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BASICITY OF 1,8-BIS(DIMETHYLAMINO) NAPHTHALENE,
CRYPTOFIX [2.2.2] AND TRIMETHYLAMINE OXIDE IN
ACETONITRILE

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The $pK_{BH}+$ values of basicity of 1,8-bis(di -
methylamine) naphthalene, cryptofix [2.2.2] and
of trimethylamine are determined by means of po -
tentiometric titration; the $pK_{BH}+$ values   for
these compounds are as follows: 18.7 $\pm$ 0.10 ,
18.6 $\pm$ 0.05, 16.6 $\pm$ 0.2 .

According to the results of the gas-phase high pres -
sure mass-spectrometric measurements by P. Kebarle et al[1]
the 1,8-bis(dimethylamino) naphthalene (the so called "pro-
ton sponge") is one of the most basic organic bases[2,3]. The
proton affinity (PA) shows that its basicity exceeds that
of ammonia by 39 kcal/mole (the PA are 246 and 207 kcal/mole,
respectively). In this respect it follows the anionic bases,
some inorganic oxides (Cs_2O, K_2O, SrO, CaO, etc.) and hy -
droxides (CsOH, KOH, NaOH, etc.) and, perhaps, also some
derivatives of guanidine and aliphatic diamines[2,3].

The compound is characterized by a rather high basici-
ty (pK = 12.1[4]) in the aqueous medium, where it exceeds the
respective Me_3N value by 2.3 pK units*. The anomalously

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* In the gas phase, the "proton sponge" exceeds trimethyl-
amine's basicity by 18 kcal/mole.

high for aromatic amines basicity of the 1,8-bis(dimethyl-amino)naphthalene might be explained either with a remar - kable steric destabilization by repulsion of the two di - methyl groups situated next to each other in the amine[1] nonprotonized form, or with the intramolecular protonated state stabilization via the hydrogen bond in that form, or with combination of these two versions[4]. Unfortunately , there is no such data yet on its super-basic behavior in the dipolar aprotic solvents, DMSO or acetonitrile.

Aliphatic monoethers show extremely low basicity in aqueous medium. Thus $pK_{BH}+ \geqslant -5.1^5$, for Et_2O in H_2O. The va-lue is by more than 15 orders of magnitude smaller than that for the isoelectric aliphatic amine Et_2NH ($pK_{BH}+ = 11.1^5$). In acetonitrile the difference between the $pK_{BH}+$ of Et_2O ($pK_{BH}+ \geqslant 0^5$)·and Et_2NH($pK_{BH}+ = 18.8^5$) is even larger than the corresponding value for the aqueous solutions , but, still being considerably smaller than the difference between the PA values of the same compounds in the gas phase ($\triangle PA = 33.7$ kcal/mole, i.e., $\triangle pK_{BH}+ \approx 25)^{2,3}$.

Owing to the intramolecular stabilization of their pro-tonated forms in acetonitrile, the basicity of some crown-ethers exceeds the basicity of Et_2O by 2÷8 $pK_{BH}+$ units (the Et_2O basicity, depending on the crown-ether structure is $2.2 \leqslant pK_{BH}+ \leqslant 8.2$, see[6]), which, for instance, is much less than that of ammonia ($pK_{BH}+ = 16.46^5$) in the same me - dium.

It should be mentioned that in the gas phase such mac-rocyclic polyethers as 18-crown-6 and 12-crown-4 appear to be much stronger (≈ 10 units of $pK_{BH}+$) bases[2,3] (PA = 224 kcal/mol) than ammonia[7] their basicities being close to that of trimethylamine (PA = 228 kcal/mol).

There has not been any data yet in literature concer - ning the basicities of macrocyclic compounds, whose mole - cules contain both oxygen and nitrogen atoms (e.g.,cryp-tofix [2.2.2] , see Scheme (1))either in water and in the dipolar aprotic solvents or in the gas phase.

Nevertheless, the trend towards increase of the basi-city of simple macrocyclic polyethers accompanying transi-

tion of these bases from acetonitrile[6] to the gas phase[2] leads to the suggestion that this cryptand has a rather high basicity. In the present report the basicity of this base in the acetonitrile medium has been determined.

In the acetonitrile medium, the pK_a values for the anionic or the anion-like oxygen-containing bases are known only for a limited number of substituted benzoate ions, phenolate ions and acetate ions[7,8].

The protonated forms of amine oxides can formally be considered as alcohols XOH containing charged substituents $(X = R_1R_2R_3\overset{+}{N})$; the basicity of their deprotonated forms (i.e. the oxides) in water[5] is 4-5 orders of magnitude lower in comparison with that of the corresponding amines. Thus, the $pK_{BH}+$ values[5] for Me_3NO and Me_3N are 4.6 and 9.8, for C_5H_5NO and C_5H_5N 0.7 and 5.2, and for the quinoline oxide and quinoline - 0.7 and 5.7, etc.

In DMSO, the trimethylamine oxide is a by ≈ 2 $pK_{BH}+$ units stronger base ($pK_{BH}+=10.6$[9]) than $Me_3N(pK_{BH}+ =8.7)$. The same tendency for this pair of compounds continues also in the gas phase, where Me_3NO is by ≈ 10 kcal/moles stronger base[2,3] than $Me_3N(PA = 238$ and 228 kcal/moles, respectively). On the other hand,[2,3] pyridine and its oxide are almost equal in their gas phase basicity, while the basicity of quinoline and especially azabicyclo [2.2.2] octane exceeds the cor - responding oxides by 2.5 and 9 kcal/moles.

In the present paper, the basicity of the trimethyl - amine oxide in the acetonitrile medium has been studied.
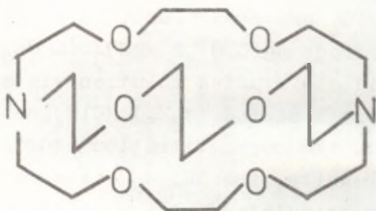
(1)

Experimental

Potentiometric method[10] based on the use of the $HClO_4$ solution in the CH_3CN medium as a titrant was used in order to determine the pK_{BH^+} values of the compounds studied in the present paper in the acetonitrile solution.

Reagents: Acetonitrile was purified according to method[10], the boiling point was 81.5°C (760 mm), the specific electrical conductance - $1.7 \cdot 10^{-7} \ \Omega^{-1} \ cm^{-1}$.

1,8-bis(dimethylamino)naphthalene was recrystallized from methanol, the boiling point at 27.5°C.

Cryptofix [2.2.2] (Fluka) was used without an additional purification.

Trimethylamine oxide was obtained after slow heating of the dihydrate (melting temperature 96.5°C) in vacuum (∼10 mm) first up to 120°, then to 150°C. The obtained anhydrous trimethylamine oxide was dried and kept at P_2O_5.

Potentiometric Procedure

The technique of potentiometric titration described in[10] has been used. The glass electrode was calibrated, taking for the reference points the pK_{BH^+} values of pyridine (12.33) and triethylamine (18.46).

If the formation of the BHB^+ type homocomplexes has been reduced to minimum, the slope of the calibrating line in the coordinates of the Nernst equation (E(mV) vs p_aH) does not differ from the theoretical one.

Diluted solutions ($\approx 10^{-4}$ mole/l) of bases were used, the titrants concentration varied in the range of $10^{-3} - 10^{-2}$ mole/l; in order to achieve a constant ionic strength, $(C_2H_5)_4NClO_4$ has been used ($\approx 5 \times 10^{-3}$ mole/l). As a reference electrode $Ag(0.01$ N $AgNO_3$ in CH_3CN) electrode connected with the studied solution via a U-shaped bridge containing 0.1 N of the $(C_2H_5)_4NClO_4$ solution is used.

Proceeding from the curve titration and from the electrode calibration results, the pK_{BH^+} values of the studied compounds were calculated:

$$pK_{BH^+} = P_aH - \log \frac{[B]}{[BH^+]} - \log f_{BH^+} \qquad (2)$$

where $[B]$ and $[BH^+]$ denote the concentration of the neutral and protonated base forms; $\log f_{BH^+} = 1.5\ I$; f – activation coefficient, I – the solution ionic strength).

Titration was repeated 3–5 times in the case of each base. From the average pK_{BH^+} values of individual measurements were calculated the arithmetic mean values of $\bar{K}_{BH^+}$, given in Table 1. Even in the case of cryptofix [2.2.2] and 1,8-bis(dimethylamino)naphthalene,only one S-shaped "jump" (deflection) was detected, corresponding to a single proton transfer to the basicity centers of the compounds, thus probably showing that the values of the second pK_{BH^+} of these compounds do not exceed 4 ++ 6 (see below).

Table 1

$p\bar{K}_{BH^+}$ of Cryptofix [2.2.2] , 1,8-bis(dimethylamino) Naphthalene and Trimethylamine Oxide in Acetonitrile

| Base	$p\bar{K}_{BH^+}$
1. 1,8-bis(dimethylamino)naphthalene	18.70 ± 0.10
2. cryptofix [2:2.2]	18.6 ± 0.05
3. Me_3NO	16.6 ± 0.2

An attempt to find the pK_{BH^+} of betaine ($Me_3\overset{+}{N}CH_2COO^-$) in the acetonitrile medium failed because of a poor solubility of the base in CH_3CN. According to the pK_{BH^+} data in water (1.8) and in DMSO (6.2)[12], betain is a much wea – ker base than the trimethylamine oxide. A value rather

close to ours $(16.9)^{x}$ has been given in report[11].

Discussion

In the case of protonation of neutral bases[9,10,12,13] the nucleophilic specific solvation of the protonated form seems to predominate over the initial state electrophilic solvation, since the $X_1X_2X_3NH^+$ acidity exceeds that of the EM:

$$X_1X_2X_3N \ldots EM \xrightarrow{\quad H^+ \quad} X_1X_2X_3NH^+ \ldots M-E, \qquad (3)$$
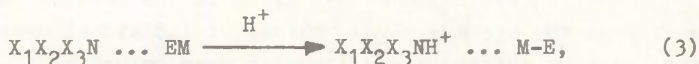
where E and M are the electrophilic and nucleophilic (basic) solvation centers of the molecules of the sol- vent E-M, respectively.

Consequently, a total gross specific medium effect solva - tion arises namely from prevalation of the specific nucleo- philic solvation of the protonated form of the amine.

Relative stabilization of the initial state of the highly polar zwitter-ionic betaine with the electrophilic molecules seems to be more significant than in the case of amines, while the stabilization of its protonated form is of minor importance, and the appearance of the medium brut- to-effect is connected with predomination of the initial state specific electrophilic solvation. Transition from aqueous solution into acetonitrile[10] (the nucleophilicities of H_2O and MeCN are practically equal, but the electrophi- lic solvating power of water remarkably exceeds that of acetonitrile) should not affect the contribution into the protonated form specific solvation and result in a sub - stantial destabilization of the neutral form of the base . This should bring about an increase of the absolute basi -

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^{x} See Ref.[8,11] for a more detailed study of the Me_3NO and some other compounds behavior depending on the correla- tion of the components and the solution pH in the ace - tonitrile medium.

city of the base. Owing to a more important role of the specific electrophilic solvation contribution in the case of Me_3NO and especially with the anionic bases ($ArCOO^-$, ArO^-, $XCOO^-$), a transition from H_2O to MeCN should in the present case cause a particularly significant $pK_{BH}+$ value increase. On the other hand, it should be taken into consideration that the transition from water to MeCN is accompanied by an almost twofold decrease of the medium dielectric permittivity and by the destabilization of both the protonated and non - protonated forms, while the contribution of the medium po - larizability change can be neglected ($n_D(H_2O) = 1.33$ $n_D(MeCN) = 1.33$).

For the purposes of comparison, in Table 2 are presented the experimentally found medium gross effects, which accompany the transition of protonation reaction of a series of neutral and anionic bases from water into acetonitrile (the data have been taken from sources[5-11]).

Table 2

Comparison of Basicities of Some Neutral and Anionic Bases in Acetonitrile and in Water[a]

No	Base	Medium, $pK_{BH}+$ or pK_a		
		acetonitrile	water	$\Delta = pK_{MeCN} - pK_{H_2O}$
1	2	3	4	5
1. NH_3		16.46	9.25	7.21
2. $MeNH_2$		18.37	10.64	7.6
3. H_2NNH_2		16.6	8.2	8.4
4. $H_2NNH_3^+$		2.8	-0.67	3.5
5. Me_3N		17.61	9.8	7.8
6. Et_3N		18.46	10.65	7.81
7. $CNNH_2$		4.0	-1.1	5.1
8. piperidine		18.9	11.1	7.8
9. morpholine		–	8.6	–
10. Et_2NH		18.75	11.1	7.6

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Table 2 continued

1	2	3	4	5
11.	C_5H_5N	12.3	5.2	7.1
12.	$C_6H_5NH_2$	10.56	5.1	5.5
13.	$2\text{-}NO_2C_6H_4NH_2$	4.9	0	4.9
14.	$MeONH_2$	10.97	4.8	6.2
15.	$CF_3\text{-}CH_2NH_2$	11.8	5.7	6.1
16.	$MeONHMe$	11.6	4.8	6.8
17.	1.8-bis(Me_2N)-naphtha-			
	lene	18.6[c]	12.1	6.5
18.	cryptofix [2.2.2]	18.6[c]	–	–
19.	Me_3NO	16.6[b]	4.6	12.0
20.	C_5H_5NO	8.26	0.7	7.6
21.	Et_2O		$-3.5 \rightleftarrows -7$	
22.	dioxane		-3	
23.	$MeO(CH_2)_2OMe$		-3.3	
24.	18-crown-6	6.5		
25.	12-crown-4	2.2		
26.	$MeCOO^-$	22.3	4.75	17.5
27.	$NCCH_2COO^-$	14.5	1.1	13.4
28.	$(COO^-)_2$	27.7	4.2	23.5
29.	$NCCH_2COO^-$	18.0	3.5	15.5
30.	CF_3COO^-	13.0	1.0	12.0
	$ArCOO^-$			
31.	H	20.7	4.2	16.5
32.	$2\text{-}NO_2$	18.3	2.2	16.1
33.	$3\text{-}NO_2$	19.3	3.5	15.8
34.	$4\text{-}NO_2$	18.7	3.4	15.3
35.	$3,5\text{-}(NO_2)_2$	16.9	2.7	14.2
36.	$2,4\text{-}(NO_2)_2$	16,2	1,4	14.8
37.	$3,5\text{-}Cl_2$	18.8	3.6	15.2
	ArO^-			
38.	H	26.9 ± 0.3	10.0	16.5
39.	$4\text{-}NO_2$	23.8	7.4	16.4
40.	$2\text{-}NO_2$	22.0	7.1	14.9
41.	$2,4\text{-}(NO_2)_2$	15.3	3.1	-12.0

Table 2 continued

1	2	3	4	5
42. $2,4,6(NO_2)_3$		7.8–11.0	0.2	9.2
43. Cl_5		16.5	4.7	11.8

a – the $pK_{BH}+$ values both for aqueous solutions and
    acetonitrile have been taken from reports [5-11]
b – this report see also[8]
c – this report[1]

Evidently, in the case of aliphatic and aromatic amines
the pK_{BH} increase amounts usually to 6-7 $pK_{BH}+$ units, thus
being a bit smaller ($\triangle$ = 3.5) than that for a successive pro-
tonation of hydrazine, while the $\triangle$ = 8.4 for the proton
transfer to the same base is a bit higher than the medium va-
lue.

As to the 1.8-bis(dimethylamino)naphthalene,its behavi-
or is similar to a typical amine ($\triangle$ = 6.5), its basicity be-
ing close to that of Et_3N and Et_2NH (the latter are by
1 $\frac{..}{..}$ 1.5 $pK_{BH}+$ units less basic in water medium).Proceeding
from the analogical behavior of hydrazine[10] (see also Ta -
bles 2, Nos 3-4), it can be expected that the second pro-
tonation of the"proton sponge" will have the $pK_{BH}+$ value so-
mewhere around 4.

Cryptofix [2.2.2] seems also to behave like a typical
amine in acetonitrile having a rather close basicity with
such strong bases (see Table 2) like pyridine, Et_2NH, etc.
in the same medium. It can also be mentioned that in the
aqueous solution, morpholine's basicity is by 2,5 $pK_{BH}+$
units weaker than piperidine. According to report[6], the
$pK_{BH}+$ values corresponding to the O-protonation of the
crown-ethers are by at least 10 pK units lower – than the
values for cryptofix [2.2.2] . It is quite possible that
the reaction of the second N-protonization of cryptofix

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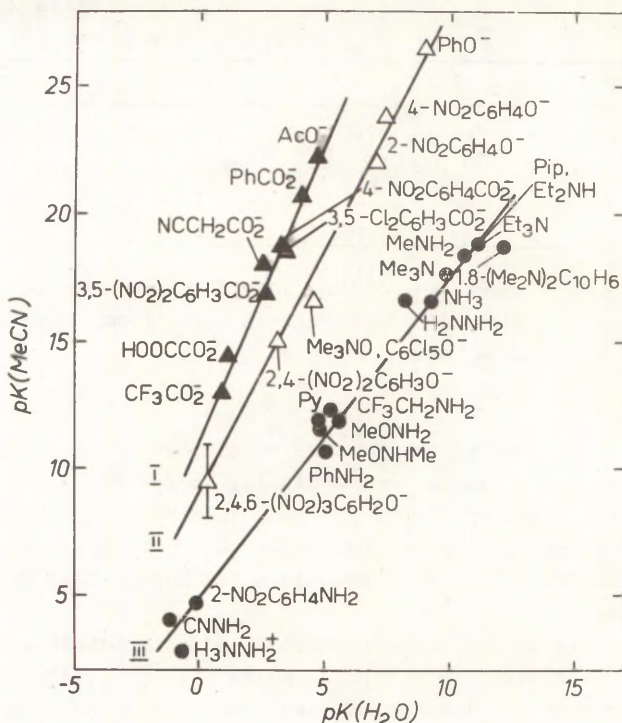
Fig. 1.   Comparison of the basicity of the anionic
          (lines I and II) and neutral (line III)
          bases in acetonitrile in the aqueous so -
          lution.

[2.2.2] (the $pK_{BH}+$ fall into the region of 4-5) and initial
O-protonation proceed in a similar pH range, being compe-
titive processes.

Table 2 shows that Δ values which characterize the
transition from water to acetonitrile ($\Delta = pK_{(MeCN)} - pK_{(H_2O)}$), the Me_3NO behavior is quite analogous to that of
anionic bases like $C_6Cl_5O^-$, CF_3COO^-, $2,4-C_6H_3O^-$, being a bit
weaker than $PhCOO^-$, CH_3COO^-, PhO^-, etc., thus once again pro-
ving the concept about the decisive role of the electrophi-
lic solvation of the non-protonated forms of anionic bases

in the case of determining their acid-base properties in solvents. If the hydrogen bond strength of the basic sol - vent molecules is either equal or weaker in comparison with either the protonated forms of the compounds of the latter group, or with the ammonium ions, then the decisive role is played by the substantial differences in the intensity of electrophilic solvation of anions, or anion-like bases, on one hand, and of amines, with the molecules of electrophilic solvent, on the other hand.

The aforesaid is illustrated by Fig. 1, which reflects the influence of the change of acetonitrile as a solvent, for water, on the structural effects, determining the basicity of the substituted amines, phenolate-ions and carbox - ylic acids. The first reaction series is $2\div2.5$ times more sensitive to the structural effects than the anionic oxy - gen-containing bases. As concerns Me_3NO, its behavior (Fig. 1) is most similar to that of the substituted phenolate ions (line II).

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CHEMICAL SHIFTS OF HYDROXYLIC PROTONS IN BINARY
MIXTURES OF FLUORINE-CONTAINING ALCOHOLS WITH
APROTIC SOLVENTS

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Chemical shifts of protons of OH-groups of
alcohols in binary mixtures of fluorine-substitu-
ted ROH alcohols (where $R=CF_3CH_2$ (TFE), $(CF_3)_2CH$
(HFP), $(CF_3)_3C$ (NFB)) with aprotic solvents have
been determined. It has been established that un-
like the alkyl-substituted alcohols, increase of
concentration of fluorine-substituted alcohol
leads to ^1H resonance shift towards a stronger
field. At a fixed mole fraction of alcohol
($N_{ROH} = 0.1$) for all studied mixtures of alcohol
and aprotic solvents (DMSO, acetone, triethyla -
mine, tetrahydrofurane and acetonitrile), chemi-
cal shifts of OH-proton are increasing in se -
quence: TFE, HFP, NFB. It has been found particu-
larly in case of DMSO that the lineshapes corres-
ponding to proton resonance of OH-group of fluo -
rine-substituted alcohol, are strongly broadened
if the N_{ROH} is changed, the maximum width of the
line is growing in succession TFE, HFP, NFB.

Dependence of chemical shifts of the proton
of the OH-group of NFB on the N_{ROH} can be used
for calculation of the association constant of

NFB with DMSO.

A nonmonotonic course of the concentration dependence of the chemical shift of the OH-group proton on the mole fraction of acid has been observed in the case of the system acetic acid-DMSO.

Introduction

In the binary systems of alcohol-aprotic solvents, the chemical shift of the proton of the OH-group of alcohol is a complex gross-value[1]. Most probably, its change in the case of dissolving alcohol in the aprotic solvent first of all carries information about two competitive processes, i.e. the self-association of alcohol molecules, on one hand and about complex formation of the alcohol molecules with the aprotic component (heteroassociation), on the other hand . Self-association according to scheme:

$$n \ ROH \rightleftharpoons (ROH)_n \qquad (1)$$

results in a shift of the OH-proton resonance towards a weaker magnetic field. The fact that the resonance of the proton of hydroxylic group is also shifted towards a stronger field[2,3] either due to the rise of the temperature or because of the dilution of the alcohols in CCl_4 is also in accordance with these findings.

The quantum-chemical calculations and results of the IR-spectrometry show that the increase of electronegativity of the substituent R is accompanied by the simultaneous increase in the OH-proton acidity, although the basic properties of the atom of the OH-group oxygen seem to weaken in a more considerable degree. It has been suggested[4,5] according to the NMR and IR spectroscopy data that the pure NFB is not actually associated. Complex-formation of the alcohol molecules with those of the aprotic solvent component (heteroassociation) is a complicated process and there is hardly any possibility for its the quantitative description yet. From a purely qualitative point of view[1], it is clear that

alcohol can participate in the above mentioned binary mix-
tures either in the form of monomers or polymeric aggre -
gates, or their associates with the aprotic component of
the mixture:

$$ROH + : B \rightleftharpoons ROH \ldots : B$$
$$(ROH)_n + : B \rightleftharpoons (ROH)_n \ldots : B \tag{2}$$
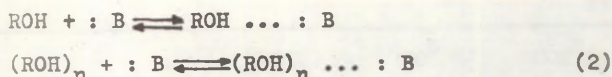
Naturally, the molecules of the aprotic solvent can
also be in the equilibrium of the $mB \rightleftharpoons B_m$ type.

It could have been expected that if both the self-as-
sociation and heteroassociation lead to the increase of
the positive charge on the hydrogen atom of the OH-groups,
it should be accompanied by a ^1H resonance shift towards a
lower field. Nevertheless, as it was shown by studying the
chemical shifts of the OH-group proton of aliphatic alco -
hols in binary mixtures with some aprotic solvents (DMSO,
acetone, triethylamine, DMF and acetonitrile[6]), an opposite
trend, i.e. a shift towards the stronger field is observed.

Experimental

Aprotic solvents (DMSO, acetone, triethylamine, tetra-
hydrofurane) and acetic acid were purified and dehydrated
according to the standard methods[7,8]. TFE, HFP and NFB were
used without an additional purification. The proton magnetic
resonance spectra of the studied systems were determined
at room temperature on a spectrometer TESLA BS
487B at operation frequency of 80 MHz relative to the
internal standard-tetramethylsilane. For the alcohol mix -
tures with DMSO, dependence of the chemical shift of the
OH-proton from the binary system was investigated in the
whole variation range of the components. As to the other
solvents, the corresponding chemical shifts have been mea-
sured at the fixed mole fraction of alcohol $N_{ROH} = 0.1$. The
results are given in Tables 1, 2 and 3.

Table 1

Chemical Shifts δ_{OH} (in ppm) and Line Halfwidth
$\Delta\nu/2$ (in Hz) of the Fluoroalkyl Alcohols in
Binary Mixtures with DMSO[x]

TFE

N_{ROH}	δ_{OH}	$\Delta\nu/2$
1.0	5.30	6
0.8	5.57	20
0.7	5.68	38
0.65	5.82	64
0.6	5.86	53
0.4	5.98	5
0.2	6.05	2
0.1	6.05	2

HFP

N_{ROH}	δ_{OH}	δ_{CH}	$\Delta\nu_{1/2}$	N_{ROH}	δ_{OH}	δ_{CH}	$\Delta\nu_{1/2}$
1.0	4.76	4.39	15	0.469	7.56	4.55	69
0.864	5.36	4.40	21	0.404	7.75	4.7	38
0.740	5.93	4.41	35	0.380	7.85	4.66	21
0.613	6.64	4.50	86	0.31	7.93	4.79	16
0.583	6.66	4.45	108	0.260	7.96	4.90	5
0.557	6.89	4.48	114	0.231	7.96	4.98	4
0.553	7.00	4.50	117	0.2	7.96	4.90	4
0.505	7.35	4.58	95	0.16	7.965	5.11	4
0.480	7.55	4.55	72	0.1	7.695	5.26	4

[x] For $(CF_3)_2CHOH$ are also given chemical shifts (in Hz) of
the proton being in the α- position relative to the
OH-group

NFB

N_{ROH}	δ_{OH}	$\Delta\nu_{1/2}$	N_{ROH}	δ_{OH}	$\Delta\nu_{1/2}$
2.00	4.18	42	0.380	9.99	85
0.771	8.05	52	0.341	10.06	62
0.725	8.20	58	0.310	10.18	54
0.706	8.24	80	0.235	10.30	25
0.651	8.39	96	0.192	10.35	19
0.629	8.57	117	0.170	10.40	21
0.600	8.78	132	0.156	10.39	11
0.562	8.80	147	0.132	10.44	9
0.531	3.05	157	0.113	10.48	8
0.478	9.49	127	1.00	10.49	8

Table 2

Chemical Shifts δ_{OH} (in ppm) of Proton of OH-group of HFP in Binary Mixtures with Aprotic Solvents at Con-centration $N_{ROH} = 0.1$

	DMSO	Acetone	Triethylamine	Tetrahydrofurane
δ_{OH}	10.41	9.275	10.24	9.21

Table 3

Chemical Shifts (in ppm) and Line Widths of COOH Group Proton of CH_3COOH in Binary Mixture of Acetic Acid-DMSO

N_{CH_3COOH}	δ_{OH}	$\Delta\nu_{1/2}$
1.00	11.76	1.1
0.8	11.46	1.3
0.6	11.48	1.6
0.5	11.53	2.8
0.4	11.56	14.9
0.2	11.61	31.9
0.09	11.84	45.6

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Discussion

Fig. 1. depicts the dependence of chemical shifts δ_{OH} and the line width $\Delta\gamma_{1/2}$ of fluoro-substituted alcohols in their mixtures with DMSO on the mole fraction N_{ROH} of alcohol.
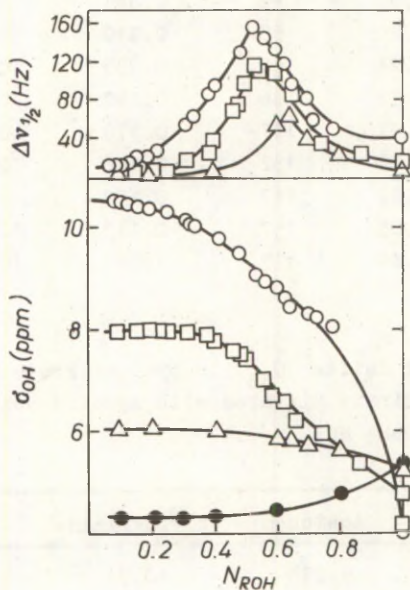
Fig. 1. Dependence of chemical shifts δ_{OH} (ppm) and the line widths at the half-hight $\Delta\gamma_{1/2}$ (Hz) of the proton of the OH-group of alcohols in their binary mixtures with DMSO on the mole fraction of alcohol N_{ROH}.

O- $(CF_3)_3COH$ △- CF_3CH_2OH

□- $(CF_3)_2CHOH$ ●- C_2H_5OH
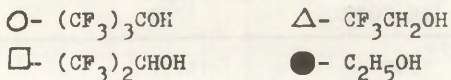
Evidently, the fluorine-containing and alkyl-substi - tuted aliphatic alcohols[1] have different concentration de - pendences. Chemical shifts of the OH-group proton of pure alcohols change in the following succession: aliphatic al- kyl-substituted alcohols, TFE, HFP, NFB towards a stronger magnetic field.

This is in keeping with the suggestion that the increase of the radical R electronegativity leads to weakening of the alcohol's self-association. After adding DMSO, the competi - tion between the self-association and heteroassociation pro- cesses should be observed. Both processes are supposed to bring about the shift of the OH-proton signal towards a lower field. For aliphatic alcohols, the influence of auto⁻ association is prevailing, while an opposite trend is noti - ced in the case of fluorine-containing alcohols where the complex-formation (heteroassociation) of alcohol with DMSO should play a more important role. This is also evidenced by the chemical shifts of the OH-proton at the concentration $N_{ROH} = 0.1$, increasing in the following succession:

aliphatic alkyl-substituted alcohols $<$ TFE $<$ HFP $<$ NFB,

i.e. with the increase of the radical R electronegativity , the signal of ^{1}H of the OH-group is shifted towards the weaker field.

Fig. 1 shows that at the lower mole fractions of alco - hol, both the chemical shifts and the line widths of the proton of the alcohol's OH-group are practically constant. At the same time it can be mentioned that the value of the mole fraction N_{ROH}, from which onwards hold the conditions $\delta_{OH} = $ const. and $\Delta\nu_{1/2} = $ const. is dropping when the radical's R electronegativity increases (see Fig. 1). But the stability of the chemical shift and of the line width of the OH-proton does not ensure the stability of chemical shift of the hyd - rogen atom, which is attached to the α- carbon atom (see Table 1, chemical shifts δ_{CH} for HFP) of $(CF_3)_2CHOH$.

The structure and composition of the complexes between DMSO and fluorine-containing alcohols have not been well studied yet. According to the IR-spectroscopy[9] data, in the case of the TFE and DMSO complexes in CCl_4, the ratio of the contributions of 1 : 1 and 2 : 1 associates is 9, while in the case of HFP and DMSO, it is increasing up to 43. It should be mentioned that the complexes between the NFB and DMSO molecules are thermodynamically very stable[10]: the cor-

responding complex-formation enthalpy is 11.8 kcal/mole!

Unlike the complexes of aliphatic alkylsubstituted alcohols, in the case of formation of the DMSO complexes with fluorine-containing alcohols, a considerable broadening of the resonance line is observed. The maximum broadening takes place at the concentration N'_{ROH}, which is half of the con-centration interval corresponding to the change of the chemical shift of the OH-group proton. A similar band widening can also be observed when studying[11] the $CF_3H \ldots N(C_2H_5)_3$ complexes in liquid argon. At 90 K, the broadening of the signal of the ^1H in CF_3H was observed. It reached the maximum in the case of comparable concentrations of the com-plex and the free fluoroform. Such a line broadening is not observed if there is no hydrogen bond acceptor and in the case of a large excess of the latter. These results have led to the conclusion[11] that the line width is determined by breaking and repeated reformation of the hydrogen bond between the H-bond donor and the acceptor.

This conclusion seems to be holding also in the case of complex-formation of the fluorine-containing alcohols with DMSO. The concentrations N'_{ROH}, corresponding to the maximum broadening of the signal from the hydroxylic proton are as follows:

	TFE	HPI	NFB
N'_{ROH}	0.7	0.63	0.56

In the case of dissolving the fluorine-containing al-cohols in other aprotic solvents, the OH-proton shift towards a weaker field also takes place. For instance, at the con-centration $N_{ROH} = 0.1$ (data of TFP and NFB from report[1]) the chemical shifts (in ppm) of the OH-proton can be cha-racterized by the following values (TMS as interal stan-dard:

	DMSO	acetone	triethylamine	tetrahydrofurane
TFE	6.05	5.43	6.54	5.15
HFP	7.965	7.10	8.21	6.83
NFB	10.41	9.275	10.24	9.21

These results again support the conclusion that the increase of the electronegativity of the radical R leads also to the increase of the OH-proton chemical shift. The results of the nonempirical quantum chemical calcula - tion[12,13] also speak in favor of this tendency, showing that in the case of the hydrogen bond formation takes place a remarkable charge transfer between the donor and the H - bond acceptor.

Simultaneously, in the complexes between two neutral partners also increases the calculated formal positive charge Mulliken's population on the hydrogen atom of the OH-group, if compared with the situation in the case of the molecules of free components.

In the case of complex-formation between the anions (XO^-, F^-) and the OH-acids (H_2O, XOH), the quantum chemical calculations predict an increase of the negative charge den- sity on the basicity center of the anion, and a simultaneous increase of the negative charge density on the oxygen atom of the H-bond donor. Therefore, accepting in a rather rough approximation, the probable change of the screening constant of the nucleus O, symbatic with that of the electron density on the mentioned atom, it can be expected that the complex- formation of the OH-acid with the hydrogen bond acceptor should cause a shift of the resonance of ^{17}O of the OH- group towards a stronger field.

Unfortunately, according to the analysis of various ex- perimental data, in the present case, no simple relation - ship has been traced between the calculated charge popu - lation on the oxygeen atom of the H-bond donor and the ex- perimentally obtained ^{17}O chemical shift in the case of the free components both in the gas phase and in solvents.

As a matter of fact the transfer of free H_2O molecules

into liquid state is alredy accompanied by the 36   ppm
shift of the ^{17}O resonance signal towards a weaker magnetic
field[14,15]. Essentially the same character have the reso -
nance shifts of the ^{17}O water towards a stronger field[x] ,
caused either by the temperature rise[16] (at transition from
25 to 215°C the shift is - 9 ppm) or by dissolving of water
in various organic solvents, thus evidencing about breaking
of hydrogen bonds between water molecules.

A qualitatively similar situation reflecting the com -
plex-formation between the DMSO and $(CF_3)_3COH$ has been ob -
served also in the present work; the ^{17}O spectrum (using a
BRUKER AM-500, frequency 67.781 MHz,   64 000 scans) of the
binary mixture of the mentioned components has been taken,
at mole fraction N_{ROH} = 0.422. The ^{17}O resonances of pure
DMSO and $(CF_3)_3COH$ were shifted by 13 and 2.0 ppm, respec-
tively, towards a weaker field in comparison with the signal
from the external standard - water. In the case of this bi-
nary mixture only one broad ($\sim$ 700 Hz) line, corresponding
to the intermolecular complex, which is situated between
the signals of the pure components and is shifted towards a
weaker field, relative to the signal of ^{17}O both   pure
alcohol (8.6 ppm) and water (10.6 ppm) has been observed at
room temperature.

In one of our previous reports[1], a linear dependence
between the chemical shift of the OH-group proton of alcohol
for the binary mixture of some alcohols with DMSO   (N_{ROH} =
0.1) and the pK_a value of the corresponding alcohol   in
the DMSO medium has been established.

In order to study the role of the structure of the hy-
droxyl-containing component of the binary mixture and par -
ticularly that of its acid-base properties, the concentra-
tion dependence of the chemical shift of the OH-group pro -

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[x] In the present paper it has actually been established
that the signal shifts of ^{17}O of water in the diluted
solutions in $(CF_3)_3COH$ and in $(CF_3)_2CHOH$ amount to-14.4
and - 15.2 ppm, respectively.

ton was studied in binary mixtures of DMSO and acidic acid . It is known that in water[18], pK_a(NFB) = 5.4, pK_a(CH$_3$COOH) = 4.75; whereas in DMSO pK_a(NBF) = 10.4[19], pK_a(CH$_3$COOH)=12.3[18]. The concentrational dependences of chemical shifts and line width of the signals from hydroxylic proton in the system acidic acid - DMSO are given in Table 3 and illustrated by Fig. 2. It can be seen that unlike the fluorine-containing alcohols, the DMSO-acidic acid mixtures are characterized by a non-monotonic cause of the concentration dependence of the chemical shift, while the stability of the OH-proton chemical shift was not traced at smaller mole fractions. The fact that the system with the smallest acidic acid content (N_{CH_3COOH} = 0.1) has the biggest line width (40 Hz), should also[3] be paid attention to.

When comparing the values of chemical shifts of alco - hols in DMSO with those of pK_a in the same solvent, a tight correlation between these values (see also report[1]) can be found. The fluorine-containing, aromatic and aliphatic al - cohols, as well as the points for the methyl alcohol and water are all situated on the general straight line.

It is possible to find the association constant for complex-formation between the NFB and DMSO. Really, at lower alcohol concentrations, the relationship[17]

$$\frac{\nu_X - \nu_{ROH}}{[D]} \quad vs \quad (\nu_X - \nu_{ROH}) \qquad (3)$$

(where ν_{ROH} is the chemical shift of pure alcohol, ν_X - the chemical shift at the DMSO concentration $[D]$) is a straight line, whose slope equals the equilibrium constant taken with the opposite sign. In the present case , for the NFP and DMSO complex, $K = 3.9 \pm 0.22$ (ppm)$^{-1}$.

These calculations cannot be carried out for the TFE and HFP, since at their low concentrations, the OH-group's proton chemical shift is a constant value.
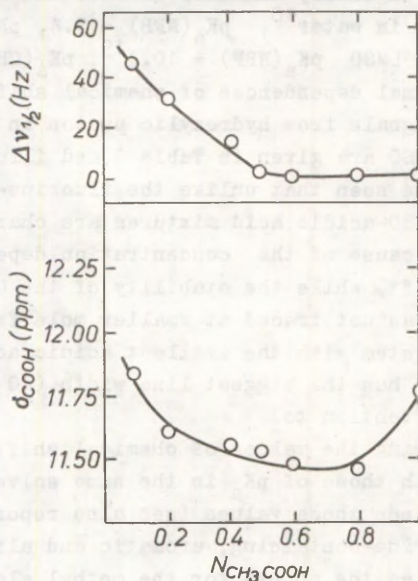
Fig. 2. Dependence of chemical shifts δ_{COOH} and the line width at half-hight $\Delta\nu_{1/2}$ of COOH - group proton on acetic acid mole fraction N_{CH_3COOH} for binary mixtures of DMSO and CH_3COOH.

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SOME STRUCTURE-REACTIVITY RELATIONSHIPS FOR ALKYL-
BROMIDES IN THE GRIGNARD REACTION

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The dependence of rate constants of alkyl -
magnesium bromide formation in pure Et_2O and TAF
was compared with that obtained in toluene in the
presence of small amounts of Et_2O and THF (less
than one mole to a mole of halide). In the last
case, both in rapid stage and in the slow one ,
the reaction followed zero-order kinetics by ha-
lide and, apparently, does not depend on   the
structure of halide. However, the rate of Würtz-
reaction as well as the activity of catalyst (the
monosolvated Grignard reagent), evidently depends
on the nature of alkyl group.

The dependence of reactivity of alkylhalides on their
structure in the Grignard reagent formation is quantitati-
vely examined only in a few papers[1-3], mainly in connection
with the mechanism of reaction.

To investigate the effect of substituents, in this stu-
dy an attempt was made to compare the conclusions concerning
the Grignard reagent formation in pure ethereous solvents
with those in toluene containing small amounts of the lat-
ter. It is known[4] that the reaction of Grignard reagent
formation in an inert media (toluene) with organic base
content being less than one mole to a mole of halide pro -
ceeds in a stepwise manner. The induction period is follo-

wed by a rapid stage with formation of the monosolvated Grignard reagent. After that takes place a slow reaction of zero-order kinetics, catalyzed by the solvated organomagnesium compound.

In our earlier work[1] it was found that in ethyl ether, butyl ether and tetrahydrofurane the rate of organomagnesium compound formation depends on the structure of alkyl group.

In this study the same relationships for the reaction between magnesium and alkylhalides in toluene mixtures with small amounts of Et_2O and THF were investigated.

Correlation analysis was made to ascertain the similarity or difference of the investigated processes in pure ethers and with their small additions.

EXPERIMENTAL

Reagents and Solvents

The organic halides were dried over calcium chloride and rectified. Toluene and ethyl ether were dried over calcium chloride and distilled over sodium wire. The THF was treated with potassium hydroxide and distilled over calcium hydride. Magnesium metal was used in the form of beads from 1.0 to 1.6 mm in diameter.

Kinetic Measurements

The reaction was carried out as described earlier[4]. The temperature in reaction flask was 30°C, the initial concentration of alkyl halide was 1.24 M and that of organic base 0.3 M (molar ratio of base to halide was 0.41), the weight of magnesium - 6 g.

The rapid stage of reaction was monitored by the thermographic method, the slow stage by the method of aliquots. The aliquots were analyzed for the content of basic magnesium and ionic halide (magnesium bromide).

When the measurements were carried out at an increased concentration of magnesium bromide a corresponding amount of 1,2-dibromoethane was introduced together with alkyl ha-

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Results of Measurements

Earlier it was determined[4,5] that in the rapid stage of reaction a certain part of the process can be described by the first-order kinetics. The rate constants were calculated by a differential method[4] from the slope of a plot of ln ($\Delta \Delta T_0 / \Delta t$) vs $\mathcal{C}$, where $\mathcal{C}$ is the time corresponding to the intermediate of the time-interval Δt. The constants obtained from such "linear" parts of differential curves were taken as some characteristics of the rapid stage of reaction. The mean values of the first-order rate constants are presented in Table 1. In this table (column 3) the average length of the linear part with regard to the time co--ordinate (from the beginning to the end of this part) is presented too. The time account starts from the introduction of halide into the reaction mixture (i.e. including the induction period). The extent (%) of the Grignard reagent formation at the end of the linear part and at the end of the whole rapid stage are represented in the next two columns respectively. It has been found earlier[4] that the rapid reaction stage is completed when the basic solvent is entirely used up for the formation of the monosolvated Grignard reagent. At the end of the rapid stage the yield of the Grignard reagent corresponds to the amount of ether (in this case ca 41%). Lower values of the yields of the Grignard reagent indicate that the Würtz reaction proceeds also in the rapid stage of the process. In order to compare better the data with those described earlier[1] the rate constants of the total reaction were recalculated to the rate constants of Grignard reagent formation taking into account the Würtz-product formation. In Table 1 the corresponding data are represented in the last column. In the same column the data for the measurements with THF were determined titri - metrically (see Discussion).

In Table 2 the kinetic characteristics of the slow stage of reaction are presented. The rate constants were calculated from the slope of a plot in coordinates: the

Table 1

Data for Rapid Stage of Reaction between Alkylbromides and Magnesium in Toluene with Small Additions of Et_2O and THF (see Exp. Part)

Alkyl group	$k_1 \cdot 10^2$ (sec^{-1})	Time interval (min) in which the k_1 is determined	Yield of Grignard Reagent		$k_1 \cdot 10^2$ (sec^{-1})
			at linear part	at rapid stage	
			Et_2O		
Et	0.81 ± 0.11	2.5 - 4.8	20	44	0.81
n-Bu	0.79 ± 0.08	3.0 - 5.0	25	30	0.58
i-Bu	0.85 ± 0.10	2.4 - 5.0	20	33	0.70
s-Bu	0.97 ± 0.15	2.5 - 3.5	8	28	0.66
			THF		
Et	-	-	-	33	0.10 ± 0.01
n-Bu	-	-	-	33	0.11 ± 0.01
i-Bu	-	-	-	26	0.11 ± 0.01
s-Bu	-	-	-	17	0.12 ± 0.01

Table 2

Data for Slow Stage of Reaction between Alkylbromides
and Magnesium in Toluene with Small Additions of Et_2O
and THF

Alkyl group	$k_o \cdot 10^4$ mole $\cdot$ l^{-1}sec^{-1}		Yield, %	
	of Grignard reagent	of halide	of Grignard reagent	of magnesium
		Et_2O		
Et	0.83 ± 0.05	1.16 ± 0.05	76	96
n-Bu	0.52 ± 0.03	0.88 ± 0.07	68	98
i-Bu	0.18 ± 0.01	0.28 ± 0.02	63	97
s-Bu	0.16 ± 0.03	0.36 ± 0.07	55	95
		THF		
Et	0.17 ± 0.02	–	51	94
n-Bu	0.098 ± 0.014	–	46	92
i-Bu	0.090 ± 0.012	–	45	97
s-Bu	0.035 ± 0.005	–	23	84

product concentration vs. time. The mean values of rate constants of Grignard reagent formation (column 2) and magnesium bromide formation (column 3) are reported. The latter data correspond to the conversion of the alkyl halide. Data for reaction of magnesium with ethyl bromide obtained by applying dibromoethane additions (and without the latter) are summarized in Table 3.

Table 3

Results of Experiment at Increased Concentration of Magnesium Bromide in Reaction Mixture

Content of Reagents, moles			$k_1 \cdot 10^2$ sec^{-1}	Yield of Grignard Reagent at Rapid Stage	$k_0 \cdot 10^4$ $mole \cdot l^{-1}, sec^{-1}$
Et_2O	C_2H_5Br	$C_2H_4Br_2$			
0.0116	0.0283	–	$0.31^{\pm}0.11$	44	$0.83^{\pm}0.05$
0.0116	0.0188	0.0094	$0.12^{\pm}0.01$	21	$0.17^{\pm}0.04$
0.0116	0.0283	0.0141	$0.14^{\pm}0.01$	18	$0.20^{\pm}0.02$

CORRELATION ANALYSIS

The following parameters were applied to quantitatively characterize the structural effects of alkyl groups: either steric constant E_s or E_s^0 of Palm[6] (free of the hyperconjuga - tion component); Taft's inductive constants σ^* or constants φ of Palm and Istomin[7,8].

It is necessary to underline that the scale of φ -con - stants for substituents is essential to describe the substi- tuent effects on the formation enthalpies of free radicals in the series of substituted methyl radicals[10,11].

The values of constants for substituted alkyl radicals used in this work are represented in Table 4.

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Table   4

Values of Substituent Constants Employed
by Data Processing

Alkyl group	$\sigma*$	φ	E_s^o	E_s	$n_{\alpha H}$
Me	0.0	3.94	0.0	0.0	3
Et	-0.100	3.38	-0.27	-0.07	2
n-Pr	-0.115	3.19	-0.56	-0.36	2
i-Pr	-0.190	2.68	-0.85	-0.47	1
n-Bu	-0.125	3.29	-0.59	-0.39	2
s-Bu	-0.210	2.87	-1.53	-1.13	1
t-Bu	-0.300	2.51	-2.14	-1.54	0
n-Pent	-0.130	3.30	-0.60	-0.40	2

STATISTICAL TREATMENT OF DATA

The program of multilinear regression analysis (MLRA) elaborated by V.Palm was employed.

During the data processing on the risk level of 0.05 statistically insignificant scales of arguments were ex - cluded. Essentially refusal lines were excluded according to the Student's criterion on the risk levels of 0.01, 0.03 and 0.05.

The final results were characterized by standard deviation in normed (s_o) and natural (s) scales; with stan - dard deviation of determined parameters and with correla - tion coefficient (R).

DISCUSSION

A. Reaction in Pure Basic Solvent

In report by Hŏrak, Palm and Soogenbits[1] only the one-parametric correlation of data was made. Authors considered that in diethyl ether kinetic data (taking into account the yield of the Grignard reagent) were described by the steric constant E_s^o.

The repeated calculation with consideration of the scales of σ^*, φ and E_s^o indicates the insignificance of the first and the second scales and the final result appears identical:

$$\log k = -1.501 \pm 0.057 + (0.529 \pm 0.058) E_s^o \qquad (1)$$
$$s_o = 0.283 \quad s = 0.101 \quad R = 0.959 \quad n = 8$$

On the risk level of 0.01 the point for sec-Bu, declining by 0.42 logarithmic units, was excluded.

In tetrahydrofurane media the dependence of reaction rate on structure of alkyl group was not revealed[1]. The repeated calculation indicates the following dependence:

$$\log k = -1.82 \pm 0.06 + (1.81 \pm 0.40) \sigma^* \qquad (2)$$
$$s_o = 0.484 \quad s = 0.067 \quad R = 0.875 \quad n = 7$$

The range of the data change in THF is very negligible. Therefore it is difficult to decide whether the distinction between equations (1) and (2) is caused by the difference of the reaction mechanism or equation (2) has only a for - mal content.

Remember, that in pure ethers the reaction proceeds by the first-order kinetics, regarding the halide and the rate of reaction depends on the structure of ether[1,12]. Data concerning the influence of the concentration of ether are somewhat contradictory. In report[12] it was found that in binary mixtures of ethyl ether with benzene or hexane the rate constants linearly depend on the molar ratio of ethyl ether. Nevertheless, one can take into consideration that the experiment was complicated by a poor solubility at the Grignard reagent at low concentrations of ether. In our later work[13] the mixtures of toluene with different organic bases (up to quite small amounts of the latter) were stu - died. The earlier described linear dependence was not re- vealed. However, it was found that at higher concentrations the base influences the reaction rate by altering the vis-

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cosity of the medium. These results coincide with the ob -
servations of Whitesides et al. [14,15].

B. The Rapid Stage of Reaction at Low Content of Basic Solvent

The values of rate constants of rapid stage in Et_2O
for different alkyl groups coincide within the limits of
exactness of experiment (Table 1). The same is valid for
the rate constants, corrected by the yield of Grignard rea-
gent at the end of rapid stage. Statistical analysis could
not reveal any correlation with constants of alkyl substi -
tuents.

In the case of the THF, the linear part of the reaction
kinetics is so limited that it is very difficult to assign
any physical sense to such a characteristic of the reaction
with variable alkyl group. However, the main part of the
kinetic curve of the reaction nearly up to the beginning of
the slow stage follows well the first-order kinetics. The
values of rate constants calculated by differential method
are presented in the last column of Table 1. The values of
these rate constants do not either depend on the structure
of the alkyl group.

One can see, that passing from the pure basic solvent
to an inert solvent with small amounts of base, the depen-
dence of rate constants on the structure of alkyl group of
halides disappears. The same phenomenon was observed also in
pure THF. However, the structure of alkyl group has an es-
sential influence upon the yield of the Grignard reagent,
i.e. upon the relative rate of the Würtz-reaction.

At the same time, the rate of reaction quite definite-
ly depends on the structure of the base, both in the case
of a pure base[1] and in the presence of additions of the
latter[5]. In the last case the rate constants linearly de-
pend on the base concentration[4,5]. Taking into account all
these facts one can conclude that the reaction follows the
zero-order kinetics by halide both in the slow and in ra -
pid stages. The observed kinetic first-order of the process

is conditioned by a rapid complexation of the catalyst e-
ther with the formed organo-magnesium compound. As it is
seen from the data for the slow step of the reaction , the
monosolvated Grignard reagent has a lower catalytic acti -
vity.

The reasons for a somewhat different course of the
process in Et_2O and THF are not quite clear yet. Probably
it is caused by distinctions in reaction rates, thermal
effects, and equilibrium constants of the processes, follo-
wing the rate determining stage. It can be concluded that
in these conditions the cleavage of the carbon-halide bond
is not the rate-determining stage , however, the organic
base takes part in this step. While the concentration of
the base markedly exceeds that of alkylhalide, and in the
case of pure base, evidently the mechanism of the reaction
is different.

C. The Slow Stage of Reaction at Low Content of Basic
Solvent

In spite of the fact, that the slow stage proceeds as
a zero-order reaction by alkyl halide, the rate constants
depend upon the structure of the alkyl group (Table 2)[x] .
The dependence is better described by the constants ψ and
E_s^o and is principally the same for the total reaction
(formation of magnesium bromides; Eq.- 3 in the case of
Et_2O) and for the formation at alkylmagnesium bromide (Eq. 4,
in the case of Et_2O).

$$\log k = -1.03 \pm 0.37 - (0.79 \pm 0.11)\psi + (0.74 \pm 0.05)E_s^o$$

$$s_o = 0.107 \quad s = 0.032 \quad R = 0.994 \quad n = 4 \qquad (3)$$

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[x] In so far as we have in our disposal the data only for
four substituents, one can consider the interpretation
of this dependence as a purely tentative one.

$$\log k = -2.17 \pm 0.01 - (0.50 \pm 0.01)\varphi + (0.77 \pm 0.01)E_s^o$$

$$s_0 = 0.003 \quad s = 0.001 \quad R = 1.000 \quad n = 4 \tag{4}$$

Somewhat worse, but quite satisfactorily the data are described by means of scales φ and E_s, or $n\alpha_H$ and E_s^o. For example, for alkylmagnesium bromide formation with additions of Et_2O, Eq.4' was obtained.

$$\log k = -3.31 \pm 0.23 - (0.21 \pm 0.07)\varphi + (0.78 \pm 0.03)E_s \tag{4'}$$

$$s_0 = 0.069 \quad s = 0.021 \quad R = 0.997 \quad n = 4$$

In the case of THF additions the rate constant of the Grignard reagent formation is described by Eq. 5.

$$\log k = -7.12 \pm 0.67 + (0.69 \pm 0.19)\varphi + (0.29 \pm 0.10)E_s \tag{5}$$

$$s_0 = 0.249 \quad s = 0.061 \quad R = 0.969 \quad n = 4$$

The values and signs of the δ parameter (susceptibility to the steric hindrance) in Eq. 3-5 appear to be reasonable. but it is difficult to explain the alteration in the sign of the term with φ constant in the case of Et_2O and THF res - pectively.

One can suppose that the obtained equations describe the summary effect of several reactions. Data in Table 3 demonstrate that magnesium bromide additions considerably suppress the rate of both the rapid and slow stages. At the same time the yield of the Grignard reagent at the end of the first stage decreases, too. Consequently, the complex of magnesium bromide with ether does not have any (or has extremely low) catalytic activity, but it binds the base firmly.

When the THF is taken for the base, during the first stage of reaction a considerable, but variable amount of magnesium bromide is formed in the case of different alkyl groups (Table 1). This does considerably influence the catalytic activity of the system in the second stage of the

reaction. Besides, we cannot yet separate the influence of
the structure of alkyl group on the reactivity of alkyl -
halide from that on the activity of catalyst (the monosol-
vated alkylmagnesium bromide). It cannot be excluded (ta-
king into account the kinetic zero-order of the reaction by
alkyl halide) that the rate constants do not depend at all
on the structure of the reagent and the obtained correlation
equations only describe the influence of the alkyl group on
the activity of catalyst under these conditions of reaction.
The influence of the structure of the base on the activity
of catalyst was established[5] earlier.

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QUANTITATIVE STATISTICAL INTERPRETATION OF KINETIC
DATA IN THE GAS PHASE HOMOLYSIS
9. Recalculation of Substituent Effects on the Con-
ventional Enthalpies and Entropies of Activation for
Substituted Methyl Radicals

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The results of the reparametrization of the
equations reflecting the effects of substituents
X on the conventional enthalpies and entropies of
activation of free radicals $X_1X_2X_3C\cdot$ are reported.
The technique of multilinear regression analysis
(MLRA) is used for this.

It is shown that the simultaneous calculation
of all parameters leads to an unsatisfactory re-
sult. More reliable values are obtained if a
smaller number of parameters are simultaneously
determined. Preliminarily the values of $\Delta H^{\neq}_{CH_3}$,
$\Delta S^{\neq}_{CH_3}$, and γ_C are calculated from the data for
alkyl radicals. The iterative procedure for the
separate calculation of enthalpic and entropic pa-
rameters is tested. However, it does not lead to
a more reliable correlation of substituent effects.
Variants of the model, where the activation entro-
py is varied, are not statistically preferred com-
paring with the isoentropic model because of a

large uncertainty of the entropy term.

Taking into account the recalculation[1] of the conventional heats of formation $\Delta H_{R.}^{\neq}$ (or $\Delta \Delta H_{R.}^{\neq}$, where $\Delta \Delta H_{R.}^{\neq} = \Delta H_{R-}^{\neq}$ $-\Delta H_{R-}^{0}$) and entropies of formation $\Delta S_{R.}^{\neq}$ for free radicals in the transition state, it is reasonable to verify the applicability of the approach described in the papers[2,3] for the correlation of substituent effects on the recalculated heats and entropies of formation of free radicals $X_1 X_2 X_3 C\cdot$, where X_1, X_2, and X_3 are hydrogen, alkyl or some other substituent. On the other hand one can try to use the applicability of this approach as a criterion for selection of different alternative versions of the $\Delta H_{R.}^{\neq}$ ($\Delta \Delta H_{R.}^{\neq}$) and $\Delta S_{R.}^{\neq}$ calculations in the communication[1].

As well as for alkanes and their polyfunctional derivatives, the $\Delta H_{R.}^{\neq}$ values of free radicals belonging to the $X_1 X_2 X_3 C\cdot$ type may be expressed by the following general initial equation[2,3]:

$$\Delta H_{X_1 X_2 X_3 C\cdot}^{\neq} = \Delta H_{CH_3\cdot}^{\neq} + \sum_i \Delta H_{X_i-}^{0} + \gamma_{C\cdot} \sum_i \gamma_{X_i} + A_{C\cdot} \sum_{i < j} \gamma_{X_i} \gamma_{X_j} +$$
$$B_{C\cdot} \gamma_{X_1} \gamma_{X_2} \gamma_{X_3} + \alpha^* \sigma_{C\cdot}^* \sum_i \sigma_{X_i}^* + \alpha^* z_{C\cdot}^* \sum_{i<j} \sigma_{X_i}^* \sigma_{X_j}^* + \sum_i \psi_{X_i} \quad (1)$$

where $\Delta H_{X_i-}^{0}$ are the additive increments for substituents X_1 ; γ_X and σ_X^* denote γ_- and the inductive sub - stituent constants for X; $\gamma_{C\cdot}$ and $\sigma_{C\cdot}^*$ are the same for the free-radical center $C\cdot$; ψ_X - the energy of the resonance interaction between substituent X and this free-radical center; $A_{C\cdot}$ and $B_{C\cdot}$ are the constants of double and triple γ- interactions through the $C\cdot$ center; α^*- the scaling constant for the inductive interaction, $z_{C\cdot}^*$ - the inductive transmission factor for the $C\cdot$ center. The scaling constant of the γ-interaction omitted in Eq (1) is equal to unity if the heats of formation are expressed in kcal/mol. Hydrogen atom serves as a standard substituent and, consequently, $\gamma_H =$

0, $\Delta H_{H-}^{O} = 0$, and $\Delta H_{X-}^{O} = \Delta H_{XH}^{O}$. For the sum of resonance energies $\sum_{i} \Psi_{X_i}$ in papers[2,3] three different terms were determined: for the double bond $C = C$ of aliphatic or the aromatic ring ($\Psi_=$), cyano (Ψ_{CN}), and nitro (Ψ_{NO_2}) groups.

For correlation of substituent effects on the entropies of activation of the substituted methyl radicals the following model was proposed[3]:

$$\Delta S_{X_1 X_2 X_3 C\cdot}^{\neq} = \Delta S_{CH_3\cdot}^{\neq} + QN + Yp \qquad (2)$$

where N is the number of substituents $X \neq H$, p denotes the number of formal pairwise interactions between these substituents, Q and Y are respective parameters.

The gas phase homolysis of covalent compounds, including the substituted methyl radical, is expressed according to the following scheme:

$$X_1 X_2 X_3 C - X_4 \longrightarrow X_1 X_2 X_3 C\cdot + X_4\cdot \qquad (3)$$
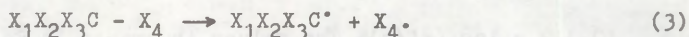
where X_4 may be also a substituted methyl of the $X_1 X_2 X_3 C$ type. Within the framework of the transition state theory one can write the following equation[3] for the value of statistically corrected rate constant logarithm k^c:

$$\log k^c = \log A - \log n - E/2.3RT = \log (k'T/h) +$$

$$+ (\Delta S_{X_1 X_2 X_3 C\cdot}^{\neq} + \Delta S_{X_4\cdot}^{\neq})/2.3R - (\Delta H_{X_1 X_2 X_3 C\cdot}^{\neq} + \qquad (4)$$

$$+ \Delta H_{X_4\cdot}^{\neq} - \Delta H_{X_1 X_2 X_3 CX_4}^{O})/2.3RT$$

where $\log A$ and E are the Arrhenius equation parameters, n is the statistical factor, R - the gas constant, T - the temperature in K, k' - the Boltzmann constant, h - the

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Planck constant, and $\Delta H^o_{X_1X_2X_3CX_4}$ is the standard heat of formation of the compound $X_1X_2X_3CX_4$.

Combining Eqs (1), (2), and (4) one can obtain an equation for treatment of primary data for the homolysis of the $X_1X_2X_3C-X_4$ compounds:

$$E + 2.3RT(\log n - \log A + 10.319 + \log T) + \Delta H^o_{X_1X_2X_3CX_4} -$$

$$- \sum_i \Delta H^o_{X_i-} + (\Delta S^{\neq}_{X_4\cdot} + \Delta S^{\neq}_{CH_3\cdot}) \, T/10^3 - \Delta H^{\neq}_{X_4\cdot} = \left\{\Delta H^{\neq}_{CH_3\cdot}\right\} +$$

$$+ \left\{\varphi_{C\cdot}\right\} \sum_i \varphi_{X_i} + \left\{A_{C\cdot}\right\} \sum_{i<j} \varphi_{X_i}\varphi_{X_j} + \left\{B_{C\cdot}\right\} \varphi_{X_1}\varphi_{X_2}\varphi_{X_3} +$$

$$+ \left\{\alpha^* \sigma^*_{C\cdot}\right\} \sum_i \sigma^*_{X_i} + \left\{\alpha^* z^*_{C\cdot}\right\} \sum_{i<j} \sigma^*_{X_i}\sigma^*_{X_j} + \left\{\psi_=\right\} N_= + \left\{\psi_{CN}\right\} N_{CN} +$$

$$+ \left\{\psi_{NO_2}\right\} N_{NO_2} - \left\{Q\right\} N \cdot T/10^3 - \left\{Y\right\} p \cdot T/10^3, \qquad (5)$$

where $10.319 = \log (k'/h)$. The values in braces in Eq. (5) and in the following equations are the coefficients to be determined. The complications arising in the calculations of the argument scales of Eq. (5) and other analogous equations for the compounds, where several halogen atoms are connected with a single carbon atom[2], were taken into account. Carry - ing out multilinear regression analysis (MLRA) in the coor - dinates of a ten-parameter Eq. (5) with the intercept ($\Delta H^{\neq}_{CH_3\cdot}$) one can attempt to determine simultaneously both the enthal- pic (first eight) and the entropic (last two) parameters . There are alternative variants for the calculation of values to be correlated (the left-hand side of Eq. (5)). Let us re- mind, that in paper[1] the values of the conventional heats of formation $\Delta H^{\neq}_{R\cdot}$ and $\Delta \Delta H^{\neq}_{R\cdot}$, and respective to them entro - pies of activation $\Delta S^{\neq}_{R\cdot}$ were calculated according to the following nine different variants of treatment:

1) Iteration B), beginning from the literature values of activation energies (E) and using the heats of formation

$\Delta_f H^o$ at 0 K for the initial compounds. In result the heats of formation of radicals at 0 K are obtained.

2) Iteration A), starting from the literature values of logarithms of the preexponential factors (log A) gives also heats of formation $\Delta H_R^{\neq}$. at 0 K.

3) The isoentropic model with constant value of the activation entropy $\Delta S_{const}^{\neq}$ = 9.8 entr. un., the heats of formation $\Delta H_R^{\neq}$. at 0 K.

4) Analogously to variant 1) but the heats of formation at 298 K.

5) Analogously to variant 2), the heats of formation at 298 K.

6) Analogously to variant 3), the heats of formation at 298 K.

7) Iteration B), the values of $\Delta \Delta H_R^{\neq}$. are obtained.

8) Iteration A), the $\Delta \Delta H_R^{\neq}$. values.

9) The isoentropic model with $\Delta S_{const}^{\neq}$ = 9.8 entr.un., the $\Delta \Delta H_R^{\neq}$. values.

The results of the statistical treatment of the gas phase homolysis data[1,4] for compounds, including the sub - stituted methyl radicals, according to Eq (5) and other equations in Tables 1-20 correspond to this numeration of the variants.

In Ref. 1, the statistical treatment of the kinetic data of the gas phase homolysis for substituted methyls was carried out proceeding from the isoentropic and isokinetic models but in paper[1] an attempt was made to parametrize the equations where both the enthalpic and entropic parameters existed. In the latter case the values to be correlated were expressed in entropic units (kcal mol^{-1} K^{-1}). A comparative processing in energic (kcal/mol) and entropic units showed their equality and all results of the statistical treatment presented lower have been obtained in units of energy.

For the inductive constant of nitro group $\sigma_{NO_2}^{*}$ = 4.5 and for the scaling constant of the inductive interaction α^{*}= 1.37 are assumed[5].

Estimating the results for the different variants of
statistical processing from the view of the quality of de-
scription a stability of solution was primarily required .
This means that only at a sufficient constancy of parame -
ters to be determined (in limits of uncertainties) during
the exclusion of significantly deviating lines one   can
further compare the values of standard deviation s or nor-
malized standard deviation s_o if the numbers of the inclu-
ded reactions are equal[2].

Results of the data treatment according to Eq. (5) for
version 1) are listed in Table 1. The other variants give
analogous results. Initial data were processed for three
different sets: the first one was a total set including all
available data, the second one consisted of the polyfunc -
tional derivatives of alkanes, and only alkanes were inclu-
ded into the third set. One can see from Table 1 that for
all three sets parameters $A_{C\cdot}$, $B_{C\cdot}$, Q, and Y are excluded
as statistically insignificant and zero values are assigned
to them already at the very beginning stage of the exclu -
sion of significantly deviating lines. Zero values for $A_{C\cdot}$
and $B_{C\cdot}$ were obtained for less representative data set of
report [2], too. The comparison of the all other parameters
distinguished from zero for the total data set and the set
without alkanes (Table 1) shows their overall mutual uncom-
patibility.

It is known[3] that the simultaneous parametrization of
the $\Delta H_R^{\neq}$ and $\Delta S_R^{\neq}$ values leads to a large effect of "o-
verpumping" between the values of the parameters to be de-
termined. Therefore, the subset of alkanes from the total
set of the present paper was separated in order to determine
some parameters ($\Delta H_{CH_3}^{\neq}$ and $Y_{C\cdot}$). However, despite a sa-
tisfactory final reliability (s = 0.69 kcal/mol) and   a
good accordance between the obtained $\Delta H_{CH_3}^{\neq}$ values and
the corresponding ones from the article[1], the value of the
$Y_{C\cdot}$ parameter (3.08) substantially differs from the values
calculated earlier (in the range 2.0 - 2.55)[2,3]. At that
time seven reactions including branched alkyls are excluded

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from the overall fourteen reactions. The homolysis data for these alkanes are hardly so unreliable that a half of the reactions must be excluded in result. Thus, the results of the data treatment in Table 1 are not satisfactory. Besides, for the set without alkanes unreasonable values for the intercept ($\Delta H^{\neq}_{CH_3.}$) are obtained, and the data treatment of the set for alkanes $X_1X_2X_3C - CX_4X_5X_6$, where $X_1 \ldots X_6$ are hydrogen atoms or alkyls, according to Eq (5), is not quite correct, because calculating the left-hand side of Eq. (5) $\Delta S^{\neq}_{X_4.} = \Delta S^{\neq}_{CH_3.}$ and $\Delta H^{\neq}_{X_4.} = \Delta H^{\neq}_{CH_3.}$ are assumed from the respective variants of the paper [1]. At the same time the $\Delta H^{\neq}_{CH_3.}$ value is a parameter to be determined in the right-hand side of Eq (5).

The data for alkanes may be more correctly processed according to the equation as follows:

$$E + 2.3RT \ (\log n - \log A + 10.319 + \log T) +$$

$$+ \Delta H^0_{X_1X_2X_3CCX_4X_5X_6} = \sum_{i=1}^{6} \Delta H^0_{X_i} - \left\{ 2 \Delta H^{\neq}_{CH_3.} \right\} +$$

$$+ \left\{ \varphi_{C.} \right\} \sum_{i=1}^{6} \varphi_{X_i} - \left\{ 2 \Delta S^{\neq}_{CH_3.} \right\} T/10^3 - \left\{ Q \right\} \ N \cdot T/10^3 -$$

$$- \left\{ Y \right\} \ p \cdot T/10^3 \tag{6}$$

While using the energies of interactions $I_{X_1X_2X_3CCX_4X_5X_6}$ between substituents $X_1X_2X_3C-$ and $X_4X_5X_6C-$ instead of the $\Delta H^0_{X_1X_2X_3CCX_4X_5X_6}$ values (for details see Ref. 1 and papers cited there) the following equation may be written:

$$E + 2.3RT \ (\log n - \log A + 10.319 + \log T) +$$

$$+ I_{X_1X_2X_3CCX_4X_5X_6} + A_C \sum_{i<j} \sum \varphi_{X_i} \varphi_{X_j} + B_C(\varphi_{X_1} \varphi_{X_2} \varphi_{X_3} +$$

$$+ \varphi_{X_4} \varphi_{X_5} \varphi_{X_6}) = \left\{ 2 \Delta \Delta H^{\neq}_{CH_3.} \right\} + \left\{ (\varphi_{C.} - \varphi_{CH_3}) \right\} \sum_{i=1}^{6} \varphi_{X_i} -$$

$$-\left\{2\Delta S^{\neq}_{CH_3\cdot}\right\} T/10^3 - \left\{Q\right\} N \cdot T/10^3 - \left\{Y\right\} p \cdot T/10^3 \qquad (7)$$

where $\Delta\Delta H^{\neq}_{CH_3\cdot} = \Delta H^{\neq}_{CH_3\cdot} - \Delta H^{o}_{CH_3-}$, $A_C = -0.200$, and $B_C = 0.020^5$ - the constants of the double and triple φ-interactions through the sp^3-carbon atom center. In the case of the isoentropic model the left sides of Eqs (6) and (7) (denoted by F_1 and F_2) are retained but the two last terms on the right-hand sides are left out:

$$F_1 = \left\{2\Delta H^{\neq}_{CH_3\cdot}\right\} + \left\{\varphi_{C\cdot}\right\}\sum_{i=1}^{6}\varphi_{X_i} - \left\{\Delta S^{\neq}_{const}\right\} T/10^3 \qquad (8)$$

$$F_2 = \left\{2\Delta\Delta H^{\neq}_{CH_3}\right\} + \left\{(\varphi_{C\cdot} - \varphi_{CH_3})\right\}\sum_{i=1}^{6}\varphi_{X_i} -$$

$$-\left\{\Delta S^{\neq}_{const}\right\} T/10^3 \qquad (9)$$

The results of the statistical data treatment for al-kanes according to Eqs (6) - (9) are presented in Tables 2, 3. The values of the determined parameters are more reaso-nable comparing with those in Table 1, and the utmost mo-ment - the number of the excluded reactions is only 1 - 2. However, there still exists a possibility for the preven-tion of a probable "overpumping" between the parameters to be determined. The iterative procedure in papers[1,3] was used for calculation of the heats of formation $\Delta H^{\neq}_{R\cdot}$ and the entropies $\Delta S^{\neq}_{R\cdot}$ for free radicals in the transition state. The analogous approach may be used for the paramet-rization of the equations reflecting the influence of the substituent effects on the substituted methyl radicals.

Let us examine this procedure within the framework of the equations using the experimental heats of formation $\Delta H^{o}_{X_1X_2X_3CCX_4X_5X_6}$ of the initial compounds for alkanes. Proceeding from the literature values of log A and using the MLRA we computed zero approximations of the entropy pa-

rameters according to equation:

$$2.3R(\log A - \log n - 10.753 - \log T) = \left\{ 2\,\Delta S^{\neq}_{CH_3 \cdot} \right\} + \left\{ Q \right\} N + \left\{ Y \right\} p \tag{10}$$

where $10.753 = \log (ek'/h)$.

In the next cycle of MLRA, zero approximations of the enthalpy parameters are obtained:

$$E + 2.3RT(10.753 + \log T + \log n - \log A + F_{calc}/2.3R) - RT + \Delta H^O_{X_1 X_2 X_3 CCX_4 X_5 X_6} - \sum_i \Delta H^O_{X_i} = \left\{ 2\,\Delta H^{\neq}_{CH_3 \cdot} \right\} + \left\{ \gamma_{C \cdot} \right\} \sum_i \gamma_{X_i} \tag{11}$$

where $F_{calc} = 2\,\Delta S^{\neq}_{CH_3 \cdot} + QN + Yp$ are the calculated values of the activation entropies proceeding from the zero approximations of the entropy parameters. Then one can calculate the first approximations of the entropy parameters:

$$2.3R \left[\log A - \log n - 10.753 - \log T + (F_{calc} + \sum_i \Delta H^O_{X_i} - \Delta H^O_{X_1 X_2 X_3 CCX_4 X_5 X_6} + RT - E)/2.3RT \right] = \left\{ 2\,\Delta S^{\neq}_{CH_3 \cdot} \right\} + \left\{ Q \right\} N + \left\{ Y \right\} p \tag{12}$$

where $F_{calc} = 2\,\Delta H^{\neq}_{CH_3 \cdot} + \gamma_{C \cdot} \sum_i \gamma_{X_i}$ are the calculated values of the activation enthalpy using the zero approximations of the enthalpy parameters. Solving then by turns the systems of Eqs (11) and (12) one can obtain the next approximations of the enthalpy and entropy parameters.

Starting from the literature values of the activation energies, at first zero approximations of the enthalpy parameters are calculated:

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$$E - RT + \Delta H^o_{X_1 X_2 X_3 CCX_4 X_5 X_6} - \sum_i \Delta H^o_{X_1-} =$$
$$\left\{ 2 \Delta H^{\neq}_{CH_3\cdot} \right\} + \left\{ \varphi_{C\cdot} \right\} \sum_i \varphi_{X_i} \tag{13}$$

and further the next approximations of the entropy and enthalpy parameters according to Eqs (12) and (11).

Results of the use of the described iterative procedure according to Eqs (10) - (13) and analogous equations in the case of the interaction energies $I_{X_1 X_2 X_3 CCX_4 X_5 X_6}$ are reflected in Table 4. From the latter one can see that there are no essential differences between the results of the iterative procedures A) and B) (compare versions 1) and 2), 4) and 5), 7) and 8) in Table 4). The iteration leads to some higher accuracy of description (Table 4) as compared with the simultaneous determination of the enthalpy and entropy parameters (Tables 2 and 3).

It must be underlined that the results listed in Tables 2-4 are obtained exclusively on the basis of the kinetic data of homolysis, and the heats of formation (interaction energies) of the initial compounds for alkanes. Moreover, the parameters $\Delta H^{\neq}_{CH_3\cdot}$ or $\Delta\Delta H^{\neq}_{CH_3\cdot}$, $\Delta S^{\neq}_{CH_3\cdot}$, $\varphi_{C\cdot}$ or $\varphi_{C\cdot} - \varphi_{CH_3}$, Q, and Y may be straightly determined from the $\Delta H^{\neq}_R$. or $\Delta\Delta H^{\neq}_R$. , and $\Delta S^{\neq}_R$. values for alkyls obtained using the technique of MLRA on the total available set of the kinetic data of homolysis[1]. In this case one can hope the parame - ters to be determined more exactly fitting the values of the heats of formation and the activation entropies for all substituted methyl radicals not only for alkyls. Thus, Eq (1) for alkyls will be reduced to the following convenient for testing simpler form:

$$\Delta H^{\neq}_{X_1 X_2 X_3 C\cdot} - \sum_i \Delta H^o_{X_i-} = \left\{ \Delta H^{\neq}_{CH_3\cdot} \right\} + \left\{ \varphi_{C\cdot} \right\} \sum_i \varphi_{X_i} +$$

$$+ \left\{A_{C^\bullet}\right\} \sum_{i<j} \sum \Upsilon_{X_i} \Upsilon_{X_j} + \left\{B_{C^\bullet}\right\} \Upsilon_{X_1} \Upsilon_{X_2} \Upsilon_{X_3} \tag{14}$$

In Ref. 1 the $\Delta H_{R^\bullet}^{\neq}$ values for eight alkyl radicals – $\cdot CH_3$, $\cdot C_2H_5$, $\cdot C_3H_7$, $\cdot CH(CH_3)_2$, $\cdot CH(CH_3)C_2H_5$, $\cdot C(CH_3)_3$, $\cdot CH(CH_3)CH(CH_3)_2$, and $\cdot C(CH_3)_2C_2H_5$ are reported. The value of $\Delta\Delta H_R^{\neq} = \Delta H_{R^\bullet}^{\neq} - \Delta H_{R^-}^{o}$ is additional for the radical $\cdot CH_2CH(CH_3)_2$. Taking into account a relatively high reliability of the experimental values of the standard heats of formation for alkanes $\Delta H_{RH}^{o} = \Delta H_{R^-}^{o}$, the $\Delta\Delta H_R^{\neq}$ values (recalculated to $\Delta H_R^{\neq} = \Delta\Delta H_R^{\neq} + \Delta H_{R^-}^{o}$) may be also used for testing Eq (14).

The data processing for the indicated eight (nine) alkyl radicals in the coordinates of Eq (14) showed that the scales $\sum_{i<j} \sum \Upsilon_{X_i} \Upsilon_{X_j}$ and $\Upsilon_{X_1} \Upsilon_{X_2} \Upsilon_{X_3}$ are excluded as statistically insignificant in all variants of treatment except some isoentropic ones (see Table 5). However, the values of the determined parameters $\Delta H_{CH_3}^{\neq}$ and $\Upsilon_{C^\bullet}$ for various comparable versions, for example variants 1) and, 2), differ significantly. Considering the largest number of the experimental data for the $CH_3\cdot$ radical, the $\Delta H_{CH_3}^{\neq}$ value may be assumed known and Eq (14) rewritten as follows:

$$\Delta H_{X_1X_2X_3C^\bullet}^{\neq} - \sum_i \Delta H_{X_i^-}^{o} - \Delta H_{CH_3}^{\neq} = \left\{\Upsilon_C\right\} \sum_i \Upsilon_{X_i} +$$
$$+ \left\{A_{C^\bullet}\right\} \sum_{i<j} \sum \Upsilon_{X_i} \Upsilon_{X_j} + \left\{B_{C^\bullet}\right\} \Upsilon_{X_1} \Upsilon_{X_2} \Upsilon_{X_3} \tag{15}$$

Results of the treatment for the same data as in Table 5 according to Eq (15) are listed in Table 6. The contradiction between the values of the parameter $\Upsilon_{C^\bullet}$ for comparable variants 1) and 2), 4) and 5) is retained then. Therefore, it is reasonable to include into the processed set instead of 8(9) radicals only the radicals methyl, ethyl, isopropyl, and tert-butyl as the most represented in

the initial data set and it is hoped that the $\Delta H_R^{\neq}$. values
for them, are the most reliable ones. Taking zero values for
the values of A_C. and B_C. a validity of two following e-
quations[2,4] for the cited four alkyl radicals may be ver-
ified:

$$\Delta H_{(CH_3)_n H_{3-n}C\cdot}^{\neq} - n\,\Delta H_{CH_4}^0 = \left\{\Delta H_{CH_3\cdot}^{\neq}\right\} + \left\{\gamma_{C\cdot}\right\}\, n\,\gamma_{CH_3} \qquad (16)$$

$$\Delta H_{(CH_3)_n H_{3-n}C\cdot}^{\neq} - n\,\Delta H_{CH_4}^0 - \Delta H_{CH_3\cdot}^{\neq} = \left\{\gamma_{C\cdot}\right\}\, n\,\gamma_{CH_3} \qquad (17)$$

where n is the number of CH_3 groups.

The results of this verification are reported in Tables
7 and 8. It can be seen that for comparable variants, the
determined parameters have stabler values than those obtained
processing all available data for alkyl radicals. However, a
little change of the γ_C. value must be admitted passing
from 0 K to 298 K. A more significant effect is observed re-
placing the iterative procedure by the isoentropic model .
The accuracy of description for the isoentropic model is to
some extent higher compared with the $\Delta H_R^{\neq}$. values obtained
by the iterative procedures. The procedure A) is just a
little preferable to the iteration B), if the values of s
and s_o are compared.

Consequently, the comparison of the results of the treat-
ment at 0 K and 298 K shows that the temperature effect on
the heats of formation is mainly expressed in the additive
terms of $\Delta H_{CH_3}^{\neq}$. but the parameters of interaction γ_C.
are compatible in the limits of uncertainties (see Tables
7 and 8).

Treatment of the $\Delta S_R^{\neq}$. values according to Eq (2) ,
where $\Delta S_{CH_3}^{\neq}$. , Q, and Y are to be determined, indicated a
lack of correlation for eight above mentioned alkyl
radicals when the data for the above cited non-isoentropic
variants were processed in separate sets. Collecting all
the $\Delta S_R^{\neq}$. values into united sets of the initial data for
eight or four (methyl, ethyl, i-propyl, and tert-butyl) radi-
cals, close final results are obtained. At that the scale of

p (the number of pairwise interactions) is excluded as statistically insignificant and other parameters have the following values:

$$\Delta S^{\neq}_{CH_3 \cdot} = 5.0 \pm 0.2 \quad \text{entr. un.}$$

$$Q = 0.59 \pm 0.08 \quad \text{entr. un.}$$

This observed correlation is characterized by the normalized standard deviation $s_o = 0.53$ and standard deviation $s = 0.42$ entr. un. This result differs essentially from that reported in Ref. 3 where $\Delta S^{\neq}_{CH_3 \cdot} = 3.2$ entr. un. and the term Yp, being proportional to the number of pairwise interactions between substituents $X \neq H$ in substituted methyl, was also significant. However, the substantial uncertainty of the activation entropy ($s_o = 0.53$) must be considered. Therefore both the entropy parameters (Y and Q) were henceforth examined as the parameters to be determined.

Proceeding from the mentioned results, the values of the respective variants in Ref. 1 served as those of $\Delta H^{\neq}_{CH_3 \cdot}$ and $\Delta S^{\neq}_{CH_3 \cdot}$, and $\mathcal{P}_C \cdot$ parameters were chosen from Table 3: 8:

Variant	$\Delta H^{\neq}_{CH_3 \cdot}$,kcal/mol	$\mathcal{P}_C \cdot$	$\Delta S^{\neq}_{CH_3 \cdot}$,entr. un.
1)	33.9	2.31	5.0
2)	33.7	2.31	4.8
3)	33.9	2.17	–
4)	31.9	2.43	4.9
5)	31.8	2.43	4.8
6)	32.0	2.27	–
7)	34.0	2.32	5.1
8)	34.1	2.33	5.4
9)	33.8	2.21	–

Next two equations are obtained proceeding from Eq (5), assuming zero values for the parameters $A_C \cdot, B_C \cdot$ and if the values of $\Delta H^{\neq}_{CH_3 \cdot}$ ($\Delta \Delta H^{\neq}_{CH_3 \cdot}$), $\Delta S^{\neq}_{CH_3 \cdot}$, and $\mathcal{P}_C \cdot$ are not to

be determined:

$$E + 2.3RT (\log n - \log A + 10.319 + \log T) + \Delta H^0_{X_1 X_2 X_3 C X_4} -$$

$$- \sum_i \Delta H^0_{X_i} + (\Delta S^{\neq}_{X_4 \cdot} + \Delta S^{\neq}_{CH_3 \cdot}) T/10^3 - \Delta H^{\neq}_{X_4 \cdot} - \Delta H^{\neq}_{CH_3 \cdot} -$$

$$- \gamma_{C \cdot} \sum_i \gamma_{X_i} = \left\{ \alpha^* \sigma^*_{C \cdot} \right\} \sum_i \sigma^*_{X_i} + \left\{ \alpha^* z^*_{C \cdot} \right\} \sum_i \sum_{i < j} \sigma^*_{X_i} \sigma^*_{X_j} +$$

$$+ \left\{ \psi_= \right\} N_= + \left\{ \psi_{CN} \right\} N_{CN} + \left\{ \psi_{NO_2} \right\} N_{NO_2} - \left\{ Q \right\} NT/10^3 -$$

$$- \left\{ Y \right\} p \ T/10^3 \tag{18}$$

$$E + 2.3RT (\log n - \log A + 10.319 + \log T) + I_{X_1 X_2 X_3 C X_4} +$$

$$+ A_C \sum_i \sum_{i < j} \gamma_{X_i} \gamma_{X_j} + B_C \gamma_{X_1} \gamma_{X_2} \gamma_{X_3} + (\Delta S^{\neq}_{X_4 \cdot} + \Delta S^{\neq}_{CH_3 \cdot}) T/10^3 -$$

$$- \Delta \Delta H^{\neq}_{X_4 \cdot} - \Delta \Delta H^{\neq}_{CH_3 \cdot} - (\gamma_{C \cdot} - \gamma_{CH_3}) \sum_i \gamma_{X_i} = \left\{ \alpha^* \sigma^*_{C \cdot} \right\} \sum_i \sigma^*_{X_i} +$$

$$+ \left\{ \alpha^* (z^*_{C \cdot} - z^*_C) \right\} \sum_i \sum_{i < j} \sigma^*_{X_i} \sigma^*_{X_j} + \left\{ \psi_= \right\} N + \left\{ \psi_{CN} \right\} N_{CN} + \left\{ \psi_{NO_2} \right\} N_{NO_2} -$$

$$- \left\{ Q \right\} NT/10^3 - \left\{ Y \right\} p \ T/10^3 \tag{19}$$

Results of the statistical treatment of data according to Eq (18) for the first six variants (from the above-men - tioned nine) are listed in Tables 9 and 10. Variants 7) -9) were processed by Eq (19) and the respective results are summarized in Table 11. One can see contradictory values of the parameters $\alpha^* \sigma^*_{C \cdot}$, $\alpha^* z^*_{C \cdot}$ or $\alpha^* (z^*_{C \cdot} - z^*_C)$, and ψ_{NO_2} for variants 1) - 2) (heats of formation at 0 K) on the one hand (unstable solutions) and for versions 3) - 9) on the other hand. At the same time the parameters $\alpha^* \sigma^*_{C \cdot}$ and ψ_{NO_2} for variants 1) and 2) become equal to zero after ex- cluding significantly deviating lines. It must be conside- red probably as a result of the "overpumping" between se-

parate scales. The values of the entropy parameters Q and Y remain unreliable. In versions 4) - 6) (heats of forma - tion at 298 K) both Q and Y have zero values, in variants 1) - 3) Y = 0 and Q $\neq$ 0 but in the case of versions 7) - 9), it is vice versa.

Taking into account the isoentropic cases for variants 3), 6), and 9), it is logical to use the following two equations instead of Eqs (18) and (19):

$$E + 2.3RT (\log n - \log A + 10.319 + \log T) + \Delta H^O_{X_1X_2X_3CX_4} -$$

$$- \sum_i \Delta H^O_{X_i^-} + \Delta S^{\neq}_{const} T/10^3 - \Delta H^{\neq}_{X_4.} - \Delta H^{\neq}_{CH_3.} - \gamma_{C} \cdot \sum_i \gamma_{X_i} =$$

$$= \left\{ \alpha^* \sigma^*_{C.} \right\} \sum_i \sigma^*_{X_i} + \left\{ \alpha^* z^*_{C.} \right\} \sum_{i<j} \sum \sigma^*_{X_i} \sigma^*_{X_j} + \left\{ \psi_= \right\} N_= +$$

$$+ \left\{ \psi_{CN} \right\} N_{CN} + \left\{ \psi_{NO_2} \right\} N_{NO_2} \tag{20}$$

$$E + 2.3RT (\log n - \log A + 10.319 + \log T) + I_{X_1X_2X_3CX_4} +$$

$$+ A_C \sum_{i<j} \sum \gamma_{X_i} \gamma_{X_j} + B_C \gamma_{X_1} \gamma_{X_2} \gamma_{X_3} + \Delta S^{\neq}_{const} T/10^3 - \Delta\Delta H^{\neq}_{X_4.} -$$

$$- \Delta\Delta H^{\neq}_{CH_3.} - (\gamma_{C.} - \gamma_{CH_3}) \sum_i \gamma_{X_i} = \left\{ \alpha^* \sigma^*_{C.} \right\} \sum_i \sigma^*_{X_i} +$$

$$+ \left\{ \alpha^* (z^*_{C.} - z^*_C) \right\} \sum_{i<j} \sum \sigma^*_{X_i} \sigma^*_{X_j} + \left\{ \psi_= \right\} N_= + \left\{ \psi_{CN} \right\} N_{CN} + \left\{ \psi_{NO_2} \right\} N_{NO_2}$$

$$\tag{21}$$

Assuming $\Delta S^{\neq}_{const} = 9.8$ entr. un. (see paper[1]), re - sults of the data treatment according to Eqs (20) and (21) reported in Table 12 are obtained. One can see that the accuracy of description and the values of parameters in Tables 12 and 9-11 differ slightly, and in the case of ver- sion 6) they even coincide because the treatment in the coordinates of Eq (18) leads to zero values of the entropy

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parameters.

In this study processing the data according to Eqs (5)-(13) and (18) - (21), an arithmetic mean T_{mean} of the lower and upper limits for each independent pair of expe - rimental log A and E values served as absolute temperature T. However, in the paper[3] two limited temperatures T_{min} and T_{max} were used for the ranges below 150 K and the values above each 100 K for a larger extent. By an analogous ap - proach, the results of the data treatment according to Eq (18) (Table 13) and Eq (19) (Table 14) for variants 1), 5), and 7) - 9) were obtained. Principal differences are not observed if these results are compared with those in Tables 9 - 11. Both the values of the parameters and the accuracy of description at comparable numbers of included reactions remain close except the more often observed zero values for the parameters $\alpha^* \sigma_C^*$, Q, and Y, if only T_{mean} are used . The entropy parameters Q and Y stay unstable and unreliable as before.

Using for every version of six (except the isoentropic model variants 3), 6), and 9)) own values of the parameters $\Delta H_{CH_3}^{\neq}$ or $\Delta \Delta H_{CH_3}^{\neq}$, φ_C , and $\Delta S_{CH_3}^{\neq}$ (see above), equations[3] for the iterative procedure, as well as Eqs(10)-(13) for alkanes, with the aim of determination of the pa - rameters in Eqs (18) and (19), could be derived. The follo- wing equation (the iteration begins from the experimental values of the activation energy) must be used for the data treatment according to variants 1) and 4):

$$E - RT + \Delta H_{X_1 X_2 X_3 C X_4}^o - \sum_i \Delta H_{X_i}^o - \Delta H_{X_4}^{\neq} - \Delta H_{CH_3}^{\neq} -$$

$$- \varphi_C \cdot \sum_i \varphi_{X_i} = \left\{ \alpha^* \sigma_C^* \right\} \sum_i \sigma_{X_i}^* + \left\{ \alpha^*_2 \sigma_C^* \right\} \sum_{i<j} \sum \sigma_{X_i}^* \sigma_{X_j}^* + \left\{ \psi_= \right\} N_= +$$

$$+ \left\{ \psi_{CN} \right\} N_{CN} + \left\{ \psi_{NO_2} \right\} N_{NO_2} \tag{22}$$

The zero approximations of the enthalpy parameters (in braces) may be obtained solving the system of Eqs (22)

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by MLRA. The solution of the next system of Eqs (23) leads to the zero approximations of the entropy parameters Q and Y:

$$2.3R\left[\log A - \log n - 10.753 - \log T + (F_{calc} + \sum_i \Delta H^o_{X_i} - \right.$$

$$- \Delta H^o_{X_1 X_2 X_3 CX_4} + RT - E + \Delta H^{\neq}_{X_4 \cdot} + \Delta H^{\neq}_{CH_3 \cdot} +$$

$$\left. + \gamma_C \cdot \sum_i \gamma_{X_i})/2.3RT\right] - \Delta S^{\neq}_{X_4 \cdot} - \Delta S^{\neq}_{CH_3 \cdot} = \left\{Q\right\} N + \left\{Y\right\} p$$

(23)

where $F_{calc} = \alpha^* \sigma^*_C \cdot \sum_i \sigma^*_{X_i} + \alpha^*_z \sigma^*_C \cdot \sum_{i<j} \sum \sigma^*_{X_i} \sigma^*_{X_j} + \psi_= N_= +$

$$+ \psi_{CN} N_{CN} + \psi_{NO_2} N_{NO_2} ,$$

using the values of the enthalpy parameters obtained in the previous cycle of MLRA. Further the first approximations of the enthalpy parameters can be obtained:

$$E + 2.3RT\left[10.753 + \log T + \log n - \log A + (\Delta S^{\neq}_{X_4 \cdot} + \right.$$

$$+ \Delta S^{\neq}_{CH_3 \cdot} + F_{calc})/2.3R - RT + \Delta H^o_{X_1 X_2 X_3 CX_4} - \sum_i \Delta H^o_{X_i} -$$

$$- \Delta H^{\neq}_{X_4 \cdot} - \Delta H^{\neq}_{CH_3 \cdot} - \gamma_C \cdot \sum_i \gamma_{X_i} = \left\{\alpha^* \sigma^*_C \cdot\right\} \sum_i \sigma^*_{X_i} +$$

$$+ \left\{\alpha^*_z \sigma^*_C \cdot\right\} \sum_{i<j} \sum \sigma^*_{X_i} \sigma^*_{X_j} + \left\{\psi_=\right\} N_= + \left\{\gamma_{CN}\right\} N_{CN} + \left\{\psi_{NO_2}\right\} N_{NO_2}$$

(24)

where $F_{calc} = QN + Yp$ at the values of Q and Y from the previous cycle of MLRA. Solving further in turn the systems of Eqs (23) and (24) the following approximations of the entropy and enthalpy parameters can be obtained.

In the case of variants 2) and 5) the first stage is the solution of the MLRA problem according to the following equation:

$$2.3R (\log A - \log n - 10.753 - \log T) - \Delta S^{\neq}_{X_4 \cdot} - \Delta S^{\neq}_{CH_3 \cdot} =$$

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$$= \left\{ Q \right\} N + \left\{ Y \right\} p \tag{25}$$

Further the solution of the systems of Eqs (24) and (23) is followed.

For variant 8) at first Eq (25) could also be used, but the next approximations of it and variant 7) demand the modifications of Eqs (22) - (24) as:

$$E - RT + I_{X_1 X_2 X_3 C X_4} + A_C \sum_{i < j} \sum \Upsilon_{X_i} \Upsilon_{X_j} + B_C \Upsilon_{X_1} \Upsilon_{X_2} \Upsilon_{X_3} -$$

$$- \Delta \Delta H^{\neq}_{X_4 \cdot} - \Delta \Delta H^{\neq}_{CH_3 \cdot} - (\Upsilon_{C \cdot} - \Upsilon_{CH_3}) \sum_i \Upsilon_{X_i} = \left\{ \alpha^* \sigma^*_{C \cdot} \right\} \sum_i \sigma^*_{X_i} +$$

$$+ \left\{ \alpha^* (z^*_{C \cdot} - z^*_C) \right\} \sum_{i < j} \sum \sigma^*_{X_i} \sigma^*_{X_j} + \left\{ \Psi_= \right\} N_= + \left\{ \Psi_{CN} \right\} N_{CN} +$$

$$+ \left\{ \Psi_{NO_2} \right\} N_{NO_2} \tag{26}$$

$$2.3R \left[\log A - \log n - 10.753 - \log T + (F_{calc} - \right.$$

$$- A_C \sum_{i < j} \sum \Upsilon_{X_i} \Upsilon_{X_j} - B_C \Upsilon_{X_1} \Upsilon_{X_2} \Upsilon_{X_3} + RT - E + \Delta \Delta H^{\neq}_{X_4 \cdot} +$$

$$+ \Delta \Delta H^{\neq}_{CH_3 \cdot} + (\Upsilon_{C \cdot} - \Upsilon_{CH_3}) \sum_i \Upsilon_{X_i}) / 2.3RT \left. \right] - \Delta S^{\neq}_{X_4 \cdot} -$$

$$- \Delta S^{\neq}_{CH_3 \cdot} = \left\{ Q \right\} N + \left\{ Y \right\} p \tag{27}$$

where $F_{calc} = \alpha^* \sigma^*_{C \cdot} \sum_i \sigma^*_{X_i} + \alpha^* (z^*_{C \cdot} - z^*_C) \sum_{i < j} \sum \sigma^*_{X_i} \sigma^*_{X_j} +$

$+ \Psi_= N_= + \Psi_{CN} N_{CN} + \Psi_{NO_2} N_{NO_2}$, and

$$E + 2.3RT \left[10.753 + \log T + \log n - \log A + (\Delta S^{\neq}_{X_4 \cdot} + \right.$$

$$+ \Delta S^{\neq}_{CH_3 \cdot} + F_{calc}) / 2.3R \left. \right] - RT + I_{X_1 X_2 X_3 C X_4} +$$

$$+ A_C \sum_{i<j} \sum Y_{X_i} Y_{X_j} + B_C Y_{X_1} Y_{X_2} Y_{X_3} - \Delta\Delta H^{\neq}_{X_4\cdot} - \Delta\Delta H^{\neq}_{CH_3\cdot} -$$

$$- (Y_{C\cdot} - Y_{CH_3}) \sum_i Y_{X_i} = \left\{ \propto^* \sigma^*_{C\cdot} \right\} \sum_i \sigma^*_{X_i} + \left\{ \propto^* (z^*_{C\cdot} - z^*_C) \right\} \sum_{i<j} \sum \sigma^*_{X_i} \sigma^*_{X_j} +$$

$$+ \left\{ \psi_= \right\} N_= + \left\{ \psi_{CN} \right\} N_{CN} + \left\{ \psi_{NO_2} \right\} N_{NO_2} \tag{28}$$

where $F_{calc} = QN + Yp$

    Using the above described iterative procedure within the framework of Eqs (22) – (28) the exclusion of lines was carried out analogously to this made in paper[1]. The values of the zero approximations for the enthalpy and entropy parameters were calculated after the exclusion of significantly deviating lines according to the Student's criterion on the risk level t = 0.01 (corresponds to the confidence level 0.99), the first order approximations on the risk level t = 0.02 etc, until the value t = 0.05 for the fourth approximations. Excluded lines were not reincluded after each cycle of MLRA.

    Results of the data treatment according to Eqs (22) – (28) for variants 1), 2), 4), 5), 7) and 8) indicate the significance of both the entropy parameters Q and Y in all the variants. These terms have opposite signs and their absolute values are decreasing during the exclusion of significantly deviating lines. The enthalpy parameters for versions 5), 7), and 8) have more or less stable values but for variants 1), 2), and 4) a significant instability of solution is observed. As an illustrative example of the iterative procedure the results for variant 7) are reported in Table 15.

    The comparison of the results of the simultaneous parametrization of the enthalpy and entropy terms by Eqs (18) and (19) (see Tables 9–11) with the above obtained results of the iterative procedure shows significant differences , between these approaches. The iteration leads in almost all the cases (except version 7)) to lower values of the stan –

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dard deviation s but at that an appreciably larger number
of lines and reactions are excluded. Thus, for variants 1),
2), and 4) the data for only 21-22 reactions from primarily
presented 66 remained valid at the end of the iterative pro-
cedure. The final accuracy of description for version 5) is
approximately similar (s = 1.66 kcal/mol, 1.88 entr.un.,and
1.61 kcal/mol, respectively) but using the same method for
the simultaneous parametrization, the number of included
reactions is larger by three and the total number of the
enthalpy and entropy parameters is smaller by two (the
values of entropy parameters became equal to zero). The re-
sult for version 7) of the simultaneous parametrization is
even more preferable: at the same number of parameters (5)
for the final results of the iteration s = 1.28 kcal/ mol
(58 reactions from 109 are included)and s = 1.21 entr. un.
(49 reactions are included)but in the case of the simultane-
ous parametrization s = 1.14 kcal/mol including 68 reactions
(see Tables 11 and 15). Consequently, application of the
iterative procedure with separate parametrization of the en-
thalpy and entropy terms does not lead to a more reliable
correlation of the substituent effects in kinetics of the
gas phase homolysis on compounds containing substituted me-
thyl radicals.

It is possible that the reason for this is a large un-
certainty (large values of s_o) for the dependence of the en-
tropy term on the number of non-hydrogen substituents (N)
and on the number of pairwise interactions (p) between them.
Therefore, an attempt was made for correlation of the entro-
py term by an even simpler model. In place of the correla -
tion of the activation entropy on N and p according to Eqs
(23) and (25) the arithmetic mean of the activation entropy
$\Delta S^{\neq}_{mean} = \sum \Delta S^{\neq}/NE$ is calculated, summing up the values
$\Delta S^{\neq} = \Delta S^{\neq}_{X_1X_2X_3C\cdot} + \Delta S^{\neq}_{X_4\cdot}$, where $\Delta S^{\neq}_{X_1X_2X_3C\cdot}$ and

$\Delta S^{\neq}_{X_4\cdot}$ are obtained in paper[1], and excluding significant-
ly deviating lines according to the Student's criterion.

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This modified iterative procedure with calculation of the $\Delta S_{mean}^{\neq}$ and the enthalpy parameters by Eq (24), where $F_{calc} = \Delta S_{mean}^{\neq}$, is carried out for variant 2). The results are listed in Table 16. When a satisfactory final accuracy of description ($s_0 = 0.081$, $s = 1.13$ kcal/mol), stability of solution and a small number of parameters are achieved, nevertheless, an excessively large number (35 from 66) of reactions is excluded. It is also seen from Table 16 that the $\Delta S_{mean}^{\neq}$ value at the end of the iteration (5.0 ± 1.1 entr.un.) significantly differs from 9.8 entr. un. assumed for the isoentropic model. However, the data set corresponding to Table 16 contains only the data for the polyfunc - tional alkanes. Inclusion of alkanes gives the value of $\Delta S_{mean}^{\neq} = 8.2 \pm 6.4$ entr. un. for 221 lines and after the exclusion of significantly deviating lines according to the Students criterion on the risk level 0.05, $\Delta S_{mean}^{\neq} = 11.0 \pm 2.6$ entr. un. for 143 lines. This result is not opposed to the effective average value of the activation entropy 9.8 entr. un. In addition to the above cited versions of the treatment the values of $\Delta H_R^{\neq}$ and $\Delta\Delta H_R^{\neq}$ for substituted methyl radicals from paper[1] were directly processed according to below reported modifications of Eq (1). For every variant among 1) - 6) four versions of the values to be correlated $F_1 - F_4$ were verified:

$$F_1 = \Delta H_{X_1 X_2 X_3 C\cdot}^{\neq} - \sum_i \Delta H_{X_i-}^o = \left\{\Delta H_{CH_3\cdot}^{\neq}\right\} + \left\{\varphi_{C\cdot}\right\}\sum_i \varphi_{X_i} + \left\{\propto^*\sigma_{C\cdot}^*\right\}\sum_i \sigma_{X_i}^* + \left\{\propto_z^*\sigma_{C\cdot}^*\right\}\sum_{i<j}\sum \sigma_{X_i}^* \sigma_{X_j}^* + \left\{\psi_=\right\} N_= + \left\{\psi_{CN}\right\} N_{CN} + \left\{\psi_{NO_2}\right\} N_{NO_2}$$

$$\tag{29}$$

$$F_2 = F_1 - \varphi_C \cdot \sum_i \varphi_{X_i} \tag{30}$$

$$F_3 = F_1 - \Delta H_{CH_3\cdot}^{\neq} \tag{31}$$

$$F_4 = F_1 - \Delta H^{\neq}_{CH_3\cdot} - \gamma_{C\cdot} \cdot \sum_i \gamma_{X_i} \tag{32}$$

For variants 7) - 9):

$$F_5 = \Delta\Delta H^{\neq}_{X_1 X_2 X_3 C\cdot} + A_C \sum_{i<j} \sum \gamma_{X_i} \gamma_{X_j} + B_C \gamma_{X_1} \gamma_{X_2} \gamma_{X_3} =$$

$$= \left\{\Delta\Delta H^{\neq}_{CH_3\cdot}\right\} + \left\{\gamma_{C\cdot} - \gamma_{CH_3}\right\} \sum_i \gamma_{X_i} + \left\{\alpha^* \sigma^*_{C\cdot}\right\} \sum_i \sigma^*_{X_i} +$$

$$+ \left\{\alpha^*(z^*_{C\cdot} - z^*_C)\right\} \sum_{i<j} \sum \sigma^*_{X_i} \sigma^*_{X_j} + \left\{\psi_=\right\} N_= + \left\{\psi_{CN}\right\} N_{CN} +$$

$$+ \left\{\psi_{NO_2}\right\} N_{NO_2} \tag{33}$$

$$F_6 = F_5 - (\gamma_{C\cdot} - \gamma_{CH_3}) \sum_i \gamma_{X_i} \tag{34}$$

$$F_7 = F_5 - \Delta\Delta H^{\neq}_{CH_3\cdot} \tag{35}$$

$$F_8 = F_5 - \Delta\Delta H^{\neq}_{CH_3\cdot} - (\gamma_{C\cdot} - \gamma_{CH_3}) \sum_i \gamma_{X_i} \tag{36}$$

Processing the values $F_2 - F_4$ and $F_6 - F_8$, $\gamma_{C\cdot}, \Delta H^{\neq}_{CH_3\cdot},$
$\gamma_{C\cdot} - \gamma_{CH_3}$ or $\Delta\Delta H^{\neq}_{CH_3\cdot}$ were naturally lacking among pa-
rameters to be determined depending on concrete forms of the
values correlated according to Eqs (30) - (32) and (34)-(36).
In addition to Eq (2), the values of the activation entro -
pies $\Delta S^{\neq}_{R\cdot}$ ($R\cdot$ belongs to the $X_1 X_2 X_3 C\cdot$ type), correspon-
ding to the values of $\Delta H^{\neq}_{R\cdot}$ and $\Delta\Delta H^{\neq}_{R\cdot}$ for variants 1),
2), 4), 5), 7) and 8), were processed likewise according to
five different versions:

$$\Delta S^{\neq}_{X_1 X_2 X_3 C\cdot} = \left\{\Delta S^{\neq}_{CH_3\cdot}\right\} + \left\{Q\right\} N \tag{37}$$

$$\Delta S^{\neq}_{X_1 X_2 X_3 C\cdot} = \left\{\Delta S^{\neq}_{CH_3\cdot}\right\} + \left\{Y\right\} p \tag{38}$$

$$\Delta S^{\neq}_{X_1X_2X_3C\cdot} - \Delta S^{\neq}_{CH_3\cdot} = \left\{Q\right\} N + \left\{Y\right\} p \tag{39}$$

$$\Delta S^{\neq}_{X_1X_2X_3C\cdot} - \Delta S^{\neq}_{CH_3\cdot} = \left\{Q\right\} N \tag{40}$$

$$\Delta S^{\neq}_{X_1X_2X_3C\cdot} - \Delta S^{\neq}_{CH_3\cdot} = \left\{Y\right\} p \tag{41}$$

where $\Delta S^{\neq}_{CH_3\cdot}$ on the left-hand side of Eqs (39) - (41) have
the values obtained in Ref. 1 for respective variants of
the treatment.

Let us discuss the results of the statistical treat -
ment according to Eqs (29) - (36). When the problems with
the intercept within the framework of Eqs (29), (30) and
(34) were solved , the values of the intercept generally
differed from those of $\Delta H^{\neq}_{CH_3\cdot}$ and $\Delta\Delta H^{\neq}_{CH_3\cdot}$ obtained in
paper[1] (maximum deviation is about 3 kcal/mole for variant
5)) but these declinations are within the range of the res-
pective standard deviations. In the case of the isoentropic
variant 9) only a precise coincidence with respective
$\Delta\Delta H^{\neq}_{CH_3\cdot} = 49.7$ kcal/mol is observed. That is why the use
of Eqs (31), (32), (35) and (36), where the values of
$\Delta H^{\neq}_{CH_3\cdot}$ and $\Delta\Delta H^{\neq}_{CH_3\cdot}$ are subtracted from the values to be
correlated F_1, is well-founded. The values of $\varphi_{C\cdot}$ and $\varphi_{C\cdot}$-
$\varphi_{CH_3\cdot}$ also in the limits of uncertainties are compatible
with the calculated above values of $\varphi_{C\cdot}$, based on the da-
ta for alkyl radicals. Therefore one can be limited only
to discussing the results of the statistical treatment of
the values processed according to Eqs (32) and (36). These
results are listed in Tables 17 - 19. As well as for pro -
cessing the data within the framework of Eqs (18) and (19)
in some variants (for the iterative procedure) zero values
for the parameters $\alpha^*\sigma^*_{C\cdot}$ and ψ_{NO_2} are obtained but in
other cases (for the isoentropic and only for the parameter
$\alpha^*\sigma^*_{C\cdot}$ also in variants 7) and 8)) these parameters are
statistically significant. In the reported variants of the
treatment a different number of radicals is excluded but

the accuracy of description is rising proportionally to the number of the excluded radicals. Therefore, the comparison of the accuracy of the description should be carried out according to the values of standard deviations s be - fore the exclusion of significantly deviating lines (radicals). One can see from Tables 17 - 19 that the data treatment according to Eq (36) leads to a higher accuracy of description compared with Eq (32), and the isoentropic model is more preferable than different versions of the iterative procedure. In the latter case besides the parameters for the enthalpies of radicals it is necessary to take into account the effects of substituents for the entropies processed by Eqs (2) and (37) - (41). A typical feature for all variants of the entropy processing for the substituted methyl radicals is a large uncertainty bordered on the lack of correlation. The results for versions 7) and 8) are listed in Table 20. MLRA with determination of intercept ac - cording to Eqs (2), (37) and (38) led in all the cases to the values of intercept remarkably differing from the re - spective $\Delta S_{CH_3}^{\neq}$ values in Ref. 1. However, a large uncertainty of the entropy parameters results also in the treatment without the intercept by Eqs (39) - (41). Thus , the values of standard deviation s before the exclusion of significantly deviating lines are similar in the ranges of 4.8 - 5.4 entr. un. . At that the results of the treatment according to Eq (40) for all six variants and for version 1) according to Eq (41) show the lack of correlation. Hence, the treatment in accordance with Eqs (2) and (29) - (36) gives evident advantage to the isoentropic model.

As a result one can conclude that the parametrization of the substituent effects for the substituted methyl radicals in the kinetics of the gas phase homolysis within the framework of the above-listed equations of the formal approach, using the technique of MLRA, does not lead to more reliable results in the case of the independent en - thalpies and entropies of activation compared with the isoentropic model. Moreover, within the reported variants

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of the treatment it is not obviously possible to prefer one
of the alternative versions of the calculated values of
$\Delta H_R^{\neq}.(\Delta \Delta H_R^{\neq}.)$ and the respective $\Delta S_R^{\neq}.$ proposed in paper[1].
Therefore, according to the isoentropic model the results
from Table 12 may be considered as conventionally recom -
mended values of parameters for substituted methyls. How -
ever, at the same time it is clear that actually one can
not deny the variance of the entropy term in free energy of
activation on the gas phase homolysis[3]. A further more ex-
act estimation of the substituent effects for substituted
methyls within formal approach lie evidently in modifica -
tion of the used models and in application of the nonlinear
least squares technique.

All calculations were performed on a computer "NORD 100"
by means of the parametrization program prepared by V.A.
Palm, making some modifications for input of the initial da-
ta.

Table   1

Results of the Data Treatment According to Eq (5) for Variant 1) (among Nine Versions Indicated in the Text)

 t   - the risk level when lines are excluded

 NE - the number of independent equations (lines)

 NRN - the number of different reactions (combinations of $X_1 X_2 X_3 C$ and X_4)

 s_o - normalized standard deviation

 s   - standard deviation in kcal/mol

The value of NRN and respective number of lines for each reaction is computed automatically by the program of MLRA only for initial and final sets of lines.

Parameters	All data			Without alkanes			Alkanes		
	Before exclusion of lines	t=0.01	t=0.05	Before exclusion of lines	t=0.01	t=0.05	Before exclusion of lines	t=0.01	t=0.05
1	2	3	4	5	6	7	8	9	10
$\gamma_C\cdot$	3.12	3.34	3.08	2.48	2.38	2.34	2.40	3.08	3.08
	$\pm$ 0.27	$\pm$0.12	$\pm$0.01	$\pm$0.33	$\pm$0.12	$\pm$0.07	$\pm$0.71	$\pm$0.06	$\pm$0.01
$\alpha^*\sigma_C^*\cdot$	- 0.10	-0.41	0	1.39	1.41	1.79	-	-	-
	$\pm$ 0.44	$\pm$0.12		$\pm$0.58	$\pm$0.23	$\pm$0.13			
$\alpha^*z_C^*\cdot$	0.65	0.67	0.67	0.47	0.46	0.44	-	-	-
	$\pm$ 0.10	$\pm$0.04	$\mp$0.01	$\pm$0.11	$\pm$0.03	$\pm$0.02			
$A_C\cdot$	0.07	0	0	0.10	0	0	0.25	0	0
	$\pm$ 0.09			$\pm$0.10			$\pm$0.23		

	1	2	3	4	5	6	7	8	9	10
$B_C.$		-0.03 ± 0.03	0	0	-0.02 ± 0.03	0	0	0.0002 ± 0.06	0	0
$\psi_=$		-11.1 ± 0.7	-12.5 ± 0.6	-12.1 ± 0.2	-7.8 ± 1.1	-7.0 ± 0.8	-4.5 ± 0.5	$-$	$-$	$-$
ψ_{CN}		-5.8 ± 1.9	-6.4 ± 1.4	-7.9 ± 0.3	-3.5 ± 1.9	-2.8 ± 1.2	-2.3 ± 0.6	$-$	$-$	$-$
ψ_{NO_2}		-5.2 ± 3.1	-4.7 ± 1.7	-9.2 ± 0.4	-4.7 ± 3.1	0	0	$-$	$-$	$-$
Q		0.19 ± 0.97	0	0	0.15 ± 1.21	0	0	-3.22 ± 2.46	0	0
Y		0.67 ± 0.96	1.32 ± 0.45	0	1.42 ± 1.23	0	0	4.39 ± 2.90	0	0
$\Delta H^{\neq}_{CH_3}.$		31.0 ± 4.1	31.4 ± 1.3	33.9 ± 0.1	29.5 ± 4.8	29.1 ± 1.5	27.7 ± 0.8	30.6 ± 12.5	31.2 ± 0.5	33.95 ± 0.09
NE		221	215	106	126	118	89	95	94	45
NRN		80		39	66		46	14	14	7
s_o		0.182	0.158	0.03	0.166	0.129	0.06	0.188	0.179	0.02
s		4.88	4.26	0.87	4.51	3.48	1.69	4.91	4.68	0.69

Table 2

Results of the Data Treatment for Alkanes by Eqs (6) and (8). The symbols are the same as in Table 1

Parameters	$\Delta H^o_{X_1X_2X_3CCX_4X_5X_6}$ at 0 K			$\Delta H^o_{X_1X_2X_3CCX_4X_5X_6}$ at 298 K					
	Eq (6)			Eq (6)			Eq (8)		
	Before exclusion of lines	t=0.01	t=0.05	Before exclusion of lines	t=0.01	t=0.05	Before exclusion of lines	t=0.01	t=0.05
	2	3	4	5	6	7	8	9	10
$2\,\Delta H^{\neq}_{CH_3}.$	67.0 ± 3.1	68.2 ± 0.9	70.1 ± 0.6	63.5 ± 3.1	64.1 ± 1.2	66.0 ± 0.7	63.5 ± 1.3	64.4 ± 0.9	66.3 ± 0.6
$\mathcal{P}_C.$	2.24 ± 0.20	2.13 ± 0.02	2.17 ± 0.01	2.31 ± 0.20	2.36 ± 0.07	2.44 ± 0.04	2.25 ± 0.03	2.23 ± 0.02	2.27 ± 0.01
$2\,\Delta S^{\neq}_{CH_3}.$	9.4 ± 1.5	9.9 ± 0.8	12.3 ± 0.5	9.5 ± 1.5	9.8 ± 0.8	12.3 ± 0.5	9.3 ± 1.2	9.8 ± 0.9	12.3 ± 0.5
Q	-0.12 ± 0.74	0	0	-0.30 ± 0.74	0	0	-	-	-
Y	+0.47 ± 0.37	0	0	0.55 ± 0.37	0.53 ± 0.26	0.71 ± 0.15	-	-	-

Table 2 continued

	1	2	3	4	5	6	7	8	9	10
NE		95	90	73	95	90	72	95	90	73
NRN		14		12	14		12	14		12
s_o		0.144	0.098	0.051	0.138	0.093	0.044	0.138	0.094	0.049
s		2.68	1.83	1.01	2.67	1.81	0.92	2.68	1.85	1.02

Table 3

Results of the Data Treatment for Alkanes by Eqs (7)
and (9). The symbols are the same as in Table 1

Parameters	Eq (7)			Eq (9)		
	Before ex-clusion of lines	t=0.01	t=0.05	Before ex-clusion of lines	t=0.01	t=0.05
$2 \Delta\Delta H^{\neq}_{CH_3}$.	98.7 ± 3.1	99.6 ± 1.2	101.9 ± 0.7	99.0 ± 1.3	100.0 ± 0.9	101.5 ± 0.5
γ_{C}. $- \gamma_{CH_3}$.	-1.64 ± 0.20	-1.62 ± 0.07	-1.55 ± 0.04	-1.76 ± 0.03	-1.78 ± 0.02	-1.74 ± 0.01
$2 \Delta S^{\neq}_{CH_3}$.	9.4 ± 1.5	9.8 ± 0.8	12.8 ± 0.5	9.4 ± 1.2	9.9 ± 0.9	12.1 ± 0.5
Q	-0.18 ± 0.74	0	0	-	-	-
Y	0.65 ± 0.37	0.66 ± 0.26	0.77 ± 0.14	-	-	-
NE	95	90	71	95	90	71
NRN	14		13	14		13
s_o	0.183	0.119	0.057	0.184	0.123	0.062
s	2.67	1.79	0.89	2.69	1.85	0.97

Table 4

Values of Enthalpy and Entropy Parameters Obtained
Resulting in the Iterative Procedure According   to
Eqs (10) – (13) for Alkanes.

Results for the fourth approximation are reported
($t = 0.05$). The first lines of NE, NRN, s_o and s va –
lues correspond to the enthalpy parameters, the second
lines to the entropy ones. Sequence numbers of variants
correspond to those nine listed in the text.

The symbols are the same as in Table 1.

Parameters	Variants					
	1)	2)	4)	5)	7)	8)
$2\Delta H^{\neq}_{CH_3\cdot}$ or $2\,\Delta\Delta H^{\neq}_{CH_3\cdot}$	68.7 ± 0.1	68.3 ± 0.1	65.0 ± 0.1	64.4 ± 0.1	100.5 ± 0.1	99.9 ± 0.1
$\gamma_{C\cdot}$ or $\gamma_{C\cdot} - \gamma_{CH_3}$	2.25 ± 0.01	2.24 ± 0.01	2.36 ± 0.01	2.36 ± 0.01	−1.66 ± 0.01	−1.66 ± 0.01
$2\,\Delta S^{\neq}_{CH_3\cdot}$	11.2 ± 0.1	10.5 ± 0.1	11.0 ± 0.1	10.4 ± 0.1	11.4 ± 0.4	10.3 ± 0.09
Q	0	0	0	0	−0.52 ± 0.13	0
Y	0.40 ± 0.05	0.42 ± 0.04	0.46 ± 0.04	0.48 ± 0.04	0.90 ± 0.12	0.49 ± 0.04
NE	63	53	61	56	58	51
	62	67	58	63	58	65
NRN	12	11	12	12	13	11
	12	11	12	12	13	13
s_o	0.043	0.029	0.038	0.030	0.046	0.036
	0.668	0.651	0.566	0.563	0.560	0.562
s	0.87	0.61	0.82	0.64	0.70	0.54
	0.82	0.84	0.73	0.75	0.69	0.76

Table 5

Results of the Data Treatment According to Eq (14) for Alkyl Radicals. The sequence
numbers 1) - 9) correspond to those listed in the text. The symbols are the same as
in Table 1

Parameters	Variants											
	1)	2)	3)	4)	5)	6)	7)*	8)*	9)*	7)**	8)**	9)**
$\Delta H^{\neq}_{CH_3\cdot}$	34.6 ± 0.6	32.7 ± 1.2	33.5 ± 0.5	32.6 ± 0.8	31.8 ± 1.5	32.0 ± 0.2	35.0 ± 0.5	35.1 ± 0.5	33.7 ± 0.4	33.2 ± 0.5	33.2 ± 0.5	31.9 ± 0.5
$\gamma_{C\cdot}$	2.18 ± 0.08	2.33 $+ -0.16$	2.19 ± 0.07	2.26 ± 0.11	2.25 ± 0.20	2.41 ± 0.08	2.21 ± 0.08	2.20 ± 0.07	2.42 ± 0.15	2.30 ± 0.08	2.28 ± 0.07	2.43 ± 0.17
$A_{C\cdot}$	0	0	0	0	0	-0.08 ± 0.03	0	0	-0.21 ± 0.06	0	0	-0.10 ± 0.02
$B_{C\cdot}$	0	0	0	0	0	0.03 ± 0.02	0	0	0.11 ± 0.03	0	0	0.04 ± 0.03
NE	8	8	8	8	8	8	9	8	8	9	8	9
s_o	0.11	0.19	0.09	0.13	0.25	0.03	0.10	0.09	0.05	0.10	0.08	0.06
s	0.90	1.64	0.75	1.14	2.17	0.24	0.85	0.75	0.44	0.86	0.73	0.50

* From $\Delta\Delta H^{\neq}_R\cdot$. values recalculated $\Delta H^{\neq}_R\cdot$. values at 0 K

** The same at 298 K

Table 6

Results of the Data Treatment by Eq (15) for Alkyl
Radicals. For comments see the previous Table

Parameters	Variants					
	1)	2)	3)	4)	5)	6)
γ_C·	2.27 $\pm$0.05	2.19 $\pm$0.08	2.13 $\pm$0.04	2.34 $\pm$0.06	2.25 $\pm$0.10	2.41 $\pm$0.05
A_C·	0	0	0	0	0	-0.08 ± 0.03
B_C·	0	0	0	0	0	0.03 ± 0.01
NE	7	7	7	7	7	7
s_o	0.16	0.24	0.12	0.18	0.31	0.04
s	0.99	1.78	0.79	1.21	2.17	0.24

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Table 7

Results of the Data Treatment by Eq (16) for Methyl, Ethyl, Isopropyl and tert-Butyl. For comments see Table 5

Parameters	Variants											
	1)	2)	3)	4)	5)	6)	7)[I]	8)[I]	9)[I]	7)[II]	8)[II]	9)[L]
$\Delta H^{\neq}_{CH_3}$.	34.3 ± 0.7	33.8 ± 0.9	34.2 ± 0.3	32.5 ± 0.8	32.1 ± 0.6	32.3 ± 0.4	34.3 ± 0.7	34.4 ± 0.7	34.3 ± 0.5	32.4 ± 0.7	32.5 ± 0.6	32.3 ± 0.5
φ_C.	2.26 ± 0.10	2.33 ± 0.12	2.14 ± 0.05	2.36 ± 0.11	2.40 ± 0.09	2.23 ± 0.05	2.29 ± 0.10	2.29 ± 0.09	2.16 ± 0.07	2.35 ± 0.09	2.36 ± 0.08	2.23 ± 0.06
NE	4	4	4	4	4	4	4	4	4	4	4	4
s_0	0.09	0.11	0.04	0.09	0.07	0.04	0.08	0.08	0.07	0.08	0.07	0.06
s	0.88	1.10	0.42	0.98	0.78	0.44	0.85	0.81	0.66	0.82	0.74	0.55

Table 8

Results of the Data Treatment by Eq (17) for Ethyl, Isopropyl and tert-Butyl.
For Comments see Table 5

Parameters	Variants											
	1)	2)	3)	4)	5)	6)	7)[x]	8)[x]	9)[x]	7)[xx]	8)[xx]	9)[xx]
$\gamma_c \cdot$	2.31 ±0.06	2.31 ±0.07	2.17 ±0.03	2.43 ±0.07	2.43 ±0.05	2.27 ±0.04	2.32 ±0.06	2.33 ±0.06	2.21 ±0.05	2.38 ±0.06	2.39 ±0.05	2.27 ±0.04
NE	3	3	3	3	3	3	3	3	3	3	3	3
s_o	0.14	0.15	0.07	0.16	0.11	0.08	0.12	0.12	0.12	0.11	0.10	0.10
s	0.95	1.10	0.49	1.10	0.81	0.53	0.89	0.86	0.78	0.84	0.77	0.65

Table 9

Results of the Data Treatment According to Eq (18) for Variants 1) - 3). The symbols are the same as in Table 1

Parameters	Variants								
	1)			2)			3)		
	Before exclusion of lines	t=0.01	t=0.05	Before exclusion of lines	t=0.01	t=0.05	Before exclusion of lines	t=0.01	t=0.05
1	2	3	4	5	6	7	8	9	10
$\alpha^* \sigma^*_{C\cdot}$	0.99 ±0.18	0.24 ±0.12	0	1.00 ±0.18	0	0	1.41 ±0.19	1.47 ±0.13	1.48 ±0.09
$\alpha^* z^*_{C\cdot}$	0.56 ±0.05	0.66 ±0.03	0.72 ±0.01	0.56 ±0.05	0.71 ±0.02	0.73 ±0.01	0.52 ±0.05	0.51 ±0.03	0.54 ±0.02
$\psi_=$	-9.5 ±0.8	-11.9 ±0.6	-10.2 ±0.24	-9.5 ±0.8	-11.5 ±0.4	-10.2 ±0.2	-8.6 ±0.9	-10.7 ±0.6	-11.6 ±0.4
ψ_{CN}	-3.7 ±1.6	-5.2 ±1.0	-3.0 ±0.5	-3.7 ±1.6	-4.1 ±1.1	-3.0 ±0.5	-4.6 ±1.7	-7.7 ±1.0	-8.4 ±0.6
ψ_{NO_2}	-3.0 ±1.8	0	0	-2.6 ±1.8	0	0	-4.0 ±1.9	-5.8 ±1.2	-7.3 ±0.8

Table 9 continued

1	2	3	4	5	6	7	8	9	10
Q	1.17 ± 0.71	-1.70 ± 0.51	-0.65 ± 0.11	1.19 ± 0.71	-1.04 ± 0.21	-0.64 ± 0.11	0.81 ± 0.74	-0.80 ± 0.39	-1.12 ± 0.25
Y	-0.68 ± 0.70	1.33 ± 0.49	0	-0.68 ± 0.70	0	0	-0.37 ± 0.73	0	0
NE	126	111	78	126	116	79	126	112	89
NRN	66		41	66		42	66		46
s_o	0.306	0.189	0.094	0.304	0.221	0.094	0.309	0.187	0.113
s	4.60	2.76	1.34	4.62	3.24	1.34	4.82	2.99	1.83

Table 10

Results of the Data Treatment According to Eq (18) for Variants 4) – 6). The symbols are the same as in Table 1

Parameters	Variants								
	4)			5)			6)		
	Before exclusion of lines	t=0.01	t=0.05	Before exclusion of lines	t=0.01	t=0.05	Before exclusion of lines	t=0.01	t=0.05
1	2	3	4	5	6	7	8	9	10
$\alpha^{\pi}_{G_C^{\pi}}$	1.04 ±0.19	1.36 ±0.07	1.43 ±0.05	1.04 ±0.19	1.36 ±0.07	1.43 ±0.05	1.47 ±0.20	1.87 ±0.07	1.71 ±0.05
$\alpha^{\pi}_{z_C^{\pi}}$	0.53 ±0.05	0.48 ±0.03	0.51 ±0.02	0.53 ±0.05	0.48 ±0.03	0.51 ±0.02	0.49 ±0.05	0.43 ±0.03	0.48 ±0.02
$\psi_=$	-9.3 ±0.9	-10.2 ±0.3	-9.8 ±0.2	-9.3 ±0.9	-10.2 ±0.3	-9.8 ±0.2	-8.5 ±0.9	-9.3 ±0.3	-8.1 ±0.2
ψ_{CN}	-3.9 ±1.7	-6.8 ±0.9	-7.3 ±0.5	-3.9 ±1.7	-6.8 ±0.8	-7.0 ±0.5	-4.7 ±1.8	-7.3 ±0.8	-7.1 ±0.5
ψ_{NO_2}	-4.3 ±1.9	-6.9 ±1.1	-7.7 ±0.7	-4.0 ±1.9	-6.6 ±1.0	-7.4 ±0.7	-5.0 ±2.0	-7.7 ±1.1	-7.0 ±0.7

Table 10 continued

	1	2	3	4	5	6	7	8	9	10
Q		0.94 ± 0.74	0	0	0.96 ± 0.74	0	0	0.51 ± 0.77	0	0
Y		-0.20 ± 0.74	0	0	-0.20 ± 0.74	0	0	0.11 ± 0.76	0	0
NE		126	110	86	126	108	87	126	108	82
NRN		66		46	66		47	66		43
s_o		0.338	0.187	0.117	0.337	0.175	0.119	0.335	0.171	0.106
s		4.85	2.72	1.64	4.86	2.57	1.66	5.04	2.65	1.51

Table 11

Results of the Data Treatment Using Eq (19). The symbols are the same as in Table 1

Parameters	Variants								
	7)			8)			9)		
	Before exclusion of lines	t=0.01	t=0.01	Before exclusion of lines	t=0.01	t=0.05	Before exclusion of lines	t=0.01	t=0.05
1	2	3	4	5	6	7	8	9	10
$\alpha^* \sigma_{C^*}^*$	1.29 ±0.15	1.44 ±0.08	1.45 ±0.04	1.29 ±0.14	1.45 ±0.08	1.49 ±0.04	1.54 ±0.15	1.40 ±0.09	1.44 ±0.04
$\alpha^*(z_{C^*}^* - z_C^*)$	0.008 ±0.044	0	0	0.006 ±0.044	0	0	-0.020 ±0.045	0	0
$\psi_=$	-8.4 ±0.6	-9.7 ±0.3	-9.1 ±0.1	-8.6 ±0.6	-9.6 ±0.3	-8.9 ±0.1	-7.8 ±0.6	-9.7 ±0.5	-9.2 ±0.2
ψ_{CN}	-4.1 ±1.6	-5.1 ±0.9	-4.9 ±0.5	-4.1 ±1.6	-5.1 ±0.9	-4.9 ±0.5	-4.5 ±1.6	-5.2 ±1.0	-4.9 ±0.4
ψ_{NO_2}	-2.6 ±1.6	-3.6 ±0.8	-3.4 ±0.5	-1.8 ±1.5	-2.9 ±0.8	-3.1 ±0.5	-4.1 ±1.6	-3.4 ±0.9	-3.8 ±0.4

Table 11 continued

	1	2	3	4	5	6	7	8	9	10
Q		1.17 ± 0.48	0	0	1.06 ± 0.47	0	0	0.88 ± 0.49	-0.80 ± 0.36	-0.56 ± 0.15
Y		-0.58 ± 0.55	0.89 ± 0.21	0.78 ± 0.11	-0.47 ± 0.54	0.89 ± 0.21	0.81 ± 0.11	-0.44 ± 0.56	1.34 ± 0.41	0.99 ± 0.17
NE	158	144	99	158	145	103	158	146		86
NRN	109		68	109			71	109		57
s_o		0.427	0.266	0.130	0.413	0.258	0.131	0.429	0.285	0.110
s		4.36	2.62	1.14	4.30	2.60	1.20	4.47	2.79	0.92

Table 12

Results of the Data Treatment, Eqs (20) and (21) Using $\Delta S^{\neq}_{const} = 9.8$ entr. un. . For versions 3) and 6) $\gamma = \alpha^{\neq} z^{\neq}_{C\cdot}$, in variant 9) $\gamma = \alpha^{\neq}(z^{\neq}_{C\cdot} - z^{\neq}_{C})$. The symbols are the same as in Table 1

Parameters	Variants								
	3) (Eq. (20))			6) (Eq. (20))			9) (Eq. (21))		
	Before exclusion of lines	t=0.01	t=0.05	Before exclusion of lines	t=0.01	t=0.05	Before exclusion of lines	t=0.01	t=0.05
1	2	3	4	5	6	7	8	9	10
$\alpha^{\neq} \sigma^{\neq}_C\cdot$	1.28 ±0.09	1.67 ±0.08	1.73 ±0.05	1.29 ±0.10	1.86 ±0.07	1.71 ±0.05	1.36 ±0.09	1.27 ±0.06	1.55 ±0.03
γ	0.54 ±0.05	0.48 ±0.03	0.51 ±0.02	0.51 ±0.05	0.43 ±0.03	0.48 ±0.02	0.005 ±0.04	0	0
$\psi_=$	-9.4 ±0.51	-9.8 ±0.4	-8.9 ±0.2	-9.0 ±0.5	-9.3 ±0.3	-8.1 ±0.2	-8.7 ±0.4	-8.8 ±0.3	-8.7 ±0.1
ψ_{CN}	-5.4 ±1.5	-6.8 ±1.0	-7.4 ±0.5	-5.2 ±1.5	-7.2 ±0.9	-7.1 ±0.5	-5.2 ±1.6	-4.8 ±1.0	-4.8 ±0.5
ψ_{NO_2}	-3.9 ±1.9	-5.9 ±1.2	-6.9 ±0.7	-4.7 ±2.0	-7.7 ±1.1	-7.0 ±0.7	-3.8 ±1.6	-2.7 ±0.8	-4.6 ±0.4

	1	2	3	4	5	6	7	8	9	10
NE		126	113	83	126	109	82	158	146	84
NRN		66		42	66		43	109		55
s_o		0.308	0.195	0.099	0.333	0.176	0.106	0.432	0.296	0.102
s		4.80	3.11	1.54	5.02	2.72	1.51	4.50	2.87	0.93

Table 13

Results of the Data Treatment According to Eq (18)
Comprising the whole Examined Temperature Range over
Each 100 K. The symbols are the same as in Table 1

Parameters	Variants					
	1)			5)		
	Before exclusion of lines	t=0.01	t=0.05	Before exclusion of lines	t=0.01	t=0.05
$\alpha^{\pi} \sigma_C^{\pi}$	1.06 ±0.11	0.27 ±0.07	0.19 ±0.06	1.17 ±0.12	1.37 ±0.06	1.46 ±0.05
$\alpha^{\pi} z_C^{\pi}$	0.56 ±0.03	0.67 ±0.02	0.69 ±0.01	0.52 ±0.03	0.50 ±0.02	0.51 ±0.01
$\psi_{=}$	-9.8 ±0.5	-12.1 ±0.3	-11.9 ±0.2	-9.4 ±0.5	-11.7 ±0.3	-11.6 ±0.2
ψ_{CN}	-2.9 ±1.0	-4.8 ±0.6	-4.5 ±0.4	-3.0 ±1.1	-7.9 ±0.5	-8.5 ±0.4
ψ_{NO_2}	-3.1 ±1.3	0	0	-4.3 ±1.4	-7.2 ±0.6	-8.2 ±0.5
Q	1.34 ±0.40	-1.51 ±0.26	-1.47 ±0.20	1.28 ±0.43	-1.11 ±0.24	-1.15 ±0.19
Y	-0.50 ±0.41	1.17 ±0.26	1.07 ±0.19	-0.04 ±0.44	1.02 ±0.25	0.86 ±0.20
NE	344	295	254	344	284	248
NRN	66		49	66		47
s_0	0.300	0.173	0.127	0.338	0.151	0.118
s	4.54	2.50	1.81	4.93	2.26	1.71

Table 14

Results of the Data Treatment According to Eq (19) Comprising the whole Examined Temperature Range over Each 100 K. The symbols are the same as in Table 1

Parameters	Variants								
	7)			8)			9)		
	Before exclusion of lines	t=0.01	t=0.05	Before exclusion of lines	t=0.01	t=0.05	Before exclusion of lines	t=0.01	t=0.05
1	2	3	4	5	6	7	8	9	10
$\alpha^* \sigma_C^*.$	1.32 ±0.09	1.37 ±0.05	1.45 ±0.02	1.33 ±0.09	1.41 ±0.05	1.52 ±0.02	1.54 ±0.09	1.39 ±0.05	1.45 ±0.03
$\alpha^*(z_C^*. - z_C^*)$	0.007 ±0.029	0	0	0.006 ±0.028	0	0	-0.014 ±0.028	0	0
$\psi_=$	-8.8 ±0.4	-10.4 ±0.2	-8.9 ±0.1	-8.9 ±0.4	-10.1 ±0.2	-8.3 ±0.1	-8.1 ±0.4	-9.9 ±0.2	-8.9 ±0.1
ψ_{CN}	-3.7 ±1.0	-5.1 ±0.5	-4.5 ±0.3	-3.7 ±1.0	-5.0 ±0.6	-5.1 ±0.3	-4.1 ±1.0	-4.9 ±0.6	-4.7 ±0.3
ψ_{NO_2}	-2.7 ±1.1	-2.9 ±0.5	0	-2.0 ±1.1	-2.6 ±0.5	-3.0 ±0.3	-4.1 ±1.1	-3.3 ±0.5	-3.6 ±0.3

Table 14 continued

1	2	3	4	5	6	7	8	9	10
Q	1.18 $\pm$0.28	-0.49 $\pm$0.17	0	1.06 $\pm$0.28	-0.43 $\pm$0.18	0.33 $\pm$0.09	0.80 $\pm$0.28	-0.75 $\pm$0.19	-0.36 $\pm$0.10
Y	-0.47 $\pm$0.32	1.33 $\pm$0.20	0.82 $\pm$0.06	-0.34 $\pm$0.32	1.30 $\pm$0.21	0.52 $\pm$0.10	-0.25 $\pm$0.32	1.28 $\pm$0.22	0.76 $\pm$0.11
NE	431	382	246	431	390	253	431	391	253
NRN	109		63	109		65	109		67
s_o	0.421	0.239	0.119	0.410	0.246	0.117	0.411	0.263	0.131
s	4.36	2.36	0.99	4.31	2.49	1.02	4.30	2.61	1.08

Table 15

Values of Enthalpy and Entropy Parameters of the Iterative Procedure Using Eqs (26)-(28) for Version 7). The symbols are the same as in Table 1

Parameters	Zero approximation					Fourth approximation			
	Before exclusion of lines	t=0.001	t=0.01	t=0.001	t=0.01	t=0.01	t=0.05	t=0.01	t=0.05
1	2	3	4	5	6	7	8	9	10
$\alpha^{\#} G_C^{\#}.$	1.26 ± 0.11	1.24 ± 0.07	1.25 ± 0.06	–	–	1.14 ± 0.03	1.13 ± 0.03	–	–
$\alpha^{\#}(z_C^{\#}. - z_C^{\#})$	0.005 ± 0.051	0	0	–	–	0	0	–	–
$\psi_=$	-12.2 ± 0.5	-12.8 ± 0.4	-12.8 ± 0.4	–	–	-11.4 ± 0.2	-10.8 ± 0.2	–	–
ψ_{CN}	-10.7 ± 1.9	-10.6 ± 1.7	-10.6 ± 1.6	–	–	-5.9 ± 0.6	-5.9 ± 0.5	–	–
ψ_{NO_2}	-6.9 ± 1.9	0	0	–	–	0	0	–	–

Table 15 continued

1	2	3	4	5	6	7	8	9	10
Q	–	–	–	-2.39 ±0.39	-2.23 ±0.29	–	–	-1.38 ±0.15	-1.31 ±0.11
Y	–	–	–	3.62 ±0.54	3.11 ±0.40	–	–	2.12 ±0.23	1.83 ±0.18
NE	158	156	154	152	138	99	87	87	76
NRN	109		105		91		58	58	49
s_o	0.426	0.369	0.350	0.884	0.857	0.165	0.137	0.766	0.821
s	5.35	4.65	4.42	5.33	3.88	1.58	1.28	1.61	1.21

Table 16

Values of the Mean Activation Entropy $\Delta S_{mean}^{\neq} = \left[\sum(\Delta S_{X_1 X_2 X_3 C\cdot}^{\neq} + \Delta S_{X_4\cdot}^{\neq})\right]/NE$ and Enthalpy Parameters of Iterative Procedure According to Eq (24), where $F_{calc} = \Delta S_{mean}^{\neq}$, for Variant 2). The symbols are the same as in Table 1

Parameters	Approximation						
	0			1	2	3	4
	Before exclusion of lines	t=0.001	t=0.01	t=0.02	t=0.03	t=0.04	t=0.05
$\Delta S_{mean}^{\neq}$	6.3 ± 6.7	6.3 ± 6.7	6.3 ± 6.7	5.5 ± 3.9	6.0 ± 3.1	5.0 ± 1.3	5.0 ± 1.1
NE	126	126	126	107	97	62	58
NRN	66	66	66	55	49	32	31
$\alpha^* \sigma_{C\cdot}^*$	1.34 ± 0.09	1.31 ± 0.09	1.34 ± 0.08	1.22 ± 0.07	1.17 ± 0.08	1.25 ± 0.07	1.24 ± 0.07
$\alpha^* z_{C\cdot}^\pi$	0.51 ± 0.05	0.48 ± 0.03	0.47 ± 0.03	0.52 ± 0.02	0.53 ± 0.03	0.52 ± 0.02	0.52 ± 0.02
ψ_a	-6.1 ± 0.5	-6.1 ± 0.5	-6.0 ± 0.5	-5.3 ± 0.3	-4.7 ± 0.3	-5.0 ± 0.2	-5.1 ± 0.2

Table 16 continued

Parameters	Approximation						
	0			1	2	3	4
	Before exclusion of lines	t=0.001	t=0.01	t=0.02	t=0.03	t=0.04	t=0.05
ψ_{CN}	-1.5 ± 1.4	0	0	0	0	0	0
ψ_{NO_2}	-2.1 ± 1.8	0	0	0	0	0	0
NE	126	126	123	101	97	60	57
NRN	66	66	63	52	49	31	31
s_0	0.321	0.320	0.297	0.197	0.194	0.090	0.081
s	4.62	4.61	4.28	2.64	2.52	1.22	1.13

Table 17

Result of the Treatment Processing Values, Obtained by
the Iterative Procedure, According to Eq (32).   The
symbols are the same as in Table 1

Parameters	Var. 1)			Var. 2)		
	Before exclusion of lines	t=0.01	t=0.05	Before exclusion of lines	t=0.01	t=0.05
$\alpha^{\ast}\,\sigma_C^{\ast}$.	1.07 $\pm$0.25	0	0	1.01 $\pm$0.25	0	0
$\alpha^{\ast}z\,\sigma_C^{\ast}$.	0.53 $\pm$0.06	0.68 $^+$0.03	0.76 $^+$0.01	0.54 $\pm$0.06	0.76 $\pm$0.02	0.75 $\pm$0.02
$\psi_=$	-13.6 $\pm$1.5	-11.7 $\pm$1.1	-12.4 $\pm$0.4	-12.8 $\pm$1.5	-12.0 $\pm$1.1	-11.1 $\pm$0.8
ψ_{CN}	-11.0 $\pm$2.7	-7.3 $\pm$1.8	-7.3 $\pm$1.8	-10.6 $^+$2.7	-7.0 $\pm$1.9	-7.0 $\pm$1.4
ψ_{NO_2}	-1.7 $\pm$2.3	3.8 $\pm$1.3	1.1 $\pm$0.5	-6.5 $\pm$2.3	0	0
NRN	46	43	30	45	42	38
s_o	0.256	0.180	0.06	0.251	0.185	0.137
s	4.42	3.09	0.97	4.36	3.23	2.40

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Table 17 continued

Parameters	Var. 4)			Var. 5)		
	Before exclusion of lines	t=0.01	t=0.05	Before exclusion of lines	t=0.01	t=0.05
$\alpha^{\pi}_{C} \sigma^{\pi}_{C'}$	0.99 ±0.27	0.87 ±0.22	0	0.97 ±0.26	0.89 ±0.21	0
$\alpha^{\pi}_{C} z^{\pi}_{C'}$	0.46 ±0.07	0.45 ±0.06	0.63 ±0.01	0.46 ±0.06	0.46 ±0.06	0.64 ±0.01
$\psi_{=}$	-13.4 ±1.6	-13.3 ±1.6	-12.1 ±0.4	-12.8 ±1.5	-12.7 ±1.5	-12.2 ±0.5
ψ_{CN}	-10.9 ±2.9	-10.5 ±2.8	-7.4 ±0.6	-10.6 ±2.8	-10.4 ±2.7	-7.3 ±0.7
ψ_{NO_2}	-1.8 ±2.4	0	0	1.3 ±2.4	0	0
NRN	46	46	30	46	46	28
s_0	0.298	0.296	0.074	0.292	0.290	0.078
s	4.70	4.67	1.08	4.60	4.56	1.17

Table 18

Results of the Treatment Processing Values, within the
Isoentropic Model, According to Eq (32). The symbols
are the same as in Table 1 except NRN - the number of
radicals

Parameters	Var. 3)			Var. 6)		
	Before exclusion of lines	t=0.01	t=0.05	Before exclusion of lines	t=0.01	t=0.05
$\alpha^{\ast}\sigma_C^{\ast}$.	2.11 ± 0.20	2.11 ± 0.20	2.03 ± 0.16	2.08 ± 0.18	2.00 ± 0.17	1.98 ± 0.14
$\alpha^{\ast} z_C^{\ast}$.	0.42 ± 0.05	0.42 ± 0.05	0.43 ± 0.04	0.35 ± 0.04	0.36 ± 0.04	0.36 ± 0.03
$\psi_=$	-11.7 ± 1.2	-11.7 ± 1.2	-11.6 ± 0.9	-11.4 ± 1.1	-11.3 ± 1.0	-10.3 ± 0.9
ψ_{CN}	-8.6 ± 2.1	-8.6 ± 2.1	-8.3 ± 1.7	-8.5 ± 1.9	-8.2 ± 1.8	-8.2 ± 1.5
ψ_{NO_2}	-8.1 ± 1.8	-8.1 ± 1.8	-8.3 ± 1.8	-7.9 ± 1.6	-7.5 ± 1.5	-8.1 ± 1.3
NRN	46	46	43	46	45	43
s_o	0.206	0.206	0.163	0.209	0.189	0.162
s	3.45	3.45	2.71	3.17	2.89	2.42

Table 19

Results of the Treatment Processing Values According to Eq (36). The symbols are the same as in Table 1 except NRN - the number of radicals

Parameters	Var. 7)			Var. 8)			Var. 9)		
	Before exclusion of lines	t=0.01	t=0.05	Before exclusion of lines	t=0.01	t=0.05	Before exclusion of lines	t=0.01	t=0.05
1	2	3	4	5	6	7	8	9	10
$\alpha^{\pi}\sigma_C^{\pi}.$	0.84 ±0.17	1.14 ±0.06	1.37 ±0.03	0.75 ±0.19	1.15 ±0.07	1.29 ±0.05	1.45 ±0.15	1.33 ±0.11	1.32 ±0.10
$\alpha^{\pi}(z_C^{\pi}.-z_C^{\pi})$	0.05 ±0.04	0	0	0.06 ±0.05	0	0	-0.01 ±0.04	0	0
$\psi_=$	-12.3 ±0.9	-12.6 ±0.8	-13.0 ±0.4	-13.0 ±1.0	-12.7 ±0.9	-13.6 ±0.7	-10.3 ±0.8	-10.2 ±0.7	-9.8 ±0.6
ψ_{CN}	-11.1 ±1.9	-12.1 ±1.7	-8.5 ±1.0	-10.7 ±2.1	-12.2 ±1.9	-10.4 ±1.4	-5.3 ±1.7	-5.0 ±1.4	-5.0 ±1.3
ψ_{NO_2}	2.0 ±1.5	0	0	2.8 ±1.7	0	0	-4.1 ±1.4	-3.4 ±1.2	-3.3 ±1.1

Table 19 continued

1	2	3	4	5	6	7	8	9	10
NRN	73	72	48	73	71	57	73	71	68
s_0	0.355	0.341	0.143	0.379	0.363	0.238	0.383	0.333	0.311
s	3.55	3.40	1.44	3.97	3.68	2.36	3.16	2.72	2.51

Table 20

Values of Entropy Parameters Obtained According to Eqs (2) and (37) - (41) for Variants 7) and 8) . For Comments see Table 17. In parentheses the values of NRN, s_o and s for the initial sets before exclusion of lines are indicated

Parameters	Var. 7)						Var. 8)					
	Eq						Eq					
	(2)	(37)	(38)	(39)	(40)[*]	(41)	(2)	(37)	(38)	(39)	(40)[*]	(41)
Q	2.37 ±0.12	1.73 ±0.29	-	-2.46 ±0.57	0.28 ±0.27	-	2.67 ±0.19	3.05	-	-2.64 ±0.59	0.03 ±0.28	-
Y	0	-	1.25 ±0.20	3.45 ±0.65	-	0.96 ±0.20	0	-	1.89 ±0.22	3.58 ±0.67	-	0.87 ±0.22
$\Delta S^{\neq}_{CH_3}$.	0	1.39 ±0.61	3.15 ±0.36	-	-	-	0	-0.97 ±1.0	1.98 ±0.52	-	-	-
NRN	55 (89)	58 (89)	57 (89)	83 (89)	89 (89)	72 (89)	78 (89)	79 (89)	70 (89)	82 (89)	89 (89)	73 (89)
s_o	0.723 (0.926)	0.793 (0.922)	0.769 (0.922)	0.853 (0.928)	0.995 (0.995)	0.885 (0.974)	0.810 (0.931)	0.808 (0.927)	0.768 (0.927)	0.859 (0.935)	1.01 (1.01)	0.911 (1.00)
s	1.90 (5.16)	2.05 (5.14)	2.00 (5.14)	4.02 (5.17)	5.55 (5.55)	3.30 (5.43)	3.66 (5.33)	3.74 (5.31)	3.11 (5.31)	4.12 (5.36)	5.80 (5.80)	3.64 (5.73)

[*] No correlation

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KINETICS OF ALKYL CHLOROFORMATES PYRIDINOLYSIS
IN ALIPHATIC ALCOHOLS

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Kinetics of ROCOCl chloroformates (R = Me,Et,
i-Pr) reaction with pyridine in R'OH alcohols
(R' = Me, Et, i-Pr) is investigated. The nature
of an alcohol is found to but slightly affect the
process. The substituent's structure in a chloro-
formate essentially influences the reaction rate;
this influence is described by the Taft equation.
A conclusion is drawn on the process's course ac-
cording to addition-elimination mechanism with
the kinetically significant stage of tetrahedral
intermediate formation.

Acylation by alkyl chloroformates in the presence of
pyridines proceeds according to the nucleophilic catalysis
mechanism[1]. The first stage of the process is pyridine and
chloroformate interaction, which leads to the aoylonic salt
(AOS) (I) formation.

$$RO-\underset{O}{\overset{\parallel}{C}}-Cl \ + \ N\hspace{-0.3em}\bigcirc \ \xrightarrow{\quad k \quad} \ \left[\ RO-\underset{O}{\overset{\parallel}{C}}-\overset{+}{N}\hspace{-0.3em}\bigcirc \ \right]_{\ I} \ Cl^{-}$$
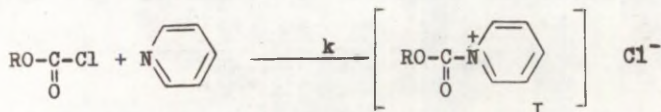
The AOS formation is considered to be proceeding according to the addition-elimination mechanism AE through rather a stable tetrahedral intermediate (II)[2,3].

$$RO-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle O^-}{|}}{C}}-\overset{+}{N}$$

II
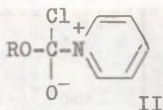
In spite of the fact, that the above mentioned reaction has been studied widely enough[2-4], the research was conducted only on the example of methyl chloroformate, and in aqueous medium solely. In this connection it seemed expedi - ent to examine the quantitative regularities of pyridine reactions with alkyl chloroformates in alcoholic media. The kinetics of the reaction was investigated by the conductometry method. The reaction has the common second order, the first order being individual for each reagent. This corresponds to the data of the works[3,5], in which the irreversi - bility of the AOS formation in protoactive media has been mentioned.

The solvent nature influence was studied on the example of methyl chloroformate. The results, represented in the Table, do show that substitution of one alcohol by another does not significantly affect the rate constant, while in acetonitrile the reaction proceeds more rapidly. This can be explained by the fact that pyridine in alcoholic media is hydrogen-bonded to a considerable extent[6]:

$$R'OH...N$$
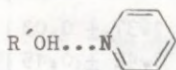
Such an association leads to the initial state stabilization, and thus, to the activation barrier increase and the rate constant decrease, when passing from acetonitrile to alcohols. These data testify to the kinetic significance of the intermediate (II) formation stage when the reac - tion proceeds according to the AE mechanism.

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Rate Constants and Activation Parameters
of ROCOCl Alkyl Chloroformates Reaction with Pyridine

R	Solvent	T, $^{\circ}$C	$k,$ $l \cdot mol^{-1} \cdot s^{-1}$	$\Delta H^{\neq},$ $\frac{kJ}{mol}$	$-\Delta S^{\neq},$ $\frac{J}{mol \cdot K}$
Me	MeCN	15	38.0 ± 5.0	-	-
	MeOH	15	6.32 ± 0.48	36.7 ± 0.8	102 ± 3
		25	11.0 ± 1.0		
		35	17.8 ± 0.9		
		45	29.8 ± 1.0		
	EtOH	15	7.82 ± 0.13	35.4 ± 1.4	105 ± 5
		25	14.4 ± 0.2		
		35	24.1 ± 0.5		
		45	33.4 ± 0.5		
	i-PrOH	15	7.30 ± 0.49	39.0 ± 1.6	93 ± 5
		25	12.5 ± 0.5		
		35	21.1 ± 0.3		
		45	39.4 ± 0.2		
Et	EtOH	15	3.36 ± 0.03	31.7 ± 1.0	125 ± 3
		25	5.67 ± 0.08		
		35	8.23 ± 0.10		
		45	13.2 ± 0.2		
i-Pr	EtOH	15	1.37 ± 0.03	36.5 ± 0.9	116 ± 3
		25	2.42 ± 0.15		
		35	4.16 ± 0.54		
		45	6.13 ± 0.10		

The reaction between alkyl chloroformates and secondary aromatic amines also proceeds according to the AE mechanism[7]. However, the pyridinolysis activation parameters (Table) are somewhat higher in comparison with the corresponding values for the reaction of alkyl chloroformate with N-alkylanilines in dioxan[7]. Apparently, this is cau - sed by the necessity of the preliminary pyridine desolva - tion in the case of the reaction in an alcohol. Neverthe - less, the $\triangle H^{\neq}$ and $\triangle S^{\neq}$ values are in quite a satisfactory agreement with the AE mechanism.

The substituent influence in an alkyl chloroformate investigation was accomplished on the example of the reaction in ethanol (Table). As can be seen from the Table, the rate decreases with the substituent volume growth. In spite of the minimal choice of the substituents, it turned out that the reaction series was well described by the Taft equation[8] with $\delta = 0.866 \pm 0.036$ (Fig.).
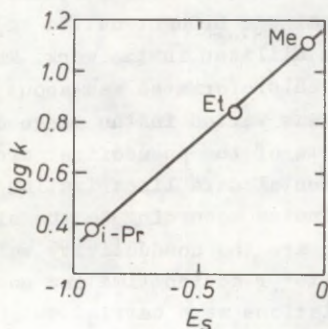
Fig. Rate constant logarithm dependence for pyridine
      reaction with chloroformates in ethanol at $25^{\circ}C$,
      r = 0.987.

The E_s constants, in accordance with the principle of isostericity, were taken for RCH_2 series. Rate decrease with the growth of the spatial hindrance means that the nucleophile attack of the intermediate (II. formation is the rate-determining stage of the reaction.

Experimental

Alkyl chloroformates and pyridine were purified by the repeated fractional distillation. Pyridine was predried over the alkali for 2 weeks. The main substance content in the reagents, which was determined titrimetrically and by the gas-liquid chromatography, constituted at least 99.5%. Acetonitrile and alcohols were dehydrated according to the known procedures[10].

Kinetic measurements were carried out by the conductometry method[11]. In polar solvents at low concentrations the AOS (I) are practically completely dissociated[12]. That is why the solution's electric conductance change is directly proportional to the AOS'concentration. A conductivity meter OK-102/1 whose signal was brought out to an automatic potentiometer KSP-4 was utilized in the work. The initial concentration of alkyl chloroformates was about 10^{-3} mol/l; pyridine concentration was varied in the range of 0.02-0.3 mol/l. The rate constants of the pseudofirst order were determined by the experimental data linearization in the $-\ln(\Lambda_{\infty} - \Lambda_t)$ – t coordinates according to the slope tangent. Here Λ_{∞} and Λ_t are the conductivity values of the solution for an "infinite" reaction time and some moment t, respectively. Calculations were carried out using a SM-4 computer by the method of the least squares, with Λ_{∞} optimization. For the AOS (I) solvolysis effect levelling the region of a kinetic curve not more than 60-65%, fractional conversion was used in calculations.

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THE RELATIVE BASICITY OF SULFONES

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The IR spectral method was employed to inves-
tigate the relative basicity of dialkyl-, aryl -
alkyl-, and cyclic sulfones. Double and multiple
correlations $\Delta \nu_{PhOH}$ with induction, steric, and
hyperconjugative constants of substituents were
found. The induction effect of substituents was
proved to determine the basicity of the sulfones
studied.

Sulfones can be usefully applied as extragents of hyd-
rocarbons and sulfur organics, components of biologically
active preparations, as electrolyte components of the li -
thium storage batteries, where the main importance is ac -
quired by their electron-donor activity. Still, literature
data concerning the sulfones basicities are scarce[1].

Taking into account the aforesaid, the shifts of the
valency vibration band of OH in phenol $\Delta \nu_{PhOH}$ have been
estimated for 23 sulfones in CCl_4 solution; besides, with
21 sulfones the shifts have been found for the first time.
The measurements were conducted in accordance with the
known[2] technique on a "Specord IR75" spectrophotometer. The
cell was 3 mm thick; the concentration of phenol in solution
amounted to 2-5 · 10^{-3} mole/l and that of sulfone – to a-
bout 10^{-2} mole/l. The data obtained (reproducibility disper-

sion 0.8 cm^{-1}) are shown in Table 1 as compared to $\Delta \nu_{PhOH}$ for the related sulfoxides and to the sums of induction $\Sigma \delta^{\pi}$, steric ΣE^{0}, and hyperconjugative constants of sub - stituents $\Sigma \Delta n$ at the SO_2-group.

Figure 1 illustrates several typical spectra of the solutions studied. The value of the maximum shift of the most intensive absorption band within 3410-3450 cm^{-1} relative to the valency vibration band of the phenol free OH-group is taken as the basicity pattern B. With aromatic sulfones, there is observed a still poor band with its maximum shifted by 44-49 cm^{-1} relative to the free OH-group peak . The proximity of these values to the $\Delta \nu_{PhOH}$ of the alkyl-substituted aromatics[1] (43-68 cm^{-1}) enables one to assign this absorption band to the hydrogen bonding OH-sulfone aromatic radical.
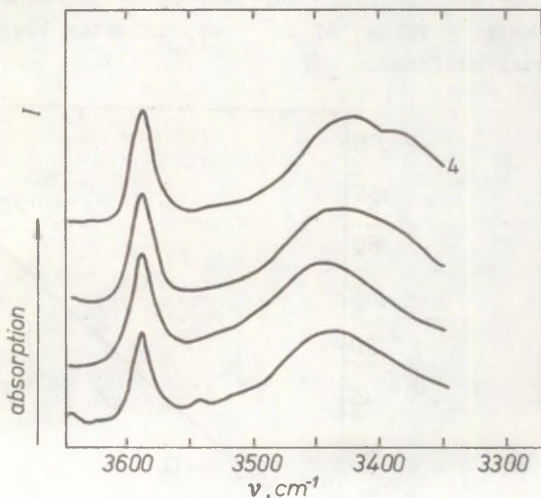
Fig. 1 IR spectra of phenol and sulfone mixtures in CCl_4 solution (C_{PhOH}=2.3 · 10^{-3}mole/l^{-1}; $C_{sulfone}$=0.9 · 10^{-2} mole.l^{-1}; T=28°C).

1 - n-tolyl-n-butylsulfone; 2 - diallylsul-fone; 3 - diethylsulfone: 4 - diisopropylsul-fone

The assymetry of the long-wave band section assigned to the complexed OH-group is inherent to the most basic aliphatic and cyclic sulfones. This assymetry increases with the growing sulfone basicity, increasing radical size, and decreasing sulfone-to-phenol ratio resulting in another low peak shifted by 190-210 cm^{-1} relative to the free OH-group band with diisopropyl-, dibutyl-, and diisobutylsulfones. Such characteristics are supposed to refer to the valency vibrations of the phenol OH-group in the three-center hydrogen bonding.

The basicity of sulfolane B=158 cm^{-1} is similar to the reported value[1]. With 2,4-dimethylsulfone, the value of B=164 cm^{-1} alongside with the data otherwise obtained is considered more reliable than the reported one (B = 181 cm^{-1})[1]. With petroleum sulfones representing a mixture of mono- and dialkylthiacyclane sulfones mainly, the obtained basicity value 167 cm^{-1} approximates the one for in - dividual sulfones.
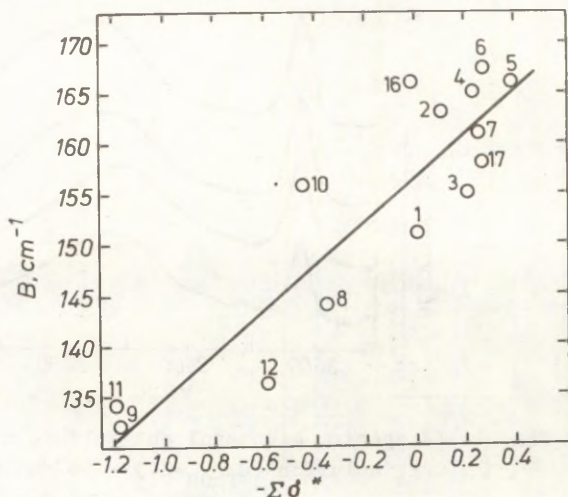
Fig. 2 The dependence of sulfone basicity B on the sum of substituent induction constants $\Sigma\sigma^{*}$. Numbered in accordance with Table 1.

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With respect to the substituents' induction properties, the sulfones possessing electron-accepting, unsaturated, and aromatic substituents reveal the lowest basicities. The dependence given in Fig. 2 can be approximated by the following equation:

$$B = 156.5 - 21.67 \sum \sigma^{\ast}$$
$$n = 10; \quad R = 0.947; \quad S_B = 4.5 \tag{1}$$

Steric and hyperconjugative constants involved into the correlation afford the improved description of basicity,

$$B = 161.9 - 21.90 \sum \sigma^{\ast} - 1.086 \sum E_S^O - 1.344 \sum \Delta n$$
$$n = 10; \quad R = 0.955; \quad S_B = 4.1 \tag{2}$$

A comparison to the correlation equation[4] derived for sulfoxides

$$B = 346 - 62.2 \sum \sigma^{\ast} - 3.7 \sum E_S^O + 2.7 \sum \Delta n$$
$$n = 22; \quad R = 0.98; \quad S_B = 6.2 \tag{3}$$

evidences about an approximately three-times lower effect of the substituent induction and steric properties on the basicity of sulfones. Taking into account the lower standard deviation with sulfones, a less close correlation of B and $\sum \sigma^{\ast}$ should be obviously explained by the lower contribution of the EDA-interactions in sulfones into the Gibbs free energy of complexation with phenol than that in sulfoxides.

Table 1. The Values of Basicity B($\Delta \nu_{PhOH}$) and Substituent Constant Sum for Sulfones and Sulfoxides

No.	Sulfones	B, cm^{-1}		$\sum \sigma^{\ast}$	$\sum E_S^O$	$\sum \Delta n$
		sulfone	sulfoxide			
1	2	3	4	5	6	7
1.	dimethyl-*	151	350[5]	0	0	6
2.	methylethyl-*	163	362[1]	-0.1	-0.37	5.4

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Table 1 (continued)

1	2	3	4	5	6	7
3. diethyl-[×]		155	360[1] 373[4]	-0.2	-0.74	4.8
4. di-n-propyl-[×]		165	378[4]	-0.23	-1.12	4.8
5. diisopropyl-[×]		166	360[5] 382[4]	-0.38	-1.70	3.6
6. di-n-butyl-[×]		167	373[5]	-0.26	-1.18	4.8
7. diisobutyl-[×]		161	392[4]	-0.25	-2.26	4.8
8. diallyl-		144	-	0.36	-	-
9. divinyl-[×]		132	284[4]	1.18	0.50	1.8
10. vinyloctyl-		156	-	0.46	-0.28	-
11. diphenyl-[×]		134.44[××]	294[1] 298[3]	1.20	0.50	3.6
12. phenylmethyl-[×]		137.47[××]	-	0.60	0.25	4.8
13. p-tolylmethyl-		149.47[××]	-	-	-	-
14. p-tolyl-n-butyl-		154.49[××]	-	-	-	-
15. (3-phenylpropyl) methyl		166.47[××]	-	0.02	-	-
16. di-p-chlorophenyl-		117.46[××] 168[×××]	-	-	-	-
17. sulfolane		158 157[1]	370[5]	-0.26	-	-
18. 3-sulfolene		137	-	-	-	-
19. 2,4-dimethylsul- folane		164 181[1]	-	-	-	-
20. 2-hexylsulfolane		168	-	-	-	-
21. 3-methoxysulfolane		148	-	-	-	-
22. benzothiophene sulfone		116	-	-	-	-
23. petroleum sulfones (210 M)		167	-	-	-	-

[×] used in correlations 1 and 2;
[××] PhOH coordinated to the sulfone aromatic radical;
[×××] "Reversed" complex of phenol[7].

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REACTIVITY OF IONS AND ION PAIRS OF 6,8-DINITRO-
1,4-DIOXASPIRO [4,5] DECA-6,9-DIENATES OF ALKALI
METALS

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Absorption spectra of 6,8-dinitro-1,4-dioxa-
spiro[4,5]deca-6,9-dienates of alkali metals   in
solvents having different polarities as well as the
kinetics of the spiro cycle opening of these   ad-
ducts have been studied.
It is shown that in solution, the spiro cy-
clic σ-complexes are in the form of various ion
pairs and free ions, whose concentration depends
on the solvent polarity. Ion pairs of spiro   ad-
ducts have proved to be more reactive than   free
ions.

We have already shown[1] that dissociation of the clas-
sical anionic Jackson-Meisenheimer σ-complexes whose struc-
ture of salts resembles that of quinolonitro acids signifi-
cantly depends on the solvent polarity. Therefore, the   de-
composition reactions characterizing these adducts, become
more complicated in the media having various dielectric per-
meabilities, since there exist different reactants, any   of
which enters the reaction at a certain individual rate   and
has a definite stereospecificity.
Nevertheless, as far as the spiro cyclic complexes are
concerned, such a relationship has not been studied yet.The
present paper deals with the absorption spectra of the 6,8-

dinitro-1,4-dioxaspiro[4,5] deca-6,9-dienate solutions of alkali metals in dimethylsulfoxide (DMSO) tetrahydrofurane (THF), in the binary mixtures DMSO-THF, DMSO-benzene and DMSO-dioxane, which essentially differ in their polarity. In a number of systems the spiro cycle opening kinetics of the dinitrocomplex spiro cycle has also been studied.

Comparison of spectral characteristics of the compounds in a medium with a high dielectric permeability (in DMSO) has shown that in this case no absorption peak shift is observed at transition from lithium salt to cesium salt. Consequently, the adducts have basically the form of free ions in this solvent, although there can also be found the solvent-separated ion pairs whose spectral characteristics do not actually differ from the absorption spectra of free ions[2].

In the low-polarity tetrahydrofurane the position of the absorption band maximum varies symbatically with the increase of cation radius. This can evidently be explained by the fact that the tendency to solvation by means of tetrahydrofurane is weakening in this direction. A comparatively small sodium ion has been rather significantly solvated, while a more volumous cesium ion has been only slightly solvated. This leads to the shift of equilibrium t to ward formation of the contact- and solvationally divided ion pairs differing in their spectral character:

$$Kt^+ An^- \rightleftharpoons Kt^+, \ An^- \rightleftharpoons Kt^+ \| An^- \rightleftharpoons Kt^+ + An^- \qquad (1)$$
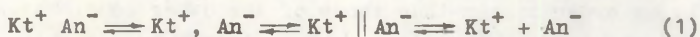
where $Kt^+ An^-$ are nondissociated molecules; Kt^+, An^- are the contact ion pairs; $Kt^+ \| An^-$ – solvent separated ion pairs; Kt^+ and An^- are free ions.

Adding of low-polarity solvents (THF, dioxane and benzene) to dimethylsulfoxide in all cases leads to a gradual absorption peak shift toward the long-wave region (Table 1). Negligible values of these changes in the case of a significantly higher low-polarity solvent concentration seems to evidence about the high level of the solvent ion

pairs formation.

Table 1

Spectral Characteristics of   Dinitrospiro Complex
in Binary Mixtures

| Binary mix- | S vol. % DMSO | | | | | | | | |
tures λ, nm	100	90	80	70	60	50	40	20	10
DMSO-benzene λ_1	502	500	500	499	499	498	497	496	496
DMSO-dioxane λ_1	502	500	499	498	497	497	496	495	492
DMSO-THF λ_1	500	500	499	498	497	496	494	492	490

Since the reactivities of free ions and the ion pairs
of various structure substantially differ[3], we have studied
the decomposition kinetics of the dinitrospiro adduct
containing different cations, in DMSO, THF and in binary
mixtures.

It is known[4] that DMSO favors the formation of free
ions and not that of solvate-dissociated ion pairs. Conse -
quently, the dinitrospiro complex's decomposition rate in
dimethylsulfoxide should not depend on the cation nature.
The data of Table 2 indicate that the decomposition rate
constants of the studied complexes have quite close values,
except the lithium complex whose decomposition rate constant
is by an order higher than those of the other complexes. We
are of the opinion that it can be explained by a rather sig-
nificant external ion pair solvation because of a high charge
density of the lithium cation, which, stabilizing the latter
retards decomposition.

In THF,   the dinitrospiro complex   decomposition pro-
ceeds at a much higher rate than in DMSO. At the   same time
the decomposition rate constant has been found to depend on
the peculiar features of the cation of the studied complexes
(Table 2). It follows from the obtained data that the ion
pairs of the latter are more reactive than the free ions.
This also explains the anomalous behavior of the lithium
complex in DMSO. The statement can be proved by the effect

Table 2

Kinetic Parameters of Decomposition Reaction of
Dinitrospiro Complex

Solvent	k ,s.$^{-1}$	Li^+	Na^+	K^+	Rb^+	Cs^+
DMSO	$k \cdot 10^4$	$24.12^{\pm}$ $^{\pm}1.45$	$3.45^{\pm}$ $^{\pm}0.19$	$3.20^{\pm}$ $^{\pm}0.20$	$3.07^{\pm}$ $^{\pm}0.21$	$3.84^{\pm}$ $^{\pm}0.18$
THF	$k \cdot 10^3$	$-$ ⱬ	$67.3^{\pm}$ $^{\pm}4.17$	$31.2^{\pm}$ $^{\pm}1.81$	$10.3^{\pm}$ $^{\pm}0.46$	$7.62^{\pm}$ $^{\pm}0.53$

ⱬ Owing to the high decomposition rate,it is not possible
to fix the decomposition time for the lithium complex in
THF.

of dibenzo-18-crown-6-ether which combines with sodium cat-
ions thus destroying the ion pairs[5] in whose presence   the
decomposition constant's rate value drops more than three
times. Decrease of k from the sodium adduct towards that of
cesium refers to higher activity of the solvate-separated
ion pairs than that of the contact one.

Research into the decomposition kinetics of the·dinit-
rospiro complex in the binary DMSO-TPF mixtures also eviden-
ces about a good reactivity of ion pairs (Table 3). It   can
be seen from the Table that adding a polar solvent into the
system leads to the growth of the number of the free   ions
being less reactive than the ion pairs. The phenomenon cau-
ses the deceleration of the spiro complex decomposition, in
case the DMSO concentration in the binary mixture increases.

Thus, the results of the present study show that in a
solvent the spirocyclic 6 - complexes are in the form of
various ion pairs and free ions, their concentration depen-
ding on the solvent's polarity.

It has been established that the reactivity of the ions
and ion particles of spiro complexes increases in the follo-
wing succession: free ions, contact ion pairs, solvate-divi-
ded ion pairs.

Table 3

Kinetic Parameters of   Dinitrospiro Complex
Decomposition Reaction in Binary DMSO-THP Mix-
tures

k, s^{-1}	S vol. % DMSO				
	100	40	20	10	0
$k \cdot 10^3$	$0.384^{\pm}$ $^{\pm}0.027$	$8.43^{\pm}$ $^{\pm}0.045$	$11.73^{\pm}$ $^{\pm}0.84$	$18.75^{\pm}$ $^{\pm}1.22$	$31.24^{\pm}$ $^{\pm}2.12$

Experimental

The dinitrospiro complexes have been obtained applying
the ordinary methods[6]. Kinetic measurements were carried out
in pseudomonomolecular conditions at a significant protic
component excess. The reaction rate constants were calcula-
ted by the first order equation[7]. The values of the cons -
tants given in Tables, have been averaged from six parallel
runs. The accuracy of kinetic measurements was assessed by
means of the mathematical statistics, the reliability coef-
ficient being 0.95 in the case of the reaction rate con -
stants calculation, the variation coefficient did not ex-
ceed 5-7%.

The solvents used were purified as described in[8].

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REACTIVITY OF AROMATIC AND HETEROCYCLIC
DERIVATIVES OF HYDRAZINE
7. Kinetics of Acylation Reaction of Hydrazides,
Derivatives of Ortho-Chlorobenzoic Acid with Ben-
zoyl Chloride in Chloroform

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The acylation reaction of 2,4-dichloro-5-
nitrobenzoic acid hydrazide with benzoyl chloride
in chloroform has been studied in 298-318 K tem -
perature range. The validity of the Arrhenius e-
quation has been proved, the activation energy and
the thermodynamic activation parameters have been
calculated. Validity of the Hammett equation   in
the acylation reaction of hydrazides of 2-chlorine-
substituted benzoic acides is proved on the basis
of experimental and literature data. The reaction
parameter ρ has been found at different tempera-
tures. Low ρ values can be explained by the iso-
lating effect of the -CO-NH-bridge groups.   The
reaction proved to be a synchronous one. A pro -
bable mechanism of acylation reaction is suggested.

The interaction of the 2,4-dichloro-5-nitro-benzoic ac-
id hydrazide with benzoyl chloride in chloroform at 298,308,
318, and 328 K has been studied in order to continue   the
series of papers[1,2] dealing with the kinetics of acylation
reactions of biologically active hydrazides of the chlorine-

substituted aromatic carboxylic acid in chloroform:
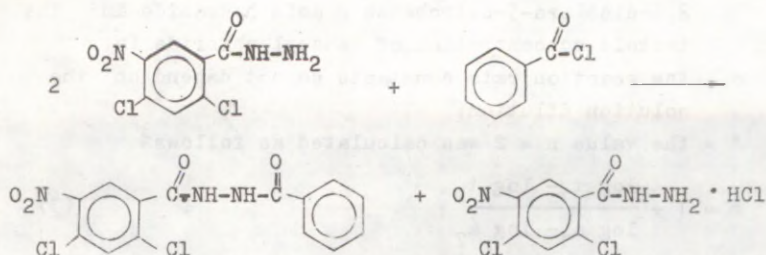
The reaction rate constants were found according to the nucleophile concentration in time. The methods of kinetic measuring were analogous to those used in previous studies[1]. The reaction has the first order according to the nucleophile and the substrate, so in total, it is the second order reaction. This is confirmed by the following facts:
a) existence of linear relationship between the current concentration reciprocal value and time (Fig. 1);
b) stability of the reaction rate constant values, calculated according to equations:

$$k = \frac{1}{2 \, \beta t} \left(\frac{1}{a - x} - \frac{1}{a} \right) \qquad (1)$$

$$k = \frac{\ln \dfrac{2x + \Delta}{2x} - \ln \dfrac{2a + \Delta}{2a}}{\Delta \beta t} \qquad (2)$$

k – bimolecular reaction rate constant ($1 \cdot mole^{-1} \, s^{-1}$);

a – initial concentration of benzoyl chloride (M);

x – benzoyl chloride concentration (M) at time moment t (s);

β – correction, taking into account the variation of the concentration of the reagents in the case of the chloroform volume extension from 298 K to the experimental temperature;

501

Δ - difference between the initial concentration of the
    2,4-dichloro-5-nitrobenzoic acid hydrazide and the
    twofold concentration of benzoyl chloride (M).
c - the reaction rate constants do not depend on the
    solution dilution;
d - the value n = 2 was calculated as follows[3]

$$n = 1 + \frac{\log t_1 - \log t_2}{\log a_1 - \log a_2} \tag{3}$$

where n denotes the reaction order,

t_1, t_2 - duration of the reaction (s) at 50%, the ini -
    tial concentrations of benzoyl chlorides being
    a_1 and a_2 (M).
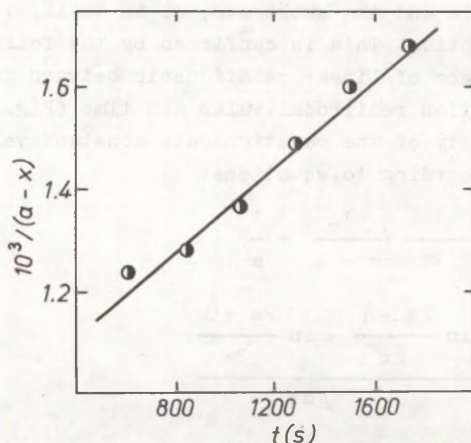
Fig. 1. Dependence of the benzoyl chloride current
         concentration reciprocal value (mole · 1^{-1})
         on time t (s) in the case of the 2,4-dichlo-
         ro-5-nitrobenzoic acid hydrazide acylation
         at 25° C.

The reaction rate constants of the 2,4-dichloro-5-nitro-
benzoic acid hydrazide at different temperatures are given in
Table 1.

Table 1

Rate Constants of Acylation Reactions (k) of 2,4-
Dichloro-5- nitrobenzoic Acid Hydrazide at Different
Temperatures

T, K	$\dfrac{k}{1 \cdot mole^{-1}}$ s^{-1}
298	0.188 ± 0.014
308	0.274 ± 0.012
318	0.425 ± 0.018
328	0.600 ± 0.023

Making use of the data of the value k, as well as those
of hydrazides (the ortho chlorobenzoic acid derivatives) ob-
tained earlier[1,2], the influence of a further substitution
of the acceptor substituents for the ortho-chlorobenzoic ac-
id can be traced in the hydrazide molecule. A successive in-
troduction of the electron-acceptor substituents ($-Cl$, $-NO_2$,
SO_2NH_2) leads to a regular deceleration of the acylation
reaction. The described effect is supposed to cause a dona-
tion of electrons by the reaction center at the transition
state formation:
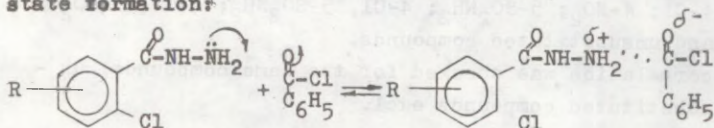
A quantitative estimation of the substituent effect on
the reactivity of hydrazides, the ortho-chlorobenzoic acid
derivatives was performed by means of the Hammett equation:

$$\log k = \log k_o + \varrho\delta \qquad (4)$$

The values δ have been taken from literature. In case
there are several substituents in the hydrazide molecule,
the algebraic total of the δ -constants of individual

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substituents must be taken. The results are presented in Table 2.

Table 2

Parameters of the Hammett Equation for Reaction of Hydrazides, Ortho-Chlorobenzoic Acid Derivatives Acylation with Benzoyl Chloride in Chloroform at Diffe - rent Temperatures

T,K	ρ	$\log k_o$	n	r	S	
298	-0.427 ± 0.056	-0.316 ± 0.035	6	0.9948	$1.76 \cdot 10^{-2}$	
308	-0.435 ± 0.072	-0.125 ± 0.041	6	0.9735	$4.11 \cdot 10^{-2}$	I
318	-0.405 ± 0.057	0.027 ± 0.028	6	0.9836	$2.98 \cdot 10^{-2}$	
328	-0.413 ± 0.046	0.189 ± 0.023	6	0.9877	$2.63 \cdot 10^{-2}$	
298	-0.464 ± 0.022	-0.290 ± 0.023	5	0.9965	$1.25 \cdot 10^{-2}$	
308	-0.531 ± 0.046	-0.055 ± 0.034	5	0.9913	$2.25 \cdot 10^{-2}$	II
218	-0.463 ± 0.048	0.070 ± 0.038	5	0.9882	$2.29 \cdot 10^{-2}$	
328	-0.452 ± 0.051	0.218 ± 0.041	5	0.9894	$2.50 \cdot 10^{-2}$	

I - the correlation was checked for the following hydra - zides, the derivatives of ortho-chlorobenzoic acid: 4-Cl; 4-NO_2; $5\text{-SO}_2\text{NH}_2$; 4-Cl, $5\text{-SO}_2\text{NH}_2$; 4-Cl, 5-NO_2 and unsubstituted compounds.

II - correlation was checked for the same compounds, un - substituted compounds excl.

It follows from the data of Table 2 that the present re-action series obeys the Hammett equation, the correlation co-efficient being rather high. Nevertheless, a separate corre-lation for the nucleophiles with electron-seeking substitu - ents improves the statistic characteristics. It is also con-firmed by the literature data about separate correlation of the analogous data for the hydrazides with electron donor and electron-seeking substituents[5]. The negative ρ value is in keeping with the scheme of the transition state formation, given earlier. The sensitivity of the electron system of the nucleophile molecule to the substituent effect found accord-

ing to the absolute value of the reaction ρ is negligible, owing to the bridge group (-CONH-) isolating influence in the hydrazide molecule[5]. Within the temperature range studied (298-328 K) the value ρ does not practically vary in case the temperature changes.

The acylation reaction rate constants of the 2,4-di-chloro-5-nitrobenzoic acid hydrazine obey the Arrhenius equations:

$$\ln k = 11.1(\pm0.9) - 31.7 \cdot 10^3(\pm824) \cdot \frac{1}{RT} \qquad (5)$$

$$n = 4, \quad r = 0.9992, \quad S = 2.51 \cdot 10^{-2}$$

The calculated activation energy values (E_A = 31.7 kJ/mole) for the 2,4-dichloro-5-nitrobenzoic acid hydrazide are compared with the E_A for the other hydrazides with electron-acceptor substituents[1,2]. The E_A values undergo but slight changes in the limits of the experiment, when the substituents acceptor qualities change.

The thermodynamic activation parameters ($\Delta H^{\neq} \Delta S^{\neq}$) for the 2,4-dichloro-5-nitrobenzoic acid hydrazide were calculated according to the Eyring equation[6].

$$\ln \frac{k}{T} \cdot \frac{h}{K} = \frac{\Delta S^{\neq}}{R} - \Delta H^{\neq} \cdot \frac{1}{RT} \qquad (6)$$

The free activation energy $\Delta G^{\neq}$ of the same compound was found by means of the Second Law of Thermodynamics (Table 3).

High negative activation entropy values (see Table 3 and our reports[1,2]) are another evidence about the fact that according to the above-given scheme the transition state formation proceeds with a better symmetry than has been observed in the case of the molecules of the initial substances. A comparatively small $\Delta H^{\neq}$ value permits us to predict the synchronism of the acylation reaction, i.e. the existence of the S_N2 mechanism. The effect of the electron-seeking substituents in the nucleophile molecule on the thermodyna-

Table 3

Thermodynamic Parameters of Activation of 2,4-Dichloro-
5-Nitrobenzoic Acid Hydrazides Acylation Reaction

$\Delta H^{\neq}$ kJ/mole	$\Delta S^{\neq}$ J/degree	T	$-T \Delta S^{\neq}$ kJ/mole	$\Delta G^{\neq}$ kJ/mole
29.1 ± 1.9	-161 ± 8	298	48.0	77.1
		308	49.6	78.7
		318	51.2	80.3
n=4 r=0.9991	S=2.64 · 10^{-2}	328	52.8	81.9

mic parameters is quite insignificant. It is interesting to
point out that the entropic contribution ($-T \Delta S^{\neq}$) into the
$\Delta G^{\neq}$ is a lot more substantial than the enthalpic one ($\Delta H^{\neq}$).

In conclusion, a following mechanism of the reaction
can be suggested:
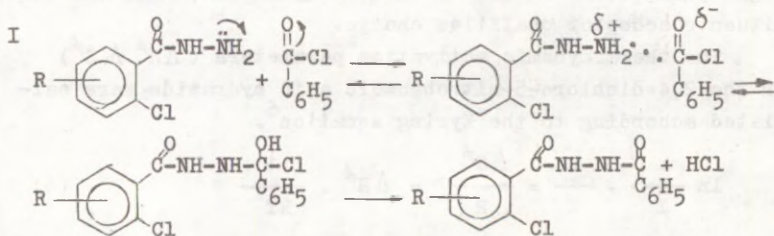
Reagents. Purification and testing of the purity level of
benzoyl chloride and chloroform have been described in[1].
The 2,4-dichloro-5-nitrobenzoic acid hydrazide was synthe -
sized according to methods[7]; it was repeatedly recrystalli-
zed; its melting point was determined and compared with the

literature data. The purity level was checked by means of
the quantitative analysis of the hydrazide group.
<u>Kinetic measurements</u> were carried out applying methods[8] .
The hydrazide concentration was found by titration with 0.01
M of the sodium nitrite solution on an EV-74 ionometer ,
using the platinum ETPL-01M and chlorosilver EVL - IMI
electrodes. The acylation reaction kinetics was studied   at
temperatures 25, 35, 45,55° C. The runs were repeated three
times, including 6-8 measurements each (the completeness of
conversion amounted to 80%). The accuracy of the calculated
parameters was estimated by means of the statistics of small
samples at the 0.95 probability level. Linear equations were
processed according to the least squares method on a micro -
calculator "Elektronika MK-52" using standard programs[9].

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