of the amino group²⁵, obviously is not the same for various bridging groups.

Inasmuch these calculations refer to the ground state it is obvious that they must correspond to the transmission factor found for IR-spectra data (ν_{NH_2}) according to which the studied bridging systems have the following order: diphenyl > -O-> -S-> -CO-> -SO₂-.

Table 4.

π -Electronic Charge Distributions
(Ground state) in



Atom number \ X	H	NO ₂	NH ₂	H	NO ₂	NH ₂
	>—<			— O —		
C ₁	-0,0450	-0,0579	-0,0362	-0,0302	-0,0427	-0,0246
C ₂	0,0103	0,0181	0,0037	-0,0377	-0,0322	-0,0409
C ₃	-0,0780	-0,0750	-0,0794	-0,0629	-0,0599	-0,0644
C ₄	0,0181	0,0283	0,0225	0,0001	0,0067	-0,0873
C ₅	-0,0783	-0,0753	-0,0796	-0,0865	-0,0852	-0,0873
C ₆	0,0103	0,0182	0,0037	-0,0357	-0,0308	-0,0384
N ₇	0,1807	0,1897	0,1761	0,1683	0,1738	0,1660
M ₈	—	—	—	0,1899	0,2019	0,1860
	— S —			— CO —		
C ₁	-0,0402	-0,0477	-0,0363	-0,0637	-0,0695	-0,0589
C ₂	-0,0134	-0,0108	-0,0146	0,0537	0,0563	0,0521
C ₃	-0,0766	-0,0736	-0,0779	-0,0783	-0,0759	-0,0796
C ₄	0,0067	0,0109	0,0047	0,0349	0,0396	0,0315
C ₅	-0,0756	-0,0738	-0,0768	-0,0813	-0,0789	-0,0832
C ₆	-0,0107	-0,0149	-0,0093	0,0273	0,0259	0,0264
N ₇	0,1723	0,1762	0,1707	0,1914	0,1963	0,1883
M ₈	0,0835	0,0947	0,0790	-0,1389 ^{II}	-0,1324 ^{II}	-0,1531 ^{III}

^{III}The total charge at carbon and oxygen atoms of CO-group.

Table 5.

The Values of $\Delta q_1 = q(\text{NO}_2) - q(\text{H})$ and
 $\Delta q_2 = q(\text{NO}_2) - q(\text{NH}_2)$ for Different Series

Δq	M	$\text{---} \text{O} \text{---}$		$\text{---} \text{S} \text{---}$		$\text{---} \text{CO} \text{---}$			
		C_4	N_7	C_4	N_7	C_4	N_7		
Δq_1		0.0102	0.0090	0.0066	0.0055	0.0042	0.0039	0.0047	0.0049
Δq_2		0.0168	0.0136	0.0100	0.0078	0.0062	0.0055	0.0081	0.0080

When comparing (Table 5) the changes in electronic charge at C_4 and N_7 in the considered series, when passing from NO_2 group to NH_2 or H-substituents, the order of changes will be the same. This sequence remains regardless whichever of the four criteria is considered: 1) Δq_1 on C_4 , 2) Δq_1 on N_7 , 3) Δq_2 on C_4 , or 4) Δq_2 on N_7 . An exception for the benzophenones, may be explained by the fact, that for this particular bridge π, π -conjugation with rings is typical, as compared with ρ, π -conjugation in case of O- and S-bridges. Thus, the quantum-chemical calculations support our conclusion on the order of transmission of electronic effects in the investigated diphenyl systems.

It should be noted that there is some disagreement between our data and the results of other workers³ who, using IR-frequencies ν_{NH_2} , have shown that the transmittability of 4-amino-4-X-diphenyl increases when introducing a sulfide bridge. Probably this discrepancy is due to inaccurate determination of these frequencies in the earlier works^{5,26,27} because of use of low resolution instruments.

As we have shown previously³, although the diphenyloxides transmit the overall electronic effect somewhat worse than the diphenyls do, a positive bridge effect (PBE)^{5,28} is observed for inductive effect. In order to find out the existence of PBE in the studied systems, the transmission factors \bar{N}_3' were estimated by dividing ρ_M^0 -values by the corresponding ρ^0 -values for diphenyls, obtained by a two-parameter correlation.³ The \bar{N}_3' values obtained in this

manner (Table 3) indicate that PBE in system I, in contrast to diphenyloxides, occurs only in the reaction state, whereas for the diphenyl sulfones, it does not exist at all.

Experimental Section

All the studied compounds were prepared and purified by the usual methods,^{24,30} and their characteristics corresponded to those available in literature.²⁹

IR-spectra were taken at least 10 times in purified³¹ dichloroethane (DCE) on a Perkin Elmer 180 spectrophotometer. The instrument was invariably calibrated against atmospheric water. Under these conditions the frequencies NH_2 were determined with the accuracy within $0.2\text{--}0.3\text{ cm}^{-1}$. Amine concentration in DCE was ca $5 \cdot 10^{-3}\text{ mol/l}$ and the path length 4 mm. Ionization constants were determined spectrophotometrically¹⁸ as described in a previous paper.⁵

The correlation parameters were calculated by the least-squares technique on a computer M-222.

The quantum-chemical calculations were performed by SCF-PPP method (H-electronic approximations) on computer BESM-4 (for the program. see Ref. 32). Values for coulombic and resonance integrals were adapted from Refs. 33-35.

*The authors are grateful to Prof. V.I. Minkin for performing the quantum-chemical calculations.

REFERENCES

1. A.Ya.Kaminsky, V.M.Ivanova, S.S.Ghitis, E.G.Kaminskaya, and L.I.Khabarova, *Reakts.Sposobn.Organ.Soedin.*, 8, 343 (1971).
2. V.M.Ivanova, A.Ya.Kaminsky, S.S.Ghitis, I.M.Sosonkin, E.G.Kaminskaya, L.I.Khabarova, G.P.Doroshina, and S.I.Buga, *ibid.*, 8, 731 (1971).
3. V.F.Andrianov, A.Ya.Kaminsky, A.V.Ivanov, S.S.Ghitis, N.V.Udris, S.S.Gluzmann, and S.I.Buga, *Organ.Reactivity*, 11, 477 (1974).
4. L.M.Litvinenko, R.S.Cheshko, and S.V.Tsukermann, *DAN SSSR*, 118, 946 (1958).
5. L.M.Litvinenko, E.V.Titov, R.S.Cheshko, M.V.Schavinskaya, and V.I.Bydachenko, *Zhurn. Org. Khim.*, 2, 1857 (1966).
6. E.V.Titov, N.G.Korzhenevskaya, R.S.Popova, and L.M.Litvinenko, *Ukr.khim.Zhurn.*, 37, 790 37, 790 (1971).
7. B.A.Korolev, Z.V.Geraschenko, and Ya.S.Vygodsky, *Reakts. Sposobn. Organ. Soedin.*, 8, 681 (1971).
8. E.Z.Katsnelson, Ch.S.Frankovsky, and T.M.Timofeyeva, *Zhurn.Org.Khim.*, 6, 1892 (1970).
9. K.Bocek, A.Mangini, and R.Zahradnik, *J.Chem.Soc.*, 1963, 255.
10. E.Z.Katsnelson. and C.S.Frankovsky, *Zhurn.Org.Khim.*, 6, 1696 (1970).
11. Ch.S.Frankovsky, Doctor Dissertation, Leningrad, 1973.
12. J.B.Hyne, *Reakts. Sposobn. Organ. Soedin.*, 5, 886 (1968).
13. L.M.Litvinenko and N.F.Levchenko, *Zhurn.Obsch.Khim.*, 31, 562 (1961).
14. G.S.Mironov, V.A.Ustinov, M.I.Farberov, and G.G.Kryukova, *Zhurn.Org.Khim.*, 2, 351 (1973).
15. S.S.Price and S.Oae. *Sulfur Bonding*, N.Y., Ronald Press, 1962, pp.32, 34, 100.
16. H.H.Jaffe, *Chem. Revs.*, 58, 191 (1958).
17. *Spravochnik Khimica (russ.)*, 2, "Khimiya", M.L., 1967, pp.98, 959.
18. A.Albert and E.Serjeant. *Ionization Constants of Acids*

- and Bases (russ.), "Khimiya", M.L., 1964.
19. P.J.Krueger, Can. J.Chem., 40, 2300 (1962).
 20. Ch.S.Frankovsky, E.Sh.Elkis, and L.D.Borodkina, Zhurn. Org. Khim., 6, 2305 (1970).
 21. R.F.Rekker and W.Th.Nauta, Rec.Trav.Chim., 80, 747 (1961).
 22. A.Ya.Kaminsky, V.F.Andrianov, and S.S.Ghitis, Zhurn. Prikl. Spekt., 1974, in press.
 23. L.M.Litvinenko, M.M.Mestechkin, E.V.Titov, L.I.Lagutskaya, and V.N.Poltavets, DAN SSSR, 179, 1110 (1968).
 24. B.Pullman and A.Pullman, Quantum Biochemistry, MIR, M., 1965, p.107 (russ.).
 25. V.I.Minkin, V.A.Bren, and E.N.Malyшева, Reakts.Sposobn. Organ. Soedin., 5, 565 (1968).
 26. E.V.Titov, L.M.Litvinenko, N.F.Levchenko. and N.A.Izmailsky, Ukr.Khim.Zhurn., 27, 481 (1961).
 27. E.V.Titov, M.V.Poddubnaya, and L.M.Litvinenko, Teor.Exper. Khimiya, 2, 271 (1966).
 28. V.A.Palm, Foundations of Quantitative Theory of Organic Reactions, "Khimiya", Leningrad, 1967 p.231.
 29. Bellst., 12, Berlin, 1931.
 30. H.Gilman and H.S.Broadbent, J.Amer.Chem.Soc., 69, 2053 (1947).
 31. A.Weissberger, E.Proskauer, J.Riddick, and E.Toops, Organic Solvents, M., 1958, Izd.inostr.lit., p.397 (russ.).
 32. G.I.Kagan, I.N.Fundlyer, and G.M.Kagan, Teor. Exper. Khimiya, 2, 589 (1966).
 33. J.Hinze and H.H.Jaffe, J.Am.Chem.Soc., 84, 540 (1962).
 34. K.Nishimoto and L.Foerster, Theor.chim.acta, 4, 155 (1966).
 35. R.Parr. Quantum Theory of Electronic Structure, N.Y. 1963.

THE POLAROGRAPHIC STUDY OF EQUILIBRIUM OF
LEVULINIC ACID HYDRAZONE FORMATION AND ITS
ACID-BASE PROPERTIES

I.A.KUZOVNICOVA, L.A.BADOVSKAYA, Ya.I.TURYAN,
and V.G.KULNEVICH

Krasnodar Politechnical Institute

Received June 2, 1975

Equilibrium constants for the formation of both unprotonated hydrazones of levulinic acid anion and protonated hydrazone of levulinic acid molecule were determined. The acid dissociation constant of the protonated hydrazone of levulinic acid anion was found. The applicability of Taft's equation for equilibrium constants mentioned has been checked up.

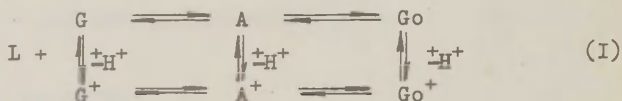
The equilibrium of the hydrazone formation and its acid-base properties were investigated on the basis of polarographic activity [1] of hydrazone (Go) of levulinic acid. The theoretical aspects of the use of the polarographic method in relation to analogous problems have been examined in papers [2,3].

The solutions for polarographic study contained: $2.0 \cdot 10^{-4}$ m/l of levulinic acid (L) + $(1.0 \cdot 10^{-3} + 0.5)$ m/l of hydrazine (G) + phosphate buffer (+ 1N KCl) with pH 3.9 + 7.25. The characteristics of capillary is $2.48 \text{ mg}^{2/3} \cdot \text{sec}^{-1/2}$ ($t = 2.78 \text{ sec}$) at -1.0V (n.c.e). All experiments were run at $25 \pm 0.2^\circ\text{C}$.

The polarographic $E_{1/2}$ value for hydrazone is dependent on pH: $E_{1/2} = -1.330 \pm 1.625\text{V}$. At $\text{pH} > 7.5$ the wave coalesces with the background electrolyte current. At $\text{pH} \leq 3.5$ the polarogram is evidently distorted by the catalytic formation of hydrogen.

Limiting current (\bar{I}_1) corresponding to the equilibrium Go formation was obtained in dependence on hydrazine concentration and pH during the time from 15 minutes up to several hours.

The following scheme [4] was assumed for equilibrium calculations:



where A - aminoalcohol; index " + " is related to the protonated forms.

A and A^+ concentrations [4,6] as well as concentrations of unprotonated form of hydrazine ($pK_a = 8,2$ [5]) and L forms with hydrated and protonated carbonyl groups [4,6] can be neglected in the range of pH ($pH \leq 7,25$).

It is necessary to pay attention to the fact that at $pH \geq 5,5$ L is present mainly in the anionic form since its $pK = 4,5$ [7]. Therefore hydrazone is present both in the form of anion and in the form of bipolar ion (nitrogen is protonated). At $pH < 5,5$ a considerable number of L molecules forms and the corresponding hydrazones are present both as unprotonated and protonated species. At $pH \leq 3,5$ the L molecular form predominates and hydrazones appear as a mixture of neutral or/and protonated forms or a protonated form only.

Let us introduce the following notations for equilibrium constants.

$$K_e^I = \frac{[Go]}{[L] \cdot [G]} \quad (2)$$

$$K_e^{II} = \frac{[Go^+]}{[L] \cdot [G^+]} \quad (3)$$

$$K_a^I = \frac{[G] \cdot [H^+]}{[G^+]} = 6,5 \cdot 10^{-9} \quad [5] \quad (4)$$

$$K_a = \frac{[Go] \cdot [H^+]}{[Go^+]} \quad (5)$$

It is easy to obtain the following relations between the above-mentioned constants:

$$K_e'' \cdot K_a = K_e^I \cdot K_a^I \quad (6)$$

$$K_{ef} = \frac{[Go] + [Go^+]}{[G^+] \cdot [L]} = K_e'' \cdot \frac{K_a + [H^+]}{[H^+]} \quad (7)$$

where K_{ef} is effective equilibrium constant, being constant only at $pH = \text{const.}$

On the basis of these equations and conditions of polarographic reduction of Go^+ we have [2,3]:

$$K_{ef} = \frac{\bar{I}_1 \cdot \bar{I}_1^0}{(\bar{I}_1^0 - \bar{I}_1) \cdot (C_G \cdot \bar{I}_1^0 - C_L \cdot \bar{I}_1)} \quad (8)$$

where \bar{I}_1^0 is limiting current corresponding practically to complete conversion of L into $Go(Go^+)$ [the lower pH^0 the bigger excess of hydrazine is required to obtain \bar{I}_1^0 (Fig.1); \bar{I}_1^0 values are shown in Fig.2; at $pH < 6.0$ the value of \bar{I}_1^0 is reached very slowly and therefore \bar{I}_1^0 value was obtained by extrapolation of the corresponding curve (Fig.2) taking into consideration that at $pH < 6.0$ \bar{I}_1^0 does not change considerably with the change of pH ; \bar{I}_1^0 found by this way is equal to $5.2 \mu a$ or $26.0 \mu a / \text{mMol/l}$ at $pH \leq 5.5$ and this corresponds to data [6] for other hydrazones], \bar{I}_1 is limiting current corresponding to the equilibrium, C_G and C_L are initial concentrations of hydrazine and L respectively. Equation (8) is true both for diffusion \bar{I}_1 value or for the kinetic one (Go protonation is retarded) [3].

The constancy of K_{ef} was observed in the broad range of C_G at $pH = \text{const.}$ This is consistent with the fact that reaction of azine formation is impossible under the investigated conditions.

The K_{ef} value decreases with the decrease of pH (Tabl. , Fig.3). This corresponds to equilibrium (7). In the interval of pH 6-7 a linear dependence of $\lg K_{ef}$

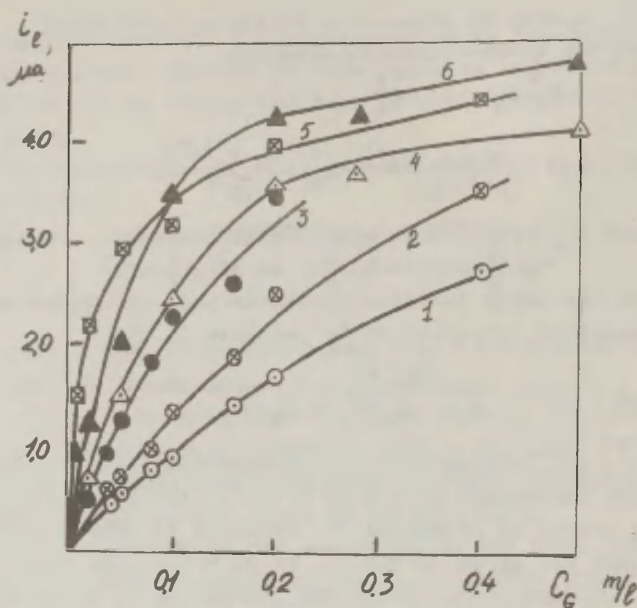


Fig.1. Dependence of Limiting Current for Levulinic Hydrazine of on the Concentration of Hydrazine.

pH: 1 - 3,90; 2 - 4,50; 3 - 4,95; 4 - 5,50;
5 - 6,00; 6 - 6,40

on pH is observed with the slope equal to 1 (Fig.3). This can be explained assuming that at $\text{pH} \geq 6,0$ $K_a \gg [H^+]$. As it will be shown later this assumption is confirmed by the experiment. On the basis of this relation from equation (7) the relationship is derived as follows:

$$\lg K_{ef} = \lg K_e \cdot K_a + \text{pH} \quad (9)$$

This equation corresponds to the experimental data at $\text{pH} \geq 6$ (Fig.3).

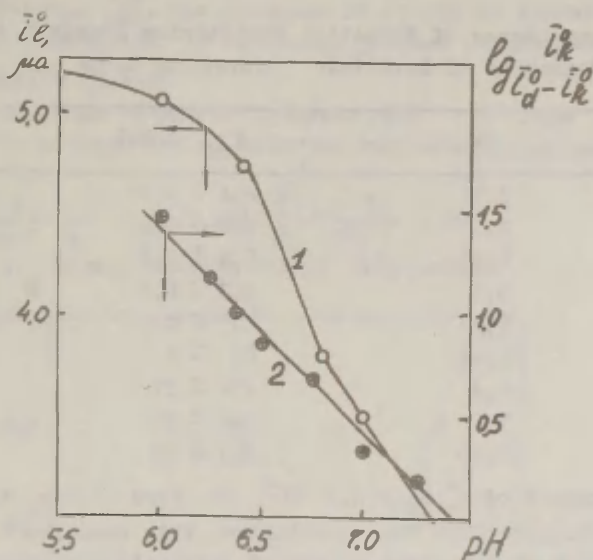


Fig.2. Dependence of Maximum Limiting Current of Levulinic Hydrazone on pH of Buffer (1) and the Check of Equation (10).

The Slope of Straight Line (2) is Equal to unity.

The value $K_a \cdot K_e'' = (2.3 \pm 0.2) \cdot 10^{-5}$ has been obtained. Taking into consideration $K_a \cdot K_e''$ value and equations (4) and (6) the equilibrium constant of formation of unprotonated form of hydrazone was obtained:

$K_e^I = (3.5 \pm 0.3) \cdot 10^3 \text{ l/mol}$. Using K_e^I and data of correlation analysis [6] it was found that $\sigma_{(CH_2)_2COO^-}^* = +0.015 \pm 0.004$. Then using this value and corresponding dependences of $lg K_e$ vs. $\Sigma \sigma^*$ and pK_a vs. $\Sigma \sigma^*$ [6] the values $K_e^* = 1.6 \pm 0.2$ and $K_a = (1.4 \pm 0.1) \cdot 10^{-5}$ were calculated.

Table

Dependence of Effective Equilibrium Constant of
Formation of Levulinic Hydrazone on pH

pH	K_{ef} l/mol
3,9	$2,4 \pm 0,05$
4,5	$3,6 \pm 0,2$
4,95	$6,9 \pm 0,1$
5,5	$9,3 \pm 0,6$
6,0	$20 \pm 0,9$
6,4	63 ± 3
6,8	174 ± 17
7,0	294 ± 20
7,25	363 ± 25

The product of $K_e'' \cdot K_a = 2,2 \cdot 10^{-5}$ is very close to the data obtained from the equilibrium. This confirms the application of the above-mentioned correlation analysis and correctness at value $\sigma^*(CH_2)_2COO^-$ found.

K_a is considerably higher than K' of hydrazine and that is typical of other hydrazones [6]. On the other hand the K_a value confirms the assumption that $K_a \gg [H^+]$ at $pH \geq 6$.

At $pH < 4,5$ K_{ef} slightly depends on pH (Fig.3). This is mainly explained by the correlation: $[H^+] > K_a$ (equation 8).

Since at $pH \leq 3,5$ whole L is practically in undissociated form the value \bar{K}_e' found corresponds to the protonated form of levulinic hydrazone:

$$K_{ef} = \bar{K}_e'' = 2,3 \pm 0,2.$$

A slight difference between \bar{K}_e'' and \bar{K}_n'' values is evidently due to a considerable distance between $-COO^-$ and $-COOH$ groups and the reaction centre.

Contrary to the region $pH < 6$ where \bar{L}_0 varies considerably with the change of $[H^+]$ (Fig.2) \bar{L}_0 decreases with the increase of $pH > 6,5$. This scheme is typical for

other hydrazones [9]. The decrease of \bar{i}_1^0 can be explained by kinetic limitation of electrode process at the stage of Go protonation [3,6,9].

In the range of kinetic current [10] in case of retarded Go protonation we have the following dependence:

$$\lg \frac{\bar{i}_k^0}{\bar{i}_d^0 - \bar{i}_k^0} = \lg 0.886 \cdot \sqrt{\frac{k_{I+} \cdot t_I}{K_a}} - \text{pH}$$

where k_{I+} is rate constant for Go protonation.

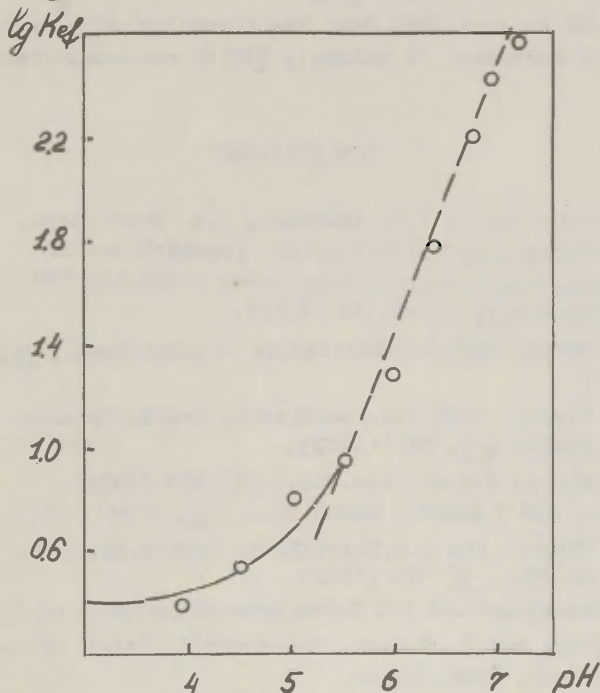


Fig.3. Dependence of Effective Equilibrium Constant of Levulinic Hydrazone Formation on pH of Buffer. The Slope of the Dotted Line Equals to unity.

Equation (10) is consistent with experimental data (Fig.2). From Fig.2 and equation (10) $k_{I+} = 4.0 \cdot 10^9 \text{ l/mol} \cdot \text{sec}$ was found.

It should be pointed out that the rate constant of protonation of hydrazones of other aliphatic compounds is higher by an order of magnitude 9. This can be expected taking into consideration the fact that in our case hydrazone exists in the anionic form and is less inclined to absorb at the negative potentials investigated. Hence the protonation occurs mainly in the volume of reaction mixture and the rate constant of this process is lower than that for the process complicated by absorption [11].

It can be concluded that the formation of pyridazone instead of hydrazone is unlikely [12] in our conditions (25°C).

BIBLIOGRAPHY

1. I.A. Kuzovnicova, V.M. Latashko, L.A. Badovskaya, Ya.I. Turyan, and V.G. Kulnevich. Transactions of Krasnodar Polytechnical Institute, Chemistry and Chemical Technology, ed. 49, 13 (1973).
2. Ya.I. Turyan and O.A. Tolstikova, J. Anal. Chem., 26, 378 (1971).
3. Ya.I. Turyan and O.A. Tolstikova. Reakts. Sposobn. Organ. Soedin., 9, 785 (1972).
4. W.P. Jencks, J. Amer. Chem. Soc., 81, 475 (1959).
5. S. Kari and L. Paavo, Suomen Kem., 40, B 55 (1967).
6. Ja.I. Turyan and O.A. Tolstikova. Reakts. Sposobn. Organ. Soedin., 9, 795 (1972).
7. A.N. Nesmeyanov and N.A. Nesmeyanov. Principles of Organic Chemistry, vol. I, Moscow, "Chemistry", vol. I, Moscow, "Chemistry", 1969, p. 410.
8. I.A. Koppel, M.M. Karelson, and V.A. Palm. Reakts. Sposobn. Organ. Soedin., 10, 497 (1973).
9. Ya.I. Turyan and O.A. Tolstikova. Transactions of Krasnodar Polytechnical Institute, Chemistry and Chemical Technology, ed. 63, 95 (1974).

10. 1a. Heyrovsky, Ya. Kuta. Principles of Polarography, Moscow, "Peace", 1965, p.339, 343.
11. S.G. Mayranovsky. Catalytic and Kinetic Waves in Polarography, Moscow, "Science", 1966.
12. W.L. Shilling and B.T. Hunter, Anal. Chem., 37, 1420 (1965).

TRIPHENYL VERDAZYL REACTIVITY, WHEN INFLUENCED BY
n-DONATING SOLVENTS IN REACTION WITH LAUROYL PEROXIDE

O.M.Polumbrik, O.I.Zaika, B.M.Yarmolyuk

All-Union Research and Design Institute of Petroleum
and Petrochemical Industry

Ukrainian SSR, Kiev-68, Palladin Avenue, 46

Received June 2, 1975

n-Donating solvents effect (dioxane, tetrahydrofuran, diethyl ether) upon the reactivity of a stable triphenyl verdazyl radical (TPV) in reaction with lauroyl peroxide (LP) $/v = k_2 (TPV)(LP)/$ has been studied. It has been shown that the specific solvation of TPV causes the decrease of reaction rate when passing from hexane to these solvents. The reaction has been carried out in the mixtures of hexane-THF and hexane-dioxane solvents. Analyzing the kinetic scheme with solvated and unsolvated TPV we have determined the equilibrium constants of solvation (20° , dioxane: $K = 3.1$ l/mol, THF: $K = 0.64$ l/mol), the coordination number of the complex ($n = 1$) and the heats of complex formation of TPV with the solvent (THF: $\Delta H = -4.6$ kcal/mol, dioxane: $\Delta H = -4.4$ kcal/mol). It has been established that solvated radicals react (20°) 45 (THF) and 310 (dioxane) times as slow as unsolvated ones. The species and the properties of ESR of TPV spectra in studied solvents are practically the same. It is supposed that specific molecular interaction contribute much to the complex formation of TPV with n-donating solvents.

It has been established that specific solvation of reacting particles causes the changes in reaction rate.¹ Medium effect may be of great importance for reactions of stable radicals too.² Solvent capacity to form hydrogen

bonds and π -complexes is often more significant, than medium polarity.³ Complex formation of stable radicals in organic solvents usually causes considerable decrease of their reactivity. For example, it takes place in the reaction of aroxyl radicals with di-tert-butyl-peroxide in nitrobenzene⁴, aromatic nitroxide radicals with 2,6-di-tert-butyl-phenol in benzene (however, in pyridine the reaction rate is 2 orders higher than that in hexane).⁵ The rate decrease takes also place in the reaction of DPPH with phenol when passing from CCl_4 to benzene.^{6,7} In aromatic solvents, which form complexes with radicals, there decreases the reactivity of alkyl radicals⁸ and Cl-radicals.⁹ Considerable decrease of the reaction rate for TPV takes place in the following cases: in dehydration reactions of hydrazobenzene¹⁰, dihydropyridines¹¹, in reaction with benzoyl peroxide¹² when passing from hydrocarbonic solvents to aromatic ones. For example, TPV solvated with pyridine reacts (50°) with 2,6-dimethyl-3,5-dicarbethoxy-1,4-dihydropyridine 23 times as slow as unsolvated one.¹¹ In reaction with benzoyl peroxide TPV complexes with benzene and anisole react 4-5 times as slow as an unsolvated radical.¹³ On the basis of kinetic and spectral data thermodynamic characteristics of TPV complexes with benzene, anisole and pyridine have been determined.^{11,13}

Up to now the reactivity of free radicals when influenced by n-donating solvents has not been studied sufficiently. The data available in literature are often contradictory. For example, DPPH is claimed to form readily complexes with n-donating solvents¹⁴ though its reaction rate with 2,4,6-tri-tert-butyl-phenol is claimed to be practically the same in hexane, dioxane and tetrahydrofuran.¹⁵ For reactions of TPV, however, with benzoyl peroxide there takes place the decrease of the reaction rate when passing from hexane to n-donating solvents (THF, acetone).¹⁶ In this paper, going on with the investigation of the influence of specific solvation upon the reactivity

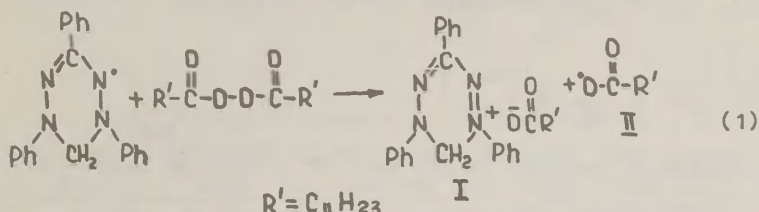
of TPV radicals, we have also studied the influence of n-donating solvents (diethyl ether, dioxane, THF) upon the interaction rate of TPV with lauroyl peroxide.

Experimental

Triphenyl verdazyl was obtained and purified as described in Ref.17. Lauroyl peroxide was obtained as described in Ref.18. Solvents were thoroughly purified before using.¹⁹ The reaction course was followed by the change in the absorption of TPV at $\lambda = 720 \text{ nm}$ (λ_{max} of TPV). At the same time both experiments were carried out in the thermostated glass-cell of spectrophotometer "OF-4" or in the radio-spectrometer ESR (P3-1301) and the maximum of the first derivative of ESR-signal of triphenyl verdazyl was measured (9 lines with intensity ratios 1:4:9:16:19:16:9:4:1; $a_N = 6 \text{ gauss}$, Ref.17).

Results and Discussion

The reaction of TPV with lauroyl peroxide takes place in accordance with Scheme (1):



The formation of triphenyl verdazylic salt has been proved spectroscopically.²⁰ The availability of free radicals II ($\text{C}_{11}\text{H}_{23}\text{CO}_2^\cdot$) in reaction (1) has been proved by experiments with traps of radicals (transformation of DPPH into DPPHH), Ref.20.

Table 1 represents the conditions and the results of some kinetic experiments in diethyl ether and Fig.1 represents the characteristic kinetic curves of the reaction of TPV with lauroyl peroxide in THF at 20° . The reaction rate in above-mentioned solvents and their mixtures can well be

described by a second-order kinetic equation (2):

$$v = k_2 \cdot (TPV) \cdot (LP) \quad (2)$$

The k_2 values are well preserved in each experiment when reaction is carried out with TPV for ~60-70%. Both parallel experiments and experiments with various initial concentrations of reagents (Fig.1, exps.1 and 2, Table 1, exps.2 and 3) result in well conforming values of rate constants. Experiments, carried out spectroscopically or by ESR-method, conform well too (Table 1, exps.5 and 6, 7 and 8).

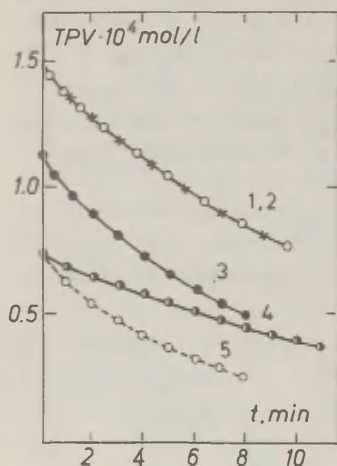


Fig.1

Kinetics of reaction of lauroyl peroxide with TPV in THF (20°)

1,2: TPV 1.48; LP 13.5

3: TPV 1.12; LP 16.8

4: TPV 0.74; LP 13.5

5: TPV 0.74; LP 27.0
· 10⁻⁴ mol/l.

Table 1

Kinetics of Reaction of TPV with LP in Diethyl Ether (20°)

NN	(LP) · 10 ⁴ mol/l	(TPV) · 10 ⁴ mol/l	k ₂ l/mol · s
1.	8.7	0.92	1.8±0.1
2.	8.7	0.46	1.9±0.1
3.	8.7	0.46	1.9±0.1
4.	17.4	0.46	2.0±0.1
5.	17.4	1.84	2.1±0.1
6*.	17.4	1.84	2.0±0.2
7.	18.8	1.60	1.7±0.1
8*.	18.8	1.60	1.8±0.2

*) Experiments 6 and 8 have been carried out by ESR-method and the rest of them spectrophotometrically.

Table 2 shows kinetic parameters of the reaction of TPV with lauroyl peroxide in organic solvents.

Table 2

Kinetic Parameters of the Reaction of TPV with LP*

Solvent	k_2 , l/mol·s			E kcal/mol	$-\Delta S^\ddagger$ e.u.
	20°	30°	40°		
Hexane	6.2±0.3	9.0±0.3	13.3±0.5	7.0±0.6	33.0±2
Benzene	3.1±0.3	5.0±0.3	7.9±0.5	8.5±0.7	29.2±2
Diethyl Ether	1.9±0.1	(1.5±0.03)**	(2.6±0.1)***	8.6±0.7	29.8±2
THF	0.82±0.04	1.50±0.04	2.77±0.10	10.8±0.6	24.1±2
Dioxane	0.17±0.01	0.33±0.01	0.63±0.03	11.9±0.6	23.4±2

*) Arithmetical means of constants (from 4-10 experiments) with a mean-square error are represented here. The values of k_2 for hexane and benzene have been taken from Ref.20.

**) At 16.1°C.

***) At 27°C.

The data of Table 2 prove that the reaction rate (1) is considerably influenced by the solvent nature. When passing from hexane to dioxane the reaction rate is 36 times as slow (20°). Earlier, while studying the reaction of TPV with benzoyl peroxide, we have proved that the decrease of rate when passing from hexane to benzene and anisole is caused by specific solvation of TPV because benzoyl peroxide in these solvents is little solvated.¹³ Assuming that lauroyl peroxide - molecule with a long alkilic chain - is also little solvated in n-donating solvents (this conforms to the fact, that the decomposition rate of lauroyl peroxide practically does not depend on the solvent nature)²¹ we can conclude that the change of the reaction rate (1) (Table 2) is caused by the specific solvation of TPV with n-donating solvents.

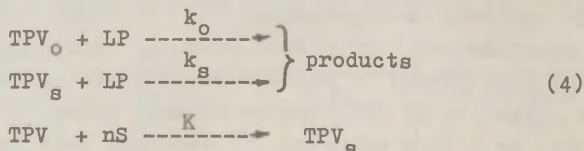
Indeed, passing from hexane to diethyl ether, THF and dioxane the energy of reaction activation increases. This is probably due to the inevitable rupture of "radical-solvent" complexes. Simultaneously the activation entropy increases since the desolvation, preceding the transition state, causes the disorder of the system.¹ When passing from hexane to aromatic and n-donating solvents (Table 2) there takes place a sympathetic increase of energy and activation entropy (compensational effect)*:

$$E = 0.477 \cdot \Delta S^{\ddagger}, r = 0.988 \quad (3)$$

Isokinetic temperature is 477°K, i.e. much higher than the used temperature interval.

Thermal decomposition of lauroyl peroxide in studied solvents takes place at a very low rate, for example, in benzene $k_1 = 2.5 \cdot 10^{-7} \cdot s^{-1}$ (30°C)(Ref.22). Decomposition of lauroyl peroxide, induced by TPV, proceeds $\sim 10^6$ - 10^7 times as rapid which is due to the sharp decrease of activation energy from 30.7 (Ref.23) to 7-12 kcal/mol (Table 2)

The capacity of triphenyl verdazyl to form complexes with the molecules of n-donating solvents and the reaction kinetics of TPV have been studied when carrying out the reaction (1) in mixtures of solvents hexane-THF, hexane=dioxane. General scheme of the reaction with the participation of n-complexes of TPV can be represented (in all experiments $[LP] \gg [TPV]$) as follows⁵:



where TPV_0 and TPV_S is a free and solvated radical, S= molecule of n-donating solvent, n = a coordinating number

*) Isokinetic temperature, determined from $\lg k_2$ (40°) versus $\lg k_2$ (20°) plot, is 467°K.

of the complex. Effective rate constant ³, observed in the experiment, is connected with the true ones in the following way (5):

$$k_{\text{eff}} = \frac{k_o + k_s \cdot K \cdot [S]^n}{1 + K \cdot [S]^n} \quad (5)$$

When $[S]$ values are small it can be supposed that k_o value and k_{eff} value $\gg k_s$ value. In this case Eq. (5) turns into Eq.(6):

$$k_o/k_{\text{eff}} = 1 + K \cdot [S]^n \quad (6)$$

Fig.2 shows the values of effective rate constants for reaction of TPV with lauroyl peroxide in mixtures of solvents hexane-THF (dioxane). These values depend on the concentration of n-donating solvent $[S]$.

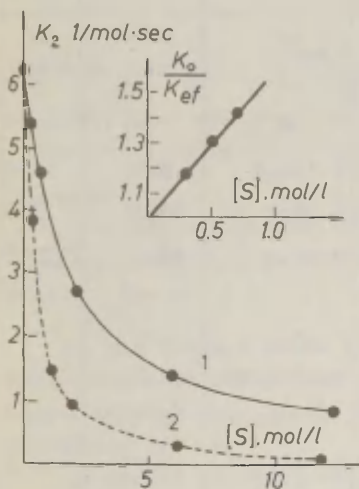


Fig.2

Relation between the rate of the reaction of TPV with lauroyl peroxide and the concentration of THF (dioxane) in mixture hexane-THF (dioxane):

1, THF; 2, dioxane.

Relation k_o/k_{eff} with the concentration of THF is shown above.

The data of Fig.2 and Table 3 prove that the reaction rate (1) decreases when the concentration of the n-donating solvent is being increased. When $[S]$ are small the linear relation between k_o/k_{eff} and $[S]$ (fig.2, above) point that

$n = 1$. In dioxane n is equal to one too. For TPV complexes $n = 1$ in benzene, anisole and pyridine (Ref.11,13). Thus, the association with only one molecule of complex-forming solvent³ is of great significance for TPV as well as for other stable radicals. Determined from Fig.2, the complex-forming constant K for dioxane equals 3.1 l/mol, for THF 0.64 l/mol (20°).

Table 3 shows kinetic parameters of the reaction of TPV with lauroyl peroxide in mixed solvents.

Table 3

Kinetic Parameters of Reaction of TPV with Lauroyl Peroxide in Mixed Solvents Hexane-THF(Dioxane)*

S mol/l	k_2 , l/mol.s			E kcal/mol	- ΔS^\ddagger e.u.
	20°	30°	40°		
THF					
0.3	5.2±0.3	-	-	-	-
0.5	4.7±0.3	-	-	-	-
0.7	4.3±0.3	-	-	-	-
2.1	2.72±0.11	4.50±0.15	7.4±0.4	9.1	28.0
5.8	1.42±0.11	2.45±0.07	4.35±0.20	10.3	26.6
12.3**	0.137	0.26	0.51	11.8	23.5
Dioxane					
0.2	3.8±0.2	-	-	-	-
1.05	1.51±0.12	2.60±0.04	4.44±0.40	9.8	26.2
1.93	0.94±0.03	(1.82±0.05)***	2.99±0.11	10.4	25.1
6.13	0.32±0.01	0.63±0.06	1.15±0.03	11.4	23.9
11.8**	0.02	0.04	0.09	13.2	23.2

*) Error of E does not exceed ±0.6 kcal/mol, ΔS^\ddagger ± 2 e.u.

**) Rate constants of solvated radicals calculated by formula (5) are given here.

***) At 31°

The data of Table 3 show that, when the concentration of n-donating solvent increases, there also takes place a sympathetic increase of energy and activation entropy. The reaction rate constants (5) of solvated radicals in THF make up 0.137 l/mol·s, and in dioxane they make up 0.02 l/mol·s, (20°) i.e. when passing from unsolvated TPV to solvated ones the reaction rate sharply decreases: in THF 45 times as slow, in dioxane 310 times as slow. After the determination of the relationships between k_{eff} and S at 30° and 40° we have determined solvation equilibrium constants as well as heats and entropies of TPV-complex formation with dioxane and THF (Table 4).

Table 4

Thermodynamic Constants of TPV Complex Formation with THF and Dioxane*

Solvent	K_{eq} , l/mol			$-\Delta H^\circ$	$-\Delta S^\circ$
	20°	30°	40°	kcal/mol	e.u.
THF	0.64	0.49	0.39	4.6	16.6
Dioxane	3.1	2.4	1.9	4.4	12.8

*) Since K has been determined from semilogarithmic anamorphosis ³ the error in ΔH is ± 2 kcal/mol.

As the Table 4 shows TPV form rather strong (often comparable with activation energies ^{8,10}) complexes with n-donating solvents. These complexes essentially affect the reactivity of TPV.

It should be mentioned that in some cases the composition in complex formation for dioxane is 2 : 1, i.e. both heteroatoms can take part in complex formation. But with weak acceptors the composition of complexes formed by dioxane is 1 : 1 and this has taken place in our experi-

ments.²⁴ The heat of TPV complex formation with dioxane is not higher than that with THF. This is probably due to the induction interaction of heteroatoms.²⁵

In ESR spectra (P9-1301) of TPV there occurs no noticeable change in the constant of superfine splitting a_N in contrast to DPPH (Ref.26). It can be assumed that a charge-transfer degree in a complex is not high (in N-oxide 0.1% (Ref.3)) as well as with N-oxide radicals³ and complex formation is due to specific intermolecular forces (induction and dispersion).

Thus, small changes in the electron structure of triphenyl verdazyl, caused by n-complex formation, may markedly affect the reactivity of this radical.

References

1. Ch.Reichardt, Solvents in Organic Chemistry, "Khimiya", L., 1973; S.G.Entelis and R.P.Tiger, Reaction Kinetics in the Liquid Phase, "Khimiya", M., 1973.
2. N.M.Emanuel, G.E.Zaikov, and Z.K.Mayzus, Solvent Effect in Radical-Chain Oxidation Reaction of the Organic Compounds "Nauka", M., 1973.
3. A.L.Buchachenko and O.P.Sukhanova, Usp.Khim., 36, 475 (1967)
4. A.I.Prokoffiev, S.P.Solodovnikov, N.N.Bubnov, and N.G.Radjabov, Izv. Akad.Nauk SSSR, ser.khim., 1969, 1664.
5. A.L.Buchachenko, O.P.Sukhanova, L.A.Kaláshnikova, and M.B.Neiman, Kinetika i kataliz, 6, 601 (1965).
6. J.C.McGrown, T.Powell, and R.Raw, J.Chem.Soc., 1959, 3103.
7. J.S.Hagg, D.M.Lohmann, and K.E.Rassell, Canad.J.Chem., 39, 1588 (1961).
8. V.L.Antonovskiy and I.V.Berezin, Dokl.Akad.Nauk.SSSR, 134, 621 (1960).
9. G.A.Russell, J.Amer.Chem.Soc., 80, 4987, 4997 (1958).
10. O.M.Polumbrik, N.G.Vasilkevich, and G.F.Dvorko, Ukr.khim.zh., 40, 1161 (1974).
11. O.M.Polumbrik, E.I.Zaika, and G.F.Dvorko, Ukr.khim.zh., 40, 963 (1974).
12. B.M.Yarmolyuk, O.M.Polumbrik, and G.F.Dvorko, Neftekhimiya, 13, 719 (1973).
13. O.M.Polumbrik, B.M.Yarmolyuk, and E.I.Zaika, Zh.Fiz.khim., 49, 742 (1975).
14. A.K.Chirkov, R.O.Matevosian, L.A.Pereliayeva, L.L.Samarin, I.I.Getsova, and B.M.Manannikov, Molecule Structure and Quantum Chemistry, "Naukova Dumka", Kiev, 106 (1970)
15. J.C.Dearden, J.Chem.Soc., B, 1971, 2251.
16. B.M.Yarmolyuk, O.M.Polumbrik, and G.F.Dvorko, Neftekhimiya, 14, 755 (1974).
17. R.Kuhn and H.Trischmann, Monatsh., 95, 457 (1964).
18. C.Beandet, Helv.Chim.Acta, 30, 1804 (1947).
19. A.Weissberger, E.Proskower, J.Riddick, and E.Toops Organic Solvents, Foreign Publs., M., 1958

20. O.M.Polumbrik, B.M.Yarmolyuk, and Niefertiekhimiya, 15, 306 (1975).
21. V.L.Antonovsky, Organic Peroxy Initiators, "Khimiya", M., 314 (1972).
22. W.E.Cass, J.Amer.Chem.Soc., 72, 4915 (1950).
23. V.L.Antonovsky and L.D.Bezborodova, Zh.Fiz.Khim., 42, 351 (1968).
24. E.N.Gurianova, I.P.Goldschtein, and I.P.Romm, Donor-Acceptor Bonding, "Khimiya", M., 354 (1973).
25. I.P.Romm, E.N.Gurianova, Zh.Obshch.Khim., 33, 1927 (1968)
26. B.Turcsanyi, G.Kosterszutz, and F.Tubos, Magyar.Kem.folyoirat, 73, 111 (1968).

Translated by V.Romanets.

DISSOCIATION CONSTANTS OF SUBSTITUTED ACETIC ACIDS AND INDUCTIVE ATTENUATION FACTORS OF SOME ALICYCLIC SYSTEMS IN AQUEOUS METHANOL

T.J. Jürjado and V.A. Palm

Chemistry Department, Tartu State University,
Tartu, Estonian S.S.R., U.S.S.R.

Received June 15, 1975

Dissociation constants of some substituted acetic acids in aqueous methanol (25 and 50 v/v) have been determined by the potentiometric titration. Those data were used to calculate inductive attenuation factors of some alicyclic systems.

The investigation of the inductive attenuation of alicyclic fragments is considered to be one of the key problems in studies of the inductive interaction. This attenuation is characterized by inductive transmission factor Z_{cycle}^* calculated as follows:¹

$$Z_{\text{cycle}}^* = \frac{\rho_{\text{X-cycle-Y}}^*}{\rho_{\text{XY}}^*} \quad (1)$$

where $\rho_{\text{X-cycle-Y}}^*$ and ρ_{XY}^* are susceptibility constants for identical reactions in the same conditions.

The necessity of the determination of the pK_a for some substituted acetic acids in aqueous methanol stems from the lack of data for calculation of the ρ_{XY}^* for the reaction series of dissociation of carboxylic acids in this solvent.

Experimental

Substituted acetic acids were synthesized, purified and kindly supplied by A.Pihl and V.Pihl.

PhCH_2COOH : m.p. 76.4-76.7°C;

HOCH_2COOH : m.p. 74-76°C;

BrCH_2COOH : m.p. 49.0°C;

ClCH_2COOH : m.p. 62.5°C;

Cl_2CHCOOH : $d_4^{20} = 1.5668$;

Cl_3CCOOH : m.p. 57.5°C.

Acetic acid, KOH, and KCl of 'pure' grade were used. Methanol was purified according to the ordinary method.² 0.01M solutions of the acids and 0.1M solution of KOH were used for titration.

The potentiometric titration was performed with a pH-meter МММ - 60M with electrodes of ЭЦЛ - 4И - 04 and 5М3.512.011Сn type. Dissociation constants were determined in 25 and 50 per cent (v/v) aqueous methanol.

The determination of the pK_a for trichloroacetic acid in 25 per cent methanol failed for known reasons.^{3,4}

The average values for 2-4 measurements are given in Table 1.

Table 1.

Acid	pK_a	
	in 25 per cent methanol	in 50 per cent methanol
CH_3COOH	5.02 ± 0.03	5.69 ± 0.03
PhCH_2COOH	4.68 ± 0.04	5.44 ± 0.04
HOCH_2COOH	4.16 ± 0.03	4.78 ± 0.06
BrCH_2COOH	3.27 ± 0.05	3.90 ± 0.05
ClCH_2COOH	3.27 ± 0.04	-
Cl_2CHCOOH	1.73 ± 0.05	2.31 ± 0.04
Cl_3CCOOH	-	1.70 ± 0.06

Treatment of Data

Substituents inductive constants δ^* calculated on the basis of aqueous dissociations of substituted acetic acids were used for the treatment of experimental pK_a .

A rigorous procedure calls for least-squares treatment using δ^* - constants calculated by the original Taft⁵ procedure from data on the rate constants of basic and acid hydrolysis of esters $XCOOR$. Such values of δ^*_X are known for 3 "electronegative" substituents (C_6H_5 , $COCH_3$ and $COOCH_3$) only. Data for a sufficient number of esters of XCH_2COOR type are also missing. Therefore, for defining δ^* values, it is necessary to make use of other reaction series for which data for as many as possible electronegative substituents, equidistant from reaction center, are available. Mainly, $pK_{a(H_2O)}^{25^\circ}$ of substituted acetic acids $XCH_2COOH^1(X_nCH_{(3-n)}COOH$ in a general case) served for that purpose. In Ref. 1 however, a universal constancy of inductive attenuation factor of methylene fragment, $Z^*_{(CH_2)} = 0.388$, was used for re-defining of δ^*_X -values. This approach causes a certain transformation of δ^* -scale as compared with those calculated by the original Taft's procedure using the value $Z^*_{(CH_2)} = 0.360$. Such a change in δ^* -scale is undesirable because for a new model series it can be a complementary reason for the incomparability of ρ^* -values calculated by means of various δ^* -scales. Moreover, the noted transformation of δ^* -scale must be considered to be unfounded because at present it is known that there is no universal value of $Z^*_{(CH_2)}$.^{6,7}

A correct re-defining of δ^*_X -values with retaining their scale requires the treatment of $pK_{a(H_2O)}^{25^\circ}$ -values for acids XCH_2COOH (for acids $XCOOH$ there are no necessary data) with δ^*_X -values calculated from the data on esters $XCOOR$. From that dependence, one can calculate new values of δ^*_X for other substituents.

Due to the lack of $pK_{a(H_2O)}^{25^\circ}$ for CH_3OOCCH_2COOH , we have only two points (C_6H_5 and $COCH_3$) covering a rather narrow range of δ^*_X to calibrate the δ^*_X -scale. Thus, it is

expedient to add the point for Cl computing $\delta_{Cl}^{\#}$ from the corresponding $\delta_{CH_2Cl}^{\#}$ - value using $Z_{(CH_2)}^{\#}=0.360$. Sure, it brings to a certain additional inaccuracy connected with the CH_3 -group as a reference substituent in both cases. It was necessary, in principle, to take H and CH_3 or CH_3 and C_2H_5 , respectively. However, bearing in mind the difference in values $Z_{CH_2}^{\#}$ for electronegative and for alkyl substituents, it turns out to be unjustified (particularly the former). Besides, an additional inaccuracy will be connected with the inevitable uncertainty of value $Z_{(CH_2)}^{\#}=0.360$ for the original $\delta_X^{\#}$ -scale.

Original values of $\delta_X^{\#}$ and $pK_a^{25^\circ}$ for acids of XOH_2OOH type used in calculations are given in Table 2. The least-squares treatment of data from Table 2 leads to the following results:

$$\delta^{\#} = (7.383 \pm 0.201) - (1.579 \pm 0.055) pK_a \quad (2)$$

$$s = 0.058, \quad r = 0.9993$$

$\delta^{\#}$ -values calculated according to Eq.(2) are given in Table 2. All other linear treatments are performed with those values except the point for $COOCH_3$ for which the original $\delta_X^{\#}$ -value was used. The parameters of these relationships are presented in Table 3.

Table 2

The $\delta^{\#}$ -Constants and Experimental $pK_a^{25^\circ}$ Values
for Substituted Acetic Acids

Substituent X_n	$pK_a^{25^\circ}$ $X_nCH(3-n)COOH$	$\delta^{\#}$	
		original Taft values ⁵	calculated according to Eq. (2)
1	2	3	4
H	4.75 ⁸	(0.49)	-0.12
F	2.66 ⁹	-	3.23
Cl	2.84 ¹⁰	2.92 ^a)	2.90
Cl ₂	1.26 ¹¹	-	5.39
Br	2.90 ¹²	-	2.80
I	3.18 ¹²	-	2.36

Table 2 (continued)

1	2	3	4
OPh	3.18 ¹³	-	2.36
OCH ₃	3.57 ¹⁴	-	1.74
OH	3.83 ¹⁰	-	1.33
COCH ₃	3.60 ^{15, b)}	1.65	1.70
COOCH ₃	-	2.00	-
NHCOCH ₃	3.67 ¹⁶	-	1.59
CH=CH ₂	4.24 ¹⁷	-	0.69
C ₆ H ₅	4.31 ¹⁸	0.600	0.58
CN	2.47 ¹⁹	-	3.48
CONH ₂	3.64 ²⁰	-	1.63
ONO ₂	2.26 ²¹	-	3.81
SH	3.75 ²²	-	1.49

a) Calculated using $\delta_{\text{CH}_2\text{Cl}}^* = 1.05$; $\delta_{\text{Cl}}^* = 1.05/0.360$

b) at 18°.

Discussion

Table 3 shows the value of ρ^* for aliphatic acids does not vary when changing solvent water for aqueous methanol. A considerable increase of the effective value of ρ^* for substituted alicyclic acids was observed by Wilcox and Leung in these conditions.²³ Consequently, the value of Z_{cycle}^* calculated according to Eq.(1) also depends on solvent. Corresponding data are presented in Table 4. $Z_{(\text{CH}_2)}^* = 0.390$ was used for re-calculation of ρ^* for acids XCH_2COOH into ρ^* values for acids XCOOH .¹ An average value for three solvents used is $\rho_{(\text{XCOOH})}^* = -1.59$.



We can calculate the values Z_{cycle}^* using the given value of $Z_{(\text{CH}_2)}^*$ and assuming the inductive influence to be transferred additively by all hydrocarbon chains according to Eq.(3).

$$Z_{\text{cycle}}^* (\text{calc.}) = \sum_i Z_{(\text{CH}_2)}^* n_i \quad (3)$$

Table 3

Correlation Parameters According to the Equation $pK_a(X) = pK_a^\circ + \rho^\Sigma \delta_X^\Sigma$ for Some Series of Acids at 25°C.

MeOH (25) and MeOH (50) denote 25 and 50 per cent (v/v) aqueous methanol. n, s, r - number of points, standard deviation, and correlation coefficient, respectively



Series of acids and solvent	pK_a°	$-\rho^\Sigma$	s	r	n and choice of substituents
$X-CH_{(3-n)}COOH$ H_2O^a	(4.67)	(0.633)	-	-	-
MeOH(25)	4.975 ± 0.025	0.600 ± 0.009	0.039	0.9995	6; H, Cl, Br, OH, C_6H_5 , Cl_2
MeOH(50)	5.672 ± 0.057	0.626 ± 0.020	0.089	0.9984	5; H, Br, OH, C_6H_5 , Cl_2
130 $X-$  $-COOH$ (data from ²³)					
H_2O	4.848 ± 0.014	0.179 ± 0.006	0.016	0.9989	4; H, Br, $COOCH_3$, CN
MeOH(25)	5.368 ± 0.008	0.201 ± 0.003	0.009	0.9997	4; Do
MeOH(50)	6.015 ± 0.006	0.224 ± 0.002	0.006	0.9998	4; Do
$X-$  $-COOH$ (data from Ref. ²³)					
H_2O	5.064 ± 0.014	0.153 ± 0.006	0.016	0.9985	4; Do
MeOH(25)	5.591 ± 0.010	0.170 ± 0.004	0.011	0.9994	4; Do
MeOH(50)	6.242 ± 0.012	0.192 ± 0.005	0.013	0.9993	4; Do

^a) pK_a and ρ^Σ values calculated using parameters of Eq.(2).

where i and n_i denote the index of hydrocarbon chain and the number of atoms in chain i , respectively. $Z_{\text{cycle}}^{\#}(\text{calc.})$ are also given in Table 4.

Table 4.

Experimental Data for $Z_{\text{cycle}}^{\#}$ and Corresponding Values Calculated According to Eq.(3) for 1.4-Bicyclo-[2.2.1]-Heptane and 1.4-Bicyclo-[2.2.2]- Octane Systems

Cycle	Solvent	$Z^{\#}$	
		experimental (calculated according to Eq.(1))	calculated according to Eq.(3)
	H ₂ O	0.113	0.111
	MeOH(25)	0.124	
	MeOH(50)	0.141	
	H ₂ O	0.096	0.077
	MeOH(25)	0.107	
	MeOH(50)	0.121	

These data show that experimental $Z_{\text{cycle}}^{\#}$ and calculated $Z_{\text{cycle}}^{\#}$ for 1.4-bicyclo-[2.2.1]-heptane fragment in water have rather similar values. In all other cases experimental values exceed remarkably the calculated ones.

It is evident without introducing any additional assumptions or empirical constants no existing model of inductive interaction does not allow to give a quantitative interpretation to the observed relationships between the $Z_{\text{cycle}}^{\#}$ values and the nature of the cycle, solvent, and reaction series. Hence the further discussion of the data from Table 4 turns out to be unfounded within the framework of the present paper.

Another point of interest is the problem of the additivity of the inductive influence of halogene atoms bonded to the same carbon atom. Assuming the pK_a of chloroacetic acid in 50 per cent methanol does not differ from that of bromoacetic acid, we can compare data for mono-, di-, and trisubsti-

tuted derivatives in this solvent. Corresponding values $\Delta pK_a(Cl_n) = pK_a^\circ - pK_a(Cl_n)$ equal to 1.79, 3.38, and 3.99 for $n=1, 2$, and 3 , respectively, proportionated as 1:1.89:2.23. These ratios evidently show the lack of additivity. We can calculate $\delta^*(Cl_2) = 6.35$ from the pK_a for trichloroacetic acid in 50 per cent methanol. If one ascribes certain approximate* value of δ^* to the CCl_3 group then using $Z_{CH_2}^* = 0.39$ $\delta^*(CCl_3) = 2.48$ follows. This value agrees well with the quantity (2.55) suggested by Taft.³

References

1. V.A. Palm, Foundations of Quantitative Theory of Organic Reactions, Khimia, Leningrad, 1967.
2. Y.K. Yur'jev, Practical Works in Organic Chemistry (in Russian), Moscow University, 1957.
3. V.F. Odyakov, Reakts.Sposbn.Organ.Soedin, 3, 1(7), 36(1966).
4. V.A. Palm and T.J. Jüriado, Reakts.Sposbn.Organ.Soedin., 7, 2(24), 449(1970).
5. R.W. Taft, Jr., in Steric Effects in Organic Chemistry, M. Newman (ed), Chapt. 13, Wiley, N.Y., 1956.
6. S.V. Bogatkov, E.Y. Borisova, G.R. Kalinina, and T.D. Sokolova, Reakts.Sposbn.Organ.Soedin., 2, 3(17), 793 (1968).
7. I.A. Koppel, M.M. Karelson, and V.A. Palm, Reakts.Sposbn.Organ.Soedin., 2, 1(39), 99 (1974).
8. H.S. Harned and R.W. Ehlers, J.Amer.Chem.Soc., 54, 1350 (1932).
9. A.L. Henhe and C.J. Fox, J.Amer.Chem.Soc., 76, 479 (1954).
10. R.P. Bell and A.T. Kuhn, Trans. Faraday Soc., 59, 1789 (1963).
11. M. Randall and C.F. Fainley, Chem. Rev., 4, 291 (1927).

In view of the uncertainty caused by the dependence of the $Z_{CH_2}^$ on the nature of reaction series.

12. D.J.G. Ives and J.H. Pryor, J.Chem.Soc., 1955, 2104.
13. D.J. Pasto. and R. Kent, J.Org.Chem., 30, 2684 (1965).
14. K. Bowden, M. Hardy, and D.C.Parkin, Can.J.Chem., 46, 2929 (1968).
15. H.M. Dawson and W. Lawson, J.Chem.Soc., 1929, 1217.
16. E.J. King, and G.W. King, J.Amer.Chem.Soc., 78, 1089 (1956).
17. M. Kilpatrick, and J.G. Morse, J.Amer.Chem.Soc., 75, 1854 (1953).
18. M. Duboux and D. Tsamadas, Helv. Chim. Acta, 7, 855 (1924).
19. B. Saxton and L.S. Darken, J.Amer.Chem.Soc., 62, 846 (1940).
20. G.H. Jeffery and A.I. Vogel, J.Chem.Soc., 1934, 1101.
21. K. McCallum and W. Emmons, J.Org.Chem., 21, 367 (1956).
22. M. Merle, G. Douheret, and M.L. Dondon, Bull.Soc.Chim. France, 1966, 159.
23. C.F. Wilcox and C. Leung, J.Amer.Chem.Soc., 90, 336 (1968).

INTERPRETATION OF ACIDITY OF CARBON ACIDS USING
 ρ -CONSTANTS OF SUBSTITUENTS. III MALONONITRILES

A. Talvik, A. Pihl, H. Timotheus, A. Osa,
J. Viira, and V. Timotheus

Department of Chemistry, Tartu State University,
202400 Tartu, Estonia, U.S.S.R.

Received June 21, 1975

The pK_a -values are determined for malononitrile (I), methyl-(II), ethyl-(III), i-propyl-(IV), i-butyl-, (cyclo-hexylmethyl)-, benzyl-, and p-nitrobenzylmalononitrile. Also the ionization rate constants by water are measured for I-IV. The pK_a and $\log k$ -values are quantitatively correlated using inductive, steric, and ρ -constants, if the σ^+ -constants for the alkyls were equalized to zero. The values of corresponding susceptibility factors are almost equal for both series.

According to the treatment of acidity of carbon acids suggested¹ the value of the sensitivity factor to the E_s' -values of substituents may be expected to depend on steric properties of a conjugated group. So, one might think that the cyano group has the lowest steric requirements. Hence, extremely low value of the sensitivity factor may characterize cyanocarbon acids. Unfortunately, acidity of simple nitriles is too low to measure precisely.² Therefore an investigation of acidity of malononitriles is undertaken to supplement the Hibbert's and Long's data³ to verify the above-mentioned idea. On the other hand, a study of ionization rates of malononitriles may be expected to give some additional information about the structure dependence of kinetic acidity of carbon acids⁴ characterized by a very "product-like"³ transition state of the ionization.

Table 1

The pK_a^0 - Values and Spectral Characteristics of Malononitriles $RCH(CN)_2$ at the Wavelength Used (25.0°). (Mean errors are shown, n is a number of runs.)

R in $RCH(CN)_2$	λ (nm)	ϵ_A - by method		pK_a^0 by method		n
		A	B	A	B	
H	225	22600 \pm 200	21900 \pm 100	11.39 \pm 0.01	11.35 \pm 0.01	18
CH ₃	237.5	20400 \pm 200	20400 \pm 100	12.77 \pm 0.01	12.74 \pm 0.01	25
C ₂ H ₅	237.5	19200 \pm 200	19200 \pm 200	12.84 \pm 0.02	12.81 \pm 0.02	18
i-C ₃ H ₇	238 ^a	17300 \pm 200	16600 \pm 100	12.93 \pm 0.01	12.91 \pm 0.01	32
i-C ₄ H ₉	238	19400 \pm 100	19400 \pm 200	12.16 \pm 0.01	12.14 \pm 0.01	34
cyclo-C ₆ H ₁₁ CH ₂	238	20200 \pm 100	19900 \pm 100	12.24 \pm 0.01	12.24 \pm 0.01	35
C ₆ H ₅ CH ₂	232	15700 \pm 200	15100 \pm 100	11.63 \pm 0.01	11.59 \pm 0.01	21
p-NO ₂ C ₆ H ₄ CH ₂	232	19700 \pm 100	18700 \pm 100	10.82 \pm 0.01	10.78 \pm 0.01	26

^a λ_{max} was at 225 nm.

The pK_a^0 and $\log k$ - values determined (see Tables 1, 2) (statistically corrected to the number of ionizable hydrogens, i.e. values of $pK_a' = pK_a^0 + n_H$ and $\log k' = \log k - n_H$) together with data for t-butylmalononitrile,³ were treated according to Eqs.(1) and (2):

$$pK_a'(-\log k') = a_0 + a_1\varphi + a_2E_s' + a_3\Delta E_s^0 \quad (1)$$

$$pK_a' = a_1\varphi + a_2E_s' + a_3\Delta E_s^0 + a_4\sigma^{\pi} \quad (2)$$

Analysis of the pK_a' - values was carried out according to following versions: (i) applying Eq.(1) to substituents H, CH_3 , C_2H_5 , i- C_3H_7 , and t- C_4H_9 ; (ii) applying Eq.(1) to all alkyl substituents, (iii) applying Eq.(2) to all substituents and equating the σ^{π} - value for p-nitrobenzyl with 0.49 (for p-nitrophenylacetic acid $pK_a = 3.87$; $\rho^{\pi} = 1.81$)^{5,6}. The φ and E_s' - values for p-nitrobenzyl were assumed equal to those for benzyl-group (see Ref.⁴ for numerical values).

Table 2

The $\log k$ - Values of Ionization of Malononitriles $RCH(CN)_2$ by Water at 25.0° and $I=0.10$ M. (Mean errors are shown, n is a number of runs.)

R in $RCH(CN)_2$	$10^3 C_{m.n.} (M)$	$C_{Br_2} (M)$	$10^4 C_{HCl} (M)$	$-\log k (sec^{-1})$	n
H	≥ 1.5	0.01-0.20	1-50	1.56 ± 0.01^a	4
CH_3	≥ 1.5	0.05-0.33	1-70	3.06 ± 0.01	13
C_2H_5	≥ 0.8	0.10-0.37	1-10	3.09 ± 0.01	13
i- C_3H_7	≥ 0.6	0.20-0.37	1-10	3.10 ± 0.01	13

^a Lit. values of k : $2.86 \cdot 10^{-2}$ (Ref.3), $2.6 \cdot 10^{-2}$ (Ref.2).

Table 3

Results of Multiple Regression Analysis of Acidity of Malononitriles. (Mean errors are shown, h is a number of degrees of freedom.)

Version Parameter	pK_a			$-\log k'$
	(i)	(ii)	(iii)	
a_0	11.72 ± 0.11	11.72 ± 0.10	-	1.88 ± 0.09
a_1	0.18 ± 0.05	0.18 ± 0.04	0.18 ± 0.03	0.22 ± 0.04
a_2	-0.35 ± 0.07	-0.35 ± 0.06	-0.36 ± 0.05	-0.32 ± 0.05
a_3	-	1.04 ± 0.10	1.05 ± 0.09	-
a_4	-	-	-3.36 ± 0.18	-
R	0.989	0.999	0.997	0.994
s	0.12	0.10	0.09	0.09
h	2	3	4	2

Table 3 demonstrates that the values of regression coefficients are independent of a set of substituents. On the other hand, taking into account the errors of pK_a' and $\log k'$ -values (as distinct from data considered earlier)^{1,4} and the 99% confidence limits (hardly higher than ± 0.04), the relationships seem to be slightly inadequate.

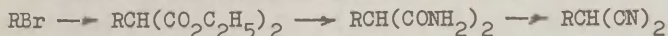
Signs of sensitivity factors agree with the previous results^{1,4} with the exception that now the φ -interaction weakens the acids. The absolute value of the sensitivity factor for the thermodynamic acidity to the E_s' -values of substituents (0.35) is much lower than the values for other carbon acids with two activating groups (from 1.56 to 3.55)¹. The ρ^* -value for dissociation (3.36) is rather reliable despite the unreliability (see Ref. 6) of the σ^* -value for p-nitrobenzyl. It is worth mentioning it is significantly higher than that of dinitroalkanes (2.29)¹.

A comparison of the values of sensitivity factors for kinetic acidity with those for the dissociation proves the activated state to be rather "product-like" as suggested by Hibbert et al.³ Moreover, the corresponding values agree within their errors.

Nevertheless, in spite of reasonable formal applicability of Eqs.(1) and (2), a problem of an interpretation of the sign of the φ -term arises. It is also necessary to deal with the problem of nonalkyl substituents considering the experimental pK_a -values of bromomalononitrile (7.8)⁷ and cyanoform (-5.1)⁸, which may be expected¹ to be lower than the values calculated by means of Eq.(2). Really it is the case for cyanoform only, whereas the experimental pK_a -value for bromomalononitrile deviates in the opposite direction by two log units (values of Table 3 for regression coefficients and those of earlier paper¹ for substituent constants are used). So, considerable deviation is hardly connected with uncertainties of regression coefficients but seems to be due to the heterogeneity of the E_s' -scale of nonalkyl substituents.

Experimental

Malononitriles were prepared as follows:



They were all repeatedly purified until an absorption at 1735 and 1200 cm^{-1} vanished and constant melting (or boiling) points were reached. Spectral measurements were made on Spectromom 2000 instrument. Elemental analysis was made on Carlo Erba analyzer 1102.

Malononitrile was purified by vacuum sublimation at 40° (1 mm), m.p. 32.1°. Calculated for $C_3H_2N_2$: C, 54.54; H, 3.05; N, 42.40. Found: C, 54.15; H, 3.71; N, 42.15.

Methylmalononitrile was recrystallized from heptane and sublimed at 40° (1 mm), m.p. 26.0°. Calculated for $C_4H_4N_2$: C, 59.99; H, 5.03; N, 34.99. Found: C, 59.03; H, 4.93; N, 35.03.

Ethylmalononitrile was fractionated, a fraction at 80-85° (12 mm) was taken, n_D^{20} 1.4156, d_4^{20} 0.9512. Calculated for $C_5H_6N_2$: C, 68.81; H, 6.43; N, 29.76. Found: C, 62.76; H, 6.19; N, 30.82.

i-Propylmalononitrile was fractionated taking a fraction at 85-90° (10 mm), n_D^{20} 1.4191, d_4^{20} 0.9501. Calculated for $C_6H_8N_2$: C, 66.64; H, 7.46; N, 25.90. Found: C, 66.07; H, 7.48; N, 26.79.

i-Butylmalononitrile was fractionated, taking a fraction at 80-85° (7 mm), n_D^{20} 1.4250, d_4^{20} 0.9122. Calculated for $C_7H_{10}N_2$: C, 68.82; H, 8.25; N, 22.94. Found: C, 67.94; H, 8.22; N, 23.84.

(Cyclohexylmethyl)malononitrile was purified by vacuum sublimation at 50° (1 mm), m.p. 33.0±0.5°. Calculated for $C_{10}H_{14}N_2$: C, 74.04; H, 8.70; N, 17.27. Found: C, 72.53; H, 8.44; N, 17.24.

Benzylmalononitrile was purified by vacuum sublimation at 140° (2 mm), m.p. 93.0°. Calculated for $C_{10}H_8N_2$: C, 76.90; H, 5.16; N, 17.94. Found: C, 76.63; H, 5.07; N, 17.79.

p-Nitrobenzylmalononitrile was recrystallized by dissolving in benzene, then adding heptane, and repeatedly from dichloroethane - heptane mixture, m.p. 165.0±0.2°. Titration after hydrolysis indicated a 99.8±0.5% purity. Calculated for $C_{10}H_7N_3O_2$: C, 59.70; H, 3.51; N, 20.88; O, 15.89. Found: C, 59.59; H, 3.55; N, 21.47; O, 16.34.

Doubly distilled water was used for all measurements. Glycine was a Reanal compound for chromatography, other compounds were of GOST "chemical pure" grade. Sodium chloride and potassium bromide were dried before use.

For pK_a - measurements several methods were proved by example of the malononitrile, for which the pK_a - value was reported to be 11.19.³ The standard potentiometric titration method gave values increasing slightly with the alkalinity of the solution. Back titrations showed the dissociation to be practically unreversible. Only by decreasing the duration of the titration a reasonable constant pK_a - value was received:

11.39 ± 0.01 as the mean of eight titrations at 25.0° and $I = 0.01$ M, the mean deviation in one titration being about 0.02 and the reversibility in an end-point more than 80%. Since the method of Hashimoto et al.⁹ was proved to give time-depending results also, dissociation constants of malononitriles in aqueous glycine buffer solutions at 25.0° and an ionic strength of 0.1 M were determined according to Hibbert, Long, and Walters.³ At the wavelength used (λ_{\max} of the anion) absorption of the malononitrile was negligible in all cases but p-nitrobenzylmalononitrile ($\epsilon 2300 \text{ cm}^2 \text{ mol}^{-1}$). Measurements were made on a Perkin Elmer 402 instrument. The pH-value of each buffer solution was confirmed with a Laborpribor LPM-60M pH-meter, standardized by tart-rate and borax solutions, and calcium hydroxide solution prepared as described by Bates.¹⁰ The experimental data were corrected using the Debye-Hückel approximation and treated by a least squares method to calculate both the extinction coefficient of the anion and a value of the dissociation constant K_a^0 , referring to infinite dilution (method A). An usual method, based on the extinction coefficient of the anion determined separately at $\text{pH} \gg \text{p}K_a$ (method B) gave nearly equal $\text{p}K_a$ -values (see Table 1). However, the results of the first were used for discussion in view of its higher sensitivity to experimental uncertainties and insufficient high pH-values possible ($\text{pH} \leq \text{p}K_a + 1.2$) for a separate determination of the extinction coefficient of the anion.

Rates of water - catalyzed bromination of malononitriles were measured at 25.0° by a conductimetric method. All reactions were carried out in excess of bromine and at the ionic strength kept at 0.1 M with sodium chloride or potassium bromide. A small amount (ca 0.15 g) of an aqueous or ethanolic solution of malononitrile was injected into the reaction mixture (15.0 cc.) in the thermostated conductance cell. The amplitude of temperature fluctuation in the cell was not higher than $\pm 0.01^\circ$. Incorporation of synchronized overheating of the contact thermometer was used.¹¹ Readings of the resistance were taken starting from the zero time mixing. An

electronic conductimeter ERCP-60 was used as a zero-instrument.¹² The plot of dR/dt vs. R was linear over the two half-lives and the gradient was independent of malononitrile, hydrochloric acid, and bromine concentrations at certain conditions only. For these conditions (see Table 2) first order ionization rate constants were determined by the Rudakov's " $\ln \phi - \tau$ method".¹³

References

1. A.I. Talvik and V.A. Palm, Organic Reactivity, 11, 2 (40) 287 (1974).
2. R.G. Pearson and K.L. Dillon, J. Amer.Chem.Soc., 75, 2439 (1953).
3. F. Hibbert, F.A. Long, and E.A. Walters, J. Amer Chem. Soc., 93, 2829 (1971).
4. A.I.Talvik, Organic Reactivity, 11, 4 (42) 977 (1975).
5. J.F.J. Dippy and F.R. Williams, J.Chem.Soc., 1934, 161.
6. V.A. Palm, Foundations of Quantitative Theory of Organic Reactions, Khimia, Leningrad, 1967, ch.7.
7. F. Hibbert and F.A. Long, J.Amer.Chem.Soc., 94, 2647 (1972).
8. R. Boyd, J.Amer.Chem.Soc., 83, 4288 (1961).
9. F. Hashimoto, J. Tanaka, and S. Nagakura, J.Molec. Spectroscopy, 10, 401 (1963).
10. R.G. Bates, Determination of pH. Theory and Practice, J. Wiley, New York, London, Sidney, 1964, ch.5.
11. Ü.L. Haldna, J.Phys.Chem., 35, 934 (1961)(Russ.).
12. V.E. Reeben, J.Phys.Chem., 37, 1644 (1963) (Russ.).
13. E.S. Rudakov, Kinetica i kataliz, 1, 177 (1960).

ESTIMATION OF "ORTHO-EFFECT" AND INDUCTIVE TRANSMITTANCY OF AROMATIC CYCLES

V.M. Nummert

Chemistry Department, Tartu State University,
Tartu, Estonian S.S.R., U.S.S.R.

Received June 18, 1975

Making use of alkaline and acidic hydrolysis data of phenyl benzoates the quantitative separation of the contributions of inductive and "ortho" effects of o-substituents has been performed. The regression analysis of the data for several reaction series for aqueous solution according to equation

$$\lg k = \rho_o^* \sigma^* + m \Delta^o + \text{const}$$

has been carried out. The linear relationship between the calculated values of inductive ρ_o^* for o-substituents and the ρ^o values was observed.

It was found that equation

$$\rho_{o,m,p}^* = 1/Z_c^* \rho^o (Z_{o,m,p}^*)_{\text{calc}}$$

enables the calculation of the inductive

$$\rho_{o,m,p}^* = Z_{o,m,p}^* (\rho_{X-Y}^*)_{\text{Ar}}$$

values related to the attenuation of the inductive effect only through σ -bonds ($Z_c^* = 0.384$).

In our previous papers¹⁻⁴ the rates of the alkaline and acidic hydrolysis of m- and p-substituted phenyl benzoates, $C_6H_5COOC_6H_4-X$, and alkyl benzoates, $C_6H_5COOCH_2-X$, with neutral and charged substituents have been investigated. After the electrostatic correction for charged substituents was introduced the data processing according to the Ingold-Taft concept⁵⁻⁷ led to an inductive attenuation factor for carbon atom $Z_c^* (=0.384)$ common for hydrocarbon, electronegative and

charged substituents in alkyl benzoates and also in substituted phenyl benzoates⁴. Taking into account the "normal" attenuation of inductive effect through the carbon chain, the present work was undertaken to examine by the analogy with aliphatic compounds the influence of o-substituents in substituted phenyl benzoates similarly as it was done by Taft^{6,7} more than twenty years ago. The polar σ_o^* constants were calculated by him for o-substituents as the characteristic of polar influence of o-substituents using the kinetic data of o-substituted benzoates with substituents in acyl part of carboxylic esters.

The results of the investigation of the alkaline and acidic hydrolysis of substituted phenyl benzoates, $C_6H_5COOC_6H_4-X$, show^{8,9} that the plot of $\Delta \lg k = \lg(k_{OH}/k_H)$ for substituted phenyl benzoates (k_{OH} and k_H denote the alkaline and acidic hydrolysis rate constants, respectively) vs. $\lg k_{OH}$ for substituted phenyl tosylates leads to the straight line common for o-, m- and p-substituted compounds as well as for neutral and charged substituents (slope 0.508 ± 0.013 , $r=0.996$, $s=0.054$). For the latter the values of rate constants k_o obtained by the extrapolation of the second-order rate constants to pure water were used (no electrostatic correction was applied):

$$\frac{\Delta \lg(k_{OH}/k_H)_{m,p}^{Benz}}{\Delta \lg(k_{OH})_{m,p}^{Tos}} = \frac{\Delta \lg(k_{OH}/k_H)_o^{Benz}}{\Delta \lg(k_{OH})_o^{Tos}} \quad (1)$$

Benz and Tos denote the series of benzoates and tosylates, and indices m, p, and o denote m-, p-, and o-substituted compounds, respectively.

When the values of $\lg k_{OH}$ for the alkaline hydrolysis of substituted phenyl benzoates are plotted versus $\lg k_{OH}$ for alkaline hydrolysis of substituted phenyl tosylates ($50^\circ C, H_2O$) the points for o-substituted compounds fit the line ($r=0.966$) different from the line for m- and p-substituted compounds ($r=0.997$). Such a situation is probably due to the steric

effect operating in the case of alkaline hydrolysis of o-substituted phenyl benzoates. For the alkaline hydrolysis of o-substituted phenyl tosylates the steric effect can be neglected¹⁰. Hence, using for benzoate series the differences $\lg(k_{OH}/k_H)$ rather than the $\lg k_{OH}$ values, influence of the steric effect can be excluded.

It is interesting to consider what kind of effects, besides the steric one, are affecting the reactivity of o-substituted phenyl benzoates in their alkaline hydrolysis.

Assuming the "normal" attenuation factor inductive effect through the carbon chain in the case of hydrolysis of benzoates one can calculate the inductive contribution (P) in the gross substituent effect as follows:

$$P = \rho_{X-Y}^* \left[(Z_c^*)^2 + (Z_c^*)^6 \right] \sigma_X^* = 2.08 \cdot 0.150 \sigma_X^* \quad (2)$$

where $\rho_{X-Y}^* = 2.08$ and $Z_c^* = 0.384$ for aliphatic substituents⁴. Calculated values of P and $\Delta \lg(k_{OH}/k_H) - P = \Delta^0$ for different o-substituents are given in Table 1.

Fig. 1 illustrates the dependence of the Δ^0 values on the resonance constants, $\sigma_R = \sigma_p^0 - Z_p^* \sigma_X^*$ ¹⁵. For comparison Fig. 1 also includes the analogous dependence of the differences $\Delta \lg(k_{OH}/k_H) - P$ on σ_R constants for m- and p-substituents. The correlation between the Δ^0 values and σ_R constants is poor the point for 2-N(CH₃)₂ substituent significantly deviating from the line for o-substituents. In analogous dependence the points for m- and p-substituted compounds form a different line with the slope considerably larger than that in the case of o-substituted compounds. For +R m- and p-substituents (resonance-acceptor) the resonance factor increases the reaction rate. At the same time for all o-substituted compounds the Δ^0 values are negative. Hence, it seems unreasonable to interpret the Δ^0 values in terms of resonance effect, only.

In order to check the applicability of the Δ^0 values in the case of other processes the treatment of the data for different reaction series according to Eq.(3) was used.

Table 1

Calculated Values of $\Delta \lg(k_{OH}/k_H) - P = \Delta^{\circ}$
 Data for Aqueous Solution at 50°C Were Used 4,8,9

Substituent X	$\lg k_{OH}$	$\lg k_H$	$\lg(k_{OH}/k_H)_X$	$\Delta \lg(k_{OH}/k_H) =$ $= \lg(k_{OH}/k_H)_X -$ $= \lg(k_{OH}/k_H)_H$	$P = \sigma_{X-Y}^* \sigma_{X-Z}^* \sigma_{X-O}^* =$ $= 2.08 \quad 0.150 \quad \sigma_X^*$	$\Delta \lg(k_{OH}/k_H) -$ $- P = \Delta^{\circ}$
2-NO ₂	0.836	-5.558	6.424	0.986	1.100	-0.114
2-F	0.536	-5.418	5.954	0.516	0.963	-0.449
2-Cl	0.406	-5.574	5.980	0.542	0.836	-0.294
2-N(CH ₃) ₂	-	-	5.495	0.057	0.242	-0.185
2-CH ₃	-0.268	-5.470	5.202	-0.236	0	-0.236

$$\lg k(pK) = \rho^* \sigma_X^* + m \Delta^0 + \text{const} \quad (3)$$

Only those reaction series in which the steric effects for o-substituted compounds were assumed to be negligible were considered. As far as the Δ^0 values are calculated from the data for aqueous solution it is possible that the Δ^0 term includes a contribution caused by specific solvation of o-substituted compounds. Therefore the data for aqueous solution only were used.

The following reaction series were processed:

1. pK_a values for dissociation of benzoic acids, 25°C, H_2O .
2. pK_a values for dissociation of phenols, 25°C, H_2O .
3. pK_a values for dissociation of anilinium ions, 25°C, H_2O .
4. $\lg k$ for alkaline hydrolysis of phenyl tosylates, 15°C, H_2O .
5. The same reaction, 50°C, H_2O .
6. The same reaction, 85°C, H_2O .

The results of the statistical treatment of data for these reaction series according to the Eq.(3) are listed in Table 2.

It is obvious that Eq.(3) describes the effects of o-substituents quite well. It was found that for all reaction series considered there exists a linear relationship between the ρ_o^* values and the ρ^0 values (Fig.2) with the slope $0.379(\pm 0.021)$ ($r=0.992$, $s=0.032$). Consequently $\rho_o^* = 0.379 \rho^0$.

On the other hand $\rho_o^* = Z_m^* \rho_o^0$ and one can conclude that $Z_m^* = \rho_o^* / \rho_o^0 = 0.379$ the Z_m^* being analogous to Z_m^* and Z_p^* transmission factor. The Z_m^* value was found from the following equation

$$\sigma_m^0 = Z_m^* \sigma_X^* + Z_m^R \sigma_R \quad \therefore (4)$$

where Z_m^* is the attenuation factor for m-phenylene system, ($Z_m^* = 0.147^{15}$), and σ_p^0 is bisected in the analogous way ($Z_p^* = 0.112^{15}$).

Table 2

Correlation of Data Y According to Equation $Y = \rho_o^* \sigma_X^* + m \Delta_X^o + \text{const.}$

Nr.	Reaction series	Y	$Y_o(X=H)$	ρ_o^*	m	const	r	s
1	2	3	4	5	6	7	8	9
1.	Dissociation of benzoic acids, 25°C, H_2O^{11} (X=2-NO ₂ , 2-F, 2-Cl, 2-CH ₃)	pK	4,17	-0.400 ± 0.020	-2.74 ± 0.23	3.25 ± 0.08	0.999	0.056
		ΔpK		0.406 ± 0.021	2.74 ± 0.25	0.915 ± 0.086	0.999	0.059
2.	Dissociation of phenols, 25°C, H_2O^{11} (X=2-NO ₂ , 2-F, 2-Cl, 2-CH ₃)	pK	9,98	-0.736 ± 0.016	-3.75 ± 0.18	9.39 ± 0.06	0.999	0.044
		ΔpK		0.739 ± 0.16	3.74 ± 0.19	0.600 ± 0.07	0.999	0.045
3.	Dissociation of anilinium ions, 25°C, H_2O^{11} (X=2-NO ₂ , 2-F, 2-Cl, 2-CH ₃ , 2-N(CH ₃) ₂)	pK	4,60	-1.00 ± 0.13	-9.12 ± 1.47	2.35 ± 0.51	0.995	0.35
		ΔpK		1.00 ± 0.13	9.12 ± 1.46	2.25 ± 0.051	0.995	0.35
4.	Alkaline hydrolysis of phenyl tosylates, 15°C, $H_2O^{12,13}$ (X=2-NO ₂ , 2-F, 2-Cl, 2-N(CH ₃) ₂)	lgk	-4.33	0.772 ± 0.130	3.15 ± 1.07	-4.09 ± 0.41	0.987	0.267
		Δlgk		0.772 ± 0.130	3.15 ± 1.07	0.23 ± 0.41	0.987	0.267

1	2	3	4	5	6	7	8	9
5. The same reaction 50°C, H ₂ O ¹⁴ , (X=2-NO ₂ , 2-F, 2-Cl, 2-CH ₃ , 2-N(CH ₃) ₂)	lg k	-2.94	0.615±0.051	2.53±0.62	-2.76±0.18	0.993	0.15	
	Δlg k		0.617±0.062	2.53±0.62	0.18±0.19	0.993	0.16	
6. The same reaction, 85°C, H ₂ O ^{12,13} (X=2-NO ₂ , 2-F, 2-Cl, 2-CH ₃ , 2-N(CH ₃) ₂)	lg k	-1.78	0.544±0.052	2.44±0.64	-1.66±0.19	0.991	0.16	
	Δlg k		0.544±0.052	2.44±0.64	0.12±0.19	0.991	0.16	

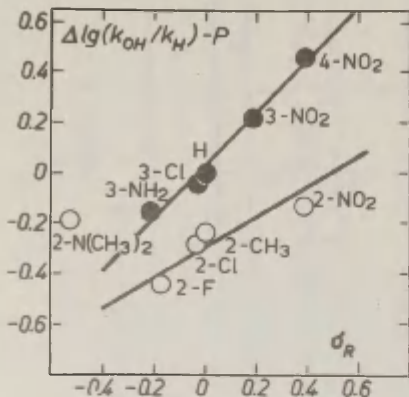


Fig. 1 Relationship $\Delta \lg(k_{OH}/k_H) - P$ vs. σ_R
 $\sigma_R = \sigma_P^0 - Z_P^{\pi} \sigma_X^{\pi} 14/$,
 $P_P = Z_P^{\pi} \cdot \Delta \lg k_{XCH_2} 4/$,
 $P_m = Z_m^{\pi} \Delta \lg k_{XCH_2} 4/$,
 $P_o = \rho_{X-Y}^{\pi} \cdot Z_o^{\pi} \cdot \sigma_X^{\pi}$

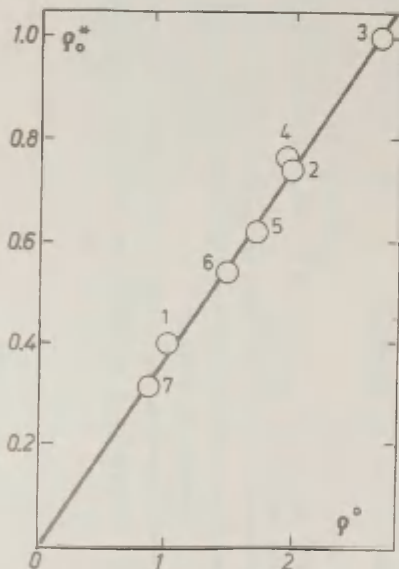


Fig. 2. Relationship between ρ_o^{π} and ρ^o . Numbering of points corresponds to reaction series in Table 2. Values of ρ^o were taken from Refs. 4, 12, 14-17. Point 7: Alkaline hydrolysis of phenyl benzoates. $50^\circ C$, H_2O $4/$. Value of ρ_o^{π} was calculated according to Eq.(2)

The ratio $Z_{\text{m}}^*/Z_{\text{o}}^*$ could be in a good approximation considered as an inductive attenuation factor Z_{c}^* for a single carbon atom:

$$Z_{\text{c}}^* = Z_{\text{m}}^*/Z_{\text{o}}^* = 0.147/0.379 = 0.388$$

The Z_{c}^* value obtained for a carbon atom involved in the aromatic cycle does not differ from these values found using pK_{a} data for aliphatic carboxylic acids¹⁵ ($Z_{\text{c}}^* = 0.388 \pm 0.015$) and $\lg(k_{\text{OH}}/k_{\text{H}})$ values for hydrolysis of benzoates⁴ ($Z_{\text{c}}^* = 0.384 \pm 0.035$).

The relationship between the pK_{meta} and the pK_{ortho} values for benzoic acids (H_2O , 25°C) gives an analogous result. As one can see from Fig. 3 fall-off plot for m- and o-substituted benzoic acids form a straight line (slope 0.346 ± 0.026 , $r=0.978$) parallel with that for aliphatic carboxylic acids. Such a relationship between the pK_{meta} and pK_{ortho} values can exist if the ratio $\rho_{\text{m}}^*/\rho_{\text{o}}^*$ nearly equals the ratio of the resonance contribution of m-substituted compounds and ortho-effects:

$$\rho_{\text{m}}^*/\rho_{\text{o}}^* \approx \Delta\text{pK}_{\text{R}}^{\text{m}}/\Delta^{\text{o}}$$

Assuming constant inductive attenuation factor Z_{c}^* for every carbon atom in benzene ring, the inductive transmission factors for o-, m- and p- phenylene systems could be calculated and these values obtained could be compared with the values of $Z_{\text{o,m,p}}^*$ obtained from correlation of the experimental data with the δ_{X}^* values.

$$(Z_{\text{o}}^*)_{\text{calc}} = (Z_{\text{c}}^*)^2 + (Z_{\text{c}}^*)^6 = 0.150;$$

$$(Z_{\text{m}}^*)_{\text{calc}} = (Z_{\text{c}}^*)^3 + (Z_{\text{c}}^*)^5 = 0.064;$$

$$(Z_{\text{p}}^*)_{\text{calc}} = 2(Z_{\text{c}}^*)^4 = 0.043$$

The value $Z_{\text{c}}^* = 0.384$ obtained for the hydrolysis data for benzoates⁴ has been used.

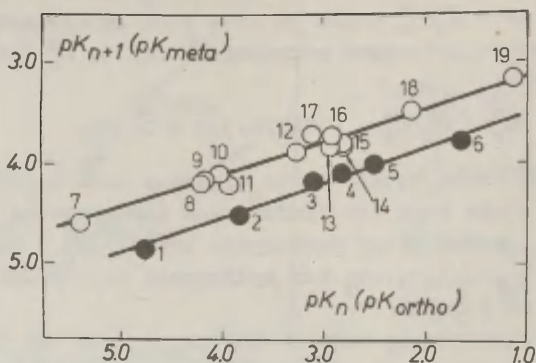


Fig. 3 Relationship between $pK_{n+1}(pK_{meta})$ and $pK_n(pK_{ortho})$. H_2O , $25^\circ C$

●: Aliphatic carboxylic acids $X(CH_2)_nCOOH$ ($n=1$)¹⁵

1. H, 2. OH, 3. CF_3 , 4. Cl, 5. CN, 6. NO_2

○: m- and o-substituted benzoic acids^{11,17,18}

7. COO^- , 8. H, 9. OEt, 10. OMe, 11. Me, 12. F, 13. Cl,

14. Br, 15. I, 16. $COOH$, 17. CN, 18. NO_2 , 19. NMe_3^+

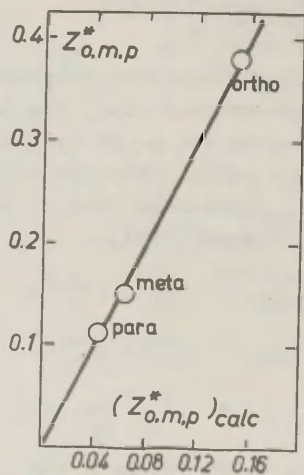


Fig. 4. Relationship between $Z_{o,m,p}^*$ and $(Z_{o,m,p}^*)_{calc}$

It is obvious that

$$Z_o^* = 0.379 \neq (Z_o^*)_{\text{calc}} = 0.150$$

$$Z_m^* = 0.147 \neq (Z_m^*)_{\text{calc}} = 0.064$$

$$Z_p^* = 0.112 \neq (Z_p^*)_{\text{calc}} = 0.043$$

At the same time the following ratios are equal each to other:

$$\frac{Z_o^*}{(Z_o^*)_{\text{calc}}} = \frac{Z_m^*}{(Z_m^*)_{\text{calc}}} = \frac{Z_p^*}{(Z_p^*)_{\text{calc}}} = 2,55 \quad (5)$$

In Fig. 4 the relationship between $Z_{o,m,p}^*$ and $(Z_{o,m,p}^*)_{\text{calc}}$ is given. Slope of the straight line is 2.55 ± 0.17

Assuming $(Z_o^*)_{\text{calc}} = (Z_c^*)^2 = 0.147$ and $(Z_m^*)_{\text{calc}} = (Z_o^*)^3 = 0.056$ the ratio (5) can be recalculated with an excellent precision*:

$$\frac{Z_o^*}{(Z_o^*)^2} = \frac{0.379}{0.147} = 2.58; \quad \frac{Z_m^*}{(Z_c^*)^3} = \frac{0.147}{0.056} = 2.62;$$

$$\frac{Z_p^*}{(Z_p^*)_{\text{calc}}} = \frac{0.112}{0.043} = 2.60 \quad (6)$$

Then the inductive attenuation factor for carbon atom Z_c^* can be expressed in the following way:

$$\frac{Z_m^*}{Z_o^*} = \frac{2.60(Z_c^*)^3}{2.60(Z_c^*)^2} = Z_c^* \quad (7)$$

Hence, assuming the transmission of inductive influence through σ -bonds, only ρ^* values for o-, m- and p- derivatives for any reaction series could be found by multiplying the ρ^0 value by 2.60.

* In the case of o- and m-phenylene systems the transmission of the inductive effect through the longer carbon chain is ignored.

$$\rho_{o,m,p}^{\#} = 2.60 \rho^{\circ}(Z_{o,m,p}^{\#})_{\text{calc}} \quad (8)$$

One can see that $\rho_o^{\#} = 0.379 \rho^{\circ} = Z_c^{\#} \cdot \rho^{\circ}$,

$$\rho_m^{\#} = 0.147 \rho^{\circ} = (Z_c^{\#})^2 \rho^{\circ} \text{ and } \rho_p^{\#} = 0.112 \rho^{\circ} = 2(Z_c^{\#})^3 \rho^{\circ}.$$

Considering $2.60 = 1/0.385 = 1/Z_c^{\#}$ one can write:

$$\rho_o^{\#} = Z_c^{\#} \rho^{\circ} = 1/Z_c^{\#} \rho^{\circ} (Z_c^{\#})^2 \quad (9)$$

$$\rho_m^{\#} = (Z_c^{\#})^2 \cdot \rho^{\circ} = 1/Z_c^{\#} \rho^{\circ} \cdot (Z_c^{\#})^3$$

$$\rho_p^{\#} = 2(Z_c^{\#})^3 \cdot \rho^{\circ} = 1/Z_c^{\#} \rho^{\circ} \cdot 2(Z_c^{\#})^4$$

The value $2.6 \rho^{\circ} = 1/Z_c^{\#} \rho^{\circ}$ could be considered as the effective reaction constant $(\rho_{X-Y}^{\#})_{\text{Ar}}$ for a hypothetical "aromatic" compounds of type X-Y where substituents are directly bonded to the reaction center:

$$(\rho_{X-Y}^{\#})_{\text{Ar}} = 2.6 \rho^{\circ} \quad (10)$$

It is necessary to underline that, in general, the values of $(\rho_{X-Y}^{\#})_{\text{Ar}}$ are not equal to the $\rho_{X-Y}^{\#}$ values found from the data for corresponding aliphatic reaction series.

In the case of "normal" reaction series, where even for m-substituted phenyls the attenuation of the inductive effect through σ -bonds characterized by strictly constant attenuation factor $Z_c^{\#}$ was found (series of hydrolysis of benzoates^{4/}) this relationship is hold, too:

$$(\rho_{X-Y}^{\#})_{\text{Ar}} / \rho^{\circ} = 2.42 \quad (\text{at } 50^{\circ}\text{C})$$

The following relationship exists:

$$(\rho_{X-Y}^{\#})_{\text{Aliph}} = (\rho_{X-Y}^{\#})_{\text{Ar}} = 2.6 \rho^{\circ}$$

In the case of this "normal" reaction series the use of the values $\sigma_{m,p}^{\#} = 0.6 + \sigma_{m,p}^{\circ}$ leads to

$$(\rho_{X-Y}^*)_{\text{Aliph}} / \rho^0 = 1/Z_c^*$$

but the use of the values $\sigma_{m,p}^* = 0.6 + Z_c^* \sigma^0$ leads to the equality:

$$(\rho_{X-Y}^*)_{\text{Aliph}} = (\rho_{X-Y}^*)_{\text{Ar}} = 1/Z_c^* \rho^0$$

In such a case the common linearity upon σ^* values for those m- and p-substituted phenyls for which ones the resonance contribution could be considered as a minor one, and for aliphatic electronegative substituents is observed (Fig.5).

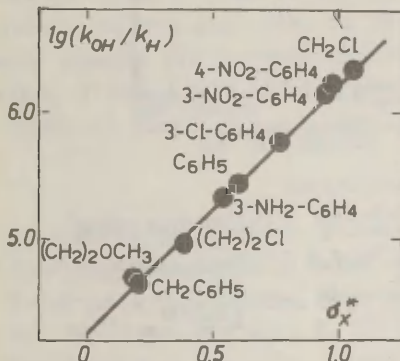


Fig. 5 Relationship between $\lg(k_{OH}/k_H)$ for hydrolysis of benzoates and σ_X^* H_2O , $50^\circ C$
 $\sigma_{m,p}^* = 0.6 + Z_c^* \sigma^0$ was used for m- and p-substituted phenyls

For reaction series considered (Table 2) the ρ^* values can be calculated as in the case of aliphatic carboxylic acids the $\rho_{X(CH_2)_2COOH}^*$ values from the ρ_{X-COOH}^* values.

Consequently:

$$\frac{\rho_{X(CH_2)_2COOH}^*}{(\rho_{X-COOH}^*)_{\text{Aliph}}} = \frac{\rho^0}{(\rho_{X-Y}^*)_{\text{Ar}}} = \frac{\rho^0}{1/Z_c^* \rho^0} = (Z_c^*)^2 \quad (11)$$

In Fig.6 the relationship between ρ_o^* (Table 2) and $(\rho_{X-Y}^*)_{Ar} = 1/Z_c^* \rho^o = 2.6 \rho^o$ is represented. One can see (the values $\rho_{X(CH_2)_2COOH}^* = 0.280 (\pm 0.026)$ and $\rho_{X-COOH}^* = 1.81^{15}$ were used) that the point for aliphatic carboxylic acid fit the common straight line with o-substituted phenyls.

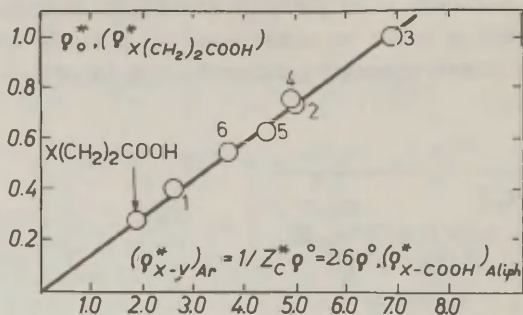


Fig.6. Relationship between $\rho_o^* (\rho_{X(CH_2)_2COOH}^*)$ and $(\rho_{X-Y}^*)_{Ar} = 1/Z_c^* \rho^o = 2.6 \rho^o ((\rho_{X-COOH}^*)_{Aliph})$. Values $\rho_{X(CH_2)_2COOH}^* = 0.28$ and $\rho_{XCOOH}^* = 1.81^{15}$ were used.

It is necessary to note that the approach presented in this paper to quantitative separation of "ortho" and inductive effects could not be considered as complete and universally applicable because the data for aqueous solution only were involved in data processing.

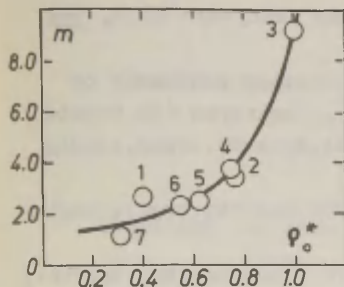


Fig.7. Relationship between m and ρ_o^* (see Table 2). Numbering of points corresponds to reaction series in Table 2. Point 7: Hydrolysis of phenyl benzoates.

In Fig.7 the relationship between the values of m and ρ_o^* (Table 2) is given. The linearity between these quantities is absent. At the same time it is obvious that the sensitivity towards the "ortho" effect increases with the increasing of the sensitivity towards the inductive effect. On condition that $\rho_o^* = 0$, the ortho effect also vanishes.

References.

1. T.O.Püssa, V.M.Nummert (Maremäe), and V.A.Palm, *Reakts. sposobn.organ.soedin.*, 9, 697 (1972).
2. T.O.Püssa, V.M.Nummert (Maremäe), and V.A.Palm, *Reakts. sposobn.organ.soedin.*, 9, 871 (1972).
3. T.O.Püssa and V.A.Palm, *Reakts.sposobn.organ.soedin.*, 9, 1209 (1972).
4. V.A.Palm, T.O.Püssa, V.M.Nummert, and I.V.Talvik, *Reakts. sposobn.organ.soedin.*, 10, 243 (1973).
5. C.K.Ingold, *J.Chem.Soc.*, 1930, 1032.
6. R.W.Taft, Jr., *J.Amer.Chem.Soc.*, 74, 3120 (1952).
7. R.W.Taft, Jr., *J.Amer.Chem.Soc.*, 75, 4231 (1953).
8. V.M. Nummert and M.V.Piirsalu, *Organic Reactivity*, 11, 899 (1975).
9. V.M.Nummert and M.V.Piirsalu, *Organic Reactivity*, 11, 911 (1975).

10. V.A.Palm and R.V.Vizgert, Doklady Akad.Nayk SSSR, 142, 1091 (1962).
11. A.Albert and E.Sergeant, "Dissociation Constants of Organic Acid and Bases", Khimia, Leningrad (in Russian).
12. V.M.Maremäe and V.A.Palm, Reakts.sposobn.organ.soedin., 11, 3(5), 209 (1965).
13. V.M.Maremäe and T.O.Püssa, Reakts.sposobn.organ.soedin., 6, 732 (1969).
14. V.M.Maremäe and V.A.Palm, Reakts.sposobn.organ.soedin., 1, 2, 85 (1964).
15. V.A.Palm, "Fundamentals of the Quantitative Theory of Organic Reactions", (Khimia, Leningrad) 1967.
16. I.A.Koppel, V.M.Maremäe, and A.V.Tuulmets, Reakts.sposobn.organ.soedin., 2, 3(5), 39 (1963).
17. G.Kortüm, W.Vogel, and K.Andrussov, "Dissoziation Konstanten Organischer Säuren in Wasseriger Lösung, London, Butterworths, 1961.
18. M.Hojo, M.Utaka and Z.Yoshida, Tetrahedron, 27, 4255 (1971).

AN ESTIMATION OF THE DEGREE OF DISSOCIATION OF ION-PAIRS IN WATER

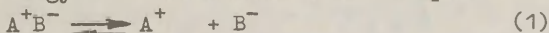
Ü. Haldna

Chemistry Department, Tartu State University,
Tartu, Estonian S.S.R.

Received June 23, 1975

The degree of dissociation of ion-pairs in water has been calculated at various concentrations of the univalent electrolyte using the electrostatic model. This treatment has led to the conclusion that the salt $(C_2H_5)_4N^+.C_3(CN)^-_5$, used in the Boyd's method, is mostly dissociated in water at the concentrations predicted by its solubility.

The free energy of dissociation of an ion-pair



is given^{1,2} by

$$\Delta F = \frac{Ne^2}{aD} = \frac{331,8}{aD} \quad (2)$$

where a is the distance between charges (in Å) and D is the dielectric constant of the medium (for water $D=78,3^3$).

Using the dissociation constant

$$K = \frac{[A^+][B^-]}{[A^+B^-]} = e^{-\frac{\Delta F}{RT}} \quad (3)$$

and the total concentration (c) of the salt, the degree of dissociation of ion-pairs can be written as follows:

$$\alpha = \frac{[A^+]}{c} = -\frac{K}{2c} + \sqrt{\left(\frac{K}{2c}\right)^2 + \frac{K}{c}} \quad (4)$$

Assuming different values for a (in Eq.2) the functions $\alpha = f(c)$ have been calculated (see Fig. 1). The plots $\alpha = f(c)$

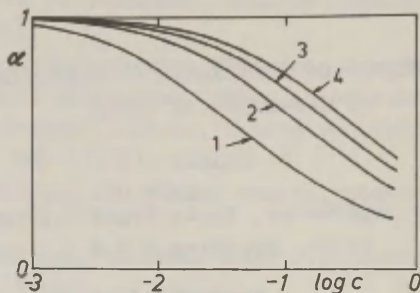
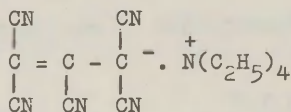


Fig. 1 The plot of the degree of dissociation of ion pairs (α) vs. total concentration of salt (c). Following distances between charges (a) are assumed: 1 - 2 Å, 2 - 3 Å, 3 - 4 Å, and 4 - 5 Å.

can be used for an estimation of the degree of dissociation of the salt PCP-TEA^+ :



in water. This case presents a remarkable interest because the Boyd's method⁴ for the determination of relative activity coefficients for ions assumes that for PCP-TEA^+ $\alpha = 1$. Since the radius of TEA^+ -ion is $2,8 \text{ \AA}$ ⁵, it follows that the distance between charges in PCP-TEA^+ is about $3\text{--}4 \text{ \AA}$. The saturated solutions of PCP-TEA^+ are not very concentrated ($c = 0,002 \text{ mole/l}$ in water and $c = 0,23 \text{ mole/l}$ in 74% w/w H_2SO_4).⁶ It is obvious from Fig. 1 that for PCP-TEA^+

$1 > \alpha > 0,5$ in 0-74% w/w H_2SO_4 . Consequently the Boyd's assumption $\alpha = 1$ does not lead to great errors. However, it should be pointed out that this conclusion is based on the applicability of Eq. 2 (with $D = \text{const.}$). The problems con-

nected with Eq. 2 are discussed in Ref. 1 and the D value will not remain constant if an electrolyte is added to water.⁷

References

1. M. Szwarc, Ed., Ions and Ion Pairs in Organic Reactions. Vol. 1, J. Wiley and Sons, New York, London, Toronto 18, (1972).
2. V.A. Palm, Reakts. sposobn. organ. soedin., 10, 413 (1973)
3. R. Robinson and R. Stokes, Electrolyte Solutions. Butterworths, London, 529 (1959).
4. R. Boyd in "Solvent-Solute Interactions" (J.F. Coetzee and C.D. Ritchie, Eds.), Marcel Dekker, N.Y., 97 (1969).
5. B.S. Krumgalz, J. Structurnoy Khimiy (in Russian), 13, 774 (1972).
6. T.K. Rodima and U.L. Haldna, Reakts. sposobn. organ. soedin. 2, 1273 (1970).
7. E. Grünwald, S. Highsmith, and Ting-Po I in M. Szwarc Ed., Ions and Ion Pairs in Organic Reactions, Vol. 2. J. Wiley and Sons, New York, London, Toronto 498 (1974).

ON THE EFFECT OF CARBOXYINVERSION ON TRIPHENYL VERDAZYL REACTION WITH SUBSTITUTED BENZOYL PEROXIDES

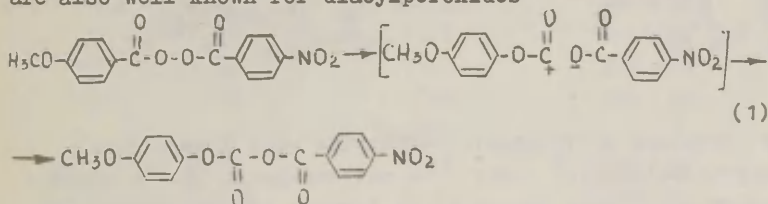
O.M.Polumbrik, V.I.Staninets, B.M.Yarmolyuk

Institute of Organic Chemistry Acad. Sci. of the
Ukr.SSR, Kiev-94, Murmanskaya, 5

Received June 25, 1975.

The kinetics of triphenyl verdazyl (TPV) reaction with p-nitro, p'-methylsubstituted benzoyl peroxide (p-NO₂, p'-CH₃-BP) in benzene, hexane and acetone has been studied spectrophotometrically. The reaction rate is described by the second order kinetic equation $v = k_2 \cdot (\text{TPV}) \cdot (\text{p-NO}_2, \text{p'-CH}_3\text{-BP})$. Carboxyinverson was found be proceed rather slow with no practical effect on the reaction rate of TPV with substituted benzoyl peroxides. The reaction mechanism including TPV attack on electroneficient peroxy oxygen is suggested.

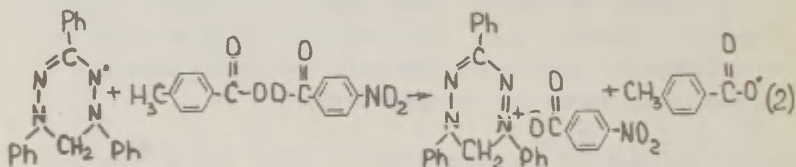
R.Criegee had shown ¹ that organic peroxides in solutions can undergo the rearrangement which results in ester formation (carboxyinverson). Such rearrangements are also well known for diacylperoxides ^{2,3}:



Carboxyinverson is supposed to occur through relatively stable ion intermediates ⁴ or through four- or six membered cyclic transition state ⁵. It is known ⁶ from the studies in this area that symmetric and unsymmetric peroxides can follow Criegee's mechanism. This reaction mechanism

can predominate even in nonpolar solvents*. Decomposition of many peroxides in nonpolar solvents (20-80 °C) results in polar products formation with considerable yield.⁷ Walling suggested⁸ that carboxyinverson occurs through mixed polar-radical mechanism including the formation of a unstable internal ion pair - radical pair type compound in a transition state.

In order to determine the significance and place of carboxyinverson in the case of triphenyl verdazylic radical (TPV) reaction with substituted benzoyl peroxides (X-BP)⁹ the kinetics of this reaction was studied in benzene, hexane and acetone for p-nitro, p-methylsubstituted benzoyl peroxide (p-NO₂, p-CH₃BP). p-Nitro, p-methyl-BP was prepared from p,p'-CH₃-BP and p-nitrobenzoylchloride as described in the work of Borsig et al.¹⁰ M.p. 134 °C. Triphenyl verdazyl was prepared and purified as described elsewhere.¹¹ The method of measurement used was described earlier.⁹ The reaction of TPV with p-NO₂, p-CH₃-BP in the solvents used occurs as follows (2):



The formation of triphenyl verdazylic salt I was proved spectroscopically.⁹ Salt I is not stable in the solvents studied and can be subjected to further transformation resulting in triphenyl verdazylic ring rupture and triphenylformazan formation.¹² p-Methylbenzoyloxy radical is unstable and can decarboxylate or split off hydrogen from solvent molecule which results in p-methylbenzoic acid formation.¹³

*) Carboxyinverson rate is known to increase with solvent polarity.⁶

Indeed the UV spectrum of the reaction product (2) in hexane shows absorption maxima at 240 and 280 nm corresponding to p-methylbenzoic acid formation.¹⁴

The rate of TPV reaction with p-NO₂, p'-CH₃-BP in benzene, hexane and acetone as well as with other substituted benzoyl peroxides⁹ is described by a second order kinetic equation (3)

$$v = k_2(\text{TPV}) \cdot (\text{p-NO}_2, \text{p}'\text{-CH}_3\text{-BP}) \quad (3)$$

Special experiments have shown the 1:1 stoichiometry for TPV/p-NO₂, p'-CH₃-BP for the reaction (2) in these solvents. Rate constants calculated by equation (3) are well maintained up to ~ 70 per cent of TPV consumption. Kinetic data are shown in the Table.

Table 1
Reaction Kinetics of TPV with p-NO₂, p'-CH₃-BP in Benzene, Hexane and Acetone, 20°

NN	(TPV) · 10 ⁴ mol/l	(p-NO ₂ , p'-CH ₃ -BP) · 10 ⁴ mol/l	k ₂ l/mol·s
Benzene			
1.	0.62	0.53	300 ± 25
2.	0.62	0.53	300 ± 25
3.	1.24	1.06	326 ± 20
4.	1.24	0.53	328 ± 20
5.	0.93	0.80	320 ± 25
Hexane			
6.	0.93	0.46	1350 ± 90
7.	0.675	0.345	1290 ± 100
Acetone			
8.	0.935	0.535	228 ± 15
9.	0.935	0.535	228 ± 15
10.	0.47	0.535	206 ± 13
11.	0.71	0.80	215 ± 15
12*	0.935	0.535	195 ± 15

*) After three days.

Rate constants for the reaction of TPV with $p\text{-NO}_2$, $p\text{-CH}_3$ -BP well fit the curve of corresponding plot $\lg k/k_0 - \sigma^\circ$ for substituted benzoyl peroxides (see Fig. 1).

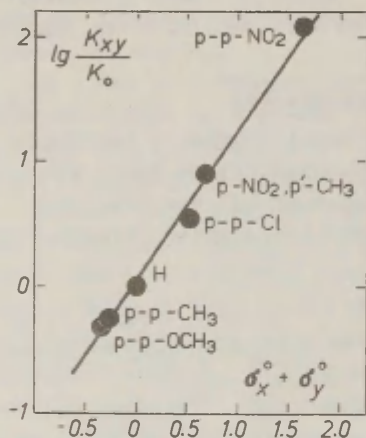


Figure 1. Taft's plot for substituted benzoyl peroxides reaction with triphenyl verdazyl (benzene, 20°).

Figure 1 represents the plot of $\lg k_{xy}/k_0$ versus Taft's σ° constants: k_{xy} - decomposition rate constant of BP, containing X and Y substituents, σ_x° and σ_y° - corresponding Taft's substituent constants. For all BP studied Taft's equation has the form:

$$\lg k_{xy}/k_0 = 1.22 \sigma^\circ, \quad r = 0.995 \quad (4)$$

As can be seen from Table 1, even in the case of acetone ($\epsilon = 21.4$) the reaction rate is somewhat lower than in benzene ($\epsilon = 2.2$) and hexane ($\epsilon = 1.9$). From these data it follows that carboxy inversion proceeds slowly and does not influence the reaction of TPV with diacyl peroxides even in the case of such very asymmetric peroxide as $p\text{-NO}_2, p\text{-CH}_3$ -BP. The same was observed for the reaction of substituted benzoyl peroxides with KI in ethanol solution.¹⁵

The reported results allow some suggestions

on this reaction mechanism. In the rate determining step TPV attacks on peroxy oxygen (rate constant correlation with Taft's σ^o constants). The experiments with benzoyl peroxide labeled by ^{18}O at carbonyl group show that the attack of trialkylstannyl ¹⁶ and triphenylmethyl ¹⁷ radicals also takes place on peroxy oxygen. Smaller substituent effect in benzoyl peroxide ⁹ as well as that of medium polarity suggest the formation of the low polarity transition state. ¹⁸ One might think that complex formation between TPV and BP proceeds through peroxy group of peroxide. Quantum chemical calculation indicating the electron density insufficiency at peroxy bond agree well with this suggestion. ¹⁹ According to polarographic data. ²⁰, the substituents in benzyl peroxide molecule have a slight influence on electron density distribution on -O-O- linkage. Nevertheless, triphenyl verdazyl reacting with p-NO₂, p'-CH₃-BP attacks a more electronegative peroxy oxygen. Thus, in accord with the conclusions of the work ¹² triphenyl verdazyl is a strong nucleophilic agent in this reaction.

References

1. R.Criegee and R.Kaspar, Ann., 560, 127 (1948).
2. J.E.Leffler, J.Amer.Chem.Soc., 72, 67 (1950).
3. F.D.Greene, H.P.Stein, C.C.Chu. and F.M.Vane, J.Amer.Chem.Soc., 86, 2080 (1964).
4. D.S.Tarbell and J.E.Longosz, J.Org.Chem., 24, 774 (1959).
5. Ya.K.Sirkin and I.I.Moiseev, Usp.khimii, 29, 425 (1960).
6. J.Lorand, The Cage Effect, in "Inorganic Reaction Mechanisms", part II, Interscience publishers, New York - Sydney - Toronto, 207 (1970).
7. J.E.Leffler and R.G.Zepp, J.Amer.Chem.Soc., 92, 3713 (1970).
8. C.Walling, H.P.Waits, J.Milovanovic, and C.G.Pappiaonnu, J.Amer.Chem.Soc., 92, 4927 (1970).
9. B.M.Yarmolyuk, O.M.Polumbrik, and G.F.Dvorko, Reakts.sposob.organ.soedin., 10, 901 (1973).
10. M.Lazar, P.Ambrovic, J.Mikovic, and E.Borsing, Thermochim.Acta, 6, 481 (1973).
11. R.Kuhn and H.Trischmann, Monatsh.Chem., 95, 457 (1964).
12. B.M.Yarmolyuk, Dissertation, Inst.Org.Khim.Akad.Nauk Ukr.SSR, Kiev. 1974.
13. T.Suehiro and M.Ishida, Bull.Chem.Soc.Japan, 44, 1692 (1971).
14. W.F.Forbes, W.A.Mueller, A.S.Ralph, and J.F.Templeton, Canad.J.Chem., 35, 1049 (1957).
15. G.T.Suchihashi, S.Miyayma, T.Otsu, and O.Simamura, Tetrahedron, 21, 1039 (1965).
16. W.P.Neumann and K.Rubsamen, Chem.Ber., 100, 1621 (1967).
17. W.E.Doering, K.Okamoto, and H.Krauch, J.Amer.Chem.Soc., 82, 3579 (1960).
18. E.M.Kosower, J.Amer.Chem.Soc., 80, 3253, 3267 (1958).
19. K.Ohkubo, H.Kitagawa, and H.Sakamoto, Bull.Jap.Petrol.Inst., 13, 184 (1971).
20. O.M.Polumbrik, B.M.Yarmolyuk, and L.V.Osadchaya, Reakts.sposob.organ.soedin., 11, 893 (1975).

THE KINETIC CH-ACIDITY OF THE IV-VII GROUP METHYL DERIVATIVES

N.N.Zatsepina, I.F.Tupitsyn, A.I.Belyaschova, and G.N.Sudakova

State Institute of Applied Chemistry, Leningrad

Received June 25, 1975

The data obtained in this work on the rate of isotopic hydrogen exchange of methyl groups in compounds of the type $(CH_3)_nM$ in solutions $ND_2^- + ND_3$, $RO^- + ROD$, $RO^- + ROD + DMSO-D_6$ are discussed in connection with the position of the central atom M in the periodic system. The general course of the kinetic CH-acidity within each period is determined by the change in the electronegativity (χ) of the atom M, and within a group, by the change of its covalent radius (r). The relative CH-acidity of all the compounds studied correlates satisfactorily with the product of χ by r . The results obtained are compared with the exchange ability of "onium" compounds $(CH_3)_nM^+X^-$ and the gas phase acidity of the hydrides MH_n . The role of the differentiating effect of the solvent in the change of the CH-acidity of these compounds is also considered.

At present, the kinetic method is still rarely used to study the dependence of the properties and physicochemical behavior of the compounds MX_n on the position of the element M in the periodic system. This is mainly associated with the difficulty of choosing a model chemical reaction which would follow a similar pathway for a sufficiently broad series of such compounds. Keeping in mind the experience gained in employing the base-catalyzed deuterium exchange for a quantitative study of the reactivity of organic compounds of different structures, we attempt to use

it in elucidating the character of the dependence of the CH-acidic properties for methyl derivatives of the IV-VII group elements on the nature of the central atom M. To be able to compare the results of this work with the earlier data on the CH-acidic properties of the methyl derivatives of nitrogen /1/, oxygen /1/, sulfur /1,2/ and phosphorus /1,3/, the relative strength of the compounds to be compared as of CH-acids was evaluated by measuring the deuterium exchange rate of the methyl group in several media: ROK+ROD, ROK+ROD+DMSO-D₆ (R= C₂H₅, t-C₄H₉) and ND₂⁻ + ND₃. The conditions and results of the kinetic studies are listed in Table 1. It was established that the exchange process of tetramethyltin in liquid ammonia is accompanied by side reactions changing the concentration of the alkaline agent in solution. To obtain comparable data on the relative mobility of methyl hydrogen in this case, the method of "competing" exchange was used. It involved adding to the mixture simultaneously with the compound under study a "witness" compound (benzene) for which the kinetics of deuterium exchange of various concentrations of the amide-ion has been investigated earlier /5/. The change in concentration of the amide ion was derived from the deviation of the experimentally observed rate constant for the "witness" in the presence of the compound under study from the value expected on the grounds of an independent study of its exchange kinetics.

Since the acidifying action of the central atom M on the methyl group can be distorted by the specific solvation effect, we will first analyze the data permitting to consider the differentiating action of the solvent on the kinetic CH-acidity of the compounds compared. The role of the solvent is revealed by the data obtained for the derivatives of sulfur, selenium and tellurium. Although, as seen from Table 1, a replacement of the solvent does not involve any change in the sequence of the CH-acidic properties, $O < S < Se < Te$, it does affect markedly the relation between the rate constants: in liquid ammonia: $k_O : k_S : k_{Se} : k_{Te} =$

Table 1. Isotopic Hydrogen Exchange in Some Methyl Derivatives.

No	Compound	Solvent ¹⁾	$t, ^\circ\text{C}$	$k \cdot 10^5$ sec^{-1}	$\log r^{2)}$	$\chi^{3)}$	$r^{4)}$
1	2	3	4	5	6	7	8
1	C_6H_{12}	A	-	-	$(-10)^{5)}$	2.50	0.77
2	$(\text{CH}_3)_4\text{Si}$	B(0.2N)	25	2.0	-3.7	1.91	1.17
3	$(\text{CH}_3)_4\text{Ge}$	B(0.2N)	25	12.0	-2.9	2.06	1.22
4	$(\text{CH}_3)_4\text{Sn}$	C($\sim 10^{-6}$) ⁶⁾	18	0.04			
		($\sim 0.03\text{N}$)	18	$(1.2 \cdot 10^3)$	(0)	1.95	1.40
5	$(\text{CH}_3)_3\text{N}$	B(0.6N)	-	-	$(-7)^{9)}$	3.0	0.70
6	$(\text{CH}_3)_3\text{P}$	B	-	-	$(-0.8)^{7)}$		
		D(0.57N)	-	-	$(5.0)^{9)}$	2.1	1.1
7	$(\text{CH}_3)_3\text{As}$	C($\sim 0.03\text{N}$)	20	2.0		2.0	1.21
8	$(\text{CH}_3)_2\text{O}$	B(0.7N)	-	-	$(-5.7)^{9)}$	3.5	0.66
9	$(\text{CH}_3)_2\text{S}/1/$	C	0	0.7	-2.2	2.5	1.04
			20	8.0			
	/2/	B(0.45N)	0	30	-1.3		
	/1/	E	135	0.15	-1.3		
			150	0.45			
	/1/	F(0.1N)	160	0.032	2.1		
			180	0.09			
10	$(\text{CH}_3)_2\text{Se}$	C($\sim 0.03\text{N}$)	-35	4.5	0.2	2.4	1.17
			-25	11.0			
		E	135	0.31	-1.0		
			150	1.1			
		F(0.1N)	180	no exchange			
11	$(\text{CH}_3)_2\text{Te}$	C($\sim 0.03\text{N}$)	-70	3.8	1.3	2.1	1.37
			-60	10.0			
		E	135	2.1	-0.04		
		F	180	no exchange			
12	CH_3F	-	-	-	$(3.0)^{8)}$	4.0	0.72
13	CH_3Cl	-	-	-	$(3.9)^{8)}$	3.0	1.14

1	2	3	4	5	6	7	8
14	CH ₃ Br	. -	-	-	(4.4) ⁸⁾	2.8	1.14
15	CH ₃ I	-	-	-	(4.9) ⁸⁾	2.5	1.33

¹⁾The notations are as follows: A-C₆H₁₁NDCs + C₆H₁₁ND₂; B- KND₂+ND₃; C-NaND₂+ND₃; D-C₂H₅OK+C₂H₅OD; E-O.1N C₂H₅OK+C₂H₅OD+DMSO-D₆(1:5), F-t-C₄H₉OK+C₄H₉OD. ²⁾ log f = log k - -log k₀ (k₀ is the deuterium exchange rate constant for toluene measured under comparable conditions /1/). ³⁾Electro-negativity by Pauling /12/. ⁴⁾Taken from refs./11,12/.

³⁾Because of the lack of data for CH acidity of neopentane we present an approximate value of log f for cyclohexane /15/ possessing in medium A a rate constant 10⁻⁸ times that of benzene for which log f = -1.9 /2,5/. ⁵⁾Estimated from data on competing benzene exchange. ⁷⁾Obtained by extrapolation: from the ratio of deuterium exchange rate constants for the methyl group C₆H₅CH₃; C₆H₅P(CH₃)₂: (C₆H₅)₂PCH₃ = 1 : 2 : 25 (medium B) /4/ it follows that a replacement of the phenyl group by the methyl radical slows down the exchange rate of phosphine by about 12 times. ⁸⁾Estimated from the correlation relation log f = 0.5 + 14.6 σ⁻(σ^o)/1/. ⁹⁾Obtained by extrapolation of data of ref./1/.

= 10 : 1 : 5·10² : 5·10³; in solution C₂H₅OK+C₂H₅OD+DMSO-D₆:
: k_S : k_{Se} : k_{Te} = 1 : 2.5 : 15.

For the reaction series considered, the changes in the deuterium exchange rate in liquid ammonia apparently reflect more fully the pattern of the intramolecular electro-nic effects. So, due to strong protophilic properties of the ND₂⁻+ND₃ solution resulting from a very high affinity of the amide ion to proton combined with a low proton-releasing and solvatating ability of liquid ammonia, the role of the solvation effect in the appearance and stabilization of the carbanion transition state in the deuterium exchange should be small in this case. When going to an alcoholic

solution of potassium alcoxide or of its mixture with DMSO, the contribution of intermolecular interactions to the change of $\log k$ increases. Depending on the nature of the substrate, the interaction with the solvent may result in a relative increase or decrease of the deuterium exchange rate. A strong positive differentiating solvent effect is found, for instance, in the deuterium exchange of trimethylphosphine in an alcoholic solution of potassium ethoxide when an additional positive charge appears on the phosphorus atom ($pK_a = 8.7$) because of its specific solvation by molecules of the alcohol /3/. On the other hand, because of both the alcohol ($t\text{-C}_4\text{H}_9\text{OD}$ or $\text{C}_2\text{H}_5\text{OD}$) and DMSO-D_6 are displaying clearly pronounced electron-releasing properties, when the substrate molecule has an electron-deficient center there appears in solution a donor - acceptor interaction by which the p-electrons of the solvent transfer partially to the molecular orbitals of the substrate thus canceling the electron-withdrawing influence of the central atom M. It is this type of interaction which is apparently responsible for the observed levelling of differences in the kinetic CH-acidity of the methyl derivatives of sulfur, selenium and tellurium in their deuterium exchange in an alcoholic medium.

If, in accordance with the above, we accept the results of kinetic measurements in a liquid ammonia as a measure of the CH- acidic properties of the compounds under study then one may conclude that the CH-acidity of the IV-VII group methyl derivatives increases from left to the right within a period of the periodic system, and from the top downwards, within a group^{*)}. Within each group, the most substantial increase in proton mobility occurs as one goes from the II to III period.

^{*)}As an exclusion may serve trimethylphosphine revealing an enhanced CH acidity also in liquid ammonia.

As seen from Fig.1, the observed pattern of $\log f$ reveals a relation with two principal parameters of the electronic shell of the atom M, viz. the electronegativity (χ) and covalent radius (r). In accordance with the fact that the electronegativity changes much stronger over the periods, and the covalent radius, within groups, the first type of relationship predominates in the change of proton mobility when going in the periodic system from the left to the right, and the second, from top downwards (cf. Figs. 1a and 1b).

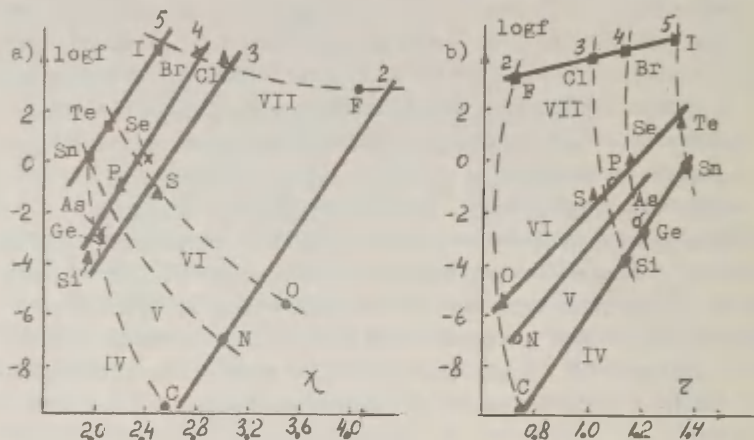


Fig.1. The plot of the kinetic CH-acidity in $(CH_3)_nM$ compounds vs. electronegativity (1a) and covalent radius (1b) of the atom M.

— changes within period (1a) and within group (1b);
 --- changes within group (1a) and within period (1b).

In the framework of the classical electron theory, the enhancement of CH-acidity with increasing electronegativity within a period reflects an increase in the electron-withdrawing inductive effect which contribution to the free energy of activation of the exchange process overrides in this case the electron-withdrawing influence of the atom M

on the reaction center by the conjugation mechanism. Variations in electronegativity within individual groups are small and antipathetic to variations in the kinetic CH acidity (Fig. 1a). One of the possible explanations for the observed increase in the CH-acidity with increasing atomic number of the element may be the theory of the nonbonded repulsion. A decrease in repulsion between the coupling and in particular between the coupling and the lone pair electrons of the valence shell of the atom M enhanced as its covalent radius increases, which causes a decrease in the valence angles from tetrahedral (for the second period elements) to close to 90° (for the third and higher period elements). It results in a decrease of the p-character of the electron pair and, hence, in a decrease of the electron-releasing conjugation ability of the atom M. In addition, an increase of the covalent radius involves ordinarily a decrease of the interatomic correction taking into account interaction between the electron pairs of the atom M and the CH-bonds of the methyl group, which causes additional polarization of the latter in the direction C^+-H^- .

The conclusion that the experimentally observed CH-acidity is determined by a simultaneous action of these factors is confirmed by the existence of a linear relationship in the $\log f - \chi \cdot r$ coordinates for all the kinetic data available (Fig. 2).

A similar pattern (when the free energy of a reaction varies in accordance with electronegativity as M varies within a given period, while within a group the main factor determines its variation is the electron repulsion which depends on atomic radius) is observed (Fig. 3) for the rate of proton abstraction from M-H bonds of the IV-VII group simple hydrides MH_n [7-9]. The existence of a linear relationship between $\log f$ and ΔH^* measured in solution and in gas phase, respectively, confirms a basic similarity between the electronic effects in the compounds compared, as well as indi-

^{*}) ΔH is the enthalpy of hydride ionization.

cates the absence of marked deviations in the sequence of relative CH-acidity of methyl derivatives which could be associated with the effects of specific solvation of the substrate by molecules of liquid ammonia. The latter follows also from a comparison of the kinetic data with results of a quantum-chemical investigation concerning the reactivity of a series of substituted methanes and methyl derivatives of elements /12/.

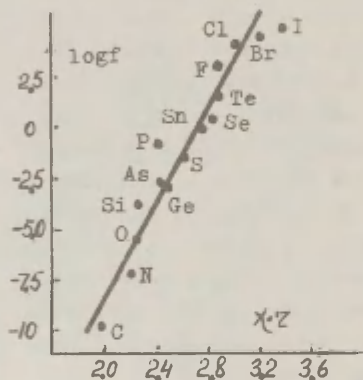


Fig.2. Correlation between $\log f$ and $\chi \cdot r$.

In contrast (Fig. 4) to the above cases the variation of the deuterium exchange rate constants for "onium" compounds of the III-IV periods/10/ depends primarily on the size of the electronic shell of the atom M characterized by its ionic (r^+) or covalent radius; the slope of the $\log k$ vs. r^+ plot (or of the $\log k$ vs. r line) turns out to be opposite to the one found for the $(\text{CH}_3)_n\text{M}$ compounds (Fig.1b). The reason for the observed differences lies apparently in the change in the nature of electronic effects of the atom M resulting from the coupling of its lone pair and appearance of excess positive charge. Quaternization is known to produce a strong enhancement of the electron-withdrawing ability due to the increase of both the inductive and d-orbital effects of the atom M. The predominant role of d-orbital stabilization of the carbanion transition state in deuterium exchange of "onium" compounds has

been demonstrated by Döering and Hoffmann /10/.

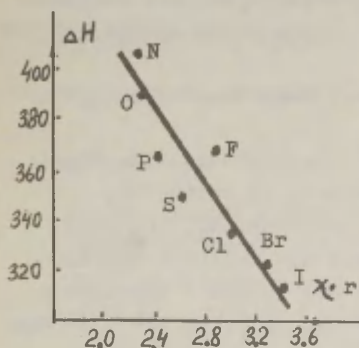


Fig.3. Correlation between ΔH and $\chi \cdot r$ for MH_n hydrides. The values of ΔH taken from refs./7-9/.

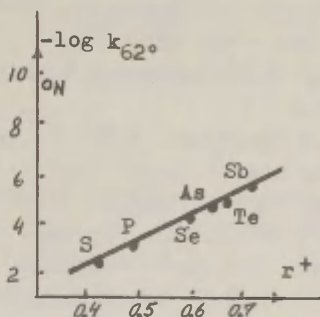


Fig.4. Correlation between $\log k$ /10/ and ionic radius of the atom M /11/ for "onium" compounds $(CH_3)_n M^+ X^-$.

Since the efficiency of delocalization of electronic density to the vacant d-orbitals increases as they become more compressed /14/, the deuterium exchange rate constants for the "onium" compounds increase with decreasing size of the electronic shell of the atom M.

EXPERIMENTAL.

In our kinetic studies we used either commercial products or compounds prepared by known procedures. The technique of studying exchange reactions has been described elsewhere/16/. The isotopic analysis was performed by means of low-voltage mass spectrometry. In most cases the compounds were analyzed either directly in the reaction solution (e.g. in the deuterium exchange in alcoholic media) or by transferring them into solution of α -methylnaphthalene which is a high boiling inert solvent (in the deuterium exchange in liquid ammonia).

REFERENCES

1. N.N.Zatsepina, I.F.Tupitsyn, A.V.Kirova, and A.I.Belyashova, Organic Reactivity(Reakts.sposobn.organ.soedin.),8,787 (1971); 11, 431(1974).
2. A.I.Shatenstein and E.A.Gvosdeva, Teor.Eksp.Khim.,1,352 (1965).
3. N.N.Zatsepina, I.F.Tupitsyn, A.I.Belyashova, B.B.Alipov, and N.S.Kolodina, Organic Reactivity,11,441(1974).
4. E.N.Tsvetkov and M.I.Kabachnik, Usp.Khim.,40,178(1971).
5. A.I.Shatenstein, Isotope Exchange and Hydrogen Substitution in Organic Compounds (Isotopnyi obmen i zameshenie vodoroda v organizheskikh soedineniakh), Moscow, Izd.Akad. Nauk SSSR, 1960.
6. R.J.Gillespie, Molecular Geometry, London, van Nostrand, 1972.
7. J.I.Brauman, J.R.Eyler, L.K.Blair, M.J.White, M.B.Comisarow, and K.C.Smyth, J.Amer.Chem.Soc.,93,6360(1971).
8. D.Holtz, J.L.Beauchamp, and J.R.Eyler, J.Amer.Chem.Soc., 92, 7045(1970).
9. O.A.Reutov, K.P.Butin, and I.P.Beletskaja, Usp.Khim.,43, 35(1974).
- 10.W.E.Döering and A.K.Hoffmann, J.Amer.Chem.Soc.,77,521(1955).
- 11.Ya.K.Syrkin and M.E.Dyatkina, The Chemical Bond and the Structure of Molecules, Moscow, State Scientific-Tech.Pub. House of Chem.Literature, 1946.
- 12.L.Pauling, The Nature of the Chemical Bond,3-rd.Ed., N.Y.,1960.
- 13.N.N.Zatsepina,A.A.Kane, and I.F.Tupitsyn,Organic Reactivity, (1975).
- 14.D.P.Craig and E.A.Magnusson, J.Chem.Soc.,1956, 4895.
- 15.A.Streitwieser and J.Richard, J.Amer.Chem.Soc.,91,529(1969).
- 16.N.N.Zatsepina,I.F.Tupitsyn, and L.S.Efros, Khim. i.Tekhnolog.Isotopov(Tr.Gos.Inst.Prikl.Khim.),No 56,113(1967).

A QUANTUM-CHEMICAL STUDY OF THE CH ACIDITY OF SUBSTITUTED ALKANES

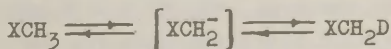
N.N.Zatsepina, A.A.Kane, and I.F.Tupitsyn

State Institute of Applied Chemistry, Leningrad

Received June 25, 1975

The CNDO/2 method was used to calculate the total energy differences for carbanions and the corresponding neutral molecules, as well as the charge on the base-attacked hydrogen atoms for a large series of substituted methanes and similar compounds. The results of calculations agree satisfactorily with the course of the kinetic and equilibrium CH-acidity of carboacids within a broad range of their variation ($\Delta pK_a^{CH} \sim 50$).

The equilibrium and kinetic CH-acidity of substituted methanes and similar compounds were studied experimentally by many authors (see e.g. Refs./1-18/). Nevertheless, the nature of the dependence of the CH-acidic properties on the electronic effect of substituents and the properties of the medium, as well as the peculiarities of the stage mechanism including the formation of a carbanion or of a carbanion transition state at the first (rate-limiting) stage of the process



require an additional investigation. The limits of applicability of the Brönsted relation

$$\log k = A + B \cdot pK_a^{CH}$$

for the series of compounds also are remaining an open question.

Useful information in this respect can be gained employing quantum - chemical methods of study-

ing the reactivity /19-21/. One may cite many examples of successful application of the latter to describe the acidic properties of both the protonic /22/ and CH-acids (polycyclic aromatic systems /22,21/, substituted toluenes /21,23/, aromatic and saturated heterocycles /24,27/). As for a theoretical interpretation of the CH-acidity of the classes of compounds discussed, the available data remain limited up to now to calculate the energy difference between the deprotonated and neutral forms for methane, ethane and some of their derivatives /28-31/.

Our calculations of the electronic structure of neutral molecules and carbanions relate to a much broader scope of compounds (Table 1). The calculations were made by the CNDO/2 method using the standard parametrization /32/ on a BESM-6 computer by a program prepared by V.Ja.Bespalov.

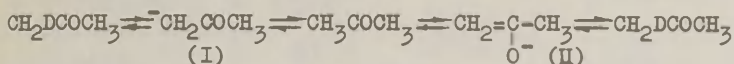
In accordance with the experimental data on the configuration of the alkyl group obtained for a number of substituted methanes /33/, we used, as a rule, the tetrahedral values of the valence angles for HCH, HCX and of the C-H bond lengths in the neutral molecule calculations. The calculations were carried out for a fixed conformation with a planar arrangement of the X, C atoms and one of the H-atoms. Additional data on the geometry of the molecules studied are listed in Table 2. Although optimization of the values of the geometrical parameters was not performed, the character of the effect of variation in the bond lengths and valence angles in a carbanion on the calculated energies was investigated on a number of compounds.

In our carbanion calculations we started from a pyramidal configuration of the anion carbon bonds with the valence angle HCH close to the tetrahedral angle. The values of all the other geometrical parameters were in most cases assumed to be equal to those of the corresponding neutral molecules.

In order to evaluate the sensitivity of the results to the effect of variation of the C⁻ atom valence state from a "pyramidal" to "planar" arrangement, the electronic structure

re calculations for carbanions of some compounds were carried out also for the "planar" configuration (with (Nos. 3,9, 20,29,36) and without (Nos.20,30,43) change in interatomic distances in the carbanion).

For some carbonyl derivatives (Nos. 13,17,35 in Table 1) the possibility for an acidic-basic process to proceed via the intermediate formation of either a carbanion (I) or enolate-anion (II) was also considered:



To elucidate the role of d-orbitals in the mechanism of activation of the exchange reaction, the calculations for the compounds containing S₁, P and S were carried out in two approximations, viz. in the minimum valence basis without including 3d-orbitals and with their inclusion /45/.

The results of various versions of calculation of the deprotonation energies ΔE, as well as of the charge on the base-attacked hydrogen atoms q_H are summarized in Table 1. Also data are given on the equilibrium (pK_a^{CH}) and kinetic (log f) CH-acidity of the compounds. The scales of the equilibrium CH-acidity are constructed on the basis of the determination of pK_a^{CH} in water and anhydrous dimethylformamide (DMFA). The values of log f characterize the mobility of hydrogen atoms of the CH-acids in the base-catalyzed deuterium exchange with respect to toluene as a reference compound (log f = Δ log k, the solvent being water, alcohol or liquid ammonia /14-16/). The experimental values of the equilibrium and kinetic CH-acidity span a range from 0 to 27 and from 4 to 50 pK_a^{CH} units, respectively.

As seen from Table 1 and Figs.1-3, the values of ΔE calculated by the CNDO/2 method agree in most cases with the trend of increasing CH-acidic properties observed for methanes and similar compounds with increasing electron-withdrawing effect of substituents. Some nonsystematic deviations of individual points from the regression lines of Figs.1-3

Table 1. CH- Acidity and Quantum-Chemical Indices of Reactivity of Substituted Alkanes.

No	Compound	ΔE , eV	q_H at, units.	$\log f^{1)}$	$pK_a^{CH} 2)$	
					(H ₂ O)	(DMF)
1	2	3	4	5	6	7
1	CH ₄	28.290	0.9876	(-10) ³⁾	40	57
2	(CH ₃) ₃ N	27.009	1.010 ⁴⁾ 1.010 1.016	-7.0	-	-
3	(OH ₃) ₂ O	27.188 (29.079) ⁵⁾	1.005 1.014 1.014	-5.7	-	-
4	CH ₃ F	27.062	0.9954	-	-	-
5	(CH ₃) ₃ As	26.857 ⁶⁾	0.9996 ⁵⁾	-2.7	-	-
6	(CH ₃) ₄ Si	26.098 (25.477) ⁷⁾	0.9896 (0.9494) ⁷⁾	-3.7		
7	(CH ₂) ₂ S	26.599 26.037 ⁷⁾	0.9920 0.9951 0.9951 0.9632 ⁷⁾ 0.9685 0.9685	-1.3	-	-
8	(CH ₃) ₃ P	26.262 (25.639) ⁷⁾	0.9914 0.9914 0.9940 0.9570 ⁷⁾ 0.9570 0.9590	-0.8	-	-
9	C ₆ H ₅ CH ₃	26.156 (25.216) ⁵⁾	1.0040 0.9914 0.9914	0	35	35
10	C ₆ H ₅ SCH ₃	26.256	0.9944 0.9971 0.9971	4.2	-	-
11	CH ₃ CN	26.096	0.9691	15.0	25	-
12	(CH ₃) ₃ N \rightarrow O	25.763	0.9767 0.9767 1.0030	-0.3	-	-
13	CH ₃ COOCH ₃	25.740 (24.568) ⁸⁾	0.9628 0.9628 0.9646	12.6	24	24

1	2	3	4	5	6	7
14	$\text{C}_6\text{H}_5\text{SOCH}_3$	25.375	0.9722 0.9764 0.9919	11.0	-	-
15	$(\text{CH}_3)_2\text{SO}$	25.278 (25.463) ⁷⁾	0.9698 0.9725 0.9907 0.9560 ⁷⁾ 0.9677 0.9677	10.0	-	-
16	$(\text{CH}_3)_3\text{P}\rightarrow\text{O}$	25.222	0.9706 0.9706 0.9810	8.7	-	-
17	$(\text{CH}_3)_2\text{CO}$	26.020 (24.482) ⁸⁾	0.9736 0.9736 0.9766	14.9	20	21 ⁹⁾
18	$\text{C}_6\text{H}_5\text{SO}_2\text{CH}_3$	24.423	0.9560 0.9677 0.9677	18.0	-	25
19	$(\text{CH}_3)_2\text{SO}_2$	24.423 (24.482) ⁷⁾	0.9492 0.9625 0.9625 0.9400 ⁷⁾ 0.9525 0.9525	17.7	23	-
20	CH_3NO_2	24.142 (23.510) ⁵⁾ (24.249) ¹⁰⁾	0.9370 0.9501 0.9501	17.3	10.2	-
21	$\text{CH}_3\text{CH}_2^*\text{CH}_3$	26.540	1.0058	-	44	60
22	$(\text{CH}_3\text{S})_2\text{CH}_2^*$	26.899 (25.438) ⁷⁾	1.0020 (0.9560) ⁷⁾	5.2 ¹¹⁾	-	-
23	$\text{CH}_3\text{CH}_2^*\text{COCH}_3$	25.271	0.9836	14.1	-	-
24	$\text{FCH}_2^*\text{COOCH}_3$	24.968	0.9829	12.9 ¹²⁾	-	22
25	$\text{C}_6\text{H}_5\text{CH}_2\text{NO}_2$	24.969	0.9521	18.7		-
26	CH_2Cl_2	24.808	0.9775	8.9	-	-
27	$\text{CH}_3\text{CH}_2^*\text{SO}_2\text{CH}_3$	24.796	0.9765	15.0	-	-
28	$(\text{CH}_3\text{CO})_2\text{CH}_2^*$	24.534	0.9649	22.4	9.0	-
29	$(\text{C}_6\text{H}_5)_2\text{CH}_2^*$	24.998 (24.411) ⁵⁾	1.0016	6.0	-	-

1	2	3	4	6	6	7
30	$(\text{CN})_2\text{CH}_2$	24.302 (24.293) ¹⁰⁾	0.9564	22.3	11.1	-
31	$\text{CH}_3\text{CH}_2\text{NO}_2$	23.997	0.9652	17.2	8.6	-
32	$\text{CH}_3\text{COCH}_2\text{COCF}_3$	23.678	0.9516	22.8	4.7 (6.79) ¹³⁾	
33	$\text{CF}_3\text{CH}_2\text{OOOCH}_3$	23.530	0.9280	-	-	15
34	$(\text{CF}_3)_2\text{CH}_2$	23.387	0.9190	12.7	-	22
35	$\text{NO}_2\text{CH}_2\text{COCH}_3$	23.056 (22.149) ⁸⁾	0.9272	23.2	5.1	-
36	$(\text{NO}_2)_2\text{CH}_2$	23.893 (20.274) ⁵⁾	0.9205	24.1	4.0	-
37	CHF_3	24.912	1.0160	9.9	-	26
38	$\text{CF}_2\text{HCOOCH}_3$	24.444	0.9965	10.4 ¹²⁾	-	25
39	FCHClCOOCH_3	23.980	0.9796	-	-	20
40	$\text{CF}_3\text{CF}_2\text{H}$	23.653	0.9803	11.1	-	-
41	CHCl_3	23.456	0.9750	-	-	15
42	CF_3CHCl_2	23.177	0.9522	15.4	-	-
43	$\text{CH}(\text{CN})_3$	23.040 (23.030) ¹⁰⁾	0.9460	-	0 (-5.1)	-
44	$\text{CF}_3\text{CFHCOOCH}_3$	22.952	0.9516	-	-	14
45	$(\text{CF}_3)_2\text{CFH}$	22.657	0.9397	15.0	-	22
46	$(\text{CF}_3)_2\text{CHCOOCH}_3$	22.419	0.9070	-	-	13
47	$\text{F}(\text{NO}_2)\text{CHCOOCH}_3$	22.400	0.9498	-	6.28	-
48	$(\text{CF}_3)_3\text{CH}$	21.796	0.8959	18.9	-	7
49	$\text{CH}_3\text{CH}(\text{NO}_2)_2$	22.585	0.9258	21.1	5.2	-
50	$\text{FCH}(\text{NO}_2)_2$	24.083	0.9318	18.4	-	-
51	$\text{CH}(\text{NO}_2)_3$	19.418 (18.650) ⁵⁾	0.8900	-	0	-

¹⁾ Taken from refs./14-16/. ²⁾ Taken from refs./1,4/. ³⁾ Because of a lack of data for methane (Continued on the next page)

(Continued from previous page) approximate value of $\log f$ for cyclohexane /16/ is presented.⁴⁾ The values of q_M are for hydrogen atoms differing in position relative to the molecule plane, minimum values of q_M being used in the correlations.⁵⁾ A "planar" model of carbanion with interatomic distances corresponding to the change the hybridization of the C⁻ atom in the direction from sp^3 to sp^2 .⁶⁾ sp-Approximation with parameters of ref./44/.⁷⁾ spd-Approximation.⁸⁾ Enolate anion as a transition state.⁹⁾ For $CH_3COC_4H_9$ /4/.¹⁰⁾ A "planar" carbanion model without change of interatomic distances.¹¹⁾ For $(C_2H_5)_2CH_2$ /14,46/.¹²⁾ Calculated from data of ref./17/.¹³⁾ Taken from ref./13/.

may be explained as due to inaccurate molecular geometry of the carbanion and errors in the selection of parameters in calculations, as well as to a weak differentiating solvent effect manifesting itself in the values $\log f$ and pK_a .

As follows from the data, the deprotonation energies calculated for the planar carbanion model depend to a smaller extent on the variation of valence angles than on the bond lengths. In accordance with the existing concepts concerning the substituent effect on the configuration stability of carbanions (see e.g. refs./1,17/), electron-withdrawing groups reduce substantially, and electron-releasing ones increase the deprotonation energy when going over from the "tetrahedral" to "planar" model.

Our calculations confirm the stabilization of the enolate form in the transition state of carbonyl compounds to be higher than that of the carbanion form.

As for the contribution of 3d orbitals of the Si, P and S atoms to variations of the calculated energy differences ΔE , it turns out that the inclusion of 3d orbitals reduces the total energies of both neutral molecules and of the corresponding carbanions while causing comparatively small dif-

ferences between the results in ΔE calculations. The differences of ΔE calculated on the sp and spd basis do not exceed 0,5 eV. An exclusion in this respect is only compound No 22 for which, in accordance with ref./46/, the contribution of the d-orbital effect is apparently substantial.

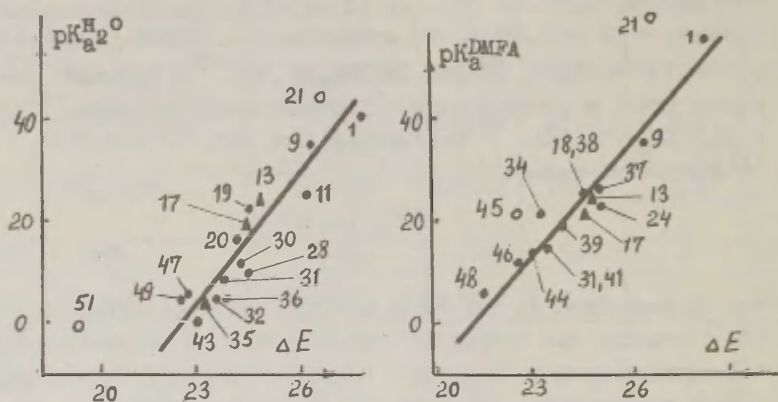


Fig.1. ▲ plot of pK_a^{CH} vs. ΔE . The numbering is as in Table 1.

O - Compounds not included in correlation analysis.

▲ - Enolate-anions.

As seen from Fig.1, the values of ΔE and pK_a^{CH} determined in water and in DMF are linearly related, the slopes of the relationships being close:

$$pK_a^{H_2O} = -178.0 + 7.9 \Delta E \quad (r=0.945, n=15) \quad (2)$$

$$pK_a^{DMFA} = -150.9 + 7.2 \Delta E \quad (r=0.963, n=15) \quad (3)$$

The variations of relative deuterium exchange rate constants for almost all of the mono- and disubstituted methanes also correlate with the value ΔE (Fig.2) over a

wide range ($\Delta \log f \approx 30$)

$$\log f = 217.8 - 8.3 \Delta E \quad (r=0.954, n=25) \quad (4)$$

However in the case of trisubstituted methanes one observes a trend toward a certain "overevaluation" of the values of $\log f$ as derived from eq.(4) compared with the experimental results.

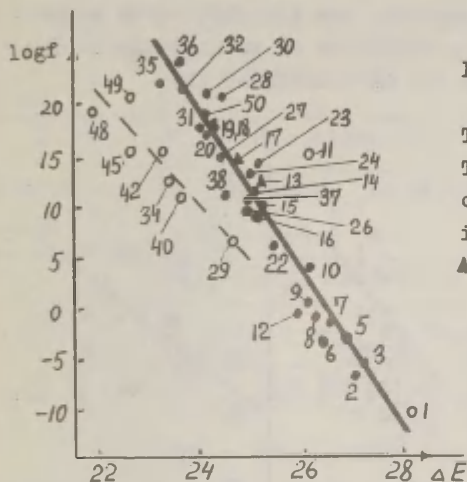


Fig.2. Δ plot of $\log f$ vs. ΔE .

The numbering is as in Table 1.

o-Compounds not included in correlation analysis
 Δ -Enolate-anions.

The similarity between relationships (2) and (4) indicates that for structurally similar compounds the behavior of the kinetic and equilibrium acidity of methanes follows the Brønsted dependence, so that the kinetic data can be used in evaluating the relative strength of weak carboacids. It should be emphasised that the results of the calculations performed refer to isolated molecular system, i.e. they should essentially characterize the kinetic CH-acidity in the gas phase. The existence of correlation between the quantum-chemical indices and the characteristics of the CH-acidity measured in solvents of different protolytic activity gives grounds to conclude that for the kind of compounds considered the solvation contribution has in most cases an appro-

ximately constant value, so that the general behavior of the relative CH-acidity in solution follows the course of the "true" acidity of carboacids in the gas phase.

Although the differences between the total energies of the carbanion and neutral molecule represent a quantum-chemical criterion of a most general nature for the exchange rate, the close similarity in the behavior of ΔE and of the charges on the base-attached hydrogen atom (q_H) which is observed for specific series of mono-, di- and trisubstituted methanes (Fig.3) indicates the possibility of an approximate description of variations in the CH-acidity of the

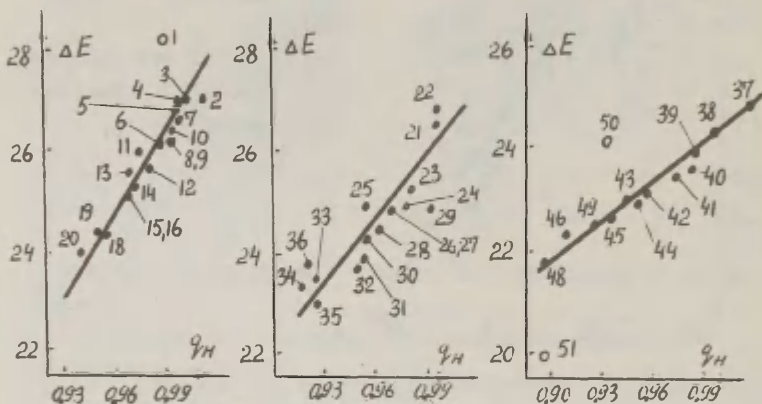


Fig.3. A plot of ΔE vs. q_H .

compounds studied also in terms of the reactivity indices introduced within the "isolated molecule" approximation:

$$\log f_{CH_3X} = 386 - 390 q_H \quad (r=0.951, n=14) \quad (5)$$

$$\log f_{CH_2XY} = 230 - 223 q_H \quad (r=0.836, n=9) \quad (6)$$

$$\log f_{CHXYZ} = 97 - 86 q_H \quad (r=0.972, n=8) \quad (7)$$

Table 2. Bond Lengths (\AA) and Valence Angles (in Degrees) Assumed in Calculations.

Compound No by Table 1	Geometric parameters	Ref.
1	2	3
1,5,6	$r_{\text{Si-C}}=1.888$, $r_{\text{As-C}}=1.98$, $r_{\text{C-H}}=1.094$	/33,44/
2,8,12,16	$r_{\text{C-N}}=1.47$, $r_{\text{N-O}}=1.44$, $r_{\text{P-C}}=1.87$, $r_{\text{P-O}}=1.48$	/33,34/
3	$r_{\text{C-O}}=1.42$, $\angle \text{OOC}=111.5$	/33/
3,34,40,42, 45,48	$r_{\text{C-F}}=1.35$, $r_{\text{C-C}}=1.54$, $r_{\text{C-Cl}}=1.77$ $\angle \text{FCF} = 109.5$	/33/
7,22	$r_{\text{C-S}}=1.802$, $\angle \text{OOC}=111.5$	/33/
9,29 ¹⁾	$r_{\text{C-C}}=1.39$, $r_{\text{C-C}\alpha}=1.52$, $\angle \text{CC}\alpha\text{C}=120$	/33,35/
10,14,18	$r_{\text{C-C}}=1.39$, $r_{\text{C-S}}=1.77$, $r_{\text{C-H}}=1.11$, $\angle \text{CSC} = 102.6$, $\angle \text{SCH}=108.5$, $\angle \text{OSO}=120$	/33/
11,43	$r_{\text{C-C}}=1.46$, $r_{\text{C-N}}=1.15$, $\angle \text{OCC}=109.5$	/37,41/
13,24,33,38, 44,46,47	$r_{\text{C-C}}=1.52$, $r_{\text{C-O}}=1.36$, $r_{\text{C=O}}=1.22$, $r_{\text{C-O}}=1.46$, $r_{\text{C-F}}=1.35$, $r_{\text{N-O}}=1.22$, $\angle \text{OCO}=116$, $\angle \text{OOO}=124$, $\angle \text{FCF}=109.5$, $\angle \text{COC}=113$, $\angle \text{ONO}=127$	/37/
15	$r_{\text{C-S}}=1.81$, $r_{\text{S-O}}=1.48$, $\angle \text{CSC}=100$, $\angle \text{CSO}=107$	/36/

1	2	3
17,23,28, ²⁾ 32,35	$r_{C-O}=1.21$, $r_{C-C}=1.52$, $r_{C-F}=1.35$, $r_{N-O}=1.22$, $\angle COO=120$, $\angle ONO=127$	/33,39/
19	$r_{S-O}=1.435$, $r_{C-S}=1.77$, $r_{C-H}=1.11$, $\angle CSC=102.6$, $\angle OSO=120$, $\angle SCH=108.5$	/38/
20,25,31	$r_{C-N}=1.47$, $r_{N-O}=1.22$, $r_{C-C}=1.52$, $r_{C-C}=1.39$, $\angle ONO=127$, $\angle NCN=109.5$	/33/
21	$r_{C-C}=1.54$, $\angle COO=111.5$	/39/
26	$r_{C-Cl}=1.778$, $r_{C-H}=1.068$, $\angle HCH=112$, $\angle ClCCl=111$	/40/
30	$r_{C-C}=1.46$, $r_{C-N}=1.158$, $\angle CCC=113.6$ $\angle HOH=105.6$	/33,41/
36,49,50, 51	$r_{C-N}=1.50$, $r_{N-O}=1.22$, $r_{C-F}=1.35$, $\angle ONO=128.6$, $\angle NCN=110.7$	/42/
37	$r_{C-F}=1.534$, $\angle FCF=108.5$	/43/
41	$r_{C-Cl}=1.76$, $\angle ClCCl=109.5$	/33/
3,9,29, ³⁾ 20,36,51	$r_{O-C^-}=1.32$, $r_{N-C^-}=1.40$, $r_{C-C^-}=1.39$, $\angle HC^-H = \angle COC^- = \angle ONC^- = \angle ONO=120$	-
20,30,43 ⁴⁾	$\angle HC^-H = \angle CC^-C = \angle ONC^- = \angle ONO=120$	-

¹⁾ The phenyl rings in diphenylmethane are turned relative to the $CC_{\alpha}C$ plane by the angle 41° . ²⁾ In the enolate anion, $r_{C-O}=1.43$, $r_{C-C}=1.37$. ³⁾ For the "planar" carbanion model with interatomic distances corresponding to the hybridization of the C^- atom changing from sp^3 to sp^2 . ⁴⁾ For the "planar" carbanion model without change of interatomic distances.

The latter apparently indicates the rule by which the potential curves do not intersect as one moves along the reaction coordinate from a state close to the initial state to the carbanion transition state to be met in the cases considered.

R E F E R E N C E S

1. D.J.Cram, Fundamentals of Carbanion Chemistry, Academic Press, New York, London, 1965.
2. A.Streitwieser and G.Hammond, In Progress in Physical Organic Chemistry, Vol.3, Wiley, New York, London, Sydney, 1965.
3. J.R.Jones, The Ionization of Carbon Acids, Academic, New York, 1973.
4. O.A.Reutov, K.P.Butin, and I.P.Beletskaya, Usp.Khim., 43, 35 (1974).
5. H.F.Ebel, Die Acidität der CH-Säuren, Georg.Thieme Verlag, Stuttgart, 1969.
6. R.C.Pearson and R.L.Dillon, J.Amer.Chem.Soc., 75, 2439 (1953)
7. F.G.Bordwell and W.S.Matthews, J.Amer.Chem.Soc., 96, 121q6 (1974).
8. F.G.Bordwell and W.J.Boyle, J.Amer.Chem.Soc., 96, 3907 (1974)
9. V.N.Dronov and I.V.Tselinsky, Reakts.Sposobn.Organ.Soedin., 7, 263 (1970); 8, 907 (1971).
10. V.N.Dronov, I.V.Tselinsky, and I.N.Shokhor, Reakts.Sposobn.Organ.Soedin., 6, 948 (1969).
11. V.K.Krylov, I.V.Tselinsky, L.I.Bagal, and M.P.Kozlova, Reakts.Sposobn.Organ.Soedin., 7, 612 (1970).
12. A.I.Talvik and V.A.Palm, Organic Reactivity, 11, 285 (1974).
13. J.R.Jones and S.P.Patel, J.Amer.Chem.Soc., 96, 574 (1974).
14. N.N.Zatsepina, I.F.Tupitsyn, A.V.Kirova, and A.I.Belyashova, Reakts.Sposobn.Organ.Soedin., (Organic Reactivity), 8, 787 (1971); 11, 441 (1974).
15. N.N.Zatsepina, I.F.Tupitsyn, B.B.Alipov, A.I.Belyashova, A.V.Kirova, and N.S.Kolodina, Organic Reactivity, (Reakts.Sposobn.Organ.Soedin.), 11, 443 (1974).

16. N.N.Zatsepina, I.F.Tupitsyn, A.I.Belyashova, and G.N.Sudakova, *Organic Reactivity*, 12, 195 (1975).
17. K.J.Klabunde and D.J.Burton, *J.Amer.Chem.Soc.*, 94, 5985 (1972).
18. J.Hine, R.B.Duke, and E.F.Gold, *J.Amer.Chem.Soc.*, 91, 3316 (1969).
19. A.Streitwieser, Jr., *Molecular Orbital Theory for Organic Chemists*, Wiley, New York, 1961.
20. M.J.S.Dewar, *The Molecular Orbital Theory of Organic Chemistry*, McGraw-Hill, New York, 1969.
21. E.D.Bergmann, B.Pullman (Ed.), *Quantum Aspects of Heterocyclic Compounds in Chemistry and Biochemistry; Proceedings of Internat.Symposium*, Jerusalem, 1969.
22. B.M.Rode and A.Engelbrecht, *Monatsheft Chemie*, 104, 893 (1973).
23. C.Weiss, *Z.Chem.*, 12, 193 (1972).
24. P.Birner, H.J.Köhler, and C.Weiss, *Chem.Phys.Lett.*, 27, 347 (1974).
25. N.N.Zatsepina and I.F.Tupitsyn, *Khim.Geterotsikl.Soedin.*, No 12, 1587 (1974).
26. N.N.Zatsepina, I.F.Tupitsyn, A.I.Belyashova, A.A.Kane, and A.V.Kirova, *Organic Reactivity*, 12, 169 (1975).
27. M.A.Schroeder and R.C.Makino, *Tetrahedron*, 29, 3469 (1973).
28. A.Streitwieser, R.H.Owens, R.A.Wolf, and J.E.Williams, *J.Amer.Chem.Soc.*, 96, 5448 (1974).
29. T.P.Lewis, *Tetrahedron*, 25, 4117 (1969).
30. D.Holtz, A.Streitwieser, and R.G.Jesaitis, *Tetrah.Lett.*, No 52, 4529 (1969).
31. S.Wolf, J.M.Tel, and J.G.Geiznadi, *Theor.Chim.Acta*, 31, 351 (1973).
32. J.A.Pople and G.A.Segal, *J.Chem.Phys.*, 44, 3289 (1966).
33. L.E.Sutton (ed.), *Interatomic Distances*, The Chemical Society, London (1958, 1965).
34. H.K.Wang, *Acta Chem.Scand.*, 19, 879 (1965).
35. M.J.Housty, *Acta Cryst.*, 14, 92 (1961).
36. H.Dreizler, G.Dend, *Z.Naturforsch.*, 19, 512 (1964).

37. Chemical Handbook, Vol.1, Leningrad, Moscow, 1962.
38. H. Oberhammer and W. Zeil, J. Mol. Struct., 6, 3999 (1970).
39. C. Kato, S. Konata, T. Iijima, and M. Kimura, Bull. Chem. Soc., Japan, 42, 2148 (1969).
40. K. Myers and W. Gwinn, J. Chem. Phys., 20, 1420 (1952).
41. C. Bigg, R. Desiderato, and R. Z. Sass, J. Amer. Chem. Soc., 86, 3157 (1964).
42. N. I. Sadova, N. I. Popik, A. V. Vilkov, Yu. A. Pankrushev, and V. A. Shljaposhnikov, Zh. Strukt. Khim., 19, 695 (1974).
43. S. Ghosh, R. Trambarulo, and W. Gordy, J. Chem. Phys. 20, 605 (1952).
44. H. Z. Hase and A. Schweig, Theor. Chim. Acta, 31, 216 (1973).
45. D. P. Santry and G. A. Segal, J. Chem. Phys., 47, 158 (1967).
46. S. Oae, W. Tagaki, and A. Ohno, Tetrahedron, 20, 417, 427 (1964).

THE BASE-CATALYZED DEUTERIUM EXCHANGE IN FIVE-MEMBERED
SATURATED HETEROCYCLES

N.N.Zatsepina, I.F.Tupitsyn, A.I.Belyashova, A.A.Kane,
and A.V.Kirova

State Institute of Applied Chemistry, Leningrad

Received June 25, 1975.

A study is made of the isotopic hydrogen exchange of α -methylene groups for a series of five-membered saturated heterocycles in alcoholic medium, both base-catalyzed (N-methylmorpholine, potassium alcocide) and without catalysis. In most of the cases the electronic effect of one or several heteroatomic groups on the exchange ability of hydrogen in alicyclics is similar to that observed for their linear analogues and correlates with the σ^- values ($\rho^- = 20$).

The course of the kinetic CH-acidity agrees satisfactorily with the differences between the total energies of carbanions and of the corresponding neutral molecules (ΔE) calculated by the CNDO/2 method, as well as with the electronic charges on the exchanging hydrogen atoms.

In recent years, a number of papers dealing with factors affecting the kinetic CH-acidity of alicyclics were published: the dependence of exchange rate on the size of the ring and on the associated change in the s-character of the reacting CH-bond was studied /1,2/; a few examples have demonstrated the steric selectivity of the exchange reaction indicating its sensitivity to variations in conformation and configuration of molecules /3-12/. However there are practically no publications devoted to a comparative study of the effect exerted by one or several heteroatomic groups incorporated in a ring on the kinetic CH-acidity. The pre-

sent work reports on such a study of a series of alicyclic compounds containing one, two, three or four heteroatomic groups.

Depending on the mobility of hydrogen atoms in the methylene groups, the kinetics of deuterium exchange was studied either in alcohol or in alcohol with an admixture of basic reagents (N-methylmorpholine, potassium alcoxide). Also, the exchange rate of thiophane, cyclopropane and spiropentane have been measured in a solution of sodium (potassium) amide in liquid ammonia.




For some compounds the rate constants of deuterium exchange were measured in various media which permitted us quantitatively estimate the relative reactivity of all the heterocycles studied. The relative rate constants ($\log f = \log k$) were calculated with respect to cyclopentanone as a reference compound. The conditions of the experiments and the kinetic data are listed in Table 1.




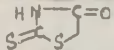
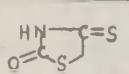

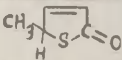


As seen from Table 1, the kinetic CH-acidity of alicyclics reveals a high sensitivity to variations in the nature of heteroatomic groups (the range of variation of the deuterium exchange rate constants spans twenty seven powers of ten). A correlation analysis of the data was carried out assuming the possibility of an approximate description of the electronic effect due to heteroatomic groups by σ -values of the corresponding substituents in the linear analogues of alicyclics. The latter are arising as the ring breaks by the bond which is the farthest from the reaction center^{*)}. The parameters of the relationship found in this way (see Fig.1)










$$\log f = -15.2 + 20.0 \sum \sigma^- (\sigma^o) \quad (r = 0.982, n=11)(1)$$

^{*)} E.g. in the deuterium exchange of cyclopentanone such an analogy is the $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$ molecule, for rhodanine - $\text{RC(S)SCH}_2\text{CONHR}$, for furanidone - $\text{CH}_3\text{COCH}_2\text{CH}_2\text{OCH}_3$, and so on.

Table 1. Kinetic Characteristics of Exchange and CNDO/2 Calculations on Alicyclics.

No	Compound	Position	Solvent ¹⁾	t, °C	k · 10 ⁵ , sec ⁻¹	E, kcal/mole	log A	log f	$\sum \epsilon_i \epsilon_j$ ²⁾	E, eV ³⁾	q _H , a.e. ³⁾
1	2	3	4	5	6	7	8	9	10	11	12
1		2,5	A	180	12.0	22.0	6.7	0	0.72	25.192	0.9776
			B	160	4.3						
				100	0.05						
				130	4.5	8.7	0.3				
			C (0.01N) D(0.001N)	105 80 20 0 25	2.1 1.0 15.0 5.2 37.0						
2		2	-	-	-	-	-	(-3.0) ⁴⁾	0.61	25.739	0.9870
3		4	B	35 15 0	10.0 3.8 1.6	8.8	2.2	1.9	0.87	25.088	0.9712
4		5	-	-	-	-	-	(-17.4) ⁴⁾	-0.11	27.099	1.0121
5		2	B	50 30	6.9 ⁵⁾ 2.2	11.4	3.6	1.6 ⁵⁾	0.84	24.484 (24.767) ⁶⁾	0.9778
6		4		10	0.56				0.87	24.864 (24.854) ⁶⁾	0.9736

1	2	3	4	5	6	7	8	9	10	11	12
7		3	C (0.1N)	70 50	4.8 0.81	19.6	8.2	-3.5	0.47	25.254	0.9726
8		2,5	C (0.6N)	105 90 75	12.0 2.5 0.54	27.0	11.7	-5.2	0.58 (0.37) ⁷⁾	25.729 (24.752) ⁶⁾	0.9707 (0.9544) ⁶⁾ (0.9696) ⁶⁾
9		2,5	C (0.1N) D (0.21N)	70 55 55 40 25	2.4 0.36 11.0 2.1 0.45	- - 20.1	- - 9.9	-3.7	0.90 (0.54) ⁷⁾	24.904 (24.826) ⁶⁾	0.9667 (0.9650) ⁶⁾
10		2	A	50 30	15.0 2.6	-	-	4.3	1.06	22.748	0.9537
11		2	A E	50 30 18	15.0 3.3 3.0	- - -	- - -	4.3	1.06	22.490 (22.096) ⁶⁾	0.9447 (0.9337) ⁶⁾
12		3	E	18	38 ⁸⁾	-	-	(5.4) ⁹⁾	-	23.897 (23.365) ⁶⁾	0.9684 (0.9635) ⁶⁾
13		5	E	18	0.15 ⁸⁾	-	-	(3.0) ⁹⁾	-	23.467 (23.281) ⁶⁾	0.9794 (0.9626) ⁶⁾
14		2	D (0.1N)	50	0.0013 ¹⁰⁾	-	-	-7.3	0.34	27.057 (25.683) ⁶⁾	0.9966 (0.9593) ⁶⁾
15		2,5	F	35	0.2 ¹¹⁾	-	-	(-2.7) ¹²⁾	1.01	-	-

1	2	3	4	5	6	9	10	11	12
16		2,5	G	25	12.0	¹³⁾ (-16.8)	0.02	26.676 ⁶⁾ (25.780)	1.0048 ⁶⁾ (0.9839)
17		1-3	G	45 25	0.86 0.2	¹³⁾ (-19.1) ¹⁴⁾ (-18.9)	-	26.713	0.9954
18		1,2 4,5	G'	25	0.66	¹³⁾ (-18.6)		26.277	0.9961
19		1-5	I	-	-	¹⁵⁾ (-23)	-0.30	26.618	1.0066
20		3		-	-	¹⁶⁾ (-2.2)	-	25.715	1.0100
21		2,5		-	-	¹⁶⁾ (1.1)	-	23.687 ⁶⁾ (23.686)	0.9544 (0.9561) ⁵⁾
22		2,5	-	-	-	⁴⁾ (-23.4)	-0.41	27.383	1.0087
23		2,5	-	-	-	⁴⁾ (-27)	-0.59	27.552	1.0342
24		2	-	-	-	⁴⁾ (0.6)	0.79	24.878 ⁶⁾ (24.175)	0.9639 (0.9437) ⁶⁾

1) The notations used: A-CH₃OD; B-0.01N N-methylmorpholine + CH₃OD; C-CH₃OK+CH₃OD; D- C₂H₅OK+C₂H₅OD; E = 0.001N C₅H₅N+ CH₃OD; F - NaOD+D₂O; G - 0.03N NaND₂+ND₃; G'-0.1N KND₂+ND₃; I -C₆H₁₁NDCs + C₆H₁₁ND₂.²⁾ ⁶⁾ values are taken from Refs. /18,19/.³⁾ For the linear analogues of compounds Nos 1,2,9, 14 the values of ΔE and q_H are, respectively: CH₃COCH₂CH₃, 25.271, 0.9836; CH₃COCH₂CH₂OH, 25.111, 0.9736; CH₃SO₂CH₂CH₃, 24.796, 0.9765; CH₃SCH₂CH₃, 26.896, 1.002 (for spd-approximation, 25.438, 0.9560).⁴⁾ Estimated by Eq.(1).⁵⁾ Mean exchange rate constants for 2- and 4-positions.⁶⁾ spd-approximation.⁷⁾ Σ σ°. ⁸⁾ From data of ref./20/. ⁹⁾ Estimated from comparison with deuterium exchange rate of isorodanine(No11). ¹⁰⁾ Measured in solution t-BuOK+t-BuOH and reduced to the specified conditions using data of ref./3/. ¹¹⁾ Taken from ref./4/. ¹²⁾ According to ref./4/(Continued on the next page),

(Continued from previous page) compound No 15 exchanges 15 times slower than trimethylsulfonium iodide whose $\log f$ estimated from data of ref./14/ is -1,5. ¹³⁾ As intermediate reference toluene /13/ was taken which in medium G exchanges 130 times faster than thiophane (No 16), and in medium G', $2.5 \cdot 10^4$ and $8 \cdot 10^3$ times faster, than cyclopropane (No 17) and spiropentane (No 18), respectively; $\log f$ for toluene estimated from data of ref./13/ is -14.7. ¹⁴⁾ Estimated from data of ref./31/. ¹⁵⁾ According to ref./1/, cyclopentane exchanges $1.6 \cdot 10^4$ times slower than cyclopropane (No 17). ¹⁶⁾ According to ref./12/, deuterium exchange rates of compounds 20 and 21 are 30 and $6 \cdot 10^4$ times larger than that for sulfolan (No 9).

are close to those found earlier for exchange in a series of substituted methanes ($\rho^- = 14.6$) /13/. Also, in most cases the conclusions drawn from the analysis of the observed correlation dependences are similar. Indeed, the influence of electron - withdrawing substituents is determined by their I-, M- and C-effects and reflected by the σ^- values whereas the electron-releasing substituents reveal an inductive and mesomeric effect reflected by the σ_P^o values. The electronic effect of two substituents at the reaction center can be described by either an additive sum of the corresponding σ^- values or (in the case of two -C substituents) a sum of the ($\sigma^- + \sigma^o$) values.

Thus the results of a correlation analysis indicate that the electronic interactions in those reaction series are of the same general nature. In most of the compounds the transformation of a molecule into a five-membered cycle does not produce any substantial changes in the mechanism of activation of the reaction center. Only three of the compounds (Nos. 8, 9, 15) display substantial deviations from the correlation curve. When the σ^- values of the sulfonyl and sulfinyl groups are replaced by the σ^o values

es, data on the kinetic acidity of the CH-acids of sulfolane and thiophane oxide fit to Eq. /1/. The elimination of the contribution from direct polar conjugation probably results from unfavorable geometric configuration of the above cyclic compounds which enhances electron repulsion between the carbanion charge and the lone pair of oxygen. This conclusion agrees with the steric selectivity of hydrogen exchange at the α -position in a heterocyclic ring established by the nuclear magnetic resonance technique for a number of sulfones and sulfoxides /8-11/*)

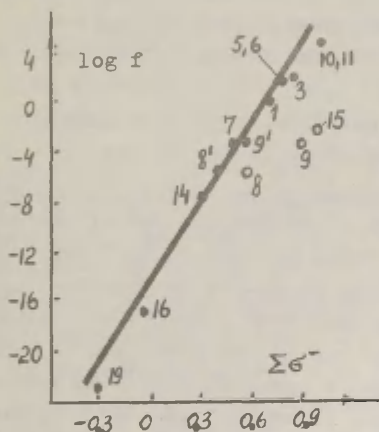


Fig.1. Correlation between the deuterium exchange rate constants and the σ^- values.

The numbering is as specified in Table 1.

As in the case of deuterium exchange of acyclic "onium" compounds of the type $(CH_3)_nM^+X^-$ /13-15/, the effect of a charged substituent on the kinetic CH-acidity of the cyclic sulfonium cation does not obey Eq. (1). The substantial slowing down of the exchange process is probably associated with a combined influence of the

*) According to Refs /4-11/, the rate of proton abstraction from trans-position relative to the lone pair of a heteroatomic group exceeds that for cis-isomer.

following two factors:

a) An unfavorable location of the CH-bond relative to the lone pair of the S^+ atom due to cyclisation. It results, in particular, in the steric selectivity in the exchange of α -hydrogen /4-7/;

b) Reduced electron-withdrawing action of a charged substituent because of a partial neutralization of charge on the S^+ atom. This is due to the interaction with the charge of the "outer" anion /14,17/. According to Refs./13-15/, the latter factor is responsible for the reduced deuterium exchange rate of "onium" compounds with an open chain (-0.3). Judging by the magnitude of deviation from correlation line of Fig.1 ($\Delta \sigma \approx -0.4$), this effect prevails also in the desactivation of the exchange process of the cyclic salt of sulfonium.

In order to elucidate the possibility of a quantum-chemical description of the observed variation of the rate constants, the CNDO/2 method was used to calculate the differences between the total energies of carbanions and of the corresponding neutral molecules (ΔE), as well as the charge on the hydrogen atoms participating in deuterium exchange (q_H). For most neutral molecules an idealized geometry was assumed, in which all C,O,N and S atoms lie in one plane and all hydrogen atoms are arranged in pairs symmetrically with respect to this plane^{*}). The structural parameters used were typical for the class of compounds considered /21-28/: $r_{C-C} = 1.54 \text{ \AA}$, $r_{C=C} = 1.37 \text{ \AA}$, $r_{(C)-(C=C)} = 1.42 \text{ \AA}$, $r_{C-O} = 1.43 \text{ \AA}$, $r_{C=O} = 1.23 \text{ \AA}$, $r_{C-S} = 1.84 \text{ \AA}$, $r_{(S)-(C=C)} = 1.71 \text{ \AA}$, $r_{C-H} = 1.09 \text{ \AA}$, $r_{S=O} = 1.47 \text{ \AA}$, $\angle HCH = 109.5^\circ$, $\angle CNC = 112^\circ$, $\angle COC = 112^\circ$, $\angle OSO = 125^\circ$, $\angle CSC = 94^\circ$. The calculations for cyclopentane, cyclopropane and spiro-pentane were based on experimental data on the geometry of the molecules involved /25-27/. The model for carbanions involves total deprotonation of the C-H bond while maintaining

^{*}) An exclusion is thiophane oxide for which, an accordance with refs./30,31/, the oxygen atom was assumed to lie out of plane ($\angle OSC = 107^\circ$).

the other bond lengths and the valence angles unchanged. Calculations for sulfur-containing compounds were carried out with or without including the d-orbitals of the sulfur atom. Calculations were performed on a BESM-6 computer by a program prepared by Dr. V. Ja. Besspalov.

As seen from Table 1 and Fig. 2 the results of calculations of ΔE and q_H follow satisfactorily the variation of relative rate of proton abstraction over a wide range of CH-acidic properties. It results from variations in the electronic nature of one or several heteroatomic groups incorporated in a ring, and different positions of exchanging hydrogen atoms in a cycle:

$$\log f = 233.0 - 9.3 \Delta E \quad (r=0.928, n=16) \quad (2)$$

$$\log f = 424.2 - 438.3 q_H \quad (r=0.948, n=19) \quad (3)$$

Except for 1,3-dithiolane (No 14 in Table 1) the inclusion of d-orbitals does not improve agreement of calculations with experiment in any case. This result supports the conclusion [3] on the essential role of d-orbitals in the stabilization of the transition state in deuterium exchange of 1,3-dithiolane.

Experiments agree also with the results on the variation of the reactivity order when going from five - membered cycles to open - chain compounds. Small differences between the calculated values of ΔE and q_H for alicyclics and disubstituted methanes representing their linear analogues (see footnote 3 to Table 1) and the closeness of the slopes of relations (2) and (3) for mono- and disubstituted methanes [28] confirm the conclusion that the cyclization effect does not involve substantial changes in the mechanism of electronic interactions in the series of five - membered rings. Finally, there is a semiquantitative agreement between the substantial decrease of ΔE and q_H and increase of CH- acidity as high as five powers of

ten as one goes from saturated to partially unsaturated cycloalkanes (Nos 20,21 in Table 1). This increase in the CH-acidity is associated with the formation of an extended conjugation system in the transition state



causing an additional stabilization of the carbanion.

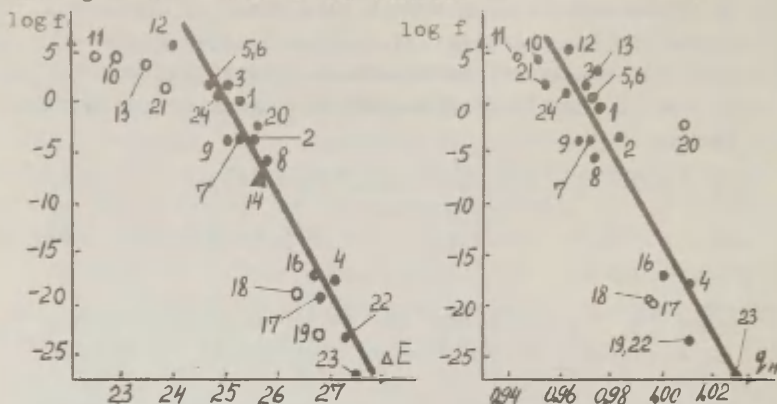


Fig.2. Plot of deuterium exchange rate of alicyclics vs. ΔE and q_H calculated in the sp-approximation.

O - Compounds not included in the correlation analysis.

Thus the data presented indicate that the quantum - chemical approach can be used in estimating the relative CH-acidity of five - membered saturated heterocycles. The CNDO/2 method exaggerates somewhat the role of electron repulsion. Therefore, attempts to use it in a description of the experimentally observed trend of the increase in CH-acidity as the cycloalkane ring decreases in size do not yield positive results (see e.g. ref./29/ and our data on cyclopentane, cyclopropane and spiropentane).

EXPERIMENTAL

Most of the compounds were prepared by standard procedures. The technique of studying the exchange reaction has been described elsewhere /32/. The deuterium content was usually determined by low - voltage mass spectrometry with the only exception of pyrrolidine-2 (No 7 in Table 1). The deuterium content in this compound was measured by a spectral emission analysis of water obtained after its combustion (deuterium from the ND group was preliminarily washed out by repeated processing with "light" ethanol).

REFERENCES

1. A.Streitwieser and J.Richard, J.Amer.Chem.Soc., 91, 529 (1969).
2. C.Rappe and W.H.Sachs, Tetrahedron, 24, 6287 (1968).
3. S.Oae, W.Tagaki, and A.Ohno, Tetrahedron, 20, 427 (1964).
4. G.Barbarella, A.Garbesi, and A.Fava, Helv.Chim.Acta, 54, 341, 2297 (1971).
5. A.Garbesi, G.Barbarella, and A.Fava, J.Chem.Soc., Chem. Commun., 1973, 155.
6. E.L.Eliel, Tetrahedron, 30, 1503 (1974).
7. O.Hofer and E.L.Eliel, J.Amer.Chem.Soc., 95, 8075 (1973).
8. S.Bradamante, S.Naiorana, A.Mangia, and G.Pagani, J.Chem. Soc., (B), 1971, 74.
9. L.A.Paquette and J.P.Freeman, J.Amer.Chem.Soc., 93, 3216 (1971).
10. R.R.Fraser, F.J.Schuber, and Y.Y.Wigfield, J.Amer.Chem. Soc., 94, 8795 (1972).
11. B.J.Hutchinson, K.K.Anderssen, and A.R.Katritzky, J.Amer. Chem. Soc., 91, 3839 (1969).
12. C.D.Broadbush, Accounts Chem. Res., 1, 231 (1968).
13. N.N.Zatsepina, I.F.Tupitsyn, and A.I.Belyashova, Organic reactivity, 11, 431 (1974).
14. N.N.Zatsepina, I.F.Tupitsyn, and A.V.Kirova, Reakts.Sposobn.Organ.Soed., 8, 787 (1971).

15. N.N.Zatsepina, I.F.Tupitsyn, A.I.Beljashova, B.B.Alipov, and N.S.Kolodina, *Organic Reactivity*, 11, 445 (1974).
16. G.Fraenkel, *J.Chem.Phys.*, 39, 1614 (1963).
17. G.Schiemenz, *Angew.Chem.Intern.Ed.*, 7, 544 (1968).
18. Yu.A.Zhdanov and V.I.Minkin, *Korrelyatsionnyi Analiz v Organicheskoi Khimii* (Comparative Analysis in Organic Chemistry), Rostov-on-Don, Izd.Rostov.Univ., 1966.
19. S.Ehrenson, R.T.C.Brownlee, and R.W.Taft, in *Progress in Physical Organic Chemistry*, Vol.10, New York, London, Sydney Toronto.
20. A.B.Hörnfeldt, *Arkiv Kemi*, 29, 455 (1968).
21. L.E.Sutton, *Tables of Interatomic Distances and Configuration in Molecules and Ions*, London, The Chem.Soc., (1958, 1965).
22. B.Bæk, D.Christensen, and W.Dixon, *J.Mol.Spectr.*, 9, 124 (1962).
23. H.J.Geise and F.C.Mijlhoff, *Rec.Trav.chim.*, 90, 577 (1971).
24. Z.Nahlovsky, B.Nahlovsky, and H.M.Seip, *Acta Chem.Scand.*, 23, 3534 (1969).
25. L.M.Sverdlov, M.A.Kovner, and E.P.Krainov, *Vibrational Spectra of Polyatomic Molecules* (Kolebatel'nye Spektry Mnogoatomnykh Molekul) Nauka, Moscow, USSR, 1970.
26. O.Bastisnsen, F.N.Fritsch, and H.Hedberg, *Acta Cryst.*, 17, 538 (1964).
27. G.Dallinga, R.K.Draai, and L.H.Toneman, *Rec.Trav.Chim.*, 87, 897 (1968).
28. N.N.Zatsepina, A.A.Kane, and I.F.Tupitsyn, *Organic Reactivity* (Reakts.Sposobn.Organ.Soedin.), 12, 179, (1975).
29. R.G.Jesaitis and A.J.Streitwieser, *Theor.Chim.Acta*, 17, 165 (1970).
30. R.Hoffman, H.Fujimoto, J.R.Swenson, and Chin-Chuen Wan, *J.Amer.Chem.Soc.*, 22, 7644 (1974).
31. M.J.Cook and A.P.Tonge, *J.Chem.Soc., Perkin Trans. II*, 1974, 767.
32. N.N.Zatsepina, I.F.Tupitsyn, and L.S.Efros, *Khim. i Tekhnolog.Isotopov* (Tr.Gos.Inst.Prikl.Khim.), No 56, 113 (1967).

THE ISOTOPIC HYDROGEN EXCHANGE IN HETEROAROMATIC TRANS-STILBENE DERIVATIVES AND SIMILAR COMPOUNDS

N.N.Zatsepina, I.F.Tupitsyn, and A.I.Belyashova

State Institute of Applied Chemistry, Leningrad

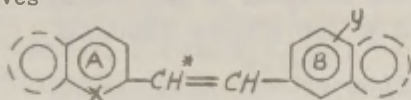
Received June 25, 1975

A study was made of the kinetics of deuterium exchange with α -hydrogen in the vinylene group for a large series of heteroarematic derivatives of trans-stilbene and of similar compounds in an alcoholic solution of potassium alkoxide. The correlation relations were found which describe the effect of substituents (heteroatoms) on the kinetic CH-acidity. The results, as well as data on the differentiating effect of the solvent and on the magnitude of the kinetic isotopic effect, permit to conclude that the mechanisms of a vinyl type reactions and of the deuterium exchange of both aliphatic and aromatic CH-bonds, reveal similar features.

Cram et al. /1/ have used the simplest stilbene systems to compare the kinetic CH-acidity of the vinyl and allyl groups, as well as to reveal some characteristic features of the mechanism of basic deuterium exchange in such systems. Still, this type of exchange processes continues to attract even greater attention of researchers (see e.g., /2-6/). However, the nature of the dependence of proton mobility on the molecular electronic structure remained poorly studied up to now. The available data are scarce and limited to the study of a few polar substituents (halogens /2/, -CN /3/, -COC₆H₅ /4,15/, -SR, -SOR, -SO₂R /5,6/) connected directly with the vinylene fragment.

The present work deals with the kinetics of basic deuterium exchange of α -hydrogen in a large number of heteroaromatic analogues trans-stilbene and some of its de-

rivatives













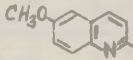

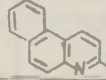

These subjects permit to follow in a stepwise manner the main features of the transmission of electronic effects to the vinyl reaction center due to the change in the nature and position of one or two heteroatoms in the A ring, or with the position of the polar substituent in the B ring. Also, changes in the π -conjugation region resulting from condensation of additional benzene rings in the A and B subsystems accompany.











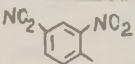



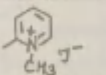




Most kinetic measurements have been carried out in alcoholic solution of potassium alkoxide. The results are presented in Tables 1 and 2. A comparison of data on the deuterium exchange of 2-styrylpyridine N-oxide labelled with deuterium in the α and β positions of the vinylene group (No 17 in Table 1) shows the exchange rate in the first case to be at least 10^6 times that for the second. Such a high selectivity of the exchange reaction affords a possibility of studying changes in the mobility of the α hydrogen atoms in the "direct" pathway (deuterium is in solvent).






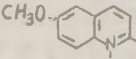

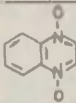



*) Although the base-catalyzed isotopic exchange of cis- and trans-stilbenes may be accompanied by their partial isomerization /1/, check experiments carried by us on "light" compounds in a "light" solvent showed that under these conditions the exchange rate for those compounds as that for stilbene (parent compound) /1/, exceeds by far the rate of isomerization. Hence, the complications associated with the configurational instability of molecules are of little importance.


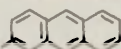
Table 1.

Isotopic Exchange of α -Hydrogen in Heteroaromatic trans-Stilbene Derivatives
in 0,6N $\text{CH}_3\text{OK}+\text{CH}_3\text{OD}$ Solution.

No	$\text{R}_1-\overset{\alpha}{\text{CH}}=\overset{\beta}{\text{CH}}-\text{R}_2$		t, °C	$k \cdot 10^5$ sec^{-1}	E, $\text{kcal} \cdot \text{M}^{-1}$	lg A	-logk _{25°}	¹⁾ $-\text{log}_{25^\circ} \text{CH}_3$	Method of pre- paration
	R ₁	R ₂							
1	2	3	4	5	6	7	8	9	10
1			180 160 145	3.0 0.73 0.24	27.0	9.2	10.6	8.2	/21/
2			160 140 120	18.0 5.3 1.4	21.6	7.2	8.7	6.3	/22/
3			160 140 120	30.0 8.1 2.0	22.9	8.5	8.3	5.4	/21/
4			105 90 75	8.7 2.6 0.61	23.6	9.7	7.6	5.1	/25/
5			160 140 120	24.0 8.3 2.6	18.8	5.7	8.1	5.7	/21/
6			160 120 105	3.5 0.6 0.1	29.3	11.6	10.5	7.2	/21/
7			160 140 115	16.0 5.7 1.1	19.7	5.6	9.8	6.4	/21/

1	2	3	4	5	6	7	8	9	10
8			140 120 100	16.0 4.8 1.5	17.1	5.2	7.4	5.1	/21/
9			75 60 45	12.0 3.5 1.0	18.3	7.5	5.9	3.5	/26/
10		 2)	60 50 40	13.0 5.4 2.1	18.9	8.5	5.4	3.2	/27/
11			120 105 90	17.0 3.8 0.74	29.5	12.6	9.1	5.6	/28/
12			120 105 85	8.1 2.3 0.4	24.0	9.4	8.2	4.9	/29/
13		 3)	45 30	9.6 4.0	(11.2)	(3.7)	3.7 ⁴⁾	1.1	/30/
14		 2)	50 40 30	15.0 7.1 2.7	15.7	7.3	4.2	1.6	/24/
15		 5)	20 10 0	16.0 6.6 2.7	14.2	6.7	-	-	10)
16		H	140 120 105	13.0 2.5 0.7	25.7	9.6	9.1	-	-
17		 6)	80 65 50	11.0 3.0 0.8	19.7	8.3	6.1	3.5	/24/

1	2	3	4	5	6	7	8	9	10
18		 7)	95 80 65	9.2 2.7 0.7	21.3	8.5	7.1	3.8	/22/
19		 8)	150 135	4.7 1.5	-	-	-	15.9	-
20		-H 8)	150 135	5.6 1.9	-	-	-	-	-
21			70 55 20	12.0 4.6 1.7	13.9	5.0	5.2	3.7	/24/
22		 9)	30 15 0	10.0 4.2 1.2	-	-	-	2.7	/31/
23			180	5.8	-	-	-	-	11)

1	2	3	4	5	6	7	8	9	10
24			180 160	6.0 1.8	-	-	-	-	11)

1) Deuterium exchange rate for the corresponding methyl derivatives in the solution 0.57N $C_2H_5OK + C_2H_5OD$ /7,8,12/. The kinetics of deuterium exchange of 1-methylisoquinoline was studied together with A. V. Kirova ($t^\circ, k \cdot 10^5, \text{sek}^{-1}$): 65.11; 50.2, 7; 35, 0.5 ($E=21.0 \frac{\text{kcal}}{\text{mole}}$, $\lg A=9.7$). 2) In the isotopic exchange of 2-styryl- $\alpha(D,T)$ -benzoxazol (60°) with the solution 0.6 N CH_3OK+CH_3OH , $k_D = 5 \cdot 10^{-5} \text{ sec}^{-1}$, $k_T = 5.8 \cdot 10^{-5} \text{ sec}^{-1}$, $k_D/k_T = 0.9$; in the exchange reaction of 2-styryl- $\alpha(D,T)$ -quinoline N-oxide (50°) $k_D = 1 \cdot 10^{-4} \text{ sec}^{-1}$, $k_T = 8 \cdot 10^{-5} \text{ sec}^{-1}$; $k_D/k_T = 1.2$. 3) In the solution 0.1 N CH_3OK+CH_3OD . 4) In the solution 0.6 N CH_3OK+CH_3OD . 5) In the solution 0.1N $(C_2H_5)_3N+CH_3OD$. 6) In the solution 0.1N $C_2H_5OK+C_2H_5OD+DMF$ (1:3) at $20^\circ k = 8 \cdot 10^{-5} \text{ sec}^{-1}$. 7) 2-styryl- $\alpha(D,T)$ -pyridine N-oxide does not exchange at 180° ($k < 10^{-7} \text{ sec}^{-1}$). 8) In the solution 0.1N $C_2H_5OK+C_2H_5OD+DMSO-D_6$ (1:5). Under the same conditions for toluene ($t^\circ, k \cdot 10^{-5} \text{ sec}^{-1}$): 150, 10; 135, 2.3/33/. 9) In the solution 0.05N $CH_3OK+CH_3OD+CHCl_3$ (2:1). 10) Obtained by quaternization of 2-styrylpyridine. 11) Obtained by deoxidation /32/ of the corresponding N-oxides (Table 2).

For trans-stilbazols differing in the structure of the heteroaromatic fragment of the molecule (nucleus A) the observed changes in the kinetic CH-acidity correlate well (Fig.1) with the σ^- values. It indicates the effect of direct polar conjugation substantially stabilizes the transition state in the exchange of α -hydrogen in the vinylene group.

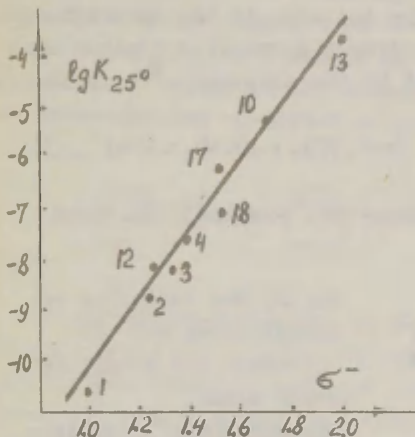


Fig.1. A plot of $\lg k$ vs. σ^- for the deuterium exchange of α -hydrogen. The numbering is as specified in Table 1. The σ^- values were taken from ref /7-9/.

These data disagree strongly with the results of a correlation treatment of the deuterium exchange rate constants for the aromatic CH-bonds of substituted benzenes and of their heteroanalogs, where the carbon atom of the reaction center is also in the sp^2 hybridization state although its activation proceeds primarily by the inductive mechanism (see e.g. /7,10,11/).

At the same time, these systems reveal a marked similarity with the corresponding methyl derivatives of aromatic heterocycles /7,8,12/ on acidifying action of various structural factors. Indeed, the electronic effect of substituents (heteroatoms) in both reaction series is characteri-

zed by correlation relations of the same type (25°)^{*)}

$$\log k_{\alpha\text{-CH}} = -16.9 + 6.7 \sigma^- \quad (r=0.985, s=0.4; n=10) \quad (1)$$

$$\log k_{\text{CH}_3} = -15.9 + 7.6 \sigma^- \quad (2)$$

The changes in the electronic structure associated with the expansion of the π -conjugation region in polycyclic heteroaromatic molecules affect the increase in the CH-acidity of the α -vinyl and methyl hydrogen atoms in a similar way. This similarity is reflected by the existence of a linear relationship

$$\log k_{\alpha\text{-CH}} = -2.6 + \log k_{\text{CH}_3} \quad (r=0.979, s=0.46, n=16) \quad (3)$$

which is valid for all the compounds studied (Fig.2).

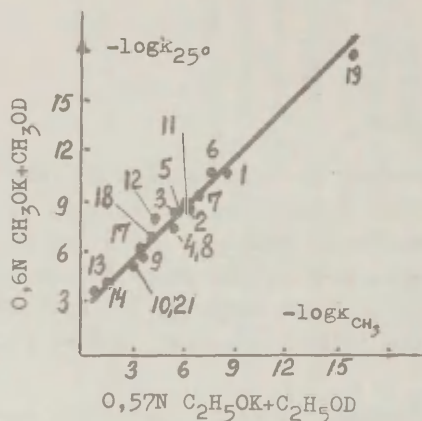


Fig.2. The deuterium exchange rates for the α -vinyl and methyl hydrogen atoms. The numbering is as specified in Table 1.

^{*)} The eqs. (1) and (2) are satisfied by the deuterium exchange rate constants measured in the solutions of 0.6N $\text{CH}_3\text{OK} + \text{CH}_3\text{OD}$ and 0.57N $\text{C}_2\text{H}_5\text{OK} + \text{C}_2\text{H}_5\text{OD}$ /7,12/, respectively. The increase in the CH-acidity affecting the magnitude of $\log k_0$ and caused by transition from the first medium to the second corresponds to $\Delta \log k \sim 0.8$.

The above gives grounds to conclude that for the series of compounds compared the hybridization state of a carbon atom is not key factor in the change of the relative kinetic CH-acidity. In terms of valence bonds theory stabilization of the deuterium exchange transition state of stilbene heteroanalogues by the conjugation mechanism which accounts for almost the same ease with which vinyl anions and anions of the benzyl type are formed, can be interpreted as resulting from an increase in the weight of the linear structure of allene in the resonance hybrid when a substituent revealing the -C-effect is present in the A ring



For better understanding of the stage mechanism of the exchange reaction of vinyl hydrogen atoms measurements of the primary kinetic effect of the substrate are of importance. The magnitude of the effect for the exchange of 2-styrylbenzoxazol- α (D,T) and of 2-styrylquinoline N-oxide- α (D,T) (Nos. 10 and 14 in Table 1) which is close to unity indicates that the "internal return" mechanism /8,14,15/ masking the isotopic effect at the CH-bond cleavage stage plays more important role than in the case of the methyl derivatives of heterocycles ($k_D/k_T \approx 2 \div 2.5$) /8,13/. This is apparently associated with a more complex and sterically more hindered geometry of the transition state in the exchange of stilbene systems. As a result of that its rate depends to a larger extent on the reorientation of the solvent molecules stabilizing the carbanion and on the possibility of their leaving the solvate shell. This interpretation is in agreement with the decrease in the exchange rate of α -vinyl hydrogen as compared with methyl hydrogen. This results from the change in the nature of the reaction center (see Table 1) and is ordinarily almost completely due to the decrea-

sing entropy term /16/ *).

In these features of the stage mechanism the exchange reaction of the stilbene systems reveals a similarity with that of the aromatic CH-bonds. This similarity manifests itself also in the character of the differentiating effect of an aprotic solvent on the kinetic CH-acidity. As is well known /17-20/, a change in the composition of the medium produced by adding an aprotic solvent (DMSO, DMF) to the alcoholic solution of potassium alkoxide affects differently the deuterium exchange rate of aliphatic and aromatic CH-bonds. In particular, as one goes from the solution of $RO^- + ROD$ to the solution of $RO^- + ROD + DMF(1:3)$, the deuterium exchange rate constant of the methyl group in 2-methylpyridine N-oxide increases by more than three powers of ten /19/ while that of the aromatic CH-bonds in the position 2 of the pyridine N-oxide ring increases only by a factor of 7-10 /20/. Although the observed differences are generally determined by several competing elementary processes, the most essential role in the systems considered is apparently played by changes in solvation associated with the degree of localization of the charge arising in the transition state of exchange at the reaction center /18/. Judging by the fact that the effect of adding an aprotic solvent (DMF) on the deuterium exchange rate of 2-styrylpyridine N-oxide

*) Just as in the case of heterocycles and of their methyl derivatives /16/, in the reaction series considered one does not observe a simple compensation dependence between the activation parameters (ΔH^\ddagger , ΔS^\ddagger). Nevertheless, there is a relationship between the characteristics of the contribution to these quantities coming from solvation. The present work does not deal with a detailed analysis of the above relationship, since the common trends of the change of the activation parameters brought about by substituents in the stilbazol series are similar to those for their heteroaromatic analogs. (See Ref./16/ for details).

($k_{\text{ROD+DMF}}/k_{\text{ROD}} \sim 10$, see Table 1) is practically identical with that observed in the deuterium exchange of pyridine N-oxide the contribution of solvation to the rearrangement of the transition state in the exchange reaction of α -vinyl hydrogen is comparable with that due to solvation on the deuterium exchange of aromatic CH-bonds.

Thus the above analysis gives grounds to conclude that, in accordance with the specific features of the electronic structure of the vinyl reaction center, the exchange reaction of the type considered reveals similarities with the process of deuterium exchange of both aliphatic and aromatic CH bonds.

A study of the kinetics of deuterium exchange of α -vinyl hydrogen in compounds with different electronic structure of the B fragment (Tables 1 and 2) permits to point out the following distinctive features of activation of the reaction center in such systems:

a) The effect of substituents in the benzene ring of 2-styrylpyridine N-oxide on the mobility of α -hydrogen depends on their inductive and mesomeric effects and correlates with the σ^0 values (Fig.3):

$$\log k = -6.0 + 2.6 \sigma^0 \quad (r = 0.995, s = 0.09, n = 11) \quad (4)$$

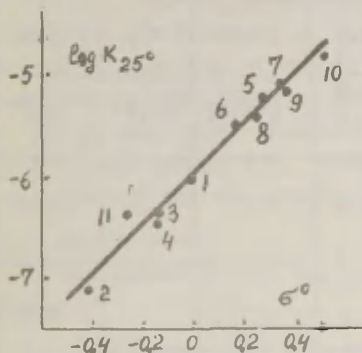
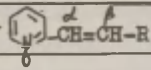

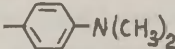
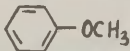
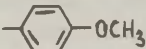
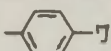



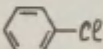
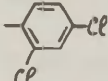
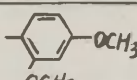



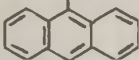


Fig.3. Correlation between the deuterium exchange rate of α -hydrogen and σ^0 values of substituent in the B ring. The numbering is as specified in Table 2.

Table 2. Isotopic Exchange of α -Hydrogen in 2-Styrylpyridine
N-oxides in 0.6N $\text{CH}_3\text{OK}+\text{CH}_3\text{OD}$ Solution.

No		t, °C	k · 10 ⁵ , sec ⁻¹	E, kcal mole	lg A	-lgk _{25°}
	R					
1	2	3	4	5	6	7
1		80	11.0	19.7	8.3	6.1
		65	3.0			
		50	0.8			
2		95	5.0	20.8	8.05	7.2
		80	1.5			
		65	0.4			
3		95	15.0	18.4	7.1	6.4
		80	5.6			
		65	1.6			
4		95	20.0	21.0	8.9	6.5
		80	6.0			
		65	1.5			
5		65	13.0	14.4	5.4	5.2
		50	4.6			
		35	1.6			
6		70	11.0	20.5	9.5	5.5
		60	4.7			
		50	1.7			
7		60	15.0	15.8	6.5	5.1
		45	5.1			
		30	1.4			
8		60	10.0	17.9	7.7	5.4
		45	2.7			
		35	1.1			
9		60	15.0	(17.8)	(7.9)	5.2
		50	6.5			
10		25	1.8	-	-	4.8
11		90	9.0	-	-	6.4
		75	2.6			
12		75	12.0	16.1	6.1	5.7
		65	5.8			
		50	2.0			

1	2	3	4	5	6	7
13		95 80 65	18.0 3.9 0.7	-	-	6.6
14		90 70 55	19.0 5.1 1.7	16.4	6.0	6.0
15		105 90 75	11.0 4.3 1.5	17.4	6.1	6.7

¹⁾ For the preparation of the compounds see ref./24/.

Thus the existence of a β -CH= bond bridge reduces strongly the transmission of electronic effects from the B ring ($\rho_B/\rho_A \approx 0.4$).

b) Replacing one of the β -hydrogen atoms in styrene and its derivatives by a phenyl radical, as well as the expansion of the π -conjugation region of the B system does not result in a substantial acceleration of the reaction (cf. Nos. 19, 20 and 1, 23, 24 in Table 1). In some cases (Nos. 1, 14, 15, in Table 2) it even slows down the exchange process.

Such a change in the rate constants which is unusual for processes involving carbanions is possibly caused by the steric effect. An increase in the size of the aromatic fragment and the possibility of steric repulsion between the β -hydrogen atom of the vinylene group and peri-hydrogen atoms of the benzene rings apparently causes the acoplanarity of the stilbene system as a whole^{*)} and thus results in destabilization of the transition state of the reaction.

^{*)} In the ground state the stilbene molecule is nearly planar

E X P E R I M E N T A L

All the compounds studied were prepared by condensation of the corresponding methyl derivatives of heteroaromatic compounds with aromatic aldehydes (Tables 1 and 2 list references to the methods used).

The procedure to study the exchange reaction is described elsewhere [28]. The deuterium content was determined from the change in the extinction coefficient of the out-of-plane bending vibration of the trans-vinylene group ($\nu \sim 960 \text{ cm}^{-1}$). The infrared spectra of compounds of interest were obtained in a chloroform solution at a concentration $\sim 0.3 \text{ M} \cdot \text{l}^{-1}$ and layer thickness 100μ .

R E F E R E N C E S

1. D.H.Hunter and D.J.Cram, J.Amer.Chem.Soc., 86, 5478 (1964).
2. D.Daloz, H.G.Viehe, and G.Chiurdoglu, Tetrah.Lett., 1969, 3925.
3. H.M.Walborsky and L.M.Turner, J.Amer.Chem.Soc., 94, 2273 (1972).
4. J.Warkenti and L.K.M.Lam, Can.J.Chem., 42, 1676 (1964).
5. C.D.Broadbent, Accounts Chem.Res., 1, 231 (1968).
6. G.Maccagnani and F.Taddei, Bull.Sci.Fac.chim.industr.Bologna, 26, 71, 83 (1968).
7. N.N.Zatsepina and I.F.Tupitsyn, Khim.Geterotsikl.Soedin., 1974, 1587.
8. N.N.Zatsepina, Yu.L.Kaminsky, and I.F.Tupitsyn, Reakts.Sposobn.Organ.Soedin., 4, 433 (1967).
9. N.N.Zatsepina, I.F.Tupitsyn, Yu.L.Kaminsky, and N.S.Kolodina, Reakts.Sposobn.Organ.Soedin., 6, 766 (1969).
10. A.I.Shatenstein, Adv.Phys.Org.Chem., 1, 155 (1963).
11. A.Streitwieser, Jr. and G.H.Hammond in Progr.Phys.Org.Chem., 1, 41 (1965).
12. N.N.Zatsepina, I.F.Tupitsyn, and A.V.Kirova, Reakts.Sposobn.Organ.Soedin., 9, 195 (1972).
13. N.N.Zatsepina, I.F.Tupitsyn, and L.S.Efros, Zh.Obshch.Khim. 33, 2705 (1963); 34, 4067, 4073 (1964).

14. D.J.Cram, Fundamentals of Carbanion Chemistry, Academic Press, New York, London, 1965.
15. J.F.Arnett and H.M.Walborsky, J.Org.Chem., 37, 3678(1972).
16. I.F.Tupitsyn, N.N.Zatsepina, A.V.Kirova, and Yu.M.Kapustin, Reakts.Sposobn.Organ.Soedin., 5, 636(1968).
17. A.I.Shatenstein, I.A.Romansky and I.O.Shapiro, Reakts.Sposobn.Organ.Soedin., 7, 337(1970).
18. Yu.I.Ranneva and A.I.Shatenstein, Zh.Obshch.Khim., 42, 2250(1972).
19. N.N.Zatsepina, A.V.Kirova, and I.F.Tupitsyn, Reakts.Sposobn.Organ.Soedin., 5, 70(1968).
20. I.F.Tupitsyn, N.N.Zatsepina, A.V.Kirova, and Yu.M.Kapustin, Reakts.Sposobn.Organ.Soedin., 5, 806(1968).
21. S.Skaup, K.Böhm., Ber., 59, 1013(1926).
22. A.R.Katritzky and P.Simans, J.Chem.Soc., 1960, 1518.
23. C.E.Kaslow and R.D.Stayner, J.Amer.Chem.Soc., 67, 1716 (1945).
24. K.Ramakan and V.R.Sumvasan, Indian J.Chem., 1, 351(1963).
25. S.Skidmore and E.Tidd, J.Chem.Soc., 1959, 1641.
26. A.M.Kiprianov and A.Ya.Ilchenko, Zh.Obshch.Khim., 35, 498 (1965).
27. D.Brown and G.Kon, J.Chem.Soc., 1948, 2147.
28. S.Roseman, J.Amer.Chem.Soc., 75, 3855(1953).
29. P.Ruggli and A.Staub, Helv.Chim.Acta, 20, 43(1937).
30. J.Thiele and R.Escales, Ber. 34, 2843(1901).
31. A.S.Elina and L.G.Tsirulnikova, Khim.Geterotsikl.Soedin., 1966, 275.
32. M.Hamana, J.Pharm.Soc., Japan, 71, 263(1951).
33. N.N.Zatsepina, I.F.Tupitsyn, and A.I.Belyashova, Organic Reactivity 11, 431(1974).
34. W.J.Hehre, L.Radom, and L.A.Pople, J.Amer.Chem.Soc., 94, 1496(1972).
35. A.R.Ager and L.Phillips, J.Chem.Soc., Perkin II, 1972, 1975.
36. N.N.Zatsepina, I.F.Tupitsyn, and L.S.Efros, Khim. i Tekhnolog. Isotopov (Tr.Gos.Inst.Prikl.Khim.). No 56, 117, 125 (1967).

THE ISOTOPIC HYDROGEN EXCHANGE IN AROMATIC NITRONES

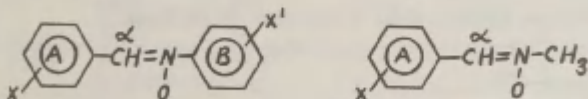
N.N.Zatsepina, I.F.Tupitsyn, A.I.Belyashova,
E.A.Medjantseva, I.M.Andreeva, and V.I.Minkin

State Institute of Applied Chemistry, Leningrad; Rostov-on-Don State University, Rostov-on-Don

Received June 25, 1975

A study of the kinetics of isotopic exchange for α -methine and N-methyl hydrogen atoms in substituted N, α -diphenyl- and N-methyl- α -phenylnitrones in an alcoholic solution of potassium alcoholate was made. The main contribution to the change in the free energy of activation for the exchange process is shown to be due to the electron-withdrawing effect of the N-oxide grouping. The effect of substituents from the phenyl rings on the kinetic CH-acidity correlates with the σ° values.

In the preceding paper /1/ a mechanism of electronic influence on the mobility of vinylene group hydrogen atoms in stilbene and its derivatives containing substituents or heteroatoms in aromatic rings was considered. The electronic effect of heteroatomic groups incorporated into the vinylene fragment of a molecule remains practically unstudied. The present work is an attempt to investigate this problem using the isotopic hydrogen exchange reaction in a series of N, α -diphenyl- and N-methyl- α -phenylnitrones.



The available data indicate the spectroscopic and physico-chemical characteristics of aromatic nitrones and similar compounds to be highly sensitive to changes in the electronic structure of their molecules (see, e.g. the results of a

polarographic study /2/, data on the NMR-, IR- and UV-spectra /3-10/, the dipole moments /8-11/ and the basic dissociation constants /12-13/).

Our kinetic studies show aromatic nitrones in an alcoholic solution of potassium alc oxide to be able to exchange fairly easily the deuterium from the alcohol for the methine- and N-methyl group hydrogen atoms (Tables 1 and 2).

As seen from Table 1, incorporation of the N-oxide function into the vinylene fragment of a molecule results in a strong enhancement of the mobility of α -hydrogen compared with that for the unsubstituted stilbene molecule. By the order of magnitude, the observed electronic effect of the N-oxide grouping ($\Delta \log k \approx 13$) is close to that occurring in the deuterium exchange of aromatic N-oxides ($\Delta \log k_{50^\circ} = \log k$ (pyridine N-oxide) - $\log k$ (benzene) ≈ 10 for the ortho hydrogen atoms of the ring /14-16/; $\Delta \log k_{25^\circ} = \log k$ (α -picoline N-oxide) - $\log k$ (toluene) ≈ 12 in deuterium exchange of the methyl group at the 2-position /14, 17/).

The total range of the rate constant variation due to all the other changes in electronic structure of the nitron molecule, including the variation of substituents in the A or B rings and the replacement of the methyl radical with the phenyl does not exceed 5 powers of ten (see Tables 1 and 2). Therefore effect of the N-oxide group connected directly with the reaction center produces the predominant contribution to the change in the free energy of activation of the exchange process.

As seen from Fig. 1, the electronic effect of substituents in the aromatic A ring on the rate of deuterium exchange in diphenylnitrones correlates with the σ° values^{*)}

$$\log k = -5.2 + 3.0 \sigma^\circ \quad (r = 0.979, n = 10) \quad (1)$$

^{*)} An exclusion to this is the nitro-group at the position 2 whose effect is described by eq. (2) with σ^- value.

Table 1. Isotopic Exchange of α -Hydrogen in α ,N-Diphenyl-nitrones in $\text{CH}_3\text{OK} + \text{CH}_3\text{OD}$ Solution.

No	Compound	$[\text{CH}_3\text{OK}]$, $\text{M}\cdot\text{l}^{-1}$	t, $^{\circ}\text{C}$	$k\cdot 10^5$ ¹⁾ , sec^{-1}	$-\log k$ _{25°} ²⁾
1		0.6	50 35 20	18.0 3.7 0.6	4.9
2		0.002	15 0	11.0 1.7	(1.1)
3		0.01	65 50 35	12.0 6.2 2.0	(3.4)
4		0.01	50 35 25	15.0 3.4 0.9	(3.3)
5		0.6	50 30 15	26.0 3.0 0.5	4.7
6		0.6	30 15	17.0 6.0	3.9
7		0.6	50 25	5.7 0.4	5.4
8		0.6	60 50 40	11.0 3.7 1.0	5.9
9		0.6	85 75 60	9.0 3.9 1.1	6.6
10		0.6	55 40	13.0 2.0	5.4
11		0.6	50 40	14.0 3.7	5.0
12		0.6	50 25	1.9 0.13	5.9
13		0.6	25	-	(17.5) ³⁾

¹⁾ Activation parameters (Compound No., E kcal/mole, log A):

1. 21.2, 10.6: 5, 21.1, 10.7: 8, 24.9, 12.4: 9, 19.9, 8.0.

²⁾ $[\text{CH}_3\text{OK}] = 0.6$ mole/l: ³⁾ Calculated from the Hammett relation using data of ref. /1/.

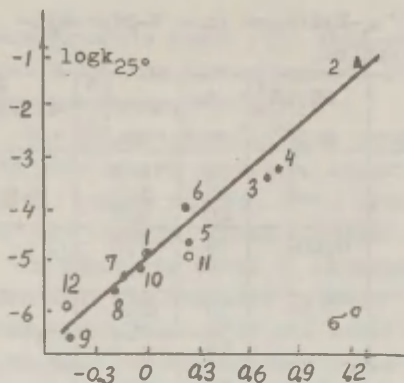


Fig.1. Deuterium exchange rate for the α -hydrogen in diphenylnitrones vs. σ values. The numbering is as specified in Table 1. σ -substituent X'.

A similar relationship for the series of substituted stilbenes can be written as [1]:

$$\log k = -16.9 + 6.7 \sigma \quad (2)$$

Thus the incorporation of the N-oxide group reduces the sensitivity of the vinyl CH bond to the electronic effects of substituents from the A ring by more than twofold. This is probably due to the fact that, as a result of considerable part of electron density displacing, from the methine reaction center to the N-oxide grouping, the carbanion transition state of the exchange process in nitrones occurs at an earlier stage and hence, in accordance with the principle of Hammond, should be less selective than in the case of deuterium exchange of stilbene and its derivatives.

Although the exchange reactions of nitrones containing substituents in the B ring have been studied by us to a lesser extent, Fig.1 reveals the possibility of using relationship (1) for an approximate description of the variation of the deuterium exchange rate constants for this class of compounds. Hence in nitrones $\rho_A \approx \rho_B$, in contrast to substituted stilbenes, where $\rho_A / \rho_B \approx 2.5$. This indicates a high mobility of the electron system of the N-oxide grouping whose effective interaction with the reaction center, on one hand, and with the B ring, on the other, is responsible for

the observed increase in the transmission of electronic influence from one electron subsystem in the nitron molecule to the other. The conclusion on the interrelated character of electronic effects in the $-\text{CH}=\text{N}-$ fragment is confirmed by the existence of a linear relationship between the rate constants of deuterium exchange for the methine α -hydrogen and the values of pK_a /12/ characterizing the basic properties of the N-oxide group (fig.2).

$$\log k = 0.5 - 0.74 \text{ pK}_a^{\text{NO}} \quad (r=0.984, n=5) \quad (3)$$

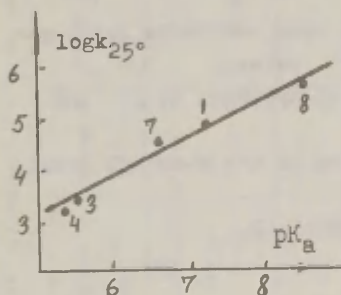


Fig.2. Dependence between CH-acidic and basic properties /12/ of diphenylnitrones. The numbering is as specified in Table 1.

A comparison of the data on the exchange rates of α ,N-diphenyl- and N-methyl- α -phenylnitrones shows (Tables 1 and 2) that a replacement of the phenyl B ring by an electron-releasing methyl group reduces the mobility of the methine hydrogen atom, on the average, by a factor of 5, whereas the reaction constant ρ remains practically unchanged (Fig.3a):

$$\log k_{25^\circ} = -5.5 + 2.2 \rho \quad (r=0.986, n=10) \quad (4)$$

The exchange rate for the N-methyl group (Fig.3b) described by relation (5)

$$\log k_{125^\circ} = -3.9 + 2.8 \rho \quad (r=0.992, n=6) \quad (5)$$

is 100-200 times smaller than that for the methine hydrogen and by at least 10^6 times higher than the deuterium exchan-

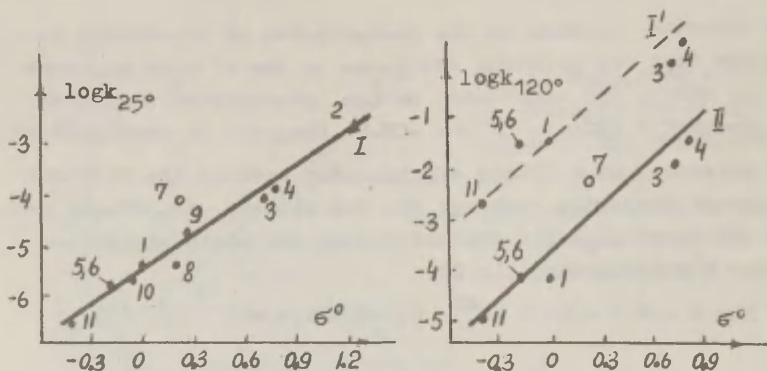


Fig.3. Correlation between the rate constants for N-methyl- α -phenylnitrones and the σ° values.

1 and 1' -deuterium exchange for α -hydrogen at 25° and 120°, respectively;

II - deuterium exchange for hydrogen of the N-methyl group at 120°.

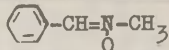
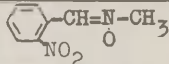
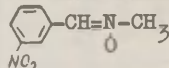
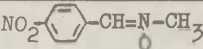
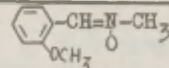
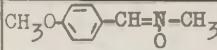
The numbering is as specified in Table 2.

ge rate for trimethylamine N-oxide^{*)}. Such a sharp increase in the kinetic CH-acidity of these compounds indicates the possibility of a sufficiently effective delocalization of the electronic charge appearing in the carbanion transition state of deuterium exchange of nitrones over the conjugated aromatic system of the $C_6H_5-CH=N-\overset{O}{\parallel}$ fragment.

^{*)}The deuterium exchange of trimethylamine N-oxide in 0.1N solution of $C_2H_5OK+C_2H_5OD+DMSO-D_6(1:5)$ proceeds at the rate $k = 1.3 \cdot 10^{-6} \text{ sec}^{-1}$ (120°) /18/. For toluene in the same solvent $k = 4.7 \cdot 10^{-6} \text{ sec}^{-1}$ (120°) /19/ and $k = 5 \cdot 10^{-12} \text{ sec}^{-1}$ (25°) /17-19/; for nitron (No 7 in Table 1), $k = 4.7 \cdot 10^{-5} \text{ sec}^{-1}$ (25°).

Table 2.

Isotopic Exchange of Hydrogen in N-Methyl- α -phenylnitrones in $\text{CH}_3\text{OK}+\text{CH}_3\text{OD}$ Solution.

No	Compound	$\alpha\text{-CH}$				N-CH_3			
		$[\text{CH}_3\text{OK}],$ $\text{M}\cdot\text{l}^{-1}$	$t,$ $^\circ\text{C}$	$k\cdot 10^5,$ sec^{-1}	$-\log k$ (25°)	$[\text{CH}_3\text{OK}],$ $\text{M}\cdot\text{l}^{-1}$	$t,$ $^\circ\text{C}$	$k\cdot 10^5,$ sec^{-1}	$-\log k$ (120°)
1	2	3	4	5	6	7	8	9	10
1		0.6	60 50 35	17.0 6.0 1.1	5.4	0.6	120 105 90	6.3 4.3 2.2	4.2
2		0.01	40 30	11.0 5.4	2.6	-	-	-	-
3		0.01	50 40	2.5 0.8	4.1	0.6	60 50 40	9.4 3.0 0.74	2.0
4		0.01	50 40 30	6.7 1.7 0.6	3.8	0.1	60 50 40	9.4 3.0 0.74	1.5
5		0.6	65 50 35	20.0 3.7 0.6	5.8	0.6	120	5.6	4.3
6		0.6	65 50 40	8.3 1.6 0.5	6.2	0.6	120 105	6.5 3.8	4.2

1	2	3	4	5	6	7	8	9	10
7		0.6	30 20 10	15.0 4.8 1.4	4.0	0.6	80 70 60	14.0 4.8 1.4	2.3
8		0.6	55 40	13.0 2.1	5.5	-	-	-	-
9		0.6	40 25 10	7.7 1.9 0.44	4.7	-	-	-	-
10		0.6	55 40 30	7.3 1.4 0.4	5.6	-	-	-	-
11		0.6	80 65 50	8.8 1.7 0.35	6.8	0.6	160 140 120	18.0 5.8 1.0	5.0

1) Activation parameters (Compound No., E kcal·M⁻¹; log A): 1, 22.3, 10.9; 5, 23.9, 11.7; 6, 22.2, 11.6; 7, 20.2, 10.8; 9, 17.6, 8.2; 10, 23.2, 11.5; 11, 23.8, 10.7.

2) $[CH_3OK] = 0.6$ M·l⁻¹.

Our attempt to measure the kinetic CH-acidity of azomethine and of its derivatives was a failure. The methine hydrogen atom participates in the isotopic exchange reaction neither in the kinetic region corresponding to the "normal" electron-withdrawing effect of a nitrogen heteroatom (see, e.g./14/) nor under much higher temperatures^{*)}. Just as in the case of isotopic exchange of aromatic CH-bonds at the position of nitrogen-containing heterocycles, the sharp decrease of the acidifying action of the nitrogen heteroatom in azomethines is undoubtedly a consequence of the " α -effect" of its lone pair /14,16,20/.

To see whether the observed changes in the CH-acidity for some of the studied compounds and those similar to them could be described from the quantummechanical standpoint, the difference between the total energies of carbanions and the corresponding neutral molecules has been calculated by the CNDO/2 method. As seen from Table 3, the results of the calculations fit correctly to the observed order of the relative mobility of hydrogen on two CH-acidic centers in the N-methyl- α -phenylnitrone molecule ($E_{\alpha-CH} < E_{N-CH_3}$) as well as to the sharp decrease in the deprotonation rate of the methyl group as one goes to trimethylamine N-oxide. As for the quantum-chemical interpretation of the electronic influence of the N-oxide grouping the differences in the rate of the deuterium exchange in nitrones and aromatic N-oxides found experimentally are considerably smaller than the calculated values ($\Delta \Delta E = \Delta E(\text{benzene}) - \Delta E(\text{pyridine N-oxide}) = 1.412 \text{ eV}$; $\Delta \Delta E = \Delta E(\text{stilbene}) - \Delta E(\text{N-methyl-}\alpha\text{-phenylnitrone}) = 1.05 \text{ eV}$), although the theory does reflect its strong acidifying action ($E_{NO} < E_N: E_{NO} < E_{CH}$).

^{*)}One does not observe an exchange reaction with unsubstituted azomethine under the following conditions: a) 0.6N $\text{CH}_3\text{OK} + \text{CH}_3\text{OD}$, 160°, 3hrs; b) 0.3N $t\text{-C}_4\text{H}_9\text{OK} + \text{C}_4\text{H}_9\text{OD}$, 70°, 2hrs; c) 0.3N $\text{CH}_3\text{OK} + \text{CH}_3\text{OD} + \text{DMSO-D}_6(1:8)$, 75°, 2hrs. The compound decomposes at higher temperatures.

Table 3.

The Difference in the Total Energy of Carbanion and Neutral Molecule Calculated by the CNDO/2 Method.

Compound ¹⁾	E, eV	Compound	E, eV
	24.160 * 24.244 **		24.683
	25.302 * 25.931 **		24.692
	25.210		25.763

¹⁾ The star *) points out the deprotonation center.

The latter disagreement can be ascribed both to the inadequacy of the CNDO/2 method and to the fact that the calculations do not include the substantial dependence of the course of the kinetic CH-acidity observed with heteroaromatic compounds on the effect of specific solvation of the substrate by molecules of a polar solvent /14,21/.

To elucidate the nature of the stage mechanism in the exchange process, we determined the kinetic isotopic effect of the reaction for diphenylnitrone- α (D,T). The values of the rate constants k_D and k_T measured at 50° in the solution 0.6N of $CH_3OK + CH_3OH$ are $1.1 \cdot 10^{-4} \text{ sec}^{-1}$ and $1.0 \cdot 10^{-4} \text{ sec}^{-1}$, respectively. The low magnitude of the kinetic isotopic effect ($k_D/k_T = 1.1$) may be considered as an evidence for the cleavage of hydrogen bonds in the carbanion transition state of the reaction being determined by the rate of the methine hydrogen atom exchange process (the "internal return" mechanism /22/). An analogous situation occurs in the isotopic exchange of substituted stilbenes /1/ and similar compounds /23/.

EXPERIMENTAL

All the compounds studied were prepared by the standard procedure /24/. The method of studying the exchange reactions

was described elsewhere /25/. The deuterium content was measured using the low voltage mass spectrometry. When determining the deuterium content in the N-methyl group of N-methyl- α -phenylnitrones, a correction was introduced to account for the fast exchange rate of the α -methine hydrogen atom of methine. The tritium activity was measured with a scintillation method.

R E F E R E N C E S

1. N.N.Zatsepina, I.F.Tupitsyn, and A.I.Belyashova, *Organic Reactivity*, 12, 207 (1975).
2. T.Kubota, H.M.Miyazaki, and Y.Mori, *Rev.Polarogr.*, 14, 313(1967).
3. K.Koyano and H.Suzuki, *Bull.Chem.Soc., Japan*, 42, 3306(1969)
4. K.Koyano and H.Suzuki, *Tetrah.Lett.*, 1968, 1859.
5. K.Tabei and E.Saiton, *Bull.Chem.Soc.Japan*, 42, 1444 (1969).
6. N.E.Alexandron and A.G.Varvoglis, *Org.Magn.Reson.*, 3, 293 (1971).
7. P.Grammaticakis and H.Textier, *Bull.Soc.Chim.Fr.*, 1971, 1323.
8. E.A.Medjantseva, I.M.Andreeva, and V.I.Minkin, *Zh.Org.Khim.*, 8, 146(1972).
9. V.I.Minkin, E.A.Medjantseva, I.M.Andreeva, and G.B.Gorshkova, *Zh.Org.Khim.*, 9, 148(1973).
10. V.I.Minkin, E.A.Medjantseva, I.M.Andreeva, and V.S.Yureva, *Zh.Org.Khim.*, 10, 2597(1973).
11. V.Baliah and V.Chandrasekharan, *Indian J.Chem.*, 8, 1096 (1970).
12. V.A.Bren, E.A.Medjantseva, and V.I.Minkin, *Reakts.Sposobn. Organ.Soedin.*, 5, 988(1968).
13. V.A.Bren, E.A.Medjantseva, I.M.Andreeva, and V.I.Minkin, *Zh.Org.Khim.*, 9, 767(1973).
14. N.N.Zatsepina and I.F.Tupitsyn, *Khim.Geterotsikl.Soedin.*, No 12, 1587(1974).
15. I.F.Tupitsyn, N.N.Zatsepina, Yu.M.Kapustin, and A.V.Kirova, *Reakts.Sposobn.Organ.Soedin.*, 5, 613(1968).

16. I.F.Tupitsyn, N.N.Zatsepina, A.V.Kirova, Yu.L.Kaminsky, and A.G.Ivanenko, *Reakts.Sposobn.Organ.Soedin.*, 10, 143 (1973).
17. N.N.Zatsepina, A.V.Kirova, and I.F.Tupitsyn, *Reakts.Sposobn.Organ.Soedin.*, 5, 70 (1968); 9, 195 (1972).
18. N.N.Zatsepina, I.F.Tupitsyn, A.V.Kirova, and A.I.Belyashova, *Reakts.Sposobn.Organ.Soedin.*, 8, 787 (1971).
19. N.N.Zatsepina, I.F.Tupitsyn, and A.I.Belyashova, *Organic Reactivity*, 11, 431 (1974).
20. R.A.Abramovitch, G.M.Singer, and A.R.Vinutha, *Chem.Comm.*, 1967, 55.
21. I.F.Tupitsyn, N.N.Zatsepina, A.V.Kirova, and Yu.M.Kapustin, *Reakts.Sposobn.Organ.Soedin.*, 5, 806 (1968).
22. D.J.Cram, *Fundamentals of Carbanion Chemistry*, Academic Press, New.York, London, 1965.
23. H.M.Walborsky and L.M.Turner, *J.Amer.Chem.Soc.*, 94, 2273 (1972).
24. O.H.Wheeler, P.H.Gore, *J.Amer.Chem.Soc.*, 78, 3363 (1956).

INFRARED STUDY OF ELECTRONIC INTERACTIONS IN SATURATED HETEROCYCLES

I.F.Tupitsyn, N.N.Zatsepina, N.S.Kolodina, and A.I.Relyashova

State Institute of Applied Chemistry, Leningrad.

Received June 25, 1975



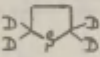
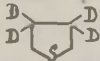

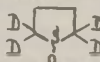

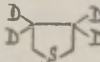

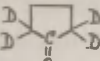

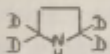
The effect of heteroatomic grouping incorporated in the ring on the band intensity of CH-stretching modes of methylene groups (Δ_{CH}) in a series of three- and five-membered saturated heterocycles is of the same type as that observed for their linear analogues and correlates with the σ° values. The fraction of the s-character of the carbon bonding orbital in the CH-bonds appearing as a result of cyclisation only weakly depends on the nature of the heteroatom and yields an approximately constant contribution to the measured value of Δ_{CH} .




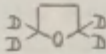

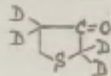
In recent years a number of papers have appeared where the integrated band intensities of the C-H stretching modes were used to elucidate the peculiarities of the mechanism of electronic effects of polar substituents and heteroatomic grouping in aliphatic /1-3/, alkyl-aromatic /4-8/ and aromatic /9,10/ compounds. The present work extends such a study to three- and five- membered alicyclic compounds.

IR spectra of mainly cycloalkanes and their heteroanalogues have been described (see e.g./11-12/). However, in most cases only the frequencies of the vibrations were studied leaving band intensities not measured. A detailed normal coordinate analysis carried out for cyclopentane /16/, tetrahydrofuran /17/ and some small rings/18/ showed the stretching CH- vibrations to be highly specific not only in frequency but in the band shape as well. This gives grounds to conclude that the variations in the CH-band intensity (Δ_{CH}) are determined primarily by the features in the electronic structure of the molecules of interest. Having in mind that the he-

heteroatomic grouping incorporated in a five-membered ring affects differently the band intensity of CH-vibrations of the methylene groups occupying α - and β -positions in the cycle, we obtained IR spectra of normal and α, α' - and β, β' -deuterio-substituted molecules, thus separating the part of the band intensity due to the CH_2 groups at the α - and β -positions of the ring (Table 1). In alicyclics the absorption bands of stretching modes in the region $2800\text{--}3000\text{ cm}^{-1}$ overlap strongly. Therefore in our study of the dependence of the quantity Δ_{CH} on characteristics of the electronic effects we used the total intensity of several bands rather than the intensity of individual bands. When comparing the band intensity of CH-vibrations per one methylene group in cycloalkanes which do not contain heteroatoms, a feature which attracts attention is a noticeable decrease of Δ_{CH} in cyclopropane and spiropentane compared with the values obtained for the methylene groups in the cyclopentane and cyclohexane molecules. As seen from Table 2, the band intensity of the CH-vibrations in cyclopentane and cyclohexane is close to the mean value of the intensity per one methylene group of the hexane aliphatic chain. The band intensity in three-membered rings lies in between the values of Δ_{CH} in saturated and unsaturated compounds. The continuous transition from the spectra of one class of compounds to another becomes particularly pronounced when the band intensity of stretching vibrations of the methylene group is compared with the s-character of the carbon hybrid orbital. The linear relationship exhibited by Fig. 1 confirms that the main structural factor determining the variation of the band intensity in cycloalkanes which do not contain a heteroatom is the hybridization state of the carbon atom which varies from sp^2 to sp^3 with increasing number of methylene groups in the ring. Combined with the other available data [19,20,24], this means that five- and six-membered rings which are low-stressed systems are closer to being analogs of saturated hydrocarbons than smaller rings whose spectral characteristics reveal a certain

Table 1. Frequencies and Band Intensities of Stretching
CH Vibrations in Five-membered Heterocycles

No	Compound	ν , cm^{-1}	$(\Delta_{\text{CH}}^{\text{sum}})^{1/2}$	$(\Delta_{\text{CH}}^{\alpha})^{1/2}$	$(\Delta_{\text{CH}}^{\beta})^{1/2}$
1	2	3	4	5	6
1		2963 2929 2873	54	54	54
2		2974 2950 2937 2903 2867	47	52 ²⁾	46 ²⁾
3		2950 2905 2867	-	-	40
4		2965 2938 2875	-	46	-
5		2955 2910 2865	36	37 ²⁾	-
6		2955 2905 2873	-	-	35
7		2972 2947 2880	24	-	30 ²⁾
8		2965 2885	22	17 ³⁾	-
9		2972 2950 2890	37	29 ²⁾	-
10		2972 2950 2890	-	-	44
11		2970 2880 2880	54	57 ²⁾	-
12		2967 2885	-	-	52

1	2	3	4	5	6
13		2984 2955 2928 2885	55	-	36 ²⁾
14		2984 2955 2928 2885	63	-	-
15		2983 29335 2870	50	52	-
16		2975 2955 2920 2880	-	-	47
17		2975 2940 2915 2875	25	20 ²⁾	20 ²⁾
18		2875 2940 2918 2875	-	17 ³⁾	-

¹⁾ Calculated per one methylene group. ²⁾ Derived from difference between the band intensities for the "light" and the corresponding deuterated compound. ³⁾ Reduced to 100% concentration of deuterium atoms in the methylene group.

similarity with unsaturated hydrocarbons. A similar conclusion can be drawn from the measurements of Δ_{CH} in the series cyclohexane-methylcyclohexane-methylcyclopentane-methylcyclobutane /21/; in a similar way a change in ring size affects the frequencies and force constants of the CH-bond /18/, the spin-spin interaction constants $J(\text{C}^{13}\text{-H})$ /25/ and the rate of proton abstraction from the methylene groups of cycloalkanes and related compounds as revealed in base-catalyzed deuterium exchange.

As seen from Tables 1 and 2, in heterocyclic compounds the band intensity in the region of the stretching CH-modes

depends strongly on the nature of the heteroatom.

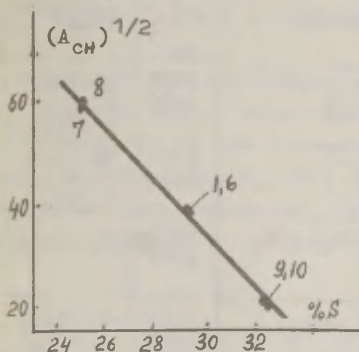


Fig.1. Plot of Δ_{CH} vs. percentage of s-character of the carbon atom hybrid orbital.

The numbering is as in Table 2.

In order to describe quantitatively the variation of Δ_{CH} of the methylene group at the α -, and β -position of a five-membered ring, we have made an assumption on the possibility of using the additive sum of the σ values of substituents in the corresponding molecule of disubstituted methane appearing as the cycle breaks by the bond farthest from the reaction center to roughly characterize the electronic effect of the heteroatoms next to the indicating CH_2 group^{*)}. Since the parameters of the relationship obtained for five-membered rings (Fig.2)

$$(\Delta_{CH}^{sum})^{1/2} = 42.5 - 37.9 \sum \sigma_p \quad (r=0.966, n=13) \quad (1)$$









are close to those in the equations established earlier for mono- and disubstituted methanes [1]:

$$(\Delta_{CH}^{sum})_{CH_3X}^{1/2} = 38.0 - 35.6 \sigma_p \quad (2)$$

$$(\Delta_{CH}^{sum})_{CH_2XY, CH_3X}^{1/2} = 35.2 - 31.7 \sum \sigma_p \quad (3)$$

^{*)}For methylene groups at the α - and β -positions of the heterocyclic ring such analogues are the molecules $CH_3X-CH_2-CH_2CH_3$ and $CH_3XCH_2-CH_2^*-CH_3$, respectively (X is the heteroatom or heteroatomic group).

Table 2. Frequencies and Band Intensities of CH Stretching Vibration in Infrared Spectra of Three-Membered Rings.

No	Compound	$\nu_{\text{cm}^{-1}}$	$(A_{\text{CH}})^{1/2}$	No	Compound	$\nu_{\text{cm}^{-1}}$	$(A_{\text{CH}})^{1/2}$
1		3090 3010	24.2(as) 29.5 (s) 38.0(sum)	6		3078 3009	21.7(as) 29.6 (s) 37.0(sum)
2		3082 3000	8.0(as) 20.6 (s) 22.4(sum)	7		2930 2875	50.0(as) 30.6 (s) 58.5(sum)
3		3095 3002	9.6(as) 8.1 (s) 12.3(sum)	8	$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	2930 2862	60 (sum)
4		3070 3002	24.0(as) 25.0 (s) 33.0(sum)	9	$\text{CH}_2=\text{CH}_2$	3095 2980	16.5(as) 12.5 (s) 20.5(sum)
5		3078 3005	27.0(as) 34.4 (s) 43.0(sum)	10		3092 3075 3040	20.4(sum)

¹⁾ Calculated per one methylene group.

variations in the band intensity in both series of compounds should be determined by similar factors. Hence it follows that the role of the ring as a structural element in molecules of five-membered saturated heterocycles is not essential in the variation of A_{CH} .

As seen from Fig.2, the electronic effect of substituents on the magnitude of A_{CH} in three-membered rings can be described in a similar way^{*)}:

$$(A_{\text{CH}}^{\text{sum}})^{1/2} = 25.0 - 33.4 \sum \sigma_p^{\circ} \quad (r=0.986, n=4) \quad (4)$$

^{*)} It should however be noted that the band intensity of asymmetric CH vibrations in thierane (No 2 in Table 2) is much lower than expected from eq.(6). The experimental value of A_{CH} agrees with the latter only if σ° value is used in place of the σ_p° value for the CH_2S group. The data available are insufficient to conclude whether the observed decrease in intensity is indeed caused by a probable displacement of electronic density from the CH-bond to the valence d-orbitals on the sulfur atom.

$$(\Delta_{CH}^S)^{1/2} = 17.8 - 28 \sum \sigma_P^\circ \quad (r=0.971, n=5) \quad (5)$$

$$(\Delta_{CH}^{as})^{1/2} = 17.6 - 19.8 \sum \sigma_P^\circ \quad (r=0.986, n=4) \quad (6)$$

The fact that the slopes of relations (1) and (4) are close together may be considered as an evidence that changes in hybridization of the CH-bond carbon atom (caused by decreasing size of the ring) are only weakly dependent on the nature of the heteroatom and therefore, make approximately a constant contribution to the magnitude of Δ_{CH}^*

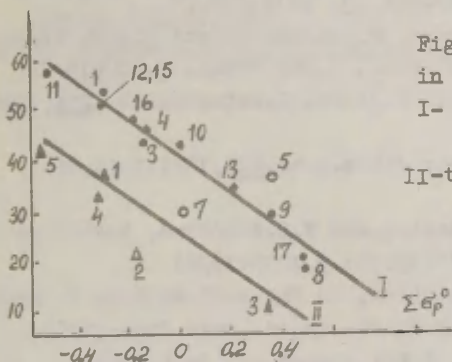


Fig.2. Variation of Δ_{CH} in saturated heterocycles.
I- five-membered rings (Table 1)
II- three-membered rings (Table 2)

EXPERIMENTAL

The compounds studied were prepared by standard procedures described in the literature, their physicochemical constants agree with the tabulated data.

The IR spectra were obtained on IKS-14 and IKS-16 spectrometers. The concentrations of compounds in the CCl_4 solution varied from 0.02 to 0.05 $M \cdot l^{-1}$. The integrated intensity was measured in practical units recommended by IUPAC.

REFERENCES

1. I.F.Tupitsyn, N.N.Zatsepina, N.S.Kolodina, and A.V.Kirova, Reakts.Sposobn.Organ.Soedin., 8, 765(1971); 11, 399(1974).
2. S.H.Pine and D.R.Steele, Spectrochim.Acta, 23A, 1509(1967).
3. S.Higuchi, E.Kuno, S.Tanaka, and H.Kamada, Spectrochim.Acta, 28A, 1335(1972).
4. I.F.Tupitsyn, N.N.Zatsepina, and N.S.Kolodina, Organic Reactivity, 11, 417(1974).
5. T.L.Brown, Chem.Rev., 58, 581(1958).
6. I.F.Tupitsyn, N.N.Zatsepina, N.S.Kolodina, and A.A.Kane, Reakts.Sposobn.Organ.Soedin., 5, 931(1968).
7. N.N.Zatsepina, A.V.Kirova, N.S.Kolodina, and I.F.Tupitsyn, Reakts.Sposobn.Organ.Soedin., 7, 667(1970); 9, 207(1972).
8. R.Joele, E.D.Schmid, and R.Mecke, Z.Naturforsch., 21A, 1906(1966).
9. E.D.Schmid et.al., Spectrochim.Acta, 22A, 1621, 1633, 1645, 1659(1966).
10. I.F.Tupitsyn, N.N.Zatsepina, and N.S.Kolodina, Reakts.Sposobn.Organ.Soedin., 6, 11(1969); 9, 1075(1972).
11. A.R.Katritzky and A.P.Ambler, in Physical Methods in Heterocyclic Chemistry, A.R.Katritzky, ed., Acad.Press, 1963.
12. B.Galabov and D.Simov, J.Mol.Struct., 11, 341(1972).
13. R.S.Lebedev and V.I.Yakimenko, Izv.Vyssh.Ucheb.Zaved.Fiz., 11, 114(1968).
14. N.D.Chizhikova, O.S. Anisimova, Yu.A.Pentin, and L.G.Yudin, Zh.Strukt. Khim., 10, 613(1969).
15. A.N.Bolotina, and L.M.Sverdlov, Zh.Prikl.Spektrosk., 7, 273(1967).
16. A.G.Finkel, N.U.Prokof'eva, and L.M.Sverdlov, Optika i spektroskopiya, 15, 195(1963).
17. L.A.Evseeva, A.G.Finkel, L.M. Sverdlov, and L.N.Pronina, Zh.Prikl.Spektrosk., 12, 301(1970).
18. E.R.Razumova and V.Y.Alexanyan, Izv.Akad.Nauk.SSSR, Ser. Khim. 1972, 1191.

19. R.N.Jones and C. Sandorfy, in Chemical Applications of Spectroscopy, Weissberger, ed., Vol. 9, Interscience, 1956.
20. S.A. Francis, J.Chem.Phys., 18, 861 (1950).
21. C.J. Boobyer and S. Weckherlin, Spectrochim. Acta, 23A, 322 (1967).
22. L.A. Evseeva and L.M. Sverdlov, Izv. Vysch. Ucheb. Zaved. Fiz., 11, 132 (1968).
23. L. Bardet, R. Granger, H. Orzaleci, and C. Sablayrolles, Trav. soc. Pharm. Montpellier, 25, 69 (1965).
24. K. Kovacevic and Z.B. Maksic, J. Org. Chem., 39, 539 (1974).
25. J.W. Emsley, J. Feeney, and L.H. Sutcliffe, High Resolution Nuclear Magnetic Resonance Spectroscopy, Vol. 2, Pergamon Press, Oxford, 1965.
26. A. Streitwieser and J. Richard, J. Amer. Chem. Soc., 91, 529 (1969).

ON THE MECHANISM OF TRANSFER OF ELECTRONIC EFFECTS
THROUGH A NITROGEN OR OXYGEN BRIDGE IN $[(CH_3)_n\bar{M}]_nX$
COMPOUNDS. IR AND PMR SPECTROSCOPIC PARAMETERS AND THE
KINETIC CH-ACIDITY OF METHYL GROUPS

N.N.Zatsepina, I.F.Tupitsyn, A.I.Belyashova, and N.S.Kolodina
State Institute of Applied Chemistry, Leningrad

Received June 25, 1975.

A correlation analysis of the measured intensities of stretching bands in infrared spectra, of the chemical proton shifts in PMR spectra and of the rate constants of base-catalyzed deuterium exchange gives grounds to conclude that the chemical behavior and spectroscopic properties of methyl groups in the specified systems are determined essentially by specific features of p, π - or p,d-conjugation in the \bar{M} -X fragment.

The electronic effects of various substituents on some spectroscopic and kinetic parameters of the methyl group (frequencies and integrated band intensities corresponding to stretching CH-vibrations /1,2/, proton chemical shifts/3-6/, the rate of base-catalyzed deuterium exchange /7,8/) in compounds CH_3X have been studied earlier. The present work reports on a similar study in $[(CH_3)_n\bar{M}]_nX$ systems where the methyl group is separated from the substituent by a nitrogen or oxygen bridge. This work is a part of a complex investigation into the main features of the mechanism of electronic interactions in organic compounds of various classes.

IR Spectra. The IR spectra of $[(CH_3)_2N]_nX$ compounds reveal several overlapping bands in the range $2760-3010\text{ cm}^{-1}$ corresponding to the stretching CH-vibrations of the methyl group /9-26/. To study the substituent electronic effects, we have chosen the lowest band ($2760-2810\text{ cm}^{-1}$) which is ascribed by some authors to the fundamental symmetric mode of the

CH bonds (ν_{CH}^S)/9-15/. However, the assignment of ν_{CH} cannot always be made unambiguously /16-26/. Therefore, besides the parameters of this band we have considered also those for sum of all the bands in the spectral region specified.

As seen from Table 1, variation of the electronic nature of the substituent affects only weakly the frequency of the stretching CH-vibration of the dimethylamine group ($\Delta\nu \approx 45\text{cm}^{-1}$) while changing substantially their intensity (A_{CH}). The plots on Fig.1 indicate the electronic effects on A_{CH}^S and A_{CH}^{sum} to be quantitatively of the same type. The general behavior of A_{CH}^S is close to that found by us earlier for a series of substituted methanes /1,2/:

$$(A_{CH}^S)^{1/2}_{CH_3X} = 24.7 - 26.4 \sigma_P^+ \quad (1)$$

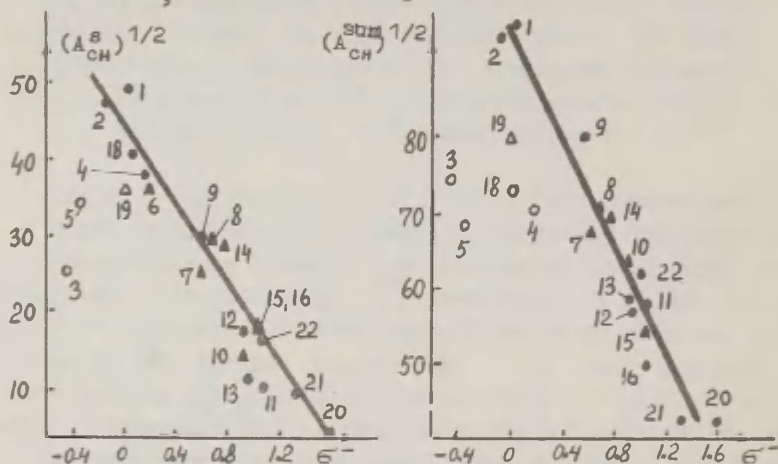


Fig.1. Correlation of A_{CH}^S and A_{CH}^{sum} of the dimethylamine-group with σ^- values.

The numbering is as in Table 1.

However, in contrast to the latter, the observed decrease of A_{CH} with increasing electron-withdrawing effect of the substituent X in the series of compounds studied correlates

Table 1. Some IR and PMR-Spectroscopic Parameters of Methyl Group in $[(CH_3)_2N]_nX$

No	Compound	ν_{CH} cm ⁻¹	$(\Delta_{CH})^{1/2}$	δ_{CH_3} p.p.m.	$\bar{\alpha}_N^{(3)}$	Method of pre- paration
1	2	3	4	5	6	7
1	$(CH_3)_2NH$	2785 2828 2865 2910 2942 2975	49 (95)	2.33 ⁴⁾ (CCl ₄)	(111.8)	-
2	$(CH_3)_3N$	2766 2816 2865 2905 2942 2973	47 (93)	2.18 ⁵⁾ (CCl ₄)	108.5	-
3	$(CH_3)_2N-N(CH_3)_2$	2772 2812 2840 2850 2950 2985	25 (74)	2.20 (CCl ₄) 2.23 (DMSO-D ₆)	-	-
4	$(CH_3)_2N-C_6H_5$	2805 2850 2880 2950 2990	37 (71)	2.90 ⁴⁾ (CCl ₄) 2.92 (DMSO-D ₆)	116	-
5	$(CH_3)_2N-NH_2$	2770 2813 2850 2890 2952 2980 3000	34 (68)	2.33 (CCl ₄)	-	-
6	$[(CH_3)_2N]_3P$	2780 2816 2854 2910	36 ⁷⁾	2.38 (DMSO-D ₆)	113.5	/40/
7	$[(CH_3)_2N]_3PS$	2795 2802 2840 2880 2920 2940 3000	24 (67)	2.63 2.73 (CCl ₄) 2.75 (DMSO-D ₆)	-	/41/

1	2	3	4	5	6	7
8	$[(CH_3)_2N]_3FO$	2800 2847 2880 2925 3000	30 (72)	$2.60^{(4)}$ (CCl ₄) 2.54 (DMSO-D ₆)	-	-
9	$(CH_3)_2NPOCl_2$	2810 2858 2900 2930 2945 3005	30 (80)	$2.7^{(4)}$ (CCl ₄)	116	/42/
10	$[(CH_3)_2N]_2CO$	2805 2825 2865 2880 2895 2935 2950	15 (64)	2.83 (CCl ₄) 2.63 (DMSO-D ₆)	117.5	/43/
11	$(CH_3)_2NCHO$	2760 2775 2795 2838 2850 2930 2940 2990	(58)	$2.85^{(4)}$ (CCl ₄) 2.93 (DMSO-D ₆)	117.5	-
12	$(CH_3)_2NCOCD_3$	2814 2875 2942 3031	17 (56)	-	-	-
13	$(CH_3)_2NCO C_6H_5$	2790 2803 2830 2855 2885 2930	10 (58)	2.98 (CCl ₄) 3.08 (DMSO-D ₆)	-	-
14	$[(CH_3)_2N]_2SO$	2780 2820 2858 2947 3000	29 (69)	2.54 (CCl ₄) 2.43 (DMSO-D ₆)	113.9 (115.3)	/38/
15	$[(CH_3)_2N]_2SO_2$	2810 2845 2880 2922 2963 3005 3020	17 (54)	$2.74^{(6)}$ (2.80) (CCl ₄)	117	/38/

1	2	3	4	5	6	7
16	$(\text{CH}_3)_2\text{NSO}_2\text{C}_6\text{H}_5$	2802 2842 2875 2910 2960	17 (49)	2.67 ⁶⁾ (CCl_4)	-	-
17	$(\text{CH}_3)_2\text{NSO}_2\text{Cl}$	2804 2828 2852 2885 2928 2945 2965 2980 3025	12 (47)	3.0 ⁶⁾ (CCl_4)	112.0	/44/
18	$(\text{CH}_3)_2\text{NSi}(\text{CH}_3)_3$	2790 2840 2865 2895 2960	40 (73) ⁹⁾	2.43 (CCl_4)	-	/45/
19	$[(\text{CH}_3)_2\text{N}]_4\text{Si}$	2795 2841 2870 2888 2925 2975	36 (80)	2.51 (CCl_4)	-	/46/
20	$(\text{CH}_3)_2\text{NNO}$	2795 2860 2910 2935 2958 3010	4 (43)	3.83 3.03 (CCl_4)	120 (123)	
21	$(\text{CH}_3)_2\text{NNO}_2$	2785 2795 2830 2855 2885 2935 2980	9 (42)	3.48 (CCl_4) 3.48 ($\text{DMSO}-\text{D}_6$)	-	/47/
22	$(\text{CH}_3)_2\text{N}-\text{N}=\text{NC}_6\text{H}_5$	2790 2840 2865 2900 2940	16 (62)	3.18 (CCl_4) 3.40 ($\text{DMSO}-\text{D}_6$)	-	/48/
23	$(\text{CH}_3)_2\text{N}-\text{SOC}_6\text{H}_5$	-	-	2.66 (CDCl_3)	-	-
24	$(\text{CH}_3)_2\text{NSOCH}_3$	-	-	2.69 (CDCl_3)	-	-

1	2	3	4	5	6	7
25	$(\text{CH}_3)_2\text{NSC}_6\text{H}_5$	-	-	2.69 ⁸⁾ (CDCl_3)	-	-
26	$(\text{CH}_3)_2\text{NSO}_2\text{CH}_3$	-	-	2.80 ⁸⁾ (CCl_4)	-	-
27	$(\text{CH}_3)_2\text{NCOC}_3\text{F}_7$	-	-	3.1 ⁴⁾ (CCl_4)	-	-

1) The values of A_{CH}^{S} ($A_{\text{CH}}^{\text{sum}}$ are given in brackets). 2) Relative to TMS, the solvent specified in brackets. 3) Taken from ref./29/. 4) Taken from ref./5/. 5) Taken from ref./35/. 6) Taken from ref./38/. 7) Measured in benzene. 8) Taken from ref./39/. 9) Calculations include data on the band intensity in the molecule $(\text{CD}_3)_2\text{NSi}(\text{CH}_3)_3$.

with the σ^- values^{*)}

$$(A_{\text{CH}}^{\text{S}})^{1/2} = 44.0 - 25.9 \sigma_{\text{P}}^- \quad (r=0.972, n=15) \quad (2)$$

A possible reason for these differences in the character of the relationships found consists in that in compounds of the type $[(\text{CH}_3)_2\text{N}]_n\text{X}$, besides the inductive effect and the effect of hyperconjugation which are responsible for the variation of A_{CH}^{S} in methanes /1,2/, a substantial role is played by the effect of p, π -conjugation between the nitrogen lone pair and the electron-withdrawing substituent X (for phosphorus-, sulfur- and silicon-containing compounds with vacant d-orbitals, interaction by the p_n-d_n -conjugation).

*) The σ^- values were taken from refs./27,28/. For a rough description of the electronic effect of complex substituents of the type $[(\text{CH}_3)_2\text{N}]_{n-1}\text{X}$ - whose nucleophilic constants are not known we used the σ^- values for the corresponding $\text{X}(\text{CH}_3)_{n-1}$ - groups (labelled with Δ in Fig.1-2).

tion mechanism is also possible^{*)}). This additional mechanism of resonance interaction promotes a more effective delocalization of electronic density from the dimethylamine - group and thus results in a more clearly pronounced character of the dependence of Δ_{CH}^S on the electronic nature of the substituent. The enhanced sensitivity of Δ_{CH}^S to the resonance influence of the substituent is confirmed by the existence of close similarity between the variations of band intensity and the mean valence angle for the nitrogen atom ($\bar{\alpha}_N$) which in this case may serve as a measure of the valence state of nitrogen (and, correspondingly, a measure of the conjugation capacity of its lone pair) /29,31/ from the essentially pyramidal for the simplest amines to the Planar (or close to planar) state in compounds where the nitrogen atom is coupled with a strong electron-withdrawing group (Fig.2).

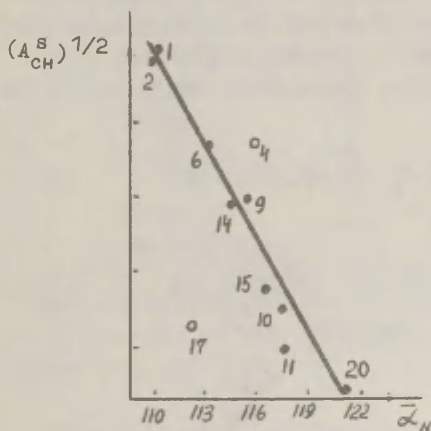


Fig.2. A plot of Δ_{CH}^S vs. $\bar{\alpha}_N$ for the dimethylamine group. The numbering is as in Table 1.

^{*)}We have not at our disposal σ^- values which should take into account the ability of the silicon atom to reveal electron - withdrawing properties /29-31/. The deviation of points 18 and 19 from a straight line in their correlation with the σ_P° values confirms a partial transfer of electronic density from the dimethylamine-group to the vacant d-orbitals of silicon.

As seen from Fig.1, the effect of strong electron-releasing substituents on the quantity Λ_{CH} is not described by relation (2). The decrease in intensity of the ν_{CH}^S band in the methyl derivatives of hydrazine as compared to the one expected from Eq.(2) is apparently associated with the electron repulsion of lone pairs in two neighboring nitrogen atoms. It is known that the dihedral angle between the orbitals of lone pairs in hydrazine and its derivatives is close to 90° /32/ which reduces strongly the possibility of conjugation between two fragments of molecules of such kind.

As seen from Table 2 listing the measured values of the frequency of the symmetric mode and the intensity corresponding to this for the methyl group in $(CH_3O)_nX$ compounds ($\nu_{CH}^S = 2840 \pm 30 \text{ cm}^{-1}$ /33,34/), the electronic effect on the quantities ν_{CH}^S and Λ_{CH}^S in oxygen-containing compounds is generally similar to the one observed in dimethylamine-derivatives. However in this case correlation analysis of the data on intensity yields close correlation coefficients for both σ_p^- values (Fig.3)

$$(\Lambda_{CH}^S)^{1/2} = 30.0 - 21.5 \sigma_p^- \quad (r=0.977, n=6) \quad (3)$$

and the σ^+ values (Fig.3)

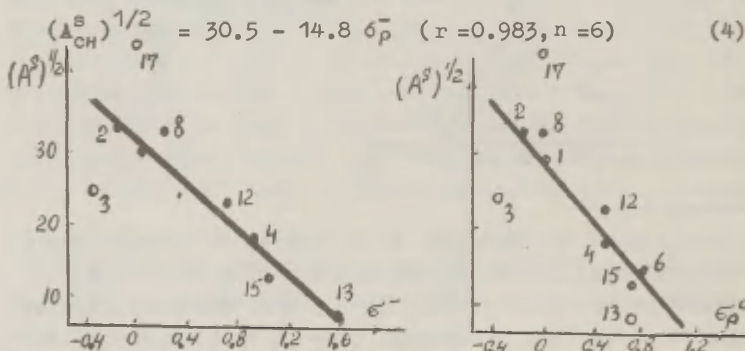


Fig.3. Correlation of Λ_{CH}^S of the methoxy-group with the σ^- and σ^+ values. The numbering is as in Table 2.

Table 2. Some IR and PMR Spectroscopic Parameters of the Methyl Group in $(\text{CH}_3\text{O})_n\text{X}$ Compound

No	Compound ¹⁾	$\nu_{\text{CH}}^{\text{S}}$	$(A_{\text{CH}}^{\text{S}})^{1/2}$	$\delta_{\text{CH}_3}^{2)}$ p.p.m.
1	CH_3OD	2834	30.0	3.38 ³⁾
2	CH_3OCH_3	2816	33.0	3.24 ³⁾
3	CH_3ONH_2	2810	24.0	-
4	$\text{CH}_3\text{OCOCH}_3$	2845	18.7	-
5	$\text{CH}_3\text{OCOC}_6\text{H}_5$	-	-	3.90
6	$\text{CH}_3\text{OCOCF}_3$	2860	15.0	3.96
7	CH_3OCHO	-	-	3.77
8	$\text{CH}_3\text{OC}_6\text{H}_5$	2835	33.0	3.73
9	$\text{CH}_3\text{OCH}_2\text{CN}$	-	-	3.47 ³⁾
10	$(\text{CH}_3\text{O})_2\text{CH}_2$	-	-	3.28 ³⁾
11	$(\text{CH}_3\text{O})_3\text{P}$	-	-	3.47 ³⁾
12	$(\text{CH}_3\text{O})_3\text{PO}$	2856	23.0	3.77
13	CH_3ONO	2825	7.8	4.06
14	CH_3ONO_2	-	-	4.15 ³⁾
15	$(\text{CH}_3\text{O})_2\text{SO}_2$	2841 2856	12.6	3.94 ³⁾
16	$(\text{CH}_3\text{O})_2\text{SO}$	-	-	3.58 ³⁾
17	$\text{CH}_3\text{OSi}(\text{CH}_3)_3$	2828	44.0	3.44

¹⁾Technique of preparation: No 3- /49/, No13- /50/, No 17 - /44/. ²⁾Measured in CCl_4 with TMS as internal standard.

³⁾Taken from ref./51/.

Although it would be difficult to make an unambiguous discrimination between these two sets of the δ values, both relationships indicate the quantity A_{CH}^{S} in the methoxy - group to be less sensitive to the electronic effect of the substituent $\text{X}^*)$ than A_{CH}^{S} in the dimethylamine - group.

^{*)}The reasons for the strong increase of intensity in compound No 17 are not clear.

The latter apparently is a consequence of a lower conjugation capacity of the oxygen lone pair compared with the nitrogen atom.

PMR Spectra. Although the proton chemical shift in methanes and similar compounds is usually assumed to be due primarily to the inductive effect of substituents /5/, in the case of the compounds under study here this conclusion appears to be inapplicable. Indeed, as seen from Fig.4, variations in the magnitude of δ_{CH_3} in dimethylamine-derivatives (Table 1) are described much better with nucleophilic than with the other sets of σ values *)

$$\delta_{CH_3} = 2.37 + 0.41 \sigma_p^- \quad (r=0.950, n=18) \quad (5)$$

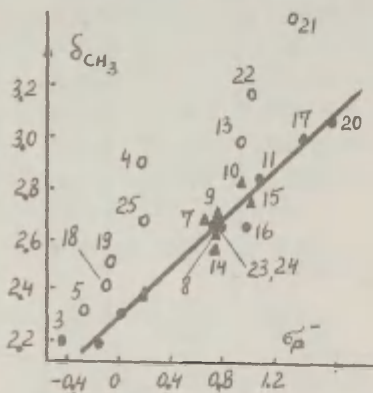


Fig.4. Correlation between δ_{CH_3} of the dimethylamine-group and the σ_p^- values. The numbering is as in Table 1.

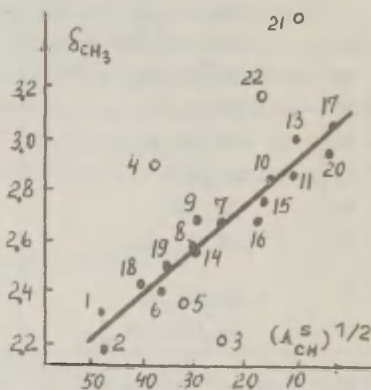


Fig.5. Plot of δ_{CH_3} vs. A_{CH}^S . The numbering is as in Table 1.

*) No correction for the magnetic anisotropy of bonds was introduced in the correlation analysis. This possibly accounts for the deviation of some points in Fig.4 and 6 from the correlation plot.

The latter fact, just as the existence in most cases of a linear relationship between the quantities δ_{CH_3} and Δ_{CH}^S (Fig.5), gives grounds to conclude that the magnitude of the chemical shift in these reaction series is primarily determined by resonance interaction of the substituent with the nitrogen bridge atom.

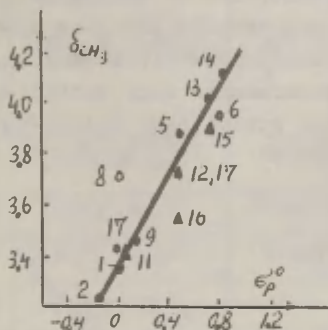


Fig.6. Correlation between δ_{CH_3} of the methoxy-group and the δ_p° values. The numbering is as in Table 2.

A fairly good correlation observed between the proton chemical shift in methoxy-derivatives and the δ_p° values (Fig.6).

$$\delta_{CH_3} = 3.38 + 0.84 \delta_p^\circ \quad (r=0.952, n=13) \quad (6)$$

indicates that in this reaction series the electronic effect of the substituent cannot be reduced to a purely inductive interaction. However, in contrast to the nitrogen-containing compounds considered above, the contribution of the -C-effect is eliminated which supports a poorer transfer of the conjugation effect via the oxygen atom compared with nitrogen.

Thus the electronic substituent effect on the quantity δ_{CH_3} in both groups of compounds studied turns out to be generally similar to the corresponding effects in the IR band intensity series.

Kinetic CH-acidity. There are only scarce data on the deuterium exchange kinetics for the series of compounds studied which were obtained for trimethyl amine /7,8/, dimethyl ether /7,8/ and their phenyl derivatives /36/, whose CH acidity could be measured only at elevated temperatures.

As follows from the results presented in Table 3, the range of kinetic CH-acidity measurements in dimethyl amine derivatives can be extended substantially by incorporating an electron-withdrawing substituents coupled directly with the nitrogen atom. Because of considerable differences in the exchange rate the kinetic measurements were carried out in media with different protolytic activities: $C_2H_5OK + C_2H_5OD$, $C_2H_5OK + C_2H_5OD + DMSO$, $KND_2 + ND_3$ *).

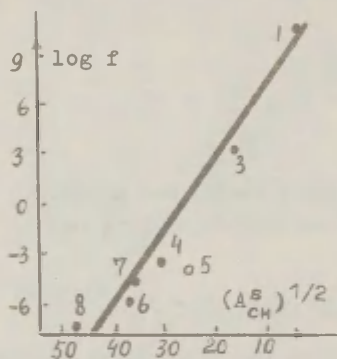


Fig. 7. A plot of $\log f$ vs. A_{CH}^S . The numbering is as in Table 3.

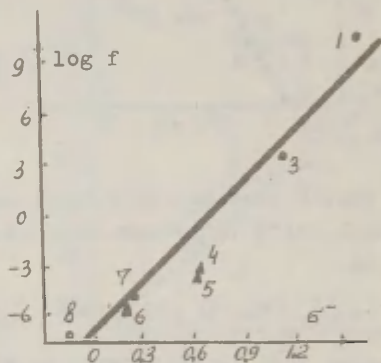


Fig. 8. Correlation between the deuterium exchange rate and the σ^- values. The numbering is as in Table 3.

*) Unfortunately, in some cases we failed to measure the deuterium exchange rate since the compounds decomposed in basic media before the kinetic region could be reached. This prevented us from searching the effect of the substituent X on the kinetic CH-acidity in oxygen-containing compounds.

Table 3. The kinetics of base-catalyzed deuterium exchange in $[(CH_3)_2N]_mX$ compounds.

No	Compound	Solvent ¹⁾	t, °C	k · 10 ⁵ , sec ⁻¹	-logk _{25°}	logf
1	$(CH_3)_2N-NO$	A(0.57N)	75 60	32 7.5	5.4	10.5
2	$CH_3N(C_6H_5)-NO$	A(0.57N)	75 60 45	31 6.6 0.4	5.4	10.5
3	$(CH_3)_2N-N=NC_6H_5$	A(0.57N) B	160 105 90 75	2.1 13 3.1 0.51	8.2	3.1
4	$[(CH_3)_2N]_3PO$	C(0.2N)	40 25	20 4.6	4.3	-3.3
5	$[(CH_3)_2N]_3P$	C(0.2N)	40	7.5	4.7	-3.7
6	$[(CH_3)_2N]_3P$	C(0.2N)	40	0.076	6.7	-5.7
7	$C_6H_5N(CH_3)_2$	C	-	-	-	-4.2 ²⁾
8	$(CH_3)_3N$	C	-	-	-	-7.0 ³⁾
9	$C_6H_5CH_3$ /8/	A(0.57N) B C(0.2N)	25	-	15.9 11.3	0

1) The notations used: A- $C_2H_5OK+C_2H_5OD$, B- $0.1N C_2H_5OK+C_2H_5OD+DMSO-D_6(1:5)$; C- KND_2+ND_3 .

2) Taken from ref. /36/.

3) Taken from ref. /8/.

To make possible their quantitative comparison, Table 3 lists relative values of the rate constants ($\log f = \Delta \log k$) calculated with respect to toluene as a reference. When presenting the kinetic data in such a way, the CH acidity of the compounds of interest may be considered on the same scale with the series of substituted methanes studied by us earlier /1,2/.

The existence of a linear relation between the quantities $\log f$ and A_{CH}^S (Fig. 7) indicates the variation of the kinetic

CH-acidity in the series of compounds studied to be determined by the same features of the mechanism of electronic interactions as revealed in the variation of A_{CH} and δ_{CH_3} . Accordingly, the deuterium exchange rate constants correlate with the σ^- values of substituent X (Fig.8):

$$\log f = -7.3 + 10.1 \sigma^- \quad (r=0.957, n=7) \quad (7)$$

Since the reaction constant in Eq. (7) is close to that obtained earlier /2/ for the series of substituted methanes ($\rho^- = 14.6$), an incorporation of a nitrogen bridge atom between the substituent and the reaction center appears only to affect slightly the intensity of transfer of electronic interactions from one subsystem of the molecule to the other.

Summing up, it may be stated that the chemical behavior and variation in the spectroscopic properties of the methyl group in $[(CH_3)_m M]_n X$ compounds is determined to a considerable extent by features in the ρ, π - or ρ, d -conjugation in the $M-X$ fragment.

EXPERIMENTAL

Most of the compounds studied were obtained by the standard procedures (the corresponding references are given in Tables 1 and 2)*); their physicochemical constants being in agreement with the published data.

The IR spectra were obtained on a IKS-16 grating spectrometer. The concentration of compounds in CCl_4 solutions ranged within $0.01-0.05 \text{ M} \cdot \text{l}^{-1}$. The values of A_{CH} listed in Tables 1 and 2 were calculated per one methyl group (in IUPAC practical units). When determining the band intensity corresponding to the symmetric CH-vibration of the methyl group

*) The authors are grateful to A.G.Ivanenko, Ju.L.Kaminski, and G.N.Sudakova for the preparation of some compounds, and to N.M.Anodina and V.F.Suslikov for the measurement of proton chemical shifts in the PMR spectra.

in dimethylamine derivatives, a graphic technique of band separation was employed.

The PMR spectra of CCl_4 or $\text{DMSO}-d_6$ solutions of the compounds studied (5-10 wt.%) were obtained with a INM-1000 instrument.

The technique used to study the exchange reactions has been described elsewhere /52/. The isotopic analysis was carried out by low-voltage mass spectrometry.

R E F E R E N C E S

1. I.F.Tupitsyn, N.N.Zatsepina, N.S.Kolodina, and A.V.Kirova, Organic Reactivity, (Reakts.Sposobn.Organ.Soedin.), 8, 765 (1971); 11, 399 (1974).
2. K.Tanabe, Spectrochim.Acta, 28A, 407 (1972).
3. S.Krishna and H.Venneth, J.Amer.Chem.Soc., 95, 6699 (1973).
4. F.Taddei, Boll.Sci.Fac.chim.industr.Bologna, 23, 273 (1963).
5. J.W.Emsley, J.Feeney, and L.H.Sutcliffe, High Resolution Nuclear Magnetic Resonance Spectroscopy, Vol.2, Pergamon Press, Oxford, 1965.
6. P.Lazzeretti and F.Taddei, Tetrah.Lett., 1969, 3025.
7. N.N.Zatsepina, I.F.Tupitsyn, A.V.Kirova, and A.I.Belyashova, Reakts.Sposobn.Organ.Soedin., 8, 787 (1971).
8. N.N.Zatsepina, I.F.Tupitsyn, and A.I.Belyashova, Organic Reactivity, 11, 431 (1974).
9. J.P.Perchard, M.T.Forel, and M.L.Josien, J.Chim.Phys. phys.-chim. Biol., 61, 652 (1964).
10. M.J.Buttler and D.C.MeKean, Spectrochim.Acta, 21, 465 (1965).
11. L.M.Sverdlov, M.A.Kovner, and E.P.Krainov, Vibrational Spectra of Polyatomic Molecules (Kolebatel'nye Spektry Mnogoatomnykh Molekul), Nauka, Moscow, USSR, 1970.
12. J.R.During and W.C.Harries, J.Chem.Phys., 55, 1735 (1971).
13. R.D.Hill and G.D.Meakins, J.Chem.Soc., 1958, 760.
14. K.Yokoboyashi, F.Watari, and K.Aida, Spectrochim.Acta, 24A, 1654 (1968).
15. G.Gamer and H.Wolf, Spectrochim.Acta, 29A, 129 (1973).

16. D.Köttgen, H.Stoll, A.Letzt, R.Pantzer, and J.Goubeau, *Z. anorg. allg.Chem.*, 385, 56 (1971).
17. F.Räuche, W.Pohl, B.Blach, and G.Goubeau, *Ber.Buns.Phys. Chem.*, 75, 67 (1971).
18. M.Goldstein, M.A.Russel, and H.A.Wollis, *Spectrochim.Acta*, 25A, 1275 (1969).
19. P.Pademacher and W.Lüttke, *Spectrochim.Acta*, 27A, 715 (1971).
20. J.W.Lewin, G.W.A.Milne, and T.Axenrod, *J.Chem.Phys.*, 53, 2505 (1970).
21. J.R.During, R.W.MacNamee, L.B.Knight, and W.C.Harris, *Inorg.Chem.* 12, 804 (1973).
22. K.V.Ramian and M.R.K.Mutry, *Current.Sci.*, 41, 673 (1972).
23. R.Paetzold and E.Rönsch, *Spectrochim.Acta*, 26A, 569 (1970).
24. H.Burger and W.Sawodny, *Spectrochim.Acta*, 23A, 2827, 2841 (1967).
25. C.Garigon-Lagrange, C.D.Loze, P.Bacelou, P.Combelas, and J.Dagaut, *J.Chim.Phys.phys.-chim.Biol.*, 67, 1936 (1970).
26. M.T.Foreil, S.Wolf, and M.Fouassier, *Spectrochim.Acta*, 28A, 1322 (1972).
27. Yu.A.Zhdanov and V.I.Minkin, *Korrelyatsionnyi Analiz v Organicheskoi Khimii* (Comparative Analysis in Organic Chemistry), Rostov-on-Don; Izd, Rostov Univ., 1966.
28. S.Ehrenson, R.T.C.Brownlee, and R.W.Taft, in *Progress in Physical Organic Chemistry*, Vol.10, New York, London, Sydney, Toronto, 1973.
29. L.V.Vilkov, L.S.Khaikin, J.J.Nazarenko, N.A.Tarasenko, and J.Hargittai, in *Sovremen.Problem.Phys.Khim.*, 7, 377 (1973).
30. R.Fessenden and J.S.Fessenden, *Chem.Rev.*, 61, 361 (1961).
31. A.Rauk, L.C.Allen, and K.Mislow, *Ang.Chem.Intern.Edit.*, 9, 400 (1970).
32. R.Hoffman, *Accounts Chem.Res.*, 4, 1 (1971).
33. M.T.Foreil, C.Garrigon-Lagrange, J.Semin, and M.L.Josien, *J.Chem.Phys.phys.-chim.Biol.*, 60, 1047 (1963).
34. J.Derouault, J.Calve, and M.T.Foreil, *Spectrochim.Acta*, 28A, 359 (1972).

35. W.O. George, J.L.S.Green, and M.J.Rix, *Spectrochim.Acta*, 26A, 2007(1970).
36. A.I.Shatenstein, *Kinetika i kataliz*, 8, 1056(1967).
37. F.A.Bovey, *NMR Data Tables for Organic Compounds*, Vol.1, Interscience, New York, London, Sydney, 1967.
38. F.Török, E.Paldi, S.Dobos, and G.Fogarasi, *Acta Chim.(Budapest)*, 63, 417(1970).
39. H.J.Jakobsen, A.Senning, and S.Kaae, *Acta Chem.Scand.*, 25, 23031(1971).
40. L.F.Fieser and M.Fieser, *Reagents for Organic Synthesis*, 1, 139 Wiley, New York-London-Sydney, 1968.
41. H.J.Vetter, H.Nöth, *Chem.Ber.*, 96, 1308(1963).
42. A.Michaelis, *Ann.Chem.*, 326, 129(1903).
43. H.Babad, *US* 3,681,457, 1969.
44. A.P.Kreshkov, L.V.Myshljaeva, and L.M.Hanoshvili, *Zh.Org.Khim.* 28, 2113(1958).
45. O.Glemser, S.P.V.Halasz, and U.Biermann, *Z.Naturforsch.*, 23B, 1381(1968).
46. H.H.Anderson, *J.Amer.Chem.Soc.*, 74, 1421(1952).
47. J.H.Robson, *J.Amer.Chem.Soc.*, 77, 107(1955).
48. F.Hauser, *Ann.*, 260, 227(1890).
49. W.Traube, H.Ohlendorf, and H.Zander, *Ber.*, 53, 1885(1920).
50. L.F.Fieser and M.Fieser, *Reagents for Organic Synthesis*, 2, 288, Wiley, New-York-London-Sydney, 1968.

IONIZATION CONSTANTS OF SOME 1-AMINO-3-
-ALKOXY-(ALKYLTHIO)-2-PROPANOLS

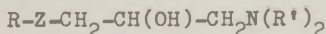
A.M.Kuliev, M.A.Allakhverdiev, E.Ya.Borisova,
V.M.Parzaliyev, and E.M.Cherkasova

Moscow M.V.Lomonosov Institute of Fine Chemical
Technology and
Institute of Chemistry of Additives, the Azerbaijan
Academy of Sciences, Baku, Azerbaijan SSR, USSR

Received July 17, 1975

The ionization constants of some 1-amino-
-3-alkoxy-(alkylthio)-2-propanols were determined
by potentiometric method in absolute ethanol
It has been established that the increase of
chain length in alkoxy- and alkylthio radicals
does not influence the base strength of amino-
alcohols. However the base strength of most ami-
no-alcohols gives a good correlation with σ^* -
constants of substituents of nitrogen atom.













As a part of the study the relationship between
the structure and properties of aminoalcohols,¹⁻³ the base
strength of some 1-amino-3-alkoxy-(alkylthio)-2-propanols
of the type



was measured.

The base strength of aminoalcohols is known to be
greatly influenced by two factors: substituents at nitrogen
atom⁴⁻⁵ and the length of carbon chain between oxygen and
nitrogen⁶. However, the effect of substituents in γ -position
on the base strength has not been studied yet.

Table
Base Strength of Aminoalcohols $R-Z-CH_2-CH(OH)-$
 $-CH_2N(R')_2$ in Ethanol Solution

N	R	Z	$-N(R')_2$	Number of points	ν^*	pK_a
I	CH_3	O		17	1.32	7.20 ± 0.02
II	C_2H_5	O		17	0.52	7.14 ± 0.02
III	C_3H_7	O		18	0.65	7.18 ± 0.02
IV	C_4H_9	O		18	0.75	7.15 ± 0.04
V	C_4H_9	O		18	1.2	7.28 ± 0.02
VI	C_4H_9	O		17	0.62	5.08 ± 0.02
VII	C_4H_9	O	$-N(C_2H_5)_2$	16	1.25	7.19 ± 0.02
VIII	C_4H_9	O	$-N(C_4H_9)_2$	18	1.82	7.03 ± 0.02
IX	C_4H_9	S		18	0.47	6.93 ± 0.02
X	C_5H_{11}	S		17	0.45	7.05 ± 0.02
XI	C_6H_{13}	S		16	0.40	7.08 ± 0.02
XII	C_7H_{15}	S		18	0.60	7.02 ± 0.02
XIII	C_4H_9	S		18	0.40	7.13 ± 0.02
XIV	C_4H_9	S		18	0.46	4.92 ± 0.02
XV	C_4H_9	S	$-N(C_2H_5)_2$	18	0.35	7.14 ± 0.02
XVI	C_4H_9	S	$-N(C_4H_9)_2$	16	1.40	6.78 ± 0.02

ν^* is an average error of volume percentage

Experimental

The aminoalcohols were synthesized by the authors according to the procedure described earlier^{9-II}. The purity of aminoalcohols was controlled by thin-layer and gas-liquid chromatography and elemental analysis. The systematic errors in potentiometric titration did not exceed 1-2%.

The ionization constants were determined by potentiometric titration method using pH-meter of pH-340 type

Discussion

It can be seen from Table that the nature of alkoxy (I-IV) and alkylthio (IX-XII) radical in aminoalcohols does not influence the base strength. On the other hand, the base strength of oxygen-containing alcohols (IV) slightly differs from the base strength of corresponding sulfur-containing aminoalcohols (IX). However, as has been shown earlier⁷, the sulphides are less basic than the esters. This is probably due to the fact that the substituents in γ -position are sufficiently removed from the reaction center.

The data in the Table indicate that the base strength of aminoalcohols is greatly influenced by amino group of the molecule. The above data made it possible to consider $R-Z-CH_2-CH(OH)-CH_2$ -group as a constant substituent.

In such a case the compounds can be expected to follow the Taft equation

$$pK_a = pK_0 + \rho \sum \sigma^*$$

as the base strength of aminoalcohols (IV-VIII-IX, XIII-XVI) depends upon the inductive effect of substituents at nitrogen atom⁸.

By the least squares treatment of the data the correlation coefficient $r=0.986$, the standard deviation $s=0.18$ and the sensitivity constant to induction effect $\rho^*=2.59$.

The equation of straight-line is as follows:

$$pK_a = (6,70 \pm 0,21) + (-2,59 \pm 0,18) \sum \sigma^*$$

with glass and silver chloride electrode filled with saturated KCl solution in ethanol. The electrodes were calibrated based on 0.05 mol of potassium biphthalate (pH=4.00) and 0.05 mol of sodium tetraborate (pH=9.16).

The titration method and calculation of pK_a are described elsewhere^I.

References

1. S.V.Bogatkov, E.Ya.Scobeleva, and E.M.Chercasova, Zh.Obtsch. Khim., 36, 134 (1966)
2. S.V.Bogatkov, V.N.Romashov, N.I.Kholdyakov, and E.M.Cherkasova, Zh. Obtsch. Khim., 39, 266 (1969)
3. I.P.Murina, E.I.Klabunovskiy, E.Ya.Borisova, and E.M.Cherkasova, Izv.AN SSSR, Otd.Khim.Nauk, 1973, 1683
4. G.Douheret, and C.C.Pariand, J.Chem.Phys., 59, 1013 (1962)
5. E.F.Leffer, H.M.Spener, and A.Burger, J.Amer.Chem.Soc., 73, 2611 (1951)
6. G.Girauet, P.Ramf, C.r., 246, 1705 (1958)
7. E.M.Arnett, Sb. "Sovremennye Problemy Fizicheskoi Organicheskoi Khimii", "Mir", M., 262 (1967)
8. V.A.Palm, Usp.Khim., 30, 1069 (1961)
9. A.M.Kuliev, V.M.Farzaliev, Z.A.Alizade, and M.A.Allakhverdiev, Tezisy dokladov XII Nauchnoi Sessii po Khimii i Tekhnologii Organicheskikh Soedinenii Sery i Sernistykh Nefti Izd. "Zinathe", Riga, 24, (1971)
10. A.M.Kuliev, M.A.Allakhverdiev, V.M.Farzaliev, and Z.A.Alizade, Azerb.Khim.Zh., N3, 35 (1975)
11. A.M.Kuliev, M.A.Allakhverdiev, V.F.Farzaliev, Z.A.Alizade, and A.A.Bairamov, Azerb.Khim.Zh., N3, 32 (1974)

TERTIARY AMINES IN REACTIONS OF ISOCYANATES AND THEIR STERIC CHARACTERISTICS

S.V.Bogatkov, N.A.Belova, and S.S.Medved
All-Union Scientific Research Institute of
Synthetic Resins, Vladimir

Received August 25, 1975

It is shown that the dependence of the reaction rate of isocyanates with some nucleophiles on the structure of tertiary amines-catalysts is described by the modified Taft equation (1). On these grounds some conclusions are made about the transition state structure in this reaction. A new E_N values are calculated also.

It was shown recently¹ that the catalytic activity of tertiary amines (TA) in acyl-transfer reactions may be described by means of modified Taft equation (1)

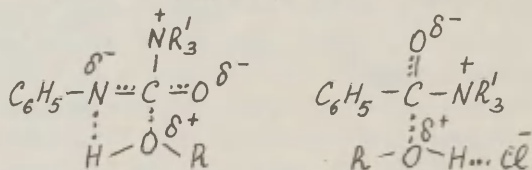
$$\lg k_{\text{cat.}} = \lg k_{\text{cat.}}^0 + \rho^* \sum \sigma^* + \delta E_N \quad (1)$$

in which the E_N constants equal to Taft's E_S constants for isosteric $R_1R_2R_3C$ are used as steric characteristics of amines $R_1R_2R_3N^+$. As it was shown in Refs. 3,4 for the alcoholysis of benzoyl chloride this equation allows the quantitative consideration of the influence of reagents structure and reaction conditions on the reaction rate. It was of interest to use this approach to the isocyanate reactions which are close in some aspects to acyl chloride reactions. These processes are of great importance in connection with the development of polyurethanes production.

The practical consideration stimulated numerous papers⁵⁻⁹ concerning the reaction kinetics of isocyanates (phenylisocyanate as a rule) with nucleophiles in the presence of TA. Nevertheless, no structure dependences observed were described quantitatively up to date. One exception is the reaction between phenylisocyanate and butanol

in toluene which was studied by Burkus⁶ and treated mathematically in paper¹. The equation used (I in Table 2) allowed to calculate for TA a number of new E_H values (see Table 3). In its turn this allowed to consider quantitatively some other reaction series which were studied in Refs.7-9. The unified experimental data are listed in Table 1 and the results of statistical treatments in Table 2.




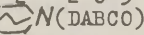
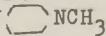
One can see from Table 2 that Eq.(1) is valid for the majority of cases with the exception of the series (IV) which has a low correlation coefficient probably due to the experimental errors. The ρ^* and δ values for the reaction of phenylisocyanates with alcohols in presence of TA (series I-III) are essentially less than those obtained for the analogous reactions of benzoyl chloride ($\rho^* \approx -2$, $\delta \approx 0,9^4$). This is believed to be because of peculiarities of the transition state structure which has (for isocyanates) more charge delocalization owing to one more heteroatom participation and less steric crowding. The latter seems to be because of more planar structure and larger interval between benzene ring and the reaction center



On the other hand the variation of the solvent and structure of analogous nucleophiles (alcohols) does not change ρ^* and δ (series I-III). This fact as well as the analogous phenomenon found for the benzoyl chloride⁴ seemingly exhibits that the polar and steric characteristics of transition state are being held constant in these reactions. On the contrary, if butylmercaptane is used as substrate the reaction sensitivity to steric and especially inductive effects increases (series V). It is apparently connected with larger volume and higher polarizability of sulfur atom compared to oxygen.

Table 1

Rate Constants for Reactions of Phenylisocyanate with Nucleophiles in the Presence of TA

Amine	$k_{III} \cdot 10^2 \text{ l}^2/\text{mol}^2 \cdot \text{sec}$				$\sum \sigma^*$	$-E_N$
	$\text{C}_4\text{H}_9\text{OH}^9$ in cyclohexanol and dioxane (2:1), 31°	$\text{C}_4\text{H}_9\text{CHCH}_2\text{OH}^8$ in benzene, 23°	H_2O^8 in dioxane, 23°	$\text{C}_4\text{H}_9\text{SH}^7$ in toluene, 25°		
$(\text{C}_2\text{H}_5)_3\text{N}$	7.33	35	46.4	103	-0.30	3.8
$(\text{C}_3\text{H}_7)_3\text{N}$	-	-	-	19	-0.35	4.1
$(\text{C}_4\text{H}_9)_3\text{N}$	2.17	-	-	22	-0.39	4.5
CH_3N 	-	-	-	55	-0.14	3.0
$\text{C}_2\text{H}_5\text{N}$ 	-	-	-	65	-0.24	3.5
$\text{C}_2\text{H}_5\text{N}$ 	1.83	8.76	22.8	1.47	+0.57	3.5
$(\text{CH}_3)_2\text{NCH}_2\text{C}_6\text{H}_5$	-	-	-	37	+0.215	2.2
N  $\text{N}(\text{DABCO})$	40.0	152	81.3	217	+0.39 ^{x)}	1.3
CH_3N  NCH_3	-	28.4	22.2	2	+0.16 ^{xx)}	3.0 ^{xx)}

x) $\sum \sigma^*$ is calculated from the Hall¹² equation ($\text{pK}_a = 9.61 - 3.30 \sum \sigma^*$) and $\text{pK}_a = 8.6$; a statistical correction is included.

xx) $\sum \sigma^*$ is calculated as $\sum \sigma^*_{\text{NR}_2} \cdot 2 \cdot Z^*_{\text{CH}_2}$, where $\sigma^*_{\text{NR}_2} = 0.6$ and $Z^*_{\text{CH}_2} = 0.36$; E_N is taken equal to E_N for isosteric N-methylpiperidine and N-methylmorpholine.

T a b l e 2

Correlation Parameters of TA Catalytic Activity in Reactions between
Phenylisocyanate and Nucleophiles by Eg (1)



NN	Nucleophile	Conditions	Number of points	Parameters of equation					Re- fe- ren- ce
				$\lg k_0$	ρ^*	δ	r	s	
I ^{x)}	C ₄ H ₉ OH	Toluene, 39.69°	4	0.9±0.2	-0.94±0.03	0.49±0.04	0.999	0.024	6 ^{x)}
II	C ₄ H ₉ OH	Cyclohexane+ dioxane(2:1), 31°	4	0.69±0.28	-0.78±0.22	0.57±0.08	0.991	0.14	9
270 III	C ₄ H ₉ CHCH ₂ OH C ₂ H ₅	Benzene, 23°	4	0.61±0.51	-0.79±0.45	0.37±0.15	0.930	0.27	8
IV	H ₂ O	Dioxane, 23°	4	0.30±0.49	-0.40±0.44	0.22±0.15	0.84	0.26	8
V	C ₄ H ₉ SH	Toluene, 25°	5 ^{xx)}	1.57±0.25	-1.90±0.23	0.67±0.09	0.990	0.15	7
Va	C ₄ H ₉ SH	Toluene, 25°	8	1.61±0.36	-1.95±0.31	0.67±0.11	0.950	0.22	7





^{x)} This series is published in ref.1.

^{xx)} The data for (C₄H₉)₃N, (C₃H₇)₃N and (C₂H₅)₃N are excluded. They probably are characterized by significant experimental errors.

Table 3

 E_N Values for Tertiary Amines

1	2	3	4
NN	Amines	$E_N(\pm 0.1-0.2)$	References
1.	$(CH_3)_3N$	1.54	a
2.	$(CH_3)_2NC_2H_5$	2.1	2
3.	$(CH_3)_2NC_3H_7$	2.2	2
4.	$(CH_3)_2NC_3H_7-i$	2.9	2
5.	$(CH_3)_2NC_4H_9$	2.2	2
6.	$(CH_3)_2NC_4H_9-s$	3.1	2
7.	$(CH_3)_2NC_4H_9-t$	3.9	a
8.	$(CH_3)_2NCH_2C_4H_9-t$	2.6	a
9.	$(CH_3)_2NC_6H_{13}-n$	2.4	b
10.	$(CH_3)_2NCH_2CH=CH_2$	1.6	b
11.	$(CH_3)_2NC_6H_{11}-Cy$	3.0	10
12.	$(CH_3)_2NCH_2C_6H_5$	2.2	10
13.	$(CH_3)_2NCH_2CH_2C_6H_5$	2.3	1
14.	$(CH_3)_2N(CH_2)_3C_6H_5$	2.0	1
15.	$(CH_3)_2NCH_2CH(C_6H_5)_2$	2.1	1
16.	$(CH_3)_2NCH_2CH_2CH(C_6H_5)_2$	2.2	1
17.	$(CH_3)_2NCH_2C\equiv CR$	1.8	1, c
18.	$CH_3N(C_2H_5)_2$	3.0	2
19.	$CH_3N(C_4H_9-t)CH_2C_4H_9-t$	4.0	a
20.	$CH_3N(C_6H_{11}-Cy)_2$	6.5	d
21.	CH_3N 	3.0	1
22.	CH_3N 	3.0	d
23.	$(C_2H_5)_3N$	3.8	a
24.	$(C_2H_5)_2NCH_2C_6H_5$	4.1	1
25.	$(C_2H_5)_2NCH_2CH_2C_6H_5$	3.9	1
26.	$(C_2H_5)_2N(CH_2)_3C_6H_5$	3.9	1
27.	$(C_2H_5)_2NCH_2CH_2CH(C_6H_5)_2$	3.6	1
28.	$(C_2H_5)_2NC_6H_{11}-cy$	5.2	1
29.	$(C_2H_5)_2NCH_2C\equiv CR$	3.4	1, c

1	2	3	4
30.	C_2H_5N 	3.5	1
31.	C_2H_5N 	3.5	e
32.	$(C_3H_7)_3N$	4.1	2
33.	$(C_3H_7)_2NCH_2CH=CH_2$	3.9	b
34.	$(C_4H_9)_3N$	4.5	2
35.	$(C_6H_{13})_3N$	4.3	b
36.	$(C_8H_{17})_3N$	4.4	10
37.	$(CH_2=CHCH_2)_3N$	3.5	b
38.	$(C_6H_5CH_2)_3N$	4.15	10
<u>Diamines</u>			
39.	N  $N(DABCO)$	1.3	d
40.	$[(CH_3)_2NCH_2]_2CH_2$	3.6	d
41.	$(O$  $N)_2CH_2$	5.7	d
42.	$[(C_2H_5)_2N]_2CH_2$	7.5	d

(a) "Original" values assigned on the basis of the isostericity principle in ref.13 (see ref.2); (b) Calculated from data of Sorokin and Schode¹⁴ for the reaction between phenylglycidilic ester and amines in phenol (50°); the correlation equation is $\lg k = -1.14 - 0.33 \sum \sigma^* + 0.63 E_N$; (c) These values are supposedly independent of R owing to geometry of compounds; (d) Calculated from data of Burkus⁶ by using a correlation equation I (Table 2); (e) Taken equal to E_N for isosteric N-ethylmorpholine (N 30).

The correlation equations from Table 2 together with those listed in refs.1,2,10 allow to calculate a lot of E_N values for TA. One can see from Table 3 that amines with the same two substituents have rather close E_N values. For example, E_N values of $(CH_3)_2NR$ are only slightly dependent on R in many cases (NN 2-6,8, 9,11-17). It is of interest to emphasize also that the E_N value for DABCO (N 39) is very low. Therefore this amine has the great

steric accessibility and, hence, the high catalytic activity in acyl-transfer reactions^{5-9,11}.

The considerable number of derived E_N values (>40) now further allows to apply of Eq (1) for the description of nucleophilicity of TA.

References

1. S.V.Bogatkov, V.G.Zaslavsky, and L.M.Litvinenko, Doklady AN SSSR, 210, 97 (1973).
2. S.V.Bogatkov, A.F.Popov, and L.M.Litvinenko, Reakts. sposobn. organ. soedin., 6, 1011 (1969).
3. Z.P.Golovina, S.V.Bogatkov, and E.M.Cherkasova, Zh. Org. Khim. (USSR), 11, 22 (1975).
4. Z.P.Golovina, S.V.Bogatkov, and E.M.Cherkasova, Org. Reactivity (Engl. Ed.), 11, 644 (1975).
5. A.Farkas, and G.Mills, in "Advances in Catalysis and Related Subjects" v.XIII, N.Y.-L., 1962.
6. J.Burkus, J. Org. Chem., 26, 779 (1961).
7. E. Dyer, J.F. Glenn, and E.G. Lendrat, J. Org. Chem., 26, 2919 (1961).
8. A.Farkas, and K.G.Flynn, J. Amer. Chem. Soc., 82, 642 (1960).
9. A.E.Oberth, and R.S.Bruenner, J. Phys. Chem., 72, 845 (1968).
10. L.M.Litvinenko, A.F.Popov, and Zh. P. Gelbina, Doklady AN SSSR, 203, 343 (1972).
11. A.I.Kirichenko, Don Thesis, Donetsk, 1969.
12. H.K.Hall, J. Amer. Chem. Soc., 79, 5441 (1957).
13. "Spravochnik Khimika", vd.3, Izd. "Khimiya" M.-L., 1965.
14. M.F.Sorokin, and L.G.Schode, Zh. Org. Khim. (USSR), 4, 666 (1968).

KINETICS OF NUCLEOPHILIC ADDITION OF ALIPHATIC
AMINES TO THE ACTIVATED ETHYLENIC BOND

G.J.Dienys, L.J.J.Kunskaitė, A.K.Vaitkevičius,
A.V.Klimavičius

Chemistry Department, Vilnius State University,
Vilnius, Lithuanian S.S.R.

Received August 25, 1975

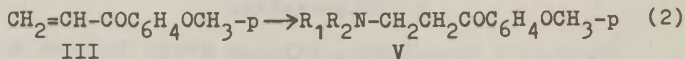
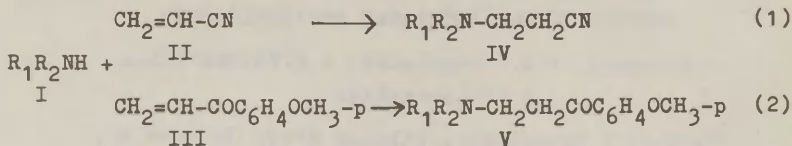
The rates of nucleophilic addition of 21 aliphatic amines to acrylonitrile in water solution and to p-methoxyphenylvinylketone in water-ethanol (9:1 by weight) at 25° were determined. The modified Taft equation with inductive (σ^*) and steric (E_N) parameters was used to correlate the rate constants. Both primary and secondary amines fitted the same correlation fairly well.

Kinetics of nucleophilic addition to the activated ethylenic bond is poorly investigated to compare with nucleophilic substitution and reactions of the carbonyl group. But in the latest 10 - 15 years the number of kinetic works increased notably making possible systematization and correlative analysis of rate constants.

A. short survey of publications on kinetics of nucleophilic addition of aliphatic amines to the activated ethylenic bond is presented below. At first the addition of some aliphatic amines to acrylonitrile was examined¹. Reports on kinetics of addition of aliphatic amines to phenylvinylketone²,³, acrylates⁴, unsaturated sulphones⁵ and sulphonamides⁶ appeared later. Extensive kinetic investigations of nucleophilic addition of morpholine and piperidine⁷ and of amino acid anions⁸ to the series of compounds containing activated ethylenic bonds were carried out by Rappoport, Friedman and others. Some kinetic data on addition of aliphatic amines to acrylonitrile was reported in our previous publication⁹.

We present now the rate constants of nucleophilic addition of 21 primary and secondary aliphatic amines to acrylo-

nitrile and p-methoxyphenylvinylketone:



Experimental

Reagents. 2-Hydroxydiethylamine was prepared by ethylation of N-(2-hydroxyethyl)-toluene-p-sulphonamide. N-Methyl-2-cyanoethylamine was prepared by cyanoethylation of methylamine. Both were purified by twicfold distillation through a Vigreux column, b.p. 166.5°/750 mm and 72.0°/8 mm, correspondingly. Liquid aliphatic amines and acrylonitrile were purified by the methods described in the literature¹⁰ followed by twofold distillation through a fractionating column of 15 t.p. efficiency. p-Methoxyphenylvinylketone was prepared as described in the literature¹¹, vacuum distilled and three times recrystallized from pentane, m.p. 20-21°.

Kinetic measurements. A. Kinetics of the reaction (1) in water at 25.00 ± 0.02° was followed conductimetrically. Conductance of the reaction mixture decreases with the course of reaction since pK_a of product IV is by 3 to 4 units lower than pK_a of corresponding amine I. From the experimental values of conductance (20-30 values up to 40-60% completion of reaction), using calibration curve, the dependance of product concentration on time, x = f(t), was obtained. The analytical expression of this dependance was found by the computer "Minsk-22" in the form:¹²

$$x = \sum_{i=0}^5 A_i t^i,$$

where A_i - coefficients, found by the least squares method. The values of reaction rate, (dx/dt)_{t=t_i}, were found for the sequence of 35-50 time moments t_i and the some number of rate constant values was calculated from the equations:

$$k_1 = \frac{dx/dt}{(a-x-y)(b-x)} ;$$

$$y = -K_b/2 + \sqrt{K_b^2/4 + K_b(a-x)} , \quad (3)$$

where a and b - initial concentrations of I and II; y - concentration of $R_1R_2NH_2^+$ ions.

The rate constant for a certain kinetic run was found as an arithmetic mean of all k_1 .

B. Kinetics of the reaction (2) in water-ethanol mixture (9:1 by weight) at $25.0 \pm 0.1^\circ$ was followed spectrophotometrically in thermostated cell of spectrophotometer SF-4A. Since the reaction (2) is notably reversible, 50 - 4000-fold excess of amine I was used. The pseudo-first-order rate constant was found by a graphical method and then divided by the concentration of amine $(a-y)^*$ to give the second-order rate constant for a given kinetic run.

From 5 to 12 runs for every amine I were carried out, using different initial concentrations of the reactants. The rate constant for every reaction (1) or (2) was found as an arithmetic mean of all runs.

Results and discussion

Quantitative evaluation of structural effects on nucleophilic reactivity of aliphatic amines presents considerable difficulties. Steric factor plays an important role in reactions of aliphatic amines, but steric effects of groups joined to nitrogen are not additive. Therefore it is impossible to use the Taft equation with steric parameters E_s (or E_s°).

The modified Taft equation was proposed in order to correlate nucleophilic reactivity of aliphatic amines with inductive and steric effects of substituents in amine molecules¹⁵. Isosteric parameters E_N (E_N°) were used in it instead

*) y was found from the equation (3) using the basicity constant of amine in water solution.

Table 1.

Rate constants ($\text{l} \cdot \text{mol}^{-1} \text{sec}^{-1}$) of the Reaction of Aliphatic Amines with Acrylonitrile and p-Methoxyphenylvinylketone at 25°.

No.	Amine	Reactant, solvent	AN ^{a)} , water $k \cdot 10^3$	VK ^{a)} , 10% ethanol k	$\Sigma \sigma^+ 13$	$-E_N 13$
1	Methylamine		$9.3 \pm 0.1^a)$	2.6 ± 0.1	0.98	0.07
2	Ethylamine		7.7 ± 0.1	2.3 ± 0.1	0.88	0.36
3	n-Propylamine		8.9 ± 0.1	-	0.86	0.37
4	Isopropylamine		2.80 ± 0.04	0.92 ± 0.02	0.72	0.93
5	n-Butylamine		10.10 ± 0.05	3.95 ± 0.15	0.85	0.40
6	Isobutylamine		9.27 ± 0.04	2.5 ± 0.1	0.86	0.35
7	sec-Butylamine		2.78 ± 0.02	-	0.77	1.10
8	t-Butylamine		-	0.080 ± 0.004	0.68	1.74
9	Cyclohexylamine		4.39 ± 0.03	1.41 ± 0.04	0.83	0.98
10	Allylamine		4.84 ± 0.03	1.49 ± 0.04	$1.14^c)$	$0.20^c)$
11	Dimethylamine		659 ± 10	-	0.49	0.47
12	Diethylamine		92.4 ± 0.5	18.3 ± 0.3	0.29	1.98
13	Dipropylamine		88.9 ± 0.5	22.3 ± 0.3	0.26	2.11
14	Diisopropylamine		0.190 ± 0.003	0.046 ± 0.003	0.11	$3.90^c)$
15	Di-n-butylamine		76.4 ± 0.8	46 ± 0.2	0.23	$2.04^c)$
16	Pyrrolidine		660 ± 10	-	0.23	0.51
17	Piperidine		508 ± 5	70 ± 2	0.31	0.79
18	Hexamethyleneimine		862 ± 10	97 ± 3	0.29	1.10
19	Morpholine		50.2 ± 0.4	7.9 ± 0.3	1.16	$0.79^d)$
20	N-Methyl-2-cyano-ethylamine		14.5 ± 0.6	-	0.99	$1.3^e)$
21	2-Hydroxydiethylamine		25.0 ± 0.8	-	$0.60^f)$	$1.1^e)$

a) abbreviations: AN - acrylonitrile, VK - p-methoxyphenylvinylketone; b) standard deviations are given; c) from 14; d) E_N for morpholine was assumed to be the same as for piperidine; e) calculated in the present work from the equation (4) with accuracy ± 0.3 ; f) from Ref.2.

of $E_{\text{N}} (E_{\text{N}}^{\circ})$:

$$\lg k = \lg k_0 + g^* \cdot \sum \sigma^* + \delta E_{\text{N}} \quad (4)$$

where $\sum \sigma^*$ is the sum of inductive effects of alkyl-groups and hydrogen atoms joined to the nitrogen atom. Parameter $E_{\text{N}} (E_{\text{N}}^{\circ})$ of amine R_1R_2N- equals to the steric parameter $E_{\text{N}} (E_{\text{N}}^{\circ})$ of radical $R_1R_2\dot{C}H-$.

Table 2.

Results of correlations

Set	Reactant ^{a)}	Solvent, temp.	n ^{b)}	$\lg k_0$	$-g^*$	δ	R	s
1 ^{c)}	AN	water, 25°	18	1.37 ± 0.57	3.07 ± 0.59	1.01 ± 0.21	0.809	0.61
2 ^{d)}	AN	- " -	16	2.20 ± 0.37	4.29 ± 0.43	1.24 ± 0.13	0.942	0.37
3 ^{e)}	AN	- " -	15	1.67 ± 0.29	3.94 ± 0.31	0.84 ± 0.14	0.963	0.26
4	VK	10% ethanol, 25°	15	3.87 ± 0.80	3.13 ± 0.78	1.09 ± 0.27	0.762	0.66
5 ^{d)}	VK	- " -	13	5.10 ± 0.58	4.77 ± 0.63	1.41 ± 0.19	0.924	0.42
6 ^{f)}	VK	- " -	11	3.58 ± 0.33	3.40 ± 0.33	0.63 ± 0.13	0.973	0.18
7 ^{g)}	VS	ethanol, 25°	11	2.07 ± 0.28	4.01 ± 0.29	1.36 ± 0.12	0.979	0.18

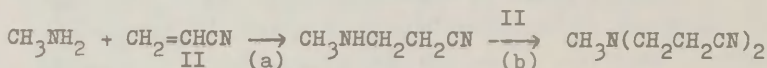
a) Abbreviations: AN - acrylonitrile, VK - p-methoxyphenylvinylketone, VS - p-tolylvinylsulphone; b) number of points in the set; c) amines No. 20,21 (Table 1) were excluded because E_{N} values were not known for them; d) the sets 2 and 5 were obtained by the exclusion of allylamine and morpholine from the sets 1 and 4, correspondingly; e) the set 3 was obtained by the exclusion of diisopropylamine from the set 2; f) the set 6 was obtained by excluding t-butylamine and diisopropylamine from the set 5; g) rate constants from the literature⁵, except morpholine.

In the previous paper⁹ we used the equation (4) for correlation of rate constants of reactions (1). We report here more rate constants for reactions (1) and a new set of reactions (2) (see Table 1). The rate constants included into Table 1 and data from literature⁵ on the nucleophilic addition of aliphatic amines to p-tolylvinylsulphone were correlated by the equation (4) (see Table 2). Correlation was better in all sets when parameter E_N was used in comparing with E_N^O . For this reason results obtained with parameter E_N^O were not included into Table 2.

As can be seen from Table 2, no correlation was obtained for the full sets of reactions (1) and (2) (sets 1 and 4). The results were improved by the exclusion of the most deviating rate constants (for allylamine, t-butylamine, diisopropylamine and morpholine). In so obtained smaller sets (3,6,7) both primary and secondary amines fitted the same correlation fairly well. The lack of correlation in the sets 1 and 4 may partly be due to the inaccuracy of rate constants and of E_N values for the amines of very low activity (t-butylamine, diisopropylamine). In the case of allylamine and morpholine deviations from correlation may be due to additional electronic effects.

Using the equation (4) from the set 3 we calculated E_N values for N-methyl-2-cyanoethylamine and 2-hydroxydiethylamine (Table 1), not reported previously.

In the reaction:



the rate constant of the step (b) is 1.6 times greater in comparing with the step (a) (No. 1, 20 in Table 1). Higher rate of the second step was reported earlier in the similar reactions of ammonia with acrylonitrile¹⁶ and of hydroxylamine with p-diphenylvinylketone¹¹.

References

1. Y.Ocata, M.Okano, Y.Furuya, and I.Tabushi, J.Amer.Chem., Soc., 78, 5426 (1956); M.Wronski and J.Bogdanski, Zeczyty Nauk Univ. Lodz, 14, 153 (1963).
2. I.Šestakova, V.Horak, and P.Zuman, Coll.Czech.Chem.Comm., 31, 3889 (1966).
3. P.Čarsky, P.Zuman, and V.Horak, Coll.Czech.Chem.Comm., 29, 3044 (1964).
4. K.Sammi and N.Ogata, Bull.Chem.Soc.Japan, 40, 1727 (1967); N.Ogata and T.Asahara, Bull.Chem.Soc.Japan, 39, 1486 (1966); K.L.Mallik and M.N.Das, Z.Phys.Chem. (BDR), 25, 205 (1960).
5. S.T.McDowell and C.J.M.Stirling, J.Chem.Soc.(B), 1967, 343. 348, 351.
6. W.G.Davies, E.W.Hardisty, T.P.Nevell, and R.H.Peters, J; Chem.Soc.(B), 1970, 1004.
7. H.Shenhav, Z.Rappoport, and S.Patai, J.Chem.Soc., (B), 1970, 469.
8. M.Friedman, J.S.Wall, J.Amer.Chem.Soc., 86, 3735 (1964); J.Org.Chem., 31, 2888 (1966).
9. G.J.Dienys, L.J.J.Kunskaitė, and A.K.Vaitkevicius, Dokl. Akad.Nauk SSSR, 216, 1300 (1974).
10. D.D.Perrin, W.L.Armarego, and D.R.Perrin, Purification of Laboratory Chemicals, Pergamon Press, 1966.
11. G.J.Dienys, J.J.Steponavičius, and R.V.Jasinskaite, Z.Org.Chim., 6, 2503 (1970).
12. G.Dienys, P.Adoméas, and A.Aleknavičiute, S.Jonaitis, Kinetika i kataliz, 15, 205 (1974).
13. Handbook of chemistry (in russian), vol.3, 1964, p.954.
14. L.M.Litvinenko, A.F.Popov, and Z.P.Gelbina, Dokl.Akad. Nauk SSSR, 205, 343 (1972).
15. S.V.Bogatkov, A.F.Popov, and L.M.Litvinenko, Reakts. sposobn.organ.soedin., 6, 1011 (1969).
16. H.Onoue and K.Minami, Kogyo Kagaku Zasshi (Industr.Chem.Soc.), 71, 1505 (1968).

РЕАКЦИОННАЯ СПОСОБНОСТЬ ОРГАНИЧЕСКИХ СОЕДИНЕНИЙ.
Том XII. Выпуск I(43). Ноябрь 1975. На англий-
ском языке. Тартуский государственный универси-
тет. ЭССР, г. Тарту, ул. Кликсоли, 18. Ответст-
венный редактор В.Палм. Сдано в печать 13/II 75.
Бумага печатная. Печ. листов 17,75 (условных
16,51). Учетно-изд. листов 13,32. Тираж 400 экз.
Типография ТТУ, ЭССР, г. Тарту, ул. Пялсони, 14.
Зак. № 1378. Цена 1 руб. 33 коп.

Rbl. 1.33