



TARTU STATE UNIVERSITY

# ORGANIC REACTIVITY

English Edition  
of

Реакционная способность  
органических соединений

Vol. XVIII  
ISSUE 3(67)  
November 1981

TARTU

TARTU STATE UNIVERSITY

# ORGANIC REACTIVITY

English Edition

of

Реакционная способность  
органических соединений

Vol. XVIII

ISSUE 3(67)

November 1981



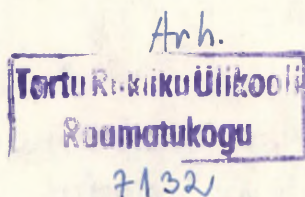
TARTU

The Editorial Board:

V. Palm, Editor-in-Chief

A. Talvik

I. Koppel



РЕАКЦИОННАЯ СПОСОБНОСТЬ ОРГАНИЧЕСКИХ СОЕДИНЕНИЙ.  
Том I/III. Вып. 3(67). Ноябрь 1981.  
На английском языке.  
Тартуский государственный университет.  
СССР, 202400, г.Тарту, ул. Пилекона, 18.  
Ответственный редактор В. Пальм.  
Подписано к печати 19.10.1982.  
Формат 60х84/16.  
Бумага писчая.  
Машинный. Ротакрифт.  
Условно-печатных листов 9,07.  
Учотно-издательских листов 7,79.  
Печатных листов 9,75.  
Тираж 400.  
Заказ № 1110.  
Цена I руб. 20 коп.  
Типографии ТГУ, СССР, 202400, г.Тарту, ул.Пилекона, 14.

KINETICS AND MECHANISM OF DIENE CONDENSATION OF HEXACHLORO-  
CYCLOPENTADIENE WITH CYCLIC DIENOPHILES

XLVI.  $\pi$ -Complexes of Hexachlorocyclopentadiene with N-(Alkenyl)Imides of Ortho-Phthalic Acid.

N.F. Musaeva, M.S. Salakhov, A.A. Gasanova, R.S. Salakhova,  
M.Ya. Salamova, and A.A. Bairamov

Institute of Chloro-organic Synthesis, Academy of Sciences  
of the Azerbaijan S.S.R., Sumgait

Received March 30, 1981

The method of PMR spectroscopy has been used to investigate charge-transfer complexes of hexachlorocyclopentadiene with N(alkenyl)imides of orthophthalic acid in cyclohexane at different temperatures. The thermodynamic parameters of complex formation were determined. Good correlations were found between the logarithms of formation constants of  $\pi$ -complexes and the rate constants of the systems studied.

The formation of complexes with charge transfer of  $\pi$ - $\pi$ -type and detection of them on the path of the reaction coordinate during the diene synthesis reactions have been reported earlier<sup>1-4</sup>. Recently we have found the formation of such complexes in the reactions of hexachlorocyclopentadiene (HCP) with N-arylimides of endo- and exo-bicyclo/2.2.1/heptene-5-dicarboxylic-2,3 acid in ethylacetate solution<sup>5,6</sup>.

It is the object of this paper to investigate the complex formation of HCP with N-(vinyl)-(I) and N-allylimides (II) of o-phthalic acid and to elucidate the relative thermodynamic stability of these complexes.

EXPERIMENTAL

N-alkenylimides (I, II) were synthesized by well-known methods<sup>7-8</sup> and purified by recrystallization to the constant melting point.

HCP and cyclohexane were used in freshly distilled



form.

The investigation of complexing was carried out on a "Tesla BS" 487 radiospectrometer, 80 mc, at different temperatures in cyclohexane solution with HMDS as an internal standard. The HCP concentration was varied from 1.5 to 12 mol/l with constant content of imides.

The complexing parameters such as the formation constant of  $\pi$ -complexes ( $K_m$ ) and chemical shifts of pure complexes ( $\Delta_m$ ) were determined by displacement of  $\beta$ -protons of N-alkenylimides (I,II) to the weak field:

$$\frac{m_D}{\Delta} = \frac{1}{K_m \cdot \Delta_m} \cdot \frac{1}{m_A} + \frac{1}{\Delta_m} \quad (1)$$

where  $m_D$  and  $m_A$  are the total concentrations of the donor and acceptor respectively;  $\Delta = (\delta_{\text{obs}} - \delta_{\text{init}})$  is the observed change of donor  $\beta$ -proton;  $\delta_{\text{obs}}$  and  $\delta_{\text{init}}$  are the chemical shifts of donor protons in a pure solvent and in the presence of acceptor;  $K_m$  is the formation constant of  $\pi$ -complex;  $\Delta_m$  is the difference of chemical shifts of protons in pure complex and in neutral solvent.

The thermodynamic parameters for complexing were derived from equations (2-4) at four temperatures.

$$\ln K_m = -\frac{\Delta H}{RT} + \text{const} \quad (2)$$

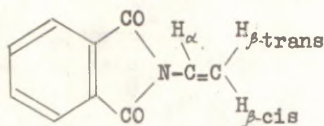
$$\Delta G = -RT \ln K_m \quad (3)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (4)$$

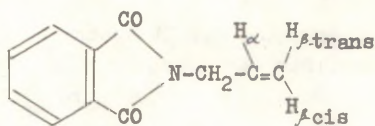
The least-squares method was used for the treatment of experimental data.

## RESULTS AND DISCUSSION

When determining complexing parameters  $K_m$  and  $\Delta_m$  we used the chemical shifts of  $H_{\beta \text{ trans}}$ -ethylenic protons of N-vinyl (I) and N-allyl-(II) imides of phthalic acid which were more remote from carboxylic groups.



I



II

The chemical shifts of these protons in a neutral solution of cyclohexane are 476 and 408 Hz for compounds (I) and (II) respectively. Upon the addition of HCP the signals of  $H_{\beta\text{trans}}$ -protons shifted to the weak field relative to the signals in neutral cyclohexane. Such shifts in signals of donor or acceptor molecules in different systems are ascribed to the formation of donor-acceptor complex<sup>10-13</sup>.

Similarly to works<sup>1-3</sup> which reported the studies of charge-transfer complexes (CTC) for a series of systems in diene synthesis with the 1:1 composition, compounds (I) and (II) can be assumed to form CTC with HCP of the same composition. The correctness of this assumption was confirmed by linearity of the dependence of  $\frac{m_D}{\Delta}$  on  $\frac{1}{m_A}$  (Fig.1).

The variation range of donor and acceptor concentrations determined from equation (1), complexing parameters, experimental temperature are given in Table 1.

Table 1  
Complexing Parameters for HCP with N-vinyl(I) and N-(allyl)-(II)-imides of o-Phthalic Acid in Cyclohexane.

$m_D'$ mol/kg	$m_A'$ mol/kg	t, °C	$K_m'$ kg/mol	$\Delta m'$ Hz	r	S	n
1	2	3	4	5	6	7	8
I 0.075	HCP 1.5-6.0	25	0.3141	34.39	0.9850	0.0036	4
		35	0.2764	31.11	0.9925	0.0032	4
		45	0.2217	28.15	0.9230	0.0145	4
		55	0.2079	24.12	0.9970	0.0033	4
		65	0.1827	19.83	0.9970	0.0033	4
II 0.200	HCP 4.0-12.0	25	0.1159	5.58	0.9981	0.0061	3
		35	0.0958	4.92	0.9995	0.0064	3
		45	0.0805	4.09	0.9995	0.0079	3
		55	0.0601	3.58	0.9997	0.0080	3

The data of Table 1 indicate that when passing from HCP+I to the HCP+II system one can observe a decrease in stability (by a factor of 2.7 to 3.5) and in the displacement of chemical shifts of pure complex protons (by a factor of 6.5 to 7.0), that pointed to a decrease in electron interaction between the addends<sup>1,4</sup>. Based on the Mulliken theory of charge transfer during  $\pi$ -complex formation<sup>15</sup> the results obtained suggest that N-vinylimide (I) has more  $\pi$ -donor ability than N-allylimide (II) of o-phthalic acid in the reaction with HCP.

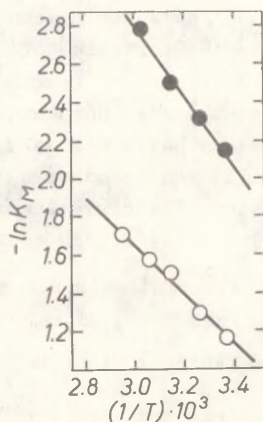
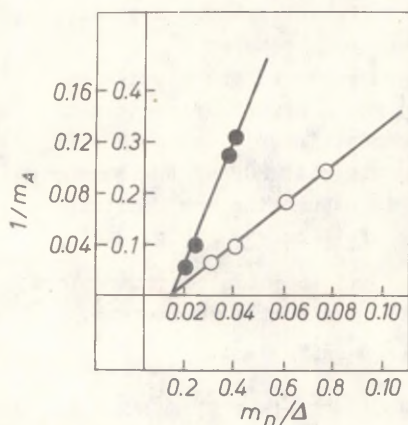


Fig. 1. Dependence of  $m_D/\Delta$  on  $1/m_A$  for complexes of HCP with N-(alkenyl)imides of ortho-phthalic acid in cyclohexane at 25°C: O-HCP+I; ●HCP+II.

Fig. 2. Dependence of  $\ln K_m$  on reciprocal temperature for complexes of HCP with imides (I) and (II): O-HCP+I; ●-HCP+II.

The thermodynamic parameters for HCP complex-formation with imides (I) and (II) were determined from temperature dependence (Fig. 2) according to equations (2-3). They are given in Table 2.

The values of thermodynamic parameters point to very weak donor-acceptor interactions in the complexes under



study and to an increase in this interaction force in passing from N-allylimide (II) to N-vinylimide (I) of o-phthalic acid that corresponds to their reactivities in the diene synthesis with HCP<sup>16,17</sup>.

Table 2

Thermodynamic Parameters for HCP Complex Formation with  
Imides (I) and (II) in Cyclohexane

Complex	t, °C	- ΔH, kcal/mole	r	S	-ΔS, e.u.	ΔG, kcal/mole
HCP-I	25	2.75±0.11	0.990	0.050	11.51	0.69
	35				11.47	0.79
	45				11.63	0.95
	55				11.49	1.02
	65				11.85	1.14
HCP-II	25	4.15 ± 0.21	0.990	0.050	18.21	1.28
	35				18.14	1.44
	45				18.04	1.59
	55				18.22	1.83

The decrease in the ΔH value (i.e. the more negative value) when introducing the methylene link is followed by a parallel decrease in the S and G values. The values of ΔH ranging from -2 to -4 kcal/mole indicate that the interaction between the components is weaker than that involving an ion bond.

As can be seen from the data in Table 1 the values of  $\kappa_m$  and  $\Delta_m$  are markedly dependent on the experimental temperature that corresponds to the literature data<sup>18</sup>. As  $\Delta_m$  characterizes the structure of intermediate complex, it follows that the complex structures undergo definite changes depending on the medium temperature. The plots of dependences  $\lg \Delta_m(I) - 1/T$  and  $\lg \Delta_m(II) - 1/T$  are linear with roughly equal slopes which can be expressed by the following empirical relationships:

$$\lg \Delta_m(I) = 0.59 \cdot 10^3 / T - 0.42 \quad r=0.978 \quad s=0.023 \quad (5)$$



$$(II) = 0.64 \cdot 10^3 / T - 1.41 \quad r=0.996 \quad s=0.009 \quad (6)$$

Satisfactory correlation relationships are found between different parameters of systems complexing under study (eqs 7-9). They can be used if necessary.

$$\lg K_m(II) = 1.39 \lg K_m(I) - 0.55 \quad r=0.953 \quad s=0.103 \quad (7)$$

$$\lg \Delta_m(II) = 0.65 \lg \Delta_m(I) - 1.23 \quad r=0.981 \quad s=0.020 \quad (8)$$

$$\Delta G(II) = 1.51 \Delta G(I) + 0.23 \quad r=0.971 \quad s=0.049 \quad (9)$$

Such relationships may help in predicting the  $\Delta G$ ,  $\lg K_m$ ,  $\lg \Delta_m$  values for complexes of one type based on the known values for the other complex when the determination of parameters for the former is complicated for some reasons. In view of difficulties that the obtaining the experimental values of these parameters presents and because of their great theoretical importance their prediction on the base of determined values of  $\Delta G$ ,  $\lg K_m$  and  $\lg \Delta_m$  is of particular significance.

Thus, the results obtained can be used for more comprehensive consideration of the mechanism of diene synthesis of HCP with N(alkenyl)imides of o-phthalic acid which will be considered in our next communication.

#### R E F E R E N C E S

1. L.J.Andrews, R.M.Keefer, J.Amer.Chem.Soc., 77, 6284(1955).
2. B.A.Arbusov, A.I.Konovalov, Izv.AN SSSR, 1959, 2130.
3. A.I.Konovalov, V.D.Kiselev, Zh.org.khim., 2, 142(1966).
4. D.Kiselev, J.G.Miller, J.Amer.Chem.Soc., 97, 4036(1975).
5. N.Musaeva, M.Salakhov, A.Bairamov, S.Suleimanov, Zh.org.khim.(in press).
6. N.Musaeva, M.Salakhov, S.Suleimanov, A.Bairamov, React.kinetics catal.lett.(in press).
7. I.Osipenko, I.Kulevskaya, G.Nikitenko, S.Mokhnach, I.Shingel, Izv.AN BSSR, ser.khim.nauk, No.3, 67(1977).
8. J.Newcomer, E.McBee, J.Amer.Chem.Soc., 71, 946(1949).
9. G.Briegleb, "Electron-Donator-Acceptor Komplexe" Sprin-

- ger Verlag, Berlin-Göttingen-Heidelberg, 1961, 227.
10. J.C.Schug, R.J.Martin, J.Phys.Chem., 66, 1554 (1962).
  11. M.W.Hanna, A.L.Ashbaugh, J.Phys.Chem., 63, 811 (1964).
  12. T.Eishun, T.Tsugikazu, S.Hideo, Makromolek.Chem., 151, 245 (1972).
  13. W.R.Carper, C.M.Buess, G.R.Hipp, J.Phys.Chem., 74, 4229 (1970).
  14. D.C.Farnum, E.R.Atkinson, W.C.Lothrop, J.Org.Chem., 26, 3204 (1961).
  15. R.S.Mulliken, J.Amer.Chem.Soc., 74, 811 (1952).
  16. M.Salakhov, N.Musaeva, O.Mamedova, R.Salakhova, T.Kopylova, Azerb.khim.zh. (in press).
  17. N.Musaeva, M.Salakhov, R.Salakhova, V.Umaeva, T.Kopylova, Organic Reactivity, 16, 398 (1979).
  18. B.Dodson, R.Foster, M.Foreman, J.Cordon, J.Chem.Soc.(B), 1283 (1971).

KINETICS AND MECHANISM OF DIENE CONDENSATION OF HEXA-  
CHLOROCYCLOPENTADIENE WITH CYCLIC DIENOPHILES  
XLVII. Structure-Reactivity Interrelation of N-(Alkenyl)  
Imides of Phthalic Acid in the Reaction with Hexachloro-  
cyclopentadiene

N.F.Musaeva, M.S.Salakhov, A.A.Gasanova, R.S.Salakhova, A.A.Bai-  
ramov, and O.M.Mamedova

Institute of Chloro-organic Synthesis, Academy of Sciences of  
the Azerbaijan S.S.R., Sumgait

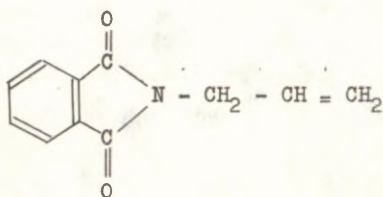
Received March 30, 1981

The kinetics of diene condensation of N-vinylimide of phthalic acid with hexachlorocyclopentadiene has been investigated and the reaction activation parameters have been estimated. A comparative analysis was carried out for kinetic parameters of the reaction studied with those for N-allylimides of phthalic acid. The chemical shifts of ethylenic protons in PMR spectra of the imides studied account for the great reactivity of N-vinylimide in the reaction.

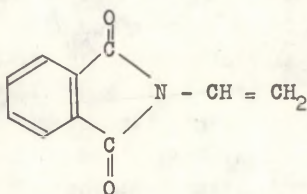
In one of our previous works<sup>1</sup> we have reported that N-allylimide of phthalic acid (I) is more reactive in the reaction of diene condensation with hexachlorocyclopentadiene (HCP) than N-allyl imides of cis-4-methyl-4-cyclohexane- and cyclohexane-1,2-dicarboxylic acid. This is so because the attraction of reaction center electrons has weakened due to the possibility of stronger absorption of electron deficiency of imide ring carbon atoms by a phenyl nucleus.

We have extended research into this area to compare the reactivities of imide (I) and N-vinylimide of phthalic acid (II) in this reaction and to elucidate the role of polar conjugation between the aromatic ring and the reaction center due to an overlap of unshared p- and  $\pi$ -electrons in dienophile (II).





I



II

With this aim in view we report here the results of kinetic studies concerning the interaction between N-alkenylimides (I)<sup>2</sup> and (II) and HCP.

## EXPERIMENTAL

Synthesis of N-vinylimide (II) of phthalic acid and its adduct with HCP viz. 1,4,5,6,7,7-hexachlorobicyclo/2.2.1/-hept-5-ene-2-phthalimide (IIa) and their characteristics are given in refs. 2,3.

The reaction rate was determined polarographically through the HCP consumption in the reaction mixture. Preliminary polarography of imide (II) and adduct (IIa) has shown that they are reduced at more negative potentials and so allow us to determine the reaction kinetics through HCP reduction waves.

To carry out the kinetic studies the HCP and N-vinylimide (II) were taken in molar ratio as 2:1; they were diluted with nitrobenzene up to the desired concentration (in this case the concentration of HCP in the mixture was 0.84 to

0.86 mole/l). The reaction was carried out in an ampule thermostated in an oil bath ( $\pm 0.1^\circ\text{C}$ ) equipped with a stirrer; sampling was done by syringe (0.2 to 0.5 ml). To stop the reaction the samples were immediately diluted with a background solution (0.1 N KCl solution in 75% acetone). The polarography conditions and procedure of kinetic measurements are similar to those of our previous works<sup>4,5</sup>.

The constants were estimated with an electronic digital computer "Elektronika" using the least-squares method.

The estimation of correctness for kinetic parameters was characterized by a value of standard deviation.

The PMR-spectra of imides (I) and (II) were obtained with a "Tesla" BS 487B radiospectrometer, 80 mc, at room temperature. All spectra were determined in the  $\text{CCl}_4$  solutions with HMDS as an internal standard. The confidence was  $\pm 0.02\text{mc}$ .

## RESULTS AND DISCUSSION

The fact that the diene condensation of N-vinylimide(II) with HCP obeys the reaction equation of the second order was confirmed by the known methods<sup>6,7</sup>. The first order with respect to HCP is shown by the linearity of semilogarithmic anamorphoses of kinetic straight lines, the line regression equations of which are:

$$\lg \frac{a-x}{a-2x} = 0.057 \cdot 10^{-2} + 5.49 \cdot 10^{-2} \tau \quad (1)$$

$$T = 120^\circ\text{C} \quad r=0.999 \quad s=0.001 \quad n \ 6$$

$$\lg \frac{a-x}{a-2x} = -0.019 \cdot 10^{-2} + 9.46 \cdot 10^{-2} \tau \quad (2)$$

$$T = 130^\circ\text{C}, \quad r=0.999 \quad s=0.001 \quad n \ 6$$

$$\lg \frac{a-x}{a-2x} = -0.954 \cdot 10^{-2} + 15.73 \cdot 10^{-2} \tau \quad (3)$$

$$T = 140^\circ\text{C} \quad r=0.999 \quad s=0.003 \quad n \ 6$$

$$\lg \frac{a-x}{a-2x} = -0.069 \cdot 10^{-2} + 26.39 \cdot 10^{-2} \tau \quad (4)$$

$$T = 150^\circ\text{C} \quad r=0.999 \quad s=0.008 \quad n \ 6$$

where  $a$  is the initial concentration of HCP, mole/l;

$x$  is the concentration of HCP consumed by the reaction, mole/l

$\tau$  is the time interval, sec.

Multiplying the right side of equations (1-4) by the parameter  $\frac{4.606}{\tau \cdot a}$  one obtains the second order rate constants for the corresponding temperatures. The mean values of these temperatures are given in Table 1. The kinetic and thermodynamic parameters of activation obtained from the Arrhenius equation within the temperature range of 110 - 150°C are presented in the same Table.

In order to carry out the comparative analysis of reactivities of N-alkenylimides (I) and (II) the Table contains kinetic data for (II) in the above reaction taken from ref.1.

As can be seen from Table 1  $k_{II}$  is twice as large as  $k_I$  at all temperatures.

The thermodynamic activation parameters of reaction are little affected in passing from compound (I) to compound (II) that points to the same type of mechanism of these reactions. Also, the uniformity of these mechanisms indicates linear dependence between the logarithms of rate constants ( $\lg k_I - \lg k_{II}$ ) with a slope of curve approximately equal to the unity at different temperatures:

$$\lg k_I = (1.03 \pm 0.008) \lg k_{II} - (0.16 \pm 0.03) \quad (5)$$

$$r=0.999 \quad s=0.006 \quad n=5$$

Considering that the carbonyl groups of the imide ring favour molecule polarization, the attraction of electrons from the reaction center can be expected to be stronger in case of N-vinylimide (II) than N-allylimide (I). Thus, the complexing properties of N-vinylimide (II) during the donor-acceptor interaction with electron-seeking HCP must be expected to be less defined than those of imide (I) and, hence, the reactivity of imide (II) should be greater than that of imide (I). However the greater activity of N-vinylimide (II) vs. N-allylimide (I) points to the reverse. Such an apparent contradiction can be explained assuming that the polarization of bonds is facilitated and the charge transfer to electron-seeking HCP takes place more readily in the case of N-allylimide (I) due to the complete conjugati-



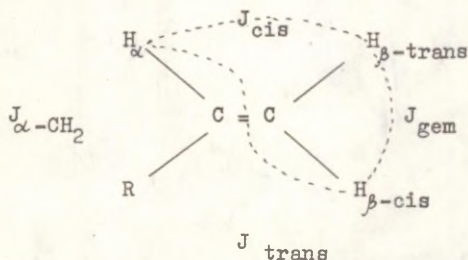
Table 1

The Comparison of Kinetic Data for Diene Condensation of N-alkyl-(I) and N-vinyl-(II)  
Imides of Phthalic Acid with HCP in Nitrobenzene at Different Temperatures

Cpd.	T, °C	$k_2 \cdot 10^6$ , l/mol · sec	lgA	Ea, kcal/mol	$\Delta H^\ddagger$ , kcal/mol	$-\Delta S^\ddagger$ , e.u.	$\Delta G^\ddagger$ , (403°K) kcal/mol	$\frac{k_{II}}{k_I}$
I	110	$8.69 \pm 0.38$	$4.94 \pm 0.18$	$17.56 \pm 0.35$	$16.76 \pm 0.34$	$38.49 \pm 0.85$		2.01
	120	$15.00 \pm 0.57$						1.97
	130	$25.56 \pm 0.51$	r 0.998		r 0.999		32.28	1.99
	140	$44.76 \pm 0.64$	S 0.014		S 0.065			1.91
	150	$76.93 \pm 0.98$	n 5		n 5			1.90
II	110	$17.52 \pm 0.41$	$4.91 \pm 0.14$	$16.98 \pm 0.26$	$16.17 \pm 0.25$	$38.62 \pm 0.65$		
	120	$29.62 \pm 0.89$						
	130	$50.90 \pm 0.39$	r 0.999		r 0.999		31.74	
	140	$85.51 \pm 1.34$	S 0.011		S 0.047			
	150	$143.79 \pm 3.44$	n 5		n 5			

on of  $\pi$ -bonds of the whole system of the N-vinylimide (II) molecule considering the unshared pairs of nitrogen p-electrons during the complex formation. This is confirmed by the values of complexing parameters in the systems studied that we have reported in the preceding communication<sup>3</sup>.

The PMR spectra give us a good idea of reactivities of these imides. Both imides have an ethylenic fragment differing in that the former has a phthalimide group (II) and the latter has a N-(methylene)phthalimide group (R) (I) in their structures. It is this character of the substituents that is responsible for intensification or weakening of the  $\pi$ -donor ability during the process of charge transfer from dienophile to diene.



In the PMR spectra of imides (I) and (II) (Fig. 1, 2) the signals of  $\beta$ -cis and  $\beta$ -trans protons of an ethylenic group appear as doublets, and those of  $\alpha$ -proton as a multiplet (Fig. 1) and a quartet (Fig. 2). They were ascribed to the corresponding protons in terms of well-known differences existing in the constants of a spin-spin splitting:  $J_{gem}$ ,  $J_{trans}$ ,  $J_{cis}$  (Table 2). The chemical shifts were defined as the average in terms of the corresponding peaks of doublets and quartets.

When comparing the chemical shifts of  $H_\alpha$ ,  $H_{\beta\text{ cis}}$  and  $H_{\beta\text{ trans}}$  - ethylenic protons of N-alkenylimides (I) and (II) one can observe the following.

The signals of  $H_\alpha$  and  $H_{\beta\text{ cis}}$  of N-vinylimide (II) as opposed to N-allylimide (I) are shifted to down fields by 76 and 64 Mz respectively that is evidently due to magnetic

anisotropy of carbonyl groups giving rise to a paramagnetic shift. As  $H_{\alpha trans}$  protons are removed from carbonyl groups their chemical shifts can be used to compare the overall electron density of imides (I) and (II) according to ref.8. The shift of the signal of the  $H_{\beta trans}$  proton of N-vinylimide (II) by 18 Hz to the upper field in comparison with that for N-alkimide I enables us to draw the conclusion that electron density is comparatively higher on the  $\beta$ -carbon atom of imide II.

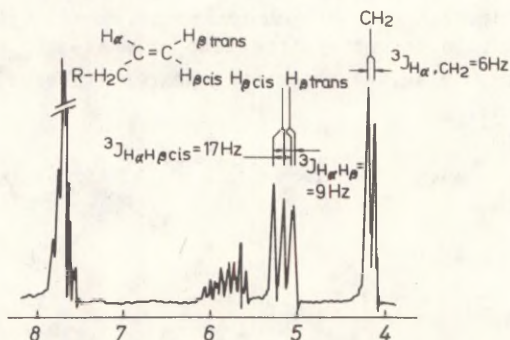


Fig.1. The PMR spectrum of N-allylimide of o-phthalic acid (I).

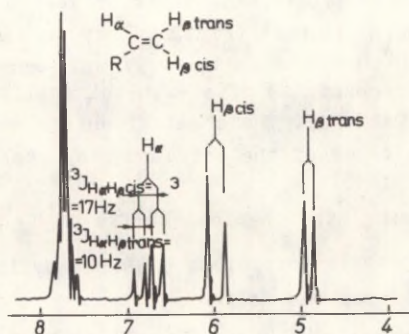


Fig.2. The PMR spectrum of N-vinylimide of o-phthalic acid (II).



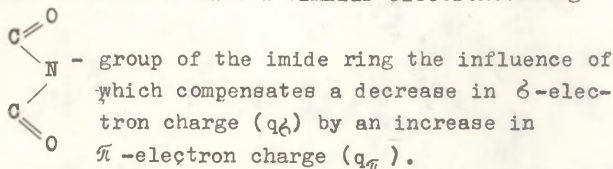
This fact could be explained as follows. The oxygen atom is known<sup>9</sup> to attract strongly  $\delta$ -electrons from surrounding carbon atoms and to manifest the donor ability of  $\pi$ -electrons toward the ethylenic  $\pi$ -bonds (i.e. the oxygen atom is  $\pi$ -donor- $\delta$ -acceptor).

Table 2

Chemical Shifts and Constants of Spin-Spin Splitting for N-Allyl(I)- and N-vinyl(II)-imides of o-Phthalic Acid

Cpd	Chemical shifts, $\delta$						Constants of Spin-Spin Splitting, Hz			
	$H_\alpha$		$H_{\beta\text{cis}}$		$H_{\beta\text{trans}}$		$J_{\text{gem}}$	$J_{\text{trans}}$	$J_{\text{cis}}$	$J_{\alpha\text{-CH}_2}$
	ppm	Hz	ppm	Hz	ppm	Hz				
I	5.80	464	5.15	412	5.10	408	0	17.0	9.0	6.0
II	6.75	540	5.95	390	4.87	390	0	17.0	10.0	-

In the compound studied we have a similar electronseeking fragment



Thus, according to refs.8,9 in the case of N-vinylimide (II), involving "direct conjugation", one observes a shift of the  $\beta$ -trans proton to the upper field in comparison with that of N-allylimide (I). The shift of the latter is due to the prevailing influence of  $\pi$ -donor ability of the imide ring undisturbed by incorporation of a  $-\text{CH}_2$ -link as with imide (I). This points to the overall electron density at the ethylenic bond of imide (II) (which plays the role of the reaction center during cycloaddition) and hence, to the greater reactivity of the latter in the reaction with HCP vs imide (I).

#### REFERENCES

1. N.Musaeva, M.Salakhov, R.Salakhova, V.Umaeva, T.Kopylova, Organic Reactivity, 16, 398(1979).
2. M.Salakhov, N.Musaeva, O.Mamedova, R.Salakhova, T.Kopylova,

DAN Azerb.SSR (in press).

3. N.Musaeva,M.Salakhov,A.Gasanova,R.Salakhova,M.Salamova,  
A.Bairamov, This Journal. Preceding Communication.
4. M.Salakhov,N.Musaeva,M.Guseinov,S.Suleimanov, Zh.org.khim.  
13, 561 (1977).
5. N.Musaeva,M.Salakhov,S.Suleimanov,R.Salakhova,A.Gasanova,  
Organic Reactivity,16, 390 (1979).
6. R.W.Wilkinson,Chem.ind.,2, 1961,1385.
7. M.Salakhov,N.Musaeva,M.Guseinov,S.Suleimanov . In: Inves-  
tigations in Polymeric and Monomeric Products 7.(1977)  
(in Russian).
8. F.Fueno,O.Kajimoto,M.Masago, Bull.Chem.Soc.Japan,46,1428  
(1973).
9. O.Kajimoto,M.Kobayashi,F.Fueno, Bull.Chem.Soc.Japan,46,  
2316 (1973).

KINETIC STUDY OF HYDROLYSIS OF BENZOATES. XIV, ALKALINE  
HYDROLYSIS IN 80% AQUEOUS DIMETHYL SULFOXIDE

V. Nummert, M. Eek, and M. Piirsalu

Laboratory of Chemical Kinetics and Catalysis,  
Tartu State University, Tartu 202400, U.S.S.R.

Received June 1, 1981

The rate constants of the alkaline hydrolysis for five substituted phenyl benzoates  $C_6H_5COOC_6H_4 - X$  ( $X = 3-Cl, 4-F, 3-NH_2, 3-CH_3, H$ ) in 80% (v/v) (50,3M%) dimethyl sulfoxide-water mixture and for two substituted phenyl benzoates ( $X = 4-F, 3-CH_3$ ) in water have been measured spectrophotometrically at 25°C.

When passing from water to 50,3M% aqueous dimethyl sulfoxide (DMSO) the  $p^o$  value for the alkaline hydrolysis of substituted phenyl benzoates increases by 0.73 units. The  $p^o$  value was found to increase to the same extent also for other reactions considered: alkaline hydrolysis of ethyl benzoates, acidic dissociation of benzoic acids and anilinium ions.

Earlier<sup>1-9</sup> we have studied thoroughly the kinetics of the alkaline hydrolysis of substituted phenyl and alkyl benzoates with electroneutral as well as with charged substituents in aqueous solution in the presence of different amounts of neutral salts like NaCl and NaClO<sub>4</sub>. It is of great interest to compare these data with those for binary mixtures of water with organic solvents.

Up to the present the alkaline hydrolysis of substituted phenyl benzoates in mixtures of water with organic solvents



has been studied insufficiently. We can find data only for 33% aqueous acetonitrile<sup>10</sup> as well as for 30, 50 and 70% aqueous dioxane<sup>11</sup>.

In the present work the kinetics of the alkaline hydrolysis of substituted phenyl benzoates  $C_6H_5COOC_6H_4-X$  ( $X=3-Cl$ ,  $4-F$ ,  $3-NH_2$ ,  $3-CH_3$ ,  $H$ ) in 80% (v/v) (50,3 M%) dimethyl sulfoxide-water mixture as well as for two phenyl benzoates ( $X=4-F$ ,  $3-CH_3$ ) in water at 25°C was measured.

#### Experimental.

As the reagent tetra-n-butylammonium hydroxide was used.

The carbon dioxide free hydroxide solution was prepared from 10% aqueous  $n-Bu_4NOH$  ("Chemapol") by passing the hydroxide solution through an ion-exchange column (Amberlite IRA-400) in argon atmosphere.

DMSO "pure" grade was dried over  $BaO$  and distilled over  $CaH_2$  in vacuo<sup>12</sup>.

The preparation and purification of phenyl benzoate as well as 3-chloro- and 3-aminophenyl benzoates has been described earlier<sup>1</sup>.

4-Fluoro- and 3-methylphenyl benzoates were synthesized by the interaction of benzoyl chloride with corresponding substituted phenol in 10% aqueous  $NaOH$  solution. 4-Fluorophenyl benzoate was several times recrystallized from 70%  $EtOH$ -water mixture. 3-Methylphenyl benzoate was recrystallized from  $EtOH$ . Both phenyl benzoates were dried over  $P_2O_5$  in vacuo.

4-Fluorophenyl benzoate, m.p. 57-58.5°C.

3-Methylphenyl benzoate, m.p. 52.0-52.5°C.

For the kinetic measurements the spectrophotometric method<sup>1</sup> was applied. The wave lengths used are given in Table 1.

The kinetic measurements were carried out under pseudo-monomolecular conditions with an excess of hydroxide. The rate constants for each phenyl benzoate were determined at 3-5 hydroxide concentrations. The measurements at each

hydroxide concentration were repeated 2-6 times and the arithmetic means of the corresponding pseudo first order rate constants  $k_1$  were calculated.

The second order rate constants were calculated as slopes of the corresponding regression plots of the pseudo-first order rate constants vs. hydroxide concentration. These plots do not go strictly through the origin of coordinates. (Fig. 1 and 2.). Such a situation can be ascribed to the fact that the determined hydroxide concentration in all the cases does not correspond to reality.

When calculating the  $k_2$  values according to the equation

$$k_1 = k_2 c_{OH^-} + \text{const}$$

the  $k_1$  values for all parallel measurements at each hydroxide concentration were embraced. The results of such preliminary kinetic data treatment are given in Table 1.

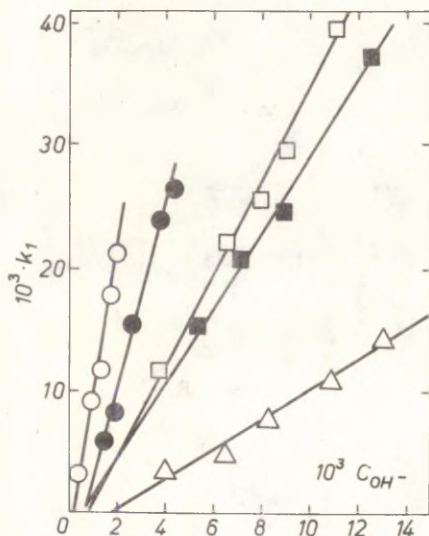


Fig. 1.  
Relationships between  
 $k_1$  of alkaline hydro-  
lysis of esters  
 $C_6H_5COOC_6H_4-X$  in 80%  
aqueous DMSO and  
hydroxide  
concentration

- -  $X = 3-Cl$
- -  $X = 4-F$
- -  $X = H$
- -  $X = 3-CH_3$
- △ -  $X = 3-NH_2$

Table 1  
Rate Constants  $k_1(\text{sec}^{-1})$  at Various  $\text{Bu}_4\text{NOH}$  Concentrations and Rate  
Constants  $k_2(\text{M}^{-1}.\text{sec}^{-1})$  for Alkaline Hydrolysis of Esters  
 $\text{C}_6\text{H}_5\text{COOC}_6\text{H}_4\text{-X}$  in 80%(v/v)DMSO-Water Mixture at 25°C

X	$10^3.\text{c}_{\text{OH}^-}$ (M)	$10^3.\text{c}_{\text{K}_1}$ ( $\text{sec}^{-1}$ )	$n_1$	$k_2$ ( $\text{M}^{-1}.\text{sec}^{-1}$ )	$n/n_0$	$10^3.\text{const}$	$\lambda$
1	2	3	4	5	6	7	8
3-Cl	0.401	$3.05 \pm 0.32$	3	$11.91 \pm 0.48$	13/15	$-2.30 \pm 1.15$	308
	1.00	$9.07 \pm 0.21$	4				
	1.30	$11.68 \pm 1.06$	2				
	1.63	$17.92 \pm 1.90$	2				
	1.92	$21.06 \pm 0.66$	4				
4-F	1.51	$5.91 \pm 0.82$	2	$8.50 \pm 0.32$	14/19	$-7.29 \pm 0.90$	316
	1.98	$8.06 \pm 0.78$	4				
	2.60	$15.57 \pm 0.30$	4				
	3.72	$23.93 \pm 1.37$	5				
	4.26	$26.46 \pm 1.71$	4				
4-F ( $\text{H}_2\text{O}$ )	4.85	$2.46 \pm 0.03$	3	$0.748 \pm 0.004$	7/10	$-1.19 \pm 0.14$	300
	12.77	$7.59 \pm 0.34$	3	$0.61 \pm 0.02^{11}$			
	29.0	$20.50 \pm 0.10$	4				



Table 1 continued

1	2	3	4	5	6	7	8
H	3.84	$12.10 \pm 0.59$	3	$3.89 \pm 0.18$ $3.41 \pm 0.07$	20/20 20/20	$-3.48 \pm 1.42$ 0	303
	6.51	$22.0 \pm 0.99$	6				
	7.81	$25.78 \pm 0.56$	3				
	8.94	$29.73 \pm 1.04$	3				
	10.8	$39.46 \pm 0.76$	5				
3-CH <sub>3</sub>	5.33	$15.74 \pm 0.40$	5	$3.00 \pm 0.12$	16/16	$-0.66 \pm 1.58$	302
	7.05	$20.73 \pm 0.55$	3	$2.94 \pm 0.04$	16/16	0	
	8.81	$24.68 \pm 0.45$	5				
	12.34	$37.13 \pm 0.73$					
3-CH <sub>3</sub> (H <sub>2</sub> O)	13.0	$4.04 \pm 0.15$	4	$0.320 \pm 0.002$	16/19	$0.039 \pm 0.259$	292
	15.61	$4.67 \pm 0.35$	3				
	30.6	$10.13 \pm 0.11$	5				
	60.33	$20.10 \pm 0.84$	3				
	106.2	$33.94 \pm 0.15$	4				

Table 1 continued

1	2	3	4	5	6	7	8
3-NH <sub>2</sub>	4.06	3.08 $\pm$ 0.05	3	1.22 $\pm$ 0.06	12/19	-1.95 $\pm$ 0.22	306
	6.51	4.55 $\pm$ 0.19	3				
	8.15	7.69 $\pm$ 0.16	6				
	10.84	10.75 $\pm$ 0.48	4				
	12.99	14.15 $\pm$ 0.12	3				

\* n<sub>1</sub> - Number of measurements at the hydroxide concentration considered,

\*\* n/n<sub>0</sub> - The denominator reflects the total number of data, involved in regression data processing and the numerator equals the number of remaining points after excluding significantly deviating points.

\*\*\* const - Value of constant in equation  $k_1 = k_2 c_{OH^-} + \text{const}$

\*\*\*\*  $\lambda$  = Wave lengths used at measurements.

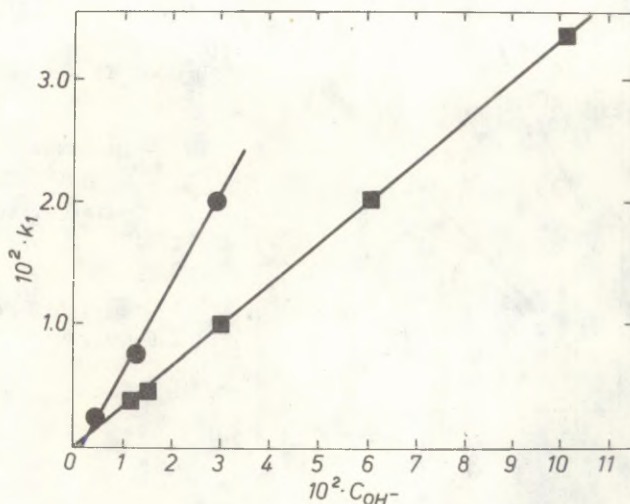


Fig. 2. Relationships between  $k_1$  of alkaline hydrolysis of esters  $C_6H_5COOC_6H_4 - X$  in water and hydroxide concentration

● - X = 4-F  
 ■ - X = 3-CH<sub>3</sub>

#### Discussion.

When passing from water to 80% (50.3M%) DMSO - water mixture the rate of the alkaline hydrolysis of substituted phenyl benzoates increases considerably and the  $\rho^\circ$  value grows by 0.75 units (see Tables 1,2 and Figure 3).



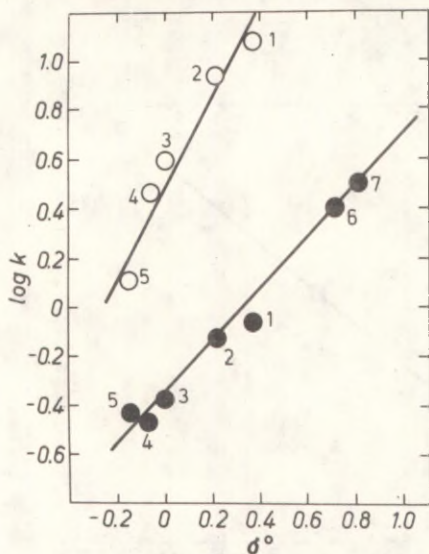


Fig. 3  
Relationships between  
log k of the alkaline  
hydrolysis of esters  
 $C_6H_5COOC_6H_4 - X$  and  $\delta^\circ$

● - in water  
○ - in 80% DMSO-  
water mixture  
X = 1. 3-Cl; 2. 4-F;  
3. H; 4. 3-CH<sub>3</sub>;  
5. 3-NH<sub>2</sub>; 6. 3-NO<sub>2</sub>;  
7. 4-NO<sub>2</sub>.

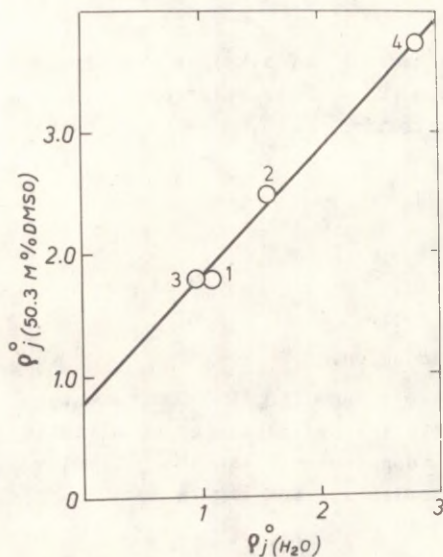


Fig. 4.  
Relationships between  
 $\rho_j^\circ (50.3 \text{ M\% DMSO})$   
and  
 $\rho_j^\circ (H_2O)$ .  
Numbers of reactions are  
those in Table 2.

Values of  $\rho_j^{\circ}(\text{H}_2\text{O})$ ,  $\rho_j^{\circ}(50.3\text{M\%DMSO})$  and  $\Delta\rho_j^{\circ}(50.3\text{M\%DMSO})$

Table 2

Reaction <sup>a</sup>	$\rho_j^{\circ}(\text{H}_2\text{O})$	$\rho_j^{\circ}(50.3\text{M\%DMSO})$	$\Delta\rho_j^{\circ}(50\text{M\%DMSO})^b$	Notes
1. $\text{C}_6\text{H}_5\text{COOC}_6\text{H}_4\text{-X+OH}^-$ , 25°C	1.05 $\pm$ 0.06	1.78 $\pm$ 0.24	0.73	
2. $\text{X-C}_6\text{H}_4\text{COOC}_2\text{H}_5\text{+OH}^-$ , 25°C <sup>15</sup>	1.52 $\pm$ 0.06	2.35 $\pm$ 0.06 2.61 $\pm$ 0.12 2.48	0.83 1.09 0.96	32.0 M%DMSO 59.0 M%DMSO c)
3. Acidic dissociation of $\text{X-C}_6\text{H}_4\text{COOH}$ , 25°C <sup>15</sup>	0.95 $\pm$ 0.02	1.88 $\pm$ 0.05 1.82 $\pm$ 0.05 1.80 1.70	0.93 0.87 0.85 0.75	48.6 M%DMSO 59.0 M%DMSO c) d)
4. Acidic dissociation of $\text{X-C}_6\text{H}_4\text{NH}_3^+$ , 25°C <sup>15</sup>	2.84 $\pm$ 0.04 <sup>e</sup>	3.84 $\pm$ 0.43 3.72	1.00 0.88	48.6 M%DMSO c)

a) Reference to the source of  $\rho^{\circ}$  values is shown.

b)  $\Delta\rho_j^{\circ}(50.3\text{M\%DMSO}) = \rho_j^{\circ}(50.3\text{M\%DMSO}) - \rho_j^{\circ}(\text{H}_2\text{O})$

c) The value of  $\rho_j^{\circ}(50.3\text{M\%DMSO})$  determined from the dependence of  $\rho_j^{\circ}(\text{M\%DMSO})$  values on M%DMSO for binary mixture  $\text{H}_2\text{O-DMSO}$ .

d) The value of  $\rho_j^{\circ}(50.3\text{M\%DMSO})$  determined from the dependence of  $\rho_j^{\circ}(\text{M\%DMSO})$  values on M%DMSO for binary mixture  $\text{H}_2\text{O-DMSO}$  according to the data of Hojo and Utaga <sup>16</sup>.

At 25°C for 50.3 M% aqueous DMSO one can write:  
 $\log k = (0.498 \pm 0.017) + (1.778 \pm 0.243) \rho^\circ$   
 and for water:

$$\log k = (-0.367 \pm 0.015) + (1.051 \pm 0.057) \rho^\circ$$

It should be noted that when passing from water to 85% DMSO-water mixture a considerable rate increase was also found in the case of alkaline hydrolysis of ethyl benzoates.<sup>13</sup>

In one of our previous works<sup>14</sup> on the basis of the  $\rho^\circ$  values belonging to different reaction series the observance of the relationship:

$$\rho_{js}^\circ - \rho_{jo}^\circ = \text{const} \quad (1)$$

was checked for individual solvents and binary mixtures as well as for concentrated aqueous solutions of different salts (j and s denote the reaction series and medium, respectively).

In order to check whether the  $\rho^\circ$  value increases in the case of alkaline hydrolysis of substituted phenyl benzoates when passing from water to 50.3 M% aqueous DMSO obey equation (1), in Table 2 the  $\rho^\circ$  values for water and 50.3 M% aqueous DMSO are given for following reaction series: alkaline hydrolysis of ethyl benzoates  $X-C_6H_4COOC_2H_5$ ; acidic dissociation benzoic acids  $X-C_6H_4COOH$  and anilinium ions  $X-C_6H_4NH_3^+$  at 25°C. The corresponding  $\rho^\circ$  values from ref.15 were used.

The  $\rho_{j((50.3 \text{ M\%DMSO})}^\circ$  values for the reaction series in Table 2 could evidently be considered as constant. Consequently, it can be assumed that there exist linear relationships between the  $\rho_{j(50.3 \text{ M\%DMSO})}^\circ$  and  $\rho_{j(H_2O)}^\circ$  values which have the slope equal to one and the intercept equal to  $\rho_{j(50.3 \text{ M\%DMSO})}^\circ$ .

The relation  
 $\rho_{j(50.3 \text{ M\%DMSO})}^\circ = (0.787 \pm 0.081) + (1.042 \pm 0.051) \rho_{j(H_2O)}^\circ \quad (2)$   
 is represented in Figure 4.



The parameters of relationship (2) indicate that the data of the alkaline hydrolysis of substituted phenyl benzoates in 50.3M% aqueous DMSO obey also equation (1).

#### References

1. T. Püssa, V. Nummert (Maremäe), and V. Palm, Reakts. sposobn. organ. soedin., 9, 697 (1972).
2. T. Püssa, V. Nummert (Maremäe), and V. Palm, Reakts. sposobn. organ. soedin., 9, 871 (1972).
3. V. Nummert and I. Alakivi, Organic Reactivity, 11, 613 (1975).
4. V. Nummert and I. Alakivi, Organic Reactivity, 11, 911 (1975).
5. V. Nummert and I. Alakivi, Organic Reactivity, 13, 105 (1976).
6. V. Nummert and I. Alakivi, Organic Reactivity, 13, 536 (1976).
7. V. Nummert and M. Piirsalu, Organic Reactivity, 14, 263 (1977).
8. V. Nummert and M. Piirsalu, Organic Reactivity, 15, 240 (1978).
9. V. Nummert and M. Piirsalu, Organic Reactivity, 16, 251 (1979).
10. J. Kirsch, W. Clewell, and A. Simon, J. Org. Chem., 33, 127 (1968).
11. Yu. Sukhorukov, V. Polonov, B. Finkelstein, and B. Istomin, Zh. Org. khim., 17, 1149 (1981).
12. D. Martin, H. Hauthal, Dimethylsulfoxide, Berlin, 1971, p. 45.

13. M. Hojo, M. Utaka, and Z. Yoshida, Tetrahedron Letters, 1, 25(1966).
14. V. Nummert and V. Palm, Organic Reactivity, 17, 331(1980).
15. V. Nummert and V. Palm, Organic Reactivity, 17, 292(1980).
16. M. Hojo, M. Utaka, and Z. Yoshida, J. Chem. Soc., Jap., Ind. Chem. Soc., 69, 885(1966).

STUDY OF 5,5-DIMETHOXYTETRACHLOROCYCLOPENTADIENE  
REACTIVITY IN THE REACTION OF DIENE CONDENSATION  
WITH CHLOROACETIC ACID ALLYL ESTERS

T.G. Kyazimova, R.S. Babayev and M.M. Guseinov  
Institute of Theoretical Problems of Chemical Tech-  
nology, Academy of Sciences of the Azerbaijan S.S.R.

Received August 5, 1981

The method of gas-liquid chromatography has been applied to study the kinetics of the reaction of diene condensation of 5,5-dimethoxytetra-  
chlorocyclopentadiene (5,5-DMTCLCPD) with chloro-  
and trichloroacetic acid allyl esters. It was shown that in the above reaction 5,5-DMTCLCPD is 4.6 times more active than hexachlorocyclopentadiene (HCLCPD).

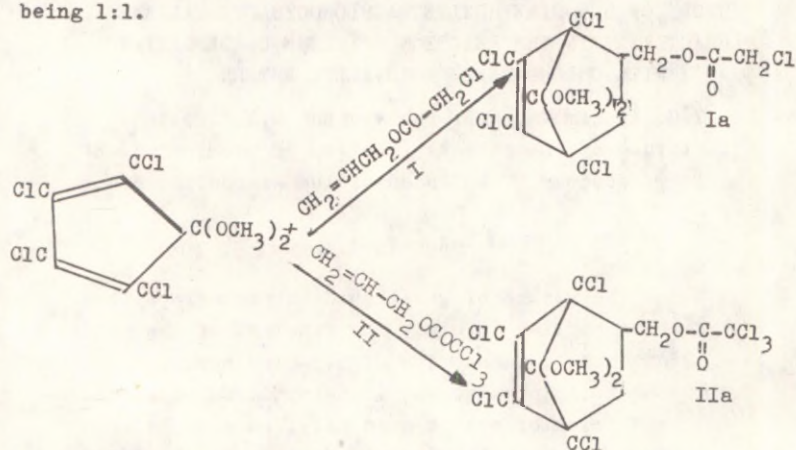
Our previous communication revealed that the reaction rate of hexachlorocyclopentadiene (HCLCPD) diene condensation is higher with monochloroacetic acid allyl esters (MCLAAAE) than with a similar ester of trichloroacetic acid (TCLAAAE). This could be ascribed to the enhancement of carbon electro-negativity by halogen atoms which will lead to a drop in both electron density at the reaction center and reactivity<sup>1,2</sup>.

With a view to continuing systematic research into this area it was of interest to check whether the noticed regularity is observed for the reaction of the above esters with 5,5-dimethoxytetrachlorocyclopentadiene (5,5-DMTCLCPD) and to compare its relative reactivity with HCLCPD.

With this aim in view we studied the kinetics of diene condensation reaction of 5,5-DMTCLCPD with MCLAAAE(I) and TCLAAAE(II) in nitrobenzene by gas-liquid chromatography (GLC). The reaction was monitored by a decrease in diene concentration.



The reaction rate of 5,5-DMTClCPD with MCLAAAE and TCLAAAE was studied in the temperature range 100° to 140°C for 6 hours, the equimolar ratio of diene and dienophile being 1:1.



It was revealed that the reaction can be described by a second order kinetic equation which can be evidenced by the constancy of rate constants calculated at various degrees of initial products transformations.

Rate constants are collected in Table 1.

Table 1

Rate Constants for the Diene Condensation  
Reaction of 5,5-DMTClCPD and HClCPD with  
MCLAAAE(I) and TCLAAAE(II)

Diene	Compound	$K \cdot 10^{-6} \text{ l/mol} \cdot \text{sec}$		
		100°C	120°C	140°C
5,5-DMTClCPD	I	30.1	81.6	205.4
	II	16.2	48.2	126.5
HClCPD	I	6.5	18.5	52.3
	II	3.5	11.26	30.49
	$K_I/K_{II}$ (DMTClCPD)	1.84	1.70	1.62

The ratio of 5,5 DMTC1CPD/HClCPD rate constants at various temperatures (Table 2) indicates that the reaction rate for DMTC1CPD is on the average 4.0 to 4.6 times higher than for HClCPD.

Table 2

The Ratio of Rate Constants  $K_{5,5\text{-DMTC1CPD}}/K_{\text{HClCPD}}$   
at Various Temperatures.

Compound	100° C	120° C	140° C
I	$\frac{30.1}{6.54} = 4.6$	$\frac{80.8}{18.5} = 4.36$	$\frac{205.4}{52.3} = 4.0$
II	$\frac{16.2}{3.5} = 4.66$	$\frac{47.8}{11.26} = 4.24$	$\frac{126.5}{30.49} = 4.11$

It is of interest to note that with a temperature jump the difference in the reaction rate of the above dienophiles regularly decreases. It can be easily seen from the dependence of logarithm ratios of 5,5-DMTC1CPD/HClCPD rate constants on the reciprocal temperature (Fig. 1). From this dependence we have calculated the value for isokinetic temperature  $481^{\circ}\text{C}^{3-4}$ . The isokinetic temperature at which the reaction rates of the studied dienes with esters (I) and (II) are to be of equal value have also been determined from the dependence of the logarithm of 5,5-DMTC1CPD and HClCPD rate constants on reverse temperature (Fig.2).

Activation energy has been calculated from the dependence of logarithms of rate constants on the reciprocal temperature. The values for kinetic and thermodynamic parameters of activation energies are displayed in Table 3.

When comparing kinetic and thermodynamic parameters it appears that 5,5-DMTC1CPD is more active in diene condensation than HClCPD. It is also proved by the values for both activation energy and activation entropy.

Table 3

Activation Parameters for the Reaction of  
Diene Condensation of 5,5-DMTC1CPD with  
Compounds (I-II)

Diene	Compound	lg A	E <sub>act</sub>	ΔH <sup>‡</sup>	ΔS <sup>‡</sup>	ΔF <sup>‡</sup>
5,5-DMTC1CPD	I	3.6	13.7	12.9	44.55	30.4
	II	3.9	14.7	13.8	42.80	30.6
HClCPD	I	3.4	14.6	13.8	45.6	31.7
	II	5.2	18.3	17.5	37.4	32.2

The analysis of the above material confirms the unity of reaction mechanism of the above esters I-II with DMO and HClCPD and the observance of the regularity found earlier about the greater dienophile activity at monochloroacetic acid allyl ester, i.e. 5,5-DMTC1CPD as well as HClCPD appear to be diene-acceptors.

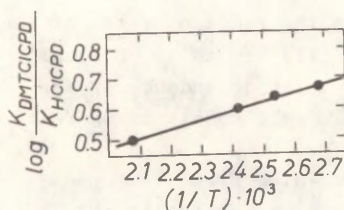


Fig. 1. The dependence of logarithms of  $K_{DMTC1CPD}/K_{HClCPD}$  rate constant ratios on temperature.

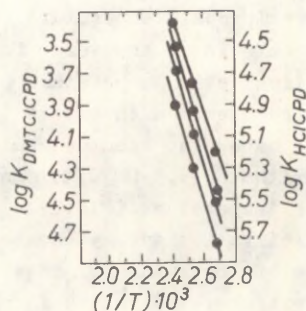


Fig. 2. The dependence of logarithms of rate constant on the reciprocal temperature for 5,5-DMTC1CPD and HClCPD diene condensation with esters I-II.



The greater activity of 5,5-DMTC1CPD in comparison with HClCPD is related to its smaller nucleophilicity caused by the partial contribution of electron pairs of oxygen atoms. Due to the smaller ionic radius of oxygen atoms than chlorine, the formation of the transitional complex in the reactions with 5,5-DMTC1CPD is more favorable.

#### EXPERIMENTAL

The esters (I-II) were synthesized by esterification of chloroacetic acids with allyl ethanol according to a well-known method<sup>5</sup>.

5,5-DMTUC1CPD was synthesized according to the method described in Ref. 6.

Adducts Ia and IIa have been synthesized and characterized earlier<sup>7,8</sup>.

Their purity was checked by the method of thin-layer chromatography on the adsorbent-aluminium oxide of second grade activity, in the system of solvents - heptane: acetone - 20:13, the developer-UV light.

#### REFERENCES

1. M.M. Guseinov, T.G. Kyazimova, R.A. Kurbanove, R.S. Babayev, and M.R. Shukyurova, *Zh. org. khim.* (in press)
2. T.G. Kyazimova, M.M. Guseinov, R.S. Babayev, and T.N. Shakhtakhtinskii, *Organic Reactivity* (in press).
3. J.E. Leffler, *J. Org. Chem.* 29, 3133(1955).
4. R.S. Petersen, *J. Org. Chem.* 29, 3133 (1964).
5. Weygand-Hilgetag. *Organisch-chemische Experimentierkunst* (Russ.transl.)
6. J. Newcomer, E. McBec, *J. Am. Chem. Soc.* 71, 946(1949)
7. M.M. Guseinov, T.G. Kyazimova, R.S. Babayev, Sh.S. Akhnazarova, and Z.Ya. Yarieva, *Az.khim.zh.*, No 3 pp.39-42, 1972.
8. M.M. Guseinov, T.G. Kyazimova, R.S. Babayev, Sh.S. Akhnazarova, and Z.K. Yarieva. *Az. khim.zh.*, No 5-6, pp-68, 1974.



THE DEPENDENCE OF IONIZATION POTENTIALS  
AND PROTON AFFINITIES ON STRUCTURE.

I. Ionization Potentials. Correlations with  
Substituent Constants and Polarizability <sup>¶</sup>.

I.A. Koppel, U.H. Mölder, and R.I. Pikver

Laboratory of Chemical Kinetics and Catalysis,  
Department of Chemistry, Tartu State University,  
202400 Tartu, Estonia, U.S.S.R.

Received December 14, 1981

The correlation of the ionization potentials (IP) with the structure has been found for the several classes of organic compounds (ethers, esters, amines, ketones, aldehydes, sulfides, etc.). Both alkyl and electronegative substituents were included. Statistical contributions of the inductive and resonance effects as well as substituent polarizability and hydrogen atom effects on the IP-s were discussed.

Several correlations of the IP of alkyl derivatives of different classes of compounds with structure in terms of the single-parameter Taft equation <sup>4-14</sup> and its more sophisticated modifications <sup>15-17</sup> were already suggested in literature. Hammett-Taft equation and some of its constraints were also used for the correlation of the IP of aromatic compounds <sup>18-23</sup>.

The correlation of alkylsubstituted compounds with the substituent constants is not accompanied at least with the practical difficulties. However, even at the first glance the situation is much more complicated for the compounds with the electronegative substituents. Several problems of prac-

---

<sup>¶</sup> See Refs. 1-3 for the preliminary communications.

tical and theoretical nature arise. The latter, probably, accounts for the fact that only one paper<sup>24</sup> with such a correlations was published. However, even in this case the amount of experimental data included was insufficient for the search of general regularities between IP and structure. In some cases generally hardly comparable<sup>25</sup> IP-s from photoionization and electron impact techniques were included simultaneously. Moreover, as a rule, these methods determine only the first IP which excludes the possibility to take into account the interaction of different orbitals.

While correlating the IP with the structure for the compounds with the electronegative substituents the following features seem to be important.

1. The competition between the orbitals of the electronegative substituent and those of the ionization center. As far as the energies of the higher occupied MO-s of electronegative substituent and ionization center (the latter is also an electronegative group) are frequently rather close each to another the gradual variation of the structure of the electronegative substituent might transfer the latter into another, competitive ionization center. On the other hand the invariability of the mechanism of the process studied is one of the major preconditions for the observance of the structure-activity relationships.

In the relatively simple case of the coexistence of two equivalent ionization centers the symmetrical splitting of the corresponding MO-s takes place. The latter could be accounted for using for the correlations the averaged IP (arithmetic mean from the IP-s corresponding to the energies of the splitting orbitals) values.

It seems evident that without the detailed assignment of the bands of the photoelectron spectrum there is no general guarantee for the correctness of the use of only the first IP-s. Instead, only IP which correspond to the orbitals of the given type should be used. On the other hand, for the compounds which possess alternative centers of ionization

( $X_1\text{COOX}_2$ ,  $X\text{CONH}_2$ ,  $X_1\text{CONX}_2X_3$ , etc.) the deviations from correlations for the compounds with well known ionization centers could be used for the assignment of the bands of their photoelectron spectra.

2. Sometimes, because of the substantial mutual shift of the potential curves of the initial and excited states there are serious problems in determining the adiabatic IP of these compounds. Therefore in several papers even no attempt was made to determine the adiabatic IP. One of the most important class of compounds whose adiabatic and vertical IP differ substantially are for example aliphatic amines. However, the use of adiabatic IP in correlations is theoretically more justified than the use of vertical IP.

3. Many authors claim the reproducibility of IP-s in the range of 0.01 eV. However, that does not mean that the corresponding absolute values determined by different techniques or even by the same technique in different laboratories agree within the same error range. On the contrary, often the adiabatic IP published by different workers differ even by  $0.1 \div 0.2$  eV.

Besides that experimental data on IP compounds with electronegative substituents is far from being systematic and homogenous (especially taking into account both experimental techniques and research groups).

4. Some compounds which include strong electronegative groups are (e.g. halide amines) are extremely unstable and therefore inconvenient for measurements of their PES. However, the instability of the compound is almost always coupled with the presence of impurities in the sample which, in their turn, might lead to the non self-consistent experimental results.

Keeping in mind the above-mentioned circumstances an attempt of systematic correlation analysis of IP of compounds containing both alkyl and electronegative substituents was undertaken in this work. For the extension of the data basis for the compounds with strong electronegative substi-



tments and/or with the several competitive ionization centers PES of more than 40 compounds were measured. The corresponding adiabatic and vertical IP are listed in the Appendix alongside with the literature data. The detailed coverage of the measured PES of the compounds of the different classes will be given in separate publications.

In a few recent years due to the fast development of such experimental techniques as spectrometry of ion cyclotron resonance and high pressure mass-spectrometry a large amount of experimental data on another important characteristic of molecules - their proton affinity (PA) - has been accumulated. Keeping in mind the existence of rather general close relationship<sup>26</sup> between PA-s and IP-s for a large variety of organic compounds (both with alkyl as well as with electronegative substituents) it is reasonable to expect the similar dependence of these parameters also on the structural factors.

Earlier<sup>27</sup> the correlation analysis of the dependence of PA for several classes of neutral and ionic aliphatic bases on structure was made in the framework of the two-parameter equation which includes inductive and polarizability terms:

$$PA = PA_0 + a_1 \sum \sigma^* + a_2 \sum \Delta R, \quad (1)$$

where  $PA_0$  refers to the PA of methyl-substituted compound,  $\sum \sigma^*$  - is the sum of the Taft inductive constants of the substituents attached to the protonization center,

$\Delta R = MR - MR(\text{methyl})$ , where MR is the calculated additive molecular refractivity of the given substituent. Also, it was found that another equation

$$PA = PA_0 + a_1 \sum \sigma^* + \ln n_1 \quad (2)$$

where  $n_1$  - is the number of hydrogen atoms immediately attached to the reaction center<sup>‡</sup>

leads to the comparable, however, statistically slightly less adequate description of the experimental data.

<sup>‡</sup> In the original work the symbol  $\Delta n$  was used.



In this series of papers the statistical least squares treatment of the data on IP as well as on PA (the following paper) was made in the framework of the more general equation (3)

$$A = A_0 + a_1 \sum \sigma^* + a_2 \sum \Delta R + a_3 \sum \sigma_R^0 + a_4 n_1 + a_5 \Delta n_2, \quad (3)$$

where  $A_0$  refers to the IP or PA of the methylsubstituted derivative

$\sum \sigma^*$  and  $\sum \Delta R$  maintain the same meaning as in Eq. (1).

$\sum \sigma_R^0$  is the sum of the substituent resonance constants  $n_1$  - is identical to the parameter used in Eq (2) (e.g., in the series of amines  $X_1X_2X_3N$   $n_1=3$  for  $NH_3$ ,  $n_1=2$  for  $X_1NH_2$ ,  $n_1=1$  for  $X_1X_2NH$  and  $n_1=0$  for  $X_1X_2X_3N$ ).

$\Delta n_2 = n_2 - n_2(\text{methyl})$ , where  $n_2$  is the number of the hydrogen atoms, attached to the  $\alpha$ -position relative to the protonization or ionization center ( $n_2(\text{methyl})=3$ ).

which as compared with Eqns (1) and (2) includes also the resonance term as well as the contributions<sup>15</sup> of hydrogen atoms attached immediately or in the  $\alpha$ -position to the reaction or ionization center.

Mostly the standard values of the substituent constants were used: Taft inductive  $\sigma^*$  constants were taken from Ref. 28 (for fluoroalkyl groups  $\sigma^*$  values were calculated according to the additive scheme using the attenuation factor  $\rho^* = 0.38$ ) and resonance constants are from Ref. 29. Molecular refractivities MR were also calculated according to the additive scheme using Vogel's refractivities for the structural elements for the sodium D-line from the compilation<sup>30</sup>.

Such a choice of scales of substituent constants is primarily caused by the practical considerations and is not strict enough and theoretically satisfactorily founded. On the contrary<sup>31</sup>, in the principle, probably two different scales of  $\sigma^*$  constants for alkyl and electronegative substituents should be used. Also, the use of two different

scales of resonance constants of  $\sigma_R^-$  and  $\sigma_R^+$  type instead of a single resonance parameter  $\sigma_R^0$  is certainly more preferable.

Detailed discussion of the alkyl substituent effects on the IP-s was given in Ref. 15 where also the importance of the effects of the number of hydrogen atoms, attached immediately and to the  $\alpha$ -position to the ionization center was duly recognized.

In the present work an attempt was made to describe the substituent effects of electronegative as well as alkyl substituents on the ionization potentials of compounds of different classes in the framework of a formalism of Eqn.(3) and its constraints.

It is evident that along other circumstances the success of this approach depends crucially on the correct recognition of the ionization center. Based on the data of PES with well identified bands one can successfully select the proper values of IP-s for the correlation analysis of compounds of the given mechanism of ionization (fixed ionization center). As it is already mentioned the use of adiabatic IP for the correlation analysis is theoretically preferable before the use of vertical IP-s. However, the major amount of the most recent IP data is derived from PES where determination of adiabatic<sup>\*</sup> IP-s (especially it refers to the higher IP-s). is not always possible. Therefore, the accompanying parallel correlation analysis was also performed for the corresponding vertical IP. Data bank of the latter is also included into the Appendix.

---

<sup>\*</sup> Strictly speaking, IP in the PES should be considered adiabatic only in the case when the analysis of the vibrational structure of the given band identifies this ionization process as a 0 - 0 transfer.

### Results

The results of the least squares statistical treatment<sup>‡</sup> of experimental IP data in terms of Eqn.(3) and its constraints are included into Tables 1 (adiabatic IP) and 2 (vertical IP). Also, the regression coefficients  $a_i$ , their statistical error limits  $sa_i$ , multiple correlation coefficients  $R$ , standard deviations  $s$  and the information on the number ( $n$ ) and identity of the points included is listed.

Pairwise correlation coefficients between  $\Sigma\sigma^*$ ,  $\Sigma\sigma_R^0$ ,  $\Sigma\Delta R$ ,  $n_1$ , and  $\Delta n_2$  were also calculated and they show that all these arguments are practically orthogonal each to another.

Figure 1 shows the lack of the general single linear dependence of IP on the measure of inductive substituent effect for the series of carbonyl compounds. However, the points for the compounds with electronegative substituents seem to group along the Milky Way-like straight line the slope of which is very much different (smaller) from the slope of the straight line for the alkylsubstituted derivatives. Despite of that one can notice from Fig.1 that compounds with substituents which have roughly the same refractivities (for example, methyl group and its flourinated or perfluorinated analogues) and other characteristics included into the Eqn.(3) fit the parallel straight lines in coordinates IP vs.  $\Sigma\sigma^*$ . It means that the inclusion of refractivity term and the other factors equalizes the slopes for compounds with alkyl and electronegative substituents. Graphically this situation is shown on Figs.2 and 3 which already display the general single line dependence (both alkyl and electronegative substituents) of IP of carbonyl compounds  $X_1COX_2$  and chlorides  $XCl$  corrected by means of Eqn.(3) for the influence of the other structural factors on the inductive constants of substituents.

<sup>‡</sup> The program written by prof. V.A. Palm was used.



Table 1  
Correlation Statistics of Regression Analysis of Adiabatic Ionization  
Potentials in Terms of Eqn. (3).

No	Class of Compounds	IP <sub>0</sub>	a <sub>1</sub>	a <sub>2</sub>	a <sub>3</sub>	a <sub>4</sub>	a <sub>5</sub>	R	s	s%	n
1	2	3	4	5	6	7	8	9	10	11	12
1.	XOH	10.78 (0.24)	0.528 (0.032)	-0.045 (0.006)	3.803 (0.443)	-0.876 (0.177)	-	0.964	0.13	5.4	18
2.	X <sub>1</sub> OX <sub>2</sub>	10.09 (0.17)	0.547 (0.017)	-0.027 (0.004)	0.493 (0.169)	0.446 (0.087)	0.057 (0.016)	0.982	0.15	3.5	34
3.	X <sub>1</sub> SX <sub>2</sub>	8.91 (0.20)	0.383 (0.030)	-0.007 (0.003)	2.016 (0.294)	0.897 (0.100)	0.211 (0.030)	0.962	0.16	4.8	41
4.	X <sub>1</sub> SX <sub>2</sub>	8.67 (0.08)	0.230 (0.009)	-0.012 (0.002)	2.237 (0.124)	0.357 (0.034)	-	0.992	0.09	1.0	37
5.	X <sub>1</sub> X <sub>2</sub> X <sub>3</sub> N	7.93 (0.30)	0.406 (0.021)	-0.023 (0.006)	0.013 (0.259)	0.277 (0.082)	-0.009 (0.018)	0.967	0.27	5.4	36
6.	X <sub>1</sub> X <sub>2</sub> X <sub>3</sub> P	8.75 (0.24)	0.249 (0.022)	0	-0.867 (0.335)	0.740 (0.073)	0.113 (0.022)	0.933	0.16	4.3	17
7.	X <sub>1</sub> COX <sub>2</sub>	9.81 (0.17)	0.311 (0.020)	-0.033 (0.004)	-0.316 (0.120)	0.228 (0.084)	0.010 (0.021)	0.963	0.15	5.0	59
8.	X <sub>1</sub> COX <sub>2</sub>	9.77 (0.13)	0.412 (0.018)	-0.026 (0.003)	-1.477 (0.143)	0.463 (0.072)	0.050 (0.017)	0.967	0.11	2.6	42
9.	X <sub>1</sub> CONX <sub>2</sub> X <sub>3</sub>	9.42 (0.15)	0.624 (0.036)	0	0	0.926 (0.090)	0.300 (0.024)	0.978	0.10	4.3	9



Table 1 continued

1	2	3	4	5	6	7	8	9	10	11	12
10. $X_1^{SOX}X_2$	8.99 (0.06)	0.303 (0.009)	-0.021 (0.001)	0.585 (0.066)	-	0	0.994	0.05	2.1	10	
11. $X_1^{CSX}X_2$	8.23 (0.29)	0.097 (0.050)	-0.073 (0.011)	0.911 (0.148)	-0.662 (0.197)	-0.231 (0.046)	0.980	0.10	4.3	17	
12. $X_1X_2X_3^{PO}$	9.58 (0.16)	0.231 (0.010)	-0.032 (0.004)	0.209 (0.086)	0.277 (0.038)	-	0.981	0.06	2.0	12	
14. $X_1^C \equiv CX_2$	9.55 (0.44)	0.273 (0.092)	-0.018 (0.012)	0.817 (0.268)	0.544 (0.314)	-0.016 (0.098)	0.970	0.16	5.7	17	

**Footnote:** The following compounds from the Appendix fit the correlation equations listed in this Table (the sequential number of the correlation from this Table is followed by the index of the reaction series and numbering of the compounds from the Appendix):

1. B:1-9, 11-13, 15, 16, 19-22; 2. B:2-5, 7-9, 11-14, 16, 19-22, 25, 28, 29, 31-33, 35-39, 41, 43, 48, 49, 51, 52, 55, 58; 3. C:1-9, 15-23, 27-32, 37-41, 44, 46, 47, 49, 50, 53-57, 59, 62; 4. C:1-8, 15-32, 37, 45, 50, 52-57, 59, 62; 5. A:1-13, 17-22, 25-35, 39-46; 6. I:1, 15, 16, 20, 22-34; 7. D:1-10, 13-32, 34, 40-51, 55, 56, 58-60, 62--76, 82, 89; 8. D:1-7, 9, 10, 12-34, 37, 40-43, 46-51; 9. D: 78-81, 83, 84, 87--89; 10. G:3, 5-13; 11. F:1-4, 6-8, 10-11, 13-20; 12. 3:4, 5, 7-11, 13, 15-18; 13. M:1-17, 22, 24, 25, 28-34, 36, 38-40, 47, 54, 55;

$IP_0$ ,  $a_1$ ,  $a_2$ ,  $a_3$ ,  $a_4$  and  $a_5$  are regression coefficients from the Eqn.(3); their statistical errors are given in the parenthesis. R - is the multiple correlation coefficient, s - the standard deviation,  $s\% = (s/\Delta IP_{\max})100$ , where  $\Delta IP_{\max}$  is the maximum range of the charge of the IP; n - the number of points involved. The zeros in the columns 4-8

Table 1 continued

refer to the statistically insignificant values of regression coefficients  $a_1$ , whereas the dash stands for the structural factor not included into the statistical treatment of the experimental data.

Table 2

Correlation Statistics of Regression Analysis of Vertical Ionization Potentials  
in Terms of Eqn.(3).

No	Class of Compounds	$IP_0$	$a_1$	$a_2$	$a_3$	$a_4$	$a_5$	R	a	s%	n
1	2	3	4	5	6	7	8	9	10	11	12
1.	XOH	9.25 (0.29)	0.664 (0.034)	-0.030 (0.007)	0.553 (0.393)	1.159 (0.215)		0.058	0.16	5.7	23
2.	XOH	9.23 (0.11)	0.776 (0.025)	-0.027 (0.003)	1.114 (0.182)	1.215 (0.081)	0.049 (0.008)	0.990	0.06	2.3	19
3.	$X_1OX_2$	10.09 (0.21)	0.670 (0.024)	-0.012 (0.003)	0	1.028 (0.089)	0.162 (0.031)	0.978	0.17	4.1	40
4.	$X_1SX_2$	8.51 (0.24)	0.314 (0.027)	-0.017 (0.005)	1.298 (0.311)	0.538 (0.102)	0	0.935	0.23	6.8	36

Continuation of Table 2

1	2	3	4	5	6	7	8	9	10	11
5.	$X_1X_2X_3N$	8.68 (0.39)	0.300 (0.019)	-0.031 (0.005)	1.027 (0.027)	0 (0.025)	-0.049 (0.025)	0.927	0.35	7.3 49
6.	$X_1X_2X_3N$	8.54 (0.25)	0.421 (0.017)	-0.020 (0.005)	-0.364 (0.169)	0.261 (0.067)	-0.023 (0.014)	0.981	0.22	4.6 37
7.	$X_1X_2X_3P$	8.25 (0.33)	0.321 (0.022)	0	0	0.645 (0.089)	0	0.937	0.31	8.9 15
8.	XCN	13.22 (0.23)	0.529 (0.057)	0	1.529 (0.294)	1.129 (0.223)	0.333 (0.060)	0.927	0.18	7.2 20
9.	XCl	11.28 (0.18)	0.551 (0.035)	-0.017 (0.005)	0.270 (0.184)	1.197 (0.190)	0.027 (0.027)	0.952	0.16	6.7 33
10.	XBr	10.45 (0.15)	0.44 (0.022)	0	0	0	0	0.937	0.14	7.4 27
11.	XI	9.78 (0.05)	0.403 (0.014)	-0.006 (0.002)	1.194 (0.108)	0.866 (0.058)	0.100 (0.014)	0.995	0.04	2.1 16
12.	$X_1COX_2$	9.79 (0.33)	0.242 (0.041)	-0.056 (0.008)	0.0004 (0.188)	-0.026 (0.182)	-0.148 (0.047)	0.914	0.25	6.4 50
13.	$X_1COX_2$	9.69 (0.25)	0.262 (0.030)	-0.064 (0.006)	-0.889 (0.182)	-0.007 (0.144)	-0.191 (0.041)	0.986	0.14	3.6 24
14.	$X_1CONX_2X_3$	9.82 (0.21)	0.630 (0.052)	0	-0.039 (0.237)	0.695 (0.139)	0.311 (0.031)	0.967	0.12	4.8 10
15.	$X_1X_2C\equiv CX_3X_4$	8.50 (0.24)	0.183 (0.013)	-0.012 (0.004)	0.758 (0.106)	0.246 (0.054)	0	0.945	0.20	5.9 36

Footnote

The following compounds from the Appendix fit equations listed in Table 2  
(for the additional explanations see Footnote to the Table 2)

1): 1. B: 1-9, 11-16, 19, 20, 21, 22, 25-27; 2. B: 1-5, 7-9, 11-15, 19, 20, 22, 25-27;  
3. B: 1-16, 19-23, 25, 38, 40, 41, 43, 48, 49, 51, 52, 57; 4. C: 1-10, 12-14, 26, 33,  
35-44, 46, 48, 51, 53, 58-65; 5. A: 1-32, 34-43, 45, 48-52; 6. A: 1-13, 17-22, 25-35,  
39-45; 7. I: 1, 2, 4, 6-8, 10, 12-19; 8. E: 1-19, 21; 9. J: 1-12, 14-22, 24, 26, 30, 31,  
33-40, 43, 44, 46, 51, 52, 53; 10. K: 2-22, 24-26, 28-30; 11. L: 1-8, 12, 16, 17,  
20-23; 12. D: 8-16, 19, 20, 30-32, 34, 35, 37, 38, 41-45, 49-66, 69, 70, 76, 81-84,  
88, 89; 13. D: 8-16, 20, 30, 32-35, 37, 39, 42-45, 49-51, 53; 14. D: 78-84, 87-89;  
15. M: 1-5, 7, 9-11, 13, 14, 16-18, 22, 24-27, 29, 31, 35, 36, 40, 41, 44-46, 48-55.



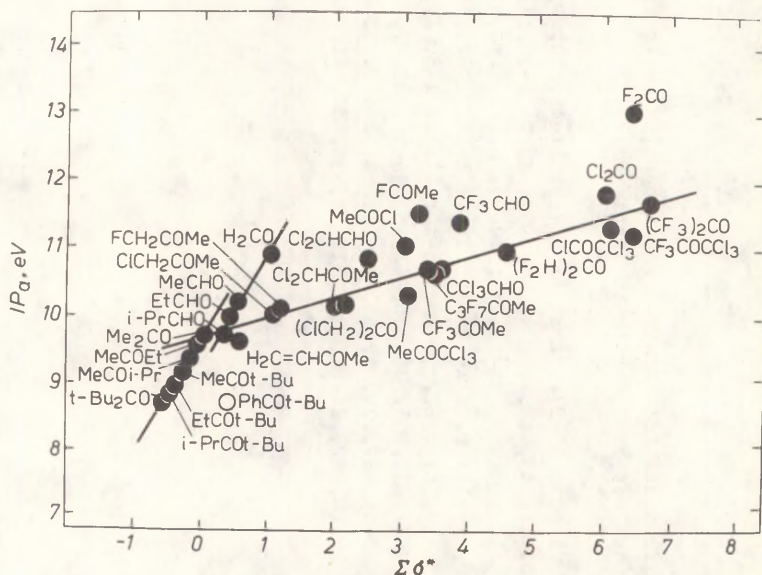


Fig. 1. The dependence of adiabatic IP of carbonyl compounds  $\text{X}_1\text{COX}_2$  on  $\Sigma\delta^*$

It follows from the above-said that for the alkyl substituents alongside with the relatively insignificant inductive effect an important role is being played by the characteristics which are connected primarily with the volume of

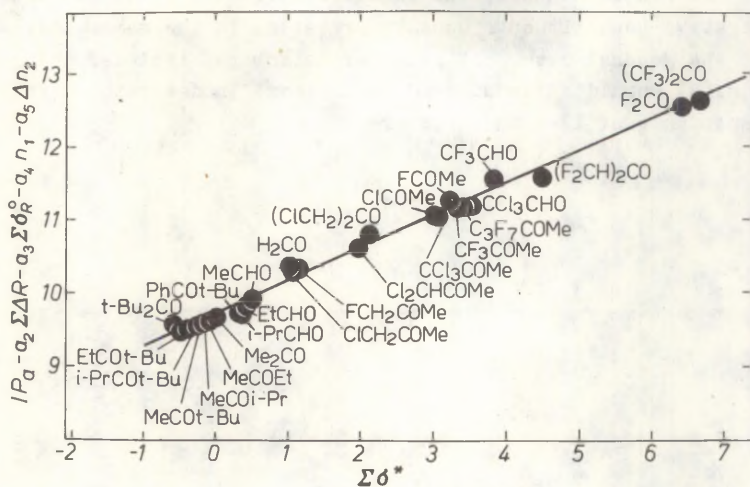


Fig. 2. The dependence of adiabatic IP of carbonyl compounds  $X_1COX_2$  corrected for the influence of the other structural factors on  $\Sigma\sigma^*$ .

the substituents connected primarily with the volume.

The molecular refractivity used for that purpose in the present work could be interpreted as a certain approximate measure of electronic polarizability of the substituents in the charge-induced dipole type interactions.

As one can expect, the inductive effect for the electro-negative substituents usually prevails. In the same time, in the general case, all structural factors, included into Eqn.(3) should be considered significant in determining the dependence of IP-s on structure.

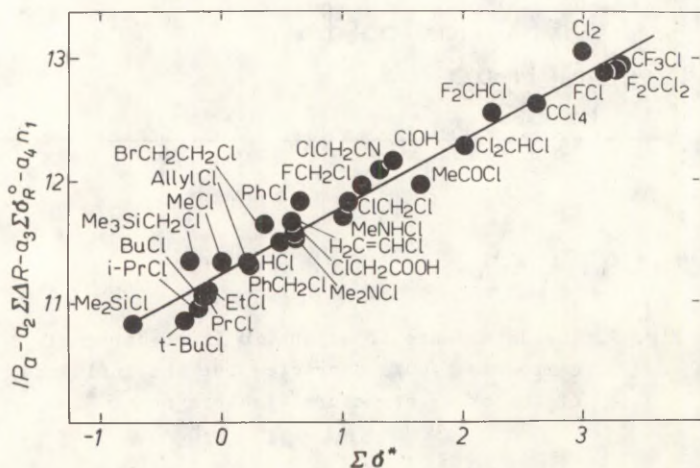


Fig. 3. The dependence of corrected IP values for IP of chlorides XCl on Taft inductive constants  $\delta^*$ .



Representation of the absolute contributions of different factors into the gross substituent effect in the form

$$\Delta IP_i = a_i \Delta X_i ,$$

where  $\Delta IP_i$  - contribution from the maximum change of  $i$ -th structural factor into IP

$a_i$  - regression coefficients from Eqn.(3)

$\Delta X_i$  - maximum range of changing the  $i$ -th factor

allows to estimate the relative importance of the maximum contributions of substituent effects of the different origin. Table 3 lists the calculated values of  $\Delta IP_v$  alongside with their relative values ( $\Delta IP_i$  for the inductive effect is taken equal to 100 per cent) for various classes of compounds.

It is evident that the relative importance of different structural factors into the gross substituent effect varies in the very wide range.

The cases of dominance of a single structural factor as well as the almost equal coexistence of all factors included are both represented.

Specifically, it follows from Tables 1, 2, and 4 that for the above-mentioned series of carbonyl compounds the non-resonance contribution (relative to the methyl group) of the alkyl substituents is mostly caused by the polarizability effect which dominates over the relatively constant contribution of the inductive effect, characteristic to the electronegative substituents. In the same time, the opposite is generally true for the electronegative substituents. It should be underlined that similar regularities hold also for the other series of compounds.

The analysis of the results of the statistical treatment of data on  $IP_a$  and  $IP_v$  in terms of Eqn.(3) leads to the following formal generalizations.

1. On condition of the inclusion of the electronegative substituents the contribution of the substituent inductive effect frequently dominates over the influence of the other

structural factors which are taken into the account by Eqn.(3). The typical  $a_1$  value of 0.5 corresponds to the "specific" inductive effect (the change of  $\sigma^*$  or  $\sum\sigma^*$  by one unit) ca 11.5 kcal/mol. However, in some real systems (the change of  $\sum\sigma^*$  values up to 9 units) the contribution of this effect into the gross substituent effect on IP values can reach much higher absolute values. For all series from Tables 1 and 2  $a_1 > 0$  which shows that the increase of the electronegativity of the substituent (the increase of the positive numerical values of  $\sigma^*$  or  $\sum\sigma^*$ ) results in the increase of the energy of the ionization of the electron from the given orbital.<sup>‡</sup>

Unfortunately, at the present moment the available experimental data on IP-s is not sufficient for the proper study of the very important problem of the attenuation of substituent inductive effect through attenuating fragments Z of aliphatic molecules  $X(Z)_nY$ , where X is the substituent, Y - ionization center and n is the integer (n= 0,1,2,3, etc.). For this purpose the statistical analysis of the data in terms of Eqn.(3) or its special variants should be made separately for the molecules with the different, fixed values of n thereby eliminating the use of the earlier assumed or fixed values of the attenuation factor of the inductive effect.

2. Polarizability term  $a_2 \sum \Delta R$  is also practically always statistically significant, whereas in all cases  $a_2 < 0$ . The latter condition manifests about the relative polarizational stabilization of the cation-radical as compared with the neutral molecule (more polarizable substituents lead to the decrease of the IP).

By its absolute value the contribution of this factor can sometimes be comparable with the influence of the inductive effect. So, despite the relatively low specific

<sup>‡</sup> Relatively high values of  $a_1$ , in its turn, are due to the very substantial differences of polarities of neutral molecule and cation-radical.

Table 4  
The Relative Contributions of Inductive and Polarizability  
Effects on IP-s of Carbonyl Compounds  $X_1COX_2$

No		$a_1 \sum \sigma^{Na}$	$a_2 \sum \Delta R^a$	%
1.	H <sub>2</sub> CO	0.43	-0.18	43
2.	MeCHO	0.22	-0.09	42
3.	EtCHO	0.17	0.00	0
4.	PrCHO	0.17	0.09	55
5.	i-PrCHO	0.13	0.09	72
6.	i-BuCHO	0.16	0.19	117
7.	MeCOEt	-0.04	0.09	233
8.	MeCOPr	-0.05	0.19	373
9.	MeCOiPr	-0.08	0.19	233
10.	Et <sub>2</sub> CO	-0.09	0.19	207
11.	MeCot-Bu	-0.13	0.28	215
12.	EtCot-Bu	-0.18	0.37	207
13.	Pr <sub>2</sub> CO	-0.10	0.37	373
14.	i-PrCot-Bu	-0.22	0.47	212
15.	i-Pr <sub>2</sub> CO	-0.17	0.37	220
16.	t-Bu <sub>2</sub> CO	-0.26	0.56	215
17.	F <sub>2</sub> CO	2.81	-0.19	7
18.	(CF <sub>3</sub> ) <sub>2</sub> CO	2.93	0.03	1
19.	FCOMe	1.40	-0.10	7
20.	ClCOMe	1.32	0.00	0
21.	ClCH <sub>2</sub> COMe	0.46	0.11	25
22.	FCH <sub>2</sub> COMe	0.51	0.00	0
23.	CF <sub>3</sub> COCCl <sub>3</sub>	2.81	0.30	II
24.	(F <sub>2</sub> CH) <sub>2</sub> CO	1.97	0.01	5
25.	t-BuCOPh	0.16	0.67	421
26.	MeCOMe	(0) <sup>b</sup>	(0) <sup>b</sup>	(100) <sup>b</sup>

a - See Footnote b for Table 3

b - By definition



the analysis of photoelectron spectra (assignment of PES bands for the molecules with several alternative ionization centers, etc.).

### Experimental

The PES spectrometer, designed and built at this university was used. The retarding field electrostatic analyser of electrons guarantees the resolution of 0.06 eV (at the electron energy of 5 eV).  $\text{HeI}_{\alpha}$  resonance line with the maximum energy 21.2 eV was used as ionization source. Argon was used for the internal reference .

Most of the reagents used in this work are commercially available. Their purity was controlled by g.l.c. Some compounds ( $\text{CF}_3\text{COH}$ ,  $\text{FCH}_2\text{CN}$ ,  $\text{CF}_3\text{CN}$ ,  $\text{MeOCH}_2\text{CF}_3$ ,  $\text{EtOCH}_2\text{CF}_3$ ,  $(\text{CF}_3\text{CH}_2)_2\text{O}$ ,  $\text{CNCH}_2\text{OMe}$ ,  $\text{HCOOCH}_2\text{CF}_3$ ,  $\text{HCOOCH}_2\text{CHF}_2$ ,  $\text{H}_2\text{NOH}$ ,  $\text{MeONH}_2$ ,  $\text{MeONMe}_2$ ,  $\text{F}_2\text{NH}$ ,  $(\text{CF}_3)_2\text{CO}$ ) were synthesized by the standard procedures. The corresponding PES and their analysis will be published in separate publication.

### References

1. I. Koppel, R. Pikver, and U. Mölder, 26th International Congress of Pure and Applied Chemistry, Tokyo, Japan, Sept. 4.-10., 1977. Abstracts, Session IV, p.909.
2. I.A. Koppel, U. Mölder, and R. Pikver, IUPAC The Chemical Society Perkin and Faraday Divisions Fourth International Symposium on Physical Organic Chemistry, York, England, 4.-8. Sept. 1978, Abstracts.
3. I. Koppel, R. Pikver and U. Mölder, in book E. Kungla et al. (Eds.), Magnetic Resonance and Related Phenomena, Springer Verlag, Heidelberg, 1979, p. 265.
4. L.S. Levitt and B.W. Levitt, I. Org. Chem., 37, 332 (1972).
5. B.W. Levitt and L.S. Levitt, Experientia, 26, 1183(1970).
6. B.W. Levitt and L.S. Levitt, Chem. Ind., 1970, 990.
7. B.W. Levitt and L.S. Levitt, Israel J. Chem., 2, 71 (1971).

8. L.S. Levitt and B.W. Levitt, Israel J. Chem., 9, 711 (1971).
9. L.S. Levitt and B.W. Levitt, G. Parkanyi, Tetrahedron, 28, 3369(1972).
10. L.S. Levitt, H.F. Widing, and B.W. Levitt, Can. J. Chem., 51, 3963(1973).
11. B.W. Levitt, H.F. Widing, and L.S. Levitt, Chem. Ind., 1973, 793.
12. F.H. van Cauwelaert, Bull. Soc. Chim. Belges, 80, 181 (1971).
13. F.I. Vilesov, Usp. phys. nauk, 81, 669 (1963).
14. F.I. Vilesov, D. Sci. Thesis, Leningrad University 1966.
15. P.K. Pöldoja and V.A. Palm, Reakts. sposobn. organ. soedin., 4, 786(1967).
16. B.A. Trofimov, U.H. Mölder, R.J. Pikver, E.P. Vyalykh and N.A. Nedolja, Izv.Akad.Nauk of U.S.S.R., Khimia, 12, 2731(1974).
17. B.A. Trofimov, U.H. Mölder, R.J. Pikver, and E.P. Vyalykh, Theor. and Exp. Khim. 11(2), 165(1975).
18. G.F. Crable and G.L. Kearns, J. Phys. Chem., 66, 436 (1962).
19. A. Foffani, S. Pignataro, B. Cantone, and F. Crasso, Z. Phys. Chem. (Frankfurt), 42, 221 (1964).
20. A. Foffani, G. Innorta, and D. Distefano, Z. Phys. Chem., (Frankfurt), 49, 291 (1966).
21. A. Streitwieser, Progress in Phys. Org. Chemistry, 1, 6, J. Wiley, N.-Y., 1963.
22. A.G. Harrison, P. Kebarle, and F.P. Lossing, J. Am. Chem. Soc., 83, 777 (1961).
23. R.F. Pollie and F.P. Lossing, J. Am. Chem. Soc., 85, 269 (1963).
24. M. Charton and B.I. Charton, J. Org. Chem., 34, 1882 (1969).
25. K. Watanabe, J. Chem. Phys., 26, 542(1957).

26. I.A. Koppel, U.H. Mölder, and R.J. Pikver, This Journal, 17, 457(1980)
27. I.A. Koppel and M.M. Karelson, This Journal, 11, 985 (1975).
28. I.A. Koppel, M.M. Karelson, and V.A. Palm, Reakts. sposobn. organ. soedin., 10, 497(1973).
29. V.A. Minkin and Yu.A. Zhdanov, Correlation Analysis in Organic Chemistry, Rostov-on-the-Don University Press, Rostov, 1966 (in Russian).
30. B.V. Ioffe, Refractometric Analysis in Chemistry, Khimia, Leningrad, 1974 (in Russian).
31. V.A. Palm, Foundations of the Quantitative Theory of Organic Reactions, Khimia, Leningrad, 1977 (in Russian).
32. The values of IP-s listed in the Appendix are mostly taken from the following sources:
  - a) Progress in Photonics, Issues 1,2, and 5, Leningrad University Press, 1969, 1971, 1975.
  - b) H.M. Rosenstock, K. Draxl, B.M. Seiner, and J.T. Heron, "Energetics of Gaseous Ions", J. Phys. Chem. Ref. Data, Suppl. nr. 1,6 (1977).
  - c) D.W. Turner, C. Baker, A.D. Baker, and C.R. Brundle, "Molecular Photoelectron Spectroscopy" Wiley, London, 1970.
  - d) Since this paper was submitted some interesting experimental data on IP have become available. In the proof stage, part of these data (IP-s of fluoramines and perfluoralkyl amines by H. Bürger, G. Pawelke, R. Dammel, and H. Bock, J. Fluorine Chem., 19, 565(1982)) was included into the Appendix and subsequently was also taken into account in the statistical treatment of IP of organic amines according to Eqn.(3).



# APPENDIX

The used values of  $IP_a$  and  $IP_v$  (in eV)<sup>a</sup>

## A. Amines.

1.  $NH_3$ :10.18, 10.84; 2.  $MeNH_2$ :9.08, 9.66; 3.  $EtNH_2$ :8.8, 9.53;
4.  $PrNH_2$ :8.78, 9.37; 5.  $i-PrNH_2$ :8.72, 9.31; 6.  $BuNH_2$ :8.71, 9.4; 7. cyclo- $C_3H_5NH_2$ :8.84, 9.43; 8.  $FCH_2CH_2NH_2$ :9.11,
- 9.86; 9.  $CF_3CH_2NH_2$ :9.97, 10.35; 10.  $CF_3(CH_2)_2NH_2$ :9.31, 9.70;
11.  $H_2C=CHCH_2NH_2$ :8.76, 9.44; 12.  $(CF_3)_3CNH_2$ :10.4, 11.10;
13.  $HOCH_2CH_2NH_2$ :8.96, 9.71; 14.  $MeONH_2$ :9.55, 10.16;
15.  $HONH_2$ :10.0, 10.56; 16.  $CINH_2$ :9.55, 10.52; 17.  $Me_2NH$ :8.3
- 8.94; 18.  $MeEtNH$ :8.15, 8.73; 19.  $Pr_2NH$ :7.84, 8.59;
20.  $i-Bu_2NH$ :7.8, 8.45; 21.  $2-Bu_2NH$ :7.63, 8.28;  $Et_2NH$ :11.93,
- 12.36; 23.  $Cl_2NH$ :9.98, 10.56; 24.  $CINHMe$ :9.19, 9.80;
25.  $Me_3N$ :7.87, 8.55; 26.  $Et_3N$ :7.42, 8.13; 27.  $Pr_3N$ :7.23,
- 7.92; 28.  $Bu_3N$ :6.98, 7.86; 29.  $Me_2EtN$ :7.79, 8.47; 30.  $MeEt_2N$ :
- 7.63, 8.35; 31.  $PNiEt_2$ :7.67, 8.32; 32.  $NCCH_2NMe_2$ :8.86, 9.22;
33.  $NF_3$ :12.97, 13.73; 34.  $CF_3NMe_2$ :9.22, 9.99; 35.  $CF_3CH_2NMe_2$ :
- 8.26, 8.98; 36.  $NCI_3$ :10.12, 10.69; 37.  $CINHMe_2$ :8.67, 9.31;
38.  $Cl_2NMe$ :9.35, 10.01; 39.  $F_2CHNF_2$ :11.5, 12.33;
40.  $(F_2CH)_3N$ :11.2, 11.65; 41.  $OF_3N(CHF_2)_2$ :11.4, 12.08;
42.  $(CF_3)_2NCHF_2$ :11.7, 12.35; 43.  $(CF_3)_2NF$ :11.6, 12.45; 44.
- $CF_3NF_2$ :11.9, 12.62; 45.  $(CF_3)_3N$ :11.7, 12.52; 46.  $(C_4F_9)_3N$ :
- 11.30, 12.00; 47.  $MeONMe_2$ :8.78, -; 48.  $H_2NNH_2$ :9.04, 9.93;
49.  $H_2NNHMe$ :8.4, 9.3; 50.  $MeHNNHMe$ :8.22, 9.00; 51.  $H_2NNMe_2$ :
- 8.05, 8.80; 52.  $Me_2NNMe_2$ :7.93, 8.27; 53.  $Et_2NCN$ :8.97, 9.32;
54.  $(NCCH_2CH_2)_3N$ :10.40, 11.26.

## B. Water, alcohols, ethers.

1.  $H_2O$ :12.62, 12.62; 2.  $MeOH$ :10.85, 10.94; 3.  $EtOH$ :10.48,
- 10.64; 4.  $PrOH$ :10.32, 10.49; 5.  $i-PrOH$ :10.16, 10.36;
6.  $t-BuOH$ :9.7, 10.23; 7.  $BuOH$ :10.04, 10.37; 8.  $2-BuOH$ :10.1,
- 10.35; 9.  $i-BuOH$ :10.09, 10.47; 10.  $HC\equiv CCH_2OH$ :10.51, 10.92;
11.  $CF_3CH_2OH$ :11.49, 11.70; 12.  $CCl_3CH_2OH$ :10.94, 11.34;
13.  $ClCH_2CH_2OH$ :10.52, 10.85; 14.  $FOH$ :12.69, 13.0; 15.  $H_2O_2$ :
- 10.62, 11.7; 16.  $(CF_3)_2CHOH$ :11.94, 12.26; 17.  $H_2C=CHCH_2OH$ :

9.63, 10.16; 18. PhOH:11.22, 11.56; 19.  $C_3F_7CH_2OH$ :11.2, 11.62; 20.  $CCl_3Me_2COH$ :10.38, 10.7; 21.  $(CF_3)_3COH$ :12.25, 12.58; 22.  $NCCMe_2OH$ :11.09, 11.32; 23.  $(CF_3)_3CCH_2OH$ :11.48, 11.68; 24.  $ClOH$ :11.12, 11.22; 25.  $FCH_2CH_2OH$ :10.8, 11.05; 26.  $C_2F_5CH_2OH$ : -, 11.68; 27.  $NH_2OH$ : -, 11.69; 28.  $Me_2O$ :9.94, 10.04; 29.  $MeOEt$ :9.74, 9.74; 30.  $Et_2O$ : -, 9.5; 31.  $Pr_2O$ : 9.28, 9.32; 32.  $i-Pr_2O$ :9.2, 9.2; 33.  $t-BuOEt$ :9.25, 9.39; 34.  $t-BuOMe$ :9.40, 9.48; 35.  $CF_3CH_2OEt$ :10.27, 10.35; 36.  $CF_3CH_2OMe$ : 10.53, 10.69; 37.  $t-Bu_2O$ :8.81, 9.16; 38.  $Bu_2O$ :9.18, 9.51; 39.  $MeOSiMe_3$ :9.61, 9.85; 40.  $(H_2C=CHCH_2)_2O$ :9.26, 9.63; 41.  $F_2O$ :13.11, 13.25; 42.  $Cl_2O$ :10.94, 11.02; 43.  $Cl_2CHOMe$ : 10.84, 10.98; 44.  $H_2C=CHOMe$ :11.8, 12.05; 45.  $PhOMe$ :10.6, 11.02; 46.  $H_2C=CHCH_2OEt$ :9.26, 9.6; 47.  $(Me_3Si)_2O$ :9.49, 9.84; 48.  $NCCH_2OMe$ :10.75, 10.96; 49.  $MeONH_2$ :10.46, 10.93; 50.  $(MeCO)_2O$ :10.42, 10.69; 51.  $MeONHMe$ : 9.97, 10.22; 52.  $((CF_3)_3C)_2O$ :12.68, 13.3; 53.  $(CF_3CO)_2O$ :11.62, 11.91; 54.  $HCF_2CF_2OEt$ :10.78, 11.80; 55.  $ClCH_2OEt$ :10.81, -, 56.  $Ph_2O$  -, 11.38; 57.  $CF_3OF$ : -, 13.63; 58.  $(ClCH_2CH_2)_2O$ :9.85, -;

#### C. Hydrogen sulfide, mercaptanes, thioethers.

1.  $H_2S$ :10.42, 10.43; 2.  $MeSH$ :9.44, 9.44; 3.  $EtSH$ :9.29, 9.29; 4.  $PrSH$ :9.19, 9.19; 5.  $BuSH$ :9.14, 9.15; 6.  $i-PrSH$ :9.14, 9.14; 7.  $i-BuSH$ :9.12, 9.12; 8.  $2-BuSH$ :9.10, 9.10; 9.  $H_2C=CHCH_2SH$ : 9.25, 9.25; 10.  $CF_3SH$ : -, 11.35; 11.  $PhSH$ :8.25, 8.51; 12.  $PhCH_2SH$ : -, 9.25; 13.  $H_2S_2$ : -, 10.01; 14.  $Me_3SiCH_2SH$ : -, 8.68; 15.  $Me_2S$ :8.68, -; 16.  $MeSEt$ :8.55, -; 17.  $Et_2S$ :8.44, -; 18.  $EtSPr$ :8.37, -; 19.  $Pr_2S$ :8.31, -; 20.  $BuS$ :8.22, -; 21.  $i-BuSPr$ :8.22, -; 23.  $i-Bu_2S$ :8.20, -; 24.  $i-Pr_2S$ :8.25, -; 25.  $i-PrSEt$ :8.35, -; 26.  $t-Bu_2S$ :8.07, 8.18; 27.  $t-BuSPr$ :8.25, -; 28.  $EtSBu$ :8.32, -; 29.  $PrSBu$ :8.26, -; 30.  $2-BuSEt$ :8.2, -; 31.  $i-BuSEt$ :8.32, -; 32.  $i-BuSBu$ :8.21, -; 33.  $t-BuSMe$ : -, 8.38; 34.  $MeSPr$ : -, 8.49; 35.  $MeSCl$ : -, 9.2; 36.  $CF_3SCl$ : -, 10.7; 37.  $(ClCH_2CH_2)_2S$ :8.52, 8.77; 38.  $H_2C=CHSEt$ :8.21, 8.50; 39.  $H_2C=CHSPr$ :8.16, 8.34; 40.  $H_2C=CHSt$ :7.92, 8.33; 41.  $(H_2C=CH)_2S$ :8.25, 8.44;

42.  $(H_2C=CHCH_2)_2S$ : 8.3, 8.55; 43.  $H_2C=CHCH_2S$ Et: -, 8.51;  
 44.  $PhSCH=CH_2$ : 7.96, 8.18; 45.  $i-BuSCH=CH_2$ : 8.62, -; 46.  $PhS$ Et:  
 7.86, 8.01; 47.  $Ph_2S$ : 7.81, -; 48.  $PhSMe$ : 7.96, 8.12; 49.  
 $PhSP$ r: 7.81, -; 50.  $(PhCH_2)_2S$ : 8.05, -; 51.  $H_2C=CHCH_2SPh$ : 7.91,  
 8.13; 52.  $Me_2S$ : 8.3, 9.01; 53.  $(CF_3)_2S$ : 11.11, 11.35;  
 54.  $(CF_3)_2S_2$ : 10.6, -; 55.  $CF_3SMe$ : 9.88, -; 56.  $MeSCN$ : 10.07, -;  
 57.  $EtSCN$ : 9.89, -; 58.  $H_2C=CHSMe$ : -, 8.45; 59.  $Cl_2S$ : 9.49, 9.7;  
 60.  $t-BuSPh$ : -, 8.17; 61.  $PhCH_2SMe$ : -, 8.42; 62.  $ClCH_2SCN$ :  
 10.29, 10.38; 63.  $(CN)_2S$ : -, 11.32; 64.  $HC=CSMe$ : -, 8.81;  
 65.  $(Me_3SiCH_2)_2S$ : -, 7.76; 66.  $NCCH_2CH_2SBu$ : 8.69, -; 67.  
 $MeOCH_2CH_2S$ Et: 8.20, 8.63.

D. Aldehydes, ketones, amides, carboxylic  
acids, esters

1.  $H_2CO$ : 10.88, -; 2.  $MeCHO$ : 10.2, -; 3.  $EtCHO$ : 9.97, -;  
 4.  $PrCHO$ : 9.86, -; 5.  $i-PrCHO$ : 9.69, -; 6.  $BuCHO$ : 9.82, -;  
 7.  $i-BuCHO$ : 9.68, -; 8.  $FCHO$ : 11.4, 12.55; 9.  $CF_3CHO$ : 11.35,  
 11.66; 10.  $CCl_3CHO$ : 10.7, 10.89; 11.  $Cl_2CHCHO$ : -, 10.83;  
 12.  $HC=CCHO$ : 10.7, 10.8; 13.  $Me_2CO$ : 9.69, 9.7; 14.  $MeCOEt$ :  
 9.51, 9.56; 15.  $MeCOPr$ : 9.39, 9.45; 16.  $i-PrCOMe$ : 9.3, 9.36;  
 17.  $Et_2CO$ : 9.33, -; 18.  $MeCOBu$ : 9.36, -; 19.  $i-BuCOMe$ : 9.34,  
 9.42; 20.  $t-BuCOMe$ : 9.14, 9.21; 21.  $i-PrCOEt$ : 9.14, -;  
 22.  $t-BuCOEt$ : 8.98, -; 23.  $Pr_2CO$ : 9.12, -; 24.  $PrCOBu$ : 9.1, -;  
 25.  $i-PrCot-Bu$ : 8.82, -; 26.  $t-Bu_2CO$ : 8.71, -; 27.  $i-Bu_2CO$ :  
 9.04, -; 28.  $i-Pr_2CO$ : 8.96, -; 29.  $EtCOBu$ : 9.15, -; 30. (cyclo-  
 $C_3H_5$ ) $_2CO$ : 9.27, 9.27; 31.  $Cl_2CO$ : 11.55, 11.83; 32.  $ClCOMe$ : 11.05,  
 11.1; 33.  $F_2CO$ : 13.02, 13.6; 34.  $(CF_3)_2CO$ : 11.67, 12.09; 35.  
 $(CN)_2CO$ : 12.56, 12.56; 36.  $Br_2CO$ : -, 11.6; 37.  $FCOMe$ : 11.51,  
 11.8; 38.  $H_2C=CHCOMe$ : -, 9.61; 39.  $(MeCO)_2$ : 9.23, 9.55;  
 40.  $ClCH_2COMe$ : 9.98, -; 41.  $(ClCH_2)_2CO$ : 10.15, 10.26; 42.  
 $CF_3COMe$ : 10.68, 10.94; 43.  $CCl_3COCF_3$ : 10.92, 11.19; 44.  $ClCOGCl_3$ :  
 11.02, 11.31; 45.  $MeCOBr$ : 10.55, 10.68; 46.  $Cl_2CHCOMe$ : 10.12,  
 -; 47.  $CCl_3COMe$ : 10.29, -; 48.  $C_3F_7COMe$ : 10.58, -; 49.  $FCH_2COMe$ :  
 10.09, 10.2; 50.  $(F_2CH)_2CO$ : 10.96, 11.23; 51.  $t-BuCOPh$ : 8.7,  
 8.98; 52.  $ClCH_2COCl$ : -, 10.3; 53.  $Cl_2CHCOCl$ : -, 11.27;



54.  $\text{HCOOH}$ :11.33, 11.51; 55.  $\text{MeCOOH}$ :10.67, 10.84; 56.  $\text{EtCOOH}$ :  
10.54, 10.72; 57.  $\text{PrCOOH}$ :10.46, 10.64; 58.  $i\text{-PrCOOH}$ :10.33,  
10.50; 59.  $\text{CF}_3\text{COOH}$ :11.46, 11.77; 60.  $\text{ClCH}_2\text{COOH}$ :10.35, 10.99;  
61.  $\text{BrCH}_2\text{COOH}$ : -, 11.0; 62.  $\text{HCOOMe}$ :10.85, 11.02; 63.  $\text{HCOOEt}$ :  
10.62, 10.96; 64.  $\text{MeCOOMe}$ :10.27, 10.48; 65.  $\text{MeCOOEt}$ :10.24,  
10.39; 66.  $\text{CF}_3\text{COOEt}$ :11.07, 11.60; 67.  $\text{EtCOOMe}$ :10.15, -;  
68.  $\text{EtCOOEt}$ :10.6, -; 69.  $\text{PrCOOMe}$ :10.07, 10.29; 70.  $i\text{-PrCOOMe}$ :  
9.98, 10.30; 71.  $\text{F}_2\text{CHCOOEt}$ :10.75, 11.09; 72.  $\text{CNCOOEt}$ :11.37, 11.89;  
73.  $\text{CNCH}_2\text{COOMe}$ : -, 10.87; -; 74.  $\text{CCl}_3\text{COOEt}$ :10.44, -;  
75.  $\text{ClCH}_2\text{COOMe}$ :10.35, -; 76.  $\text{H}_2\text{C}=\text{CHCOOMe}$ : -, 11.12;  
77.  $(\text{MeOCO})_2$ : -, 10.36; 78.  $\text{HCONH}_2$ :10.13, 10.32;  
79.  $\text{HCONHMe}$ :9.79, 9.87; 80.  $\text{HCONMe}_2$ :9.14, 9.25; 81.  $\text{MeCONH}_2$ :  
9.62, 9.95; 82.  $\text{MeCONHMe}$ :9.79, 9.87; 83.  $\text{MeCONMe}_2$ :8.82, 9.43;  
84.  $(\text{H}_2\text{N})_2\text{CO}$ :9.8, 10.28; 85.  $\text{H}_2\text{NCONHMe}$ :9.25, 9.66;  
86.  $(\text{MeNH})_2\text{CO}$ :8.9, 9.23; 87.  $(\text{Me}_2\text{N})_2\text{CO}$ :8.46, 8.72;  
88.  $\text{CF}_3\text{CONH}_2$ :10.77, 11.23; 89.  $\text{FCH}_2\text{CONH}_2$ :10.19, 10.38;  
90.  $(\text{FCH}_2)_2\text{CO}$ :10.46, 10.58.

#### E. Nitriles<sup>b</sup>

1.  $\text{HCN}$ :13.82; 2.  $\text{MeCN}$ :13.11; 3.  $\text{EtCN}$ :12.85; 4.  $(\text{CN})_2\text{CH}_2$ :  
13.91; 5.  $\text{FCH}_2\text{CN}$ :13.60; 6.  $(\text{CN})_2$ :14.68; 7.  $\text{CCl}_3\text{CN}$ :13.87;  
8.  $\text{ClCH}_2\text{CN}$ :13.59; 9.  $\text{ClCN}$ :13.80; 10.  $\text{BrCN}$ :13.54; 11.  $\text{PhCN}$ :  
12.62; 12.  $\text{MeSCN}$ :12.85; 13.  $\text{Me}_2\text{NCN}$ :11.87; 14.  $\text{H}_2\text{C}=\text{CHCN}$ :  
13.00; 15.  $\text{CF}_3\text{CN}$ :14.39; 16.  $\text{ClCH}_2\text{CH}_2\text{CN}$ :13.24; 17.  $\text{HC}\equiv\text{CCN}$ :  
13.54; 18.  $\text{ICN}$ :13.41; 19.  $\text{Cl}_2\text{CHCN}$ :13.92; 20.  $\text{FCN}$ :14.56;  
21.  $\text{H}_2\text{NCN}$ :12.98.

#### F. Compounds $\text{X}_1\text{X}_2\text{CS}^b$

1.  $\text{H}_2\text{CS}$ :9.33; 2.  $\text{Cl}_2\text{CS}$ :9.84; 3.  $(\text{NH}_2)_2\text{CS}$ :8.41;  
4.  $\text{H}_2\text{N}(\text{CS})\text{NHMe}$ :8.29; 5.  $\text{Me}_2\text{N}(\text{CS})\text{NH}_2$ :8.34; 6.  $\text{Me}_2\text{N}(\text{CS})\text{NHMe}$ :  
7.93; 7.  $(\text{Me}_2\text{N})_2\text{CS}$ :7.84; 8.  $(\text{MeHN})_2\text{CS}$ :8.08; 9.  $\text{F}_2\text{CS}$ :10.64;  
10.  $\text{F}(\text{CS})\text{Cl}$ :10.2; 11.  $\text{H}(\text{CS})\text{NH}_2$ :8.69; 12.  $\text{H}(\text{CS})\text{NMe}_2$ :8.16;  
13.  $\text{Me}(\text{CS})\text{NH}_2$ :8.36; 14.  $\text{Me}(\text{CS})\text{NMe}_2$ :7.86; 15.  $\text{CF}_3\text{S}(\text{CS})\text{F}$ :  
10.12; 16.  $\text{CF}_3\text{S}(\text{CS})\text{Cl}$ :9.57; 17.  $(\text{CF}_3\text{S})_2\text{CS}$ :9.25;  
18.  $(\text{MeS})_2\text{CS}$ :8.5; 19.  $(\text{MeO})_2\text{CS}$ :8.99;  $\text{Me}(\text{CS})\text{MeO}$ :8.71.

### G. Sulfoxides<sup>b</sup>

1.  $\text{F}_2\text{SO}$ :12.6; 2.  $\text{Cl}_2\text{SO}$ :11.13; 3.  $\text{Br}_2\text{SO}$ :10.54; 4.  $(\text{MeO})_2\text{SO}$ :10.25; 5.  $(\text{Me}_2\text{N})_2\text{SO}$ :8.53; 6.  $\text{Me}_2\text{SO}$ :9.01; 7.  $\text{Et}_2\text{SO}$ :8.76; 8.  $t\text{-Bu}_2\text{SO}$ :8.18; 9.  $\text{Pr}_2\text{SO}$ :8.60; 10.  $i\text{-Pr}_2$ :8.46; 11.  $\text{H}_2\text{C}=\text{CH}(\text{SO})\text{Me}$ :9.02; 12.  $\text{Me}(\text{SO})\text{Ph}$ :8.79; 13.  $\text{Ph}_2\text{SO}$ :8.58.

### H. Phosphine oxides

1.  $\text{Me}_3\text{PO}$ : -, 9.90; 2.  $\text{H}(\text{PO})\text{Me}_2$ : -, 10.32; 3.  $\text{F}_3\text{PO}$ :12.77, 13.52; 4.  $\text{Cl}_3\text{PO}$ :11.49, 11.91; 5.  $\text{Cl}_2(\text{PO})\text{NMe}_2$ :10.73, 11.28; 6.  $(\text{NMe}_2)_3\text{PO}$ :9.68, 10.44; 7.  $(\text{MeO})_3\text{PO}$ :10.24, 10.81; 8.  $\text{EtO}(\text{PO})\text{Cl}_2$ :11.05, 11.46; 9.  $(\text{EtO})_3\text{PO}$ :9.79, 10.54; 10.  $\text{Me}(\text{PCl})\text{Cl}_2$ :10.92, 11.49; 11.  $(\text{ClCH}_2)_2(\text{PO})\text{Cl}$ :10.46, 10.75; 12.  $(\text{ClCH}_2)_2(\text{PO})\text{OEt}$ : -, 10.19; 13.  $(\text{EtO})_2(\text{PO})\text{Cl}$ :10.29, 10.96; 14.  $(\text{Me}_2\text{N})_2(\text{PO})\text{Cl}$ : -, 10.90; 15.  $\text{H}(\text{PO})(\text{MeO})_2$ :10.53, 11.10; 16.  $\text{Me}(\text{PO})(\text{MeO})_2$ :10.0, 10.53; 17.  $\text{H}(\text{PO})(\text{EtO})_2$ :10.31, 10.86; 18.  $\text{H}_2\text{C}=\text{CH}(\text{PO})\text{Cl}_2$ :10.81, 11.24; 19.  $\text{Me}_2(\text{PO})\text{Cl}$ : -, 10.77; 20.  $\text{ClCH}_2(\text{PO})\text{Cl}_2$ : -, 11.50; 21.  $(\text{EtO})_2(\text{PO})\text{SMe}$ :8.93, 9.26; 22.  $\text{Cl}_2(\text{PO})\text{SMe}$ :9.82, 10.20.

### I. Phosphines.

1.  $\text{PH}_3$ :9.96, 10.6; 2.  $\text{H}_2\text{PMe}$ :9.12, 9.6; 3.  $\text{HPMe}_2$ :8.47, -; 4.  $\text{PMe}_3$ : -, 8.60; 5.  $\text{H}_2\text{PEt}$ : -, 8.36; 6.  $(\text{CF}_3)_3\text{P}$ : -, 11.57; 7.  $\text{Bu}_3\text{P}$ : -, 8.0; 8.  $\text{HPF}_2$ : -, 11.0; 9.  $\text{PF}_3$ :11.66, 12.29; 10.  $\text{ClPF}_2$ : -, 11.5; 11.  $\text{PCl}_3$ : -, 10.51; 12.  $\text{F}_2\text{PCN}$ : -, 11.9; 13.  $(\text{CF}_3)_2\text{PCl}$ : -, 11.13; 14.  $\text{CF}_3\text{PCl}_2$ : -, 10.70; 15.  $\text{ClCH}_2\text{PCl}_2$ :9.58, 10.17; 16.  $(\text{ClCH}_2)_2\text{PCl}$ :9.38, 9.85; 17.  $(\text{CF}_3)_2\text{PH}$ : -, 11.50; 18.  $\text{H}_2\text{PCF}_3$ : -, 11.18; 19.  $\text{MePBu}_2$ : -, 8.20; 20.  $t\text{-Bu}_3\text{P}$ :7.70, -; 21.  $t\text{-Bu}_2\text{PMe}$ :8.35, -; 22.  $t\text{-Bu}_2\text{PCl}$ :8.45, -; 23.  $t\text{-Bu}_2\text{PF}$ :8.50, -; 24.  $\text{Me}_2\text{PCl}$ :9.20, -; 25.  $t\text{-BuPH}_2$ :9.30, -; 26.  $t\text{-BuPCl}_2$ :9.30, -; 27.  $\text{Me}_2\text{PF}$ :9.35, -; 28.  $\text{MePCl}_2$ :9.85, -; 29.  $t\text{-BuPF}_2$ :9.65, -; 30.  $\text{MePF}_2$ :10.35, -; 31.  $\text{HPEt}_2$ :8.52, -; 32.  $i\text{-PrPH}_2$ :9.43, -;  $\text{BuPH}_2$ :9.50, -; 34.  $\text{PrPH}_2$ :9.54, -.

# J. Chlorides<sup>b</sup>

1. HCl:12.78; 2. MeCl:11.33; 3. EtCl:11.01; 4. PrCl:10.88; 5. BuCl:10.84; 6. i-PrCl:10.78; 7. t-BuCl:10.61; 8. i-BuCl:10.66; 9. cyclo-C<sub>6</sub>H<sub>11</sub>Cl:10.67; 10. CCl<sub>4</sub>:12.39; 11. ClCH<sub>2</sub>Cl:11.81; 12. Cl<sub>2</sub>CHCl:12.19; 13. FeCl<sub>3</sub>:12.6; 14. CF<sub>3</sub>Cl:13.0; 15. F<sub>2</sub>CHCl:12.6; 16. FCHCl<sub>2</sub>:12.45; 17. FCH<sub>2</sub>Cl:11.9; 18. F<sub>2</sub>CCl<sub>2</sub>:12.9; 19. CFCF<sub>3</sub>:12.65; 20. ClCH=CHCH<sub>2</sub>Cl:11.5; 21. H<sub>2</sub>C=CHCl:11.61; 22. H<sub>2</sub>C=CHCH<sub>2</sub>Cl:11.23; 23. ClCH=CHCl:11.90; 24. PhCl:11.51; 25. Cl<sub>2</sub>CO:12.66; 26. MeCOCl:12.0; 27. ClCH<sub>2</sub>CHO:11.75; 28. CCl<sub>3</sub>CHO:12.42; 29. ClCH<sub>2</sub>COCl:11.81; 30. ClCH<sub>2</sub>COOH:11.5; 31. ClCH<sub>2</sub>CN:12.05; 32. Cl<sub>2</sub>CHCN:12.4; 33. FeCl<sub>2</sub>:12.86; 34. Cl<sub>2</sub>S:12.46; 35. Cl<sub>2</sub>:12.36; 36. ClCF<sub>2</sub>CF<sub>2</sub>Cl:12.89; 37. PhCH<sub>2</sub>Cl:10.9; 38. BrCH<sub>2</sub>CH<sub>2</sub>Cl:11.46; 39. ClCH<sub>2</sub>CH<sub>2</sub>Cl:11.5; 40. Me<sub>2</sub>SiCH<sub>2</sub>Cl:11.0; 41. NCCl<sub>2</sub>CH<sub>2</sub>Cl:11.6; 42. H<sub>2</sub>NCI:11.95; 43. Me<sub>2</sub>NCI:11.19; 44. HOC1:12.27; 45. Cl<sub>2</sub>CHCHO:12.36; 46. MeCHCl<sub>2</sub>:11.58; 47. CF<sub>3</sub>COCCl<sub>3</sub>:12.7; 48. CCl<sub>3</sub>CH<sub>2</sub>OH:12.5; 49. ClCH<sub>2</sub>SCN:11.77; 50. CCl<sub>3</sub>CMc<sub>2</sub>OH:12.41; 51. MeNHCl:11.47; 52. Me<sub>3</sub>SiCl:10.58; 53. ClNO<sub>2</sub>:12.08; 54. PF<sub>2</sub>Cl:12.8; 55. SiH<sub>3</sub>Cl:11.65; 56. SiF<sub>3</sub>Cl:13.44.

# K. Bromides<sup>b</sup>

1. HBr:11.83; 2. MeBr:10.69; 3. EtBr:10.44; 4. PrBr:10.34; 5. BuBr:10.30; 6. i-PrBr:10.23; 7. t-BuBr:10.10; 8. i-BuBr:10.25; 9. Br<sub>2</sub>:11.83; 10. FeBr:11.78; 11. BrCH<sub>2</sub>Br:11.0; 12. CHBr<sub>3</sub>:11.19; 13. CF<sub>3</sub>Br:12.0; 14. H<sub>2</sub>C=CHBr:10.87; 15. H<sub>2</sub>C=CHCH<sub>2</sub>Br:10.65; 16. PhBr:10.9; 17. PhCH<sub>2</sub>Br:10.36; MeCOBr:11.1; 19. BrCN:11.94; 20. BrCH<sub>2</sub>CH<sub>2</sub>OH:10.63; 21. Me<sub>2</sub>SiBr:10.24; 22. BrCH<sub>2</sub>CH<sub>2</sub>Br:10.81; 23. BrCF<sub>2</sub>CH<sub>2</sub>Br:11.28; 24. ClCH<sub>2</sub>CH<sub>2</sub>Br:10.8; 25. BrCF<sub>2</sub>CF<sub>2</sub>Br:11.9; 26. cyclo-C<sub>6</sub>H<sub>4</sub>Br:10.13; 27. H<sub>2</sub>NBr:11.27; 28. Me<sub>2</sub>NBr:10.56; 29. MeNHBr:10.92; 30. BrCH<sub>2</sub>COOH:10.8.

# L. Iodides<sup>b</sup>

1. HI:10.71; 2. MeI:9.81; 3. EtI:9.65; 4. PrI:9.56; 5. BuI:9.5; 6. i-PrI:9.44; 7. i-BuI:9.46; 8. t-BuI:9.27; 9. SiH<sub>3</sub>I:



polarizability effect (for  $a_2 = -0.03$  and  $\Delta R = 1.0$  it equals 0.7 kcal/mol) for the average values of  $a_2 = -0.03$  and  $\Sigma \Delta R = 10.0$  corresponds the change (decrease) of IP by almost 7 kcal/mol.

3. In most series the contribution from the resonance effect is also significant. As a rule  $a_3 > 0$  which refers to the relative resonance stabilization of the cation-radical. Only for the series of carbonyl compounds ( $X_1COX_2$ ,  $X_1COOX_2$ ) and phosphine oxides the statistical treatment leads to the negative values of  $a_3$ . Formally, the latter, corresponds to the extra resonance stabilization of the neutral molecule. Depending on the concrete molecule the absolute contribution of this effect could be rather substantial. For example, for  $a_3 = 1.0$  and  $\sigma_R^0 = -0.20$  the total effect from this factor equals 4.0 kcal/mol which corresponds to the specific resonance effect (for  $\Sigma \sigma_R^0 = -1.0$ ) of ca 23 kcal/mol.

4. As it was shown already in Ref. 15 the presence of the hydrogen atom, immediately attached to the ionization center might result in a very large contribution into the gross substituent effect. Present results again confirm this conclusion showing that for the typical value  $a_4 = 1.0$  the effect of introduction of one immediately attached hydrogen amounts to ca 23 kcal/mol.

5. By its absolute value the effect of  $\alpha$ -hydrogen atoms seems to be of somewhat lower intensity. For the typical conditions  $a_5 = 0.1$  and  $\Delta n_2 = -5$  this results in a value of 11 kcal/mol which corresponds to the specific effect (for  $\Delta n_2 = 1$ ) of 2.3 kcal/mol.

In most cases  $a_5 > 0$  and  $\Delta n_2 < 0$ , that in terms of Eqn.(3) indicates to the decrease of the gross IP-s of the given compound (relative to the methyl derivative). According to the statistical characteristics of correlations reported in Tables 1 and 2, keeping in mind a certain inhomogeneity of the data used and taking into account a very wide range of variation of IP-s one should acknowledge that Eqn.(3) gives,

Table 3

Estimation of Statistical Contributions from Different Structural Factors into Gross Substituent Effects on IP

No	Class of compounds	$\Delta IP_I^a$	$\Delta IP_2^a$	% <sup>b</sup>	$\Delta IP_3^a$	%	$\Delta IP_4^a$	%	$\Delta IP_5^a$	%
1.	XOH	2.62	0.90	34	0.53	20	1.22	46	0.15	6
2.	X <sub>1</sub> OX <sub>2</sub>	5.66	0.39	7	0	0	2.11	37	1.04	18
3.	X <sub>1</sub> SX <sub>2</sub>	2.42	0.99	49	0.93	39	1.08	44	0	0
4.	X <sub>3</sub> N	4.38	0.82	19	0.33	8	0.78	18	0.20	5
5.	X <sub>3</sub> P	3.27	0	0	0	0	1.94	59	0	0
6.	XCN	1.93	0	0	0.99	51	1.13	59	1.0	52
7.	XCl	1.97	0.49	25	0.29	14	1.18	60	0	0
8.	XBr	1.80	0	0	0	0	0	0	0	0
9.	XI	1.55	0.18	II	0.56	36	0.87	56	0.3	19
10.	X <sub>1</sub> COX <sub>2</sub>	1.89	2.67	142	0.99	52	0	0	1.11	59
11.	X <sub>1</sub> CSX <sub>2</sub> <sup>c</sup>	0.45	1.87	241	1.03	44	1.26	36	1.25	36
12.	X <sub>1</sub> X <sub>2</sub> X <sub>3</sub> PO	2.68	0.67	25	0.42	16	0.47	17	0.89	33
13.	X <sub>1</sub> COOX <sub>2</sub>	0.68	0	0	0.63	93	0	0	0	0
14.	X <sub>1</sub> CONX <sub>2</sub> X <sub>3</sub>	2.29	0	0	0.17	7	0.75	33	1.59	69
15.	X <sub>1</sub> C=CX <sub>2</sub> <sup>c</sup>	4.66	5.98	128	0.14	3	0.74	16	0.29	6
16.	X <sub>1</sub> X <sub>2</sub> C=CX <sub>3</sub> X <sub>4</sub>	2.51	0.56	22	1.35	54	0.75	30	0	0

a - For definition see the text. Subscript i refers to the i-th factor included into Eqn.(3)

b - The quantity  $(\Delta IP_i / \Delta IP_1)100$

c - Based on Table 1, the other items are calculated on the basis of Table 2.

as a rule, at least satisfactory quantitative description of the dependence of the large variety of IP of different classes of molecule on their structure. Therefore it seems that the present approach could serve as a certain starting point for the prediction of the experimentally unavailable IP values as well as for the solving some theoretical problems. For example, formalism of Eqn.(3) could be useful in

10.06; 10.  $I_2$ :10.54; 11.  $ICH_2I$ :10.0; 12.  $CF_3I$ :11.09; 13.  $ICH_2CH_2OH$ :9.96; 14.  $ICH_2CH_2OMe$ :9.72; 15.  $PhI$ :10.05; 16.  $ICH_2COOH$ :10.0; 17.  $ICN$ :11.18; 18.  $ICF_2CF_2I$ :10.59; 19.  $ICH_2CH_2I$ :9.85; 20.  $H_2C=CHCH_2I$ :9.8; 21.  $H_2C=CHI$ :9.72; 22.  $CF_3CH_2I$ :10.25; 23.  $PhCH_2I$ :9.63.

#### M. Substituted ethylenes.

1.  $H_2C=CH_2$ :10.51, 10.51; 2.  $MeCH=CH_2$ :9.72, 9.88; 3.  $EtCH=CH_2$ :9.58, 9.72; 4.  $MeCH=CHMe$ :9.11, 9.37; 5.  $Me_2C=CH_2$ :9.23, 9.45; 6.  $Me_2C=CHMe$ :8.67, -; 7.  $Me_2C=CMe_2$ :8.30, 8.42; 8.  $MeEtC=CH_2$ :9.12, -; 9.  $FCH=CH_2$ :10.37, 10.63; 10.  $F_2C=CH_2$ :10.29, 10.70; 11.  $F_2C=CHF$ :10.14, 10.62; 12.  $FCH=CFCl$ :9.83, -; 13.  $FCH=CHF$ :10.21, 10.62; 14.  $F_2C=CF_2$ :10.12, 10.52; 15.  $ClCH=CHF$ :9.87, -; 16.  $CF_3ClC=CClCF_3$ :10.36, 10.55; 17.  $H_2C=CHCl$ :10.0, 10.18; 18.  $Cl_2C=CH_2$ :9.74, 10.0; 19.  $Cl_2C=CHCl$ :9.48, 9.65; 20.  $Cl_2C=CCl_2$ :9.34, 9.51; 21.  $FCF_3C=CF_3$ :11.25, 11.55; 22.  $H_2C=CHCN$ :10.91, 10.91; 23.  $H_2C=CHCH_2CN$ :10.39, -; 24.  $FCH_2CH=CH_2$ :10.11, 10.6; 25.  $ClCH_2CH=CH_2$ :10.05, 10.38; 26.  $t-BuCH=CH_2$ : -, 9.7; 27.  $t-BuCH_2CH=CH_2$ : -, 9.6; 28.  $ClCH_2CCl=CH_2$ :9.82, -; 29.  $F_2C=CFCl$ :9.84, 10.24; 30.  $F_2C=CCl_2$ :9.65, 9.84; 31.  $PrCH=CH_2$ :9.50, 9.54; 32.  $i-PrCH=CH_2$ :9.51, -; 33.  $BuCH=CH_2$ :9.46, -; 34.  $Et_2C=CH_2$ :9.21, -; 35.  $ClCH=CHCl$ :9.68, 9.93; 36.  $(CN)_2C=C(CN)_2$ :11.77, 11.79; 37.  $CF_3CF=CF_2$ :10.62, 11.29; 38.  $EtCH=CHBu$ :8.86, -; 39.  $PrCH=CHPr$ :8.84, -; 40.  $ClCH=CF_2$ :9.84, 10.04; 41.  $NCC=CHCN$ : -, 11.15; 42.  $t-Bu_2C=CH_2$ :8.80, -; 43.  $NCCMe=CH_2$ : -, 10.51; 44.  $NCCH=CHMe$ : -, 10.23; 45.  $(CN)_2C=CH_2$ : -, 11.38; 46.  $NCCCl=CH_2$ : -, 10.58; 47.  $Et_2C=CHMe$ :8.53, -; 48.  $t-Bu_2C=CHt-Bu$ : -, 8.5; 49.  $t-BuCH=CHt-Bu$ : -, 8.99; 50.  $i-Pr_2C=Ci-Pr_2$ : -, 8.13; 51.  $i-PrCMe=CMei-Pr$ : -, 8.27; 52.  $BuCMe=CH_2$ : -, 9.04; 53.  $PrCMe=CH_2$ : -, 9.00; 54.  $PrCH=CH_2$ :9.52, 9.69; 55.  $i-BuCH=CH_2$ :9.45, 9.62.

#### N. Substituted acetylenes

1.  $HC\equiv CH$ :11.4, 11.4; 2.  $MeC\equiv CH$ :10.37, 10.54; 3.  $EtC\equiv CH$ :10.18, -; 4.  $MeC\equiv CMe$ :9.59, 9.79; 5.  $MeC\equiv CPr$ :9.37, -; 6.  $EtC\equiv CEt$ :9.34, -; 7.  $PrC\equiv CPr$ :9.2, -; 8.  $NCC\equiv CH$ : -, 11.6; 9.  $NCC\equiv CCN$ :11.81, 11.81; 10.  $FC\equiv CH$ :11.26, 11.50; 11.  $Cl\equiv CH$ :10.63, 10.63;



12.  $\text{ClC}\equiv\text{CCl}$ :10.09, 10.25; 13.  $\text{PrC}\equiv\text{CH}$ :10.1, -; 14.  $\text{BuC}\equiv\text{CH}$ :  
 10.05, -; 15.  $\text{BuC}\equiv\text{CMe}$ :9.34, -; 16.  $\text{EtC}\equiv\text{CPr}$ :9.28, -;  $\text{EtC}\equiv\text{CBu}$ :  
 9, 23, -; 18.  $\text{HOCH}_2\text{C}\equiv\text{CH}$ :10.51, 10.59; 19.  $\text{H}_2\text{C}=\text{CHC}\equiv\text{CH}$ :10.61,  
 10.61; 20.  $\text{FC}\equiv\text{CF}$ :11.18, 11.6; 21.  $\text{CF}_3\text{C}\equiv\text{CH}$ :11.96, 12.1;  
 22.  $\text{CF}_3\text{C}\equiv\text{CCF}_3$ : -, 12.8; 23.  $\text{t-BuC}\equiv\text{CH}$ : -, 10.08; 24.  $\text{MeC}\equiv$   
 $\equiv\text{CSiMe}_3$ : -, 9.57; 25.  $\text{FC}\equiv\text{CSiMe}_3$ : -, 10.2; 26.  $\text{ClC}\equiv\text{CSiMe}_3$ :  
 -, 9.7.

a-- If not specially indicated the chemical formula of the  
 compound is followed by the adiabatic and subsequently  
 by the vertical ionization potentials. As a rule, data  
 were taken from Ref. 32. The values of IP measured in  
 this work are underlined.

b - Vertical IP only.

CNDO/2 CALCULATIONS OF MOLECULES.

3. Ionization Potential and Charge Distribution

I.A. Koppel and U.H. Mõlder

Laboratory of Chemical Kinetics and Catalysis,  
Tartu State University 202400 Tartu, Estonia,  
USSR.

Received December 25, 1981

For several classes of aliphatic compounds the linear relationship was established between ionization energy of the electron localized on a certain atom and semiempirical CNDO/2 charge on the latter. The charge distribution was calculated according to the Mulliken's procedure. The correction for the intramolecular Madelung potential was introduced into the valence shell ionization potentials. The method for the determination of the ionization potential (IP) of the lone pair from photoelectron spectra (PES) was suggested. The linearity between CNDO/2 and *ab initio* (STO-3G and 4-31G basis sets) charge densities was found.

In the previous publications<sup>1a,b</sup> of this series the applicability of semiempirical CNDO/2 method for the calculation of proton affinities (PA) and ionization potentials was considered. In Ref.2 the empirical linear energy-structure type correlation equation was suggested for the quantitative description of the dependence of the IP-s on the structure. In the present communication an attempt will be made to establish the dependence of IP of molecules on CNDO/2 charges on the corresponding ionization center. The relationship between PA of several molecules or anions and the CNDO/2 charge on the protonization center is the subject of Ref. 3.

All calculations were performed according to the standard procedure using the original parametrization of Pople and Beveridge<sup>4</sup>. The charge distribution was calculated using the formalism of the Mulliken's population analysis<sup>5</sup>. Geometries of molecules used are given in the Appendix to the Ref. 1a.

It follows from the population analysis that the correctly predicted dipole moment of the given molecule is not necessarily connected with the "real" charge distribution on the atoms of this system. However, it is still interesting to compare in that respect the results of the different quantum chemical methods. Using the corresponding data from Refs. 6a, b and some other literature sources the comparison of values of experimental dipole moments  $\mu$  with their CNDO/2 or ab initio Gaussian 70 (STO-3G and 4-31G basis sets) values leads to the Equations (1)-(3):

$$\begin{aligned} \mu &= 0.95(0.05) \mu_{\text{CNDO}} - 0.03(0.11); \quad r = 0.937 & (1) \\ s &= 0.61; \quad n = 50 \end{aligned}$$

$$\begin{aligned} \mu &= 1.15(0.06) \mu_{3\text{G}} + 0.21(0.09) \quad r = 0.961; & (2) \\ s &= 0.32; \quad n = 29 \end{aligned}$$

$$\begin{aligned} \mu &= 0.97(0.04) \mu_{4-31\text{G}} - 0.49(0.10); \quad r = 0.979 & (3) \\ s &= 0.22; \quad n = 25 \end{aligned}$$

where  $r$  is the correlation coefficient,  $s$  - standard deviation (in Debyes),  $n$  - number of points; standard deviations of the corresponding regression coefficients are given in parentheses.

Eqns. (1)-(3) lead to the well-known<sup>7</sup> consequence that 4-31G basis set overestimates the polarity of the molecule. The opposite is true for the STO-3G basis set. In other words, STO-3G basis set underestimates the electronegativity of strong electronegative substituents whereas 4-31G basis set leads to the reversed results. Eqn. (2) does not describe



the behavior of chlorine compounds. According to the statistical characteristics of these correlations Eqn. (3) (4-31G basis set) offers the best fit of experimental values to their predicted values. However, the latter correlation is characterized by the largest intercept (ca 0.5 Debyes). On the contrary, Eqn. (1) despite its large standard deviation leads to  $\mu$  values which practically do not need any additional correction. In Table 1 the vertical IP<sup>2</sup> derived from PES and CNDO/2 atomic charges on the ionization center are listed. The Mulliken atomic charges do not follow inherently from the concrete quantum mechanical model and are not part of the physical reality. In that sense they are analogous to atomic orbital coefficients through which the atomic charges are being calculated. It seems reasonable to consider these charges determined by the Mulliken's procedure as some parameters which characterize the given atom (in a special case - ionization center) in the molecule. In principle MO-s are delocalized all over the molecule. However, in several special cases some MO-s are with high probability mostly localized on a certain atoms. This situation probably holds for nonbonding orbitals. In such a cases the use of the term "ionization center" seems to be justified.

In the presence of two equivalent ionization centers in the molecule the symmetrical splitting of the corresponding MO-s takes place. This relatively simple situation can be taken into account using in correlation equations the arithmetic mean value from the corresponding ionization potentials.

Statistical least squares treatment of the data from Table 1 results in linear relationships between IP and charge q on the ionization center for the different classes of molecules:

$$IP = aq + b \quad , \quad (4)$$

where a is the slope and b intercept. The corresponding correlation statistics is listed in Table 2.

It should be mentioned that the hydrogen atoms immediately attached to the ionization center lead to the parallel shifts

Table 1  
Ionization Potentials CNDO/2 Charges on Ionization  
Center, and Madelung Corrections<sup>a</sup>

No	Molecules	IP	q <sub>o</sub>	q/r
1	2	3	4	5
Compounds with sp <sup>3</sup> Oxygen				
1.	H <sub>2</sub> O	12.6	-0.265	3.72
2.	MeOH	10.96	-0.231	3.03
3.	EtOH	10.65	-0.243	2.99
4.	PrOH	10.52	-0.259	-
5.	BuOH	10.43	-0.259	-
6.	t-BuOH	10.26	-0.261	3.42
7.	FOH	13.00	-0.063	1.00
8.	ClOH	11.22	-0.188	2.47
9.	CF <sub>3</sub> CH <sub>2</sub> OH	11.70	-0.227	3.76
10.	(CF <sub>3</sub> ) <sub>2</sub> CHOH	12.21	-0.215	4.23
11.	(CF <sub>3</sub> ) <sub>3</sub> COH	12.58	-0.200	4.41
12.	CCl <sub>3</sub> CH <sub>2</sub> OH	11.34	-0.239	3.88
13.	CCl <sub>3</sub> Me <sub>2</sub> COH	10.7	-0.264	4.10
14.	FCH <sub>2</sub> CH <sub>2</sub> OH	11.05	-0.249	3.64
15.	ClCH <sub>2</sub> CH <sub>2</sub> OH	10.85	-0.261	3.99
16.	H <sub>2</sub> O <sub>2</sub>	11.7	-0.115	1.11
17.	HC≡CCH <sub>2</sub> OH	10.92	-0.245	3.36
18.	Me <sub>2</sub> SO	9.01	-0.312	3.31
19.	F <sub>2</sub> SO	12.58	-0.19	3.67
20.	Me <sub>2</sub> O	10.04	-0.212	2.86
21.	MeOEt	9.80	-0.213	2.71
22.	Et <sub>2</sub> O	9.60	-0.223	2.91
23.	t-Bu <sub>2</sub> O	9.16	-0.259	3.41
24.	F <sub>2</sub> O	13.26	0.141	-1.73
25.	Cl <sub>2</sub> O	11.02	-0.029	0.27
26.	CF <sub>3</sub> OF	13.63	-0.085	3.20
27.	CF <sub>3</sub> CH <sub>2</sub> OMe	10.69	-0.189	2.97

## Continuation of Table 1

1	2	3	4	5
28.	$\text{CF}_3\text{CH}_2\text{OEt}$	10.27	-0.202	2.74
29.	$\text{ClCH}_2\text{OMe}$	10.25	-0.193	-
30.	$\text{Cl}_2\text{CHOMe}$	10.98	-0.181	2.86
31.	$\text{HCOQH}$	11.51	-0.237	4.05
32.	$\text{CF}_3\text{COQH}$	13.2	-0.221	5.17
33.	$\text{MeCOQH}$	12.05	-0.255	4.55
34.	$\text{MeONH}_2$	10.28	-0.143	1.25

B. Compounds with  $\text{sp}^3$  Nitrogen

1.	$\text{NH}_3$	10.72	-0.218	2.94
2.	$\text{MeNH}_2$	9.64	-0.206	2.72
3.	$\text{t-BuNH}_2$	9.25	-0.221	2.36
4.	$\text{ClNH}_2$	10.52	-0.148	2.30
5.	$\text{FCH}_2\text{CH}_2\text{NH}_2$	9.86	-0.194	2.74
6.	$\text{F}_2\text{CHCH}_2\text{NH}_2$	10.15	-0.185	3.01
7.	$\text{CF}_3\text{CH}_2\text{NH}_2$	10.35	-0.177	3.30
8.	$(\text{CF}_3)_3\text{CNH}_2$	11.10	-0.193	4.39
9.	$\text{MeONH}_2$	10.28	-0.047	0.20
10.	$\text{HOCH}_2\text{CH}_2\text{NH}_2$	9.7	-0.210	-
11.	$\text{N}_2\text{H}_4$	10.3	-0.111	1.07
12.	$\text{HCONH}_2$	10.52	-0.243	4.69
13.	$\text{MeCONH}_2$	10.32	-0.257	4.63
14.	$\text{Me}_2\text{NH}$	8.94	-0.181	2.68
15.	$\text{EtNH}_2$	8.62	-0.183	2.27
16.	$\text{F}_2\text{NH}$	12.36	0.203	-2.23
17.	$\text{Cl}_2\text{NH}$	10.56	-0.072	1.25
18.	$\text{MeNHCl}$	9.8	-0.104	1.48
19.	$\text{MeCONHMe}$	9.85	-0.212	3.98
20.	$\text{Me}_3\text{N}$	8.55	-0.140	2.07
21.	$\text{Me}_2\text{NEt}$	8.38	-0.152	2.23
22.	$\text{Et}_3\text{N}$	8.19	-0.163	1.93
23.	$\text{NF}_3$	13.73	0.402	-4.65
24.	$(\text{CF}_3)_3\text{N}$	12.52	-0.326	9.99



Continuation of Table 1

1	2	3	4	5
25.	$(CF_3)_2NF$	12.45	-0.108	5.58
26.	$CF_3NF_2$	12.62	0.129	0.45
27.	$(CF_3)_2NCHF_2$	12.35	-0.308	9.44
28.	$(CF_3)_2NCl$	11.45	-0.218	6.13
29.	$CF_3NMe_2$	9.99	-0.202	4.82
30.	$CF_3CH_2NMe_2$	8.98	-0.130	2.14
31.	$CNCH_2NMe_2$	9.22	-0.131	2.40
32.	$CCl_3$	10.69	0.03	-0.25
33.	$MeNCI_2$	10.01	-0.001	0.03
34.	$Me_2NCI$	9.31	-0.063	0.75
35.	$MeCNMe_2$	9.43	-0.157	3.13
36.	$EtNCN$	9.32	-0.123	2.52
37.	$H_2NCN$	10.65	-0.168	3.40
38.	$Me_2NCN$	9.44	-0.114	2.25
39.	$(CNCH_2CH_2)_3N$	11.26	0.167	5.56

## C. Compounds with sp-Nitrogen

1.	$HCN$	13.82	-0.106	0.74
2.	$MeCN$	13.11	-0.163	1.36
3.	$FCN$	14.56	-0.147	2.54
4.	$ClCN$	13.80	-0.065	0.95
5.	$CF_3CN$	14.39	-0.058	1.20
6.	$FCH_2CN$	13.60	-0.137	1.42
7.	$ClCH_2CN$	13.59	-0.163	1.68
8.	$Cl_2CHCN$	13.92	-0.142	1.77
9.	$CCl_3CN$	13.87	-0.141	1.87
10.	$(CN)_2$	14.49	-0.076	1.05
11.	$NCCH_2CN$	13.41	-0.195	2.12
12.	$H_2C = CHCN$	13.00	-0.168	1.55
13.	$H_2NCN$	12.98	-0.213	2.06
14.	$Me_2NCN$	12.79	-0.190	1.84
15.	$Et_2NCN$	12.6	-0.221	1.93
16.	$CNCH_2NMe_2$	13.74	-0.180	2.19

## Continuation of Table 1

1	2	3	4	5
17.	NCCOOEt	13.80	-0.079	0.80
18.	(CN) <sub>2</sub> CO	14.41	-0.101	1.36
19.	(CN) <sub>2</sub> S	14.02	-0.075	0.80
20.	ClCH <sub>2</sub> SCN	14.44	-0.031	0.53

D. Compounds with sp<sup>2</sup> oxygen

1.	H <sub>2</sub> CO	10.88	-0.196	2.28
2.	MeCHO	10.20	-0.248	2.71
3.	PrCHO	9.83	-0.254	2.76
4.	t-BuCHO	9.82	-0.271	2.91
5.	FCHO	12.54	-0.245	3.71
6.	CF <sub>3</sub> CHO	11.66	-0.140	2.50
7.	Me <sub>2</sub> CO	9.70	-0.260	2.87
8.	MeCOEt	9.52	-0.296	2.99
9.	(cyclo-C <sub>3</sub> H <sub>5</sub> ) <sub>2</sub> CO	9.27	-0.314	3.17
10.	F <sub>2</sub> CO	13.6	-0.284	5.06
11.	Cl <sub>2</sub> CO	11.84	-0.140	2.99
12.	(CN) <sub>2</sub> CO	12.56	-0.194	3.12
13.	FCH <sub>2</sub> COMe	10.20	-0.238	2.94
14.	CF <sub>3</sub> COMe	10.94	-0.188	2.79
15.	(CF <sub>3</sub> ) <sub>2</sub> CO	12.09	-0.117	2.93
16.	(F <sub>2</sub> CH) <sub>2</sub> CO	11.23	-0.143	2.63
17.	CF <sub>3</sub> COCCl <sub>3</sub>	11.19	-0.168	3.12
18.	HCOOH	11.51	-0.290	3.32
19.	MeCOOH	10.84	-0.343	3.90
20.	EtCOOH	10.72	-0.328	3.76
21.	CF <sub>3</sub> COOH	12.00	-0.259	3.82
22.	MeCOOMe	10.59	-0.347	4.06
23.	F <sub>2</sub> CHCOOEt	11.58	-0.268	3.62

## E. Chlorides

1.	HCl	12.78	-0.096	1.09
2.	MeCl	11.33	-0.122	0.77

Continuation of Table 1

1	2	3	4	5
3.	$\text{CF}_3\text{Cl}$	13.00	-0.100	2.17
4.	$\text{FCl}$	12.86	0.152	-1.34
5.	$\text{ClCN}$	12.37	-0.014	0.43
6.	$\text{Cl}_2\text{CH}_2$	11.81	-0.090	0.97
7.	$\text{Cl}_3\text{CH}$	12.19	-0.066	0.92
8.	$\text{CCl}_4$	12.39	-0.049	0.87
9.	$\text{Me}_2\text{NCl}$	11.19	-0.103	0.37
10.	$\text{MeNHC1}$	11.47	-0.080	0.39
11.	$\text{MeNCl}_2$	11.71	-0.051	0.28
12.	$\text{NHC1}_2$	11.88	-0.027	0.04
13.	$\text{NCl}_3$	12.25	-0.004	0.06
14.	$\text{ClOH}$	12.27	0.023	-0.51
15.	$\text{Cl}_2\text{O}$	12.37	0.061	-0.64
16.	$(\text{CF}_3)_2\text{NCl}$	13.0	0.048	0.26
17.	$\text{CCl}_3\text{CN}$	12.3	-0.052	0.91
18.	$\text{ClCH}_2\text{CN}$	12.05	-0.104	1.05
19.	$\text{ClCH}_2\text{SCN}$	11.69	-0.089	0.64

## F. Sulfur Compounds

1.	$\text{H}_2\text{S}$	10.43	0.005	-0.08
2.	$\text{MeSH}$	9.44	-0.034	-0.01
3.	$\text{CF}_3\text{SH}$	11.35	-0.040	1.73
4.	$\text{Me}_2\text{S}$	8.71	-0.076	0.23
5.	$(\text{CF}_3)_2\text{S}$	11.35	-0.094	3.30
6.	$(\text{CN})_2\text{S}$	11.32	0.057	0.02
7.	$\text{MeSCN}$	10.06	-0.039	0.28
8.	$\text{ClCH}_2\text{SCN}$	10.38	-0.014	0.25
9.	$\text{H}_2\text{S}_2$	10.14	-0.001	0.01

a IP and Madelung corrections are given in eV and charges are in atomic units



Table 2  
Correlation of Vertical IP and Charges on the  
Ionization Center According to Eqn.(4).<sup>a, b</sup>

No	Class of Compounds	a	b	r	s	n	Typical Com- pounds Devia- ting From Eqn.(4)
1.	XOH	24.24 (1.41)	17.08 (0.34)	0.975	0.23	17	H <sub>2</sub> O, FOH, ClOH, H <sub>2</sub> O <sub>2</sub>
2.	X <sub>2</sub> O	26.23 (1.13)	15.62 (0.21)	0.993	0.18	10	F <sub>2</sub> O, Cl <sub>2</sub> O
3.	X <sub>2</sub> CO	14.99 (0.76)	13.74 (0.16)	0.986	0.15	13	FCO, F <sub>2</sub> CO; (CN) <sub>2</sub> CO
4.	XCOOX	15.31 (0.83)	15.38 (0.21)	0.988	0.14	10	
5.	XNH <sub>2</sub>	17.57 (3.80)	13.32 (0.73)	0.918	0.22	6	NH <sub>3</sub> , MeONH <sub>2</sub> , N <sub>2</sub> H <sub>4</sub> , HCONH <sub>2</sub> , MeCONH <sub>2</sub>
6.	X <sub>2</sub> NH	12.19 (2.59)	11.25 (0.37)	0.958	0.29	4	F <sub>2</sub> NH, MeCONHMe
7.	X <sub>3</sub> N	13.28 (1.93)	10.56 (0.17)	0.951	0.32	7	NF <sub>3</sub> , (CF <sub>3</sub> ) <sub>3</sub> N, (CF <sub>3</sub> ) <sub>2</sub> NF, CF <sub>3</sub> NF <sub>2</sub> , (CF <sub>3</sub> ) <sub>2</sub> NCHF <sub>2</sub> , (CF <sub>3</sub> ) <sub>2</sub> NCl, CF <sub>3</sub> NMe <sub>2</sub>

a - Correlations are holding for the limiting set of compounds. Typical molecules which do not fit the given equations are listed in the last column of this Table ( see also the text)

b - IP-s are in eV.

of straight lines in terms of Eqn. (4) towards the higher values of IP. So, the points for aliphatic alcohols XOH are shifted upwards relative to the ethers by 2 eV, whereas the point for water lies, in its turn, by 1.8 eV higher than the ethers line (See Fig.1). For the nitrogen compounds the analogous relationships are statistically somewhat less reliable. Probably, it is due to the low population of the nonbonding orbitals of the nitrogen, i.e. because of the rather significant delocalization of the charge in these systems. Despite of that, statistically the parallel straight lines for the primary, secondary and tertiary amines are separated indeed. The shift between these lines is ca 1 eV, whereas the point for ammonia is also shifted upwards from the line of primary amines by the same increment. That means that the effect of the introduction of the hydrogen atom immediately to the ionization center is roughly additive (See also Fig.2). Similar situation holds also for the correlation of proton affinities with the charge on the protonization center<sup>3</sup>.

For the oxygen compounds there are different slopes a for the  $sp^3$  and  $sp^2$  oxygen atom. It is somewhat surprising to notify that there is no effect of the hydrogen atom, immediately attached to the carbonyl group: the points for the aldehydes, ketones and also formaldehyde lie on the same straight line (See Fig. 3). The carbonyl compounds which contain a electron donating functional group attached to the ionization center form a separate straight line. For example, points for carboxylic acids and esters (and on some reason, also  $(CN)_2CO$ ) where the  $sp^2$  oxygen of the carbonyl group is considered as an ionization center are shifted upwards by 1.6 eV from the line for ketones and aldehydes (See Fig. 3).

As a rule, very substantial deviations from relationships listed in Table 2 occur when the fluorine atom or perfluoroalkyl group (e.g.,  $CF_3$ ) are attached immediately to the ionization center. At the same time, the former leads to too low and the latter to too high values (by several eV) of IP. The

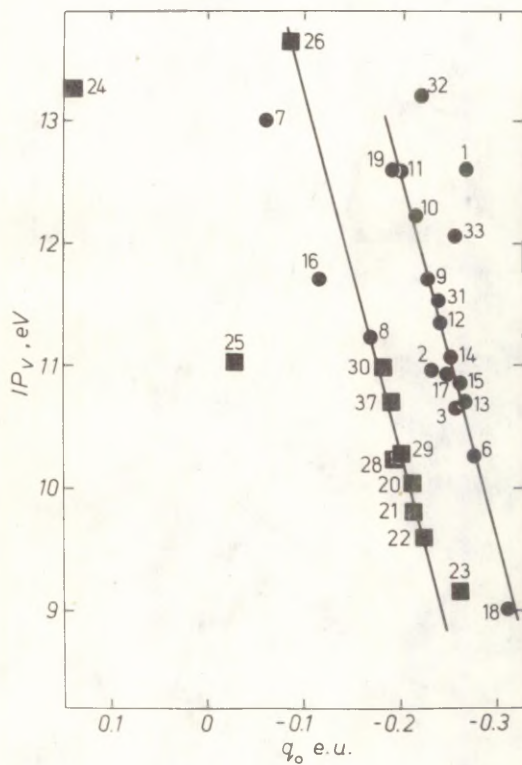


Fig. 1. The dependence of vertical IP on the charge of the  $sp^3$  oxygen. The numbering of the points corresponds to Table 1.

- - alcohols, KOH and water
- - ethers,  $X_1OX_2$



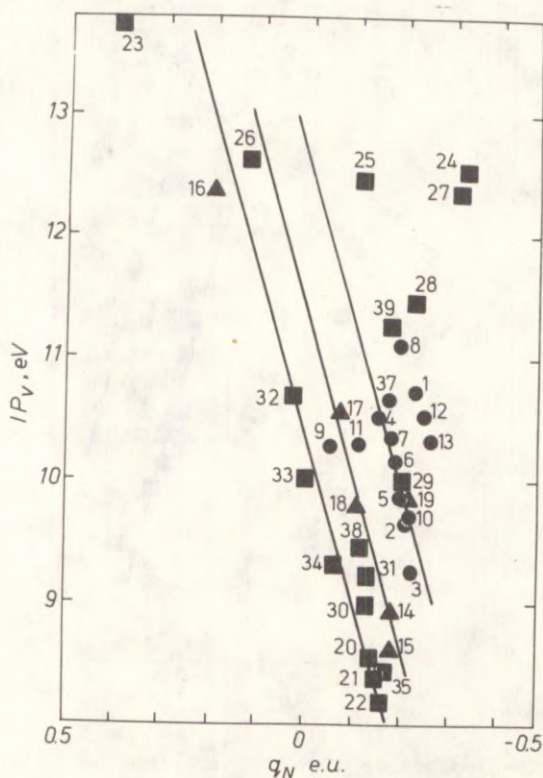


Fig. 2. The dependence of vertical IP on the charge of the  $sp^3$  nitrogen. The numbering of the points corresponds to Table 1.

- - primary amines  $XNH_2$  and ammonia
- ▲ - secondary amines  $X_1X_2NH$
- - tertiary amines  $X_1X_2X_3N$

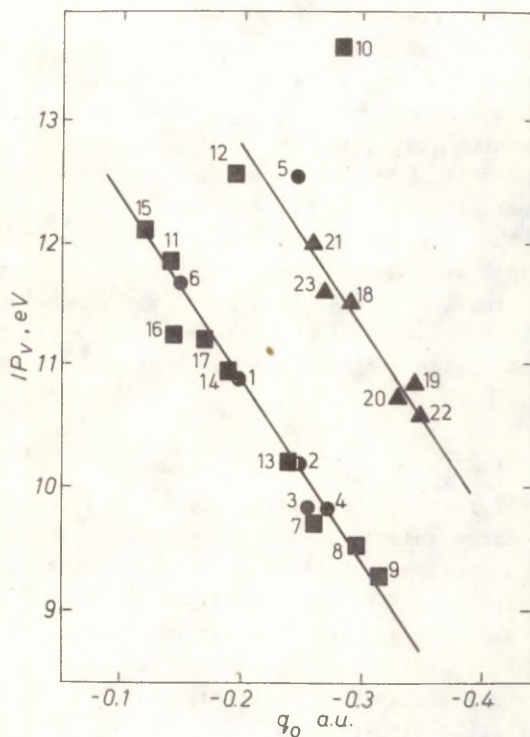


Fig. 3. The dependences of vertical IP on the charge of the  $sp^2$  oxygen. The numbering of points corresponds to Table 1.

- - Compounds  $XCHO$  and  $H_2CO$
- - Compounds  $X_1COX_2$
- ▲ - Carbonyl compounds  $XCOM$  with the adjacent donor group  $M$

behavior of the carbonyl compounds is again exceptional:  $\text{CF}_3$  derivatives ( $\text{CF}_3\text{CHO}$ ,  $\text{MeCOCF}_3$ ,  $(\text{CF}_3)_2\text{CO}$ , etc.) do not deviate from the straight line, determined by the corresponding equation from Table 2 whereas fluoro-substituted compounds still do not fit the general relationship deviating by several eV towards the higher IP values.

Significant systematic deviations of several points from relationships listed in Table 2 evidence about a certain fundamental shortcomings of the simplified approach formally represented by Eqn.(4). It seems to the present authors that the solution of the problem could be found using the method used by Siegbahn et al.<sup>8</sup> for the analysis of the ESCA spectra. The point charge model was suggested which takes into account the electrostatic potential  $E_i$  on the  $i$ -th atom generated by the arbitrary charge distribution in the given system.

$$E_i = E_0 + kq_i + \sum_{i \neq j} q_j / r_{ij} , \quad (5)$$

where  $E_0$  is the reference energy level,  $kq_i$  - the potential of the  $i$ -th charge and the last term represents the intra-molecular Madelung-type potential which takes into account the influence of all other atomic charges in the molecule ( $r_{ij}$  is the distance between the  $i$ -th and  $j$ -th point charge). The use of this equation for the binding energies  $E_B$  of inner shell electrons leads to the linear dependence of  $E_B$  on the charge of the ionization center:<sup>9,10</sup>

$$E_B - V = kq_i + l , \quad (6)$$

where  $V = \sum_j q_j / r_{ij}$  is the Madelung correction term for the experimental  $E_B$ ,  $l$  is the intercept and  $k$  the slope of the straight line. The absolute value of the latter depends on the definition of the charge on the atom, on the basis set used and is proportional to the one center repulsion integral.

For the Slater type basis functions the calculated value<sup>11</sup> of the integral



$$k = \langle \psi_{\text{core}} (1) \psi_{\text{core}} (1) \frac{1}{r_{12}} \psi_V (2) \psi_V (2) \rangle, \quad (7)$$

where  $\psi_{\text{core}}$  and  $\psi_V$  are the orbitals of the inner and valence shell, respectively is 22.0 eV. Eqn.(6) was used<sup>12-18</sup> for the several classes of compounds. The value of the coefficient  $k$  was found to depend somewhat on the nature of the compounds.

It was recently shown<sup>2</sup> that for the aliphatic oxygen and nitrogen compounds the linear relationship holds between the energies of nonbinding valence and core electrons. At the same time the sensitivity of the valence and inner shell ionization potentials towards structural effects is approximately the same. The similar behavior of these two quantities suggests that Eqn.(6) might be valid also for the IP-s valence electrons. That idea was checked up in the present work. The calculated Madelung correction terms are listed in the 5th column of the Table 1.

It is evident that the point charge model for the valence electrons (the lack of central symmetry, etc.) is rather rough approximation. Still the results of the use of this approach are interesting and encouraging. Some differences emerge while compared with the use of Eqn.(4) instead of Eqn.(6).

In Fig. 4 the dependence of corrected for the Madelung-type potentials IP-s on the charge on the oxygen atom  $q_o$  is shown for alcohols (Eqn.(8)), ethers (Eqn.(9)) and similar compounds in coordinates of Eqn.(6).\*

$$\begin{aligned} \text{IP-V} &= 25.24(0.77)q_o + 13.55(0.17); \quad r = 0.994 \\ s &= 0.18 \text{ eV}; \quad n = 16 \end{aligned} \quad (8)$$

$$\begin{aligned} \text{IP-V} &= 22.20(0.89)q_o + 11.87(0.14); \quad r = 0.993; \\ s &= 0.33 \text{ eV}; \quad n = 11 \end{aligned} \quad (9)$$

---

\* In the following, the error limits of the regression coefficients are given in the parenthesis.

In Fig. 5, analogous linear relationships between corrected IP-s and  $q_N$  for primary (Eqn.(10)), secondary (Eqn.(11)) and tertiary (Eqn.(12)) amines are shown.

$$\text{IP-V} = 21.76 (1.47)q_N + 11.27(0.27); r = 0.980; \\ s = 0.28 \text{ eV}; n = 11 \quad (10)$$

$$\text{IP-V} = 22.20 (0.89)q_N + 11.87(0.14); r = 0.997 \\ s = 0.29 \text{ eV}; n = 6 \quad (11)$$

$$\text{IP-V} = 21.93 (0.46)q_N + 9.64 (0.05); r = 0.996; \\ s = 0.32 \text{ eV}; n = 20 \quad (12)$$

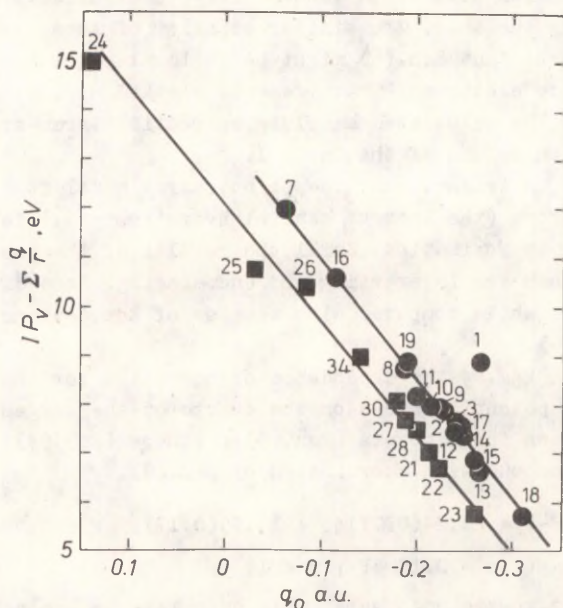


Fig. 4. The dependence of vertical IP-s corrected for the Madelung potential on the charge of the  $sp^3$  oxygen. See footnotes to Fig. 1.

Based on the CNDO/2 calculations of Clark<sup>14</sup> the similar relationship (Eqn.(13)) holds also for pyridine, perfluoropyridine, pyridazine, pyrimidine, and pyrazine:

$$\begin{aligned} \text{IP-V} &= 22.08 (2.42) q_N + 11.52 (0.36); \quad r = 0.982; \\ s &= 0.27 \text{ eV}; \quad n = 5 \end{aligned} \quad (13)$$

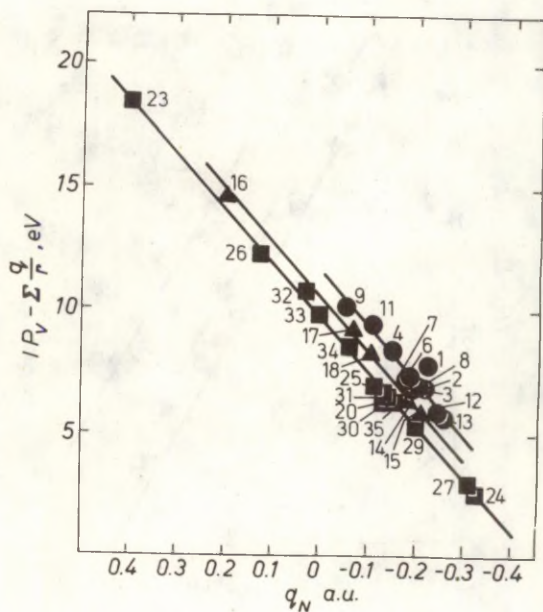


Fig. 5. The dependence of vertical IP-s corrected for the Madelung potential on the charge of the  $sp^3$  nitrogen. See footnotes to Fig. 2.



In all of these cases the Madelung correction allows one to consider from the one viewpoint all molecules of those classes. Strong electronegative groups and halide atom substituents immediately attached to the ionization center are also included. Such molecules as  $\text{H}_2\text{O}_2$ ,  $\text{Me}_2\text{SO}$  and  $\text{F}_2\text{SO}$  fit the same relationship (Eqn.(8)) for the alcohols.

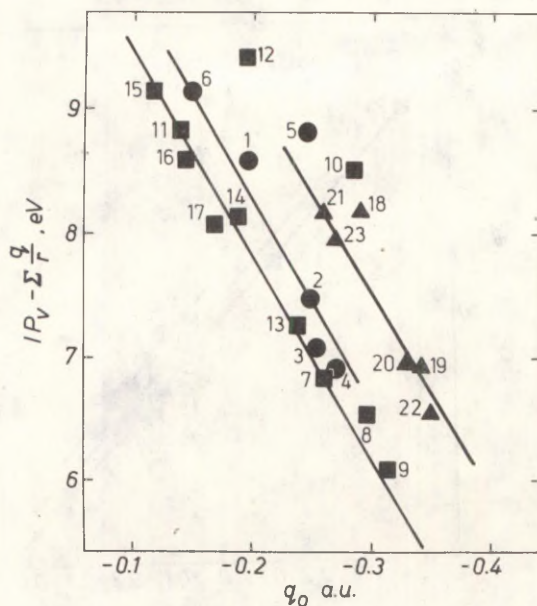


Fig. 6. The dependence of vertical IP-s corrected for the Madelung potential on the charge on the  $\text{sp}^2$  oxygen. See footnotes to Fig. 3.

In some cases the Madelung potential method enables one to assign unambiguously the IP from the PES which corresponds to the given ionization center. So, in Table 1 we have listed the ionization energies of nitrogen atom for hydroxylamines and amides as well as for substituted cyanoamides  $X_1X_2NCN$ . Also, the ionization energies of hydroxylic oxygen atom in some carboxylic acids were identified from PES using the present approach.

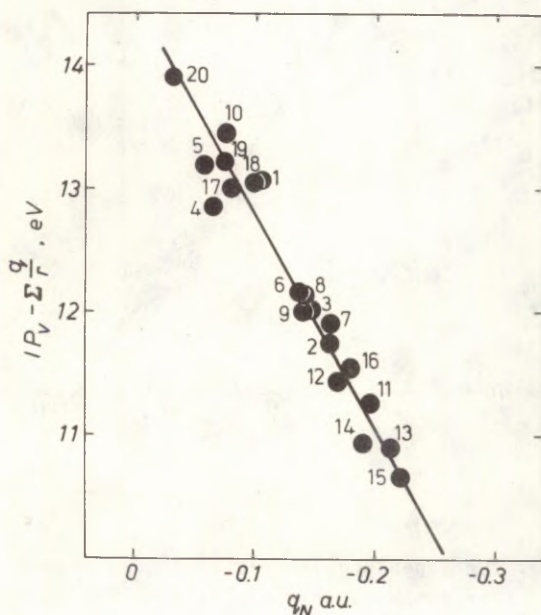


Fig. 7. The dependence of vertical IP-s corrected for the Madelung potential on the charge of the  $sp$  nitrogen. The numbering of points corresponds to Table 1.

Naturally the Madelung correction does not take into account the extra resonance interaction between the positively charged ionization center and lone electron pair

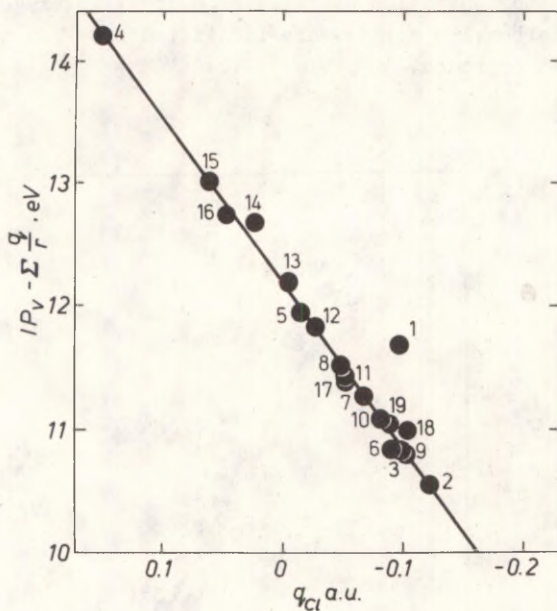


Fig. 8. The dependence of vertical IP-s corrected for the Madelung potential on the charge of the chlorine atom. The numbering of the points corresponds to Table 1.



functional group (e.g., OH, OR, NH<sub>2</sub> etc.). Therefore, not surprisingly, in the case of carbonyl compounds such a compounds (see Eqn. (14)) still deviate from

$$\begin{aligned} \text{IP-V} &= 16.77(1.64)q_o + 12.49(0.51); r = 0.986 \\ s &= 0.14 \text{ eV, } n = 5 \end{aligned} \quad (14)$$

the relationships (see Fig.6) of the aldehydes (Eqn.(15)) and ketones (Eqn.(16)):

$$\begin{aligned} \text{IP-V} &= 18.54(1.62)q_o + 11.93(0.37); r = 0.992 \\ s &= 0.15 \text{ eV, } n = 4 \end{aligned} \quad (15)$$

$$\begin{aligned} \text{IP-V} &= 15.23(0.53)q_o + 10.91(10.11); r = 0.996 \\ s &= 0.11 \text{ eV, } n = 8 \end{aligned} \quad (16).$$

Probably on the same reason the points for FCHO, F<sub>2</sub>CO, Cl<sub>2</sub>CO (and also (CN)<sub>2</sub>CO) exercise the very close behavior to the carboxylic acids (adjacent OH) and their esters (OR group).

An interesting and important cases for the interpretation of photoelectron spectra are nitriles and halogen compounds. So, based on the relationship (17) for the nitriles (see Fig.7) we suggest (see Table 1) the values of IP which refer to the ionization of the lone pair of the nitrogen of the cyano group (H<sub>2</sub>NCN, MeNCN, Et<sub>2</sub>NCN, CNCH<sub>2</sub>NMe, NCCOOEt, (CN)<sub>2</sub>CO and (CN)<sub>2</sub>S).

$$\begin{aligned} \text{IP-V} &= 16.86(0.75)q_N + 14.47(0.10); r = 0.985 \\ s &= 0.17 \text{ eV ; } n = 18 \end{aligned} \quad (17)$$

With one exception (Me<sub>2</sub>NCN) all these quantities agree with the corresponding values, predicted in Ref.19 on the basis of the linear relationship between experimental PA values and vertical IP-s from PES. In the case of Me<sub>2</sub>NCN, however, Ref.19 predicts a value 11.77, whereas Eqn.(17) leads to a higher value 12.79 eV which agrees with the interpretation of the PES spectrum of this compound suggested by Stafast<sup>20</sup>.

The assignment of the bands of the lone pairs of halogen

atoms makes the interpretation of the PES of organic halides an extremely difficult task. So, the chlorine bands are frequently located in the same region with the lone electron pair bands of the other atoms. In this paper we suggest the Eqn.(18) for the interpretation of PES of chloro-compounds (see also Fig. 8):

$$\begin{aligned} \text{IP} - V &= 13.56(0.27)q_{\text{Cl}} + 12.18(0.01); r = 0.997 \\ s &= 0.08 \text{ eV}, n = 15 \end{aligned} \quad (18)$$

Some examples of the use of Eqn.(18) are given in Table 1. It is worth-while to mention that the IP values for chloro-methanes predicted from Eqn.(18) agree well with the earlier literature values which were determined taking into account of the degeneration of the energy levels.

Similar relationship holds also for the sulfides:

$$\begin{aligned} \text{IP} - V &= 21.59(1.71)q_{\text{S}} + 10.28(0.04); r = 0.979 \\ s &= 0.22 \text{ eV}, n = 9 \end{aligned} \quad (19)$$

The use of literature values and our data from Refs. 6a, b allows one to compare the numerical values of atomic charges determined by ab initio techniques from one hand and by semiempirical CNDO/2 procedure from another.

Statistical treatment shows that for the different basis sets ab initio Gaussian-70 charges are in a good agreement with each other:

$$\begin{aligned} q_{4-31\text{G}} &= 2.803(0.184)q_{3\text{G}} + 0.162(0.040); r = 0.961 \\ s &= 0.116; n = 21 \end{aligned} \quad (20)$$

Also the linear relationship holds between the charges derived from 4-31G basis set and CNDO/2 procedure:

$$\begin{aligned} q_{4-31\text{G}} &= 2.188(0.115)q_{\text{CNDO}} + 0.101(0.013); r = 0.979 \\ s &= 0.098, n = 18 \end{aligned} \quad (21)$$

The latter equation suggests that the dependence of IP values on ab initio atomic charges on the ionization center should follow the similar regularities outlined in this paper for CNDO/2 charges.

In conclusion it should be underlined that the use of Madelung correction factor leads for the localized lone electron pairs to the relatively reliable identification of the bands in photoelectron spectra. It is especially helpful for the rather complicated cases of the coexistence of several alternative ionization center in the same molecule. Somewhat surprisingly, the satisfactory results were already gotten using the simplified semiempirical CNDO/2 procedure.

#### References

1. a) I.A. Koppel and U.H. Mölder, *Organic Reactivity*, 18, 43 (1981).  
b) I.A. Koppel, U.H. Mölder, and R.I. Píkver, *Organic Reactivity*, 18, 84(1981).
2. I.A. Koppel, U.H. Mölder, and R.J. Pikver, *Organic Reactivity*, 18, 380 (1981).
3. I.A. Koppel and U.H. Mölder, *This Journal*, 18, (1981).
4. J.A. Pople and D.L. Beveridge, *Approximate Molecular Orbital Theory*, Mc Graw-Hill Book Company, 1970.
5. R.S. Mulliken, *J. Chem. Phys.*, 23, 1833 (1955).
6. a) I.A. Koppel and M.B. Comisarow, *Organic Reactivity*, 17, 498 (1980).  
b) I.A. Koppel, U.H. Mölder, and M.B. Comisarow, *Organic Reactivity*, 18, 21 (1981)
7. P. Kollman and S. Rothenberg, *J. Am. Chem. Soc.*, 99, 1333 (1977).
8. U. Gelius, B. Roos, and P. Siegbahn, *Chem. Phys. Lett.*, 4, 471 (1970).
9. H. Basch, *Chem. Phys. Lett.*, 5, 337 (1970).
10. M.E. Schwartz, *Chem. Phys. Lett.*, 6, 631 (1970).
11. D.T. Clark and D. Kilcast, *J. Chem. Soc. (A)*, 3286 (1971).



12. D.T. Clark, D. Kilcast, and W.K.R. Musgrave, Chem. Comm., 516 (1971).
13. D.T. Clark and D. Kilcast, J. Chem. Soc. (B), 2243 (1971).
14. D.T. Clark, R.D. Chambers, D. Kilcast, and W.K.R. Musgrave, Farad. Trans.II, 2, 309 (1972).
15. P. Baybutt, W.N.E. Meredith, M.F. Guest, V.R. Sannders, J.H. Hillier, J.A. Conner, and M. Barber, Mol. Phys., 25, 1011 (1973).
16. T.K. Ha and L.C. Allen, Int. J. Quant. Chem., 15, 199 (1967).
17. H. Bash and L.C. Snyder, Chem. Phys. Lett., 3, (1969).
18. M.E. Schwartz and L.C. Allen, J. Am. Chem. Soc., 92, 1466 (1970).
19. I.A. Koppel, U.H. Mölder, and R.J. Pikver, This journal, 17, 458(1980).
20. H. Stafast and H. Bock, Chem.Ber.,107, 1882 (1974).

ON THE KINETICS OF 5-CHLOROANTHRA (I,9-CD)-6-  
-ISOXAZOLONE AMINATION

L.M. Gornostayev, G.I. Zolotaryeva and D.Sh. Verkhodova

Krasnoyarsk State Pedagogical Institute, Krasnoyarsk

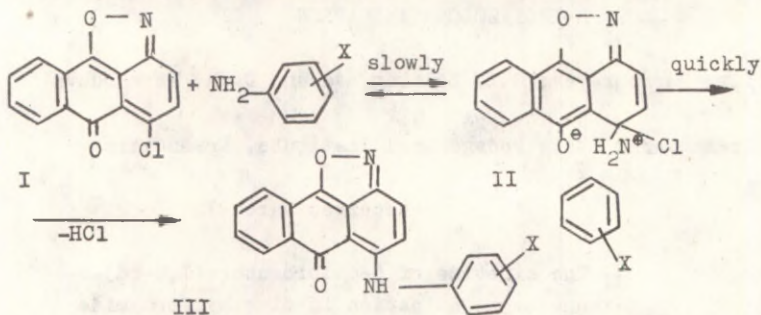
Received March 12, 1982

The kinetics of 5-chloroanthra(I,9-cd)-6-isoxazolone amination in dimethylformamide has been investigated. Amination of the above isoxazolone obeys the Hammett equation. It was shown that the studied reaction is not catalyzed by arylamine. The activities of 5-chloroanthra(I,9-cd)-6-isoxazolone and I-halogen-anthraquinones toward piperidine were compared.

So far the reactivity of anthraquinone derivatives in relation to the I,10-quinoid system as well as heterocyclic anthrone analogs with similar distribution of multiple bonds has been studied insufficiently. Reference 1 reports a number of active positions in the molecule of I,10-anthraquinone (ana-quinone) in relation to the nucleophilic attack:  $9 > 4 > 2$  which is in agreement with quantum-mechanical calculations on the distribution of  $\pi$ -electron density in the ground state<sup>2</sup>. It was shown<sup>3-4</sup> that 5-chloroanthra(I,9-cd)-6-isoxazolone(I) which contains a fragment of I,10-anthraquinone-I-imine in its structure interacts easily with various amines. The high activity of compound I in amination reactions has been attributed to the enhanced stability of intermediate(2) resulting from the appearance of aromaticity in the central ring of anthrone<sup>4</sup>.

Since it is uncommon for the intermediate to enhance its stability in the reactions of aromatic nucleophilic sub-

stitution in this way, it was of interest for us to study the amination reaction of 5-chloroanthra(1,9-cd)-6-isoxazolone and compare the obtained kinetic results with similar data for the amination reaction of I-halogenanthraquinones<sup>5</sup>.



The kinetics of 5-chloroanthra(1,9-cd)-6-isoxazolone amination was studied spectrophotometrically in dimethylacetamide at 95 $\pm$ 0.1°C. The values for second order rate constants ( $k_2$ ) are displayed in Table I.

Table I  
Rate constants of amination of  $k_2$  (l/mol $\cdot$ sec) $\cdot$   
 $\cdot 10^3$  5-chloroanthra(1,9-cd)-6-isoxazolone with  
arylamines  $\text{NH}_2\text{-C}_6\text{H}_4\text{-X}$

N n/n	I	2	3	4	5	6	7	8
X	n-OC <sub>2</sub> H <sub>5</sub>	n-OCH <sub>3</sub>	n-CH <sub>3</sub>	m-CH <sub>3</sub>	H	m-OCH <sub>3</sub>	n-Br	m-NO <sub>2</sub>
$k_2$	27.58	20.51	8.847	4.014	3.181	2.645	0.7205	0.1127

According to Fig. I there is a linear correlation between the values of  $\log k_2$  and Hammett's  $\sigma$ .

The low absolute value of  $\rho$  could be ascribed to a drop in the polarity of intermediate (2) resulting from the formation of an intramolecular hydrogen bond, but also to the high temperature of the reaction and to the use of a polar



solvent.

Judging by the sign of  $\rho$  and also by the lack of absorption in the UV spectra of intermediate (II) it can be assumed that the rate-determining step of the reaction is the step of forming this compound.

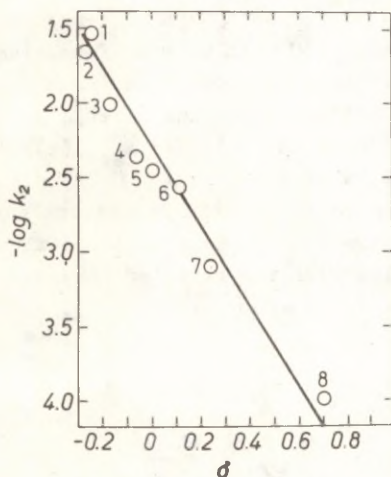


Fig.1. The dependence of  $\log k_2$  on Hammett's  $\sigma$  for the amination of 5-chloroanthra(1,9-cd)-6-isoxazolone in dimethylacetamide at 95°C.  $\rho = -2.38^{\pm}$   
 $r = 0.979$ ,  $s = 0.184$ . (The numbering of points corresponds to Table I).

Lack of the primary kinetic isotope effect speaks for the proposed mechanism. As a matter of fact,  $k_2$  (1/mol\*sec) have rather close values ( $k_{2H} = 0.00318$ ,  $k_{2D} = 0.00328$ ) for the amination of isoxazole (I) with aniline ( $k_{2H}$ ) and N,N,2,4,6-pentadeuteroaniline ( $k_{2D}$ ) at a temperature of 95°C.

We have established another fact that supports the proposed mechanism - lack of basic catalysis at the interaction of substrate (I) with n-toluidine in dimethylacetamide at 95°C at the following ratios 1:5, 1:10, 1:20, 1:30, 1:50

(in these cases  $k_2$  (1/mol $\cdot$ sec) have the following values: 0.00885; 0.00879; 0.00816; 0.00767; 0.00772).

For the reaction of isoxazolone (I) with n-toluidine at the ratio 1:5 we have determined activation parameters in the temperature range 87-95°C. We established that  $E_{act}$  (kJ/mol) = 77.42;  $\Delta s^\ddagger$  = -78 J/mol $\cdot$ K.

In ref.5 the kinetics of interaction of I-halogenanthraquinones with piperidine at 50°C in dimethylformamide has been studied. When applying I-fluoroanthraquinone as the substrate in this reaction the following kinetic parameters were obtained:  $k_2$ (1/mol $\cdot$ sec) $\cdot 10^2$  = 1.211;  $E_{act}$  (kJ/mol) = 50.58;  $\Delta s^\ddagger$ (J/mol $\cdot$ K) = -146.30.

We have determined similar kinetic parameters for the reaction of 5-chloroanthra(I,9-cd)-6-isoxazolone with piperidine in dimethylformamide with the ratio of the substrate and reagent being 1:5.

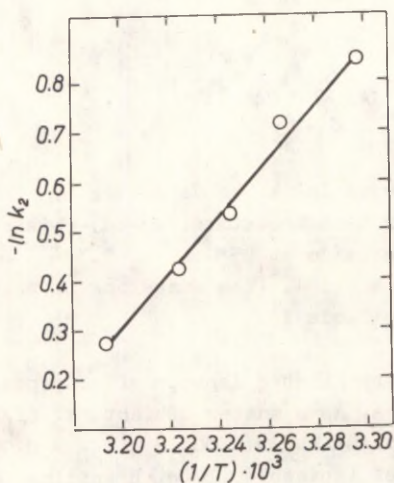


Fig.2. Determination of activation parameters for the interaction of 5-chloroanthra(I,9-cd)-6-isoxazolone with piperidine in dimethylformamide in the temperature range 30-40°C.  $E_{act}$  (kJ/mol) = 46.545  $\pm$  3.741;  $\Delta s^\ddagger$ (J/mol $\cdot$ K) = -98.762.

It was revealed that the  $k_2(1/\text{mol}\cdot\text{sec})\cdot 10^2(134.95)$  of this reaction at  $50^\circ\text{C}$  is considerably higher than the one for the interaction of I-fluoroanthraquinone with piperidine found in the literature.  $E_{\text{act}}$  of the process which we have studied (Fig.2) has a somewhat lower value than in the case compared.

The results obtained enable us to state that halogen (chlorine) in the position of 5-anthra(I,9-cd)-6-isoxazolones has high mobility which exceeds the mobility of fluorine in I-fluoroanthraquinone in the reaction of nucleophilic substitution.

## EXPERIMENTAL

### Initial Products and Reaction Products

5-chloroanthra(I,9-cd)-6-isoxazolone was obtained by a well-known method<sup>6</sup>. The synthesis of 5-arylaminoanthra(I,9-cd)-6-isoxazolones has been reported earlier<sup>4</sup>. Similarly to the well-known method<sup>4</sup> the following products were synthesized:

#### 5-m-nitroanilinoanthra(I,9-cd)-6-isoxazolone

0.64 g (0.0025m) of 5-chloroanthra(I,9-cd)-6-isoxazolone and 1.725 g (0.0125m) of m-nitroaniline in 10 ml of dimethylacetamide was heated in hot water bath for 15 hours, then the reaction volume was cooled, the residue was filtered off and washed with ether. After recrystallization of the latter 0.69 g (77.18%) of 5-m-nitroanilinoanthra(I,9-cd)-6-isoxazolone was obtained from toluene. The melting point was  $246-247^\circ\text{C}$ .  $\lambda_{\text{max}}$ , nm (log  $\epsilon$ ) (ethanol) 253 (4.48) ; 269 (4.47) ; 350 (4.017) ; 490 (4.25) ; 520 (4.29). The obtained per centage: N 11.79.  $\text{C}_{20}\text{H}_{11}\text{N}_3\text{O}_4$ . The calculated per centage: N 11.76.

#### 5-piperidinoanthra(I,9-cd)-6-isoxazolone

1.28 g (0.005m) of 5-chloroanthra(I,9-cd)-6-isoxazolone was suspended in 25ml of methanol. The suspension was heated up to  $50^\circ\text{C}$ . When mixing without further heating of the suspension, 1.94 g (0.02m) of piperidine in 5 ml of methanol



was gradually added to the suspension. The reaction volume was mixed three times. Having been cooled to 0-5°C the residue fell out, it was filtered and washed over ether. After recrystallization from the mixture of ethanol and toluene (2:1 by ratio) 1.22 g (80.26%) of 5-piperidinoanthra(I,9-cd)-6-isoxazolone was obtained. The melting point was 160-162 C.  $\lambda_{\max}$ , nm (log  $\epsilon$ ) (ethanol) 260 (4.44), 267 (4.40), 350 (3.95), 500 (4.21), 538 (4.24). The obtained per centage: N 9.12, C<sub>19</sub>H<sub>17</sub>N<sub>2</sub>O<sub>3</sub>. The calculated per centage: N 9.21.

The solvents involved in the study of kinetics were purified according to a well-known method<sup>6</sup>.

#### Kinetic Measurements

The kinetics of the reaction was studied by the method of sampling. The concentration of 5-chloroanthra(I,9-cd)-6-isoxazolone in the temperature-controlled reaction flask in the case of amination was  $0.5 \cdot 10^{-1}$  mol and in the case of interaction with piperidine  $0.5 \cdot 10^{-2}$  mol. After a 100-fold dilution (toluene applied as diluent) the resulting mixture was analyzed on a spectrophotometer Specord UV-Vis at definite intervals, the width of the slot being Imm-Icm. In all the cases the spectral curves passed through the isobestic point. The data for calculating the rate constants were obtained at the wavelengths 510-530 nm where the initial isoxazolone (I) does not practically absorb. The calculation of rate constants was done by the least squares method<sup>7</sup>.

The activation parameters were calculated by a well-known method<sup>8</sup>.

#### REFERENCES

1. M.V. Gorelik, S.P. Titova, and V.A. Trdatyan, Zh.org.khim., 16, 167 (1980).
2. A. Topp, P. Boldt, and H. Scmandt, Lieb. Ann., 1974, 1167.
3. A.M. Galushko, and N.S. Dokunikhin, Zh.org.khim., 15, 575 (1979).
4. L.M. Gornostayev, G.F. Zeibert, and G.I. Zolotaryeva,

I980,9I2.

5. J. Mindl, J. Slosar, and M. Vecera, Coll. Czech. Chem. Commun., 33, 2895 (I968).
6. H. Becker et al., Organicum (Russ. transl.), "Mir", vol. 2, 360 (I979).
7. E. A. Moelwyn-Hughes, The Chemical Statics and Kinetics of Solutions (Russ. transl.), "Khimiya", I33 (I975).
8. A. Gordon and R. Ford, The Chemist's Companion (Russ. transl.), "Mir", I57 (I976).

APPLICATION OF THE ELECTROSTATIC THEORY TO THE  
KINETICS OF THE FORMATION OF LEUCONITRILES  
OF TRIARYLMETHANE DYES

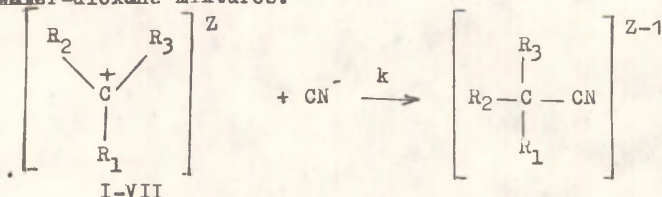
T.Ä. Nikolova and V.V. Sinev

Leningrad Lenseviet Institute of Technology

Received March 30, 1982

On the basis of the spectrophotometric investigation of the kinetics of interaction of some triarylmethane dyes with cyanide anion it has been shown, that the influence of the ionic strength and dielectric constant of the medium on the rate constants of the reactions studied obeys the electrostatic theory of Brönsted-Christiansen-Scatchard.

Continuing the investigations of the influence of medium polarity on the kinetics of the slow ionic reactions<sup>1-7</sup> we have studied the kinetics of interaction of some triarylmethane conjugated ions (I-VII), differing by the value and sign of the charge (z), with cyanide-anion in water and water-dioxane mixtures.



I  $R_1 = Ph$ ;  $R_2 = R_3 = 4-Me_2NPh$ ;

II  $R_1 = Ph$ ;  $R_2 = 4-Me_2NPh$ ;  $R_3 = A$  (antipyryl)

III  $R_1 = 4-Me_2NPh$ ;  $R_2 = R_3 = A$

\* All the rate constants are corrected for the reaction of samples (I-VII) with alkali (0.001M.), introduced for suppression of the cyanide-ion hydrolysis.



IV  $R_1 = \text{Ph}; R_2 = R_3 = 3\text{-OMe}, 4\text{-O}^-\text{Ph};$

V  $R_1 = R_2 = R_3 = 3\text{-OMe}, 4\text{-O}^-\text{Ph};$

VI  $R_1 = 4\text{-Me}_3\text{N}^+\text{Ph}; R_2 = R_3 = 4\text{-Me}_2\text{NPh};$

VII  $R_1 = R_2 = R_3 = 4\text{-Me}_2\text{NPh}.$

Increase in ionic strength has been found to decelerate the reaction between the cyanide ion and the cations and it accelerates the interaction of the anionic nucleophile with the negative ions, which is in full accordance with the predictions of the electrostatic theory<sup>8-11</sup>. As it should be expected, the dependence of the logarithm of the rate constant on the  $\frac{\sqrt{\mu}}{1+\sqrt{\mu}}$ -parameter is expressed by the straight line with the slope being in agreement with the product of charges of the reacting ions.

Table 1.

THE RESULTS OF STATISTICAL TREATMENT (IN ACCORDANCE WITH EQUATION 1) OF THE DATA ON THE IONIC STRENGTH INFLUENCE ON THE KINETICS OF INTERACTION OF TRIARYLMETHANE DYES WITH CYANIDE ION IN AQUEOUS SOLUTION AT 20°C

R	$(Z_a \cdot Z_b)$	tg α <sup>a)</sup>	-lg k <sub>0</sub> <sup>b)</sup>	r	s	n
I	-1	-1.05	0.355	0.998	0.003	11
II	-1	-0.98	0.376	0.994	0.004	13
III	-1	-0.96	1.188	0.996	0.003	11
IV	+1	0.91	2.521	0.993	0.005	7
V	+2	1.92	3.920	0.999	0.007	4
VI	-2	-1.99	-0.189	0.995	0.009	11

a, b) the slope and intercept of the dependence

$$\lg k = f\left(\frac{\sqrt{\mu}}{1+\sqrt{\mu}}\right)$$

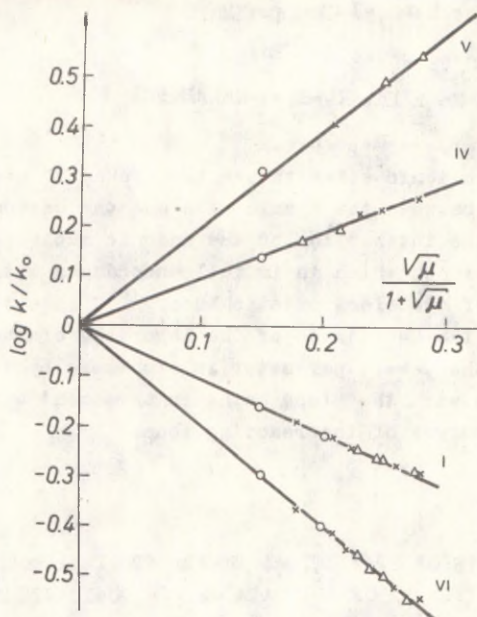


Fig. 1 The influence of the ionic strength on the rate constant of the formation of the leuconitriles of triarylmethane dyes in water at 20° C.

- o - no salt added
- x - in the presence of KCL
- Δ - in the presence of  $\text{NaNO}_3$

It should be emphasized, that for each examined conjugated ion the linear dependence includes the data obtained both in the presence of different added salts and in the absence of the latter. It completely confirms non-specific nature of the primary studied salt effect.

The investigation carried out in mixed water-dioxane solvents allowed us to find out that the influence of the binary system on the kinetics of all the studied reactions also agrees with the predictions of the electrostatic theory.

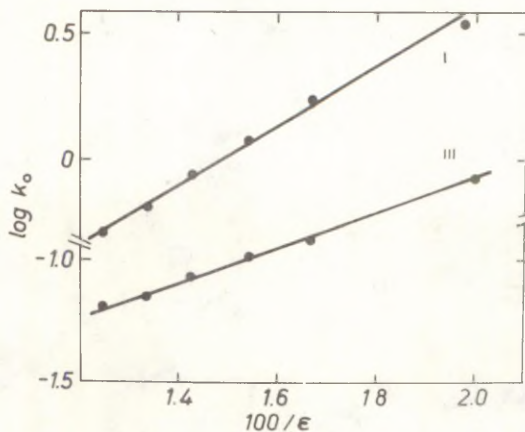


Fig. 2. The influence of dielectric constant (water-dioxane) on the rate constant of the formation of leuconitriles of cations I and III. The normalized values are given.

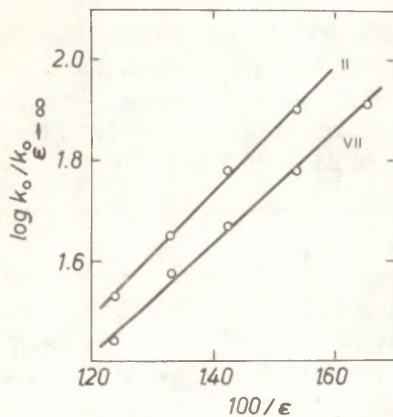


Fig. 3. The dependence of the rate constant of interaction of triarylcarbocations with the cyanide-anion on the dielectric constant of the mixed water-dioxane solvent.



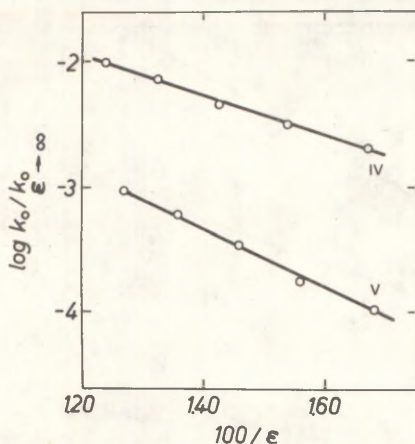


Fig. 4. The dependence of the rate constant of interaction of triarylmethane anions with cyanide-anion on dielectric constant of the water-dioxane solvent system.

Table 2

THE RESULTS OF THE STATISTICAL TREATMENT (BY THE SCATCHARD EQUATION) OF THE DATA ON THE DIELECTRIC CONSTANT OF THE WATER-DIOXANE MIXTURES INFLUENCE ON THE KINETICS OF THE FORMATION OF TRIARYLMETHANE DYES LEUCONITRILES AT 20°C.<sup>a)</sup>

R	$z_a$	$\lg d^b$	$-\lg k_0^c$	$r, \text{\AA}$	r	s	n
I	1	122	1.800	2.0	0.999	0.060	6
II	1	124	1.920	2.0	0.999	0.015	4
III	1	68	2.047	3.6	0.998	0.013	6
IV	-1	162	0.476	1.5	0.998	0.030	5
V	-2	238	0.702	2.1	0.997	0.032	6
VII	1	115	2.823	2.2	0.992	0.028	6

<sup>a)</sup> 25°C; <sup>b), c)</sup> the slope and intercept of the straight line

$$\lg k = f\left(\frac{1}{\epsilon}\right)$$

Addition of a non-polar component to the solvent results in the acceleration of the reaction between the  $\text{CN}^-$ -anion and the cations, but decelerates the interaction of the uni-charged ions. The logarithm of the rate constant is found to be linearly dependent on the  $\frac{1}{\epsilon}$ -parameter for all of the ions under consideration, the above dependence also includes the rate constants obtained in pure water (Fig. 2-4, Table 2 ).

Thus, the influence of the polar properties of the medium on the kinetics of the reactions studied is described by the Brönsted-Christiansen-Scatchard equation<sup>8-11</sup>.

$$\lg K = \lg K_{\epsilon \rightarrow \infty} + \frac{Z_A Z_B^A \sqrt{\mu}}{1 + \sqrt{\mu}} - \frac{Z_A Z_B^N e^2}{2.303 RT r^{\#} \epsilon} \quad (1)$$

It should be noted, that the above equation properly describes the influence of the dielectric constant on the kinetics of the formation of leuconitriles of those aminotriphenylmethane dyes, for which considerable deviations from the electrostatic theory have been found in the case of their interaction with the hydroxide-ion in the solvent system under consideration<sup>12,13</sup> and in other water-organic solvent systems<sup>5,14</sup>. Such a result makes it possible to come to the conclusion that the mentioned deviations for the formation of the triarylcarbinols result from some specific details of the interaction mechanism of the  $\text{OH}^-$ -ion with the water molecules, bound in the hydration sphere of the aminotriphenylcarbocations<sup>15</sup>.

The radii of the activated complex of the reactions studied calculated in accordance with eq. 1 appeared to be close enough to the corresponding values obtained for the reaction of triarylcarbinols formation<sup>3,4,16,17</sup>, such a result being in agreement with the supposition about the frontal attack of the carbonium center of the conjugated ions by the anions.

## References

1. V.V. Sinev, Reakts. sposobn. organ. soedin., 3, v.1, 191 (1966).
2. V.V. Sinev and M.M. Livshits, Reakts. sposobn. organ. soedin., 6, 292 (1969).
3. V.V. Sinev and M.M. Livshits, Reakts. sposobn. organ. soedin., 8, v.2, 557 (1971).
4. E.A. Shaykova and V.V. Sinev, Reakts. sposobn. organ. soedin., 10, 547 (1973).
5. V.V. Sinev, E.A. Shaykova, and O.F. Ginzburg, Zh. org. khim., 10, 1912 (1974).
6. V.V. Sinev, T.V. Proskuriakova, A.V. Alexander, and O.F. Ginzburg, Zh. org. khim., 14, 1676 (1978).
7. A.V. Alexander, V.V. Sinev, and O.F. Ginzburg, Zh. org. khim., 17, 800 (1981).
8. G. Scatchard, Ann. N.Y. Acad. Sci., 39, 342 (1940).
9. S. Glasstone, K.J. Laidler, and H. Eyring, The Theory of Rate Processes, N.Y.-L., (1940).
10. E.S. Amis, Solvent Effects on Reaction Rates and Mechanisms, N.Y.-L., (1966).
11. S.G. Entelis and R.P. Tiger, Kinetics of Reactions in the Liquid Phase, "Khimiya", (1973).
12. J.C. Turgeon and V.K. LaMer, J. Am. Chem. Soc., 74, 5989 (1952).
13. V.V. Sinev and G.K. Semenova, Reakts. sposobn. organ. soedin., 10, 43 (1973).
14. M.M. Livshits, V.V. Sinev, and O.F. Ginzburg, Zh. org. khim., 8, 1907 (1972).
15. D. Bethell and V. Gold, Carbonium Ions, (Russian translation), Mir, (1970).
16. V.V. Sinev, G.K. Semenova, and O.F. Ginzburg, Zh. org. khim., 8, 1205 (1972).
17. G.K. Semenova, V.V. Sinev, and O.F. Ginzburg, Zh. org. khim., 8, 301 (1972).



A THERMOCHEMICAL STUDY OF THE ASSOCIATION AND  
DONOR CAPACITY OF DIAMINES IN SOLUTIONS

V.G. Tsvetkov, M.N. Buslayeva, Yu.P. Klapshin  
and K.T. Dudnikova

N.S. Kurnakov Institute of General and Inorganic Chemistry,  
USSR Academy of Sciences, Moscow; Institute of Chemistry  
at Gorky State University, Gorky

Received April 8, 1982

The enthalpies of mixing 1,2-propylene diamine, 1,3-trimethylene diamine and 1,6-hexamethylene diamine with hexane and chloroform have been determined for a number of concentrations. From the data obtained the association energies and the donor capacity of these diamines have been estimated. The donor capacity, as compared with ethylene diamine, is shown to increase, which is explained by inductive effects.

In our previous works<sup>1,2</sup> the association and electron-donor-acceptor capacity of ethylene diamine were studied in detail. Ethylene diamine was shown to be a good donor (the donor number  $DN_{SbCl_5}$  was estimated by us as equal to  $50 \pm 3$ ) and a bad acceptor of electrons<sup>1</sup>. This explains the comparatively weak hydrogen bond in liquid ethylene diamine (the association energy amounts to  $3.8 \text{ kcal/mol}^2$ ). The objective of the present work is to study thermochemically the donor capacity and association variation in diamines with the introduction of a  $CH_3$  end group (1,2-propylene diamine) and  $CH_2$  bridged groups (1,3-trimethylene diamine and 1,6-hexamethylene diamine) into the ethylene diamine molecule. To solve this problem we have chosen the thermochemical method previously used by us in studying liquid ethylene diamine<sup>1,2</sup>.

The enthalpies of mixing diamines with hexane and chloroform were determined in an adiabatic calorimeter in the medium of dry nitrogen at  $293^\circ K$  for 1,2-propylene diamine and 1,3-trimethylene diamine, and at  $318^\circ K$  in the

case of 1,6-hexamethylene diamine, as its melting point is  $312^{\circ}\text{K}$ . The accuracy of determining the enthalpy variation was  $\pm 1.5\%$ . The experimental procedure was described in <sup>3,4</sup>

Diamines were dehydrated by twice performed distillation over metallic sodium, hexane and chloroform - by conventional techniques <sup>5</sup> ,.

The results obtained on the enthalpies of mixing with hexane are shown in Table 1 for 1,2-propylene diamine and 1,3-trimethylene diamine and in Fig.1 for 1,6-hexamethylene diamine.

From the results obtained the enthalpies of mixing of diamines with hexane are seen to be positive and to increase with dilution, which is characteristic of associated liquids.

Thermochemical investigation of the solutions of associated liquids in alkanes is often used to estimate the association energy of these compounds. It is shown in <sup>6</sup> that the quantity of the first integral heat of solution in hexane is close to the association energy of the liquids in question if this energy is not very high ( $E_{\text{ass}}$  lower than 10 kcal/mol). According to our data this quantity amounts to 3.6 kcal/mol for 1,2-propylene diamine, 4.0 kcal/mol for 1,3-trimethylene diamine and 3.5 kcal/mol in the case of 1,6-hexamethylene diamine. It is thus seen that 1,3-trimethylene diamine is associated more than ethylene diamine (association energy of ethylene diamine amounts to 3.8 kcal/mol <sup>2</sup> ), and 1,2-propylene diamine and 1,6-hexamethylene diamine - less.

The second objective of the present work was to study the variation of the donor capacity of diamines with the introduction of  $\text{CH}_3$  and  $\text{CH}_2$  groups into the ethylene diamine molecule. As already noted <sup>1</sup> , direct determination of Gutmann's donor number in the case of diamines (from the heats of mixing with  $\text{SbCl}_5$  in the medium of dichloroethane at the ratio of components 1:1) is impossible because of a strong exoeffect leading to the combustion of diamine, so, following works <sup>1,7,8</sup> , we have estimated the donor capacity

Table 1

Enthalpies of mixing 1,2-propylene diamine (PDA) and 1,3-trimethylene diamine (TDA) with hexane at 298°K

mol.% of di- amines	$C_6H_{14}$ - PDA		$C_6H_{14}$ - TDA	
	$\Delta H_2$ $\frac{\text{cal}}{\text{mole of PDA}}$	$\Delta H^m$ $\frac{\text{cal}}{\text{mole of mixture}}$	$\Delta H_2$ $\frac{\text{cal}}{\text{mole of TDA}}$	$\Delta H^m$ $\frac{\text{cal}}{\text{mole of mixture}}$
0	3600		4000	
1	3400	34	-	
2	3200	64	3500	70
4	2800	112	3200	128
6	2400	144	3000	150

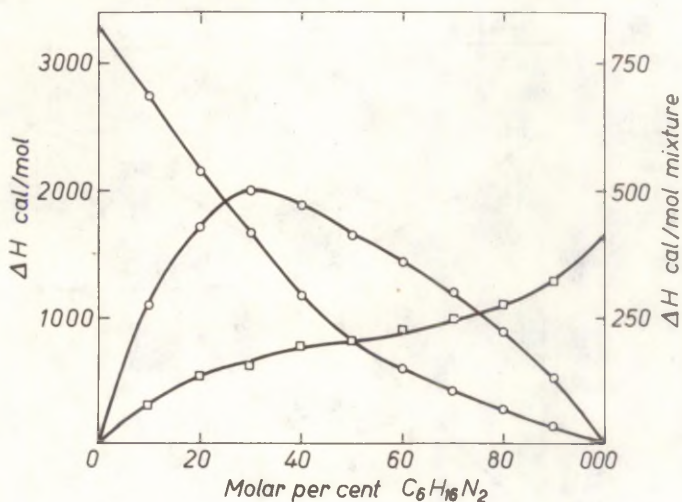


Fig.1. Enthalpies of mixing hexane with 1,6-hexamethylene diamine at 318°K

a)  $\Delta H$  of mixing cal/mol mixture

b)  $\Delta H$  of mixing cal/mol  $C_6H_{16}N_2$

c)  $\Delta H$  of mixing cal/mol  $C_6H_{14}$



Table 2

Enthalpies of mixing 1,2-propylene diamine (PDA) and 1,3-trimethylene diamine (TDA) with chloroform at 298°K

mol.% of di- amines	CHCl <sub>3</sub> - PDA		CHCl <sub>3</sub> - TDA	
	$-\Delta H_2$	$-\Delta H^m$	$-\Delta H_2$	$-\Delta H^m$
	cal mole of PDA	cal mole of mixture	cal mole of TDA	cal mole of mixture
0	4400		5000	
5	3800	190	4300	215
10	3300	330	3500	350
15	2900	435	3353	503
20	2600	520	3000	600
30	2100	630	2300	690
40	1650	660	1900	760
50	1300	650	1500	750

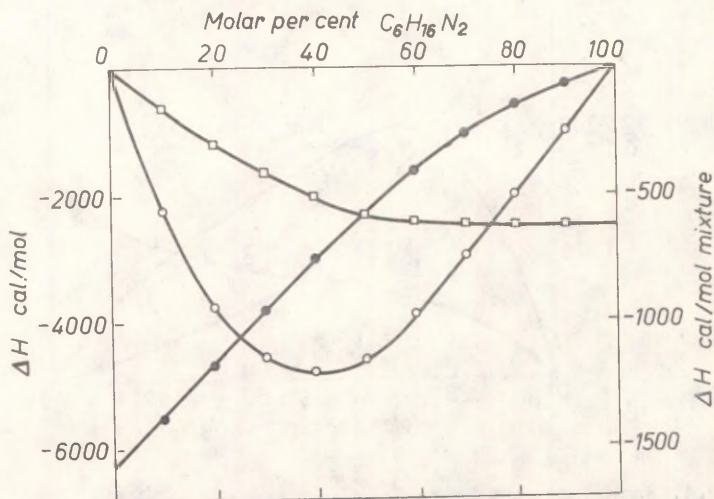


Fig.2. Enthalpies of mixing chloroform with 1,6-hexamethylene diamine at 318°K  
 a)  $\Delta H$  of mixing cal/mol mixture  
 b)  $\Delta H$  of mixing cal/mol C<sub>6</sub>H<sub>16</sub>N<sub>2</sub>  
 c)  $\Delta H$  of mixing cal/mol CHCl<sub>3</sub>

of the diamines in question from the enthalpies of mixing with chloroform. The results obtained are shown in Table 2 and Fig.2.

The enthalpies of mixing diamines with an excess of chloroform amounted to: -4.4 kcal/mol for 1,2-propylene diamine, -5.0 kcal/mol for 1,3-trimethylenediamine and -6.2 kcal/mol for 1,6-hexamethylene diamine. Taking into account the previously found association energies of pure diamines, one can estimate the energy of hydrogen bond between chloroform and diamines at 8 kcal/mol in the case of 1,2-propylene diamine, 9 kcal/mol in the case of 1,3-trimethylene diamine and 9.7 kcal/mol in the case of 1,6-hexamethylene diamine. It should be noted that these values are greater than the energy of hydrogen bond of chloroform with ethylenediamine (7.8 kcal/mol<sup>1</sup>).

All the diamines studied by us thus possess a higher donor capacity than ethylene diamine. We are inclined to explain this by the inductive effects of both the end  $\text{CH}_3$  group and the bridged  $\text{CH}_2$  groups introduced into the ethylenediamine molecule<sup>9,10</sup>. A lower association of 1,2-propylene diamine and 1,6-hexamethylene diamine we have explained by steric factors. Indeed, the presence of an end  $\text{CH}_3$  group hinders the free rotation of the amine group, necessary to reach the configuration most favourable during association. In the case of 1,6-hexamethylene diamine, however, the molecule proves to be too large, and the contacts needed for association are found with a smaller probability than for ethylene diamine.

#### REFERENCES

1. V.G. Tsvetkov, M.N. Buslayeva, and A.I. Krugliak, *Reakts. sposob. org. soedin.* 17, iss. 2 (62), 129 1980.
2. V.G. Tsvetkov, A.I. Krugliak, and M.N. Buslayeva, *Vestnik KhGU* 1982 (in print).
3. P.N. Nikolajev and I.B. Rabinovich, *Tr. po khimii i khim. tekhnologii*, iss. 2, Gorky, 83 1971.

4. V.G. Tsvetkov, Ye.F. Kuprianov, and I.B. Rabinovich, Tr. po khimii i khim. tekhnologii, iss.1, Gorky, 83 1974.
5. A. Weissberger, E. Proskauer, J. Riddick, and E. Toops, Organic Solvents, Foreign Languages Publishing House, Moscow, 1958.
6. Yu. A. Aleksandrov, V.G. Tsvetkov, and Ye.I. Soloviova, Zh. fiz. khim., 51, iss. 8, 2137 1977.
7. V.P. Belousov, A.M. Starodubtsev, T.D. Boliakina, and M.Ye. Obukhova, Tr. po khimii i khim. tekhnologii, iss. 4 (43), Gorky, 85 1975.
8. V.G. Tsvetkov, B.P. Kozyrkin, L.Ya. Tsvetkova, and I.B. Rabinovich, Zh. obshch. khim., 48, iss. 10, 2162 1978.
9. Ye. N. Guryanova, I.P. Goldshtein, and I.P. Romm, Donor-Acceptor Bond. "Khimiya", Moscow, 1973.
10. V. Gutmann, The Donor-Acceptor Approach in Molecular Interactions, Plenum Press. N.Y. and London, 1978.



STUDY OF 2-OXOINDOLINE DERIVATIVES  
BY OXIDIZING VOLTAMMETRY

V.I. Makurina and V.V. Bolotov

Kharkov State Pharmaceutical Institute  
Kharkov, the Ukrainian SSR

Received April 24, 1982

Electrochemical oxidation of 3,3-diphenyl-2-oxoindolines on the rotating platinum microanode in acetonitrile has been studied. The dependence of limiting currents ( $i_l$ ) of electrooxidation on temperature, rotation rate of the electrode and concentration was studied and the diffusion-limited character of  $i_l$  was established. The influence of electronic effects of substituents in the molecules of the studied substances on electrochemical properties was established. The equation of correlation dependences of the half-waves potentials  $E_{I/2}$  on Hammett's  $\sigma$  constants was obtained. The established dependence of  $i_l$  on the concentration of the depolarizer was applied to work out methods of quantitative determination of 2-oxoindoline derivatives. The error limit of analysis is under 2 per cent.

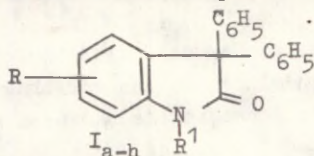
2-oxoindoline derivatives reveal antiinflammatory activity<sup>1,2</sup>. Therefore it is of interest to study the electrochemical properties of the above compounds with a view to determining their structure, studying their reactivity and establishing the possible relationship between their electrochemical properties and biological activity. The results

obtained could be applied to reveal the metabolic mechanism and biotransformations of bioactive substances in the living cell<sup>3</sup>.

To solve the above objectives we applied the method of electrochemical oxidation on the rotating platinum micro-anode.

Anodic oxidation was applied to 3,3-diphenyl-2-oxoindoline derivatives ( $I_{a-h}$ ) the structure of which is displayed in the Table.

Table  
ELECTROCHEMICAL PROPERTIES OF ELECTROOXIDATION  
OF 2-OXOINDOLINE DERIVATIVES IN ACETONITRILE



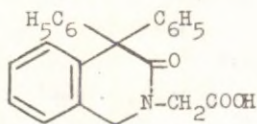
Compound	R	R <sup>I</sup>	E <sub>i</sub> , B	E <sub>I/2</sub> , B	K <sub>d</sub> ·10 <sup>3</sup>	Peculiarities of electro- oxidation
I <sub>a</sub>	4-COOH	H	2.0	-	-	x
I <sub>b</sub>	5-COOH	H	-	-	-	xx
I <sub>c</sub>	7-COOH	H	1.86	1.79	1.25	xxx
I <sub>d</sub>	H		1.78	1.74	2.26	xxx
I <sub>e</sub>	5-CH <sub>3</sub>		1.70	1.60	1.32	xxxx
I <sub>f</sub>	5,7-(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>2</sub> COOH	1.56	1.52	1.21	xxxx
I <sub>g</sub>	5-OCH <sub>3</sub>		1.34	1.30	0.93	xxxx
I <sub>h</sub>	5-Cl		1.86	1.82	2.40	xxx

Note. x indistinct polarization curves,  
 xx oxidizes with the supporting electrolyte,  
 xxx well-defined polarization curves,  
 xxxx volt-ampere curves suitable for analytic  
 purposes

On volt-ampere curves of compounds  $I_{a-h}$  a wave can be observed which characterizes the involvement of molecules of the studied substances in the electrochemical process.

The electrochemical properties of the studied substances are influenced by the position and character of substituents in the annelated benzene ring. The presence of 2-oxoindolines of the methoxy group ( $I_g$ ) facilitates electrooxidation, but when changed by more electronegative substituents, the oxidation potentials shift to the more negative range of potentials ( $I_h$ ).

For 2-oxoindolines, which contain a carboxyl group in various positions of the benzene ring of the oxindol cycle, the following regularity can be observed: the COOH group in position 5 ( $I_b$ ) considerably hinders electrooxidation (no oxidation can be observed on the polarogram), but when transferring it to position 4 or 7 the polarograms reveal electrooxidation of the studied substances. It gives evidence of the fact that in the electrooxidation processes of 5- and 7-substituted 2-oxoindolines (similarly to O- and p-substituted benzene<sup>4</sup>) an important role is played by the effects of direct polar resonance of the substituents with the reaction center, which for the above depolarizers is evidently the C-N bond between the hydrogen of the annelated benzene ring and the atom of nitrogen. The above assumption is reinforced also by the fact that the model compound (II), where the conjugation of  $\pi$ -electrons of the nitrogen atom with the benzene ring is out of the question, does not undergo electrooxidation.



II

When analyzing the influence of the character of substituents on the electrochemical properties of the studied substances from the point of view of the principle of linearity of free energies we have obtained a correlation equation

between the  $E_{1/2}$  bond and Hammett's  $\sigma$  constants for compounds  $I_{d-h}$  which is the following:  $E_{I/2} = 1.7I_{\pm} - 0.53^{\pm}$



( $r=0.998$  ;  $s=0.233$ ). It should be noted that a point corresponding to  $E_{I/2}$  of compound  $I_g$  which contains a  $OCH_3$  group in position 5 deviates from the general correlation.

The study of the dependence of limiting currents on the concentration, temperature and rotation speed of the electrode (Figures 1 and 2)

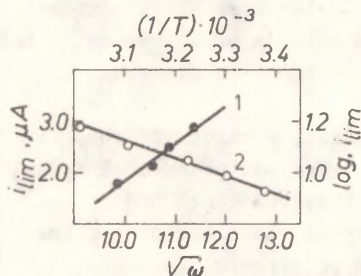


Fig.1.

The dependence of the limiting current on  $\sqrt{\omega}$  ( $\omega$  is in rad/sec for the solution of compound  $I_f$  in acetonitrile (I). The temperature dependence of electrooxidation of compound  $I_f$ , the concentration of the solution is 0.40 mmol/l (2).

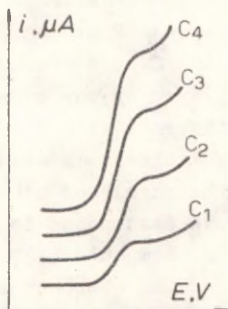


Fig.2.

The polarization curves for the solutions of compound  $I_g$  in acetonitrile (c - concentration of the solution, mmol/l ;  $c_1=0.33$  ,  $c_2=0.57$  ,  $c_3=0.75$  ,  $c_4=0.89$ ).

confirmed the diffusive character of  $i_l$ . The existence of a satisfactory correlation between the value of the limiting current and concentration has enabled us to work out methods of quantitative determination of 2-oxoindolines according to which the analysis of 3,3-diphenyl-5-methoxy-6-oxoindoline-I-acetic acid ( $I_g$ ) was carried out. The error limit of the suggested method is under 2 per cent.

## EXPERIMENTAL

Volt-ampere curves were recorded on a polarograph LP-7e, the scanning rate of the potential being 400 mv/min. The indicator electrode was a rotating platinum microdisk anode with a surface of  $5 \cdot 10^{-3} \text{ cm}^2$ ; the reference electrode was an external aqueous saturated calomel half-cell. The solvent was acetonitrile, purified according to the method described in ref. 5, the indifferent electrolyte - the 0.1 M solution of lithium perchlorate, the concentration of the studied substances was 0.3-0.9 mmol/l. Depolarization of the indicator electrode was carried out by cleaning the latter with a piece of fine emery cloth after recording volt-ampere curves.

## REFERENCES

1. V.V. Bolotov, V.V. Drugovina, P.A. Petyunin, Z.S. Spesivtseva, and S.M. Drogozov, *Khim.-pharm.zh.*, 13, No. II, 45 (1979).
2. V.V. Bolotov, P.A. Petyunin, V.V. Drugovina, and A.I. Berezhnyakova, *Khim.-pharm.zh.*, 14, No. I2, 39 (1980).
3. *Electrosynthesis and Bioelectrochemistry*, Ed. by V.N. Frumkin, Ya.P. Stradyn, and L.G. Feoktistov, Moscow, "Nauka", 343, (1975).
4. Ya.P. Stradyn, *Izv. AN Latv. SSR*, No. 8, 95 (1979).
5. I.M. Sosonkin, A.P. Domarev, Z.G. Kaminskaya, A.I. Tolstikov, F.F. Lakomov, and G.Ya. Kaminski, *Zh. prikladn. khim.*, 950 (1971).

QUANTITATIVE STATISTICAL INTERPRETATION  
OF KINETIC DATA IN THE GAS PHASE HOMOLYSIS.

I. Modified Calculation Scheme for Formation  
Enthalpies in the Gas Phase at 0°K.

V. Palm and R. Hiob

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

Received August 5, 1982

Applicability of the calculation scheme to formation enthalpies ( $\Delta H_O^0$ ) of organic compounds based on conceptions of  $\Psi$ - and inductive interactions has been proved for the gas phase at 0° K. The values of parameters A, B and C related to pairwise, triple and quaternary interactions of groups connected with the same  $sp^3$  carbon atom are specified. Complementary rules are suggested reflecting the absence of any interaction between halogen atoms connected with a single carbon atom but the vicinal one between two fluorine atoms. The substituent constants  $\Psi$  and additive increments for halogen atoms and the nitro group are specified. The applicability of universal values of the inductive transmission constant  $z_C^*$  for carbon atom and scaling constant  $\alpha^*$  is demonstrated to enable one reasonably describe the  $\Delta H_O^0$  values of polyfunctional derivatives of alkanes.

The use of the value of  $G_{NO_2}^* = 4.48$  instead of the previously used (3.55) leads to a more precise description of  $\Delta H_O^0$  values for polynitro substituted alkanes. This is accompanied with a considerable change in the inductive scaling constant  $\alpha^*$  value (1.35 instead of 2.2, in kcal/mole).



The subject of the present and following papers of this series is a detailed representation of the results of the quantitative statistical treatment of the kinetic data for the gas phase homolytic dissociation. A formal approach to structure-reactivity relations is used. A preliminary survey of these results has been presented recently<sup>1</sup>.

Homolytic dissociation with the fission of the ordinary covalent bond according to the scheme:



is characterized by the activation free energy  $\Delta G^\ddagger$ . It is the difference between G values for activated and initial states, the latter being represented by the molecule  $R_1 - R_j$ . The activated state is considered as a combination  $[R_1 \cdot R_j \cdot]^\ddagger$  of two free radicals. To calculate the  $\Delta G^\ddagger$  value one has to be able to calculate the formation free energies both for initial and activated states. For the calculation of free energies the evaluation of corresponding formation enthalpies is required. Therefore, following the purpose of quantitative interpretation of kinetic data for reactions (1), it is desirable to use a sufficiently reliable scheme for the quantitative interpretation of formation enthalpies of covalent compounds.

A formal calculation scheme for formation enthalpies of organic compounds has been presented earlier<sup>2-15</sup>. According to this scheme the formation enthalpy of any compound  $RX$  is represented as a sum of the additive terms of substituents R and X and contributions of  $\varphi$ - and inductive interaction energies. Resonance and steric energies may be added. This is represented by the following equation:

$$\Delta H_{RX} = \Delta H_R + \Delta H_X + \alpha \varphi_R \varphi_X + \alpha^{\pi} G_R^{\pi} G_X^{\pi} + \dots \quad (2)$$

$\Delta H_R$ ,  $\Delta H_X$  are additive substituent increments,  $\alpha \varphi_R \varphi_X$  is

energy of  $\varphi$ -interaction,  $\alpha^{\pi} \sigma_R^{\pi} \sigma_X^{\pi}$  - energy of inductive interaction,  $\varphi$  and  $\sigma^{\pi}$  denote corresponding substituent constants,  $\alpha$  and  $\alpha^{\pi}$  are scaling constants for  $\varphi$ - and inductive interactions. The scale of substituent constants  $\varphi$  is obtained assuming  $\alpha = 1$  kcal/mole.

Standard formation enthalpies  $\Delta H_{f,298}^{\circ}$  in the gas phase served as experimental data for the parametrization of the calculation scheme considered. However, from the point of view of reactions of type (1), values of  $\Delta H_f^{\circ}$  at  $0^{\circ}\text{K}$  ( $\Delta H_0^{\circ}$ ) are needed. Therefore it is expedient to modify the calculation scheme on the basis of  $\Delta H_0^{\circ}$  values.

A statistical verification of the equation

$$\Delta H_f^{\circ}(\text{RX}) - \Delta H_f^{\circ}(\text{RH}) = \Delta H_X + \varphi_R \varphi_X \quad (3)$$

has been performed on the basis of  $\Delta H_0^{\circ}$  values. These were calculated proceeding from the  $\Delta H_{f,298}^{\circ}$  values compiled in literature<sup>4,5</sup>. The results are represented in Table 1. As a rule the  $\varphi_X$  values obtained are close to those gained by using the enthalpy data for  $298.15^{\circ}\text{K}$ . However, some deviations have to be mentioned (CN and  $\text{C}_6\text{H}_5$ ).

The recalculation of  $\Delta H_0^{\circ}$  from the values of  $\Delta H_{f,298}^{\circ}$  was performed according to the equation:

$$\Delta H_0^{\circ} = \Delta H_{f,298}^{\circ} - (\text{H}_{298}^{\circ} - \text{H}_0^{\circ})_{\text{compound}} + \sum_i n_i (\text{H}_{298}^{\circ} - \text{H}_0^{\circ})_i \quad (4)$$

where  $i$  is the index of the element and  $n_i$  - the number of atoms of the  $i$ -th element in the molecule considered.

The values of  $(\text{H}_{298}^{\circ} - \text{H}_0^{\circ})_{\text{compound}}$  were estimated using group additivity rules<sup>16</sup> if they were lacking in the literature<sup>16,17</sup>. For example, the value  $(\text{H}_{298}^{\circ} - \text{H}_0^{\circ})_{\text{C}_6\text{H}_5\text{CF}_3}$  was estimated by the equation:

$$\begin{aligned} (\text{H}_{298}^{\circ} - \text{H}_0^{\circ})_{\text{C}_6\text{H}_5\text{CF}_3} &= (\text{H}_{298}^{\circ} - \text{H}_0^{\circ})_{\text{C}_6\text{H}_5\text{C}_2\text{H}_5} + \\ &+ (\text{H}_{298}^{\circ} - \text{H}_0^{\circ})_{\text{CF}_3\text{CH}_3} - (\text{H}_{298}^{\circ} - \text{H}_0^{\circ})_{\text{C}_2\text{H}_5\text{CH}_3} = \\ &= 5.34 + 3.64 - 3.51 = 5.47 \text{ kcal/mole.} \end{aligned}$$

Using this value  $(H_{298}^{\circ} - H_0^{\circ})$ ,  $\Delta H_0^{\circ}$  was calculated:

$$\begin{aligned}\Delta H_0^{\circ} &= \Delta H_{f,298}^{\circ}(C_6H_5CF_3) - (H_{298}^{\circ} - H_0^{\circ})(C_6H_5CF_3) + \\ &+ 7(H_{298}^{\circ} - H_0^{\circ})(C) + 2.5(H_{298}^{\circ} - H_0^{\circ})(H_2) + 1.5(H_{298}^{\circ} - H_0^{\circ})(F_2) = \\ &= -141.9 - 5.47 + 7 \cdot 0.25 + 2.5 \cdot 2.024 + 1.5 \cdot 2.108 = \\ &= -137.4 \text{ kcal/mole.}\end{aligned}$$

For nitrocompounds we could find the value of  $(H_{298}^{\circ} - H_0^{\circ})(CH_3NO_2)$ , only.<sup>16</sup> The  $(H_{298}^{\circ} - H_0^{\circ})$  values for other nitrocompounds were estimated using additive increment 1.76 kcal/mole for the nitro group calculated from the data for nitromethane and additive terms for other groups.

The values of  $\Delta H_{f,298}^{\circ}$  (kcal/mole) reported by Pittam and Pilcher<sup>18</sup> for methane (-17.80), ethane (-20.04), n-propane (-25.02), n-butane (-30.03), and 2-methyl-propane (-32.07) were used.

The polylinear development leads to the representation of the  $\gamma$ -values for trisubstituted methyls and standard formation enthalpies for tetrasubstituted methanes by equations as follows:

$$\begin{aligned}\gamma_{CX^1X^2X^3} &= \gamma_{CH_3} + A \sum_i \gamma_X^i + B \sum_{i < j} \gamma_X^i \gamma_X^j + \\ &+ C \gamma_X^1 \gamma_X^2 \gamma_X^3\end{aligned}\quad (5)$$

$$\begin{aligned}\Delta H_{f(R^1R^2R^3R^4C)}^{\circ} &= \Delta H_{f(CH_4)}^{\circ} + \sum_i \Delta H_{f(R^iH)}^{\circ} + \\ &+ \gamma_{CH_3} \sum_i \gamma_{R^i}^1 + A \sum_{i < j} \gamma_{R^i}^1 \gamma_{R^j}^1 + \\ &+ B \sum_{i < j < k} \gamma_{R^i}^1 \gamma_{R^j}^1 \gamma_{R^k}^1 + C \gamma_{R^1}^1 \gamma_{R^2}^1 \gamma_{R^3}^1 \gamma_{R^4}^1\end{aligned}\quad (5,a)$$



The parameters A, B and C could be evaluated using the data only for those compounds for which the only intramolecular interaction present is the one related to  $\varphi$  constants. This means that there will be neither steric strain nor inductive interaction between functional groups. Therefore these parameters could be evaluated using the data for sterically nonstrained alkanes, only.

The values of  $\Delta H_{f,298}^{\circ}$  and  $\Delta H_0^{\circ}$  for most simple alkanes could be considered as precise enough to establish whether there exists any difference between A, B and C values for 298.15 °K and absolute zero. This is equivalent to the analogous consideration for  $\varphi_R$  values. And another problem exists. According to the logic of Eqs. (5) and (5,a), the  $\varphi_R$  values for normal alkyls should hold the rule as follows:

$$\varphi_{RCH_2} = \varphi_{CH_3} + A \varphi_R \quad (6)$$

This means that the interaction terms between two carbon atoms isolated by n carbon atoms make significant contributions equalling  $A^n \varphi_{CH_3}^2$ . Such interaction should take place also in the case of those pairs of atoms, which are isolated by more than one carbon atom.

Treatment of the corresponding experimental data leads to the conclusion that Eq. (6) does not hold in the case of normal alkyls and for two carbon atoms isolated by more than a single carbon atom ( $n > 1$ ) the interaction is absent. This is in fact another manifestation of the well-known constancy of the methylene group additive contribution into  $\Delta H_{f,298}^{\circ}$  or  $\Delta H_0^{\circ}$  values starting from the transition from propane to n-butane. Proceeding from the data for normal alkanes up to octane inclusively and assuming the absence of the interaction terms  $A^n \varphi_{CH_3}^2$  for any value of  $n > 1$  for 298.15 °K the following figures were obtained:  $\varphi_{CH_3} = 3.945$ ,  $\varphi_{RCH_2} = 3.254 \pm 0.008$  and  $A = -0.1760 \pm 0.0008$ . If those terms are included for  $n > 1$  the result is  $A = -0.1976 \pm 0.0110$ .

Comparison of standard deviations for the parameter A clearly indicates that the first version is to be preferred.

For 0°K the first version leads to  $\varphi_{CH_3} = 3.934$ ,  $\varphi_{RCH_2} = 3.114 \pm 0.041$  and  $A = -0.2065 \pm 0.0070$ .<sup>3</sup> According to the second one  $A = -0.2381 \pm 0.0234$ .

From these results one can conclude that the differences between  $\varphi_R$  and A values, estimated for 298.15°K and 0°K, are significant ones. Consequently, Eqs. (5) and (5,a) do not describe the data for alkyls and alkanes precisely enough and the  $\varphi$  values for alkyls are, in principle, temperature-dependent. To put it in other words the  $\Delta H_{f,298}^0$  and  $\Delta H_0^0$  values could not be described with ideal precision using the unique formal approach. But, one has to realize that the experimental uncertainties in  $\Delta H_f^0$  values for other classes of compounds considerably exceed those ones for alkanes. Therefore, the introduction of additional specifications at this stage is hardly any practical importance.

In fact, the value  $\varphi_{CH_3} = 3.94^2$  has been accepted. As an estimate the value  $A = -0.200^3$  for 0°K was chosen. From  $\Delta H_0^0$  values for 2-methylpropane and 2,2-dimethylpropane the values of parameters  $B = 0.020$  and  $C = -0.002$  were obtained. These conventional estimates were used in the following calculations but they can not be considered to be figures reliable enough (see Table 4).

The original version of calculation scheme fails to describe satisfactorily the  $\Delta H_f^0$  values for compounds the molecules of which ones contain several halogen atoms connected with a single carbon atom. Therefore we had to reconsider the regularities connected with  $\Delta H_0^0$  values of polyhalo substituted methanes. The successive substitution of halogen atoms for hydrogen ones in the methane molecule leads to rather additive changes in  $\Delta H_0^0$  values of chloro-, bromo- and iodosubstituted methanes. Using compatible experimental estimates<sup>19</sup> of  $\Delta H_0^0$  (kcal/mole) for  $CH_3Cl$  (-18.8; -18.7; -18.5),  $CH_2Cl_2$  (-20.8; -20.5; -20.9);  $CHCl_3$  (-23.5; -23.8;

-23.8),  $\text{CCl}_4$  (-25.0; -25.0; -25.4),  $\text{CH}_3\text{Br}$  (-4.7; -4.9; -5.3),  $\text{CH}_2\text{Br}_2$  (6.1),  $\text{CHBr}_3$  (16.2),  $\text{CBr}_4$  (26.1; 27.1),  $\text{CH}_3\text{I}$  (5.4; 5.6; 5.7; 6.3, 6.9; 7.3),  $\text{CH}_2\text{I}_2$  (29.25) and  $\text{CHI}_3$  (52.9), the following linear dependences are obtained:

$$\Delta H_0^\circ(\text{CH}_{4-n}\text{Cl}_n) = -(16.5 \pm 0.3) - (2.22 \pm 0.10)n \quad (7, a)$$

$$n = 1, 2, 3 \text{ and } 4, \quad s = 0.4, \quad r = 0.9904$$

$$\Delta H_0^\circ(\text{CH}_{4-n}\text{Br}_n) = -(15.4 \pm 0.3) + (10.5 \pm 0.1)n \quad (7, b)$$

$$n = 1, 2, 3 \text{ and } 4, \quad s = 0.4, \quad r = 0.9996$$

$$\Delta H_0^\circ(\text{CH}_{4-n}\text{I}_n) = -(17.1 \pm 0.5) + (23.3 \pm 0.3)n \quad (7, c)$$

$$n = 1, 2 \text{ and } 3, \quad s = 0.7, \quad r = 0.993$$

The intercepts of these dependences are close to the value of  $\Delta H_0^\circ(\text{CH}_4) = -15.9^{18, 16}$ .

The slopes representing the additive terms of changes in  $\Delta H_0^\circ$  caused by the substitution of a halogen atom for a hydrogen one are not equal to  $\Delta H_0^\circ$  values of respective halogen hydrides (-22.0, -6.8 and 6.9 kcal/mole<sup>19</sup>, respectively). According to the  $\varphi$ -interaction scheme this means that although there exists  $\varphi$ -interaction between the substituted methyl and halogen atoms, the  $\varphi$ -constant of the former is independent of the number of substituents (halogen atoms) and is equal to  $\varphi_{\text{CH}_3}$ . Moreover, there is no any inductive interaction between<sup>3</sup> halogen atoms connected with a single carbon atom.

As the constants A, B and C characterize the intensity of the pairwise, triple and quarternary interactions between the substituents connected with the same carbon atom this conclusion means that all these parameters will be equal to zero if all these interacting substituents are halogen atoms.

One can generalize these results in the form of the following supplementary postulate, not deduced from the general equations of the formal theory: there exists no inter-



action ( $\gamma$ - or inductive) between halogen atoms connected with the same  $sp^3$ -carbon atom.

For polyfluoro substituted methanes the additivity of the substituent effect considered is not observed. Besides, there are no reliable experimental estimates for  $\Delta H_{F,298}^0$  and  $\Delta H_0^0$  values of  $CH_3F$ .

Proceeding from the additivity of the effect of the substitution of halogen atom for hydrogen one in chloro-, bromo- and iodosubstituted methanes the relationships could be formulated as follows:

$$\begin{aligned}\Delta_X &= \Delta H_0^0(CH_{4-n}X_n) - \Delta H_0^0(CH_{4-n+1}X_{n-1}) = \\ &= \Delta H_0^0(HX) + \gamma_{CH_3} \gamma_X\end{aligned}\quad (8)$$

Consequently,

$$\gamma_X = (\Delta_X - \Delta H_0^0(HX)) / \gamma_{CH_3} \quad (9)$$

The slopes of linear relationships (7,a), (7,b) and (7,c) do not represent the most reliable estimates of the  $\Delta_X$ -values as the intercepts rather significantly differ from the  $\Delta H_0^0(CH_4)$  value.

Seeking for a way to the extrapolative estimation of  $\Delta_F$  and  $\gamma_F$  values the possible linearities of  $\Delta_X$  and  $\gamma_X$  on the sequence number N of halogen in the order F, Cl, Br and I were tested. The slopes of linearities (7,a) : (7,c) depend linearly on N but the extrapolated value  $\Delta_F = -15.0$  kcal/mole. There is no way for any simple use of this value for the interpretation of  $\Delta H_0^0$  values for fluorine derivatives of methane.

There was made use from the  $\Delta H_{O(HX)}^0$  values cited earlier and the mean value of mean  $\Delta_{Cl}$ -values, calculated for  $CH_3Cl$ ,  $CH_2Cl_2$ ,  $CHCl_3$  and  $CCl_4$ , the mean value of  $\Delta_{Br}$  for  $CH_3Br$ ,  $CH_2Br_2$ ,  $CHBr_3$  and  $CBr_4$  ignoring alternative  $\Delta H_0^0$  estimates for  $CH_3Br$  and  $CBr_4$  equal to -5.3 and 26.1 kcal/mole, respectively, and the mean value of  $\Delta_I$  obtained

using for  $\text{CH}_3\text{I}$  the  $\Delta\text{H}_0^\circ$  estimates equal to 6.3 and 6.9 and ignoring the ones equal to 5.4, 5.6 and 5.7 kcal/mole. This procedure results in  $\Delta_{\text{Cl}} = -2.4$ ,  $\Delta_{\text{Br}} = 11.0$  and  $\Delta_{\text{I}} = 22.6$  kcal/mole and  $\varphi_{\text{Cl}} = 4.98$ ,  $\varphi_{\text{Br}} = 4.52$  and  $\varphi_{\text{I}} = 4.02$ . The last ones are linearly dependent on N and the extrapolated value  $\varphi_{\text{F}} = 5.45$  can be obtained. According to Eq. (8) this corresponds to  $\Delta_{\text{F}} = -43.3$  and  $\Delta\text{H}_0^\circ(\text{CH}_3\text{F}) = -59.2$  kcal/mole if  $\Delta\text{H}_{\text{F}} = \Delta\text{H}_0^\circ(\text{HF}) = -64.8$  kcal/mole<sup>19</sup> is assumed.

These estimates of  $\varphi_{\text{X}}$  for F, Cl and Br agree with the values from Table 1 ( $6.24 \pm 0.67$ ,  $4.92 \pm 0.28$  and  $4.36 \pm 0.54$  for F, Cl and Br, respectively) obtained by the use of Eq. (3) when the points for HF, HCl and HBr are involved into the data set for linear regression. But the last ones lead to a less precise description of  $\Delta\text{H}_0^\circ$  values for polyhalogensubstituted methanes and other alkanes. Therefore the specification of  $\varphi_{\text{X}}$  values making use from Eqs. (8) and (9) seems to be a procedure justified enough.

For polyfluoro substituted alkane derivatives an additional artificially introduced postulate has to be formulated. According to the latter each coupling interaction between two fluorine atoms vicinally connected with a single  $\text{sp}^3$  carbon atom is accompanied by the stabilizing energetical effect  $a_{\text{F},\text{F}}^{1,3} = -5.5$  kcal/mole.

Any approach to the parametrization of an empirical calculation scheme is heavily dependent on the experimental data used. In the case of thermochemical data including those for halogen derivatives this problem is a complicated one. The alternative estimates of  $\Delta\text{H}_\text{F}^\circ$  values for a given compound are frequently significantly different. Therefore the possibility remains to select for parametrization the values suiting better for the model used as it was done above in the case of  $\Delta\text{H}_0^\circ$  values for  $\text{CH}_3\text{I}$ . If such kind of selection has enough wide statistical foundation it is a justified procedure and can serve as an additional criterion for the reliability of experimental data. But, the scarcer the used set of data the more arbitrary become the criteria used

for such a selection.

In the case under consideration it would be incorrect to ignore the new specified experimental  $\Delta H_{f,298}^{\circ}$  values for a selected set of methane halogen derivatives suggested by V.P. Kolesov<sup>20</sup> proceeding from the critical analysis of recent publications related to this topic. In the same paper the attempt is made to calculate the  $\Delta H_{f,298}^{\circ}$  values for other halogen derivatives of methane.

From the viewpoint of the model used in this paper most important are the specified  $\Delta H_{f,298}^{\circ}$  and based on them  $\Delta H_0^{\circ}$  values for chlorine derivatives of methane,  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{I}$ . The  $\Delta H_{f,298}^{\circ}$  values suggested by this author ( $-19.58 \pm 0.16$ ,  $-22.76 \pm 0.08$ ,  $-24.54 \pm 0.37$  and  $-22.86 \pm 0.16$  kcal/mole for chloro-, dichloro-, trichloro- and tetrachloromethane, respectively) do not lead to the linearity of type (7,a) either for  $298.15^{\circ}$  or for  $0^{\circ}\text{K}$ . It is so because the dependence of  $\Delta H_f^{\circ}$  on  $n$  is represented by the curve with a maximum. Further, the specified estimates suggested by Kolesov for chloro-, bromo- and iodomethane, after recalculation into corresponding  $\Delta H_0^{\circ}$  values, using Eq. (8) lead to the estimates of  $\Delta_X$  as follows:  $\Delta_{\text{Cl}} = -1.79$ ,  $\Delta_{\text{Br}} = 8.86$  and  $\Delta_{\text{I}} = 21.2$  kcal/mole. If the use is made from Eq. (9) the corresponding  $\varphi_X$  values are  $\varphi_{\text{Cl}} = 5.13$ ,  $\varphi_{\text{Br}} = 4.42$  and  $\varphi_{\text{I}} = 3.72$ . The linearity of the latter on  $N$  is obeyed precisely and the extrapolated value  $\varphi_{\text{F}} = 5.83$  is closer to the figure  $6.24 \pm 0.67$  from Table 1 than the above estimate 5.45. For the vicinal pairwise interaction between fluorine atoms the value becomes  $a_{\text{F},\text{F}}^{1,3} = -6.8$  kcal/mole.

The scheme developed in this paper results in a simple additive formula for the calculation of  $\Delta H_0^{\circ}$  values for halogen derivatives of methane:

$$\Delta H_0^{\circ} = \Delta H_0^{\circ}(\text{CH}_4) + \sum_i n_i \Delta_{X_i} + n_{\text{F},\text{F}}^{1,3} a_{\text{F},\text{F}}^{1,3} \quad (10)$$



where  $i$  is a sequence index of halogen,  $n_i$  - the number of atoms for  $i$ -th halogen and  $n_{F,F}^{1,3}$  - the number of pairwise vicinal interactions between fluorine atoms.

For  $\Delta H_{f,298}^0$  a similar formula can be written. Assuming that  $\varphi_X$  values are temperature independent the  $\Delta_X$  values change as much as the  $\Delta H_{f,298}^0$  values differ from  $\Delta H_0^0$  ones for corresponding HX. Such differences are significant only for HBr and HI and for 298,15°K  $\Delta_{Br}^{298} = 9.11$  and  $\Delta_I^{298} = 22.14$  kcal/mole. Accepting the  $\varphi_X$  values estimated by the use of the  $\Delta H_{O(CH_3X)}^0$  based on the data reported by Kolesov one obtains  $\Delta_{Br}^{298} = 8.71$  and  $\Delta_I^{298} = 20.96$  kcal/mole.

Kolesov<sup>20</sup> reports critically selected experimental values of  $\Delta H_{f,298}^0$  also for  $CH_2F_2$ ,  $CHF_3$ ,  $CF_4$ ,  $CCl_3Br$ ,  $CF_3Br$ ,  $CF_2Cl_2$ ,  $CFCl_3$ ,  $CF_3Br$  and  $CF_3I$ . The data for these compounds were not used for the estimation of  $\Delta_X$  or  $\varphi_X$  values. The parameter  $a_{F,F}^{1,3}$  has been estimated using the data for three first compounds from this set. The  $\Delta H_{f,298}^0$  values for 8 of these compounds, excepting  $CCl_3Br$ , are described by Eq. (10) with standard deviations equalling 1.70 and 2.75 kcal/mole, using parameters established, respectively, without and with the use of the  $\Delta H_{f,298}^0$  values, re-examined by Kolesov for  $CH_3Cl$ ,  $CH_3Br$  and  $CH_3I$ .

Tables<sup>19</sup> list the experimental values of  $\Delta H_{f,298}^0$  for several other mixed polyhalogen substituted methanes. Leaving alone fluorine derivatives which in the majority of cases are obviously related to systematic negative deviations (5 + 8 kcal/mole), the corresponding standard deviations for the remaining 15 compounds equal 1.89 and 2.39 kcal/mole for calculations by Eq. (10).

So one can conclude that the modified parametrization on the basis of data for  $CH_3Cl$ ,  $CH_3Br$  and  $CH_3I$  reported in ref. 20 does not improve the agreement between the calculated and experimental values. Therefore we have no reason to accept this modified parametrization.

It has to be mentioned that the precision of calculated values for 298,15 and 0°K is different. For example the deviations of the calculated value from that of experimental for  $\text{CCl}_4$  at 298,15°K range from -1.3 up to 4.5 kcal/mole depending on the selected experimental value. For 0°K these deviations range from -0.1 up to -3.2 kcal/mole (the latter corresponds to the experimental value reported by Kolesov<sup>20</sup>). Depending on the parametrization used this is due to the inequality in the values of the difference  $\Delta H_{f,298}^\circ - \Delta H_0^\circ$  for  $\text{CH}_4$  (-1.4 kcal/mole) and  $\text{CCl}_4$  (-0.5 kcal/mole) as the  $\Delta H_f^\circ$  for HCl is practically temperature independent and the same was assumed for the  $\varphi_{\text{Cl}}^\circ$  value.

As for the experimental values of  $\Delta H_f^\circ$  for fluorine containing halogen derivatives of methane which have not been specified in the cited paper by Kolesov<sup>20</sup>, the possibility of large errors could be demonstrated when different alternative values are being compared. So for  $\text{CHCl}_2\text{F}$  two values - -73.0 and -66.5 kcal/mole are listed<sup>19</sup>. The estimate by Eq. (10) is -65.3 kcal/mole. The value -73.0 is rather too negative by the 7 kcal/mole mentioned above. For  $\text{CH}_2\text{FCl}$  experimental values -63 and -64.5 kcal/mole are listed<sup>19</sup> and the calculated value equals -63.5 kcal/mole. It seems that the calculation by the use of Eq.(10) leads generally to more reliable results than the existing experimental estimates.

Ref. 20 lists the calculated  $\Delta H_{f,298}^\circ$  values for a number of halogen derivatives of methane including those 15 compounds which contain no fluorine and for which experimental data are available<sup>19</sup>. For the latter the standard deviation of the calculated values equals 7.8 kcal/mole. This indicates rather a low degree of reliability of the comparative calculations for short series of compound used in ref. 20.

One can realize that the whole body of experimental data available is compatible with the additional rules introduced by us for halogen containing compounds.

It should be emphasized that the applicability of Eq.(10)

to polyhalogen substituted methanes does not mean that the substituent effects in  $\Delta H_f^\circ$  values caused by halogen atoms could be in all cases reduced to additive increments  $\Delta_X$  and  $a_{F,F}^{1,3}$ . The interaction is absent only for two vicinal halogen atoms (excepting the fluorine ones). But halogen atoms do interact with other groups in vicinal position. So, the  $\Delta H_f^\circ$ ,<sub>298</sub> or  $\Delta H_0^\circ$  values for polyhalogen substituted ethane and other alkanes could not be described satisfactorily enough if the explicit reflection of  $\varphi$ - and also inductive interactions is ignored. The corresponding examples will be considered in the final part of this paper.

It is reasonable to modify also  $\varphi_{NO_2}$  and  $\Delta H_{NO_2}$  values. The correlation of  $\Delta H_f^\circ$ ,<sub>298</sub> values reported in ref.<sup>52</sup> and recalculated to the absolute zero was performed. Using

$\varphi_R$  values based on  $\Delta H_0^\circ$  values of alkanes  $RCH_3$  the result obtained is:

$$\begin{aligned}\varphi_{NO_2} &= 7.42 \pm 0.61, \\ \Delta H_{NO_2} &= -27.29 \pm 1.85 \text{ kcal/mole.}\end{aligned}$$

Using  $\varphi_R$  values calculated according to Equation (5) ( $A = -0.200$ ,  $B = 0.020$  and  $C = -0.002$ , see Table 1) the result is:

$$\begin{aligned}\varphi_{NO_2} &= 7.12 \pm 0.68 \\ \Delta H_{NO_2} &= -26.83 \pm 2.11 \text{ kcal/mole.}\end{aligned}$$

A more correct procedure is the treatment of all alternative 23 estimates of  $\Delta H_f^\circ$ ,<sub>298</sub> available for seven nitroalkanes. After exclusion of two significantly deviating alternative points the result is obtained as follows:

$$\begin{aligned}\varphi_{NO_2} &= 6.01 \pm 0.46 \\ \Delta H_{NO_2}(298^\circ K) &= -24.2 \pm 1.5 \text{ kcal/mole} \\ \Delta H_{NO_2}(0^\circ K) &= -23.4 \pm 1.5 \text{ kcal/mole}\end{aligned}$$



Using the averaged values of  $\Delta H_{f,298}^0$  for nitromethane, 2-nitropropane and 2-nitromethyl propane only, the result for 0°K is obtained as follows:

$$\gamma_{\text{NO}_2} = 6.1$$

$$\Delta H_{\text{NO}_2} = -22.7 \text{ kcal/mole}$$

This recalculation of  $\Delta H_{\text{NO}_2}$  and  $\gamma_{\text{NO}_2}$  values leads to corresponding changes into the estimates of  $\gamma$ -interaction and inductive contributions to the formation enthalpies of polynitro compounds. The inductive contribution is essential for the estimation of the scaling factor  $\alpha^*$  for inductive interaction.

A special problem is the value  $G^*$  for the nitrogroup. Proceeding from the data of six reaction series the averaged value of  $G_{\text{NO}_2}^* = 4.48$  was obtained<sup>15</sup> which is essentially higher when compared with the previous estimate<sup>21</sup> (3.55).

The inductive effect caused by several halogen atoms connected with a single carbon atom does not show an additivity<sup>21,15,90</sup>. Proceeding from the existing  $G^*$ -values for mono- and polyhalogen substituted methyls the empirical equation for these values could be constructed as follows<sup>1</sup>:

$$G_{X_1X_2X_3C}^* = 0.39 \sum_i^* G_{X_i}^* - 0.0275(\text{NHAL}-1) \sum_i 2^{(4-n_{X_i})}$$

where NHAL is the number of halogen atoms among substituents  $X_i$  and  $n_{X_i}$  denotes the number of halogen atom in the sequence F, Cl, Br and I.

Taking into account all the assumptions and results presented above, the statistical data treatment was performed as described in the following part of this paper.

The available data for  $\Delta H_0^0$  (gas phase) of 24 polynitro compounds (31 independent estimates of  $\Delta H_0^0$  values) were processed. The inductive contribution  $\Delta H_{(\text{ind})}$  was separated from the  $\Delta H_0^0$  values making use of the equation<sup>11</sup>:

$$\Delta H_{(\text{ind})} = \Delta H_0^0 - \Delta H_0^0(\text{calc}) \quad (11)$$

$\Delta H^0_{\text{O(calc)}}$  was calculated according to Equation (5,a) ( $R = H, CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, t-C_4H_9$  and  $NO_2$ ) and using the values of  $A, B$ , and  $C$  estimated above.

$\Delta H_{\text{(ind)}}$  can be expressed by the formula <sup>11,15</sup> :

$$\Delta H_{\text{(ind)}} = \alpha \sum_{i < j} z_C^{\pi} n_{ij} G_i^{\pi} G_j^{\pi}, \quad (12)$$

where  $\alpha$  is the scaling factor of  $G^{\pi}$  constants,  $n_{ij}$  - the number of carbon atoms between  $i$ -th and  $j$ -th substituents,  $z_C^{\pi}$  - the inductive transmission factor for the carbon atom.

The treatment of  $\Delta H_{\text{(ind)}}$  values was performed using the method of Nonlinear Least Squares (NLS). For this purpose Eq. (12) was transformed into the expression as follows:

$$\Delta H_{\text{(ind)}} = X_0 (A_0 X_1 + A_1 X_1^2 + A_2 X_1^3 + A_3 X_1^4 + A_4 X_1^5) \quad (13)$$

where  $X_0 = \alpha G_{NO_2}^{\pi 2}$ ,  $X_1 = z_C^{\pi}$ , and  $A_0, A_1, A_2, A_3$  and

$A_4$  - the numbers of the coupling interactions between nitro groups isolated by 1,2,3,4 and 5 carbon atoms, respectively. Unfortunately, Eq. (13) does not allow the calculation of  $\alpha$  and  $G_{NO_2}^{\pi}$  values separately.

The results<sup>2</sup> of this treatment of  $\Delta H_{\text{(ind)}}$  values are represented in Table 2.

It was also of interest to attempt a simultaneous calculation of different combinations of parameters from the set  $\alpha G_{NO_2}^{\pi 2}, z_C^{\pi}, \gamma_{NO_2}, \Delta H_{NO_2}, A, B$  and  $C$  proceeding from the all available data for nitro compounds (poly- and mononitro substituted alkanes). To do this the function was linked with the NLS program to calculate the  $\Delta H^0_{\text{O}}$  values according to the following equation:

$$\Delta H^0_{\text{O}} = \Delta H^0_{\text{O(calc)}} + \Delta H_{\text{(ind)}}, \quad (14)$$

where  $\Delta H^0_{\text{O(calc)}}$  is the same quantity as in Eq. (11) and  $\Delta H_{\text{(ind)}}$  is given by Eq.(12).

As the unknown parameters  $\alpha^{\pi} \sigma_{\text{NO}_2}^{\pi 2}$ ,  $z_{\text{C}}^{\pi}$ ,  $\rho_{\text{NO}_2}$ ,  $\Delta H_{\text{NO}_2}^{\circ}$ , A, B and C were considered fixing some of them (A, B and C or  $\rho_{\text{NO}_2}$  and  $\Delta H_{\text{NO}_2}^{\circ}$ ) at constant values estimated independently of the given run of data processing. The results of the treatment according to Eq.(14) of 53 experimental points for 31 compounds are presented in Table 3. The indexes of the obtained results in Table 3 (and also in Table 2) are presented as N.M. N represents the sequence number of a treatment version defined by parameters to be determined, the values of fixed coefficients and by the selection of the data set used. M denotes the sequence number of the (intermediate) result for a given version, characterized by N. The results were printed when the NLS iterative treatment cycle was completed. Then the significantly deviating points were excluded and the next data processing cycle started. The last value of M for each N corresponds to the final result when there remain no significantly deviating points according to the Student criterion.

The last version 5, presented in Table 3 is analogous to version 1. However, the experimental values  $\Delta H_{f,298}^{\circ}$  were used instead of the  $\Delta H_0^{\circ}$  values.

The final values of  $\alpha^{\pi} \sigma_{\text{NO}_2}^{\pi 2}$ ,  $z_{\text{C}}^{\pi}$  and  $\rho_{\text{NO}_2}$  for the versions 1 and 5 are very close,  $\rho_{\text{NO}_2}$  being somewhat lower for  $\Delta H_{f,298}^{\circ}$  values as it is expected. This is an additional proof of the sufficient accuracy of the calculation of  $\Delta H_{f,298}^{\circ}$  values into the  $\Delta H_0^{\circ}$  values.

The results represented in Tables 2 and 3 prove that the data for nitro compounds could be successfully described using the unique value of  $z_{\text{C}}^{\pi}$  for any number of carbon atoms isolating the interacting nitro groups. This  $z_{\text{C}}^{\pi}$  value obtained proceeding from  $\Delta H_0^{\circ}$  values ranges from 0.41 up to 0.45.

The value of  $\alpha^{\pi}$  at the given level of  $\alpha^{\pi} \sigma_{\text{NO}_2}^{\pi 2}$  is completely defined by the value accepted for  $\sigma_{\text{NO}_2}^{\pi 2}$ .



The  $\alpha_{\text{NO}_2}^*$  value is practically independent of the number of points considered. The trend is observed to increase of this value if the absolute value of  $\Delta H_{\text{NO}_2}^*$  is increased (see version 4 in Table 3). Assuming  $G_{\text{NO}_2}^* = 3.55$ ,  $\alpha_{\text{NO}_2}^*$  yields a values close to 2.2 calculated in Ref.<sup>15</sup> from results of paper<sup>11</sup>, and to 2.05 in Ref.<sup>12</sup>. It is of interest to mention that proceeding from values  $\gamma_{\text{NO}_2} = 6.1$ ,  $\Delta H_{\text{NO}_2}^* = -22.7$  kcal/mole and  $\Delta H_0^*$  values of di-,<sup>2</sup> tri-,

tetranitro methane and hexanitro ethane one obtains also  $\alpha^* = 2.2$  kcal/mole (for  $G_{\text{NO}_2}^* = 3.55$ ).

Accepting  $G_{\text{NO}_2}^* = 4.48$  the values for  $\alpha^*$  range between 1.2 + 1.3 kcal/mole<sup>2</sup> (at earlier fixed A, B and C).

The results for version 4 from Table 3 prove the necessity of the specification of  $\gamma_{\text{NO}_2}$  and  $\Delta H_{\text{NO}_2}^*$  values if the previously used figures are<sup>2</sup> considered<sup>2</sup> ( $\gamma_{\text{NO}_2} = 6.96$  and  $\Delta H_{\text{NO}_2}^*(298^\circ) = -27.65$  kcal/mole).

If the values A, B and C are included in the set of parameters to be determined for A the values close to -0.200 will be obtained, the latter is based on the data for alkanes. Parameter B is excluded as statistically insignificant and for C the positive values are obtained. The choice between three alternative pairs of  $\gamma_{\text{NO}_2}$  and  $\Delta H_{\text{NO}_2}^*$  values (6.1 and -22.7, 6.01 and -23.4, 6.35 and<sup>2</sup> -24.6)<sup>2</sup> is rather difficult. Fortunately, the alternative values are close enough.

There remains the problem of the choice between two alternative values for  $G_{\text{NO}_2}^*$ . To solve this problem and to specify the  $\alpha^*$  value, all available data for polyfunctional alkanes were involved in the NLS treatment according to the following equation:

$$\Delta H_{\text{(ind)}} = X_0(A_0 + A_1X_1 + A_2X_1^2 + A_3X_1^3 + A_4X_1^4 + A_5X_1^5) \quad (15)$$

where  $X_0 = \alpha^*$ ,  $X_1 = z_C^*$ ,  $A_0$ ,  $A_1$ ,  $A_2$ ,  $A_3$ ,  $A_4$  and  $A_5$  denote the sums of the  $\sum_i \sum_j G_{ij}^*$  type between functional groups isolated by 0, 1, 2, 3, 4 and 5 carbon atoms, respectively.

The results of this treatment are listed in Table 4. Altogether 150 values of  $\Delta H_{(ind)}$  for 116 compounds were processed. The inductive contribution  $\Delta H_{(ind)}$  was separated from  $\Delta H_0^0$  as described above by using specified values of A, B, C, and  $\varphi_X$  and  $\Delta H_X$  for halogens. The used values  $\Delta H_{F,298}^0$ ,  $\Delta H_{O,298}^0$ ,  $\Delta H_{(ind)}$  with references to the sources of  $\Delta H_{F,298}^0$  are presented in Table 5.  $G$  values correspond to the recommended values in Tables<sup>90</sup>. For nitrogroup two pairs of  $\varphi_{NO_2}$  and  $\Delta H_{NO_2}$  values, giving close results (see for example versions 3 and 9 in Table 4), were used. The comparison of the results for two alternative values of

$G_{NO_2}^*$  obviously speaks for the value 4.48. For  $G_{NO_2}^* = 3.55$  the standard deviation is  $0.4 \pm 0.9$  kcal/mole higher at the comparable level of statistical degrees of freedom. The use of  $G_{NO_2}^* = 3.55$  leads to the enhanced value for  $z_C^*(0.55 \pm 0.47$

in versions 1 and 8) when compared with the results from Tables 2 and 3 and with the other variants from Table 4. The value  $z_C^* = 0.49$  for compounds without nitro groups (version 7.1) has no the special significance since after exclusion of four most deviated points  $z_C^* = 0.40$  (version 7.2). Of course, the lower value for standard deviation s of the results in Table 4 has to be desired. It is hard to say whether it is the consequence of the inaccuracy of experimental data or indicates the insufficient adequacy of the model used<sup>\*</sup>.

---

<sup>\*</sup> Special additional rules were introduced only for halogen atoms. It would be reasonable to test the generalization of these rules for other functional groups (OH, OCH<sub>3</sub>, NH<sub>2</sub>, NR<sub>2</sub> etc.) with more electronegative than sp<sup>3</sup> carbon first atom with unshared electron pairs. The study of this possible way of the improvement of the model could be the subject of a separate paper.

Preferring the value  $G_{NO_2}^{\pi} = 4.48$  all versions of data processing (the set of nitro compounds, the whole set of polyfunctional derivatives and the latter excluding the nitro compounds) lead to a lower value for  $\alpha^{\pi}$  when compared with those reported earlier<sup>11,15,22</sup>. These ones were calculated from  $\Delta H_{f,298}^0$  values of polyfunctional derivatives of alkanes assuming  $G_{NO_2}^{\pi} = 3.55$ <sup>11</sup> and from  $\varphi^{\pi}$ -values for several reaction series<sup>22</sup>.

All calculations were performed using a small universal computer Nairi-2 and programs written by us in the language of special directives for this computer.

As one can conclude from the consideration of the results of data processing there is no possibility to establish the absolutely unique values for parameters  $\alpha^{\pi}$ ,  $z_C^{\pi}$ ,  $\varphi_{NO_2}$  and  $\Delta H_{NO_2}$ . The reason is that the NLS program used does not enable one to get a fully unique solution for the problem of total parametrization of the equation of type (14) for the available data set as it is impossible to consider all the 7 parameters cited above to be the unknown ones simultaneously. The value of  $\alpha^{\pi}$  depends on whether the parameters A, B, C and also  $z_C^{\pi}$  are fixed at certain selected standard values or not. Proceeding from the fixed values of A, B, C,  $G_{NO_2}^{\pi} = 4.48$ ,  $\varphi_{NO_2} = 6.1$  and  $\Delta H_{NO_2} = -22.7$  kcal/mole the values  $\alpha^{\pi} = 1.19 \pm 0.07$  kcal/mole and  $z_C^{\pi} = 0.43 \pm 0.02$  are obtained (version 3.4 in Table 4). If the value of  $z_C^{\pi}$  is fixed at continual level  $z_C^{\pi} = 0.39$  the result is  $\alpha^{\pi} = 1.35 \pm 0.02$  kcal/mole (version 4.3 in Table 4). The recommended conventional combinations of parameters for the calculation scheme, specified from the results of this study are listed in Table 6.

Let us consider now some examples of the use of the calculation scheme when the additional rules for the halogen atoms connected with a single carbon atom are taken into account. To avoid the inaccuracies connected with the recalculation of the data for absolute zero the calculations



will be presented for  $\Delta H_{f,298}^{\circ}$ . Keeping in mind that for HF and HCl the values of  $\Delta H_0^{\circ}$  and  $\Delta H_{f,298}^{\circ}$  does not differ and assuming for 298.15°K the same  $\gamma$ -values of halogens that were used for 0° K. The only difference is reduced to the use of the value  $\Delta H_{f,298}^{\circ} = -17.8$  instead of  $\Delta H_0^{\circ} = -15.9$  kcal/mole for methane.

### 1,2-Dichloroethane.

Although the sequence of fragmentation has no influence on the final result it is convenient to start considering this molecule as a combination of two groups  $\text{CH}_2\text{Cl}$ :

$$\Delta H_f^{\circ}(\text{ClCH}_2\text{CH}_2\text{Cl}) = 2\Delta H(\text{CH}_2\text{Cl}) + \gamma_{\text{CH}_2\text{Cl}}^2 + \alpha^* \bar{G}_{\text{CH}_2\text{Cl}}^2$$

For  $\text{CH}_2\text{Cl}$  one can write

$$\gamma_{\text{CH}_2\text{Cl}} = \gamma_{\text{CH}_3} + A\gamma_{\text{Cl}} = 3.94 - 0.200 \times 4.98 = 2.94$$

$$\begin{aligned} 2\Delta H(\text{CH}_2\text{Cl}) &= 2 \times \Delta H_f^{\circ}(\text{CH}_3\text{Cl}) = 2\Delta H_f^{\circ}(\text{CH}_4) + 2\Delta_{\text{Cl}} = \\ &= 2 \times (-17.8) + 2 \times (-2.4) = -40.4 \text{ kcal/mole} \end{aligned}$$

Taking into account that  $\bar{G}_{\text{CH}_2\text{Cl}}^* = 1.04$  the result is:

$$\begin{aligned} \Delta H_f^{\circ}(\text{ClCH}_2\text{CH}_2\text{Cl}) &= -40.4 + 2.94^2 + 1.35 \times 1.04^2 = \\ &= -30.3 \text{ kcal/mole.} \end{aligned}$$

In Tables<sup>19</sup> two experimental values -31.3 and -30.3 kcal/mole are listed.

### Hexachloroethane

$$\Delta H_f^{\circ}(\text{CCl}_3\text{CCl}_3) = 2\Delta H(\text{CCl}_3) + \gamma_{\text{CCl}_3}^2 + \alpha^* \bar{G}_{\text{CCl}_3}^2$$

$$\gamma_{\text{CCl}_3} = \gamma_{\text{CH}_3} + 3A\gamma_{\text{Cl}} + 3B\gamma_{\text{Cl}}^2 + C\gamma_{\text{Cl}}^3 =$$

$$= 3.94 - 3 \times 0.200 \times 4.98 + 3 \times 0.020 \times 4.98^2 +$$

$$-0.002 \times 4.98^3 = 2.20$$

$$\bar{G}_{\text{CCl}_3}^* = 2.60$$

$$\Delta H_f^\circ(\text{CCl}_3\text{CCl}_3) = 2 \cdot \Delta H_f^\circ(\text{CH}_4) + 6 \Delta_{\text{Cl}} + \varphi_{\text{CCl}_3}^2 + \alpha \cdot \overline{G}_{\text{CCl}_3}^{\text{M2}} =$$

$$= 2 \times (-17.8) + 6 \times (-2.4) + 2.20^2 + 1.35 \times 2.60^2 = -36.0 \text{ kcal/mole}$$

Experimental values are  $-36.0^{50}$ ,  $-35.3^{52}$  and  $-33.8^{51}$  kcal/mole.

### 1,1,1-Trifluoroethane

$$\Delta H_f^\circ(\text{CH}_3\text{CF}_3) = 2 \Delta H_f^\circ(\text{CH}_4) + 3 \Delta_{\text{F}} + 3 a_{\text{F},\text{F}}^{1,3} +$$

$$+ \varphi_{\text{CH}_3} \varphi_{\text{CF}_3}$$

$$\varphi_{\text{CF}_3} = \varphi_{\text{CH}_3} + 3A \varphi_{\text{F}} + 3B \varphi_{\text{F}}^2 + C \varphi_{\text{F}}^3 =$$

$$= 3.94 - 3 \times 0.200 \times 5.45 + 3 \times 0.020 \times 5.45^2 +$$

$$- 0.002 \times 5.45^3 = 2.14$$

$$\overline{G}_{\text{CF}_3}^{\text{M}} = 2.50$$

$$\Delta H_f^\circ(\text{CH}_3\text{CF}_3) = 2 \times (-17.8) + 3 \times (-43.3) + 3 \times (-5.5) +$$

$$+ 3.94 \times 2.14 = -173.6 \text{ kcal/mole}$$

The experimental values reported are  $-174.1^{19}$  and  $-175.6^{30,36}$  kcal/mole.

These examples show that simple additive estimates of  $\Delta H_f^\circ$  values are significantly less reliable. Using the  $\Delta_{\text{Cl}}$ ,  $\Delta_{\text{F}}$  and  $a_{\text{F},\text{F}}^{1,3}$  values as additive increments for the three halogen derivatives considered the calculated

$\Delta H_f^\circ$ ,<sub>298</sub> values are  $-24.8$ ,  $-34.4$  and  $-165.5$  kcal/mole, respectively.

Table 1

The Values of Correlation Parameters of Eq. (3)  
for Different Functional Groups X.

I, Ia - the treated data set includes the experimental point for the corresponding hydride ( $R_1 = H$ ).

II, IIa - the experimental point for the corresponding hydride has been excluded from the data set.

I, II - the  $\varphi_R$ - values calculated from  $\Delta H_O^0$  for alkanes were used.

Ia, IIa - the  $\varphi_R$ - values calculated according Eq.(5) were used ( $A = -0.200$ ,  $B = 0.020$  and  $C = -0.002$ ).

n - the number of points (lines)

r - correlation coefficient

s - standard deviation

$\Delta H_X$  and s values are represented in kcal/mole.

X		$\Delta H_X$	$\varphi_X$	n	r	s
1	2	3	4	5	6	7
NH <sub>2</sub>	I	-9.48 $\pm$ 0.30	5.97 $\pm$ 0.10	20	0.9976	0.36
	II	-9.73 $\pm$ 0.54	6.05 $\pm$ 0.17	19	0.9932	0.37
	Ia	-9.37 $\pm$ 0.68	5.81 $\pm$ 0.21	21	0.9873	0.82
	IIa	-9.36 $\pm$ 1.26	5.81 $\pm$ 0.39	20	0.9621	0.84
OH	I	-58.06 $\pm$ 0.64	7.06 $\pm$ 0.21	29	0.9884	0.75
	II	-62.56 $\pm$ 0.66	8.43 $\pm$ 0.21	24	0.9932	0.37
	Ia	-57.59 $\pm$ 0.95	6.64 $\pm$ 0.30	30	0.9727	1.13
	IIa	-58.74 $\pm$ 1.75	6.99 $\pm$ 0.54	29	0.9269	1.14
SH	I	-19.52 $\pm$ 0.07	4.22 $\pm$ 0.03	13	0.9998	0.08
	II	-19.33 $\pm$ 0.46	4.19 $\pm$ 0.16	15	0.9911	0.24
	Ia	-19.09 $\pm$ 0.47	3.98 $\pm$ 0.16	16	0.9889	0.55
	IIa	-16.00 $\pm$ 0.48	2.91 $\pm$ 0.16	13	0.9833	0.23
CH=CH <sub>2</sub>	I	13.87 $\pm$ 0.59	2.39 $\pm$ 0.20	14	0.9614	0.64
	II	10.15 $\pm$ 1.07	3.58 $\pm$ 0.35	13	0.9525	0.44
	Ia	13.96 $\pm$ 0.63	2.27 $\pm$ 0.20	14	0.9551	0.68
	IIa	11.01 $\pm$ 1.36	3.18 $\pm$ 0.42	13	0.9143	0.58



Table 1 (continued)

1	2	3	4	5	6	7
CN	I	29.49 $\pm$ 1.70	0.50 $\pm$ 0.61	10	0.2821	1.88
	II	21.39 $\pm$ 2.60	3.20 $\pm$ 0.88	9	0.8103	1.22
	Ia	29.40 $\pm$ 1.68	0.53 $\pm$ 0.58	10	0.3049	1.87
	IIa	19.90 $\pm$ 3.50	3.76 $\pm$ 1.14	10	0.7596	1.75
F	I	-63.05 $\pm$ 2.06	6.24 $\pm$ 0.67	11	0.9520	2.34
	II	-56.95 $\pm$ 3.93	4.38 $\pm$ 1.22	10	0.7866	2.11
	Ia	-63.40 $\pm$ 1.82	6.25 $\pm$ 0.58	11	0.9634	2.05
	IIa	-58.21 $\pm$ 3.63	4.70 $\pm$ 1.10	10	0.8327	1.89
Cl	I	-22.60 $\pm$ 0.82	4.92 $\pm$ 0.28	17	0.9760	0.91
	II	-25.25 $\pm$ 1.80	5.80 $\pm$ 0.61	16	0.9414	0.86
	Ia	-22.32 $\pm$ 0.74	4.72 $\pm$ 0.25	17	0.9793	0.84
	IIa	-23.46 $\pm$ 1.60	5.09 $\pm$ 0.53	16	0.9328	0.85
Br	I	-8.34 $\pm$ 1.59	4.36 $\pm$ 0.54	14	0.9178	1.74
	II	-13.00 $\pm$ 1.58	6.05 $\pm$ 0.51	11	0.9689	0.64
	Ia	-8.20 $\pm$ 1.59	4.17 $\pm$ 0.53	14	0.9157	1.76
	IIa	-14.88 $\pm$ 2.39	6.39 $\pm$ 0.77	12	0.9346	1.14
NO <sub>2</sub>	II	-27.20 $\pm$ 1.85	7.42 $\pm$ 0.61	7	0.9836	0.75
	IIa	-26.83 $\pm$ 2.11	7.12 $\pm$ 0.68	7	0.9780	0.87
C <sub>6</sub> H <sub>5</sub>	I	23.79 $\pm$ 0.72	2.07 $\pm$ 0.27	9	0.9460	0.83
	II	22.52 $\pm$ 2.15	2.48 $\pm$ 0.70	8	0.8210	0.87
	Ia	23.94 $\pm$ 0.91	1.90 $\pm$ 0.31	9	0.9232	0.99
	IIa	23.61 $\pm$ 2.58	2.07 $\pm$ 0.83	8	0.7155	1.06

Table 2  
Results of the Data Processing According to Eq.(13)

n - the number of experimental points

s - standard deviation

Values of  $X_0$ , s and  $\alpha^*$  are represented in kcal/mole

No	NO <sub>2</sub> para- meters	$X_0 = \alpha^* G_{NO_2}^2$	$X_1 = z_C^*$	n	s	$G_{NO_2}^* = 3.55$	$G_{NO_2}^* = 4.48$
1.1	$\varphi_{NO_2} = 6.1$ ; $\Delta H_{NO_2} =$ $= -22.7$	$24.18 \pm 2.03$	$0.436 \pm 0.027$	31 <sup>a</sup>	2.53	1.92	1.20
1.2		$24.52 \pm 1.71$	$0.426 \pm 0.023$	29 <sup>b</sup>	2.00	1.95	1.22
2.1	$\varphi_{NO_2} = 6.01$ ; $\Delta H_{NO_2} =$ $= -23.4$	$25.91 \pm 2.32$	$0.434 \pm 0.029$	31 <sup>a</sup>	2.87	2.06	1.29
2.2		$26.09 \pm 1.65$	$0.434 \pm 0.021$	29 <sup>b</sup>	2.01	2.07	1.30
2.3		$25.47 \pm 1.32$	$0.446 \pm 0.017$	28 <sup>c</sup>	1.69	2.02	1.27

<sup>a</sup> Taking into account the additional point which coincides with the beginning of coordinates by definition.

<sup>b</sup> Owing to significant deviations at the level  $t = 0.95$ , alternative points for  $C_2(NO_2)_6$  and  $(CH_3)_2C(NO_2)_2$  were excluded.

<sup>c</sup> For the same reason the parallel point for  $(CH_3)_2C(NO_2)_2$  and the point for  $(NO_2)_3C(CH_2)_3NO_2$  were excluded.

<sup>d</sup> Another alternative point for  $C_2(NO_2)_6$  is excluded.

Results of the statistical treatment of  $\Delta H_O^\circ$  and  $\Delta H_{f,298}^\circ$  values for nitrocompounds according to Eq.(14).

The values for other parameters were obtained after neglecting the argument scale corresponding to the statistically insignificant coefficient.

Versions 1.÷ 4. correspond to the processing of  $\Delta H_0^0$  and version 5 of  $\Delta H_{f,298}^0$  values.

s - standard deviation

Values of  $\alpha^* \pi_{\text{NO}_2}^2$ ,  $\alpha^*$ ,  $\Delta H_{\text{NO}_2}$  and  $s$  are represented in kcal/mole.

No	$\chi_{\text{NO}_2}^{\text{H}}$	$\chi_{\text{NO}_2}^{\text{G}}$	$\chi_{\text{NO}_2}^{\text{H}}$	$\chi_{\text{NO}_2}^{\text{G}}$	$\chi_{\text{C}}^{\text{H}}$	$\chi_{\text{NO}_2}^{\text{H}}$	$\Delta H_{\text{NO}_2}$	A	B	C	n	s
		$\chi_{\text{NO}_2}^{\text{H}} = 3.55$	$\chi_{\text{NO}_2}^{\text{G}} = 4.48$									
1	2	3	4	5	6	7	8	9	10	11	12	
1.1	25.3 $\pm$ 2.0	2.01	1.26	0.44 $\pm$ 0.02	5.7 $\pm$ 0.5	-22.4 $\pm$ 1.4	-0.20	0.020	-0.002	53	1.97	
1.2	26.1 $\pm$ 1.5	2.07	1.30	0.45 $\pm$ 0.02	6.4 $\pm$ 0.4	-24.6 $\pm$ 1.2	-0.20	0.020	-0.002	48	1.36	
2.1	26.2 $\pm$ 2.4	2.08	1.31	0.42 $\pm$ 0.03	6.1	-22.7	-0.18 $\pm$ 0.02	0.001 $\pm$ 0.010	0.007 $\pm$ 0.005	53	2.14	



Table 3 (continued)

1	2	3	4	5	6	7	8	9	10	11	12
2.2	24.7 $\pm$ 1.4	1.96	1.23	0.43 $\pm$ 0.02	<u>6.1</u>	-22.7	-0.17 $\pm$ 0.01 (0.0)		0.009 $\pm$ 0.001	44	1.28
3.1	27.8 $\pm$ 2.2	2.20	1.38	0.41 $\pm$ 0.02	<u>6.01</u>	-23.4	-0.17 $\pm$ 0.01 0.005 $\pm$ 0.009	0.004 $\pm$ 0.005	53	1.88	
3.2	28.6 $\pm$ 1.3	2.27	1.43	0.42 $\pm$ 0.02	<u>6.01</u>	-23.4	-0.17 $\pm$ 0.01 (0.0)		0.006 $\pm$ 0.001	48	1.30
4.1	28.8 $\pm$ 2.3	2.29	1.44	0.41 $\pm$ 0.02	<u>6.35</u>	-24.6	-0.17 $\pm$ 0.01 0.008 $\pm$ 0.008	0.003 $\pm$ 0.004	53	1.88	
4.2	30.3 $\pm$ 1.4	2.40	1.51	0.41 $\pm$ 0.02	<u>6.35</u>	-24.6	-0.17 $\pm$ 0.005 (0.0)		0.005 $\pm$ 0.001	48	1.31
5.1	22.8 $\pm$ 1.7	1.81	1.14	0.46 $\pm$ 0.02	5.3 $\pm$ 0.5	-21.8 $\pm$ 1.4	<u>-0.200</u>	<u>0.020</u>	<u>-0.002</u>	53	1.86
5.2	23.9 $\pm$ 1.2	1.89	1.19	0.47 $\pm$ 0.01	6.0 $\pm$ 0.3	-24.3 $\pm$ 1.0	<u>-0.200</u>	<u>0.020</u>	<u>-0.002</u>	48	1.18
5.3	26.0 $\pm$ 1.1	2.06	1.29	0.45 $\pm$ 0.01	6.4 $\pm$ 0.3	-25.5 $\pm$ 0.9	<u>-0.200</u>	<u>0.020</u>	<u>-0.002</u>	44	0.92

Table 4

Results of the Statistical Treatment of the  
Values of Inductive Contribution  $\Delta H_{(ind)}$  for  
Polyfunctional Alkanes in Terms of Eq. (11)

Version	$\varphi_{NO_2}$	$\Delta H_{NO_2}$ , kcal/mole
1. $\pm$ 7.	6.10	-22.7
8. $\pm$ 9.	6.01	-23.4

n - the number of points

s - standard deviation

Values  $\alpha^*$  and s are represented in kcal/mole.

No	$\sigma_{NO_2}^*$	$X_0 = \alpha^*$	$X_1 = z_C^*$	n	s
1	2	3	4	5	6
1.1	3.55	$1.34 \pm 0.14$	$0.53 \pm 0.04$	150	6.71
1.2	3.55	$1.52 \pm 0.11$	$0.50 \pm 0.03$	134	4.34
1.3	3.55	$1.65 \pm 0.11$	$0.47 \pm 0.02$	123	3.73
2.1	3.55	$1.93 \pm 0.05$	<u>0.39</u>	150	7.05
2.2	3.55	$2.06 \pm 0.04$	<u>0.39</u>	134	4.53
2.3	3.55	$2.09 \pm 0.03$	<u>0.39</u>	122	3.82
3.1	4.48	$1.22 \pm 0.13$	$0.42 \pm 0.03$	150	5.82
3.2	4.48	$1.29 \pm 0.09$	$0.41 \pm 0.02$	133	3.83
3.3	4.48	$1.23 \pm 0.08$	$0.43 \pm 0.02$	122	3.82
3.4	4.48	$1.19 \pm 0.07$	$0.43 \pm 0.02$	144	2.85
4.1	4.48	$1.34 \pm 0.03$	<u>0.39</u>	150	5.82
4.2	4.48	$1.38 \pm 0.02$	<u>0.39</u>	133	3.82
4.3	4.48	$1.35 \pm 0.02$	<u>0.39</u>	112	2.79
5.1	3.55	$1.83 \pm 0.33$	$0.42 \pm 0.06$	44 <sup>a</sup>	7.31
5.2	3.55	$1.91 \pm 0.15$	$0.42 \pm 0.03$	39 <sup>a</sup>	3.25
5.3	3.55	$1.81 \pm 0.11$	$0.45 \pm 0.02$	34 <sup>a</sup>	2.30
6.1	4.48	$1.36 \pm 0.17$	$0.39 \pm 0.04$	44 <sup>a</sup>	4.97
6.2	4.48	$1.40 \pm 0.12$	$0.38 \pm 0.03$	39 <sup>a</sup>	3.01
6.3	4.48	$1.25 \pm 0.07$	$0.42 \pm 0.02$	35 <sup>a</sup>	2.02
7.1	-	$1.09 \pm 0.20$	$0.49 \pm 0.11$	106 <sup>b</sup>	6.15
7.2	-	$1.39 \pm 0.18$	$0.40 \pm 0.07$	102 <sup>b</sup>	5.01

Table 4(continued)

1	2	3	4	5	6
7.3	-	1.37 $\pm$ 0.15	0.41 $\pm$ 0.06	95 <sup>b</sup>	4.28
8.1	3.55	1.32 $\pm$ 0.14	0.55 $\pm$ 0.04	150	7.11
8.2	3.55	1.51 $\pm$ 0.10	0.53 $\pm$ 0.03	134	4.58
8.3	3.55	1.60 $\pm$ 0.10	0.51 $\pm$ 0.02	124	3.97
9.1	4.48	1.21 $\pm$ 0.13	0.44 $\pm$ 0.04	150	6.03
9.2	4.48	0.44 $\pm$ 0.08	0.44 $\pm$ 0.02	126	3.54
9.3	4.48	1.17 $\pm$ 0.06	0.47 $\pm$ 0.02	144	2.97

<sup>a</sup> For a set including nitro compounds, only.

<sup>b</sup> For a set of data for compounds excluding the nitro ones.

Table 5

The Formation Enthalpies  $\Delta H_{f,298}^{\circ}$ ,  $\Delta H_0^{\circ}$ , the Sums of Group Additive Increments and  $\phi$ -interaction Terms  $\Delta H_{(calc)}$  and the Inductive Contributions  $\Delta H_{(ind)}$  for Polyfunctional Derivatives of Alkanes (in kcal/mole).

No	Compound	$\Delta H_{f,298}^{\circ}$	$\Delta H_0^{\circ}$	$\Delta H_{(calc)}$	$H_{(ind)}$	References
1	2	3	4	5	6	7
0.	-	0	0	0	0	-
1.	$\text{CH}_2(\text{NO}_2)_2$	-14.3	-10.3	-20.7	10.4	11
2.	$\text{CH}(\text{NO}_2)_3$	- 0.2	4.8	-29.8	34.6	23
3.	- " -	- 3.2	1.8	-29.8	31.6	24
4.	$\text{C}(\text{NO}_2)_4$	18.5	24.4	-40.2	64.7	11
5.	$\text{CH}_3\text{CH}(\text{NO}_2)_2$	-24.4	-18.8	-27.8	9.0	25
6.	- " -	-24.6	-19.0	-27.8	8.8	26
7.	$\text{O}_2\text{NCH}_2\text{CH}_2\text{NO}_2$	-22.9	-17.6	-21.7	4.1	11
8.	$\text{CH}_3\text{C}(\text{NO}_2)_3$	-12.6	- 6.1	-37.8	31.7	25
9.	- " -	-11.6	- 5.1	-37.8	32.7	26
10.	$\text{C}_2(\text{NO}_2)_6$	36.9	45.6	-55.5	101.5	25
11.	- " -	45.5	54.6	-55.5	110.1	27, 25
12.	$\text{C}_2\text{H}_5\text{CH}(\text{NO}_2)_2$	-28.6	-21.7	-29.9	8.3	25



Table 5 (continued)

1	2	3	4	5	6	7
13.	- " -	-26.8	-19.9	-29.9	10.1	25
14.	$O_2N(CH_2)_3NO_2$	-31.6	-25.1	-25.1	0.0	11
15.	$(CH_3)_2C(NO_2)_2$	-31.0	-24.0	-35.5	11.5	25
16.	- " -	-25.9	-18.9	-35.5	16.6	28
17.	$C_2H_5C(NO_2)_3$	-18.4	-10.6	-39.7	29.2	11
18.	$CH_3C(NO_2)_2C(NO_2)_3$	8.1	17.8	-53.4	71.2	11
19.	$C_3H_7CH(NO_2)_2$	-34.1	-25.9	-33.0	7.1	11
20.	$O_2N(CH_2)_4NO_2$	-38.7	-30.9	-28.0	-2.9	11
21.	$O_2N(CH_2)_3C(NO_2)_3$	-24.9	-14.9	-45.5	30.7	11
22.	$O_2NCH_2CH(CH_3)C(NO_2)_3$	-20.0	-9.6	-46.4	36.8	11
23.	$(O_2N)_2CHCH_2C(NO_2)_2CH_3$	-28.7	-18.3	-48.3	30.0	11
24.	$CH_3C(NO_2)_2C(NO_2)_2CH_3$	-20.2	-9.9	-51.2	41.3	11
25.	$C_4H_9CH(NO_2)_2$	-38.2	-28.6	-37.0	8.4	11
26.	$C_4H_9C(NO_2)_3$	-29.0	-17.7	-46.8	29.1	11
27.	$/(O_2N)_3CCH_2/CHNO_2$	-9.2	4.8	-71.9	76.7	11
28.	$(CH_3)_2(NO_2)C-$ $-C(NO_2)_2C_2H_5$	-47.1	-34.9	-51.5	16.6	11
29.	$(CH_3)_2(NO_2)C-$ $-C(NO_2)(CH_3)_2$	-53.2	-41.7	-47.5	5.9	25
30.	$CH_3C(NO_2)_2CH_2-$ $-C(CH_3)_2C(NO_2)_3$	-4.19	-25.1	-70.8	45.7	11
31.	$C_6H_5CH_2NO_2$	6.7	12.9	15.0	-2.1	11
32.	$C(NO_2)_3^F$	-44.3	-39.3	-93.0	53.8	29, 30
33.	- " -	-43.8	-38.8	-93.0	54.3	24
34.	$C(NO_2)_3Cl$	5.3	10.3	-50.4	60.7	24
35.	$C(NO_2)_3Br$	14.6	21.4	-35.3	56.7	11
36.	$CF_2(NO_2)_2$	-96.4	-92.5	-131.8	39.3	31
37.	$CF(C_6H_5)(NO_2)_2$	-44.2	-37.6	-52.7	15.2	11
38.	$CH(NO_2)_2C_6H_5$	8.3	15.4	7.3	8.1	11
39.	$(O_2N)_3CCH_2C_6H_5$	15.7	25.0	-5.7	30.7	11
40.	$CF_2NO_2CF_2NO_2$	-194.1	-189.8	-229.6	39.8	31
41.	$CF_2NO_2CF(NO_2)_2$	-143.7	-138.2	-189.1	50.9	31
42.	$CF(NO_2)_2CF(NO_2)_2$	-84.2	-77.5	-148.6	71.1	31

Table 5(continued)

1	2	3	4	5	6	7
43. $\text{CF}(\text{NO}_2)_2\text{C}(\text{NO}_2)_3$	-20.6	-12.7	-102.1	89.4	31	
44. $\text{C}_2\text{F}_6$	-322.0	-320.0	-323.0	3.0	32, 30	
45. - " -	-308.0	-306.0	-323.0	17.0	33, 30	
46. $\text{CH}_2\text{FCHF}_2$	-159.1	-156.3	-161.0	4.8	34, 30	
47. $\text{CF}_3\text{CH}=\text{CH}_2$	-144.5	-141.6	-145.8	4.2	35, 36, 30	
48. $\text{CF}_3\text{CH}_2\text{CF}_3$	-331.5	-328.2	-327.7	-0.5	37, 36, 30	
49. $\text{CF}_2\text{ClCCl}_3$	-120.1	-118.7	-129.4	10.6	38, 30	
50. $\text{CF}_2\text{ClCFCl}_2$	-165.8	-164.7	-170.3	5.7	38, 30	
51. - " -	-183.2	-182.1	-170.3	-11.7	39, 30	
52. $\text{CF}_2\text{ClCF}_2\text{Cl}$	-212.4	-210.9	-217.3	6.4	40, 30	
53. - " -	-216.4	-214.9	-217.3	2.4	33, 30	
54. - " -	-227.8	-226.3	-217.3	-9.0	39, 30	
55. $\text{CF}_3\text{CH}_2\text{CH}_2\text{Cl}$	-184.0	-180.1	-179.3	-0.9	36	
56. $\text{CF}_3\text{CH}_2\text{CHCl}_2$	-189.7	-186.4	-183.5	-2.9	36	
57. $\text{CF}_3\text{CH}_2\text{CCl}_3$	-189.8	-187.1	-186.8	-0.3	36	
58. $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$	-271.9	-268.8	-274.8	6.0	41	
59. - " -	-271.4	-268.3	-274.8	6.5	42	
60. $\text{CF}_2\text{ICF}_2\text{I}$	-159.1	-156.4	-167.1	10.7	43	
61. $\text{CH}_2\text{FCH}_2\text{OH}$	-100.3	-96.4	-103.5	7.1	17, 30	
62. $\text{CF}_3\text{CH}_2\text{OH}$	-210.2	-206.8	-210.0	3.2	37	
63. - " -	-213.6	-210.2	-210.0	-0.2	17	
64. $\text{CF}_3\text{CH}_2\text{CH}_2\text{OH}$	-217.8	-213.1	-213.9	0.8	30, 36	
65. $\text{CHF}_2\text{CF}_2\text{CH}_2\text{OH}$	-251.3	-247.1	-257.4	10.3	44, 36	
66. $\text{CF}_3\text{CF}_2\text{CH}_2\text{OH}$	-309.0	-305.4	-313.2	7.8	45, 36	
67. $\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}_2\text{OH}$	-410.4	-406.2	-416.5	10.2	45, 30	
68. $\text{HOCH}_2(\text{CF}_2)_4\text{CH}_2\text{OH}$	-492.0	-485.7	-509.8	24.2	46	
69. $\text{CF}_3\text{COOH}$	-244.2	-241.8	-255.1	13.3	47	
70. - " -	-244.7	-242.3	-255.1	12.8	17	
71. $\text{CF}_3\text{CH}_2\text{NH}_2$	-170.1	-166.0	-160.0	-6.0	48, 30	
72. - " -	-171.2	-167.1	-160.0	-7.1	17	
73. $\text{CF}_3\text{C}_6\text{H}_5$	-141.9	-137.4	-136.1	-1.2	30, 36	

Table 5(continued)

1	2	3	4	5	6	7
74.	$\text{CH}_2\text{ClCH}_2\text{Cl}$	-31.2	-28.5	-27.9	-0.7	49
75.	- " -	-30.3	-27.6	-27.9	0.2	19
76.	$\text{CH}_2\text{ClCHCl}_2$	-45.0	-42.4	-31.8	-10.6	50
77.	$\text{CHCl}_2\text{CHCl}_2$	-33.0	-31.0	-35.5	4.5	50
78.	- " -	-36.5	-34.5	-35.5	1.0	51
79.	$\text{CHCl}_2\text{CCl}_3$	-35.4	-34.1	-38.5	4.4	50
80.	- " -	-34.0	-32.7	-38.5	5.8	51
81.	$\text{C}_2\text{Cl}_6$	-36.0	-35.4	-41.4	6.0	50
82.	- " -	-35.3	-34.7	-41.4	6.7	52
83.	- " -	-33.8	-33.2	-41.4	8.2	51
84.	$\text{Cl}(\text{CH}_2)_3\text{Cl}$	-38.6	-34.7	-31.0	-3.7	53,54
85.	$\text{CH}_2\text{ClCHClCH}_3$	-40.0	-36.1	-34.5	-1.6	53
86.	- " -	-39.6	-35.7	-34.5	-1.2	55
87.	$\text{CH}_2\text{ClCHClCH}_2\text{Cl}$	-44.4	-41.0	-39.2	-1.7	56
88.	$\text{CCl}_3\text{CH}_2\text{CH}_2\text{Cl}$	-38.7	-35.4	-38.4	3.0	36
89.	$\text{CH}_2=\text{CHCH}_2\text{Cl}$	-0.2	2.9	2.7	0.2	57
90.	$\text{CH}_3\text{OCH}_2\text{CH}_2\text{Cl}$	-65.2	-61.2	-52.4	-8.8	11
91.	$\text{ClCH}_2\text{CH}_2\text{OH}$	-64.0	-60.2	-62.3	2.2	11
92.	$\text{CH}_2\text{ClCOOH}$	-105.1	-102.3	-106.2	4.0	17
93.	- " -	-105.6	-102.8	-106.2	3.5	51,17
94.	$\text{CHCl}_2\text{COOH}$	-104.6	-101.8	-110.7	8.9	17
95.	$\text{CCl}_3\text{COOH}$	-106.5	-104.3	-114.2	9.9	51,17
96.	- " -	-104.8	-102.6	-114.2	11.6	17
97.	$\text{CH}_2\text{BrCH}_2\text{Br}$	-9.3	-3.1	-0.6	-2.5	58
98.	- " -	-10.2	-4.0	-0.6	-3.4	53
99.	$\text{CHBr}_2\text{CHBr}_2$	-9.6	-0.7	18.7	-19.4	17
100.	$\text{CH}_3\text{CHBrCH}_2\text{Br}$	-24.6	-17.1	-6.9	-10.2	53
101.	- " -	-17.4	-9.9	-6.9	-3.0	59
102.	$\text{C}_2\text{H}_5\text{CHBrCH}_2\text{Br}$	-24.5	-15.7	-9.2	-6.5	51
103.	- " -	-24.4	-15.6	-9.2	-6.4	60
104.	$\text{C}_6\text{H}_5\text{CH}_2\text{Br}$	15.1	21.9	25.6	-3.8	61
105.	- " -	18.8	25.6	25.6	-0.1	53
106.	- " -	20.0	26.8	25.6	1.1	62



Table 5(continued)

1	2	3	4	5	6	7
107.	- " -	16.5	23.3	25.6	-2.4	63,53
108.	$\text{CH}_2=\text{CHCH}_2\text{Br}$	11.8	16.6	16.4	0.2	59
109.	$\text{CH}_2\text{ICH}_2\text{I}$	15.9	19.3	23.3	-4.0	64
110.	$\text{CH}_3\text{CHICH}_2\text{I}$	8.6	13.3	17.3	-4.0	65,64
111.	$\text{I}(\text{CH}_2)_3\text{I}$	10.6	15.3	20.3	-5.0	64
112.	$\text{C}_6\text{H}_5\text{CH}_2\text{I}$	23.9	29.2	37.6	-8.4	61
113.	- " -	30.4	35.7	37.6	-1.9	66,67
114.	$\text{CH}_2=\text{CHCH}_2\text{I}$	22.9	26.3	28.4	-2.1	68
115.	$\text{HO}(\text{CH}_2)_3\text{OH}$	-93.7	-87.9	-100.2	12.3	69
116.	$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{OH}$	-100.7	-94.9	-104.3	9.4	69
117.	$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{OH}$	-103.0	-95.9	-106.7	10.8	69
118.	$\text{HOCH}_2\text{CH}_2\text{OH}$	-92.8	-88.3	-96.7	8.4	70
119.	- " -	-95.1	-90.6	-96.7	6.1	71
120.	- " -	-92.5	-88.0	-96.7	8.7	72,69
121.	$\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$	-104.0	-98.2	-86.7	-11.5	11
122.	$\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$	-53.6	-48.3	-46.6	-1.7	11
123.	$\text{CH}_2=\text{CHCH}_2\text{OH}$	-31.6	-27.5	-32.0	4.4	73
124.	- " -	-29.6	-25.5	-32.0	6.4	74
125.	$\text{HC}\equiv\text{CCH}_2\text{OH}$	10.1	13.5	5.2	8.3	11
126.	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	-22.4	-16.6	-22.6	5.9	11
127.	$\text{CH}_3\text{OCH}_2\text{CH}=\text{CH}_2$	-25.5	-20.4	-22.0	1.5	11
128.	$\text{CH}_3\text{OCH}_2\text{C}\equiv\text{CH}$	19.7	23.1	15.2	7.9	11
129.	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$	-4.1	1.9	3.6	-1.7	11
130.	$\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2\text{NH}_2$	-12.8	-5.2	-3.6	-1.5	75
131.	$\text{C}_2\text{H}_5\text{CH}(\text{NH}_2)\text{CH}_2\text{NH}_2$	-17.7	-9.1	-5.8	-3.3	75
132.	$(\text{CH}_3)_2\text{C}(\text{NH}_2)\text{CH}_2\text{NH}_2$	-21.6	-12.3	-11.5	-0.8	75
133.	$\text{CH}_2=\text{CHCH}_2\text{NH}_2$	6.9	11.7	18.3	-6.6	11
134.	$\text{C}(\text{CN})_4$	160.8	161.2	113.0	48.2	76
135.	$\text{NCC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{CN}$	24.2	32.9	28.6	4.4	77

Table 5(continued)

1	2	3	4	5	6	7
136.	$\text{CH}_2=\text{CHCH}_2\text{CN}$	37.7	40.7	43.3	-2.6	11
137.	$\text{NC}(\text{CH}_2)_4\text{CN}$	35.7	42.1	47.2	-5.1	77
138.	$\text{CH}_2=\text{CHCH}_2\text{CH}=\text{CH}_2$	25.3	29.7	30.6	-0.9	78,19
139.	$\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}=\text{CH}_2$	20.0	25.7	27.7	-2.0	79
140.	$\text{HC}\equiv\text{CCH}_2\text{CH}_2\text{C}\equiv\text{CH}$	99.4	101.7	102.3	-0.6	11
141.	$\text{HC}\equiv\text{C}(\text{CH}_2)_4\text{C}\equiv\text{CH}$	91.9	96.8	96.3	0.5	80
142.	- " -	90.2	95.1	96.3	-1.2	81
143.	$\text{CH}_2(\text{C}_6\text{H}_5)_2$	37.4	45.8	48.9	-3.1	82,83
144.	$\text{CH}(\text{C}_6\text{H}_5)_3$	63.7	75.4	78.9	-3.5	84,85
145.	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$	32.4	42.1	45.9	-3.8	86
146.	$\text{C}_6\text{H}_5\text{CH}_2\text{SH}$	6.8	10.3	11.9	-1.6	87,88
147.	$\text{C}_6\text{H}_5\text{CH}_2\text{SCH}_3$	3.8	10.6	13.0	-2.4	11
148.	$\text{HSCH}_2\text{CH}_2\text{SH}$	-32.5	-28.4	-28.0	-0.4	89
149.	$\text{HS}(\text{CH}_2)_3\text{SH}$	-37.5	-32.1	-31.0	-1.1	89

Table 6.

Conventionally Recommended Parameter Sets for the Calculation Scheme of  $\Delta H_0^0$  values Specified in This Study.

The value of the scaling constant for the  $\mathcal{V}$ -interaction

$$\alpha = 1 \text{ kcal/mole.}$$

Parameter	Value
1	2
$\mathcal{P}_{\text{CH}_3}$	3.94 <sup>2,15</sup>
A (kcal/mole)	-0.200
B (kcal/mole)	0.020
C (kcal/mole)	-0.002
$\mathcal{P}_F$	5.45
$\mathcal{P}_{\text{Cl}}$	4.98
$\mathcal{P}_{\text{Br}}$	4.52

Table 6 (continued)

1	2	3
$\varphi_I$	4.02	
$a_{F,F}^{1.3}$ (kcal/mole)	-5.5	
$\varphi_{NO_2}$	6.1	
$\Delta H_F$ (kcal/mole)	-64.8	
$\Delta H_{Cl}$ (kcal/mole)	-22.0	
$\Delta H_{Br}$ (kcal/mole)	- 6.8	
$\Delta H_I$ (kcal/mole)	6.9	
$\Delta H_{NO_2}$ (kcal/mole)	-22.7	
$G_{NO_2}$	$4.48 \pm 0.14^{15}$	
$z_C^{\pi}$	$0.39^{15}$	$0.43 \pm 0.02$
$\alpha^{\pi}$ (kcal/mole)	$1.35 \pm 0.02$	$1.19 \pm 0.07$

## REFERENCES

1. V.A. Palm and R.J. Hiob, Organic Reactivity, 18, 152 (1981)
2. B.I. Istomin and V.A. Palm, Reakts. sposobn.organ. soedin., 8, 845(1971) (in Rus.)
3. B.I. Istomin and V.A. Palm, Reakts. sposobn.organ. soedin., 2, 433(1972) (in Rus.)
4. B.I. Istomin and V.A. Palm, Reakts.sposobn.organ. soedin., 2, 469(1972) (in Rus.)



5. B.I. Istomin and V.A. Palm, Reakts.sposobn.organ. soedin., 9, 847(1972)(in Rus.)
6. B.I. Istomin and V.A. Palm, Reakts.sposobn.organ. soedin., 9, 1089(1972)(in Rus.)
7. B.I. Istomin and V.A. Palm, Reakts.sposobn.organ. soedin., 9, 1105(1972)(in Rus.)
8. B.I. Istomin and V.A. Palm, Reakts.sposobn.organ. soedin., 9, 1225(1972)(in Rus.)
9. B.I. Istomin and V.A. Palm, Reakts.sposobn.organ. soedin., 10, 537(1973)(in Rus.)
10. B.I. Istomin and V.A. Palm, Reakts.sposobn.organ. soedin., 10, 567(1973)(in Rus.)
11. B.I. Istomin and V.A. Palm, Reakts.sposobn.organ. soedin., 10, 583(1973)(in Rus.)
12. B.I. Istomin and V.A. Palm, Reakts.sposobn.organ. soedin., 10, 1005(1973)(in Rus.)
13. B.I. Istomin and V.A. Palm, Reakts.sposobn.organ. soedin., 10, 1011(1973)(in Rus.)
14. B.I. Istomin and V.A. Palm, Reakts.sposobn.organ. soedin., 10, 1025(1973)(in Rus.)
15. V.A. Palm, Foundations of Quantitative Theory of Organic Reactions, "Khimia", Leningrad, 1977(in Rus.)
16. V.A. Kireev, Methods of Practical Calculations in Thermodynamics of Chemical Reactions. "Khimia", Moscow, 1975 (in Rus.)
17. Thermal Constants of Substances. Handbook ed. by V.P. Glushko, Issues 1-5, Publ. House of Acad.Sci. U.S.S.R., Moscow, 1965-1971 (in Rus.)
18. D.A. Pittam and G. Pilcher, J. Chem.Soc., Faraday Trans.I, 2224(1972).
19. M.Kh. Karapetyants and M.A. Karapetyants. Fundamental Thermodynamic Constants of Anorganic and Organic Substances. "Khimia", Moscow, 1968 (in Rus.)
20. V.P. Kolesov, Uspekhi khimii, 47, 1145 (1978)(in Rus.)
21. V.A. Palm, Foundations of Quantitative Theory of Organic Reactions. "Khimia", Leningrad, 1967(in Rus.)

22. I.A. Koppel, M.M. Karelson, and V.A. Palm, Reakts. sposobn.organ.soedin., 10, 497(1973) (in Rus.)
23. E.A. Miroshnichenko, Yu.A. Lebedev, S.A. Shevelev, V.I. Gulevskaya, A.A. Fainzilberg, and A.Ya. Apin, Zh. phys.khim., 41, 1477(1967)(in Rus.)
24. G.A. Carpenter, M.F. Zimmer, E.E. Baroody, and R.A. Robb, J.Chem.Eng.Data, 15, 553(1970).
25. Yu. A. Lebedev, E.A. Miroshnichenko, and Yu. K. Knobel. Thermochemistry of Nitrocompounds. "Nauka", Moscow, 1970 (in Rus.)
26. E.A. Miroshnichenko, Yu. K. Knobel, and Yu.A. Lebedev, Dep. VINITI No 3037-71; Zh.phys.khim., 45, 2372 (1971) (in Rus.)
27. P. Noble, W.L. Reed, C.J. Hoffman, J.A. Callaghan, and F.G. Borgardt, Am.Inst.Aeron. Astronaut.J., 1, 395(1963).
28. D.E. Holcomb, and C.L. Dorsey, Ind.Eng.Chem., 41, 2788(1949).
29. M.F. Zimmer, R.A. Robb, E.E. Baroody and G.A. Carpenter, J.Chem.Eng.Data, 11, 577(1966).
30. V.P. Kolesov, Some Questions of Thermochemistry of Fluorine Organic Compounds in "Contemporary Problems of Physical Chemistry", vol. 6, pp.124-164, Moscow State University, Moscow, 1972 (in Rus.)
31. V.I. Pepekin, Yu.A. Lebedev, and A.Ya. Apin, Dokl.AN SSSR, 208, 153(1973)(in Rus.)
32. G.S. Sinke, J.Phys.Chem., 70, 1326(1966).
33. F.W. Kirkbride and F.G. Davidson, Nature, 174, 79(1954).
34. J.R. Lacher, A. Kianpour, F. Oetting, and J.D. Park, Trans.Faraday Soc., 52, 1500(1956).
35. V.P. Kolesov, A.M. Martynov, and S.M. Skuratov, Zh.phys.khim., 41, 913(1967) (in Rus.)
36. V.P. Kolesov, Papers on Chemistry and Chemical Technology (Gorki), Iss.2(31), pp.3-11(1972) (in Rus.)
37. V.P. Kolesov, First International Conference on Calorimetry and Thermodynamics, Warsaw, 1969 (in Rus.)
38. H. Wartenberg and J. Schiefer, Z.anorg.Chem., 278, 326 (1955).

39. V.P. Kolesov, O.G. Talakin, and S.M. Skuratov, Zh.phys.khim., 42, 3033(1968) (in Rus.)
40. J.R. Lacher, J.M. McKinley, C.M. Snow, L. Michel, G. Nelson, and J.D. Park, J.Am.Chem. Soc., 71, 1330(1949).
41. G.M. Slavetskaya, V.P. Kolesov, and G.S. Durkina, Zh.phys.khim., 47, 2723(1973)(in Rus.)
42. V.P. Kolesov, G.M. Slavetskaya, and T.S. Papina, in Sixth All-Union Conference on Calorimetry, pp.118-122(1973) (in Rus.)
43. E.Chung Wu, J.M. Pickard, and A.S. Rodgers, J.Phys.Chem., 79, 1078(1975).
44. D.A. Brandreth, S.P. O'Neill, and R.W. Missen, Trans. Faraday Soc., 62, 2355(1966).
45. A.C. Meeks and I.J. Goldfarb, J.Chem.Eng.Data, 12, 196(1967).
46. V.P. Kolesov, G.M. Slavetskaya, Yu.I. Aleksandrov, V.P. Vartanov, and G.A. Novikov, Zh.phys.khim., 48, 790(1974)(in Rus.)
47. V.P. Kolesov, G.M. Slavetskaya, and T.S. Papina, Dep. VINITI No 3819-71; Zh.phys.khim., 46, 815(1972)(in Rus.)
48. E.R. Bissel and M. Finger, J.Org.Chem., 24, 1256(1959).
49. A.M. Rozhnov, Neftekhimika, 8, 431(1968) (in Rus.)
50. K.A. Kobe and R.H. Harrison, Petrol.Refiner., 36, 155(1957).
51. L. Smith, L. Bjellerup, S. Krook, and H. Westermarck, Acta Chem., Scand., 7, 65(1953).
52. A.S. Rodgers, J.Phys.Chem., 71, 1996(1967).
53. D.N. Andreevski, Zh.phys.khim., 43, 2713(1969)(in Rus.)
54. K.K. Kelley, US Bur. Mines.Bull., 584(1960).
55. K.K. Kelley, J.Am.Chem.Soc., 51, 1400(1929).
56. Landolt-Börnstein Tabellen, Band II, Teil 4, Springer-Verlag, Berlin, 1961.
57. J.E. Kilpatrick and K.S. Pitzer, J. Chem. Phys., 17, 1064(1949).
58. W.D. Gwinn and K.S. Pitzer, J. Chem. Phys., 16, 303(1948).
59. K.A. Kobe and R.H. Harrison, Petrol. Refiner., 30, 151(1951).



60. L. Bjellerup, *Acta Chem. Scand.*, 15, 231, (1961).
61. S.J. Ashcroft, A.S. Carson, and J.B. Pedley, *Trans. Faraday Soc.*, 59, 2713(1963).
62. S.W. Benson and J.H. Buss, *J. Chem. Phys.*, 29, 546(1958).
63. T. Holm, *J. Organometal. Chem.*, 56, 87(1973).
64. S.W. Benson and A. Amano, *J. Chem. Phys.*, 36, 3464(1962).
65. K.A. Kobe and R.E. Pennington, *Petrol. Refiner.*, 29, 93(1950).
66. J.D. Cox, H.A. Gundry, and A.J. Head, *Trans. Faraday Soc.*, 60, 653(1964).
67. R. Walsh, D.M. Golden, and S.W. Benson, *J. Am. Chem. Soc.*, 88, 650(1966).
68. J.K. Koehler, and W. Giaque, *J. Am. Chem. Soc.*, 80, 2659(1958).
69. P.J. Gardner and K.S. Hussain, *J. Chem. Thermodyn.*, 4, 819(1972).
70. S.W. Benson, *J. Am. Chem. Soc.*, 86, 3922(1964).
71. J.H.S. Green, *Quart Rev.*, 15, 125 (1961).
72. G.S. Parks, T.J. West, B.F. Naylor, P.S. Fujii, and L.A. McClaine, *J. Am. Chem. Soc.*, 68, 2524(1946).
73. J.H.S. Green, W. Kynaston, and H.M. Paislay, *J. Chem. Soc.*, 473(1963).
74. M.A. Dolliver, T.L. Gresham, G.B. Kistiakowsky, E.A. Smith, and W.E. Vaughan, *J. Am. Chem. Soc.*, 60, 440(1938).
75. W.D. Good and R.T. Moore, *J. Chem. Eng. Data*, 15, 150(1970).
76. D.S. Barnes, C.T. Mortimer, and E. Mayer, *J. Chem. Thermodyn.*, 5, 481(1973)
77. N.D. Lebedeva and Yu.A. Katin, *Dep. VINITI No 5505-73; Zh. phys.khim.*, 47, 1620(1973) (in Rus.)
78. J.F. Messerly, S.S. Todd and H.H. Finke, *J. Phys. Chem.*, 62, 4304(1965).
79. G.B. Kistiakowsky, J.R. Ruhoff, H.A. Smith, and W.E. Vaughan, *J. Am. Chem. Soc.*, 58, 146(1936).

80. H.A. Skinner and A. Snelson, *Trans. Faraday Soc.*, 55, 404(1959).
81. F.D. Rossini, K.S. Pitzer, R.L. Arnett, R.M. Braun, and G.C. Pimental, *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*, Pittsburgh, 1953.
82. N.V. Lavrov, V.V. Korobov, and V.I. Filippova, *Thermodynamics of Gasofication Reactions and Gas Synthesis*. Publ. House of Acad. Sci. U.S.S.R., Moscow, 1960 (in Rus.)
83. E. Morawetz, *J.Chem.Thermodyn.*, 4, 455(1972).
84. G.S. Parks, W.D. Kennedy, R.R. Gates, J.R. Mosley, G.E. Moore, and M.L. Renquist, *J.Am.Chem.Soc.*, 78, 56(1956).
85. V.I. Pepekin, R.D. Erlich, Yu.N. Matyushin, and Yu.A. Lebedev, *Dokl. AN SSSR*, 214, 865(1974) (in Rus.)
86. D.J. Coleman and G. Pilcher, *Trans. Faraday Soc.*, 62, 821(1966).
87. W.D. Good, *J.Chem.Eng. Data*, 17, 28(1972).
88. H. Mackle and R.T.B. McClean, *Trans. Faraday Soc.*, 58, 895(1962).
89. M. Mansson and S. Sunner, *Acta Chem.Scand.*, 16, 1863(1962).
90. *Tables of Rate and Equilibrium Constants of Heterolytic Organic Reactions*. Ed. V.A. Palm, vol. 5(II), VINITI, Moscow, 1979, pp. 161-162 (in Rus.)

# CONTENTS

N.F. Musaeva, M.S. Salakhov, A.A. Gasanova, R.S. Salakhova, M.Ya. Salamova, and A.A. Bairamov, Kinetics and Mechanism of Diene Condensation of Hexachlorocyclopentadiene with Cyclic Dienophiles. XLVI. $\pi$ -Complexes of Hexachlorocyclopentadiene with N-(Alkenyl)Imides of Ortho-Phthalic Acid . .	347
N.F. Musaeva, M.S. Salakhov, A.A. Gasanova, R.S. Salakhova, A.A. Bairamov, and O.M. Mamedova, Kinetics and Mechanism of Diene Condensation of Hexachlorocyclopentadiene with Cyclic Dienophiles XLVII. Structure-Reactivity Interrelation of N-alkenylimides of Phthalic Acid in the Reaction with Hexachlorocyclopentadiene . . . . .	354
V. Nummert, M.EEK, and M. Piirsalu, Kinetic Study of Hydrolysis of Benzoates. XIV. Alkaline Hydrolysis in 80% Aqueous Dimethyl Sulfoxide . . . . .	363
T.G. Kyazimova, R.S. Babayev and M.M. Guseinov, Study of 5,5-Dimethoxytetra- chlorocyclopentadiene Reactivity in the Reaction of Diene Condensation with Chloroacetic Acid Allyl Esters . . . . .	375
I.A. Koppel, U.H. Mölder, and R.J. Pikk- ver, The Dependence of Ionization Potentials and Proton Affinities on Structure. I. Ionization Potentials. Correlations with Substituent Constants and Polarizability . . . . .	380



I.A. K o p p e l and U.H. M ö l d e r, CNDO/2 Calculations of Molecules. 3. Ionization Potential and Charge Distribution . . . . .	411
L.M. G o r n o s t a y e v, G.I. Z o l o t a r y e - v a and D.Sh. V e r k h o d o v a, On the Kinetics of 5-Chloroanthra (1,9-CD)-6-Isoxazolone Amination . . . . .	435
T.A. N i k o l o v a and V.V. S i n e v, Application of the Electrostatic Theory to the Kinetics of the Formation of Leukonitriles of Triarylmethane Dyes . . . . .	442
V.G. T s v e t k o v, M.N. B u s l a y e v a, Yu. P. K l a p s h i n and K.T. D u d n i k o v a, A Thermochemical Study of the Association and Donor Capacity of Diamines in Solutions . . . . .	449
V.I. M a k u r i n a and V.V. B o l o t o v, Study of 2-Oxoindoline Derivatives by Oxidizing Voltammetry . . . . .	455
V. P a l m and R. H i o b, Quantitative Statis- tical Interpretation of Kinetic Data in the Gas Phase Homolysis. I. Modified Calculation Scheme for Formation Enthalpies in the Gas Phase at 0°K. . . . .	460