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STUDY OF SOLVENT DEPENDENCE OF THE pK_a^O VALUES OF ACIDS.
1. Verification of Brønsted Postulate

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It is known that the relationship

$$pK_{AHS_2} - pK_{AHS_1} = \cdot const \qquad (1)$$

derived from the Brønsted equation is
generally not valid.

In the present work it was assumed
that the "differentiating" and "lev-
elling" effects of solvents on the
pK_a values are caused by the influence
of substituents depending on the medi-
um. The veracity of this working hypo-
thesis could be checked on the basis
of the pK_a values of acids if the
influence of substituents could be
considered negligible.

The statistical verification of
relationship (1) was performed accord-
ing to the equation:

$$pK_{js}^O = -pK_{oo}^O + (pK_{jo}^O + pK_{os}^O) \qquad (2)$$

using 317 pK_a values of OH and SH
acids with various hydrocarbon radicals

(aliphatic, aromatic, alicyclic, bicyclic, condensed aromatic cycles) in various individual solvents and binary mixtures (about one hundred media all in all). In equation (2) j and s denote the reaction series of the type of acids and solvent. The upper index "o" emphasizes that only unsubstituted acids (i.e. the substituent is the hydrogen atom)are considered. The latter could correspond to a standard compound in the reaction series with a varying substituent.

Benzoic acid was chosen as a general standard compound (j=o) and water as a standard medium (s=o).

It was found that in the case of all individual solvents and binary mixtures the Brønsted postulate (1) is applicable to acids with hydrocarbon radicals the electronegativities of which do not differ considerably from each other.

According to the Brønsted theory[1-4] all acids of the same charge type similarly change their strength when passing from one medium to another:

$$pK_{AHS_2} - pK_{AHS_1} = const \ (Z) \tag{1}$$

where const (Z) is the characteristic constant for the solvents considered depending on the charge type of the acid AH.

For the uncharged acids

$$const(o) = \lg \frac{K_{aS_2H^+}}{K_{aS_1H^+}} + \frac{e^2N}{2.3RTr} \; (1/D_2 - 1/D_1) \quad (2)$$

where

$K_{aS_1H^+}$ is the acidic constant of lyate ions for solution S_1 under the standard conditions; r is the radius of the solvated ions (for simplicity it was assumed $r_{A^-} = r_S$); and D_1 denotes the dielectric permittivity of solvent S_1.

From equation (1) it follows that the plotting of pK_a values in one solvent against the pK_a values in another solvent should give a linear relationship with the unit slope.

On the basis of comparing the numerous experimental pK_a values of various acids of the same type it was concluded[3] that relationship (3) could be observed only for the acids of the same "nature". At this it was not explained what was understood by the term "nature".

It should be noted that if we plot the pK_a values in one solvent against the pK_a values for another solvent in the case of the same reaction series with varying substituents then the slope of that plot is defined as ratio ρ_{S_1}/ρ_{S_2}[5,6]

$$pK_{S_1}^{x} = \frac{\rho_{S_1}}{\rho_{S_2}} \; pK_{S_2}^{x} + pK_{S_1}^{o} - \frac{\rho_{S_1}}{\rho_{S_2}} \; pK_{S_2} \quad (3)$$

Relationship (3) is often used to check the applicability of the Brønsted postulate (1). However, the ratio ρ_{S_1}/ρ_{S_2} depends on both the reaction series and the nature of the solvent. For example, the ratio $\rho_{DMSO}^{o}/\rho_{H_2O}^{o} = 2.76$ for the acidic dissociation of benzoic acids in DMSO and water, and $\rho_{DMSO}^{o}/\rho_{H_2O}^{o} = 1.70$ for the acidic dissociation of phenols. Such a result is quite natural considering equation (5) (see further).

In the present work it was assumed that the "differentiating" and "levelling" effects of solvents on the pK_a values are caused by the influence of substituents depen-

ding on medium.

Proceeding from this working hypothesis the purpose of this paper was to verify the applicability of the Brønsted postulate (1) or the relationship

$$pK_{js} - pK_{jo}^O = pK_{os}^O - pK_{oo}^O = \Delta pK_s^O \qquad (4)$$

in the case of the pK_a values for the uncharged OH and SH acids when the substituents effect could be considered as negligible.

In equation (4) the following symbols are used:

pK_{oo}^O is the pK_a value for a standard reaction in standard medium;

pK_{os}^O is the pK_a value for a standard reaction in medium S:

pK_{jo}^O is the pK_a value for the given reaction in standard medium ;

pK_{js}^O is the pK_a value for the considered reaction in medium S.

The upper index "o" emphasizes that only unsubstituted acids (i.e. substituent is an atom of hydrogen) are considered. The latter should correspond to a standard compound in the reaction series with varying substituents.

For the present work we chose the dissociation of benzoic acid as the standard reaction (j=o) and water as standard medium (s=o).

The value of pK_{oo}^O = 4.20 equalled the pK_a of benzoic acid in water at 25°C.

In one of our previous works[7] it was found that in the case of various reaction series including m- and p- substituted derivatives of benzene, the medium effects on the ρ^O values (i.e. on the substituents effect) do not depend on the reaction series and should be considered as the characteristic constants of media

$$\rho_{js}^O - \rho_{jo}^O = \rho_{os}^O - \rho_{oo}^O = \Delta\rho_s^O \qquad (5)$$

The meanings of the ρ^o_{oo}, ρ^o_{os}, ρ^o_{jo} and ρ^o_{js} constants are analogous to the pK^o_{oo}, pK^o_{os}, pK^o_{jo} and pK^o_{js} values in equation (4).

Relationship (5) means that one and the same substituent in various reaction series influences the pK_a value to the same extent when passing from one medium to another.

Consequently, if equation (4) is applicable to the acids with standard substituents, then analogous relationships should hold also for the substituted acids considered.

$$pK^x_{js} - pK^x_{jo} = pK^x_{os} - pK^x_{oo} = \triangle pK^x_s \qquad (6)$$

The applicability of the Brønsted postulate (1) for acids with a standard substituent or relationship (4) could be checked using the following modifications of equation (4):

$$pK^o_{oo} = (pK^o_{os} + pK^o_{jo}) - pK^o_{js} \qquad (7)$$

$$pK^o_{js} = -pK^o_{oo} + (pK^o_{os} + pK^o_{jo}) \qquad (8)$$

$$pK^o_{js} = (pK^o_{jo} - pK^o_{oo}) + pK_{os} \quad (j = const) \qquad (9)$$

$$pK^o_{js} = (pK^o_{os} - pK^o_{oo}) + pK^o_{jo} \quad (s = const) \qquad (10)$$

We performed the data treatment according to equations (7) - (10) embracing the pK_a values for the following acids: phenol, thiophenol, phenyl acetic, phenyl propionic, acetic, formic, cyclohexanecarboxylic, cyclopentanecarboxylic, cyclobutanecarboxylic, 1,4-bicyclo[2,2,2]octanecarboxylic, 1,4-bicyclo[1,2,2]heptanecarboxylic, α- and β-naphthoic acids. Strictly speaking, the radicals of the acids considered as to their effective electronegativities are to some extent different from each other. However, we suppose that such a difference has little influence on the dependence of the pK_a values upon medium (see reference 14).

For the sake of comparison the values of pK_{a_1} and pK_{a_2} for dicarboxylic acids $HOOC(CH_2)_n COOH$ where n=0,1,2,3 and the pK_a values for hydrochloric acid were embraced in

data treatment as well.

It should be emphasized that the verification of the applicability of relationship (4) has sense only for the solvents in which the uncomplicated acid dissociation scheme is realized. Taking into account such a restriction, the data processing was performed including the data nearly for one hundred various media : alcohols, glycols, acetone, acetophenone, dimethyl sulfoxide, formamide, N,N-dimethylformamide, N-methylacetamide, hexamethylphosphortriamide, acetonitrile, nitromethane, and binary mixtures of water with alcohols, dioxane, acetone, DMSO, N,N-dimethylformamide, N-butylacetamide, N-methylpyrrolidine, 1,2-dioxyethane, tetrahydrofurane and concentrated aqueous solution of tetrabutylammonium bromide.

The abbreviations given in Tables[8] stand for the solvents used.

Tables[8,9] served as the main source of initial data. If some data are not embraced by these editions the corresponding references are given in Table 1. If some pK_a constants are essentially the same for one and the same acid, the corresponding arithemetic means were used. If the disagreement between the data of different authors was more than 0.3 logarithmic unit , all the parallel pK_a values were involved in the data treatment.

As far as possible, we applied pK^o_{js} and pK^o_{os} values by same author which were estimated by one and the same experimental method. In the case of dicarboxylic acids the statistical correction 0.3 logarithmic units was not taken into account because in differences these terms cancel out.

First the observance of the relationship was verified by comparing the pK^o_{oo} values calculated by Eq.(7) with the experimental value equal to 4.20. The corresponding results for 22 acids in various media are represented in Table 1.

The general statistical verification of the observance of condition (4) was performed according to linear relationship (8) in two different ways.

Firstly the data for 13 uncharged acids in about hundred various media were treated.

Secondly, the pK_a values for HCl and the pK_{a_1} and pK_{a_2} values for bicarboxylic acids $HOOC(CH_2)_n COOH$ (n=0,1,2,3) in the case of media the electrophilicity parameters $E^{10,11}$ of which did not essentially differ from such a parameter for water, were included as well. Significantly deviating values of pK_a were preliminarly excluded from the data set used in statistical data treatment (see Table 1).

In connection with data processing we should note the following. 13 uncharged acids were involved, the initial sampling was 317 pK_a values for 271 combinations of j and s indices (in some cases several alternative pK_a values were used). The linear regression in coordinates of equation (8) is characterized by the following parameters (see Fig. 1):

$$pK^o_{oo} = 4.481 \pm 0.061; \quad slope = 1.012 \pm 0.005$$
$$r = 0.996 \qquad s = 0.307$$

After excluding (according to the Student test on the confidence level of 0.95) 50 significantly deviating points for the set of 267 pK_a values for 242 various combinations of j and s the following result was obtained:

$$pK^o_{oo} = 4.364 \pm 0.048, \quad slope = 1.001 \pm 0.004$$
$$r = 0.998 \qquad s = 0.199.$$

Among 50 significantly deviating pK_a values 21 pK_a values belong to alternative values of pK_a embraced in data processing (see Table 1.).

The inclusion of pK_a values for HCl and pK_{a_1} and pK_{a_2} for 4 bicarboxylic acids (initial sampling of 422 pK_a values, see Table 1) does not significantly influence the parameters of equation (8):

$$pK^o_{oo} = 4.506 \pm 0.056; \qquad slope = 1.016 \pm 0.004$$
$$r = 0.996 \qquad s = 0.312$$

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After excluding 58 significantly deviating points the following result was obtained:

$$pK^o_{oo} = 4.378 \pm 0.043; \quad slope = 1.002 \pm 0.003$$

$$r = 0.998 \quad s = 0.201$$

It should be noted that when processing the data according to equation (8) the excluded points include a relatively large number of pK_a values for H_2O-DMSO binary mixtures.

If relationship (3) is valid, linearities (9) and (10) should also work for separate acids and media.

The results of the treatment of pK^o_{js} values by Eqs.(9) and (10) are listed in Tables 2 and 3 (see Fig.2 and 3).

According to Eq.(9) we treated the pK^o_{js} values for 19 acids in various media and according to Eq.(10) the pK^o_{js} values for 30 media of various acids.

It should be noted that Eq.(9) (and consequently relationship (3)) is satisfactorily applicable to HCl and bicarboxylic acids as well, if we do take into aonsideration the media where the electrophilicity parameter E considerably differs from such a parameter for water.

The values of deviations $(pK^o_{oo})_{calc} - pK^o_{oo}$ for pK_{a_2} bicarboxylic acids of type $^-OOC(CH_2)_nCOOH$ (Z = -1) are given in Table 4. Table 5 lists the analogous values for pK_{a_2} of o-, m- and p- phtalic acids. The greatest deviations (from - 3 to -8 logarithmic units) both for acids $^-OOC(CH_2)_nCOOH$ and o-phthalic acid are observed in the case of DMSO, dimethylformamide and acetonitrile.

Thus, in the case of all individual solvents and binary mixtures a number of unchanged OH (and SH) acids change their strength to the same extent when passing from a given medium to another i.e. the Brønsted postulate (1) is applicable to the acids with the same standard substituent (in the present case X=H) or with radicals, the effective electronegativities of which do not differ considerably from each other.
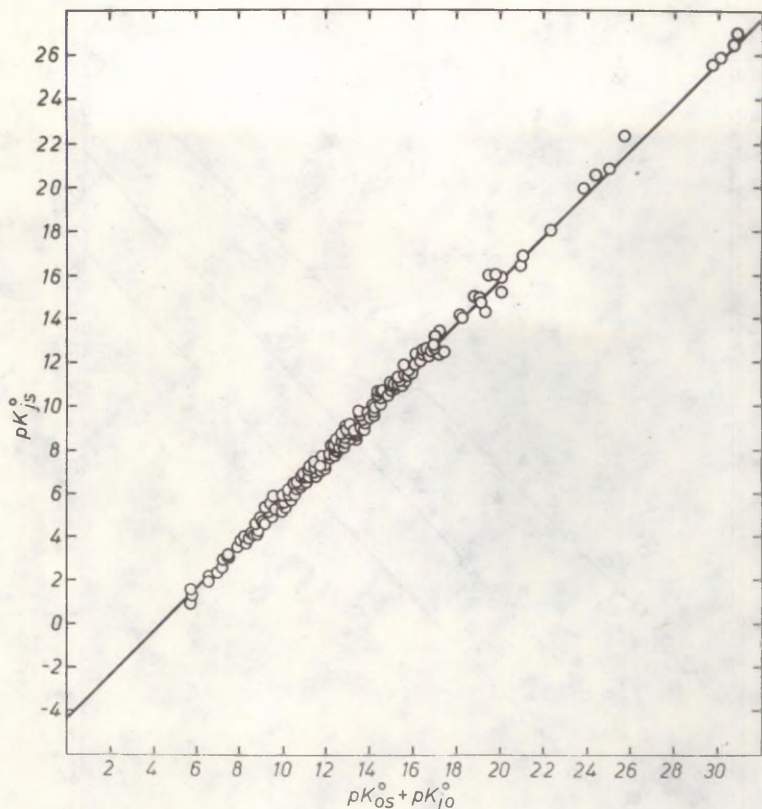
Fig. 1. Plot of pK_{js}^O vs. $(pK_{os}^O + pK_{jo}^O)$.
The figure displays the values of pK_{js}^O for uncharged acids and pK_1 and pK_2 for bicarboxylic acids which were included in data treatment by Eq. 8 (see Table 1).

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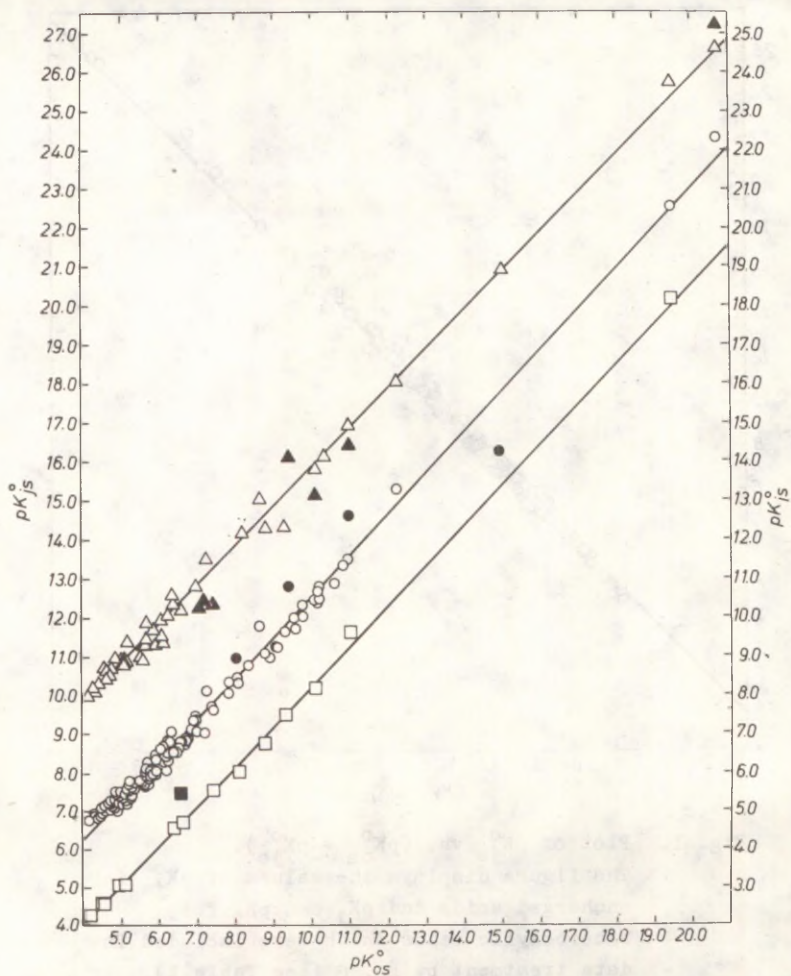
Fig. 2. Plot of pK^O_{js} vs. pK^O_{os} for phenol ($\triangle$), phenyl acetic acid ($\square$, left scale), and for acetic acid ($\bigcirc$, right scale). Shaded points correspond to significantly deviating alternative values.

Fig. 3. Plot of pK^o_{js} vs. pK^o_{jo} for the following media:

H_2O - EtOH(23.6M%)	(●)
Bu_4NBr (7.75 m)	(△)
EtOH	(○)
DMSO	(▲)
DMFA	(□)

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Table 1

Parameters of Equation (7)

$$(pK^o_{oo})_{calc} = (pK^o_{os} + pK^o_{jo}) - pK^o_{js}$$

	Medium	pK^o_{js} *	pK^o_{os} *	$(pK^o_{oo})_{calc}$	Notes
1	2	3	4	5	6

C_6H_5OH

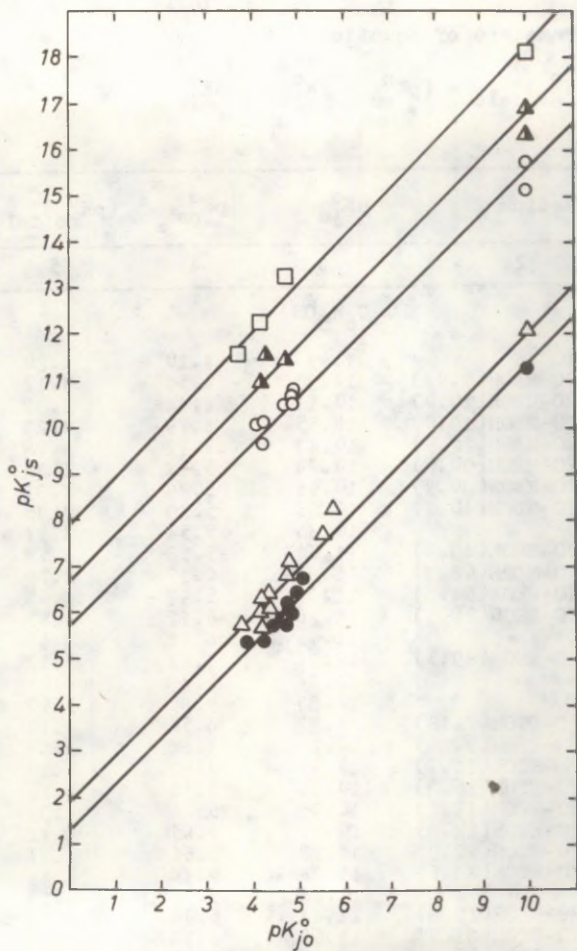|	Medium	pK^o_{js}	pK^o_{os}	$(pK^o_{oo})_{calc}$	Notes
1	H2O	9.99	4.20	4.20	1)
2	H2O-MEOH(9.94)	10.33	4.51	4.17	
3	H2O-MEOH(10.0)	10.11	4.44	4.32	
4	H2O-MEOH(19.0)	10.55	4.79	4.23	
5	H2O-MEOH(22.9)	10.43	4.72	4.28	
6	H2O-MEOH(30.0)	10.80	5.14	4.38	
7	H2O-MEOH(30.9)	10.91	5.29	4.37	
8	H2O-MEOH(40.1)	10.86	5.23	4.36	
9	"	10.86	5.54	4.67	
10	H2O-MEOH(43.9)	11.04	5.58	4.53	
11	H2O-MEOH(62.3)	11.37	6.17	4.79	
12	H2O-MEOH(64.1)	11.33	5.97	4.63	
13	H2O-MEOH(80.1)	11.56	6.12	4.55	
14	"	11.95	6.12	4.16	
15	H2O-MEOH(89.5)	12.34	7.47	5.12	2)
16	"	12.34	6.43	4.08	
17	MEOH	14.33	9.36	5.02	2)
18	H2O-ETOH(7.18)	10.32	4.50	4.17	
19	H2O-ETOH(9.35)	10.76	4.64	3.87	2)
20	H2O-ETOH(11.7)	10.67	4.82	4.14	
21	H2O-ETOH(16.3)	10.96	5.16	4.19	
22	H2O-ETOH(17.1)	10.93	5.26	4.32	
23	H2O-ETOH(22.2)	10.92	5.65	4.72	
24	H2O-ETOH(22.8)	11.28	5.66	4.37	
25	H2O-ETOH(23.6)	11.28	5.70	4.41	
26	"	11.28	5.48(31)	4.19	
27	H2O-ETOH(29.8)	11.44	5.76	4.31	
28	H2O-ETOH(31.7)	11.68	5.94	4.25	
29	H2O-ETOH(55.3)	12.18	6.65	4.44	
30	H2O-ETOH(69.6)	12.44	7.25	4.80	2)
31	"	12.44	6.70	4.25	3)
32	H2O-ETOH(85.5)	12.82	7.00	4.17	
33	ETOH	15.12	10.12	4.99	2)

Table 1 continued

1	2	3	4	5	6
34	ETOH	15.80	10.12	4.31	
35	H2O-DMSO(2.72)	10.19(12)	4.33(12)	4.13	
36	H2O-DMSO(9.67)	10.70(12)	4.70(12)	3.99	
37	H2O-DMSO(14.0)	10.99(12)	4.92(12)	3.92	
38	H2O-DMSO(19.5)	11.41(12)	5.25(12)	3.83	2)
39	H2O-DMSO(26.7)	11.90(12)	5.74(12)	3.83	2)
40	H2O-DMSO(35.5)	12.60(12)	6.40(12)	3.79	2)
41	H2O-DMSO(48.6)	13.52(12)	7.30(12)	3.77	2)
42	H2O-DMSO(59.4)	14.33(12)	8.08(12)	3.74	2)
43		14.33(12)	8.97	4.62	4)
44	H2O-DMSO(70.0)	15.05(12)	8.69(12)	3.63	2)
45	H2O-DMSO(83.0)	16.12(12)	9.45(12)	3.32	2)
46	"	16.12(12)	10.44	4.31	5)
47	DMSO	16.40	11.00	4.59	
48	"	16.90	11.00	4.09	
49	H2O-D(5.13)	10.96(13)	4.83(13)	3.86	2)
50	H2O-D(12.4)	11.50(13)	5.67(13)	4.16	
51	H2O-D(24.1)	12.26	6.16	3.89	
52	"	12.36(13)	7.12(13)	4.85	2)
53	H2O-D(45.9)	14.70(13)	9.22(13)	4.51	
54	HMPTA	14.15	8.25	4.09	
55	DMFA	18.00	12.26	4.25	
56	T-BUOH	20.84(14)	15.10(15)	4.18	6)
57	BU4NBR(7.75M)	12.08	6.30	4.21	
58	CH3NO2	25.70(16)	19.50(17)	3.79	2)
59	CH3CN	26.60	20.70	4.09	
60	"	27.20	20.70	3.49	2).

$$C_6H_5SH$$

1	2	3	4	5	6
61	H2O	6.54	4.20	4.20	1)
62	H2O-ETOH(7.18)	6.82	4.50	4.22	
63	H2O-ETOH(17.1)	7.45	5.26	4.35	
64	H2O-ETOH(22.3)	7.76	5.65	4.43	
65	H2O-ETOH(85.5)	9.28	7.00	4.26	

$$C_6H_5CH_2COOH$$

1	2	3	4	5	6
66	H2O	4.31	4.20	4.20	1)
67	H2O-MEOH(89.5)	7.57	7.47	4.21	
68	"	7.57	6.43	3.17	1)
69	MEOH	9.39	9.36	4.38	
70	ETOH	10.20	10.12	4.23	
71	H2O-AN(2.66)	4.57	4.45	4.19	
72	H2O-AN(3.33)	4.57	4.50	4.24	3)
73	H2O-AN(7.57)	5.07	5.00	4.24	3)

Table 1 continued

1	2	3	4	5	6
74	H2O-AN(9.37)	5.07	5.09	4.33	3)
75	H2O-MCS(48.6)	6.72	6.64	4.23	
76	(CH2OH)2	8.06	8.16	4.41	
77	CH3CH(OH)CH2OH	8.78	8.83	4.36	
78	DMSO	11.6	11.00	3.71	2)
79	CH3NO$_2$	20.1(17)	19.5(17)	3.71	2)
80	FA	6.57(18)	6.36(18)	4.10	

$$C_6H_5(CH_2)_2COOH$$

1	2	3	4	5	6
81	H2O	4.68	4.20	4.20	1)
82	H2O-ETOH(8.2)	5.02	4.68	4.34	3)
83	H2O-ETOH(18.9)	5.58	5.36	4.46	3)
84	H2O-ETOH(23.6)	5.88	5.70	4.50	
85	"	5.88	5.48(31)	4.28	
86	H2O-ETOH(34.4)	6.24	5.95	4.39	3)
87	H2O-ETOH(57.7)	6.96	6.50	4.22	3)
88	H2O-AN(3.33)	4.90	4.50	4.28	3)
89	H2O-AN(14.1)	5.92	5.52	4.28	3)
90	H2O-D(4.86)	5.30	4.86	4.24	
91	H2O-D(12.0)	6.16	5.76	4.28	
92	H2O-D(23.5)	7.28	7.04	4.44	3)

$$CH_3COOH$$

1	2	3	4	5	6
93	H2O	4.75	4.20	4.20	1)
94	H2O-MEOH(9.94)	5.02	4.51	4.24	
95	H2O-MEOH(10.0)	4.96	4.44	4.23	
96	H2O-MEOH(19.4)	5.27	4.89	4.37	
97	H2O-MEOH(22.9)	5.32	4.72	4.15	
98	H2O-MEOH(30.9)	5.55	5.24	4.44	
99	H2O-MEOH(40.1)	5.81	5.23	4.17	
100	"	5.81	5.54	4.48	
101	H2O-MEOH(45.8)	5.96	5.71	4.50	
102	H2O-MEOH(64.1)	6.44	5.97	4.28	
103	H2O-MEOH(69.2)	6.56	6.44	4.63	
104	H2O-MEOH(80.1)	6.66	6.12	4.21	
105	H2O-MEOH(83.5)	7.10	6.90	4.55	
106	H2O-MEOH(89.5)	7.86	7.47	4.34	
107	MEOH	9.64	9.36	4.47	
108	H2O-ETOH(3.18)	4.94	4.37	4.22	
109	H2O-ETOH(6.85)	5.07	4.63	4.31	
110	H2O-ETOH(7.18)	4.94	4.50	4.31	
111	H2O-ETOH(9.10)	5.14	4.77	4.38	
112	H2O-ETOH(11.7)	5.12	4.82	4.45	
113	H2O-ETOH(14.4)	5.28	4.92	4.39	

Table 1 continued

1	2	3	4	5	6
114	H2O-ETOH(16.3)	5.35	5.16	4.56	
115	H2O-ETOH(17.1)	5.38	5.26	4.63	
116	H2O-ETOH(23.6)	5.68	5.70	4.77	
117	"	5.68	5.48(31)	4.55	
118	"	5.84(19)	5.70	4.61	
119	"	5.84(19)	5.48(31)	4.39	
120	H2O-ETOH(28.1)	5.84	5.75	4.66	
121	"	5.84	5.57	4.48	
122	H2O-ETOH(29.8)	5.85	5.76	4.66	
123	H2O-ETOH(31.7)	6.06	5.94	4.63	
124	H2O-ETOH(37.0)	6.12	5.70	4.33	
125	H2O-ETOH(41.9)	6.34	6.14	4.55	
126	H2O-ETOH(42.2)	6.32	6.19	4.62	
127	H2O-ETOH(51.9)	6.56	6.57	4.76	
128	"	6.56	6.30	4.49	3)
129	H2O-ETOH(55.3)	6.69	6.65	4.71	
130	"	6.69	6.40	4.46	3)
131	H2O-ETOH(60.9)	6.87	6.79	4.67	
132	"	6.87	6.50	4.38	3)
133	H2O-ETOH(61.0)	6.84	6.77	4.68	
134	H2O-ETOH(69.6)	7.06	7.25	4.94	2)
135	"	7.06	6.70	4.39	3)
136	H2O-ETOH(73.6)	7.10	6.91	4.56	
137	"	7.10	6.52	4.17	
138	H2O-ETOH(77.9)	7.40	7.30	4.65	
139	"	7.40	6.90	4.25	3)
140	H2O-ETOH(88.1)	8.80	8.40	4.35	
141	ETOH	10.41	10.12	4.46	
142	H2O-AN(5.79)	5.17	4.75	4.33	
143	H2O-AN(7.20)	5.20	4.90	4.45	
144	H2O-AN(9.53)	5.43	5.09	4.41	
145	H2O-AN(11.7)	5.63	5.34	4.46	
146	H2O-AN(17.1)	6.01	5.76	4.50	
147	H2O-AN(19.7)	6.00	5.86	4.61	
148	H2O-AN(23.7)	6.45	6.25	4.55	
149	H2O-AN(31.8)	7.00	6.79	4.54	
150	H2O-AN(42.0)	7.70	7.42	4.47	
151	H2O-AN(55.4)	8.78	8.40	4.37	
152	AN	12.55	11.95(32)	4.15	
153	H2O-D(4.86)	5.29	4.86	4.32	
154	H2O-D(12.7)	6.16	5.85	4.44	
155	H2O-D(18.0)	6.73	6.20	4.22	
156	"	6.30	6.20	4.65	
157	H2O-D(24.6)	7.52	7.01	4.24	
158	H2O-D(24.9)	7.26	7.01	4.50	
159	H2O-D(29.0)	8.06	7.88	4.57	

3

Table 1 continued

1	2	3	4	5	6
160	H2O-D(33.6)	8.48	8.11	4.38	
161	H2O-D(45.0)	9.97	9.57	4.35	
162	H2O-DMSO(2.50)	4.89	4.36	4.22	
163	H2O-DMSO(2.72)	4.91(12)	4.33(12)	4.17	
164	H2O-DMSO(4.52)	5.05	4.52	4.22	
165	H2O-DMSO(5.96)	5.24	4.72	4.23	
166	H2O-DMSO(9.67)	5.25(12)	4.70(12)	4.20	
167	H2O-DMSO(13.3)	5.47	4.94	4.22	
168	H2O-DMSO(14.0)	5.50(12)	4.92(12)	4.17	
169	H2O-DMSO(18.7)	5.81	5.28	4.22	
170	H2O-DMSO(19.5)	5.82(12)	5.25(12)	4.18	
171	H2O-DMSO(26.7)	6.32(12)	5.74(12)	4.17	
172	H2O-DMSO(35.5)	7.08(12)	6.40(12)	4.07	
173	H2O-DMSO(48.6)	8.10(12)	7.30(12)	3.95	
174	H2O-DMSO(59.4)	8.98(12)	8.08(12)	3.85	2)
175	"	8.98(12)	8.97	4.74	4)
176	H2O-DMSO(70.0)	9.77(12)	8.69(12)	3.67	2)
177	H2O-DMSO(83.0)	10.77(12)	9.45(12)	3.43	2)
178	"	10.77	10.44	4.42	5)
179	DMSO	11.47	11.0	4.28	
180	"	12.60	11.0	3.15	1)
181	H2O-DMFA(18.9)	5.78	5.25	4.22	
182	H2O-DMFA(41.2)	8.35	7.90	4.30	
183	H2O-DMFA(67.8)	10.65	10.20	4.30	
184	DMFA	13.24	12.26	3.77	2)
185	H2O-MCS(2.48)	4.91	4.38	4.22	
186	H2O-MCS(5.42)	5.07	4.60	4.28	
187	H2O-MCS(8.94)	5.27	4.86	4.34	
188	H2O-MCS(13.3)	5.47	5.16	4.44	
189	H2O-MCS(18.6)	5.81	5.52	4.46	
190	H2O-MCS(48.6)	6.84	6.64	4.55	
191	H2O-NMP(20W%)	4.95	4.53	4.33	9)
192	H2O-NMP(30W%)	5.11	4.73	4.37	9)
193	H2O-NMP(40W%)	5.31	4.99	4.43	9)
194	H2O-NMP(50W%)	5.63	5.31	4.43	9)
195	H2O-NBA(20W%)	4.88	4.59	4.43	9)
196	H2O-NBA(40W%)	5.02	4.95	4.68	9)
197	H2O-NBA(60W%)	5.18	5.19	4.76	9)
198	H2O-DME(10W%)	4.93	4.42	4.24	9)
199	H2O-DME(20W%)	5.13	4.71	4.33	9)
200	H2O-DME(30W%)	5.37	5.04	4.42	9)
201	H2O-DME(40W%)	5.65	5.41	4.51	9)
202	H2O-DME(50W%)	6.05	5.88	4.58	9)
203	H2O-THF(10W%)	4.92	4.49	4.32	9)
204	H2O-THF(20W%)	5.14	4.87	4.48	9)
205	H2O-THF(30W%)	5.39	5.33	4.69	9)

Table 1 continued

1	2	3	4	5	6
206	H2O-THF(40W%)	5.70	5.78	4.83	2)9)
207	H2O-THF(50W%)	6.08	6.23	4.90	2)9)
208	I-PROH	11.30(15)	10.88(14)	4.33	7)
209	FA	6.82	6.36	4.29	
210	BU4NBR(7.75M)	6.85	6.30	4.20	
211	DG	7.35	6.96	4.36	
212	T-BUOH	10.30	9.80	4.25	
213	"	14.22(15)	15.10(15)	5.63	1)
214	BUOH	9.22	9.18	4.71	
215	"	10.43	10.24	4.56	
216	I-BUOH	10.35	10.20	4.60	
217	(CH2OH)2	5.60	5.19	4.34	
218	"	8.32	8.16	4.59	
219	C6H13OH	9.26	9.11	4.60	
220	C6H5CH2OH	9.71	9.63	4.67	
221	CH3CH(OH)CH2OH	9.10	8.83	4.48	
222	CH3COC6H5	10.03	9.80	4.52	
223	CH3COCH2COOC2H5	10.84	10.62	4.53	
224	CH3CN	22.30	20.70	3.15	1)
225	CH3NO2	20.50(17)	19.50(17)	3.75	2)
226	MACA	7.14(20)	6.60(20)	4.21	

HCOOH

1	2	3	4	5	6
227	H2O	3.72	4.20	4.20	1)
228	H2O-MEOH(10.0)	3.84	4.44	4.32	
229	H2O-MEOH(22.9)	3.97	4.72	4.47	
230	H2O-MEOH(40.1)	4.60	5.54	4.66	
231	"	4.36	5.23	4.59	
232	H2O-MEOH(64.1)	5.28	5.97	4.41	
233	"	4.78	5.97	4.91	2)
234	H2O-MEOH(89.5)	6.54	7.47	4.65	
235	"	5.30	6.43	4.85	2)
236	H2O-ETOH(3.18)	3.80	4.37	4.29	
237	H2O-ETOH(6.85)	3.92	4.63	4.43	
238	H2O-ETOH(7.18)	3.80	4.50	4.42	
239	H2O-ETOH(9.10)	4.02	4.77	4.47	
240	H2O-ETOH(17.1)	4.13	5.26	4.85	
241	H2O-ETOH(28.2)	4.60	5.75	4.87	2)
242	"	4.60	5.57	4.69	
243	H2O-ETOH(48.1)	5.14	6.28	4.86	2)
244	H2O-ETOH(50.0)	5.25	6.30	4.77	3)
245	H2O-ETOH(55.3)	5.30	6.65	5.07	2)
246	H2O-ETOH(60.9)	5.63	6.79	4.88	2)
247	"	5.63	6.50	4.59	3)
248	H2O-ETOH(84.4)	6.62	7.00	4.01	

Table 1 continued

1	2	3	4	5	6
249	H2O-ETOH(85.5)	5.75	7.00	4.97	2)
250	H2O-D(4.86)	4.18	4.86	4.40	
251	H2O-D(14.3)	5.09	5.80	4.43	3)
252	H2O-D(17.0)	6.12	6.32	3.92	
253	H2O-D(32.3)	7.02	7.70	4.40	3)
254	H2O-D(48.2)	8.80	9.20	4.12	3)
255	"	9.14	9.20	3.78	2)3)
256	H2O-DMFA(18.9)	4.90	5.25	4.07	
257	H2O-DMFA(41.2)	7.15	7.90	4.47	
258	H2O-DMFA(67.8)	9.35	10.20	4.57	
259	DMFA	11.60	12.26	4.38	
260	FA	5.50	6.26	4.58	
261	BU4NBR(7.75M)	5.74	6.30	4.28	
262	DG	6.64	6.96	4.04	
263	BUOH	8.03	9.18	4.87	2)
264	C6H13OH	7.92	9.11	4.91	2)
265	I-BUOH	8.85	10.20	5.07	2)
266	T-BUOH	8.82	9.80	4.70	
267	C6H5CH2OH	8.34	9.62	5.00	2)
268	CH3COC6H5	8.61	9.80	4.91	2)

c - Hex COOH

1	2	3	4	5	6
269	H2O	4.90	4.20	4.20	1)
270	H2O-MEOH(30.9)	6.11	5.24	4.03	
271	H2O-MEOH(36.0)	6.11	5.33	4.12	3)
272	MEOH	10.04	9.36	4.22	
273	H2O-ETOH(23.6)	6.45	5.70	4.15	
274	"	6.45	5.48(31)	3.93	
275	H2O-ETOH(28.1)	6.30	5.75	4.35	
276	"	6.30	5.57	4.17	
277	H2O-ETOH(48.1)	7.10	6.28	4.08	
278	H2O-ETOH(85.5)	7.83	7.07	4.14	
279	ETOH	10.77	10.12	4.25	
280	H2O-MCS(48.6)	7.47	6.64	4.07	
281	H2O-DMFA(31.2)	7.82	6.70	3.78	2)3)
282	H2O-DMSO(2.72)	5.03(21)	4.33(12)	4.20	
283	H2O-DMSO(5.96)	5.23(21)	4.72(12)	4.39	
284	H2O-DMSO(9.67)	5.53(21)	4.70(12)	4.07	
285	H2O-DMSO(14.0)	5.84(21)	4.92(12)	3.98	
286	H2O-DMSO(19.5)	6.29(21)	5.25(12)	3.86	
287	H2O-DMSO(26.7)	6.83(21)	5.74(12)	3.81	2)
288	H2O-DMSO(35.5)	7.56(21)	6.40(12)	3.74	2)
289	H2O-DMSO(48.6)	8.56(21)	7.30(12)	3.64	2)
290	H2O-DMSO(59.4)	9.44(21)	8.08(12)	3.54	2)
291	"	9.44(21)	8.97	4.43	4)

Table 1 continued
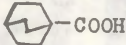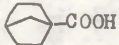
1	2	3	4	5	6
292	H2O-DMSO(70.0)	10.21(21)	8.69(12)	3.38	2)
293	H2O-DMSO(83.0)	11.23(21)	9.45(12)	3.12	2)
294	"	11.23(21)	10.44	4.11	5)
295	(CH2OH)2	8.03	7.65	4.52	
296	T-BUOH	15.82(15)	15.10(15)	4.18	
297	CH3CN	23.3(15)	20.70	2.30	1)

c – BuCOOH

298	H2O	4.79	4.20	4.20	1)
299	MEOH	9.89	9.36	4.26	
300	H2O-ETOH(23.6)	6.21	5.70	4.28	
301	"	6.21	5.48(31)	4.06	
302	ETOH	10.63	10.12	4.28	
303	(CH2OH)2	7.88	7.65	4.56	

c – PeCOOH

304	H2O	4.99	4.20	4.20	1)
305	MEOH	10.15	9.36	4.20	
306	H2O-ETOH(23.6)	6.48	5.70	4.21	
307	"	6.48	5.48(31)	3.99	
308	ETOH	10.76	10.12	4.36	
309	(CH2OH)2	8.05	7.65	4.59	

⬡–COOH

310	H2O	5.08	4.20	4.20	1)
311	H2O-MEOH(13.0)	5.61	4.60	4.07	3)
312	H2O-MEOH(30.9)	6.26	5.24	4.06	
313	MEOH	10.23	9.36	4.21	
314	H2O-ETOH(23.6)	6.75	5.70	4.03	
315	"	6.75	5.48(31)	3.81	2)
316	H2O-ETOH(28.1)	6.87	5.75	3.96	
317	"	6.87	5.57	3.78	2)

⬠–COOH

318	H2O	4.88	4.20	4.20	1)
319	H2O-MEOH(13.0)	5.39	4.60	4.09	3)
320	H2O-MEOH(30.9)	6.04	5.24	4.08	

1 – NaphtCOOH

| 321 | H2O | 3.69 | 4.20 | 4.20 | 1) |
| 322 | H2O-ETOH(23.6) | 5.50 | 5.70 | 3.89 | |

Table 1 continued

1	2	3	4	5	6
323	H2O-ETOH(23.6)	5.50	5.48(31)	3.67	2)
324	H2O-BCS(12.1)	5.89	5.69	3.49	2)
325	H2O-AN(7.57)	4.74	5.00	3.95	
326	H2O-D(4.86)	4.53	4.86	4.02	

2 - NaphtCOOH

327	H2O	4.17	4.20	4.20	1)
328	H2O-ETOH(23.6)	5.67	5.70	4.20	
329	"	5.67	5.48(31)	3.98	
330	H2O-ETOH(43.1)	6.10	6.24	4.31	
331	H2O-BCS(12.1)	5.95	5.69	3.91	
332	H2O-AN(7.57)	4.94	5.00	4.23	
333	H2O-D(4.86)	4.89	4.86	4.14	

HCl

334	H2O	-7.00(22)	4.20	4.20	1)
335	CH3NO2	8.10(17)	19.50(17)	4.40	
336	CH3CN	8.90(17)	20.70	4.80	1)

HOOCCOOH

337	H2O	1.29	4.20	4.20	1)
338	H2O-MEOH(10.0)	1.65	4.40	4.04	
339	MEOH	5.34(23)	9.36	4.31	
340	H2O-ETOH(7.18)	1.38	4.50	4.41	
341	H2O-ETOH(8.91)	1.44(24)	4.77	4.62	
342	H2O-ETOH(17.1)	1.97	5.26	4.58	
343	H2O-ETOH(20.7)	2.03(24)	5.33	4.59	
344	H2O-ETOH(31.7)	2.52	5.94	4.71	
345	H2O-ETOH(37.0)	2.54(24)	5.98	4.73	
346	H2O-ETOH(61.0)	3.39(24)	6.74	4.64	
347	ETOH	6.58	10.12	4.83	1)
348	"	6.91(24)	10.12	4.40	
349	H2O-MCS(48.6)	3.24	6.63	4.68	
350	BU4NBR(7.75M)	2.91	6.30	4.68	
351	FA	2.83	6.36	4.82	1)
352	DMFA	8.2(20)	11.55(20)	4.64	
353	DMSO	6.2	11.0	6.09	1)
354	CH3CN	14.50(25)	20.70	7.49	1)
355	MACA	3.55(20)	6.6(20)	4.34	

⁻OOCCOOH

356	H2O	4.29	4.20	4.20	1)

Table 1 continued

1	2	3	4	5	6
357	H2O-MEOH(10.0)	4.81	4.44	3.92	
358	MEOH	8.27(23)	9.36	5.38	1)
359	H2O-ETOH(3.32)	4.19	4.31	4.41	
360	H2O-ETOH(7.18)	4.41	4.50	4.38	
361	H2O-ETOH(8.91)	4.84(24)	4.77	4.12	
362	H2O-ETOH(11.7)	4.71	4.82	4.40	
363	H2O-ETOH(17.1)	5.11	5.26	4.44	
364	H2O-ETOH(20.7)	5.45(24)	5.33	4.17	
365	H2O-ETOH(37.0)	6.06(24)	5.98	4.21	
366	H2O-ETOH(61.0)	7.28(24)	6.74	3.75	1)
367	ETOH	10.12(24)	10.12	4.29	
368	H2O-MCS(48.6)	6.85	6.63	4.07	
369	BU4NBR(7.75M)	6.09	6.30	4.50	
370	FA	6.39(18)	6.36	4.26	
371	DMFA	14.15(20)	11.55(20)	1.69	1)8)
372	DMSO	14.9	11.0	0.39	1)
373	CH3CN	27.7(25)	20.70	-2.61	1)
374	MACA	7.05(20)	6.6(20)	3.79	1)

$$HOOCCH_2COOH$$
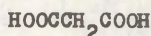
375	H2O	2.82	4.20	4.20	1)
376	H2O-MEOH(10.0)	2.91	4.44	4.35	
377	H2O-MEOH(22.9)	3.29	4.87	4.40	
378	H2O-MEOH(64.1)	4.14	5.97	4.65	
379	H2O-MEOH(80.1)	4.42	6.12	4.52	
380	MEOH	7.66(23)	9.36	4.52	
381	H2O-ETOH(7.18)	3.05	4.50	4.27	
382	H2O-ETOH(8.91)	3.16(24)	4.77	4.43	
383	H2O-ETOH(17.1)	3.36	5.26	4.72	1)
384	H2O-ETOH(20.7)	3.42(24)	5.33	4.73	
385	H2O-ETOH(31.7)	3.76	5.94	5.00	1)
386	H2O-ETOH(37.0)	3.78(24)	5.98	5.02	1)
387	H2O-ETOH(55.3)	4.24	6.65	5.00	1)
388	H2O-ETOH(61.0)	4.37(24)	6.74	5.19	1)
389	ETOH	7.91	10.12	5.03	1)
390	H2O-MCS(48.6)	4.28	6.63	5.17	1)
391	BU4NBR(7.75M)	3.43	6.30	5.69	1)
392	FA	4.38(18)	6.36	4.80	1)
393	DMFA	7.8(20)	11.55(20)	7.28	1)8)
394	DMSO	7.2(26)	11.0	6.62	1)
395	CH3ON	15.3(25)	20.70	8.22	1)
396	MACA	4.30(20)	6.6(20)	5.12	1)8)

$$^{-}OOCCH_2COOH$$
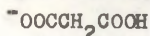
| 397 | H2O | 5.69 | 4.20 | 4.20 | 1) |

Table 1 continued

1	2	3	4	5	6
398	H2O-MEOH(10.0)	5.76	4.44	4.37	
399	H2O-MEOH(22.9)	6.34	4.87	4.22	
400	H2O-MEOH(40.1)	6.99	5.23	3.93	
401	H2O-MEOH(64.1)	7.65	5.97	4.01	
402	MEOH	10.64(23)	9.36	4.52	
403	H2O-ETOH(7.18)	5.80	4.50	4.39	
404	H2O-ETOH(8.91)	6.36(24)	4.77	4.10	
405	H2O-ETOH(17.1)	6.49	5.26	4.46	
406	H2O-ETOH(20.7)	7.06(24)	5.33	3.96	
407	H2O-ETOH(31.7)	7.22	5.94	4.41	
408	H2O-ETOH(37.0)	7.77(24)	5.98	3.90	
409	H2O-ETOH(55.3)	7.97	6.65	4.37	
410	H2O-ETOH(61.0)	9.02(24)	6.74	3.41	1)
411	ETOH	12.72(24)	10.12	3.09	1)
412	H2O-MCS(48.6)	8.83	6.63	3.49	1)
413	BU4NBR(7.75M)	8.30	6.30	3.69	1)
414	FA	8.34(18)	6.36	3.71	1)
415	DMFA	20.8(27)	12.26	-2.85	1)
416	DMSO	18.55(26)	11.0	-1.86	1)
417	CH3CN	30.5(25)	20.70	-4.11	1)
418	MACA	9.0(20)	6.6(20)	3.24	1)8)

$$HOOC(CH_2)_2COOH$$

1	2	3	4	5	6
419	H2O	4.19	4.20	4.20	1)
420	H2O-MEOH(10.0)	4.73	4.87	4.33	
421	H2O-MEOH(40.1)	5.20	5.23	4.22	
422	H2O-MEOH(64.1)	5.77	5.97	4.39	
423	H2O-MEOH(80.1)	6.09	6.12	4.22	
424	MEOH	9.32(23)	9.36	4.22	
425	H2O-ETOH(3.18)	4.34	4.37	4.22	
426	H2O-ETOH(6.85)	4.50	4.63	4.32	
427	H2O-ETOH(7.18)	4.35	4.50	4.34	
428	H2O-ETOH(8.91)	4.55(24)	4.77	4.41	
429	H2O-ETOH(17.1)	4.82	5.26	4.63	
430	H2O-ETOH(20.7)	5.02(24)	5.33	4.50	
431	H2O-ETOH(31.7)	5.36	5.94	4.77	
432	H2O-ETOH(37.0)	5.53(24)	5.98	4.64	
433	H2O-ETOH(55.3)	6.02	6.65	4.82	1)
434	H2O-ETOH(61.0)	6.14(24)	6.74	4.79	
435	H2O-ETOH(73.6)	6.36	6.91	4.80	1)
436	"	6.36	6.52	4.35	
437	ETOH	9.58	10.12	4.73	
438	H2O-MCS(48.6)	6.07	6.63	4.75	
439	BU4NBR(7.75M)	5.59	6.30	4.90	1)

Table 1 continued

1	2	3	4	5	6
440	FA	6.00(18)	6.36	4.55	
441	DMFA	10.4(27)	12.26	6.05	1)
442	DMSO	9.5(26)	11.0	5.65	1)
443	CH3CN	17.6(25)	20.70	7.29	1)

$$^-OOC(CH_2)_2COOH$$

1	2	3	4	5	6
444	H2O	5.58	4.20	4.20	1)
445	H2O-MEOH(10.0)	5.71	4.44	4.31	
446	H2O-MEOH(22.9)	6.17	4.87	4.28	
447	H2O-MEOH(40.1)	6.70	5.23	4.11	
448	H2O-MEOH(64.1)	7.39	5.97	4.16	
449	H2O-MEOH(80.1)	7.76	6.12	3.94	
450	MEOH	11.19(23)	9.36	3.75	2)
451	H2O-ETOH(7.18)	5.72	4.50	4.36	
452	H2O-ETOH(8.91)	6.24(24)	4.77	4.11	
453	H2O-ETOH(17.1)	6.25	5.26	4.59	
454	H2O-ETOH(20.7)	6.79(24)	5.33	4.12	
455	H2O-ETOH(31.7)	6.86	5.94	4.66	
456	H2O-ETOH(37.0)	7.51(24)	5.98	4.05	
457	H2O-ETOH(55.3)	7.64	6.65	4.59	
458	H2O-ETOH(61.0)	8.54(24)	6.74	3.78	2)
459	ETOH	12.11	10.12	3.59	1)
460	H2O-MCS(48.6)	8.11	6.63	4.10	
461	BU4NBR(7.75M)	7.71	6.30	4.17	
462	FA	8.03(18)	6.36	3.81	2)
463	DMFA	19.9(27)	12.26	-2.06	1)
464	"	17.21(28)	12.26	-0.63	1)
465	DMSO	16.7(26)	11.0	-0.12	1)
466	CH3CN	29.0(25)	20.70	-2.62	1)

$$HOOC(CH_2)_3COOH$$

1	2	3	4	5	6
467	H2O	4.33	4.20	4.20	1)
468	H2O-ETOH(7.18)	4.44	4.50	4.39	
469	H2O-ETOH(8.91)	4.73	4.74	4.34	
470	H2O-ETOH(17.1)	4.96	5.26	4.63	
471	H2O-ETOH(20.7)	5.22	5.47	4.58	
472	H2O-ETOH(31.7)	5.56	5.94	4.71	
473	"	5.89	5.94	4.38	
474	H2O-ETOH(37.0)	5.89	5.98	4.42	
475	H2O-ETOH(55.3)	6.36	6.65	4.62	
476	H2O-ETOH(61.0)	6.70	6.77	4.40	
477	ETOH	10.22	10.12	4.23	
478	H2O-MCS(48.6)	7.17	6.63	3.79	2)
479	BU4NBR(7.75M)	6.47	6.30	4.16	

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Table 1 continued

1	2	3	4	5	6
480	FA	6.22(18)	6.26	4.37	
481	DMFA	10.85(20)	11.55(20)	5.05	1)8)
482	CH3CN	19.20(25)	20.70	5.83	1)
483	MACA	6.85(20)	6.6(20)	4.08	

$$^-OOC(CH_2)_3COOH$$

1	2	3	4	5	6
484	H2O	5.43	4.20	4.20	1)
485	H2O-ETOH(7.18)	5.58	4.50	4.35	
486	H2O-ETOH(8.91)	5.85	4.77	4.35	
487	H2O-ETOH(17.1)	6.13	5.26	4.56	
488	H2O-ETOH(20.7)	6.37	5.33	4.39	
489	H2O-ETOH(31.7)	6.73	5.94	4.64	
490	"	7.22	5.94	4.15	
491	H2O-ETOH(37.0)	7.22	5.98	4.19	
492	H2O-ETOH(55.3)	7.51	6.63	4.55	
493	H2O-ETOH(61.0)	8.25	6.74	3.92	2)
494	ETOH	11.86	10.12	3.69	1)
495	BU4NBR(7.75M)	7.22	6.30	4.51	
496	FA	8.21(18)	6.36	3.58	1)
497	DMFA	13.8(20)	11.55(20)	3.18	1)8)
498	CH3CN	29.95(25)	20.70	-3.82	1)

x If a reference to the source of pK_a is not indicated in brackets it was given in publication[8,9]

1) The pK_{js}^o value preliminarily excluded from the data set used in data treatment by Eq.(8).

2) The pK_{js}^o value excluded during the data treatment by Eq.(8).

3) The pK_{os}^o value was found from the relationship pK_{os}^o vs. molar per cent (M%) of the organic component of the binary aqueous-organic solvent.

4) The pK_{os}^o value for 59.0 M% DMSO.

5) The pK_{os}^o value for 82.8 M% DMSO.

6) The pK_{js}^o value, found from the relationship pK_{js}^o vs. δ^o.

7) The pK_{os}^o value, found from the relationship pK_{os}^o vs. δ^o.

8) pK_a at 40^oC.

a) By W% the volume per cents are denoted.

Table 2

Results of pK_{js}^{o} Values Treatment by Eq. (9)

$$pK_{js}^{o} = (pK_{jo}^{o} - pK_{oo}^{o}) + \varkappa\, pK_{os}^{o} \qquad (\text{ j = const })$$

NO	Acid (j)	$(pK_{jo}^{o}-pK_{oo}^{o})_{calc}$	$pK_{jo}^{o}-pK_{oo}^{o}$	Slope $\varkappa$	r	s	n_s/n_s^o
1	2	3	4	5	6	7	8
1.	PhOH	$5.63^{\pm}0.09$	5.79	$1.020^{\pm}0.012$	0.996	0.349	60/60
		$5.67^{\pm}0.09$	5.79	$1.019^{\pm}0.009$	0.997	0.276	55/60
		$5.79^{\pm}0.06$	5.79	$1.007^{\pm}0.008$	0.998	0.211	47/60
2.	PhSH	$2.41^{\pm}0.19$	2.34	$0.969^{\pm}0.036$	0.996	0.080	5/5
3.	$PhCH_2COOH$	$-0.007^{\pm}0.167$	0.11	$1.021^{\pm}0.021$	0.997	0.305	14/14
		$-0.143^{\pm}0.068$	0.11	$1.029^{\pm}0.008$	0.999	0.123	13/14
4.	$PhCH_2CH_2COOH$	$0.614^{\pm}0.174$	0.48	$0.952^{\pm}0.031$	0.993	0.087	12/12
5.	CH_3COOH	$0.107^{\pm}0.057$	0.55	$1.038^{\pm}0.003$	0.996	0.232	130/130
		$0.292^{\pm}0.055$	0.55	$1.006^{\pm}0.008$	0.996	0.200	125/130
		$0.512^{\pm}0.050$	0.55	$0.972^{\pm}0.007$	0.996	0.146	113/130
6.	HCOOH	$-0.621^{\pm}0.177$	-0.48	$0.968^{\pm}0.025$	0.986	0.321	41/42
		$-0.543^{\pm}0.143$	-0.48	$0.947^{\pm}0.022$	0.991	0.254	37/42
		$-0.428^{\pm}0.126$	-0.48	$0.925^{\pm}0.019$	0.993	0.210	33/42
7.	c-HexCOOH	$0.776^{\pm}0.177$	0.70	$1.020^{\pm}0.026$	0.992	0.307	27/27
		$0.839^{\pm}0.050$	0.70	$0.987^{\pm}0.007$	0.996	0.081	16/27

Table 2 continued

1	2	3	4	5	6	7	8
8.	c-PeCOOH	0.990±0.222	0.79	0.963±0.031	0.997	0.164	6/6
9.	c-BuCOOH	0.998±0.125	0.79	0.971±0.018	0.999	0.094	5/6
		0.695±0.187	0.59	0.974±0.026	0.998	0.138	6/6
10.	⬡-COOH	1.21±0.20	0.88	0.975±0.034	0.995	0.144	8/8
11.	(COOH)$_2$	-2.91±0.19	-2.91	0.940±0.028	0.994	0.235	15/15
		-3.19±0.12	-2.91	0.986±0.018	0.998	0.133	13/15
12.	$^-$OOCCOOH	-0.045 ±0.216	0.09	1.022±0.037	0.990	0.214	15/15
		-0.068 ±0.13	0.09	1.010±0.022	0.997	0.122	12/15
13.	HOOCH$_2$COOH	-1.36±0.18	-1.38	0.949±0.031	0.995	0.143	9/9
14.	$^-$OOCCH$_2$COOH	1.63±0.23	1.49	0.972±0.042	0.988	0.185	13/13
15.	HOOC(CH$_2$)$_2$COOH	0.029±0.17	-0.01	0.950±0.028	0.991	0.190	19/19
16.	$^-$OOC(CH$_2$)$_2$COOH	0.827±0.26	1.38	1.099±0.045	0.985	0.223	18/18
		0.839±0.120	1.38	1.112±0.032	0.995	0.144	15/18
17.	HOOC(CH$_2$)$_3$COOH	-0.197±0.174	0.13	1.029±0.029	0.996	0.148	14/16
18.	$^-$OOC(CH$_2$)$_3$COOH	1.03 ±0.43	1.23	1.010±0.076	0.970	0.206	11/11
		1.47 ±0.35	1.23	0.921±0.063	0.978	0.152	10/11
19.	HCl	-11.1±0.2	-11.2	0.973±0.011	0.999	0.150	3/3

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Table 3

Results of pK_{js}^o Values Treatment by Eq. (10)

$$pK_{js}^o = (pK_{os}^o - pK_{oo}^o) + \varkappa\, pK_{jo}^o \qquad (s = const)$$

No	Medium	$(pK_{os}-pK_{oo}^o)_{calc}$	$pK_{os}^o-pK_{oo}^o$	Slope $\varkappa$	r	s	n_j/n_j^o
1	2	3	4	5	6	7	8
1. H_2O-MeOH(10.0)		0.251 ± 0.068	0.24	0.978 ± 0.014	0.999	0.098	9/10
2. H_2O-MeOH(22.9)		0.517 ± 0.112	0.67	1.011 ± 0.021	0.998	0.126	8/8
3. H_2O-MeOH(30.9)		1.22 ± 0.16	1.04	0.970 ± 0.028	0.997	0.138	6/6
4. H_2O-MeOH(40.1)		1.02 ± 0.15	1.19	1.006 ± 0.029	0.997	0.170	8/8
5. H_2O-MeOH(64.1)		1.61 ± 0.21	1.77	0.997 ± 0.040	0.993	0.234	8/8
6. H_2O-MeOH(89.5)		2.69 ± 0.48	2.23	0.978 ± 0.095	0.968	0.521	6/6
		3.43 ± 0.17	2.23	0.892 ± 0.031	0.997	0.161	4/6
7. H_2O-EtOH(11.7)		0.320 ± 0.119	0.62	1.034 ± 0.020	0.999	0.099	4/4
8. H_2O-EtOH(17.1)		0.485 ± 0.146	1.06	1.048 ± 0.027	0.996	0.152	11/11
9. H_2O-EtOH(23.6)		1.59 ± 0.17	1.38	0.965 ± 0.034	0.992	0.184	11/12
10. H_2O-EtOH(31.7)		1.05 ± 0.221	1.74	1.071 ± 0.041	0.992	0.224	11/11
11. H_2O-EtOH(55.3)		1.62 ± 0.17	2.32	1.070 ± 0.030	0.997	0.159	8/9
12. Bu_4NBr(7.75m)		1.99 ± 0.13	2.10	1.008 ± 0.025	0.992	0.133	9/11
13. EtOH		6.00 ± 0.17	5.63	0.947 ± 0.029	0.995	0.208	9/11
14. MeOH		5.76 ± 0.12	5.16	0.858 ± 0.021	0.998	0.102	6/6
15. DMSO		7.17 ± 0.27	6.80	0.948 ± 0.040	0.996	0.248	5/5

Table 3 continued

1	2	3	4	5	6	7	8
16.	DMFA	8.17 $\pm$0.26	8.06	0.989$\pm$0.045	0.996	0.227	4/4
17.	CH$_3$CN	16.49 $\pm$0.14	16.50	1.061$\pm$0.031	0.998	0.431	5/5
		16.30 $\pm$0.07	16.50	1.059$\pm$0.015	0.999	0.214	4.5
18.	CH$_3$NO$_2$	15.40 $\pm$0.05	15.30	1.038$\pm$0.014	0.999	0.174	5/5
19.	HMPTA	3.97 $\pm$0.10	4.05	1.02	0.999	-	2/2
20.	t-BuOH	10.97 $\pm$0.00	10.9	0.984	0.999	-	2/2
21.	H$_2$0-DMS0(2.72)	0.098$\pm$0.013	0.13	1.010$\pm$0.002	0.999	0.009	4/4
22.	H$_2$0-DMS0(9.67)	0.331$\pm$0.011	0.50	1.037$\pm$0.001	0.999	0.008	4/4
23.	H$_2$0-DMS0(14.0)	0.519$\pm$0.008	0.72	1.048$\pm$0.001	0.999	0.002	4/4
24.	H$_2$0-DMS0(19.5)	0.769$\pm$0.009	1.05	1.065$\pm$0.001	0.999	0.006	4/4
25.	H$_2$0-DMS0(26.7)	1.267$\pm$0.008	1.54	1.064$\pm$0.001	0.999	0.002	4/4
26.	H$_2$0-DMS0(35.5)	1.978$\pm$0.054	2.20	1.063$\pm$0.008	0.999	0.038	4/4
27.	H$_2$0-DMS0(48.6)	2.958$\pm$0.124	3.10	1.058$\pm$0.019	0.999	0.089	4/4
28.	H$_2$0-DMS0(59.4)	3.796$\pm$0.182	3.88	1.056$\pm$0.028	0.999	0.130	4/4
29.	H$_2$0-DMS0(70.0)	4.465$\pm$0.283	4.49	1.062$\pm$0.044	0.997	0.203	4/4
30.	H$_2$0-DMS0(83.0)	5.172$\pm$0.409	5.25	1.099$\pm$0.064	0.995	0.293	4/4

Table 4

Deviation from Eq. (7)

$$\Delta pK = (pK^O_{oo})_{calc} - pK^O_{oo} \text{ for Anionic Acids } {}^-OOC(CH_2)_n COOH$$

No	Medium	n=0	n=1	n=2	n=3
1.	H_2O	0	0	0	0
2.	MeOH(10.0)	-0.08	0.17	0.11	-
3.	MeOH(64.1)	-	-0.19	-0.04	-
4.	MeOH	1.10	0.21	-0.45	-
5.	H_2O-EtOH(7.18)	0.18	0.19	0.16	0.15
6.	H_2O-EtOH(8.91)	-0.08	-0.10	-0.09	0.15
7.	H_2O-EtOH(17.1)	0.24	0.26	0.39	0.36
8.	H_2O-EtOH(20.7)	-	-0.24	-0.08	0.19
9.	H_2O-EtOH(31.7)	-	0.21	0.46	0.44, -0.05
10.	H_2O-EtOH(37.0)	-	-0.30	-0.15	-0.01
11.	H_2O-EtOH(55.3)	-	0.15	0.39	0.35
12.	H_2O-EtOH(61.0)	-	-0.79	-0.42	-0.28
13.	EtOH	0.09	-1.11	-0.61	-0.51
14.	Bu_4NBr(7.75m)	0.30	-0.51	-0.03	0.31
15.	FA	0.06	-0.49	-0.39	-0.72
16.	DMFA	-2.51	-7.76, >-2.96	-6.26, -4.83	-1.02
17.	DMSO	-3.81	-6.06	-4.32	-
18.	CH_3CN	-6.81	-6.31	-6.82	-8.02
19.	MAcA	-0.41	-0.96	-	-

Table 5

pK_2 Values and Deviations from Eq. (7)

$$\triangle pK = (pK_{oo}^{o})_{calc} - pK_{oo}^{o} \quad \text{for Phthalic Acids} \quad {}^-OOC-C_6H_4COOH$$

No	Medium	Ortho [*]		Meta [*]		Para [*]	
		pK_2	$\triangle pK$	pK_2	$\triangle pK$	pK_2	$\triangle pK$
1.	H_2O	5.40	0	4.62	0	4.46	0
2.	MeOH(64.1)	7.74	-0.57				
3.	MeOH	9.79(23)	0.76	10.61(29)	-0.84	10.30(29)	-0.68
4.	"	12.1(29)	-1.54				
5.	"	11.65	-1.09				
6.	H_2O-EtOH(7.18)	5.65	0.05				
7.	H_2O-EtOH(17.1)	6.56	-0.10				
8.	H_2O-EtOH(31.7)	7.43	-0.29				
9.	H_2O-EtOH(55.3)	8.11	-0.26				
10.	EtOH	12.17	-0.85				
11.	Bu$_4$NBr(7.75m)	8.25	-0.75	5.95	0.73	6.58	-0.02
12.	FA	7.72(18)	-0.16				
13.	DMFA	>16.0(20)	>-3.25			12.15(18)	-0.74
14.	DMSO	16.0	-3.80	12.3(29)	-0.88	12.1(29)	-0.84
15.	CH_3CN	29.8(30)	-7.90	23.0(29)	-1.88		
16.	MAcA	8.80(18)	-0.60			7.10(18)	-0.24

[*] If reference to the source of pK_a is not indicated in brackets it was given in publication[8,9].

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A STUDY OF ACID-BASE EQUILIBRIA IN AQUEOUS
DIOXANE SOLUTIONS OF PHENYLANTHRANYL
ACID DERIVATIVES

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The method of potentiometric titration in 60%
aqueous dioxane at 25°C has been applied to mea-
sure the ionization constants of phenylanthranyl
acid derivatives. The pK_a values were correlated
with Hammett σ constants and σ° with Hammett-Taft
constants. The mechanism which transmits the sub-
stituents effect on the reaction center is dis-
cussed.

Phenylanthranyl acids are widely used in analyti-
cal practice as redox indicators when determining quantita-
tively a number of substances[1,2]. However, they are also of
interest as compounds with a versatile pharmacological ef-
fect[3-6]. Besides, phenylanthranyl acids serve as the initial
reagents for the synthesis of a set of acridine derivatives
which are biologically active[7,8].

Therefore, it was of interest to study the acid-
base equilibria of a number of phenylanthranyl acid deriva-
tives with the aim to study their reactivity and establish
a possible relationship between the acid-base properties
and pharmacological effect.

To fulfil this task the method of potentiometric
titration was applied to determine the acid ionization con-
stants of phenylanthranyl acid derivatives of the following
structure at 25°C
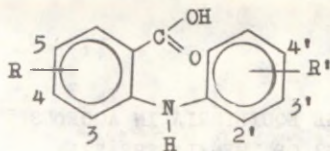
(the values for R and R' are presented in Table 1)
Due to low solubility in water the measurements of pK_a were carried out in 60% aqueous dioxane.

Table 1

IONIZATION CONSTANTS OF PHENYLANTHRANYL
ACID DERIVATIVES IN 60% AQUEOUS DIOXANE

Series	R / R'	pK_a					
		H	4-Cl	3-NO$_2$	4-NO$_2$	5-NO$_2$	3,5-NO$_2$
1	2	3	4	5	6	7	8
A	H	6.96*	6.50	–	5.42	5.51	–
	2 - CH$_3$	7.00	6.65	–	5.54	5.60	4.44
	3 - CH$_3$	–	6.54	–	–	–	4.48
B	4 - CH$_3$	7.00	6.62	–	5.55	5.63	4.48
C	2 - OCH$_3$	7.12	6.60	5.79	5.65	5.69	4.57
	3 - OCH$_3$	–	–	5.59	–	5.48	4.40
D	4 - OCH$_3$	7.06	6.61	5.65	5.58	5.65	4.53
	2 - Cl	6.82	6.31	–	5.38	–	–
	3 - Cl	–	6.26	–	–	5.30	–
	4 - Cl	6.84	6.29	–	5.25	–	–
	2 - Br	–	–	–	–	–	4.35
	3 - Br	–	–	–	–	–	4.21
E	4 - Br	–	6.34	–	5.23	5.29	4.26
	3 - J	–	–	–	–	–	4.27
	4 - J	–	6.35	–	–	–	4.26
Series		F	G		H	I	J

* The mean deviations of pK_a values don't exceed 0.09 units.

It was established that the pK_a values (Table 1)

which characterize carboxyl group protonation change in the
range 4.21 - 7.12 units and are largely dependent on the
nature of the substituents in the anthranyl part of the mo-
lecules (ΔpK_a in series A-E is equal to 2.5 units). Electron
acceptor substituents in the benzene ring of the anthranyl
fragment bring about a considerable increase in acidity
when compared to their nonsubstituted analogs. 3,5-dinitro-
derivatives of phenylanthranyl acid (series J) are charac-
terized by especially high acidity. The quantitative estima-
tion of the influence of the electron nature of radicals in
the benzene ring of the anthranyl part of the studied mole-
cules on pK_a values was done according to the Hammett equa-
tion (Table 2, equations 1-5). The values of reaction con-
stants (ρ = 1.69-1.78) evidence that the reaction center
is highly sensitive to the polar influences of substituents.

The nature of the radical in the benzene ring
which does not contain a carboxyl group exerts less influe-
ence on the pK_a value (ΔpK_a in series F-J is equal to 0.3-
0.4 unit). This can be explained by the formation of the
intramolecular hydrogen bond (IHB) between the carbonyl
oxygen and the hydrogen atom of the amino group, the pres-
ence of which has been proved by electron spectroscopy and
quantum chemistry[9]:
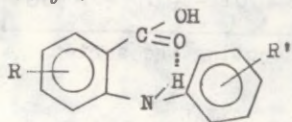
IHB stabilizes the anthranyl fragment of the phe-
nylanthranyl acid molecule and the phenyl ring appears to
be turned at an angle of 70° from the surface[9]. Such geometry
of the studied compounds is unfavorable for p-π-conjuga-
tion of the lone electron pair of the nitrogen atom with
each phenyl ring and eliminates the possibility to alternate
the electronic effects of the substituents according to
the mechanism of polar resonance of the latter with the re-
action center.

The pK_a values of phenylanthranyl acids of series F–J correlate satisfactorily with Hammett-Taft σ^0 constants[10] (Table 2, equations 6-10).

Table 2

Correlation Equations of pK_a Dependences of Substituted Phenylanthranyl Acid on Hammett σ Constants and on Hammett-Tafts σ^0 Constants

№ eq.	Series	Correlation Equation	r	s
1	A*	$pK_a = 6.87 \pm 0.04 - (1.72 \pm 0.05)\sigma$	0.999	0.02
2	B	$pK_a = 6.96 \pm 0.10 - (1.78 \pm 0.13)\sigma$	0.993	0.03
3	C	$pK_a = 6.95 \pm 0.09 - (1.69 \pm 0.11)\sigma$	0.996	0.03
4	D	$pK_a = 6.94 \pm 0.08 - (1.70 \pm 0.09)\sigma$	0.991	0.04
5	E	$pK_a = 6.63 \pm 0.10 - (1.72 \pm 0.12)\sigma$	0.992	0.06
6	F	$pK_a = 6.96 \pm 0.02 - (0.46 \pm 0.09)\sigma^0$	0.997	0.02
7	G	$pK_a = 6.51 \pm 0.02 - (0.66 \pm 0.05)\sigma^0$	0.980	0.01
8	H	$pK_a = 5.46 \pm 0.01 - (0.76 \pm 0.02)\sigma^0$	0.999	0.01
9	I	$pK_a = 5.54 \pm 0.01 - (0.72 \pm 0.05)\sigma^0$	0.997	0.01
10	J	$pK_a = 4.43 \pm 0.01 - (0.58 \pm 0.03)\sigma^0$	0.995	0.01

* See Table 1 for denoting the series

EXPERIMENTAL

The ionization constants have been determined by the potentiometric titration of 0.001 M of solutions of the studied compounds at 25°C on a device pH = 340. As a standard the ionization constant of acetic acid in 60% aqueous dioxane has been determined ($pK_a = 7.50$, $pK_a = 7.52$ and 7.49 [11]). The pK_a values were determined by the method of half-neutralization. The data presented in Table 1 are the mean values out of 3–4 measurements.

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ACID-BASE EQUILIBRIA IN SOLUTIONS OF ARYLAMIDES AND
2-OXOINDOLIN-3-GLYOXYL ACID ARENSULFONYLAMIDES

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The method of potentiometric titration in 60% aque-
ous dioxane at 25°C has been used to determine the
pK_a values of arylamides and 2-oxoindolin-3-glyoxyl
acid arensulfonylamides. It was established that the
arylamides of 2-oxoindolin-3-glyoxyl acid are monobasic
but the corresponding arensulfonylamides are dibasic
acids. The pK_{a_1} value of the latter characterizes the
acidity of the sulfamide group and pK_{a_2} -the acidity
of the OH group of the enol form of these compounds.

Earlier[1] we have studied the electrochemical proper-
ties of a number of 2-oxoindolin derivatives that are of
interest for biology.When doing further research in order
to establish the interrelation between the structure,
physico-chemical properties and the biological activity of
2-oxoindolin derivatives,we determined the pK_a values of
the acidic ionization of arylamides (I) and arensulfonyl-
amides of 2-oxoindolin-3-glyoxyl acid (II).

Due to the fact that compounds I and II do not solve
in water the measurement of pK_a values was done by apply-
ing the method of potentiometric titration in 60% aqueous
dioxane. The obtained experimental data are presented in
Table. As can be seen,amides I appear to be monobasic
acids,their pK_a values are in range 6.92-7.15 units.Accor-
ding to ref.2 3-acylderivatives of 2-oxoindolin(compounds
I included) are characterized by a high degree of enol-

ization. Therefore the acid—base equilibria for amides I
could be presented by scheme A.
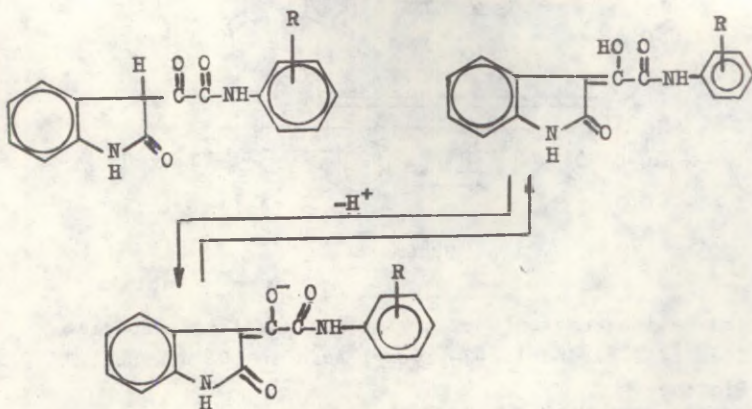
Scheme A

The pK_a values of compounds I are rather independent
of the nature of radicals in the benzene ring.This is so
because of their considerable remoteness from the reaction
center.

Arensulfonylamides II ionize in two steps.The pK_{a_1}
values of these compounds vary in the range 3.42-4.75 units,
but pK_{a_2} - 8.55-8.22 units.

The comparison of the obtained pK_a values of the am-
ides of both groups of substances indicates that pK_{a_1} of com-
pounds II are characterized by the acidity of the sulfamide
group. pK_{a_2} and pK_a of amides I are related to the OH group
ionization of the enol form of substances II.Therefore,the
acid—base equilibria for the latter could be presented by
scheme B.

The nature of the radicals in the benzene ring of arensul-
fonylamides II exerts considerable influence on the pK_{a_1}

value of these compounds and little influence on the pK_{a_2} value for the same reasons as for compounds I.
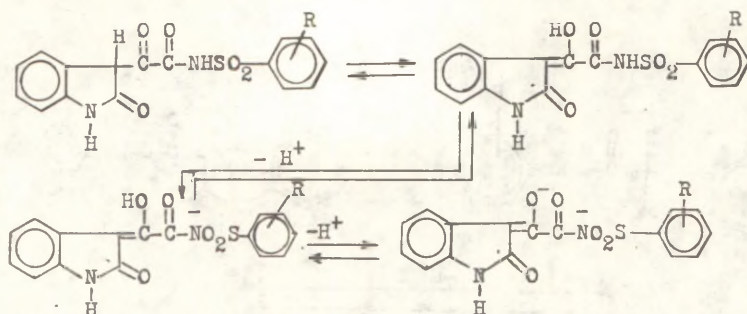
Scheme B

Table

Ionization Constants of Arylamides and Arensulfonylamides of 2-oxoindolin-3-glyoxyl Acid in 60% Aqueous Dioxane

Compounds I		Compounds II		
R	pK_a	R :	pK_{a_1}	pK_{a_2}
H	6.81	H	4.25	8.05
4-CH$_3$	7.01	4-NH$_2$	4.85	8.22
4-OCH$_3$	7.15	3-CH$_3$	4.45	8.05
4-OH	7.01	4-CH$_3$	4.43	8.16
3-CL	6.95	4-NO$_2$	3.42	8.09
4-CL	7.05	3,5-Br$_2$,		
4-Br	7.07	4-NH$_2$	4.48	8.11
4-NO$_2$	6.92			
2-COOH	5.43			
	7.53*			

Note. The mean deviations of pK_a values do not exceed 0.09 log unit.

* pK_{a_2}

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It is interesting to note that pK_{a_2} of substances II exceed pK_a of compounds I almost by a unit. This is due to the influence of the negative charge in the anion which forms in the first step of ionization.

The quantitative estimation of the influence of the nature of the substituents in the benzene ring of substances II on the pK_{a_1} values has been done according to the Hammett-Taft equation. The correlation equation of the above dependence ,which has been obtained by the least squares method, is the following:

$pK_{a_1} = 4.28 \pm 0.09 - (0.76 \pm 0.19)6^o$;r =0.99, S =0.09

The 6° values - substituents constants have been taken from ref.3.

A rather small value of the reaction constant ($\rho = 0.76$) gives evidence of low sensitivity of the reaction center (the sulfamide group) to the polar influences of substituents in the benzene ring in the arensulfonylamide part of the molecule of compounds II.

<center>EXPERIMENTAL</center>

The ionization constants were determined by potentiometric titration of 0.001 M of the solutions of the studied compounds in 60% aqueous dioxane at 25^oC on a device pH-340.

Previously it was established that the glass electrode used for titration had satisfactory hydrogen function. As a standard, pK_a of acetic acid was determined in 60% aqueous dioxane ($pK_a^{exp} = 7.51$; $pK_a = 7.52$ and 7.49^4).

The measurement and calculation of pK_a were done by the method described in ref.5. Only those substances were used for titration the individuality of which was confirmed by the data of elemental analysis and infrared spectra.

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QUANTITATIVE STATISTICAL INTERPRETATION OF
KINETIC DATA IN THE GAS PHASE HOMOLYSIS.
5. Correlation of Substituent Effects on Conventional
Formation Enthalpies of Substituted Methyl Radicals
Proceeding from Isoentropic and Isokinetic Models

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The parametrization of the equations reflec-
ting the influence of substituent effects on
the conventional formation enthalpies for sub-
stituted methyl free radicals $X_1X_2X_3C^{\cdot}$ has
been described. These equations are based on
an analogy with those applicable to the for-
mation enthalpies of compounds with the cova-
lent bonds taking into account γ , inductive
and resonance interactions.

The different hypothesis of relationships valid for the
activation energy (E) and the preexponential factor (A) val-
ues in the gas phase homolysis were checked in the previ-
ous reports[1-3] of this series. It was shown that log A and
E values are independent of each other and the dependence
of log k on the structure is mainly determined by the
changes in the E value. Taking into account this result
one can describe the kinetic parameters of the gas phase
homolysis formally in terms of the isoentropic and iso-
kinetic models[3]. For this purpose the conventional forma-
tion enthalpies of free radicals at $0^{\circ}K$ in the transition
state were calculated using the least-squares method. The
listed $\Delta H_R^{\neq}$. or $\Delta \Delta H_R^{\neq}$. values, where $\Delta \Delta H_R^{\neq}. = \Delta H_R^{\neq}. - \Delta H_{OR}^{O}$-
(see ref. 2), are conventional and not standard. The as-
sumption about the constancy of internal temperature contri-

butions in the transition state is introduced (i.e. the cor-
responding heat capacity change is ignored). Besides, the
real variation of log A values is not taken into account
and $\Delta H_R^{\neq}$. or $\Delta \Delta H_R^{\neq}$. values are calculated assuming either
the universal log A_o value or within the framework of the
isokinetic dependence.

If $\Delta H_R^{\neq}$. or $\Delta \Delta H_R^{\neq}$. values are known one can estimate
the rate constants for the gas phase homolysis in all combi-
nations of R if the experimental formation enthalpy value

$\Delta H_{OR_i R_j}^O$ is known or the value of the interaction energy
$(I_{R_i R_j})$ between the radicals-substituents in the initial
compound may be calculated.

The $\Delta H_R^{\neq}$. values for the free radicals belonging to
types $XO^{\cdot}$, $X_1 X_2 N^{\cdot}$, $X_1 X_2 X_3 C^{\cdot}$ etc, depend on the nature of
substituents X which are connected with the free-radical
center. Except the trivial contributions caused by the
additive increments of these substituents generally the
terms caused by the interaction between the reaction center
and the substituents as well as between the substituents
themselves must exist as well. The quantitative estima-
tion of all these contributions enables us to estimate the
$\Delta H_R^{\neq}$. or $\Delta \Delta H_R^{\neq}$. values for a large number of free radi-
cals. This is a way to extend significantly the predictive
power of the calculation scheme for the estimation of the
rate constants of the gas phase homolysis.

The substituted methyl radicals are the most important
and complicated case since the joint influence of three
substituents must be considered. Proceeding from the analo-
gous influence of substituents on the formation enthalpies
of alkanes and their polyfunctional derivatives[4,5], one
can express the following equation for the formation enthal-
pies in the transition state of free radicals belonging to
$X_1 X_2 X_3 C^{\cdot}$ type:

$$\Delta H^{\neq}_{X_1X_2X_3C^\cdot} = \Delta H^{\neq}_{CH_3^\cdot} + \sum_i \Delta H_{X_i} + \varphi_{C^\cdot} \cdot \sum_i \varphi_{X_i} +$$
$$+ A_{C^\cdot} \sum_{i<j} \varphi_{X_i} \varphi_{X_j} + B_{C^\cdot} \varphi_{X_1} \varphi_{X_2} \varphi_{X_3} + \alpha^{\ast} \sigma^{\ast}_{C^\cdot} \cdot \sum_i \sigma^{\ast}_{X_i} +$$
$$+ \alpha^{\ast} z^{\ast}_{C^\cdot} \cdot \sum_{i<j} \sigma^{\ast}_{X_i} \sigma^{\ast}_{X_j} + \sum_i \psi_{X_i} \qquad (1)$$

where $\Delta H^{\neq}_{CH_3^\cdot}$ is the formation enthalpy of the free methyl radical, ΔH_{X_i} denotes additive increments for substituents X_i, φ_X and $\sigma^{\ast}_X$ are φ- and inductive substituent constants, $\varphi_{C^\cdot}$ and $\sigma^{\ast}_{C^\cdot}$ are the same for the free-radical center, ψ_X - the energy of the resonance interaction between substituent X and the free-radical center, $A_{C^\cdot}$ and $B_{C^\cdot}$ - the constants of double and triple φ-interactions through the $C^\cdot$ center, $\alpha^{\ast}$ - the scaling constant for the inductive interaction, $z^{\ast}_{C^\cdot}$ - the inductive transmission factor for the $C^\cdot$ center. The scaling constant of the φ-interaction omitted in equation (1) is equal to unity if the formation enthalpies are expressed in kcal/mol.

Actual data treatment in the coordinates of this equation is complicated by the fact that the ΔH°_0 values are known to be either of unsufficient reliability or unknown for many compounds from which the $\Delta H^{\neq}_{X_1X_2X_3C^\cdot}$ values are calculated. Therefore for the reaction:

$$X_1X_2X_3C - X_4 \rightarrow X_1X_2X_3C^\cdot + X_4^\cdot \qquad (2)$$
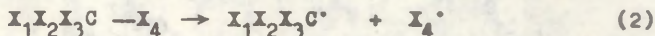
it is most expedient to process only the respective D or D^1 values calculated[2,3] according to the formulas:

$$D_{ij} = E_{ij} + 2.3RT_{mean} (\log A_o - \log A_{ij} + \log n_{ij}) \qquad (3)$$
$$D^1_{ij} = \left[2.3RT_{mean}/\beta (\log A_{ij} - \alpha - \log n_{ij}) - E_{ij}\beta \right]/(T - \beta) \qquad (4)$$

where R is the gas constant, T_{mean} represents the mean temperature for the temperature range studied to calculate

the log A and E values, $\log A_o$ is the logarithm of the universal preexponential factor, n denotes the statistical factor, ß is the isokinetic temperature and $\propto$ is the intercept of the isokinetic dependence between the "true" $\log A^{\ddagger}$ and E^1 values in the form $\log A^1 = \propto + E^1/2.3\,R\beta$. Equation (4) is reduced to eq. (3) in the isoentropic special case $(1/\beta = 0)$. At that $\propto = \log A_o$.

Proceeding from the expression[2]:

$$\Delta\Delta H^{\ddagger}_{X_1 X_2 X_3 C\cdot} + \Delta\Delta H^{\ddagger}_{X_4\cdot} = D_{X_1 X_2 X_3 C - X_4} + \varphi_{X_1 X_2 X_3 C}\,\varphi_{X_4} + \propto^{\ast} \sigma^{\ast}_{X_1 X_2 X_3 C}\,\sigma^{\ast}_{X_4} \tag{5}$$

where $\Delta\Delta H^{\ddagger}_{X_1 X_2 X_3 C\cdot} = \Delta H^{\ddagger}_{X_1 X_2 X_3 C\cdot} - \Delta H_{X_1 X_2 X_3 CH}$,

eq. (1), and the analogous equation for the compound $X_1 X_2 X_3 CH$ the D value can be written as follows:

$$D_{X_1 X_2 X_3 C - X_4} = \Delta\Delta H^{\ddagger}_{CH_3\cdot} + \Delta\Delta H^{\ddagger}_{X_4\cdot} + \varphi_{C\cdot} \sum_{i=1}^{3} \varphi_{X_i} +$$
$$+ A_{C\cdot} \sum_{\substack{i<j \\ (i=1)}}^{2}\sum^{3} \varphi_{X_i}\varphi_{X_j} + B_{C\cdot} \varphi_{X_1}\varphi_{X_2}\varphi_{X_3} + \propto^{\ast}\sigma^{\ast}_{C\cdot} \sum_{i=1}^{3}\sigma^{\ast}_{X_i} +$$
$$+ \propto^{\ast} z^{\ast}_{C\cdot} \sum_{\substack{i<j \\ (i=1)}}^{2}\sum^{3}\sigma^{\ast}_{X_i}\sigma^{\ast}_{X_j} + \sum_{i=1}^{3}\gamma_{X_i} - A\sum_{\substack{i<j \\ (i=1)}}^{3}\sum^{4}\varphi_{X_i}\varphi_{X_j} -$$
$$- B\sum_{\substack{i<j<l \\ (i=1)}}^{2}\sum^{3}\sum^{4}\varphi_{X_i}\varphi_{X_j}\varphi_{X_l} - \propto^{\ast} z^{\ast}_{C}\sum_{\substack{i<j \\ (i=1)}}^{3}\sum^{4}\sigma^{\ast}_{X_i}\sigma^{\ast}_{X_j} -$$
$$- \varphi_{X_1 X_2 X_3 C}\,\varphi_{X_4} - \propto^{\ast}\sigma^{\ast}_{X_1 X_2 X_3 C}\,\sigma^{\ast}_{X_4} - \varphi_{CH_3}\sum_{i=1}^{4}\varphi_{X_i} \tag{6}$$

The complications arising in the calculations of formation enthalpies for the compounds where several halogen atoms are connected with a single carbon atom[5] are not evidently reflected in this expression. Moreover, one must consider the nonadditivity of the $\sigma^{\ast}$ values for the substi-

tuted methyls with several halogen atoms at the first atom. Generalizing the corresponding relationships observed for polyhalogen substituted methyls the following equation was obtained[5]:

$$\sigma^{\ast}_{X_1X_2X_3C} = 0.39 \sum_{i=1}^{3} \sigma^{\ast}_{X_i} - 0.0275(\text{NHAL}-1) \sum_i 2^{(4-n_{X_i})} \quad (7)$$

where NHAL denotes the total number of halogen atoms among substituents X_i at the first atom of the substituted methyl, n_{X_i} is the position number of halogen in the sequence of F, Cl, Br and I if starting from zero.

One does not know anything in advance about the relationships reflecting the interactions between the halogen atoms connected with the free-radical center $C^{\cdot}$.

The parameters to be determined are β, $\propto$, $\gamma_{C^{\cdot}}$, $A_{C^{\cdot}}$, $B_{C^{\cdot}}$, $\propto^{\ast}$, $\sigma^{\ast}_{C^{\cdot}}$, $z^{\ast}_{C^{\cdot}}$ as well as $\sigma^{\ast}_{NO_2}$.

Assuming for D eq (3) the parametrization of eq. (6) proceeding from the known D, $\Delta\Delta H^{\neq}_{CH_3}$ and $\Delta\Delta H^{\neq}_{X_4}$ values reduces to the multilinear regression analysis (MLRA) in the respective coordinates. Since one was faced with many different versions of data treatment connected with the change not only in the list of arguments but some values of them e.g. ($\sigma^{\ast}_{NO_2}$), the usual MLRA technique requires labour-consuming alteration of initial data. Therefore we attempted to find preliminary promising versions using the nonlinear least squares (NLLS) method.

A respective universal program was written by us for a small universal computer "Nairi-2". An algorithm for the calculation of the $D_{X_1X_2X_3C} - X_4$ values according to eq.(6) taking into account all known complications for halogen derivatives of methane[5] and supposed for the halogen substituted free-radical center $C^{\cdot}$ was programmed as a function for this NLLS program.

Several hypotheses were checked for the set of D values for 45 compounds (reactions) assuming $\log A_o = 14.64$ (the

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total data set is listed in ref. 2). It was achieved by
simply realized variation of sets where different parame-
ters have unknown or fixed values. Sometimes slight changes
in the subprogram for the calculation of the $D_{X_1 X_2 X_3 C-X_4}$
values were made. At that any parameter from eq. (6) may
be served as a quantity to be determined in the course of
data treatment.

It is reasonable to estimate the values of parameters
$\mathcal{V}_{C^\bullet}$, $A_{C^\bullet}$ and $B_{C^\bullet}$ proceeding from the $\Delta H_R^{\neq}$ values for
methyl, ethyl, i-propyl and t-butyl which are obtainable
with a relatively high precision[2]. If one examines the
values:

$$\Delta n = \Delta H^{\neq}_{(CH_3)_n H_{3-n}C^\bullet} - n \Delta H^o_{OCH_4} - \Delta H^{\neq}_{CH_3^\bullet} = n \mathcal{V}_{C^\bullet} \cdot \mathcal{V}_{CH_3} \quad (8)$$

where the right-hand side of the equation is written assum-
ing zero values for $A_{C^\bullet}$ and $B_{C^\bullet}$, then the following results
are obtained:

Radical	Δn	$\mathcal{V}_{C^\bullet} \cdot \mathcal{V}_{CH_3}$
ethyl	$8.0^{\pm}0.5$	$8.0^{\pm}0.5$
i-propyl	$16.5^{\pm}0.5$	$8.3^{\pm}0.3$
t-butyl	$25.7^{\pm}0.5$	$8.6^{\pm}0.2$

The Δn values were calculated from the $\Delta H_R^{\neq}$ values
for these free radicals obtained by the different versions
of the data treatment in refs. 2, 3. Taking into account
the known value $\mathcal{V}_{CH_3} = 3.94$ the estimates for $\mathcal{V}_{C^\bullet}$ in the
range of 2.03-2.18 are obtained. $\mathcal{V}_{C^\bullet} = 2.11$ corresponds
to $\mathcal{V}_{C^\bullet} \cdot \mathcal{V}_{CH_3} = 8.3$. Taking into account only the results
obtained using $\log A_o = 14.64$ $\mathcal{V}_{C^\bullet} = 2.20^{\pm}0.10$. These values
indicate zero or very close to zero $A_{C^\bullet}$ and $B_{C^\bullet}$ values.

The data treatment using the NLLS technique for the
set including 45 reactions with $\mathcal{V}_{C^\bullet}$, $A_{C^\bullet}$, and $B_{C^\bullet}$ values
to be estimated and using the values $\sigma^{\neq}_{NO_2} = 3.55$ and
$\alpha^{\neq} = 2.2$ leads to the zero values of $A_{C^\bullet}$ and $B_{C^\bullet}$ and

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$\mathcal{P}_{C}.$ = 2.04. One can conclude that the result is to a high degree of persistence since the data for the compounds $(CH_3)_4H_{3-n}C-CH_3$ were not included in the indicated set. Therefore the subsequent data processing was performed by fixing $A_{C}.=0.0$ and $B_{C}.=0.0$.

The assumption about the existence of $\mathcal{P}$ and inductive interactions between halogen atoms connected with the free-radical center $C^{\cdot}$ led to worse statistical characteristics and a large number of excluded points during the treatment at any combination of other initial assumptions made. Therefore it was necessary to expand the special additional postulate for halogens interacting via the center $C^{\cdot}$ as well. To be concrete this means that in the cases when both X_i and X_j are halogens the value $z_{C}.$ = 0 has to be used. As regards $\mathcal{P}$-interaction through the $C^{\cdot}$ center then it is lacking not only for halogens but also for all other substituents. This fact is reflected by in the zero values of $A_{C}.$ and $B_{C}.$ parameters.

The simultaneous estimation of the $\sigma_{NO_2}^{\ast}$ and $\alpha^{\ast}$ values is impossible since only the products of $\alpha^{\ast} \cdot \sigma_{X}^{\ast}$ type are present in eq. (6).

Fixing the value $\sigma_{NO_2}^{\ast}$ = 4.5 and including $\alpha^{\ast}$ into the list of parameters to be determined the final $\alpha^{\ast}$ value is established close to 1.8. But assuming $\sigma_{NO_2}^{\ast}$ = =3.55 the $\alpha^{\ast}$ value is established in the range 2.2-2.5.

If the parameters $\alpha^{\ast}$, $\mathcal{P}_{C}.$, $\alpha^{\ast}\sigma_{C}^{\ast}$ and $\alpha^{\ast}z_{C}^{\ast}.$ are estimated simultaneously then their final values are 2.47, 2.03, 2.01 and 1.01, respectively. The $\alpha^{\ast}z_{C}^{\ast}.$ value shows that $z_{C}^{\ast}$ and $z_{C}^{\ast}.$ values are close and therefore in the subsequent MLRA treatment the version $z_{C}^{\ast}.=z_{C}^{\ast}$ was always tested as well.

When calculating D values according to eq. (4) the parameters to be estimated being α and β, assuming $A_{C}.=0$, $B_{C}.=0$, A= -0.2, B=0.02 and $\mathcal{P}_{CH_3}$ = 3.94, eq.(6) transforms into the following expression:

$$\gamma_{X_1 X_2 X_3} \; \gamma_{X_4} - 0.2 \sum_{\substack{i < j \\ (i=1)}}^{2} \sum^{3} \gamma_{X_i} \gamma_{X_j} + 0.02 \, \gamma_{X_1} \gamma_{X_2} \gamma_{X_3} - \Delta \Delta H^{\neq}_{X_4 \cdot} - $$

$$- \Delta \Delta H^{\neq}_{CH_3 \cdot} = \left[2.3 R T_{mean} \, (\log n_{ij} - \log A_{ij}) + E_{ij} + \right.$$

$$\left. + 2.3 R T_{mean} \propto \right] \, \beta / (T_{mean} - \beta) + \propto^{\ast} \; \sigma^{\ast}_{C \cdot} \; \sum_{i=1}^{3} \sigma^{\ast}_{X_i} - $$

$$- \propto^{\ast} \; \sigma^{\ast}_{X_1 X_2 X_3 C} \; \sigma^{\ast}_{X_4} + \propto^{\ast} (z^{\ast}_{C \cdot} - z^{\ast}_{C}) \sum_{i < j}^{2} \sum^{3} \sigma^{\ast}_{X_i} \; \sigma^{\ast}_{X_j} + $$

$$+ \psi_{=} \, N_{=} + \psi_{CN} \, N_{CN} + \psi_{NO_2} \, N_{NO_2} + (\, \gamma_{C \cdot} - 3.94) \sum_{i=1}^{3} \gamma_{X_i}$$

$$(9)$$

γ with subscripts denote the contributions of the resonance of substituents X_i to the free-radical center $C \cdot$ $\gamma_{=}$ corresponds to the resonance contribution of double bond in unsaturated or aromatic systems, ψ_{CN} is the same for cyano, and ψ_{NO_2} - for nitro group. $N_{=}$, N_{CN} and N_{NO_2} denote the numbers of respective substituents connected with the $C \cdot$ center. In the case of several nitro groups connected with $C \cdot$ it was assumed that $N_{NO_2} = 1$ taking into account the steric hindrance of the resonance. For that reason only one of them is able to retain the coplanarity necessary for the resonance or there exists a propeller-like structure where the resonance interactions are weakened for all (two or three) nitro groups. Taking into account the limited reliability of the experimental E_{ij} and $\log A_{ij}$ values and the simplified model used one can consider any further refinement of the details on the steric hindrance of the resonance as sense-less.

The solution of eq. (9) with parameters β, $\propto$, $\propto^{\ast}$, $\sigma^{\ast}_{C \cdot}$, $(z^{\ast}_{C \cdot} - z^{\ast}_{C})$, $\psi_{=}$, ψ_{CN}, ψ_{NO_2} and $\gamma_{C \cdot}$ to be estimated leads to the use of the NLLS technique. The algorithm of the calculations according to eq. (9) was programmed as a function for the NLLS program. The set of reactions pro-

cessed according to eq. (9) is listed in Table 3. 96 values
for 76 reactions were used. After the exclusion of 17
points 79 points for 63 reactions remained, and assuming
$\sigma_{NO_2}^* = 4.5$ the following results were obtained:

$$1/\beta = 0.0000 \pm 0.00002$$
$$\alpha = 13.58 \pm 0.52$$
$$\alpha^* = 1.14 \pm 0.12$$
$$\sigma_{C^\cdot}^* = 1.52 \pm 0.14$$
$$\psi_= = -10.4 \pm 0.7$$
$$\psi_{CN} = -5.8 \pm 1.1$$
$$\psi_{NO_2} = -3.3 \pm 1.0$$
$$\rho_{C^\cdot} = 2.01 \pm 0.06$$
$$z_{C^\cdot}^* - z_C^* = -0.08 \pm 0.03$$

The standard deviation was 1.70 Kcal/mol. This data treat-
ment confirms the purely formal isokinetic behavior of the
reactions belonging to type (2) and the lack of the improve-
ment of description if one compares this result with the
one for the formal isoentropic case[3]. Therefore, taking
into account also the unwieldiness of eq. (9), further data
processing was performed according to eq. (6) where D_{ij} is
held according to eq. (3). At that the log A_o value can be
either included into the list of parameters to be estimated
or fixed at the previously estimated value (e.g. 14.64).

The above preliminary results made it possible to spe-
cify the form of the tested relationships using the MLRA
technique. The treatment was performed by two basic ver-
sions using either the $\Delta H^{\neq}_{X_1X_2X_3C^\cdot}$ values according to
eq. (1) or the D values expressed by eq. (6).

For the treatment of the $\Delta H^{\neq}_{X_1X_2X_3C^\cdot}$ values eq. (1)
was transformed into the following concrete expression:

$$\delta \Delta H^{\neq}_{X_1X_2X_3C^\cdot} = \Delta H^{\neq}_{X_1X_2X_3C^\cdot} - \Delta H^{\neq}_{CH_3^\cdot} - \sum_i \Delta H_{X_i} =$$
$$= \left\{ \rho_{C^\cdot} \right\} \sum_i \rho_{X_i} + \left\{ \alpha^* \sigma_{C^\cdot}^* \right\} \sum \sigma_{X_i}^* + \left\{ \alpha^* z_{C^\cdot}^* \right\} \sum_i \sum_{i<j} \sigma_{X_i}^* \sigma_{X_j}^* +$$

$$+\left\{\psi_{=}\right\} N_{=} +\left\{\psi_{CN}\right\} N_{CN} +\left\{\psi_{NO_2}\right\} N_{NO_2} \tag{10}$$

The values in braces are the coefficients to be determined.

The data treatment according to eq. (10) was based on the $\Delta H_R^{\neq}$. values calculated using two log A_o values – 14.64 (Table 1 in ref. 2) and 13.92 from the paper[3]. The set of $X_1X_2X_3C^{\cdot}$ radicals and respective $\delta\Delta H_{X_1X_2X_3C^{\cdot}}^{\neq}$ values is listed in Table 1 and the results of the data treatment according to eq. (10) at the $\sigma_{NO_2}^{\neq}$ values 3.55 and 4.48 in Table 2. At that the data were processed taking into account the point for $(C_6H_5)_3C^{\cdot}$ radical and with the omission of this point since the inclusion of it evidently distorts the value of the $\psi_{=}$ parameter. One can see from Table 2 that eq. (10) really well describes the $\delta\Delta H_{X_1X_2X_3C^{\cdot}}^{\neq}$ values while all initially set up coefficients are statistically significant. The $\psi_{C^{\cdot}}$ values in the range 2.03 – – 2.15 are compatible with the above calculated values from the data for methyl and its methyl derivatives. One can conclude once more the good applicability of the substituent constants to describe the substituent effects on the formation enthalpies of free radicals . Other determined coefficients are stable enough as well, except $\psi_{=}$ and, to less extent, $\alpha^{\neq}\sigma_{C^{\cdot}}^{\neq}$. . However, this is related to the exclusion of the point for $(C_6H_5)_3C^{\cdot}$ which have $N_{=}$ = 3 and the steric hindrance to resonance is evident. It is of interest to mention that in the case log A_o= 14.64 the point for $(C_6H_5)_3C^{\cdot}$ is excluded during the procedure of point exclusion but at log A_o = 13.92 this point remains in the final set and distorts the $\psi_{=}$ value. These results confirm the higher reliability of log A_o=14.64. Without taking into account the triphenyl methyl radical the $\psi_{=}$ and ψ_{CN} values are each indistinguishable from the other, and for ψ_{NO_2} the 1.5 – 2.5 times lower value is

is obtained reflecting the essential energetic effect of the resonance:
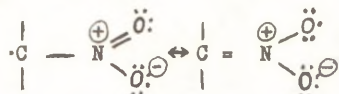
The standard deviation of the results for $\sigma^*_{NO_2} = 4.48$ is somewhat lower than for $\sigma^*_{NO_2} = 3.55$ and the first value may be preferred. A similar result was obtained when the formation enthalpies for the polyfunctional alkanes were processed[5].

Taking into account s values the comparison of the results for the two values of log A_o tested (14.64 and 13.92) are practically indistinguishable.

Assuming eq. (3) for D values eq. (6) was transformed into the following concrete expression:

$$Y = \varphi_{X_1 X_2 X_3 C} \, \varphi_{X_4} - 0.2 \sum_{\substack{i<j \\ (i=1)}}^{2} \sum_{i=1}^{3} \varphi_{X_i} \varphi_{X_j} + 0.2 \varphi_{X_1} \varphi_{X_2} \varphi_{X_3} -$$

$$- \Delta\Delta H^{\neq}_{X_4.} - \Delta\Delta H^{\neq}_{CH_3.} + 2.3 RT_{mean} (\log n_{ij} - \log A_{ij}) +$$

$$+ E_{ij} + 3.94 \sum_{i=1}^{3} \varphi_{X_i} = -\left\{ \log A_o \right\} 2.3 RT_{mean} + \left\{ \alpha^* \sigma^*_{C.} \right\} \sum_{i=1}^{3} \sigma^*_{X_i} -$$

$$- \left\{ \alpha^* \right\} \sigma^*_{X_1 X_2 X_3 C} \, \sigma^*_{X_4} + \left\{ \alpha^* (z^*_{C.} - z^*_C) \right\} \sum_{\substack{i<j \\ (i=1)}}^{2} \sum_{i=1}^{3} \sigma^*_{X_i} \sigma^*_{X_j} +$$

$$+ \left\{ \psi_= \right\} N_= + \left\{ \psi_{CN} \right\} N_{CN} + \left\{ \psi_{NO_2} \right\} N_{NO_2} + \left\{ \varphi_{C.} \right\} \sum_{i=1}^{3} \varphi_{X_i} \qquad (11)$$

In addition to the Y values to be correlated the following values were processed as well:

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$$Y_1 = Y + 2.3RT_{mean} \log A_o \tag{12}$$

$$Y_2 = Y + \alpha^{\neq} \sigma^{\neq}_{X_1X_2X_3C} \sigma^{\neq}_{X_4} \tag{13}$$

$$Y_3 = Y - \varphi_C \cdot \sum_{i=1}^{3} \varphi_{X_i} \tag{14}$$

$$Y_4 = Y + 2.3RT_{mean} \log A_o - \varphi_C \cdot \sum_{i=1}^{3} \varphi_{X_i} \tag{15}$$

$$Y_5 = Y + \alpha^{\neq} \sigma^{\neq}_{X_1X_2X_3C} \sigma^{\neq}_{X_4} - \varphi_C \cdot \sum_{i=1}^{3} \varphi_{X_i} \tag{16}$$

$$Y_6 = Y + 2.3RT_{mean} \log A_o + \alpha^{\neq} \sigma^{\neq}_{X_1X_2X_3C} \sigma^{\neq}_{X_4} - $$
$$- \varphi_C \cdot \sum_{i=1}^{3} \varphi_{X_i} \tag{17}$$

Processing the values $Y_1 \div Y_6$ the terms $\left\{ \log A_o \right\} \times$ $\times 2.3RT_{mean}$, $\left\{ \alpha^{\neq} \right\} \sigma^{\neq}_{X_1X_2X_3C} \sigma^{\neq}_{X_4}$, and $\left\{ \varphi_C \cdot \right\} \sum_{i=1}^{3} \varphi_{X_i}$ from the right-hand side in eq. (11) were omitted according to eqs. (12)-(17).

If the radicals-substituents X_4 also belong to the $X_1X_2X_3C$ type then $\Delta\Delta H^{\neq}_{X_4} = \Delta\Delta H^{\neq}_{CH_3}$ and the summation was performed over all the six substituents X_i. The $\Delta\Delta H^{\neq}_{X_4}$ and $\Delta\Delta H^{\neq}_{CH_3}$ values were obtained by corresponding MLRA data treatments according to equations of type (5) (see refs. 2,3). If a radical X_4 was lacking in the set of the most represented radicals then $\Delta\Delta H^{\neq}_{X_4}$ (denote $\Delta\Delta H^{\neq}_{R_i}$) was calculated according to equation:

$$\Delta\Delta H^{\neq}_{R_i} = D_{ij} + I_{R_iR_j} - \Delta\Delta H^{\neq}_{R_j} \tag{18}$$

where the subscript j denotes a free radical characterized by $\Delta\Delta H^{\neq}_{R_j}$ either as a result of the MLRA technique (primary value) or it had been obtained earlier by eq. (18).

An exception was made in the case of Y_4 and Y_6 values when $\triangle\triangle H^{\neq}_{X_4}$ for Cl, Br and I were calculated as the differences $\triangle\triangle H^{\neq}_{X_4} = \triangle H^{\neq}_{X_4} - \triangle H_{XH}$ while the $\triangle H^{\neq}_{X_4}$ values were obtained from the data treatment for 97 radicals[2].

The set of 96 Y values for 76 reactions listed in Table 3 was used for MLRA according to eqs. (11)-(17).

The scheme reflected by eqs. (11)-(17) was tested in four basic versions: assuming two alternative $\mathcal{G}^{*}_{NO_2}$ values (3.55 and 4.48) and both these versions with a single and two log A_o values to be estimated. One of them was related to the $X_1X_2X_3C - NO_2$ compounds and another to the remaining set. Within these four basic versions the zero values for the α^{*} ($z^{*}_C - z^{*}_C$) and $\mathcal{V}_{NO_2}$ parameters were fixed according to eqs. (11)-(17). As the Y and Y_1-Y_6 values do not belong to primary experimental values one must attach special importance to the absolute value of standard deviation (s) at the prescribed number of accounted points.

Beside the s value one can use some additional criteria proceeding from the constancy of solution (in the course of point exclusion and the accordance between α^{*} values calculated from the treatment of Y type values and determined from the formation enthalpies for polyfunctional alkanes[5].

It has to be mentioned that the number of excluded (or vice versa accounted) points is not a sufficiently adequate criterion since part of the reactions is represented by several parallel Y values[**] in the initial data set. Therefore as a more correct characteristic of the representativeness of the final data set is the number of different reactions (NRN) covered. Naturally the NRN value does not decrease if only part of the available parallel points is excluded.

In principle this characteristic may be also unsatisfactory. If the same reaction is represented by two sharply

[**] Parallel Y values arise either due to several parallel log A_{ij} and E_{ij} values or using alternative $\triangle\triangle H^{\neq}_{X_4}$ values.

different alternative Y (Y_1-Y_6) values   and both of them
are excluded with opposite signs of the corresponding devi-
ations then the average from these Y values is close to the
regression hypersurface. Particularly this case is realized
for the homolysis of $CH_2=CHCH_2-CH_2CH=CH_2$.

Thus, more preferable are the versions where the s value
is lowest at the prescribed number of points, the solution
is stable at the minimum number of excluded points or maxi-
mum number of reactions covered, and the α^* value   is
closest to the values obtained for the polyfunctional alka-
nes. Besides, as the results of the data treatment for the
Y values do not depend on the experimental ΔH_0^o values of
the initial compounds, both the agreement between the re-
sults of the $Y_{X_1X_2X_3C-X_4}$ values treatment in the coordi-
nates of eqs.(11)-(17) and the $\delta\Delta H_{X_1X_2X_3C}$ values treat-
ment according to eq.(10) serve as an important criterion.

Some results of the treatment of Y and Y_1 - Y_6 values
are listed in Table 4. Each version has four subversions
corresponding to different numbers of points included. The
first of them corresponds to initial data sets including
96 points for 76 reactions presented in Table 3. After the
exclusion of the most deviating points according to Stu-
dent's criterion the following relatively stable inter-
mediate results are listed. Therefore the comparison of the
results for the initial data set before the exclusion of
points is probably senseless (especially for α^* σ_C^* val-
ues). The last subversion corresponds to the final result
when there remain no significantly deviating points.

Proceeding from the indicated criteria one can draw the
following conclusions proceeding from the results of data
treatment according to eqs. (11) - (17).

Processing the Y values all the parameters listed are
statistically significant if a single (not two) universal
log A_o value is assumed. The results for $\sigma_{NO_2}^*$ = 3.55 and
$\sigma_{NO_2}^*$ =4.5 are practically indistinguishable from the

position of s values. The $\alpha^{\mathbf{x}}$ values are very close (1.64-
-1.53 and 1.37-1.23) to the values from the data of poly-
functional alkanes (1.34-1.65 and 1.39-1.19)[5]. At that
relatively constant results (versions 2.1-2.3 and 3.1-3.3
in Table 4) for the Y values are compared.

If the special log A_{oNO_2} parameter is drawn for nitro
compounds the different log A_o and log A_{oNO_2} values are
obtained only assuming $\psi_{NO_2} = 0$. Hence a question may
arise whether the special log A_{oNO_2} or the resonance contri-
bution ψ_{NO_2} should be introduced for nitro compounds. How-
ever, the absolute value for ψ_{NO_2} is even increasing and
not approaching zero as hoped if ψ_{NO_2}, log A_o and log A_{oNO_2}
parameters are estimated simultaneously. At that s is not
lowered essentially. Assuming $\psi_{NO_2} = 0$ the comparable
results from the position of s values are obtained both
for the universal log A_o and separate preexponential factors.
Consequently it is (statistically) groundless to use the
special log A_{oNO_2} value for the $C-NO_2$ bond fission reactions.

From the viewpoint of the minimum s value one can con-
clude that the best version is obtained as a result of the
treatment of Y_2 values according to eq. (13) if $\sigma^{\mathbf{x}}_{NO_2} = 4.5$
and $\alpha^{\mathbf{x}} = 1.37$ kcal/mol. Thus, the solution become steady
after the exclusion of seven points for five reactions, and
s was equal to 2.32 kcal/mol (log A_o = 14.61). At the end
of the procedure when the exclusion of significantly devi-
ating points was finished 73 points for 59 reactions re-
mained which had the corresponding standard deviation equal-
ing 1.39 kcal/mol (version 4 in Table 4). This result is
well compatible with the result obtained according to eq.(10)
listed in Table 2, with the exception of the ψ_{NO_2} param-
eter (values -3.0 ± 0.6 and -5.3 ± 0.9 kcal/mol, respectively).

A similar version for $\sigma^{\mathbf{x}}_{NO_2} = 3.55$ (version 5 in Table
4) is unique because the ψ_{NO_2} parameter is excluded as
statistically insignificant (for the same reason $\alpha^{\mathbf{x}}(z^{\mathbf{x}}_{c\cdot} - z^{\mathbf{x}}_c)$

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is excluded as well). However, this result is likewise not compatible with the treatment according to eq. (10) with respect to the ψ_{NO_2} value estimated within the range $-3.1 \div -4.5$ kcal/mol. Fixing $\psi_{NO_2} = 0$ the standard deviation for the use of eq. (10) is enhanced approximately by 0.3 kcal/mol and the φ_{C}. value somewhat drops becoming equal to 2.00 ± 0.08 (version 9 in Table 2). One can conclude from these results that the assumption $\psi_{NO_2} = 0$ is scarcely justified.

The values obtained for the coefficient $\alpha^*(z_{C}^* - z_{C}^*)$ are in all versions different from zero ($-0.05 \div -0.10$ kcal/mole) if the special log A_{ONO_2} for the $C-NO_2$ bond homolysis was not included. Using the $\sigma_{NO_2}^* = 3.55$ value the $\alpha^*(z_{C}^* - z_{C}^*)$ coefficient is equal either to $-0.13 \div -0.15$ or it is excluded as a statistically insignificant parameter (at the fixed $\alpha^* = 2.2$ kcal/mol).

The value of the φ_{C}. parameter obtained using eqs. (11)-(17) is compatible with the values obtained proceeding from eqs. (8) and (10).

The compatibility between the result of the best version from the viewpoint of s for the Y_2 values according to eq. (13) and the $\delta \Delta H_{R}^{\neq}$. values expressed by eq. (10) is observed likewise with respect to the $\alpha^* \sigma_{C}^*$. , $\psi_=$ and ψ_{CN} parameters. At the same time one must consider that ψ_{CN} has been calculated only on the ground of two points using eq.(10), and according to 3-4 points using the scheme (11).

Taking into account the results obtained for the treatment of the formation enthalpies of polyfunctional alkanes[5], and the results of the present study one can prefer the value $\sigma_{NO_2}^* = 4.5$.

The general compatibility between the results for the treatment of the $\delta \Delta H_{X_1 X_2 X_3 C}^{\neq}$. values in the coordinates of eq. (10) and the scheme reflected in eqs. (11)-(17) was mentioned already. However, these two approaches are not always equivalent to one another from the viewpoint of the

reliability for the special cases. Discrepancies between the experimental and calculated ΔH_0^0 values for respective initial compounds are certainly one of the real reasons for arising these disagreements. Before corresponding examples are compared a correction may be inserted taking into account some real difference in the formulation of initial postulates. The right-hand side of eq. (10) includes the $\alpha^* z_C^* \cdot \sum\limits_{i}^{2} \sum\limits_{<j}^{3} \sigma_{X_i}^* \sigma_{X_j}^*$ term and the $\alpha^*(z_C^* \cdot - z_C^*) \sum \sum \sigma_{X_i}^* \sigma_{X_j}^*$ contribution is present in eq. (11). One can define a certain type of radicals $(X_1 X_2 X_3 C^\cdot)$ for which the equalling of the $\alpha^*(z_C^* \cdot - z_C^*)$ factor to zero is not an adequate simple reflection of the equality $z_C^* \cdot = z_C^*$. This is due to the nonadditivity of the inductive influence for halogen atoms connected with the same sp^3 carbon atom. If this nonadditivity occuring in the initial state is lacking in a free radical (eq.(10) namely reflects such an assumption) then in the cases where X_1 and X_2 are halogen atoms, and X_3 nitro group or some other "normal" polar substituent, a correction term ΔZ (see eq. (7)) must be added to the right-hand side of eq. (11) according to the following expression:

$$\Delta Z = 0.0275 \, \alpha^* \, \sigma_{X_3}^* \left[2^{(4-n_{X_1})} + 2^{(4-n_{X_2})} \right] / 2$$

If $X_3 = NO_2$, $\sigma_{NO_2}^* = 4.48$, $\alpha^* = 1.37$, the ΔZ

value varies from 0.3 kcal/mol for $\cdot CI_2 NO_2$ to 2.7 kcal/mol for $\cdot CF_2 NO_2$.

In all other cases when both X_1 and X_2 are not halogen atoms or X_3 does not belong to the "normal" substituents (i.e. not halogen-like), $\Delta Z = 0$.

We should note once more that the introduction of the correction ΔZ is not a doubtless procedure. It is justified only if the interaction of halogen atoms with "normal" electronegative substituents via the $C^\cdot$ center is additive and at the same time the analogous interaction via sp^3 carbon atom is nonadditive. If one postulates the indicated

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interaction via the C° center nonadditive and subjected to the same relationships as the interaction via the sp^3 carbon atom there is no reason for introducing the correction ΔZ.

For version 6 of Table 4 the correction ΔZ was introduced. Standard deviation s remains approximately on the same level as in the similar version 2 when ΔZ was not introduced. One can consider some decrease in deviations for the corresponding points from dependence (11) for the Y_2 values (see Table 5) as an indirect indication in favor of introducing this correction. However, there are other origins of even larger uncertainties.

The accordance between the results of the data treatment in the coordinates of eq. (10) and eqs. (11)-(17) shows the sufficient reliability of the parametrization for the influence of substituent effects on the $\Delta H_R^{\neq}$. values of substituted methyl radicals. One can extract some additional information with respect to this topic from the comparison of the deviations for separate radicals and the corresponding homolysis reactions observed using eqs.(10) and (11)--(17), respectively. It is meaningful to compare these deviations in the cases when at least one of them is large. If these deviations are caused by inaccuracies in the ΔH_0^O values the uncertainties in respective experimental values are reflected by larger deviations of the corresponding points for the data treatment according to eq. (10). At the same time inaccuracies in the estimates of the intramolecular interactions for the initial state and to the same degree uncertainties in the $\Delta \Delta H_{X_4}^{\neq}$. values must be reflected by analogous deviations when[4] using eqs.(11)-(17).

The corresponding concrete data are listed in Table 5 (deviations for the estimates from the experimental values in kcal/mol). One can see that for 7 cases out of 9 processed both by eq. (10) and the values according to eqs. (11) and (13) a large deviation is observed only within the framework of one scheme of the data treatment. This confirms the reliability of the initial D values for respective

reactions. One must suppose larger uncertainty in the experimental values in four cases from the indicated seven ones and in the calculative estimations of the ΔH_0^o values in three cases.

The triphenyl methyl radical represents evidently the case of the steric hindrance to the resonance between phenyl groups and the $C^{\cdot}$ center. There remains only the homolysis of $BrCH_2$-Br serving as a single origin for the estimation of $\Delta H^{\neq}_{BrCH_2}$ to be probably characterized by a roughly uncertain D value (in the present case the experimental and calculated ΔH_0^o values coincide). There remains some doubt with respect to other compounds connected with significant deviations when eqs.(11)-(17) are used _ (see Table 3). One may try to explain some of them by the ΔZ correction term but generally the points for fluorine-containing compounds are strongly deviating. For instance for the $CF_3\cdot$ free radical one obtains the following data (in kcal/mol) if log A_0=14.0 is assumed:

Homolyzing compound	D	$I_{R_iR_j}$	$\Delta\Delta H^{\neq}_{CF_3}.$
CF_3-Br	68.0	17.8	49.2
CF_3-I	43.0	15.8	34.3
CF_3-CF_3	61.3	12.9	37.1
	70.4		41.7

The estimated $\Delta\Delta H^{\neq}_{CF_3}$ value is equal to 49.1 kcal/mol[xx] proceeding from the parametrization according to eq.(11) of the Y_2 values ($\sigma^{\neq}_{NO_2}$ = 4.5), and 48.6[xx] proceeding from the treatment according to eq. (10) (version 8.4 in Table 2). Proceeding from the above one must consider the D values for CF_3-I and CF_3-CF_3 as roughly erroneous.

On the other hand it is not fully clear how reliable is

[xx] At that the contribution of 15.0 kcal/mol caused by threefold double interaction between F atoms in CHF_3 is considered.

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the ΔH_0^o estimate for C_2F_6 indirectly used for the calcula-
tion of the interaction energy $I_{R_iR_j}$. So the experimental
values ΔH_0^o for CF_3H are ranging from -168.4 to -160.9
kcal/mol[6] and for C_2F_6 there are two values: -306.0 and
-320.0 kcal/mol (for refs. see paper[5]). Applying these val-
ues the interaction energy $I_{CF_3-CF_3}$ may be estimated in the
range from 1.8 up to 30.8 kcal/mol (according to the ex-
pression $I_{R_iR_j} = \Delta H_{R_iR_j} - \Delta H_{R_i} - \Delta H_{R_j}$), and the $\Delta\Delta H_{CF_3}^{\neq}$.
value from 31.6 to 50.6 kcal/mol. All $\Delta\Delta H_{CF_3}^{\neq}$. values cited
lie in this range. Consequently an additional check of the
experimental values is extremely needed in this case espe-
cially taking into account the large discrepancies between
the two alternative $D_{CF_3-CF_3}$ values.

It has to be mentioned, however, that this divergence
between the parallel $D_{CF_3-CF_3}$ values is obtained artifi-
cially.

Arrhenius parameters for this reaction are from the
same author[7,8] while the activation energy is equal to
94.4 kcal/mol in both papers, and the log A value is cor-
rected from 18.22[7] to 17.62[8]. The temperature range is
approximately 1300-1600°K in both cases. However in the
handbook[9] the temperature range is presented erroneously
1573-1873°K and therefore T_{mean} = 1720°K. Owing to this
enhanced temperature the D value obtains a lower value
still. Using T_{mean} = 1450°K for the calculation of both D
values the discrepancy is not very large (66.4 and 70.4
kcal/mol). This instance indicates the limitations of the
used model at temperatures significantly differing from the
general mean temperature range 700-800°K (see ref.1).

One can conclude that the parametrization of the equa-
tion type (10) reflects the influence of substituent effects
on the formation enthalpies of the free radicals $X_1X_2X_3C^{\cdot}$
reliably enough. The results are unique for the $\rho_{C^{\cdot}}$, $\alpha^* \sigma_{C^{\cdot}}^*$,
$\alpha^* z_C^*$. and $\psi_=$ values. The ψ_{CN} value determined by two
points proceeding from eq. (10) and by four or three points
within eqs. (11)-(17) is less defined. It is natural for

this limited basic data set. The identity of the ψ_{CN} and $\gamma_=$ values processing the data according to eq. (10) draws by the simplicity of the representation of the resonance contribution especially if the extrapolation of the $\psi_= = -9.2$ kcal/mole value to all other $\overline{\pi}$-electron systems except nitro group is accepted.

The disagreement between the ψ_{NO_2} parameter values obtained using eq. (10) on the one hand, and eqs. (11)-(17) on the other hand, assuming $\sigma^{*}_{NO_2} = 4.5$ was already mentioned. The ψ_{NO_2} values are in the ranges $-5.3 \div -6.2$ and $-2.1 \div -3.9$ kcal/mol, respectively. At that the s value for the treatment according to eq. (10) is raised by 0.7-0.8 kcal/mol if $\psi_{NO_2} = 0$ is assumed when compared with the version with ψ_{NO_2} included into the set of parameters to be estimated.(see versions 8 and 10 in Table 2).

Assuming $\sigma^{*}_{NO_2} = 3.55$ the ψ_{NO_2} values for the treatment according to eq. (10) varies in the range $-3.1 \div -4.5$ kcal/mol and the assumption that $\psi_{NO_2} = 0$ enhances the s value insignificantly (see version 9 in Table 2). The scheme expressed by eqs. (11) - (17) at $\sigma^{*}_{NO_2} = 3.55$ leads to the ψ_{NO_2} values from -2.7 to -4.4 kcal/mol, which agrees well with the results obtained by using eq. (10). But supposing that $\alpha^{*} = 2.2$ kcal/mol and $\rho_{C.} = 2.20$ the ψ_{NO_2} value becomes close to zero (from -1.0 to -1.3 kcal/mol) or zero (the final $\rho_{C.}$ value is equal to 2.10). Besides, the $\alpha^{*}(z^{*}_{C.} - z^{*}_{C})$ coefficient is also excluded as statistically insignificant.

One can see from the above that although the assumption that $\sigma^{*}_{NO_2} = 3.55$ allows to decrease the number of parameters for the scheme reflected in eqs. (11) - (17) by two but the standard deviation s is at the some increased.

A more thorough investigation of the formal reason for the appearance of significant ψ_{NO_2} contribution leads to the conclusion that ψ_{NO_2} is necessary to describe the Y_2

values characterizing the homolysis of CCl_3-NO_2, $CH_3CCl_2-NO_2$ and $C_2H_5CCl_2-NO_2$ as well. If it is assumed that $\Psi_{NO_2}=0$ the negative deviations for the estimates compared to the experimental values in the order of 4-7 kcal/mol for the indicated compounds are observed ($\sigma^{\ast}_{NO_2}$ = 3.55 and $\alpha^{\ast}$ = = 2.2 kcal/mol are assumed). However, assuming $\sigma^{\ast}_{NO_2}$ = =4.5 the mentioned effect is not observed (see Table 3 as well).

The results of the data treatment in the coordinates of eqs. (11)-(17) allows, in principle, to select between significantly different experimental Y values. One must consider those values more correct which correspond to the minimum deviations of the respective points from the hypersurface determined by the indicated equations (see Table 3). As one can see from Table 3 the values of deviations Δ for different versions of the treatment are rather close and essential distinctions are not observed. Taking into account the degree of reliability of the initial experimental data, and the conventionality for both the formation enthalpies of free radicals and the activation energies D one can consider the results of the parametrizations for eqs. (10) and (11) to be quite satisfactory. One can suppose version 4.3 in Table 2 for eq. (10) and version 4.3 in Table 4 for eq. (11) to be conventionally recommended values of the parameters. However, other combinations of parameters are apparently acceptable as well, especially if is assumed that log A_o = 14.64. As was shown in ref. 3 the inclusion of the log A_o value into the set of the parameters to be estimated does not improve the precision of description and leads only to some drop in the log A_o values (close to 14). However, higher log A_o values are likely to be preferable[2].

Table 1

The Set of Free Radicals of the $X_1X_2X_3C^{\cdot}$ Type for MLRA Treatment in the Coordinates of Eq.(10) of the Values:

$$\delta \Delta H^{\neq}_{X_1X_2X_3C^{\cdot}} = \Delta H^{\neq}_{X_1X_2X_3C^{\cdot}} - \Delta H^{\neq}_{CH_3^{\cdot}} - \sum_i \Delta H_{X_i}$$

The deviations from the regression hypersurfaces at the values of the coefficients for eq.(10) after the exclusion of significantly deviating points for versions 4.3 and 8.4 in Table 2 are presented in columns entitled Δ . + and - in columns 5 and 8 denote the points included and excluded from the final data sets, respectively. The $\delta \Delta H^{\neq}_{X_1X_2X_3C^{\cdot}}$ and Δ values are represented in kcal/mol.

No	Free Radical $X_1X_2X_3C^{\cdot}$	$\log A_0 = 14.64$			$\log A_0 = 13.92$		
		$\delta \Delta H^{\neq}_{X_1X_2X_3C^{\cdot}}$	Δ	The status of point	$\delta \Delta H^{\neq}_{X_1X_2X_3C^{\cdot}}$	Δ	The status of point
1	2	3	4	5	6	7	8
1.	$CH_3CH_2\cdot$	9.2	−0.8	+	7.1	1.4	+
2.	$C_2H_5CH_2\cdot$	5.1	1.7	+	3.4	3.3	−
3.	$(CH_3)_2CH^{\cdot}$	17.0	−0.1	+	15.6	1.3	+
4.	$(CH_3)_3C^{\cdot}$	26.2	−0.8	+	26.1	−0.8	+
5.	$C_2H_5(CH_3)CH^{\cdot}$	14.3	0.9	+	13.8	1.4	+
6.	$C_2H_5(CH_3)_2C^{\cdot}$	23.2	0.5	+	24.4	−0.7	+
7.	$CH_2 = CHCH_2\cdot$	−1.5	0.6	+	−1.6	1.0	+
8.	$CH_2=CH(CH_3)CH^{\cdot}$	6.6	1.0	+	7.3	0.5	+
9.	$CH_2=CH(CH_3)_2C^{\cdot}$	14.7	1.4	+	15.4	0.9	+
10.	$ClCH_2\cdot$	18.4	−2.7	+	18.0	−2.7	+
11.	$BrCH_2\cdot$	20.8	−6.3	−	20.4	−6.2	−
12.	$NCCH_2\cdot$	10.1	−1.0	+	10.2	−1.0	+
13.	$C_6H_5CH_2\cdot$	−1.1	−0.7	+	−0.9	−0.6	+
14.	$Cl_2CH^{\cdot}$	30.6	0.7	+	30.6	0.0	+
15.	$F_3C^{\cdot}$	52.3[x]	−0.1	+	51.6[x]	−0.5	+
16.	$Cl_3C^{\cdot}$	49.4	−2.4	+	49.6	−3.7	−
17.	$Br_3C^{\cdot}$	40.7	2.7	+	41.1	1.3	+

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Table 1 continued

1	2	3	4	5	6	7	8
18.	$C_6H_5(CH_3)CH^{\bullet}$	9.1	-2.4	+	9.0	-2.0	+
19.	$(NO_2)_2CH^{\bullet}$	50.3	-3.8	-	50.8	-4.1	-
20.	$(NO_2)_2FC^{\bullet}$	79.4	-1.7	+	79.8	-1.6	+
21.	$(NO_2)_2ClC^{\bullet}$	73.8	0.3	+	74.4	0.2	+
22.	$(NO_2)_2BrC^{\bullet}$	67.9	4.6	-	68.5	4.5	-
23.	$(NO_2)_3C^{\bullet}$	89.4	-1.6	+	89.9	-1.4	+
24.	$(C_6H_5)_3C^{\bullet}$	7.1	-11.9	-	5.4	-9.3	-
25.	$ClCH_2CH_2C^{\bullet}$	13.2	-5.0	-	13.9	-5.8	-
26.	$CH_3(NO_2)CH^{\bullet}$	23.7	0.0	+	24.0	-0.1	+
27.	$CH_3(NO_2)_2C^{\bullet}$	55.0	0.0	+	55.4	-0.2	+
28.	$(NO_2)_2CF(NO_2)_2C^{\bullet}$	80.4	-0.1	+	81.2	-0.1	+
29.	$(NO_2)_3C(NO_2)_2C^{\bullet}$	82.4	1.7	+	83.1	1.8	+
30.	$C_2H_5(NO_2)CH^{\bullet}$	22.5	-0.5	+	21.9	0.3	+
31.	$NC(CH_3)_2C^{\bullet}$	25.0	1.0	+	25.0	1.0	+
32.	$(CH_3)_2(NO_2)C^{\bullet}$	34.3	-2.1	+	34.8	-2.4	+
33.	$C_2H_5(NO_2)_2C^{\bullet}$	50.7	2.6	+	51.2	2.3	+
34.	$C_3H_7(NO_2)CH^{\bullet}$	20.7	1.4	+	21.0	1.3	+

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[*] Proceeding from $\Delta H^{\neq}_{CF_3}$. calculated using the D_{CF_3} values.

[**] (+) denotes inclusion,
(-) the exclusion of the point

Table 2

The Results of Processing the $\delta\Delta H^{\neq}_{X_1X_2X_3C\cdot}$ Values from Table 1 in the
Coordinates of Eq. (10).

NE – the number of considered equations (points)
s – standard deviation in kcal/mol
All coefficients are in kcal/mol

No	$\log A_o$	$\sigma^*_{NO_2}$	$\gamma_{C\cdot}$	$\alpha^* \sigma^*_{C\cdot}$	$\alpha^* z^*_{C\cdot}$	$\gamma_=$	γ_{CN}	γ_{NO_2}	NE	s
1	2	3	4	5	6	7	8	9	10	11
1.1	14.64	3.55	2.03 ± 0.13	2.14 ± 0.29	0.75 ± 0.07	-6.8 ± 0.9	-9.3 ± 2.2	-3.7 ± 1.6	34	2.96
1.2	14.64	3.55	2.05 ± 0.11	2.06 ± 0.24	0.79 ± 0.06	-6.8 ± 0.8	-9.1 ± 1.9	-3.4 ± 1.3	32	2.48
1.3	14.64	3.55	2.13 ± 0.08	1.87 ± 0.18	0.82 ± 0.04	-9.5 ± 0.9	-9.3 ± 1.3	-4.2 ± 1.0	29	1.77
1.4	14.64	3.55	2.11 ± 0.07	2.03 ± 0.16	0.77 ± 0.04	-9.5 ± 0.8	-9.6 ± 1.1	-4.5 ± 0.8	27	1.48
2.1	14.64	3.55	2.10 ± 0.12	2.02 ± 0.28	0.77 ± 0.06	-9.4 ± 1.4	-9.5 ± 2.1	-4.0 ± 1.5	33	2.75
2.2	14.64	3.55	2.12 ± 0.09	1.93 ± 0.22	0.80 ± 0.05	-9.5 ± 1.1	-9.3 ± 1.6	-3.7 ± 1.2	31	2.17
2.3	14.64	3.55	2.11 ± 0.07	2.03 ± 0.16	0.77 ± 0.04	-9.5 ± 0.8	-9.6 ± 1.1	-4.5 ± 0.8	27	1.48
3.1	14.64	4.48	2.05 ± 0.11	2.10 ± 0.26	0.45 ± 0.04	-6.8 ± 0.8	-9.3 ± 2.0	-6.0 ± 1.5	34	2.69
3.2	14.64	4.48	2.04 ± 0.10	2.03 ± 0.23	0.46 ± 0.04	-6.7 ± 0.7	-9.0 ± 1.7	-5.6 ± 1.3	32	2.32
3.3	14.64	4.48	2.13 ± 0.08	1.89 ± 0.18	0.49 ± 0.03	-9.5 ± 0.9	-9.3 ± 1.3	-5.7 ± 1.0	30	1.75
3.4	14.64	4.48	2.15 ± 0.07	1.83 ± 0.16	0.50 ± 0.03	-9.6 ± 0.8	-9.3 ± 1.2	-6.1 ± 0.9	29	1.62
4.1	14.64	4.48	2.13 ± 0.11	1.97 ± 0.24	0.47 ± 0.04	-9.6 ± 1.2	-9.5 ± 1.8	-6.2 ± 1.3	33	2.41
4.2	14.64	4.48	2.12 ± 0.09	1.90 ± 0.20	0.48 ± 0.03	-9.5 ± 1.0	-9.2 ± 1.5	-5.8 ± 1.1	31	1.94

Table 2 continued

1	2	3	4	5	6	7	8	9	10	11
4.3	14.64	4.48	2.15 ± 0.07	1.83 ± 0.16	0.50 ± 0.03	-9.6 ± 0.8	-9.3 ± 1.2	-6.1 ± 0.9	29	1.62
5.1	13.92	3.55	2.03 ± 0.12	2.14 ± 0.29	0.77 ± 0.06	-7.1 ± 0.9	-9.2 ± 2.2	-3.5 ± 1.6	34	2.92
5.2	13.92	3.55	2.03 ± 0.09	2.06 ± 0.22	0.81 ± 0.05	-7.0 ± 0.7	-8.9 ± 1.7	-3.1 ± 1.2	31	2.23
5.3	13.92	3.55	2.04 ± 0.08	2.03 ± 0.20	0.79 ± 0.05	-7.0 ± 0.6	-8.9 ± 1.5	-3.5 ± 1.1	29	1.96
6.1	13.92	3.55	2.08 ± 0.12	2.05 ± 0.28	0.78 ± 0.06	-9.0 ± 1.4	-9.4 ± 2.1	-3.7 ± 1.5	33	2.83
6.2	13.92	3.55	2.08 ± 0.09	1.96 ± 0.21	0.82 ± 0.05	-9.0 ± 1.0	-9.1 ± 1.5	-3.3 ± 1.1	30	2.06
6.3	13.92	3.55	2.09 ± 0.08	1.94 ± 0.17	0.80 ± 0.04	-9.0 ± 0.9	-9.1 ± 1.3	-3.8 ± 1.0	28	1.72
7.1	13.92	4.48	2.05 ± 0.10	2.10 ± 0.26	0.46 ± 0.04	-7.1 ± 0.8	-9.2 ± 2.0	-5.8 ± 1.4	34	2.63
7.2	13.92	4.48	2.04 ± 0.09	2.03 ± 0.22	0.47 ± 0.04	-7.0 ± 0.7	-8.9 ± 1.7	-5.3 ± 1.2	32	2.21
7.3	13.92	4.48	2.05 ± 0.09	2.02 ± 0.20	0.48 ± 0.03	-7.0 ± 0.6	-8.9 ± 1.6	-5.3 ± 1.1	31	2.07
8.1	13.92	4.48	2.11 ± 0.11	2.00 ± 0.25	0.47 ± 0.04	-9.2 ± 1.3	-9.4 ± 1.9	-5.9 ± 1.4	33	2.48
8.2	13.92	4.48	2.10 ± 0.09	1.93 ± 0.20	0.48 ± 0.03	-9.1 ± 1.0	-9.1 ± 1.5	-5.5 ± 1.1	31	2.01
8.3	13.92	4.48	2.13 ± 0.08	1.87 ± 0.17	0.50 ± 0.03	-9.2 ± 0.9	-9.1 ± 1.3	-5.8 ± 1.0	29	1.71
8.4	13.92	4.48	2.14 ± 0.07	1.72 ± 0.16	0.52 ± 0.03	-9.2 ± 0.8	-8.8 ± 1.1	-5.3 ± 0.9	27	1.48
9.1	13.92	3.55	1.97 ± 0.13	2.04 ± 0.31	0.72 ± 0.06	-8.3 ± 1.5	-8.3 ± 2.3	0.0	33	3.07
9.2	13.92	3.55	1.99 ± 0.10	1.96 ± 0.24	0.77 ± 0.05	-8.4 ± 1.2	-8.1 ± 1.7	0.0	30	2.36
9.3	13.92	3.55	2.00 ± 0.08	1.87 ± 0.21	0.76 ± 0.05	-8.4 ± 1.0	-8.0 ± 1.5	0.0	27	1.96
10.1	13.92	4.48	2.01 ± 0.14	1.79 ± 0.31	0.44 ± 0.05	-8.4 ± 1.6	-7.7 ± 2.3	0.0	33	3.19
10.2	13.92	4.48	2.00 ± 0.12	1.74 ± 0.27	0.45 ± 0.04	-8.3 ± 1.4	-7.5 ± 2.1	0.0	31	2.78
10.3	13.92	4.48	2.02 ± 0.10	1.63 ± 0.25	0.47 ± 0.04	-8.4 ± 1.2	-7.3 ± 1.8	0.0	29	2.40
10.4	13.92	4.48	2.03 ± 0.09	1.69 ± 0.22	0.46 ± 0.04	-8.5 ± 1.1	-7.6 ± 1.6	0.0	27	2.10
10.5	13.92	4.48	2.05 ± 0.07	1.80 ± 0.17	0.44 ± 0.03	-8.7 ± 0.8	-8.2 ± 1.2	0.0	25	1.66

Table 3

The Set of Reactions, Y values for MLRA in the
Coordinates of Eqn. (11), and Deviations Δ from the
Regression Hypersurface for the Coefficients after the
Exclusion of Significantly Deviating Points for Versions
1-6 in Table 4. Y and Δ in kcal/mol

NO	Homolyzing compound	Y	Δ for Versions in Table 5					
			1	2	3	4	5	6
1	2	3	4	5	6	7	8	9
0	$CH_2=C(CH_3)CH_2-H$	-71.4	4.9	5.2	5.3	5.4	5.4	5.4
1	$NCCH_2 - H$	-66.6	-0.5	0.4	0.7	0.8	0.7	0.8
2	$C_6H_5CH_2 - H$	-67.1	1.1	1.4	1.6	1.7	1.7	1.7
3	"	-69.3	0.0	0.4	0.5	0.7	0.7	0.7
4	$2-CH_3-C_6H_4CH_2-H$	-74.7	5.4	5.7	5.9	6.1	6.1	6.0
5	$3-CH_3-C_6H_4CH_2-H$	-73.1	2.5	2.9	3.1	3.2	3.2	3.2
6	$4-CH_3-C_6H_4CH_2-H$	-75.1	3.8	4.3	4.4	4.6	4.6	4.6
7	"	-84.1	4.6	5.3	5.6	5.8	5.7	5.7
8	"	-60.8	4.8	4.8	4.8	4.9	5.0	4.9
9	$ClCH_2CH_2-Cl$	-37.0	-1.6	-0.5	-0.2	0.1	-0.8	-0.1
10	$BrCH_2-Br$	-43.4	-7.1	-6.0	-5.1	-4.8	-4.9	-5.2
11	Br_2CH-Br	-24.2	-2.7	-2.7	-2.0	-1.4	-1.9	-2.0
12	Br_3C-Br	-6.6	1.3	0.2	0.7	1.6	0.8	0.7
13	CF_3-Br	-16.3	-1.0	-1.9	-1.3	-0.1	-1.2	-1.2
14	CH_2Cl-Br	-43.5	-4.7	-3.8	-2.9	-2.6	-2.7	-3.0
15	$CHCl_2-Br$	-25.0	-0.1	-0.2	0.4	1.0	0.5	0.4
16	CCl_3-Br	-5.3	1.3	0.1	0.6	1.5	0.7	0.6
17	CF_3-I	-6.5	15.0	13.4	13.2	14.7	13.3	13.7
18	$C_6H_5CH_2-C_3H_7$	-54.1	0.1	0.1	0.0	0.1	0.1	0.1
19	"	-50.4	-1.9	-1.9	-2.0	-2.0	-1.9	-2.0
20	$(C_6H_5)_3C - H$	-56.6	-5.6	-8.6	-9.6	-10.0	-9.4	-9.8
21	$NCCH_2-CH_3$	-52.3	-1.4	-0.9	-0.6	-0.6	-0.7	-0.6
22	$NC(CH_3)_2C-CH_3$	-34.2	4.4	4.4	4.3	4.2	4.1	4.2
23	$C_6H_5CH_2-CH(CH_3)_2$	-52.0	-3.4	-3.2	-3.4	-3.4	-3.4	-3.4
24	$CH_2=CHCH_2-C(CH_3)_3$	-45.2	1.4	1.3	0.9	0.8	0.9	0.9

Table 3 continued

1	2	3	4	5	6	7	8	9
25	$CH_2=CHCH_2-CH_2CH=CH_2$	-54.9	-2.3	-3.9	-4.4	-4.6	-4.4	-4.5
26	"	-71.6	6.9	5.6	5.1	5.0	5.2	5.1
27	$CH_2=CHCH_2-Cl$	-62.1	1.1	1.3	1.6	1.4	1.3	1.4
28	$CH_2=CHCH_2-Br$	-54.2	1.2	1.1	1.4	1.1	1.1	1.1
29	$CH_2=CHCH_2-I$	-61.1	1.8	2.0	1.9	2.0	1.6	2.0
30	$C_6H_5CH_2-Br$	-55.9	0.7	0.7	1.0	0.7	0.7	0.7
31	$CF_2NO_2-NO_2$	-0.8	-5.4	-5.1	-7.2	-5.6	-7.7	-3.2
32	$CH(NO_2)_2-NO_2$	-11.1	-1.9	-1.3	-2.0	-1.9	-2.5	-2.0
33	$CF(NO_2)_2-NO_2$	-0.6	-5.1	-4.7	-6.8	-5.2	-6.8	-5.3
34	$CCl(NO_2)_2-NO_2$	-3.4	1.1	1.4	-0.2	0.8	-0.2	0.7
35	$CBr(NO_2)_2-NO_2$	-4.6	2.2	2.6	0.6	1.9	0.5	1.9
36	$C(NO_2)_3-NO_2$	-7.8	-1.1	-0.5	-1.4	-1.0	-1.4	-1.1
37	"	1.0	-2.2	-1.9	-2.8	-2.4	-2.8	-2.5
38	$CH_3CHNO_2-NO_2$	-16.0	-0.6	0.0	-0.5	-0.4	0.3	-0.7
39	$CH_3C(NO_2)_2-NO_2$	-4.7	0.6	1.0	0.1	0.2	-0.4	0.1
40	$(NO_2CFC(NO_2)_2-NO_2$	-9.9	0.6	1.1	0.0	0.8	0.1	0.7
41	$(NO_2)_3CC(NO_2)_2-NO_2$	-9.8	0.2	0.7	0.2	0.4	0.0	0.4
42	$C_2H_5CH(NO_2)-NO_2$	-18.4	-1.0	-0.2	-0.8	-0.7	0.1	-1.0
43	$(CH_3)_2C(NO_2)-NO_2$	-5.6	0.0	0.4	-0.4	-0.3	0.4	-0.7
44	$C_2H_5C(NO_2)_2-NO_2$	-6.0	0.6	1.0	0.2	0.2	-0.2	0.1
45	$C_3H_7CHNO_2-NO_2$	-18.1	-1.0	-0.2	-0.8	-0.6	0.1	-1.0
46	$CF_3 - CF_3$	-39.4	23.2	21.4	19.5	23.7	15.4	22.4
47	"	-13.0	14.9	12.6	10.4	14.6	6.3	13.3
48	$C_6H_5CH_2 - SH$	-56.7	1.5	1.6	1.6	1.6	1.5	1.6
49	$C_6H_5CH_2 - SCH_3$	-55.2	-0.1	-0.1	0.1	-0.1	0.0	-0.1
50	$C_6H_5CH_2 - Cl$	-65.3	0.1	0.5	0.8	0.6	0.5	0.7
51	$C_6H_5CH_2 - NH_2$	-65.2	-0.5	-0.2	0.0	0.1	0.1	0.0
52	"	-63.1	0.2	0.4	0.5	0.6	0.6	0.6
53	"	-74.4	-1.9	-1.3	-1.1	-0.9	-1.0	-1.0
54	$(CH_3)(C_6H_5)(CN)C-CH_3$	-36.3	2.0	0.5	-0.2	-0.4	-0.1	-0.3
55	$CH_2=$ $=CHCH(CH_3)-CH(CH_3)_2$	-43.9	0.1	0.0	-0.4	-0.4	-0.4	-0.4
56	$CH\equiv CCH_2-CH(CH_3)_2$	-51.2	-1.0	-1.1	-1.3	-1.1	-1.2	-1.2
57	$CH_3CH(CH)-C(CH_3)_3$	-19.5	-1.2	-0.4	-0.7	-0.4	-0.7	-0.5

Table 3 continued

1	2	3	4	5	6	7	8	9
58	$CH_3OCH_2 - Cl$	-37.0	10.5	11.0	11.6	11.6	11.7	11.4
59	$CCl_3 - NO_2$	4.1	-0.2	-0.4	-0.5	-1.0	-6.6	-0.5
60	"	4.4	-0.7	-0.8	-0.9	-1.4	-7.0	-1.0
61	$CCl_2NO_2 - NO_2$	-1.3	1.0	1.2	-0.5	0.5	-1.4	1.7
62	$CHFNO_2 - NO_2$	-13.1	-4.4	-3.8	-5.0	-4.2	-5.3	-4.5
63	$CFClNO_2 - NO_2$	2.2	-5.0	-4.9	-6.8	-5.4	-7.5	-3.7
64	$CFBrNO_2 - NO_2$	-0.3	-2.9	-2.8	-5.2	-3.3	-5.9	-1.8
65	$CFINO_2 - NO_2$	-1.7	-1.5	-1.3	-4.0	-1.8	-4.7	-0.7
66	$CI(NO_2)_2 - NO_2$	-5.6	2.8	3.1	1.1	2.5	0.9	2.4
67	$CH_3CFNO_2 - NO_2$	-5.5	-2.3	-1.9	-3.2	-2.5	-3.5	-2.8
68	$CH_3CClNO_2 - NO_2$	-7.0	2.9	3.3	2.0	2.5	1.7	2.3
69	$CH_3CBrNO_2 - NO_2$	-8.0	2.6	2.9	1.9	2.2	1.7	2.0
70	$CH_3CCl_2 - NO_2$	-3.7	0.4	0.5	0.5	0.0	-4.1	0.4
71	$(NO_2)_2CFCF(NO_2)-NO_2$	-8.9	-1.6	-1.1	-3.4	-1.6	-3.3	-1.6
72	$C_2H_5CCl_2 - NO_2$	-6.1	0.1	0.4	0.4	-0.1	-4.1	0.4
73	$C_3H_7C(NO_2)_2 - NO_2$	-6.2	1.1	1.5	0.7	0.8	0.2	0.7
74	$CH_3OCH_2-CH_2OCH_3$	-17.0	0.9	1.0	0.8	1.6	0.6	1.3
75	$C_6H_5CH_2-COOH$	-59.7	-2.4	-2.2	-1.9	-2.0	-2.0	-2.0
76	"	-61.8	-0.4	-0.2	0.2	0.0	0.1	0.0
77	$(C_6H_5)_2CH-COOH$	-53.5	0.5	-1.1	-1.6	-1.9	-1.9	-1.7
78	"	-48.5	-4.6	-6.2	-6.6	-7.1	-7.0	-6.9
79	$C_6H_5CH_2-NHCH_3$	-57.5	-0.1	-0.1	-0.1	0.0	-0.1	0.0
80	"	-72.3	-0.7	-0.1	-0.1	0.1	0.0	0.1
81	$(CH_3)_2C(OH)-CH(CH_3)_2$	-27.0	-1.0	0.1	-0.1	0.1	-0.2	0.0
82	$C_6H_5CH_2-N(CH_3)_2$	-62.7	-0.4	-0.2	0.0	0.0	0.0	0.0
83	$CH_2=CHCH_2-CH_3$	-62.7	1.3	1.4	1.5	1.6	1.6	1.6
84	"	-51.4	-3.7	-3.7	-3.7	-3.7	-3.6	-3.7
85	"	-63.6	-0.8	-0.5	-0.4	-0.3	-0.2	-0.3
86	"	-49.8	2.8	2.6	2.5	2.5	2.6	2.5
87	$CH_2=CHCH(CH_3)-CH_3$	-38.0	1.0	0.5	0.3	0.2	0.3	0.2
88	$CH_2=CHC(CH_3)_2-CH_3$	-29.6	3.0	2.3	1.8	1.7	1.8	1.7
89	$C_6H_5CH_2-CH_3$	-58.5	-0.7	-0.6	-0.5	-0.4	-0.4	-0.5

Table 3 continued

1	2	3	4	5	6	7	8	9
90	$C_6H_5CH_2-CH_3$	-58.9	-0.4	-0.2	-0.2	-0.1	-0.1	-0.1
91	"	-60.8	-1.1	-1.0	-0.9	-0.8	-0.7	-0.8
92	"	-63.5	0.2	0.4	0.5	0.6	0.6	0.6
93	$C_6H_5CH(CH_3)-CH_3$	-51.4	-1.9	-1.9	-2.0	-2.0	-1.9	-2.0
94	$C_6H_5CH_2-C_2H_5$	-51.9	-2.0	-1.9	-2.0	-2.0	-1.9	-2.0
95	"	-50.8	-2.5	-2.5	-2.6	-2.5	-2.5	-2.5

Table 4

Some Results of MLRA of Y, Y_1, and Y_2 Values for Homolysis of $X_1X_2X_3C - X_4$ Type Compounds from Table 3 in the Coordinates of Eq. (11).

$\sigma^*_{NO_2} = 4.5$ is assumed except versions 3 and 5 where $\sigma^*_{NO_2} = 3.55$. The $\triangle Z$ correction is considered in version 6. (0.0) denotes the coefficients which appeared statistically insignificant proceeding from intermediate results of the data treatment. The values of other coefficients are obtained as a result of the data treatment without taking into account the scales of arguments corresponding to statistically insignificant coefficients. The previously fixed values of parameters not included into unknown coefficients in this version are underlined.

NE - the number of considered equations (points)

NRN - the number of considered reactions

s - standard deviation in kcal/mol

All coefficients except $\log A_o$ (sec^{-1}) are in kcal/mol

No	$\log A_o$	$\alpha\,\sigma^*_{C.}$	α^*	$\alpha^*(z^*_{C.}-z^*_C)$	$-\psi_=$	$-\psi_{CN}$	$-\psi_{NO_2}$	$\varphi_{C.}$	NE	NRN	s
1	2	3	4	5	6	7	8	9	10	11	12
1.0	14.64	1.07±0.21	1.01±0.20	-0.05±0.06	6.8±0.5	4.2±1.8	1.4±2.0	2.23±0.09	96	76	3.54
1.1	14.64	1.92±0.21	1.35±0.15	-0.08±0.04	7.3±0.4	6.9±1.3	2.6±1.3	2.21±0.06	87	69	2.29
1.2	14.64	1.92±0.15	1.37±0.11	-0.08±0.03	7.0±0.3	6.9±0.9	3.0±0.9	2.20±0.04	76	62	1.66
1.3	14.64	1.92±0.14	1.37±0.10	-0.08±0.03	7.1±0.3	5.8±1.0	3.1±0.9	2.20±0.04	74	60	1.57
2.0	14.43±0.28	1.04±0.22	0.98±0.21	-0.05±0.06	7.3±0.9	4.5±1.9	1.5±2.0	2.19±0.10	96	76	3.55

Table 4 continued

1	2	3	4	5	6	7	8	9	10	11	12
2.1	14.73±0.23	1.94±0.22	1.37±0.16	−0.08±0.04	7.0±0.8	6.8±1.3	2.5±1.3	2.22±0.07	87	69	2.31
2.2	14.08±0.18	1.77±0.15	1.26±0.11	−0.07±0.03	8.8±0.6	7.6±0.9	3.4±0.9	2.11±0.05	75	62	1.56
2.3	14.21±0.13	1.67±0.11	1.23±0.08	−0.07±0.02	8.5±0.5	6.1±0.7	2.9±0.6	2.16±0.04	62	52	1.07
3.0	14.49±0.27	1.12±0.22	1.27±0.26	−0.09±0.07	7.2±0.9	4.5±1.9	2.1±1.8	2.19±0.10	96	76	3.49
3.1	14.73±0.23	1.86±0.22	1.64±0.20	−0.14±0.05	7.0±0.8	6.5±1.3	3.2±1.2	2.22±0.07	86	68	2.32
3.2	14.10±0.16	1.66±0.13	1.53±0.12	−0.13±0.03	8.9±0.6	6.2±0.9	4.0±0.7	2.13±0.05	71	57	1.37
3.3	14.07±0.14	1.68±0.11	1.53±0.10	−0.15±0.03	8.9±0.5	6.2±0.7	4.1±0.6	2.11±0.04	65	54	1.13
4.0	14.56±0.27	1.20±0.20	_1.37_	0.03±0.04	7.1±0.9	5.0±1.9	−1.2±1.4	2.22±0.11	96	76	3.60
4.1	14.61±0.21	1.96±0.16	_1.37_	−0.08±0.03	7.4±0.7	7.2±1.3	2.7±1.0	2.20±0.07	89	71	2.32
4.2	13.99±0.16	1.89±0.11	_1.37_	−0.06±0.02	9.1±0.6	8.2±0.8	2.8±0.7	2.08±0.05	75	61	1.49
4.3	13.99±0.15	1.85±0.10	_1.37_	−0.05±0.02	9.2±0.5	7.1±0.9	3.0±0.6	2.10±0.04	73	59	1.39
5.0	14.97±0.27	1.70±0.18	_2.20_	(0.0)	6.2±0.9	5.6±2.0	(0.0)	2.28±0.11	96	76	3.80
5.1	14.80±0.20	1.90±0.13	_2.20_	(0.0)	6.6±0.6	6.7±1.4	(0.0)	2.24±0.07	89	71	2.54
5.2	14.14±0.17	1.80±0.09	_2.20_	(0.0)	8.4±0.6	7.8±1.0	(0.0)	2.12±0.06	76	62	1.75
5.3	14.04±0.11	1.70±0.06	_2.20_	(0.0)	8.9±0.4	6.5±0.7	(0.0)	2.10±0.03	61	51	1.07
6.0	14.41±0.27	1.03±0.21	0.98±0.20	−0.07±0.06	7.4±0.8	4.6±1.9	1.9±1.9	2.19±0.10	96	76	3.48
6.1	14.33±0.22	1.86±0.20	1.33±0.15	−0.07±0.03	8.3±0.7	7.5±1.2	3.0±1.2	2.17±0.07	86	69	2.12
6.2	13.90±0.17	1.76±0.15	1.26±0.11	−0.07±0.03	9.3±0.6	8.0±0.9	3.5±0.9	2.08±0.05	76	62	1.54
6.3	14.01±0.16	1.74±0.13	1.25±0.10	−0.06±0.02	9.0±0.6	6.6±0.9	3.8±0.8	2.10±0.05	71	57	1.34

Table 5

The Comparison of Some Results of the Data Treatment
in the Coordinates of Eqs. (10) and (11).

Units - kcal/mol. The data corrected by ΔZ are in
parenthesis. α^{x} = 1.37 kcal/mol is assumed.

No	Free Radical $X_1X_2X_3C^{\cdot}$	Deviation using eq. (10)	Homolyzing compound	Deviation using eq. (11) for the values according to eq. (13)
1.	$(C_6H_5)_3C^{\cdot}$	-9.3	$(C_6H_5)_3C-H$	-10.0
2.	$(NO_2)_2CH^{\cdot}$	-4.1	$(NO_2)_2CH-NO_2$	-1.9
3.	$(NO_2)F_2C^{\cdot}$	-2.3	$(NO_2)F_2C-NO_2$	-5.6(-2.9)
4.	$(NO_2)_2FC^{\cdot}$	-1.6	$(NO_2)_2FC-NO_2$	-5.2
5.	$(NO_2)_2BrC^{\cdot}$	4.5	$(NO_2)_2BrC-NO_2$	1.9
6.	$NC(CH_3)_2C^{\cdot}$	1.0	$NC(CH_3)_2C-CH_3$	4.2
7.	$BrCH_2^{\cdot}$	-6.2	$BrCH_2-Br$	-4.8
8.	$ClCH_2CH_2^{\cdot}$	-5.8	$ClCH_2CH_2-Cl$	0.1
9.	$F_3C^{\cdot}$	-0.5^{x}	F_3C-Br	-0.1
			F_3C-I	14.7
			F_3C-CF_3	23.7
				14.6
10.	$Cl_3C^{\cdot}$	-3.7	Cl_3C-Br	1.5
			Cl_3C-NO_2	-1.2
			$(NO_2)Cl_2C-NO_2$	0.5(1.9)
			$(NO_2)FClC-NO_2$	-5.4(-3.4)
			$(NO_2)FBrC-NO_2$	-3.3(-1.6)
			$(NO_2)FIC-NO_2$	-1.8(-0.3)

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^{x} Calculated from the data for $CF_3 - Br$

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PHOTOELECTRON SPECTRA OF MOLECULES
4. AMINES

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Photoelectron spectra (PES) of some amines
($CF_3CH_2NH_2$, Me_2NCl, $MeNCl_2$, $(n-C_4F_3)_3N$,
$(NCCH_2CH_2)_3N$, $(Me_2Si)_2NH$, Me_3SiNEt_2, and
$3,5-(CF_3)_2C_6H_3NH_2$) were obtained. The linear re-
lationship between valence shell lone electron
pair ionization potentials (IP) and nitrogen
atom ESCA shifts was found.

The IP-s of amines were also compared with
the corresponding quantities for the lone electron
pair in the substituted phospines. Semiempirical
(CNDO/2) and ab initio (Gaussian 70) calculations
were used for the assignment of the PES bands.

In the previous publications of these series PES of
alcohols[1a], ethers[1b], and nitriles[1c] were analyzed. In the
present communication PES of some aliphatic amines with
the electronegative substituents as well as of
$3,5-(CF_3)_2C_6H_3NH_2$ were studied.

For the simple fluoro-and chlorosubstituted amines the
calculation of the spectrum of eigenvalues was performed
by the semiempirical CNDO/2 method as well as by the non-
empirical Gaussian 70 (STO-3G and 4-31G basis sets) proce-
dure. PES of fluoro-substituted derivatives of ammonia

(F_2NH and NF_3) were studied in Refs. 2 and 3. Photoelectron spectra of some perfluoroalkyl substituted amines were analyzed in Ref.4 whereas several 1st IP of fluorinated alkylamines were reported in Ref. 5. The analysis of chloro-substituted amines was presented in Ref. 6. PES of one trimethylsilyl-substituted amine (($Me_3Si)_3N$) was studied in Ref. 7 and some SIH_3 substituted derivatives of amines were discussed in Ref. 8.

In the present paper the PES of $(n-C_4F_9)_3N$ is also reported. It well agrees with such in a recent publication by S. Elbel.[4a]

Experimental

Photoelectron spectrometer used and the experimental technique were already described earlier[1a]. Some commercial chemicals ($CF_3CH_2NH_2$, $(n-C_4F_9)_3N$, $(Me_3Si)_2NH$, Me_3SiNEt_2, $HOCH_2CH_2NH_2$ and $3,5-(CF_3)_2C_6H_3NH_2$) were used. Their purity was checked by g.l.c. Before the recording the spectra the samples were subjected to several freeze--pump -thaw cycles.

($NCCH_2CH_2)_3N$ was synthesized by the standard technique from $(HOCH_2CH_2)_3N$.

Me_2NCl and $MeNCl_2$ were obtained by the chlorination of the corresponding amines. HNF_2 was synthesized in the sample ampoule immediately before measurement by the inter-action of concentrated sulfuric acid and $(C_6H_5)_3CNF_2$. Due to the presence in the reaction mixture of several impuri-ties in this case only the first adiabatic (11.93 eV) and vertical (12.36 eV) ionization potentials were determined. These values were already reported and used in our earlier communications[9a,c] and their agreement with the literature data is excellent.

The present experimental PES are visualized in Fig. 1. Table 1 lists adiabatic and vertical IP-s determined from PES.

Quantum chemical calculations of amines were mostly performed using the semiempirical CNDO/2 procedure with the original parametrization.

The following bond distances (if not shown otherwise) were used (in nm units):
CH=0.119; CC=0.1457; CN=0.147; NH=0.107; NCl=0.156; CF=0.1343; CO=0.143; OH=0.096. SiN=0.170; SiC=0.187. Tetrahedral valence angles were used except in the case of NCl_3 where $\angle$ ClCCl=90° (experimental [10] value is 107.4°) gives lower total energy.

For anilines CC=0.14 and CH=0.1112 were used for the benzene ring and $N-C_{arom}$=0.137 and $C-C_{arom}$=0.145 for the distances between the aromatic ring and the substituent (CF_3 or NH_2). NH_2 group was assumed to be coplanar with the benzene ring, the HNH angle was taken to be 120°.

The corresponding total energies E_{tot}, Koopmans' MO energies ε, symmetries of MO-s and their approximate characters are also given in Table 1.

Table 1.

Experimental ionization potentials and the calculated orbital energies ($-\varepsilon$) of some amines. All values are in eV units.

1. $CF_3CH_2NH_2$ 2. Me_2NCl

	IP_v^a	CNDO/2[b]		STO-3G		IP_v^a	CNDO/2[b]		
		$-\varepsilon$	MO	$-\varepsilon$			$-\varepsilon$	MO	
1	2	3	4	5	1	2	3	4	5
1.	10.35	14.59	n_N	9.17	1.	9.45	13.17	8a'	n_N, n_{Cl}
2.		15.95	σ_{NH}	12.19	2.	11.26	14.17	5a''	n_{Cl}
3.	13.86	18.72	σ_{CN}	12.81	3.	12.05	14.30	7a'	σ_{NCl}
4.		19.37	n_F	12.81	4.	13.21	16.34	6a'	n_{Cl}, n_N
5.		19.81	n_F	13.30	5.	14.21	16.71	4a''	π_{CH_3}
6.		20.12	n_F	13.57					
7.	15.18	21.02	n_F	13.84					
8.		21.52	n_F	14.14					
9.		21.88	n_F	14.63					
10.	16.91	23.35	π_{CH_2}	16.92					
11.	17.70	25.35		17.95					

II

Table 1 continued

1	2	3	4	5	
12.	19.19	27.09		18.39	
13.	20.29	27.34		18.47	
14.				21.46	

a - $IP_a^{(1)}$ = 9.97; $IP_a^{(2)}$ = 13.21;   a - $IP_a^{(1)}$ = 8.75; $IP_a^{(2)}$ = $IP_v^{(2)}$;

    see also Refs. 5,9.   see also Refs. 6,11,12

b - E_{tot} = -112.2508 a.u.   b - E_{tot} = -46.6913 a.u.

c - E_{tot} = -424.9975 a.u.

3. $HOCH_2CH_2NH_2$ 4. $(NCCH_2CH_2)_3N$

	IP_v^a	CNDO/2[b]			IP_v^a	CNDO/2[b]
		$-\varepsilon$	MO			$-\varepsilon$
1.	9.71	11.26	n_O, $\widetilde{\pi}_{CH_2}$	1.	11.26	12.96
2.	10.54	12.38	σ_{CO}	2.	12.97	13.95
3.	11.98	14.22	n_N	3.	14.73	14.81
4.	12.92	16.02	σ_{NH}			14.97
5.	14.07	17.51	$\bar{n}_O$			15.37
6.	15.33	19.89	σ_{NC}			15.72
						16.12

a - $IP_a^{(1)}$ = 8.96;   a - $IP_a^{(1)}$ = 10.40[9b],

    see also Refs. 1a,9,13 $IP_a^{(2)}$ = 12.97

b - E_{tot} = -49.4221 a.u.   b - E_{tot} = 119.2867 a.u.

Table 1 continued

5. $(n-C_4F_9)_3N$ 　　　　6. $MeNCl_2$

IP_v^a			IP_v^a	CNDO/2[b]		
				$-\varepsilon$		MO
1.	12.00^{9a}		1.	10.02	11.93	$5a''$	n_{Cl}, n_N
2.	13.56		2.	11.36	13.32	$8a'$	n_N, n_{Cl}
3.	14.90		3.	11.54	14.05	$4a''$	n_{Cl}
4.	16.24		4.	11.95	15.75	$7a'$	n_{Cl}
5.	17.06				15.91	$3a''$	
6.	17.7				18.33	$6a'$	
					21.30	$5a'$	

a – $IP_a^{(1)} = 11.30^{9a}$;　　　　a – $IP_a^{(1)} = 9.52$;
　　see also Ref. 4a　　　　　　　see also Ref. 6.

　　　　　　　　　　　　　　b – $E_{tot} = -53.5975$ a.u.

7. $(Me_3Si)_2NH$ 　　　　8. Me_3SiNEt_2

IP_v^a	CNDO/2[b]		IP_v^a	
	$-\varepsilon$	MO		
1.	8.76	11.96	14b	1.	7.90
2.	10.10	12.86	14a	2.	10.13
3.	10.53	13.55	13b	3.	10.76
4.		14.20	13a	4.	12.95
5.		14.61	12b		
6.		15.32	12a		
7.	13.16	15.55	11b		
8.	13.68	16.56	10b		

a – $IP_a^{(1)} = 8.55$; $IP_a^{(2)} = 9.54$　　　a – $IP_a^{(1)} = 7.68$

b – $E_{tot} = 76.3653$ a.u.

Table 1 continued

9. $3,5-(CF_3)_2C_6H_3NH_2$

	IP_v^a	CNDO/2[b]	
		$-\varepsilon$	MO
1.	8.84	12.19	$22a'\ \pi$
2.	10.21	14.26	$19a''$
3.	11.59	15.01	$18a''\ \pi$
4.		15.16	$21a'\ \sigma_{CC}$
5.		17.75	$20a'\ n_F$
6.	12.70	17.84	$17a''\ \sigma_{CH}$
7.	13.29	18.00	$16a''n_N$
8.	14.40	18.54	$15a''\pi_{NH_2}$
9.	14.92	18.91	$14a''\ n_F$
10.		19.37	$19a'$
11.	15.53	19.66	$18a'$
12.		19.73	$13a''$
13.		20.40	$17a'$
14.		20.70	$12a''$
15.	16.71	20.76	$16a'$
16.		21.24	$11a''$
17.		21.28	$16a'$
18.		21.65	$10a''$
19.	18.71	22.94	$15a'$
20.	18.85	23.12	$9a''$
21.	20.19	24.11	$8a''$

a – $IP_a^{(1)}=$ 8.59, $IP_a^{(2)}=$ 10.02, $IP_a^{(3)}=$ 11.45

b – $E_{tot}=$ -238.8506 a.u.
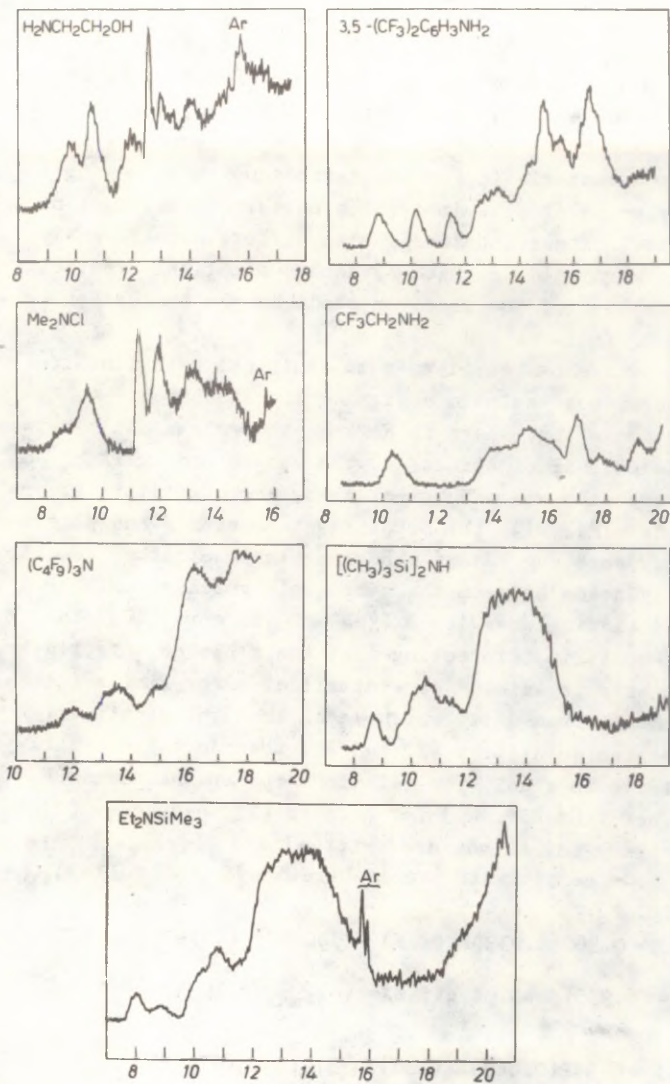
Fig. 1. Photoelectron Spectra of Some Amines.

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Discussion

The lone electron pair of amines has a relatively low bonding energy and, as a rule, gets preferentially ion-ized at the excitation by photons. However, for this class of compounds the corresponding band is not as sharp as it is usually characteristic for the typical peaks belonging to the lone pairs of some ionization centers (chlorine, bro-mine, etc.). The adiabatic IP also differs significantly from the vertical one which evidences about the drastic reorganization of the electron shell in the ionization pro-cess.

As it was shown earlier[9] some empirical relationships could be of some help in assigning the PES bands.

So, among the others in Ref. 9a the relationship between the lone pair IP of amines and the corresponding PA of these compounds was discussed. Also, the quantitative cor-relations of IP with the substituent constants and polar-izability were suggested[9b]. Besides that, a rather general linearity holds between the nitrogen's valence shell IP-s and ESCA binding energies $E_B(1sN)$ of its core level 1s electrons. It is interesting that the slope of this linear relationship is within its statistical error limits indis-tinguishable from unity which means that the sensitivity of these two quantities (IP and E_B) towards the substitu-ent effects is equal. The relationships of this kind (E_B values are from Ref. 14) for primary (1), secondary (2), and tertiary (3) amines are written (the errors of the regression coefficients are in parentheses) as follows (see also Fig. 2):

$$IP_v(n_N) = 0.962(0.039)E_B(1sN) - 380.286 \ (15.920) \qquad (1)$$

$$r = 0.995; \ s = 0.04 \ eV; \ s\% = (\Delta IP_{max}/s)100 = 3.6; \ n = 8$$

$$IP_v(n_N) = 0.942(0.068)E_B(1sN) - 372.862 \ (27.795) \qquad (2)$$

$$r = 0.990 \ ; \ s = 0.03 \ eV; \ s\% = 5.5; \ n = 6$$

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$$IP_v(n_N) = 0.796(0.009)E_B(1sN) - 313.813(3.735) \qquad (3)$$

$r = 0.999$; $s = 0.003$ eV; $s\% = 0.7$; $n = 3$,

where r – the correlation coefficient,

   s – standard deviation,

   ΔIP_{max} – the maximum range of variation of the IP

   n – the number of points.

Unfortunately there is not enough E_B data for the compounds with the electronegative substituents ($CF_3CH_2NH_2$ fits Eqn.(1) but NF_3 deviates[x] significantly from Eqn.(3)) to explore the range of applicability of those relationships (see also Ref. 9a).
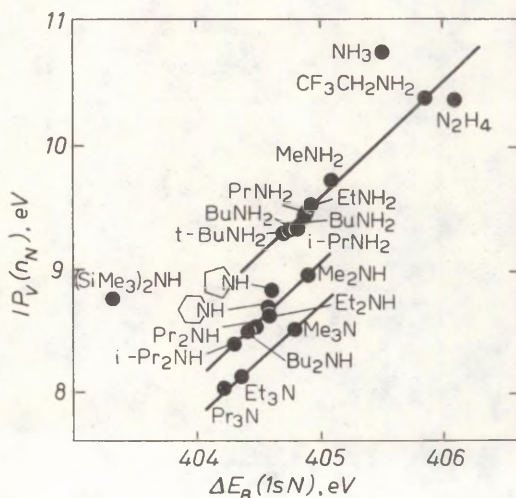
Fig. 2. The dependence of $IP_v(n_N)$ on the binding energies E_B of core level electrons for some amines.
[x] The amine (($Me_3Si)_2NH$) which has the silicon-containing substituent attached immediately to the lone pair ionization center (N) deviates from Eqn.(2) towards the higher values of IP_v-s (Compare also with Ref. 1b).

The comparison[1c] of IP-s of various ionization centers in classes of compounds of the similar structure proves itself to be rather useful for the assignment of IP-s to the electrons localized at different atoms.

The comparison of IP of the nitrogen and phosphor lone pairs in amines and phosphines leads to the linearity(4)[15]

$$IP_v(n_N) = 1.346(0.054)IP(n_P) - 3.17(0.52) \qquad (4)$$

$r = 0.982; \ s = 0.28 \ eV; \ s\% = 4.8; \ n = 25$

which could be visualized in Fig. 3.
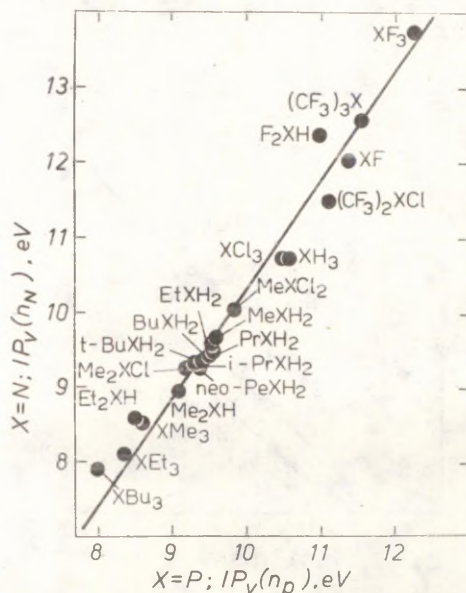
Fig. 3. The comparison of ionization potentials of the nitrogen ($IP_v(n_N)$) and phosphor ($IP_v(n_P)$) lone electron pairs in amines and phosphines.

For the interpretation of PES bands in terms of molecular orbitals the semiempirical CNDO/2 calculations of several amines were undertaken. As it was already noticed in the previous communications of this series[1] this method not always reproduces the order of MO-s predicted by the nonempirical quantum chemical calculations. It seems that alongside with the problems connected with the use of the Koopmans' approximation there are also errors of interpretation introduced by the nature of the CNDO/2 method. From that point of view it is interesting to compare the results of these quantum chemical calculations on the different levels of theory. In the present work such a comparison was made for a few simple fluorosubstituted amines (see Table 2).

Table 2

MO energies ($-\varepsilon$) for some fluorosubstituted amines as calculated by semiempirical CNDO/2 and nonempirical Gaussian 70 methods. All values are in eV units.

1. FNH_2 2. F_2NH

4-31G[a]		3G[b]	CNDO/2[c]		4-31G[a]		3G[b]	CNDO/2[c]	
$-\varepsilon$	MO	$-\varepsilon$	$-\varepsilon$	MO	$-\varepsilon$	MO	$-\varepsilon$	$-\varepsilon$	MO
1	2	3	4	5	1	2	3	4	5
11.48	7a'	8.62	14.85	5a'	14.04	8a'	10.18	15.50	6a'
16.09	2a''	12.68	17.27	2a''	17.34	7a'	12.96	18.87	5a'
18.25	6a'	14.69	22.47	4a'	17.43	5a''	13.06	19.97	4a''
18.22	5a'	15.72	24.34	3a'	18.73	4a''	14.27	21.96	3a''
20.02	1a''	17.30	25.23	1a''	20.47	3a''	16.52	25.62	2a''

Table 2 continued

1	2	3	4	5	1	2	3	4	5
30.63	4a'	28.23	32.88	2a'	20.67	6a'	16.52	26.24	4a'
43.55	3a'	40.94	49.20	1a'	22.12	5a'	18.47	27.83	3a'
424.37	2a'	417.60				4a'		32.50	2a'
714.44	1a'	707.04				2a''		43.38	1a''
						3a'		53.31	1a'
						2a'			
						1a''			
						1a'			

a – E_{tot} = –154.7372 a.u.,
NF= 0.140 nm, NH=0.101 nm,
∠ MNF = 120°, ∠HNH= 107.0°;

a – E_{tot} = –253.4155 a.u.
NF=0.140 nm, NH=0.1026 nm
∠ FNF=102.0°, ∠ HNF=99.8°;

b – E_{tot} = –152.8492 a.u.;
for the geometry and MO-s
see the previous footnote

b – E_{tot} = –250.3012 a.u.;
for the geometry and MO-s
see the previous footnote.

c – E_{tot} = –40.9679 a.u.

c – E_{tot} = –68.0579 a.u.,
NF=0.125 nm, NH=0.109 nm,
∠ HNF= ∠NFF=105.2°

3. NF_3 4. CF_3NH_2

4-31G[a]		3G[b]		CNDO/2[b]		3G[a]		CNDO/2[b]	
$-\varepsilon$	MO	$-\varepsilon$	MO	$-\varepsilon$	MO	$-\varepsilon$	MO	$-\varepsilon$	MO
1	2	3	4	5	6	1	2	3	4
15.36	6a₁	10.63	6a₁	16.72	4a₁	10.39	14a'	16.59	10a'
18.72	5e	13.58	5e	20.02	4e	12.29	13a'	18.02	9a'
18.91	1a₂	14.23	1a₂	21.60	1a₂	12.76	7a''	19.26	6a''
20.35	4e	15.25	4e	22.98	3e	12.78	12a'	19.93	8a'
23.19	3e	18.64	5a₁	28.07	2e	13.27	6a''	20.72	5a''
23.24	5a₁	18.71	3e	28.75	3a₁	13.87	5a''	21.22	4a''
30.61	4a₁	26.72	4a₁	31.99	2a₁	14.25	11a'	22.01	7a'

Table 2 continued

1	2	3	4	5	6	1	2	3	4
45.51	2e	41.69	2e	47.47	1e	15.94	$4a''$	22.23	$3a''$
49.53	$3a_1$	45.58	$3a_1$	56.41	$1a_1$	18.06	$10a'$	25.83	$6a'$
432.15	$2a_1$	424.18	$2a_1$				$3a''$	26.75	$5a'$
716.91	1e	708.27	1e				$9a'$	26.92	$2a''$
716.92	$1a_1$	708.27	$1a_1$				$8a'$	28.61	$4a'$
							$7a'$	40.01	$3a'$
							$6a'$	47.03	$1a''$
							$2a''$	47.08	$2a'$
							$5a'$	52.85	$1a'$
							$4a'$		
							$3a'$		
							$2a'$		
							$1a''$		
							$1a'$		

a – E_{tot} = -352.0756 a.u.,   a – E_{tot} = -386.4314 a.u.,
NF= 0.137 nm,   CN=0.1486 nm, CF=0.136 nm,
$\angle$FNF=102.2°.   NH=0.1033 nm, $\angle$HNC=109.5°

b – E_{tot} = -347.7537 a.u.,   b – E_{tot} = -103.5745 a.u.,
for the geometry see the   CN=0.147 nm, CF=0.1332 nm,
previous footnote   NH=0.104 nm, $\angle$HNC=112.0°

c – E_{tot} = -95.1586 a.u.,
NF=0.125 nm, $\angle$FNF=104.6°

As one can see from Table 2 the CNDO/2 order of MO-s
for simple amines is in satisfactory agreement with that
calculated on ab initio level. The same seems also to be
true for the calculated charge distribution in the mole-
cule (see Table 3).

Table 3

Charge distribution in some simple aliphatic amines

		FNH_2	F_2NH	NF_3	CF_3NH_2
Localization of HOMO on $2p_z N(\%)$	4-31G	27	10	12	-
	3G	63	20	21	64
	CNDO/2	60	35	42	69
Mulliken charge q_N (a.u.)	4-31G	-0.402	0.239	0.779	-
	3G	-0.325	-0.052	0.173	-0.400
	CNDO/2	-0.023	0.203	0.402	-0.267
Dipole moment μ Debyes	4-31G	2.91	2.57	0.04	--
	3G	1.65	1.48	0.04	1.91
	CNDO/2	2.14	1.75	0.05	2.46
	experimental		1.93	0.24	-

It is important to notify that all methods considered predict the similar significant mixing of the orbitals of the lone pairs of nitrogen and fluorine.

The comparison of the results on two different levels of calculations can be continued on the example of $CF_3CH_2NH_2$ (see Table 1 and Fig. 1). This molecule belongs to the C_1 symmetry group and therefore its MO-s are characterized only by their localization characters. According to Table 1 the results of STO-3G and CNDO/2 calculations are in a reasonable agreement. The STO-3G bond lengths for this molecule are as follows: CN=0.154, CF=0.136, NH= =0.1033 CC=0.155, CH=0.1089 nm. The Mulliken charge on the nitrogen atom is -0.38 a.u. and the dipole moment 1.62 D.

For the CNDO/2 calculations the experimental geometry was used (CN=0.143, CC=0.154, CF=0.1332, NH=0.107, $\angle$CNH= = 107°, $\angle$FCC = 110.9, $\angle$FCF = 108.8°). The HOMO belongs by 42 per cent to 2p AO of nitrogen atom, q_N = -0.177 a.u. and dipole moment 1.95 D.

It could be concluded that the introduction of fluorine into amines leads to the significant delocalization of their HOMO-s. It is interesting to notice that the comparable CNDO/2 calculation of methylamines gives the following localization of HOMO on 2p AO of nitrogen atom: $MeNH_2$-59 per cent, Me_2NH-57 per cent and Me_3N-55 per cent.[x]

The behavior of chlorosubstituted derivatives of ammonia (see Table 1, No 2,6) is in general features similar to that of fluorosubstituted ones. Again, CNDO/2 calculations predict the rather extensive mixing of the orbitals of the lone pairs of nitrogen and chlorine atoms whereas the order of MO-s agrees with such for the fluorosubstituted derivatives from Table 2.[xx]

In the case of NCl_3 CNDO/2 calculations lead to rather unexpected result. So, the use of experimental geometry (NCl=0.176 nm, $\angle$ ClNCl = 107°) leads to E_{tot}= -60.1659 a.u. and to the same order of MO-s as given in Table 2 for NF_3. However, the use of another geometry (NCl=0.156 nm and ClNCl=90°) results in significantly lower E_{tot}= -60.5191 a.u. and in the following order of MO-s : $4e, 1a_2, 4a_1, 3e, 2e, 3a_1, 2a_1, 1e, 1a_1$.

In the earlier paper [1c] from this series some IP-s were listed for Et_2NCN. In Ref. 16 the analysis of its analogue Me_2NCN was performed in terms of the modified CNDO treatment.

Our CNDO/2 calculations of Et_2NCN lead to the similar conclusions whereas the MO order is $12a', 8a'', 7a'', 11a', 6a'', 10a', 9a', 5a''$ and the HOMO is by 49 per cent localized on the nitrogen atom of the Et_2N group.

Calculations of $(NCCH_2CH_2)_3N$ were made assuming the C_{3v} symmetry (E_{tot}= -119.2867 a.u.). Its HOMO has by 42 per-

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[x] As in the case of oxygen compounds[1a,b] the CNDO/2 calculations lead to the not very probable conclusion that HOMO-s in compounds with large bulky alkyl substituents (e.g., tertiary butyl) are practically fully delocalized from the ionization center.

[xx] Somewhat different order of MO-s for X_2NH and X_3N is suggested in Ref. 6.

cent of the character of the lone pair of the "tertiary" nitrogen atom.

PES of $H_2NCH_2CH_2OH$ was thoroughly studied in Ref. 13 where the authors monitored the temperature dependent spectrum which evidences on the intramolecular hydrogen bond. The PES of this molecule reported by us in Table 1 is in a good accordance with the literature[13] one. CNDO/2 calculations evidence for a rather intense intramolecular hydrogen bond between OH group and nitrogen atom. (C_1 symmetry, E_{tot}= -49.4221 a.u.). The HOMO of this molecule is also significantly delocalized and has a somewhat prevailing n_O character.

According to the Ref. 8 we assumed the "planar" structure (SiNSiH) for the $(Me_2Si)_2NH$ molecule (C_2 symmetry). On the contrary to the expected $(p \to d)_\pi$ effect CNDO/2 calculations do not reveal any participation of the silicon orbitals in the HOMO. However, there is still a very definite interaction of the orbitals.

CNDO/2 calculations of the aniline lead to the MO sequence $3b_1$, $6b_2$, $1a_2$, $8a_1$, $5b_2$, $2b_1$ which differs from the "experimental" order b_1, a_2, b_1, a_1, b_1. Introduction of two CF_3 groups into 3 and 5 positions of the benzene ring initates only a small changes in the CNDO/2 charge distribution in the aniline molecule. MO-s of the parent compound and its 3,5-bis-trifluoromethyl derivative MO-s are highly delocalized and n_N character is present only for the $3b_1$ and $2b_1$ MO-s of the aniline and for the $22a'$ and $16a''$ orbitals of $3,5-(CF_3)_2C_6H_3NH_2$.

The analysis of PES of the substituted hydroxylamines $X_1X_2NOX_3$ will be presented in one of the forthcoming papers simultaneously with the discussion of the effect of the immediately attached lone pair substituent on the behavior of the ionization or reaction center of the same type (the so called α -effect).

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15. The exclusion of the points for $F_3X, F_2XH, (CF_3)_3X$,
     $(SiH_3)_3X$, and $(GeH_3)_3X$ leads to somewhat changed reg-
     ression coefficients and statistical characteristics:

$$IP_v(n_N) = 1.127(0.028)IP(n_P) - 1.21(0.26)$$
$$r=0.995 , s=0.09 \text{ eV, } s\%=2.5 , n=20.$$

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NONLINEAR PARAMETRIZATION OF EQUATIONS FOR
ATOMIC SPECTRAL TERMS
1. Specification of General Character of
Dependence on Orbital-Orbital Shielding
Constants

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Making use of the model[1,2] of the additive
shielding and nonshielding interactions of elec-
trons eqs. (5) and (7) are derived. To obtain
these equations a certain interdependence between
the two interactions referred to is assumed and
the single-electron hydrogen-like approach is
employed. Eqs. (5) and (7) enable one to describe
the ionization potentials of both neutral and
several ionized atoms with variable charges and
electronic configurations. The parametrization
of these equations has been achieved by the non-
-linear least squares treatment of the 221 values
of spectral terms.

The results of statistical treatment of the ionization
potentials of neutral atoms and atomic ions according to
eq. (1) were reported previously[1,2]:

$$I_j = \frac{I_H}{n^2}(Z - \sigma_j)^2 - \beta_j Z , \qquad (1)$$

Where σ_j and β_j denote the constants characteristic
of the jth isoelectronic series, I_H is the ionization po-
tential for hydrogen atom, n denotes the principal quantum
number and Z is equal to the charge of nucleus. For the lin-
earization of eq.(1) it was transformed as follows:

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$$W_j = \frac{I_H}{n^2} Z^2 - I_j = a_j + b_j Z$$

Application of the last equation to the data sets for isoelectronic series (the linearity of W_j on Z) leads to the confirmation of the reliability of eq. (1). The a_j and b_j values for different isoelectronic series were estimated and the corresponding σ_j and β_j values calculated as follows:

$$\sigma_j = \sqrt{-a_j n^2 / I_H} \quad ; \quad \beta_j = b_j - 2 I_H \sigma_j / n^2 .$$

Data sets for isoelectronic series covered, in average, $4 \div 6$ experimental points and the parameters σ_j and β_j were calculated at low numbers of statistical degrees of freedom. Nevertheless, it was established that the parameters σ_j and β_j could be represented in some approximation as the sums of additive contributions $\sigma_{j(i)}$ and $\beta_{j(i)}$ each of them representing the interaction of the given jth electron with a shielding electron located on the ith orbital:

$$\sigma_j = \sum_{i=1}^{j-1} \sigma_{j(i)} \quad ; \quad \beta_j = \sum_{i=1}^{j-1} \beta_{j(i)} \tag{2}$$

A rough dependence represented by eq. (3) has also been noticed between $\sigma_{j(i)}$ and $\beta_{j(i)}$ values

$$n^2 \beta_{j(i)} = C_f (1 - \sigma_{j(i)}) . \tag{3}$$

The proportionality coefficient C_f is a constant in case one or several orbital characteristics (n_i for shielding orbital, the total spin quantum number etc.) are fixed. Considering eq. (1) a conclusion can be drawn that the σ_j values represent the shielding of the jth electron and the β_j values are related to the contribution into the jth electron interaction energy with all other ones which cannot be represented in the terms of the shielding of nucleus charge.

A correct approach to the problem of estimation of effective charges of nuclei and the corresponding shielding constants require that the equation for I_j values should contain all the terms present in the precise relationship for hydrogen-like atom energies. The only essential changes to be done are the substitution of the effective value Z^* of nucleus charge for Z, and the addition of the term related to the non-shielding potential. Consequently, the Rydberg constant R_∞ for the infinity mass of nucleus should be introduced instead of I_H. The dependence of the system reduced mass on the atomic mass should be reflected as well. Besides that, the spin and relativistic effects and the Lamb shift should be taken into account. Nevertheless, in this study the corresponding more complicated version of Eq. (1) has not been applied yet. Our primary task was to check the reliability and the limits of applicability of the relationship (3) as well as a more accurate estimation of the constants $\sigma_{j(i)}$ representing the coupling orbital-orbital shielding. The possibility of the observation of some secondary regularities for those constants was also kept in mind. All this can result in a remarkable reduction of the number of parameters to be estimated and promote a further specification of the significance and the values of the terms related to different effects.

That was the reason why the statistical treatment of the values of spectral terms for the three first electronic shells has been performed. The parameters to be estimated were $\sigma_{j(i)}$ as well as the values of coefficients C_f from relationship (3). The application of the non-linear least square (NLLS) treatment of experimental data is also required.

The first variant of data processing was performed according to the following equation:

$$I_j = \frac{I_H}{n^2} (Z - \sum_{i=1}^{j-1} \sigma_{j(i)})^2 - Z \sum_{i=1}^{j-1} B_{j(i)} \tag{4}$$

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The aim was to check the additivities according to relationships (2) using the ionization potentials of atoms and positively charged ions in ground and different excited states as I_j values.

After that the possibility to reduce the number of empirical parameters was studied combining eqs. (3) and (4). The resulting equation could be represented as follows:

$$I_j = \frac{I_H}{n^2} \left(Z - \sum_{i=1}^{j-1} \sigma_{j(i)}\right)^2 - \frac{Z}{n^2} \sum_{i=1}^{j-1} C_{j,f}(N_i - \sigma_{j(i)}) \tag{5}$$

N_i denotes the number of electrons (1 or 2) occupying the shielding orbital.

The reduction of the number of parameters to be estimated is possible if the $C_{j,f}$ value remains constant for several levels of the subscript i that means a certain degree of its independence from the actual shielding orbital.

The substitution of the relationship (3) for the $\beta_{j(i)}$ value is consistent with the interpretation of the latter value as a constant of the nonshielding interaction[1,2] between electrons, as $\beta_{j(i)}$ is assumed to be proportional to the fraction $(N_i - \sigma_{j(i)})$ of the charge of the ith electron exerting no shielding effect on the jth electron considered.

The number and type of coefficients $C_{j,f}$ may be, in principle, different. I.e., one can assume for the electronic configuration $1s^2 2s^2 2p^6 3s^2$ a relationship as follows:

$$I_j = \frac{I_H}{9} \left(Z - \sigma_{3s(1s^2)} - \sigma_{3s(2s^2)} - 3 \cdot \sigma_{3s(2p^2)} - \sigma_{3s^2}\right)^2 -$$

$$- \frac{Z}{9} \left\{ C_{3s(s)} \left[(2 - \sigma_{3s(1s^2)}) + (2 - \sigma_{3s(2s^2)}) + (1 - \sigma_{3s^2}) \right] + \right.$$

$$\left. + C_{3s(p)} \cdot 3 \cdot (2 - \sigma_{3s(2p^2)}) \right\}$$

The shielding configuration is specified in the parenthesis of the subscript for constants σ. These parenthesis are omitted for two electrons occupying a single orbital.

This relationship is deduced for 3s orbital shielded, assuming that in eq. (5) for all shielding s-electrons a single value of coefficient $C_{3s(s)}$ and for p-orbitals — another value $C_{3s(p)}$ could be used.

For the same configuration another relationship could be written if two coefficients $C_{j,f}$ ($C_{3s(1s,2s)}$ and $C_{3s(3s)}$) instead of a single one ($C_{3s(s)}$) are introduced.

It is well known that the contribution of the additional minor effects cited above is represented by terms, proportional to higher powers of $Z(Z^{*})$ (particularly, the fourth one). It was already stated that in this study those effects are not introduced explicitly. Nevertheless, the data processing technique allowed quite easily to check whether the accuracy of the description is enchanced if to the right hand side of eqs. (4) and (5) a purely formal term proportional to Z^{*3} is added. The third power of the effective nucleus charge was chosen because for the hydrogen-like series 1s and 2p the contribution proportional to Z^3 appears to be significant if the correction reflecting the influence of the variable reduced mass is not introduced. Thus, modified eqs. (6) and (7) were obtained:

$$I_j = \frac{I_H}{n^2}(Z - \sum_{i=1}^{j-1} \sigma_{j(i)})^2 - Z \sum_{i=1}^{j-1} \beta_{j(i)} + \delta(Z - \sum_{i=1}^{j-1} \sigma_{j(i)})^3 \quad (6)$$

$$I_j = \frac{I_H}{n^2}(Z - \sum_{i=1}^{j-1} \sigma_{j(i)})^2 - \frac{Z}{n^2} \sum_{i=1}^{j-1} C_{j,f}(N_i - \sigma_{j(i)}) +$$

$$+ \delta(Z - \sum_{i=1}^{j-1} \sigma_{j(i)})^3 \quad (7)$$

δ is a parameter to be estimated for a given type of the orbital occupied by the jth electron.

Procedure and Results of Data Processing

The values of spectral terms* of atoms and different positively charged ions covering the three first electron shells were processed statistically. The total number of I_j values used for the parametrization of eqs. (4)-(7) was 221 (for 39 electonic configurations, listed in Table 1).

For several configurations with occupied d-orbitals only 1-4 belong to the most reliable experimental data: I_j for neutral and sometimes also for onefold ionized atoms corresponds to configurations $3p^6 3d^n 4s^2$ and $3p^6 3d^n 4s$, but not to $3p^6 3d^n$. As the first electrons removed are the 4s ones, it is possible to use for configurations $3p^6 3d^n$ the I_j values starting with twofold and sometimes onefold ionized atoms (see the data represented in Ref. 3). Besides that, already for three- or fourfold ionized atoms the parallel experimental data for the same ion extracted from different sources represent a significant scatter. Data sets used include such parallel values for which the I_j value's difference does not exceed 1.8eV.

As to the excited states of atoms and ions, only the data for such isoelectronic series were used for which the shielding electronic configuration is represented by orbitals occupied by electron pairs. Configurations 5 and 19 from Table 1 are the only exclusions.

This limitation allows to avoid the dependence of the $\sigma_{j(i)}$ and $\beta_{j(i)}$ values estimated on the spin quantum number. At the same time this grants a full correspondence between the electronic configuration and the energy level (in case fine structure of the terms is neglected). The situations when several energetic levels correspond to a single electronic configuration (e.g. to the configuration $1s^2 2s^2 2p3p$ correspond the terms ^1S, ^1P, ^1D, ^3S, ^3P and ^3D) could not be correctly interpreted in the framework of any single-electron approximation.

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* Here spectral term is a synonym of the ionization potential I_j – the energy of the removal of the electron occupying the jth orbital to the infinity.

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Table 1

Electron Configurations for the Spectral Terms
Used for Statistical Data Processing
n – the number of experimental points for the actual
data set

Subset of configurations	Seq. No	Electronic configuration	Term symbol	n
1	2 .	3	4	5
1s	1	$1s^2$	^1S	9
2s	2	$1s^2 2s$	^2S	8
	3	$1s^2 2s^2$	^1S	7
2p	4	$1s^2 2p$	$^2P^o$	8
	5	$1s^2 2s 2p$	$^3P^o$	7
	6	$1s^2 2s^2 2p$	$^2P^o$	6
	7	$1s^2 2s^2 2p^2$	^3P	6
	8	$1s^2 2s^2 2p^3$	$^4S^o$	6
	9	$1s^2 2s^2 2p^4$	^3P	6
	10	$1s^2 2s^2 2p^5$	$^2P^o$	6
	11	$1s^2 2s^2 2p^6$	^1S	6
3s	12	$1s^2 3s$	^2S	8
	13	$1s^2 2s^2 3s$	^2S	6
	14	$I, II, 3s^{\ast}$	^2S	6
	15	$I, II, 3s^2$	^1S	6
3p	16	$1s^2 3p$	$^2P^o$	8
	17	$1s^2 2s^2 3p$	$^2P^o$	6
	18	$I, II, 3p$	$^2P^o$	6
	19	$I, II, 3s 3p$	$^3P^o$	7
	20	$I, II, 3s^2 3p$	$^2P^o$	6
	21	$I, II, 3s^2 3p^2$	^3P	5
	22	$I, II, 3s^2 3p^3$	$^4S^o$	5
	23	$I, II, 3s^2 3p^4$	^3P	5
	24	$I, II, 3s^2 3p^5$	$^2P^o$	5
	25	$I, II, 3s^2 3p^6$	^1S	5

Table 1 continued

1	2	3	4	n
	26	$1s^2 3d$	^2D	8
	27	$1s^2 2s^2 3d$	^2D	6
	28	$I,II,3d$	^2D	6
	29	$I,II,3s^2 3d$	^2D	6
	30	$I,II,3s^2 3p^6 3d$	^2D	7
3d	31	$I,II,3s^2 3p^6 3d^2$	^3F	4**
	32	$I,II,3s^2 3p^6 3d^3$	^4F	4**
	33	$I,II,3s^2 3p^6 3d^4$	^5D	4**
	34	$I,II,3s^2 3p^6 3d^5$	^6S	4**
	35	$I,II,3s^2 3p^6 3d^6$	^5D	1
	36	$I,II,3s^2 3p^6 3d^7$	^4F	1
	37	$I,II,3s^2 3p^6 3d^8$	^3F	4**
	38	$I,II3s^2 3p^6 3d^9$	^2D	2
	39	$I,II,3s^2 3p^6 3d^{10}$	^1S	5

* I,II denote the completely filled first and second shells.

** The data set includes the alternative experimental values for the ion with a maximal positive charge.

As a source of experimental data for the three first rows Table 4 and for the fourth row elements References 5 and 6 were employed.

In the case of the spin-orbital splitting the arithmetical mean values were used.

The whole body of the electronic configurations was divided into subsets, each corresponding to the shielded electron (removed in the course of ionization) belonging to a single subshell (constant n and l values) as represented in Table 1. For any of these subsets an independent set of parameters to be estimated in the course of data processing is defined. Therefore, the simultaneous statistical tratment of the data corresponding to a single subset of electronic

configurations was used.

For NLLS calculations a computer "Nairi-3" was employed. The program was written by the authors of the paper. The principal description of the corresponding algorithm is presented in the Appendix of the present communication.

The results of the statistical treatment of I_j values according to eqs. (5) and (7) are listed in Table 2. The results obtained according to eqs. (4) and (6) are omitted, excluding the corresponding standard deviations S', only. The reason is that the I_j values could be described with almost equal precision by eqs. (5) and (7), containing in total a considerably smaller number of empirical parameters.

The arrows in the column "Type of Interaction" indicate the mutual orientation of the spins. The denotations 2p(2p), 3p(3p) and 3d(3d) correspond to the electrons occupying different orbitals regardless of the orientation of spins[*].

In column $C_{j,f}$ second subscripts (f) denote the shielding orbitals (or their types specified by the value of 1) related to a single constant value of this coefficient according to eqs. (5) and (7).

S_o and S denote the standard deviations for normalized and natural scalings ($S_o = S/\sigma$ where σ^2 is equal to the dispersion of the experimental values for the corresponding data set).

In the last column n_o and n denote the initial and final (after exclusion of significantly deviating points according to the Student's criterion on the level of .95) numbers of experimental points in the data set processed.

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[*] The results of data processing according to Eq.(4) lead to the conclusion that the introduction of additional parameters $\sigma_{2p(2p)}^{\uparrow\downarrow}$ and $\beta_{2p(2p)}^{\uparrow\downarrow}$ as well as $\sigma_{3p(3p)}^{\uparrow\downarrow}$ and $\beta_{3p(3p)}^{\uparrow\downarrow}$ does not improve the precision of the description.

Table 2

The Results of Data Processing According to Eqs. (5) and (7)

The dimensions of $c_{j,f}$, δ, S and S' is eV,

$\sigma_{j(i)}$ are given in elementary charge units.

Type of Interaction	Equation	$\bar{\sigma}_{j(i)}$	$c_{j,f}$	δ	S_o, S and S'	n/n_o
1	2	3	4	5	6	7
$1s^2$	5	0.5088 ± 0.0006	$c_{1s(1s)} = 6.012 \pm 0.061$		$S_o = 0.00060$ $S = 0.232$ $(S' = 0.235\ )$	9/9
$1s^2$	7	0.55768 ± 0.00006	$c_{1s(1s)} = 4.155 \pm 0.008$	$2.12 \cdot 10^{-3} \pm$ $\pm 3 \cdot 10^{-5}$	$S_o = 6.8 \cdot 10^{-5}$ $S = 0.026$ $(S' = 0.027)$	9/9
$2s(1s^2)$ $2s^2$	5	1.4401 ± 0.0012 0.5301 ± 0.0016	$c_{2s(1s)} = 7.248 \pm 0.094$ $c_{2s(2s)} = 1.619 \pm 0.065$		$S_o = 0.0015$ $S = 0.111$ $(S' = 0.112)$	15/15
$2s(1s^2)$ $2s^2$	7	1.4903 ± 0.0003 0.5220 ± 0.0004	$c_{2s(1s)} = 6.267 \pm 0.028$ $c_{2s(2s)} = 2.025 \pm 0.017$	$1.52 \cdot 10^{-3} \pm$ $\pm 4 \cdot 10^{-5}$	$S_o = 0.00040$ $S = 0.030$ $(S' = 0.030)$	15/15
$2p(1s^2)$ $2p(2s)^{\uparrow\uparrow}$	5	1.8794 ± 0.0012 0.4093 ± 0.0035	$c_{2p(s)} = 4.992 \pm 0.028$ $c_{2p(p)} = 3.087 \pm 0.018$		$S_o = 0.0036$ $S = 0.228$	51/51

Table 2 continued

1	2	3	4	5	6	7
$2p(2s^2)$		1.0196 ± 0.0023			$(S' = 0.182)$	
$2p(2p)$		0.6193 ± 0.0006				
$2p^2$		0.8837 ± 0.0020				
$2p(1s^2)$	7^*	1.9075 ± 0.0008	$c_{2p(s)} =4.576\pm0.020$	$2.84\cdot10^{-3}\pm1.2\cdot10^{-4}$	$S_o = 0.0024$	50/51
$2p(2s)$↑↑		0.4233 ± 0.0023	$c_{2p(p)} =3.126\pm0.012$		$S = 0.153$	
$2p(2s^2)$		1.0446 ± 0.0015			$(S' = 0.149)$**	
$2p(2p)$		0.6236 ± 0.0004				
$2p^2$		0.8856 ± 0.0013				
$3s(1s^2)$	5	1.6839 ± 0.0049	$c_{3s(1s,2s)}=5.240\pm0.092$		$S_o = 0.0093$	26/26
$3s(2s^2)$		1.3138 ± 0.0095	$c_{3s(2p)} =3.477\pm0.052$		$S = 0.279$	
$3s(2p^2)$		1.5520 ± 0.0025	$c_{3s(3s)} =2.61\pm0.17$		$(S' = 0.282)$	
$3s^2$		0.5200 ± 0.0082				
$3s(1s^2)$	7^*	1.7324 ± 0.0040	$c_{3s(1s,2s)}=4.884\pm0.080$	$1.76\cdot10^{-3}\pm2.4\cdot10^{-4}$	$S_o = 0.0078$	26/26
$3s(2s^2)$		1.3200 ± 0.0077	$c_{3s(2p)} =3.692\pm0.044$		$S = 0.235$	
$3s(2p^2)$		1.5520 ± 0.0022	$c_{3s(3s)} =2.69\pm0.14$		$(S' = 0.242)$	
$3s^2$		0.5200 ± 0.0069				
$3p(1s^2)$	5	1.9073 ± 0.0039	$c_{3p(s)} =3.828\pm0.036$		$S_o = 0.0123$	56/58
$3p(2s^2)$		1.5894 ± 0.0086	$c_{3p(p)} =3.036\pm0.024$		$S = 0.357$	
$3p(2p^2)$		1.7144 ± 0.0023			$(S' = 0.335)$	
$3p(3s)$↑↑		0.307 ± 0.011				

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Table 2 continued

1	2	3	4	5	6	7
$3p(3s^2)$		0.8842 ± 0.0071				
$3p(3p)$		0.5320 ± 0.0022				
$3p^2$		0.8700 ± 0.0073				
$3p(1s^2)$	7	2.0	$c_{3p(s)} = 3.181 \pm 0.031$	$4.38 \cdot 10^{-3} \pm 1.8 \cdot 10^{-4}$	$S_o = 0.0094$	56/58
$3p(2s^2)$		1.5693 ± 0.0030	$c_{3p(p)} = 3.000 \pm 0.019$		$S = 0.272$	
$3p(2p^2)$		1.7311 ± 0.0017			$(S' = 0.276)$	
$3p(3s)^{\uparrow\uparrow}$		0.3864 ± 0.0076				
$3p(3s^2)$		0.9873 ± 0.0050				
$3p(3p)$		0.5474 ± 0.0017				
$3p^2$		0.8700 ± 0.0056				
$3d(1s^2)$	5	1.9920 ± 0.0059	$c_{3d(s)} = 3.900 \pm 0.087$		$S_o = 0.0151$	51/62
$3d(2s^2)$		1.8260 ± 0.0114	$c_{3d(p)} = 5.132 \pm 0.019$		$S = 0.545$	
$3d(2p^2)$		1.9800 ± 0.0042	$c_{3d(d)} = 2.044 \pm 0.040$			
$3d(3s^2)$		1.4920 ± 0.0099				
$3d(3p^2)$		1.0688 ± 0.0040				
$3d(3d)$		0.7402 ± 0.0016				
$3d^2$		1.0				

* The Student's criterion has been used for the exclusion of significantly deviating points on the level of .99.

** Corresponds to the data set of 51 experimental points.

Discussion

Relatively low values of standard deviations S' prove that the spectral terms of atoms and ions related to the three first electron shells are well represented by eqs.(4) and (6). Therefore, one can conclude that the additivity of the constants 6_j and β_j of the interelectronic interaction is well established.

The introduction of the term $\delta(Z - \sum_{i=1}^{j-1} 6_{j(i)})^3$ leads to some additional increase of the precision of the description. This holds especially for 1s- and 2s- orbitals being in an excellent agreement with the experimental values.

The results obtained are in favor of the relationship (3), too. The reduction of the number of empirical parameters does not bring about a significant decrease in the precision of the description.

Now we shall give a more detailed discussion of some examples. In 1s and 2s subsets standard deviations S (for eq. (5)) and S' (for eq. (4)) do not practically differ. This result is trivial as the corresponding numbers of empirical parameters coincide. For subset 3s the decrease in the number of parameters by one unit is connected with the decrease of S value from .282 to 279. If the number of parameters is reduced by one more unit due to the use of a single value of the coefficient $C_{3s(s)}$ for all shielding s-electrons the S value increases up to .322, and the values of $6_{j(i)}$ are noticeably changed (the value of $6_{3s}2$, in particular). According to the Fisher criterion the parameter excluded is statistically significant.

The use of two parameters $C_{3p(s)}$ and $C_{3p(p)}$ instead of seven $\beta_{j(i)}$ values for the 3p subset is accompanied by an obviously insignificant increase of the S value (from .335 to .357). Such a comparison would be impossible for the 3d subset, as a considerably more scarce data set was used

for data processing according to Eq. (4).

Thus, the results obtained prove that the $\beta_{j(i)}$ values are proportional to the nonshielding part of the charge of shielding electrons.

The introduction of the term $\delta(z - \sum_{i=1}^{j-1} \sigma_{j(i)})^3$ into the nonshielding potential makes the description more precise as it was stated for eq. (4). As this does not concern 3d set, the respective results are not reflected in Table 2.

There is a tendency towards the increase of the value of standard deviation S for atomic particles with greater numbers of electrons (see Table 2).

The values of $\sigma_{j(i)}$ (Table 2) obtained depend, in general, on the corresponding quantum numbers. Some of those relationships are illustrated in Figs. 1 ÷ 3. Proceeding from the parametrization of eq. (5) the regularities could be detected as follows:

i. Very close values for constants $\sigma_{1s}2$, $\sigma_{2s}2$ and $\sigma_{3s}2$ (.509 .530 and .520 , respectively) justify the conclusion that the shielding of one s-electron by another occupying the same s-orbital does not depend on the principal quantum number. The $\sigma_{2p}2$ and $\sigma_{3p}2$ values (.884 and .870) are also close enough. It results from the aforesaid that for electrons occupying a single orbital the shielding constant does not depend on the principal quantum number and is, consequently, fully defined by the orbital quantum number l, only.

In Fig. 2 this dependence is demonstrated for the averaged (for s- and p- orbitals) values of $\sigma_{j(i)}$. One can see that the $\sigma_{j(i)}$ values for shielding and shielded electrons occupying a single orbital, increase with the increase of l value.

ii. If two electrons are occupying different orbitals in the same shell, the corresponding $\sigma_{j(i)}$ values decrease , when the principal quantum number n increases if the l-values for both orbitals are fixed·

$$\sigma_{2p(2p)} = .619 > \sigma_{3p(3p)} = .532$$
$$\sigma_{2p(2s)} = .510 > \sigma_{3p(3s)} = .442$$
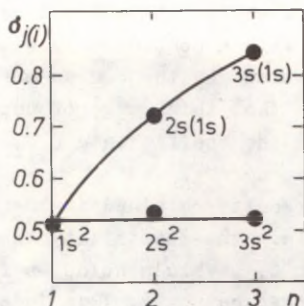
Fig. 1. Dependence of $\sigma_{j(i)}$ values on the principal quantum number n (according to the parametrization of eq. (5)).
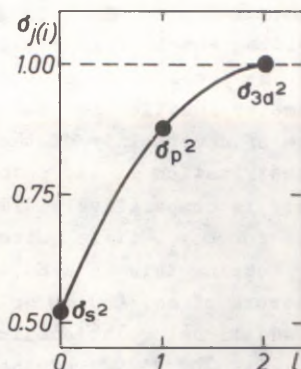
Fig. 2. Dependence of averaged (for s- an p-orbitals) values of $\sigma_{j(i)}$ on the orbital quantum number l (according to the parametrization of eq. (5)).
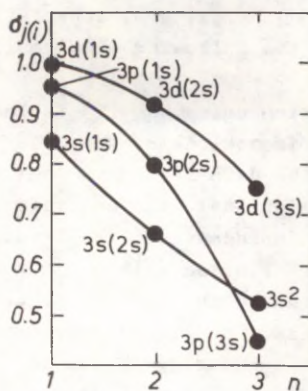
Fig. 3. Dependence of $\sigma_{j(i)}$ values on the principal quantum number n (according to the parametrization of eq. (5)).

iii. Figs. 1 and 3 demonstrate that $\delta_{j(i)}$ depends monotonically on the principal quantum number (in Fig.I the shielding and in Fig. 3 the shielded orbitals are fixed).

The problem of non-linear parametrization for a multi-parameter function is connected with a considerably wide range of uncertainty of the solution. In the course of the parametrization it was concluded that this range of uncertainty is comparatively wide for the coefficients $C_{j,f}$, while for $\delta_{j(i)}$ it is quite the contrary.

Keeping this in mind, the results obtained in the framework of eq. (5) do not exclude the possibility that the additional relationships for $C_{j,f}$-values holds as follows: iv. The value of the coefficient $C_{ns(1s)}$ is independent of the principal quantum number n for the orbital shielded.

v. $C_{2s(2s)} = C_{3s(3s)} = (C_{ns(ns)}$ for $n > 1)$

vi. $C_{2p(s)} = C_{3p(s)} = (C_{np(s)})$

vii. $C_{2p(p)} = C_{3p(p)} = (C_{np(p)})$

In the parenthesis the hypothetical generalizations for higher n values are presented.

viii. Rather close values of δ for different types of orbitals shielded including the value $\delta = 2,33 \cdot 10^{-3} \pm 0,3 \cdot 10^{-3}$ for hydrogen-like series 1s can be noticed.

These regularities could also be used for a further reduction of the number of empirical parameters, especially when the data for the fourth and the following electronic shells should be covered.

The accuracy of the description using eq. (5) is lower than that for the respective experimental data. The uncertainty of the latter, excluding the data for the 3d set, is hardly ever more than .1 eV. Besides that, the analysis of residues discloses their obvious dependence on the Z value for different isoelectronic series (curves with minimum). Eq. (7) leads to a considerable enhancement of the accuracy and to the disappearance of the above mentioned dependence for the residues. Nevertheless, the accuracy of the description of the I_j values does not become fully adequate.

Comparatively large deviations for neutral atoms become es-
pecially remarkable.[*] Still greater deviations are observed
for the electron affinities of the second row elements.

The use of eq. (7) instead of eq. (5) also leads to a
considerable change in the numerical values of the parame-
ters estimated. For the parameters obtained according to
eq. (7) the dependences on the quantum numbers hold less
strictly.

It follows from the aforesaid that the version of para-
metrization applied in this study should not be taken as
the final one. It would be reasonable to test an equation
which represents a closer imitation of the influence of the
effective nucleus charge according to the theoretical (or
empirical) relationship which adequately describe the terms
for hydrogen atom and hydrogen-like ions.

It is interesting to point out a comparatively high ac-
curacy of the total energies for the second row atoms which
could be calculated using eq. (7). The corresponding figures
are represented in Table 3.

Table 3

Comparison of Experimental and Calculated Total
Energies (in eV) for the 2nd Row Atoms

Total energies E are calculated as the negative sums
of the first, the second etc. ionization potentials. When
calculating E_{calc} by the use of eq. (7) for the last ioniza-
tion potentials the value $I_j = I_H Z^2 + 2.33 \cdot 10^{-3} Z^3$ was used.

Atom	$-E_{exp}$ [**]	$-E_{calc}$, this study	ΔE
1	2	3	4
Li	203.48	203.43	0.05
Be	399.14	399.11	0.03
B	670.97	671.00	-0.03
C	1030.08	1030.03	0.05

[*] For carbon, nitrogen and oxygen atoms these deviations
are equal to .20, .32 and -.35 eV, respectively, and for Na
and Mg .43 and .56 eV.

Table 3 continued

1	2	3	4
N	1486.03	1485.75	0.28
O	2043.80	2043.94	-0.14
F	2715.80	2715.95	-0.15
Ne	3511.54	3511.42	0.12

*** The ionization potentials from Ref. 6 were used.

Appendix

The Algorithm of Nonlinear Least Squares (NLLS) Used.

As a base the standard principle of NLLS[7] was used. According to that each step in the iteration scheme is reduced to the solution of the multilinear regression analysis (MLRA) problem for a system of equations with a matrix of coefficients formed by vector-rows of partial derivatives of the function to be parametrisized on the parameters to be estimated. The vector-row of the right sides of these equations represents the differences between the assigned and the calculated values of the quantities to be described. The solution represents temporal corrections for the parameters to be estimated.

$Y(I)$, $I = 1, ...,M$ denote a set of quantities to be described and $F(I, ...,X(J),...)$, $J=1,111,N$ - a function to be parametrisized, where $X(J)$ represents the parameters to be estimated. The set of $X(J)$ values minimizing the sum $\sum_{I=1}^{M} \left[Y(I) - F(I,...,X(J)...) \right]^2$ has to be obtained.

The initial approximation $XO(J)$ for the running set $X(J)$ of the parameters to be estimated should be defined. By numerical differentiation* the partial derivatives

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* From the function the intercept and the linear part could be extracted, if present. Corresponding partial derivatives are defined trivially and do not require numerical differentiation.

$$D(I,J) = \partial F(I,\ldots,X0(J),\ldots)/\partial X(J), \quad J=I,\ldots,N;$$
$$I=I,\ldots,M,$$

as well as the differences

$$DY(I) = Y(I)-F(I,\ldots,X0(J)\ldots), \quad I=1,\ldots M$$

are calculated.

The system of linear equations is defined as follows:

$$\sum_{J=1}^{N} D(I,J) * DX(J) = DY(I), \quad I = 1,\ldots,M; \; M > N$$

For this system the MLRA procedure is applied resulting in the calculation of a set of corrections $DX(J)$.

The MLRA procedure used demands an exclusion of the statistically non-significant (in program the probability level of .95 was used) vector-rows $D(I,J)$ $(I=1,\ldots M)$ according to the Fisher criterion. For corresponding $DX(J)$ zero values are assigned. To avoid an excessively high level of nonorthogonality of the linear problem, a vector-row for which the normalized standard deviation $SDX0(J)$ of the coefficient $DX(J)$ exceeds the limit SK (in program SK=.5[*]) has to be excluded as well.

---

[*] Normalized scaling of $D(I,J)$ and $DY(I)$ is used. Scaling factors are equal to the reciprocals of the root squares from the dispersions of corresponding vector-rows. As a criterion of the significant nonorthogonality the relation $\sum [SDX0(J)]^2 > S_0^2$ is used where S_0 denotes total standard deviation in normal scaling. The criterion $SDX0(J) > .5$ brings about a considerable degree of nonorthogonality, resulting in the enchancement of the uncertainty of $DX(J)$ values at the expense of each other (the s.c. "overpumping" effect). Accepting a lower SK value may result in an untimely stopping of the determination of temporary corrections for some parameters to be estimated.

The MLRA subprocedure dictates also the preliminary exclusion of statistically insignificant vector-rows $D(I,J)$ if the scaled covariation matrix is so insufficiently defined that it could not be rearranged without a considerable reduction of accuracy. As a criterion of a corresponding situation the satisfaction of the relation DET < CRT was used, where DET is the value of a determinant of the scaled covariation matrix and CRT is a limit for the reduction of accuracy (in program CRT=$1.0 \cdot 10^{-9}$). First of all these vector-rows $D(I,K)$ are excluded for which the following relation is satisfied :

$$1 - \left[R(J,K)\right]^2 < CRT; \quad K > J,$$

where $R(J,K)$ is the correlation coefficient between vector-rows $D(I,J)$ and $D(I,K)$.

If this procedure does not lead to successful effect, the vector-row, the removal of which results in the minimal value of the ratio $\mathcal{R}$ = DETO/DET > CRT is temporarily excluded. DETO denotes the value of the determinant of the modified scaled covariation matrix. The latter is obtained by the addition of a line and a row corresponding to the inclusion of the additional vector-row $DY(I)$.

If all values $\mathcal{R}$<CRT, the temporary exclusion of that vector-row is performed, the removal of which results in the maximal value of DET.

If DET > CRT and DETO < CRT this vector-row $D(I,J)$ has to be eliminated, the removal of which results in the minimal value of DETO. If the situation DETO < CRT continues after the removal of more than a single vector-row, that row should be temporarily eliminated the removal of which results in the maximal value of DET. After satisfaction of the condition DETO > CRT the vector-row, the exclusion of which leads to the minimal value of the ratio $\mathcal{R}$= DETO/DET, is detected. This vector-row has to be eliminated if this is not accompanied by the increase of the ratio $\mathcal{R}$ by factor exceeding a limiting value R. The value R=1.2 accepted in program grants the preservation of all vector-rows significant on the level .95.

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The procedure of a preliminary selection of the vector-
-rows $D(I,J)$ for MLRA terminates with the gradual reinclu-
sion of temporarily eliminated vector-rows in case some of
them appear to be statistically significant. The vector-row,
the reinclusion of which leads to the maximal value of
DET > CRT and to the decrease of the ratio æ by more than
R times, has to be reincluded, etc. Application of the MLRA
procedure described eliminates the need for the rearrangement
of the insufficiently determined matrix, and grants the
calculation of statistically significant and not exceedingly
"overpumped" corrections $DX(J)$.

As to the calculation technique employed for calculation
of the determinant and the rearrangement of the normalized
covariation matrix, only the elements of the upper triangle
and the diagonal ones were used. A temporary removal of the
vector-rows was carried out assigning zero values to the
corresponding elements of the upper triangle, and unity val-
ues to the diagonal ones without changing the actual range
of the matrix. To restore the starting matrix, the elements
of the lower triangle as well as those of the diagonal were
used. These details are important as they reduce considera-
bly the computer time.

After any temporary or final exclusion of the vector-
-row $D(I,J)$ the whole procedure of MLRA is repeated.

After the subsequent set of statistically significant
corrections of $DX(J)$ the new approximates of the parameters
to be estimated are assigned:

$XO(J) = XO(J) + DX(J)$.

For the excluded vector-rows the corresponding $DX(J)$
values are equalized to zero. The iteration cycle is com-
pleted if all the corrections $DX(J)$ are statistically insig-
nificant.

If the addition of the temporary correction $DX(J)$ re-
sults in the $XO(J)$ value exceeding the maximal or minimal
restrictions, the corresponding limiting value is assigned
to $XO(J)$. This fixed value could be changed during some fol-
lowing steps of iteration if the addition of the correction
results in the value of $XO(J)$ not exceeding the restriction
limits.

If the limiting value is assigned to the parameter to be estimated, all the calculations for the temporary iteration steps are repeated, whereas the corresponding vector-row $D(I,J)$ is excluded and for the correction $DX(J)$ zero value is assigned.

After the completion of the temporary iteration cycle follows the elimination of significantly deviating points according to the Student's criterion. If they are present, data processing for the remaining data set is repeated starting from the very beginning.

If these significantly deviating points are not present, the statistical significancy of the $XO(J)$ values obtained is checked. For the standard deviations $SX(J)$ of them, these of the corresponding last corrections $DX(J)$ which are not equal to zero are accepted. The satisfaction of the condition

$\eta = |(XO(J) - XS(J))/SX(J)| < SCR$ is checked for all the parameters. Here $XS(J)$ is the standard value of the Jth parameter which corresponds to the absence of this parameter in the model tested[*], SCR=constant (in program SCR=2). For all the parameters satisfying this condition the standard values are assigned and they are omitted from the set of parameters to be estimated. Then a new cycle of data processing follows and the significance of the parameters omitted is checked using the Fisher criterion. If the positive result is obtained, the exclusion of the parameters undergoing the check of their significance is confirmed, otherwise they are reincluded. Then the analogical check of the significance follows for the parameter with a minimal value of the criterion η. If this appears to be insignificant, the following one will be considered, etc. until a limiting value of η (in program 8) is reached.

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[*] Mostly $XS(J)$ equals zero but it can equal unity, too, if the exponent of the "true" parameter is accepted for the working one.

If the statistically insignificant parameters are de-
tected and eliminated from the set of those to be estima-
ted, the procedure of the exclusion of significantly devi-
ating points is repeated and another check of the signifi-
cance of the parameters to be estimated follows.The solution
procedure is terminated when no statistically insignificant
parameter is detected to be present. Conventional standard
deviations for the parameters to be estimated are calculated.
These are equalized to the standard deviations $SX(J)$ of the
corrections calculated one by one for the final set of
$X0(J)$ values. Doing that all the $DX(K)$ $K \neq J$ are not con-
sidered as the parameters to be estimated (i.e. monolinear-
ity on $D(I,J)$ vector). The $SX(J)$ values obtained by means
of this procedure do not reflect the uncertainty of the
solution caused by the "overpumping" effect cited above.

The values of the standard deviations in natural and
normal scalings are calculated according to the convention-
al formulae using the function to be parametrisized with
a running set of the values of the parameters to be esti-
mated.

The algorithm described does not allow to continue the
specification of the solution within the limits of its
uncertainty (e.g. via the minimization of the relative val-
ues of $DX(J)$ up to some limiting value assigned). No special
procedure is included to overcome the difficulties caused
by the presence of deep canyons with slanting bottom in the
space of the solutions approximates.

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NON-ELECTROLYTE EFFECTS ON THE STRUCTURE OF
THE LITHIUM CHLORIDE SOLUTIONS
IN ETHANOL.

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Differential-conductometric effect
caused by the additions of several organic
non-electrolytes (methanol, isopropyl alco-
hol, isobutyl alcohol, isoamyl alcohol) and
water in the solutions of the lithium chlo-
ride in ethanol is measured. The "structur-
ization" volumes V_s were calculated for the
molecules of the additions. A linear rela-
tionship between the volumes V_s and intrin-
sic molecular volumes is found.

Many different experimental measurements and theoreti-
cal calculations are indicating that the water and aliphatic
alcohols have significant structure of hydrogen bonds be-
tween hydroxyl groups of neighbouring molecules. Thus they
are characterized as highly structurized systems. An addi-
tion of other neutral or ionic chemical substances to such
solvents can either strengthen or loosen this structure.
According to the model of the electrolyte solutions, given
in Ref. 1 , an addition of the second substance to the
electrolyte solution causes the change in the electrical
conductivity of the latter. The increase of the number of
structural bonds leads to the decrease of the conductivity
of the solution, whereas the lowering of the number of
structural bonds results higher conductivity. This effect
is quantitatively described by the parameter of the addition

V_S which is equal to the mean volume in the 1 l of solution, where ions change their conductive activity. In case of the positive values of V_S ions pass to the non-conductive state, and if negative values of V_S they become conductive.

It was shown that in the case of aqueous solutions the so-called structurization volumes V_S are approximately proportional to the intrinsic volumes of the addition molecules. Different neutral organic compounds[2] and alkylammonium salts[3] were used as additions to the electrolyte solutions. In the number of cases the quantities V_S were calculated from the two different sets of data. These were the electrical conductivity in binary mixed solvents and the results of differential-conductometric measurements[2].

The equivalent conductivity of the electrolyte solutions in the mixed binary solvents is described by the following equation:

$$\lambda = \lambda_o \exp(- V_S c_S) , \qquad (1)$$

where λ_o is the limiting equivalent conductivity of electrolyte in the basic pure solvent (in water), and C_s denotes the molar concentration of the second solvent. Clearly the parameter V_S can be evaluated from the least--squares treatment of the limiting conductivity data for the electrolyte solutions in binary solvents.

In the differential conductometry the quantity

$$y = \frac{k \cdot 10^3}{C_s} (\frac{1}{R_o + \Delta R} - \frac{1}{R_x}) \qquad (2)$$

is found. In this formula k denotes the cell constant (cm^{-1}), C_s is the molar concentration of the small addition to the electrolyte solution, R_o and R_x are the resistances (Ω) of this solution before and after adding the second substance to the solution respectively. The quantity ΔR describes the change in the resistance of the solution caused by the dilution in the process of the addition. The quantity y (Eq. 2) is therefore simply the change of the specific conductivity of the solution per mole of added

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non-electrolyte, i.e. $\Delta\varkappa/C_S$.

It was shown by us[1] , that this quantity is simply
related to the volume of structurization V_S:

$$y = V_S \cdot \varkappa. \qquad (3).$$

There is a significant importance to investigate the
influence of the different non-electrolytes to the structure
of other solvents. In the present work we present the data
of the influence of several hydroxylic substances (the wa-
ter, methanol, isopropyl alcohol, isobutyl alcohol, and
isoamyl alcohol) on the conductivity of the lithium chlo-
ride solutions in ethanol. The choice of this system was
governed by the good solubility of lithium chloride in
ethanol, which enables to measure the differential-conducto-
metric effect in the wide range of electrolyte concentration.

Experimental

Methanol (grade "Pure") was distilled. The fraction
used had b.p. $65.0^{\circ}C$, $d_{25}^{25} = 0.7962$ g/cm^3 and $n_D^{20} = 1.3312$.

Ethanol (grade "Pure for analysis") was dried on the
CaO and distilled. The fraction used had b.p. $78.4^{\circ}C$ and
$d_{25}^{25} = 0.7898$.

Isopropyl alcohol (grade "Pure") was distilled. The
fraction used had b.p. $82.0^{\circ}C$, $d_{25}^{25} = 0.7870$ and $n_D^{20} = 1.3780$.

Isobutyl alcohol (grade "Pure for analysis") was dis-
tilled. The fraction used had b.p. $107.5^{\circ}C$, $d_{25}^{25} = 0.8019$
and $n_D^{20} = 1.3960$.

Isoamyl alcohol (grade "Pure") was distilled. The frac-
tion used had b.p. $130.5^{\circ}C$, $d_{25}^{25} = 0.8123$ and $n_D^{20} = 1.4080$.

The water used was deionized and bidistilled. The
differential-conductometric measurements were carried out
on the apparatus described elsewhers[4]. All the measurements
were made at the temperature $25.0\pm0.1^{\circ}C$, maintained constant
with the accuracy of $\pm0.001^{\circ}C$. The conductance cell was
isolated from the surrounding atmosphere by CaO tubes to
prevent the absorption of the water. The cell constant
k = 19.60 cm^{-1}. A constant resistance R_p = 9907.0 Ω was

used in parallel joint to the conductance cell for the investigation of the dilute solutions.

The quantity y was calculated according to the Eq.(2) by the program y ARV in the computer EC-1010B. The dilution term ΔR was calculated by the following procedure.

The equivalent conductivity of the lithium chloride solutions in ethanol is given by the following formula

$$\lambda = \lambda_o + A \sqrt[3]{C} + BC, \qquad (4)$$

where C is the molar concentration of the LiCl, and the constants λ_o, A and B have the values (at 25°C):

$$\lambda_o = 26.94$$
$$A = -27.13$$
$$B = 4.78$$

Therefore the term ΔR:

$$\Delta R = \frac{\partial R}{\partial C} \Delta C \qquad (5)$$

can be evaluated analytically.

Really, the derivative of the solution resistance against concentration equals :

$$\frac{\partial R}{\partial C} = - \frac{R^2}{k} \frac{\partial \varkappa}{\partial C} = - \frac{R^2 \cdot 10^{-3}}{k} (\lambda_o + \frac{4}{3} A \sqrt[3]{C} + 2 BC), \quad (6)$$

and the change in the concentration of electrolyte is
$$\Delta C = \frac{C \Delta V}{V_o} \qquad (7)$$

where ΔV and V_o are the volume of added substance and the total volume of solution respectively.

Discussion.

The numerical values of the quantity y for different hydroxylic compounds in the wide range of the lithium chloride concentration in ethanol are given in Table 1. An approximate proportionality between the values of y and

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specific conductivities of the corresponding solutions was observed (see Fig. 1). This allows to calculate the structurization volumes V_s for the added substances according to the Eq. (3):

$$V_s = \frac{y}{\mathscr{x}} \qquad (8).$$

Mean values of V_s for the all compounds investigated are given in Table 1. It should be noticed that the numerical values of V_s determined in the ethanol solutions differ substantially from those in aqueous solutions. Moreover, practically all the compounds studied in the aqueous solutions have positive values of V_s, i.e. they strenghten the hydrogen-bonded structure of water. However, the additions of water and methanol to the ethanol solutions are characterized by negative values of V_s, which means that these compounds are loosening the structure of ethanol.

In spite of this interesting inversion, a relationship between the V_s values and intrinsic molecular volumes (calculated as the sum of bond refractions) for the series of hydroxylic compounds is found. In a good approximation this relationship is linear (See Fig. 2) and it could be described by the following equation:

$$V_s(EtOH) = (-163.8 + 6.8) + 12.2 \pm 0.4) \ \sum R_D \qquad (9)$$

$$r = 0.997$$
$$s = 7.65$$
$$s_o = 0.032$$

The abscissa intercept of this linearity is equal to the intrinsic volume of ethanol, consequently $V_s = 0$ for its molecule. This result is quite natural, because the addition of ethanol to itself should not change its structure. The similar phenomenon for the water additions to the aqueous solutions was observed earlier[1].

The slope of the relationship (9) slightly differs from the slope of the similar linearity for the aqueous solutions (See Fig. 2.). Evidently further experimental investigations are necessary to generalize the relationships of type Eq. (2).
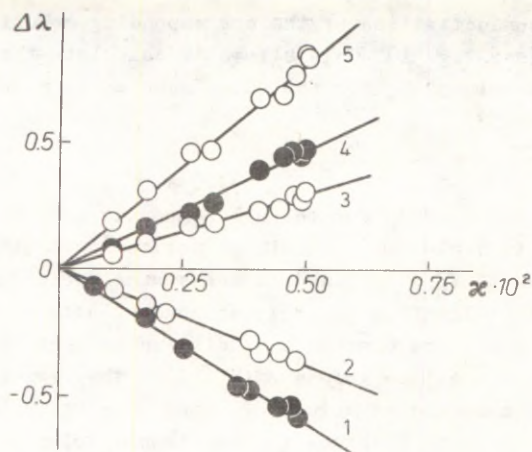
Fig. 1. Dependence of the differential-conductometric quantities Y(2) on the specific conductivity of the LiCl ethanolic solutions (1-H_2O, 2-CH_3OH, 3-$(CH_3)_3$ 3-$(CH_3)_2CHOH$, 4-$(CH_3)_2CHCH_2OH$, 5-$(CH_3)_2CHCH_2OH$)
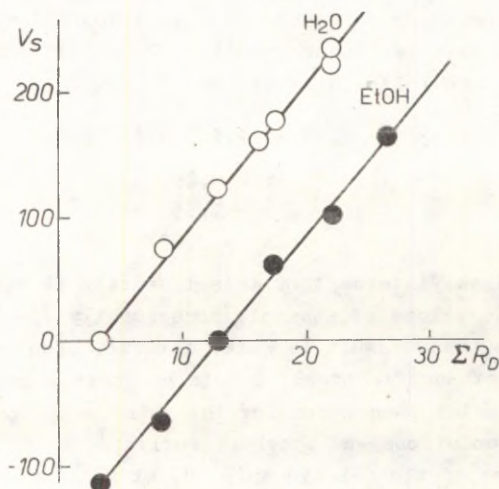
Fig. 2. Relationship between the structure-formation volumes V_s of hydroxylic compounds and their intrinsic volumes ΣR_D in the water and in ethanol.

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Table 1

Differential-conductometric $\Delta\lambda$ =y values for hydroxylic solvent additions in the lithium chloride ethanol solutions

c_{LiCl}(M)	$\varkappa \cdot 10^2$ ($\Omega^{-1}_{cm^{-1}}$)	$\Delta\lambda$ values				
		H_2O	MeOH	1-PrOH	1-BuOH	1-AmOH
0.038	0.072	-0.065 ± 0.006	–	–	–	–
0.072	0.114	–	-0.079 ± 0.011	0.067	0.085	0.198
0.135	0.177	-0.187 ± 0.005	-0.145 ± 0.008	–	–	–
0.147	0.183	–	-0.175 ± 0.003[6a]	0.107	0.168	0.316
0.237	0.255	-0.314 ± 0.007	–	–	–	–
0.254	0.267	–	–	0.171 ± 0.009	0.230 ± 0.003	0.465 ± 0.008
0.350	0.318	–	–	0.185 ± 0.048	0.264 ± 0.015	0.469 ± 0.015
0.445	0.363	-0.457 ± 0.010	–	–	–	–
0.619	0.420	–	-0.336 ± 0.009	–	–	–
0.795	0.459	–	–	0.249 ± 0.022	0.459 ± 0.015	0.687 ± 0.023
0.882	0.476	-0.535 ± 0.005	–	–	–	–
0.932	0.482	–	-0.368 ± 0.022	–	–	–
1.292	0.503	–	–	0.302 ± 0.005	0.472 ± 0.008	0.844 ± 0.005
1.525	0.497	–	–	0.270 ± 0.005	0.451 ± 0.065	0.869 ± 0.012
1.744	0.489	-0.596 ± 0.014	–	–	–	–
1.879	0.477	–	–	0.290 ± 0.020	0.478 ± 0.002	0.774 ± 0.032
2.160	0.450	-0.532 ± 0.019	-0.325 ± 0.060	–	–	–
2.506	0.408	-0.476 ± 0.026	-0.273 ± 0.026	0.231 ± 0.019	0.398 ± 0.095	0.666 ± 0.010
V_s		−115	−76	61	100	164

(a c_{LiCl} = 0.178M, $\varkappa$ = 0.00216

Therefore the influence of non-electrolyte additions
to the structure of electrolyte solutions in hydroxylic
solvents will be studied using different salts (NaI, NaSCN)
and different solvents (methanol, isoamyl alcohol).   The
results of these investigations will be discussed elsewhere.

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QUANTITATIVE STATISTICAL INTERPRETATION OF KINETIC
DATA IN THE GAS PHASE HOMOLYSIS
6. Attempt of Simultaneous Estimation of Entropy
and Enthalpy Contributions in Free Energy of
Activation

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The results of the calculation of the mu-
tually independent conventional enthalpies
of formation $\Delta H_R^{\neq}$. and entropies $\Delta S_R^{\neq}$. for
free radicals in the transition state are
presented. Impossibility of the simultaneous
parametrization of the $\Delta H_R^{\neq}$. and $\Delta S_R^{\neq}$. val-
ues has been proved. The entropy and enthalpy
contributions are estimated within the frame-
work of an iterative procedure by two paths:
proceeding the iteration from either the lit-
erature log A or E values.

The equations reflecting the influence of
the substituent effects on the conventional
formation enthalpies and entropies of substi-
tuted methyl radicals are parametrized.

In the previous papers[1-3] of this series for the estima-
tion of the rate constants of the gas phase homolysis:

$$R_i - R_j \xrightarrow{k} R_i \cdot + R_j \cdot \qquad (1)$$
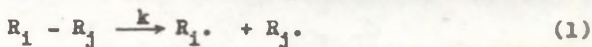
the statistical verification of the isoentropic and isokine-
netic models has been carried out.

However, even with superficial understanding of the

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gas phase homolysis one can consider the applicability of the isoentropic and isokinetic models to be purely formal. It is caused by the fact that the dependence of log k on the structure is mainly determined by the changes in E values, while the variation of log A values makes an essentially smaller contribution[1]. So, the attempts to establish the presence and values of possible real variations in the log A values are justified.

The unimolecular reaction theory has been developed during more than a half of century by now. The Lindemann scheme which may be represented by the following two-stage process:

$$R_i R_j + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R_i R_j^{\textbf{x}} + M \qquad (2)$$

$$R_i R_j^{\textbf{x}} \xrightarrow{k^{\textbf{x}}} R_i R_j^{\neq} \longrightarrow R_i^{\cdot} + R_j. \qquad (3)$$
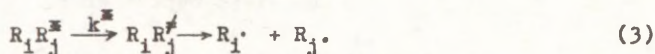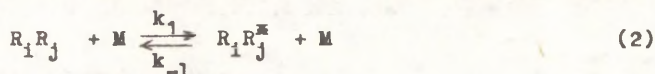
has served as the foundation for all modern theories. At that, the stage (2) corresponds to the activation and deactivation of molecules and the stage (3) to the fission. The whole reaction is described by the macrokinetic law determined from the relation of rates of these two stages. There are two limiting cases: low and high pressure limits. In the high pressure range the dependence of the limiting rate constants on temperature may be represented by the simple Arrhenius equation:

$$k_{\infty} = A_{\infty} \exp(-E_{\infty} /RT) \qquad (4)$$

Within the framework of the transition state theory the Arrhenius parameters are related with the entropy and the enthalpy of activation:

$$A_{\infty} = (ekT_{mean}/h) \exp(\Delta S^{\neq}/R) \qquad (5)$$

$$E_{\infty} = \Delta H^{\neq} + RT_{mean} \qquad (6)$$

Information on unimolecular reaction theory and existing calculation methods for the rate constants of the gas phase homolysis may be found in the literature[5-33].

Despite many other developments and much criticism it is pointed out[10] that RRKM theory should be considered as the very basis of the unimolecular reaction theory. However, any attempts to estimate the values of the parameters of the transition state retain a part of them inevitably unknown and they become fitting parameters. So, the RRKM theory does not allow to calculate the Arrhenius parameters for the high-pressure limit but it is supposed that one of them must be previously known.

Proceeding from such estimation of the problem it is reasonable to try to establish some quantitative relationships to which the log A values are subordinated using the statistical treatment within the framework of the formal model.

The list of the activation parameters for the gas phase homolysis reactions (1) used in the given study are presented in paper[2]. Seeking for the way of revealing the "real" variations of the log A values, one has to consider significant uncertainties of the corresponding values obtained from the experimental data according to the Arrhenius equation. The absence of parallel data for a large number of reactions leads to the situation where the uncertainty of the log A values for a single reaction is comparable with the whole range of the variation of the log A values observed. For that reason one can hardly expect to get the full picture of the dependence of the log A values on the structure of compounds undergoing homolysis, proceeding from the data available.

The calculation of the conventional formation enthalpies of free radicals within the framework of the isoentropic or isokinetic models, or proceeding from the experimental activation energies was based on the following equation for the activation enthalpy:

$$D_{ij} = \Delta H^{\neq}_{R_i\cdot} + \Delta H^{\neq}_{R_j\cdot} - \Delta H^o_{OR_iR_j} \tag{7}$$

This relationship assumes the absence of interaction between free radicals formed in the activated state. It supposes also the constancy of the intrinsic temperature-contributions of enthalpies during the transition state.

Instead of the experimental formation enthalpies for reactants one can use respective energies of interaction $(I_{R_1 R_j})$ between substituents R_i and R_j for these compounds according to the method described in ref. 2. Then, instead of equation (7), one can write:

$$D_{ij} = \Delta\Delta H^{\neq}_{R_1 \cdot} + \Delta\Delta H^{\neq}_{R_j \cdot} - I_{R_1 R_j} \tag{8}$$

where

$$\Delta\Delta H^{\neq}_{R_1 \cdot} = \Delta H^{\neq}_{R_1 \cdot} - \Delta H^{0}_{OR_1 -} \tag{9}$$

$$\Delta\Delta H^{\neq}_{R_j \cdot} = \Delta H^{\neq}_{R_j \cdot} - \Delta H^{0}_{OR_j -} \tag{10}$$

$$I_{R_1 R_j} = \gamma_{R_1} \gamma_{R_j} + \alpha^{\neq} \sigma_{R_1} \sigma_{R_j} \tag{11}$$

Conformably to the transition state theory[4] for unimolecular reactions of the type (1) the log k value (subscript ∞ is omitted) is given by:

$$\log k = \log (k'T/h) + \Delta S^{\neq}/2.3R - \Delta H^{\neq}/2.3RT =$$
$$= \log (ek'T/h) + \Delta S^{\neq}/2.3R - E/2.3RT \tag{12}$$

taking into account the expressions (5) and (6). k' denotes the Boltzmann and h - the Planck constant, E is an experimental activation energy calculated according to the Arrhenius equation, $\Delta H^{\neq} = E - RT$ represents the activation enthalpy and $\Delta S^{\neq}$ - the activation entropy.

For the $\Delta S^{\neq}$ value it is reasonable to test an additive hypothesis analogously to the enthalpy of activation:

$$\Delta S^{\neq}_{R_1 R_j} = \Delta S^{\neq}_{R_1 \cdot} + \Delta S^{\neq}_{R_j \cdot} \tag{13}$$

Here $\Delta S_{R\cdot}^{\neq} = S_{R\cdot}^{\neq} - S_{R-}^{o}$ where $S_{R\cdot}^{\neq}$ is the entropy of a free radical in the transition state and S_{R-}^{o} denotes the additive contribution to the entropy of the initial state by a substituent R.

Additivity rule for entropy has been discussed for example, in papers by Benson and co-workers both for compounds[34-35] and free radicals[24] at different levels. Three approximations are revealed: the zero order approximation for atomic properties, the first order approximation of bond properties, and the second order approximation of group properties. The reliability of the description has been enhanced in the same sequence. For the latter case the uncertainty of the S_{298}^{o} values is about 0.5-1.0 e.u. [27] for compounds.

Statistically corrected value of the rate constant $\log k^{c}$ may be represented as follows:

$$\log k^{c} = \log A_{ij} - \log n_{ij} - E_{ij}/2.3RT =$$

$$= \log (k'T/h) + (\Delta S_{R_1\cdot}^{\neq} + \Delta S_{R_j\cdot}^{\neq})/2.3R \div$$

$$\div (\Delta H_{R_1\cdot}^{\neq} + \Delta H_{R_j\cdot}^{\neq} - \Delta H_{OR_1R_j}^{o})/2.3RT \qquad (14)$$

Analogously one can obtain the following equation:

$$\log A_{ij} \sim \log n_{ij} - E_{ij}/2.3RT = \log (k'T/h) +$$

$$+ (\Delta S_{R_1\cdot}^{\neq} + \Delta S_{R_j\cdot}^{\neq})/2.3R - (\Delta\Delta H_{R_1\cdot}^{\neq} + \Delta\Delta H_{R_j\cdot}^{\neq} - I_{R_1R_j})/2.3RT \qquad (15)$$

The $\Delta S_{R\cdot}^{\neq}$ and $\Delta H_{R\cdot}^{\neq}$ or $\Delta\Delta H_{R\cdot}^{\neq}$ values in eqs. (14) and (15) are regarded as completely independent of one another. For the statistical treatment these equations may be transformed as follows:

$$\Delta H_{R_1\cdot}^{\neq} + \Delta H_{R_j\cdot}^{\neq} - T\Delta S_o^{\neq} - T\Delta S_{R_1\cdot}^{\neq} - T\Delta S_{R_j\cdot}^{\neq} =$$

$$= \Delta H_{OR_1R_j}^{o} + E_{ij} + 2.3RT(\log n_{ij} - \log A_{ij} + \log (k'T/h)) \qquad (16)$$

$$\Delta\Delta H^{\neq}_{R_i\cdot} + \Delta\Delta H^{\neq}_{R_j\cdot} - T\Delta S^{\neq}_0 - T\Delta S^{\neq}_{R_i\cdot} - T\Delta S^{\neq}_{R_j\cdot} =$$

$$= I_{R_iR_j} + E_{ij} + 2.3RT(\log n_{ij} - \log A_{ij} + \log(k'T/h)) \quad (17)$$

where $\log (k'T/h) = 10.319 + \log T$. $\Delta S^{\neq}_0$ is the nonadditive contribution of the activation entropy which should be indistinguishable from zero.

Equations (16) and (17) may be modified taking into account the substituent effects in the radicals of the $X_1X_2X_3C\cdot$ type and in the corresponding initial compound[36]. The $\Delta H^{\neq}$ and $\Delta\Delta H^{\neq}$ values for substituted methyls are given by following expressions:

$$\Delta H^{\neq}_{X_1X_2X_3C\cdot} = \Delta H^{\neq}_{CH_3\cdot} + \sum_i \Delta H_{X_1-} + \rho_{C\cdot}\sum_i \rho_{X_i} +$$

$$+ \alpha^x \sigma_{C\cdot} \sum_i \sigma_{X_i} + \alpha^x z^x_{C\cdot} \sum_{i<j}\sum \left\{\sigma_{X_i} \sigma^x_{X_j}\right\} +$$

$$+ N_= \psi_= + N_{CN} \psi_{CN} + N_{NO_2} \psi_{NO_2} \quad (18)$$

$$\Delta\Delta H^{\neq}_{X_1X_2X_3C\cdot} = \Delta\Delta H^{\neq}_{CH_3\cdot} + (\rho_{C\cdot} - \rho_{CH_3})\sum_i \rho_{X_i} -$$

$$- A\sum_{i<j}\sum\left\{\rho_{X_i} \rho_{X_j}\right\} - B\left\{\rho_{X_1} \rho_{X_2} \rho_{X_3}\right\} + \alpha^x \sigma_{C\cdot}\sum_i \sigma_{X_i} +$$

$$+ \alpha^x(z^x_{C\cdot} - z^x_C)\sum_{i<j}\sum\left\{\sigma_{X_i} \sigma_{X_j}\right\} + N_= \psi_= + N_{CN}\psi_{CN} + N_{NO_2}\psi_{NO_2}$$

$$\quad (19)$$

The products in braces are equalled to zero if all substituents are halogen atoms the ρ or σ^x constants for which are multiplied[37]. $\psi_=$, ψ_{CN} and ψ_{NO_2} denote energies of resonance for $\overline{\pi}$-electron systems, cyano- and nitro groups connected with the free radical center $-\overset{\cdot}{\underset{|}{C}}\cdot$, respectively, $N_=$ and N_{CN} are the numbers of the $\overline{\pi}$-electron systems or cyano groups at this center. N_{NO_2} equals unity if one or several nitro groups are connected with the

center $-\overset{|}{\underset{|}{C}}\cdot$, otherwise it equals zero. In this way the steric hindrance of the resonance caused by the interaction of several nitro groups is indirectly taken into consideration.

A dependence of the $\Delta S^{\neq}$ values for substituted methyls on the substituent effects is previously unknown. Testing different reasonable hypothesis one must admit the sufficiently rigid conditions of the parametrization related to the form of this relationship. It appears from the requirement to have a sufficient number of statistical degrees of freedom. For instance, any scheme must be precedingly rejected if it demands new empirical parameters for each substituent X connected with the center $-\overset{|}{\underset{|}{C}}\cdot$, for the data set considered. Therefore, one must be limited to schemes which are taking into account only the number of such substituents in a given radical. For example, it can be considered that only the numbers of these substituents and their pairwise interactions are significant:

$$\Delta S^{\neq}_{X_1 X_2 X_3 C\cdot} = \Delta S^{\neq}_{CH_3\cdot} + NQ + pY \tag{20}$$

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

In fact, this model assumes that the "entropic" substituent constants for all substituents except hydrogen equal to unity.

An actual data treatment showed the statistical insignificance of the term NQ. Therefore, this value in the right hand side of eq. (20) is omitted below.

The data treatment according to eqs. (16) and (17) is technically possible using the multilinear regression analysis (MLRA) program and taking the $\Delta H^{\neq}_{R\cdot}$ or $\Delta\Delta H^{\neq}_{R\cdot}$ and $\Delta S^{\neq}_{R\cdot}$ as unknown parameters to be determined. The results of different versions of this treatment are presented in Tables 1 and 2. A minimum (T_{min}) and maximum (T_{max}) temperature values of investigated ranges, beside mean values (T_{mean}) , are used. Likewise earlier [2,3] only the data for the most

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frequently occurring radicals were processed instead of the complete data set. One can see from Tables 1 and 2 that sufficiently high final (after the exclusion of significantly deviated points according to Student's criterion) accuracy of description is achieved. Especially it is related to the results obtained by processing the data for three temperatures (T_{min}, T_{mean} and T_{max}) of investigated temperature ranges for each reaction. At that the standard deviation is 0.54 (2.05) kcal/mol, the number of the points involved equals 199 (300), and the number of the reactions involved is 32 (35). Using the data only for T_{mean} the standard deviation equals 1.35 (2.22) kcal/mol, the number of points involved equals to 88 (100), and the number of reactions involved - 32 (35). In parentheses respective characteristics for initial data sets before the exclusion of significantly deviating points are indicated.

Nevertheless, the actual results (the $\Delta H_R^{\neq}$. and $\Delta S_R^{\neq}$. values for free radicals listed in Tables 1 and 2) obtained by this way hardly reflect the real situation with sufficient accuracy. It can be seen particularly on corresponding $\Delta S_R^{\neq}$. values. Their dependence on the structure of free radicals is deprived of any logic. For instance, the $\Delta S_R^{\neq}$. values $10.1^{\pm}0.6$, $5.5^{\pm}1.1$, $2.5^{\pm}0.5$ and $11.4^{\pm}0.7$ (see Table 2) for the radicals CH_3., C_2H_5., $(CH_3)_2CH^{\cdot}$ and $(CH_3)_3C^{\cdot}$, respectively, are obtained using the data at three temperatures for each independent combination of data (the total number of them is NE) and the combinations for 14 radicals are covered. Very uncertain and at the same time high absolute values of $\Delta S_R^{\neq}$. for halogen atoms seem to be illogical as well. The activation entropy constant contribution ($\Delta S_0^{\neq} = -6.3^{\pm}0.5$) does not equal zero and increases essentially in result of the procedure of the exclusion of points. This value arises if the entropy contribution is expressed as follows:

$$\Delta S_{R_i R_j}^{\neq} = \Delta S_0^{\neq} + \Delta S_{R_i}^{\neq}. + \Delta S_{R_j}^{\neq}. \tag{21}$$

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The $\Delta S_0^{\neq}$ value differing from zero is equivalent to the introduction of a correction into the constant log (k'/h), which is fully unjustified. To these contradictions one can add completely absurd $\Delta S_R^{\neq}$. values for halogens obtained by processing the data at a single temperature (for Br. 206 ± 126, for I. 27.8 ± 14 after the exclusion of points, and for Cl· -18.3 ± 25749 before the exclusion of points). Besides, a significant unstableness of solution during the exclusion of points should be noted.

All above is easily explained if the statistical effect of "overpumping" between pairs of parameters $\Delta H_{R_i.}^{\neq}$ - $\Delta S_{R_j.}^{\neq}$ is considered. Coefficients in front of unknown $\Delta H_{R_i.}^{\neq}$ values are equal to 0, 1 or 2 (for symmetrical combinations $R_i - R_j$), and ahead of $\Delta S_{R_i.}^{\neq}$ - 0, T or 2T, respectively. Since T value varies in limited[1] ranges, the significant correlation between columns of coefficient matrix corresponding to $\Delta H_{R_i}^{\neq}$ and $\Delta S_{R_i.}^{\neq}$ for each value of a subscript i is a direct reason for the indicated "overpumping". It is known that essential uncertainties of the initial experimental data are able to favor the "overpumping".

The conclusion may be drawn that the simultaneous parametrization of the $\Delta H_R^{\neq}$. and $\Delta S_R^{\neq}$. values for free radicals using the MLRA procedure does not lead to the sufficiently reliable results in the present case if the separation of the entropy and enthalpy contributions is considered.

A sequential processing of the entropy and enthalpy contributions in eqs. (16) and (17) within the iterative procedure directed to obtain the self-consistent result is an alternative method. Actually, it means that eq. (16) is replaced by two following equations (assuming $\Delta S_0^{\neq} = 0$):

$$\Delta S_{R_i.}^{\neq} + \Delta S_{R_j.}^{\neq} = 2.3R(\log A_{ij} - \log n_{ij} - \log(ek' T_{mean}/h)) \tag{22}$$

and

$$\Delta H_{R_i.}^{\neq} + \Delta H_{R_j.}^{\neq} = E_{ij} - RT_{mean} + \Delta H_{OR_i R_j}^o \tag{23}$$

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The enthalpy contribution in the case of the iterative procedure for eq. (17) is expressed as follows:

$$\triangle\triangle H^{\neq}_{R_i.} + \triangle\triangle H^{\neq}_{R_j.} = E_{ij} - RT_{mean} + I_{R_i R_j} \qquad (24)$$

Two parallel procedures A) and B) are possible. The former starts from the literature values of $\log A_{ij}$, and the latter — from E_{ij}. Let us examine them more thoroughly within the framework of eqs. (22) and (23).

A) Procedure

The zero order approximations of the $\triangle S^{\neq}_{R.}$ values for free radicals were computed in result of the MLRA in the coordinates of eq. (22). Proceeding from these $\triangle S^{\neq}_{R.}$ values, corrected values of the $\log A_{ij}$ for all combinations of i and j were further calculated:

$$\log A_{ij(corr)} = \log(ek'/h) + \log T_{mean} + (\triangle S^{\neq}_{R_i.} + \triangle S^{\neq}_{R_j.})/2.3R \quad (25)$$

Proceeding from these values corrected values of $E_{i.}$ were calculated:

$$E_{ij(corr)} = E_{ij} + 2.3RT_{mean}(\log A_{ij(corr)} - \log A_{ij} + \log n_{ij}) \quad (26)$$

Then the zero order approximations of the $\triangle H^{\neq}_{R_i.}$ and $\triangle H^{\neq}_{R_j.}$ values were calculated using the MLRA in the coordinates of the following equation:

$$\triangle H^{\neq}_{R_i.} + \triangle H^{\neq}_{R_j.} = E_{ij(corr)} - RT_{mean} + \triangle H^{O}_{OR_i R_j} \qquad (27)$$

Further, new $E_{ij(corr)}$ values were calculated:

$$E_{ij(corr)} = \triangle H^{\neq}_{R_i.} + \triangle H^{\neq}_{R_j.} - \triangle H^{O}_{OR_i R_j} + RT_{mean} \qquad (28)$$

From these values new $\log A_{ij(corr)}$ were calculated in turn:

$$\log A_{ij(corr)} = \log A_{ij} + (E_{ij(corr)} - E_{ij})/2.3RT_{mean} \qquad (29)$$

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The obtained log $A_{ij(corr)}$ values were inserted into
eq. (22) instead of log A_{ij} and the whole procedure was
repeated once again leading to the first order approxima-
tions for $\Delta S_R^{\neq}.$ and $\Delta H_R^{\neq}.$.

B) Procedure

The MLRA in the coordinates of eq. (23) was carried out
resulting in the zero order approximations of the $\Delta H_R^{\neq}.$ val-
ues for free radicals. Proceeding from the latter the
$E_{ij(corr)}$ values were calculated according to eq. (28). From
$E_{ij(corr)}$ the log $A_{ij(corr)}$ values were calculated according
to eq. (29). These values were inserted into eq. (22) in-
stead of the log A_{ij} values and in result of the MLRA in the
coordinates of this equation the zero order approximations
of the $\Delta S_R^{\neq}.$ values for free radicals were calculated. The
procedure was continued according to eqs. (25), (26) and
(27) resulting in the first order approximations of the
$\Delta H_R^{\neq}.$ values for free radicals. Proceeding from the latter
the first order approximations of the $\Delta S_R^{\neq}.$ values for free
radicals were calculated using eqs. (28), (29) and (22).

The sense of the both procedures leads to the removal
of the "noise" background during the realization of the
exclusion of significantly deviating points in each cycle
of the MLRA. Since in these cycles the parameters to be
determined were either $\Delta S_R^{\neq}.$ or $\Delta H_R^{\neq}.$ for free radicals the
possibility of the above "overpumping" is at least essenti-
ally decreased.

The results obtained using the described A) and B) pro-
cedures according to eqs. (22) and (23) are presented in
Tables 3 - 6. One can see that a high degree of self-consis-
tency for the data is achieved already as a result of two
iterative cycles on the level of the first order approxi-
mations while the A) and B) procedures lead to almost iden-
tical results. For the majority of radicals, except halogen
atoms the first order approximations are nearly close to
those of zero order. This result confirms quick convergence
of the described iterative procedure.

It should be underlined that the first order approximations $\Delta S_R^{\neq}$. for the halogen atoms $Cl^\bullet$, $Br^\bullet$ and $I^\bullet$ are indistinguishable from zero and the analogous $\Delta H_R^{\neq}$. values for $Br^\bullet$ and $I^\bullet$ represented by more than single equations are close to the known values ($\Delta H_{0(Br^\bullet)}^{0} = 28.18$ and $\Delta H_{0(I^\bullet)}^{0} = 25.63$ kcal/mol[38]) estimated on the ΔH_0^0 values of Br_2 and I_2 molecules and their dissociation energies D_o, if the A) procedure is used. This result seems fully reasonable. B) procedure leads to negative $\Delta S_R^{\neq}$. values for halogen atoms and the closeness of the $\Delta H_R^{\neq}$. values for $Br^\bullet$ and $I^\bullet$ with above mentioned values retains only assuming $\Delta S_{Br^\bullet}^{\neq}$. $= \Delta S_I^{\neq}$. $= 0$ (see Table 6). At the same time the $\Delta S_R^{\neq}$. values for other radicals keep their values and the accuracy of description remains on the same level. When the $\Delta S_H^{\neq}$. value is included into the set of unknown parameters its value is indistinguishable from zero. Using B) procedure the $\Delta H_H^{\neq}$. value as a parameter to be determined is equal to 51.6 ± 1.6 kcal/mol for the initial data set (before the exclusion of points) in the case of the zero order approximation. This result coincides with the value based on ΔH_0^0 and D_o for H_2[38]. After the exclusion of points the $\Delta H_H^{\neq}$. value is dropped to 48.9 ± 0.5 kcal/mol. Proceeding from the above one can from the very beginning equalize the $\Delta S_R^{\neq}$. values for the halogen atoms with zero, and assume $\Delta S_H^{\neq}$.$=0$, $\Delta H_H^{\neq}$.$=51.6$ kcal/mol.

The largest discrepancy between A) and B) procedures occurs in the case of the methyl radical characterized by the $\Delta S_{CH_3}^{\neq}$. values 3.1 ± 0.2 and 5.2 ± 0.1 e.u. and the $\Delta H_{CH_3}^{\neq}$. values 32.0 ± 0.1 and 34.1 ± 0.2 kcal/mol, respectively. If the whole set of the radicals belonging to $(CH_3)_n H_{3-n} C^\bullet$ type is examined the known linearity on n for the corresponding $\Delta H_n^{\neq}$ values is observed:

$$\Delta H_n^{\neq} = \Delta H_0^{\neq} + nx \qquad (30)$$

One can interpret this equation as the additivity of the γ-interaction[2,36]. For the $\Delta S_n^{\neq}$ values obtained using A) procedure the following relationship holds excellently ($s = 0.08$ e.u.):

$$\Delta S_n^{\neq} = \Delta S_0^{\neq} + pY \tag{31}$$

where p is the number of interactions between methyl groups. If n=0 or 1 p=0, if n=2 p=1, and n=3 corresponds to p=3.

The values of $\Delta H_{CH_3}^{\neq}$, $\Delta S_{CH_3}^{\neq}$ and $\Delta S_{(CH_3)_3C}^{\neq}$ obtained using B) procedure remarkably deviate from these relationships.

A) and B) procedures give compatible results in the limits of combined uncertainties for the radicals $NH_2^{\cdot}$, $NO_2^{\cdot}$; $SH^{\cdot}$, $CH_3O^{\cdot}$, $C_2H_5O^{\cdot}$, $CH_2=CHCH_2^{\cdot}$ and $C_6H_5CH_2^{\cdot}$.

Proceeding from the above results one can prefer the $\Delta S^{\neq}$ and $\Delta H^{\neq}$ estimates obtained using A) procedure.

The following parameters of the linear regressions in the coordinates of eqs. (30) and (31) are obtained using the $\Delta S^{\neq}$ and $\Delta H^{\neq}$ values for alkyl radicals $(CH_3)_3H_{3-n}C^{\cdot}$ resulting from the use of the A) procedure:

$$\Delta H_0^{\neq} = \Delta H_{CH_3}^{\neq} = 31.7 \pm 0.2 \text{ kcal/mol} \tag{32}$$

$$\mathscr{x} = Y_{CH_3} Y_{C^{\cdot}} = 10.06 \pm 0.15 \tag{33}$$

$$\Delta S_0^{\neq} = \Delta S_{CH_3}^{\neq} = 3.2 \pm 0.02 \text{ e.u.} \tag{34}$$

$$Y = 1.43 \pm 0.02 \tag{35}$$

The $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values for alkyl radicals should found on these parameters. From eq. (33) and Y_{CH_3} = 3.94 the values of $Y_{C^{\cdot}}$ = 2.55 and ($Y_{C^{\cdot}} - Y_{CH_3}$) = -1.39 are obtained, somewhat higher than the values[36] obtained using the isoentropic and isokinetic models ($Y_{C^{\cdot}}$ in the ranges of 2.0 - 2.2).

The results of using the iterative A) and B) procedures according to eqs. (22) and (24) are listed in Tables 7-10. Generally they are analogous to the results achieved applying the experimental enthalpies of formation and the conclusions drawn above, hold. Thus, A) procedure leads to nearly zero values of $\Delta S^{\neq}$ for halogens while sig-

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nificantly negative values are obtained using B) procedure.
The quick convergence of the iterative procedure is taking
place as well. The results of the data treatment for the
enthalpy contribution of the second order approximation are
presented in Table 10 suplementally to the results of the
zero and first order approximations. However, the result
remains identical. By analogy of eq. (30) the linearity on
n for the radicals of type $(CH_3)_n H_{3-n} C^\cdot$ is valid:

$$\Delta\Delta H_n^{\neq} + n\,\Upsilon_{CH_3}^2 + p\Delta\,\Upsilon_{CH_3}^2 + B\Upsilon_{CH_3}^3 = \Delta\Delta H_{CH_3}^{\neq} + n\,\Upsilon_{C^\cdot}\cdot\Upsilon_{CH_3^\cdot} \quad (36)$$

p denotes the number of interactions between methyl groups,
A= -0.2 and B= 0.02 are the constants enabling the calcula-
tion of the contributions of the pairwise and triple inter-
actions via the C atom to the total energy of the Υ-inter-
action for polysubstituted alkanes[37].
The value of $\Upsilon_{CH_3}\Upsilon_{C^\cdot}$ is close to 10 as well. A good linear
relationship according to eq. (31) is not observed for the
$\Delta S_n^{\neq}$ values, however, they are located around the straight
line based on the values of (34) and (35). A) procedure
remains also somewhat more preferable.

Thus, we have determined the $\Delta S_R^{\neq}.$ and $\Delta H_R^{\neq}.$ or $\Delta\Delta H_R^{\neq}.$
values for the 15 most represented radicals. These values
for all other radicals which are not covered by the iter-
ative procedure may be calculated according to the equations:

$$\Delta S_{R_i}^{\neq}. = 2.3R(\log A_{ij} - \log n_{ij} - \log(ek\,^\prime T_{mean}/h)) - \Delta S_{R_j}^{\neq}. \quad (37)$$

and

$$\Delta H_{R_i}^{\neq} = E_{ij} - RT_{mean} + \Delta H_{OR_i R_j}^o. \quad (38)$$

or

$$\Delta\Delta H_{R_i}^{\neq}. = E_{ij} - RT_{mean} + I_{R_i R_j} - \Delta\Delta H_{R_j}^{\neq}. \quad (39)$$

where the subscript j denotes a free radical the values
$\Delta S^{\neq}$ and $\Delta H^{\neq}$ or $\Delta\Delta H^{\neq}$ of which are known either as a result

of the iterative procedure (primary values), or may be obtained earlier by eqs. (37) – (39). If parallel estimates were available the mean values would be calculated after the exclusion of significantly deviating points according to the Student's criterion on the confidence level 0.95. The list of the results obtained by this procedure for 15 radicals which are represented in more than single combinations of the type $R_i R_j$ is presented in Table 11. For comparison the $\Delta H_{R}^{\neq}$. values calculated proceeding from the isoentropic model according to equations:

$$\Delta H_{R_i}^{\neq}. + \Delta H_{R_j}^{\neq}. = D_{ij} + \Delta H_{OR_i R_j}^{o} \qquad (39)$$

where

$$D_{ij} = E_{ij} + 2.3RT_{mean}(14.64 - \log A_{ij} + \log n_{ij}) \qquad (40)$$

are listed.

The estimates of $\Delta H_{R}^{\neq}$. for the most represented radicals obtained both as a result of the iterative A) procedure and proceeding from the isoentropic model with $\log A_o = 14.64$ are also compared in Table 5. In paper[2] the assumption of 1.5 kcal/mol served as an estimate of the upper limit of the standard deviation for the data treatment in the coordinates of eq. (39) and the analogous data treatment using D_{ij} values according to eq. (8). One can see that the estimates of $\Delta H_{R}^{\neq}$. values both taking into account the variation of the $\log A$ values caused by the inconstancy of the $\Delta S_{R}^{\neq}$. values and these obtained proceeding from $\log A_o = 14.64$ differ by more than the indicated 1.5 kcal/mol for 7 radicals in Table 5, as well as for 7 radicals in Table 11 (are underlined). It is of interest to note that they include all the radicals which have the negative $\Delta S_{R}^{\neq}$. values. Generally, it is hard to imagine the transition state for the gas phase homolysis being less "loose" than the initial state. Consequently, the negative $\Delta S_{R}^{\neq}$. values are hardly ever justified. Among the other underlined radicals different alkyl radicals (except $C_6H_5CH_2$.) are included. They have higher $\Delta S_{R}^{\neq}$. values than the effective mean value of 2.3 e.u.

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corresponding to the log $A_o=14.64$ at $T = 750^oK$. These estimates should be evidently considered as the statistically justified ones and they are in accordance with the transition state theory. Unfortunately, a great uncertainty of single log A values prevents a real estimation of the $\Delta S_R^{\neq}$. values for the radicals which occur only in single combinations of R_iR_j.

Thus the log k values may be calculated using the values of $\Delta H_R^{\neq}$. either based on the effective mean value of log $A_o=14.64$ (denote as $\Delta H_R.)^2$ or on the values calculated in the present paper and conjugated by the respective $\Delta S_R^{\neq}$. values. Although the latter approach should undoubtedly be considered a more preferable one, its applicability range is limited because of the lack and unreliability of corresponding experimental data.

One can show that the $\Delta H_R.$ and $\Delta H_R^{\neq}$. values are related by the equation as follows:

$$\Delta H_R. = \Delta H_R^{\neq}. + T_e . 10^{-3}(\Delta S_o - \Delta S_R^{\neq}.), \qquad (41)$$

where $\Delta S_o = 2.3R(\log A_o - \log(ek^*/h) - \log T_e)/2$ equals the half value of the activation entropy corresponding to the effective mean value of log A_o, T_e is some kind of averaged temperature for the data set used for the estimation of the given $\Delta S_R^{\neq}$. value. It should be noted that assuming the universal log A_o value the log k_T estimates would be the less reliable the farther the considered temperature lies from this temperature range on which respective $\Delta H_R.$ values are parametrized.

Estimation of the Substituent Effects for Substituted Methyls

The value of $\gamma_C. = 2.55$ follows from eq. (33) as it was mentioned already. This value is somewhat higher than those obtained using the isoentropic model[36]. Taking into account this $\gamma_C.$ value, applying eqs. (30) and (31) to any substituted methyls, and combining eqs. (16) and (18) or (17) and (19) one can obtain following equations for the treatment of initial data of homolysis for the com-

pounds $X_1X_2X_3C - X_4$ where one of the forming radicals represents a substituted methyl:

$$pY - (\alpha^{\neq} \, \delta_C^{\cdot} \sum_{i=1}^{3} \delta_{X_i} + \gamma \sum_{i<j}^{2} \sum_{j}^{3} \left\{ \delta_{X_i}^{\neq} \, \delta_{X_j} \right\} + N_{\equiv} \psi_{\equiv} +$$

$$+ N_{CN} \psi_{CN} + N_{NO_2} \psi_{NO_2})10^3/T = F_{X_1X_2X_3C} - X_4 \qquad (42)$$

In the case of eqs. (16) and (18)

$$\gamma = \alpha^{\neq} \, z_C^{\neq} \cdot \qquad (43)$$

and

$$F_{X_1X_2X_3C-X_4} = 2.3R(\log A_{ij} - \log n_{ij} - 10.319 - \log T) -$$

$$- \Delta S_{CH_3}^{\neq} \cdot - \Delta S_{X_4}^{\neq} \cdot + (\Delta H_{CH_3}^{\neq} \cdot + \Delta H_{X_4}^{\neq} \cdot + \sum_{i=1}^{3} \Delta H_O^o(X_i-) +$$

$$+ \varphi_C \cdot \sum_{i=1}^{3} \varphi_{X_i} - \Delta H_O^o(X_1X_2X_3C-X_4) - E_{ij})10^3/T \qquad (44)$$

For the combination of eqs. (17) and (19):

$$\gamma = \alpha^{\neq} (z_C^{\neq} \cdot - z_C^{\neq}) \qquad (45)$$

and

$$F_{X_1X_2X_3C-X_4} = 2.3R(\log A_{ij} - \log n_{ij} - 10.319 - \log T) -$$

$$- \Delta S_{CH_3}^{\neq} \cdot - \Delta S_{X_4}^{\neq} \cdot + (\Delta\Delta H_{CH_3}^{\neq} \cdot + \Delta\Delta H_{X_4}^{\neq} \cdot + (\varphi_C \cdot - \varphi_{CH_3}) \sum_{i=1}^{3} \varphi_{X_i} -$$

$$- A \sum_{i<j}^{2} \sum_{j}^{3} \left\{ \varphi_{X_i} \, \varphi_{X_j} \right\} - B \left\{ \varphi_{X_1} \varphi_{X_2} \varphi_{X_3} \right\} - I_{ij} - E_{ij}) 10^3/T \qquad (46)$$

The subscript i is related to the radical $X_1X_2X_3C^{\cdot}$, j - to X_4. (except substituents X_1 and X_3). I_{ij} was calculated by eq. (11) assuming $\alpha^{\neq} = 1.37$ and $\delta_{NO_2}^{\neq} = 4.5$ (see[37]).

The value of F on the right hand side of eq. (42) may
be calculated either according to (44) or (46). Unknown pa-.
rameters are Y, $\alpha^{\Xi} \bar{G}_{C^{\cdot}}$, γ, $\psi_{=}$, ψ_{CN} and ψ_{NO_2}. The
number of points for each independent set of the log A_{ij},
B_{ij} and $\Delta H^{\circ}_0(X_1X_2X_3G-X_4)$ or I_{ij} values depends on the
range of investigated temperature limits. The data over
each hundred degrees were used if the temperature range cov-
ered several hundreds of grade. The two limited temperatures
T_{min} and T_{max} were used for the ranges below 150° ᵡᵡ . Thus,
the whole investigated range of temperatures is covered for
each reaction.

The results of the data treatment according to eq. (42)
are presented in Tables 12 and 13.

The results from Table (12) and for the version I from
Table (13) are comparable taking into account the identical
sets of the reactions applied. It appears that the use of
the experimental formation enthalpies for compounds R_1-R_j
leads to somewhat worse statistical characteristics (the
standard deviation s is higher at the lower numbers of
considered points and reactions, the constancy of the solu-
tion is significantly lower if the confidence level is
changed from 0.99 to 0.95) compared with the results ob-
tained by the use of $F_{X_1X_2X_3G-X_4}$ values according to eq.(46)
employing the calculated values of interaction (I_{ij}) between
substituents R_1 and R_j in the initial compounds.

From the viewpoint of the obtained z^{Ξ}_C. values there is
a quite excellent coincidence for the both indicated cases:
0.360 and 0.346, respectively. The $\alpha^{\Xi} \bar{G}_{C^{\cdot}}$ values equal-
ling correspondingly to $1.60^{\pm}0.09$ and $1.75^{\pm}0.09$ are also
indistinguishable in the ranges of combined uncertainties.
However, the resonance contributions $\psi_{=}$ = (-11.2$^{\pm}$0.2 and

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ᵡᵡ The data at only single temperature were used if the
temperature range was not indicated in a source.

-10.0 ± 0.2) and ψ_{NO_2} = (-8.0 ± 0.4 and -6.5 ± 0.4) differ significantly and only the ψ_{CN} (-9.6 ± 0.7 and -8.0 ± 0.8) is the case where the values are indistinguishable because of the larger ranges of uncertainties for the values compared. The greatest differences are, however, observed for the Y values (0.95 ± 0.29 and 1.94 ± 0.22) while in the first case a significant trend of solution occurs (the descent from the value of 2.54 ± 0.45 to 0.95 ± 0.29 if the confidence level is changed from 0.99 to 0.95).

However the comparison of the results for the versions I and II in Table 13 convince that the difference ($z_{C\cdot}^{x}-z_{C}^{x}$) is rather indistinguishable from zero. Equalling $\gamma =$ $= \alpha^{x}(z_{G\cdot}^{x} - z_{C}^{x}) = 0$ the s value is only insignificantly enhanced while this difference disappears after the exclusion of four points for two reactions. At that the significant change of the Y and $\alpha^{x} \sigma_{C\cdot}^{x}$ values occurs showing an essential correlation between the p, $\sum\limits_{i} \sigma_{X_i}^{x}$ and

$$\sum\limits_{i < j} \sum \left\{ \sigma_{X_i}^{x} \sigma_{j}^{x} \right\} \text{ scales.}$$

The parameter γ turns out to be statistically insignificant and the values of the rest of the parameters are indistinguishable from those for the version II listed in the same table for the case of the more representative set of reactions (the variant III in Table 13). For that reason one can consider the results of the version III from Table 13 as the most reliable ones. At the same time it should be stressed that almost indistinguishable values for the Y parameter are obtained from (35) and according to the indicated version from Table 13 (1.43 ± 0.02 and 1.19 ± 0.18, respectively). It shows a general applicability of eq. (31) for the calculation of the $\Delta S^{\neq}$ values for substituted methyl radicals.

If the result for the version III from Table 13 is compared with an analogous result obtained using the isoentropic model, it should be mentioned that for the latter case the accuracy of description is characterized by s=1.07 kcal/mol for 62 points at T_{mean} for 52 reactions[36] (see Table 4

from[36], the version 2.4). In the case of the considered
version from Table 13 s= 1.97 e.u. for 130 points related
to 51 reactions. In kcal/mol this s value for T=800°K is
expressed by the value ≈1.6. Therefore, in the formal-sta-
tistical sense a more precise description is achieved using
the isoentropic approach. In fact, it is the result of the
inclusion of points related to different temperatures and
reflected in the larger number of points considered in the
data treatment (130 points against 62). Actually, the iso-
entropic model becomes less adequate if the existing data
for essentially different temperatures are considered for
separate reactions. In this connection it should be once
more underlined that the Y parameter reflecting the effect
of the substitution of the hydrogen atoms in methyl radicals
as well the $\Delta S^{\neq}_{CH_3.}$ and $\Delta S^{\neq}_{X_4.}$ values for X_4. radicals cov-
ered by the set of reactions for the version III in Table
13 are doubtless statistically significant.

Table 1

Results of Data Treatment in the Coordinates of
Eq. (16) at T_{mean}.
$\Delta H_R^{\neq}$. - in kcal/mol, $\Delta S_R^{\neq}$. - in e.u., assuming
$\Delta S_o^{\neq} = 0$.

NE - the number of independent equations (points).
NRN - the number of different reactions (combinations
      of R_i and R_j).
s   - standard deviation in kcal/mol

The number of independent equations (points) used
for the calculation of the present parameter is given in
parenthesis.

R°	Set of Data			
	Initial		After Exclusion of Points	
	$\Delta H_R^{\neq}$.	$\Delta S_R^{\neq}$.	$\Delta H_R^{\neq}$.	$\Delta S_R^{\neq}$.
Cl	11.5 ± 23689	$-18.3\pm25749(1)$	-	-
Br	-12.3 ± 137.9	$-48.2\pm170.0(4)$	-140.9 ± 1027	$-206.4\pm126(3)$
I	44.8 ± 17.6	$19.8\pm21.5(9)$	51.2 ± 11.4	$27.8\pm14(9)$
NH_2	51.9 ± 3.5	$8.0\pm2.9(5)$	51.9 ± 2.1	$8.0\pm1.8(5)$
NO_2	9.0 ± 1.1	$16.4\pm1.8(16)$	8.8 ± 0.7	$7.2\pm1.1(14)$
SH	10.8 ± 13.1	$-7.7\pm14.0(4)$	8.6 ± 7.9	$-10.1\pm8.5(4)$
OCH_3	5.8 ± 2.1	$7.7\pm4.3(7)$	5.9 ± 1.3	$8.2\pm2.6(6)$
OC_2H_5	-10.0 ± 2.1	$-13.2\pm4.5(15)$	-10.1 ± 1.3	$-13.5\pm2.7(15)$
CH_3	30.3 ± 1.4	$1.0\pm1.4(44)$	31.8 ± 0.9	$2.8\pm1.0(37)$
C_2H_5	10.0 ± 9.9	$-13.1\pm10.6(13)$	6.9 ± 6.1	$-16.5\pm6.5(13)$
$CH(CH_3)_2$	13.3 ± 3.2	$-0.5\pm3.2(9)$	16.1 ± 2.0	$1.1\pm2.0(7)$
$C(CH_3)_3$	16.9 ± 4.6	$9.7\pm4.6(10)$	16.2 ± 2.8	$8.9\pm2.8(10)$
$CH_2CH=CH_2$	47.8 ± 6.8	$10.0\pm7.2(10)$	60.3 ± 7.5	$23.1\pm7.6(7)$
$CH_2C_6H_5$	43.6 ± 11.1	$-5.0\pm11.5(12)$	46.5 ± 6.8	$-1.9\pm7.0(11)$
NE	100		88	
NRN	35		32	
s	2.22		1.35	

Table 2

Results of Data Treatment in the Coordinates of
Eq. (16) at Three Temperatures T_{min}, T_{mean}, and T_{max}
including $\Delta S_0^{\neq}$ into the Parameters to Be Determined.
The symbols are the same as in Table 1.

$R°$	Set of Data			
	Initial		After Exclusion of Points	
	$\Delta H_R^{\neq}$.	$\Delta S_R^{\neq}$.	$\Delta H_R^{\neq}$.	$\Delta S_R^{\neq}$.
Cl	15.8±22.7	−7.9±24.6(3)	27.0±6.0	5.3±6.5(3)
Br	23.0±10.7	−3.2±13.0(12)	31.2±3.2	6.4±3.9(9)
I	28.1±4.9	1.4±6.0(27)	21.7±2.5	−4.3±3.4(13)
NH_2	45.5±1.3	3.9±1.2(15)	47.8±0.5	6.9±0.5(5)
NO_2	8.8±0.6	7.5±1.0(48)	8.2±0.2	8.7±0.3(36)
SH	9.5±5.6	−7.3±6.0(12)	6.9±1.5	−8.9±1.6(10)
OCH_3	5.9±1.1	9.3±2.3(21)	2.9±0.4	5.6±0.8(9)
OC_2H_5	−8.7±1.0	−9.0±2.2(45)	−7.7±0.3	−5.6±0.7(36)
CH_3	31.9±0.8	4.2±1.3(132)	35.5±0.4	10.1±0.6(82)
C_2H_5	20.0±3.2	−1.3±3.5(39)	24.7±1.0	5.5±1.1(33)
$CH(CH_3)_2$	12.5±1.6	0.1±1.6(27)	13.8±0.6	2.5±0.5(17)
$C(CH_3)_3$	15.9±2.3	10.1±2.3(30)	15.3±0.6	11.4±0.7(29)
$CH_2CH=CH_2$	44.6±3.0	8.1±3.2(30)	33.3±1.1	−1.5±1.2(15)
$CH_2C_6H_5$	48.1±4.0	1.2±4.3(36)	44.1±1.2	−1.8±1.3(28)
$\Delta S_0^{\neq}$	−2.8±1.0		−6.3±0.5	
NE	300		199	
NRN	35		32	
s	2.05		0.54	

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Table 3

$\Delta S_R^{\neq}$. Values Obtained in Result of the Iterative
A) Procedure According to Eqs. (22) and (23) for Free
Radicals.

      a - the results for the initial set of data in the
          stage of the MLRA

      b - the results for the final set of data after the
          exclusion of points.

The rest of symbols are the same as in the previous tables.

$R^{\cdot}$	Zero-order Approximation		First-order Approximation	
	a	b	a	b
H^{x}	0.0	0.0	0.0	0.0
Cl	$-1.7 \pm 5.8(1)$	$-1.7 \pm 3.4(1)$	$0.2 \pm 3.1(1)$	$-0.02 \pm 1.2(1)$
Br	$-2.4 \pm 4.1(2)$	$-3.6 \pm 2.5(2)$	$1.4 \pm 1.7(4)$	$-0.06 \pm 0.7(3)$
I	$-2.4 \pm 2.8(5)$	$-0.8 \pm 1.8(4)$	$-1.1 \pm 1.2(9)$	$0.3 \pm 0.5(6)$
NH_2	$-3.2 \pm 1.2(5)$	$-3.2 \pm 0.7(5)$	$-4.8 \pm 0.7(5)$	$-3.2 \pm 0.3(3)$
NO_2	$2.5 \pm 1.4(14)$	$3.8 \pm 1.0(10)$	$3.0 \pm 0.7(16)$	$3.6 \pm 0.3(10)$
SH	$-2.9 \pm 3.3(3)$	$-3.9 \pm 2.0(3)$	$-3.7 \pm 1.6(4)$	$-3.8 \pm 0.6(4)$
OCH_3	$4.6 \pm 1.7(5)$	$3.9 \pm 1.1(4)$	$3.9 \pm 0.7(7)$	$2.9 \pm 0.3(3)$
OC_2H_5	$1.6 \pm 1.2(9)$	$-1.6 \pm 0.9(5)$	$-1.0 \pm 0.4(15)$	$-1.6 \pm 0.2(11)$
CH_3	$4.1 \pm 0.7(42)$	$3.2 \pm 0.5(30)$	$3.2 \pm 0.4(44)$	$3.1 \pm 0.2(28)$
C_2H_5	$2.2 \pm 1.8(9)$	$3.3 \pm 1.1(7)$	$3.2 \pm 0.9(13)$	$3.3 \pm 0.4(10)$
$CH(CH_3)_2$	$8.2 \pm 1.8(7)$	$4.6 \pm 1.3(4)$	$6.7 \pm 0.9(9)$	$4.5 \pm 0.4(5)$
$C(CH_3)_3$	$7.2 \pm 1.6(10)$	$7.5 \pm 1.0(9)$	$7.3 \pm 0.9(10)$	$7.5 \pm 0.3(10)$
$CH_2CH=CH_2$	$-0.9 \pm 1.5(10)$	$-0.9 \pm 1.0(8)$	$-1.1 \pm 0.8(10)$	$-0.9 \pm 0.5(6)$
$CH_2C_6H_5$	$-1.0 \pm 2.0(9)$	$1.9 \pm 1.4(7)$	$1.8 \pm 1.0(12)$	$1.9 \pm 0.4(11)$
NE	82	64	100	70
NRN	35	34	35	30
s	5.58	3.31	2.98	1.05

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^{x} The value $\Delta S_H^{\neq}$. = 0 is fixed prior data processing.

Table 4

$\Delta S_R^{\neq}$. Values Obtained in Result of the Iterative B) Procedure According to Eqs. (22) and (23) for Free Radicals.

The symbols are the same as in Table 3

$R^\cdot$	Zero-order Approximation		First-order Approximation	
	a	b	a	b
H^x	0.0	0.0	0.0	0.0
Cl	$-4.5\pm3.3(1)$	$-4.6\pm1.1(1)$	$-4.2\pm3.3(1)$	$-4.3\pm1.1(1)$
Br	$-3.8\pm1.8(4)$	$-5.3\pm0.6(3)$	$-3.9\pm1.8(4)$	$-5.4\pm0.6(3)$
I	$-2.6\pm1.2(9)$	$-1.3\pm0.5(6)$	$-2.6\pm1.2(9)$	$-1.2\pm0.5(6)$
NH_2	$-3.5\pm0.7(5)$	$-2.1\pm0.3(3)$	$-3.6\pm0.7(5)$	$-2.1\pm0.3(3)$
NO_2	$5.9\pm0.7(16)$	$6.5\pm0.2(12)$	$5.9\pm0.7(16)$	$6.5\pm0.2(12)$
SH	$-4.0\pm1.7(4)$	$-4.1\pm0.5(4)$	$-4.7\pm1.7(4)$	$-4.8\pm0.5(4)$
OCH_3	$4.6\pm0.7(7)$	$4.6\pm0.3(3)$	$5.0\pm0.7(7)$	$5.1\pm0.3(3)$
OC_2H_5	$-0.8\pm0.5(15)$	$-1.4\pm0.2(11)$	$-0.8\pm0.5(15)$	$-1.4\pm0.2(11)$
CH_3	$5.3\pm0.4(44)$	$5.2\pm0.1(27)$	$5.3\pm0.4(44)$	$5.2\pm0.1(27)$
C_2H_5	$3.4\pm0.9(13)$	$3.5\pm0.3(10)$	$3.4\pm0.9(13)$	$3.5\pm0.3(10)$
$CH(CH_3)_2$	$8.5\pm0.9(9)$	$5.3\pm0.3(5)$	$8.3\pm0.9(9)$	$5.2\pm0.3(5)$
$C(CH_3)_3$	$5.6\pm0.9(10)$	$5.9\pm0.3(10)$	$5.5\pm0.9(10)$	$5.8\pm0.3(10)$
$CH_2CH=CH_2$	$1.9\pm0.8(10)$	$2.0\pm0.5(6)$	$1.5\pm0.8(10)$	$1.6\pm0.5(6)$
$CH_2C_6H_5$	$1.2\pm1.1(12)$	$1.4\pm0.3(11)$	$1.5\pm1.1(12)$	$1.7\pm0.3(11)$
NE	100	70	100	70
NRN	35	30	35	30
s	3.15	0.95	3.15	0.95

x The value $\Delta S_H^{\neq}$. = 0 is fixed prior data processing.

Table 5

$\Delta H_R^{\neq}$. Values Obtained in Result of the Iterative A) Procedure According to Eqs. (22) and (23), and Proceeding from the Isoentropic Model[2] According to Eqs. (39) and (40) for Free Radicals.

The symbols are the same as in Table 3.

The radicals for which the $\Delta H_R^{\neq}$. estimates in result of the Iterative A) Procedure differ from the estimates according to eqs. (39) and (40) more than 1.5 kcal/mol are underlined.

R·	Zero-order Approximation		First-order Approximation		According to eq.(39), D_{1j} according to eq.(40)	From ΔH_0^o and D_0 for diatomic molecules
	a	b	a	b		
1	2	3	4	5	6	7
H*	<u>51.6</u>	<u>51.6</u>	<u>51.6</u>	<u>51.6</u>	<u>51.6</u>	51.63
Cl	$24.4^{\pm}2.5(1)$	$24.4^{\pm}1.0(1)$	$24.4^{\pm}2.5(1)$	$24.4^{\pm}1.0(1)$	$27.4^{\pm}1.2$	28.59
Br	$26.7^{\pm}1.4(4)$	$27.8^{\pm}0.6(3)$	$26.7^{\pm}1.4(4)$	$27.8^{\pm}0.6(3)$	$30.0^{\pm}0.7$	28.18
I	$27.1^{\pm}1.0(9)$	$26.3^{\pm}0.4(2)$	$27.1^{\pm}1.0(9)$	$26.3^{\pm}0.4(7)$	$29.3^{\pm}0.5$	25.63
NH_2	$38.7^{\pm}0.5(5)$	$37.1^{\pm}0.3(3)$	$38.7^{\pm}0.5(5)$	$37.1^{\pm}0.3(3)$	$44.8^{\pm}0.3$	−
NO_2	$7.5^{\pm}0.5(16)$	$7.4^{\pm}0.2(12)$	$7.4^{\pm}0.5(16)$	$7.3^{\pm}0.2(12)$	$7.2^{\pm}0.3$	−
SH	$13.4^{\pm}1.3(4)$	$13.5^{\pm}0.5(4)$	$13.5^{\pm}1.3(4)$	$13.6^{\pm}0.5(4)$	$18.7^{\pm}0.7$	−
OCH_3	$4.0^{\pm}0.6(7)$	$4.1^{\pm}0.2(5)$	$3.5^{\pm}0.6(7)$	$3.6^{\pm}0.2(5)$	$4.2^{\pm}0.3$	−
OC_2H_5	$-4.7^{\pm}0.4(15)$	$-4.5^{\pm}0.2(11)$	$-4.7^{\pm}0.4(15)$	$-4.5^{\pm}0.2(11)$	$-2.2^{\pm}0.2$	−

Table 5 continued

1	2	3	4	5	6	7
CH_3	$32.3^{\pm}0.3(44)$	$32.1^{\pm}0.1(28)$	$32.2^{\pm}0.3(44)$	$32.0^{\pm}0.1(28)$	$31.9^{\pm}0.2$	–
C_2H_5	$25.8^{\pm}0.7(13)$	$25.7^{\pm}0.3(11)$	$25.8^{\pm}0.7(13)$	$25.7^{\pm}0.3(11)$	$25.2^{\pm}0.4$	–
$CH(CH_3)_2$	$17.9^{\pm}0.7(9)$	$19.4^{\pm}0.3(6)$	$17.8^{\pm}0.7(9)$	$19.3^{\pm}0.3(6)$	$17.1^{\pm}0.3$	–
$\overline{C(CH_3)_3}$	$14.7^{\pm}0.7(10)$	$14.7^{\pm}0.3(10)$	$14.7^{\pm}0.7(10)$	$14.7^{\pm}0.3(10)$	$10.4^{\pm}0.3$	–
$\overline{CH_2CH=CH_2}$	$37.5^{\pm}0.6(10)$	$37.4^{\pm}0.4(6)$	$37.5^{\pm}0.6(10)$	$37.4^{\pm}0.4(8)$	$40.9^{\pm}0.5$	–
$\overline{CH_2C_6H_5}$	$50.1^{\pm}0.8(12)$	$50.1^{\pm}0.3(11)$	$50.1^{\pm}0.8(12)$	$50.1^{\pm}0.3(11)$	$51.8^{\pm}0.4$	–
NE	100	74	100	74	231	–
NRN	35	31	35	31	125	–
s	2.44	0.91	2.44	0.91	1.10	–

x The value $\Delta H_H^{\neq} = 51.6^{38}$ is fixed prior data processing.

Table 6

$\Delta H_R^{\neq}$. Values Obtained in Result of the Iterative B) Procedure According to Eqs.(22) and (23) for Free Radicals.

The symbols are the same as in Table 3.

R°	Zero-order Approximation		First-order Approximation I[**], II[**]			
	a	b	a	b	a	b
1	2	3	4	5	6	7
H[*]	51.6	51.6	51.6	51.6	51.6	51.6
Cl	$23.0\pm3.9(1)$	$20.1\pm1.4(1)$	$24.4\pm2.6(1)$	$24.4\pm0.8(1)$	$20.1\pm2.6(1)$	$20.4\pm0.7(1)$
Br	$25.6\pm2.1(4)$	$23.5\pm0.8(4)$	$26.8\pm1.4(4)$	$27.8\pm0.5(3)$	$22.4\pm1.4(4)$	$23.4\pm0.4(3)$
I	$24.9\pm1.5(9)$	$24.9\pm0.6(7)$	$27.0\pm1.0(9)$	$26.0\pm0.4(6)$	$25.8\pm1.0(9)$	$24.9\pm0.3(6)$
NH_2	$38.7\pm0.8(5)$	$38.6\pm0.4(3)$	$40.0\pm0.6(5)$	$38.6\pm0.2(3)$	$40.0\pm0.6(5)$	$38.5\pm0.2(3)$
NO_2	$6.6\pm0.8(16)$	$8.6\pm0.4(6)$	$9.0\pm0.6(16)$	$8.7\pm0.2(13)$	$8.9\pm0.6(16)$	$8.6\pm0.1(12)$
SH	$14.8\pm2.0(4)$	$13.3\pm0.7(4)$	$13.6\pm1.3(4)$	$13.0\pm0.5(3)$	$13.3\pm1.3(4)$	$12.6\pm0.4(3)$
OCH_3	$4.4\pm0.9(7)$	$4.4\pm0.3(6)$	$4.3\pm0.6(7)$	$4.4\pm0.2(5)$	$4.3\pm0.6(7)$	$4.6\pm0.2(4)$
OC_2H_5	$-3.5\pm0.6(15)$	$-4.4\pm0.2(11)$	$-4.6\pm0.4(15)$	$-4.5\pm0.1(11)$	$-4.6\pm0.4(15)$	$-4.4\pm0.1(11)$
CH_3	$33.1\pm0.5(44)$	$34.1\pm0.2(25)$	$34.2\pm0.3(44)$	$34.0\pm0.1(27)$	$34.2\pm0.3(44)$	$34.1\pm0.1(23)$
C_2H_5	$24.8\pm1.1(13)$	$26.1\pm0.4(10)$	$24.9\pm0.7(13)$	$24.8\pm0.3(10)$	$26.2\pm0.7(13)$	$26.1\pm0.2(10)$

Table 6 continued

1	2	3	4	5	6	7
$CH(CH_3)_2$	$20.7 \pm 1.1(9)$	$20.8 \pm 0.4(7)$	$18.5 \pm 0.7(9)$	$20.7 \pm 0.3(5)$	$18.6 \pm 0.7(9)$	$20.7 \pm 0.2(5)$
$C(CH_3)_3$	$14.3 \pm 1.1(10)$	$13.1 \pm 0.4(7)$	$13.1 \pm 0.7(10)$	$13.1 \pm 0.2(10)$	$13.1 \pm 0.7(10)$	$13.0 \pm 0.2(10)$
$CH_2CH=CH_2$	$37.3 \pm 1.0(10)$	$40.2 \pm 0.5(7)$	$37.4 \pm 0.7(10)$	$37.5 \pm 0.4(6)$	$40.2 \pm 0.7(10)$	$39.8 \pm 0.3(5)$
$CH_2C_6H_5$	$47.7 \pm 1.3(12)$	$49.6 \pm 0.5(10)$	$49.8 \pm 0.9(12)$	$49.9 \pm 0.3(11)$	$49.6 \pm 0.9(12)$	$49.9 \pm 0.2(10)$
NE	100	69	100	72	100	66
NRN	35	34	35	29	35	29
s	3.76	1.34	2.51	0.76	2.50	0.60

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* The value of $\Delta H_H^{\neq} = 51.6^{18}$ is fixed prior data processing

** In the version I of the first order approximation $\Delta S_R^{\neq} = 0$ is assumed for H, Cl, Br and I (see Table 3). In the version II only $\Delta S_H^{\neq} = 0$ and for other radicals the values from Table 4 are used.

Table 7

A) $\Delta S_R^{\neq}$. Values Obtained in Result of the Iterative Procedure According to Eqs. (22) and (24) for Free Radicals.

I and II differ by the numbers of the fixed values of $\Delta S_R^{\neq}$. = 0.

The $\Delta S_R^{\neq}$. values of the zero order approximation are taken from Table 3.

The symbols are the same is in Table 3.

R°	First - order Approximation			
	I		II	
	a	b	a	b
H	0[*]	0[*]	0[*]	0[*]
Cl	$1.2^{\pm}2.1(2)$	$0.5^{\pm}1.1(2)$	0[*]	0[*]
Br	$1.3^{\pm}2.1(2)$	$0.5^{\pm}1.1(2)$	0[*]	0[*]
I	$0.3^{\pm}1.4(5)$	$0.3^{\pm}0.7(5)$	0[*]	0[*]
NH_2	$-2.3^{\pm}1.9(3)$	$-2.8^{\pm}1.0(3)$	$-2.6^{\pm}1.8(3)$	$-2.9^{\pm}0.9(3)$
NO_2	$2.8^{\pm}1.0(9)$	$4.3^{\pm}0.6(7)$	$2.8^{\pm}1.0(9)$	$4.4^{\pm}0.6(7)$
SH	$-3.6^{\pm}1.7(3)$	$-3.7^{\pm}0.8(3)$	$-3.7^{\pm}1.6(3)$	$-3.7^{\pm}0.8(3)$
OCH_3	$4.0^{\pm}2.0(2)$	$4.1^{\pm}1.0(2)$	$4.0^{\pm}2.0(2)$	$4.1^{\pm}1.0(2)$
OC_2H_5	$-1.8^{\pm}3.0(1)$	$-1.6^{\pm}1.5(1)$	$-1.9^{\pm}3.0(1)$	$-1.7^{\pm}1.5(1)$
CH_3	$3.2^{\pm}0.4(43)$	$3.1^{\pm}0.2(33)$	$3.2^{\pm}0.4(43)$	$3.1^{\pm}0.2(33)$
C_2H_5	$3.5^{\pm}1.0(9)$	$3.3^{\pm}0.5(9)$	$3.6^{\pm}0.9(9)$	$3.4^{\pm}0.4(9)$
$CH(CH_3)_2$	$6.8^{\pm}0.9(8)$	$3.8^{\pm}0.5(4)$	$6.8^{\pm}0.8(8)$	$3.8^{\pm}0.5(4)$
$C(CH_3)_3$	$7.9^{\pm}0.8(10)$	$8.1^{\pm}0.4(10)$	$7.9^{\pm}0.8(10)$	$8.1^{\pm}0.4(10)$
$CH_2CH=CH_2$	$-2.7^{\pm}0.7(10)$	$-1.8^{\pm}0.6(7)$	$-2.5^{\pm}0.7(10)$	$-1.0^{\pm}0.4(8)$
$CH_2C_6H_5$	$1.1^{\pm}1.0(13)$	$1.6^{\pm}0.5(13)$	$1.3^{\pm}0.9(13)$	$1.7^{\pm}0.5(13)$
NE	70	58	70	59
NRN	31	29	31	30
s	2.79	1.40	2.74	1.40

[*] The value of zero is previously fixed.

Table 8

$\Delta S_R^{\neq}$. Values Obtained in Result of the Iterative
B) Procedure According to Eqs. (22) and (24) for Free
Radicals.

The symbols are the same as in Table 3.

$R^\cdot$	Zero-order Approximation		First-order Approximation	
	a	b	a	b
$H^{\bar{x}}$	0	0	0	0
Cl	$-4.5\pm2.3(2)$	$-5.5\pm1.1(2)$	$-4.6\pm2.1(2)$	$-5.7\pm1.2(2)$
Br	$-4.6\pm2.3(2)$	$-5.6\pm1.1(2)$	$-4.7\pm2.1(2)$	$-5.7\pm1.2(2)$
I	$-2.6\pm1.5(5)$	$-2.6\pm0.7(5)$	$-2.3\pm1.4(5)$	$-2.5\pm0.8(5)$
NH_2	$-4.9\pm2.1(3)$	$-5.7\pm1.0(3)$	$-5.3\pm1.9(3)$	$-5.9\pm1.1(3)$
NO_2	$2.3\pm1.1(9)$	$4.1\pm0.6(7)$	$3.4\pm1.0(9)$	$4.5\pm0.6(8)$
SH	$-4.5\pm1.8(3)$	$-4.6\pm0.9(3)$	$-4.4\pm1.7(3)$	$-4.5\pm0.9(3)$
OCH_3	$5.3\pm2.2(2)$	$5.6\pm1.1(2)$	$5.8\pm2.1(2)$	$6.0\pm1.1(2)$
OC_2H_5	$-4.1\pm3.2(1)$	$-3.8\pm1.6(1)$	$-4.0\pm3.0(1)$	$-3.8\pm1.7(1)$
CH_3	$4.9\pm0.4(43)$	$4.6\pm0.2(32)$	$4.4\pm0.4(43)$	$4.3\pm0.2(34)$
C_2H_5	$4.2\pm1.1(9)$	$3.9\pm0.5(9)$	$3.9\pm1.0(9)$	$3.8\pm0.5(9)$
$CH(CH_3)_2$	$8.8\pm0.9(8)$	$4.5\pm0.9(3)$	$6.7\pm0.9(8)$	$3.6\pm0.6(4)$
$C(CH_3)_3$	$4.8\pm0.9(10)$	$5.2\pm0.4(10)$	$5.8\pm0.8(10)$	$6.0\pm0.5(10)$
$CH_2CH=CH_2$	$2.2\pm0.8(10)$	$3.4\pm0.5(7)$	$1.9\pm0.8(10)$	$3.4\pm0.5(8)$
$CH_2C_6H_5$	$0.8\pm1.1(13)$	$1.6\pm0.5(13)$	$1.2\pm1.0(13)$	$1.8\pm0.6(13)$
NE	70	57	70	60
NRN	31	29	31	30
s	3.06	1.49	2.85	1.58

$^{\bar{x}}$ $\Delta S_H^{\neq}$. = 0 is previously fixed.

Table 9

$\Delta\Delta H_R^{\neq}$. Values Obtained in Result of the Iterative
A) Procedure According to Eqs. (22) and (24) for Free Radicals.

The symbols are the same as in Table 3.

R°	Zero-order Approximation		First-order Approximation	
	a	b	a	b
H[x]	51.6	51.6	51.6	51.6
Cl	46.3±1.8(2)	47.2±1.1(2)	46.3±1.8(2)	46.8±1.1(2)
Br	34.2±1.8(2)	35.1±1.1(2)	34.2±1.8(2)	34.6±1.1(2)
I	21.9±1.2(5)	22.2±0.7(5)	21.9±1.2(5)	22.0±0.7(5)
NH_2	46.2±1.7(3)	46.6±1.0(3)	46.5±1.7(3)	46.7±0.9(3)
NO_2	29.5±0.9(9)	28.9±0.5(8)	30.0±0.9(9)	29.5±0.5(8)
SH	32.5±1.5(3)	32.7±0.8(3)	32.7±1.5(3)	32.8±0.8(3)
OCH_3	51.9±1.8(2)	51.9±1.0(2)	52.0±1.8(2)	52.2±1.0(2)
OC_2H_5	56.2±2.6(1)	56.1±1.5(1)	56.0±2.6(1)	56.0±1.5(1)
CH_3	48.3±0.3(43)	48.2±0.2(35)	48.2±0.3(43)	48.1±0.2(36)
C_2H_5	42.2±0.9(9)	42.3±0.5(9)	42.3±0.9(9)	42.4±0.5(9)
$CH(CH_3)_2$	37.9±0.8(8)	39.8±0.5(5)	37.2±0.8(8)	38.7±0.5(6)
$C(CH_3)_3$	39.1±0.7(10)	39.1±0.4(10)	39.7±0.7(10)	39.7±0.4(10)
$CH_2CH=CH_2$	29.7±0.7(10)	28.2±0.5(8)	29.6±0.6(10)	28.9±0.6(7)
$CH_2C_6H_5$	33.8±0.9(13)	33.4±0.5(13)	33.6±0.9(13)	33.4±0.5(13)
NE	70	61	70	61
NRN	31	31	31	30
s	2.49	1.41	2.46	1.39

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[x] The value of $\Delta\Delta H_H^{\neq}$. = 51.6 is previously fixed.

Table 10

$\Delta\Delta H_R^{\neq}$. Values Obtained in Result of the Iterative B) Procedure According to Eqs.(22) and (24) for Free Radicals.

The entropy values for halogens (Cl, Br and I) differing from zero are used passing from the zero order approximation to the first. Passing from the first order approximation to the second the values of $\Delta S_R^{\neq} = 0$ for Cl, Br and I are fixed.

R•	Zero-order Approximation		First-order Approximation		Second-order Approximation	
	a	b	a	b	a	b
	1	2	3	4	6	7
H*	51.6	51.6	51.6	51.6	51.6	51.6
Cl	49.6±3.1(2)	41.9±1.9(1)	41.1±1.9(2)	41.9±1.1(2)	46.4±1.9(2)	47.2±1.1(2)
Br	32.7±3.1(2)	30.2±1.4(2)	29.4±1.9(2)	30.2±1.1(2)	34.3±1.9(2)	35.1±1.1(2)
I	19.9±2.1(5)	19.8±1.0(4)	19.7±1.3(5)	20.0±0.7(5)	21.8±1.3(5)	22.1±0.7(5)
NH_2	49.8±2.9(3)	44.1±1.5(2)	43.6±1.7(3)	43.8±1.0(3)	43.5±1.7(3)	43.8±1.0(3)
NO_2	26.1±1.5(9)	28.4±0.8(6)	29.5±0.9(9)	29.2±0.5(8)	30.2±0.9(9)	29.8±0.6(8)
SH	33.1±2.5(3)	32.0±1.1(3)	31.9±1.5(3)	32.1±0.9(3)	32.3±1.5(3)	32.5±0.9(3)
OCH_3	53.4±3.0(2)	53.0±1.3(2)	53.1±1.8(2)	53.4±1.0(2)	53.4±1.8(2)	53.6±1.1(2)
OC_2H_5	55.1±4.5(1)	54.0±1.9(1)	54.1±2.7(1)	54.1±1.5(1)	54.8±2.7(1)	54.8±1.6(1)
CH_3	49.4±0.6(43)	49.7±0.3(30)	49.7±0.3(43)	49.3±0.2(35)	49.4±0.3(43)	49.2±0.2(36)

* The value of $\Delta\Delta H_{H.}^{\neq} = 51.6$ is previously fixed.

Table 10 continued

1	2	3	4	5	6	7
C_2H_5	$41.9^{\pm}1.5(9)$	$43.0^{\pm}0.7(7)$	$42.9^{\pm}0.9(9)$	$42.8^{\pm}0.5(9)$	$42.0^{\pm}0.9(9)$	$42.0^{\pm}0.5(9)$
$CH(CH_3)_2$	$41.1^{\pm}1.3(8)$	$40.8^{\pm}0.6(8)$	$37.7^{\pm}0.8(8)$	$39.1^{\pm}0.5(6)$	$36.8^{\pm}0.8(8)$	$38.3^{\pm}0.5(6)$
$C(CH_3)_3$	$38.6^{\pm}1.2(10)$	$36.9^{\pm}0.6(7)$	$36.9^{\pm}0.7(10)$	$37.8^{\pm}0.5(9)$	$37.9^{\pm}0.7(10)$	$38.0^{\pm}0.4(10)$
$CH_2CH=CH_2$	$29.2^{\pm}1.1(10)$	$32.6^{\pm}0.6(7)$	$33.6^{\pm}0.7(10)$	$32.3^{\pm}0.5(8)$	$29.7^{\pm}0.7(10)$	$28.3^{\pm}0.5(8)$
$CH_2C_6H_5$	$31.4^{\pm}1.5(13)$	$33.0^{\pm}0.8(9)$	$33.5^{\pm}0.9(13)$	$33.3^{\pm}0.5(13)$	$33.6^{\pm}0.9(13)$	$33.3^{\pm}0.5(13)$
NE	70	51	70	60	70	62
NRN	31	30	31	30	31	31
s	4.23	1.83	2.56	1.44	2.52	1.50

Table 11

$\Delta S_R^{\neq}$. Values and Different Estimates of the $\Delta H_R^{\neq}$. Values for Less Represented Radicals but Occuring more than in a Single Combination Like $R_i R_j$.

The radicals are underlined for which the estimates of $\Delta H_R^{\neq}$. obtained as a result of the iteration procedure differ from those obtained proceeding from the value $\log A_o = 14.64$ more than 1.5 kcal/mol

No	R°	Secondary values, obtained proceeding from the results of the iterative A)procedure for most frequently occuring radicals from Tables 3 and 5		Total set of data	Eq.(39), D_{ij} from Eq.(40) Secondary values obtained proceeding from the results for the 15 most frequently occurring radicals
		$\Delta S_R^{\neq}$, e.u.	$\Delta H_R^{\neq}$, kcal/mol		
1.	FO	4.8±0.4	28.3±0.1	28.2±0.8	28.3±0.1
2.	C_3H_7O	0.8±0.3	-8.5±0.1	-8.0±0.7	-10.9±0.1
3.	$(CH_3)_3CO$	5.7±0.1	-15.1±0.1	-15.9±0.2	-15.9±0.2
4.	F_2N	3.9±0.4	8.8±0.2	8.6±0.4	8.6±0.0
5.	$C_6H_5\underline{NH}$	-4.6±1.0	55.0±1.5	60.0±0.6	59.8±1.4
6.	$\overline{NO}$	3.8±0.6	20.5±0.3	21.2±0.4	24.3±1.5
7.	CH_3Cd	-12.5±1.5	41.1±0.6	53.8±0.6	53.7±1.3
8.	$\overline{CH_3Hg}$	-1.5±0.9	47.5±0.7	51.1±0.3	51.2±0.9
9.	$\overline{C_3H_7}$	6.2±3.3	22.9±2.8	20.7±0.7	19.5±2.7
10.	$\overline{C_2H_5(CH_3)CH}$	4.9±0.3	16.6±0.6	14.0±0.5	13.9±0.3
11.	$\overline{C_2H_5(CH_3)_2C}$	7.1±0.4	11.0±0.1	7.0±0.8	7.7±0.4
12.	$\overline{CF_3}$	5.4±3.2	-121.5±2.6	-122.7±0.5	-121.4±7.4
13.	$\overline{CCl_3}$	-1.6±0.5	11.2±0.4	15.3±1.0	15.1±0.4
14.	$\overline{C_6H_5}$	3.0±1.2	73.2±0.8	73.4±0.6	74.1±0.6
15.	CH_3CO	-0.8±0.6	-8.8±0.7	-5.8±0.4	-7.7±3.5

Table 12

Results of the Data Treatment According to Eqs.(42)
and (44) if the Total Investigated Temperature Range is
Covered.

t - the confidence level of the exclusion of points
s and Y are in $e.u$, the other parameters in kcal/mol.
The number of points (NE) and reactions (NRN) for the
initial set of data are given in parenthesis.

Parameter	Values	
	$t = 0.99$	$t = 0.95$
Y	$2.54^{\pm}0.45$	$0.95^{\pm}0.29$
$\alpha^{x}\sigma_{C}^{x}$	$1.98^{\pm}0.14$	$1.60^{\pm}0.09$
$\gamma = \alpha^{x}z_{C}^{x}$	$0.46^{\pm}0.02$	$0.50^{\pm}0.01$
γ_{H}	$-12.5^{\pm}0.4$	$-11.2^{\pm}0.2$
γ_{CN}	$-9.6^{\pm}1.5$	$-9.6^{\pm}0.7$
γ_{NO_2}	$-8.4^{\pm}0.7$	$-8.0^{\pm}0.4$
NE	132(150)	94
NRN	43(47)	33
s	4.00	1.88

Table 13

Results of Data Treatment According to Eqs.(42) and (46) if the Total Investigated Temperature Range is Covered ($\sigma^{*}_{NO_2}$ = 4.5).

Variants: I – the set of reactions is the same as in Table 12

II – continuation of the solution for the version I when the value $\alpha^{*}(z^{*}_{C.} - z^{*}_{C}) = 0$ is fixed without the inclusion of excluded points

III – the set of reactions for the variant I is completed by those for which enthalpies of formation for initial compounds are unknown but the calculation of I_{ij} values is possible.

The symbols are the same as in Table 12.

Parameters	Values of parameters in versions					
	I		II		III	
	t = 0.99	t = 0.95	t = 0.99	t = 0.95	t = 0.99	t = 0.95
Y	$2.12^{\pm}0.33$	$1.94^{\pm}0.22$	$1.24^{\pm}0.18$	$0.89^{\pm}0.18$	$1.96^{\pm}0.29$	$1.19^{\pm}0.18$
$\alpha^{*}\sigma^{*}_{C.}$	$1.81^{\pm}0.14$	$1.75^{\pm}0.09$	$1.39^{\pm}0.05$	$1.34^{\pm}0.04$	$1.39^{\pm}0.07$	$1.34^{\pm}0.04$
$\gamma = \alpha^{*}(z^{*}_{C.} -z^{*}_{C})$	$-0.07^{\pm}0.02$	$-0.06^{\pm}0.01$	(0)	(0)	0^{**}	0^{**}
$\psi_{=}$	$-11.5^{\pm}0.3$	$-10.0^{\pm}0.2$	$-9.9^{\pm}0.3$	$-9.7^{\pm}0.2$	$-10.9^{\pm}0.4$	$-9.5^{\pm}0.2$
ψ_{CN}	$-8.5^{\pm}1.2$	$-8.4^{\pm}0.7$	$-8.0^{\pm}0.8$	$-8.2^{\pm}0.7$	$-5.8^{\pm}1.3$	$-7.3^{\pm}0.7$
ψ_{NO_2}	$-6.7^{\pm}0.7$	$-6.5^{\pm}0.4$	$-5.6^{\pm}0.4$	$-5.7^{\pm}0.4$	$-5.4^{\pm}0.6$	$-5.1^{\pm}0.3$
NE	124(130)	97	97	93	175(184)	130
WRN	44(47)	36	36	34	66(69)	51
s	2.89	1.73	1.92	1.72	3.72	1.97

x x The parameter Y is excluded as statistically insignificant during the data processing.

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TRANSESTERIFICATION OF ESTERS OF CARBOXYLIC
ACIDS BY TITANIUM ALCOHOLATES
III. Transesterification of Esters of Aliphatic Acids

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Transesterification kinetics of butylic
esters of ten aliphatic carboxylic acids has
been studied in heptane. Activation parame-
ters of the reactions have been determined.
The coefficients of a regression model de-
scribing the acyl group substituent and
temperature effects upon the reactivity of
esters in this reaction have been determined.
The separation of overall steric effect of
substituents into terms influencing the en-
tropy and enthalpy of activation is accom-
plished. The mechanism of the reaction is
discussed.

The second communication of this series reported the
results of the study of transesterification kinetics of
butylic esters of three meta-substituted benzoic acids by
sec-butyl orthotitanate in heptane in the temperature range
from 25 to 75°C. Activation parameters of the reaction and
a two-factorial regression model with a cross term present
adequately describing the influence of substituent and
temperature effects upon the reactivity of butyl benzoates
in this reaction were reported.

The subject of the present study is the transesterifi-
cation kinetics of butylic esters of aliphatic carboxylic

acids by sec-butyl orthotitanate. The transesterification of ten esters RC(O)OBu (R=H, Me, Bu, t-Bu, $CHCl_2$, CCl_3, CH_2Br, CH_2OPh, CH_2CH_2Cl and $CHPh_2$) has been studied in heptane in a wide temperature range.

EXPERIMENTAL

Reagents. The purification of heptane has been reported earlier[1]. The methods of preparation, purification and determination of the concentration of orthotitanate have been published in the first communication of this series[2].

Butylic esters were prepared from butanol and the corresponding acid or the commercial products of "Reachim" were used. The purity of esters used was not lower than 98% (GLC).

Kinetic measurements. The methods of carrying out the kinetic runs and GLC analysis as well as the calculation of rate coefficients have been published earlier[2]. A glass column (0.3 x 300 cm) with 7% fluoro-silicone elastomer SKTFT - 100 on a support Chromaton-N Super was used for GLC analysis of reaction mixtures. Normal alkanes were used as internal standards.

RESULTS AND DISCUSSION

In kinetic runs the pseudo-first-order conditions were granted by the use of a large (not less than 20-fold) excess of orthotitanate over the esters. The first-order rate coefficients were calculated from the relationship $\ln \varphi$ -t (φ is the ratio of peak heights of the initial ester and the internal standard, t is reaction time) by the least squares method. Since the first-order rate constants k_I for transesterification by sec-butyl orthotitanate depend proportionally on the concentration of alcoholate in a wide range of its variation[1,2], the kinetic measurements were carried out at only 2-3 concentrations of ortho-titanate and the second-order rate constants were calculated as follows:

$$k_{II} = k_I / c_{Ti}$$

The rate constants obtained are listed in Table 1. The values of activation parameters calculated by the method of least squares are listed in Table 2.

Table 1.

Rate Constants k_{II} of Transesterification of butyl Esters of Aliphatic Acids RC(O)OBu by sec-Butyl Orthotitanate in Heptane

No	R	t, ^{o}C	$10^3(k_{II} \pm s)$, $M^{-1} \cdot s^{-1}$
1	2	3	4
1.	H	0.0	1.79 ± 0.16
2.	H	25.0	7.98 ± 0.30
3.	H	50.0	25.3 ± 2.1
4.	Me	25.0	0.552 ± 0.030
5.	Me	50.0	2.09 ± 0.08
6.	Me	75.0	6.34 ± 0.60
7.	n-Bu	25.0	0.260 ± 0.023
8.	n-Bu	50.0	0.968 ± 0.077
9.	n-Bu	75.0	2.93 ± 0.30
10.	t-Bu	25.0	0.0223 ± 0.0012
11.	t-Bu	50.0	0.0913 ± 0.0043
12.	t-Bu	75.0	0.265 ± 0.015
13.	$ClCH_2$	0.0	2.32 ± 0.11
14.	$ClCH_2$	25.0	8.59 ± 0.29
15.	$ClCH_2$	55.0	30.9 ± 1.3
16.	Cl_2CH	0.0	4.45 ± 0.57
17.	Cl_2CH	25.0	12.7 ± 0.5
18.	Cl_2CH	50.0	32.8 ± 1.9
19.	Cl_3C	0.0	2.61 ± 0.04
20.	Cl_3C	25.0	8.30 ± 0.42
21.	Cl_3C	50.0	20.2 ± 0.8
22.	$BrCH_2$	0.0	2.52 ± 0.02
23.	$BrCH_2$	25.0	9.34 ± 0.51
24.	$BrCH_2$	50.0	24.7 ± 1.1
25.	$PhOCH_2$	0.0	1.27 ± 0.16
26.	$PhOCH_2$	25.0	4.85 ± 0.17

Table 1 continued

1	2	3	4
27.	$PhOCH_2$	50.0	14.6 ± 0.8
28.	$ClCH_2CH_2$	25.0	0.641 ± 0.015
29.	$ClCH_2CH_2$	50.0	2.27 ± 0.05
30.	$ClCH_2CH_2$	75.0	6.53 ± 0.42
31.	Ph_2CH	25.0	0.0293 ± 0.0055
32.	Ph_2CH	50.0	0.126 ± 0.07
33.	Ph_2CH	75.0	0.370 ± 0.049

[*] Values of k_{II} from Ref. 2.

Table 2

Activation Parameters of Transesterification of
Butylic Esters of Aliphatic Acids $RC(O)OBu$ by sec-Butyl
Orthotitanate in Heptane[+]

R	$\log A$	$E, \frac{kcal}{mole}$	$\Delta H^{\neq}, \frac{kcal}{mole}$	$-\Delta S^{\neq}, entr. un.$	$\Delta G^{\neq}, \frac{kcal}{mole}$
1	2	3	4	5	6
H	4.73 ± 0.13	9.34 ± 0.17	8.75	38.89	20.35
Me	4.13 ± 0.12	10.08 ± 0.18	9.49	41.65	21.91
Bu	3.74 ± 0.18	10.01 ± 0.26	9.41	43.41	22.35
tBu	2.87 ± 0.12	10.26 ± 0.18	9.67	47.11	23.72
$ClCH_2$[**]	4.08 ± 0.07	8.40 ± 0.09	7.81	41.85	20.29
Cl_2CH	3.26 ± 0.17	7.03 ± 0.23	6.44	45.60	20.04
Cl_3C	3.17 ± 0.09	7.18 ± 0.12	6.59	46.05	20.32
$BrCH_2$	3.81 ± 0.11	8.00 ± 0.15	7.41	43.08	20.26
$PhOCH_2$	3.97 ± 0.14	8.58 ± 0.19	7.99	42.38	20.63
$ClCH_2CH_2$	3.85 ± 0.08	9.61 ± 0.12	9.02	42.92	21.82
Ph_2CH	3.20 ± 0.29	10.54 ± 0.43	9.95	45.89	23.63
Ph[***]	4.70 ± 0.06	12.14 ± 0.09	11.55	39.0	23.18

[*] The values of E and log A are calculated from the Arrhenius equation by the least squares method (including $\log k_{II}$ values of individual determinations). $\Delta H^{\neq}, \Delta S^{\neq}$ and $\Delta G^{\neq}$ are calculated from the values of E and log A.
[**] Data from Ref. 2.
[***] Data from Ref. 1.

Table 3

Values of Substituent Constants Used for Data Treatment

R	$E_S^{(a)}$	$E_S^{o(b)}$	$\nu^{(c)}$	$E_S^{isod(d)}$	$n_{HC}^{(e)}$	$\sigma^{*(f)}$	$\sigma^{*(g)}_{Alc=o}$
H$^{(h)}$	0	0	0	0	0	0	0
Me	-1.24	-0.25	0.52	-1.24	3	-0.49	0
Bu	-1.63	-0.84	0.68	-1.63	2.4	-0.62	0
tBu	-2.78	-2.39	1.24	-2.78	1.2	-0.79	0
CH_2Cl	-1.48	-0.82	0.60	-1.31	2	0.52	1.01
$CHCl_2$	-2.78	-2.45	0.81	-1.71	1	1.52	2.01
CCl_3	-3.30	-3.30	1.38	-2.78	0	1.99	2.48
CH_2Br	-1.51	-0.85	0.64	-1.31	2	0.59	1.08
CH_2OPh	-1.57	-0.91	0.74	-1.63$^{(i)}$	2	0.43	0.92
CH_2CH_2Cl	-2.14	-1.35	0.97	-1.60	2.4	-0.11	0.38
$CHPh_2$	-3.00	-2.67	1.25	-3.22$^{(j)}$	1	-0.03	0.46

(a) Taft's steric constants[3], shifted by 1.24 units to the more negative values compared with the original. Taft's scale (hydrogen atom is the standard substituent).

(b) Palm's steric constants[22] derived from Taft's E_S values taking into account the hyperconjugation contribution to the latter by the equation: $E_S^o = E_S + 0.33(n_H + 0.4\ n_{HC})$. (hydrogen atom is the standard substituent).

(c) Charton's steric constants[21,22], calculated from the difference of van der Waals radii of substituent R and hydrogen

(d) Isosteric values for steric substituent constants E_S.

(e) $n_{HC} = n_H + 0.4\ n_C$, where n_H and n_C are the numbers of hydrogen and sp^3 carbon atoms connected with the reaction centre

(f) Uniform scale of polar constants[11] for the hydrogen atom, alkyl groups and the functional derivates of the latter (for a more detailed description of the scale see the text).

(g) Scale of polar constants[11] for functional derivates of alkyl groups (see the text).

(h) Standard substituent

(i) E_S for n-Bu

(j) E_S for $CHEt_2$

Table 4
Results of Data Treatment According to Equations (1) and (2)[a]

Number of correlation	$\log k_o$	a_1 [b]	a_3	a_5 [c]	R [d]	s [e]	s_o [f]
[1A]	5.63 ± 0.46	$0.949\pm0.039(E_S)$	-2.28 ± 0.13	0.387 ± 0.014	1-11	0.161	0.192
[1B]	5.28 ± 0.10	$0.902\pm0.009(E_S)$	-2.21 ± 0.03	0.405 ± 0.003	1-6, 8, 9	0.030	0.037
[1C]	5.37 ± 0.08	$0.892\pm0.009\ (E_S)$	-2.24 ± 0.02	0.407 ± 0.003	2-6, 8, 9	0.024	0.029
[1D]	5.09 ± 0.11	$0.901\pm0.008\ (E_S)$	-2.15 ± 0.03	–	1-4	0.024	0.029
[1E]	$5.2\ \pm0.08$	$0.898\pm0.008\ (E_S)$	-2.21 ± 0.03	–	2-4	0.016	0.021
[2A]	5.39 ± 0.43	$0.944\pm0.036\ (E_S^0)$ $-0.237\pm0.033\ (n_{HC})$	-2.25 ± 0.12	0.395 ± 0.013	1-11	0.150	0.178
[2B]	5.31 ± 0.10	$0.898\pm0.009\ (E_S^0)$ $-0.307\pm0.007\ (n_{HC})$	-2.21 ± 0.03	0.404 ± 0.003	1-6, 8, 9	0.029	0.036
[2C]	5.11 ± 0.12	$0.898\pm0.008\ (E_S^0)$ $0.300\pm0.007\ (n_{HC})$	-2.15 ± 0.04	–	1-4	0.025	0.030
[3]	5.06 ± 0.67	$0.737\pm0.052\ (E_S)$	-2.03 ± 0.19	$0.343\pm0.019(g)$	1-11	0.241	0.287
[4]	4.87 ± 0.43	$0.889\pm0.034\ (E_S^{189})$	-2.06 ± 0.12	0.290 ± 0.011	1-11	0.154	0.183
[5]	5.05 ± 0.70	$-2.04\ \pm0.13\ (\nu)$	-2.12 ± 0.20	0.322 ± 0.019	1-11	0.248	0.295
[6]	-2.11 ± 0.03	$0.91\ \pm0.009\ (E_S)$	(298.2K)	1.366 ± 0.011	1-6, 8, 9	0.019	0.021
[7]	-2.10 ± 0.03	$0.911\pm0.009\ (E_S^0)$ $-0.309\pm0.008\ (n_{HC})$	(298.2K)	1.362 ± 0.011	1-6, 8, 9	0.020	0.021

Table 4 continued

(a) Since in the course of data treatment according to equations (1) and (2) the terms with coefficients a_2, a_4 and a_7 turned out to be statistically insignificant, Table 4 lists the coefficients and the statistics for the equation $\log k = \log k_o + a_1 E_S + a_3 \cdot 1000/T + a_5 \cdot \sigma^{\ast} \cdot 1000/T + (a_6 n_{HC})$.

(b) The scale of steric constants used in the correlation is given in brackets after the coefficient a_1.

(c) In all correlations the $\sigma^{\ast}_{Alk=o}$ scale of polar constants was used; except the correlation [3], where the $\sigma^{\ast}$ scale was used.

(d) The numbers correspond to the substituents R in the esters RC(O)OBu included in the correlation: H(1), Me(2), Bu(3), t-Bu(4), CH_2Cl(5), $CHCl_2$(6), CCl_3(7), CH_2Br(8), CH_2OPh(9), CH_2CH_2Cl(10), $CHPh_2$(11).

(e) Standard deviation from the hyperplane of the regression in the scale of correlated values ($\log k_{II}$).

(f) Standard deviation in the normalized scale (the normalization is obtained[1] by the division of the corrected values and arguments by the square roots of the corresponding dispersions).

The statistical treatment of the kinetic data was carried out by using a program[1] of multifactorial regression analysis written for the computer Nairi-3. Table 3 lists the scales of substituent constants used in data treatment.

In the present work we studied the effect of two factors - the structure of the substituent in the acyl portion of the ester and the temperature upon the transesterification kinetics. For aliphatic esters the former factor includes at least two formal types of interaction, steric and polar. The values of $\log k$ for constant temperature follow Taft's equation[3]:

Table 5

Values of Activation Energy and Entropy Contributions to
the Total Steric Effect of Aliphatic Groups for Trans-
esterification by Sec-Butyl Orthotitanate in Heptane .

R	$\sigma^*_{Alk=0}$	E_a, kcal/mole	E_{calc}, $\frac{kcal}{mole}$	E_a-E_{calc}, kcal/mole	$-T\Delta\Delta S^*$ (25°C), kcal/mole
H	0(0.49)	9.34 ± 0.17	10.25(9.96)	-0.90(0.0)	0.0[b]
Me	0	10.08 ± 0.18	10.25	-0.2	0.8
Bu	0	10.01 ± 0.26	10.25	-0.2	1.4
t-Bu	0	10.26 ± 0.18	10.25	0.0	2.5
CH_2Cl	1.01	8.40 ± 0.09	8.37	0.0	0.9
$CHCl_2$	2.01	7.03 ± 0.23	6.51	0.5	2.0
CCl_3	2.48	7.18 ± 0.12	5.63	1.6	2.1
CH_2Br	1.08	8.00 ± 0.15	8.24	0.2	1.3
CH_2OPh	0.92	8.58 ± 0.19	8.54	0.0	1.0
CH_2CH_2Cl	0.38	9.61 ± 0.12	9.54	0.1	1.2
$CHPh_2$	0.46	10.54 ± 0.43	9.39	1.2	2.1
Ph	0.60	12.14 ± 0.09	9.10	3.0[c]	0.0

[a] Values of activation energy, calculated according to
equation [1C] (see Table 4): $E_{calc}=2.303 \cdot R \cdot a_3 - 2.303 R \cdot a_5 \sigma^*$

[b] Standard substituent

[c] Resonance energy E_v between the benzene ring and carbonyl group (see text).

$$\log k = \log k_0 + \delta E_S + \rho^* \cdot \sigma^* ,$$

where E_S and σ^* are the steric and polar substituent
constants of R; δ and ρ^* are the reaction constants
measuring the susceptibility of the reaction series to the
steric and polar effects.

A combined influence of the structure of an ester and
temperature on the rate of the process studied can be
described by a non-additive equation (1):

$$\log k = \log k_o + a_1 E_S + a_2 \sigma^* + a_3 \cdot 1000/T + a_4 E_S \cdot 1000/T + a_5 \sigma^* \cdot 1000/T$$
(1)

Table 4 lists the results of data treatment according to equation (1). Since in all correlations the terms with coefficients a_2 and a_4 turned out to be statistically[1] insignificant, these terms are not listed in Table 4. The results obtained correspond to the isoentropic polar effect and isoenthalpic steric effect of substituents in the acyl part of an ester.

The results of two alternative data treatment have been obtained. One of them makes use of polar substitution constants $\sigma^*_{Alk=o}$ [the scale[11] of polar constants for functional derivates of alkyl groups, calculated mostly from the pK_a values of substituted acetic acids $RCH_3C(O)OH$ in water ($25^{\circ}C$); the $\sigma^*_{Alk=o}$ values for the hydrogen atom and saturated hydrocarbon radicals are equalized to zero] . The other was based on the use of uniform σ^* scale[11] of polar constants for the hydrogen atom, alkyl groups and the functional derivates of the latter, accepting the hydrogen atom for the standard substituent ; for alkyls original Taft's values and for functional derivates of alkyls values calculated mostly from the pK_a-s of the corresponding substituted acetic acids in water ($25^{\circ}C$). The comparison of these alternative results confirms the assumption made by some authors[4-9] that the σ^* values for alkyl groups may be equalized to zero (at least in the acyl transfer reactions): the regression [1A] leads to a much better fit than regression [3] (see Table 4).

The influence of variable steric effect originating from the acyl portion of an ester was reflected least properly in terms of Charton's ν-parameters (cf. statistical indices of equation [5] with the corresponding indices of equations [1A] and [4] in Table 4).

The application of equation (1) to the complete series of results (33 values of $\log k_{II}$, Table 1) results in a relatively poor correlation, as shown in Table 4 (correlation [1A]). At the confidence level of 0.95 the significantly deviating points for esters $R=CH_2CH_2Cl$, $CHPh_2$ and

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CCl_3 (at all temperatures) were excluded. After that a much better correlation was obtained (regression [1 B] in Table 4) and the equation [1 B] adequately describes the acyl group substituent and temperature effects upon the reactivity of esters in this reaction. The values of constants obtained in regression [1 B] for log k_o, a_1 and a_3 do not differ within the limits of their uncertainties from the corresponding values in regression [1 E] (when only alkyl substituents R = Me, Bu and t-Bu were included into the data treatment)

Number [2] of Table 4 lists the results of data treatment according to equation (2) with hyperconjugation terms included:

$$\log k = \log k_o + a_1 E_S + a_2 \, \sigma^* + a_3 \cdot 1000/T + a_4 \cdot E_S \cdot 1000/T + \quad (2)$$
$$+ \, a_5 \, \sigma^* \cdot 1000/T + a_6 n_{HC} + a_7 \cdot n_{HC} \cdot 1000/T$$

where $\quad n_{HC} = n_H + 0.4 \, n_C$,
and $\quad n_H$ and n_C are the numbers of α-C-H and α-C-C bonds involved in hyperconjugation.

The terms with coefficients a_2, a_4 and a_7 in regressions [2] proved to be statistically insignificant. The comparison of the statistical indices of the corresponding (with the same substituents involved) regressions according to equations (1) and (2) (Table 4) shows that the significance of the corresponding correlations is statistically essentially identical in spite of one additional term in regressions according to equation (2). The coefficients a_1 in correlations according to equations (1) and (2) are almost equal and the ratio of coefficients a_6/a_1 in correlations [2 B] and [2 C] does not essentially differ from the ratio (0.33) used for calculating the values of E_S^o:

$$E_S^o = E_S + 0.33 \, (n_H + 0.4) \, n_C \, .$$

Consequently, the relative susceptibility of the process under discussion for heptane solution (in the conditions when specific solvation is lacking) to the supposed hyperconjugation and steric effects is the same as that for acid

catalysed hydrolysis of esters in aqueous ethanol.

In connection with the results cited above it is of considerable interest to compare the behaviour of the formic ester (R=H) to other esters. Often the compounds with hydrogen related to the reaction centre are excluded from the correlations where the E_S scale of steric constants is used[4,10]. In the case of the present process the points for R=H were not excluded at the 0.95 confidence level (the value $\sigma^* = 0$ was used for hydrogen). But the tendency of the hydrogen points to deviate from the hyperplane as described by equation [1 B] in one direction at lower temperatures and in the other at higher temperatures and the difference between the value of log A for formic ester and the values of log k_o from correlations [1 B] , [1 C] and [1 D] are likely to indicate some specific mode of interaction for the hydrogen substituent.

We established in our earlier paper[1], that the chemical reactivity of butylic esters of meta-substituted benzoic acids in the reaction with sec-butyl orthotitanate in heptane is adequately described by the relationship:

$$\log k = (4.37^{\pm}0.07) - (2.55^{\pm}0.02) \cdot 1000/T +$$
$$+ (0.329^{\pm}0.004) \cdot \sigma^o \cdot 1000/T$$
$$s = 0.024; \; s_o = 0.040$$

It should be noted that as a result of the isoentropic inductive effect in this aromatic series as well as in the aliphatic series studied in the present work the coefficients before the terms $\sigma^o \cdot 1000/T$ in equation (3) and $\sigma^* \cdot 1000/T$ (correlation [1 C] in Table 4), 0.329 and 0.407 respectively, are equivalent to the corresponding ρ^o and ρ^* values at the same single temperature. The ratio of these values $(0.407^{\pm}0.003)/(0.329^{\pm}0.004)=1.24^{\pm}0.03$ ($\cong \rho^*/ \rho^o$) is significantly different from one. The well-known fact that the ρ^* value is seldom exactly the same as the ρ^o value in the corresponding reaction series indicates that the construction of a common scale of polar constants for functional groups and aliphatic substituents on the one hand, and

substituted phenyls on the other hand, is impossible[12].

Let us consider now the substituent effects on the entropy and enthalpy of activation, obtained in the present study. The values of activation parameters are summarized in Table 2.

We found that the equation [1 B] adequately describes (after excluding points for esters $R = CHPh_2$, CCl_3 and CH_2CH_2Cl) the influence of the substituent in the acyl portion of an ester and temperature upon transesterification kinetics. The result obtained corresponds to the isoentropic inductive and isoenthalpic steric effects of the substituent. The isoentropic inductive effect presumes a linear relationship between activation energy (E_a) and σ^{x} constants. This relationship is visualized in Fig.1. A comparison of experimental (E_a values listed in Table 2) and calculated by equation [1 C]

$(E_{calc} = 2.303 \ R \ a_3 - 2.303 \ R \ a_5 \ \sigma^{\text{x}} = 10.25 - 2.303 \ R \ a_5 \sigma^{\text{x}} \text{kcal/mole})$

values of activation energy shows that the corresponding values are significantly different in the case of three esters, $R = CCl_3$, $CHPh_2$, and $CHCl_2$ (Table 5). The inadequacy of these values ($E_a - E_{calc} \neq 0$) may result either from incorrect σ^{x} values for these substituents or from the effect of any other, besides inductive, type of interaction upon activation energy. The former assumption hardly proves to be correct since it requires (see Fig. 1) unlikely low σ^{x} values for these substituents (e.g., $\sigma^{\text{x}} < 0$ for $R = CHPh_2$). On the other hand an increase in the activation energy ($E_a - E_{calc} > 0$) may result from the non-zero energy term of the total steric effect (steric strain) for these three esters with bulky substituents in their acyl portion. Within the framework of the transition slate theory Taft[3,13] accomplished the separation of the overall steric effect of a substituent as measured by E_s into "steric strain" and "steric hindrance of motions". On the basis of Taft's assumptions the appearance of the "steric strain" term of total steric free energy being expressed by an increase in the activation energy is expected for every branched substituent attached to the reaction centre. In the present reaction

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series no such increase of activation energy was established in the case of butyl pivalate (R = t-Bu), the ester with a bulky substituent in its acyl portion. This result is in some contradiction with Taft's assumptions.

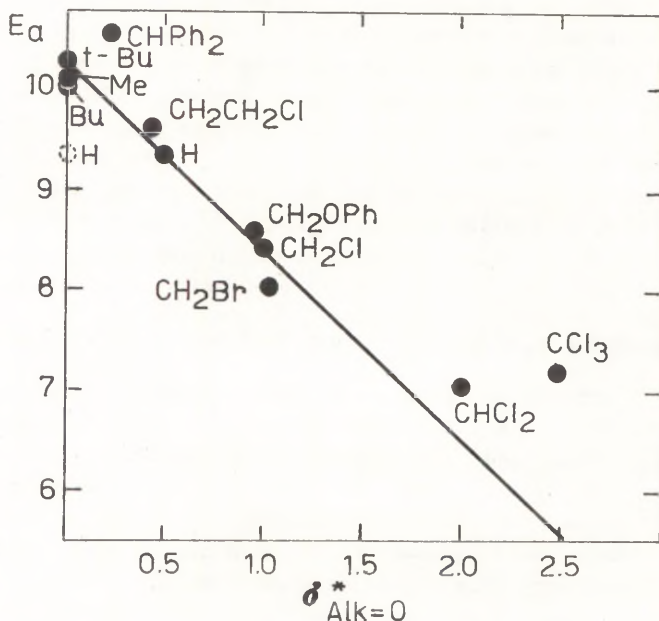Fig. 1. Energies of activation E_a plotted against polar constants $\sigma^*_{Alk=o}$. The line corresponds to the relation $E_{calc}=10.25 - 2.303\ R\ a_5\ \sigma^*$, were $a_5 = 0.407$ (correlation [1 C] in Table 4).

The values listed in the first entry of Table 5 show that the use of $\sigma^*=0$ for butyl formiate (R=H) leads to an unlikely value of "steric strain" energy ($E_a - E_{calc}= 9.34 - 10.25= -0.91$ kcal/mole) while the use of Taft's original value σ^* (hydrogen)=0.49 leads to the expected result ($E_a - E_{calc}=0.0$). We may obtain a new value $E_s(H)=$

= -0.71 for hydrogen by applying the value $\sigma^* = 0.49$ in equation [1 C].

The points for the ester with $R=CH_2CH_2Cl$ too (like that of $R=CHPh_2$ and CCl_3 discussed above), deviate significantly from the hyper-plane described by equation [1 B]; while its activation energy (E_a) does not differ from the calculated E_{calc} value (see Table 5 and Fig. 1). Since the substituent $R=CH_2CH_2Cl$ is characterized by unexpectedly high (if compared to the isosteric substituent, $R=Pr$) E_s value [$E_s(CH_2CH_2Cl)= -2.14$; $E_s(Pr)= -1.60$] , the deviation of the points for this ester may be caused by the inaccurate E_s value. A new E_s value obtained from equation [1 C] (or equation [6]) is $E_s(CH_2CH_2Cl)= -1.76$ (-1.75), which only slightly differs from the corresponding isosteric value.

To estimate the value of the resonance effect for the phenyl group (E_ψ) on the kinetics of butyl benzoate in the process under discussion, we can start from the assumption[3] that the steric effect on E_a is negligible, since the $T\Delta\Delta S^{\neq}$ term for this ester equals zero within its experimental uncertainty (see the last entry of Table 5). Therefore we can obtain the E_ψ value for butyl benzoate from the following relationship:

$$E_\psi = E_a - E_{calc.} = 12.1 - 9.1 = 3.0 \text{ kcal/mole}$$

Almost the same E value can be obtained from another procedure as well. Since the values of log A (and $\Delta S^{\neq}$) coincide for butyl formiate ($R=H$) and butyl benzoate ($R=Ph$), and assuming the isoentropicity of polar and resonance effects, the steric effects for these substituents must be equal: $E_s(H)=E_s(Ph)= -0.71^*$. Using the value of E_s(phenyl)

* Almost the same E_s values for R=H and Ph are obtained from equation [1 C] , using the corresponding log A values:

$$E_s = \frac{\log A - \log k_o}{a_1} \text{ , where log } k_o = 5.37 \text{ and } a_1 = 0.892.$$

The obtained values $E_s(H)= -0.72$ and $E_s(Ph)= -0.75$ within the experimental uncertainty do not differ from the value $E_s = -0.71$.

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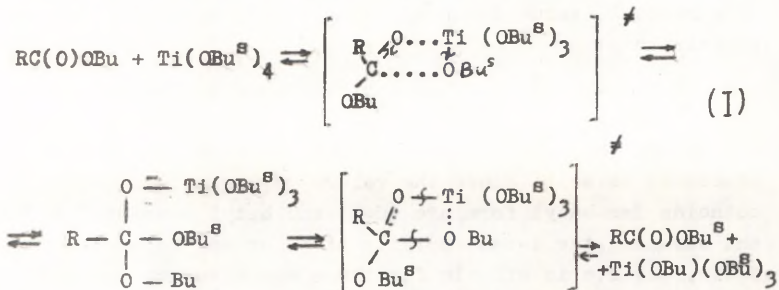in equation [1 C], the magnitude of resonance effect for butyl benzoate can be calculated:

$$E_\psi = -2.303 \, R \, T(\log k_{exp} - \log k_{calc}) = 3.12 \text{ kcal/mole},$$

where $\log k_{calc}$ is calculated by equation [1 C],

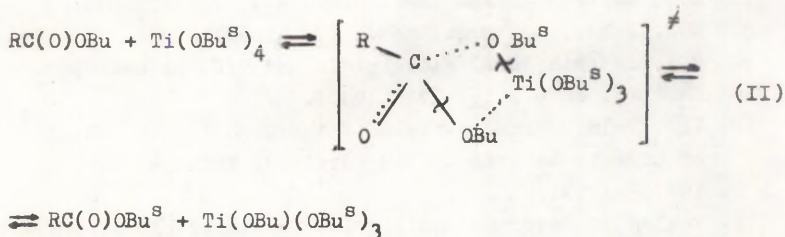$E_B(Ph) = -0.71$; $\sigma^{\mathsf{X}}(Ph) = 0.64$ and $\log k_{exp}^{25^{\circ}C} = -4.19$ (reported in our previous publication[1]);

The value $E_\psi = 3.0$ kcal/mole for transesterification of butyl benzoate by sec-butyl orthotitanate in heptane obtained in this work is lower than the corresponding values[3] for acid ($E_\psi = 4.6$ kcal/mole) and base-catalysed ($E_\psi = 5.0$ kcal/mole) hydrolysis of esters. In the case of hydrolysis reactions proceeding via tetrahedral intermediate the resonance between phenyl substituent and carboxyl group that stabilizes the ground state is assumed[3] to be almost completely missing in the transition state. A somewhat smaller value of resonance energy E_ψ for transesterification by orthotitanate may be an indicator of an "earlier" (more reagent like) transition state for this reaction. For transesterification according to this mechanism the following scheme (I) has been supposed[14]·

$$RC(O)OBu + Ti(OBu^s)_4 \rightleftharpoons \left[\begin{array}{c} R \diagup O \cdots Ti \, (OBu^s)_3 \\ {}^\diagdown C \cdots\cdots OBu^s \\ OBu \end{array} \right]^{\neq} \rightleftharpoons \quad (I)$$

$$\rightleftharpoons \quad \begin{array}{c} O = Ti(OBu^s)_3 \\ | \\ R - C - OBu^s \\ | \\ O - Bu \end{array} \rightleftharpoons \left[\begin{array}{c} O \dashv Ti \, (OBu^s)_3 \\ R \diagup {}^{\vdots} \\ {}^\diagdown C \dashv O \, Bu \\ \diagup \\ O \, Bu^s \end{array} \right]^{\neq} \rightleftharpoons \begin{array}{c} RC(O)OBu^s + \\ + Ti(OBu)(OBu^s)_3 \end{array}$$

In this scheme the dotted lines stand for the forming bonds and the crossed out lines for the breaking bonds (when going from reagents towards products).

On the other hand, one-step cyclic concerted mechanism has been proposed[15,16] for non-catalysed aminolysis of

esters in non-polar aprotic media. The delivery of the pro-
ton to the departing oxygen is assumed without the formation
of a tetrahedral intermediate . A similar path of amino-
lysis reaction is suggested by DeTar[17] on the basis of the
comparison of ρ values for acyl and having groups. This
author concludes that the aminolysis of esters does not
involve a kinetically significant tetrahedral intermediate,
but that some kind of direct displacement (of the S_N^2 type)
occurs instead. Since the E_ψ value obtained in this work
for the reaction under discussion is lower than the resonance
energy between the benzene ring and the carbonyl group ($E^{18} =$
$= 7$-11 kcal/mole), we may assume a similar to that one for
the aminolysis mechanism for transesterification as well:

$$RC(0)OBu + Ti(OBu^s)_4 \rightleftharpoons \left[\begin{array}{c} R \diagdown \\ C \cdots\cdots O\ Bu^s \\ \diagup \diagdown \diagup Ti(OBu^s)_3 \\ 0 \qquad OBu \end{array} \right]^{\neq} \rightleftharpoons \qquad (II)$$

$$\rightleftharpoons RC(0)OBu^s + Ti(OBu)(OBu^s)_3$$

Comparatively low phenyl-carbonyl resonance effect is
also characteristic of the aminolysis reaction.[19] Low val-
ues ($\rho \approx 1.0$ for the reactions of pyrrolidine[20] with substi-
tuted p-nitrophenyl benzoates and p-chlorophenyl benzoates
in acetonitrile at $25^\circ C$), low $\Delta H^{\neq}$ and high negative $\Delta S^{\neq}$
values[19] also indicate the similarity of these two processes

But taking into account that the mechanism (I) also
leads to a non-polar cyclic transition state without a
considerable separation of charges the values of ρ^*, $\Delta H^{\neq}$
and $\Delta S^{\neq}$ obtained in the present study for transesterifica-
tion reaction are also consistent with this mechanism. So,
on the basis of the data available we cannot categorically
dismiss any of these two mechanisms.

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