ISSN 0206-4766

TARTU STATE UNIVERSITY

ORGANIC REACTIVITY

Vol. XXIV
ISSUE 3(87)
September 1987

TARTU

TARTU STATE UNIVERSITY

ORGANIC REACTIVITY

Vol. XXIV

ISSUE 3(87)

September 1987

TARTU

Title of original:

Реакционная способность органических соединений,
Том XXIУ, вып. 3(87), Сентябрь I987.
Тартуский государственный университет

Organic Reactivity
Vol. 24 3(87) 1987

AB INITIO SCF LCAO MO CALCULATIONS OF MOLECULES.

VI. EFFECT OF SOLVENT-SOLUTE INTERACTIONS ON STRUCTURE AND BASICITY OF ANIONS OF OH-ACIDS

I.A. Koppel
Laboratory of Chemical Kinetics and Catalysis,
Tartu State University, 202400 Tartu, Estonian S.S.R.

Received August 26, 1987

Nonempirical model calculations (supermolecular approach, STO-3G basis set, full optimization of geometry by the gradient method) were performed in order to study the effect of specific solvation on the energetic and structural characteristics of anions XO^-, their protonated forms XOH and on the corresponding hydrates $XO^-...nH_2O$ and $XOH...nH_2O$ (where $n \leq 3$; X = H, Me, Et, i-Pr, t-Bu, F, HO, O^-, H_2N, CH_2F, CF_3, CF_3CH_2, $(CF_3)_2CH$, $(CF_3)_3C$, Me_3N^+, NO_2, ClO_3 and $C(H) = C(H)NO_2$).

Specific solvation of the compounds of this type causes substantial changes in their geometry and energetics as well as in charge distribution. Relative susceptibility of a given reaction series to substitutent effects undergoes remarkable changes as a result of a gradual attachment of water molecules to the deprotonated and/or protonated forms of the base. In other words, intermolecular interactions can substantially alter not only the intensity but even the direction of intramolecular interactions. It has been shown that in the approximation used, the gas phase basicity of XO^- anions should be ≈ 2.2 times more susceptible to structural effects than that of their trihydrates, while comparison of experimentally obtained basicities in the gas phase and in water (the solvent) makes the susceptibility drop more than three times. It has been found (3-21G* basis set) that the DMSO molecules can form stable solvation complexes with the anions of F^- and OH^- types. For the latter anion, the calculated complex formation energy equals 24.3 kcal/mol.

In the Appendix information about geometry and distribution of electron density for 95 neutral and anionic species and their hydration complexes is given.

Nonempirical model calculations of the specific solvation effect on the structure and energetics of ions and neutral molecules of different classes in the "supermolecular" approximation can sometimes yield the results[1-7] which are in satisfactory agreement with the experiment. As far as the adequacy of the results and the frequency of references are concerned, the LCAO MO calculations of solvation complexes of small neutral molecules and positive ions[8-11] dominate in the literature.

Due to the importance of the problem of considering the correlation effects the calculations of structure and energetics of solvation complexes of anions are significantly less spread.

A rather limited number of small anions and their solvation (hydration) complexes[4-6, 9-14] has been discussed on various levels of one-electron approximation, or even according to the schemes taking into account the correlation energy corrections.

Analysis of the results has shown[4,9] that even at a primitive STO-3G level, the nonempirical quantum chemical theory can foretell the basic regularities of the specific solvation effect on the solvation complexes' structure and on the energetics of the proton transfer processes which they take part in. Therefore we have also made an attempt (using the nonempirical model calculation in the supermolecular approximation) to carry out a systematic study of the specific solvation effect on the energetic and structural parameters of the species participating mainly in the following transformations:

$$XOH...n(H_2O) + MeO^-...n(H_2O) \xrightarrow{PA_{XO^-...nH_2O}} XO^-...n(H_2O) + + MeOH...n(H_2O), \quad (1)$$

where $n \leq 3$, but X = H, Me, Et, i-Pr, t-Bu, F, HO, O^-, NH_2, CF_3, CF_3CH_2, $(CF_3)_2CH$, $(CF_3)_3C$, Me_3N, NO_2, ClO_3, MeCO, $C(H)=C(H)NO_2$.

Geometries of neutral molecules, anions and their hydration complexes were found using full optimization of the bond lengths as well as the valence and conformation angles. The calculations were based on the Gaussian-80[19] and Gaussian-82[20] program systems on the minimum (STO-3G) basis set. The main results are given in Tables 1-3. Some pecularities of the energetics and geometry of molecules, ions and the corresponding solvation complexes are given in the Appendix (see also reports[15,16,17]).

For the purposes of comparison, model calculations (STO-3G, 3-21G, 3-21G* basis sets) of the specific solvation effect on the structure and energetics of solvation complexes of dimethyl sulfoxide with some anions (F^-, OH^-) and neutral molecules (HF, H_2O) were performed. Essential results of these calculations are visualized in Fig. 1.

---

[*] Some of the results obtained were reflected in papers[15-18].

Table 1

Total Energies E_{tot} (STO-3G basis set, a.u.) of Nonhydrated (n=0) Neutral Molecules XOH, Anions XO$^-$, Proton Affinities (PA$_{cal}$ – present calculation, PA$_{exp}$ – experimental value) of the Latter (in kcal/mol units) and Differences of Total Formal Charges (Δq) on the Reaction Center in Protonated and Deprotonated Forms of the Base^a.

	X	$-E_{tot(XOH)}$	$-E_{tot(XO^-)}$	PA_{calc}	$-\Delta PA_{calc}$	Δq	PA_{exp}	$-\Delta PA_{exp}$
	2	3	4	5	6	7	8	9
1	H	74.9659	74.0650	565	-36.0	0.600	390.8	-11.6
2	Me	113.5492	112.7064	529	0	0.537	379.2	0
3	Et	152.1331	151.2960	526.4	2.6	0.600	376.1	3.1
4	i-Pr	190.7165	189.8840	522.2	6.8	0.490	374.1	5.1
5	t-Bu	229.2994	228.4720	519.4	9.6	0.475	373.3	5.9
6	F	172.3742	171.5531	515.4	13.6	0.600	-	-
7	HO	148.7650	147.9366	520.0	9.0	-	367.9	11.3
8	O$^-$	147.9366	146.6230	824.5	-295.5	0.571	-	-
9	H_2N	129.2631	128.4265	521.6	7.4	0.58	-	-
10.	CH_2F	211.0080	210.1961	509.6	19.4	0.55	-	-
11.	CF_3	405.9571	405.2064	470.7	58.3	0.512	348	-

Continuation of Table 1

1	2	3	4	5	6	7	8	9
12.	CF_3CH_2	444.5136	443.7170	500.0	29.0	0.490	364.4	14.8
13.	$(CF_3)_2CH$	775.4753	774.7108	479.9	49.1	0.470	347.9	31.3
14.	$(CF_3)_3C$	1106.3866	1105.6731	447.9	81.1	0.452	334.3	44.9
15.	$Me_3\overset{+}{N}$	245.4341	244.8884	342.5	186.5	0.517	235	144.2
16.	NO_2	275.6585	274.9690	432.8	96.2	0.460	324.6	54.2
17.	NO	201.9156	201.1640	471.3	57.7	-	338.3	40.9
18.	ClO_3	749.9337	749.2985	398.0	131.0	0.354	280	99.2
19.	CN	165.5112	164.8060	442.7	86.3	-	-	-
20.	MeCO	224.8102	224.0483	478.2	50.8	0.414	350.9	28.3
21.	CF_3CO	517.1805	516.4620	451.0	78.0	0.450	325.7	53.5
22.	HCO	186.2179	185.4563	478.0	51.0	0.458	347.6	31.6
23.	Ph	300.9872	301.7280	465.0	64.0	0.393	351.4	27.8
24.	$O_2NC(H)=C(H)$	350.9400						

a - See also the Appendix and [15].

Table 2

Ab initio Calculation of Energetics and Charge Distribution for Solvation Complexes Taking Part in Transfer (1).[a,b]

		$XO^-...HOH$			$XOH...OH_2$					
		$-E_{tot}$	$E_{HB(XO^-)}$	$\Delta 1$	$-E_{tot}$	$E_{HB(XOH)}$	$\Delta 2$	ΔE_{HB}	$PA_{XO^-...HOH}$	Δq_{H_2O}
1	2	3	4	5	6	7	8	9	10	11
1.	H	149.1432	70.5	–	149.9398	5.9	–	64.6	500	–
2.	Me	187.7489	48.1	0.290	188.5251	6.3	0.051	41.8	487.2	0.393
3.	Et	226.3342	45.4	0.291	227.1076	5.4	0.048	39.0	485.5	0.394
4.	i-Pr	264.9188	43.2	0.281	265.6888	4.0	0.068	39.2	483.3	0.390
5.	t-Bu	303.5023	39.2	0.266	304.2702	3.1	0.061	36.1	482.0	0.376
6.	F	246.5971	49.0	0.290	247.3540	8.7	0.068	40.3	472.6	0.427
7.	HO	222.9766	46.1	0.282	223.7430	7.6	–	38.9	481.1	0.282
8.	O^-	222.0016	(259)[c]	0.53	222.9766	46.5	–	(212.5)[c]	613	–
9.	H_2N	203.4679	47.4	0.294	204.2406	7.3	–	40.1	485.0	–
10.	CF_3	480.2163	27.6	0.182	480.9410	11.3	0.082	16.3	454.6	0.418
11.	CF_3CH_2	518.7423	37.3	0.252	519.4934	7.8	–	29.5	471.4	0.407

Continuation of Table 2

1	2	3	4	5	6	7	8	9	10	11
12.	$(CF_3)_2CH$	849.7210	27.8	0.200	850.4560	9.3	0.069	18.5	461.4	0.411
13.	$(CF_3)_3C$	1180.6723	20.9	0.154	1181.3701	11.0	0.061	9.9	438.0	0.384
14.	Me_3N^+	319.8782	15.0	0.124	320.4200	12.6	0.139	2.4	340.1	0.419
15.	ClO_3	824.2840	12.3	0.086	824.9309	19.6	0.145	-7.3	400.1	0.294
16.	NO_2	349.9690	19.6	-	350.6480	14.8	-	4.8	428.0	0.412
17.	MeCO	299.0538	25.3	0.108	299.7875	9.4	0.069	15.9	460.5	0.393

[a] Total energies (columns 3 and 6, E_{tot}, a.u., STO-3G basis set) of hydration complexes (n=1), hydrogen bond complex-formation energies (kcal/mol) for the monohydration of anions XO^- ($E_{HB(XO^-)}$, column 5) or neutral molecules XOH ($E_{HB(XOH)}$, column 7), the differences between the latter two quantities $\Delta E_{HB} = E_{HB(XO^-)} - E_{HB(XOH)}$ column 9, (in kcal/mol), and proton affinities of monohydrated anions (column 10, kcal/mol) are given. The quantity $\Delta 1$ (column 5, a.u.) characterizes the net transfer of the negative charge from the anion XO^- to the molecule of water in the hydration complex $XO^-...HOH$; the analogous quantity $\Delta 2$ is equal to the net positive charge transforred in the hydration complex $XOH...OH_2$ from XOH to the water molecule. The quantity Δq_{H_2O} is the difference between the total charge on the hydrated reaction center (O^- or OH)^2 in protonated and deprotonated forms of the base.

[b] See also Appendix. [c] Full proton transfer from H_2O molecule to O_2^{2-} anion takes place.

Table 3

Total Energies (STO-3G Basis Set, a.u.) of Hydration Complexes (n=3) from Scheme (1), the Hydrogen Bond Formation Energies (kcal/mol) Between XO^- and XOH and 3 Water Molecules (correspondingly, $E_{HB(XO^-)}$ and $E_{HB(HOH)}$ are Given in Columns 3,4,6 and Proton Affinities of Trihydrated Base XO^- are given (kcal/mol) in Column 10. The Quantities $\Delta 1$, $\Delta 2$ and Δq_{H_2O} Are Analogous to Those From Table 2.[a]

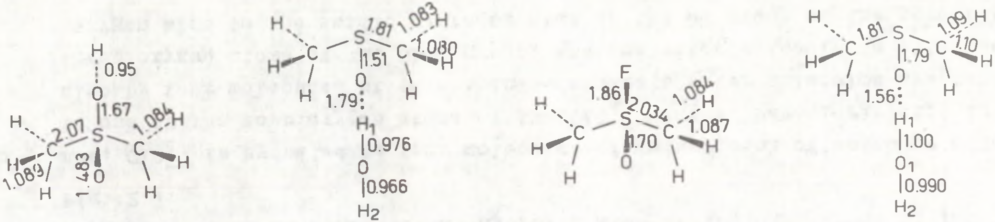
X		$XO^-...n(H_2O)$			$XOH...n(H_2O)$					
		$-E_{tot}$	$E_{HB}(XO^-)$	$\Delta 1$	$-E_{tot}$	$E_{HB}(XOH)$	$\Delta 2$	ΔE_{HB}	$PA(XO^- n(H_2O))$	Δq_{H_2O}
1	2	3	4	5	6	7	8	9	10	11
1.	H	299.1779	135.1	-	299.8860	14.1		121.0	444.5	
2.	F	396.6085	99.0	0.401	397.3115	24.9	0.120	74.1	441.3	0.387
3.	Me	337.7647	79.3	-	338.4770	18.8	0.100	60.5	447.1	-
4.	CF_3	630.2086	65.6	0.356	630.9010	29.0	0.158	36.6	434.6	0.360
5.	Me_3N^+	469.8340	30.1	0.328	470.3670	22.1	0.268	8.0	334.5	0.33
6.	ClO_3	1049.2292[b]	42.2[b]	0.26[b]	974.8962[c] 1049.8390[b]	41.8 26.2[b]	0.290	0.4	397.3 382.8[b]	-
7.	Et	376.3509	101.3	0.467	-	-	-	-	-	-
8.	Ph	525.9664	50.8		526.6577	19.7		31.1	433.9	+13.4

Table 3 continued

a - In monofunctional anions XO^- three separate molecules of water are attached to three lone pairs of oxygen (see Fig. 2, No 3), whereas in neutral molecules XOH the solvation of the latter takes part by the water trihydrate which, by its central oxygen atom, is attached to the hydrogen atom of the OH- group of XOH (see also Fig. 2.).

b - n=4; ClO_4^- is hydrated by four molecules of water, each of which is attached to one of the four oxygen atoms of the ClO_4^- anion. Perchloric acid is solvated also by four molecules of water: three separate water molecules are bonded to three oxygen atoms of the ClO_3 group, and one water molecule is attached by its oxygen atom to the acidic hydrogen atom of the OH group of the perchloric acid.

c - n=3; complex formation between the central oxygen atom of water trimer and hydrogen atom of the OH-group of the perchloric acid was assumed.



(1) (2) (3) (4)

Fig. 1. Nonempirical calculation (Gaussian-82 system) of complex formation energy.

Figure 1 continued

(1) - Between DMSO molecule and OH^- anion ($3\text{-}21G^*$ basis set) $\angle(OSO) = 108.55^\circ$, $\angle(SOH) = 103.3^\circ$, $E_{tot(complex)} = -623.7540$ a.u., $E_{tot(DMSO)} = -548.8467$ a.u., $E_{tot(OH^-)} = -74.8686$ a.u., $\Delta E = 24.3$ kcal/mol;

(2) - Between molecules of DMSO and H_2O ($3\text{-}21G^*$ basis set); $\angle(CSO) = 103.5^\circ$, $\angle(SOH1) = 109.9^\circ$, $\angle(H1OH2) = 107.6^\circ$, $E_{tot(complex)} = -624.4420$ a.u., $E_{tot(H_2O)} = -75.5860$ a.u., $\Delta E = 5.9$ kcal/mol;

(3) - Between molecule of DMSO and F^- anion (STO-3G basis set); $\angle(FSO) = 86.0^\circ$, $\angle(FSC) = 131.0^\circ$, $q_F = -0.496$, $q_S = 0.638$, $q_O = -0.513$, $q_C = -0.3103$, $E_{tot(complex)} = -642.8470$ a.u., $E_{tot(DMSO)} = -545.1921$ a.u., $q_S = 0.4063$, $q_C = -0.2687$, $q_O = -0.372$ $E_{tot(F^-)} = -97.6133$ a.u.; $\Delta E = 26.1$ kcal/mol.

For the complex between molecules of DMSO and HF (STO-3G basis set) $E_{tot(complex)} = -643.7841$ a.u., $q_S = 0.442$, $q_C = -0.267$, $q_O = -0.368$, $q_H(HF) = 0.212$, $q_F = -0.316$, $E_{tot(HF)} = -98.5729$ a.u., ($q_H = 0.210$, $q_F = -0.210$) $\Delta E = 12.1$ kcal/mol

(4) - Between molecules of DMSO and H_2O (STO-3G basis set): $\angle(CSO) = 103.5^\circ$, $\angle(SOH1) = 103.61^\circ$, $\angle(H1OH2) \approx 101.0^\circ$, $q_{O_1} = -0.4073$, $q_O = -0.379$, $q_S = 0.444$, $q_C = -0.2658$, $q_{H_1} = 0.202$, $q_{H_2} = 0.1205$, $E_{tot} = -620.1725$ a.u., $E_{tot(H_2O)} = -74.9659$ a.u., $\Delta E = 9.1$ kcal/mol, $\mu = 5.7D$

Discussion

Analysis of these results of nonempirical quantum chemical model calculations of the effects of both specific (this report and[1,8,15,17,18]) and nonspecific solvation[21] on the structure and energetics of ions and neutral molecules of various classes shows that in both cases transition of the particle which is not solvated in the gas phase into the solution is accompanied by remarkable changes both in the structure (bond lenths, the charge of the effective radius of the reagent, etc.) and charge distribution. The changes are especially significant in the case of ionic molecules. The present data (see the Appendix) refer to the effect of stepwise attachment of water molecules to some anions (alkoxide ions, perchlorate, etc.) and to their conjugated acids in the gas phase. Evidently, (see Tables 2,3) the anion hydration is generally followed by the charge transfer from the oxygen atom of the anion as well as from the latter as a whole to the water molecule. In this case the level of the charge transfer (Δ_1) from the ion to the water molecule depends both on the nature of the ion and on the number of molecules of the solvent in the hydration cell of the latter. For instance, according to calculations, the Mulliken charge on the oxygen atom of the EtO^- anion (-0.625) decreases on additon of the 1st H_2O molecule to -0.515 charges of the electron whereas (see the Appendix, Nos 30, 32) two more water molecules initiate a further drop to -0.468, while at protonation it equals -0.300 a.u. (see the Appendix, Nos 34,30). The charge transfer to the solvent molecules is smaller, for example in the case of hydration of the acetate ion, CF_3O^-, $(CF_3)_2CHO^-$, $(CF_3)_3CO^-$, Me_3NO (see the Appendix, Nos 43, 45, 47, 53, 55, 57, 59, 67 - 70, 75 - 79) and especially in the case of the phenolate and perchlorate ions (see the Appendix, Nos 82-84,87), characterized by the extensive internal charge delocalization and by a comparatively low basicity. On the other hand, "hydration" of superbase O_2^{2-} is accompanied by a full charge transfer from the latter to the H_2O molecule and leads to a full proton transfer from H_2O to the base ($O_2^{2-} + H_2O \longrightarrow HOO^- + HO^-$ (see Table 2, No 8 and the Appendix, No 17). We should also like to pay attention to the charge transfer in the case of small hard single-atom anions. Thus, for the F^- (STO-3G calculations), the Δ_1 value for the transition of the negative charge to the water molecule (Appendix, No 95) is 0.466 a.u., while in the case of the charge transfer to the DMSO molecule (Fig. 1, No 3) this value is equal to 0.504 a.u. . In the case of a full protonation, negative charge on the F atom drops from -1 to -0.209 a.u. (Appendix, No 94), i.e. by 0.791 a.u.

Charge transfer from the anion to the water molecule results in the increase of the negative charge on the oxygen atoms of H_2O. The negative charge transfer from the anion or anion-like (Me_3NO) base to the solvent molecules proceeds not only from the basicity center (e.g. oxygen atom) but also from the substitutent. Therefore, the gross effect of the negative charge transfer from the anion as a whole to the solvent molecules is much greater, being-0.15 to-0.35 electron charge units (Tables 2,3, Δ_1 values). For alkyl-substituted alkoxide ions and FO^- the Δ_1 value is mainly -0.25 ÷ -0.30, while in the case of perfluoro derivatives ($(CF_3)_3CO^-$, $(CF_3)_2CHO^-$, CF_3O^-) $-0.15 \geqslant \Delta_1 \geqslant -0.20$; for ClO_4^- $\Delta_1 = -0.09$, for CH_3COO^- $\Delta_1 = -0.108$; for O_2^{2-} $\Delta_1 = -0.53$. It can be seen from Table 3 that under similar conditions, the absolute value of the charge transfer degree Δ_1 increases proportionally to the increase of the number of water molecules, attached to the anion. Thus, if n = 3, the Δ_1 values for X = CF_3, F and Et are respectively -0.36, -0.40 and -0.467 a.u.. Still, in the case of an internally more stabilized anion, ClO_4^-, the increase of the Δ_1 value is more moderate, at n = 4 reaching -0.26 electron charge units only (see also the Appendix, No 87).

Naturally, from the "solvent's point of view", the effect of negative charge transfer from the anion to the solvent molecule is equivalent to a positive charge transfer from the latter (especially, from the water molecule) to the solute, i.e. in the case of the protic solvent of its partial protonization.

The effect of comparative intensity of solute-solvent transfer was recently predicted[1] also for the hydration process of the positively charged RNH_3^+ ions (see Appendix No 7).

Initiating the intermolecular charge transfer between the solute and the solvent molecules, solvent-solute interactions efficiently (up to the turning off) compete[8,15,17,18] the mechanisms of intramolecular (by means of different types of resonance, inductive, polarization, etc. interactions) stabilization or destabilization of solutes. Really, it can be seen from the Appendix that as a rule, owing to the action of the mentioned intramolecular mechanisms (especially that of anionic conjugation[22-24]) in alkoxide ions, in the vicinity of the protonation center, the C-O bond lengths are shorter, while the legths of the C-C and C-H bonds in α-position and C-F bonds in α- and ß-positions are longer than in the corresponding protonated forms, XOH[*]. It can be seen from the Appendix that the negative charge transfer to the water molecules accompanying the XO^- solvation, and a partial proton transfer from the molecules of the latter to the solute, which is equal to the former process, are accompanied by a rather significant change in the geometry of ions.

It can be seen that even addition of the first water molecule stretches (see the Appendix) the C-O bond length in the majority of XO^- anions from ≈ 1.30 Å to 1.35-1.41 Å, which is quite close to the calculated (and experimental) bond length (1.43 Å) in a completely protonated anion, i.e. in the XOH molecule. In its turn, the alkoxide ion hydration is also followed by shortening of the α-C-C, α-C-H and α-C-F bonds (Appendix, Nos 23-62, etc.). The consecutive attachment of additional water molecules causes a much smaller increase of the lengths of these bonds, thus, the latter are practically indistinguishable from those in the XOH molecules.

A qualitatively different situation is observed for the HO^- anion and some other (relatively small) anions (FO^-, HOO^-, H_2NO^-, O_2^{2-}, etc.), containing the electron-donor group in the immediate vicinity of the protonation center which is unable for the intramolecular stabilization via the mechanism characterizing the donor reaction center interaction

---

[*] The statement holds in the case of the deprotonated forms of amines, mercaptanes and alkanes[22-24].

with electron-acceptor substituents.[*]

Geometry of these anions is relatively insensitive to the attachment of water molecules (a certain decrease of the X-O bond length is observed; X = F, HO, H_2N, O^- and H), although a very significant charge redistribution between the solute and the solvent molecules takes place (see Appendix). It can be seen in Fig. 1 that this tendency is observed also in the case of the OH^- ion solvation (in this ion the OH bond length is 1.029 Å, 3-21G basis set) by the DMSO molecule.

Alongside making use of intermolecular solvational interactions in order to turn on or off the resonance or hyperconjugative mechanisms of intramolecular stabilization or destabilization of the reagent, analogous changes in the geometry and energetics of the latter can be reached also (or even primarily) purely "intramolecularly", for instance, by the selection of conformations where separate fragments of the system cannot interact with each other according to the mentioned mechanisms because of the special orientation (e.g. the absence of the coplanarity of the subsystems).[22] Take, for example, a typical case of anion $O_2NC(H) = C(H)O^-$ (see Appendix, No 91). In the case of a perpendicular conformation (the NO_2 is turned 90° relative to the OC(H)CH plane) the majority of the elements of the anion's geometry resemble those corresponding to the hydrated to the O^- form of the anion (Appendix, No 93) (alkoxide oxygen atom is the acceptor of the H-bond) where the NO_2 group and the OC(H)CH plane are coplanar.

The aforesaid holds also in the case of some other systems discussed in the present paper where the intensity of intramolecular stabilization or destabilization according to the negative hyperconjugation or dipolar interactions may

---

[*] Naturally, variation of the qualitative and quantitative distribution of electron density in an ion or in a molecule should lead to substantial changes in the intensity of intramolecular interactions of the charge-charge, charge-dipole, dipole-dipole and ion-induced dipole types (vide infra).

largely depend on the conformation (the gauche-trans(cis) orientation of the alcohol's OH-group relative to some electronegative (F), electropositive or H-atoms in the substituent, etc.).[*]

The results of the present paper (see Appendix, Nos 6, 11, 12, 28, 29, 33, 42, 46, 48, 56, 60, 66, etc.) agree with the supposition[1, 8, 15-18] that the geometry of neutral XOH molecules remarkably less depends on the presence of solvent molecules than that of ionic particles. Specific solvation (hydration) or (in the limiting case) a complete protonization of XO^- should lead to the decrease of the negative charge on the protonization center and to a smaller availability of lone electron pairs of the oxygen atom in their stabilizing or destabilizing interaction with the group orbitals of electron-acceptor (e.g., CF_3, $C(CF_3)_3$, NO_2, etc.), alkyl (CH_3, $(CH_3)_3C$, etc.) or with potentionally electron-donor (HO, O^-, F, NH_2, etc.) substituents. Therefore, in the hydrated or protonated forms of XO^- the processes of the above-mentioned intramolecular stabilization via the anionic hyperconjugation or some other mechanisms which assume the intramolecular charge redistribution, interaction of orbitals, etc., are expressed more weakly than in the corresponding deprotonated, specifically nonsolvated XO^- forms. Therefore, it is not surprising that the geometry of the neutral polar XOH molecules remarkably less depends on the presence of solvent molecules. Nevertheless, the charge is again redistributed between the solute and molecules of the solvent (e.g., water). Direction of the charge transfer either from the neutral proton-donor XOH acids (e.g., XOH, CH_3COOH, $HClO_4$, etc.)[15,17] or from the protonated forms of neutral bases (e.g., XNH_3^+[1], Me_3NOH^+[15])

---

[*] In the Appendix, for XOH the data for the most stable conformations are reported. A more detailed analysis of the mutual orientation effect of the fragments of molecules and ions on the existence and intensity of their intramolecular stabilization or destabilization mechanisms can be found in the review by Radom.[22]

is opposite to that which is characteristic of the hydration of anions.

In this case, charge redistribution results in the gross effect of the positive charge transfer ($\Delta_2 = 0.05 - 0.15$ a.u. from the solutes of XOH type and ≈ 0.34 a.u. for XNH_3^{+1}), to the solvent or in the equivalent transfer of the corresponding negative charge from the H_2O molecule as the basic solvent onto the electrophilic solute.* A certain correlation holds between the proton-donor capacity of the electrophile and the amount of the charge Δ_2 transferred to the solvent (water) molecule. So, in the case of neutral particles XOH, the Δ_2 is the greatest (+0.15) for perchloric acid (for alcohols $0.05 \leq \Delta_2 \leq 0.09$, whereas for Me_3NOH^+ $\Delta_2 = 0.14$). In the case of the XOH molecules, such a charge redistribution results in the increase of both the positive charge at the hydrogen atom and the negative charge on oxygen atoms of the XOH hydroxylic group. This kind of specific hydration increases the polarity of the XOH solute, while the calculated dipole moments of the XOH...(OH_2) complexes reach rather high values, in some cases exceeding the totals of dipole moments of the separate components.

It should be mentioned that solvation of a water molecule by the DMSO molecule is accompanied by a rather weakly expressed transfer of the positive charge from the H_2O molecule to that of DMSO (0.085 a.u., STO-3G basis set) (see Fig. 1, Nos 2,4).

It follows from the aforesaid that both owing to the intermolecular solute-solvent charge transfer and accompanying variations of the geometry and charge distribution in the charged solute, the effective size(distance between the centroid of the negative (positive for the XNH_3^{+1} system) charge and the substituent dipole)increases, while the effective

---

[*] In the above-mentioned case of hydration of the F^- anion the H_2O molecule functions as the XOH acid; the amount of the positive charge transferred to the base (F^-) forms 0.466 a.u. The Δ_2 value for the trihydrate of H_3O^+ (Appendix, No 7) is practically the same (0.45 a.u.).

charge (i.e. its absolute value) at the protonation center decreases.

Admitting the existence of the above-mentioned mechanism of the specific influence of intermolecular interactions on the intramolecular interaction between the substituent and the reaction center and taking for a rather rough approximation simple model approaches of the charge-charge, charge-dipole, dipole-dipole and charge-induced dipole interaction types, it should be expected that the specific solvation of ions (e.g. XO^-) and their transfer from the gas phase into the solvent is accompanied by the remarkable decrease of both the energy of intramolecular interactions of the charge-charge (Eq. (2)), charge-dipole (Eq. (3)) and dipole-dipole (Eq. (4)) types, and that of polarization interactions between the charge and the induced dipole (Eq. (5)):

$$E_{ion-ion} = q_i q_j / D r_{ij} , \qquad (2)$$

where q_i and q_j are point charges, being situated at the distance of r_{ij} in the medium with the dielectric constant D,

$$E_{ion-dipole} = q \mu \cos Q / D r^2 , \qquad (3)$$

where Q = orientation angle of substituent dipole
D = dielectric constant
r = distance between point charge q on the reaction center and the center of point dipole of the substituent (dipole moment μ),

$$E_{dipole-dipole} = \mu_1 \cos Q_1 \mu_2 \cos Q_2 / D r^3 , \qquad (4)$$

where μ_1 and μ_2 are the dipole moments of the fragments,
Q_1, Q_2 = the orientation angles of the dipoles
r = distance between the dipole centers,

$$E_{pol} = - \alpha q^2 / 2 D r^4 , \qquad (5)$$

where q = the charge on the reaction center
α = substituent's polarizability.

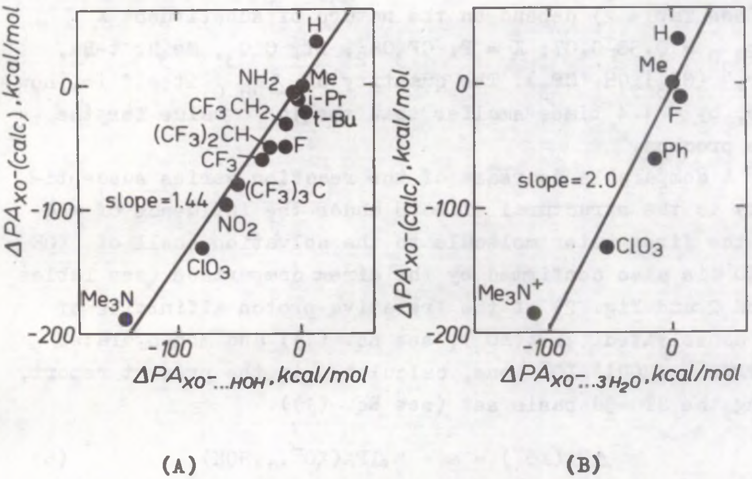


Fig. 2. Comparison of relative changes of the calculated proton affinities of nonsolvated XO^- ions (STO-3G basis set) with the relative affinities of monohydrated (A) and trihydrated (B) ions of $XO^-...n(HOH)$.

Besides, owing to the r^{-4} dependence of the energy of the latter interaction, in the case of transition from gas to the solvent the medium effect should be especially remarkable.

It is noteworthy that similarly to the gas phase results for the nonsolvated species, a comparative independence of the differences between the gross Mulliken charges Δq (see Table 1) at the reaction center in the initial (deprotonated) and terminal states (e.g., for transformation

$XO^- + H^+ \longrightarrow XOH$ $\Delta q = q_{OH} - q_{O^-}$) in the limits of the reaction series holds also for the analogous transition (the Δq_{H_2O} value) between the monosolvated particles, $XO^-...HOH$ and $XOH...OH_2$, for which the Δq_{H_2O} value does not actually (see Table 2) depend on the nature of 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 of Δq_{H_2O} itself is, however, by ≈ 1.4 times smaller than the Δq value for the same process.*

A comparable decrease of the reaction series susceptibilty to the structural effects under the influence of adding the first water molecule to the solvation shell of XOH or XO^- is also confirmed by the direct comparison (see Tables 1 and 2 and Fig. 2) of the relative proton affinities of the nonsolvated ($\Delta PA(XO^-)$, see Eq. (1)) and monohydrated ($\Delta PA(XO^-...HOH)$) XO^--ions, calculated in the present report, using the STO-3G basis set (see Eq. (1)).

$$\Delta PA(XO^-) = a + b\Delta PA(XO^-...HOH) \qquad (6)$$

The slope of the dependence varies somewhat, depending on the inclusion or exclusion of the points for Me_3NO and O_2^{2-}. Without these points slope b = 1.61, with the Me_3NO exclusion b = 1.44; with inclusion of the points for O_2^{2-}, b = = 1.85. The former value, i.e. b = 1.61, seems to be statistically more reliable. The consequtive addition of two more H_2O molecules to XOH and XO^- leads (see Table 3) to a further decrease of the Δq_{H_2O} value (by ≈ 15-20 %) and to an additional drop of the susceptibility of the reaction series to the structural effects.

Thus, it follows from the comparison of the relative calculated values of proton affinities of the monohydrated and trihydrated anions (see Fig. 2) that the reaction se-

---

* q_{H_2O} is found as the 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.

ries susceptibility to the structural effects decreases 1.4 times due to the attachment of two more water molecules into the solvation shell. Consequently, a more or less reliable calculated gross effect of the successive hydration influence on the proton affinities of the XO^- anions by 3 water molecules amounts to $1.6 \cdot 1.4 = 2.24$ times (including the point for Me_3NO, the effect is equal to $1.44 \cdot 1.4 = 2.0$, and including also the point for O_2^{2-}, $1.85 \cdot 1.4 = 2.01$ times).

On the other hand, a direct comparison of the gas phase and liquid phase basicity of some anions XO^- shows the susceptibility of the reaction series to the structural effects decrease during the transition from the gas phase into water approximately 3.7 ± 0.3 times, i.e. by 40 % more than it was predicted on the basis of the above-mentioned simple nonempirical calculations within the framework of a rather primitive model, in the present case taking into consideration only three water molecules. Therefore, it is clear that in this case the adequate consideration of solvation effects during transition from the gas phase into water cannot be limited to that of specific solvation only. Nevertheless, at least one case can be mentioned[1,8] (protonation of primary amines) when the simple model of specific solvation leads to the adequate description of the medium effects already on the level of STO-3G simple calculations.

A somewhat smaller (≈2 times) experimentally observed gross effect of a drop of the reaction series (1) susceptibility towards the structural effects characterizes the transition from the gas phase to the DMSO. On its turn, transition from the latter into water almost equally (1.9 ± 0.2) reduces the susceptibility of this reaction series to the gross effects of the structure. Changes having quite similar values characterize transiton from the gas phase into the solvent also from the point of view of the a_1 coefficient from Eq.[15, 17,18,25,26]

$$A = A_o + a_1\sum\sigma^* + a_2\sum\Delta R + a_3\sum\sigma^o_R + a_4 n_1 + a_5 \Delta n_2 \,, \quad (7)$$

Table 4

Typical Regression Coefficients≠ a_1 and a_2 of Eq. (7), ρ^o and $\rho_R^{\pm}$ in Eq. (8) for Some Solvents and Gas Phase

Medium	XO^-		$XCOO^-$		ArO^-		$ArCOO^-$	
	$-a_1$	$-a_2$	$-a_1$	$-a_2$	$-\rho^o$	$-\rho_R^-$	$-\rho^o$	$-\rho_R^+$
GP	10.4	0.52	7.8	0.22	18.1	8.9	15.0	3.0
DMSO	7.6	0.17	3.91	0.08	6.6	2.7	3.6	0.04
CH_3CN	-	-	4.73	0.042	5.9	3.4	3.5	1.4
DMP	-	-	-	-	6.5	-	3.2	1.9
CH_3NO_2	-	-	4.54	0.027	4.8	-	3.5	-
CH_3OH	-	-	2.3	0.035	3.5	1.9	1.9	0.5
C_2H_5OH	-	-	2.21	-	3.4	1.9	2.1	0.53
$(CH_3)_2CHOH$	-	-	2.48	-	4.6	2.8	2.1	0.52
$(CH_3)_3COH$	-	-	2.98	-	7.7	-	4.2	-
H_2O	3.84	0.049	2.46	0.11	2.48	0.68	1.37	0.34

≠ Regression coefficients (see also[15,17,18,25,26]) are given in kcal/mol units.

where A denotes the gas or liquid phase basicity of the base; $\sum\sigma^*$ and $\sum\sigma_R^o$ are the sums of Taft's inductive an and resonance constants at the reaction center, $\Delta R = MR - MR$ where MR is the calculated additive molecular substituent refraction, n_1 is the number of hydrogen atoms, directly attached to the protonization center, $\Delta n_2 = n_2 - n_2$(methyl) is the relative number of H-atoms in the α-position to the reaction vcenter; A_o, a_1, a_2, a_3, a_4, a_5 are the constants both for this series as well as for that of substituted aliphatic carboxylate ions of $XCOO^-$ (see Table 4).

In a very nonrigid and a rather rough approximation, often[8,15,17,18] the induction effect in the terms of Eq.(7) or its analogues can be visualized via the ion-dipole or dipole-dipole interactions expressed by Eqs. (3) and (4). The polarization contribution ($a_2\sum\Delta R$) can be analogously visualized in Eq. (7) in the terms of the interactions of the point-charge (reaction center)-induced dipole (substituent) type, expressed via Eq. (5) (see above).

For the purposes of comparison, in Table 4 are given some typical data [17,18,25,26] concerning the a_1 and a_2 coefficients for the two above-mentioned aliphatic reaction series as well as the ρ^o and $\rho_R^{\pm}$ coefficients[17,18,25] from Eq. (8)

$$A = A_o + \rho^o\sigma^o + \rho_R^{\pm}\sigma_R^{\pm}\ , \qquad (8)$$

where σ^o and $\sigma_R^{\pm} = \sigma^{\pm} - \sigma^o$ (σ^+ and σ^- are the electrophilic and nucleophilic substituent constants, respectively) - substituent constants[27]; A_o, ρ^o and $\rho_R^{\pm}$ are the reaction series constants, A is either the gas phase basicity or the pK_a of the corresponding base (in the present case, the anionic one) in liquid phase.

which refer to the acidic dissociation (i.e., the basicity of the corresponding conjugated anions of the substituted benzoic acids and phenols in the gas phase and in other solvents.

Table 4 shows that in all cases observed, transition from the gas phase into the solvent does not alter conditions $a_1 < 0$ and $\rho^0 < 0$, $\rho^{\pm}_R < 0$, although the values itself can drop rather substantially. One can see that the largest changes (Table 4, e.g., dissociation of alcohols, phenols and benzoic acids) are related to the transition from the gas phase into water. For the reactions of dissociation of neutral OH-acids the latter can be, at least qualitatively explained by the prevalation of the specific electrophilic solvation in the anionic (A^-...H-OH) form over the nucleophilic solvation of neutral acid (AH...OH_2). Running ahead, one can say that the same conclusion emerges as a result of the analysis of the data of Table 4 in terms of the empirical equation (see below) for consideration of individual contributions of nonspecific and specific solvation in the gross solvent effects.

Naturally, the Mulliken charge redistribution which accompanies the solvate formation and variation of the effective dimensions of the reagents (see above) must also affect the intensity of the influence of nonspecific solvent-solute interactions (polarity and polarizability of the medium)[8,17,18,28]. Under the medium influence the intermediate position of the solvent attenuation factors of the structure effects (the a_1 values of Eq. (7) and those of the ρ^0 coefficient from Eq. (8)) for DMSO (see Table 4 and ref. [8,25]) is usually explained by the absence (against the background of the nonspecific solvent-solute interactions) of electrophilic solvation by the molecules of DMSO via the hydrogen bond in the anionic form of the acid (XO^-, $XCOO^-$, etc.) and by the possible prevalence of the stabilizing nucleophilic solvation in the neutral acid of the XCOOH...$OSMe_2$, XOH...$OSMe_2$ type and by the proposed[29] simultaneous negligibility of the contribution from the specific electrophilic solvation of the anion by the interaction with the DMSO molecules. However, it should be taken into consideration that according to the results of our nonempirical calculations (3-21G* basis set) (see Fig. 1 and reports[15,17]), DMSO is capable of electrophilic solvation of anions like HO^-, F^-, FO^-, etc. via the positive end of the S-O dipole. Most probably it also concerns alcoholate and carboxylate ions.

Evidently, (see Fig. 1) the interaction energy here is of the same order or even exceeds the energy of the DMSO interaction with the XOH and XCOOH type electrophiles in the gas phase. This statement was recently confirmed[30] by a direct experimental monitoring of the DMSO complexes with the Cl^-, NO_2^-, etc. anions in the gas phase.

The influence of less intensive specific solvation interactions in comparison with DMSO is expected to appear in the case of nitromethane[31] and acetonitrile. This way or another, in connection with that attention should be drawn to a rather low ratio of the a_1 values (Table 4) observed for the dissociation reactions of XCOOH in gas phase on one hand, and in DMSO, $MeNO_2$ and MeCN, on the other. For the $X_1X_2X_3C^-$ system the transition from the gas phase into DMSO this ratio of a_1 values does not exceed 1,2[18].

As it might have been expected on the basis of Eq. (5) and of the results of model calculation[8,15,18], the a_2 value changes (decreases) considerably more than the susceptibility to the influence of polar (inductive) effects. Thus, for the XO^- series, transition from the gas phase into water reduces a_2 5.7 times, in the case of transition into DMSO it is reduced 3 times, whereas for the $XCOO^-$ series the susceptibility constant a_2 drops in both cases ≈ 3.7 times. Simple model calculation on the basis of Eqs. (3), (5) (the r and D values are supposed to be identical in both equations) shows that qualitatively, the range of changes of the a_1 and a_2 values do not contradict each other. So, the changes of a_1 (2.3 times) and a_2 (5.1 times) refer to the change of r from 2 to 3 Å due to the hydration of XO^-, and a very possible increase of r from 3 to 4 Å corresponds to the changes of a_1 and a_2 values 1.8 and 3.2 times, respectively.

For evaluation of the relative contributions of the nonspecific and specific solvent-solute interactions into the characteristics of the reaction series towards the structural effects (a_i, ρ^0, $\rho_R^{\pm}$) (or to the pK_a values) some additional information can be obtained applying the corre-

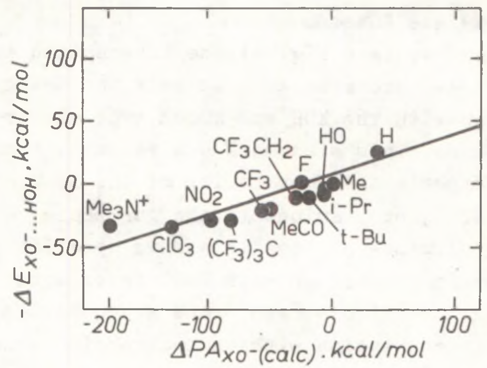


Fig. 3. Relationship between the relative enthalpies of ($\Delta E_{XO^-...HOH}$) of hydrogen bond formation between the XO$^-$ anions and a water molecule on the relative basicity of the donor XO$^-$(ΔPA_{XO^-}(calc)).

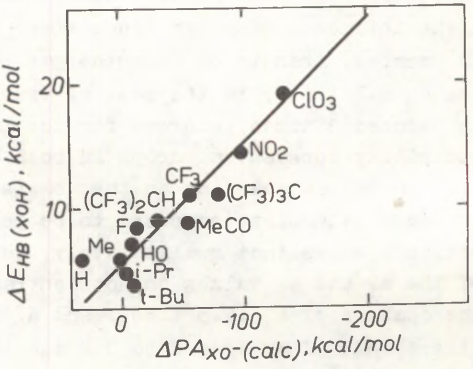


Fig. 4. Dependence of the relative strength of hydrogen bond ΔE_{HB}(XOH) between the neutral XOH acid and a water molecule (the base) on the relative basicity of the conjugated XO$^-$ (ΔPA_{XO^-}(calc)) base.

lation equation[28], which takes into account individual contributions of polarity, polarizability, electrophilicity, and the general basicity of the solvent:

$$A = A_o + yY + pP + eE + bB, \qquad (9)$$

where $Y = f(D)$ and $P = f(n_D)$, respectively are the polarity and polarizability of the solvent, D and n_D - the dielectric permittivity and solvent refraction index; E and B are the empirical measures of electrophility and general basicity of the solvent; A_o, y, p, e and b are the constants, $A_o = A$ for the gas phase (A - log k, pK_a, spectral characteristic, etc.)

A few typical examples of application of this equation in the case of some ρ^o and $a_1(\rho^*)$ regression coefficients of Eqs. (7) and (8) from Table 4 can be found in Table 5.

One can see that in the case of the basicity of aliphatic carboxylate ions $XCOO^-$ and the basicity of the substituted benzoate and phenolate ions, respectively, Eq. (9) shows that the susceptibility of the basicity of anionic bases to the structural effect decreases in the last two cases with the transition from the gas phase into a more polar and electrophilic medium (in case of $ArCOO^-$, the medium polarizability is also of some significance). At the same time, according to rather poor data for the aliphatic anions $XCOO^-$, the a_1 value drops with the transition from the gas phase into the liquid one mainly thanks to the electrophilic component of the solvent-solute interactions, which stabilizes the anionic form, the conjugated base A^- of the AH acid, thus increasing the acid strenth of the latter (specific solvation of the acid AH in this case stabilizes the initial state and reduces the acidity of the acid). Negligibility of the contribution of the nucleophilic solvation effect on the gross ρ^o values in the case of the series of benzoate and phenolate ions and a relatively weak effect of the factor for the series of $XCOO^-$ is somewhat unexpected. It could be connected with a relatively weak dependence of

Table 5

Analysis of Influence of Nonspecific and Specific Solvation Effects on Some Regression Coefficients (ρ^o from Eq. (8), for Acid-Base Equilibria with Participation of Substituted Benzoate- and Phenolate-Ions, and a_1 Value from Eq. (7) for Derivatives of Aliphatic Carboxylate Ions) Using Multiparameter Equation (9)[a]

	Correlated A value	A_o	y	p	e	-b	R	s %	n
1.	ρ^o, substituted benzoate ions	-10.84 (2.23)	5.87 (1.96)	10.69 (6.63)	0.113 (0.031)	0	0.964	4.3	12
2.	ρ^o, substituted phenolate ions	-13.13 (0.88)	9.10 (0.76)	0	0.151 (0.033)	0	0.965	5.7	10
3.	a_1, substituted aliphatic $XCOO^-$	-5.03 (0.17)	0	0	0.127 (0.035)	0.0065 (0.0020)	0.724	16.3	9

[a] - In parentheses under the regression coefficients of Eq. (9) is given their confidence range, 0 marks negligibility of the medium factor, R is the multiple regression coefficient, s % = $(s/\Delta A_{max})100$, where s is the standard deviation, a and ΔA_{max} - the variation range of the correlated value, n is the number of points.

(free) stabilization energy of the neutral acid on its structure as compared with a rather noticeable simultaneous change of the acidity of the latter. The model nonempirical calculations of hydration of the XOH molecules and XO^- anions by water molecules seems also to evidence about it. It follows from the data of Tables 2,3 that both the complex formation energy between the water molecule and the XO^- anion itself and its variation with structure X (Fig. 3), considerably exceed the absolute level and the change of the neutral XOH as an electrophile and water molecule (Fig. 4), as the nucleophilic (basic) solvating agent.

Really, Figs. 3 and 4 show that in the first case, the linear dependence of the relative calculated complex formation energies of XO^- with H_2O on the anion proton affinity[*] has an average slope value (0.375 ± 0.10) almost four times exceeding that of (0.10) the dependence of the energy of complex-formation of the neutral XOH acid as an electrophile with the water molecule on the $\Delta PA_{calc}(XO^-)$ (i.e., on the calculated acidity of the XOH acid).

One cannot either overlook the fact[**] that the data of different authors do not always agree with each other in the limits of various experimental errors (see refs. [7a, 7b] where, for instance, the hydrogen bond strengths found for

---

[*] It should be mentioned that according to the data of the present paper (see Fig. 3), the linearity between the experimental hydrogen bond strength and the experimental proton affinity of the XO^- anion established[17] on the bases of a rather limited XO^- set, seems to be an exception rather than a rule.

[**] Experimental values for a series of $XO^- \ldots H_2O$ complexes are as follows: X = H[7a, 8] : 25.0 kcal/mol, Me : 19.9[7a] kcal/mol and 23.9 [7b] kcal/mol, t-Bu [7b] : 23.4 kcal/mol, C_6H_5 [7b] : 15.4 kcal/mol, NO_2 [14]: 12.4 kcal/mol.

the $MeO^-...H_2O$ complex differ by ≈ 4 kcal/mol; the same value for the $t\text{-}BuO^-...H_2O$ given in [7b] seems to have been exaggerated, etc.).

Tendency towards the prevalence of stabilization of the anionic form of XO^- usually weakens when the anion's size increases and/or while introducing the electronegative substituents X. These phenomena have complicated reasons. Thus, the increase of the ion's effective radius caused either by its greater size or by a more favorable charge delocalization, should bring about a reduction in the intensity of the nonspecific electrostatic and the electrophilic specific solvation of the acid's anionic form. Introducing more electronegative substituents, in its turn leads to the decrease of the real basicity of the XO^- anion (i.e., to the decrease of electrophilic stabilization via the hydrogen bond, as reflected by the $E_{HB}(XO^-)$ value (Tables 2, 3) and to the increase of the acid's acidity, which should result in a greater nucleophilic stabilization of the XOH neutral form (see $E_{HB}(XOH)$ values in Tables 2, 3). It can be mentioned that according to the results of these model calculations, stabilization intensity via the specific XOH solvation in the case of $HClO_4$ and Me_3NOH^+ exceeds the stabilizing effect by water molecules as the electrophiles- of the corresponding deprotonated forms, ClO_4^- and Me_3NO.

It was suggested in literature[8,9,15,17,18,22] that even at a minimal basis set level, modern nonempirical calculations of various fundamental properties (energetics, structure, etc.) of molecules often correctly reflect some basic regularities of the changes of the experimentally recorded values, on the structural and medium factors.

This also concerns the calculation of the gas phase basicity or the proton affinity of organic molecules and anions. It is especially remarkable [15,32] that regardless of the fact that the PA_{calc} values predicted in the minimal base substantially differ from the absolute experimental values PA_{exp}, there is a satisfactory correlation between them, making it possible to assess on the basis of different values probable expected values of the yet unknown experimental values PA_{exp}.

For 61 anionic bases, the corresponding correlation equation is:[32]

$$PA_{exp} = 108(16) + 0.536(0.033)PA_{calc} , \qquad (10)$$

where in parentheses is given the reliability range of the regression coefficients.

Standard deviation from the regression line equals 9 kcal/mol, although the greatest absolute deviations of some calculated PA_{exp} values amount to 92 kcal/mol on the average. The mentioned equation includes also (ClO_4^- excluded) a series of anions of the OH-acids discussed in the present communication. To the time being, the gas phase basicity of only a limited number of XO^- monohydrates (X = H, Me, etc.)[7] and a few alkyl-substituted XO^-, solvated by alcohol molecules[7] has been established.[8] Therefore, analogous equations connecting the corresponding calculations and the experimental proton affinity values (gas phase basicity) of the hydrated or solvated XO^- particles are still absent.

Perhaps it would be sensible, before accumulation of a sufficient experimental data set concerning the proton affinities of the mono-, di-, tri-, etc. hydrated XO^- bases to make use of the above-mentioned relationship (10), where instead of the PA_{calc} were used the corresponding values, calculated in the present work for the $XO^-...n(H_2O)$ hydrated complexes. It would permit us to give a rough estimation of the mentioned values.

It should be said in conclusion that alongside with prediction of the exaggerated absolute PA values, calculations in the minimal basis set clearly overestimate the strength of the hydration bond between XO^- and HOH, as well as between the neutral acids XOH and OH_2. The deviations are especially remarkable in the case of small and hard substituents (H,F).[8]

There are reasons to believe that tranfer to a higher level of the theory (a more complete and flexible basis set, applying the diffuse functions[9] for anions; transfer behind the limits of the Hartree-Fock theory, either in the framework of the direct method of configurational interactions or by means of using the Møller-Plesset perturbation theory etc.) permits us to determine accurately enough these values as well as the proton affinities of the anionic bases[7,9,15,33].

We are carrying out theoretical investigation in this direction. Experimental studies (ICR) have also been started in order to directly determine the gas phase basicity values of the hydrated or solvated anions of organic acids, the OH-acids included.

On the other hand, it must be admitted that the combined approaches, incorporating the essential features of different methods should be considered the most prospective ones in the development of theoretical quantum chemical and statistical calculation methods of medium effects. Here should, for instance, belong the combination of the supermolecular approach and the model hamiltonian methods with the formalism of the Monte Carlo and molecular dynamics methods, constructing of more efficient intermolecular potentials, combination of the supermolecular approach with the methods of model hamiltonian (see [10,34,35] for references). Quite recently, a rather promising progress has been made in this direction (see, e.g., reviews [10,35], reports [36-38], etc.).

The author would like to thank professors R.W. Taft and W.J. Hehre for stimulative discussions, valuable advice and support in conducting the present study during his stay at the Department of Chemistry, the University of California (Irvine) in 1981-82.

References

1. M.Taagepera, D. DeFrees, W.J. Hehre, and R.W. Taft, J. Am. Chem. Soc., 102, 424 (1980).
2. J. Bromilow, J.L.M. Abboud, C.B. Lebrilla, R.W. Taft, G.

G. Scorrano, and V. Lucchini, ibid., 103. 5448 (1981).

3. S. Yamabe, T. Minato, and K. Hirao, J. Chem. Phys., 80, 1576 (1984).
4. W.L. Jorgensen and M. Ibrahim, J. Comput. Chem., 2, 7 (1981).
5. a) S. Ikuta, ibid., 5, 374 (1984).
   b) S. Ikuta, Mass Spectrometry, 30, 297 (1982).
6. M.M. Szczczniak and S. Scheiner, J. Chem. Phys., 77, 4586 (1982).
7. a) G. Caldwell, M.D. Rozeboom, J. Kiplinger, and J.E. Bartmess, J. Am. Chem. Soc., 104, 4660 (1984).
   b) M. Meot-Ner and L.W. Sieck, J. Am. Chem.Soc., 108, 7525 (1986).
8. R.W. Taft, Progr. Phys. Org. Chem., 14, 247 (1983).
9. W.J. Hehre, L. Radom, P.v.R. Schleyer, and J.A. Pople, Ab Initio Molecular Orbital Theory, New York, Interscience, 1985.
10. V.A. Zubkov, B.I. Kolegov, and T.M. Birshtein, Usp. khim., 52, 1057 (1983).
11. I.G. Kaplan, Introduction into the Theory of Intermolecular Interactions, (in Russian), Moscow, Nauka, 1982.
12. M.D. Newton and S. Ehrenson, J. Am. Chem. Soc., 93, 4971 (1971).
13. W.P. Kraemer and G.H.F. Diercksen, Theor. Chim. Acta, 23, 398 (1971).
14. J.M. Howell, A.M. Sapse, E. Singman, and G. Synder, J. Phys. Chem., 86, 2345 (1982).
15. a) I.A. Koppel and U.H. Mölder, This journal, 20, 2 (1983).
    b) I.A. Koppel, U.H. Mölder, and V.A. Palm, this journal, 22, 3 (1985).
16. I.A. Koppel, a) Abstracts of the 9th All-Union Conference on Quantum Chemistry, 10-12 June 1985, Ivanovo, (in Russian), part 1, p. 13.
    b) the International Conference "Chemical Physics of Enzyme Catalysis", 21-24 September 1987, Tallinn, p.99.
17. I.A. Koppel, Dr. Sci. Thesis, (in Russian), IKhF AN SSSR, Moscow, 1986.

18. I.A. Koppel, U.H. Mölder, and R.J. Pikver, Ch. 5 in book Ion-Molecular Reactions of Organic Compounds in Gas Phase , O.S. Chizhov (Ed.), (in Russian), Nauka, Ufa, 1987.

19. I.S. Binkley, R.A. Whiteside, R. Krishnan, et al., QCPE, No 406, 437, 446, 500.

20. R.F. Hout, M.M. Francl, E.S. Blurock, et al., Univ. of California, Irvine, 1977-1983.

21. M.M. Karelson, this journal, 17, 371 (1980).

22. L. Radom, Progress in Theoretical Organic Chemistry, v. 3, I.G. Csiszmadia (Ed.), Amsterdam, Elsevier, 1983, p. 1.

23. P.v.R. Schleyer, and A. Kos, Tetrahedron, 39, 1141(1983).

24. D.S. Friedman, M.M. Francl, and L.C. Allen, ibid., 41, 449 (1985).

25. I.A. Koppel and M.M. Karelson, this journal, 11, 985 (1975).

26. I.A. Koppel and U.H. Mölder, in book QSAR Strategies in the Design of Bioactive Compounds, J. Seydel (Ed.), Weinheim: VCH, 1984, p. 281.

27. V.A. Palm, Foundations of Quantitative Theory of Organic Reactions, (in Russian), Leningrad, Khimiya, 1977.

28. I.A. Koppel,and V.A. Palm, in book N.B. Chapman and J. Shorter (Eds.), Advances in LFER, London, Plenum, 1972, Ch. 5.

29. A.J. Parker, Chem. Rev., 69, 1 (1969).

30. a) T.F. Magnera, G. Caldwell, J. Sunner, S. Ikuba, and P. Kebarle, J. Am, Chem. Soc., 106, 6140 (1984).
    b) L.W. Sieck, J. Phys. Chem., 89, 5552 (1985).

31. K.M. Dyumaev and B.A. Korolev, Usp. Khim., 49, 2065(1980). (1980).

32. I.A. Koppel and M.B. Comisarow, this journal, 17, 495 (1980).

33. T. Clark, J. Chandrasekhar, G.W. Spitznagel, and P.v.R. Schleyer, J. Comput. Chem., 4, 294 (1983).

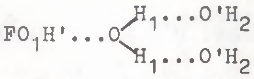
34. G.M. Zhidomirov, A.A. Bagaturyants, and I.A. Abronin, Applied Quantum Chemistry (in Russian), Moscow, Khimiya, 1979.

35. B.Ya. Simkin and I.I. Sheikhet, in book: Physical Chemistry. Contemporary Problems. (in Russian), Moscow, Nauka, 1983.
36. E. Clementi, G. Gorongiu, M. Gratorola, et al., Int. J. Quant. Chem., 16, 409 (1982).
37. E. Clementi and G. Gorongiu, Studies in Physical and Theoretical Chemistry, 27, 397 (1983).
38. J. Chandrasekhar, S.F. Smith, and W.L. Jorgensen, J.Am. Chem. Soc., 107, 154 (1985).

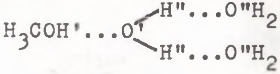
APPENDIX

Some Characteristic Features of Geometry and Distribution of Charges in Systems $XO^- \ldots n(H_2O)$ and $XOH \ldots n(H_2O)^{\neq}$

System	Geometry and Charge Distribution
1	2
1. HO^-	$HO=1.045$, $q_O=-0.760$
2. HOH	$HO=0.989$, $HOH=100.02$, $q_O=-0.330$, $q_H=0.165$
3. $HO^- \ldots H_1OH_2$	$HO=1.035$, $H_1O=1.01$, $OH_2=1.007$, $OH_1=1.199$, $HOH_1=100.9$, $H_1OH_2=$ $=100.9$
4. $HO_1^- \ldots 2(H'OH'')$	$HO_1=1.033$, $O_1H'=1.30$
5. $HO_1^- \ldots 3(H'OH'')$	$HO_1=1.030$, $O_1H'=1.40$, $H'O=1.0$, $OH''=0.985$, $HO_1H'=110.0$, $H'OH''=$ $=100.5$
6. $H_2O \ldots H'O_1H'' \ldots OH_2$	$OH'=0.981$, $H'O(H_2)=1.84$, $OH=0.988$, $q_{O_1}=-0.412$, $q_O=0.330$, $q_{H'}=$ $=0.174$, $q_H=0.18$
7. $OH_3^+ \ldots 3(O'H_2')$	$OH=1.018$, $HO'=1.379$, $HOH=120.0$, $q_O=-0.45$, $q_{O'}=-0.348$, $q_H=0.331$, $q_{H'}=0.25$, $\triangle_2=0.45$, $E_{tot}=-300.4170$ a.u.
8. FO^-	$FO=1.55$, $q_{O^-}=-0.553$, (6-31G*: $FO=1.49$)
9. FOH	$FO=1.355$, $OH=1.006$, $FOH=101.01$, $q_O=-0.149$, $q_H=0.195$, $q_F=-0.046$
10. $FO^- \ldots H\text{-}O'\text{-}H_1$	$FO=1.373$, $OH=0.957$, $OH_1=1.00$, $FOH=103.6$, $HOH_1=100.9$, $FH=1.294$, $q_{O^-}=-0.444$, $q_{O'}=-0.509$, $q_H=0.216$

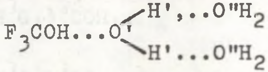
	1	2
11.	$FOH'\ldots O'H_2$	$FO=1.355$, $OH'=1.011$, $H'O'=1.63$, $O'H=0.986$, $FOH'=101.4$, $HOH=114.3$, $q_O=-0.214$, $q_{O'}=-0.333$, $q_{H'}=0.231$
12.	 $FO_1H'\ldots O\begin{matrix}H_1\ldots O'H_2\\ H_1\ldots O'H_2\end{matrix}$	$FO_1=1.356$, $O_1H'=1.027$, $H'O=1.488$, $OH_1=0.987$, $OH_2=0.988$, $H_1O'=1.70$, $FO_1H'=101.6$, $H_1OH_1=112.9$, $H'OH_1=117.3$, $q_{O_1}=-0.253$, $q_{H'}=0.245$, $q_O=-0.427$, $q_{H_1}=0.221$, $q_{O'}=-0.334$, $q_{H_2}=0.189$
13.	$FO_1^-\ldots 3(H'OH)$	$FO_1=1.362$, $O_1H'=1.49$, $H'O=1.016$, $OH=0.993$, $FO_1H'=107.8$, $H'OH=100.3$, $q_{O_1^-}=-0.382$, $q_F=-0.187$, $q_{H'}=0.224$, $q_O=-0.446$, $q_H=0.07\div0.08$,
14.	O_2^{2-}	$OO=1.4605$, $q_O=-1.0$
15.	HO_1O^-	$OO=1.4492$, $OH=1.021$, $HOO=105.36$, $q_{O^-}=-0.57$, $q_{O_1}=-0.42$
16.	HOOH	$OO=1.3964$, $HO=1.001$, $HOO=101.12$, $\theta=125,3$
17.	$(O-O_1)^{2-}\ldots HO'H'$	$OO_1=1.449$, $O_1H=1.021$, $HO^1=\infty$, $O'H'=1.045$, $OO_1H=105.36$, $q_O=-0.57$, $q_{O_1}=-0.42$, $q_{O'}=-0.76$
18.	$HOO_1^-\ldots H'O'H_1$	$HO=1.01$, $OO_1=1.42$, $O_1H=1.30$, $O'H'=1.09$, $O'H_1=1.00$, $HOO_1=102.1$, $OO_1H'=102.5$, $HO'H_1=100.8$, $q_O=-0.318$, $q_{O_1}=-0.446$, $q_{O'}=-0.505$, $q_H=0.22$, $q_{H_1}=0.003$, $q_H=0.046$
19.	$HOO_1^-\ldots 3(H'O'H'')$	$OO_1=1.41$, $O_1H'=1.50$, $H'O'=1.02$, $O'H''=0.99$, $HO=1.0099$, $HOO_1=103.24$, $OO_1H'=99.57$, $H'O'H''=100.5$

1	2
20. HONH$_2$	NO=1.427, NH=1.04, OH =0.995, NOH=101.4, $q_O=-0.210$
21. H_2NO^-	NO=1.48, NH=1.051, $q_{O^-}=-0.587$, $q_H=-0.012$
22. $H_2NO^-\ldots H'O_1H''$	NO=1.45, HN=1.057, OH'=1.28, $H'O_1=1.10$, $O_1H''=0.999$, $H'O_1H''=100.99$, HNO=107.4, NOH'=105.9, $q_{O^-}=-0.443$, $q_{O_1}=-0.515$, $q_{H'}=0.217$, $q_{H''}=0.004$, $q_N=-0.349$, $q_H=0.043$
23. H_3CO^-	CO=1.368, CH=1.132, HCO=117.12, $q_O=-0.658$
24. H_3COH'	CO=1.433, CH=1.095, OH'=0.991, COH'=103.86, $q_O=-0.295$, $q_{H'}=0.177$, $q_C=-0.065$, $q_H=0.061$
25. $H_3CO^-\ldots H'O_1H''$	CO=1.407, CH=1.108, $H'O_1=1.096$, $O_1H''=0.999$, OH'=1.274, COH'=107.7, $H'O_1H''=100.8$, $q_{O^-}=-0.515$, $q_{O_1}=-0.517$, $q_C=-0.073$, $q_{H'}=0.222$, $q_{H''}=0.0047$, $q_H=-0.04$
26. $H_3CO^-\ldots 2(H'O_1H'')$	CO=1.41, CH=1.10, OH'=1.36, $H'O_1=1.05$, $O_1H''=0.995$, HCO=113.7, $H'O_1H''=100.5$, COH'=108.7, $E_{tot}=-262.7650$
27. $H_3CO^-\ldots 3(H'O_1H'')$	CO=1.425, CH=1.095, OH'=1.458, $H'O_1=1.023$, $O_1H''=0.991$, HCO=112.95, COH'=109.0, $H'O_1H''=100.3$

1		2
28.	$H_3COH'\ldots O'H''_2$	CO=1.424, CH=1.0926, OH'=0.984, H'O'=1.715, O'H"=0.985, COH'=104.17, H'O'H"=114.04, q_O=-0.336, $q_{O'}$=-0.335, $q_{H'}$=0.214, q_H=0.042÷÷0.05, $q_{H''}$=0.193, q_C=-0.069
29.	 $H_3COH'\ldots O'\begin{matrix}H''\ldots O''H_2\\ H''\ldots O''H_2\end{matrix}$	CO=1.430, CH=1.095, H'O'=1.58, O'H"=0.983, H"O"=1.71, OH'=1.00, O"H=0.985, HCO=109.8, COH'=104.36, H'O'H"=114.8, H"O"H=115.8, q_C=-0.073, q_O=-0.372, $q_{O'}$=-0.438, $q_{O''}$=-0.344, $q_{H'}$=-0.344, $q_{H'}$=0.240, q_H=0.03÷÷0.045, $q_{H''}$=0.216, $q_H(O''H_2)$=0.195
30.	$H_3C'CH_2O^-$	CO=1.348, C'C=1.62, CH=1.133, C'H=1.090, C'CO=116.7, HC'C=112.9, O is in trans-position relative to C'H bond, q_O=-0.625, q_C=0.0432, $q_{C'}$=-0.204, $q_H(CH_2)$=-0.097, $q_H(C'H_3)$=0.002
31.	$H_3C'CH_2OH$	C'C=1.547, CO=1.434, OH=0.991, CH=1.086, C'H=1.0936÷÷1.0974, COH=103.98, gauche-conformation, q_O=-0.300, $q_H(OH)$=0.175
32.	$H_3C'CH_2O^-\ldots H'O_1H''$	CO=1.40, CC'=1.57, CH=1.111, C'H=1.086÷÷1.090, OH'=1.27, H'O_1=1.099, O_1H"=0.994, C'CO=112.68, HC'C=112.19, COH'=1069, H'O_1H"=100.7, q_O=-0.519, q_C=0.014, $q_{C'}$=-0.188, $q_H(CH_2)$=-0.035, $q_H(C'H_3)$=0.004, $q_{H'}$=0.222, q_{O_1}=-0.515, $q_{H''}$=0.0025

	1	2
33.	$H_3C'CH_2OH'...O'H''_2$	CO=1.430, CH=1.085, C'H=1.099, CC'=1.544, OH'=0.992, H'O'=1.72, O'H"=0.987, HC'C=110.3, C'CO=108.7, COH'=104.28, H'O'H"=114.5, $q_O=-0.333$, $q_{C'}=-0.188$, $q_C=0.005$, $q_{O'}=-0.335$, $q_{H''}=0.190$, $q_{H'}=0.2085$
34.	$H_3C'CH_2O^-...3(H'O_1H'')$	CC'=1.55, CO=1.41, CH=1.084, C'H=1.095, OH'=1.45, $H'O_1=1.025$, $O_1H''=0.996$, C'CO=114.06, HC'C=111.32, $H'O_1H''=100.25$, COH'=108.56, $q_O=-0.4676$, $q_{O'_1}=-0.4565$, $q_C=0.008$, $q_{C'}=-0.1932$, $q_{H'}=0.228$, $q_{H''}=0.0727$, $q_H(CH_2)=0.004$, $q_H(C'H_3)=0.02 \div 0.046$
35.	$(H_3C')_2C(H)O^-$	CO=1.337, C'H=1.087÷1.090, CH=1.13, CC'=1.62, HC'C=113.6, HCO=117.07, $q_O=-0.6142$, $q_C=0.122$, $q_{C'}=-0.203$, $q_H(CH)=-0.0892$
36.	$(H_3C')_2C(H)OH'$	CO=1.421, CH=1.097, C'H=1.085, OH'=0.957, CC'=1.55, HCO=104.55, COH'=103.0, HC'C=110.12, $q_O=-0.293$, $q_{H'}=0.1691$, $q_C=0.0844$, $q_{C'}=-0.1923$, $q_H(CH)=0.060$, trans-conformation
37.	$(H_3C')_2C(H)O^-...H'O'H''$	CO=1.40, CH=1.1107, CC'=1.575, C'H=1.088, OH'=1.270, H'O'=1.098, O'H"=1.003, HCO=111.9, COH'=107.0, H'O'H"=100.69, HC'C=112.4, $q_O=-0.522$, $q_C=0.0886$, $q_{C'}=-0.1941$, $q_{O'}=-0.5127$, $q_{H'}=0.2214$, $q_{H''}=0.010$

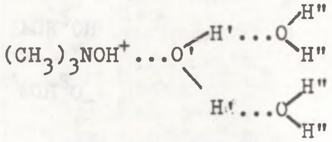
	1	2
38.	$(H_3C')_2C(H)O^-...3(H'O'H'')$	CO=1.42, CH=1.105, CC'=1.572, C'H=1.087, C'H=1.105, OH'=1.51, H'O'=1.013, O'H"=0.990, COH'=104.5, HCO=113.23, H'O'H"=100.88, q_O=-0.498, q_C=0.0882, q_H=-0.017, $q_{C'}$=-0.1969, $q_{H'}$=0.2193, $q_{O'}$=-0.475, $q_{H''}$=0.1215
39.	$(H_3C')_3CO^-$	CO=1.33, CC'=1.62, C'H=1.085÷1.088, C'CO=115.49, HC'C=113.05, q_O=-0.607, q_C=0.181, $q_{C'}$=-0.2022
40.	$(H_3C')_3COH'$	CO=1.44, OH'=1.00, CC'=1.57, C'H=1.095, COH'=102.0, HC'C=109.5, q_O=-0.297, $q_{H'}$=0.165
41.	$(H_3C')_3CO^-...H'O'H''$	CO=1.39, CC'=1.576, C'H=1.085÷1.090, OH'=1.28, H'O'=1.097, O'H"=1.00, C'CO=110.62, HC'C=112.5, COH'=108.7, H'O'H"=100.53, q_O=-0.5212, q_C=0.1612, $q_{C'}$=-0.188÷0.194, $q_{H'}$=0.236, $q_{O'}$=-0.5109, $q_{H''}$=0.099
42.	$(H_3C')_3COH'...O'H''_2$	CO=1.44, CC'=1.55, OH'=0.996, O'H"=0.986, C'H=1.092, H'O'=1.61, C'CO=106.17, COH'=106.9, HC'C=110.8, q_O=-0.363, $q_{O'}$=-0.3298, q_C=0.1507, $q_{C'}$=-0.181÷-0.191, $q_{H'}$=0.219, $q_{H''}$=0.195
43.	F_3CO^-	CO=1.275, CF=1.423, FCO=117.01, q_O=-0.572, q_F=-0.286, q_C=0.430
44.	F_3COH	CO=1.401, OH=0.991, CF=1.380, COH=104.0, FCO=110.4

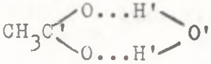
	1	2
45.	$F_3CO^-\ldots HO'H'$	$CO=1.31$, $CF=1.402\div1.407$, $OH=1.40$, $O'H'=0.994$, $HO'=1.037$, $COH=115.14$, $FCO=116.6$, $HO'H'=100.55$, $q_O=-0.5296$, $q_C=0.4586$, $q_F=-0.242\div-0.253$, $q_H=0.2332$, $q_{O'}=-0.4676$, $q_{H'}=0.0541$
46.	$F_3COH\ldots O'H'_2$	$CO=1.40$, $CF=1.366\div1.375$, $OH=0.997$, $HO'=1.589$, $O'H'=0.985$, $COH=105.6$, $HO'H'=114.2$, $FCO=108.88$, $q_O=-0.358$, $q_C=0.520$, $q_H=0.2494$, $q_F=-0.152\div0.174$, $q_{O'}=-0.33$, $q_{H'}=0.207$
47.	$F_3CO^-\ldots 3(HO'H')$	$CO=1.35$, $CF=1.387\div1.394$, $OH=1.53$, $HO'=1.00$, $O'H'=0.990$, $FCO=113.7$, $COH=113.9$, $HO'H'=99.9$, $q_O=-0.4935$, $q_{O'}=-0.4321$, $q_F=-0.2095\div0.2127$, $q_C=0.4805$, $q_H=0.2241$, $q_{H'}=0.093$
48.	 $F_3COH\ldots O'\genfrac{}{}{0pt}{}{\diagup H'\ldots O''H_2}{\diagdown H'\ldots O''H_2}$	$CO=1.385$, $CF=1.37\div1.378$, $OH=1.028$, $HO'=1.39$, $O'H'=0.985$, $H'O''=1.63$, $O''H=0.988$, $COH=106.23$, $FCO=110.1$, $HO'H'=112.8$, $H'O''H=116.96$, $q_O=-0.3999$, $q_{O'}=-0.440$, $q_{O''}=-0.3336$, $q_F=-0.1681\div-0.186$, $q_H(OH)=0.2684$, $q_{H'}=0.2335$, $q_H(O''H_2)=0.204$
49.	$CF_3CH_2O^-$	$CO=1.32$, $CF=1.383\div1.389$, $CH=1.129$, $CC=1.687$, $CCO=116.95$, $FCC=112.96$, $q_O=-0.5786$, $q_C(CH_2)=0.039$, $q_C(CF_3)=0.3266$, $q_F=-0.2127\div-0.2243$, $q_H=-0.0687$

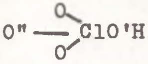
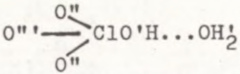
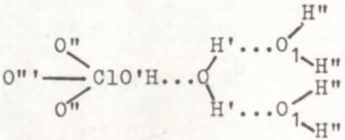
1	2
50. $CF_3C'H_2OH'$	q_{CO}=1.432, CF=1.373, CC=1.576, OH'=0.991, C'H=1.097, COH'=103.87, CCO=107.48, FCC=110.27, q_O=-0.2747, $q_{H'}$=0.1883, q_H=0.070, $q_{C'}$=-0.0264, q_C=0.427, q_F=$-0.149\div0.156$
51. $CF_3C'H_2O^-$...H'O'H"	C'O=1.39, CC'=1.60, C'H=1.11, CF=$1.380\div1.387$, OH'=1.31, H'O'=1.077, O'H"=0.999, C'OH'=110.2, FCC'=112.17, CC'O=111.78, H'O'H"=100.6, q_O=-0.5067, $q_{C'}$=0.011, q_C=0.3782, $q_{O'}$=-0.4987, $q_{H'}$=0.2252, $q_{H''}$=0.0214, q_F=$-0.188\div0.204$
52. $CF_3C'H_2O^-$...2(H'O'H")	E_{tot}=-593.7520 a.u., C'O=1.397, CC'=1.59, C'H=1.106, CF=1.38, OH'=1.40, H'O'=1.036, O'H"=0.993, C'OH=108.95, H'O'H"=100.5, FCC'=112.1, q_O=-0.474, $q_{O'}$=-0.467, $q_{C'}$=-0.02, q_C=0.388, q_H=0.0108, $q_{H'}$=0.2297, $q_{H''}$=0.06
53. $(CF_3)_2CHO^-$	CO=1.30, CF=1.38, CH=1.13, CC=1.67, FCC=116.0, q_O=-0.540, q_F=$-0.196\div-0.204$, q_C(CH)=-0.095, $q_C(CF_3)$=0.341, q_H=-0.043
54. $(CF_3)_2CHOH'$	CO=1.430, CH=1.094, OH'=0.993, CF=1.370, CC=1.587, HCO=108.16, COH'=104.0, FCC=111.5, q_O=-0.267, $q_{H'}$=0.198, q_H=0.088, q_F=$-0.142\div0.152$, q_C(CH)=0.013, $q_C(CF_3)$=0.417

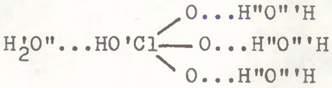
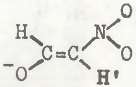
1	2
55. $(CF_3)_2CHO^-...H'O'H''$	CO=1.367, CC=1.62, CF=1.383, CH=1.112, OH'=1.375, H'O'=1.045, O'H"=0.994, COH'=113.6, FCC=113.2, HCO=116.4, H'O'H"=100.4, q_O=-0.4998, q_C(CH)=0.042, $q_C(CF_3)$=0.377, q_F=-0.171++-0.182, $q_{O'}$=-0.477, $q_{H'}$=0.225, q_H=-0.0036, $q_{H''}$=0.051
56. $(CF_3)_2CHOH'...O'H''_2$	CO=1.43, CF=1.37, CC=1.59, OH'=1.01, H'O'=1.61, O'H"=0.995, COH=106.53, H'OH'=112.98, FCC=111.53, q_O=-0.319, $q_C(CF_3)$=0.415, q_C(CH)=0.11, q_H=0.088, $q_{H'}$=0.2315, q_F=-0.148++-0.164, $q_{H''}$=0.225++0.250
57. $(CF_3)_3CO^-$	CO=1.294, CC=1.69, CF=1.36, FCC=115.5, CCO=114.6, q_O=-0.514, q_C=0.1477, $q_C(CF_3)$=0.3502, q_F=-0.186++-0.189
58. $(CF_3)_3C'OH$	C'O=1.424, CC'=1.616++1.622, OH=0.997, CF=1.36++1.37, CC'O=106.1, C'OH=103.4, FCC'=113.2, q_O=-0.269, $q_{C'}$=0.039, q_C=0.455++0.469, q_H=0.207, q_F=-0.145++-0.159
59. $(CF_3)_3C'O^-...HO'H'$	C'O=1.27, CC'=1.59, CF=1.361, OH=1.45, HO'=1.037, O'H'=0.994, C'OH=115.1, HO'H'=100.2, CC'O=114.55, FCC'=115.48, q_O=-0.4898, $q_{C'}$=0.1504, q_C=0.3613++0.3657, q_F=-0.1700++-0.1800, q_H=0.224, $q_{O'}$=-0.443, $q_{H'}$=0.067

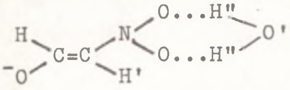
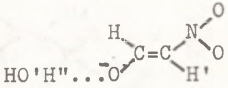
1	2
60. $(CF_3)_3C'OH...O'H'_2$	CO=1.42, CF=1.36, OH=0.990, O'H'=1.00, CC'=1.62, HO'=1.62, C'OH=103.2, HO'H'=113.0, CC'O=106.8, q_O=-0.3388, q_C=0.410++0.433, $q_{C'}$=0.049, q_F=-0.130++-0.14, $q_{O'}$=-0.322, q_H=0.243, $q_{H'}$=0.19
61. FCH_2O^-	CO=1.315, CF=1.445, CH=1.147, FCO=114.9, q_O=-0.6114, q_H=-0.114, q_F=-0.3031, q_C=0.1352
62. FCH_2OH	CO=1.425, CF=1.381, CH=1.03++1.075, OH=0.991, FCO=110.6, COH=104.2, q_O=-0.297, q_H(OH)=0.191, q_F=-0.160, q_C=0.132
63. NO_3^-	NO=1.315, q_O=-0.384, q_N=-0.152
64. $HO'NO_2$	NO=1.27, NO'=1.444, O'H=0.998, NO'H=100.5, q_O=-0.1548, $q_{O'}$=-0.1578, q_N=0.233, q_H=0.234
65. $O''_2NO^-...HO'H$	NO=1.35, NO"=1.30, q_O=-0.370
66. $O''_2NON...O'H'_2$	NO=1.43, q_O=-0.231, $q_{O''}$=-0.184, q_H=0.273, $q_{O'}$=-0.335, q_N=0.221
67. $(CH_3)_3NO$	NO=1.546, CN=1.522, CH=1.09, CNO=108.14, q_O=-0.377, q_N=-0.129, q_C=-0.09, q_H=0.07++0.095, μ=4.26D
68. $(CH_3)_3NOH^+$	NO=1.446, CN=1.527, OH=1.002, CH=1.09, NOH=102.91, CNO=103.92, q_O=-0.118, q_C=-0.080, q_N=-0.0625, q_H=0.13

1	2
69. $(CH_3)_3NO...H'O'H''$	$NO=1.51$, $CN=1.53$, $OH'=1.54$, $H'O'=1.00$, $O'H''=0.987$, $NOH'=109.82$, $H'O'H''=100.34$, $CNO=111.7$, $q_O=-0.3451$, $q_{O'}=-0.437$, $q_N=-0.110$, $q_C=-0.085$, $q_{H'}=0.210$, $q_{H''}=0.1027$
70. $(CH_3)_3NO...3(H'O'H'')$	$NO=1.4706$, $CH=1.09$, $OH'=1.58$, $H'O'=1.00$, $O'H''=0.992$, $CN=1.533$, $HCN=109.5$, $NOH'=111.14$, $H'O'H''=102.05$, $CNO=109.75$, $q_O=-0.3028$, $q_N=-0.0902$, $q_C=-0.08$, $q_H=\sim 0.09$, $q_{O'}=-0.430$
71. $(CH_3)_3NOH^+...O'H'_2$	$NO=1.43$, $CN=1.54$, $OH=1.027$, $O'H'=0.988$, $HO'=1.47$, $CH=1.09$, $NOH=107.45$, $HO'H'=115.82$, $CNO=101.0$, $q_O=-0.211$, $q_N=-0.0763$, $q_C=-0.076$, $q_H=0.2847$, $q_{O'}=-0.3374$, $q_{H'}=0.225$
72. 	$NO=1.451$, $CN=1.54$, $HO'=1.235$, $H'O_1=1.56$, $OH=1.10$, $O'H'=0.99$, $HO'H'=113.6$, $CNO=104.3$, $NOH=106.2$, $H'O_1H''=130.7$, $O_1H''=0.99$, $q_O=-0.250$, $q_N=-0.837$, $q_C=-0.08$, $q_H(OH)=0.2895$, $q_{O'}=-0.457$, $q_{H'}=0.260$, $q_{O_1}=-0.436$, $q_{H''}=0.265$
73. $HCOO^-$	$q_O=-0.5147$, $q_C=0.1582$, $q_H=-0.1288$
74. $HC(O')OH'$	$q_{O'}=-0.270$, $q_O(OH)=-0.260$, $q_H=0.074$, $q_{H'}=0.203$, $q_C=0.255$
75. $CH_3C'O_2^-$	$CC'=1.63$, $CH=1.087$, $CO=1.263$, $OCO=130.5$, $HCC=111.4$, $q_O=-0.5048$, $q_C=-0.2317$, $q_{C'}=0.2313$, $q_H=0.05$

	1	2
76.	$CH_3C'(O')OH'$	CH=1.085, CC'=1.537, CO'=1.2164, OH'=0.4899, C'OH=104.6, CC'O'=126.8, O'C'O=121.8, $q_{O'}=-0.2692$, $q_O=-0.2943$, $q_{H'}=0.2026$, $q_{C'}=0.3157$, $q_C=-0.2070$, $q_H=0.0834$
77.		CC'=1.61, CH=1.087, C'O=1.267, OH'=1.82, O'H'=0.995, HCC'=110.6, C'OH'=105.3, CC'O=115.8, H'O'H'=95.5, OH'O'=141.0
78.	$CH_3C'(O')OH'...O''H''_2$	CC=1.54, CO'=1.222, OH'=1.00, CH=1.085, H'O"=1.55, O'H"=0.982, CO=1.376, C'OH'=105.15, O'C'O=122.5, CC'O=125.1, H'O"H"=116.7, HCC'=110.1, $q_{O'}=-0.2917$, $q_O=-0.337$, $q_{H'}=0.234$, $q_{O''}=-0.3518$, $q_{H''}=0.2140$
79.	$CH_3C'(O_2^-)...2(H'O'H'')$	C'O=1.269, CC'=1.588, CH=1.086, OH'=1.53, H'O'=1.01, O'H"=0.985, HCC'=110.5, H'O'H"=100.1, CC'O=115.2, C'OH'=121.95, $q_{C'}=0.244$, $q_C=-0.224$, $q_O=-0.483$
80.	$CF_3C'O_2^-$	CC'=1.705, C'O=1.254, CF=1.38, FCC'=113.6, CC'O=112.6, $q_O=-0.4602$, $q_C=0.3126$, $q_{C'}=0.2399$, $q_F=-0.2098\div-0.2123$
81.	$CF_3C'(O')OH$	CC'=1.590, C'O'=1.213, C'O=1.213, OH=0.989, CF=1.37, CC'O'=123.11, CC'O=111.47, C'OH=104.33, FCC'=108.6, $q_C=0.4140$, $q_{C'}=0.2914$, $q_{O'}=-0.2783$, $q_O=-0.2315$, $q_H=0.2204$, $q_F=-0.139$
82.	ClO_4^-	ClO=2.00, OClO=109.5, $q_O=-0.2037$, $q_{Cl}=-0.1851$

	1	2
83.		HO'=1.006, ClO'=1.75, ClO"=2.26, (in trans-position relative to H-atom), ClO=2.32, ClO'H=99.38, OCl'=101.25, $q_{O'}=-0.1103$, $q_O=-0.0603$, $q_{O''}=-0.0447$, $q_{Cl}=0.0142$, $q_H=0.261$, $\mu=2.44D$
84.	$O'_3ClO^- \ldots HO''H'$	ClO=1.98, ClO'=1.99, OH=1.61, HO"=1.00, O"H'=0.984, O'ClO=109.23, ClOH=109.1, HO"H=99.9,
85.		O'H=1.049, ClO"'=2.33, ClO"=2.26, ClO'=1.77, HO=1.39, OH'=0.987, ClO'H=95.8, HOH'=104.08, O"ClO"'=101.3, $q_{O'}=-0.1647$, $q_H=0.295$, $q_{Cl}=-0.0894$, $q_{O'''}=-0.0501$, $q_{O''}=-0.0680$, $q_{\ddot{O}}=-0.3266$, $q_{H'}=0.230$, $\mu=5.29D$
86.		O'H=1.139, HO=1.178, OH'=0.990, $O_1H''=0.985$, ClO'=1.77, O"ClO"'=101.3, ClO"'=2.33, ClO"=2.26, ClO'H=100.06, HOH'=122.3, $H'O_1H''=128.3$, $q_H=0.3136$, $q_{O'}=-0.2142$, $q_{O'''}=-0.0588$, $q_{O''}=-0.0826$, $q_O=-0.4547$, $q_{O_1}=-0.344$, $q_{H'}=0.2783$, $q_{H''}=0.228$, $q_{Cl}=-0.165$, $\mu=10.78D$
87.	$ClO_4^- \ldots 4(HO'H')$	ClO=2.00, OH=1.73, H'O'=0.990, HO'=0.995, ClOH=99.9, HO'H=99.6, OClO=109.5, $q_O=-0.1484 \div -0.1504$, $q_{Cl}=-0.150$, $q_H=0.204$, $q_{O'}=-0.392$, $q_{H'}=0.122$

	1	2
88.	 $H_2'O''\ldots HO'Cl(O\ldots H''O'''H)_3$	HO'=1.096, H'O"=0.987, O"H=1.37, H"O"'=0.974, OH"=1.89, ClO=2.26÷÷2.33, ClO'=1.77, ClO'H=111.8, H'O"H=117.5, O'ClO=101.3, ClOH"=100.05, H"O"'H=99.7, $q_{O'}=-0.175$, $q_H(O'H)=0.303$, $q_{O''}=-0.341$, $q_O=-0.382$, $q_{O'''}=-0.366$, $q_{H'}=0.24$, $q_{H''}=0.190$, $q_H(O'''H)=0.176$, $q_{Cl}=-0.0793$, $q_O=-0.014$÷÷-0.041
89.	NO_2^-	NO=1.294, ONO=114.3, $q_O=-0.454$
90.	HONO'	NO'=1.224, NO=1.42, OH=0.993, ONO'=108.3, NOH=101.5, $q_{O'}=-0.09$, $q_O=-0.217$, $q_H=0.213$, $q_N=0.095$
91.		a) $E_{tot}=-350.9400$ **a.u.** CO=1.27, CC=1.42, CH=1.11, CH'=1.078, CN=1.38, NO=1.31, HCO=121.2, CCH'=121.7, CCN=122.4, CNO=120.2, CCO=126.28, $q_{O^-}=-0.335$, $q_C(CHO)=0.1025$, $q_C(CH')=-0.1646$, $q_H=0.0095$, $q_{H'}=0.0128$, $q_N=0.0816$, $q_O(NO)_2=-0.3385$, NO_2-group is coplanar with the $HC(O^-)CH'$ group, b) $E_{tot}=-350.9050$ **a.u.** CO=1.24, CC=1.385, CH=1.114, CH'=1.071, CN=1.495, NO=1.28, HCO=120.44, CCH'=123.8, CCN=122.07, CNO=120.38, CCO=126.7, $q_{O^-}=-0.4316$, $q_C(CHO)=0.0924$, $q_C(CH')=0.211$, $q_{H'}=0.00$, $q_N=0.1096$, $q_O(NO_2)=-0.2623$, NO_2-group is in perpendicular position relative to $HC(O^-)CH'$ plane

1	2
92. 	E_{tot}=-425.9360 a.u. CO=1.24, CC=1.43, CH=1.08, CH'=1.075, CN=1.38, NO=1.32, OH"=1.77, O'H"=0.990, HCO=120.7, CCH'=122.4, CCN=121.7, CNO=120.4, CCO=126.6, OH"O'=146.2, H"O'H"=96.4, NOH"=108.6, q_{O^-}=-0.3373, q_C(CHO)=0.1075, q_C(CH')=-0.1382, q_N=0.0801, q_O(NO_2)=-0.325, q_O(H_2O)=-0.4604, q_H(H_2O)=0.1784, NO_2-group is coplanar with the HC(O^-)CH' plane
93. 	E_{tot}=-425.9300 a.u. CO=1.26, CC=1.396, CH=1.105, CH'=1.07, CN=1.43, NO=1.30, OH"=1.477, O'H"=1.013, O'H"=0.987,HCO=119.95, CCH=123.3, CCN=121.8, CNO=119.9, CCO=126.3, COH"=106.83, HC'H"=100.23, q_{O^-}=-0.3823, q_C(CHO)=0.1123, q_C(CH')=-0.1517, q_H(CHO)=0.033, $q_{H'}$=0.0242, q_N=0.0935, q_O(NO_2)=-0.30, $q_{O'}$=-0.4423, $q_{H''}$=0.229, q_H=0.0885, NO_2 group is coplanar with the OCH=CH fragment
94. HF	E_{tot}=-98.5729, HF=0.956, q_F=-0.209
95. F^-...HOH'	FH=1.071, OH=1.227, OH'=1.015, HOH'=101.2, q_F=-0.534, q_H=0.195, q_O=-0.587, $q_{H'}$=-0.074, E_{tot}=-172.1540 a.u.

≠ As a rule, data for the most stable conformations are given. With a few exceptions (Nos 52, 91-93) the total energies of the systems considered are recorded in Tables 1-3. The following simplified representation of the geometries in the 2nd column of the present Table is accepted:

a) the bond lengths (in Å) are given after the symbols of atoms forming the given bond (e.g., HO=1.045);

b) valence angles (in degrees) follow after the indication of the atoms forming the given angle (e.g., in the case of water molecules: HOH=100.02). As a rule, conformation angles are not indicated. Atomic charges (Mulliken population) are in the units of the charge of the electron. It seems that in the case of systems 57-60, the full optimization of the geometry was not reached.

Organic Reactivity
Vol. 24 3(87) 1987

PHOTOELECTRON SPECTRA OF MOLECULES
9. HYDROXYLAMINES

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

Department of Geophysics, Laboratory of Chemical
Kinetics and Catalysis, The Computing Center,
Tartu State University, Tartu, Estonian SSR

Institute of Chemical and Biological Physics,
Academy of Sciences of the Estonian SSR,
Tallinn, Estonian SSR

Received September 23, 1987

Photoelectron spectra (PES) of 6 methyl substituted hydroxylamines were studied using nonempirical (Gaussian-80 program system, STO-3G, 3-21G and 4-31G basis sets) and semiempirical (HAM/3 and CNDO/2) methods of quantum chemical calculations. Photoelectron spectra of $HONMe_2$, $MeONH_2$ and MeONHMe molecules were measured.

The present series of reports[1-8] has dealt with the analysis of the PE spectra of various classes of organic molecules, making use of both empirical relationships (IP dependence on the bonding energy of inner shell electrons, on proton affinities; comparison of the PE spectra of homological series, etc.) and quantum chemical calculations. In this communication, the experimental PE spectra of some N-and O-alkyl substituted hydroxylamines $R_1R_2ONR_3R_4$ have been compared with the energy eigenvalues according to the

Koopman's theorem on the nonempirical calculation level (the STO-3G and 3-21G basis sets in the Gaussian-80 system) and on the level of semiempirical calculations using the CNDO/2 and HAM/3 methods.

Experimental

The equipment and the experimental technique used were described in report[1]. Since the retarding field spectrometer operates rather efficiently, collecting electrons and as the susceptibility of electrons of different kinetic energy does not differ very significantly, the current of photoelectrons is registered by means of a dynamic electrometer. The given spectra have been obtained in the result of a repeated scanning. Vertical IP were determined at the maximums of the corresponding peaks, the accuracy being 0.05-0.1 eV. Strictly saying, the IP found from the PE spectra can be considered adiabatic only if the analysis of the band's vibrational structure identifies the transition as the 0-0 one. Our experience has shown that the IP determined as the beginning of the spectral band, shifted at the energy scale by the half-width of the obtained argon line, coincides with the IP found by means of photoionization, the accuracy being ±0.03 eV.

The PE spectra of three methyl substituted hydroxylamines are visualized in Fig. 1. Some data about the spectra of these compounds were given in report[9].

The compounds measured were liberated from the corresponding hydrochlorides using standard methods during the experiment. The synthesis obeyed the following scheme:

$$HONHCH_3 \cdot HCl + KOH \longrightarrow HONHCH_3 + H_2O + KCl$$

Since the PE spectrum susceptibility to the compounds present does not differ remarkably, there are certain difficulties in identification of the lines of water and the corresponding hydroxyl amine in the spectrum of the mixture.

Each sample was subjected to several freeze-pump-thaw cycles. Owing to a good volatility of hydroxylamines it

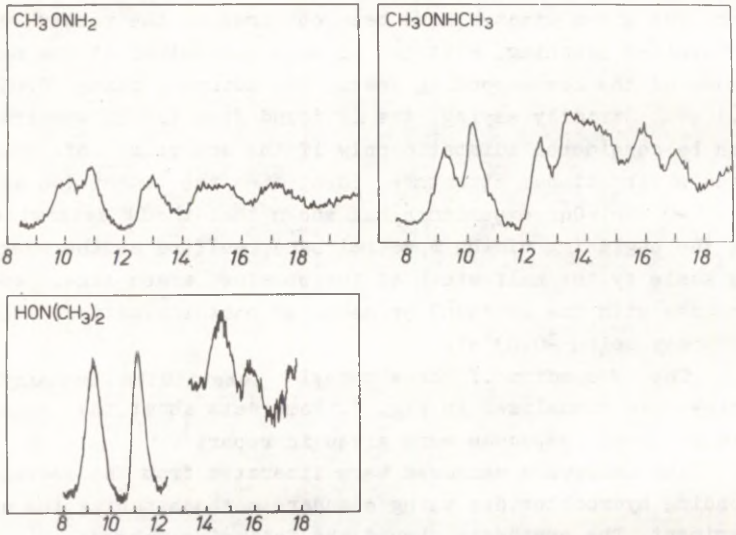


Fig. 1. PE spectra of hydroxylamine methyl derivatives.

was usually possible to suppress the water spectrum and thus obtain reliable PE spectra of those compounds.[*] The hydroxylamine and O-methyl hydroxylamine spectra agree well with those given in[10]. These methods did not work in the case of a heavier $H_3CON(CH_3)_2$ amine, so only the first adiabatic and vertical IP can be considered reliable.

Table 1 presents the IP values given both in literature and those found according to the PE spectra as well as the results of quantum chemical calculations.

In keeping with the Koopman's theory, the IP_i values have been compared with the calculated eigenvalues of energy ($-\varepsilon_i$). Alongside the MO symmetry and their approximate localization character have been given (commonly accepted symbols are used). The calculated total energies of molecules have also been given. All nonempirical calculations were carried out using a full optimization of the geometry. Similar calculations in a split-valence 3-21G basis set practically reproduce the experimental geometries of molecules, therefore Table 1 provides optimum bond lengths and valence angles, calculated using the 3-21G basis set for the whole set of molecules studied. Literature provides data about the experimental geometry of H_2NOH, determined from the microwave spectra. For $MeONH_2$, trans-position of the NH_2 group relative to the OC bond was established (see references in[10]).

Discussion

The compounds in which the adjacent atoms have a lone pair of electrons (e.g., of the $X_1X_2NNX_3X_4$ type)[10] or two lone pairs (in peroxides of the X_1OOX_2 type)[11] each, have been thoroughly studied. In hydroxylamines there are one and two lone pairs of electrons, respectively, on the adjacent nitrogen and oxygen atoms. We have investigated the PE

---

[*] The exception is $HONMe_2$ whose low volatility did not enable us to firmly establish even its first ionization potential.

Table 1

Ionization Potentials of Hydroxylamines, Determined from PE Spectra and Orbital Energies ($-\varepsilon_i$),eV Calculated by Means of Different Methods

1. $HONH_2$

IP_v[a]	CNDO/2[b]		HAM/3[c]		STO-3G[d]	
	$-\varepsilon_i$	MO	$-\varepsilon_i$	MO	$-\varepsilon_i$	MO
10.59	15.05	5a' n_N, σ_{OH}	10.59	5a' n_N	9.14	7a' n_N
11.70	15.77	2a" n_O	11.50	2a" n_O	10.34	2a" n_O
15.50	20.37	4a' σ_{NO}	15.33	4a' σ_{NO}	14.24	6a' σ_{NO}
16.80	22.30	3a' σ_{OH}, n_N	16.32	3a' σ_{OH}, n_N	15.59	5a' σ_{OH}
(17.0)	22.86	1a" π_{NO}, π_{NH_2}	17.68	1a" π_{NH_2}	16.56	1a" π_{NH_2}

3-21G[e]		4-31G[f]		6-31G[g]	
$-\varepsilon_i$	MO	$-\varepsilon_i$	MO	$-\varepsilon_i$	MO
11.04	7a' n_N	11.55	7a' n_N	11.59	7a' n_N
12.69	2a" n_O	13.14	2a" n_O	13.19	2a" n_O
15.76	6a' σ_{NO}	16.32	6a' σ_{NO}	16.38	6a' σ_{NO}
17.46	5a' σ_{OH}	18.05	5a' σ_{OH}	18.11	5a' σ_{OH}
18.48	1a" π_{NH_2}	18.83	1a" π_{NH_2}	18.87	1a" π_{NH_2}

a-- see[10] and[11]; this report: $IP_a^{(1)}$ = 10.00 eV, $IP_a^{(2)}$ = 11.5 eV, $IP_v^{(1)}$ = 10.56 eV, $IP_v^{(2)}$ = 11.69 eV.

b - E_{tot} = -32.4204 a.u., this report.

c - this report, experimental geometry.

d - E_{tot} = -129.2631 a.u., this report.

e - E_{tot} = -130.2564 a.u., this report; optimum geometry: NH = 1.008 Å, NO = 1.468 Å, OH = 0.967 Å, HNO = 104.54°, NOH = 102.87°, HNH = 108.88°.

f - E_{tot} = -130.7918 a.u., see[10,12], this report, $E_{tot}(HONH_3^+)$ = -131.1158 a.u.,; optimum geometry: NO = 1.440 Å, H1N = 1.0113 Å, NH = 1.0098 Å, OH = 0.965 Å, HON = 110.41°, HNO = 106.6°, H1NO = 113.3°;

$E_{tot}(H_2NO^-)$ = -130.1392 a.u., optimum geometry: NO = = 1.506 Å, HN = 1.015 Å, HNO = 106.5°, HNH = 105.7°, PA_{calc} = 409.3 kcal/mol.

g - E_{tot} = -130.9232 a.u., see[10]; experimental geometry:[13] NH = 1.016 Å, NO = 1.453 Å, OH = 0.962 Å, HNH = = 107.1°, HNO = 103.25°, NOH = 101.4°, NH_2 trans relative to OH.

2. HONHMe[≠]

CNDO/2[a]		HAM/3[b]		STO-3G[c]		3-21G[d]	
$-\varepsilon_i$	MO	$-\varepsilon_i$	MO	$-\varepsilon_i$	MO	$-\varepsilon_i$	MO
13.17	n_N	9.65	n_N	8.51	n_N	10.44	n_N
14.69	n_O	10.91	n_O	10.17	n_O	12.42	n_O
17.58	π_{CH_3}, σ_{NO}	13.62	π_{CH_3}	13.10	σ_{NO}	14.36	σ_{NO}
19.30	σ_{OH}, π_{CH_3}	14.05	π_{CH_3}	13.92	σ_{OH}, π_{CH_3}	15.26	σ_{OH}, π_{CH_3}
21.37	σ_{NC}, σ_{NH}	14.71	σ_{NO}	14.28	σ_{NC}, σ_{CH}	15.84	σ_{NC}, π_{CH_3}
						17.82	σ_{OH}, π_{CH_3}

≠ - PE spectrum is not known (see text).

a - E_{tot} = -41.0848 a.u., this report.

b - optimum 3-21G geometry.

c - E_{tot} = -167.8409 a.u., this report.

d - E_{tot} = -169.0723 a.u., this report; optimum geometry: NO = 1.467 Å, NH = 1.008 Å, OH = 0.967 Å, CN = 1.478 Å, H1C = 1.079 Å, HC = 1.083 Å, CNO = 105.60°, HCN = = 109.95°, H1CN = 108.36°, HNO = 103.62°, NOH = 103.89°.

Table 1 continued

3. $HONMe_2$

IP_v^a	CNDO/2^b $-\varepsilon_i$	CNDO/2^b MO	HAM/3^c $-\varepsilon_i$	HAM/3^c MO	STO-3G^d $-\varepsilon_i$	STO-3G^d MO	3-21G^e $-\varepsilon_i$	3-21G^e MO
9.22	12.67	8a" n_N	9.46	8a' n_N	8.11	11a' n_N	10.02	11a' n_N
11.08	14.22	5a" n_O	10.71	5a" n_O	9.95	6a" n_O	12.20	6a" n_O
			13.21	4a" π_{CH_3}	12.57	10a' σ_{NO}	13.99	19a' σ_{NO}
			13.45	3a" π_{CH_3}	13.14	5a" π_{CH_3}	14.19	5a" π_{CH_3}
(13.0)			13.72	7a' σ_{NO}				
			14.08	6a' σ_{OH}, π_{CH_3}				
14.55	17.35	7a' σ_{NO}, π_{CH_3}	14.95	2a" σ_{NC}	13.93	9a' σ_{OH}	15.04	4a" π_{CH_3}
	17.44	4a" n_O, π_{CH_3}	15.21	5a'	14.17	4a" π_{CH_3}	15.29	9a' σ_{OH}
15.8	19.12	3a" π_{CH_3}	16.24	4a'	15.45	3a"	16.97	3a" σ_{NC}

a - $IP_a^{(1)}$ = 8,60 eV, $IP_a^{(2)}$ = 10.80 eV; this report, the spectrum was recorded by J.J. Villem (Tartu State University).

b - E_{tot} = -49.7681 a.u., this report; c - this report, optimum 3-21G geometry.

d - E_{tot} = -206.4263 a.u., this report; e - E_{tot} = -207.8906 a.u.; optimum geometry: NO = = 1.466 Å, OH = 0.968 Å, CN = 1.472 Å, H1C = 1.086 Å, HC = 1.080 Å, CNO = 104.89°, HCN = 108.65°, H1CN = 111.28°, HON = 103.97°.

Table 1 continued

4. $MeONH_2$

IP_v[a]	CNDO/2[b] $-\varepsilon_i$	MO		HAM/3[c] $-\varepsilon_i$	MO	
10.16	13.87	7a'	n_N	9.77	7a'	n_N
10.93	14.14	3a"	n_O, π_{NH_2}	10.34	3a"	n_O
12.94	17.39	6a'	π_{CH_3}, σ_{NO}	13.15	6a'	π_{CH_3}
15.0	19.15	2a"	π_{CH_3}, π_{NH_2}	14.70	2a"	π_{CH_3}
	21.23	5a'	σ_{CO}, σ_{NO}	14.89	5a'	σ_{CO}
17.31	24.34	4a'	π_{CH_3}, σ_{NO}	16.55	4a'	σ_{NO}
17.31	25.14	1a"		17.20	1a"	π_{NH_2}, n_O

STO-3G[d] $-\varepsilon_i$	MO		4-31G[e] $-\varepsilon_i$	MO		3-21G[f] $-\varepsilon_i$	MO	
8.68	10a'	n_N	11.25	10a'	n_N	10.84	10a'	n_N
9.58	3a"	n_O	12.39	3a"	n_O	11.54	3a"	n_O
12.46	9a'	σ_{NO}, π_{CH_3}	13.96	9a'	$\bar{n}_O$	13.65	9a'	σ_{NO}, π_{CH_3}
14.36	8a'	σ_{CO}	17.21	2a"	π_{CH_3}, π_{NH_2}	15.93	8a'	σ_{CO}
14.78	2a"	π_{CH_3}	17,62	8a'	σ_{CO}	16.11	2a"	π_{CH_3}
16.12	7a'	π_{CH_3}	18.32	7a'	π_{CH_3}	17.35	7a'	π_{CH_3}
17.21	1a"	π_{NH_2}, n_O	19.41	1a"	π_{NH_2}, π_{CH_3}	18.67	1a"	π_{NH_2}

a - $IP_a^{(1)} = 9.55$ eV, $IP_a^{(2)} \approx 10.5$ eV; this report, see also[10,11]

b - $E_{tot} = -41.0869$ a.u., this report

c - optimum 3-21G geometry; this report

d - $E_{tot} = -167.8447$ a.u.; trans-conformation is by 1.82 kcal/mol less stable than cis-conformation: for protonated form, $MeONH_3^+$ $E_{tot} = -168.2483$ a.u.

e - $E_{tot} = -169.7077$ a.u.; see[11]

f - $E_{tot} = -169.0672$ a.u.; this report: optimum geometry: NO = 1.463 Å, NH = 1.009 Å, CO = 1.447 Å, HC = 1.081 Å, HNO = 104.05°, CON = 110.44°, HCO = 108.92°, H1CO = = 109.66°.

Table 1 continued

5. MeONHMe

IP_v[a]	CNDO[b]		HAM/3[c]		3-21G[d]	
	$-\varepsilon_i$	MO	$-\varepsilon_i$	MO	$-\varepsilon_i$	MO
9.39	13.45	n_N	9.48	n_N	10.31	n_N
10.22	15.51	n_O	9.95	n_O	11.39	n_O
12.61	16.22	σ_{NC}, π_{CH_3}	12.28	σ_{NO}, π_{CH_3}	13.24	σ_{NO}, π_{CH_3}
13.95	16.27	σ_{CO}, σ_{NH}	13.46	σ_{NO}	14.61	σ_{CO}, π_{CH_3}
			13.67	π_{CH_3}, σ_{NC}	15.06	π_{CH_3}, σ_{NC}
			14.62	π_{CH_3}	19.95	π_{CH_3}
(14.5)			14.94	σ_{CO}, π_{CH_3}	16.85	σ_{CO}, π_{CH_3}
			15.66	σ_{NO}		
16.11	18.10	π_{CH_3}	16.38		17.06	π_{CH_3}, σ_{NO}
17.25	20.75	π_{CH_3}	20.89		18.39	

a - $IP_a^{(1)} = 8.92$ eV, $IP_a^{(2)} = 10.0$ eV, $IP_a^{(3)} = 12$ eV; this report

b - $E_{tot} = -49.7207$ a.u., this report

c - optimum 3-21G geometry, this report

d - $E_{tot} = -207.8833$ a.u., this report; optimum geometry: NO = 1.461 Å, NH = 1.009, CO = 1.448 Å, HC = 1.81 Å, CN = 1.479 Å, CNO = 105.82°, H1CN = 112.16°, HCN = = 108.53°, HNO = 103.15°, CON = 110.67°, HCO = 109.13°, H1CO = 109.71°.

6. $MeONMe_2$

IP_v[a]	CNDO/2[b]		HAM/3[c]	
	$-\varepsilon_i$	MO	$-\varepsilon_i$	MO
9.33	12.43	10a' n_N	9.09	10a' n_N
	13.64	6a" n_O	9.94	6a" n_O
	16.24	9a' σ_{NO}, π_{CH_3}	12.29	9a' σ_{NO}, π_{CH_3}
	16.99	5a" π_{CH_3}	12.81	5a" π_{CH_3}
	18.45	8a' σ_{CO}	13.41	4a" π_{CH_3}

Table 1 continued

CNDO/2[b]			HAM/3[c]		
$-\varepsilon_i$	MO		$-\varepsilon_i$	MO	
19.01	4a"	π_{CH_3}	13.43	8a'	$\bar{n}_O$
19.75	3a"	π_{CH_3}, σ_{NO}	13.84	3a"	σ_{NC}, π_{CH_3}
20.35	7a'	π_{CH_3}	14.23	7a'	

STO-3G[d]			3-21G[e]		
$-\varepsilon_i$	MO		$-\varepsilon_i$	MO	
8.06	14a'	n_N	9.91	14a'	n_N
9.28	7a"	n_O	11.26	7a"	n_O
11.68	13a'	σ_{NO}	13.00	13a'	σ_{NO}
12.99	6a"	σ_{NC}, π_{CH_3}	14.06	6a"	σ_{NC}, π_{CH_3}
13.14	12a'	σ_{CO}	14.38	12a'	σ_{CO}
14.17	5a"	π_{CH_3}	14.94	5a"	π_{CH_3}
14.42	4a"	π_{CH_3}	15.72	4a"	π_{CH_3}
14.86	11a'	π_{CH_3}	15.85	11a'	π_{CH_3}
			17.50		
			17.55		

a - this report, $IP_a^{(1)}$ = 8.78 eV

b - E_{tot} = -58.4508 a.u., this report

c - optimum 3-21G geometry, this report

d - E_{tot} = -245.0109 a.u., this report

e - E_{tot} = -246.7016 a.u., this report; optimum geometry: NO = 1.460 Å, CO = 1.448 Å, CN = 1.473 Å, H1C = 1.086Å, HC = 1.080 Å, H1C (in MeO) = 1.079 Å, HC (in MeO) = = 1.082 Å, CNO = 104.95°, H1CN = 111.28°, HCN = 108.71°, CON = 111.11°, H1CO = 109.65°, HCO = 109.18°.

spectra of the O-methyl as well as the N-methyl hydroxylamines.

The compounds having lone electron pairs in the α-position relative to the nucleophilic center are considered "supernucleophilic"[14] and show the so called α-effect[11], which is mainly caused by the interaction of the lone electron pairs via space.[15]

Earlier calculations for these compounds were carried out without optimization of the geometry, using the experimental or the standard bond lengths and valence angles values in order to find certain parameters of molecules, including the conformational barrier.[16] In communication[17], the PE spectra of hydroxylamine and O-methyl hydroxylamine were interpreted on the basis of the semiempirical CNDO/2 calculations. Only in report[12] the nonempirical calculation of hydroxyl amine and its flurroderivatives has been carried out with a full optimization of geometry using the STO-3G and 4-31G basis sets.

The semiempirical CNDO/2 calculations applying experimental geometry do not correctly reflect the conformation of hydroxylamine molecules. The structure whose conformational angle $\varphi = 180^\circ$ (see Fig. 2) has turned out to be by 2.13 kcal/mol more stable than the experimentally established value ($\varphi = 0^\circ$). This result fits those of report[18], but contradicts some other results.[17] Semiempirical HAM/3 calculations of different structures obtained via the OH-bond rotating relative to the lone nitrogen pair (angle φ) refer (in the case of fixed bond lengths) to some preference of the experimentally established conformations. In Fig. 2 is given the dependence of the MO energies on angle φ, calculated by means of the HAM/3 method. It should be taken into consideration that the n_O and n_N orbitals form the mixture in which their statistical weight depends on the angle φ.

The following conclusion can be drawn on the basis of these results and of the results of nonempirical calculations of the molecules using a full optimization of their geometry: in hydroxylamine and in its methyl derivatives, the conformation in which the α-effect or the mutual repulsion of lone electron pairs is minimal, appears to be the most stable one. As it was indicated in report[16], the above-given rule need not stay valid in the case of electronegative substituents. From the viewpoint of quantum chemical analysis of the PE spectra, the alkyl substituted hydroxyl amines can be studied quite easily, since they have two well resolved bands corresponding to the ionization of nitrogen and oxygen lone pairs. Methyl substitution at nitrogen and oxygen induces the band shift of the lone electron pairs of these atoms in accordance with the substituents' induction effect. In this case, overlapping of these bands is not observed. Fig. 3 presents the correlation diagram of the MO($-\varepsilon_i$) energies of all six methyl substituted hydroxylamines, the data of nonempirical calculation in the 3-21G basis set were used.

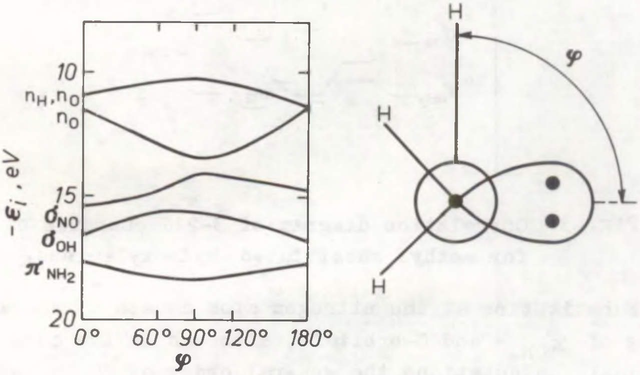


Fig. 2. The Walsh diagram of $HONH_2$ molecule according to the calculations using HAM/3 (fixed 3-21G optimum geometry).

If the number of methyl groups grows, the energy of σ-orbitals of the N-O bond will be growing, while the methyl substitution at oxygen atom leads to the mixing of these orbitals with the π_{CH_3} orbitals.

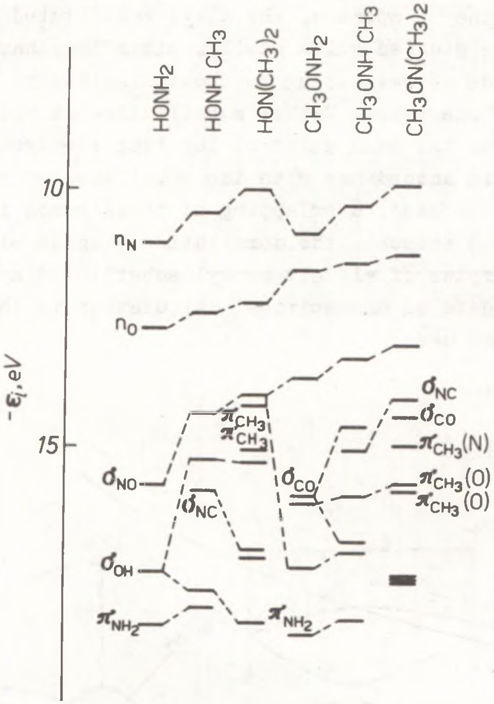


Fig. 3. Correlation diagram of 3-21G energies of MO for methyl substituted hydroxylamines.

Substitution at the nitrogen atom causes a remarkable mixing of π_{CH_3}- and σ-orbitals, although in the case of non-empirical calculations the general order of MO is retained. Mixing is less clearly expressed in the case of the HAM/3 method and the orbitals of the methyl group of the π_{CH_3} character lie higher than the σ_{NO} orbitals. Similar changes in the spectrum are traced if oxygen attaches the methyl group.

The results of statistical treatment of the experimental and calculated PE spectra (i.e. eigen values $-\mathcal{E}_i$) of some molecules in terms of Eq. (1)

$$IP_i = a + b(-\mathcal{E}_i), \qquad (1)$$

are given in Table 2; a and b are constants, IP_i are the successive experimental ionization potentials of the PE spectra.

Table 2

Results of Regression Analysis of Spectra According to Eq. (1)[*]

Compound	Method	a	b	r	S	n
1. H_2NOH	CNDO/2	-1.804(0.903)	0.841(0.049)	0.997	0.30	4
	HAM/3	-0.534(0.414)	1.055(0.030)	0.999	0.15	4
	STO-3G	1.739(0.017)	0.966(0.004)	0.999	0.03	4
	3-21G	-0.842(1.068)	1.017(0.075)	0.995	0.38	4
	4-31G	-1.142(0.988)	1.001(0.066)	0.996	0.34	4
	6-31G	-1.149(0.989)	0.998(0.066)	0.996	0.34	4
2. $HONMe_2$	CNDO/2	-3.900(1.265)	1.041(0.077)	0.997	0.37	4
	HAM/3	-1.375(0.606)	1.140(0.049)	0.998	0.23	4
	STO-3G	2.137(0.237)	0.885(0.019)	0.999	0.12	4
	3-21G	-0.683(0.811)	0.982(0.059)	0.996	0.32	4
3. $MeONH_2$	CNDO/2	1.666(0.904)	0.647(0.049)	0.989	0.45	6
	HAM/3	0.362(0.737)	0.999(0.056)	0.995	0.33	6
	STO-3G	2.250(0.447)	0.905(0.036)	0.998	0.23	6
	3-21G	-1.047(0.440)	1.033(0.031)	0.999	0.18	6
	4-31G	-0.447(1.270)	0.927(0.085)	0.992	0.53	6
4. MeONHMe	CNDO/2	-2.621(1.604)	0.892(0.090)	0.980	0.69	6
	HAM/3	-0.846(0.341)	1.094(0.026)	0.999	0.17	6
	3-21G	-2.319(0.790)	1.119(0.050)	0.995	0.35	6

---

[*] r - correlation coefficient, s - standard deviaton(in eV), n - number of points. Confidence range for a,b is in parenthesis.

In the case of these compounds whose PE spectra are not known, correlation between the independent HAM/3 and nonempirical 3-21G calculations, the correlation coefficient value reached 0.990 for both HONHMe and $MeONMe_2$, standard deviation being 0.2 ÷ 0,35 eV.

The statistical characteristics of Table 2 reveal that all calculation methods satisfactorily characterize the molecules studied. The conditions for the greatest closeness of the regression coefficients in Eq. (1) to the ideal values ($a = 0$ and $b = 1.0$) make us admit that here both the semiempirical CNDO/2 method, as well as nonempirical calculations in the minimum (STO-3G) basis set clearly fall behind the calculations using the HAM/3 method and also those applying the split-valence 3-21G, 4-31G and 6-31G basis sets.

The proton affinity can be considered a certain (though not full) characteristic of nucleophility of molecules. In the compounds studied, the nitrogen atom[19-22] is the prime candidate for the protonation center. The CNDO/2 calculation of proton affinities (in kcal/mol) of the molecules, taking into account the correlational relationship[23] between the experimental and calculated proton affinity values predicts the following PA values for hydroxylamines (not corrected calculated PA values are in parentheses):

$HONH_2$	196.0(277.7)	HONHMe	209.6(300.3)
$MeONH_2$	210.1(301.1)	$HONMe_2$	215.3(309.8)
MeONHMe	201.0(286.0)	$MeONMe_2$	218.3(314.6)

Recalculation of the PA_{calc} values for $HONH_2$ which were found by means of nonempirical methods using correctional relationships from report[20], yields the following probable "experimental" PA_{exp} values:

Basis set	PA_{calc}	PA_{exp}[a,b]
STO-3G	246.7[20,21a]	201.7
3-21G	209.9[21]	195.5
4-31G	204.1[a]	195.8
6-31G*	205.9[21]	198.9
MP4/6-31G*	189.9[24]	190.3

Mean value: 196.4

---

a - this report, b - PA value for NH_3 is taken to equal 207 kcal/mol[17,18].

PA(H_2NOH) = 199.7 kcal/mol was obtained from the linear dependence[9] of the proton affinities of the molecule on their ionization potential (provided that the protonation center and the ionization center coincide). According to the nonempirical calculation with a full optimization of geometry on the STO-3G basis set of the O-methyl hydroxyl amine protonated form, while taking also into consideration the rlationships from ref.[20], the predicted value of $PA_{exp}(MeONH_2)$ = 204.6 kcal/mol (PA_{calc} = 253.2). The proton affinity of this compound (205.4 kcal/mol) established experimentally[22] using the ICR spectrometry practically coincides with the given value, as well as that (206 kcal/mol) presented in ref.[9] owing to the linear relationship between the PA and IP_v.

The difference between the experimental PA value of this compound and the mean value of PA_{exp} for $HONH_2$ is 9.0 kcal/mol, which quite correctly reflects the effect of the methyl substitution effect for the hydrogen atom (≈ 8 kcal/mol) in methanol and in the acetic acid.[17]

It can be said in conclusion that the PA values for $HONMe_2$ and $MeONMe_2$ predicted[9] on the basis of linear dependence between the proton affinities and the ionization potential of the protonation center, are equal to ≈214 and 220 kcal/mol respectively.

The authors are grateful to J.J. Villem for recording the PE spectrum of $HONMe_2$.

References

1. I.A. Koppel, U.H. Mölder, and R.J. Pikver, Organic Reactivity, 20, 45 (1983).
2. U,H. Mölder, R.J. Pikver, and I.A. Koppel, ibid., 20,208 (1983).

3. U.H. Mölder, R.J. Pikver, and I.A. Koppel, ibid., 20, 230 (1983).
4. U.H. Mölder, R.J. Pikver, and I.A. Koppel, ibid., 20, 355 (1983).
5. U.H. Mölder and I.A. Koppel, ibid., 20, 483 (1983).
6. U.H. Mölder and I.A. Koppel, ibid., 21, 27 (1984).
7. U.H. Mölder, R.J. Pikver, and I.A. Koppel, ibid.,24, 97 (1987).
8. U.H. Mölder, R.J. Pikver, and I.A. Koppel, ibid., 24, 213 (1987).
9. I.A. Koppel, U.H. Mölder, and R.J. Pikver, ibid., 17, 457 (1980),
10. K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, and S. Iwata, Handbook of HEI Photoelectron Spectra of Fundamental Organic Molecules, Japan Scientific Societies Press, Tokyo; Halsted Press, New York, 1981.
11. P. Rademacher and B. Freckmann, J. Electron Spectrosc. Relat. Phenom., 19, 251 (1980).
12. I.F. Olsen and J.M. Howell, J. Fluorine Chem., 12, 123 (1978).
13. K.-H. Hellwege and A.M. Hellwege (Eds.), Landolt-Börnstein Numerical Data and Functional Relationships in Science and Technology, New Series, Vol. 7, Springer-Verlag, Berlin, Heidelberg, New York, 1976.
14. I.A. Zoltewicz and L.W. Deady, J. Am. Chem. Soc., 94, 2765 (1972).
15. R. Hoffmann, Acc. Chem. Res., 4, 1 (1971).
16. L. Radom, W.J. Hehre, and J.A. Pople, J. Am. Chem. Soc., 93, 289 (1971); ibid., 94, 2371 (1972).
17. K. Kimura and S. Katsumata, J. Chem. Phys., 67, 1225 (1977).
18. M.S. Gordon, J. Am. Chem. Soc., 91, 3122 (1969).
19. H. Johansson, P.A. Kollman, J.F. Liebman, and S. Rothenberg, J. Am. Chem. Soc., 96, 3750 (1974).
20. I.A. Koppel, U.H. Mölder, and V.A. Palm, Organic Reactivity, 22, 3 (1985).
21. R.A. Whiteside, M.J. Frisch, J.S. Binkley, et al., CMU Quantum Chemistry Archive, 2nd Edition, 1981, CMU,

Pittsburgh, PA. 15213.

22. I.A. Koppel, Dr. Sci. Thesis (in Russian), Moscow, 1986.
23. I.A. Koppel and U.H. Mölder, Organic Reactivity, 18, 42 (1981).
24. J.E. DelBene, U.J. Frisch, K. Raghavachari, and J.A. Pople, J. Phys. Chem., 86, 1529 (1982).

Organic Reactivity
Vol. 24 3(87) 1987

DIFFERENTIAL-CONDUCTOMETRIC STUDY OF THE AMINOACID ADDITIONS ON THE CONDUCTIVITY OF AQUEOUS ELECTROLYTE SOLUTIONS

H. Kuura and M.M. Karelson

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

Received December 2, 1987

Differential-conductometric effect of the glycine, ß-alanine and γ-aminobutyric acid on the electrical conductivity of the potassium chloride aqueous solutions is measured at 25°C. The relationship between the structure-formation parameters, V_s in solution and the intrinsic volume of the aminoacid is obtained.

In a series of papers[1-4] by our group the results of the differential-conductometric investigation of the influence of small additions of neutral non-electrolytes on the structure of electrolyte aqueous and nonaqueous solutions were given. The characteristic linear relationships between the structure-formation volume in solution V_s, and the intrinsic volume V_i of the non-electrolyte were obtained in the solvents of the same chemical nature. There is also a good correlation between the volumes V_s and the various hydrophobicity parameters for the electroneutral organic substances in a given solvent (π , log P)[5]. Consequently, these volumes can be used for the measurement of hydrophobic influence of the substances on the solvent as well.

Thus, it is of a considerable interest to use the differential conductometry for the estimation of the hydrophobicity of various biomolecules in different solvents. In this paper we present the preliminary results of the investigation of the aminoacid addition influence on the structure of the potassium chloride aqueous solutions.

Experimental

In the differential conductometry the quantity

$$Y = \frac{k \cdot 10^3}{c_s} \left(\frac{1}{R_o + \Delta R} - \frac{1}{R_x} \right) \qquad (1)$$

is studied. In this formula k denotes the cell constant (cm^{-1}), c_s is the molar concentration of the substance added to the electrolyte solution, R_o and R_x are the resistances (Ω) of this solution before and after the addition, respectively. The term ΔR accounts for the change of the resistance of the solution due to the dilution in the process of addition.

It was shown earlier[1] that the quantity Y is simply related to the volume of structure-changing in the solvent, V_s by the given additions according to the following proportional relationship:

$$Y = V_s \cdot \varkappa \qquad (2)$$

where $\varkappa$ denotes the specific conductivity of the initial electrolyte solution. The volume V_s corresponds to that part of the total volume of the solution where the mobility of ions has been changed according to the two-structure model of solutions[6]. In the case of positive V_s values, the ions are converted from the conducting state to the non-conducting state, and in the case of negative V_s values, the opposite process is observed. Thus, the parameter V_s is characterizing the specific influence of the solute addition on the structure of electrolyte solution.

The differential-conductometric measurements were made on the apparatus, whose principal scheme has been described elsewhere.[7] All the measurements were made at 25°C±0.1°C. The temperature was preserved with the accuracy of ±0.001°C. The measurement cell was isolated from the atmosphere by the anidrome tubes to avoid the absorption of water. The cell constant was 19.40 cm^{-1}. A constant resistance R_p = = 9907.0 Ω was used in parallel joint to the conductivity cell for the investigation of the dilute solutions of electrolytes with the low values of specific conductivity. The dilution correction ΔR in Eq. (1) was calculated according to the procedure given elsewhere.[2]

The preparations of glycine, ß-alanine and γ-aminobutyric acid by "Renal" (Hungary) were used. The bidistilled deionized water was used for the aqueous solutions.

The potassium chloride used had the grade "Purest".

Discussion

The results of the experimental measurements of the influence of amino acids on the electrical conductivity of potassium chloride aqueous solutions are given in Tables 1-3. It should be mentioned that a good linear relationship between the quantity Y(1) and the specific conductivity of the initial electrolyte solution $\varkappa$ is observable in the case of any amino acid (glycine, ß-alanine, γ-aminobutyric acid) studied (cf. Fig. 1). Therefore, the constant values of the structure-formation parameters V_s for every substance can be estimated from the slopes of these relationships in the wide range of the electrolyte (0.01-3.0 mol/l). The mean values of the parameters V_s are also given in Tables 1-3.

It is known from the previous investigations[1-4] that the linear relationship is valid between the volume V_s and the intrinsic volume of the non-electrolyte added to the electrolyte solution in the solvent of similar chemical nature (hydroxylic compounds, aprotic solvents, etc.). In the case of hydroxylic additions to the aqueous solutions this linear relationship has the following form:[1]

$$V_s = -27.9 + 11.5 \Sigma R_D, \tag{3}$$

where ΣR_D is the intrinsic volume of the given hydroxylic molecule estimated as the sum of the corresponding molar refractions.[8]

Table 1

The Experimental Values of the Differential Conductometric Effects Y of Glycine on the Potassium Chloride Aqueous Solution at 25°C

C_{KCl} (mol/l)	$\varkappa \cdot 10^2$ (Ω^{-1} cm^{-1})	Y	V_s (cm^3/mol)
0.013	0.180	0.151	84.1
0.055	0.722	0.685	94.9
0.116	1.471	1.29	88.1
0.234	2.830	2.48	87.6
0.57	6.524	5.70	87.4
0.87	9.597	8.50	88.6
2.00	20.484	19.11	93.2
3.22	30.712	27.82	90.6
			$\bar{V}_s = 89.3 \pm 3.5$

However, for the zwitterionic amino acid additions significant deviations from the linearity (3) in the direction of smaller V_s values are observable in comparison with the hypothetic hydroxylic compounds of the same intrinsic volumes (cf. Fig. 2). According to our interpretation of the

Table 2

The Experimental Values of the Differential Conductometric Effects of the ß-Alanine on the Potassium Chloride Aqueous Solutions at 25°C

C_{KCl} (mol/l)	$\varkappa \cdot 10^2$ (Ω^{-1} cm)	Y	V_s (cm^3/mol)
0.012	0.171	0.256	150.0
0.054	0.704	1.05	149.2
0.120	1.511	2.26	149.6
0.18	2.210	3.21	145.3
0.50	5.681	7.92	139.4
1.07	11.565	16.60	143.5
1.86	19.037	28.24	148.3
3.12	29.789	45.11	151.4

$\bar{V}_s = 147.1 \pm 4.1$

Table 3

The Experimental Values of the Differential Conductometric Effects of the γ-Aminobutyric Acid on the Potassium Chloride Aqueous Solutions at 25° C

C_{KCl} (mol/l)	$\varkappa \cdot 10^2$ (Ω^{-1} cm)	Y	V_s (cm^3/mol)
0.012	0.171	0.346	202.3
0.051	0.674	1.56	231.5
0.110	1.457	3.24	222.4
0.20	2.614	5.64	215.7
0.49	5.613	12.50	222.7
0.81	11.758	26.11	222.0
1.88	19.389	43.03	221.8
2.79	27.639	55.59	201.1

$\bar{\bar{V}}_s = 217.5 \pm 10.6$

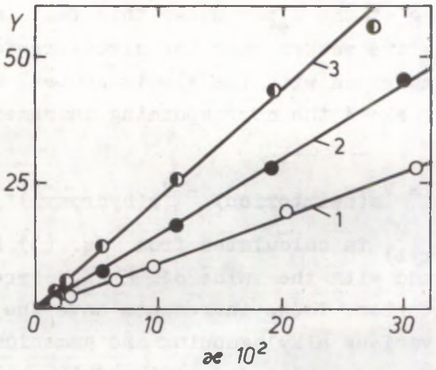


Fig. 1. The proportional relationship between the differential conductivity Y and the equivalent conductivity of the solution, for some zwitterionic compounds in the aqueous solutions of potassium chloride at $25^{\circ}C$ (1 - glycine, 2 - ß-alanine, 3 - γ -aminobutyric acid).

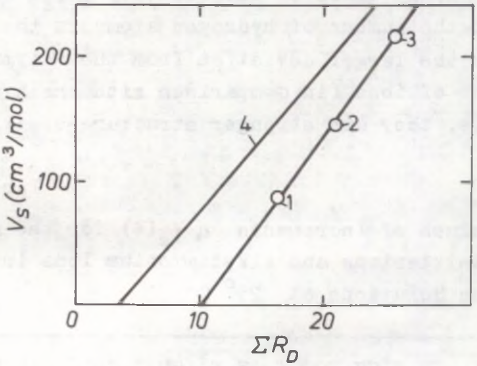


Fig. 2. The relationship between the parameters V_s and the intrinsic volume of zwitterionic compounds (ΣR_D). (1 - glycine, 2 - ß-alanine) 3- γ aminobutyric acid, 4 - the straight line for the hydroxylic electroneutral compounds).

physical meaning of the V_s parameter this fact implies that the zwitterions are weaker than the structure-forming agents in water in comparison with the electroneutral hydroxylic compounds. In Table 4 the corresponding increments V_s are given:

$$\Delta V_s = V_{s(\text{zwitterion})} - V_{s(\text{hydroxyl})}, \qquad (4)$$

where $V_{s(\text{hydroxyl})}$ is calculated from Eq. (3) for the hydroxylic compound with the value of ΣR_D, corresponding to the given zwitterion. These increments have the same (negative) sign as various alkylammonium and ammonium ions in aqueous solutions, calculated from the data published elsewhere.[9,10] Consequently, the structural unit causing the negative deviations from Eq. (3) for zwitterions (structure breaking in the solution) is the ionized amino group in their molecules. The increment ΔV_s is a constant for a given series of amino acids in the limits of the experimental error. However, the alkylammonium ions of a different degree of substitution at nitrogen atom have significantly different numerical values of the quantity ΔV_s. Obviously, the decrease of the number of hydrogen atoms in the ammonium ion leads to the larger deviation from the "normal" hydrophobic behavior of ions (in comparison with the hydroxylic compounds), i.e. they are stronger structure-breaking agents.

Table 4

The Values of Increments ΔV_s(4) for the Amino Acid Zwitterions and Alkylammonium Ions in Aqueous Solutions at 25° C

Ion	$H_3N^+CH_2COO^-$	$H_3N^+(CH_2)_2COO^-$	$H_3N^+(CH_2)_3COO^-$
ΔV_s	-70.4	-66.0	-49.1

Table 4 continued

Ion	NH_4^+	$C_2H_5NH_3^+$	$(C_2H_5)_2NH_2^+$	$(C_2H_5)_3NH^+$
ΔV_s	-85.0	-116.7	-117.9	-154.9

Ion	$(C_2H_5)_4N^+$	$C_5H_5NH^+$	$(OHCH_2CH_2)_3NH^+$
ΔV_s	-240.0	-167.9	-151.6

In conclusion it has to be said that differential conductometry proves to be a valuable method for investigation of the solvation mechanism of zwitterions and other biologically active polyelectrolytes. The results of the corresponding research will be published elsewhere.

References

1. **M.M. Karelson, This journal, 14, 74 (1977).**
2. **M.M. Karelson and H. Kuura, This journal, 20, 397(1983).**
3. **M.M. Karelson and H, Kuura, This journal, 21, 330(1984).**
4. **H. Kuura and M.M. Karelson, This journal, 23, 472(1986).**
5. **C. Hansch and A.J. Leo, Substituent Constants for Correlation Analysis in Chemistry and Biology, J. Wiley & Sons, N.Y., 1979.**
6. **M.M. Karelson, This journal, 21, 160 (1984).**
7. **Ü.L. Haldna and V.A. Palm, Dokl. AN SSSR, 135, 667(1960). (1960).**
8. **Handbook of Chemistry, Part 1 (in Russian), GHTIIHL, Moscow-Leningrad, 1962, p. 391.**
9. **M.M. Karelson, V.A. Palm, and Ü.L. Haldna, This journal, 9, 831(1972).**
10. **Ü.L. Haldna and L.R. Oraste, This journal, 14, 357(1977).**

Organic Reactivity
Vol. 24 3(87) 1987

SOLVENT INFLUENCE ON α-ALKYLACROLEINS OXYDATION RATE

J.J. Yatchishin, Ya.N. Pirig, and R.G. Makitra
Polytechnical Institute, Lvov
Institute of Physical Chemistry, Academy.Sci.Ukrainian SSR
Division in Lvov

Received November 11, 1987

Kinetics of acrolein, metacrolein, and ethylacrolein oxydation by peracetic acid in I2 solvents is investigated. The oxydation rate increases with the growth of the electrophilicity, polarity, and polarizability of solvents, but diminishes with the growth of their self-association. The reaction is realized via the step of donor-acceptor complex formation from the peracetic acid and aldehyde while the electrophilic solvation of the latter favors the reaction proceeding.

The aldehydes oxydation by peracetic acid is a heterolytic reaction in contrast to their radical oxydation by oxygen. N.M.Emanuel et al.[I-3] established that the acetaldehyde interaction with peracetic acid results in an intermediate formation which then gradually converts into two molecules of acetic acid; but the structure of this intermediate is unclear yet.

Some information about the reaction mechanism of aldehyde oxydation by peracids may be received by means of studying the effect on the process kinetics. However, in contrast to the peracid reaction with olefines (the Prileshaev's reaction) or the sulfide oxydation the literature data on the solvent influence on the aldehydes oxydation by peracids are very poor. Only Ref.[3] reports that the reaction rate decreases significantly in acetone, nitromethane, and methanol as compared to toluene or CCl_4 probably in the consequence of the hydrogen bond formation between aldehydes and peracetic acid. During the following 30 years from the appearence of that article no investigation in this field has been published. In this paper we report the results of studying the medium influence on the rate of the unsaturated aldehydes (acrolein, metacrolein, and α-ethylacrolein) oxydation by the peracetic acid - PAA (Table).

Experimental

The reaction is realized in the thermostated reactor at the reagents' ratio I:I and the PAA and aldehydes' concentration 2-3 mole/l. The hydroquinone is added to the reaction mixture in ratio of I% from the aldehyde weight in order to suppress the possible polymerization.

The rate constants of metacrolein oxydation in the acetic acid medium at 20^{o} in both the presence and absence of hydroquinone do not exceed the experimental error limits and are equal to $(1.17\pm0.03).10^{3}$ and $(1.21\pm0.03).10^{3}$, correspondingly. We found that the PAA in the experimental conditions at 20^{o} practically does not decompose. The conversion level of the initial substances was 70-80%. The rate of the PAA loss in aldehyde oxydation reaction is described by the second order reaction equation. The PAA concentration in the process was determined iodometrically. The composition of oxydation products was controlled chromatographically[4].

The oxydation process in the indifferent solvents yields merely the unsaturated acids and only insignificant amounts (1-3%) of epoxyaldehydes and lower acids. The oxydation in alcohols leads besides the unsaturated acid formation, to the formation of their esters with the corresponding alcohols, the yield being 10-15% on aldehyde.

Table

Rate Constants of α-Alkylacrolein Oxydation by Peracetic Acid at 20° in Some Solvents

No	Solvent	E_T	Rate constants, $k.10^3$ l/mole min		
			acrolein	metacrolein	ethylacrolein
1	$CHCl_3$	39.1	1.41±0.05	0.87±0.04	0.74 ±0.05
2	CCl_4	42.5	1.43±0.03	0.85±0.03	0.85±0.05
3	Chlorobenzene	37.5	1.75 ±0.10	1.06±0.09	0.77±0.06
4	Benzene	34.5	1.85±0.05	1.42±0.10	0.74±0.03
5	Dioxane	36.0	1.44±0.05	0.92±0.05	0.89±0.08
6	Acetone	42.2	1.77±0.05	0.89±0.02	0.82±0.02
7	Ethylacetate	38.1	2.98±0.03	0.62±0.02	0.42±0.04
8	Methanol	55.5	4.31±0.10	2.33±0.01	1.68±0.02
9	Ethanol	51.9	4.95±0.10	2.66±0.01	1.94±0.03
10	Propanol	50.7	6.39±0.20	2.72±0.01	1.89±0.08
11	Water	63.1	4.28±0.20	1.58±0.10	1.44±0.12
12	Acetic acid	51.2	1.78±0.05	1.17±0.03	0.90±0.01

Results

As can be seen from the data of the Table, in contrast to Ref.[3], the process rate is maximal in alcohols and minimal in donor solvents, e.g. ethylacetate, but on the whole the rate constants do not differ more than 4 times. The α-alkylacrolein's oxydation rates are 1.5-2 times lower than that of acrolein.

It is noticeable that the reaction studied is realized in the relatively concentrated (2-3 molal) solutions, i.e. the total content of the reagents and products of the reaction was equal to 30-50% of reaction mixture. Therefore, the aldehyde-peracid interaction is expected to predominate in the mixture, which leads ultimately to the formation of a compound. Significant differences in the interaction rates in different solvents (3-4 times) do indicate that the solvation of the reagents and the reaction complex by the solvent molecules is shifting the interaction equilibrium. Since the ratio of the reagents was equal to 1:1 in all studied cases and their molar concentration in the mixture was almost the same, it was possible to make an attempt to establish a numerical correlation between the reaction rates and the physico-chemical properties of the solvents.

An attempt to correlate the process rate with the empirical Dimroth-Reichardt[5] E_T parameters of the medium solvation ability ("polarity") was unsuccessful (Figure). As can be seen from the Fig., no distinct connection between the log k and E_T can be found. The solvents can be divided into two groups. The first one includes the solvents whose solvation ability is smaller than that of acetic acid in which the process rate is almost independent of the E_T value. It is possibly caused by the presence of the admixture of acetic acid in solution, added with the PAA and formed in the reaction which leads to but a small degree of solvation by these solvents in favor of predominating solvation by CH_3COOH. The other group of solvents is represented by water and alcohols characterized by E_T values near to or greater than that of the acetic acid (E_T=51.2) and which accelerate the process. However, this accelerating effect weakens with the growth of the E_T value. Presumably this accelerating effect is caused by the specific solvation of the intermediate aldehyde-peracid complex by the hydroxylic solvents.

In order to ascertain a more detailed character both of solvents influence and solvation processes, the obtained results are treated by means of a linear free-energy five-parameter equation:

$$\log k = a_o + a_1 \cdot \frac{n^2 - 1}{n^2 + 2} + a_2 \cdot \frac{\varepsilon - 1}{2\varepsilon + 1} + a_3 \cdot \delta^2 + a_4 \cdot B + a_5 \cdot E$$

which takes into account the solvent's ability to the specific and nonspecific solvation[6] and to the self-association[7]; n and ε are the refraction index and the dielectric permittivity of the solvent respectively, B and E its basicity and electrophilicity according to Ref.[6], δ^2 is its cohesion energy density in cal/l.

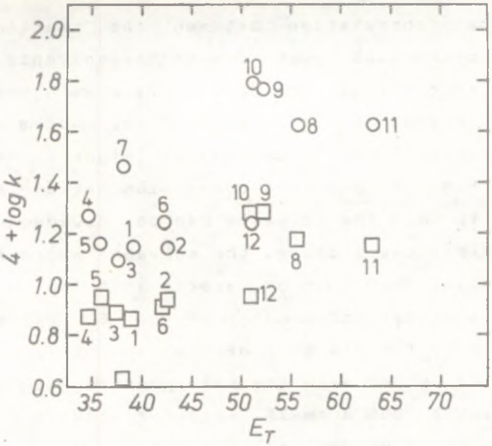


Fig.1. Dependence of rate constant log of α-alkylacroleins oxydation on E_T: ○-acrolein, □ - α-ethylacrolein. Number of points corresponds to the solvents in the Table.

In the case of acrolein, the degree of interaction is low for all the solvents: the gross correlation coefficient value equals R=0.946 only. But the exclusion of the data for the two solvents, namely for $CHCl_3$ (N^o 1) and propanol (N^o 10) leads to a satisfactory value of R:

$$\log k = -3.089 + 0.580 \frac{n^2 - 1}{n^2 + 2} + 0.758 \frac{\varepsilon - 1}{2\varepsilon + 1} - 0.001 \cdot \delta^2 -$$

$$-0.004 \cdot B + 0.041 \cdot E; \quad N=9; \quad R=0.974; \quad s=0.081$$

The paired correlation coefficients of separate parameters are equal to: $r_{01}=0.678$; $r_{02}=0.770$; $r_{03}=0.627$; $r_{04}=0.451$; $r_{05} = 0.879$. Thus, the determining influence on the process rate is caused by the electrophilic solvation of the intermediate complex but some "corrective" influence is shown by other solvation processes, too. In particular, growth of medium's basicity decelerates the process (the sign "minus" at the corresponding term) in the result of the competetive bonding of the PAA molecule like in the epoxidation reaction.[9]

Investigation of the validity of the initial parameters of the equation by means of their successive exclusion shows the relative negligibility of polarizability and basicity of solvents. The influence of solvent on the investigated reaction rate may be satisfactorily described by the following three-parameter equation, which takes into account the electrophilicity, polarity and cohesion energy density of solvents:

$$\log k = -2.929 + 0.556 \frac{\varepsilon - 1}{2\varepsilon + 1} - 0.00076.\delta^2 + 0.034.E ;$$

$$N = 9; \quad R = 0.957; \quad s = 0.089$$

If the other parameters are excluded, the degree of correlation will diminish more significantly, up to $R<0.95$.

For the two other aldehydes we obtained the following equations:

a) for metacrolein -

$$\log k = -4.271 + 4.264 \frac{n^2 - 1}{n^2 + 2} + 0.496 \frac{\varepsilon - 1}{2\varepsilon + 1} - 0.00174.\delta^2 +$$

$$+ 0.063\cdot E; \; N = 11; \; R = 0.955; \; s = 0.085; \; r_{OE} = 0.700$$

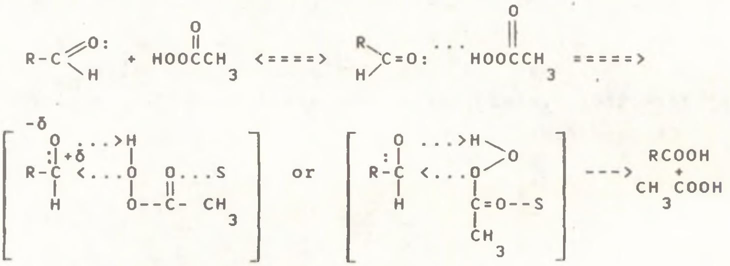
b) for ethylacrolein (after the exclusion of the data for CCl_4 and ethylacetate):

$$\log k = -3.541 + 1.131 \frac{n^2 - 1}{n^2 + 2} + 0.459 \frac{\varepsilon - 1}{2\varepsilon + 1} - 0.000113.\delta^2 +$$

$$+ 0.042\, E; \; N = 9; \; R = 0.957; \; s = 0.087; \; r_{OE} = 0.795$$

Thus, the solvation effects in the oxydation of all the three unsaturated aldehydes have identical character. The most important factor is the electrophilic solvation of intermediate which leads to the acceleration of conversion. It is proved by the maximal values of the paired correlation coefficient of log k with this parameter and the maximal decrease of the total correlation coefficient value if this parameter is excluded from the calculations. The process rate will be raised (the sign "plus" at the corresponding term) by the growth of the medium's polarity which favors the separation of charges in the intermediate. The increase of the cohesion energy density reduces in all cases the reaction rate which is connected, probably, not so considerably with the energy expenditure on the cavity formation for the intermediate placing in medium as with the necessity of destruction of the alcohol associates, since the monomeric alcohol molecules only undergo intermediate solvation. For solvents NN^{o} 1-7 with low polarity the δ^2 values are close and change within the limits of 0.08 - 0.11 kcal/mole while for alcohols and water the δ^2 values are 2-5 times higher.

The formation of an intermediate with H-bond between the aldehyde molecule and the acyclic form of PAA is the first stage in the aldehyde oxydation[1-3]. Then the oxygen atom of peroxy group approaches the electron-deficient carbon atom of aldehyde and rearrangement of the intermediate into products will be realized[4]. This process is favored both by the electrophilic solvation of oxygen atom of the peracid carbonyl and the nonspecific solvation which leads to the charge separation in the intermediate:



S - solvent molecule

In contrast to the epoxydation of olefines by the PAA[8], in the present case the role of basicity is insignificant. Only low process rates in the aromatic solvents and the insignificance of the basicity permit to make an assumption that there exists some difference between the oxydation mechanism of aldehydes and the epoxydation of olefines by PAA. In the case of epoxidation, complex formation between the double bond of olefine and the cyclic form of PAA ("butterfly" mechanism) takes place and the basic solvents decelerate the rate in the result of transformation of the active cyclic form of PAA into the inactive one. At the same time the aldehydes carbonyl group is a significantly stronger electron donor than the double bond of olefines and the complexation with PAA can be realized more easily probably by means of the H-bond formation with the lone electron pair. Nevertheless, a certain decrease of the process rate in the strong basic solvents (ethylacetate, acetone) and the sign "minus" at the basicity term permit to suppose a possibility of some rivalry between the oxydable aldehyde and the basic solvent for the PAA molecule. It can be assumed that in the more basic solvents than the investigated ones, e.g. the DMFA, the rate process is diminished more significantly.

REFERENCES

1. R.F.Vassilev and N.M.Emanuel, Acad.Sci USSR,ser.khim., 1956,No4,pp.378-396.
2. R.F.Vassilev, A.I.Terenin, and N.M.Emanuel, Ibid, 1956, No4,pp.397-402.
3. R.F.Vassilev, A.I.Terenin, and N.I.Emanuel, Ibid, 1956, No4,pp.403-409.
4. M.D.Fedevich, J.J.Yatchishin, Ya.N.Pirig, and M.V. Kaspruk, Neftekhimija,15,n.3.,449-453(1975).
5. Chr.Reichardt, Solvents in the organic chemistry. (in Russian),"Khimija",Leningr.1973
6. V.A.Palm Principles of quantitative theory of organic reactions. "Khimija",Leningr.1977,p.87-126.(in Russian)
7. R.G.Makitra, V.Ya.Zhukovskij, and Ya.N.Pirig Kinetika i kataliz. 23,No5,1262-1265 (1982).
8. R.G.Makitra and Ya.N.Pirig, Zh.Fiz.Khim.,52,3,785-787 (1978).
9. B.M.Lynch and K.H.Pausacker, J.Chem.Soc.,No5,p.1525-1531 (1955).

Organic Reactivity
Vol. 24 3(87) 1987

REACTIVITY OF DERIVATIVES OF PHENYL-ANTHRANILIC ACID

III. Kinetics of Alkaline Hydrolysis Reaction of Methyl Ester of 4-Chloro-5-Nitro-N-Phenyl-Anthranilic Acid in Binary Dioxane-Water Solvent

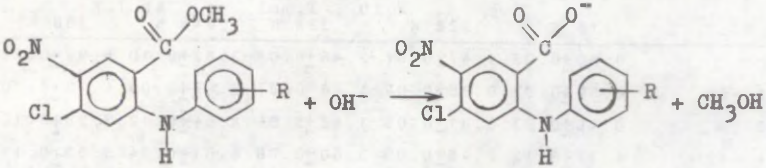
A.N. Gaidukevich, E.N. Svechnikova, and
E.E. Mikitenko
Kharkhov State Pharmaceutical Institute,
Kharkhov, the Ukrainian SSR

Received December 3, 1987

Kinetics of alkaline hydrolysis reactions of 8 derivatives of 4-chloro-5-nitro-N-phenyl anthranilic acid methyl ester was studied in mixed dioxane-water solvent in the temperature range 45-85 ^{o}C. Bimolecular reaction rate constants, energy, enthalpy, entropy and free activation energy have been calculated. Effects of electronic nature and position of substituents in non-anthranilic molecule fragment of substrate on above-mentioned parameters have been analyzed. It has been established that reaction series studied obeys general equation of Hammett for 2' and 4' substituents. Validity of isokinetic correlation with enthalpic control has been shown, and isokinetic temperature was determined.

The kinetics of alkaline hydrolysis reactions of 2',4'-derivatives of methyl ester of 4-chloro-5-nitro-N-phenyl anthranilic acid in the mixed dioxane-water solvent (60 volume % of dioxane) has been studied at various temperatures (45-85 °C) in order to continue the series of papers[1-2] investigating the reactivity of biologically active derivatives of phenyl-anthranilic acid.

The reaction fits the following equation:



The process can be described by the second order equation:

$$\frac{dx}{dt} = k(a-x)(b-x) \qquad (1)$$

where a,b are the initial concentrations of ester and alkali (mol/l), respectively,

x - denotes the current concentration of the reaction product (mol/l);

t - time (s);

k - reaction rate constant (l/mol.s).

Division of the variables and integration of Eq.(1) enables us to find the reaction rate constant:

$$k = \frac{2.303}{t(b-a)} \log \frac{a(b-x)}{b(a-x)} \qquad (2)$$

The obtained k value is corrected to the volume expansion of the solvent in temperature range of 25 °C - t °C, multiplying it by factor $\tau = d_{25}/d_t$, where d_{25}, d_t denote the density of the binary dioxane-water solution at temperatures 25° and t °C.

The reaction rate constants were calculated via the concentraction change of sodium hydroxide in time according to Eq.(2). The concentrations of the nucleophile and the substrate were varied, but the reaction rate constant remained the same in the limits of the experiment error. Consequently, the reaction has the second order.

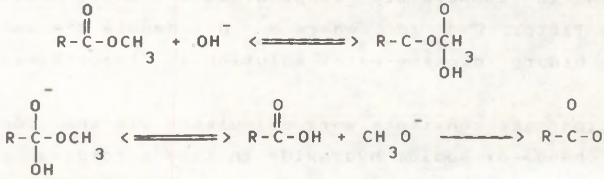
12

Table 1.

Rate Constants of Alkaline Hydrolysis Reaction of Methyl Ester Derivatives of 4-Chloro-5-Nitro-N-Phenyl-Anthranilic Acid at Various Temperatures.

	$k.10^3$, l.mol^{-1} s^{-1} at T,K				
R	318 K	328 K	338 K	348 K	358 K
H	0.80±0.02	1.47±0.07	2.45±0.08	3.82±0.10	6.92±0.12
4'-CH_3	0.50±0.03	0.95±0.04	1.78±0.07	2.69±0.08	4.79±0.10
3',4'-CH_3	0.46±0.03	0.81±0.06	1.48±0.04	2.64±0.12	3.98±0.10
4'-Cl	1.37±0.12	2.45±0.09	3.80±0.06	6.61±0.04	9.55±0.11
2',4'-CH_3	0.32±0.03	0.59±0.05	1.10±0.08	1.86±0.07	3.16±0.10
2'-CH_3	0.45±0.04	0.76±0.07	1.38±0.11	2.23±0.03	3.76±0.05
2'-OCH_3	0.35±0.03	0.63±0.04	1.05±0.07	2.04±0.11	3.31±0.09
2'-Cl	1.04±0.08	1.95±0.09	3.02±0.11	5.25±0.08	8.13±0.08

The rate constants of this reaction series are also remarkably affected by the electronic nature and position of the substituents in the non-anthranilic fragment of the molecule (Table 1): introduction of donor substituents decelerates the process, while acceptor substituents have an opposite effect thus stabilizing the anion of the phenyl-anthranilic acid derivatives at the expense of a greater delocalization of its charge. Consequently, in the case of the alkaline hydrolysis reactions of 4-chloro-5-nitro-N-phenyl-anthranilic acid derivatives, operates the $B_{AC}2$ mechanism of alkaline hydrolysis known from literature[3]:



$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}OCH_3 + OH^- \rightleftharpoons R\text{-}\underset{OH}{\overset{O}{C}}\text{-}OCH_3$$

$$R\text{-}\underset{OH}{\overset{O^-}{C}}\text{-}OCH_3 \rightleftharpoons R\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH + CH_3O^- \longrightarrow R\text{-}\overset{O}{C}\text{-}O^- + CH_3OH$$

It is worth mentioning that the esters have a poorer reactivity with 2'-substituents than with 4'-substituents.

Quantitative estimation of the electron substituent effect on the reactivity of methyl esters of 4-chloro-5-nitro-N-phenyl-anthranilic acid was performed by means of the Hammett equation (Table 2) separately and simultaneously for 2',4'-derivatives.

The data of Table 2 show that the values of reaction parameter ρ are positive at all temperatures studied, thus confirming the validity of the $B_{AC}2$ alkaline hydrolysis mechanism of the reaction series. 2' and 4'-derivatives of methyl esters of 4-chloro-5-nitro-N-phenyl-anthranilic acid obey the Hammett equation, the correlation coefficient being rather high. The ρ values for 2' and 4'-derivatives are not large. This can be explained by the situation that the substituents are placed rather far from the substrate's reaction center. It should also be mentioned that the ρ values for the alkaline hydrolysis reaction of 4-derivatives of β-dimethyl-aminoethyl ester of 4-chloro-N-phenyl-anthranylic acid, methyl esters of 2',4'-derivatives of 4-nitro-N-phenyl-anthranilic acid and 2',4'-derivatives of 4-chloro-5-nitro-N-phenyl-anthranilic acid are quite close.
This should most probably be connected with a rather similar mechanism of electron transfer effects to the reaction center. The ρ values for 2'-substituents are smaller than those for 4'-substituents, although the differences are not significant. Therefore a simultaneous correlation for compounds with 2',4'-substituents was carried out. The linear relationship was statistically significant (it was checked by means of the Fischer F-criterion[4]), though the correlation coefficient value has dropped and the dispersion values S tend to be greater than in the case of a separate correlation . The ρ value is decreasing if the temperature rises.

The Arrhenius equation holds for all compounds of this reaction series:

$$\ln k = \ln A - \frac{E_A}{RT} \qquad (3)$$

Table 2.

Parameters of the Hammett Equation of Alkaline Hydrolysis Reactions of Methyl Esters of 4-Chloro-5-Nitro-N-Phenyl-Anthranilic Acid in Dioxane-Water Solution at Various Temperatures: $\log k = \log k_o + \rho\sigma$

T,K	ρ	log k	r	s
318[a]	1.104±0.022	-3.060±0.049	0.9968	0.023
328[a]	1.078±0.012	-2.844±0.026	0.9983	0.016
338[a]	0.927±0.017	-2.617±0.038	0.9952	0.024
348[a]	0.923±0.021	-2.400±0.048	0.9922	0.030
358[a]	0.852±0.019	-2.191±0.042	0.9927	0.027
318[b]	0.982±0.022	-2.926±0.057	0.9948	0.030
328[b]	0.961±0.010	-3.187±0.026	0.9989	0.014
338[b]	0.860±0.031	-2.708±0.079	0.9873	0.042
348[b]	0.842±0.026	-2.467±0.066	0.9907	0.035
358[b]	0.771±0.023	-2.263±0.057	0.9918	0.030
318[c]	1.046±0.019	-3.139±0.042	0.9826	0.046
328[c]	1.018±0.020	-2.941±0.045	0.9810	0.049
338[c]	0.917±0.024	-2.655±0.053	0.9650	0.058
348[c]	0.882±0.031	-2.504±0.025	0.9612	0.065
358[c]	0.833±0.019	-2.221±0.043	0.9723	0.047

a - correlation data for 4'-derivatives

b - correlation data for 2'-derivatives

c - correlation data for 2' and 4'-derivatives taken together

The values of activation energy E_A and preexponential factor A calculated according to Eq.(3) are given in Table 3. Conducting electron-donor substituents into the ester molecule leads to the expected increase of activation energy; electron-acceptor substituents cause opposite effect. Correlation of the E_A dependence on the Hammett σ constants is not statistically significant.

The Eyring equation[5] was applied in order to calculate the activation enthalpy ($\Delta H^{\neq}$) and entropy ($\Delta S^{\neq}$), the free activation energy ($\Delta G^{\neq}$) was calculated according to the second law of thermodynamics. The obtained data are pre-

Table 3

Kinetic Activation Parameters (E_A and ln A) of Alkaline Hydrolysis Reactions of Methyl Ester Derivatives of 4-Chloro-5-Nitro-N-Phenyl-Anthranilic Acid.

R	E_A kJ/mol	ln A	r	S
H	49.8±0.5	11.7±1.6	0.9988	0.048
4'-CH_3	52.7±0.5	12.4±1.9	0.9986	0.054
3',4'-CH_3	52.2±0.4	12.1±1.5	0.9991	0.043
4'-Cl	47.4±0.5	11.3±1.7	0.9984	0.052
2',4'-CH_3	54.6±0.2	12.6±0.6	0.9997	0.015
2'-CH_3	50.5±0.3	11.4±0.9	0.9996	0.027
2'-OCH_3	53.8±0.4	12.4±1.7	0.9988	0.052
2'-Cl	48.4±0.4	11.4±1.3	0.9991	0.039

sented in Table 4. Activation entropy is negative for all compounds, which once again confirms the $B_{AC}2$ mechanism of the reaction. Large absolute $\Delta S^{\neq}$ values refer to the formation of a highly symmetric intermediate. Itroduction of the acceptor substituents into the molecule leads to an increase the absolute $\Delta S^{\neq}$ value and to a decrease of $\Delta H^{\neq}$. Small $\Delta H^{\neq}$ values evidence about a synchronic mechanism of the reaction. Linear dependence of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ on the σ constants of substituents cannot be considered statistically reliable, substituent effect on the free activation energy value is similar with their effect on $\Delta H^{\neq}$. It is interesting also to mention that the contributions of enthalpy and entropy to the $\Delta G^{\neq}$ value are quite close.

In order to check the existence of the isokinetic correlation in the reaction series studied, the correlations $\Delta H^{\neq}$ - $\log k_T$, $\Delta H^{\neq}$ - $\Delta S^{\neq}$, ϱ-1/T (Table 5) were studied. Their linear character was demonstrated by means of the regression analysis, using the F-criterion of Fischer. The values of isokinetic temperature β found are rather similar to those calculated separately applying equation[6] (Table 6):

$$\log k_{T_2} = \text{const} + x\log k_{T_1}$$

The β value exceeds the given temperature range, which refers to the enthalpic control type of the alkaline hydrolysis reaction of methyl ester derivatives of 4-chloro-5-nitro-N-phenyl-anthranilic acid.

Experimental

Reagents. Purification of solvents and the control of their purity level have been described earlier[1].

Methyl esters of 4-chloro-5-nitro-N-phenyl-anthranilic acid were synthesized according to the known methods[7]. Their purity was checked by means of elemental analysis and thin layer chromotography in mixtures (acidic acid-water 1:1, propanol-water 1:1) on "Silufol" plates.

For preparation of sodium hydroxide solutions, solid sodium hydroxide, purified from carbonates according to methods[8] was used.

Kinetic measurements were conducted according to methods[1]. Sodium hydroxide concentration in the solution was determined by means of potentiometric titration on an EV-74 monomer using the HCl solution. Reaction kinetics was studied at 45,55,65,75,85 C. Experiments were repeated three times, including 6-8 measurings each (depth of transformation being at least 80%). The accuracy of the obtained parameters was assessed by means of the methods of mathematical statistics for small sets[4] (with a 0.95 probability). Linear equations were treated using the least squares method on a micro computer "Elektronika MK-52", applying standard programs[9].

Table 4.

Thermodynamic Activation Parameters ($\Delta H^{\neq}$, $\Delta S^{\neq}$, $\Delta G^{\neq}$) of Alkaline Hydrolysis Reaction of Methyl Ester Derivatives of 4-Chloro-5-Nitro-N-Phenyl-Anthranilic Acid

R	$\Delta G^{\neq}$ kJ/mol 318K	328K	338K	348K	358K	$\Delta H^{\neq}$ kJ/mol	$\Delta S^{\neq}$ J/d	r	S	t ΔS kJ/mol 318K
H	96.9	98.5	100.0	101.6	103.2	47.0±0.4	-157±2	0.9670	0.047	-49.9
4'-CH_3	98.1	99.7	101.2	102.7	104.2	49.9±0.2	-152±1	0.9994	0.033	-48.2
3',4'-CH_3	98.4	99.9	101.5	103.0	104.6	49.4±0.4	-154±3	0.9989	0.043	-49.0
4'-Cl	95.4	97.1	98.7	100.3	102.0	43.4±0.4	-164±2	0.9987	0.043	-52.0
2',4'-CH_3	99.4	100.9	102.4	103.9	105.4	51.8±1.3	-150±4	0.9998	0.015	-47.6
2'-CH_3	98.5	100.1	101.7	103.3	104.9	47.7±0.8	-160±6	0.9996	0.026	-50.8
2'-OCH_3	99.1	100.7	102.2	103.7	105.2	51.0±0.4	-151±3	0.9986	0.052	-48.1
2'-Cl	96.2	97.8	99.4	101.0	102.6	45.6±1.6	-159±2	0.9990	0.039	-50.6

Table 5

Determining of Isokinetic Temperature. Correlation Parameters of Equations y=a+bx of Relationship of Kinetic and Activation Parameters of Alkaline Hydrolysis Reactions of Methyl Ester Derivatives of 4-Chloro-5-Nitro-N-Phenyl-Anthranilic Acid and Isokinetic Temperature β.

x	y	a	b	r	S	β K
log k_{318}	$\Delta H^{\neq}$	$(10.0\pm1.1).10^{3}$	$(-11.8\pm0.4).10^{3}$	0.915	0.91	657
log k_{328}	$\Delta H^{\neq}$	$(14.1\pm1.2).10^{3}$	$(-11.5\pm0.4).10^{3}$	0.915	1.10	686
log k_{338}	$\Delta H^{\neq}$	$(13.1\pm1.4).10^{3}$	$(-12.8\pm0.5).10^{3}$	0.925	1.16	683
log k_{348}	$\Delta H^{\neq}$	$(15.0\pm1.3).10^{3}$	$(-13.2\pm0.5).10^{3}$	0.905	1.12	701
[illegible] k_{358}	$\Delta H^{\neq}$	$(16.0\pm1.4).10^{3}$	$(-14.0\pm0.6).10^{3}$	0.918	1.25	700
ΔS	$\Delta H^{\neq}$	$(56.4\pm1.1).10^{3}$	556 ± 16	0.931	3.78	556
1/T	ϱ	-0.872 ± 0.068	609 ± 22	0.987	0.032	698

Data for 2' and 4'-derivatives were correlated simultaneously

Table 6

Determining of Isokinetic Temperature β. Correlation Parameters of Equation log k_{T_2} = const + x log k_{T_1} of Alkaline Hydrolysis Reaction of Methyl Ester of 4-Chloro-5-Nitro-N-Phenyl-Anthranilic Acid.

Temperature, K					
T_1	T_2	x	r	S	β K
318	338	0.885	0.9889	0.029	657
328	348	0.858	0.9944	0.023	551
328	358	0.798	0.9973	0.015	560
338	358	0.896	0.9941	0.022	731
348	358	0.914	0.9865	0.033	517

Data for 2',4'-derivatives were correlated simultaneously.

References

1. A.N.Gaidukevich, E.N.Svechnikova, G.P.Kazakov, and T.A. Kostina, Organic Reactivity,23,442(1986).
2. A.N.Gaidukevich, G.P.Kazakov, A.A.Kravchenko, E.E.Mikitenko, E.N.Svechnikova, and G.Sim., Abstracts of XV Republican Conference on Organic Chemistry of the Ukrainian SSR (in Russian),Uzhgorod,1986,p.353.
3. R.Carry and R.Sandberg, "Advanced Course in Organic Chemistry"(Russian translation),Moscow, "Khimiya",1981, p.300.
4. E.N.Lvovsky "Statistical Methods of Construction of Empirical Formulas",(in Russian),Moscow, "Vysshaya Shkola", 1982.
5. H.Eyring "Foundations of Chemical Kinetics",(Russian translation),"Mir",Moscow,1983.
6. V.A.Palm "Foundations of Quantitative Theory of Organic Reactions",(in Russian),Leningrad,"Khimiya",1977.
7. "Synthesis and Transformations of Organic Compounds taining Hetero Atoms",(in Russian),Baku,1981,p.68.
8. A.Albert and E.Serjeant, "Ionization Constants of Acids and Bases",(in Russian),Moscow, "Khimiya",1964.
9. Ya.K.Trokhimenko, Programming of Micro Calculators "Elektronika-52" and "Elektronika MK-61",(in Russian), "Tekhnika",1987.

Organic Reactivity
Vol. 24 3(87) 1987

NUCLEOPHILIC SUBSTITUTION AT TETRACOORDINATED ATOM OF SULFUR. II. REACTIVITY OF THIOALCOHOLATE IONS

Yu.S. Simanenko, T.M. Prokopeva, I.A. Belousova,
V.A. Savylova, A.F. Popov, and G.S. Sakulin

Institute of Physico-Organic Chemistry and Coal
Chemistry, Acad. Sciences of the Ukrainian SSR,
Donetsk, 340114

Received November 23,1987

Kinetic and thermodynamic analysis of thioalcoholysis of arylsulfonates has been conducted. It has been established that the reaction includes thioalcoholate ion nucleophilic attack at tetracoordinated atom of sulfonate sulfur, while existence of such acid-base centers as $-COO^{\ominus}$, $>N$, $>\overset{\oplus}{N}H$ and OH-groups in molecule does not promote the intramolecular transfer of sulfonyl group. Rate of thioalcoholysis does not depend much on structure of attacking nucleophile (β_N =0.25) and of leaving group nature (β_X =-0.32). Quantitative comparison of reactivity of $RS^{\ominus}$ anions and RNH_2 amines shows that the former are more efficient nucleophiles, and the character of substituent effect in nucleophile on transition state of acyl and sulfonyl groups turns out to be analogous. It has also been found that unlike aminolysis of arylsulfonates, in case of thioalcoholysis, early transition stage is observed. Factors determining the rate of nucleophilic attack of thioalcoholate ions have also been discussed.

Thioalcoholate and thioarylate anions have proved to be efficient nucleophilic reagents for substrates of various nature[1-6]. Being highly polarizable nucleophiles, they react abnormally rapidly with "soft" substrates, but in the reactions with arylvinylsulfonates[1] and arylthioisocyanates[2] the reaction rate is 10^4 times higher than that of interaction with the alcoholate-anions which have similar structure. Nevertheless, increased reactivity of thioalcoholate ions in comparison with amines and alcoholate anions was also established in the reactions with oxygen and thiol esters of carboxylic acids[3,4] and in the case of addition to the carbonilic group of aldehydes[5]. But if 4-nitrophenyl-4'-toluene sulfonate (NPTS) is used, the thiophenolate ion reacts 100 times faster than aliphatic amines having approximately the same basicity and it has only a slightly smaller reactivity than such α-nucleophiles as oxymate ions[6]. Still higher nucleophilicity of the thioalcoholate ion being in correlation with that of hypochlorite and acethydroxymate anions, was noticed in the thiobutylate ion reaction with disulfones[7]. The substrates do not actually belong to the group of "soft" electrophiles (v.v. - they are "hard" substrates). Therefore, to solve our problem[8] of finding scientifically grounded highly efficient nucleophilic reagents and catalytic systems which can rapidly decompose the substrates stable in water, it was expedient to carry out a detailed kinetic research into the reactions of nucleophilic substitution at the tetracoordinated atom of sulfur with participation of thioalcoholate anions and aryl esters of 4-toluene-sulfonic acid[9]. It is known that aryl esters of 4-toluene-sulfonic acid are "hard" electrophiles. They are stable in water and, thus, information about their interaction with different nucleophiles can be useful for establishing the factors which determine the reactivity of "soft", easily polarizable nucleophiles - thioalcoholate ions.

Experimental results

The nature of the effect of acid-base properties of substituted mercaptothioalcohols on the rate of their reaction with aryl esters of 4-toluenesulfonic acid was studied using the interaction of mercapto derivatives with NPTS as an example. Kinetic analysis of the process shows that the reactive particle is the anionic form of thiol alcohols. The reaction rate increases both with rising of the thioalcohol gross concentration and with the increase of the medium pH (Figs.1,2). The reaction proceeds only via the sulfur - leaving group bond cleavage (4-nitro-phenolate ion) and, consequently, it includes the nucleophilic attack at the tetracoordinated atom of sulfur of NPTS.

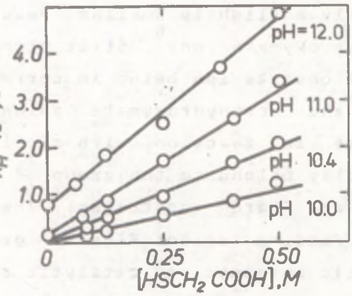


Fig.1. Dependence of the observed pseudofirst order rate constants k_H (s^{-1}) for reaction of thioglycolic acid with NPTS on $[HSCH_2COOH]_0$ at various pH values; 25 °C, μ=1.0 (KCl)

At least we could not succeed in registering the reaction corresponding to the nucleophilic attack at the aromatic atom of carbon of 4-nitrophenylic ring. Absence of the deuterium isotopic solvent effect for the reactions with participation of the methyl ester of thioglycolic acid ($k(H_2O)/k(D_2O)=1.03$) is also in accordance with the assumption about the nucleophilic substitution taking place and not with the general base catalysis of the NPTS hydrolysis by means of thioalcoholate ion.

Quantitative estimation of the reactivity of thioalcoholate ions (Nos 1-4, Table 1) is not complicated since the reaction rate obeys Eq(1), and if the pK_a values of their

Table 1

Conditions of Carrying out Experiment, Basicity of Thioalcoholate Ions (pK_a) and Their Reactivity (k_2, M^{-1}, s^{-1}) with Reference to NPTS in 5% Aqueous Ethanol; 25°C; $\mu = 1.0$ (KCl)

Nucleophile	pK_a	pH	$[RCH_2SH]_0$ [a]	n [b]	k_2
1	2	3	4	5	6
1. $^{\ominus}OOCCH_2-S^{\ominus}$	10.20±0.06	10.0-12.0	0.06-0.5	20	$(8.5\pm0.1).10^{-4}$
2. $CH_3CONH\underset{\substack{\vert\\ COO}}{C}HCH_2-S^{\ominus}$	9.63±0.03	9.6-10.0	0.06-0.5	8	$(8.9\pm0.2).10^{-4}$
3. $HOCH_2CH_2-S^{\ominus}$	9.58±0.03 10.02±0.06 c)	9.2-11.0	0.05-1.0	11	$(6.6\pm0.2).10^{-4}$
4. $CH_3OOCCH_2-S^{\ominus}$	7.70±0.03	10.0	0.05-0.5	5	$(1.8\pm0.1).10^{-4}$
5. $^{\oplus}NH_3\underset{\substack{\vert\\ COO^{\ominus}}}{C}HCH_2-S^{\ominus}$	8.45 d)	9.0-10.2	0.5	5	$(2.1\pm0.2).10^{-4}$
6. $NH_2\underset{\substack{\vert\\ COO}}{C}HCH_2-S^{\ominus}$	9.91 e)	10.8-11.8	0.5	5	$(3.9\pm0.4).10^{-4}$ f)
		9.0-10.2	0.5	5	$(3.5\pm0.2).10^{-4}$ f)

Table 1 continued

1	2	3	4	5	6
7. $NH_2\underset{\mid \atop COO^{\ominus}}{CH}CH_2SCH_3$	8.77±0.04	8.7-10.0	0.5	5	$(1.1\pm0.2).10^{-5}$
8. $\overset{\oplus}{N}H_3CH_2CH_2-S^{\ominus}$	$8.49^{d)}$	9.0-10.0	0.5	5	$(3.4\pm0.2).10^{-4}$
9. $NH_2CH_2CH_2-S^{\ominus}$	$9.85^{e)}$	10.4-11.6	0.5	5	$(6.0\pm0.4).10^{-4}$
10. $NH_2CH_2CH_2SCH_3$	9.50±0.03	9.5-10.5	0.5	5	$(4.1\pm0.4).10^{-5}$
11. $(C_2H_5)_2\overset{\oplus}{N}H(CH_2)_2-S^{\ominus}$	$8.11^{d)}$	8.5-9.8	0.2	5	$(2.0\pm0.3).10^{-4}$
12. $(C_2H_5)_2N(CH_2)_2-S^{\ominus}$	$9.70^{e)}$	10.0-10.5	0.2	6	$(4.0\pm0.4).10^{-4}$
13. $(C_2H_5)_2N(CH_2)_2SCH_3$	9.71 0.06	10.7	0.2	5	$(1.2\pm0.1).10^{-5}$

a) gross concentration of thioalcohol; b) number of Experiments; c) pK_a value in 30% ethanol; d) pK_1 value (see Scheme (2)); e) pK_4 value (see Scheme (2)); f) calculated according to Eq. (12) (see Fig.4).

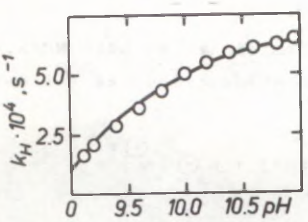
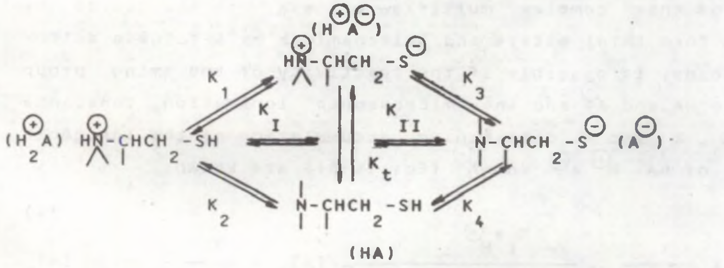


Fig.2. The pH profile for mercaptoethanol reaction with NPTS; 25 °C, $\mu = 1.0$ (KCl); $[HOCH_2CH_2SH]_0 = 1.0$ M

conjugate acids are known, it permits to conduct the reaction at optimum pH values, to find the concentration of the reacting thioalcoholate ions and, consequently, to calculate the k_2, $M^{-1}s^{-1}$ values

$$k_H = k_2[RCH_2S^{\ominus}] = \frac{k_2K_a}{K_a + a_{H^{\oplus}}}[RCH_2SH]_o \qquad (1)$$

Actually, the situation is quite different in the case of cysteine, cysteamine and N,N-diethylcysteamine being in aqueous solutions in four different forms (Scheme 2), while three of them: the zwitter-ionic $H^{\oplus}A^{\ominus}$, the neutral HA and the monoanionic $A^{\ominus}$ - are potential nucleophilic reagents.



(2)

Existence of two acid-base centers -SH and $\geqslant$N in the molecules of cysteine, cysteamine, and N,N-diethylcysteamine leads to the situation where depending on the pH medium, the aminogroup of either the HA and $A^{\ominus}$ form, or the thioalcoholate group of $H^{\oplus}A^{\ominus}$ and $A^{\ominus}$ form can react with NPTS. Consequently, the reaction rate can be described as follows:

$$k_H = k_{H^{\oplus}A^{\ominus}}[H^{\oplus}A^{\ominus}] + k_{HA}[HA] + k_{A^{\oplus}}[A^{\ominus}] =$$

$$= k_{H^{\oplus}A^{\ominus}} \frac{K_t}{1 + K_t} \alpha_{HA^{\pm}}[A]_o + k_{HA} \frac{1}{1 + K_t} \alpha_{HA^{\pm}}[A]_o + \qquad (3)$$

$$+ k_{A^{\ominus}} \alpha_{A^{\ominus}}[A]_o$$

$[A]_o$ - is the gross concentration of the mercapto derivative, conducted into the reaction system, K_t - is the constant of tautomeric transformation of the zwitter anion $H^{\oplus}A^{\ominus}$ into the neutral HA form; $\alpha_{HA^{\pm}}$ denotes the ratio of the mercapto derivative having the monoanionic $A^{\ominus}$ form ($[HA^{\pm}] = [HA] + [H^{\oplus}A^{\ominus}]$), $\alpha_{A^{\ominus}}$ denotes the contribution of the mercapto derivatives being in the monoanionic form $A^{\ominus}$; $k_{A^{\ominus}} = k_{\gg N} + k_{S^{\ominus}}$ - characterizes the overall reactivity of amino- and thioalcoholate groups in monoanion $A^{\ominus}$ and it can be considered the second order rate constant. Quantitative description of this complex multiflow process, in the course of which form thiol esters and sulfonamides of 4-toluene sulfonic acids, is possible if the reactivity of the amino group in the HA and $A^{\ominus}$ and the "microscopic" ionization constants K_1, K_2, K_3 and K_4 determining accumulation of the ionogenic forms of HA, $H^{\oplus}A^{\ominus}$ and $A^{\ominus}$ (Eqs.(4-6)) are known.

$$[HA] = \frac{1}{1 + K_t} \cdot \frac{K_I a_{H^{\oplus}}}{K_I K_{II} + K_I a_{H^{\oplus}} + a^{2}_{H^{\oplus}}} [A]_0 = \frac{1}{1 + K_t} \alpha_{HA^{\pm}} [A]_0 \qquad (4)$$

$$[H^{\oplus}A^{\ominus}] = \frac{K_t}{1 + K_t} \cdot \frac{K_I a_{H^{\oplus}}}{K_I K_{II} + K_I a_{H^{\oplus}} + a^{2}_{H^{\oplus}}} [A]_0 = \frac{K_t}{1 + K_t} \alpha_{HA^{\pm}} [A]_0 \qquad (5)$$

$$[A^{\ominus}] = \frac{K_I K_{II}}{K_I K_{II} + K_I a_{H^{\oplus}} + a^2_{H^{\oplus}}} [A]_0 = \alpha_{A^{\ominus}} [A]_0 \qquad (6)$$

Therefore the analysis of these processes was done in two stages. First the potentiometric titration was used in order to determine the "macroscopic" constants of acidic ionization K_I and K_{II}[7,8] for cysteine, cysteamine and N,N-diethylcysteamine, as well as the equilibrium constants for their S-methyl derivatives (9), modeling the ionization stage, characterized by the K_2 value.

$$K_I = \frac{([H^{\oplus}A^{\ominus}] + [HA])a_{H^{\oplus}}}{[H_2^{\oplus}A]} = K_1 + K_2 \qquad (7)$$

$$K_{II} = \frac{[A^{\ominus}]a_{H^{\oplus}}}{([H^{\oplus}A^{\ominus}] + [HA])} = \frac{K_3 K_4}{K_3 + K_4} \qquad (8)$$

$$\overset{|\oplus}{\underset{|}{HN}}-\underset{|}{C}HCH_2-SCH_3 \xrightleftharpoons{K_a} \overset{|}{\underset{|}{N}}-\underset{|}{C}HCH_2-SCH_3 \qquad (9)$$

Since the change of the standard free energy of the transfer of $H_2^{\oplus}A$ in $A^{\ominus}$ does not depend on the transition method, but $pK_1 + pK_3 = pK_2 + pK_4 = pK_I + pK_{II}$, thus, proceeding from (7), (10), (11) and from the measured values K_I, K_{II}, K_a (if $K_a = K_2$), it is possible to find the "microscopic" ionization constants K_1, K_3 and K_4 (Table 2).

$$K_3 = \frac{K_I K_{II}}{K_I - K_2} = \frac{K_I K_{II}}{K_1} \qquad (10)$$

$$K_4 = \frac{K_I K_{II}}{K_I - K_1} = \frac{K_I K_{II}}{K_2} \qquad (11)$$

Then the second order rate constants, quantitatively characterizing the aminogroup reactivity to NPTS, for the S-methyl derivatives of cysteine were established. The second order rate constants found can be approximated as the k_{HA} values for their non-metallic analogs. It is confirmed by the fact that the log k_2 values for these nucleophiles obey the Brønsted relationship for the NPTS reactions with amines (Fig. 3).

Table 2

Values of "Microscopic" and "Macroscopic" Ionization Constants and Constants of Tautomeric Equilibrium for Cysteine, Cysteamine and N,N-Diethylcysteamine in 5% Aqueous Ethanol; 25^{o} C; μ=1.0 (KCl)

pK_a	Cysteine	Cysteamine	N,N-Diethylcysteamine
pK_I	8.28±0.04	8.45±0.03	8.10±0.04
pK_{II}	10.40±0.03	10.90±0.06	11.30±0.06
pK_1	8.45	8.49	8.11
pK_2	8.77±0.04	9.50±0.03	9.71±0.06
pK_3	10.23	10.86	11.29
pK_4	9.90	9.85	9.69
K_t	2.1	10.2	39.8

A substantial negative deviation from the Brønsted plot in the case of S-methyl-N,N-diethylcysteamine seems to be caused by the susceptibility of the reaction to the steric substituent effects[6,8].

During the 2nd stage of the analysis, the reactivities of the $H^{\oplus}A^{\ominus}$ and $A^{\ominus}$ forms as thioalcoholate anions, were calculated from the pH dependences. The reaction was carried out under the conditions (see Table 1) where the contributions of the routes with the $H^{\oplus}A^{\ominus}$ and HA participation into the process rate were compared with those of the routes with participation of $A^{\ominus}$. When transforming expression (3) into (12),

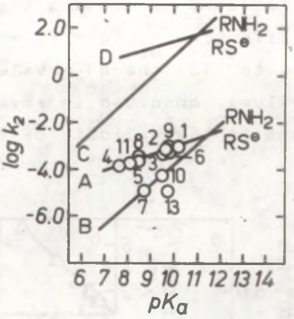


Fig.3. Brønsted relationships for reaction of thyoalcoholate ions and amines with 4-nitrophenyl-4'-tolyene sulfonate (straight lines A and B; numeration of points coincides with those of Table 1) and 4-nitrophenyl acetate (straight lines C and D). Straight lines C and D were made up on the basis of data of reports[4, 10,11], - straight line B was constructed according to the data of[8].

it is easy to find the $k_{2\,obs}$, and $k_{A^{\ominus}}$ values in the coordinates "$k_{2,obs}$ - $\alpha_{A^{\ominus}} / \alpha_{HA^{\pm}}$" (see Fig.4a).

$$k'_{2,obs} = \frac{k_H}{\alpha_{HA^{\pm}}[A]_0} = \left[k_{H^{\oplus}A^{\ominus}}\frac{K_t}{1+K_t} + k_{HA}\frac{1}{1+K_t}\right] + $$

$$+ k_{A^{\ominus}}\frac{\alpha_{A^{\ominus}}}{\alpha_{HA^{\pm}}} = k_{2,obs} + k_{A^{\ominus}}\frac{\alpha_{A^{\ominus}}}{\alpha_{HA^{\pm}}} \qquad (12)$$

Then, proceeding from the $k_{2,obs}$ values, and the measured values of K_t and k_{HA}, were found the constants $k_{H^{\oplus}A^{\ominus}}$. Individual rate constants, characterizing the nucleophilic reactivity of the anionic center $-\overset{\ominus}{S}$ ($k_{-S^{\ominus}}$) and the neutral center $\geqslant N$ ($k_{\geqslant N}$) in molecule $A^{\ominus}$ were established, assuming that the $A^{\ominus}$ behavior like that of amine, obeys the

Brønsted equation[8]; and $k_{-S^{\ominus}} = k_{A^{\ominus}} - k_{>N}$ (see Table 1). If pH≥10, $A^{\ominus}$ being the basic form reacting with NPTS and the contributions of the flows involving the $H^{\oplus}A^{\ominus}$ and HA form are insignificant (i.e., $k_{2,obs} \approx 0$), it will be possible to determine according to (12) the $k_{A^{\ominus}}$ value only (Fig.4b). Similarity of $k_{A^{\ominus}}$ values, observed in several pH regions (see Table 1, No6) refers to the validity of the kinetic equation (3).

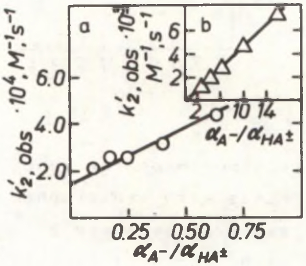


Fig.4. NPTS reaction with cysteine in 5% aqueous ethanol; 25 °C; μ=1.0(KCl). The results of measuring were treated applying Eq.(12): a) pH=9.0-10.2; b) pH=10.8-11.6

Interaction of 2-mercaptoethanol with the arylic esters of 4-toluene sulfonic acid was studied in 30 volume per cent of aqueous ethanol, which ensured a good solubility of the reagents and the forming reaction products. Transition from a 5% to a 30% aqueous ethanol does not affect the nucleophilicity of the mercapto derivative anionic form (of the k_2 values for NPTS and 2,5-DNPTS[*] in 5% and 30% ethanol in Table 3), although in these conditions the reactivity of ammonia relative to NPTS decrases ~50 times[12]. Evidently, it is connected with the fact that in the case of the NPTS thioalcoholysis at transition from the 30% ethanol simultaneously with the increase of the leaving group basicity in the substrate leads also to the higher basicity of the attacking

---

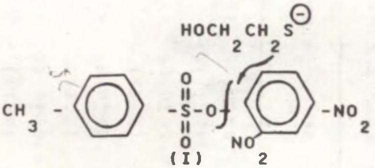
[*] For explanation of abbreviation see Table 3.

thioalcoholate ion (see Tables 1,3), while the ammonia basicity seems to decrease[13] rather substantially.

The rate of the 2-mercaptoethanol anion reaction does not especially depend on the basicity of the leaving arylate anion (Eq.(13)). $\log k_2 = (-0.99\pm0.30)+(-0.32\pm0.04)pK_a$;

$S_{tot}=0.13$; r=0.984 (13)

The leaving group basicity decreases $\sim 10^5$ times, during the transition from CPTS to 2,5-DNPTS, while the rate of nucleophilic attack with the $-\overset{\|}{\underset{\|}{S}}\wr OAr$ bond breaking increases 20 times only (see Table 3). Still, the interaction rate of thiol with 2,4-DNPTS, is almost 3.10^4 times higher than with 2,5-DNPTS in spite of the fact that the basicities of the corresponding arylate ions are very close (Table 3). This is caused by the reaction mechanism change: unlike arylsulfonates Nos 2-5 (Table 3) where the sulfur atom of the sulfonylic group is attacked, in the reaction with 2,4-DNPTS thioalcoholate anion attacks the aromatic carbon atom of phenol fragment and breaking of the $-\overset{\|}{\underset{\|}{S}}-O\wr C\!\!\swarrow$ bond (I) takes place. This process results in a quantitative and irreversible formation of 2-oxyethyl-2,4-dinitrophenyl sulfide and 4-toluene sulfonic acid (see Experimental). The second order rate constant for this reaction was calculated according to Eq.(1).



(I)

The ability of dinitrosulfonates to function as arylating agents has been observed earlier[14].

DISCUSSION

Nucleophilic reactivity of thioalcoholate ions to NPTS does not especially depend on their basicity (see Table 1) and it obeys the Brønsted equation:

$\log k_2 = (-5.7\pm0.47)+(0.25\pm0.05)pK_a$; $S_{tot}=0.10$; r=0.936 (14)

Data for all mercapto derivatives fall onto the same

Table 3

Conditions of Experiment, Basicity of Leaving Group in Substrate (pK_a) and 2-Mercaptoethanol Reactivity (k_2, $M^{-1} \cdot s^{-1}$) to Arylic Esters of 4-Toluene Sulfonic Acid in 30% Ethanol; 25 °C, $\mu = 1.0$(KCl)

	Substrate	pK_a^{a}	λ, nm	pH	$[HOCH_2CH_2SH]_o$ M	k_2
1.	2,4-dinitrophenyl-4'-toluene sulfonate (2,4-DNPTS)	3.88±0.02 (4.11)	370	6.09-9.4	0.0625-1.0	55.7±0.1 b)
2.	2,5-dinitrophenyl-4'-toluenesulfonate (2,5-DNPTS)	5.26±0.06 (5.22)	440	10.50	0.0625-1.0	0.0018±0.0001
				9.50	0.1-1.0	0.0015±0.0001 c)
3.	4-nitrophenyl-4'-toluenesulfonate (NPTS)	7.51±0.03 (7.14)	410	9.2-11.0	0.0625-1.0	0.0005±0.00001
				9.50	0.1-1.0	0.00066±0.00002 c)
4.	2,4-dibromophenyl-4'-toluenesulfonate (2,4-DBPTS)	8.56±0.02 (7.74)	315	10.20	0.125-1.0	0.00012±0.00001
5.	3-chlorophenyl-4'-toluenesulfonate (CPTS)	9.67±0.04 (9.02)	300	11.0	0.1-1.0	0.000079±0.000003

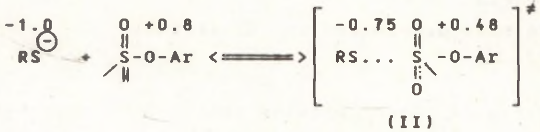
a) Ionization constants of substituted phenols have been found spectrophotometrically in 30% ethanol; pK_a values in water[12,15] are given in parentheses.

b) k_2 characterizes the arylation rate of 2-mercaptoethanol anion of 2,4-DNPTS.

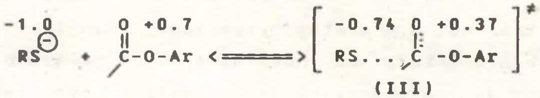
c) k_2 values have been determined in 5% ethanol.

straight line (Fig.3), thus proving that such acid-base groups as $-COO^{\ominus}$, $>N$, $>\overset{\oplus}{N}H$ and -OH which are the components of cysteine, cysteamine, N,N-diethylcysteamine, thioglycolic acid and 2-mercaptoethanol do not have any remarkable stabilizing effect during the transition state of the rate limiting stage of thioalcoholysis. It means that these functional groups are catalytically indifferent both in the reaction studied and in that of mercapto derivatives with 4-nitrophenyl acetate (NPA)[3].

There are several common features between the kinetic regularities of the thioalcoholysis and aminolysis of aryl esters of acidic and para-toluene sulfonic acid. In the case of the rate determining attack of the carbon atom of the carbonylic group of arylacetates by thioalcoholate ions, the sensitivities to the nucleophile and leaving group basicities equal $\beta_N^4=0.27$ and $\beta_X^4=-0.33$ respectively. These values practically coincide with those of β in case of the 4-toluene sulfonate group transition to thiol (Eqs.(13) and (14)). Such a coincidence of the β values cannot be occasional. Most probably, it reflects the structural similarity of transition states of the reactions and the identity of distribution of effective charges (δ) at the attacking and leaving groups in the transition state. The effective charge value at the ester atom of arylsulfonate oxygen was found to be $\delta=+0.8$[12]. Making use of this value and $\delta=-1.0$ for thioalcoholate anion, we calculated the effective charges on the reacting atoms in the triangular bipyramidal state (II) in the case of reactions of the 4-toluene sulfonate group transition (see Scheme (15a)). For the purposes of comparison (15b), the variation of effective charges in the transition state (III), when the nucleophilic attack of the carbon atom by the thioalcoholate ion is the rate determining stage[4] has been shown.

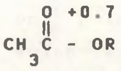


(15a)



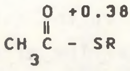
(15b)

It will be possible to establish the degree of similarity of the transition states (II) and (III) by means of a reagent or reaction product if we know the variation of the effective charges at the reacting atoms during the transition from the initial state to the reaction products.[4] In the case of formation of thiol esters of acetic acid, the overall variation of the charge at the sulfur atom is 1.38[4], at the complex esteric oxygen atom the charge value equals -1.70[4]. The effective charge value on the sulfur atom in the thiol esters of arylsulfonic acids is not known. Nevertheless, comparing the electron acceptor ability of the acylic and aryl sulfonylic groups in compounds (IV) and (VI), we came to the conclusion that, evidently, in the thiol esters of arylsulfonic acids, the effective charge on the sulfur atom should be close to $\delta \approx +0.4$ (VII).



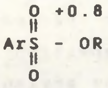
$CH_3\overset{O\ +0.7}{\overset{\|}{C}} - OR$

(IV)



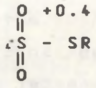
$CH_3\overset{O\ +0.38}{\overset{\|}{C}} - SR$

(V)



$Ar\underset{\overset{\|}{O}}{\overset{O\ +0.8}{\overset{\|}{S}}} - OR$

(VI)



$Ar\underset{\overset{\|}{O}}{\overset{O\ +0.4}{\overset{\|}{S}}} - SR$

(VII)

Therefore the formation of the thiol esters of arylsulfonic acids is followed by changing of the charges on the reacting atoms of sulfur (+1.4) and oxygen (-1.8). Consequently, the rate determining transition states (II) and (III) form rather early both in the case of the acylic group transition to the thiolate anion[4] and in the case of the 4-toluene sulfonate group transition, since during the transition from the initial to the transition states (II) and (III), the effective charge changes ≈ 20%.

Small sensitivity of thiolate anions to the basicity in the reactions with various substrates seems to be a regular phenomenon rather than an exception. Beside NPTS and NPA, small β_N values are characteristic of the reactions of thioalcoholate ions with acetyl-imidazole cations ($\beta_N \approx 0.2$[16]) but they are also quite common with the addition of acetaldehyde ($\beta_N \approx 0.1$[5]) and methyl cobaloxime ($\beta_N \approx 0$[17]) to the carbonyl group. An early transition state with an insignificant change of the charge on the nucleophilic sulfur atom is typical of these processes. This is in keeping with the variation of the activation entropy value in the case of transition from the NPTS reaction with anion of 2-mercaptoethanole to the reaction with piperidine. The difference between the $T\Delta S^{\neq}$ (piperidine) and $T\Delta S^{\neq}$ (2-mercaptoethanol) is -5 kcal/mol (see Table 4), i.e. the transition state for the reactions with piperidine is more regulated than that for the process with the participation of 2-mercapto ethanol.

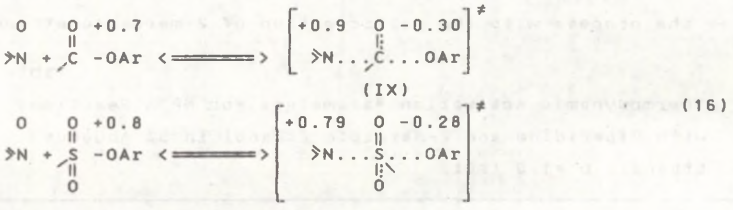
Table 4

Thermodynamic Activation Parameters for NPTS Reactions with Piperidine and 2-Mercapto Ethanol in 5% Aqueous Ethanol: μ =1.0 (KCl)

Nucleophile	$\Delta G^{\neq}$ (298 K) kcal/mol	$\Delta H^{\neq}$ kcal/mol	$\Delta S^{\neq}$ a.u.	$T\Delta S^{\neq}$ kcal/mol
Piperidine	21.5	9.0±1.1	-(42.1±0.7)	-12.5
2-Mercapto-ethanol	21.8	14.3±1.1	-(25.2±1.0)	-7.5

According to the Hammond postulate[18] in the case of an early transition state, the susceptibility of the reaction rate to the structure effects should be insignificant. At the same time in the reactions of thioalcoholates with aryl and thioaryl esters of carbonic acids[4], and methiodide of O-acetylpyridine-4-aldoxime[19], the rate determining stage undergoes a change and a later transition stage is realized, the sensitivity to the thiolate anions' nature is growing ($\beta_N \sim 0.9$). Unfortunately, we did not succeed in studying the reactivity of thioalcoholate ions whose pK_a were smaller than those of the leaving group in NPTS. Therefore, it is not quite clear whether the change of the transition state from the reagent like to the product-like one takes place or not in the reaction studied, in case the attacking nucleophile basicity is smaller than that of the leaving group.

Unlike thioalcoholysis the aminolysis of aryl acetates and aryl sulfonates is much more sensitive to the peculiarities of the attacking amine and those of the leaving group (in the case of the aminolysis of aryl sulfonates $\beta_N = 0.79$[8], $\beta_X = -1.08$[12]; for the aminolysis of aryl acetates $\beta_N = 0.9$[4], $\beta_X = -1.0$[20]). Large β values in the case of aminolysis of these two classes of "rigid" substrates refer to the situation that in the transition states (IX) and (X) (Scheme (16)) form almost integral positive charges on the nitrogen atom of the nucleophile; charges close to zero are observed on the oxygen of the leaving group of phenolate ion.



(IX)

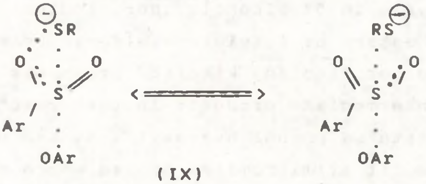
(16)

(X)

These transition states, evidently being on halfway from reagents to the reaction products, resemble the intermediate products of addition, and, as to the aminolysis, a series of convincing facts proving that the process proceeds via formation of the tetrahedral intermediate addition product (IAP). The value $\beta_N = 0.9$, in general reflects the substituent effect on the equilibrium constants of the IAP formation[4]. At the same time, a remarkable sensitivity to the nature of the attacking nucleophile and leaving group can be explained by means of the coordinated reaction mechanism, where as the β values, characterizing the variations of the effective charges on the reacting atoms, do not practically carry any information about the order of the forming and breaking bonds with the attacking and leaving groups in the transition state. The aminolysis of NPTS in 41% alcohol proceeds in two parallel routes, one of them having the second order according to amine[6]. Such a behavior can principally be caused by the formation of penta-coordinated intermediate addition product. Nevertheless, the catalysis by other amine molecules was not observed neither in the case of the NPTS aminolysis in 5% alcohol[8], nor in the case of aminolysis of aryl esters of 4-toluene-sulfonic acid in 30% ethanol[12]. We could not find any kinetic arguments proving the existence of intermediate products in the reactions of sultones with substituted phenol hydroxyl ions and phosphate anions[21]. Therefore, it still remains opened which mechanism of aminolysis of arylsulfonates is realized, either the correlation or the stepwise one, although the sensitivity of aminolysis of arylsulfonates and arylacetates to the nucleophile and leaving group practically coincides.

Thioalcoholate anions react with NPTS more quickly than amines, but the nucleophilicity of thiol anions having small basicities whose $pK_a \approx 8.0$ almost 100 times exceeds the reactivity of amines with the comparative pK_a values. If the basicity of thioalcoholate ions and amines increases, the differences in their reactivity smooth out but the correlation straight lines A and B (Fig.3) intersect at $pK_a \approx 11.4$, corresponding to the basicity of the hypothetical thioalcoholate ion. Thus, in the case of any pK_a values attainable, thioalcoholate anions turn out to be more effective nucleophiles than amines. Analogous behavior of the $RS^{\ominus}$ ions and amines can be traced in the reactions with NPA (see Fig.3), while intersection of correlation lines C and D takes place at $pK_a \approx 11.0$. Such a behavior of thioalcoholate ions in the reactions with NPTS and NPA must be caused by their smaller β_N values.

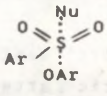
Thioalcoholate ions, as also the majority of "soft" easily polarizable nucleophiles have the characteristic attainable α-orbitals, which can accept the lone electron pair of the substrate, having the form of the Lewis acid, and thus stabilize the transition state of the reaction. This can be the essential factor, leading to the high reaction rates with NPTS at the expense of giving away the electrons from the oxygen atoms of sulfonyl group to the free α-orbitals of the nucleophilic center of thiol (XI). A similar transition state is evidently realized also for the reactions of the $RS^{\ominus}$ anions with methyl cobaloxim[17].



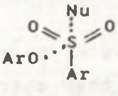
(IX)

This can hardly be an exhaustive interpretation of kinetic data, since the chemical behavior of $\overset{\ominus}{C}H_2SH$ and $\overset{\ominus}{C}H_2OH$ carbanions cannot be directed only by the existence of the $(p\text{-}d)_\pi$ - interactions in their molecules. The reasons of the differences in the properties of these carbanions can be easily understood if we bear in mind that the sulfur atom has a greater polarizability in comparison with oxygen, the $-\overset{|}{\underset{|}{C}}-SH$[22] bond is also longer. Nevertheless, the EPR spectra evidence about a remarkable delocalization of the non-paired electron on the chlorine atom in β-chloroethyl radical[23]. The latter leads to the assumption that the atoms which are more easily polarizable, sulfur incl., participate in the stabilization of transition states of type (XI) owing to the delocalization of electrons on free α-orbitals.

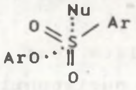
Nucleophilic attack at the tetracoordinated sulfur atom of aryl sulfonates may cause the formation of the isomeric transition states (XII-XIV) having a bipyramidal structure with different states of attacking and leaving groups.



(XII)



(XIII)



(XIV)

A more favorable direction of the attack is achieved when the attacking and the leaving group are in axial positions, while the oxygen atoms of the sulfonyl group and the carbon of the phenyl nucleus are in the equatorial positions thus forming the basis for the bipyramide (XII). Such a transition state is more stable energetically and less sensitive to the steric substituent effects in the leaving group if compared with transition states (XIII) and (XIV) (there the attacking and leaving groups are in the axial and equatorial states, respectively). Introduction of the orto-substituents into the phenyl nucleus of the leaving group does not actually bring about any remarkable negative deviations in the correlation dependences of type (13) neither in the cawe of thioalcoholysis nor of the arylsulfonates ammonolysis[12], although in the latter case, a late transition state can be observed and consequently, it should be fairly sensitiv to the steric substituent effects. Most probably, the theoretical regularities explaining the locations of the polar substituents in the maximums of the bipyramidal transition state of the substitution reactions at the tetracoordinate phosphorus atom, can succesfully be applied also to the penta-coordinated sulfur atom. Studies of the organic penta-coordinated sulfur compounds -sulfuranes- have shown their structure to be bipyramidal, thus corresponding to the distribution rules of ligands[25], which have been drawn for the penta-coordinated phosphorus compounds.

EXPERIMENTAL

Thioglycolic acid, methyl ester of thioglycolic acid, N,N-diethylcepteamine, and 2-mercaptoethanol were several times distilled over in the argon current. Cysteine, cysteamine, and N-acetyl cysteine (commercial preparations of "chemically pure" grade) were used for an additional purification. S-methyl esters of cysteamine and N,N-diethyl cysteamine were synthesized according to the following methods: thiol (0.1M) was dissolved in 150ml of methanol, containing 0.12M of sodium methylate, when cooling ($t=5\,^{o}C$), 0.12M of methyl iodide was added by dropping. The solution was kept for ≈ 12 hours in the refrigerator. Methanol, saturated with hydrogen chloride was added to the mixture, and the solvent was subjected to steaming until dry. Chlorohydrates of S-methyl esters of cysteamine and N,N-diethyl cysteamine were extracted by means of hot isopropanol. At cooling, the latter dropped taking the form of colourless crystals. Chlorohydrate of S-methyl ester of N,N-diethyl cysteamine was recrystallized three times from isopropanol, melting point being 101-103 °C. The halogen ion concentration in the analyzed sample corresponds to the theoretical values. Chlorohydrate of S-methyl ester of cysteamine was turned into base by means of sodium methylate in methanol, sodium chloride was filtered, the solvent underwent steaming until drying but S-methyl ester of cysteamine was distilled under the argon atmosphere, boiling point 147 °C (cf. boiling point 146.8 °C[26]). S-methyl ester of cysteine was obtained and purified as indicated in[27]. In all cases, the purity level of thiols was controlled by iodometric titration[28]; concentration of sulfohydrylic groups in the analyzed sample was at least 97%.

Aryl esters of 4-toluene sulfonic acid were obtained from the corresponding phenols (0.1 M) and 4-toluene sulfochloride (0.1 M) in presence of triethyl amine (0.1 M) in absolute dioxane. At termination of the reaction, dioxane was steamed till the minimum volume, and the solution was poured out on ice. The crystals dropped were filtrated, washed with 0.1 M of HCl solution and dried in air. Aryl esters of 4-toluene sulfonic acid were recrystallized up to a stable melting point (see Table 5).

Table 5

Melting Points and Solvents for Recrystallizing Aryl Esters of 4-Toluene Sulfonic Acid

No	Ester	Melting point °C	Solvent for recrystallization
1.	2,4-DNPTS	123(122-123[12])	Absolute ethanol
2.	2,5-DNPTS	116(115-117[12])	Absolute ethanol
3.	NPTS	98(97-97,5[12])	Absolute ethanol
4.	2,4-DBPTS	120(120[29])	Toluene hexane
5.	CPTS	42-43	Toluene hexane

Inorganic reagents of "extra pure" and "chemically pure" grade were applied without additional purification; D_2O and solutions of deuterium chloride in D_2O were used, the concentration of isotope-substituted substance being 99.8%; deuterium oxide of sodium was prepared as suggested in[30].

Ionization constants of mercapto derivatives were determined potentiometrically at 25°C, ionic strength μ=1.0 kept in KCl in a 5% ethanol; those of substituted phenols (30% ethanol; μ =1.0(KCl)) were found spectrophotometrically[15]. The pK_a values were calculated according to the Henderson-Hasselbach equation.

The reaction of aryl esters of 4-toluene sulfonic acids with nucleophiles was monitored by means of UV-spectrophotometry according to the accumulation of the corresponding arylate ion at the wave lengths given in Table 3 at 25±0.5°C. In all kinetic experiments, the initial concentration of the substrate (1.10^{-5} - 5.10^{-5} M) is much smaller than the initial concentration of nucleophile (0.06-1.0 M). The constants of pseudofirst order were calculated as in[8]. Solutions of nucleophilic reagents were prepared directly before each series of kinetic measuring; their initial concentrations were simultaneously functioning as a buffer. The necessary pH values were found by means of the concentrated solutions of NaOH and HCl. The ionic strength of the solution was established by introducing IM KCl. The acidity of the reaction medium was monitored before and after each kinetic test. If the pH variation exceeded 0.05 pH units at termination of the first reaction the results were not taken into consideration.

The reaction products were analyzed by means of the UV spectrophotometry. In all cases (2,4-dinitrophenyl-4'-toluene sulfonate excluded), the UV spectra of reaction products coincided with those of model solutions, made up of the suggested reaction products forming in the case of the S-O bond breaking of aryl esters of 4-toluene sulfonic acid. In the case of 2-mercapto ethanol interaction with 2,4-DNPTS, 4-toluene sulfonic acid and 2-oxyethyl-2,4-dinitrophenyl sulfide accumulate in the reaction mixture. The latter component is intensively absorbed in the same region that 2,4-dinitro phenolate ion, i.e. if λ=370 nm. Since no variation of absorption was observed at this wave length of the reaction and the standard mixture, consisting of 4-toluene sulfonic acid and 2-oxyethyl-2,4-dinitrophenyl sulfide in the case of acidification of the solutions to pH$\sim$1.0, it refers to breaking of the $-\overset{\|}{\underset{\|}{S}}-O\int Ar$ but not of the $-\overset{\|}{\underset{\|}{S}}\int O-Ar$ bond. Thus in the 2,4-dinitrophenyl-4'-toluene sulfonate reaction with 2-mercapto ethanol the attack at the carbon of 2,4-dinitrobenzene aromatic nucleus will be realized and the attack is not directed at the tetracoordinated sulfur atom.

The activation parameters for the piperidine and 2-mercapto ethanol reaction with NPTS were found on the basis of the temperature dependence (25,40,50 ^{o}C) of the aminolysis and thioalcoholysis rate constants. The values are given in Table 4.

REFERENCES

1. P.De Maria and A.Fini, J.Chem.Soc.,Perkin Trans,Part II, 1773(1973).
2. L.Drobnica, D.Podhradsky, and P.Gemeiner, Collect.Czech. Chem.Commun.,40,3688(1975).
3. J.W.Ogilvie, J.T.Tyson, and B.S.Strauch, Biochemistry,3, 754(1964).
4. D.J.Hupe, and W.P.Jencks, J.Am.Chem.Soc.,99,451(1977).
5. J.E.Lienhard and W.P.Jencks, J.Am.Chem.Soc.,88,3982 (1966).
6. P.Monjoint, G.Guillot, and M.Laloi-Diard, Phosphorus and Sulfur,2,192(1976).
7. J.L.Kice and E.Legan, J.Am.Chem.Soc.,95,3912(1973).
8. Yu.S.Simanenko, T.M.Prokopeva, V.A.Savyolova, A.F.Popov, G.S.Sakulin, and I.A.Belousova, Organic Reactivity,23, 209(1986).
9. J.L.Kice, Adv.Phys.Org.Chem.,17,65(1980).
10. W.P.Jencks and M.Gilchrist, J.Am.Chem.Soc.,90,2622 (1966).
11. W.P.Jencks and J.Carriuolo, J.Am.Chem.Soc.,82,1788 (1960).

12. N.A.Suttle and A.Williams, J.Chem.Soc., Perkin Tran., Part II,1563(1983).
13. G.Gordon, "Organic Chemistry of Electrolytic Solutions", (in Russian),Mir,1979.
14. R.V.Vizgert, I.M.Ozdrovskaya, S.G.Sheiko, and E.S. Mitchenko "Reactions of Nucleophilic Substitutions in Series of Activated Sulfonic Acids", - In book: "Structure and Reactivity of Organic Compounds" (in Russian), Kiev: Naukova dumka, 1981, pp.104-140.
15. A.Albert and E.Serjeant, Ionization Constants of Acids and Bases (Russian translation), "Khimija", Moscow - Leningrad,1964.
16. W.P.Jencks and K.Salvesen, J.Am.Chem.Soc.,93,1419(1971).
17. K.L.Brown and R.G.Kallen, J.Am.Chem.Soc.,88,3577(1972).
18. G.S.Hammond, J.Am.Chem.Soc.,77,334(1955).
19. J.J.O'Neill, H.Kohl, and J.Epstein, Biochem.Pharmacol.,8, 399(1961).
20. W.Jencks, "Catalysis in Chemistry and Enzymology", (Russian translation), "Mir", Moscow,1972.
21. T.Deacon, C.R.Farrer, B.J.Sikkel, and A.Williams, J.Am. Chem.Soc.,100,2525(1978).
22. F.Bernardi, J.G.Csizmadia, A.Mangini, H.B.Schlegel M.-H.Whangbo, and S.Wolfe, J.Am.Chem.Soc.,97,2209(1975).
23. T.Kawamura, D.J.Edge, and J.K.Kochi, J.Am.Chem.Soc.,94, 1752(1972).
24. F.H.Westheimer, Acc.Chem.Res.,70(1968).
25. E.F.Pezozzi, J.C.Martin, and J.C.Paul, J.Am.Chem.Soc.,96, 6735(1974).
26. C.J.Hawkins and D.D.Perrin, J.Chem.Soc.,1351(1962).
27. M.D.Armstrong and J.D.Lewis, J.Org.Chem.,16,749(1951).
28. Houben-Weyl, "Methods of Organic Chemistry", (in Russian), Goskhimizdat, Moscow,1963.
29. C.Stewter, "Chemistry of Organic Sulfur Compounds", (Russian translation), "Inostrannaya Literatura",Moscow, 1951,p.376.
30. A.K.Covington, R.A.Robinson, and R.G.Bates, J.Phys.Chem., 70,3820(1966).

CONTENTS

РЕАКЦИОННАЯ СПОСОБНОСТЬ ОРГАНИЧЕСКИХ СОЕДИНЕНИЙ.
Том XXIУ. Вып. 3(87). Сентябрь I987.
На английском языке.
Тартуский государственный университет.
ЭССР, 202400, г.Тарту, ул.Юликооли, I8.
Vastutav toimetaja V. Palm.
Paljundamisele antud 29.03.1988.
Formaat 60x84/16.
Kirjutuspaber.
Masinakiri. Rotaprint.
Tingtrükipoognaid 7,21.
Arvestuspoognaid 6,79. Trükipoognaid 7,75.
Trükiarv 350.
Tell. nr. 315.
Hind rbl. 1.40.
TRÜ trükikoda. ENSV, 202400 Tartu, Tiigi t. 78.