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THE DEPENDENCE OF IONIZATION POTENTIALS AND PROTON AFFINITIES ON STRUCTURE. II. PROTON AFFINITIES. CORRELATIONS WITH SUBSTITUENT CONSTANTS AND POLARIZABILITY*

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The correlation of proton affinities (PA) with the structure holds for the several classes of organic compounds including alkyl as well as electronegative substituents. The analysis of the relative contributions of different structural factors (inductive and resonance effects, polarizability of the substituent and effects of hydrogen atoms) into the gross substituent effect has been performed.

Earlier[4] the correlation analysis of the dependence of PA on structure for several aliphatic series in terms of the two-parameter equation including inductive and polarizability terms was made by one of the present authors:

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

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* See also the preliminary communications[1-3].

where PA_o refers to the methyl-substituted derivative, $\sum\sigma^*$ - the sum of the inductive constants at the protonization center, and $\Delta R = MR - MR(\text{methyl})$, where MR is the calculated additive molecular refractivity (at the sodium D-line) of the substituent.

It was also found that Eqn. (2)

$$PA = PA_o + a_1\sum\sigma^* + hn_1 \qquad (2)$$

where n_1 is the number of the hydrogen atoms, immediately attached to the protonization center leads to the similar, however statistically slightly less satisfactory results.

The alternative, and according to its results equivalent approach for the quantitative calculation of the polar and polarizability effects on the gas phase basicity of some classes of organic compounds was also suggested by R.W.Taft[5].

In the very recent years, due mainly to the fast progress of ICR spectroscopy and high pressure mass-spectrometry a large amount of new important experimental data on PA-s of compounds of various classes has been accumulated. It calls for the certain revision and development of the empirical quantitative schemes of the correlation of the gas phase basicity of (mostly) the aliphatic compounds with their structure.

In the present work the statistical treatment of the proton affinity data available was performed in terms of more general aquation (3)

$$PA = PA_o + a_1\sum\sigma^* + a_2\sum\Delta R + a_3\sum\sigma_R^o + a_4 n_1 + a_5\Delta n_2, \qquad (3)$$

where $\sum\sigma^*$, $\sum\Delta R$ and n_1 are as defined for Eqns.(1) and (2),

$\sum\sigma_R^o$ is the sum of Taft resonance constants of the substituents attached to the protonization center, and

$\Delta n_2 = n_2 - n_2(\text{methyl})$, where n_2 is the number of the hydrogen atoms in the α-position to the reaction center ($n_2(\text{methyl})=3$).

which was already used[6] in the present series of papers for the correlation of the dependence of ionization potentials on structure.

One can see, that as compared with Eqn. 1 the present approach takes into account also the contribution of resonance effects and the influence of the hydrogen atoms attached immediately or at the α-position to the reaction center.

As a rule standard values of the substituent constants were used. Taft's inductive σ^* constants were mostly taken from Ref. 7 (for the fluoroalkyl groups the additive values were calculated using the attenuation factor $Z^* = 0.35$). Resonance constants are from Ref.8 and the molecular refractivities MR of the complex substituents were calculated according to the additive scheme using Vogel's refractivities[9,10] for the structural elements determined at the D-line of sodium.

Analogously to the earlier works[4,6], mostly due to the practical considerations, an attempt was made to characterize the influence of alkyl as well as electronegative groups in the framework of a single, however theoretically[11] not very strict scheme[6]. Most of the PA values were taken from our compilation[20] and references given therein. Some other sources[12-18] were used for the more recent data. The complete list of compounds included into correlations is given in the footnotes to the Table 1.

Results

The results of the statistical least squares treatment of the data according to Eqn (3) and its constraints are listed in Table 1. The regression coefficient a_i, the standard deviations (in the parentheses), multiple correlation coefficients R, standard deviations of the correlation s, s% values defined as $s\% = (s/\Delta PA_{max})100$ (where ΔPA_{max} is the maximum range of the change of PA), as well as the number of points involved are reported.

The independence (orthogonality) of the different scales of substituent constants upon each other was also checked.

Discussion

One can see that Eqn.(3), similar to the correlations of ionization potentials with structure[3,6] and with a reasonable accuracy (as a rule $s = 1 \div 2$ kcal/mol and $s\% = 2 \div 7$), describes the dependence of PA values of various classes of neutral and anionic bases on their structural characteristics (inductive and resonance effects, polarizability, the effects of hydrogen atoms attached to the basicity center). Keeping in mind rather general close linear relationship[20]

$$PA = \alpha' IP + \beta$$

between PA and IP such a situation was not surprising. As far as the slope of this linearity $\alpha' = -0.67 \pm 0.20$, one has to expect that the dependence of PA values on the structure should be characterized by the regression coefficients a_i which have the opposite sign and are approximately 1.6-1.7 times smaller than the corresponding values for the correlation of IP values with structure in terms of the analogue of Eqn.(3).

The survey of Table 1 shows that, in the general case, similarly to the treatment of IP-s, in terms of the counterpart of Eqn.(3), several influencing factors should be taken into account simultaneously. It was demonstrated earlier[3,4] and reconfirmed by the data from Table 1 (see also Fig.1) that the single-parameter correlations of type $PA = PA_0 + a_1 \sum \sigma^*$, as a rule, do not lead to the adequate quantitative description of the dependence of the proton affinities on the structural factors (compare with Fig.2).

The earlier conclusion[4-6] about the nature of the non-resonance contribution of the alkyl groups is also confirmed. It follows from Table 1 that the relative contribution of the polarizability effect into the gross substituent

Table 1

The Results of Regression Analysis of Proton Affinities According to Eqn. (3)

Class of Compounds			PA_o	$-a_1$	a_2	a_3	$-a_4$	$-a_5$	R	s	s%	n
1	2		3	4	5	6	7	8	9	10	11	12
I.	X_1OH	a	201.6 (5.2)	12.33 (1.67)	0.150 (0.089)	48.47 (16.80)	18.64 (3.00)	2.24 (0.68)	0.965	1.2	5.0	II
		b	195.4 (2.3)	11.83 (1.22)	0.567 (0.096)	-	-	-	0.923	2.1	8.8	11
		c	197.4 (3.4)	10.60 (1.80)	-	-	-	-	0.748	3.1	14.1	11
	X_1OH $(X_1 \neq H)$	d	185.8 (5.6)	13.70 (2.29)	0.232 (0.121)	46.80 (24.17)	-	1.72 (0.93)	0.920	1.8	8.2	11
		e	196.1 (1.5)	11.50 (0.81)	0.415 (0.079)	-	-	-	0.958	1.3	5.9	10
2.	X_1OX_2	a	196.8 (3.4)	7.39 (1.02)	0.476 (0.107)	-10.55 (9.28)	1.79 (1.95)	-0.249 (0.381)	0.915	2.8	7.0	32
		b	193.5 (2.3)	8.01 (0.61)	0.640 (0.058)	0	0	0	0.948	2.3	5.8	28
		c	194.3 (2.1)	8.12 (0.55)	0.579 (0.057)	0	0	0	0.952	2.0	5.3	27
		d	200.5 (4.5)	10.25 (1.02)	-	-	-	-	0.760	4.5	11.8	31

Continuation of Table 1

1	2		3	4	5	6	7	8	9	10	11	12
3.	X_1OX_2 (X≠H)		195.0 (2.2)	7.95 (0.58)	0.528 (0.077)	-	-	-	0.954	1.9	5.3	17
4.	X_1O^-	a	374.7 (6.9)	10.70 (1.17)	-	-	-	-	0.819	6.8	10.3	18
		b	381.3 (4.5)	11.44 (0.75)	-0.480 (0.090)	-	-	-	0.975	2.4	3.6	18
		c	379.4 (1.8)	10.36 (0.44)	-0.524 (0.075)	-8.67 (4.49)	-18.06 (2.42)	-0.985 (0.589)	0.994	1.3	1.9	18
5.	$XCOO^-$	a	344.4 (0.8)	7.07 (0.60)	-	-	-	-	0.959	2.3	9.1	14
		b	346.8 (1.1)	7.76 (0.54)	-0.216 (0.076)	-	-	-	0.976	1.9	7.5	14
		c	348.2 (1.5)	5.11 (0.65)	-0.300 (0.055)	-33.37 (7.90)	-4.29 (1.74)	-0.689 (0.453)	0.981	1.1	4.3	14
6.	$X_1X_2X_3C^-$		389.8 (5.5)	3.28 (0.51)	-0.274 (0.075)	-43.41 (1.91)	-12.23 (1.84)	-1.79 (0.54)	0.971	2,2	4.1	21
7.	XCH_2^-		-19.0 (2.7)	5.86 (0.70)	-0.656 (0.125)	-25.35 (4.47)	-21.71 (3.35)	0	0.986	2.2	3.9	10
8.	$XC \equiv C^-$		371.9	6.75	-	-	-	-	-	-	-	2
9.	XCN	a	195.2 (4.3)	5.29 (0.76)	-	-	-	-	0.718	4.2	15.8	18

Continuation of Table 1

1	2		3	4	5	6	7	8	9	10	11	12
		b	189.6 (2.7)	5.16 (0.54)	0.607 (0.107)	–	–	–	0.903	2.6	9.8	16
		c	189.4 (2.2)	5.03 (0.58)	0.311 (0.086)	-27.67 (3.46)	10.20 (2.54)	2.27 (0.66)	0.974	1.5	4.2	19
10.	XNH_2	a	235.2 (4.8)	9.24 (0.62)	0.177 (0.048)	0.768 (3.01	6.27 (1.70)	0.709 (0.390)	0.966	1.1	5.7	19
		b	235.3 (1.50)	7.65 (0.24)	0.179 (0.015)	6.62 (1.05)	8.13 (0.54)	0.848 (0.118)	0.996	0.3	1.7	17
11.	X_1X_2NH $(X_1, X_2 \neq H)$		224.1 (2.5)	7.30 (0.84)	0.188 (0.057)	7.62 (3.71)	–	0.616 (0.318)	0.947	1.5	6.8	15
12.	$X_1X_2X_3N$ $(X_1, X_2, X_3 \neq H)$		226.2 (1.7)	8.92 (0.34)	0.134 (0.040)	-7.60 (2.95)	–	0.694 (0.463)	0.997	1.2	1.4	15
13.	$X_1X_2X_3N$	a	230.4 (2.3)	11.21 (0.39)	–	–	–	–	0.943	2.2	2.6	49
		b	226.1 (1.9)	7.67 (0.33)	0.301 (0.028)	–	–	–	0.981	1.9	2.2	49
		c	225.9 (2.0)	8.72 (0.22)	0.173 (0.029)	-3.88 (1.97)	1.75 (0.80)	0.741 (0.201)	0.990	1.4	1.6	49
14.	X_1X_2CO $(X_1, X_2 \neq H)$		198.8 (4.0)	5.00 (0.91)	0.292 (0.125)	-10.26 (4.17)	–	1.59 (0.98)	0.968	2.1	5.1	14
15.	X_1X_2CO	a	201.7 (6.5)	6.43 (0.56)	–	–	–	–	0.827	6.4	12.5	27

Continuation of Table 1

1	2	3	4	5	6	7	8	9	10	11	12
15.	X_1COX_2 b	196.3 (3.5)	4.68 (0.34)	0.659 (0.070)	–	–	–	0.946	3.4	7.10	25
	c	198.5 (3.0)	6.49 (0.53)	0.349 (0.081)	0.426 (2.62)	9.35 (1.94)	1.54 (0.58)	0.989	1.6	3.2	23
	d	197.8 (5.5)	4.21 (0.60)	0.638 (0.110)	−16.47 (3.38)	0.982 (2.38)	−0.206 (0.498	0.848	5.0	10.1	55
	e	198.7 (1.9)	3.21 (0.23)	0.558 (0.042)	−20.88 (1.26)	1.02 (0.87)	−0.671 (0.174)	0.976	1.7	3.4	40
	f	207.9 (4.3)	7.70 (1.02)	0	28.27 (10.65)	12.55 (2.24)	1.84 (0.74)	0.989	0.6	3.5	8
	g	215.8 (0.8)	4.82 (0.23)	0.710 (0.041)	0	0	0	0.993	0.7	2.6	7

Footnotes:

Ia. X=H,Me,Et,Pr,i-Pr,Bu,t-Bu, CCl_3CH_2, F_2CHCH_2, $F(CH_2)_2$, $HC{\equiv}CCH_2$

Ib. X=H,Me,Et,Pr,i-Pr,Bu,t-Bu,CCl_3CH_2, F_2CHCH_2, CF_3CH_2, $F(CH_2)_2$

Ic. The same as 1a with the exception of exclusion of X=H and inclusion of X=CF_3CH_2

Id. The same as 1c except X=$HC{\equiv}CCH_2$

Ie. The same as 1c

2a. X_1,X_2=H,H;Me,H; Et,H; Pr,H; i-Pr,H; Bu,H; t-Bu,H; CCl_3CH_2,H; F_2CHCH_2,H; CF_3CH_2,H; $HC{\equiv}CCH_2$,H; Me_2; Me,Et; Et_2; Pr_2; Et,i-Pr; Et,t-Bu; $(i\text{-}Pr)_2$; Me,t-Bu; Me,i-Pr; $(t\text{-}Bu)_2$; Me,$SiMe_3$; $(CF_3CH_2)_2$; Et,CF_3CH_2; Me,CF_3CH_2; $(H_2C{=}CHCH_2)_2$; $(HC{\equiv}CCH_2)_2$;

Footnotes to Table 1 (continuation)

CF_3CH_2, CH=CH_2; Me, CH_2CN; Me, CH=CH_2; Et, CH=CH_2.

2b. The same as 2a except X_1, X_2=Me, $SiMe_3$; H_2C=CH, Me; H_2C=CH, Et; CCl_3CH_2, H.

2c. The same as 2b except $X_1=X_2\neq H$.

2d. The same as 2a except $X_1=X_2\neq H$.

3. X_1, X_2=Me_2; Et_2; Me, Et; Pr_2; Et, i-Pr; Me, i-Pr; Et, t-Bu; $(i\text{-}Pr)_2$; Me, t-Bu; $(t\text{-}Bu)_2$; Me, $SiMe_3$; $(CF_3CH_2)_2$; CF_3CH_2, Et; CF_3CH_2, Me; $(H_2C=CHCH_2)_2$; $(HC\equiv CCH_2)_2$; Me, CH_2CN; Me, CH=CH_2; Et, CH=CH_2.

4a,b. X=H, HO, Me, Et, Pr, Bu, i-Pr, i-Bu, t-Bu, t-BuCH_2, PhCH_2, $F(CH_2)_2$, F_2CHCH_2, CF_3CH_2, $(CF_3)_2CH$, $(CF_3)_3C$, $C_2F_5CH_2$, NO_2.

4c. The same as 4a exeept F_2CHCH_2, Bu, PhCH_2.

5a. X=Me, Et, Pr, Bu, $Cl(CH_2)_2$, FCH_2, $ClCH_2$, F_2CH, Cl_2CH, CF_3, $BrCH_2$, PhCH_2, Ph, t-Bu.

5b. The same as 5a

5c. X=H, Me, Et, Pr, Bu, t-Bu, $Cl(CH_2)_2$, FCH_2, $ClCH_2$, F_2CH, Cl_2CH, CF_3, PhCH_2, $BrCH_2$.

6. X_1, X_2, X_3=Ph,H,H; F,F,F; F,F,H; Cl,Cl,Cl; F,F,Me; F,H,H; Ph,Me,Me; Ph,Me,H; Me,Me,NO_2; H,Me,NO_2; H,H,NO_2; H,H,CN; H,CN,MeO; H,CN,Ph; H,CN, CN; F,F,CF_3; PhCO, Me,H; H,H, MeCO; H,Me,MeCO; Me,Me,MeCO; H,MeCO,MeCO.

7. The correlation of the relative PA values[17]: PA-PA(X=H); X=H, CN, COOMe, NO_2, Ph, NH_2, MeNH, $MeSO_2$, MeSO.

8. Me and CF_3 substituents only[16].

9a. X=Me, Et, Pr, Bu, i-Pr, t-Bu, $CNCH_2$, FCH_2, CN, CCl_3, $ClCH_2$, Br, Ph, MeS, H_2C=CH, CF_3, $Cl(CH_2)_2$

9b. X=H, Me, Et, Pr, Bu, i-Pr, t-Bu, $CNCH_2$, FCH_2, CN, CCl_3, $ClCH_2$, Ph, H_2C=CH, CF_3, $Cl(CH_2)_2$

9c. X=H, Me, Et, Pr, Bu, i-Pr, t-Bu, $CNCH_2$, FCH_2, CN, CCl_3, $ClCH_2$, Cl, Br, Ph, MeS, Me_2N, H_2C=CH, CF_3, $Cl(CH_2)_2$.

10a. X=H, Me, Et, Pr, i-Pr, Bu, i-Bu, 2-Bu, t-Bu, t-Am, t-BuCH_2, $CN(CH_2)_2$, $F(CH_2)_2$, CF_3CH_2, $CF_3(CH_2)_2$, $H_2C=CHCH_2$, PhCH_2, $HC\equiv CCH_2$, MeNH.

10b. The same as 10a except CF_3CH_2 and $CF_3(CH_2)_2$.

Footnotes to Table 1 (continuation)

11. X_1,X_2=Me,Me;Me,Et; Pr,Pr; Bu,Bu; i-Pr,i-Pr; i-Pr,Et; i-Bu,i-Bu; 2-Bu,2-Bu; t-Bu,t-Bu; t-Am,t-Bu; CF_3CH_2,Me; $(HC{\equiv}CCH_2)_2$; $(CH_2{=}CHCH_2)_2$;Me,NH_2.

12. X_1,X_2,X_3=Me,Me,Me; Me, Me, Et; Me_2, Et; Me_2, i-Pr; Et_2, Pr; Me_2,t-$BuCH_2$; $CNCH_2$,Me_2; F,F,F; Me_2,CF_3; CF_3CH_2,Me_2; Me_3SiCH_2,Me_2; H_2N,Me_2; Et_3; Pr_3; Bu_3.

13. X_1,X_2,X_3=H,H,H;Me,H,H;Et,H,H; Pr,H,H; i-Pr,H,H; Bu,H,H; i-Bu,H,H; 2-Bu,H,H; t-Bu,H,H; t-Am,H,H: t-$BuCH_2$,H,H; $CN(CH_2)_2$,H,H; $F(CH_2)_2$,H,H; CF_3CH_2,H,H;$CF_3(CH_2)_2$,H,H; $H_2C{=}CHCH_2$,H,H; $PhCH_2$,H,H;; $HC{\equiv}CCH_2$,H,H; Me,NH_2,H; Me_2,H; Me,Et,H;Et_2,H; Pr_2,H; Bu_2,H; i-Pr_2,H; i-Pr,Et,H; i-Bu_2, H; 2-Bu_2,H; t-Bu_2,H; t-Am,t-Bu,H; CF_3CH_2,Me,H; $CNCH_2$,H, Me; H_2N,Me_2; Me_3; Et_3; Pr_3; Bu_3; Me_2,Et; Me,Et_2; i-Pr, Me_2; Pr,Et_2; t-$BuCH_2$,Me_2; $CNCH_2$,Me_2; F.F,F; CF_3,Me_2; CF_3CH_2, Me_2; Me_3SiCH_2, Me_2; MeO,H,H; H_2N, H,H;

14. X_1,X_2=Me_2; Me,Et; Et_2; i-Pr,Me; Me,cy-Pr; Ph_2; Ph,Me; $(MeO)_2$; Me,CF_3; $(CF_3)_2$; Me,FCH_2; $(F_2CH)_2$; $(cy\text{-}Pr)_2$; Me,SMe.

15a: X_1,X_2=Me,H; Et,H; Pr,H; Bu,H; i-Pr,H; t-Bu,H; CF_3,H; Me_2; Me,Et; Et_2; Me,i-Pr; Me,t-Bu; Me,cy-Pr; Me,Ph; $(MeCO)_2$; Me,CF_3; $(CF_3)_2$; FCH_2,Me; $(F_2CH)_2$; $(FCH_2)_2$; $(cy\text{-}Pr)_2$; Me,SMe; Me,CH_2Ph; CF_3,F; CH_3,F; F_2CH,CH_2F; F,F.*

15b. X_1,X_2=H,H; Me,H; Et,H; Pr,H; Bu,H; i-Pr,H; t-Bu,H; CF_3, H; Me_2; Me,Et; Et_2; Me,i-Pr; Me,t-Bu; Me,cy-Pr; Ph_2; Me, Ph; Me,CF_3; $(CF_3)_2$; FCH_2,Me; $(FCH_2)_2$; $(F_2CH)_2$; $(cy\text{-}Pr)_2$; Me,SMe; F,F; CF_3,F.*

15c. X_1,X_2=H,H; Me,H; Et,H; Pr,H; i-Pr,H; t-Bu,H; CF_3,H; Me_2; Me,Et; Et_2; Me,i-Pr; Me,cy-Pr; Ph_2; Me,Ph; Me,CF_3; $(CF_3)_2$; FCH_2,Me; $(FCH_2)_2$; $(F_2CH)_2$; $(cy\text{-}Pr)_2$; F,F; Bu,H; CF_3,F*.

15d. X_1,X_2=H,H; Me,H; Et,H; Pr,H; i-Pr,H; t-Bu,H; CF_3,H; Me_2; Me,Et; Et_2; i-Pr,Me; Me,t-Bu; Me,cy-Pr; Ph_2; Me, Ph; $(MeCO)_2$; $(MeO)_2$; Me,CF_3; $(CF_3)_2$; Me,CH_2F; $(FCH_2)_2$; $(F_2CH)_2$; $(cy\text{-}Pr)_2$; Me,SMe; F,F; $PhCH_2$,Me;Me,F; CF_3,F;

Footnotes to Table 1 (continuation)

F_2CH, CH_2F; H, OH; Me, OH; Pr, OH; FCH_2, OH; $ClCH_2$, OH; CF_3, OH; H_2NCH_2, OH; F_2CH, OH; H, OMe; H, OEt; Me, OMe; Pr, OMe; Et, OMe; i-Pr, OMe; EtO, OMe; t-Bu, OMe; cy-Pr, OMe; CF_3, OMe; CF_3, OEt; CN, OEt; F_2CH, OEt; Ph, OMe; $ClCH_2$, OEt; FCH_2, OEt.*

15e. The same as 15d except X_1, X_2=Me, F; $PhCH_2$, Me; F_2CH, CH_2F; $(MeCO)_2$; F, F; Pr, OH; CF_3, F; Et, OH; $(cy\text{-}Pr)_2$; t-Bu, H; $ClCH_2$, OH; Me, OH; F_2CH, OH; cy-Pr, Me; Me, SMe; $(FCH_2)_2$.*

15f. X_2=OH; X_1=H, Me, Et, Pr, FCH_2, $ClCH_2$, CF_3, F_2CH.

15g. X_1, X_2=H, NHMe; H, NMe_2; Me, NH_2; Me, NMe_2; EtO, NMe_2; CF_3, NH_2; Me_2N, Me_2N.

effect of alkyl (non-electronegative) groups clearly dominates for these substituents over the influence of the inductive effect which is characteristic to the electronegative substituents. On the other hand, while comparing the substituents with approximately equal polarizability (for example, X=CF_3CH_2 and CH_3CH_2 or $(CF_3)_3C$ and $(CH_3)_3C$) but with different electronegativity, the contribution of the inductive effect could reach very substantial absolute and relative values which heavily dominate over the polarizability effects.

Table 2 visualizes the distribution of the contributions of different structural factors into the gross substituent effects in the case of the gas phase protonization of XO^- anions.

Correlation statistics from Table 1 shows that the contribution of inductive effect formally represented in Eqn.(3) by the $a_1\sum\sigma^*$ is significant for all reaction

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* In Table 1 (series 14 and 15) the correlations which included data for the fluorinated substituents from Refs.13 and 14 were reported. The use of the corresponding data from Ref. 20 leads to practically indistinguishable results.

Table 2

The Separation of Contributions[a] of Different Structural Factors on the Proton Affinity of Anionic Bases XO^- in Gas Phase

No	X	$a_1\sigma^*$	$a_2\Delta R$	$a_3\sigma^o_R$	a_4n_1	$a_5\Delta n_2$	Gross Substituent Effect Calculations	Gross Substituent Effect Experiment
1.	H	-5.1	2.4	-0.95	18.1	-2.96	11.5	11.7
2.	Me	0	0	0	0	0	0	0
3.	Et	1.0	2.4	-0.17	0	-0.99	-2.6	-3.0
4.	Pr	1.2	-4.9	-0.17	0	-0.99	-4.9	-4.4
5.	Bu	1.3	-7.3	-0.17	0	-0.99	-7.2	-10.3
6.	i-Pr	2.0	-4.9	-0.17	0	-1.97	-5.0	-5.0
7.	i-Bu	1.3	-7.3	-0.17	0	-0.99	-7.2	-5.7
8.	t-Bu	3.1	-7.3	-0.17	0	-2.96	-7.3	-5.8
9.	$t\text{-}BuCH_2$	1.7	-9.7	0	0	-0.99	-9.0	-7.3
10.	O_2N	-50.1	-0.56	-2.3	0	-2.96	-55.9	-54.5
11.	HO	-14.6	1.6	2.51	0	-1.97	-12.4	-11.2
12.	$F(CH_2)_2$	-4.0	-2.5	-0.08	0	-0.99	-7.6	-8.6
13.	CF_3CH_2	-12.1	-2.7	-0.78	0	-0.99	-16.6	-14.7
14.	$C_2F_5CH_2$	-12.2	-5.0	-0.78	0	-0.99	-18.9	-17.6
15.	$(CF_3)_2CH$	-24.2	-5.5	-0.78	0	-1.97	-32.5	-33.6[16]
16.	$(CF_3)_3C$	-36.1	-8.2	-0.78	0	-2.96	-48.1	-49.1[16]
17.	CF_3	-34.5	0.3	-1.65	0	-2.96	-38.8	(-33±3)[16]

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[a] Calculated according to correlation 4c from Table 1. All quantities are given in kcal/mol.

series (simultaneously alkyl, as well as electronegative substituents were included). Besides that, without any exceptions for all reactions of proton transfer to electroneutral or negatively charged bases (basicity of anions A^- or acidity of their conjugated acids AH) the a_1 values are negative showing that the increase of the substituent electronegativity (higher positive values of σ^*) results

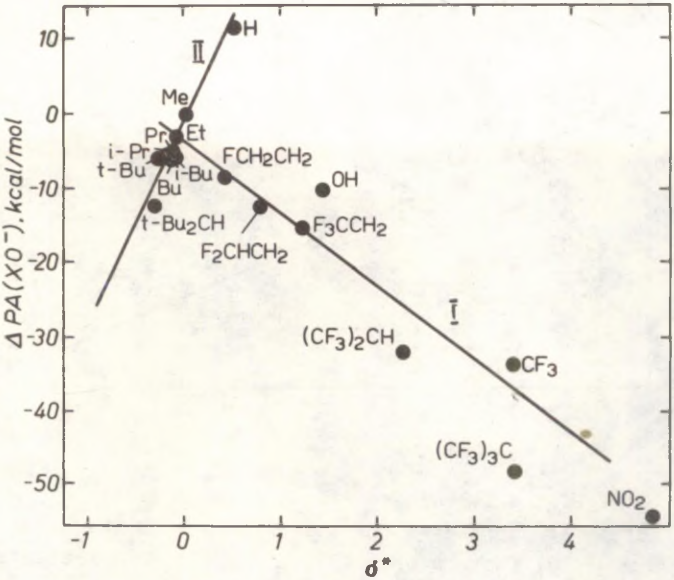

Fig.1. The dependence of gas phase basicity of XO^- anions on Taft's σ^* constants. Line (I) is drawn through the points for fluorosubstituted ethoxide-ions and $C_2H_5O^-$, line (II) is drawn for OH^- and alkylsubstituted anions.

in the decrease of the basicity of the base of any charge type.

In the very rough approximation the inductive field effect is sometimes[21-23] visualized by the interaction energy

$$E = q \mu \cos \Theta \; / Dr^2, \qquad (5)$$

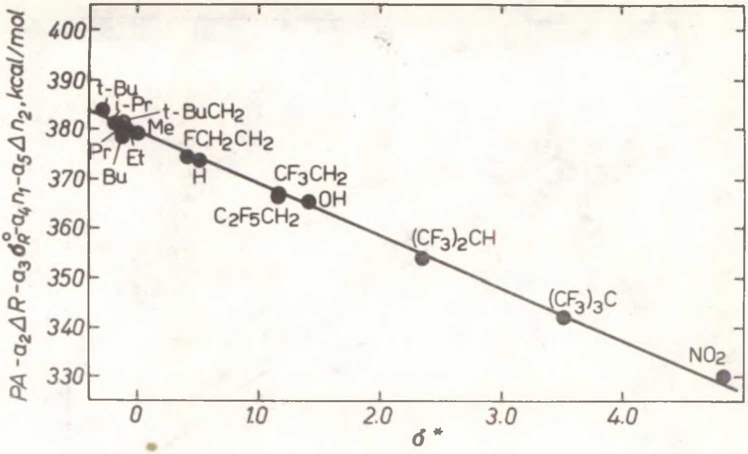

Fig. 2. The dependence of gas phase basicity of anions XO^- corrected for the influence of the other structural factors (Eqn.(3)) on Taft's σ^* constants. The straight line corresponds to correlation 4 c from Table 1.

where q – is the charge on the reaction center
D – is the dielectric constant
Θ – is the orientation angle
μ – is the dipole moment of substituent X
r – is the distance between the point charge on the reaction center and dipole of the substituent

between the point charge localized on the reaction center and the (point) dipole of the substituent. It is evident that interactions of this type could contribute very substantionally into the energetics of gaseous ions. So, for $q=1$, $\mu=1$ (Debye), $r=2A$, $D=1$ and $\Theta=0$ $E=28.3$ kcal/mol. The energy[23] of electrostatic dipole-dipole interaction between the dipoles of the fragments of polar molecules (e.g., neutral bases and acids) is substantially lower:

$$E = \mu_1 \cos \Theta_1 \mu_2 \cos \Theta_2 / r^3 D \qquad (6)$$

where μ_1 and μ_2 are the dipole moments of the fragments
Θ_1 and Θ_2 are the orientational angles of the dipoles
r - is the separation between the centers of dipoles

The analysis of the energetics of the proton transfer reactions in terms of Eqn.5 shows that the stabilization or destabilization energies which accompany the conversion of the reaction center of the basis of the different charge type (for the protonated form of the neutral base $q > 0$ (in the ideal case $q= +1$), and for the A^- $q < 0$ (in the limiting case $q= -1$), however in both ionic forms BH^+ and A^- the charge q by its absolute value significantly exceeds the charges on the reaction center in the corresponding electroneutral form B or AH) should have (on conditions of Θ=const) the opposite signs which essentially is evidenced by the general condition $a_1 < 0$ for the compounds of these classes. The absolute values ($-3 \geqslant a_1 \geqslant -11$) of a_1 which are less than for the case of ionization potentials^6 but significantly enhanced relative to the proton transfer reactions in the solution (see the following paper in this issue and Refs. 3 and 4) formally certify about the very substantional differences in the polarities of the neutral molecule and its protonated or deprotonated forms.

In terms of the approach^4 based on the Hine's equation the quantity a_1 (or ρ^*) could be represented as the difference between the Taft's σ^* constants of the reaction center in the final and initial states of the reaction. On condition of the constant orientation and separation of the substituent and reaction center (Θ, r_j = const) one can, on the basis of modelling the inductive field effect as the interaction between the point charge (of the reaction center) and the point dipole (of the substituent), write for the transfer[*] $X_iY'_j \rightarrow X_iY_j$ an expression[**]

$$E_{ij} = (q_{Y_j} - q_{Y'_j})\mu_i \cos\Theta / Dr^2_j = A_j\mu_i \tag{7}$$

which is formally analogous to the Hine's equation. In Eqn.(7) the dipole moment μ_i stands for the characteristics of the i-th substituent and the quantity

$$A_j = (q_{Y_j} - q_{Y'_j}) \cos\Theta / Dr^2_j \tag{8}$$

plays the role of the reaction constant a_1 from Eqn.(3).

As evidenced (see Table 3) by the nonempirical quantum chemical calculations[16,24] (STO-3G, total optimization of geometries using Gaussian 70[25] and Gaussian 82[26] systems of programs) an approximate invariability of the calculated differences of Mulliken charges in the final and initial states of the proton transfer reaction center $\Delta q = q_{Y_j} - q_{Y'_j}$ holds over a wide range of variation of X_i (for j=const). Due to the not quite representative set of Δq-values and because of their rather uncomparable statistical weights for some reaction series, the rigorous comparison of the A_j and a_1 values should be postponed.

Only the preliminary conclusion (see Fig 3) could be made by observing that the comparison at a_1 and Δq values for neutral and anionic bases leads to the grouping of the points into two different families with significantly different slopes. It is worthwhile to notify that the slope for the anions A^- exceeds that for the neutral bases B ca by 1.6 times which, in terms of Eqns (5),(7), and (8) formally hints to the lower r_j value for the former class of

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[*] subscripts i and j refer to the i-th substituent X_i and the j-th reaction center Y_j whereas superscript marks the latter in the initial (deprotonated) state.

[**] For the sake of simplicity Eqn.(6) was used instead of Eqn.(5) for the neutral molecule .

Table 3

The Differences Δq of Mullinen Charges (STO-3G Basis) on the Reaction Center for Some Proton Transfer Reactions[16,24].

Reaction Series 1	q_{Y_j} 2	$q_{Y'_j}$ 3	$\Delta q = q_{Y_j} - q_{Y'_j}$ 4	Substituents Involved 5
1. $XO^- + H^+ \rightarrow XOH$	$0.15 \geqslant q_{OH} \geqslant -0.43$	$-0.2 \geqslant q_{O^-} \geqslant -1$	0.52 ± 0.07	X=H, F, NO_2, ClO_3, HO, F_3N, Me_3N, Ph, Me, Et, i-Pr, t-Bu, CF_3, CF_3CH_2, $(CF_3)_2$ $(CF_3)_2CH$, $(CF_3)_3C$.
2. $XNH^- + H^+ \rightarrow XNH_2$	$0.14 \geqslant q_{NH_2} \geqslant -0.4$	$-0.377 \geqslant q_{NH^-} \geqslant -0.70$	0.63 ± 0.10	X=NO_2, F, CF_3
3. $X_1X_2N^- + H^+ \rightarrow X_1X_2NH$	$q_{NH} = 0.14$	$q_{N^-} = -0.414$	0.55	X_1, X_2=F
4. $XC\equiv C^- + H^+ \rightarrow XC\equiv CH$	$q_{CH} = 0.047$	$q_{C^-} = -0.334$	0.381	X=CF_3
5. $XCOO^- + H^+ \rightarrow XCOOH$	$-0.01 \geqslant q_{OH} \geqslant -0.092$	$-0.46 \geqslant q_{o^-} \geqslant -0.515$	0.42 ± 0.03	X=H, Me, CF_3 Me_3NCH_2

Table 3 continued

1		2	3	4	5
6.	$XS^- + H^+ \rightarrow XSH$	$q_{SH} = 0.063; 0.114$	$q_{S^-} = -0.517, -0.63$	0.662 ± 0.030	X=Me, CF_3
7.	$XNH_2 + H^+ \rightarrow XNH_3^+$	$0.66 \geqslant q_{NH_2^+} \geqslant 0.52$	$-0.04 > q_{NH_2} > -0.096$	0.711 ± 0.05	X=Me, CF_3, Et, CH_2CN, CF_3CH_2
8.	$X_1X_2CO + H^+ \rightarrow X_1X_2COH^+$	$0.26 \geqslant q_{OH^+} \geqslant 0.217$	$-0.117 \geqslant q_O \geqslant -0.236$	0.416 ± 0.050	X_1X_2=H,F; F_2; H,CN; $(CN)_2$; CF_3,H; $(CF_3)_2$
9.	$XCN + H^+ \rightarrow XCNH^+$	$q_{NH^+} = 0.24; 0.311$	$q_N = -0.106; -0.138$	0.397 ± 0.020	X=CN, CF_3
10.	$XOH + H^+ \rightarrow XOH_2^+$	$q_{OH_2^+} = 0.584$	$q_{OH} = -0.105$	0.749	X=H.

Footnote : The quantity Δq is calculated as a difference between the total charge on the reaction center on the final and initial states. For example for series 2 from this Table $\Delta q = q_{NH_2} - q_{NH^-}$, for series 7 $\Delta q = q_{NH_3^+} - q_{NH_2}$, etc.. The q values are given in charges of the electron.

bases[x].

The aforesaid agrees with the results[16,24-33] of the nonempirical quantum chemical calculations of the structure and charge distribution for the systems of different chemical nature $X(Z)_nY^{+}_{-}H^+$, where X - is the substituent, Z - the attenuating fragment, (e.g., CH_2-group) n=0,1,2,etc., Y - the reaction center ($OH, NH_2, SH, \equiv CH$, CO, CN, etc.). According to that, as a rule, the C-O, C-NH, C-S, C-C distances at the immediate vicinity of the reaction center in the deprotonated forms of alcohols, amines, mercaptanes, alkanes are significantly <u>shorter</u>[xx] than in the corresponding protonated systems and <u>longer</u> in the α-and β-positions

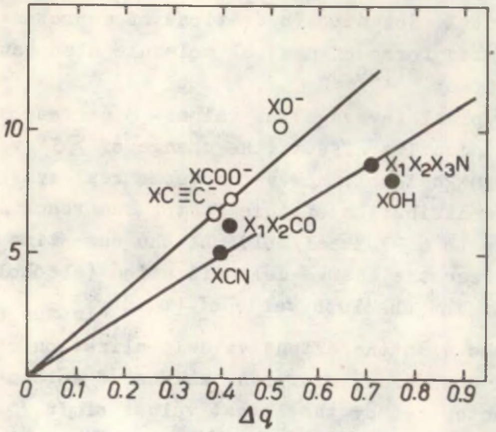

Fig.3. The dependence of a_1 values on the differences Δq of the Mulliken charges on the reaction center in the initial and final states of some proton transfer equilibria.

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[x] For example, assuming $r_j = 3\mathring{A}$ for A^- and $r_j = 4\mathring{A}$ for BH^+ leads already to the ratio 1.77.

[xx] When both X and Y are electrondonating (n=0) groups posessing lone electron pairs ($HONH_2, H_2NNH_2$, FOH, FNH_2, HOOH,etc.) the deprotonation of the neutral molecule results in the increase of the distance between X and Y.

(see Fig.4). Simultaneously, due to the intramolecular stabilizing interactions the center of gravity of the negative charge in the anion moves from the protonation center towards the substituent which corresponds to the shortening of the distance r_j. Vice versa, as a rule,[16,24,27,29,29,30,33] the protonation of the neutral molecule (ROH, RNH_2, R_1COR_2, etc.) is accompanied by the increase of the bond length between the substituent and reaction center and by the shift of the centroid of the positive charge farther off from the substituent into the peripheral region of the protonation center (hydrogens of the NH_3^+, OH_2^+ and, OH^+-groups,etc.). This, in its turn leads to the increase of the effective distance between the centroid of the positive charge and substituent X. Solvation(hydration) of deprotonated as well as protonated forms of neutral molecule also causes the similar effect.[21,29,34]

The typical (average) a_1 value - 8 corresponds to the specific inductive effect (the change of $\sum\sigma^*$ values by one unit),8 kcal/mol, however in some real systems the absolute contribution of this factor can reach much higher values (up to 60-70 kcal/mol). At the same time it seems that the less the charge delocalization (alcohols, amines) the higher the absolute value of a_1. In the opposite, the systems with the extensive delocalization of the charge (carbonyl compounds, nitriles, anions of carbon-acids,etc.) are characterized by the lowest values of $/a_1/$.

The assumption of the equality of the absolute contributions of inductive and polarizability effects in the following series of protonation and deprotonization equilibria of alcohols XOH

$$XOH_2^+ + MeOH \longrightarrow XOH + MeOH_2^+ \qquad (9)$$

and

$$XO^- + MeOH \longrightarrow XOH + MeO^- \qquad (10)$$

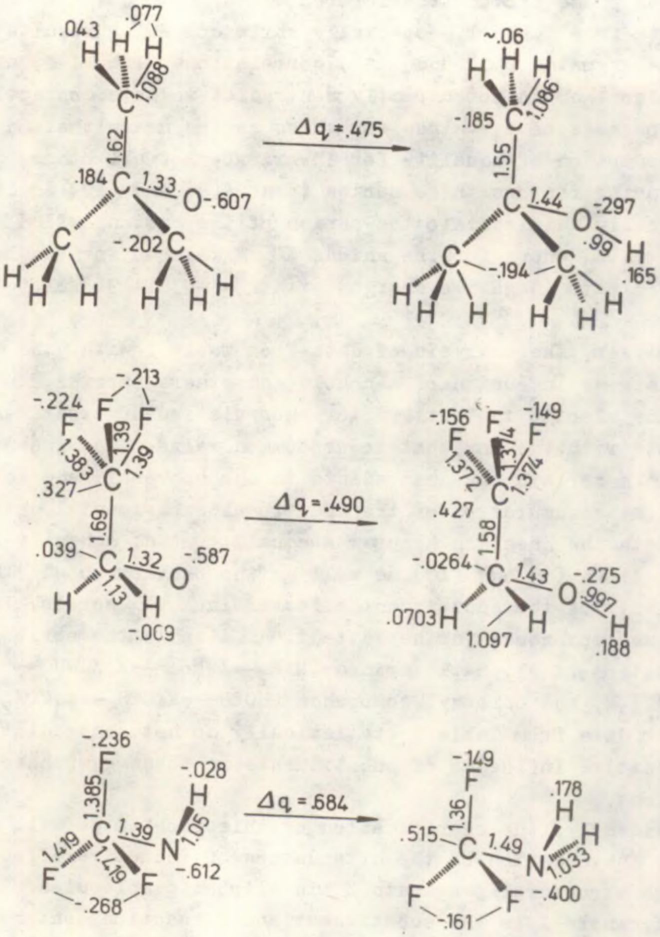

Fig. 4. STO-3G structure and Mulliken charge distribution[16,24] for some neutral molecules and anionic bases.

serves as a basis for the alternative approach[5] suggested for the separation of these types of substituent effects in some gas phase proton transfer reactions.

Data from Table 1, especially while comparing results of two-parameter (σ^* and ΔR) correlations (1 b, 1 f, and 4 b, also 4 c) do not directly contradict to this concept. The closeness of a_1 values for these series means that on the assumption of equality (or invariance) of all other influencing factors these series (Eqns. (9) and (10)) could be formally unified into the series of the protonization of ethers X_1OX_2 where for the anions XO^- X_2 stands for the lone electron pair (negative charge) with $\sigma^*_2 = -(381-196)/11.5 = -16$.

However, the analysis of data from Table 1 with the simultaneous inclusion of alcohols and ethers (series 2 and 3) leads also to the satisfactory correlation of experimental data with the somewhat <u>lower</u> common value of a_1 (ca-8). This in a certain way contradicts to the abovesaid and leads, until the accumulation of the additional experimental data, open both the question about the equality of a_1 and a_2 values in reactions (9) and (10) as well as the problem about the additivity of the substituent effects in X_1OX_2 series. The last question needs further attention. Also in the series of protonation of aliphatic amines ($HNH_2 \rightarrow X_1NH_2 \rightarrow X_1X_2NH \rightarrow$ $\rightarrow X_1X_2X_3N$) and carbonyl compounds ($HCOH \rightarrow X_1COH \rightarrow X_1COX_2$), however, data from Table 1 statistically do not contradict to the additive influence of substituents in these gas phase reactions.

Evidently, the clarification of this problem as well as, ,e.g., the question of the attenuation of inductive effect through structural fragments Z in aliphatic molecules $X(Z)_nY$, where X is the substituent and Y-reaction center ($n=0,1,2,3$, etc.) calls for additional accumulation of extensive and systematic new experimental data for several classes of compounds (e.g., X_1X_2NH, XOH, XCH_2OH, X_1OX_2,

$X_1CH_2OCH_2X_2$, XSH, XCH_2SH, X_1SX_2, etc.)*

According to Table 1 the <u>polarizability</u> term $a_2\sum\Delta R$ is always statistically significant for determining the gas phase basicity of neutral and anionic bases. For neutral bases $a_2 > 0$ and for anions (acidity of their conjugated acids) $a_2 < 0$ which manifests about the relative polarizational stabilization of the corresponding ionic forms (BH^+ and A^-) as compared with the neutral species B and AH. In other words, the increase of the polarizability of the substituent leads to the increase of the basicity of neutral bases (higher values of PA) and to the decrease of the basicity of anionic bases (lower values of PA because of the extra stabilization of the initial state A^-).

According to the rather simplified model[21-23] based on the point charge - induced dipole type interactions the energetics of this effect could be visualized by the equation

$$E_{pol} = -\alpha q^2/2Dr^4 \quad , \qquad (11)$$

where α is the polarizability (of the substituent)
q and D are as above (see Eqn. (5),
r is the distance between the reaction center (charge q) and polarizable matter

One can see that the energy of this interaction is independent of the sign of q. On the other hand, E_{pol} decreases much faster with the distance than the energy of charge-dipole interaction (compare Eqn.(5). At completely realistic values of $\alpha = 10Å^3$, $q = \pm 1$ and D=1 this effect can reach significant values (at $r=3Å$ $E_{pol}= 18.3$ kcal/mol; at $r=4Å$ $E_{pol}= 5.8$ kcal/mol). Typical values of a_2 from Table 1

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* There is a new evidence[16] showing on the basis of the gas phase acidity measurements (substituted bicyclo /2.2.2/ octane- and octenecarboxylic acids and 4-substituted cubane carboxylic acids) that in alicylic systems the inductive effect of electronegative substituents is attenuated to the reaction center through the space (field effect) but not via the C-C bonds (see also Ref.35).

(a_2 = 0.3, ΔR = 10) correspond to the energetic effect of 3 kcal/mol (i.e., the specific polarizability effect ΔR=1 is 0.3 kcal/mol). However, for some systems (XO^-, X_1COX_2, X_1COOX_2, X_1OX_2, $X_1X_2X_3N$) its contribution can already reach 5-10 kcal/mol.

Enhanced sensitivity of charge - induced dipole interactions on the separation (r^{-4}) between reaction center and polarizable substituent makes this type of substituent effects especially sensitive relative to any intra- (resonance, hyperconjugation) or intermolecular (solvation) channels of charge delocalization or transfer. It seems, that due to the theoretically predicted[16] noncoincidence of the distances of the centroids of the effective charge on the reaction center (with a common atom but of the opposite sign) from the dipole of substituent, one hardly has to to expect for the reaction of types (9) and (10) the equivalence of the corresponding values of a_1 and (especially) a_2 on the basis of Eqns.(5) and (11).

Concluding the discussion on the use of the molecular refractivity as a measure of the substituent polarity one has to mention that this quantity (ΔR) is not able to account for the (possible) influence of the difference of the polarizabilities of isomeric radicals (e.g., $CH_3(CH_2)_3$ and $(CH_3)_3C$, etc.) on the reactivity of the correspon compounds.

Either due to not enough represe nonalkyl elementary substituents (NO_2, NH_2, N $_2$, OH, OMe, etc.) immediately attached to the reaction center capable to the resonance interaction, or because of the inability of the σ_R^o constants to be an adequate measure of this interaction, the sensitivity a_3 of the given reaction series towards the resonance interactions is as a rule, statistically less reliable than the corresponding values of a_1 and a_2. In some cases even its sign depends on the set of substituents (amines,ether, carbonyl compounds). However, in most cases $a_3 < 0$ which formally refers to the relative resonance stabilization of the initial state (XO^-,

X_3N, $XCOO^-$, $X_1X_2X_3C^-$) by the acceptor groups or to the preferred stabilization of the protonated form (for X_1OOX_2+ + X_1COOX_2, XCN) by the donor substituents. Positive values of a_3 for X_1OH and secondary amines X_1X_2NH are probably artefacts caused by the extremely narrow and statistically nonrepresentative set of σ_R^0 constants for the substituents involved.[x]

According to Table I the absolute contribution of the resonance contribution can change in the very wide range. So, it is almost negligible for the amines ($X_1X_2X_3N$), less than 2-3 kcal/mol for series 4, 15 (XO^-, X_1COX_2,[xx] X_1COOX_2) and up to to one electronvolt for the reaction of dissociation of C-H acids.

As in the case of ionization potentials[6] the presence of the hydrogen atom immediately attached to the reaction center might result in a very significant contribution into the gross substituent effect on the basicities of neutral and anionic bases. For neutrals $a_4 \leq 0$ which. refers to the decrease of the basicity of the compound upon the introduction of the hydrogen atom into the immediate vicinity of the basicity center. According to Table 1 the absolute value of this effect reaches in some cases more than 10 kcal/mol being the smallest for the tertiary amines and carbonyl compounds.

For the anions, however, $a_4 > 0$ which formally shows that in this case hydrogen atom of this type causes the increase of the basicity of the anion.

The lowest specific effect (4.3 kcal/mol) belongs to carboxylate ions, the highest - to alcoholate ions. In practice, however, the effect of hydrogen atom immediately

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[x] This situation, similar to the abovesaid in the case of inductive and polarizability effects, urgently calls for a new, systematic and purposeful experimental studies in order to significantly expand the number and nature of the substituents (both + R as well as -R substituents) as well as the reaction series.

[xx] For the series of aldehydes and ketones this effect seems to be (almost) negligible.

attached to the reaction center is largest for carbanions $X_1X_2X_3C^-$ where the gross effect of introducing 3 hydrogen atoms amounts up to 36 kcal/mol.

Possibly the introduction of the hydrogen atom into the immediate vicinity of the reaction or ionization center (for the proton transfer reactions (PA) as well as for the process of extracting electron[6] from the highest occupied moleculal orbital (IP)) serves as a certain trigger "turning off" with its presence the resonance and hyperconjugative stabilization between nonhydrogen substituent and reaction or ionization center in protonated forms of neutral (BH^+) and anionic bases (A^-) and in cation-radical $B^{+\cdot}$.

It is not surprising, that for both of these processes (see a_i values for the correlation of IP-s from Ref. 6) holds a closely opposite trend of changing the a_4n_1 and $a_5\Delta n_2$ values.

According to Table 1 $a_5 > 0$ for anions and $a_5 < 0$ for neutral bases. Keeping in mind that $\Delta n_2 < 0$, one can see that the effect of α-hydrogen atoms leads to the increase of the basicity of neutrals and to the decrease of the basicity of the anionic base relative to the corresponding methylsubstituted derivatives (compare also with the discussion of the effect of the immediately attached hydrogen).

The specific effect of α-hydrogen atoms is less than that of the hydrogen atom immediately connected to the reaction center (at $a_5=1.0$ (XO^-) and $\Delta n_2=-1$ $a_5\Delta n_2= -1$ kcal/mol). However, its contribution into the gross substituent effect on PA values in some cases could be very substantial. So, for the carbanions $X_1X_2X_3C^-$ ($a_5= 1.8$ and $\Delta n_{2(max)}= -9$) this effect can easily exceed 16 kcal/mol.

Resonance and hyperconjugative stabilization of some protonated neutral bases BH^+ and anions A^- could be visualized by results of the ab initio quantum chemical calculations[16,24,27-32,34,36,37] of the energetics, geometry and charge distribution (systems of programs Gaussian-82[26] and Gaussian 70[25]).

In the liquid phase all solutes (ions,neutral molecules, free radicals) are influenced by the nonspecific and specific solvent-solute interactions.[21,40-46]

Quantum chemical nonempirical model calculations of the influence of the specific [16,29] as well as nonspecific[47] solvation the ions and neutral molecules of various classes show that in both cases the transfer of nonsolvated gaseous particles into the solution is accompanied by the rather significant changes in their structure (variation of bond lengths, valence and conformational angles, and effective radius) as well as in the charge distribution. Such changes are most noticeable in the case of ionic molecules. In particular, Fig. 5 which is based on the results of ab initio calculations from Refs. 16 and 24 visualizes the effect of the stepwise addition of water molecules to some anions (alkoxide-ions, perchlorate-ion, etc.) and their conjugated acids AH in the gas phase. One can see that the hydration of the anion is accompanied by the significant charge transfer from the oxygen atom of the anion as well as from the whole base to the water molecules. In the same time the intensity of charge transfer from the ion to the water molecule depends on the nature of the ion as well as on the number of the solvent molecules in the hydration shell the latter. For example, calculations show that the Mulliken charge on the oxygen atom of the $CH_3CH_2O^-$ anion (-0.625) decreases on addition of the 1st H_2O molecule to -0.519 charges of the electron (see Fig.5., 1 and 2), whereas the hydration by three molecules of water leads to further decrease of this quantity to -0.468 units. In the case of bases with relatively extensive internal charge delocalization and lower basicity (CH_3COO^-,CF_3O^-, $(CF_3)_3CHO^-$, ClO_4^-, Me_3NO, etc.) the decrease of the formal charge on the basicity center is less significant. From the other hand, however, the "hydration" of the superbase O_2^{2-} is accompanied with the full charge transfer from the latter

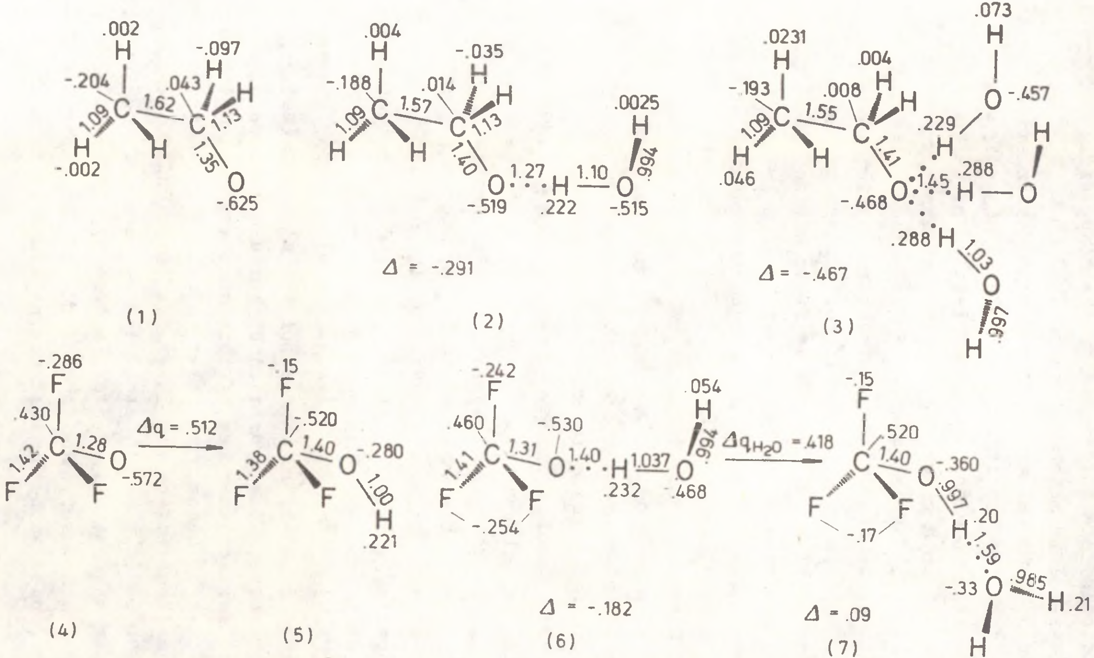

Fig. 5. The calculated[16,24] (STO-3G basis) bond lengths and Mulliken charges for some molecules, ions, and solvation complexes.

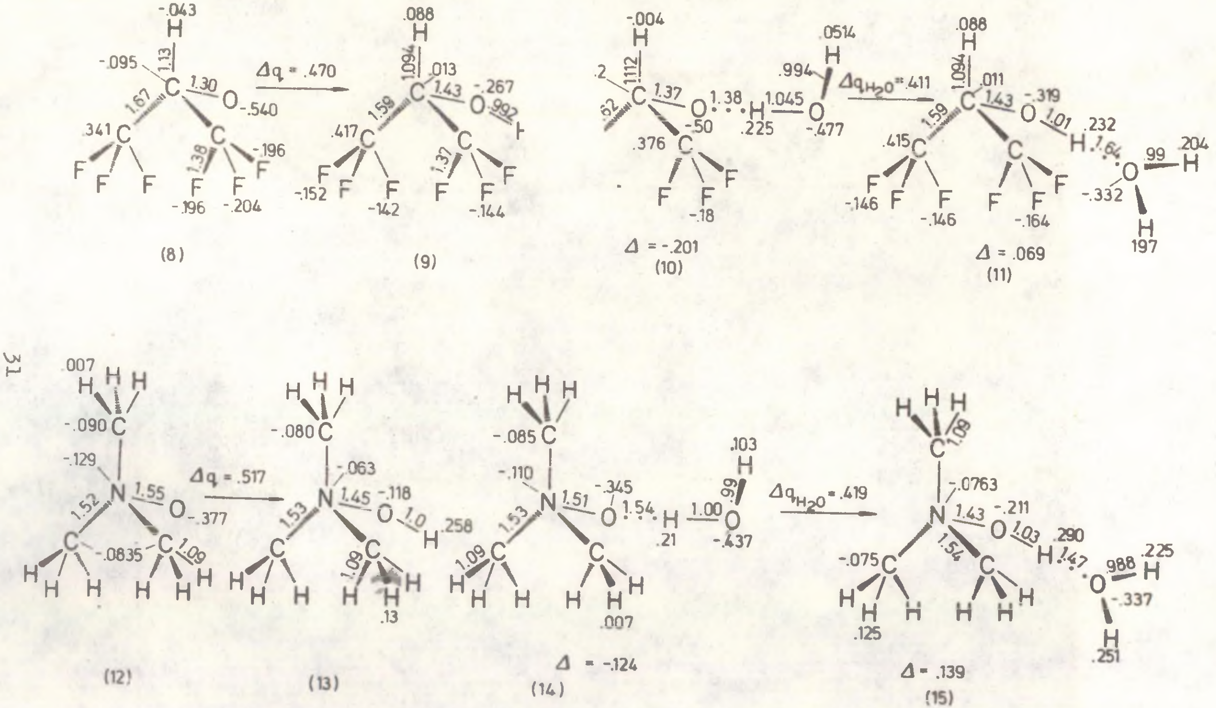

Fig. 5.(continued from p.30)

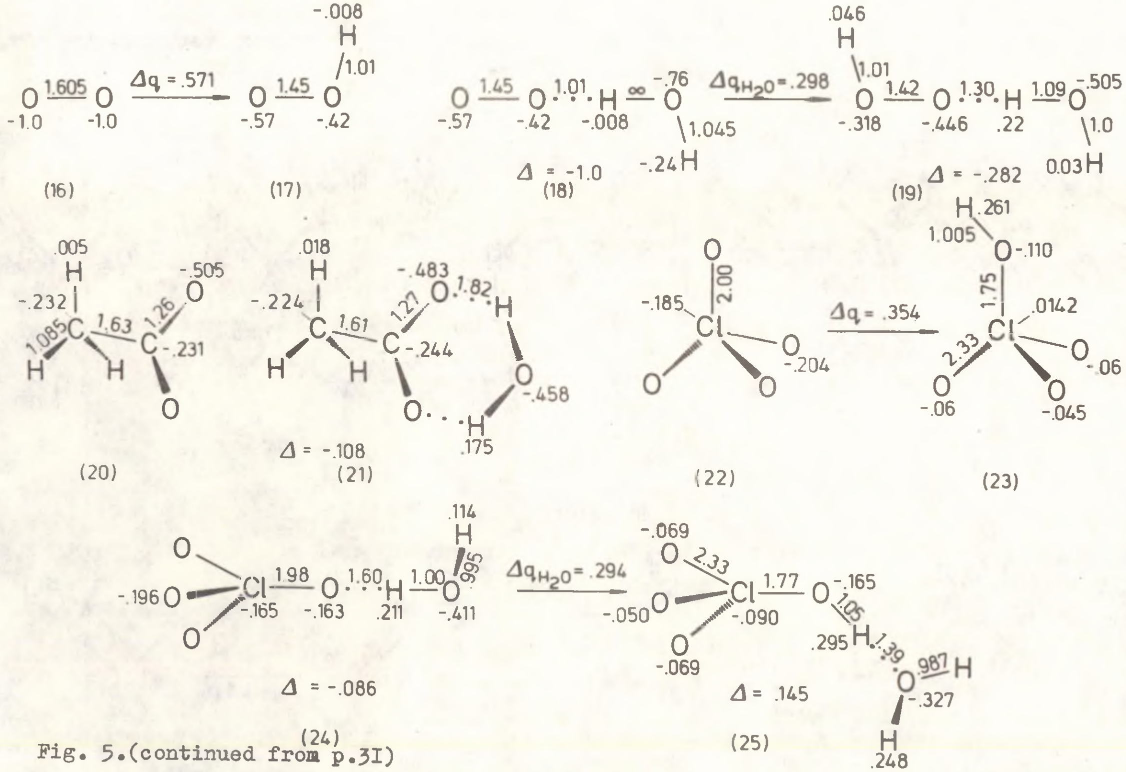

Fig. 5.(continued from p.3I)

to the water molecule and leads to the complete proton transfer from H_2O to the base (i.e. $O_2^{2-} + H_2O \longrightarrow HOO^- + HO^-$). In its turn, the above-said transfer of the negative charge from the anion to water molecules results in the corresponding increase of it on the oxygen atom of H_2O. The "leakage" of the negative charge from the anions or anion-like (Me_3NO) bases to the molecules of the solvent takes place not only from the basicity center (e.g., oxygen atom) itself but also from the substituent. Therefore, the gross base-to-solvent charge transfer effect is even more significant[16] ranging from -0.15 to -0.35 units of the electron charge (see Fig.5, the Δ-values). For alkylsubstituted alkoxide anions and FO^- $-0.25 \geqslant \Delta \geqslant -0.30$, whereas for perfluorinated derivatives ($(CF_3)_3CO^-$, $(CF_3)_2CHO^-$, CF_3O^-) $-0.15 \geqslant \Delta \geqslant -0.20$ for ClO_4^- $\Delta = -0.09$, CH_3COO^- $\Delta = -0.108$ and, from the other hand, for O_2^{2-} $\Delta = -0.53$.

Naturally, from the "viewpoint" of the solvent the effect of the transfer of the <u>negative</u> charge from the anions to the molecules of solvent is equivalent to the transfer of the <u>positive</u> charge from the solvent (e.g., from the molecules of H_2O) to the solute and to the partial protonization of the latter (in the case of hyrogen-bond-donor-solvents).

The solute-solvent charge transfer effect of comparable intensity was recently predicted[29] also for the case of hydration of positively charged ions (XNH_3^+).

Calling for the <u>intermolecular</u> charge transfer between the solute and solvent molecules the solvent-solute interactions effectively compete (up to the turning off) with the mechanisms of <u>intramolecular</u> (via interactions of different nature-resonance, hyperconjugation, etc.) stabilization or destabilization of the solute.

Fig. 5 shows that the intermolecular charge transfer between solute and solvent and the partial protonization of the solute lead also to rather significant change in the geometry of ions.

Indeed, frequently, the addition of the first water molecule to the XO^- anion (see Fig.5) increases the C-O bond distance from 1.30 Å (see also the diagram (Fig.4) in this issue) to 1.35-1.41 Å which is rather close to the calculated (and experimental) C-O bond length in the fully protonated anion, i.e. in the alcohol molecule XOH. The consecutive attachment of additional water molecules leads already to much less significant changes in this bond distance.

The qualitatively different situation[16] takes place for the HO^- anion and for the other (relatively small) anions (FO^-, HOO^-, H_2NO^-, O_2^{2-}, etc.) which contain the electron donor group in the immediate vicinity of the protonation center and are unable for the intramolecular stabilization via interaction of the (donor) reaction center with the substituent (see the previous paper in this issue). Despite the rather significant redistribution of the charges between the solute and solvent molecules. The geometry of these anions is relatively unaffected by the addition of water molecules (some <u>decrease</u> of the $X-O^-$ bond distance takes place for X=F,HO,H_2N,O^- and H)

As it was already mentioned the gradual ("sufficient") increase of the basicity of the solute XO^- (e.g., for $X=O^-$) is expected to lead to the complete proton transfer from the water molecules to the anion (see p.32)

As it follows from the aforesaid, due to the solute-solvent charge transfer and the accompanying changes in the geometry and in the charge distribution of the solute the effective distance between the centroid of the negative (for the system XNH_3^+[29] - positive) charge and the dipole of the substituent changes (as a rule, increases), whereas the net Mulliken charge (i.e. its absolute value) on the protonization center, in its turn, decreases.

Due to these circumstances the simple model considerations suggest that the specific solvation of ions (e.g.,XO^-) and the transfer of the latter from the gas phase into solution should lead to the significant reduction of the energies

(Eqn.(5) and(11)) of intramolecular charge-dipole and charge-induced dipole interactions. In the same time, due to the r^{-4} dependence of the energy of the latter interaction on the distanoe, the solvent effects accompanying the transfer from the gas phase into solution should be especially noticeable for this mechanism of intramolecular interactions.

Fig.5 supports the supposition[29] that the geometry of the neutral solutes practically does not depend on the presence of the solvent molecules. However, the significant redistribution of the formal atomic charges between the solute and solvent molecules (e.g.,water) takes place even in this case.

The direction of the charge transfer between the neutral protic acids AH (e.g.,XOH,CH_3COOH,$HOClO_3$,etc.) or the cationic acids (e.g. XNH_3^{+}[29],Me_3NOH^{+}[16]) and solvent (H_2O) molecules is reversed as compared with the situation in the case of the hydration of anionic bases. Due to the charge redistribution the gross effect of the transfer of the positive charge (0.05-0.15 units of the electron charge from solutes of type XOH[16] and about 0.35 units for the system XNH_3^{+}[16]) from the electrophilic solute to the molecules of water takes place .

A certain correlation holds between the proton donor capacity of the electrophile and the amount of the formal charge transferred to the molecules of the solvent. So, from the neutral proton donors the largest Δ value (+0.15) belongs to perchloric acid, for the alcohols $0.05 \leq \Delta \leq 0.09$, whereas $\Delta = 0.14$ for the Me_3NOH^+. Due to such a redistribution the positive Mulliken charge on the hydrogen atom of the OH group of compounds XOH increases simultaneously with the increase of the negative charge on the oxygen atom of the same group. As a result, the specific hydration of this kind increases the polarity of the solutes XOH whereas the calculated dipole moments of the complexes $XOH...OH_2$ reach rather significant values which exceed the additive values calculated on the basis of the dipole moments of the component.

It is noticeable that similar to the gas phase results the relative independence within the given reaction series of the difference of the gross Mulliken charges (Δq) on the reaction center in the initial (deprotonated) and final (protonated) states (e.g., for the transfer $XO^- + H^+$ XOH $\Delta q = q_{OH} - q_{O^-}$) holds also for the corresponding monosolvated species $XO^-...HOH$ and $XOH...:OH_2$ (the quantity Δq_{H_2O} in Fig.1) over the wide range of the variation of the substituent X($\Delta q^{*}_{H_2O} = 0.38 \pm 0.07$; X= F, CF_3CH_2, Et, ClO_3, Me_3N, t-Bu, i-Pr, $(CF_3)_2CH$, CF_3). The quantity Δq_{H_2O} itself is, however, by 1.37 times smaller than the corresponding gas phase quantity Δq. The comparable decrease of the sensitivity of the given reaction series towards the substituent effects with the introduction of the 1st water molecule into the solvation shell of XOH and XO^- follows also from the comparison (Fig.6) of the calculated[16,24] (STO-3G basis set) relative proton affinities of the nonsolvated $\Delta PA(XO^-)$ and monohydrated $\Delta PA(XO^-...HOH)$ XO^- ions:

$$XOH + MeO^- \xrightarrow{\Delta PA(XO^-)} XO^- + MeOH \qquad (12)$$

$$XOH\cdots{:}OH_2 + MeO^-\cdots HOH \xrightarrow{\Delta PA(XO^-\cdots HOH)} XO^-\cdots HOH + MeOH\cdots{:}OH_2 \qquad (13)$$

It is interesting to notify that the perchlorate ion and trimethylamine oxide follow the same pattern with the alcoholat-anions.

The consecutive addition[16] of two more water molecules to XOH and XO^- leads to the further reduction of the Δq values as well as to the additional decrease (by 15-20 per cent) of the sensitivity of this reaction series towards

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* Δq_{H_2O} is calculated as a difference between the gross Mulliken charge on the solvated OH-group and the charge on the solvated O^- atom. The charges on the H_2O molecule are not taken into account for the calculation of this quantity.

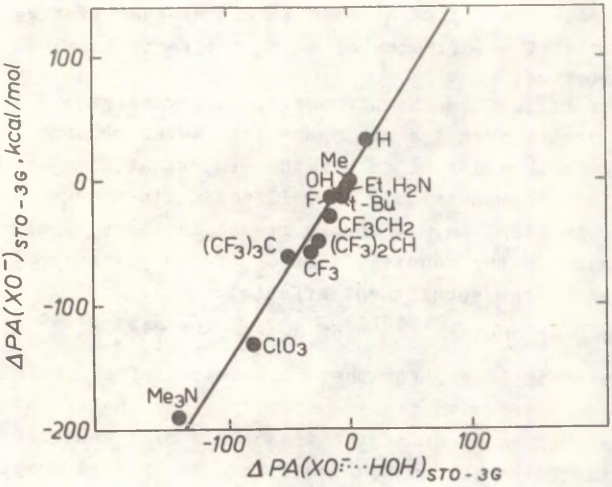

Fig. 6. Comparison of calçulated[16,24] (STO-3G basis) relative proton affinities of nonsolvated and monosolvated XO^- ions in the gas phase (the slope is 1.35±0.08, the intercept equals -1.6±2.2).

the substituent effects. However, it is evident that in the general case the adequate quantitative description of the change of the a_i values while substituting the gas phase for the solution is unachievable only in terms of specific solvent-solute interaction mechanisms. On the other hand, we are aware of at least about one case[29] (protonation of substitueted amines) where the simplified (STO-3G basis) specific solvation approach leads to almost quantitative description of the influence of solvent effects on the organic reactivity

As it follows from the aforesaid, the transfer of the reacting species from the gas phase into water or some other solvent should lead to a rather important changes in the structure (composition), as well as in its charge distribution. In its turn, it should result in the very significant changes in the sensitivities a_i of the given reaction series towards the substituent effects.

The largest changes[4,40,48] of a_1 for the same proton transfer process (e.g., for the dissociation of alcohols XOH) are connected with the transfer from gas phase into water. For the reactions of the dissociation of neutral OH-acids the latter situation could be qualitatively explained of the electrophilic solvation of the anionic form (A^-...HOH) over the nucleophilic solvation of the electroneutral acid (AH...OH_2).

Naturally, the redistribution of formal Mulliken charges and the changes of the effective dimensions of the reagents (vide supra) which accompany the formation of solvates should also result in the intensity of the nonspecific solvent-solute interactions (polarity and polarizability of the solvent).[40-42,44,47]

The intermediate nature of the a_1 values for DMSO solvent[48] could be explained by the absence (on the background of the nonspecific solvent-solute interactions) of the electrophilic (hydrogen bond assisted) solvation[+] in the anionic form (XO^-,$XCOO^-$, etc.) of the neutral acid and by the (probable) domination of the stabilizing nucleophilic solvation in the neutral acids, e.g. by formation of complexes $XCOOH...OSMe_2$, $XOH...OSMe_2$, etc.

It is suggested that nitromethane[40] and acetonitrile exercise on these solutes even weaker specific solvent-solute interactions than DMSO. This way or another, in all those three cases the rather low ratio of a_1 values for the dissociation of XCOOH in the gas phase and DMSO,$MeNO_2$, and MeCN calls for attention.

As one can expect on the basis of Eqn.(11) and on the results of the above-mentioned model calculations[16,29] the a_2 values should change significantly more than the sensitivity towards the polar (inductive) effects.

Simple calculations (the identity of r and D values is assumed in both Eqns.(5) and (11)) on the basis of Eqns.(5) and (11) of the ratios of a_1 and a_2 values predict that for the increase of the r value due to the hydration from 2 to 3Å should result in the decrease of the a_1 value by 2.3 times and of the a_2 value by 5.1 times. Equally realistic change of r from 3Å to 4Å should decrease these values by 1.8 and 3.2 times.

According to the aforesaid, the a_3,a_4, and a_5 values are also connected with the intramolecular stabilizing interactions, the intensity of which heavily depends (up to the turning off) on the presence and nature of the solvent molecules.

[+] Nonempirical quantum chemical calculations[16] on the STO-3G^x basis (with the inclusion of the diffuse (d) orbitals), however, suggest that DMSO is also potentially able for the electrophilic solvent-solute stabilization of the anions HO^-,F^-,FO^- (and probably, also, alcoholate and carboxylate anions) by the positive end of the dipole of the SO group. The energy of such an interaction (up to 20 kcal/mol) is of the same order (or even higher) than the energy of the interaction of DMSO with electrophiles XOH or XCOOH.

It seems evident that for the systematic comparison of the role of the substituent effects in solution and in the gas phase an extensive and carefully designed accumulation of a new experimental data for the proton transfer reactions as well as the analysis of the existing data on the types of chemical reactions should be undertaken.

Concluding the brief analysis of some consequences of using the present empirical multiparameter approach to the correlation of ionization potentials and proton affinities of organic compounds of various classes with their structure one has to underline the necessity of the further check of Eqn. (3) and its special variants. Along with the further inclusion of the new experimental data for a wider range of compounds on ionization potentials, proton affinities and affinities towards the other electrophilicity centers as well as quantities measured in solution[34] one naturally has to consider the modification of the approach itself. So, evidently, instead of the single σ_R^o scale of resonance constants two separate scales (σ_R^+ and σ_R^-) should be used.

The problems of the use of a single scale (σ^*, σ_I, etc.) or two different (separately for the alkyl and electronegative substituents) scales of inductive constants also need further reconsideration. Further study of role of cross terms[x] should be undertaken . Most serious attention should be given to the idea[38] of inclusion into the correlation equations of the special electrostatic correction term even in the absence in the molecule of ionic substituents (compare with Ref. 39 and 7)[xx].

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[x] The preliminary calculations by the present authors show that the inclusion of some cross terms (n_1^2, $n_1\sigma^*$, etc.) improves the correlations for some reaction series.

[xx] For example, the electrostatic correction calculated for the gross PA values of benzoate anions using the group dipole moments of substituents reduces ca by 30 per cent the ρ^o value for this reaction series.

Keeping in mind for the future these and other goals it still seems, however, that the present approach which in most cases gives at least satisfactory adequate quantitative description of the dependence of PA and IP values of a large quantity of organic compounds on their structure could serve as a certain starting point for the further development of the formalism based on the LFER principle.

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PHOTOELECTRON SPECTRA OF MOLECULES
I. ALCOHOLS

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HeI photoelectron spectra (PES) of 14 aliphatic alcohols are measured. In some cases the 1st adiabatic ionization potentials (IP) were also determined by the photoionization (PI) technique. Mostly the halogen derivatives were considered. Semiempirical and ab initio quantum chemical calculations were used for the interpretation of the spectra.

Photoelectron spectroscopy is one of the major tools for the study of the electronic structure of molecules of different classes[1]. Amongst the various problems which could be solved by means of PES is also the study of the substituent effects on the molecular structure. In several papers using either the retarding field analyser[2,3] or the high resolution[4-6] instruments the PES spectra of several alkyl-substituted alcohols were measured and thoroughly analyzed. The spectra of some halogen substituted derivatives[8-10] (including FOH[11] and ClOH[12]) were also reported. However, the study of molecules with electronegative substituents has still not been enough extensive and systematic mostly because of the problems related to the interpretation of complex molecules. In those systems the unambigous identification of the ionization center is frequently complicated due to the competition between different ionization centers and because of the interdependence of the properties of structural elements .

In relatively large molecules of the low symmetry the strong overlapping of PES bands and charge delocalization initiated broadening of the latter also take place.

As a consequence of that the PES themselves usually offer no explicit and easily accessible information and it is necessary to use various indirect methods for their interpretation.

In order to clarify the various aspects of the substituent effects on the behavior of ionization centers in the gas phase the extensive and systematic study of the influence of carefully chosen representative (both alkyl and electronegative) sets of substituents on the PES of different classes of compounds needs to be undertaken. The present series of papers was designed for the partial fulfillment of this goal[13].

In this paper the HeI photoelectron spectra of some alcohols with electronegative substituents were recorded. The semiempirical (CNDO/2) and (in some cases) ab initio calculations (STO-3G basis set) were performed in order to interprete the experimental PES data.

Experimental.

The photoelectron spectrometer[14], designed and built at this university was used. The glowing of the positive column of the helium discharge in the quartz capillary was used as a photon source.

The resonance HeI line with the maximum energy of 21.22 eV(58.4 nm)is being excited. The retarding field electrostatic analyzer consists of two cilindrical electrodes which are coaxial relative to the photon beam. The screen from μ-metal shields the analyzer from the external magnetic fields. The present design of the analyzer quarantees the retarding of the electrons mainly in direction of the radial component of their velocity.

The sample vapor pressure in the analyzer is kept lower than 0.1 Pa. The resolution of the analyzer by energy $\Delta E/E \approx$

≈1.2 per cent, i.e. the limiting resolution for the electrons of the energy of 5 eV is about 0.06 eV. Such a resolution is sufficient for measurements of spectra of relatively complex molecules which are characterized by the significant overlapping of the closely situated bands and, as a rule, by the lack of the vibrational structure.

Argon doublet (15.759 and 15.937 eV) was used as an internal reference. The PES reported in the present work are the averaged representations of the results of several separate measurements. The vertical IP-s are determined as the locations of the maximums of the corresponding peaks. The errors of this procedure never exceeded 0.05-0.1 eV.

On the other hand, ionization potentials in PES should be considered strictly adiabatic only in the case when the analysis of the vibrational structure of the given band identifies this ionization process as a 0 - 0 transfer.

However, our experience shows that the IP-s determined at the beginning of the slope of the spectral band, which is shifted on the energetic scale by the half width of the argon line, coincide with the (adiabatic) values determined by the photoionization technique within ±0.03 eV. The vacuum monochromator (with the resolution of ≤ 0.03 nm) Seya-Namioka was used for the determination of IP by this method[14]. The 1st adiabatic ionization potential was determined as a breaking point in the region of the ionization threshold on the dependence of the logarithm of the photoionization efficiency on the energy of photons.

The relative error of this method usually does not exceed ±0.01 eV.

Most of the reagents used throughout of the present series of paper are commercially available. The purity was controlled by g.l.c.

H_2NOH was liberated from its triphosphate salt by heating immediately before measurements.

Before recording the spectra all compounds were carefully degassed by the repeated freeze-pump-thaw-freeze-pump cycles.

Photoelectron spectra recorded in this work are shown on Fig. 1. The values of adiabatic and vertical ionization potentials determined either by PES of by PI techniques are given in Table 1. Some literature PES data for a few other aliphatic alcohols is also reported for comparison in the same Table.

Semiempirical quantum chemical CNDO/2 calculations are performed using the original parametrization[15] of Pople and Beveridge. Bond lengths, suggested in Ref.16 were used: OH=1.034, CO=1.367, CO = 1.457, CH=1.119, CF = 1.343, CCl= =1.67, C≡N=1.191, ≡C–C=1.425, C≡C=1.205, ≡C – H = 1.092. All sp^3 valence angles were assumed tetrahedral. The problems of the choice of the "proper" conformation are discussed later in the next section of the present report.

For $(CF_3)_2CHOH$ and $(CF_3)_3COH$ molecules the ab initio calculations[17] were made using the Gaussian 82 system of programs[18] on the STO-3G level with the full geometry optimization using the method of analytical gradients.

Discussion

In some of our papers[13,21] the influence of electronegative and alkyl substituents on the reaction or ionization center was considered.

A certain empirical relationships between different energetic parameters (proton affinity, ionization potentials of valence and core electron shells, etc.) as well as the dependences of the latter on the structure were found to hold. These regularities could be used for the prediction of the otherwise unaccessible parameters or for the identification of the ionization reaction center on the basis of the known data set. Both problems are equally important for the study of the nature of the processes investigated.

So, in Ref. 13b a rather general linearity between the proton affinities PA and ionization potentials of bases of the different classes was established. For the aliphatic alcohols this kind of relationship is shown on Fig. 2.

Table 1

Ionization Potentials of Some Alcohols Determined From PES and Calculated MO-Energies ($-\varepsilon$). All Figures in eV Units.

1. EtOH

	IP_v^a	4-31G^a		STO-3G^b		CNDO/2^c	
		$-\varepsilon$	MO	$-\varepsilon$	MO	$-\varepsilon$	MO
1.	10.64	11.89	3a'' n_O	9.57	3a''	14.35	3a'' n_O
2.	12.18	13.15	10a' $\sigma_{CC}, \bar{n}_o$	10.78	10a'	15.50	7a' σ_{CC}, σ_{OH}
3.	13.21	14.22	2a'' π_{CH_3}, n_O	12.85	9a'	16.98	6a' σ_{CH}, σ_{CO}
4.	13.86	14.37	9a' π_{CH_3}, σ_{CO}	13.20	2a''	18.19	2a'' n_O, π_{CH_3}
5.	(14.5)	15.32	8a' σ_{CO}, σ_{CC}	13.89	8a'	20.65	5a' π_{CH_3}, n_O
6.	15.85	17.64	1a'' π_{CH_3} n_O	16.37	1a''	24.11	4a' σ_{CH}, σ_{OH}
7.	17.35	18.72	7a' σ_{OH}	16.52	7a'	25.67	1a'' π_{CH_2}
8.	20.7			21.63	6a'	28.07	
9.	24.2			26.31	5a'	36.94	

a - From Ref. 10; b - From Ref. 19.; c - This work, E_{tot}= -37.2772 a.u.

Table 2 continued

2. FCH_2CH_2OH

	IP_v^a	CNDO/2[b]		
		$-\varepsilon$	MO	
1.	11.05	14.65	$4a''$	n_O
2.	12.65	15.36	$9a'$	σ_{CC}, σ_{OH}
3.	13.09	17.19	$3a''$	n_O, π_{CH_3}
4.	14.00	17.46	$8a'$	σ_{CO}
5.	15.00	19.39	$7a'$	$n_F, \bar{n}_O$
6.	16.00	21.72	$2a''$	n_F, π_{CH_2}
7.	17.35	23.41	$6a'$	σ_{CF}, σ_{OH}

3. $ClCH_2CH_2OH$

	IP_v^a	4-31G[b]		CNDO/2[c]		
		$-\varepsilon$		$-\varepsilon$	MO	
1.	10.88	11.95	n_{Cl}	13.81	$9a'$	n_{Cl}
2.	11.46	12.11	$_{Cl}$	13.85	$4a''$	n_{Cl}
3.	11.69	12.68	n_O	15.01	$3a''$	n_O, n_{Cl}
4.	12.67	13.51	$\bar{n}_O$	15.87	$8a'$	σ_{CCl}
5.	13.91	14.58	σ_{CCl}	16.50	$7a'$	σ_{CC}, σ_{OH}
6.	14.67	16.30	π_{CH_3}	19.41	$2a''$	n_O, π_{CH_3}
7.	15.78	16.83	π_{CO}	21.44	$6a'$	σ_{CO}, σ_{CC}
8.	16.48	18.17	π_{CH_2}	22.49	$5a'$	σ_{OH}
9.	17.95	19.17	σ_{OH}	26.70	$1a''$	π_{CH_2}

---

a - From Ref. 9

b - This work: $E_{tot} = -64.2545$ a.u.

a - This work : $IP_a^{(1)} = 10.66$; see also Ref.9,10.

b - From Ref. 10

c - This work: $E_{tot} = -52.6964$ a.u.

Table 1 continued

4. CF_3CH_2OH

	IP_v^a	CNDO/2[b] $-\varepsilon$	MO	
1.	11.70	15.60	12a′	σ_{CC}, σ_{OH}
2.	13.29	16.02	7a″	n_O
3.	15.35	18.87	11a′	σ_{CO}
4.	16.46	19.44	6a″	n_F
5.	17.01	19.70	10a′	n_F
6.	18.01	21.10	5a″	n_F
7.	20.56		9a′	σ_{OH}, n_F

---

a - This work. The 1st three IP_a-s are: 11.49, 12.75 and 14.62 eV. See also Ref. 8.

b - This work: E_{tot}= :-118.2479a.u.

5. $NCMe_2COH$

	IP_v^a	CNDO/2[b] $-\varepsilon$		
1.	11.32	13.75	6a″	n_O
2.	12.13	14.39	11a′	σ_{CC}, σ_{OH}
3.	12.85	15.54	10a′	π_{CN}, σ_{CO}
4.		16.86	5a″	π_{CN}
5.		17.39	9a′	σ_{OH}
6.	14.38	17.45	4a″	n_O
7.		19.04	8a′	n_N
8.	16.30	19.88	3a″	π_{CH_3}

a - This work: $IP_a^{(1)}$= 11.09 eV

b - This work: E_{tot}= -63.7318 a.u.

Table 1 continued

6. CCl_3CH_2OH

	IP_v^a	CNDO/2^b	
		$-\varepsilon$	MO
1.	11.34	13.58	7a'' n_{Cl}
2.		13.65	12a' n_{Cl}
3.	11.78	13.84	11a' n_{Cl}
4.		14.34	6a'' n_{Cl}
5.	12.21	14.91	5a'' n_{Cl}, n_O
6.	12.72	15.31	10a' n_{Cl}
7.	13.29	15.96	4a'' n_O, n_{Cl}
8.	14.91	17.54	9a' σ_{OH}
9.	15.46	18.53	8a' $\sigma_{OH}, \sigma_{CCl}$
10.	16.76	19.17	3a'' n_O, n_{Cl}
11.	18.31	21.55	7a' $\bar{n}_O$
12.		22.14	6a' σ_{CO}

a – This work: $IP_a^{(1)}$: 10.94 eV

b – This work : E_{tot}=-83.5930 a.u.

7. $CF_3C(OH)_2H$

	IP_v^a	CNDO/2^b	
		$-\varepsilon$	MO
1.	10.80	14.85	13a' n_O
2.	11.81	16.79	12a' $\sigma_{CH_2}, \bar{n}_O$
3.		17.40	9a'' n_O
4.	13.26	19.48	8a'' n_F
5.		19.65	11a' n_F
6.		20.34	10a' n_F
7.		20.71	7a'' σ_{OH}
8.		20.96	6a''
9.		21.24	5a''
10.	15.38	21.83	9a'
11.		22.24	4a''
12.	16.83	24.33	8a'

a – This work: $IP_a^{(1)}$= 10.49 eV

b – This work: E_{tot}= -136.6604 a.u.

Table 1 continued

8. $HC\equiv CCH_2OH$

	IP_v^a	CNDO/2^b	
		$-\varepsilon$	MO	
---	---	---	---	---
1.	10.59	14.15	$3a''$	n_O, π_{CC}
2.	10.92	15.46	$8a'$	π_{CC}, n_O
3.	11.53	16.50	$7a'$	σ_{OH}
4.	13.40	17.38	$2a''$	n_O, π_{CC}
5.		20.54	$6a'$	σ_{CO}
6.	16.26	22.83	$5a'$	σ_{CH}
7.	17.51	25.08	$1a''$	π_{CC}, π_{CH_2}
8.	18.58	25.74	$4a'$	π_{CH_2}, σ_{OH}
9.	22.5^d	31.85	$3a'$	
10.	23.9^d	37.84	$2a'$	

---

a - This work $IP_a^{(1)}$= 10.56 (PI method); $IP_a^{(1)}$= 10.51 (PES).

b - This work: E_{tot} = -42.5302 a.u.

c - For $HC\equiv CC(CH_3)_2OH$ $IP_a^{(1)}$= 10.21 (PI) d - From Ref. 19.

9. t - BuOH

	IP_v^a	CNDO/2^b		
		$-\varepsilon$	MO	
1.	10.25	13.52	$6a''$	n_O
2.	11.48	14.04	$10a'$	σ_{CC}, σ_{OH}
3.	12.39	15.86	$9a'$	σ_{CO}
4.	12.75	17.08	$5a''$	n_O
5.	13.20	17.18	$4a''$	π_{CH_3}
6.	13.64	17.61	$8a'$	σ_{CH}, σ_{OH}
7.	14.07	19.89	$3a''$	n_O, σ_{CH}
8.	14.60	20.20	$7a'$	σ_{OH}
9.	15.56	23.70	$2a''$	π_{CH_3}
10.	15.89	23.85	$6a'$	π_{CH_3}
11.	16.68	24.70	$5a'$	σ_{CO}, π_{CH_3}

a - From Ref. 6

b - This work: E_{tot} = = -54.6489 a.u.

Table 1 continued

10. i - PrOH

	IP_v^a	4-31G^a		CNDO/2^b	
		$-\varepsilon$		$-\varepsilon$	
1.	10.36	11.60	n_O	13.94	n_O
2.	11.75	12.48	σ_{CC}	14.58	σ_{CC}
3.	12.58	13.94	π_{CH_3}	16.19	σ_{CO}
4.	13.06	14.42	σ_{CO}	17.47	π_{CH_3}
5.	13.66	14.62	π_{CH_3}	18.43	n_O
6.	14.0	14.89	π_{CH_3}	19.04	π_{CH_3}
7.	15.11	16.49	$\tilde{\pi}_{CH_3}$	22.77	σ_{OH}
8.	15.88	16.99	σ_{CC}	23.35	π_{CH_3}
9.	17.22	19.08	σ_{OH}	24.84	$\tilde{\pi}_{CH_3}$

a - From Ref. 10
b - This work: E_{tot}= -45.9647 a.u.

11. CCl_3CMe_2OH

	IP_v^a	CNDO/2^b		
		$-\varepsilon$	MO	
1.	10.70	13.11	10a″	n_{Cl}, σ_{CCl}
2.		13.35	15a′	n_{Cl}, σ_{CC}
3.	11.30	13.50	14a′	n_{Cl}
4.		14.14	9a″	n_{Cl}
5.		14.60	8a″	n_{Cl}, n_O
6.		15.10	13a′	n_{Cl}
7.		15.32	7a″	n_{Cl}, n_O
8.	12.45	16.02	12a′	$\bar{n}_O$, n_{Cl}
9.	13.48	17.31	11a′	$\bar{n}_O$
10.		17.70	6a″	n_O
11.		18.09	5a″	π_{CH_3}
12.		18.48	10a′	σ_{OH}, σ_{CCl}
13.	15.93	20.77	4a″	π_{CH_3}
14.		21.19	9a′	σ_{OH}
15.	17.42	22.26	8a′	σ

a - This work; $IP_a^{(1)}$= 10.38 eV
b - This work: E_{tot} =-100.9795 a.u.

Table 1 continued

12. $(CF_3)_3COH$

	IP_v^a	STO-3G^b		CNDO/2^c		
		$-\varepsilon$	MO	$-\varepsilon$	MO	
1.	12.58	9.51	$24a''$	15.75	$19a''$	n_O
2.	13.85	10.22	$33a'$	16.18	$24a'$	σ_{CC}, σ_{OH}
3.		12.59	$23a''$	18.71	$23a'$	σ_{CO}
4.		12.66	$32a'$	20.31	$18a''$	n_O, n_F
5.	15.88	12.79	$22a''$	20.41	$17a''$	n_F
6.		13.29	$31a'$	20.45	$22a'$	n_F
7.		13.44	$21a''$	20.63	$16a''$	n_F
8.		13.47	$30a'$	20.73	$21a'$	n_F
9.		13.58	$20a''$	20.88	$20a'$	n_F
10.		13.59	$29a'$	21.26	$15a''$	n_O
11.		13.80	$19a''$	21.58	$19a'$	σ_{OH}
12.		13.89	$28a'$	21.94	$14a''$	n_F
13.		14.03	$18a''$	22.14	$13a''$	n_F
14.		14.11	$17a''$	22.15	$18a'$	n_F
15.		14.12	$27a'$	22.49	$12a''$	n_F
16.		14.39	$16a''$	22.52	$17a'$	n_F
17.	16.93	14.40	$26a'$	22.60	$11a''$	n_F
18.	17.51	15.06	$25a'$	22.77	$16a'$	σ_{OH}, n_F

a - This work; $IP_a^{(1)} = 12.25$ eV

b - This work: $E_{tot} = -1106.3806$ a.u.

c - This work: $E_{tot} = -297.5614$ a.u.

Table 1 continued

13. $(CF_3)_2CHOH$

	IP_v^a	STO-3G^b		CNDO/2^c		
		$-\varepsilon$	MO	$-\varepsilon$	MO	
1.	12.21	9.97	$18a''$	15.80	$14a''$	n_O
2.	13.8	11.51	$23a'$	16.11	$17a'$	σ_{CC} σ_{OH}
3.	15.6	12.98	$17a''$	18.91	$16a'$	σ_{CO}
4.		13.06	$16a''$	19.98	$13a''$	n_O
5.		13.08	$22a'$	20.02	$12a''$	n_F
6.		13.10	$21a'$	20.15	$15a'$	n_F
7.		13.15	$15a''$	20.42	$14a'$	σ_{OH}
8.		13.57	$14a''$	20.99	$11a''$	n_O
9.	15.81	13.63	$20a'$	21.56	$13a'$	n_O, n_F
10.		14.11	$19a'$	21.67	$10a''$	n_F
11.		14.24	$13a''$	21.96	$12a'$	n_F
12.		14.38	$18a'$	22.08	$9a''$	n_F
13.		14.39	$12a''$	22.24	$11a'$	n_F
14.	16.72	14.62	$17a'$	22.53	$8a''$	n_F
15.	17.41	15.46	$16a'$	23.23	$10a'$	n_F
16.		17.71	$11a''$	24.38	$9a'$	σ_{OH}
17.		17.87	$15a'$	25.21	$7a''$	n_F
18.		18.06	$10a''$	26.36	$6a''$	n_F
19.		18.46	$14a'$	27.31	$8a'$	n_F
20.		19.13	$9a''$	27.85	$5a''$	n_F
21.	21^d	19.37	$13a'$	28.21	$7a'$	n_F
22.	22.8^d	21.42	$12a'$	29.65	$6a'$	σ_{CH}

---

a - This work; $IP_a^{(1)} = 11.94$ eV; $IP_a^{(2)} = 13.23$. See also Ref. 8

b - This work: $E_{tot} = -775.4753$ a.u.

c - This work: $E_{tot} = -207.9051$ a.u. d - From Ref. 8.

Table 1 continued

14. $(CF_3)_3CCH_2OH$

	IP_v^a	CNDO/2[b]		
		$-\varepsilon$	MO	
1.	11.68	15.70	23a''	n_O
2.		16.23	23a'	σ_{CC}
3.	13.09	16.98	22a'	σ_{CC}, σ_{OH}
4.		17.52	22a''	n_O
5.	14.19	19.45	21a'	σ_{CO}
6.		20.25	21a''	n_F
7.		20.29	20a''	n_F
8.		20.35	20a'	n_F
9.		20.39	19a'	n_F
10.		20.49	18a'	n_F
11.		20.49	19a''	n_F
12.	15.71	21.35	17a'	σ_{CO}
13.		21.76	18a''	
14.		21.92	16a'	
15.		21.98	17a''	
16.		22.04	15a'	
17.		22.36	16a''	
18.	16.58	22.49	15a''	
19.		22.51	14a''	
20.		22.74	14a'	
21.		22.91	13a''	
22.	17.46	23.54	12a''	
23.		24.10	11a''	
24.		25.77	10a''	
25.	18.68	25.88	9a''	

a - This work; $IP_a^{(1)}$ = 11.48 eV

b - This work: E_{tot} = -306.2476 a.u.

15. n-PrOH Table 1 continued

	I_v[a]	4-31G[a]		CNDO/2[b]		
					MO	
1.	10.49	11.80	n_O	14.24	$4a''$	n_O
2.	11.70	12.41	σ_{CC}	14.39	$9a'$	σ_{CC}
3.	12.24	13.09	π_{CH_3}, π_{CH_2}	15.82	$3a''$	n_O, π_{CH_3}
4.	12.79	13.36	σ_{CO}	16.32	$8a'$	n_O
5.	13.4	14.44	π_{CH_3}, n_O	17.67	$7a'$	σ_{OH}
6.	14.52	15.73	σ_{CO}	20.81	$2a''$	n_O, π_{CH_3}
7.	15.3	15.91	π_{CH_3}, π_{CH_2}	22.33	$6a'$	σ_{CO}
8.	16.03	17.67	π_{CH_2}	23.18	$5a'$	π_{CH_2}, σ_{OH}
9.	17.23	19.14	σ_{OH}	27.88	$1a''$	π_{CH_2}

a - From Ref.10

b - This work; E_{tot}= -45.9634 a.u.

Table 1 continued

16. $ClCH_2CH_2(Br)CHOH$ 17. $C_3F_7CH_2OH$ 18. $H_2NCH_2CH_2OH$[a] 19. H_2NOH[a]

	IP_v^b		IP_v^c		IP_v^d		IP_v^e
1.	10.36	1.	11.62	1.	9.71	1.	10.56
2.	10.69	2.	13.23	2.	10.54	2.	11.69
3.	11.23	3.	13.87	3.	11.98	3.	12.04
4.	12.4	4.	15.8	4.	12.92	4.	12.63
5.	13.16			5.	14.07		
6.	16.66			6.	15.33		

a - The PES of this compound will be discussed in the following papers of this series

b - This work; $IP_a^{(1)}$= 10.31 eV

c - This work; $IP_a^{(1)}$= 11.20 eV

d - This work; $IP_a^{(1)}$= 8.96 eV. See also Refs. 10, 18

e - This work; $IP_a^{(1)}$= 10.00 eV; See also Ref. 10.

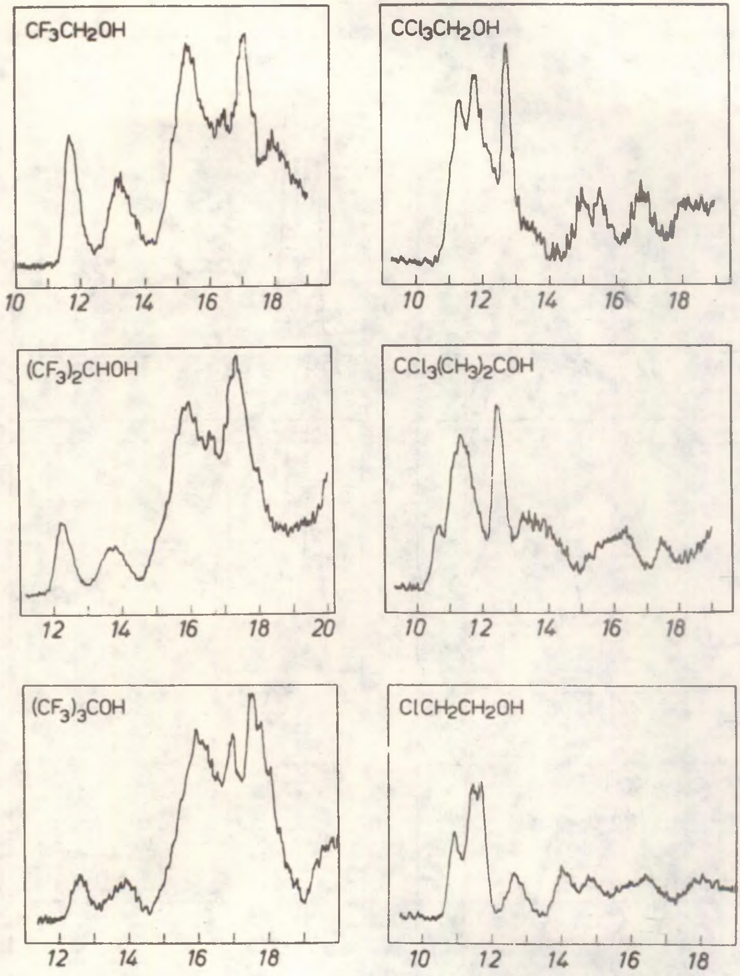

Fig.I. Photoelectron spectra of some alcohols

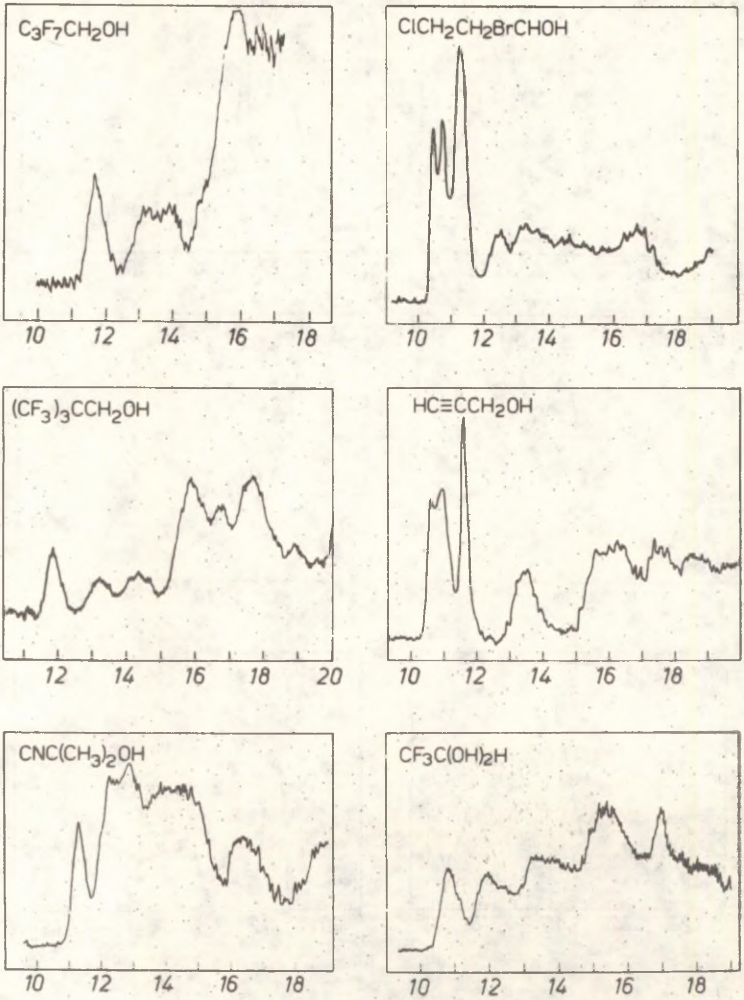

Fig.I.(continuation)

In the present case this could be expressed mathematically for the adiabatic and vertical ionization potentials as follows:

$$IP_a = -0.076(0.007)PA + 25.02(1.33) \qquad (1)$$

$$r = 0.972;\ s = 0.13\ \text{eV};\ s\% = 7.4 \qquad n = 10$$

and

$$IP_v = -0.070(0.003)PA + 24.14(0.61), \qquad (2)$$

$$r = 0.993;\ s = 0.07\ \text{eV};\ s\% = 4.1; \qquad n = 10$$

where r - is the correlation coefficient,
s - standard deviation[‡],
$s\% = (s/\Delta IP_{max})100$ - where ΔIP_{max} is the maximum range of the variation of IP_a or IP_v
n - the number of points

The proton affinity scale (adjusted to the $PA_{NH_3} = 207.0$ kcal/mol) was used.[13b] All the 1st IP-s except that of $HC\equiv CCH_2OH$ fit Eqns.(1) and (2). Instead of that in the case of latter compound the 2nd IP_v = 10.92 eV belongs to the oxygen atom and therefore also obeys Eqn.(2).

Relationships (1) and (2) can be used for the prediction of the still experimentally unavailable PA values of some alcohols with strongly electronegative substituents. Some of the values are given in Table 2 (see also Ref. 13b).

Table 2

The Predicted PA (in kcal/mol) Values for Some Aliphatic Alcohols

$(CF_3)_2CHOH$	170.4	$C_2F_5CH_2OH$	178.0
$(CF_3)_3COH$	165.1	$C_3F_7CH_2OH$	178.9
$(CF_3)_3CCH_2OH$	178.0	$ClCH_2CH_2OH$	189.1[*]
CCl_3CMe_2OH	192.0	$NCMe_2COH$	183.1

[*] Calculated on the assumption that the 1st IP-s of these compounds refer to the oxygen atom.

[‡] The standard deviations of the regression coefficients are given in equations in parenthesis.

There exists also the rather close relationship[13b] between the IP of the valence electron shell and the corresponding bonding energies E_B of the inner shell (1s) electrons determined from ESCA. Eqn. (3) and Fig. 3

$$IP_v = 1.126(0.048)E_B(O1s)-596.01(26.41) \qquad (3)$$
$$r = 0.985;\ s = 0.15\ eV;\ s\% = 4.7;\ n = 18.$$

describe this situation in the case of the molecules of alcohols and ether which does not involve structural fragments capable to the direct resonance interaction with the ionization center. Water and its fluorinated analog F_2O do not fit Eqn.3. However, it is interesting that the points for the esters and carboxylic acids obey the aforesaid relationship on condition that the sp^3 oxygen of the OAlk or OH group is considered as an ionization center. In the latter case the 2nd ionization potential of these compounds was used as belonging to the oxygen lone pair.

Along with the correlations of IP values with the gas phase intrinsic basicity measures it is also reasonable to compare IP values with some other empirical basicity measure, e.g. with the base induced shifts of the stretching frequencies of the OH group of phenol $\Delta\nu_{PhOH}$ (in CCl_4 solvent).[22,23] The latter are sometimes[22] considered as a measure of the specific nucleophilic solvation ability of the solvents (the so called solvent B parameters.[22,23]). It is clear from Fig.4 that analogous to Eqn.(1) and (2) but rather approximate linearity exists between the ionization potentials $IP(n_o)$ of the aliphatic alcohols (and phenol) and the corresponding $\Delta\nu_{PhOH}$ values for the latter compounds in CCl_4 solution. One can see from Fig.4. that the points for CH_3OH and CCl_3Me_2COH deviate from the straight line determined by the Eqn. (4):

$$IP_v = -0.0091(0.0012)\Delta\nu_{PhOH} + 12.62(0.13) \qquad (4)$$
$$r = 0.980;\ s = 0.11\ eV,\ s\% = 7.5;\ n = 11 .$$

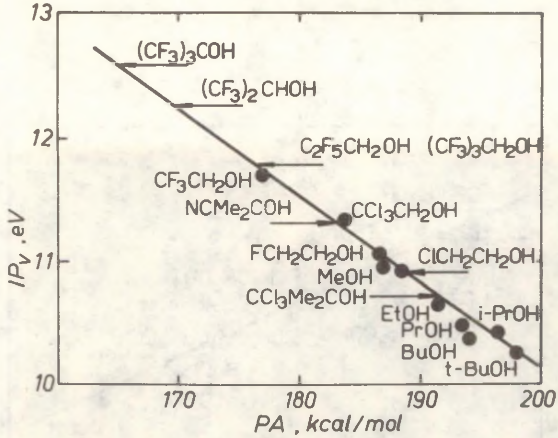

Fig. 2. The dependence of the vertical ionization potentials of alcohols on their proton affinities. The arrows refer to the IP values of some alcohols with electronegative substituents which were used for the prediction of PA values of these bases (see the Text).

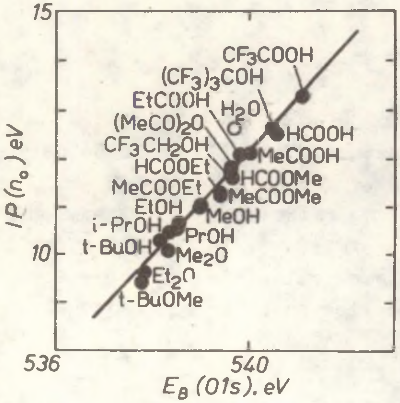

Fig. 3. The dependence of IP-s of the sp^3 oxygen on the corresponding core level 1s electron binding energies for some oxygen containing compounds.

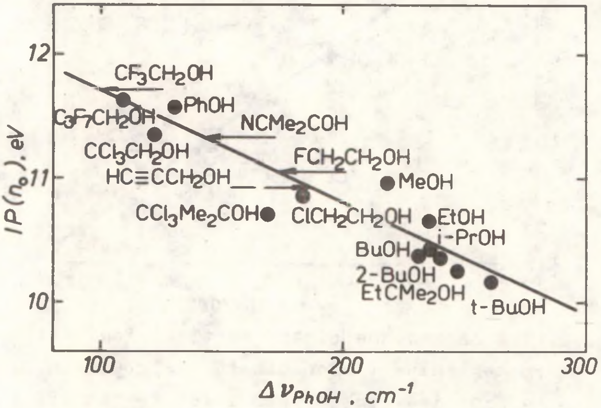

Fig. 4. The dependence of IP(n_o) of alcohols on the IR-shifts $\Delta\nu_{PhOH}$ of the OH-group of C_6H_5OH on complex formation in CCl_4 solution.

Despite its approximate nature, Eqn. (4) could be used either for the identification of the n_o band in PES or, vice versa, for the prediction of the $\Delta\nu_{PhOH}$ values on the basis of the known values of IP(n_o). In Table 3 a few approximate solvent B parameters, calculated on the basis of Eqn.(4), are given for some low basicity aliphatic alcohols.

Table 3.

Solvent B-parameters (in cm^{-1}) of Some Aliphatic Alcohols Calculated from Eqn.(4).

CF_3CH_2OH	102	FCH_2CH_2OH	174
$(CF_3)_2CHOH$	46	$(CF_3)_3CCH_2OH$	104
$(CF_3)_3COH$	4	$HC{\equiv}CCH_2OH$	189
$C_2F_5CH_2OH$	104	$NCMe_2COH$	144

Earlier, the multiparameter Equation (5)

$$IP = IP_o + a_1\sum\sigma^* + a_2\sum\Delta R + a_3\sum\sigma_R^o + a_4 n_1 + a_5\Delta n_2, \quad (5)$$

where IP_o refers to the methylsubstituted derivative
σ^* and σ_R^o are Taft's inductive and resonance constants
ΔR = MR-MR(methyl), where MR is the calculated additive molecular refractivity of the substituent,
$\Delta n_2 = n_2 - n_2$(methyl) where n_2 is the number of α-hydrogen atoms (n_2(methyl)=3)
n_1 = 0,1,2,3 is the number of atoms attached immediately to the ionization center

was suggested[13e] by the present authors for the quantitative correlation of the adiabatic and vertical IP-s on the structure of molecules of different classes.

In the present case the data for the aliphatic alcohols and water obey the following special variants of Eqn.(5) (see also Fig. 5):

$$IP_a = 10.78 + 0.528\sum\sigma^* - 0.045\sum\Delta R + 3.803\sum\sigma_R^o - 0.876\, n_1 \quad (6)$$

R = 0.964; s = 0.13 eV; s% = 5.4 ; n = 18

$$IP_v = 9.23 + 0.776\sum\sigma^* - 0.027\sum\Delta R + 1.114\sum\sigma_R^o + 1.215\, n_1 + 0.049\,\Delta n_2 \quad (7)$$

R = 0.990; s = 0.06 eV; s% = 2.3 ; n = 19

As a rule the use of Eqns. (6) and (7) for the calculation of IP(n_o) values leads to quantities which coincide (within the error limits determined by the standard deviations s) with the values determined for the 1st bands in PES. From the viewpoint of identification of the ionization center the $ClCH_2CH_2CH(Br)OH$ molecule which involves three different lone pair heteroatoms is a rather interesting example. In this case Eqn.(7) predicts the IP(n_o)=11.15 eV which is close to the ionization energy determined from the 3rd band (11.23 eV) of PES. For the bromine atom one can expect the splitting of the corresponding band due to the spin-orbital interaction. In the case of HBr the intensity of this interaction (the separation between two adjacent band) is 0.33 eV which exactly coincides with the separation of the first two bands in the PES of $ClCH_2CH_2CH(Br)OH$. The arithmetic average from the IP-s of the two bands is 10.53 eV whereas the average IP(n_{Br}) value calculated (with the correction for the spin-orbital interaction) from Eqn.(10) of Table 2 from Ref 13e is 10.72 eV while the IP(n_{Cl}) value according to Eqn.(9) from the same Table is 11.10 eV. From that one might conclude that the 3rd band of this alcohol is formed due to the overlapping of the bands corresponding to IP(n_o) and IP(n_{Cl}).

The use of Eqn.(9) from the same Table of Ref. 13e for the calculation of the average values of IP(n_{Cl}) gives for $ClCH_2CH_2O$ 11.30 eV (11.58 from the spectrum), for CCl_3CH_2OH 12.36 eV (12.16 from the spectrum), and 12.04 eV for CCl_3CMe_2OH (11.9 from PES).

IP-structure relationships of type (5) could be successfully used for identification of PES bands also for several other classes of molecules. For example, Eqn.(8) from Table 2 of Ref 13e leads to IP(n_N) = 13.68 eV for $CNMe_2COH$ molecule (1st IP_v = 11.32), etc.

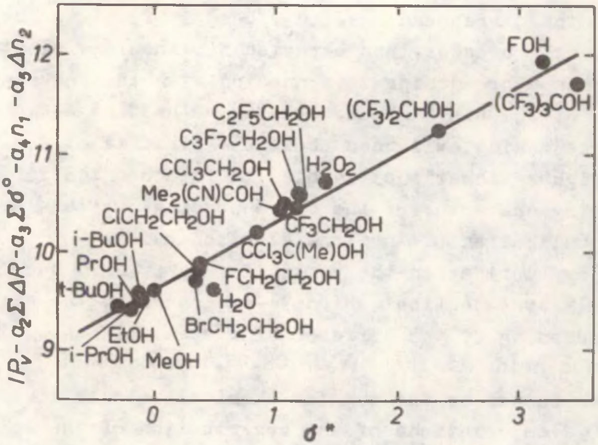

Fig. 5. The dependence of vertical IP of the aliphatic alcohols corrected for the influence of the other structural factors on $\sum\sigma^*$.

In the spectra of alkylsubstituted alcohols one can expect the presence of the rather intense sharp band from the nonbonding 2p-electrons of oxygen IP(n_o), the series of wide band characteristic to the alkanes, and bands due to the electrons of the C-O and O-H bonds.

However, the corresponding IP(n_o) band is found to be significantly broader than expected for the lone electron pairs. Such a broadening is connected with the increase of the size of the alkyl group. Sometimes the fine structure is observed which evidences about the significant population of the higher vibrational levels. It is accounted for by the bonding character of the corresponding orbitals or by the delocalization of the lone electron pairs.

On perfluorination the vertical excitation becomes noticeably less vertical which is evidenced by the significant broadening of the corresponding spectral band. This phenomenon holds in the row CF_3CH_2OH, $(CF_3)_2CHOH$, $(CF_3)_3COH$ and is supported by the quantum chemical calculations. So, the CNDO/2 calculations of the contribution of the 2p AO-s of the oxygen give the following figures for the n_o-character: C_2H_5OH-43 per cents, FCH_2CH_2OH - 41 per cents, $(CF_3)_3COH$ 27 per cents. IP of the molecule is the measure of the difference in the energies of the molecule and its molecular ion (cation-radical). The substitution of the hydrogen atom in the molecule for the alkyl group results in the stabilization of the ion (lower IP-s), whereas the substitution for fluorine atom leads to the reversed effect. As far as the polarizabilities of the hydrogen and fluorine atoms are approximately equal for this respect the behavior of methyl and CF_3-groups is also rather similar.[13e] Hence, the substitution of the methyl-group for the CF_3-group reduces mostly to the polar effects. From this viewpoint F atom and CF_3 group are considered as σ-acceptors whereas the latter trend is partially compensated by their π-donicity. It has been argued[24-26] that in the planar molecules the substitution of the hydrogen atom for the fluorine atom leads to the more preferable σ-than π-stabilization of MO-s. This predominantly σ-stabilizing effect of fluorosubstitution is (the so called"perfluoro effect") sometimes successfully used for he identification of the order of the molecular orbitals in the planar molecules. The preference of the F sustitution consists also in the fact that it does not create additional lines below 17 eV which excludes the problem of resolution of the new lines from the shifted bands.

In the recent years the substitution of the perfluoroalkyl groups (CF_3, etc.) for the corresponding alkyl groups (the so called perfluoroalkyl effect) has been widely studied (See Ref. 27 and the references therein. Some other aspects of the perfluoroalkyl effect were also discussed in Refs. 21, 28, 29). As compared with their alkyl analogs this effect leads to the almost equal stabilization of all MO energy levels. The latter circumstances were used as a starting point for the more detailed interpretation of the PES of some alkylsubstituted derivatives.
Their analysis is significantly complicated by the presence of the broad structureless C-H bands which overlap with the rest of the spectrum. Using successfully the concept of the perfluoroalkyl effect it was suggested[27] that the substitution of the alkyl group for C_nF_{2n+1} substituent lead to the parallel shifts of the n and σ MO-s of the ionization center without any inversion of their order and the type of their symmetry.

In the fluorine substituted compounds studied in this work the CF_3-group is not attached immediately to the ionization center.but separated by the latter by the attenuating fragment ($-CH_2-$, $\rightarrow$CH or $\equiv$C-). From one hand ,this somewhat complicates the spectrum, from the other, however, excludes (or reduces) the π-donating effect of the fluorine atom. The energies and assignment of σ- MO-s deduced by the comparison of the spectra of alkyl- and perfluoroalkyl substituted derivatives are given in Table 4.

Table 4

The energies of σ-MO-s (in eV) Determined on the Basis of Perfluoroalkyl Effect

Compound	n_O	σ_{CC}	σ_{CO}	σ_{OH}
CH_3CH_2OH	10.64	12.18	14.5	15.85
CF_3CH_2OH	11.70	13.29	15.35	17.01
$(CH_3)_2CHOH$	10.36	11.75	14.0	15.11
$(CF_3)_2CHOH$	12.21	13.8	15.81	16.72
$(CH_3)_3COH$	10.25	11.48	13.64	14.60
$(CF_3)_3COH$	12.58	13.85	15.88	16.93
$C_2H_5CH_2OH$	10.49	11.70	12.79	14.52
$C_2F_5CH_2OH$	11.68	13.2	14.1	15.7

Some uncertainty accompanies the determination of the character of the MO from which the ionization takes place. The assignment of MO-s listed in Table 4 is based on the following order of the MO-s derived on the basis of ab initio calculations[10]: n_O, σ_{CC}, σ_{CO} and σ_{CH}. However, different quantum chemical methods, depending on the approximation used (semiempirical or ab initio calculations, the nature of the basis set, etc.) sometimes lead to the different and even contradictory results. Also, along those factors the MO-character is rather sensitive to the molecular conformation chosen.

Some idea about the results of the analysis of PES performed using different quantum chemical SCF MO methods could be gained from Table 1 where alongside Koopmans' ionization energies calculated using the nonempirical (STO-3G and 4-31G basis sets) and semiempirical (HAM-3,CNDO/2) methods are given.

It was shown earlier[10,13b,d] that the linear relationship

$$IP_i = a\varepsilon_i + b \ , \tag{8}$$

where a and b are constants, holds between the experimental set of the consequtive IP_i-s determined from PES and the corresponding calculated MO energies ε_i of the single molecule or, in some cases, for the classes of molecules.

As a rule Eqn.(8) leads[13b,d] to the statistically satisfactory description of the data[*]. The results (see Table 5 and Refs.[13b,d]) of the least squares correlation treatment of the IP_i and ε_i values from Table 1 confirm this statement.

Also, one can see that as a rule, the correlations of the experimental PES IP-s with the ε_i values derived from the ab initio calculations lead to better statistical characteristics of the fit (see also Fig.6.).

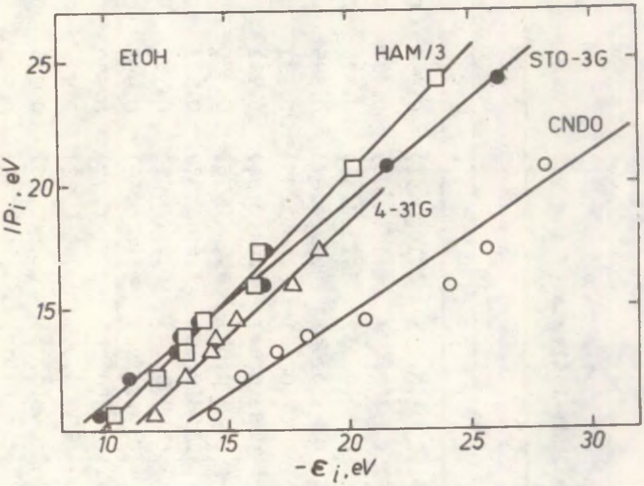

Fig.6. The comparison of the PES of EtOH and the spectrum of the MO energies ε_i calculated by the different quantum chemical methods.

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[*] However, the absolute values of the IP-s calculated on the basis of the Koopmans' theorem might significantly differ (even by a few eV) from the experimental ones.

Table 5

The Results of the Statistical Analysis of the PES of Alcohols in Terms of Eqn.(8).

No	Compound	Method	a	-b	r	s	s%	n
1	2	3	4	5	6	7	8	9
1.	EtOH	HAM/3	1.02(0.03)	0.15(0.51)	0.996	0.40	2.9	9
		4-31G	0.92(0.07)	0.17(1.00)	0.987	0.39	5.7	7
		STO-3G	0.80(0.03)	3.23(0.45)	0.996	0.44	2.6	9
		CNDO/2	0.59(0.04)	2.77(0.87)	0.985	0.80	3.5	9
2.	FCH_2CH_2OH	CNDO/2	0.67(0.06)	1.80(1.05)	0.983	0.44	5.1	7
3.	$ClCH_2CH_2OH$	4-31G	0.87(0.04)	0.81(0.64)	0.992	0.32	4.4	9
		CNDO/2	0.54(0.04)	4.00(0.76)	0.980	0.52	4.8	9
4.	CF_3CH_2OH	CNDO/2	1.08(0.10)	4.60(1.87)	0.983	0.49	7.8	6
5.	CCl_3CH_2OH	CNDO/2	0.89(0.04)	0.75(0.69)	0.995	0.30	4.2	10
6.	i-PrOH	4-31G	0.91(0.04)	0.10(0.66)	0.992	0.29	3.9	9
		CNDO/2	0.53(0.04)	3.70(0.77)	0.980	0.45	4.1	9
7.	$HC{\equiv}CCH_2OH$	HAM/3	0.98(0.03)	0.83(0.52)	0.996	0.47	3.5	9
		CNDO/2	0.68(0.03)	0.75(0.58)	0.995	0.45	2.5	8
8.	$(CF_3)_2CHOH$	STO-3G	0.91(0.02)	3.39(0.36)	0.998	0.24	2.1	7
		CNDO/2	0.69(0.05)	1.77(1.05)	0.988	0.62	4.5	7

Table 5 continued

1	2	3	4	5	6	7	8	9
9.	t-BuOH	CNDO/2	0.49(0.03)	4.52(0.64)	0.979	0.42	3.7	11
10.	$(CF_3)_3COH$	STO-3G	0.84(0.06)	4.96(0.77)	0.992	0.31	5.6	5
		CNDO/2	0.60(0.07)	3.59(1.31)	0.982	0.46	6.6	5
11.	CCl_3CMe_2OH	CNDO/2	0.69(0.04)	I.95(0.66)	0.993	0.34	4.9	6
12.	$NCCMe_2OH$	CNDO/2	0.79(0.02)	0.52(0.36)	0.999	0.11	1.8	5
13.	PrOH	4-31G	0.87(0.05)	0.77(0.79)	0.987	0.37	5.0	9
		CNDO/2	0.46(0.04)	4.91(0.72)	0.977	0.49	3.6	9
14.	$(CF_3)_3CCH_2OH$	CNDO/2	0.68(0.03)	1.15(0.57)	0.996	0.24	2.4	7
15.	$CF_3C(OH)_2H$	CNDO/2	0.65(0.04)	0.93(0.70)	0.995	0.27	2.8	5

Excellent results by the HAM/3 method are explained by the fact that this semiempirical method was specially parametrized for the analysis of the PES. It is also instructive that this method, as well as the ab initio split valence calculations (the 4-31G basis set) lead to the slopes a which are the closest to the unity. This circumstance could be used for the more or less reliable analysis of the PES which contain bands which are very hard to identify because of their overlapping.

Formally, the statistical characteristics of the correlation of IP_i values with the CNDO/2 orbital energies are somewhat less reliable. The slope a from Eqn.(8) varies moderately from molecule to molecule; its average value for the alcohols is 0.67±0.17.

For the methanol molecule all quantum chemical methods suggest the self-consistent order and characters of the localization of the MO[*]-s:

$$2a''(n_O),\ 7a'(\pi_{CH_3}),\ 6a'(\sigma_{CO}),\ 1a''(\pi_{CH_3}),\ 5a'(\sigma_{OH}).$$

However, there already is a certain disagreement between the interpretations of the PES of ethanol by the different SCF MO methods. So, HAM/3 gives[19] the MO order as $3a''$, $10a'$, $9a'$, $2a''$, $8a'$, $1a''$, $7a'$, $6a'$, $5a'$, whereas the ab initio calculations using the 4-31G split valence base predict a somewhat different arrangement of MO-s (see Table 1). As indicated by various calculations the trans-$\underline{C}H_3$ CH_2 $\underline{O}H$ conformation of the C_s symmetry is the most stable one which is in agreement with the corresponding electron diffraction results (see Ref. 10,30,31 for the literature sources). CNDO/2 method also leads to the slightly different order of the MO energies and characters of localization. The results of the present CNDO/2 calculations of the alcohols are shown on the correlation diagram of their eigenvalues (see Fig.7).

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[*] Throughout this paper the symbols of the dominant characters of localization the MO-s are conventional (n, π, σ pseudo- π_{CH_2} or pseudo-π_{CH_3} etc.).

There are even some contradictory results in determining IP from the PES of ethanol. So, the authors of Ref.10 locate the band at 14.5 eV which in Ref. 6 has the energy 15.2 eV and is absent in the spectrum of EtOH reported in Ref. 9. The existence of the abovesaid band could be confirmed by the relationship (8) which for on all levels of SCF calculations predicts the presence of the $8a'$ ($5a'$ in CNDO/2) MO at ca 14.5 eV.

The trans-$X\underline{C}H_2CH_2\underline{O}H$ of the C_s group of symmetry is also the most stable CNDO/2 conformation for the halogenethanols.*

On the correlation diagram (Fig.7) the MO-s of the same symmetry and, as a rule, of the same character are connected by the dotted line for the similar molecules. In the chloro-substituted alcohols there is an important question about the origin of the predominant character of the HOMO (the lone pair of the oxygen or halogen atom). Qualitatively, several circumstances should be taken into account. So, in XCH_2CH_2OH the polar (inductive) effect of X should increase the IP of the ethanol's lone pair of the oxygen atom, whereas the influence of the F atom should be probably more pronounced than that of chlorine. For the F-substituted derivative no polarizability effects is expected. On the contrary (the counteracting to the inductive effect), noticeable polarizability effects[13e] should stabilize the cation-radical for the Cl-compounds. On that basis one can expect that the IP(n_0) of the $ClCH_2CH_2OH$ is lower then IP(n_0) for its F-counterpart. (In its turn the possible[3] interaction of n_0 and n_{Cl} orbitals should result in the further reduction of IP(n_0). As a matter of fact, CNDO/2 calculations reproduce this mixing of orbitals which naturally is absent in fluorocompounds.

The spin-orbital splitting of the chlorine bands is in

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* For X=Cl the experimentally more favorable cis-conformation is found to be 1.8 kcal/mol less stable than the trans form. The corresponding figure for the X=F is 2.6 kcal/mol.

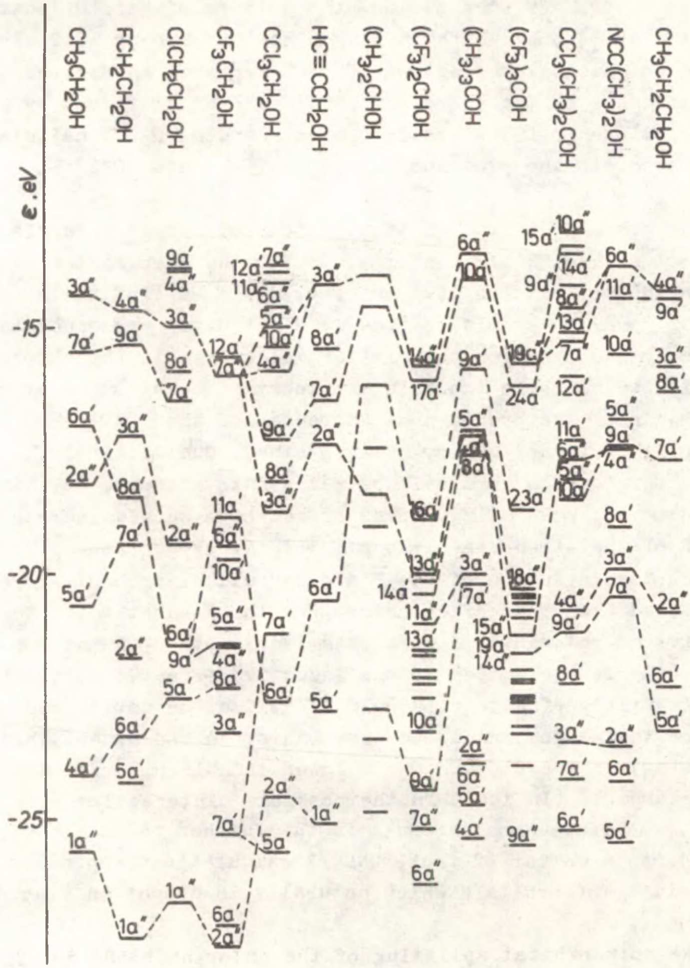

Fig.7. Correlation diagram of CNDO/2 eigenvalues for some aliphatic alcohols.

$ClCH_2CH_2OH$ of the same order (the difference between 2nd and 3rd bands is 0.26 eV) as in the hydrogen chloride molecule (0.09 eV).

On the substitution of H atom for halogen the IP of the electrons of the C-O bond should increase due to the inductive effect of the more electronegative atom. In most cases the MO of this chemical bonds is not free from a certain contribution from the orbitals of the C-H bond and or from the other MO-s. It, naturally, complicates the analysis of the substituent effects on the corresponding PES.

According both to the nonempirical (4-31G basis) and CNDO/2 calculations the eigenvalue spectrom of the $ClCH_2CH_2OH$ molecule has two closely situated bands which belong to the higher occupied orbitals and have the character of the chlorine lone pairs. Not until the 3rd MO has the n_O character. That reflects the general rule that the HOMO of the chlorosubstituted alcohols refer to the chlorine lone pairs.

It is also interesting to note that the 4a MO of EtOH (σ_{OH} character by CNDO/2) is destabilyzed by the halogenatin.

Trans-conformation seems to the most stable CNDO/2 structure (cis form is 1.9 kcal/mol less stable) for the $\underline{C}F_3CH_2\underline{O}H$ (C_s symmetry) and in all conformations the HOMO 12a$'$ belongs to the C-C bond and has σ-but not n_O character. However, on the contrary, the ab initio calculations[17] (Gaussian 82[18] system of programs with a full optimization of the geometry by the method of gradients) using the STO-3G basis set (E_{tot} = -444.5136 a.u.) still predicts that the HOMO (8a$''$ symmetry) has predominantly n_O character. Probably, the failure to reach that conclusion using CNDO/2 method is connected to the problem of finding the best optimized geometry using the standard Pople and Dobosh version of the program.

On the CNDO/2 level trans- $\underline{C}Cl_3CH_2\underline{O}H$ conformation is slightly (1.3 kcal/mol) more preferable than the cis-form and its HOMO-s belong to the chlorine lone pairs.
The strong orbital interaction of chlorine and oxygen lone

pairs splits the $7a''(n_O)$ MO in CF_3CH_2OH into the doublet $5a''(n_{Cl}, n_O)$, $4a''(n_O,n_{Cl})$ characteristic to CCl_3CH_2OH. As predicted on the basis of the empirical analysis the $9a'$, $8a'$ and $3a''$ MO-s really have the σ-character. However, there are no MO-s with the predominant σ_{CO} and σ_{CC} character. Most MO-s include the contributions from the chlorine lone pairs.

HAM/3 calculations[19] of the $HC{\equiv}CCH_2OH$ molecule predict the following order of MO-s: $3a''$, π_{CC}, $12a'$, π_{CC}, $2a''$, n_O, $11a'$, $10a'$, $1a''$, $9a'$. Comparison of these results with the CNDO/2 calculations (the same trans-C_s conformation was used) shows (see Table 1) that in the latter case $2a''$ and $1a''$ MO-s are shifted by one level upwards on the energy scale. CNDO/2 also predicts the existence of the interaction between the lone pairs of the oxygen and of the CC triple bond which should result in appearance of the doublet of MO-s: $3a''(n_O,\pi_{CC})$ and $2a''(n_O,\pi_{CC})$.

The study of the perfluoroalkyl effect on the structure and PES of the branched alcohols could by started with the calculation of i-PrOH molecule. The latter has an experimental geometry[30,31] with the preferred gauche-conformation (C_1 symmetry).

One can see from Fig.7 that in branched molecules σ_{CO} MO is destabilized by the increase of the size of the alkyl group. In its turn, the same time, σ_{CC} MO approaches n_O MO. Both phenomena are paralleled also by the experimental evidence.

The spectrum of $(CF_3)_2CHOH$ is characterized by the strong overlapping of bands and therefore the determination of the low-lying orbitals is somewhat complicated. As in the case of CF_3CH_2OH the CNDO/2 calculations of this as well as $(CF_3)_3COH$ molecule were suppored with the ab initio Gaussian 82[18] (STO-3G basis set) calculations using the method of gradients for the finding the fully optimized structures of the species.

According to the CNDO/2 calculations the energy of the gauche-conformation of $(CF_3)CHOH$ is only slightly different (lower by 1 kcal/mol) from its trans structure. Semiempirical calculations of this molecule were performed for trans form only. The other of CNDO/2 eisenvalues is characterized by the fact that all its antisymmetric MO-s are shifted relative to the molecule's symmetry plane towards the higher energies. It is interesting to note that CNDO/2 $17a'$ level belongs to the same σ-orbitals as the analogous MO in $(CH_3)_2CHOH$. However, it has now the σ_{OH} character (σ_{CC} - in the $(CH_3)_2CHOH$). According to our non-empirical calculations (STO-3G basis set), in the range of MO-s from $17a''$ to $17a'$ (according to correlation 8 from Table 5 this corresponds to the interval from 15.5 to 16.8 eV) there is a multipliplicity of near lying MO-s. In the experimentally determined PES this corresponds to the area with the extensive overlapping of the different bands.

In calculations of tert-BuOH the C_s symmetry was always assumed. According to the Table 4 of this paper CNDO/2 MO-s $6a''$, $10a'$, $9a'$, $8a'$, and $7a'$ are σ- orbitals. Two additional MO-s are ($8a'$ and $7a'$) generated by the hybridization of σ_{CH} and σ_{OH} orbitals. As in the case of $(CF_3)_2CHOH$, both CNDO/2 and STO-3G calculations again predict the multiplicity of spectral lines in the range between 15.5 and 17 eV which again corresponds to the area in the real PES which is characterized by the unresolved broad bands.

The Fig.7 and data from Table 1. confirm the rather strict observance of the above mentioned rule[27] about the effect of perfluoroalkyl substitution on the shifts of the MO energies in alkyl- and perfluorinated derivatives. Indeed, MO-s of $(CH_3)_2CHOH$ and $(CF_3)_2CHOH$ on the one hand, and MO-s of $(CH_3)_3COH$ and $(CF_3)_3COH$ on the other hand change in the very similar, almost parallel mood without inverting their order. In the same time, the bands corresponding to the alkyl substituent are absent in perfluoro-compounds. Instead of that the proper number of fluorine bands is now present.

Concluding the study of the $(CF_3)_2CHOH$ and $(CF_3)_3COH$

it is worthwhile to compare their spectra of eigenvalues calculated on the semiempirical CNDO/2 and ab initio STO-3G levels. Rather satisfactory linear relationships hold in both cases:

$$(CF_3)_2CHOH: \quad -\varepsilon_{CNDO} = 1.22(0.05)(-\varepsilon_{3G}) + 4.11(0.75 \qquad (9)$$

$$r = 0.984;\ s = 0.75\ \text{eV};\ s\% = 4.7\ ;\ n = 22$$

$$(CF_3)_3COH: \quad -\varepsilon_{CNDO} = 1.18(0.06)(-\varepsilon_{3G}) + 5.02(0.88)$$

$$r = 0.972;\ s = 0.58\ \text{eV};\ s\% = 5.9\ ;\ n = 22 \qquad (10)$$

Standard deviations of these linearities are similar to those from Table 5. Therefore, one might expect that in general lines both of these methods should lead in most cases to the comparable assignment of PES using the Koopmans' approach.

The introduction of the CCl_3 group into $(CH_3)_3COH$ molecule complicates significantly the interpretation of PES. In that case the energies of the chlorine lone pairs and of the oxygen atom are rather close. Therefore the additional possibilities for their mixing arise whereas the broad structureless bands of two methyl groups are still present.

In the present calculations of $CCl_3(CH_3)_2COH$ the C_s symmetry was assumed. The symmetry characteristics of the MO and the characters of their approximate localization are given in Table 1. The interaction of the chlorine and oxygen lone pairs is responsible for the presence in the spectrum of two lines, with the mixed characters n_{Cl}, n_O, and n_O, n_{Cl}, correspondingly. As it is typical for the chlorosubstituted alcohols the highest occupied MO-s belong to the chlorine lone pairs.

CNDO/2 calculations of $NC(CH_3)_2COH$ molecule were made assuming the C_s symmetry. As far as the CN group has the ionization levels around 13 eV the PES of this compound is less complicated due to the interactions of different MO-s. However, two broad structureless CH_3 bands are still present and complicate the analysis of PES significantly. The CNDO/2 spectrum of eigenvalues is similar to that of $(CH_3)_3COH$. Two additional MO-s characterize the CN group (π_{CN} and n_N, two others (10a$'$) have the mixed characters (π_{CN} and σ_{CO}).

CNDO/2 method fails to predict the experimentally favored gauche-conformation for the n-C_3H_7OH. Instead of that the trans-form appears to be significantly more stable. The orders of MO-s for the CNDO/2 trans-conformation and for the gauche conformation calculated[10] using ab initio 4-31G basis set, however, generally coincide with the exception of 1a$''$ and 9a$'$ MO-s.

The spectra of $C_2F_5CH_2OH$, $C_3F_7CH_2OH$, and $(CF_3)_3CCH_2OH$ seem to be closely similar (see Table 1). The analysis of the PES of the latter compound in terms of the perfluoroalkyl effect is unfortunately impossible due to the lack of the PES for the $(CH_3)_3CCH_2OH$. The trans-structure for the $(CF_3)_3CCH_2OH$ (C_s symmetry) seems to be slightly favored by CNDO/2 calculations.

The calculations of trans conformation of the $CF_3C(OH)_2H$ (C_s symmetry) suggest that the interaction of the lone pairs of two oxygen atoms takes place (splitting into 13a$'$ and 9a$''$ MO-s).

The analysis of the PES of $H_2NCH_2CH_2OH$ and hydroxylamine will be given in the forthcoming papers of this series of papers.

Conclusion

The complex approach which uses empirically established relationships (the dependence of IP on PA, on the core level ionization energies, on the structure and quantum chemical calculations seems to be the most effective tool for the analysis of PES which have several overlapping and structureless bands and which reflect the competition between different ionization centers.

Rather useful are the linearities between the IP_i determined from PES and the calculated spectrum of eigenvalues of the molecules. Even more general linearities of this kind frequently hold within the different classes of similar molecules.

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THE EFFECT OF SUBSTITUENTS ON CHEMICAL SHIFTS OF AMINOGROUPS OF 5-SUBSTITUTED 2-PYRIMIDINECARBOXYLIC ACIDS HYDRAZIDES IN THE ^{1}H-NMR SPECTRA

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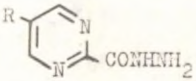
By the method of ^{1}H-NMR spectroscopy hydrazides of 5-substituted 2-pyrimidinecarboxylic acids in the solutions of dimethyl sulphoxide and deuterochloroform have been investigated. With the help of correlative analysis the dependences between the chemical shifts of protons of -NH- and $-NH_2$ groups and electronic effects of substituents were studied. Comparing the obtained correlation parameters to those analogical for hydrazides of p-substituted benzoic acids a similarity of the transmission of electronic effects of the substituents from the 5th position of pyrimidine and p-position of the benzene rings was established.

The combination of two biologically important fragments in the hydrazine derivatives of pyrimidinecarboxylic acids - the pyrimidine ring and the hydrazide grouping - defines the practical importance of this series of compounds. Among them the compounds possessing biological activity have been found[1-3]. However, the data on the structure, reactivity and other physicochemical properties of this series of compounds are not available for the present. In connection with this and continuing our studies of hydrazine derivatives of pyrimidinecarboxylic acids[3-5], we have synthesized some hydrazides of 5-substituted 2-pyrimidinecarboxylic acids (I) and studied their ^{1}H-NMR spectra. To provide more reliable interpretation of some data received in the pyrimidine series under analogous conditions the spectra of hydrazides of the p-substituted benzoic acids (II)[*] have been recorded as well.



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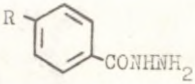

II

R = NH_2, CH_3O, CH_3, H, CI, Br.

The ^{1}H-NMR spectra of compounds I and II have been recorded in dimethyl sulphoxide (DMSO) and deuterochloroform ($CDCl_3$) solutions. In the ^{1}H-NMR spectra besides the signals of the aromatic protons the signals of protons of the primary ($-NH_2$) and those of the secondary (-NH-) aminogroups of the hydrazide grouping are being observed with the values of chemical shifts presented in Tables 1,2.

When diluting dimethyl sulphoxide solutions of hydrazides I and II an unsignificant shift of the signals of -NH- and $-NH_2$ groups protons takes place to the higher field. At concentrations of hydrazides equal to 0.005 m.f. and lower the chemical shifts of the groups mentioned remain constant. When the temperature of solutions of the studied compounds I and II in DMSO is increased a similar shift of the signals of protons of the primary and secondary aminogroups towards the higher field is observed. Taking into account, that DMSO is capable of forming complexes with the help of the hydrogen bond[7], it is possible to suppose that in the diluted solutions of hydrazides I and II the formation of complexes between the proton-donor -NH- and $-NH_2$ groups and DMSO takes

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[*] Hydrazides of aromatic acids by the ^{1}H-NMR method were studied by E.V. Titov and co.[6].

Table 1

Chemical Shifts* of Protons of -NH- and $-NH_2$ Groups of Hydrazides of 5-Substituted 2-Pyrimidinecarboxylic Acids (I)

R	$(CH_3)_2SO$		$CDCI_3$		$\Delta\delta^{I**}_{NH}$	$\Delta\delta^{I}_{NH_2}$
	δ_{NH}, ppm	δ_{NH_2}, ppm	δ_{NH}, ppm	δ_{NH_2}, ppm		
NH_2	9.49	4.47	-	-	-	-
CH_3O	9.85	4.59	8.66	4.08	1.19	0.51
CH_3	9.92	4.64	8.97	4.20	0.95	0.44
H	10.01	4.68	8.82	4.12	1.19	0.56
CI	10.13	4.71	8.86	4.15	1.27	0.56
Br	10.10	4.71	8.88	4.13	1.22	0.58

Table 2

Chemical Shifts* of Protons of -NH- and $-NH_2$ Groups of Hydrazides of p-Substituted Benzoic Acids (II)

R	$(CH_3)_2SO$		$CDCI_3$		$\Delta\delta^{II**}_{NH}$	$\Delta\delta^{II}_{NH_2}$
	δ_{NH}, ppm	δ_{NH_2}, ppm	δ_{NH}, ppm	δ_{NH_2}, ppm		
NH_2	9.26	4.31	-	-	-	-
CH_3O	9.60	4.44	7.40	4.06	2.20	0.38
CH_3	9.67	4.46	7.42	4.06	2.25	0.40
H	9.76	4.51	7.57	4.11	2.19	0.40
CI	9.86	4.54	7.42	4.06	2.44	0.48
Br	9.86	4.54	7.55	4.02	2.31	0.52

* Chemical shifts δ_{NH} and δ_{NH_2} in DMSO are measured relatively to the methyl protons of DMSO and re-counted for TMS scale with the help of equation $\delta = \delta_{(CH_3)_2SO} + 2.59$.

** $\Delta\delta_{NH} = \delta_{NH}^{(CH_3)_2SO} - \delta_{NH}^{CDCI_3}$; $\Delta\delta_{NH_2} = \delta_{NH_2}^{(CH_3)_2SO} - \delta_{NH_2}^{CDCI_3}$.

place. In favour of this tells the fact that the signals of -NH- and $-NH_2$ groups protons in $CDCI_3$ solutions are in the higher field than the signals in DMSO (Table 1,2).

It is known that the chemical shift of protons of the primary and secondary aminogroups of aromatic acids hydrazides is generally determined by the value of diamagnetic screening of the resonating proton and is in good correlation with the Hammett - Taft substituent constants σ [8]. Assuming that the contribution of electronic, steric and magnetic factors of the pyrimidine ring inside one and the same reactionary series is constant[9], it is possible to admit, that the chemical shifts of protons of hydrazides aminogroups (I) will depend on the electronic density of nitrogen and, subsequently, on the substituents electronic effects. Really, the data of correlation analysis show that the chemical shifts of protons of -NH- and $-NH_2$ groups are in good correlation with σ substituent constants (Table 3, eq. 1,2). The data of analogous equations for hydrazides of p-substituted benzoic acids, are presented as well (Table 3, eq. 3,4).

Table 3

Parameters of Correlation Equation $y = y_o + \rho\sigma$

Eq.No.	Series	y	y_o	ρ	s^a	r^b	n^c
1	I	δ_{NH}	9.99± ±0.01	0.679± ±0.03	0.023	0.983	6
2	I	δ_{NH_2}	4.66± ±0.004	0.268± ±0.012	0.009	0.983	6
3	II	δ_{NH}	9.74± ±0.009	0.655± ±0.03	0.02	0.985	6
4	II	δ_{NH_2}	4.49± ±0.003	0.253± ±0.01	0.008	0.985	6

a - standard deviation, b - correlation coefficient, c - number of points used in correlation.

Comparison of the values of the ρ coefficient in equations (1,3), as well as in equations (2,4) indicates that the substituent effects of substituents R on the chemical shifts of protons of -NH- and $-NH_2$ groups are similar in both series of compounds.

It is necessary to note that the correlations of chemical shifts of protons of aminogroups of hydrazides I, II with σ° substituent constants are pure. For example, the values of correlation coefficients r of the relationships between δ_{NH} and δ_{NH_2} of hydrazides I and σ° constants are equal to 0.927 and 0.917, respectively. The same is observed for hydrazides II (for $\delta_{NH} - \sigma^{\circ}$ and $\delta_{NH_2} - \sigma^{\circ}$ $r = 0.931$ and 0.932). Thus, the better correlations of the chemical shifts of protons of aminogroups with σ constants indicate the existence of the polar resonance effect between substituents R and aminogroups in series I, II[10]. In order to evaluate the contribution of polar resonance effect of substituents to the chemical shifts of protons of -NH- and $-NH_2$ groups the two-parameter correlation equations, using σ°, σ_R^+ substituent constants, have been calculated. The parameters of these equations are presented in Table 4.

Table 4

Parameters of Correlation Equation

$$y = y_o + \rho\sigma^{\circ} + \rho_R^+\sigma_R^+$$

Eq.No.	Series	y	y_o	ρ	ρ_R^+	s	r	n
5	I	δ_{NH}	10.03± ±0.034	0.491± ±0.126	0.266± ±0.069	0.047	0.959	6
6	I	δ_{NH_2}	4.68± ±0.005	0.168± ±0.02	0.121± ±0.011	0.007	0.993	6
7	II	δ_{NH}	9.78± ±0.029	0.473± ±0.106	0.257± ±0.058	0.04	0.968	6
8	II	δ_{NH_2}	4.51± ±0.011	0.182± ±0.039	0.10± ±0.02	0.015	0.971	6

Comparing the values of ρ and ρ_R^+ coefficients in equations (5,7) it can be concluded that the transmission of inductive and polar resonance effects to the secondary aminogroup is practically equal in both series of compounds. A similar result was obtained by investigating 5-substituted 2-aminopyrimidines[11]. However, the influence of the polar resonance effect on the δ_{NH} is almost two times lower than the influence of the inductive effect of substituents (ρ_R^+/ρ =0.54).

The comparison of ρ and ρ_R^+ in equations (5,6) shows that in series I the role of the inductive effect of substituents on δ_{NH_2} decreases by a higher degree than the resonance effect. And an analogous comparison of ratio ρ_R^+/ρ in equations (7,8) indicates that in hydrazides of p-substituted benzoic acids (II) the relative influence of substituent inductive and polar resonance effects on δ_{NH_2} remains the same as on δ_{NH}.

The comparison of the chemical shifts of protons of the primary and secondary aminogroups shows the chemical shifts of protons of -NH-group to be changing by 2.5 times stronger than those of the protons of -NH_2 group (eq.9,10) which is in good agreement with the data[6] and the idea of the "barrier role" of the link -NH- is confirmed[12.13].

Series I

$$\delta_{NH}=(2.52\pm0.066)\delta_{NH_2} -(1.78\pm0.305) \quad s=0.014 \quad r=0.994 \quad (9)$$

Series II

$$\delta_{NH}=(2.58\pm0.034)\delta_{NH_2} -(1.86\pm0.152) \quad s=0.007 \quad r=0.998 \quad (10)$$

As has been mentioned above, the signals of protons of -NH- and -NH_2 groups in the solutions of $CDCI_3$ are in the higher field in comparison with the signals in DMSO solutions (Table 1,2). The chemical shifts of protons of the secondary aminogroups of hydrazides I in DMSO differ insignificantly from the analogous chemical shifts of hydrazides II. Nevertheless, this difference becomes essential in $CDCI_3$. Comparing $\Delta\delta^{I}_{NH}$ and $\Delta\delta^{II}_{NH}$ it is possible to assume that in the chloroform solutions of hydrazides of 5-substituted 2-pyrimidinecarboxylic acids there exists an intramolecular hydrogen bond between the heterocyclic nitrogen atom and the proton of the secondary aminogroup.

Finally, it is necessary to note that no linear correlation was observed between the chemical shifts of protons of aminogroups of hydrazides I, II in $CDCI_3$ solutions and substituents constants. Evidently this may be accounted by the following reasons: in the hydrazides I - by a possible formation of the hydrogen bond between the nitrogen of pyrimidine ring and proton of -NH- group, while in the hydrazides II - by an inconstant effect of the magnetic anisotropy of the ring, caused by its rotation around the C_{aryl}-C bond.

Experimental

Parameters of correlation equations were calculated on a computer "Minsk-22" using the programs elaborated by Cand. of phys.-math. sci. V. Balevičius. The substituent constants were taken: σ - from[10]; σ^{o}, σ_{R}^{+} - from[14].

Synthesis of compounds

The initial materials for the synthesis of hydrazides of 5-substituted 2-pyrimidinecarboxylic acids (I) were the amides of the corresponding acids, which were obtained from 2-cianpyrimidines. 2-Cianpyrimidine was synthesized according to the method[15], 5-dimethylaminomethyleneamino-2-cianpyrimidine according to[16], 5-methoxy-, 5-methyl-, 5-chlor-, 5-brom-2-cianpyrimidines according to the method[17]. Amide of 2-pyrimidinecarboxylic acid was obtained according to[18], amides of 5-chlor- and 5-brom-2-pyrimidinecarboxylic acids according to[17], the amide of 5-amino-2-pyrimidinecarboxylic acid according to the method described in[19].

Amide of 5-methoxy-2-pyrimidinecarboxylic acid. To a stirred mixture of 1 g. (0.0074 moles) of 5-methoxy-2-cianpyrimidine, 6 ml. of ethanol and 30 ml . of 30% hydrogen peroxide 0.4 ml. of 5 M solution of potassium hydroxide in water was added dropwise, When the exothermic reaction was over the reaction mixture was stirred at 50°C for 0.5 h. After cooling the precipitated material was removed by filtration and recrystallized. Yield 71%, m.p. 219.5-220.5°C (from water). Found, %: C 47.42; H 4.62; N 27.60. $C_6H_7N_3O_2$. Calculated, %: C 47.06; H 4.61; N 27.44.

Amide of 5-methyl-2-pyrimidinecarboxylic acid. A mixture of 5.0 g. (0.042 moles) of 5-methyl-2-cianpyrimidine, 50 ml. of water and 1.5 ml. of 25% ammonia was heated in the boiling water bath for 6 h. Then the mixture was evaporated in vacuum to dryness, the residue was washed with ether and crystallized. Yield 88%, m.p. 192-193°C (from ethanol). Found, %: C 52.43; H 5.25; N 30.81. $C_6H_7N_3O$. Calculated, %: C 52.55; H 5.14; N 30.64.

Hydrazides of 5-substituted 2-pyrimidinecarboxylic acids. 2 g. (0.04 moles) of 99% Hydrazine hydrate was added to a hot solution of 0.01 moles of amide of corresponding 2-pyrimidinecarboxylic acids and the reaction mixture was refluxed under stirring for 1.5-2 h /In the case of synthesis of compounds I ($R=NH_2$, CH_3O) 0.13 moles of hydrazine hydrate was used/. After cooling the precipitated material was removed by filtration, washed with ethanol and recrystallized. The data of synthesized hydrazides I are presented in Table 5. Compound I ($R=CH_3O$) was synthesized in the solution of ethylcelozolve, and in the use of compound I ($R=NH_2$) - no solvent was used.

Hydrazides of p-substituted benzoic acids were synthesized from methyl esters of the corresponding benzoic acids in the solutions of ethanol analogically to the synthesis of hydrazides I. Their constants were in good agreement with literature data[20,21].

Purity of the synthesized compounds was controlled chromatographically.

^{1}H-NMR spectra

^{1}H-NMR spectra of compounds in DMSO solutions were recorded on a spectrometer BS 487 C "TESLA" (80 MHz), and in $CDCI_3$ - on a spectrometer Hitachi R 22 (90 MHz) at 33±1°C with an accuracy ±0.01 ppm. Chemical shifts are given in the scale of tetramethylsilane. The concentrations of compounds were 0.005 m.f., DMSO and $CDCI_3$ were purified as described in[22] and were dried by storing molecular sieve 4A. The samples were prepared in the box, preliminarily dried by anhydrone.

Table 5

Characteristics of Hydrazides of 5-Substituted 2-Pyrimidinecarboxylic Acids (I).

R	M.p., °C	Brutto f-la	Found/Calculated,%		
Yield,%	(solvent)		C	H	N
NH_2	268-269	$C_5H_7N_5O$	39.41	4.50	45.39
80	(water)		39.22	4.61	45.73
CH_3O	200-201.5	$C_6H_8N_4O_2$	42.51	5.20	33.53
58	(izopropanol)		42.86	4.79	33.32
CH_3	158.5-160	$C_6H_8N_4O$	47.41	5.15	36.83
79	(ethanol)		47.36	5.30	36.82
H	178-179	$C_5H_6N_4O$	43.80	4.28	40.50
75	(ethanol)		43.48	4.38	40.56
CI	209-200	$C_5H_5N_4CIO$	34.58	3.21	32.54
72	(ethanol)		34.80	2.92	32.47
Br	208.5-209.5	$C_5H_5N_4BrO$	27.53	2.60	25.52
75	(ethanol)		27.67	2.32	25.82

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ACIDO-BASIC PROPERTIES OF THE SUBSTITUTED AMIDES AND HYDRAZIDES OF SUCCINIC ACID ARENSULFOHYDRAZIDES

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The method of potentiometric titration in water and 60% aqueous dioxane at 25°C has been applied to determine the acid ionization constants of methylamides and hydroxyamides of succinic acid arensulfohydrazides as well as the acid and basic ionization constants of arensulfohydrazide hydrazides of succinic acid and a number of its hydrazones. The correlation equations were obtained which chracterize the electronic influence of the substituents on the ionization of the sulfohydrazide group.

Previously[1] we have conducted research into the physicochemical properties /ionization constants, infrared and UV spectra/ of arensulfohydrazide hydrazides of oxalic acid and established the regularities with regard to the structure influence of the studied compounds on the above properties.

Continuing the study of dicarboxylic acid derivatives we determined the acid ionization constants of methylamides /series A/ and hydroxyamides /series B/ of succinic acid arensulfohydrazides, the acid and basic ionization constants of arensulfohydrazide hydrazides of succinic acid /series C/ as well as the pK_a values of the acid ionization of the interaction products of the latter with carbonyl containing reagents: benzylidenehydrazides /series D/, 4-methoxy and 2-hydroxybenzylidenehydrazides, furfurylidenehydrazide and indolinone-2-ilidene-3-hydrazide of succinic acid benzenesulfohydrazide /series E/. The experimental data are represented in Table 1.

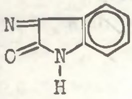
The methylamides of series A are characterized by low acidity: the pK_a value of these compounds in 60% aqueous dioxane ranges from 8.82 to 10.11 units. The substitution of the methyl radical for the hydroxyl one /series B/ does not influence the ionization of the sulfohydrazide group /compare the pK_a values of compounds 2,3 and 10-11/. When passing over from methylamides /series A/ and hydroxyamides /series B/ to the hydrazides /series C/ of succinic acid arensulfohydrazides no signifacent change in pK_a values was observed either: the pK_avalues of the acid ionization of hydroxyamides in water are close to the pK_a values of the corresponding hydrazides. The comparison of the acid-base properties of arensulfohydrazide hydrazide of oxalic acid and analogous hydrazides of succinic acid /series C/ revealed that the latter are characterized by higher basicity /~to 0.2-0.3 units/ and lower acidity: the pK_a values of the acid ionization of succinic acid hydrazides were by~ a unit higher the pK_a values of oxalic acid hydrazides[1]. This can be explained by the fact that the introduction of a $-CH_2-CH_2-$ grouping between the two carboxylic groups into the structure of the molecules of oxalic acid hydrazides will lead to the isolation of the electron acceptor influence of the second carbonyl.

Due to the low solubility in water the pK_a values of the acid ionization for methylamides /series A/ and the hydrazones of series D and E were determined in 60% aqueous dioxane. Since the studied compounds are from the viewpoint of biology promising, it was of practical interest to estimate the ability of the sulfohydrazide

Table 1

Ionization constants of the substituted amides and hydrazides of arensulfohydrazides of succinic acid and its derivatives

Compound	Series	R	X	R′	pK_a of acid ionization in water	pK_a of acid ionization in 50% aqueous dioxane	pK_a of basic ionization in water
1	2	3	4	5	6	7	8
1	A	H	–	CH_3	7.64*	9.65*	
2		CH_3	–		7.98*	9.99*	
3		CH_3O	–		8.10*	10.11	
4		Cl	–		7.40*	9.41	
5		Br	–		7.37*	9.38	
6		NO_2	–		6.81*	8.82	
7		H	CH_2		8.09*	10.10	
8	B	H	–	CH	7.86	–	
9		CH_3	–		8.05	9.97	
10		CH_3O	–		8.12	10.09	
11		Br	–		7.65	9.48	
12		NO_2	–		7.02	–	
13		H	CH_2		8.26	–	
14	C	H	–	NH_2	7.92	–	3.42
15		CH_3	–		8.11	–	3.43
16		CH_3O	–		8.18	–	3.45
17		Cl	–		7.64	–	3.41
18		Br	–		7.58	–	3.42
19		NO_2	–		7.05	–	3.40
20		H	CH_2		8.34	–	3.43
21	D	H	–	$N{=}CHC_6H_5$	7.96*	9.89	

1	2	3	4	5	6	7	8
22		CH_3	–	$N{=}CHC_6H_5$	8.04*	10.07	
23		CH_3O	–		8.20*	10.23	
24	D	Br	–		7.49*	9.52	
25		NO_2	–		6.92*	8.95	
26		H	CH_2		8.08*	10.11	
27		H	–	 N=CH-	–	9.89	
28			–	$N{=}CH{-}C_6H_4CH_3O{-}4$	–	10.01	
29	E		–	$N{=}CH{-}C_6H_4OH{-}2$	–	10.05	
30			–		–	10.28	

*Calculated by taking into account the corrections Δ, found according to equations 1 and 2, Table 2.

*The mean deviations of pK_a values do not exeed 0.09 unit..

Table 2

The dependence of the pK_a values of the acid ionization of methylamide /compound 2/ and benzylidenehydrazide /compound 22/ of succinic acid p-toluenesulfohydrazide on the dioxane weight fraction /m/ in the solvent

compound		m				Correction Δ
		0.4	0.5	0.6	0.7	
2	pK_a	9.33	9.61	9.99	10.32	2.01
22		9.42	9.69	10.07	10.42	2.03

Correlation parameters of pK_a – m

Compound	Correlation equation	№ equation	r	s
2	$pK_a=7.98\pm0.08+(3.35\pm0.15)\cdot m$	1	0.996	0.03
22	$pK_a=8.04\pm0.09+(3.38\pm0.16)\cdot m$	2	0.997	0.02

group of these compounds for ionization in water. Therefore, on the example of methylamide /series A, compound 2/and the benzylidenehydrazides /series D, compound 22/ of succinic acid p-toluenesulfohydrazide we have studied the dependence of pK_a on the dioxane part by weight /m/ in the solvent and the equations of this dependence /Table 2/ have been obtained.

The found corrections Δ which characterize the change in the pK_a values of methylamide 2 and hydrazone 22 when passing over from water to 60% aqueous dioxane were applied to calculate the pK_a values of acid ionization in water and other compounds of series A and D /Table 1/. The calculated pK_a values are close to the values of ionization constants of succinic acid hydroxyamides and hydrazides in water which were obtained experimentally. This indicates that the ionization mechanism of the sulfohydrazide group in water and in 60% aqueous dioxane is homogeneous for all the compounds studied.

The nature of the radical in the amide and hydrazide fragments of molecules does not exert influence on the ionization of the sulfohydrazide group due to the considerable remoteness of these substituents from the reaction center.

The constant values of the acid ionization of methylamides, hydroxyamides, hydrazides and benzylidenehydrazides of succinic acid arensulfohydrazides depend largely on the electronic nature of the substituents in the benzene ring of the sulfohydrazide part of the molecule. The quantitative estimation of this dependence was carried out according to the Hammett equation /Table 3/. The value of the σ-constant is taken from[2].

Existance of linear correlation between pK_a values and the Hammett σ-constants most probably related with the fact, that reaction centre /α-atom of nitrogen of the sulfohydrazide group/ is connected with the substituents in the benzene ring by direct polar conjugation.

Table 3

The parameters of the correlation dependence of the pK_a values on the Hammett σ-constants for the substituted hydrazides of arensulfohydrazides of succinic acid and its derivatives

series	correlation equation	№ equation	r	s
A	$pK_a=9.73\pm0.03-(1.34\pm0.07)\cdot\sigma$	3	0.998	0.03
B	$pK_a=7.85\pm0.02-(1.04\pm0.04)\cdot\sigma$	4	0.998	0.02
C	$pK_a=7.89\pm0.03-(1.10\pm0.06)\cdot\sigma$	5	0.997	0.02
D	$pK_a=9.86\pm0.03-(1.21\pm0.07)\cdot\sigma$	6	0.997	0.03

The values of the reaction constants for equations 3-6 are close to each other (the tendency to an insignificent increase of ρ value observed in 60% aqueous dioxane, eguations 3,6) which indicate that the influence of the electronic nature of substituents in the benzene ring of the sulfohydrazide part of the molecule on the ionization of the sulfohydrazide group for all the reaction series is nearly the same.

The close values of the reaction constants for the hydrazides of succinic ($\rho=1.10$; equation 3) and oxalic acids ($\rho=1.23^1$) evidence the same sensitivity of the reaction center (the sulfohydrazide group) to the polar influences of the substituents in the sulfohydrazide fragment of the molecules of both groups of substances.

EXPERIMENTAL

The pK_a values were determined by the potentiometric titration of 0.001 M of the solutions of the studied substences at 25°C on a device pH-340 in water and 60% aqueous dioxane. The glass electrode was calibrated in a water-organic solvent[3] and it was established that the electrode used in the later had a satisfactory hydrogen function. As a standard, the acid ionization constant of acetic acid was determined in 60% aqueous dioxane (pK_a exp.=7.50; pK_a=7.52 and 7.49[4]).

The pK_a values were found as pH values at the point of half neutralisation. The pK_a values presented in Table 1 are the mean values of 3-4 determinations. The mean deviations of the pK_a values do not exceed 0.09 pK_a units

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THE INFLUENCE OF THE NATURE OF THE HALOGEN ATOM IN BUTYRYL HALIDE ON THE KINETICS OF THE REACTION WITH BUTANOL IN THE PRESENCE OF ACID ADDITIONS

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The results of the catalytic influence of monofunctional and bifunctional acid additions on the rate of the reaction of butyryl halides (RCOX) with butanol have been compared. It was demonstrated that the rate constants of the reaction of acid halides with the above alcohol catalyzed by acetic acid can be described by the modified correlation equation for the departing group X. The results obtained agree with the bifunctional mechanism of carboxylic acid in the above reaction.

It has been shown earlier[1] that acetic acid which contains an electron donor (C=O) and an electron acceptor (OH) group in its molecule catalyzes the reaction of butyrylchloride with alcohol in toluene twice stronger than 3,4-dinitrophenol which is by acidity almost equal to the former and contains the OH-group only. When passing over to butyrylfluoride the catalytic activity of the same acetic acid increases greatly.

In order to investigate the mechanism of the catalytic process and particularly to reveal the contribution of the hydrogen bond in the transient state, we have devoted the present paper to the study of the kinetics of the reaction of butyrylbromide with butanol in toluene in the presence of acetic acid and 3,4-dinitrophenol additions as well as to the reaction of butyrylchloride with butanol in the presence of thioacetic acid additions.

In the course of the studied reaction:

$$RCOX + Alk\,OH \longrightarrow RCOOAlk + HX \qquad (1)$$

hydrogen halides separate, which, as is known[2], react with the alcohol. In connection with this the rate constants were calculated on the basis of initial rates.

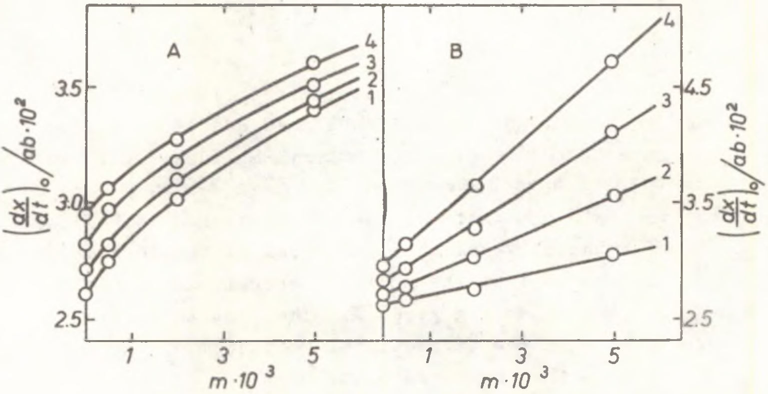


Fig. 1. The dependence of the values $\left(\frac{dx}{dt}\right)_0 / a.b\ 10^2$ (l/mol . sec) on acetic acid (A) and 3,4 dinitrophenol (B) additions m (mol/l) for the reaction of butyrylbromide with butanol at various b (mol/l)
1 -- 0.05, 2 -- 0.01, 3 -- 0.015, 4 -- 0.02.

Fig. 1. (A) presents the dependences of the values $\left(\frac{dx}{dt}\right)_0 / a \cdot b$, which are effective rate constants of the second order, on the concentration of acetic m (mol/l). Here a and b denote the initial concentrations of butyrylbromide and butanol. The above values increase with an increase in both the catalyzer and alcohol concentrations. The absence of linear dependence on the analytical concentra-

tion of acetic acid proves that the monomer form is the catalytically active one. According to the data for various alcohol concentrations we have calculated the effective rate constants of the catalytic process $k_{A,eff}$, which numerically equal the tangents of the slope angle in the points at m → 0. Fig. 2 (straight line 1) indicates that the constants $k_{A,eff}$ do not increase with an increase in alcohol concentration. Consequently, in this case only one catalytic stream occurs in which one molecule of the reagents and one molecule of the catalyzes are involved.

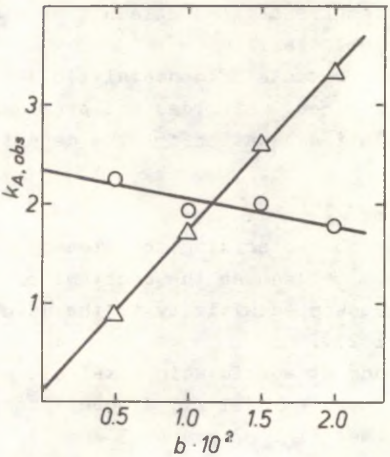


Fig.2. The dependence of the constants $k_{A,eff}$ ($l^2/mol^2.sec$) on b (mol/l) for the reaction of butyrylbromide with butanol catalyzed by acetic acid (1) and 3,4-dinitrophenol(2).

An insignificant drop in $k_{A,eff}$ is caused by the partial formation of catalytically inactive associates between the alcohol and the acetic acid. The individual rate constant for the above catalytic stream corresponds to the section k_A = = $(2.32 \pm 0.15) l^2/mol^2.sec$ intercepted by the straight line on the axis of ordinates .

The study of the catalytic influence of 3,4-dinitrophenol on the reaction of butyrylbromide with butanol was also conducted at various alcohol concentrations in the presence of different catalyzer additions. As can be seen in

Fig. 1 (B), there is a rectilinear dependence of the values $(\frac{dx}{dt})_o$ / a.b on m. The tangents of the slope angles appear to be in this case effective rate constants of the catalytic process $k_{A,eff}$. Differently from the catalysis of acetic acid, the constants $k_{A,eff}$ (Fig.2, straight line 2) increase with an increase in alcohol concentration. The intercepted section of the ordinate axis corresponds to the rate constant of the catalytic stream with the participation of one alcohol molecule and one phenol molecule $k_A = (9.20 \pm 0.56)$. (10^{-2}, l^2/mol^2 . sec) and the tangent of the slope angle corresponds to the rate constant of the catalytic stream with the participation of two alcohol molecules and one molecule of dinitrophenol $k_{A,2} = (163 \pm 4)$, l^3/mol^3.sec.

The second order rate constants of noncatalytic processes k_2 in a number of acid fluorides, chlorides and bromides can be described by the correlation equation for the departing group X^3:

$$\lg k - \lg k_{ref} = \gamma\tau \qquad (2)$$

where τ is the value characterizing the cleavage ability of the departing group; γ denotes the constant of the reaction series which expresses sensitivity to the nature of the departing group (γ =1.27).

The rate constants found at acetic acid catalysis as well as those which were found earlier for diphenylphosphoric acid[4] do not obey eq.(2) (see Fig. 3, graphs 1 and 2). It is caused by the appearance of two oppositely acting factors: on the one hand in several acylhalides of F, Cl and Br the cleavage ability of the departing group is enchanced, on the other hand - in reverse order the ability to form a hydrogen bond in the transient state increases which favors the acceleration of the catalytic process when passing over from Br to F. In this case the constants k_A could be described by the following dependence[5]:

$$\lg k - \lg k_{ref} = \gamma\tau + \varphi \cdot \varkappa \qquad (3)$$

where $\varkappa$ is the value which characterizes the influence of the ability of the departing group to form a hydrogen bond in the transition state on the catalyzer activity; ψ is the constant which characterizes the sensitivity of the given reaction series to the above property of the departing groups. As characteristics of the ability of the departing groups to form the hydrogen bond we have applied the association constants of phenol with cyclohexylhalides K_{ass} in CCl_4 at 25° [6].

As can be seen in Fig.3 (straight lines 3 and 4), dependence (3) is really observed for the reaction which is catalyzed by acetic and diphenylphosphoric acids. If the catalysis is carried out with the above acids the correlation equations are respectively as follows:

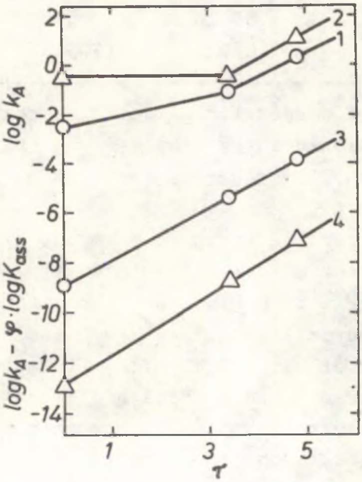


Fig.3. The dependence of lg k_A(1,2) and (lg k_A - ψ lg K_{ass}) (3,4) on the values of the departing τ groups for the reaction of butyrylhalides with butanol in toluene catalyzed by acetic and diphenylphosphoric acids.

$$\lg k_A = -8.91 + 1.07\tau + 6.68 \lg K_{ass} \quad (4)$$

$$\lg k_A = -12.9 + 1.24\tau + 13.0 \lg K_{ass} \quad (5)$$

It should be noted that the ability of the departing group X to form the hydrogen bond exerts great influence on the efficiency of the catalysis. This is proved by the data in Table which present the rate constants and their relationships characterizing catalytic activity (k_A/k_2) with regard to noncatalytic (k_2) reactions and those catalyzed by acetic acid (k_A).

Table

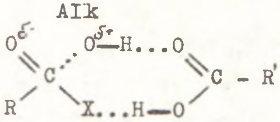
Rate Constants k_2 (l/mol . sec), k_A (l^2/mol^2.sec) and Their Relationships for the Reaction of Butanol Acylation with Butyrylhalides in the Presence of Autic Acid

Acid halides	k_2	k_A	k_A/k_2
Butyrylbromide	$2.53.10^{-2}$	2.32	90
Butyrylchloride	$1.90.10^{-4}$	$9.50.10^{-2}$	500
Butyrylfluoride	$1.79.10^{-8}$	$3.05.10^{-3}$	170000

The catalytic activity of carboxylic acid in the reaction involving acid halides is abruptly enhanced when passing over from acid bromide to acid fluoride (cf. ref.8).

If the ability of the departing group to form the hydrogen bond exerts great influence on catalysis intensity, then the ability of the catalyzer to form the above bond should also exert great influence on catalysis. We have studied the kinetics of the reaction of butyrylchloride with butanol in toluene in the presence of thioacetic acid additions which do not form a strong hydrogen bond[7]. It was proved that the latter do not accelerate the reaction , i. e. also the ability of the catalyzer to form the hydrogen bond has a major role in the given catalytic system.

Taking into account the existing data we are of the opinion that the bifunctional mechanism of carboxylic acid catalysis is more likely in the reaction where acid halides are involved.



The following circumstances speak for the bifunctional mechanism of catalysis.

Firstly, the catalytic activity of acetic acid in the reaction where butyrylchloride is involved exceeds (although not significantly, twice) the catalytic activity of 3,4-dinitrophenol which by its acidity is almost equal to the former.

Secondly, at the carboxylic acid catalysis of the reaction of butyrylhalides with alcohol the same tendency in the change of catalytic activity is manifested as in the reaction of benzoylhalides with amines where the bifunctional mechanism is simple[8].

Thirdly, the 3,4-dinitrophenol catalysis in the reaction of butyrylchloride with alcohol manifests itself in two parallel streams (with the involvement of one and two molecules of alcohol) but the acetic acid catalysis manifests itself only in the stream of one molecule of alcohol. The latter is caused by the fact that not only the hydroxyl group of the carboxylic acid but also the carbonyl group is involved in the catalytic act.

Fourthly, 3,4-dinitrophenol does not accelerate the reaction of butyrylfluoride with butanol. At present there is no definite answer to the question why this phenol does not accelerate the reaction with acid fluoride and why it does accelerate the process with the involvement of acid chloride. Nevertheless, the absence of catalysis with 3,4-dinitrophenol and the extremely high catalytic effect of carboxylic acid in the reaction with acid fluoride also agree with the bifunctional mechanism of catalysis.

EXPERIMENTAL

Toluene[9], butanol[10], acetic acid[11], 3,4-dinitrophenol[12] were purified as has been indicated earlier. Butyrylbromide[13] was purified by distillation at atmospheric pressure. Air--dry glassware was additionally dried in the vacuum box (110°,2 mm) for two hrs, before cooling dry air was introduced.

When conducting the experiment, an airtight camera dried with phosphoric pentoxide was used. The course of the process was monitored chromatographically by the bulk of forming butylbutyrate[1]. At this the reaction with the involvement of butyrylbromide (due to its high rate) was preliminarily stopped by adding an excess of toluene solution of diethylamine. The check tests proved that during the working period the bulk of the forming ether does not change in the presence of diethylamine. All the calculations were done by the least squares method. The confidence level was characterized by mean squares deviations.

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REACTIVITY OF 9-CHLORACRIDINE AND ITS DERIVATIVES

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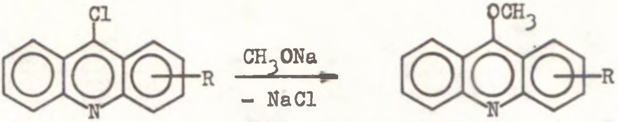
The kinetics of the reaction of 9-chloracridine with sodium methanolate in absolute methanol has been studied in the temperature range 328-346 K. The rate constants and activation energies have been calculated. The potentiometric method was applied to determine the pK_a values of 9-chloracridine basic ionization in 60% aqueous dioxane at 298 K. It is shown that chlorine reactivity in position 9 in the reaction of its nucleophilic substitution for sodium methanolate depends on the electronic nature of the substituents in the molecule of 9-chloracridines as well as on the basicity of the latter. The correlation of the logarithms of rate constants, activation energies and pK_a values was done. It was established that the studied reaction series is isokinetic.

9-chloracridines are widely applied to obtain a number of medicinal compounds, new biologically active compounds[1-3] but they are also used as analytical reagents[4]. To select the optimum synthesis conditions for 9-aminoacridine derivatives which have from the viewpoint of biology great prospects and also to provide the relative evaluation of 9-chloracridines as analytical reagents, we have studied the influence of substituents in their molecules on the reactivity of chlorine in position 9. To solve this problem, we have applied the reaction of nucleophilic substitution for sodium methanolate in absolute methanol:



$R = H, CH_3, OCH_3, NO_2$.

The chloride-ion which separates as a result of the reaction was determined by the method of Vohlhard[5]. The choice of sodium methanolate as the nucleophilic reagent was conditioned by its considerable reactivity as well as by the data that its interaction with aromatic halogen derivatives, differently from the reaction with amines[6], is not complicated by autocatalysis. In kinetic studies we used the methods which have been applied to study the reactivity of 4-chloroquinolines and 9-chloro-ß-quinindanes[7].

The reaction of 9-chloroacridines with sodium methanolate is irreversible, it proceeds with the formation of 9-methoxysubstituted acridines (Table 1) and obeys the second order kinetic reaction, which is proved by the constancy of rate constants (Table 2) calculated according to the equation:

$$k = \frac{2.303}{t(a-b)} \cdot \lg \frac{b(a-x)}{a(b-x)} ,$$

where k is the rate constant of the reaction (mol^{-1}, sec^{-1});

a,b are the initial concentrations of sodium methanolate and corresponding 9-chloracridines (M);

x is the concentration of 9-methoxyacridines (M) after moment t (sec).

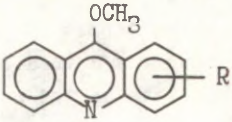
The reaction under discussion obeys the Arrhenius equation, since for 2-methyl-9-chloracridine the equation has the following formula:

$$\lg k = 10.36 - \frac{44.13 \cdot 10^2}{T} \quad (r = 0.996).$$

The existence of a linear dependence between the loga-

Table I

9- methoxyderivatives Of Acridine

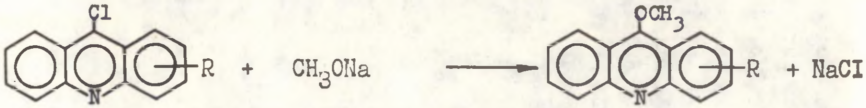


Value R[x]	Yield per cent	Melting point °C	Found, % :N	Brutto-formula	Calculated, % :N
2-CH_3	84	80-3	6,39	$C_{15}H_{13}NO$	6,27
4-CH_3	78	83-5	6,32	$C_{15}H_{13}NO$	6,27
2-Cl	76	127-8	5,82	$C_{14}H_{10}ClNO$	5,74
4-Cl	73	108-110	5,86	$C_{14}H_{10}ClNO$	5,74
2-OCH_3	86	150	5,97	$C_{15}H_{13}NO_2$	5,85
4-OCH_3	82	105-6	5,88	$C_{15}H_{13}NO_2$	5,85

x) Benzene served as the solvent for crystallization

Table 2

Kinetic And Thermodynamic Reaction Parameters



R	$K \cdot 10^2$, mol^{-1} sec^{-1}				E_a kJ/mol
	328 K	333 K	342 K	346 K	
H	0.262 ± 0.002	0.408 ± 0.019	0.815 ± 0.066	1.402 ± 0.028	72.52
2-CH$_3$	0.068 ± 0.004	0.124 ± 0.008	0.247 ± 0.020	0.323 ± 0.032	77.36
4-CH$_3$	0.033 ± 0.006	0.062 ± 0.002	0.127 ± 0.005	-	75.29
2-Cl	0.832 ± 0.013	2.604 ± 0.194	4.550 ± 0.307	-	58.59
4-Cl	0.720 ± 0.005	I.693 ± 0.138	2.921 ± 0.203	-	57.27
2-OCH$_3$	-	0.043 ± 0.007	0.091 ± 0.004	0.126 ± 0.002	78.71
4-OCH$_3$	-	0.055 ± 0.005	0.117 ± 0.002	0.188 ± 0.004	79.26
2-NO$_2$	13.687 ± 0.021	53.214 ± 1.051	78.060 ± I.820	-	40.23

rithms of rate constants and the inverted temperature values enabled us to calculate the activation energy of the interaction of 9-chloracridines with natrium methanolate which is presented in Table 2.

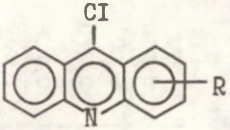
The values of the rate constants of the studied reaction depend on the nature and position of the substituent in the molecule of 9-chloracridine. The introduction of electron acceptor substituents (the NO_2 group in particular) into the latter will result in a significant increase in the reactivity of 9-chloracridines. The electron donor substituents exert an opposite effect. The established regularity proves that the reaction rate of the nucleophilic chlorine substitution for **sodium** methanolate is determined mainly by electron density at the reaction center.

The electron density at the carbon atom in the 9th position of the acridine cycle which determines the reactivity of 9-chloracridines is related to the basicity of the latter which is confirmed by the existence of a linear correlation between the logarithms of the rate constants and the pK_a values (Tables 3 and 4). 9-chloracridines which contain methoxygroups in positions 2 and 4 manifest more basic properties. The substitution of the latter for electronegative atoms of chlorine leads to a decrease in the basicity of the above substances. Due to the low solubility of 2-nitro-9-chloracridine in 60% aqueous dioxane we could not measure its pK_a value. It was calculated in accordance with the dependence equation $lgk-pK_a$ (Table 4). obtained by the least squares method.

The logarithms of the rate constants of the studied reaction, the activation energies (E_a) and the pK_a values of basic ionization are in correlation for 2-derivatives with the constants of quinoline substituents[8] and for 4-derivatives with σ constants of acridine substituents found earlier[9] (Tables 3 and 4). The values of the reaction constants (5.575 and 5.471) in equations 1 and 2 (Table 4) evidence the high sensitivity of the studied reaction se-

Table 3

Ionization Constants For 9-chloracridine And Its Derivatives



R	pK_a in 60 per cent aqueous dioxane	Parameters of correlation dependences $pK_a^{*}-\sigma$
H	3.29*	$pK_a = 3.34 \pm 0.03$ $-(1.98 \pm 0.21)\ \sigma$; r= 0.998. S = 0.03
2-CH_3	3,38	
4-CH_3	3,45	
2-Cl	3.10	
4-Cl	3.06	
2-OCH_3	3.56	
4-OCH_3	3.52	
2-NO_2	2.68**	

* The mean deviations of pK_a values do not exceed 0.08 units.

** Calculated according to eq. (4) of the dependence lgk us pK_a (Table 4).

Table 4

The Parameters Of The Correlations lgk and E_A and σ - constants, lgk^{341} us lgk^{333} and lgk^{333} us pK_a For The Reaction Of 9-chloracridine And Its Substituents With Sodium Methanolate

The correlation equation of the reaction	r	S	№ Equation
$lgk^{333} = -2.692 - 0.120 + (5.575 \pm 0.308) \cdot \sigma$	0.992	0.058	1
$lgk^{342} = -2,399 \pm 0,082 + (5.471 \pm 0.436) \cdot \sigma$	0.993	0.091	2
$E_A = 71,20 \pm 0,67 - (71.80 \pm 3.32) \cdot \sigma$	0.980	0.570	3
$lgk^{333} = 9.505 \pm 0.119 - (3,643 \pm 0.216)\ pK_a$	0.984	0.118	4
$lgk^{342} = -0.139 \pm 0.011 + (0.937 \pm 0.031) lgk^{333}$	0.992	0.009	5
T isokin. = 528.2 K			

ries to the polar influences of the substituents. The positive values of the reaction constants reinforce the conclusion that a decrease of electron density in the reaction center will lead to an increase in the reactivity of the substances under discussion.

The existence of a linear dependence between the logarithms of the rate constants at various temperatures (equation 5 Table 4) indicate, that the studied reaction series is an isokinetic one[10]. The isokinetic temperature (528.2K), calculated from eq.(4) lies above the temperature range in which the kinetic studies were carried out. It proves that with an increase of the temperature the sensitivity of the reaction to structural changes in the molecule decreases.

EXPERIMENTAL

The Methods For The Study Of The Reaction Kinetics Of 9-chloracridines With Sodium Methanolate.

In a 50 ml measuring flask pulves of 9-chloracridines are dissolved in 30-40 ml of absolute methanol in the cold, the calculated amount 0.01 M of sodium methanolate is added in absolute methanol and it is increased up to the mark by methanol.

5 ml of the prepared solution of the reaction mixture is placed in glass ampules, they are sealed up and plunged into the thermostat with the accuracy of temperature regulation ± 0.1°C. The concentrations of chloracridines ranged 0.001-0.025 M and that of sodium methanolate from 0.00408 to 0.108 M. As the beginning of the reaction we took the moment the ampule was plunged into the thermostat.

After a certain period of time the ampule is cooled down and its contents is transferred into 10 ml of 0.3 normal solution of nitric acid. The contents of the chloride ion were determined according to Vohlhard. When calculating the rate constants we took the mean values of three tests as the final results, each of the tests included eight measurements. The accuracy of the obtained rate constants was estimated by the method of mathematical statistics (the confidence level being 0.95)[11].

Potentiometric titration was carried out with the help of a potentiometer pH-340 with glass and chlorargentite electrodes in 60% aqueous dioxane at 298 K. The pK_a value was calculated as pH in the point of 50% neutralisation.

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TRANSESTERIFICATION OF ESTERS OF CARBOXYLIC ACIDS BY TITANIUM ALCOHOLATES

II. Transesterification of Esters of Aromatic Acids

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Transesterification kinetics of butylic esters of three meta-substituted benzoic acids has been studied in heptane in the temperature range from 25 to 75°C. It is proved that a two-factoral regression model with a cross term present adequately describes the acyl group substituent and temperature effect upon the reactivity of butyl benzoates in this reaction.

In the first paper of this series[1] it has been established that the transesterification by titanium alcoholates can be used as a model reaction when studying the influence of structural factors, solvent and temperature on the reactivity of esters in aprotic solvents. The reaction under discussion is of the second order (the first in each reagent) and is not complicated by side reactions. The subject of the present study is the transesterification kinetics of butylic esters of meta-substituted benzoic acids. The kinetics of this reaction for esters $XC_6H_4C(O)OBu$ (X=H,m-Cl, m-NO_2) has been studied in heptane at temperatures 25,50 and 75°C. The choice of substituents in benzoates and temperatures of kinetic measurements corresponds to the wide enough ranges of the variation of the polar substituent constant σ^0 and temperature achieved by the minimum number of experiments.

EXPERIMENTAL

Reagents. Heptane was shaken with the mixture of concentrated sulphuric and nitric acids, washed with water and redistilled over calcium hydride in the atmosphere of dry argon. It was stored over granules of molecular sieves 4 Å. The esters were prepared from butanol and the corresponding acid, their purity was not less than 98% (GLC). The preparation and purification of sec-butyl orthotitanate has been reported earlier[1].

Kinetic measurements. The methods of carrying out the kinetic runs, GLC analyses as well as the calculation of rate constants have been published in the first report of this series[1]. The conditions of GLC analysis are listed in Table 1.

Table 1.

Conditions of GLC Analysis (glass column 0.3x300 cm, 7% fluoro-silicone elastomer SKTFT-100 on a support Chromaton-N Super, carrier-gas-nitrogen).

Ester	Internal standard	Column temperature
Butyl benzoate	Diphenyl methane	182°C
Butyl m-chlorobenzoate	Fluorene	190°C
Butyl m-nitrobenzoate	Triphenyl methane	240°C

RESULTS AND DISCUSSION

The kinetic data for the transesterification of three substituted butyl benzoates by sec-butyl orthotitanate in heptane were obtained at 25,50 and 75°C. The pseudo-first-order conditions were granted by the use of a large (not less than 20-fold) excess of orthotitanate. The first-order rate constants 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. 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. Therefore the kinetic measurements were carried out at 2-3 concentrations of ortho-titanate and the second-order rate constants were calculated as follows:

$$k_{II} = k_I / \sigma_{Ti}$$

The rate constants obtained are listed in Table 2.

Table 2

Rate Constants of Transesterification of Meta-Substituted Butyl Benzoates $XC_6H_4C(O)OBu$ by Sec-Butyl Orthotitanate $Ti(OBu^S)_4$ in Heptane.

	X	t, °C	$c_{Ti,M}$	$10^4 . k_I$, s^{-1}	$10^4 . k_{II}$, $M^{-1} . s^{-1}$	$10^4 . (k_{II} \pm S)$, $M^{-1} . s^{-1}$
1	2	3	4	5	6	7
0	H	25.0	0.0342	0.0211	0.618	0.643±0.015
I		25.0	0.0635	0.0420	0.661	
2		25.0	0.0868	0.0556	0.641	
3		25.0	0.1068	0.0695	0.651	
4		25.0	0.1068	0.0696	0.652	
5		25.0	0.1068	0.0680	0.697	
6	H	50.0	0.1050	0.333	3.17	3.25±0.07
7		50.0	0.1050	0.347	3.30	
8		50.0	0.1050	0.344	3.28	
9	H	75.0	0.0486	0.561	11.55	12.08±0.46
10		75.0	0.0486	0.615	12.66	
II		75.0	0.1016	1.213	11.94	
12		75.0	0.1016	1.235	12.16	
13	m-Cl	25.0	0.0868	0.156	1.80	1.90±0.18

Table 2 continued

1	2	3	4	5	6	7
14		25.0	0.0868	0.159	1.83	
15		25.0	0.0342	0.0739	2.16	
16		25.0	0.0635	0.114	1.80	
17	m-Cl	50.0	0.1050	0.770	7.33	7.58±0.38
18		50.0	0.1050	0.776	7.39	
19		50.0	0.0502	0.409	8.14	
20		50.0	0.0502	0.374	7.44	
21	m-Cl	75.0	0.0486	1.171	24.09	25.20±0.99
22		75.0	0.1016	2.642	26.00	
23		75.0	0.1016	2.591	25.50	
24	m-NO_2	25.0	0.0518	0.219	4.22	4.33±0.08
25		25.0	0.0518	0.228	4.40	
26		25.0	0.1083	0.474	4.38	
27		25.0	0.1083	0.470	4.34	
28	m-NO_2	50.0	0.0502	0.762	15.17	16.23±0.76
29		50.0	0.0502	0.837	16.67	
30.		50.0	0.1050	1.770	16.86	
31	m-NO_2	75.0	0.0486	2.638	54.29	50.99±2.63
32		75.0	0.0486	2.518	51.82	
33		75.0	0.1016	4.910	48.33	
34		75.0	0.1016	5.031	49.52	

Activation parameters calculated by the least squares method, are listed in Table 3.

Table 3

Activation Parameters of Transesterification
of Butylic Esters of Meta-Substituted Benzoic Acids
$XC_6H_4C(O)OBu$ in Heptane (at 25°C).

X	log A	E, $\frac{kcal}{mole}$	$\Delta H^{\neq}$ $\frac{kcal}{mole}$ *	$\Delta S^{\neq}$, entr. un.*	$\Delta G^{\neq}$, $\frac{kcal}{mole}$ *
H	4.70±0.06	12.14±0.09	11.55	39.0	23.18
m-Cl	4.11±0.13	10.70±0.19	10.11	41.7	22.55
m-NO_2	4.09±0.09	10.18±0.12	9.59	41.8	22.05

* calculated from the values of E and log A.

The values of the activation entropy are more negative by 15-20 e.u. than it is observed for the hydrolysis[2] and alcoholysis (transesterification)[3] of benzoic esters. The figures obtained are close to the result obtained for the transesterification of butyl chloroacetate by sec-butyl orthotitanate ($\Delta S^{\neq} = -42$ e.u.[1]).

The statistical treatment of the data has been carried out by using a program written for the computer Nairi-3 by one of the authors of the present report. This program is based on the modified algorithm. The preliminary automatic exclusion of the statistically nonsignificant argument scales is carried out granting minimally required orthogonality of these scales. The subsequent exclusion of argument scales is based on the comparison of the ratios of the determinants of two correlation matrices. One of them includes the row and column constituted from the correlation coefficients of the vector of the measured values (log k) with argument vectors and the other does not. The changes in this ratio due to the exclusion of the argument scales by turns have been used as a relative criterion for statistical significance levels of the scales excluded. The resulting set of scales includes only those significant on the level

0.95 and meeting the orthogonality requirement. As a criterion of satisfactory orthogonality the relationship

$$s_j^{\circ} < s_{\circ} ,$$

is employed, where so is the normalized standard deviation from the hyperplane of the regression and s_j° is the normalized* standard deviation for j-th regression coefficient. Out of the scales for which this condition does not hold the one corresponding to the maximum relative value of its standard deviation has to be excluded.

The resulting general degree of orthogonality of argument scales is represented by the trace SP of the inversed correlation matrix which is equal to the ratio of the sum of the squares of the normalized standard deviations of the coefficients and the square of the normalized general standard deviation:

$$SP = \sum_j (s_j^{\circ})^2 / s_{\circ}^2$$

The relative goodness of the correlation is characterized by $s_{\circ}$ and KEF[4]:

$$KEF = 1 / s_{\circ} F (f_1, f_2) ,$$

where F is the Fisher criterion,
$f_1 = m-1$; $f_2 = m-n-1$; m-number of experimental points,
n - number of coefficients

The absolute level of adequacy of the description is represented, as usual, by the value S of the standard deviation from the hyperplane of the regression, scaled as the original values to be correlated (log k).

Several progressively decreasing significance levels may be used for the exclusion of significantly deviating points according to the Student criterion. In this work the sequence of levels 0.99; 0.97 and 0.95 was chosen.

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* The normalization was obtained by the division of the corrected values and arguments by the square roots of the corresponding dispersions.

A more detailed description of the algorithm and program will be published separately.

The combined influence of the structure of a ester and temperature on the rate of the process studied can be described by a non-additive equation (1):

$$\log k = \log ko + a_1 \cdot \sigma^0 + a_2 . 1000/T + a_{12} . \sigma^0 . 1000/T \quad (1)$$

Two sets[5] of σ^0(Table 4) were used for data treatment:

a) σ^0_{rec} (calculated proceeding from three certain reference data sets)

b) σ^0_{av} (averaged figures obtained from the data processing for 34 different reaction series)

Table 4.

Alternative Values of σ^0 Used in Correlations.

R	σ^0_{rec}	σ^0_{av}
H	(0)	(0)
m-Cl	0.37	0.39
m-NO_2	0.71	0.69

Table 5 lists the results of data processing according to eq.(1) (position numbers 1. and 2.). In both cases the significantly deviating point no. 15 (Table 2) was excluded. The term $a_1 \cdot \sigma^0 (\equiv \rho \cdot \sigma^0)$ turned out to be statistically insignificant and the result obtained corresponds to the isoentropic substituent effect. Both regressions are characterized by high statistical indices.

The alternative (additive) model without the cross term was tested as well. The latter corresponds to the isoenthalpic substituent effect. The corresponding results are represented in rows 3. and 4. of Table 5. One can conclude that the first (non-additive) scheme indeed corresponds to the significantly better statistics than the additive one. Since

Table 5

Coefficients and Statistics of the Correlation of the Rate Constants for Transesterification of Meta-Substituted Benzoic Esters $XC_6H_4C(O)OBu$ by $Ti(OBu^5)_4$ in Heptane with Equation (1).

No	σ^o	l_gk_o	a_1	a_2	a_{12}	$n(n_o)$	s	s_o	SP	KEF
1.	σ^o_{rec}	4.37±0.07	0	-2.55±0.02	0.329±0.004	34(35)	0.024	0.040	0.059	289
2.	σ^o_{av}	4.36±0.07	0	-2.55±0.02	0.337±0.005	34(35)	0.026	0.044	0.059	243
3.	σ^o_{rec}	3.99±0.13	1.03±0.03	-2.42±0.04	-	35(35)	0.045	0.075	0.057	83.2
4.	σ^o_{av}	3.98±0.13	1.05±0.05	-2.42±0.04	-	35(35)	0.045	0.075	0.057	84.3
5.	σ^o_{rec}	-4.19±0.01	1.17±0.01		(298.2K)	13(14)	0.011	0.032	0.077	273
6.	σ^o_{av}	-4.19±0.01	1.20±0.01		(298.2K)	13(14)	0.012	0.033	0.077	249
7.	σ^o_{rec}	-3.49±0.01	0.98±0.02		(323.2K)	10(10)	0.019	0.069	0.100	50.7
8.	σ^o_{av}	-3.50±0.03	1.01±0.03		(323.2K)	10(10)	0.024	0.088	0.100	31.2
9.	σ^o_{rec}	-2.92±0.02	0.88±0.02		(348.2K)	11(11)	0.018	0.068	0.091	54.5
10:	σ^o_{av}	-2.93±0.03	0.90±0.02		(348.2K)	11(11)	0.024	0.092	0.091	30.2

So for correlations 1. and 2. (Table 5) only slightly exceeds the standard deviation of the experimental data in normalized scale $S_o^{exp} = 0.037$, these equations adequately describe the substituent and temperature effects on the process under discussion and the latter belongs to the isoentropic reaction series.

In Table 5 the results of the treatment of the experimental data according to the Hammett-Taft equation ($\log k = \log k_o + a_1 \sigma^o$) are listed as well (position numbers 5-10, see also Fig. 1).

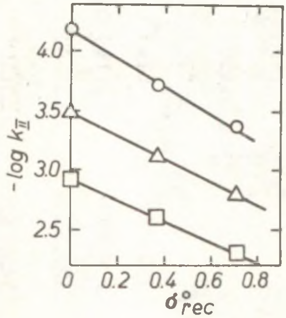

Fig. 1. Plot of $\log k_{II}$ vs. σ^o_{rec} for transesterification by sec-butyl orthotitanate in heptane at temperatures 25(O), 50 (△) and 75°C (□).

Comparison of the values of $\rho (\equiv a_1)$ to the corresponding values for base-catalysed transesterification (ethanolysis[3], $\rho_{25^o} = 2.53$) shows, that transesterification by titanium alcoholates is less sensible to substituent inductive polar effect and its transition state is obviously less polar.

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AB INITIO SELF-CONSISTENT REACTION FIELD CALCULATIONS
III. MOLECULAR IONS.

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The results of ab initio self-consistent reaction field calculations of the molecular ions H_3O^+, OH^-, FO^-, CH_3O^-, and fluoro-substituted derivatives of ammonia and their corresponding protonated ions have been given. The calculations of the hydration complexes of hydroxyl and hydroxonium ions are also proceeded. Relative sensitivity to the non-specific solvation effects is estimated for the dissociation energy of simple alcohols and substituted ammonium ions.

1. Introduction.

The investigation of the solvent effects on the various properties of the molecules has an important role in the theory of chemical reactivity. In different theoretical and semiempirical descriptions these effects are mainly divided into two classes: that of (1) nonspecific macroscopic electrostatic interactions, and (2) specific short-range interactions[1,2]. During the last decade there have been several attempts to account solvent effects in quantum-chemical calculations[3-6]. Short-range specific interactions (chemical complex-formation, hydrogen bonding etc.) are usually described using the so-called supermolecule calculations, where the solute particle is surrounded by a small number of solvent molecules and the traditional SCF wavefunction is calculated for the whole system. Macroscopic electrostatic effects are taken into account in the framework of Kirkwood's reaction field model[7].

In the first paper of this series[8] an ab initio self-consistent reaction field (SCRF) method was proposed for the neutral molecular species. Here this method is extended to the interaction between ionic molecules and dielectric medium.

Following the classical Kirkwood theory the modified hamiltonian for the molecular ion in the homogeneous dielectric medium can be written as[3]:

$$\hat{H} = \hat{H}_o + \hat{U}_o \ , \qquad (1)$$

where H_o denotes the hamiltonian of the isolated molecule, and the operator

$$\hat{U}_o = -\frac{1}{2} \quad \frac{Q^2}{2} \left(\frac{\varepsilon - 1}{\varepsilon} \right) + \frac{2(\varepsilon - 1)}{2\varepsilon + 1} \quad \frac{\hat{\mu}^2}{a_o^3} \qquad (2)$$

describes its interaction with the reaction field in the medium of dielectric permittivity ε. It is also assumed that the solute particle is embedded in solvent into a cavity of radius a_o, and whereas having a total ionic charge Q, it is also characterized by the dipole moment operator . The Roothaan-Hall -type equations are iteratively solved using the following modified one-electron hamiltonian[4]:

$$\hat{H}(\Phi) = \hat{H}_o + \bar{\bar{g}} \cdot \vec{r} \cdot \langle \Phi | \hat{\mu} | \Phi \rangle \qquad (3)$$

where $\bar{\bar{g}}$ denotes the tensor of reaction field permittivity:

$$\bar{\bar{g}} = \frac{2(\varepsilon - 1)}{(2\varepsilon + 1)a_o^3} \ , \qquad (4)$$

$\vec{r}$ is the radius-vector of an electron and Φ is the molecular wavefunction at the previous steps of self-consistent field iteration. The total energy of a molecule which consists of M nuclei with the radius-vectors $\vec{R}_\nu$ and charge Z_ν , is expressed by the following formula:

$$E_{tot} = E_{el} + \bar{g} \sum_{\nu}^{M} Z_\nu \cdot \vec{R}_\nu \cdot \langle \Phi | \hat{\mu} | \Phi \rangle + \sum_{\nu<\mu} \frac{Z_\mu \cdot Z_\nu}{|R_\mu - R_\nu|} - \frac{Q^2}{2a_0}\left(\frac{\varepsilon - 1}{\varepsilon}\right) \quad (5)$$

Here the electronic energy is:

$$E_{el} = \sum_{ij} P_{ij} H_{ij} + \frac{1}{2} \cdot \sum_{ijkl} P_{ij} P_{kl} \left[2(ij/kl) - (ik/jl) \right], \quad (6)$$

P_{ij} are the elements of the density matrix, (ij/kl) - interelectronic repulsion integrals, and

$$H_{ij} = \langle i / \hat{H}_{core} / j \rangle + \bar{g} \cdot \langle i / \vec{r}_1 \cdot \langle \Phi | \hat{\mu} | \Phi \rangle / j \rangle \quad (7)$$

denote the elements of the modified core hamiltonian matrix.

The above-described computational scheme is realized as a modification of the standard ab initio GAUSSIAN 70 program[9], which allows to proceed the calculations using simple STO-N6 and extended N-31G bases.

2. Results.

a) Simple molecular ions.

Numerical data of the SCRF LCAOMO calculations of the H_3O^+, OH^-, FO^-, and CH_3O^- ions are given in Tables 1-4. The value of the solvent dielectric constant corresponding either to the gaseous phase ($\varepsilon = 1$), 1,4-dioxane(ε=2.209[10]), ethanol (ε=20.74[10]) or water (ε= 80,1[10]) were assumed in the calculations. The cavity radii for these ions were calculated from the van der Waals radii of the individual atoms or from their molecular refractions. The following numerical values were used for different molecular ions:

a_o = 1.95Å for H_3O^+
a_o = 1.41Å for OH^-
a_o = 1.95Å for FO^-
a_o = 2.25Å for CH_3O^-

Full bondlength optimization was carried out for the first three species, for the methoxede-ion STO-3G the optimum geometry of the isolated molecule was assumed (l_{CO}= =1.43Å, l_{CH}=1.083Å, ∠HCO=110° ,∠HCH=107.92°). STO-3G basis was used throughout the calculations. For the H_3O^+ ion the dependence of the molecular properties on the basis set size was also examined.

b) Solvational complexes.

The results of the SCRF LCAOMO calculations of the complexes $H_3O^+(H_2O)_3$, $OH^-(H_2O)_4$, and $H_2O(H_2O)_4$ using STO-3G basis set are produced in Table 5. The value of the dielectric constant of the medium was taken to be equal either ε =1 (gaseous phase) or ε =80.1 (the water). The pyramidal structure, i.e. three water molecules bound to the three hydrogen atoms of the hydroxonium ion, was assumed for the complex $H_3O^+(H_2O)_3$. The complexes $OH^-(H_2O)_4$ and $H_2O(H_2O)_4$ were expected to have the tetrahedral ice-like structure. The cavity radius for all complexes was a_0= 4.564Å.

c) Fluoro-substituted derivatives of ammonia and ammonium ions.

The numerical data of the SCRF LCAO MO calculations of the molecules NH_3, NH_2F, NHF_2, and NF_3, and the corresponding protonated ions NH_4^+, NH_3F^+, $NH_2F_2^+$, and NHF_3^+ are presented in Tables 6-9. Instead of the simple STO-3G basis an extended 4-31G basis was used throughout these calculations. One of the following values was given to the dielectric constant of the medium: ε =1 (gaseous phase), ε =2.209 (1,4-dioxane), ε =48.9 (dimethyl sulfoxide), or ε =80.1 (the water). The cavity radius for every species was taken equal to a_0=3Å. For the neutral molecules (except NF_3, which has planar geometry) the pyramidal structure and for the protonated ions the tetrahedral structure was assumed. Optimum SCF bondlengths were used for every molecule.

Table 1.

The results of the SCRF LCAO MO calculations on the H_3O^+ ion [a]

Dielectric constant of the medium	Basis set	Configuration	Total energy (a.u.)	Dipole moment (D)	Bondlength r_{OH} (Å)	δ_o^b	ΔF_{el}^c $(\frac{kcal}{mol})$
1 1	STO-3G	pyramidal	-75.329301	2.250	0.9934	-0.2366	(0)
		planar	-75.342027	0	0.9752	-0.2486	(0)
	4 - 31G	pyramidal	-76.1875502	2.524	0.9701	-0.6811	(0)
		planar	-76.200600	0	0.9621	-0.7495	(0)
	6 - 31G	pyramidal	-76.263057	2.524	0.9671	-0.6838	(0)
		planar	-76.276331	0	0.9612	-0.7554	(0)
2.209	STO-3G	pyramidal	-75.412113	2.265	0.9959	-0.2437	-49.30
	4-31G	planar	-76.271572	2.590	0.9776	-0.7021	-49.94
80.1	STO-3G	pyramidal	-75.480576	2.283	0.9977	-0.2533	-90.09
		planar	-75.470032	0	0.9752	-0.2486	-84.06
	4-31G	pyramidal	-76.345124	2.662	0.9829	-0.7295	-92.25
		planar	-76.334593	0	0.9629	-0.7495	-84.06
	6-31G	pyramidal	-76.421027	2.660	0.9788	-0.7330	-92.23
		planar	-76.410321	0	0.9612	-0.7554	-84.06

(a The cavity radius was equal to a_o=1.95Å (b Partial charge on the oxygen atom
(c Free energy of the electrostatic solvation

Table 2.

The results of the SCRF LCAO MO calculations on the OH^- ion(a (STO-3G basis set).

Dielectric constant of the medium	Total energy (a.u.)	Dipole moment (D)	Bondlength r_{OH}(Å)	δ_O(b	ΔF_{el} $\left(\frac{kcal}{mol}\right)$
1	-74.064663	0.5898	1.0451	-0.7577	(0)
2.209	-74.169046	0.6549	1.0551	-0.7385	-64.80
20.74	-74.248971	0.9105	1.0759	-0.7005	-113.66
80.1	-74.256438	0.9538	1.0793	-0.6942	-118.15

(a The cavity radius was equal to a_o=1.41Å

(b Partial charge on the oxygen atom.

Table 3.

The results of the SCRF LCAO MO calculations on the FO^- ion(a (STO-3G basis set).

Dielectric constant of the medium	Total energy (a.u.)	Dipole moment (D)	Bondlength r_{OF}(Å)	δ_O	ΔF_{el} $\left(\frac{kcal}{mol}\right)$
1	-171.533695	1.5718	1.2842	-0.6600	(0)
2.209	-171.619394	1.7569	1.3083	-0.6408	-47.23
20.74	-171.690174	2.1046	1.3531	-0.6063	-83.44
80.1	-171.697305	2.1717	1.3620	-0.5998	-86.86

(a The cavity radius was equal to a_o = 1.95Å.

Table 4.

The results of the SCRF LCAO MO calculations on the CH_3O^- ion$^{(a}$ (STO-3G basis set).

Dielectric constant of the medium	Total energy (a.u.)	Dipole moment (D)	δ_o	δ_c (b	ΔF_{el}
1	-112.629310	1.7975	-0.6578	-0.1334	(0)
2.209	-112.760710	2.1512	-0.6894	-0.1346	-42.93
20.74	-112.824806	2.4429	-0.7263	-0.1375	-76.87
80.1	-112.829875	2.4761	-0.7305	-0.1378	-80.05

(a The cavity radius was equal to a_o=2.25Å

(b The partial charge on the carbon atom.

Table 5.

The results of the SCRF LCAO MO calculations on the solvational complexes $H_3O^+(H_2O)_3$, $OH^-(H_2O)_4$, and $H_2O(H_2O)_4$$^{(a}$ (STO-3G basis set).

Complex	Dielectric constant of the medium	Total energy (a.u.)	Total energy of the solvational sphere(a.u.)$^{(b}$
$H_3O^+(H_2O)_3$	1	-300.341657	-224.881344
	80.1	-300.399348	-224.881448
$OH^-(H_2O)_4$	1	-373.988427	-299.792220
	80.1	-374.046939	-299.793115
$H_2O(H_2O)_4$	1	-374.851885	-299.845246
	80.1	-374.854901	-299.846091

(a The cavity radius was equal to a_o= 2.25Å

(b The energy of the complex without the central particle (H_3O^+, OH^-, or H_2O).

Table 6.

The results of the SCRF LCAO MO calculations on the molecule NH_3 and ion NH_4^+ (4-31G basis set).

Species	Dielectric constant of the medium	Total energy (a.u.)	Dipole moment (D)	ΔF_{el} (kcal/mol)
NH_3	1	-56.097263	2.109	(0)
	2.209	-56.098799	2.128	-0.539
	48.9	-56.100997	2.153	-1.198
	80.1	-56.101088	2.154	-1.213
	1	-56.455516	0	(0)
	2.209	-56.503624	0	-30.137
	48.9	-56.541907	0	-54.211
	80.1	-56.542610	0	-54.652

Table 7.

The results of the SCRF LCAO MO calculations on the molecule NH_2F and ion NH_3F^+(4-31G basis set).

Species	Dielectric constant of the medium	Total energy (a.u.)	Dipole moment (D)	ΔF_{el} (kcal/mol)
NH_2F	1	-154.751357	2.873	(0)
	2.209	-154.754580	2.940	-1.024
	48.9	-154.758724	3.024	-2.321
	80.1	-154.758790	3.025	-2.393
NH_3F^+	1	-155.057231	2.128	(0)
	2.209	-155.116850	2.187	-30.802
	48.9	-155.147232	2.262	-55.522
	80.1	-155.148465	2.264	-55.990

Table 8.

The results of the SCRF LCAO MO calculations on the NHF_2 molecule and $NH_2F_2^+$ ion (4-31G basis set).

Species	Dielectric constant of the medium	Total energy (a.u.)	Dipole moment (D)	ΔF_{el} (kcal/mol)
NHF_2	1	-253.407272	2.541	(0)
	2.209	-253.409824	2.621	-0.896
	48.9	-253.413057	2.681	-1.869
	80.1	-253.413138	2.682	-1.884
$NH_2F_2^+$	1	-253.665392	2.272	(0)
	2.209	-253.715524	2.320	-30.927
	48.9	-253.756465	2.384	-55.742
	80.1	-253.757125	2.386	-56.144

Table 9.

The results of the SCRF LCAO MO calculations on the NF_3 molecule and NHF_3^+ ion (4-31G basis set).

Species	Dielectric constant of the medium	Total energy (a.u.)	Dipole moment (D)	ΔF_{el} (kcal/mol)
NF_3	(a)	-352.062906	0	(0)
NHF_3^+	1	-352.273792	1.841	(0)
	2.209	-352.347101	1.889	-30.586
	48.9	-352.414098	1.926	-55.387
	80.1	-352.415426	1.927	-55.804

(a The molecule NF_3 has at optimum the planar structure and therefore it does not interact with the surrounding medium with the framework of SCRF model ($\hat{\mu}$ =0).

3. Discussion.

The electrostatic interaction between any ionic molecule and dielectric medium can be divided into two parts. The first term in Eq. 2. corresponds to the Born point-charge solvation energy and the second is that of Kirkwood's dipole-solvent interaction energy. The Born term does not appear in the electronic hamiltonian (cf.Eq.3.) and therefore exerts no influence on the electronic wavefunction and electronic energy. Its numerical value however is normally an order larger than that of the dipole-dielectrics interaction (See Tables 6-9 for the substituted ammonia molecules and molecular ions). Nevertheless, the latter term may have a substantial importance in the determination of the geometrical structure of a molecular ion. An interesting example of that is the hydroxonium ion, for which the ordinary ab initio SCF calculations without polarization functions give the planar structure as more stable[11]. The addition of the dipole-dielectrics interaction potential to the hamiltonian however predicts the greater relative stability of the pyramidal configuration (See Table 1.)

No doubt it is of interest to study the influence of the dielectric medium on the chemical reactivity of the molecules using quantum-chemical calculations. We have made a preliminary attempt to estimate solvent effects on one of the simplest reactions, i.e. on the protonation equilibria of organic bases. Using also the computational results from Ref.8., the reaction energies (potential energy differences between reagents and products) were calculated for the equilibria:

$$XO^- + H_3O^+ \rightleftharpoons XOH + H_2O, \tag{8}$$

and

$$NX_3 + H_3O^+ \rightleftharpoons NX_3H^+ + H_2O \tag{9}$$

The reaction energies are accordingly:

$$\Delta E_1 = E_{H_2O} - E_{H_3O^+} + E_{XOH} - E_{XO^-} \quad , \qquad (10)$$

and

$$\Delta E_2 = E_{H_2O} - E_{H_3O^+} + E_{NHX^+_3} - E_{NX_3} \qquad (11)$$

In the solvents of higher dielectric constant value the energy differences (10,11) are smaller (cf.Fig. 1 for the dissociation of alcohols), and the equilibria (9.9) are therefore shifted to the left, which fact conforms to the classical electrostatic depictions. The estimation of the relative magnitude of the electronic substituent effects in the media of different dielectric permittivity is also possible. Thus the sensitivity of the reaction energy to the substituent effects in the alcohol molecules is increasing if we reduce the dielectric constant of the medium. The difference between the reaction energies (10) for the FOH(X=F) and H_2O(X=H) molecules is 51.7 kcal/mol in the gaseous phase and only 28.4 kcal/mol in the dielectrics of ε=80.1 (that of the water). These quantities correspond to the reaction constant values ρ^*(g.p.)=19.81. and $\rho^*(\varepsilon=80.1)=$ =10.88 respectively.

An interesting example of the inversion of the substituent effects on the chemical reactivity in different media is the experimentally well-known fact about the different trends of acidities of alcohols in the gaseous phase and in water[12]. According to the computational data (cf.Fig. 1) the main reason for this phenomenon is the difference in non-specific electrostatic solvation of the alkoxy and hydroxyl ions in these media.

In fact, the alkyl groups do have significantly larger polarizability in comparison with the hydrogen or fluorine, which makes the corresponding alkoxy anions more sensitive to the stabilizing electrostatic solvent effects.

Even from the brief comparison of the calculated and

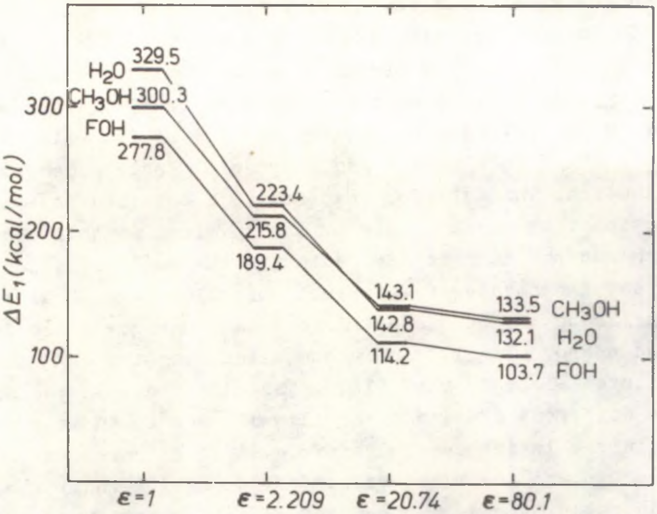

Fig. 1. Computational energies of Equilibrium (ε) for several hydroxylic compounds in the media of different dielectric permittivity.

experimental energy absolute values an essential role of the specific solvation for the protonation equilibria (8.9) can be seen. The calculated energies of the equilibrium

$$H_3O^+ + OH^- \rightleftharpoons 2H_2O \qquad (10)$$

with the inclusion of the specific solvation in the first coordination sphere around the species are given in Table 5. It follows from these results that the specific hydrogen-bonding has the effect of the same order on the energy of equilibrium (10) as the nonspecific electrostatic interaction. The respective contributions when going from the gaseous phase to liquid water are $\Delta E(\text{specific})=105.6$ kcal/mol and $\Delta E(\text{non-specific})=197.4$ kcal/mol. The calculated reaction energy in water $\Delta E\ (H_2O)= -26.5$ kcal/mol is comparable with the experimental reaction free energy $\Delta G= -24.1$ kcal/mol.

Generally two main characteristics of a molecule determine its interaction with the surrounding dielectric medium. Firstly, it is the size of the molecule, which determines the energy of "hole-formation" in the solvent. The second factor is the polarity and polarizability of the molecule, given by its dipole moment and intrensic electron density distribution. The data for reaction (9), obtained on the assumption that any molecule or ion involved in this equilibrium has the same cavity radius in the medium, indicate the great importance of the right molecular size. Really, the influence of the dielectric constant change on the calculated energy ΔE_2 (11) is much smaller than that of the substituted alcohols (ΔE_1(10)). The difference in the size of the different species in equilibrium was taken into account in the latter case. Therefore it is of paramount importance to use the right values of the cavity radii throughout the calculations. The consistent determination of these parameters in the SCRF calculations will be the object of our further investigations.

The basis set, which gives the best description of the electron distribution in the molecule should be used due to the importance of the dipole moment operator in the SCRF calculations. Also it is of significant theoretical interest to take into account the higher electrical moments (quadrupole, octopole etc.) with the dielectric medium in such calculations. The discussion of the corresponding modifications of the SCRF LCAO MO method will be published elsewhere.

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