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SOLVENT EFFECT ON KINETICS OF HOMOLYTIC REACTIONS.
I. THERMOLYSIS OF ETHERS OF PERACIDS.

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The data of the medium effect on the rate of thermal decomposition of tert.-butyl ethers of perbenzoic and o-thiophenyl perbenzoic acids are generalized by means of the multi-parameter linear free energy relationship.

Unlike heterolytic reactions, the solvent effect on the rate of homolytic processes has not been studied very thoroughly yet, and the conducted studies have been of qualitative nature mainly. Owing to the complex and multi-phase character of the reactions with participation of free radicals, the quantitative generalizations of the medium effect have been carried out concerning the simplest cases only: the non-induced decomposition of tert.-butyl ether of performic acid[1,2] and tert.-butyl-peroxide[1], rearrangement of cumyl perbenzoate[1], decompostion of the diacyclic peroxides[3,4] as well as the dimerization of phenoxylic radicals[2,5]. Therefore the further investigation into this field will be of remarkable interest.

It was established in R.E.Pincock's[6] well-known study on the thermolysis of tert.-butylperformate (TBPF) catalyzed with pyridine in 20 solvents at 90°C that the rate of the process during the transition from the non-polar n-heptane to nitrobenzene is increasing by a factor of 10^2, but only the values of a few solvents suit the linear dependence of log k on the Kirkwood parameter. The existence of even two linear dependences can be expected: those in case of polar solvents and hydrocarbons (Fig. 1).

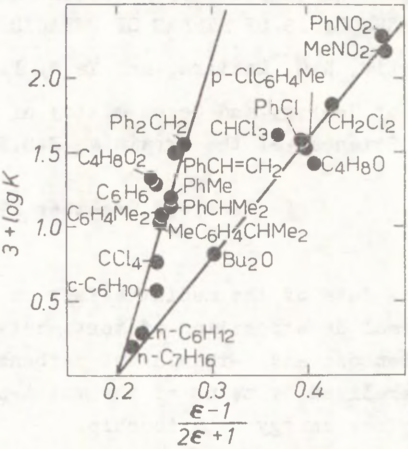
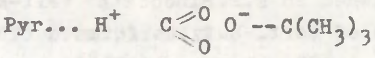


Fig. 1. Dependence of tert.-butylperformate decomposition rate on polarity according to[6] (1). An alternative dependence in case of hydrocarbons (2).

The latter dependence has not been discussed. In the case of low-polarity solvents the linear dependence of log k on the medium polarizability[6] has also been observed. It has been found that in certain solvents there is also connection between the TBPF decomposition rate and that of amines' quaternization in similar media. The author assumes that the decomposition is of ionic character conditioned by the catalytic effect of pyridine:



$$\text{Pyr... H}^{+}\quad \text{C}\overset{\text{O}}{\underset{\text{O}}{\lessgtr}}\ \text{O}^{-}\text{--C(CH}_3)_3$$

which is actually not in keeping with the independence of the process rate of its concentration. In a number of solvents (e.g. in ethers) another mechanism may exist which is characterized by the HCOOH formation instead of CO_2 suppressed by the quinone or oxygen additions. It is more characteristic of the induced radical decomposition of peroxide compounds.

These works[6] were generalized quantitatively by V.A.Palm and I.A. Koppel.[1] They showed that in accordance with the assumptions of report[6], the reaction rate is determined by the nonspecific solvation. However, the correlation coefficient value R = 0.895 is rather small. Our additional research[2] has proved that if the specific electrophilic solvation of the activated state of perether is taken into consideration, it will be possible to get a satisfactory generalization of the data of its decomposition rate in 18 solvents, R = 0.987. An attempt to consider the medium effect on this process by means of the electrophilicity parameter E_T only, leads to remarkably poorer results: in case of 13 solvents R = 0.929[7]. At the same time, the possibility of the catalysis with pyridine is rather doubtful since any notable dependence of the rate on the medium basicity was not observed. Probably, the role of the catalysis is to suppress the induced radical decomposition. The absence of the induced process is also confirmed by the fact that the rate does not depend on the cohesion energy density of the medium, thus characterizing its selfassociation, and finally, by the cage effect which plays a vital part in the radical reactions.

As to the tert.- butylperbenzoate (TBPB), it cannot be catalyzed with the bases suggested in the scheme of[6] owing to the absence of the formyl atom of hydrogen but the decomposition process must have a clearly homolytic character. It has been established in[8] that decomposition takes place at differentiated rates in aliphatio solvents being practically similar in the aromatic ones which are more favorable to the induced decomposition.In order to find out the effect of the medium properties on the rate of a typical homolytic decomposition of perethers, we compared the data[8-11] on the TBPB decomposition rate at 110°C and 119.4°C in 15 solvents. (see Table 1). The induced decompostion was suppressed by the addition of diphenyl ether.

Table 1

Tert-Butylperbenzoate Decomposition Rate Constants at 110°C and Parameters of Solvents[x]

No	Solvent	$\frac{n^2-1}{n^2+2}$	$\frac{\varepsilon-1}{2\varepsilon+1}$	δ^2	B	E_T	Ref.	$k.10^4$ (110°)	$k.10^4$ (119.4°)	log k_{110}	log k 119.4
1	2	3	4	5	6	7	8	9	10	11	12
1.	Chlorobenzene	0.3064	0.377	385.9	38	157.0	8	0.384	1.115	-4.4157	-3.9527
2.	n-butanol	0.2421	0.457	553.9	231	210.2	8	7.440	18.400	-3.1284	-2.7352
3.	dibutyl ether	0.2421	0.289	250.4	285	139.8	8	1.800	3.793	-3.7447	-3.4210
4.	acetic acid	0.2270	0.387	427.1	139	214.4	8	1.140	9.058	-3.9431	-3.0430
5.	benzene	0.2947	0.231	349.8	48	144.4	8	0.350	1.041	-4.4559	-3.3825
6.	xylene	0.2968	0.256	327.2	68	143.6	8	0.380[xx]	1.092	-4.4202	-3.9618
7.	p-chlorotoluene	0.3037	0.386	388.6	41	161.6	8	0.342	1.010	-4.660	-3.9957
8.	diphenyl ether	0.3340	0.321	358.8	123	147.8	9	0.228	0.900	-4.6421	-4.0458
9.	butylacetate	0.2393	0.364	302.3	158	155.8	8	1.056	2.676	-3.9763	-3.5725
10.	cumene	0.2898	0.239	319.1	56	141.6	11	0.396	-	-4.4023	-
11.	undecane	0.2536	0.203	250.9	0	129.4	11	0.425	0.170	-0.3716	-3.3799

Table 1 continued

1	2	3	4	5	6	7	8	9	10	11	12
12.	bromobenzene	0.3232	0.373	422.4	40	157.0	8	-	1.325	-	-3.8778
13.	ethylbenzene	0.2921	0.242	325.7	58	142.3	8	-	1.065	-	-3.9727
14.	t-butylbenzene	0.2905	0.239	289.0	60	141.1	8	-	1.032	-	-3.9863
15.	methyl benzoate	0.3025	0.394	408.8	160	164.2	8	-	0.784	-	-4.1073

* - parameters of solvents δ^2 and E_T in kJ/mole, Ref. 12.

** - the initial value $k_{119.4} = 1.10 \cdot 10^{-4}$ recalculated for temperature 110°C on the basis of $E_{act} = 33.8$ kcal/mol.

The obtained data can be generalized by the multiparameter LFER equation (the probability level being rather high) and taking into account the solvation parameters of the Koppel-Palm equation[1] and the possible influence of the breaking of the cage effect the cohesion energy density according to Hildebrand is as follows: $\delta^2 = \Delta H_{vap} - RT/V_{mol}$ kJ/mol. Since report[6] suggests a possible influence of the Kosower parameter on the decomposition rate $Z \equiv E_T$, in the present research for comparison, the parameter E_T according to Reichardt is used in order to characterize the electrophilicity. The proportionality of this parameter to E was proved in[13]. The following expressions have been obtained:

a) at 110°C

$$\log k \cdot 10^4 = -1.406 - 10.566 f(n) + 0.355 f(\varepsilon) + 0.0054\,\delta^2 + 0.00218 B - 0.0135 E_T;$$

$N=11$; $R=0.996$; $S=0.055$; $r_1=0.765$; $r_2=0.563$; $r_3=0.494$; $r_4=0.798$; $r_5=0.646$.

b) at 119.4°C

$$\log k \cdot 10^4 = -1.174 - 10.931 f(n) - 0.555 f(\varepsilon) + 0.0032\,\delta^2 + 0.00057 B - 0.00393 E_T;$$

$N=13$ (without No 13); $R=0.954$; $s=0.167$;
$r_1=0.843$; $r_2=0.342$; $r_3=0.354$; $r_4=0.523$; $r_5=0.653$

It is in keeping with the conclusion of reports[1,2,6] that it is the polarizability of the medium that has a decisive effect on the decomposition rate, although a relatively small value of the pair-wise correlation coefficient according to the parameter $r = 0.764$ refers that other factors also significantly affect the rate. In case of analyzing the equation at 119.4°C, the alternate checking of their significance permits us to exclude the polarity factor: $\log k = f(n, \delta^2, B, E_t)$, but $R=0.996$. The effect of electrophilic solvation is also rather insignificant: $\log k = f(n, E, \delta^2, B)$, $R=0.961$. The process can also be described with an acceptable accuracy by four - or even three-parameter equations;

$$\log k\cdot 10^4 = -1.484 - 10.375 f(n) + 0.00548\delta^2 + 0.00227B - 0.012E_T;\ R = 0.996;\ s = 0.054$$

$$\log k\cdot 10^4 = -3.370 - 6.350 f(n) + 0.00197\delta^2 + 0.00220B$$

$$R = 0.961;\ s = 0.146.$$

In Figs. 2 and 3 the connection between the log k_{calc}. (according to the three-parameter equations taking into consideration n, B and δ^2) and log $k_{exp.}$ at temperatures 110°C and 119.4°C is shown. Term numbers correspond to those of Table 1.

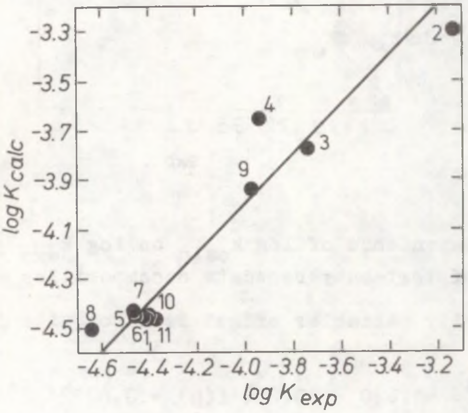


Fig. 2. Dependence of log $k_{calc.}$ on log k_{exp} in case of tert-butylperbenzoate decomposition at 110°C.

Exclusion of other solvation factors decreases the value even more substantially, e.g. f(n) to 0.87, δ^2 or B to 0.92.

In case of 119.4°C the general dependences are the same: the medium polarity does not affect the log k value, if it is excluded, R will drop from 0.954 to 0.953. The electrophilic solvation is also negligible, its exclusion leads to the three-parameter equation while R=0.948;

$$\log k\cdot 10^4 = -1.057 - 11.216 f(n) + 0.00345\ \delta^2 + 0.00044\ B - 0.0048\ E_T;$$

$$R = 0.953,\ s = 0.158$$

$$\log k\cdot 10^4 = -1.795 - 9.655\ f(n) + 0.00217\ \delta^2 + 0.00041\ B$$

$$R = 0.948;\ s = 0.166$$

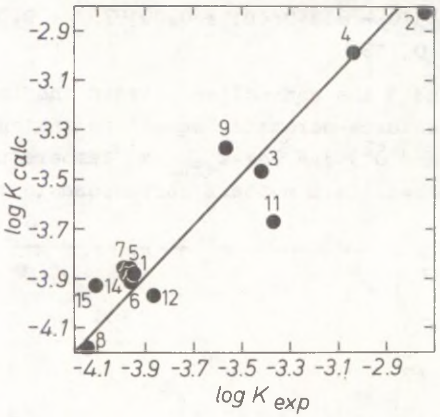


Fig. 3. Dependence of log k_{calc} on log k_{exp} in case of tert-butylbenzoate decomposition at 119.4°C.

The basicity parameter effect is also quite insignificant:

$$\log k \cdot 10^4 = -1.620 - 10.224\, f(n) + 0.00224\, \delta^2$$

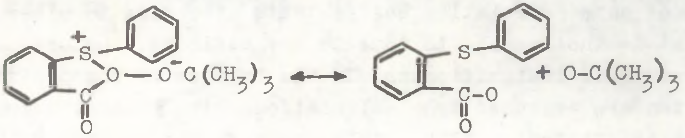
$$R = 0.146$$

At the same time the exclusion of energy expense for the cavity formation in the reaction medium ($\equiv \delta^2$) breaks the correlation: R = 0.854.

In case of comparison of the calculation date with those of the TBPF thermolysis, one should first of all pay attention to a remarkable medium basicity effect, the rising of which brings about the acceleration of the decomposition rate. It confirms the assumption[6] that the perethers decomposition can be catalyzed with the bases solvating their molecule and favoring this reaction because of the electron shifts. However, owing to the absence of formyl hydrogen in case of TBPB, the solvation of the acylic fragment will probably take place. Still, the set of solvents studied in[8-11] did not include any strong pyridine-like bases.

Unlike TBPF, growing of the medium polarizability does not accelerate but slows down the TBPB decomposition. It may probably be caused by the aromatic nature of the TBPB, which leads to the predominance of the stabilizing solvation of the initial molecule. A certain although rather insignificant effect of the cohesion energy density factor on the decomposition rate makes us to suppose that the diphenyl oxide is a weaker inhibitor than pyridine and as a result the induced TBPB decomposition can take place. The insignificance of the medium polarizability and electrophilicity parameters refers to the more polar character of the TBPB state in comparison with TBPB or of the complex TBPF- pyridine. Remarkably higher decomposition rates of the TBPF- pyridine complex in comparison with those of TBPB are also in agreement with this assumption. In case of the reactions in benzene, the second order rate constant of the TBPF decomposition at 90°C equals $21.5 \cdot 10^{-3}$ l/mol·s, while the first order rate constant of TBPB at 110°C is $0.35 \cdot 10^{-4}\ s^{-1}$ only.

In[14] the decomposition of the tert-butyl ether of o-thiophenylperbenzoic acid inhibited by the styrene addition at 40°C has been studied. The authors have observed the existence of the linearity between the log k of decomposition in alcohols, acetone, DMSO, acetonitrile and the Kosewer Z parameter. The authors admit on the basis of increasing of the rate with growth of Z, as well as according to the data of the salt and substituent effects that the formation of the polar transition state should be considered the initial stage of the homolytic decomposition:



However, there is a number of experimental values which do not suit this dependence.

Generalization of the data[13] (Table 2) leads to the equation with a sufficient probability of the dependence involving all the 11 solvents, without taking into account the results for the mixed solvents water-dioxane.

Table 2.

Rate Constants of t-Butyl-o-Thiophenylperbenzoate[14]

No	Solvent	$k \cdot 10^4, sec^{-1}$	E_T
1.	Cyclohexane	0.0686	31.2
2.	tetrahydrofurane	0.300	37.4
3.	chlorobenzene	0.490	37.5
4.	nitrobenzene	0.880	42.0
5.	acetone	1.220	42.2
6.	tert-butanol	3.240	43.9
7.	acetonitrile	5.440	46.0
8.	DMSO	6.020	45.0
9.	iso-propanol	7.250	48.6
10.	ethanol	16.500	51.9
11.	methanol	47.500	55.5

$$\log k = -8.421 + 0.174 \frac{n^2-1}{n^2+2} + 0.0903 \frac{\varepsilon - 1}{2\varepsilon + 1} + 0.0006\, B + 0.017\, E_T + 0.00263\, \delta^2,\quad N=11,\ R= 0.989,$$

$$s = 0.176,\ r_1= 0.506,\ r_2= 0.769,\ r_3= 0.560,\ r_4= 0.985,\ r_5= 0.930$$

The log k value is practically determined by the factor of electrophilic solvation effect only. Relatively small values of pair correlation coefficients according to other factors do not enable to come to any definite conclusions about their insignificance. If the factors of nonspecific solvation are excluded from calculations, the general correlation coefficient will remain unchanged: $\log k = f(B, E_t, \delta^2)$, R = 0.989; while the exclusion of the electrophilic solvation parameter decreases the multiple correlation coefficient to 0.973. Nucleophilic solvation and the cohesion energy density of the medium correct the log k and E_t dependence very insignificantly. However, there is a relatively firm dependence between the log k and δ^2 and it could be possible to describe the medium effects by means of combination of the δ^2 and B parameters: log k = f(B,δ^2) R = 0.948. Evidently, these pecularities result from a specific solvent selection (preferably the strongly polar ones).

The decisive role of electrophilic solvation, which according to[13] favors the appearance of a positive charge on the sulphur atom, and the absence of the dependence of the process rate on the medium polarity (r=0.769) refer to the essential difference between the decomposition mechanisms in the both cases observed. Their only common feature is the nucleophilic solvation effect promoting the polarization of the O-O bond and the selfassociation effect of the medium. Such a drastic difference of the substrates whose structures are not basically different in their sensitivity to the solvation effects in the thermolysis reaction of perether leads to the conclusion that on one hand, these studies should be extended, and on the other hand they speak about the effective application of the LFER methods for their investigation.

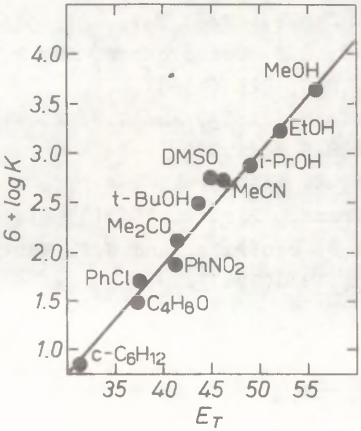


Fig. 4. Dependence of log k on E_T.

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SOLVENT EFFECT ON KINETICS OF HOMOLYTIC REACTIONS

II. SOME DIFFICULTIES IN APPLICATION OF LFER. DEVIATIONS FROM HAMMETT EQUATION.

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Fundamental reasons leading to the complications in the use of LFER in the analysis of medium and substituents' effect on the homolytic reactions rate are discussed.

Hammett-Taft and Koppel-Palm linear free energy relationships (LFER) have been very evidently used for generalization of the influence of substituents or correspondingly of the medium on the rate of heterolytic reactions. However, they are comparatively rarely used in case of the homolytic reactions in consequence of several both experimental and theoretical difficulties. Yet it is necessary to point out that only few examples are known of a successful quantitative description of the experimental data about the solvent effect on the homolytic reactions' data (see part I of this series). Therefore we consider that it will be useful to dwell on some most important causes of the above mentioned difficulties and in the first place on the study of the medium effect.

I. Complexity of the reactions with participation of the radicals which proceed through many steps. Therefore the determined value of the rate constant is a resultant and depends on the ratio of the rates of separate stages. Because of the experimental difficulties, the data permitting a qualitative comparison of solvents or substituents on the rates of separate elementary stadiums of radical reactions are nearly absent. However, in some cases in which the reaction mechanism permits a certain determination of the limiting stage, a numerical approximation of the most probable expression for the rate and the data treatment of the received rate constants which are nearly equal to the values of the limiting stage rate constants is possible, as it has been suggested in the case of the butyric aldehyde oxidation in several solvents[1].

2. For the reactions with the formation of free radicals, two or more parallel ways of conversion are possible. E.g., in the case of the thermolysis of the benzoyl peroxide[2] or organic peracids[3], alongside their pure monomolecular decomposition a parallel process of decomposition induced by the formed radicals which are characterized by quite different kinetic and energetic parameters is realized. The gross rate of decomposition may be described by the following equation:

$$-\frac{[ROOR']}{dt} = k_I[ROOR'] + k_{ind}[ROOR']^{n^2}$$

As the effective rate constant of the process which is determined in the case of the peroxycompounds' decomposition by means of the O-O group content diminishing is a resultant and the effects of solvation or of substituent influence act according to different laws, the treatment of the k effective values by means of the LFER equations is as a rule not successful. However, if one leads the reaction in the presence of inhibitors or in a medium of solvents which can suppress the radical stages, it will be possible to determine the uninitiated process rate constants and also the rate constants of the initiated decomposition by the difference of the summary and inhibited process rates. As we shall show later on, each of these processes can be described by means of the LFER equations. We should point out here that the hydrocarbons used as solvents favor, on the whole, the initiated radical process.

3. The role of the solvent does not lead only to the suppression or development of the radical stages of the process. In many cases the character of the solvent may influence the chemical nature of the process. Such values of the inhibited decomposition of the polymeric peroxyde of azelaic acid in the ethers (Bu_2O, THF, dioxane) do not correlate with the common dependence for the other 15 solvents, which leads to the supposition that they have another transformation mechanism, probably a partial bimolecular interaction of peroxyde with these solvents[4]. And in pyridine the decomposition is of an autocatalytic character. Some deviations from the common regularities of the influence of solvents have been observed also in case of ethers in the reaction of the pyridine catalyzed thermal decomposition of tert-butylperformate[5].

4. The rate constant values of the reactions with the participation of radicals depend on the substrate concentration. In the result of the summation of contributions of the reactions of different order, the observed order differs from order one and may change with the change of the concentration, e.g. in the case of decomposition of peracids[6] or benzoyl peroxide[7,8]. The same phenomenon occurs in the case of ion-radical reactions. This pecularity as well as the super-sensitivity of homolytic reactions even towards the traces of impurities especially of the heavy metal ions of changing valency make us regard the selection and comparison of the data of various authors with maximum care, which in the case of heterolytic reactions in general does not cause any problems.

5. In some homolytic reactions, the diffusion phenomena have also some significance, particularly in the oxidation processes by means of gaseous oxygene. A significant role have the cage effects connected with the ability of the medium to selfassociate around the reacting particles thus leading to the growth of the radicals "activity". This phenomenon is of practical use in the polymer chemistry[9].

As a result it is possible that in the equations which connect the reaction rate with the medium properties, some new terms may appear, e.g. the cohesion energy density $\delta^2 = (\Delta H_{vap} - RT)/V$ which is proportional to the medium's self-association ability and therefore is responsible for the development of the "cage effect". Thus in Ref.[10] the rate of the decomposition of p-nitrophenylazotriphenylmethane in alkanes correlates with their viscosity. In Ref.[11] the presence of a linear correlation between the log k of the dicumylperoxide thermolysis in the alkenes and the viscosity has also been established. However, it is necessary to note that this comparison was realized only in case of the homologous hydrocarbons and the data obtained in other solvents do not agree with the obtained dependence and so the possibility of the influence of any other characteristics which also regularly changes with the change of the molecular weight cannot be excluded. E.g. it is known that for the homologous solvent series the cohesion energy density δ^2 is proportional to their viscous flow activation energy[12].

6. When generalizing the data of the correlation between the σ-constants of substituents and the rate of conversion for homolytic reactions, a number of deviations from the Hammett equation may be found which cannot be explained, thus leading to the supposition that with a sharp change of the electron density on the reaction center caused by the influence of some substituents, especially the NO_2 group, the reaction mechanism most probably changes. The following examples can be adduced. It has been shown in Ref.[13] that the noninduced decomposition of tert-butyl perbenzoates in the diphenyl ether at 120° for the five substituents (OMe, Me, H, Cl, NO_2) may be excellently described by the Hammett equation with the r 0.990-0.996 (at various temperatures). The decomposition rate diminishes with the growth of the attraction of electron to the phenyl cycle in consequence of the decrease of the electron density at the oxygen atom being connected with the carbonyl group and the increase of the O-O bond polarity (ionic character) and correspondingly the increase of their stability. This result was confirmed

in Ref.[20] for the reaction in n-undecane at 110°. However, the thermolysis of peresters in chlorobenzene and toluene obeys the Hammett equation with the exception of the data for the p-NO_2 substituent in chlorobenzene and for those of p-OMe in toluene[14]: Fig. 1.

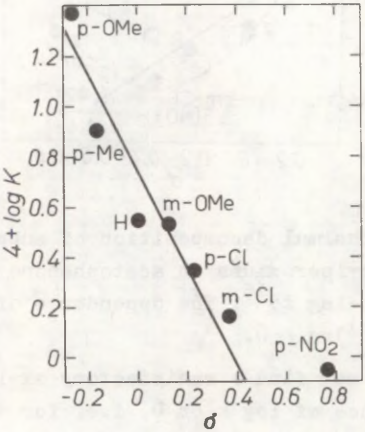

Fig. 1. Thermolysis of tert-butylphenylperacetates in chlorobenzene at 90° according to[14]. The dependence of log k(min^{-1})vs. σ . The data for p-OMe extrapolated.

Still more substantial deviations for the nitrogroups have been observed in the case of noninduced decomposition of substituted benzoylperoxides in acetophenone in Ref.[15]: Fig. 2. The correlation coefficient for all substituents is according to review[16] equal to 0.687 only, or after checking the σ values, it is 0.769. Even after the exclusion from our calculations of the most deviating data for the nitrosubstituted peroxydes (o- and p-nitro, and 3,5-di - nitro) r = 0.835 only. Nevertheless, the isokinetic dependence in this reaction is unexpectedly well realized:

$$\Delta H^{\neq}(26.66 \pm 0.30) + (0.617 \pm 0.064)\Delta S^{\neq}$$

N = II, r = 0.955; s = 0.25

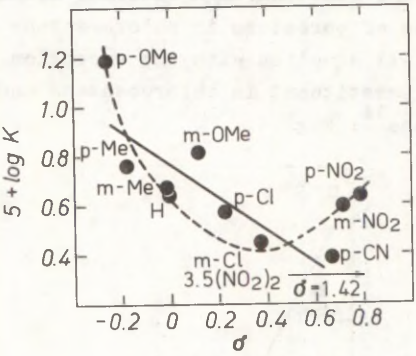

Fig. 2. The thermal decomposition of substituted benzoylperoxides in acetophenone at 80°C according to [15]. The dependence of log k (min^{-1})vs. б.

The authors do not find a satisfactory explanation for the V-like dependence of log k on б, i.e. for the effect of the rate increase of strong electronegative nitrogroups.

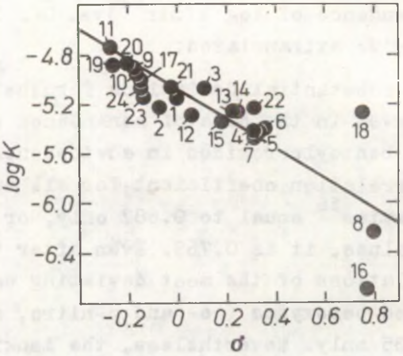

Fig. 3. The thermal decomposition of substituted benzoylperoxides according to [17]. The dependence of log k on б. The N^oN^o of experimental points according to Table 1.

However, the decomposition rates for the same peroxydes determined dilatometrically at 70° in styrene according to its polymerization rate, correlate with the σ values considerably better, though some deviations can also be found[17]. For the 21 points (see Table) r = 0.819 only but when we exclude the data for p-cyanocompound which deviates the most, we receive an equation with an acceptable, though small degree of concordance: $\log k = (-5.098 \pm 0.044) - (1.410 \pm 0.136)\,\sigma$

$$N = 20; \quad R = 0.925; \quad s = 0.179$$

Table

Thermolysis of Substituted Benzoyl Peroxides
In Styrene at 70°C According to Ref.[17]

No	substituent	log k	σ^+	No	substituent	log k	σ^+
1.	H	-5.155	0.000	13.	p-Cl	-5.268	0.227
2.	m-Me	-5.222	-0.069	14.	p-Br	-5.284	0.232
3.	m-OMe	-5.046	0.115	15.	p-I	-5.268	0.180
4.	m-F	-5.444	0.337	16.	$p\text{-}NO_2$	-6.699	0.778
5.	m-Cl	-5.444	0.337	17.	p-Et	-5.004	-0.151
6.	m-Br	-5.420	0.391	18.	p-CN	-5.268	0.660
7.	m-I	-5.444	0.352	19.	p-i-Pr	-4.975	-0.280
8.	$m\text{-}NO_2$	-6.155	0.710	20.	p-t-Bu	-4.896	-0.197
9.	p-Me	-4.963	-0.170	21.	$p\text{-}C_6H_5$	-5.071	-0.010
10.	p-OMe	-4.773	-0.268	22.	$p\text{-}OCOCH_3$	-5.222	0.310
11.	p-OEt	-4.731	-0.240	23.	$3,5\text{-}(CH_3)_2$	-5.114	-0.140
12.	p-F	-5.276	0.062	24.	$3,4\text{-}(OMe)_2$	-5.052	-0.153

For the σ^+ constants of para-substituents the correlation is only slightly worse: for 14 substituents r = 0.816 and after the exclusion from the calculations of the data for the p-CN compound, r = 0.904.

The decomposition rate (and, probably the initiation of styrene polymerization) for the substituted benzoyl peroxydes increases in case of the electron-drawing substituents and decreases in case of electron-attracting ones[18]. I.e., according to Walling's opinion the transition state depends on the electron effects. It is necessary to mention the fact stated by the authors of Ref.[19] that the orto-substituted peroxydes decompose significantly faster especially in the case of substituents of large volume as the result of combination of the steric and polarizability effects. This observation agrees with the same results about the influence of the sterically hindered substituents on the decomposition of tert-butyl esters of the aliphatic peracids[20]. When the authors found for the II unbranched peresters an excellent correlation between the rates of thermolysis at 110° and the Taft's constants ($r = 0.995$, $\rho = 1.237$), the branched peracids as well as those containing the voluminous substituents in the α- or β -positions (Cl, phenyl) deviate from the rectilinear dependence on σ and the rate of their decomposition was found to be on the average for one order higher. The common E_s-scale at steric constants is in this case unapplicable.

The above mentioned examples illustrate the difficulties appearing in the application of the LFER equations even in relatively simple cases of generalization of electron effects. One may anticipate more substantial complications caused by the above considered reasons in case of examination of medium effects. Nevertheless, in a number of cases such a qualitative examination is possible and this permits to foresee the rates of the process in other solvents not investigated yet and to present the mechanism of homolytic rections in a more detailed way.

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COMPARISON OF SOLVATION EFFECTS IN EPOXYDATION AND OXYDATION REACTIONS BY PERACETIC ACID

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The activity of peracetic acid in the reactions both of epoxidation of olefines and oxidation of alkynes, sulfides and nitrosocompounds diminishes with the growth of basicity of solvents. However, an exact proportionality between the rates of these reactions cannot be observed owing to a different sensitivity of these substrates toward the solvation effects. An adequate generalization of the medium properties' influence may be realized only by the Koppel--Palm LFER multiparameter equation.

On the basis of the investigation of medium effects the authors of Ref.[1] expressed an opinion that the mechanisms of both epoxydation and oxydation of sulfides, thio- and nitrosocompounds as well as alkynes by means of peracids are identical. According to Lynch and Pausacker[2], the active form of the peracid is a cyclic one with the intramolecular H-bond which forms in the reaction a chelate complex with the unshared electron pair of the substrate. According to this mechanism the reaction rates slow down in the basic solvents as the result of partial conversion of peracids to the less active form with the intermolecular H-bond.

However, there is no strong proportionality between the rates of the corresponding reactions. The authors of Ref.[1] compared the rates of oxidation of the p-dinitrodibenzyl sulphide with perbenzoic acid and of nitrosobenzene with m-chloroperbenzoic acid and established that the data for the oxidation in benzene and ethanol deflect from a linear interdependency. Some deviations occur when comparing the rates of nitrobenzene oxidation and the epoxidation of cyclohexene in several solvents according to the data of Ref.[3], or when comparing also the epoxidation rates of some substrates by peroxides[4].

Most probably such a behavior can be explained by the different sensitivity of the substrates to the medium solvation effects whose total accounting is possible only by means of the LFER multiparameter equation proposed by I.A. Koppel and V.A. Palm[5]. Though the medium's basicity is the factor which determines the reaction rate of the substrates with peracids, a certain contribution to the same value is made also by other solvation effects.

Thus, we have established[4,6] that in the epoxidation reactions the correlation coefficient between the process rate and the medium's basicity, which decelerates the process, is in limits of 0.85-0.95, but its value is remarkably increasing if we take into account the other solvation effects, in the first place the electrophilic solvation. In the case of the sulfides oxidation, more significant is the account of nonspecific solvation.[7]

Table 1

Constants of Oxidation Rates of Nitrosonobenzene k_1 and 4-Octyne k_2 With M-Chloroperbenzoic Acid in Several Solvents at 25°C According to Ref.[8,9].

No	Solvent	$\log k_1 \cdot 10^4$ exp.	$\log k_1 \cdot 10^4$ calc.	Δ expr.-calc.	$\log k_2 \cdot 10^4$ exp.
1	2	3	4	5	6
1.	$CHCI_3$	2.556	2.425	0.131	1.3263
2.	CCI_4	2.117	2.284	- 0.167	0.7300

Table 1 continued

1	2	3	4	5	6
3.	Benzene	2.299	2.282	0.017	0.8407
4.	Nitrobenzene	2.539	2.550	-0.011	-
5.	Sulfolane	2.0414	2.027	0.015	-
6.	DMFA	1.029	1.207	-0.178	-
7.	Dioxane	1.441	1.356	0.085	-0.4089
8.	Tert-Butanol	1.301	1.233	0.068	-
9.	I-Propanol	1.425	1.372	0.053	-0.4815
10.	Ethanol	1.537	1.485	0.052	-
11.	Methanol	1.660	1.722	-0.062	-0.4089
12.	CH_2CI_2	-			1.0867

With the purpose of establishing the relative significance of separate solvation effects in the interaction of peracids with other substrates we have generalized the data on the oxidation of nitrobenzene[8] and 4-octyne[9] with the m-chloroperbenzoic acid (Table 1) by means of the Koppel-Palm equation which includes also the cohesion energy density term.

For the nitrosobenzene we obtained the following equation:

$$\log k_1 \cdot 10^4 = 0.665 + 9.507\,\frac{n^2-1}{n^2+2} - 0.251\,\frac{\varepsilon - 1}{2\varepsilon + 1} - 0.045\delta^2 -$$

$$- 0.00357 \cdot B + 0.024 \cdot E$$

$m=11$; $R=0.986$; $s=0.123$; $r_1=0.746$; $r_2=0.321$; $r_3=0.262$; $r_4=0.925$; $r_5=0.444$

Thus, the medium's basicity is a determining factor as in the case of peracids interaction with other substrates, but the value of correlation coefficient R between log k and basicity B is relatively small, 0.925 only. If we take into account other solvation factors, it is possible to attain an excellent correlation. The examination of the validity of regression coefficients in case of separate factors shows that the medium's polarity is negligible and the sensitivity of the reaction towards the electrophilicity of the medium is small. A successive exclusion of these parameters reduces the R value to 0.985 and 0.982 correspondingly. At the same time the exclusion from calculations of the polarizability term reduces the R value to 0.955, and the cohesion energy density to 0.965. In this way it is possible to adequately describe the influence of solvents on the oxidation process rate by the following three-parameter equation:

$$\log k_1 \cdot 10^4 = 0.029 + 6.83(n^2-1)(n^2+2) + 0.0051\delta^2 - 0.0388B;$$

$$R = 0.982; \quad s = 0.119$$

$$F_{calc.} = 19.4 > 8.89 = F_{T/0.05;\ 7;\ 3/}$$

Thus, the influence of the medium on the rate of nitrosobenzene oxidation reaction is the same as in case of the sulfide oxidation. For the dinitrodibenzyl sulfide oxidation we have established the following dependence:

$$2 + \log k = -0.164 + 8;\ 580\,\frac{n^2-1}{n^2+2} - 1.496\delta^2 - 0.00426.B\ ;$$

$$m = 12;\ R = 0.984;\ s = 0.132;\ r/OB/ = 0.953$$

Some deviations from the linearity which are marked in[1] between the rates of these processes are caused by a smaller influence of nonspecific solvation on the second reaction. though the role of the polarizability in both cases is identical and opposite to the influence of the basicity. The influence of cohesion energy density, i.e. the energy expense on cavity formation is of smaller significance, especially in the first case.

For the 4-octyne oxidation, calculation by means of the five-parameter equation is of smaller statistical probability in consequence of a small number of studied solvents (only seven). However, approximate calculations show that the δ^2 and E terms are negligible. The studied process may be satisfactorily described by the following equation:

$$\log k_2 \cdot 10^4 = -2.523 + \frac{n^2-1}{n^2+2} + 2.050 \frac{\varepsilon-1}{2\varepsilon+1} - 0.0050\, B;$$

$$m=7;\ R=0.998;\ s=0.172;\ r_1=0.793;\ r_2=0.247; r_3=0.463$$

$$F_{calc.} = 20.8 > 9.28 = F_{T(0.05;3;3)}$$

As in the previous case, the medium's basicity is the rate process determining factor and the solvent ability to the nonspecific solvation favors the proceeding of the process in consequence of an active complex solvation. However, in this case the validity of both terms $f(n^2)$ and $f(\varepsilon)$ is equally significant and the exclusion of any of these two factors diminishes the R value to 0.968. It is interesting to note that the oxidation reactions in contrast to those of epoxidation are practically insensitive to the influence of a possible electrophilic solvation of the reaction complex.

Thus, the adduced analysis vividly supports the opinion that the medium's influence on even similar reactions may appreciably differ in the result of differences in their solvation phenomena. A complete description of this influence may be possible only by means of multiparameter LFER equations if all solvation processes are taken into account.

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SOLUBILITY OF GASES

I. GENERALIZATION OF SOLVENT PROPERTIES' INFLUENCE ON SOLUBILITY OF GASES BY MEANS OF MULTIPARAMETER LINEAR FREE ENERGY RELATIONSHIPS

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At present theoretical calculations do not permit to exactly determine solubility of gases in diverse solvents.A satisfactory connection between any medium property and the solubility of gases may be obtained only for a number of solvents with similar structures and for gases which are not capable of specific interaction. According to Pierotti's theory a process of gas solubility in liquids is determined by the expanding of energy on the formation of a cavity in the liquid medium and by the energetic effect of interaction between a gas and a solvent. At present theoretical calculation of these terms does not give a satisfactory result; however, it is possible to do an adequate generalization of the available experimental data of gas solubilities in diverse solvents by means of the multiparameter linear free energy relationships (LFER) which take into account the

cohesion energy density of a liquid and its solvation effects according to Koppel and Palm.

The submission of real gases to the ideal gas laws is rather an exclusion than a rule and any satisfactory connection of both the experimental and the calculated data may be observed only for the noninteractioning matters and in extremely low concentration limits. An especially complicated influence on the gas solubility is caused by the solvent's nature. A.I. Brodskij wrote in 1947: "Solubility of gases depends in most cases extremely strongly on the solvent's nature ... The problem of the influence of solvent's nature on the solubility is complex and has still not been quantitatively solved... This is connected with the absence of the sufficiently distinct and general ideas about the intermolecular forces which operate in the solvents and define the solubility and with the absence of a general theory of liquids."[1].

At present the most widely developed are both Hildebrand's regular solutions theory[2] and Pierotti's theory of cavity formation[3]. According to the former, the process of solution of gases should be formally considered as consisting of the following three stages: 1) isothermal compression of the considered gas to a hypothetical liquid state, 2) dissolution of this hypothetical pseudoliquid in the solvent, and 3) isothermal expansion of the solution[2]. For the calculation of the gas solubility the following expression is suggested:

$$-\log X_2 = -\log X_2^T + \frac{0.4343 \cdot V_2}{RT} (\delta_1 - \delta_2)^2$$

in which X_2 is the solubility of a gas in the mole parts, X_2^T - the theoretical solubility according to Raoult's rule, V_2 is the partial molar volume of the gas in the liquid and the δ -terms are correspondingly the solubility parameters of the solvent and the gas. For the solutions in which the molar volumes of the components differ significantly, it is necessary to take into account in accordance with the Flory-Huggins model a correction on the medium volume V_I:

$$-\log X_2 = -\log X_2^T + \log \frac{V_2}{V_I} + 0.4343\left(I - \frac{V_2}{V_I}\right) + \frac{0.4343\, V_2}{RT}(\delta_1 - \delta_2)^2$$

According to the cavity formation theory, the gas solubility is determined by the sum of both the energy expense on the formation of a cavity for placing gas molecule and the energetic effect of interaction of the gas with the solvent. This point of view has received the most complete development in Pierotti's work[3]. The author proceeds from the model of a hard sphere introduction in a liquid medium; the proposed equations for the calculation of Henry's constants and the enthalpies of the solution, which present the subsequent development of the Rice theory, summarize a two-step process, which includes a formation of a cavity of fitting dimensions in the medium and the subsequent introduction of the gas molecule in the formed cavity which interacts with the medium.

However, at present all these equations give satisfactory results only in case of the systems with low polarity and incapable of interacting chemically; the numerical divergencies between the values received on the basis of the existing theories of solutions and the experimental values may reach considerable magnitudes. Besides, in these calculations it is necessary to introduce, as a rule, various corrective empirical parameters[4] the more the components interact and the more the behavior of the system deflects from the model of a simple physical interaction.

Obviously, numerous divergencies of calculated and experimentally obtained values are caused by the effects of solvation and association; such an explanation for the deviations of binary liquid system properties from the ideal state was given as far back as at the beginning of the 20th century in the letters of von Zawidsky[5], Dolezalek[6] and others. The same cause of the discrepancies in calculation of gas solubilities was adduced by de Ligny[7,8] in his paper devoted to the verification of Pierotti's equation.

Chemical interaction causes an enormally high solubility of some gases in the chemically active solvents. Marvel and coworkers [9,10] established that the C-H group of halogenohydrocarbons forms a H-bond with the O,N, or S-containing organic donors (ethers, ketones, trialkylamines a.o.) and that the solubility of haloforms vastly diminishes in alcohols and also in other associated solvents. It is clear that when dealing with the non-aqueous solutions it is necessary to take into account both the physical and chemical (donor-acceptor) interactions.

Recently, Abraham has verified in a series of papers[11,12] the applicability of Pierotti's theory particularly in case of great spheric nonpolar molecules such as $Sn(CH_3)_4C(Ph)_4$ a.o. The authors compared the thermodynamic characteristics of dissolution calculated both by the scale particles theory SPT of Pierotti[13] and the Sinanoglu-Reisse-Mouras-Ramos theory SRMR[14] with the corresponding values determined calorimetrically or chromatographically. In general the thermodynamic parameters of dissolution present a sum of energetic effects of cavity formation therm, the interaction therm and a compensation term which takes into account the difference in the standard states of the gas phase and the solution:

$$\Delta G^o_{sol} = G_{cav} + G_{int} + RT \ln - \frac{V_{gas}}{V_{sol}}$$

However, neither of the calculation variants gives satisfactory results in all cases. We should like to add that the cited calculations are not applicable in all systems with a specific interaction between the gas and the medium. Therefore for the technically important gases the empirical formulas for the generalization of experimental data of gas solubilities in diverse solvents are proposed. However, all of them are completely empirical, their predictability is rather insignificant and there are many exclusions and deviations.

We proceeded from the assumption that any physico-chemical process should be accompanied by a corresponding change of isobaric thermodynamic potential (Gibb's free energy) and that this change may be characterized in accordance with the LFER-principle as the sum of contributions of separate changes of ΔG which correspond to different kinds of interaction between the dissolved particle and medium:

$$\Delta G_{sol} = \sum \Delta G_i$$

According to academician Ya. I. Frenkel's theory of the hole structure of liquids, any liquid represents a more or less structured medium into which an outside molecule can be introduced after spending additional energy for the formation of a cavity with the corresponding dimensions. Such an opinion is given by Pierotti too - according to the scaled particles theory one of the terms, which determines the ΔG_{sol} value is the energy consumption for the formation of a cavity ΔG_{cav}. The value of this term will be determined both by the dimensions of the introduced molecule and by the properties of the same liquid. The more complicated is its structure,the higher is the level of self-association, the greater will be the energy consumption in case of the cavity formation.

However, it is obvious that if the process of introduction of a gas molecule demands spending of energy on the cavity formation, the interaction of the very molecule with the medium will be accompanied by the release of the energy which will be the more noticeable the stronger this interaction is. It is clear that side by side with a relatively weak universal (physical, nonspecific) interaction a much stronger acid-base (specific, chemical) interaction is possible. The presence of these two types of interaction for both gas and liquid solutions has been taken into account in the letters of Prausnitz[15-18] and this presents the advantage of the NRTL theory in comparison with that of Pierotti. Thus, the change of the thermodynamic potential of the system,when a gas is dissolving,is equal to the summary energetic effect of the cavity formation of the specific interaction and also of the change of the aggregative state of the gas. As the problem refers to the energy of the cavity formation, it is very probable that this will be proportional to the cohesion energy density of the solvent according to Hildebrand: $\delta^2 = (\Delta H_{vap}-RT)/ V_{mol}^{-I} = (\Delta H_{vap}-RT).\ d/M$, or in the first approximation to its enthalpy of vaporization. Besides the general theoretical reasons, including those taken for the basis of the NRTL theory, a number of experimental observations speak in favor of such an assumption. It is stated e.g. in Hildebrand's work that the log of solubility of simple gases which was expressed in mole fractions diminishes ca. proportinally to the growth of the solubility parameter δ of solvents^4.(p. 409).

The problem concerning the choice of solvent characteristics which define their ability to the specific and non-specific interaction is still more complicated. In a common case one cannot neglect a single aspect of reagent-medium interaction. This has led to the development of a multiparameter equation conception (Koppel-Palm, Meyer, Krygowski-Fawcett, Kamlet-Taft). We used the Koppel-Palm model - the four-parameter equation which takes into account separately: the non-specific solvation by means of the introduction of two terms which characterize the polarity and polarizability of a solvent, and the ability to the acid-base interaction by means of its basicity and electrophilicity. The positive side of such a model is the separate consideration of all the solvation factors known by now and the possibility to determine the significance of each of them. The increase of the number of parameters leads to the increase of the volume of calculations and complicates the interpretation of the character of the occurring process on the initial stage. However, the successive exclusion of separate terms followed always either by the determination of the multiple correlation coefficient or of the significance of separate regression terms by means of Student's criterion (t-analysis) permits to exclude the terms with a negligible or only small significance and thus to diminish the number of the factors, considered in the process.

Thus, we propose for studying the connections between the gas solubility and the solvent properties the following equation:

$$G = a_o + a_I \frac{n^2-I}{n^2+2} + a_2 \frac{\varepsilon -I}{2\varepsilon +I} + a_3 B + a_4 \cdot E + a_5 \delta^2$$

the applicability of which will be illustrated with several examples. It is necessary to mark that as the presented model is based on the principle of free energy linearity either the ΔG or log γ of dissolved gas, or its Henry constants or solubility values given in molar fractions, can be equally used as the correlated parameters, since:

$$\Delta G_i = -RT \ln K_{Hi} \equiv -RT \ln \frac{N_i}{p} \equiv -RT \ln \gamma_i$$

It is also interesting to indicate that the free term a_o in the equations is not only a formal mathematical symbol but should even correspond to the gas solubility in an ideal solvent which is not able either to self-association (i.e. $\delta=0$) or to the interaction with a soluted (i.e. n, ε = I; B,E =0). Indeed, as we shall further show, in very many cases this term is close to the gas solubility value calculated by the laws of ideal gas although an excellent coincidence cannot be expected here as in this term all the systematic errors of experiments are summarized too. Such a calculation which at first was proposed purely empirically only, permits to establish an adequate connection between the solvent properties and the solubility of freones[19], acetylene[20], propylene[21], C_2H_5F[22], H_2S[23], and some simple gases[24] in these solvents - as well as to explain the solvation phenomena realized in case of gas dissolvation, e.g. to confirm the presence of acid-base interaction of $CHClF_2$ with the basic solvents[25]. Therefore we think it important to verify the applicability of the cited equation for the generalization of the solubility data for some other gases.

It should be mentioned that in their method of description of solvent effect on the physico-chemical processes by means of the multiparameter LFER equations, Kamlet and Taft[26] have proposed to describe the ΔG_{sol} changes as the sum of the solubility parameter effect according to Hildebrand δ_H=

$:\sqrt{\delta^2}$ and the effect of non-specific solvation of a gas, determined by the bipolarity parameter π^*

$$\Delta G = g + h\,\delta_H + s\pi^*$$

The corresponding calculations were realized for 40 substances in 5-12 (in some cases more) solvents and in a number of cases, e.g. alkanes, simple gases the equations with a high degree of reliability $r=0.98-0.99$ were obtained. However, in many cases the correlation is unsatisfactory, especially for substances capable of the H-bond formation, e.g. C_2H_4 $m=6$, $r=0.256$; benzene $m=II$, $r=0.785$; C_2H_5I $m=12$, $r=0.729$; C_2H_5OH $m=17$, $r=0.877$. Most probably it is mainly caused by the fact that the specific (donor-acceptor) interaction was not taken into account. The authors also admit that e.g. in the case of ethanol the accounting of the third solvatochromic basicity parameter permits to raise the value of the multiple correlation coefficient from 0.877 to 0.972.

An additional source of inaccuracies may be the fact that in their formula the authors of Ref.[26] do not use the same cohesion energy δ^2 in order to characterize the expense of energy in the cavity formation but apply the solubility parameters, i.e. the square root of the energy. It should be pointed out that the formal dimensions of the δ_H parameter $ccal/l.mole^{1/2}$ do not permit to use it immediately in the LFER. For example, we may point out that in the papers by Hildebrand and Prausnitz we came across the following expression $(\delta_I - \delta_2)^2$ only. However, this discrepancy was eliminated by these authors in one of their recent papers[27]. The comparison of the results obtained on several examples by the two-parameter Kamlet-Taft-Abraham equation and by the five-parameter LFER evidences in favor of the latter version.[28]

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INFLUENCE OF MEDIUM EFFECT ON DECOMPOSITION RATE OF 6,8-DINITRO-1,4-DIOXASPIRO[4,5]DECA-6,9-DIENATE SODIUM

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Decomposition kinetics of 6,8-dinitro-1,4-dioxaspiro[4,5]deca-6,9-dienate sodium has been studied in binary mixtures of dimethylsulfoxide-protic components in the form of aliphatic alcohols with various structures and water in temperature range 25-45°C. Activation parameters of the reaction have been determined. It has been established that the decomposition reaction of spirocyclic complex proceeds according to bimolecular mechanism, and remarkably depends on acidity and structure of profic component. This has been confirmed by correlations established on one hand, between log k of decomposition rate and on the other hand, between σ^* values, pK of alcohol and E_s^c of its radicals.

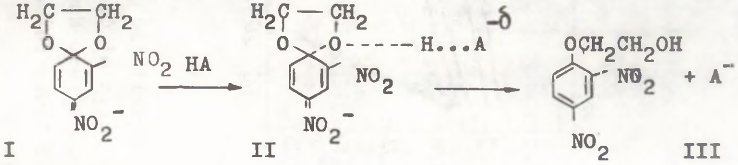
Such problems as establishing interdependence between the reactivity structure of the Jackson-Meisenheimer anionic σ-complexes, as well as detecting the effects of different medium factors on their stability have been discussed thoroughly enough in literature[1,2]. However, these studies have not dealt so much with the anionic spirocyclically structured σ-complexes.

Therefore the aim of the present research was to study the effects of acidity, medium structure and temperature on the stability of spirocomplexes on the example of 6,8-dinitro-1,4-dioxaspiro[4,5]deca-6,9-dienate sodium. The dissociation reaction started in binary mixtures, consisting of the aprotic polar solvent dimethylsulfoxide (DMSO) and protic components (water and aliphatic alcohols with various structures).

The studied anion spirocyclic complex having the structure of the quinolonitro acid salt is completely dissociated in the dimethylsulfoxide medium, since the solvents with a high dielectric constant tend to favor the formation of free ions rather than that of solvationally separated ion pairs[3].

The reaction rate was measured spectrophotometrically according to the variation of the optic density at the absorption peak (λ = 502 nm), which is characteristic to the spirocyclic complex. The linear nature of the corresponding kinetic dependences (Figs 1,2) indicate that in case of small concentrations in the alcohol-water mixture the reaction has the first order, concerning these components as well as the decomposed complex.

Thus, the decomposition reaction of the 2,4-dinitrospiro complex, accompanied by the opening of the cycle and the 1-(ß-oxyethony)-2,4-dinitrobenzene formation is a protolytic reaction, proceeding according to the bimolecular mechanism, which includes the coordinated protonation of the spirocycle oxygen atom and the C-O bond decompostion[4]:



The results of kinetic measurements given in Table 1 evidence that the decomposition rate of the C-O bond of spirocycle depends linearly on the acidity of the proton com-

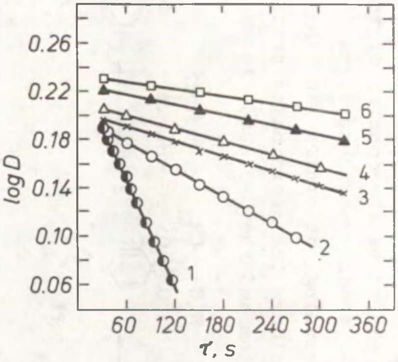


Fig. 1. Semilogarithmic anamorphosis of kinetic curve of decomposition reaction of spirocomplex. Numeration of kinetic straight lines corresponds to that of Table 1.

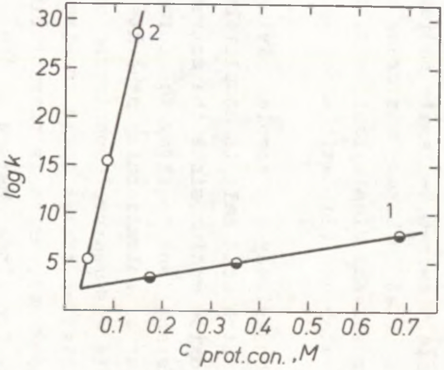


Fig. 2. Dependence of log k on proton concentration. 1-H_2O; 2-CH_3OH.

Table 1

Kinetic and Thermodynamic Parameters of Decomposition Reaction of 6,8-Dinitro-1,4-Dioxaspiro[4,5]Deca-6,9 -Dienate Sodium

No	Proton component*	$k \cdot 10^4$, s^{-1}			pK	σ^*	E_s^c	E, kJ/mol	$\Delta S^{\neq}$ J/mol.
		298°	308°	318°					
1	CH_3OH	28.85±0.11	39.72±0.79	57.77±3.96	15.09	0.000	0.000	28.83	-196.68
2	C_2H_5OH	7.84±0.43	12.56±0.72	19.26±0.66	15.93	-0.100	- 0.38	35.44	-185.33
3	C_3H_7OH	5.37±0.53	7.89±0.43	14.63±0.34	16.10	-0.115	-0.67	39.67	-174.28
4	C_4H_9OH	4.23±0.11	6.91±0.12	10.24±0.63	16.10	-0.130	-0.70	45.33	-157.28
5	i-C_3H_7OH	2.93±0.11	5.21±0.21	9.32±0.15	17.10	-0.190	-1.08	45.65	-159.25
6	t-C_4H_9OH	0.49±0.01	0.92±0.01	1.89±0.06	19.00	-0.300	-2.46	53.05	-149.14
7	H_2O	3.50±0.13	-	-	15.74	-0.490	0.32	-	-

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[*] Molar concentration of proton complex equals 0.17 M,

ponent and undergoes the following transformation: $CH_3OH >$ $> C_2H_5OH > C_3H_7OH > C_4H_9OH > H_2O > i - C_3H_7OH >$ tert. - - C_4H_9OH.

The least squares calculations have shown that there is a satisfactory correlation dependence between the log k and pK of alcohols ($r = 0.969$; $s = 0.161$). The acidity of aliphatic alcohols remarkably depends on the electron-donor properties of alkylic groups, which evidently affects the decomposition rate of the spiro-complex. It must be admitted that an excellent correlation ($r = 0.996$; $s = 0.061$) between the logarithms of decomposition rate constants and the σ-constant values of alcohol radicals (σ^*) can really be observed.

The reaction constant ρ calculated for the given isokinetic series by equation $\log k = -3.76 + 5.74\,\sigma^*$ has a positive value thus evidencing about a remarkable polarity of the transition state[6].

Investigation into the 2,4-dinitrospirocomplex proved that the reaction rate does not only depend on the medium's acidity but also on the proton component structure. The data treatment (Table 1) refers to the existence of the interdependence between log k of opening of the spiro cycle and E_S^c of alkyl radical of alcohols, confirmed by the correlation dependence between these two parameters ($r = 0.975$; $s = 0.151$). Branching of the alkyl radical of alcohol seems to cause the diminishing of the role of specific solvation of oxygen atoms of spirocycle. As a result the decomposition process is slowing down.

The anomalous behavior of water in whose participation the rate of the C-O bond breaking of spiro cycle is smaller than in case of alcohols having smaller acidity and polarity values can be explained by the formation of the $DMSO \cdot 2H_2O$[7]-type structures, interacting with the complex slower than water.

Slowing down of the reaction rate can probably also be conditioned by the product stabilization owing to the formation of hydrates in nitro groups. It has been shown when studying the classical Jackson-Meisenheimer[8] σ-complexes.

In order to determine the effect of variation of composition of binary mixtures on the energetic parameters of the studied decomposition reaction, the temperature dependence on the rate of the spirocycle opening in the presence of any alcohol was studied. Fig. 3 shows that the experimental points are quite well located on the straight within the log k-1/T coordinates.Consequently,the Arrhenius equation can be applied in case of these systems and it is also possible to figure the energetic parameters of the decomposition reaction.

It can be said on the basis of the obtained data (Table 1) that the activation energy is increasing during the transition from methanol to tert.-butanol. Besides that, a certain influence of the entropy factor on the reaction rate can be observed. It is probably connected with solvation of the complex by the binary mixture components.Negative values established for the activation entropy correspond to the earlier suggested[9] bimolecular scheme of decomposition of the anionic σ-complexes. Our data prove that the limiting stage of the reaction is the period of interaction of the complex with the proton component resulting in the formation of the medium product of type II which is connected with a greater regulation of the whole system,and thus, the entropy is decreasing.

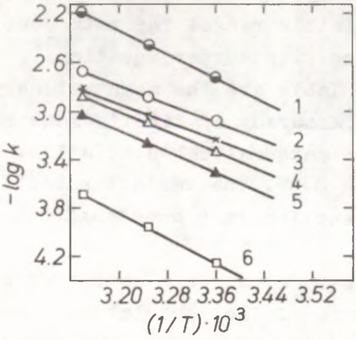

Fig. 3. log k - 1/T dependence in case of decomposition reaction of spirocomplex under the action of proton components. Numeration of straights corresponds to that of Table 1.

The results of the present investigation show that the decomposition reaction of 6,8-dinitro-1,4-dioxaspiro-[4,5]-deca-6,9-dienate sodium proceeds by the bimolecular mechanism and it remarkably depends on the acidity and structure of the proton component. Besides, the rate of decomposition of spirocycle is controlled by the entropy factor.

Experimental

6,8-Dinitro-1,4-dioxaspiro[4,5]deca-6,9-dienate sodium was obtained in the inner molecular cyclization reaction under the effect of tret.-butylate on the 1-(ß-oxyethoxy)-2,4-dinitrobenzene dioxane solution. The yield of the product was 95%. The established % of metal: Na 9.16; the calculated % : Na 9.20. 1-(ß-oxyethoxy)-2,4-dinitrobenzene was obtained according to the known methods[10].

The solvents used were purified as described in[11].

Kinetic measurements were conducted under the pseudomonomolecular conditions at a substantial excess of the proton component. The studied complex was added to the thermostatically treated reaction solution. The moment of introduction of the complex was considered the beginning of the processes. Then the studied solution was placed into the cell of SF-14 spectrometer, thermostated at the same temperature. After certain time intervals the absorption spectra were taken in the visible range. The rate constants were determined applying the first-order equation[12]. The rate constants given in the Table are the mean values of six parallel measurings. The accuracy of kinetic measurings was checked by the methods of mathematical statistics. The probability coefficient being 0.95. The variation coefficient in case of calculation of reaction rate constants did not exceed 5 - 7%.

The activation parameters were estimated according to the equations given in[13]. The correlation parameters were calculated applying the methods of mathematical statistics.

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SOME SPECIFIC FEATURES OF APPLICATION OF LFER AND PPL TO KINETICS OF COMPETITIVE REACTIONS

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The initiative modelling method has enabled us to analyze situations when the overall rate constants of competitive reactions which depend on variable parameters are described. The results of this modelling have been compared to the experimental dependences observed in case of reactions of alkaline hydrolysis of different esters in ethanol-water mixtures; the competitive processes in this case are (i) the reaction with HO^- and (ii) the reaction with EtO^-.

In classical correlation analysis* has always existed a question of proper application of LFER for rate constants of competitive reactions. Actually the answer is clear: LFER may be correctly applied only in case of kinetic characteristics of one-step reactions, or if the complex constants (k_{obs}) are obtained via multiplication or devision of these values. In practice however, usually a more common rule is used (see[2-5]): the observance of LFER for any reaction series in the whole range of a variable parameter is treated as the constancy of reaction mechanism; on the contrary, the

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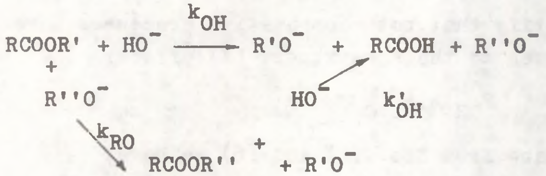
* Exner[1] uses the term "classical correlation analysis", unlike the term "chemometric" for LFER with parameters which are characteristics of the defined type of intra- or intermolecular interactions.

non-linear nature of correlations, breakdown of correlation and considerable deviations of individual points show the change of reaction mechanism. Thus, the fact of observance of LFER is considered as the criterion of the reaction mechanism's constancy.But Istomin[6] managed to show that this was largerly oversimplified. With the help of the imitative modelling method he found out that under certain conditions good correlations may be observed also in case of composite rate constants of competitive processes. As the results of Istomin's work are based on the simple correlation analysis, it is interesting to continue with the idea and to study multiple parameter correlations.

The results of imitative modelling are of interest if they enable us to explain some experimental material. Our analysis will be restricted to competitive reactions only. As an example the alkaline hydrolysis of esters in water-alcohol mixtures may be taken because in this case the hydrolysis competes with re-esterification[7,8] (see Scheme 1).



(1)

If the reaction kinetics is followed by the decreasing concentration of RCOOR', or by the increasing concentration of RO^-, the observed rate constant is the compositive quantity:

$$k_{obs} = (1 - \alpha)k_{OH} + \alpha k_{RO} \qquad (2)$$

Here, α is the degree of conversion of HO^- into anion $R''O^-$.

$$\alpha = [R''O^-]/[HO^-]_0 = 1/(1 + 1/K(N_{H_2O}/N_{R''O})) \qquad (3)$$

α depends both on the ethanol content in the mixture solvent and on the quantity of equilibrium constant (K):

$$R''OH + HO^- \overset{K}{\rightleftharpoons} R''O^- + H_2O \qquad (4)$$

This constant depends also on the composition[9] of the mixture , so the ratio k_{OH} and k_{RO} will be changed with alteration composition of the mixture from $k_{obs} = k_{OH}$ in water, to $k_{obs} = k_{RO}$ in absolute ethanol.

Simple Correlations

If LFER is applied to describe a medium effect, the following equation will be observed:

$$\log k_{obs}(X_1)_i = a_0 + a_1 \log k_{obs}(X_2)_i \qquad (5)$$

Where, $k_{obs}(X_1)_i$ and $k_{obs}(X_2)_i$ are rate constants for two esters with substituents X_1 and X_2 respectively in the i-th solvent. Let us assume that linear dependences are obeyed in case of each of competitive reactions and for each reaction the Hammett-Taft equation is strictly observed. It is possible if in case of all esters in the same solvent mixture the rate constants k_{OH} and k_{EtO} obey the following relationship:

$$k_{OH} = \beta k_{EtO} \qquad (6)$$

which testify that both competitive processes have similar sensitivites to the substituent (X) effect:

$$\rho_{OH} = \rho_{EtO} \qquad (7)$$

In this case from Eqs. (2) and (6) we have:

$$k_{obs} = (1 - \alpha + \alpha\beta)k_{OH} = \gamma k_{OH} \qquad (8)$$

and $$\log k_{obs} = \log k_{OH} + \log\gamma \qquad (8')$$

Calculated values for selected values α and β are in Table 1.

Table 1.

% EtOH	α	$\beta = 50$		$\beta = 25$		$\beta = 10$		$\beta = 5$	
		γ	$\log\gamma$	γ	$\log\gamma$	γ	$\log\gamma$	γ	$\log\gamma$
0	0	1	0	1	0	1	0	1	0
50	0.09	5.41	0.733	3.16	0.50	1.81	0.26	1.36	0.13
90	0.74	37.3	1.57	18.8	1.27	7.66	0.88	3.96	0.60

Values α have been calculated by Eq. (3) and correspond to 0, 50, 90% ethanol content in water-ethanol mixtures. Values β have been chosen at random with the aim to achieve a wide range of these values.

To reduce the analysis, let us rewrite Eq. (5) so that it would go through zero:

$$\log k_{obs}(X_1)_i - \log k_{obs}(X_1)_0 = A(\log k_{obs}(X_2)_i - \\ - \log k_{obs}(X_2)_0 \qquad (10)$$

or

$$\Delta \log k_{obs}(X_1) = A \Delta \log k_{obs}(X_2) \qquad (10)$$

Proceeding from the initial conditions and Eq. (10), the next equation is to be applied using the data of alkaline hydrolysis:

$$\Delta \log k_{OH}(X_1) = B \Delta \log k_{OH}(X_2) \qquad (11)$$

Now we can examine the application of LFER for values k_{obs} if we substitute Eq. (8') for Eq. (10):

$$\Delta \log k_{OH}(X_1) + \log \gamma = A'(\Delta \log k_{OH}(X_2) + \log \gamma) \qquad (12)$$

The initial data are given in Table 2, the results are illustrated in Fig. 1 and in Table 3.

The form of Eq. (12) proposes that maximum deviations of data points in the analyzed correlations will be observed when the slope of the straight line is near -1. This is evident because the transition from the straight line (from Eq. (11)) to correlations which describe the values k_{obs}, results from the shift of the values of the abstsissae and the intercept by the log γ value. In Fig. 1 it is given as the shift of the initial points along the slope line equal to a unit. So the maximum deviations of points are observed for correlations which have slope close to -1. In cases examined in Fig. 1 the deviations reach their maximum when the slopes of the initial line are -1 and -2. When the initial line slopes are not far from 1, e.g. 1/3 and 2, the observed correlations are well approximated with straight lines (see Fig. 1 and Table 3). We must note that in every set of correlations, in every "bunch" of lines, the best straight lines are observed when β has the highest value (in our case when $\beta = 50$[*].

Table 2.

B	x^a	y^a	$\beta = 50$		$\beta = 25$		$\beta = 10$		$\beta = 5$	
			X^b	Y^b	X^b	Y^b	X^b	Y^b	X^b	Y^b
2	0.5	1	1.23	1.73	1	1.5	0.76	1.26	0.63	1.13
	1	2	2.57	3.57	2.27	3.27	1.88	2.88	1.6	2.6
-1	-1	1	-0.27	1.73	-0.5	1.5	-0.74	1.26	-0.87	1.13
	-2	2	-0.43	3.57	-0.73	3.27	-1.12	2.88	-1.4	2.6
1/3	-3	-1	-2.27	-0.27	-2.5	-0.5	-2.74	-0.74	-2.87	-0.87
	-6	-2	-4.43	-0.43	-4.73	-0.73	-5.12	-1.12	-5.4	-1.4
-2	0.5	-1	1.23	-0.27	1	-0.5	0.76	-0.74	0.63	-0.87
	1	-2	2.57	-0.43	2.27	-0.73	1.88	-1.12	1.6	-1.4

[a] $x = \Delta \log k_{OH}(X_2)$; $y = \Delta \log k_{OH}(X_1)$ in Eq. (11).

[b] $X = \Delta \log k_{OH}(X_2) + \log \gamma$; $Y = \Delta \log k_{OH}(X_1) + \log \gamma$ in Eq. (12).

In reality, B in Eq. (11) has a negative sign if the reaction rates of compounds with substituents X_1 and X_2 turn directly opposite when the variable parameter (in our case it is the water-ethanol mixture composition) changes. It may be in case the given compounds are on different sides of the isoparametric point (for the isoparametricity phenomenon see[10]).

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[*] It is necessary to note that in all cases we have supposed that the β is the constant, while the contents of the mixture change. On one hand, this is not right, e.g. in hydrolysis and re-esterification of arylacetates β decreases (35, 9, 3) when the ethanol content increases (0, 50, 90% respectively)[8]. But on the other hand, the latter results are not quite correct, because there have been some assumptions when k_{obs} has been separated into k_{OH} and k_{EtO}, for example, it has been supposed that LFER had to be applied to k_{obs} strictly.

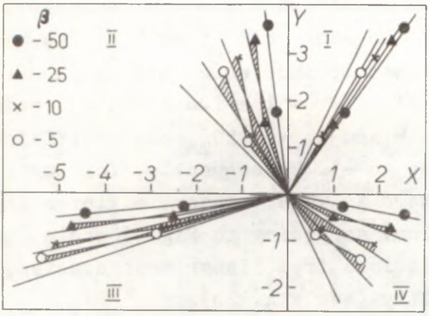

Fig. 1.
The graphical illustration of Eq.(12) in case of varied initial data

All the previous reasons can be illustrated by the alkaline hydrolysis of $MeC(O)SC_6H_4X$ (I) and $MeC(O)OC_6H_4X$ (II) in water-ethanol mixtures. In case of hydrolysis of the esters (I) in water-dioxan mixtures ("pure" hydrolysis, with-

Table 3

B	a)	β = 50	β = 25	β = 10	β = 5
2	A'	1.392±0.005	1.450±0.016	1.550±0.031	1.648±0.041
	r	1.000	0.9999	0.9996	0.9994
	s_o	0.0136	0.0385	0.0628	0.0699
1/3	A'	0.102±0.006	0.164±0.013	0.230±0.015	0.269±0.013
	r	0.9962	0.9936	0.9957	0.9977
	s_o	0.0313	0.0714	0.0877	0.0786
-2	A'	-0.177±0.014	-0.351±0.047	-0.649±0.093	-0.943±0.112
	r	0.9935	0.9828	0.9801	0.9837
	s_o	0.0409	0.1155	0.1883	0.2007
-1	A'	-7.767±0.603	-4.007±0.488	-2.307±0.283	-1.702±0.177
	r	0.9940	0.9855	0.9853	0.9894
	s_o	0.3064	0.4315	0.3793	0.2917

a) Coefficients and statistics of the regressions corresponding to Eq. (12).

out re-esterification) the Hammett equations are well applied in case of every data set in each mixture, moreover, all correlations intersect the same point (see Fig. 2a), as PPL demanded. If we take the compounds which are at the same distance of the both sides from the isoparametric point, i.e. the esters where $X_1 = H$ and $X_2 = p\text{-}NO_2$, the coefficient B in Eq. (11) will be close to -1. Consequently, for log k' of hydrolysis of these esters in water-ethanol mixtures (hydrolysis + re-esterification) according to Fig. 1 would be expected considerable deviations from linear dependencies, which was observed in reality (see Fig. 2b).

In case of the hydrolysis of esters (II) in water-dioxan mixtures[13] the situation is similar to that shown in Fig. 2a for esters (I), so in case of phenyl acetates with X_1=H and H_2= p-NO_2 the slope of Eq. (11) will be near -1. However, as it was pointed out in Ref. [14], LFER holds in case of the medium effect in hydrolysis of esters (II), i.e. the deviation of points from straight lines has not been observed. If the previous analysis is correct, this situation may be explained by two reasons:

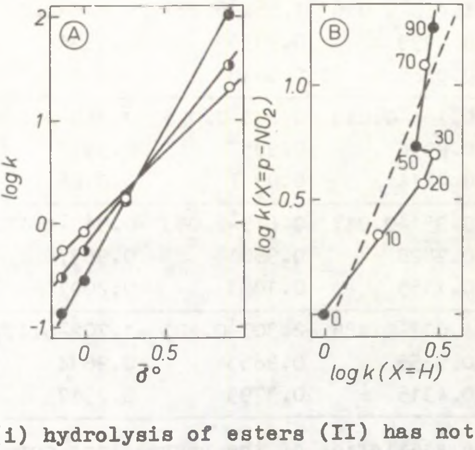

Fig. 2. Plots of log k_{exp} vs σ^{o} for alkaline hydrolysis of esters (1) in water-ethanol mixtures (a). Examination of the LFER applicability in case of the medium effect in this reaction (b) (the ethanol content is given in volume %).

(i) hydrolysis of esters (II) has not been studied thoroughly enough, rate constants have been studied in 0, 50, 90% ethanol content mixtures only. Using these points, it is possible to make up a straight line for esters (I), too (see dotted line in Fig. 2b); (ii) β is 8.2 for esters (I) and 17.1 for esters (II), but as we could see earlier when β increases - the application of Eq. (12) is better.

Double Parameter Correlations

If LFER is applied to each of the competitive processes and also to each of the variable parameters, the PPL must be obeyed in case of any complex reaction according to the results of Ref.[10]. We decided to examine if PPL is really observed in case of k_{obs} which were calculated by Eq. (2). We chose at random a couple of equations, calculated the hypothetic rate constants by these equations, then summed up the constants by Eq. (2), approximated them to two significant figures. The results of PPL application to the constants calculated in this way are given in Table 4.

1. Initial processes are Reg. 1 and 2 in Table 4. (Equations describing k_{OH} and k_{EtO} respectively are taken from Ref.[8]. The summary constants k_{obs} are described very well within the framework of the polylinear equation (see Reg.5). The latter regression has better statistics than the regres-

Table 4

Coefficients and Statistics of the Initial and Resulting Regressions[a]. The Form of Equations is: $\log k = a_0 + a_1 \bar{\sigma}^0 + a_2 S + a_3 \bar{\sigma}^0 S$

	Reg.1	Reg.2	Reg.3	Reg.4	Reg.5	Reg.6
a_0	0.15	1.66	1.0	1.66	0.142-0.008	0.120-0.032
a_1	0.95	0.95	1.0	-0.5	0.959-0.017	1.062-0.075
a_2	0.92	1.0	1.0	0.5	-0.001-0.023	0.069-0.067
a_3	-1.6	-0.4	-0.6	-0.2	1.118-0.050	1.105-0.155
R					0.9997	0.996
S_0					0.015	0.059

[a] As the measures of structural effect $\bar{\sigma}^0$ values for substituents p-Me, H, p-Br and p-NO_2 are taken. The measures of the medium effect are: 0, -0.25, -0.37 for Reg. 1; 0, -0.86, -1.43 for Reg. 2 and 4; 0, -0.8, -1.0 for Reg. 3.

sion for experimental data which have been taken from[4] (see Reg. 6).

2. Initial processes are Reg. 1. and 3. If to compare these regressions with the previous example, there are different sensitivities to the effect of one of the factors in this case. As a result PPL cannot be applied to the summary constants - the Hammett equations do not intersect one point (Fig. 3a). Moreover, LFER is impossible to apply in case of medium effect (medium effect is the factor to which the sensitivities of both processes have been taken differently).

3. Initial processes are Reg. 1 and 4. Here we have the dependences with different sensitivities to the effect of both the factors. Moreover, the sensitivities to medium effect in these regressions have different signs. No linear correlations are applied in this case (Fig. 3b).

The last two examples are similar to the situation which has been analyzed earlier[5]. Example 2 is of special interest because the situation is similar to that observed in case of hydrolysis of esters $PhCOOC_6H_4X$ in water-ethanol mixtures at 25° (Fig. 3c). The correlation line which denotes the Hammett equation in water intersects the correlations for 50

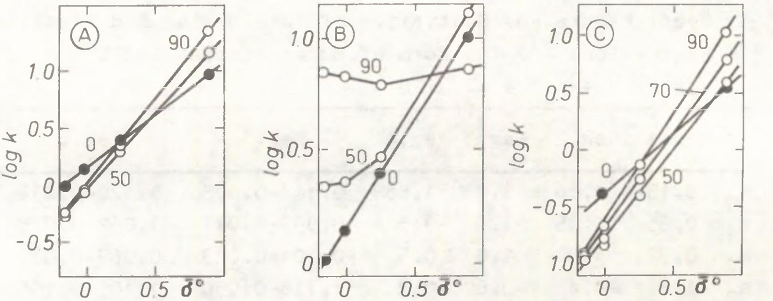

Fig. 3. The Hammett plot for calculated rate constants (A, B) and experimental rate constants (C) of the alkaline hydrolysis of substituted phenyl benzoates in water-ethanol mixtures, at 25°C (see Table 4).

Table 5

Coefficients and Statistics of the Equation[a] $\log k = b_0 + b_1\bar{\sigma}^0 + b_2 S + b_3\tau + b_4\bar{\sigma}^0 S + b_5\bar{\sigma}^0\tau + b_6 S\tau + b_7\bar{\sigma}^0 S\tau$

	Reg.1	Reg.2	Reg.3	Reg.4	Reg.5	Reg.6	Reg.7	Reg.8	Reg.9
b_0	0.15	1.66	0.15	1.66	0.142±0.005	0.181±0.009	0.143±0.005	0.142±0.004	0.587±0.016
b_1	0.95	0.95	0.95	0.95	0.959±0.010	0.879±0.024	0.959±0.010	0.959±0.009	1.060±0.033
b_2	0.92	1.00	0.92	1.00	-0.001±0.013	0.000	0.001±0.013	0.001±0.013	-0.096±0.039
b_3	-2.50	-2.50	-3.00	-2.00	-2.500±0.024	-2.292±0.044	-3.027±0.049	-2.516±0.023	-2.092±0.057
b_4	-1.60	-0.40	-1.60	-0.40	1.118±0.028	1.168±0.049	1.118±0.028	1.118±0.027	1.278±0.084
b_5					-0.001±0.052	0.000	-0.007±0.103	-0.005±0.050	0.000
b_6					0.001±0.070	0.000	1.682±0.139	0.823±0.067	0.000
b_7					0.007±0.149	0.000	-0.015±0.296	-0.007±0.142	1.022±0.296
R					0.9999	0.997	0.9998	0.9999	0.998
S_0					0.013	0.045	0.014	0.013	0.048

[a] The measures of the structural effect are the same as in the Table 4. The measures of the medium effect are: 0. -0.25, -0.37 for Reg.3 - 4. In the Reg.5-9 the measures of the medium effect are taken from the calculated (Reg.5,7,8) or the experimental (Reg.6,9) data of log k. They have been calculated as: $S = \log k(X = p\text{-NO}_2;\ i\text{-th solvent};\ 25^\circ\text{C}) - \log k(X = p\text{-NO}_2;\ H_2O;\ 25^\circ\text{C})$. The measure of temperature is $\tau = 10^3(1/T - 1/298.16)$ [16].

and 90% ethanol content mixtures. Perhaps, this situation is the result of different sensitivities to medium effect for reactions with HO^- and EtO^-.

Three-Parameter Correlations

To the two factors modelling the substituent and medium effects, we have added now the third factor modelling the temperature influence,(the conditions remained the same).

1. Initial processes are Reg. 1 and 2 in Table 5. These regressions are transformed from Reg. 1 and 2 of Table 4, by adding the third factor (which is the same for both competitive processes) modelling the temperature effect and corresponding to the activation energy 47.5 kJ/mol (this value is observed for hydrolysis of esters (II) in water[14]). We observed the additive behavior of the structure and temperature factors, of the medium and temperature factors,and these three factors together.

As the temperature effect is the same for both the competitive reactions, the gross log k_{obs} values fit accurately the polylinear equation (Reg. 5, Table 5). Moreover, all cross terms except term $b_4\bar{\sigma}^{o}S$ are not significant, as

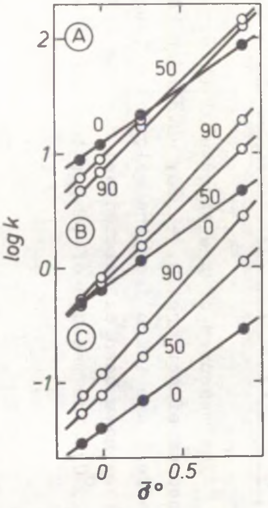

Fig. 4. The Hammett plot for calculated rate constants for two competitive processes at different temperatures (see text and Table 5).

they are taken into the initial equations. This situation can be showed as a vertical displacement of a "bunch" of straight lines (which reflect double-parameter correlations) with temperature changing.

As an example there is the experimental case of alkaline hydrolysis of aryl acetates (II) in ethanol-water mixtures[14] (see Reg. 6, Table 5), which illustrates our situation.

2. Initial processes are Reg. 3 and 4. In this case the activation energy of ethanolysis is taken as 40 kJ/mol (it corresponds to the activation energy of phenolysis[17]) which is less than that of the hydrolysis - 55.5 kJ/mol (it corresponds to the hydrolysis of esters (I)[12]). The results of log k_{obs} treated are given in Fig. 4. At 25°C and close temperatures, the situation is similar to that described in Table 5, Reg. 5. As an example in Fig. 4b the Hammett correlations at 15°C are given. All these correlations cross at one point. So, the whole set of the log k_{obs} values in the small temperature range must well obey the same polylinear equation. In fact, the calculated log k_{obs} values in temperature range 15+35°C fit the equation (see Reg. 7) whose statistics are quite good[x].

In case of a wide temperature range, the correlation for water deviates from the common dependence for the 50-÷90% ethanol content mixtures owing to the differences of the activation energies of two competitive processes. There are two examples in Fig. 4: (i) the straight line for water crosses the lines for water-ethanol mixtures more than once (Fig. 4a); (ii) the water data are situated below those of aqueous ethanol (Fig. 4c). The former situation is similar to that shown in Fig. 3a, b. The latter corresponds to the alkalyne hydrolysis of esters (II) in water-ethanol mixtures[12]. It is possible that the difference in the activation energy of hydrolysis and re-esterification of esters (I) explains why the LFER cannot be applied in case of the medium effect in the whole range of variation:

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[x] In Reg. 7 there is the term $b_6 \tau S$, which did not exist in initial equations. The reason why it appears will be discussed below.

3. Initial processes are Reg. 1 and 4. The energies of activation of the two competitive processes are less different than in the previous example. The calculated k_{obs} values are adequately described by one polylinear equation (Reg. 8, Table 5). But unlike the initial processes, in this case there is the term $b_6 \tau S$. It is necessary to note that this term appears, not because of the nonorthogonality of the variables (the scales of variables are the same as in Reg. 5), i.e. it is not caused by the "number game" and so this result is mathematically correct. But from the point of view of chemical logic (if we want to interpret the terms of polylinear equation in the framework of the significance which has been attributed to them a priori) the term $b_6 \tau S$ in Reg. 8 is an artefact. The aforesaid concerns also the same term in Reg. 7.

There are a lot of examples when some unexpected terms appear in multiple correlations. One of them is alkaline hydrolysis of esters $PhCH_2C(O)OC_6H_4X$ in water-ethanol mixtures[18] (see Reg. 9). We may suppose that an appearance of an unexpected cross term in this case is the result of slight differences between the activation energies of competitive reactions (hydrolysis and ethanolysis) of the given esters*.

Conclusion

All correlations discussed in the present paper (polylinear equations) are not true correlations from the point of view of classical correlation analysis since they are the result of superposition of two real correlation dependences. However, when the sensitivities of identical factors in competitive reactions are the same then the polylinear equation characterizing complex processes has good statistics. So, the fact of observance of polylinear equations itself cannot be regarded as a criterion of the single route of reaction, and thus a criterion of constancy of the reaction mechanisms. Certainly, it should be borne in mind that the requirement of equal sensitivities of the effects

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* Unfortunately, there are no experimental data on the energy

of definite factors on the competitive reactions speaks about identical reaction mechanisms of these processes.

If the sensitivites of competitive processes are different, the particular single correlations are not observed, and the total k_{obs} values do not fit PPL. If the differences of sensitivities are not significant, then PPL may be applied but unexpected terms will be observed in polylinear equations.

We consider the results shown in the part "Simple Correlations" to be of special interest. We analyzed the situation when the deviations of the points from linear dependences are caused by the mathematical reasons only (i.e. by the form of the equation).

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of activation of phenylacetic acid esters. However, it may be supposed that the activation energies of ethanolysis and phenolysis are close. For Hydrolysis and phenolysis of esters (II) these values are 46.7 and 41.6 kJ/mol respectively. In example 2 (PPL does not apply to the whole range of the temperature change) the differences between hydrolysis and phenolysis energy of activations are more considerable (55.5 and 43.0 kJ/mol respectively).

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REACTIVITY OF AROMATIC AND HETEROLYTIC HYDRAZINE DERIVATIVES. V. INTERDEPENDENCE OF IR SPECTRA AND KINETIC CHARACTERISTICS OF ACYLATION REACTION OF 6-CHLORINE-9-HYDRAZINOACRIDINE DERIVATIVES

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The IR spectra of 6-chlorine-9-hydrazinoacridine derivatives have been studied. Linear correlation between the stretching frequencies of symmetrical and asymmetric vibrations of the terminal aminogroup with the Hammett σ-constants has been established. The $\nu^{as}_{NH_2} - f(\sigma)$ relationship is considered antibatic, that of $\nu^{s}_{NH_2} - f(\sigma)$ - symbatic. The analogues of these regularities and the dependences of kinetic and activation parameters of acylation reaction of 6-chlorine-9-hydrazinoacridines with benzoylchloride on the Hammett σ--constants have been discussed. The data of the IR spectra of hydrazinoacridines can be employed in order to interprete kinetic dependences.

In order to continue the studies of reactivity of heterocyclic derivatives of 1-3 hydrazine, the IR spectra of the 6-chlorine-9-hydrazinoacridine (I-VIII) derivatives in chloroform (Table 1) have been studied. In the spectra, the absorption bands of practically all functional groups belonging to the composition of the studied compounds can be identified.

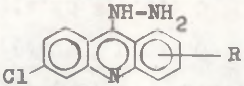
Thus, there is an absorption band of a medium intensity in the 3425-3410 cm^{-1} range corresponding to $\nu^{as}_{NH_2}$, while the $\nu^{s}_{NH_2}$ is displaced up to 3220-3180 cm^{-1}. The frequency of the stretching vibration band of the secondary amino group is stable for the whole series of compounds; the δ_{NH_2} and δ_{NH} vibrations appear as the overlapping bands in the 1600-1670 cm^{-1} range. The absorption bands of the aromatic structure are situated in the same region thus making their interpretation more complicated. The absorption corresponding to the alkoxylic fragment vibration can be identified in the spectra of mixtures according to their bands being in the range of 1280-1270 cm^{-1} and 2850-2840 cm^{-1}.

Kinetic characteristics of the acylation reaction of hydrazinoacridines (I-VIII) with benzoylchloride have been given in our previous report[3].

The frequencies of both symmetrical and asymmetric valence vibration shifts of the terminal amino group as well as the rate constants of the acylation reaction and the activation energy and ethalpy are in linear correlation with the σ-constants of Hammett (Table 2) at various temperatures. Note that the angle coefficients of correlation equations connecting the $\nu^{as}_{NH_2}-f(\sigma)$, $\nu^{s}_{NH_2}-f(\sigma)$ have different signs. A similar relationship has been detected earlier also in case of hydrazides of carbonic acids, while in the case of aromatic amines the both dependences are symbatic.[5] The similarity of the IR spectra of hydrazines and hydrazides of carboxilic acids is proved by the kinetic data of the acylation reaction of the derivatives of 9-hydrazinoacridine[3] and the hydrazides of benzoic acid[1,2]. Rather small correlation coefficients for Eqs. 1,3 are still statistically significant and their values are substantially increasing (Eqs.2, 4) if the data for 2-methoxy-6-chlorine-9-hydrazinoacidine will be excluded. Anomalous behavior of 2-methoxy-6-chlorine-

Table 1

Wave Number of Absorption Bands in IR Spectra of 6-Chlorine-9-Hydrazinoacridine in Chloroform in cm^{-1}



	R	ν_{NH}	$\nu^{as}_{NH_2}$	$\nu^{s}_{NH_2}$	δ_{NH_2}	δ_{NH}	$\nu_{C \cdots C}$
I.	H	3160	3418	3245	1570	1580	1590
II.	2-CH_3	3170	3420	3230	1570	1580	1600
III.	4-CH_3	3170	3420	3225	1570	(1570)	1590
IV.	2-OCH_3	3170	3425	3240	1570	1580	1600
V.	4-OCH_3	3170	3427	3180	1580	(1580)	1590
VI.	2-CI	3170	3415	3260	1580	(1580)	1600
VII.	4-CI	3160	3412	3250	1590	1570	1600
VIII.	2,3-CH_3^*	3175	3425	3220	1570	(1570)	1590

Table 2

Correlation Dependences of Wave Numbers of IR Spectra, Kinetic and Activation Parameters of 6-Chlorine-9-Hydrazinoacridines on the Hammett σ Constants

	Equation	r	s	n
1.	$\nu^{as}_{NH_2} = (3420 \pm 127) + (-27.9 \pm 2.1)\,\sigma$	0.910	1.96	8
2.	$\nu^{as}_{NH_2} = (3418 \pm 112) + (-26.9 \pm 1.8)\,\sigma$	0.941	1.82	7
3.	$\nu^{as}_{NH_2} = (3238 \pm 21) + (135 \pm 2.1)\,\sigma$	0.930	8.23	8
4.	$\nu^{s}_{NH_2} = (3235 \pm 19) + (141 \pm 1.9)\,\sigma$	0.98	5.37	7
5.	$\log k^{298} = (-1.411 \pm 0.008) + (-1.278 \pm 0.017)\,\sigma$	0.994	0.071	6
6.	$\log k^{308} = (-1.258 \pm 0.013) + (-1.123 \pm 0.077)\,\sigma$	0.963	0.028	6
7.	$\log k^{318} = (-1.094 \pm 0.020) + (-1.009 \pm 0.024)\,\sigma$	0.990	0.016	6
8.	$\log k^{328} = (-0.960 \pm 0.013) + (-0.987 \pm 0.019)\,\sigma$	0.995	0.010	6
9.	$\Delta H^{\neq} = (6.61 \pm 0.06) + (4.75 \pm 0.04)\,\sigma$	0.991	0.013	6
10.	$E_A = (6.78 \pm 0.09) + (4.40 \pm 0.03)\,\sigma$	0.990	0.015	6

Table 3

Correlation Equations of Kinetic and Activation Parameters of 6-Chlorine-9-Hydrazinoacridine on their Wave Numbers

	Equation	r	s	n
1.	$\log k^{298} = (-135.6 \pm 2.9)+(3.925\ 10^{-2} \pm 1.3\ 10^{-2})\ \nu^{as}_{NH_2}$	0.986	0.078	6
2.	$\log k^{298} = (24.9 \pm 0.5)+(-8.131\ 10^{-3} \pm 1.5\ 10^{-4})\ \nu^{s}_{NH_2}$	0.954	0.083	6
3.	$E_A = (456.4 \pm 9.9)+(-0.131 \pm 0.013)\ \nu^{as}_{NH_2}$	0.910	0.317	6
4.	$\Delta H^{\neq} = (492.6 \pm 9.9)+(-0.142 \pm 0.013)\ \nu^{as}_{NH_2}$	0.907	0.346	6
5.	$\Delta G^{\neq} 298 = (216.6 \pm 4.5)+(-0.0577 \pm 0.0061)\ \nu^{as}_{NH_2}$	0.968	0.089	6
6.	$E_A = (-87.2 \pm 2.0)+(2.90\ 10^{-2} \pm 2.6\ 10^{-3})\ \nu^{s}_{NH_2}$	0.949	0.237	6
7.	$\Delta H^{\neq} = (-95.6 \pm 2.5)+(3.16\ 10^{-2} \pm 2.8\ 10^{-3})\ \nu^{s}_{NH_2}$	0.984	0.248	6
8.	$\Delta G^{\neq}_{298} = (-16.2 \pm 0.5)+(1.10\ 10^{-2} \pm 6.8\ 10^{-4})\ \nu^{s}_{NH_2}$	0.912	0.147	6

-9-hydrazinoacridine is evidently connected with the charge transfer between the electron donor methoxy-group and the chlorine atom in position 6, the π-electron system of the acrydine molecule being included as it happens also in case of 2-methoxy-6-nitro-9-amino-acridine.[6]

The methods of linear regression analysis have been applied in order to study the dependence of kinetic and activation parameters of the acylation reaction on the wave number of valence shifts of the aminogroup (Table 3). The obtained correlation coefficients of Eqs. 1-8 are statistically significant inspite of a wide variation of the r values in case of a similar sample.

Owing to the absence of the Hammett σ-constants for the derivatives of hydrazinoacridines, it is advisable to use the IR-spectroscopy data for interpretation of kinetic dependences.

Experimental

The synthesis, identification and purity tests of the 6-chlorine-9-hydrazinoacridines have been described earlier[3]. The IR spectra of the solutions were recorded on a double-beam IR-spectrophotometer Specord 75-IR, at concentration of ~0.05 mol/l in the cells with windows of potassium bromide whose thickness d= 0.427 mm. The correlation analysis was conducted according to the known formulae[7] on a micro computer "Electronika B3-34", using the standard algorithms[8].

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KINETICS OF NADH OXIDATION BY SINGLE-ELECTRON ACCEPTORS

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During the oxidation of reduced nicotinamide adenine dinucleotide (NADH) by ferricyanide and quinoidal radicals the reduced acceptors inhibit the reaction, thus reducing NADH$^{+\cdot}$. The potential of the redox pair NADH$^{+\cdot}$/NADH, calculated according to the reaction rate with ferri/ferrocyanide is equal to 966 mV. With the use of quinoidal acceptors this value is decreased. The possibility of hydrogen transfer in the oxidation of NADH by quinoidal radicals is discussed.

Single- or multi-step (e$^-$, H$^+$, e$^-$ or H$^\cdot$, e$^-$) hydride-ion transfer schemes can be used to describe the oxidation reactions of reduced nicotinamide adenine dinucleotide (NADH), a cofactor of dehydrogenases and its analogues by flavin and quinoidal compounds[1-11]. The choice of a scheme is based on different estimation of the potential of a single-electron oxidation of dihydropyridines and the proton transfer rate to an acceptor[3-11] that is greatly complicated by the instability of cation-radicals of dihydropyridines. Much valuable information on the energetics of single-electron processes may be acquired through the use of single-electron acceptors - inorganic complexes and free radicals[11-14]. Reaction inhibition by a reduced low-potential acceptor, reducing back the cation-radical of dihydropyridine, leads to the conclusion that the electron transfer takes place in the rate limiting step[14]. However, the question on the possibility of hydrogen transfer to an acceptor in a single-electron oxidation has been studied insufficiently.

The aim of the present work is to study the kinetics of NADH oxidation by ferricyanide and quinoidal radicals, which are able to receive a proton in the reduction process, and the reaction inhibition by the reduced forms of these compounds.

EXPERIMENTAL

NADH (Reanal, Hungary), tetracyano-p-quinodimethane (TCNQ) (Chemapol, Czechoslovakia), N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) (BDH Chemicals Ltd., Great Britain) were used as received. Lithium salt of $TCNQ^{-\cdot}$ and perchlorate of $TMPD^{+\cdot}$ were synthesized according to Melby[15] and Michaelis[16], respectively. Potassium ferri- and ferrocyanide (pure) were recrystallized twice from water. Kinetic measurements were carried out spectrophotometrically with a spectrophotometer Specord UV-VIS in an anaerobic medium at $25 \pm 0.1\,^{\circ}C$[6,11]. The concentrations of $TCNQ^{-\cdot}$, $TMPD^{+\cdot}$ and ferricyanide were 15-70 and 150-500 uM, respectively. During the measurements NADH was in 10-30-fold excess. In calculations $\Delta\varepsilon_{570} = 11\ nM^{-1}cm^{-1}$ ($TMPD^{+\cdot}$) and $\Delta\varepsilon_{730} = 10.8\ nM^{-1}cm^{-1}$ ($TCNQ^{-\cdot}$) were used. The measurements were carried out in 0.1 M K-phosphate-citrate buffer solutions, pH 7.0 and 5.0 containing 1 mM EDTA. Li-phosphate-citrate buffer solutions (0.1 M) were used in the experiments with $TCNQ^{-\cdot}$. The data obtained were processed with a computer D 3-28.

RESULTS AND DISCUSSION

During the oxidation of NADH by ferricyanide the reaction is first order up to a 85-90% conversion of ferricyanide. The obtained pseudofirst order rate constants are proportional to NADH concentrations, and the initial reaction rate is proportional to reagents concentrations. Thus it follows, that the oxidation of NADH by ferricyanide is the second order reaction. The presence of milimolar concentrations of the reaction product - ferrocyanide reduces markedly the reaction rate (Fig. 1).

The oxidation of NADH by free radicals $\text{TMPD}^{+\cdot}$ and $\text{TCNQ}^{-\cdot}$ also follows a bimolecular mechanism, since the initial reaction rates are directly proportional to the reagent concentrations, however, at a comparatively low oxidant reduction a deviation from the linearity in coordinates ln A - t is observed.

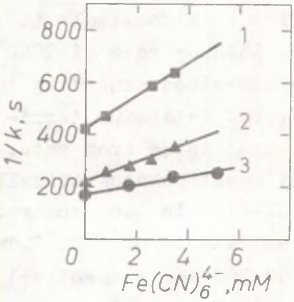

Fig. 1. The effect of ferrocyanide on the NADH oxidation rate by ferricyanide, pH 7.0. NADH concentration - 1.95 mM (1), 3.5 mM (2), 5.2 mM (3).

It is due to the reaction inhibition by the reduced form of an acceptor, since the addition of TMPD (10-90 µM) decreases the reduction rate of $\text{TMPD}^{+\cdot}$ considerably (Fig. 2). In the presence of 10-12 µM (pH 7.0) and 25-30 µM (pH 5.0) TCNQH^{-}, formed in situ, the pseudofirst order rate constant of $\text{TCNQ}^{-\cdot}$ reduction is decreased twice.

The data given indicate that the oxidation of NADH by single-electron acceptors can be described by a scheme, presented by Bruice et al.[14]:

$$\mathrm{NADH}\ \underset{k_{-1}[\mathrm{Red}]}{\overset{k_1[\mathrm{Ox}]}{\rightleftarrows}}\ \mathrm{NADH}^{+\bullet}\ \xrightarrow{k_H}\ \mathrm{NAD}^{\bullet}\ \xrightarrow{k_3[\mathrm{Ox}]}\ \mathrm{NAD}^{+} \qquad (1)$$

Due to the high exothermicity of $NAD^{\bullet}$ oxidation the oxidation constant is expressed as $k_1k_H/(k_H + k_{-1}[Red])$.

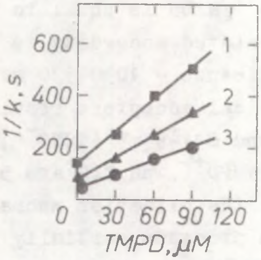

Fig. 2. The effect of TMPD on the NADH oxidation rate by $TMPD^{+\bullet}$, pH 7.0. NADH concentration - 0.3 mM (1), 0.5 mM (2), 0.75 mM (3).

The k_1 values, obtained by extrapolating the rate constants to the zero product concentrations, and the k_1/k_{-1} ratios, calculated with $k_H = 1.2\cdot10^7\ s^{-1}$ for free $NADH^{+\bullet}$[12], are summarized in the table.

Table

Kinetic Parameters of NADH Oxidation by Single-Electron Acceptors

Redox pair	pH	E^1, mV	k_1, $l\cdot mole^{-1}s^{-1}$	k_1/k_{-1}
Ferri/ferrocyanide	7.0	430	1.2±0.1	$(8.1\pm1.6)\cdot10^{-10}$
$TMPD^{+\bullet}/TMPD$	7.0	270[17]	25±5	$(9.7\pm1.1)\cdot10^{-11}$
$TMPD^{+\bullet}/TMPDH^{+}$	5.0	357	37±2.8	$(9.2\pm2.5)\cdot10^{-11}$
$TCNQ^{-\bullet}/TCNQH^{-}$	7.0	110[6]	4±1.2	$(2.5\pm0.6)\cdot10^{-12}$
$TCNQ^{-\bullet}/TCNQH^{-}$	5.0	228	20.3±4.5	$(5.7\pm1.8)\cdot10^{-11}$

The increase of k_1 values of quinoidal acceptors at pH 5.0 is due to the increase of their single-electron reduction potential (E^1), since the proton is transferred in the reduction process (pK_a $TMPDH^+$ = 6.5[17], pK_a $TCNQH^-$ - 7.2[6]).

The k_1/k_{-1} ratio, being the equilibrium constant of redox reactions, enables us to calculate the potential of single-electron oxidation of NADH. As it follows from the data on the reaction with ferri/ferrocyanide (Table), the potential of the pair $NADH^{+\bullet}/NADH$ is equal to 966±6 mV, that is close to that calculated according to the data on the NADH oxidation by ferricenes - 1030-930 mV[12]. At the same time the use of quinoidal acceptors results in lower potential values - 792±6 and 831±9 mV ($TCNQ^{-\bullet}$, pH 7.0 and 5.0), 861±3 and 952±7 mV ($TMPD^{+\bullet}$, pH 7.0 and 5.0) that indicates some difference in the oxidation mechanism. It is possible that the reaction proceeds partially with a hydrogen transfer in the limiting step, where the product inhibition does not take place[14]:

$$NADH + TCNQ^{-\bullet} \rightleftharpoons NAD^{\bullet} + TCNQH^{-} \qquad (2)$$

$$NAD^{\bullet} + TCNQ^{-\bullet} + H^{+} \xrightarrow{\text{fast}} NAD^{+} + TCNQH^{-}$$

The other possibility may be the formation of a charge transfer complex in the reaction where the dissociation of $NADH^{+\bullet}$ is accelerated or the proton transfer to the acceptor takes place. Such a possibility is supported by the high negative activation entropy of NADH oxidation by $TMPD^{+\bullet}$ that is close to $\Delta S^{\neq}$ for p-quinones[11] for which the formation of charge transfer complexes in the oxidation of dihydropyridines is characteristic[8].

It is known, that the reactivity of quinoidal radicals with respect to NADH is close to that of p-quinones with the same single-electron reduction potentials[11]. Despite the formation of biradical charge transfer complexes in the oxidation of dihydropyridines by quinones[8,9] and the character of the kinetic isotope effect variation, that is unexplainable in terms of a single-step hydride transfer[8,9,11], the single-electron oxidation high endothermicity of dihydropyridines is a strong evidence against a multi-step hydride-ion transfer mechanism[7,10,12]. The data presented in this work indicate that a partial transfer of proton or hydrogen atom in the limiting step is possible that may considerably decrease the endothermicity of the process.

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EFFECT OF STRUCTURAL FACTORS ON STABILITY AND SPECTRAL CHARACTERISTICS OF 3,3-DIPHENYL-1-ARYLTHIOPHTHALYLIUM IONS

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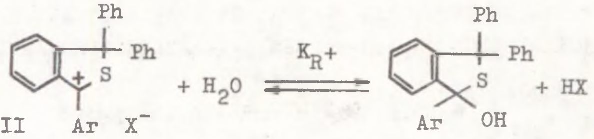
The electron spectra and acid-base conversions in a series of 3,3-diphenyl-1-arylthiophthalylium ions [$Ar=C_6H_5$, p,m-$CH_3C_6H_4$, p-$CH_3OC_6H_4$, p-$(CH_3)_2NC_6H_4$, p-$(C_2H_5)_2NC_6H_4$, m-FC_6H_4] have been studied. The effects of hetero atom, substituents in aryl and at position 3 on their stability and spectral characteristics are discussed.

Studies on the effect of structural factors on the stability and reactivity of carbenium ions, intermediates of various chemical conversions, are important for understanding the mechanisms of these conversions and contribute to conscious regulation of them. In this respect rather convenient research objects are stable annelated five-member heterocarbenium ions with one hetero atom: phthalylium, thiophthalylium, isoindolynium ions. However, the effect of different structural elements on the cation stability has presently been sufficiently studied and quantitatively estimated only for phthalylium ions [1]. With the sulfuric analogs of phthalylium ions data are only available on the effect of substituents at position 1 on the stability of 3,3-dimethyl-1-arylthiophthalylium ions [2,3].

To obtain more detailed information on the effect of the nature of the hetero atom and the substituents at C_1 and C_3 of the hetero ring on the stability of thiophthalylium ions, we studied spectrophotometrically the acid-base conversion in a series of 3,3-diphenyl-1-arylthiophthalylium ions (I-VII). The constants of equilibrium between thiophthalylium ions and the appropriate carbinol bases were used as quantitative characteristics of cation stability.



I-VII

$Ar=C_6H_5$(I), 4-$CH_3C_6H_4$(II), 4-$CH_3OC_6H_4$(III), 4-$(CH_3)_2NC_6H_4$ (IV), 4-$(C_2H_5)_2NC_6H_4$(V), 3-$CH_3C_6H_4$(VI), 3-FC_6H_4(VII);$X=CIO_4$.

In analyzing the acid-base equilibrium constants (Table 1) three circumstances draw one's attention. First, as with 3,3-dimethyl-1-arylthiophthalylium ions and their oxygen analogs, the substitution of oxygen by sulfur results in stabilization of cations, with no additivity of the contribution being observed. For example, for 3,3-dimethylsubstituted ions with $Ar=C_6H_5$ $\Delta pK_{R^+} = pK_{R^+}(S)-pK_{R^+}(O)$ amounts to 1.05 log units, whereas with 3,3-diphenylsubstituted ions $\Delta pK_{R^+} = 0.59$. Second, according to their influence on the cation stability, the substituents at the carbenium center and the hetero atom are in competitive relationships: an increase in the electron-donating properties levels the hetero atom stabilizing effect. And the third, the comparison of the stabilities of 3,3-diphenyl- and 3,3-dimethylsubstituted [3] thiophthalylium ions shows that the substitution of the methyl groups by the phenyl ones decreases the stability of cations on an average by 2.4 log units regardless of the nature of 1-aryls. Analogous effect is also observed with phthalylium ions. However, it is less pronounced (ΔpK_{R^+av} = 1.9) [4], which provides evidence for greater electronic conduction of sulfur as compared with oxygen.

In the series studied, the logarithms of the equilibrium constants correlate with the Brown and Okamoto σ^+-constants (Figure).

The comparison of the reaction constants for the series

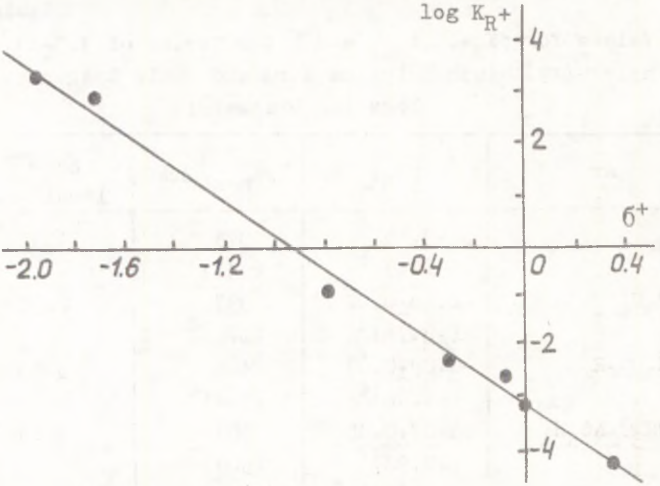
Table 1

Values for pK_{R^+}, λ_{max} and ε for Series of 3,3-Diphenyl-1-Arylthiophthalylium Ions and their Oxygen Analogs (in brackets)

Ar	pK_{R^+}	λ_{max}, nm	$\varepsilon \cdot 10^{-4}$, $l \cdot mol^{-1} \cdot cm^{-1}$
C_6H_5	-3.15 [5] (-3.74) [6]	375 [5] (347)[6]	1.95 [5]
$4\text{-}CH_3C_6H_4$	-2.18±0.02 (-2.74)[4]	397 (376)[4]	2.35
$4\text{-}CH_3OC_6H_4$	-0.83±0.02 (-1.06)[4]	468 (414)[4]	3.05
$4\text{-}(CH_3)_2NC_6H_4$	+3.07±0.05 (+2.98)[7] +3.05±0.07* (+3.17)* [7]	567 (509)[7]	3.79
$4\text{-}(C_2H_5)_2NC_6H_4$	+3.39±0.05 (3.33)[7] +4.25±0.03* (4.40)* [7]	569 (511)	4.10
$3\text{-}CH_3C_6H_4$	-2.52±0.06 (-3.21)[4]	376 (350)	2.15
$3\text{-}FC_6H_4$	-4.33±0.08 (-)	368 (-)	2.09

* pK_{R^+} values for dialkylamino groups in 1-aryl.

of 3,3-diphenyl- (ρ = 3.44±0.14) and 3,3-dimethyl-1-arylthiophthalylium (ρ = 3.25±0.12) [3] ions shows statistically insignificant differences between them. Thus, the sensitivity of thiophthalylium ions to the effect of the substituents at position 1 of the hetero ring is independent of the nature of the substituents at C_3. The same regularity is observed with the oxygen analogs: ρ = 3.62±0.10 for 3,3-dimethyl-1-arylphthalylium ions, whereas for 3,3-diphenyl-1-arylphthalylium ones ρ = 3.74±0.12 [4]. It is worth noting that the greater sulfur contribution to the stabilization of the cyc-



log K_R+ = f(б +) dependence
(ρ =3.44±0.14,log K_R^o+=3.12±0.30, r=0.996, n=7)

lic heterocarbenium ions considered results in an 1.1-fold decrease in the sensitivity of thiophthalylium ions to the effect of the substituents at C_1 in comparison with phthalylium ions.

With cations IV and V containing dialkylamino groups in 1-aryl and within the range of pH values from 3.1 to 4.5, an equilibrium is set up not only between the carbocations R^+ and the carbinol bases ROH but also between the base ROH and oxyammonium ions HR^+OH: $R^+ + H_2O \rightleftharpoons ROH + H^+ \rightleftharpoons HR^+OH$. Table 1 lists the pK_a values for $NAlk_2$ groups calculated by the method[8].

The analysis of the pK_a values shows that the substitution of methyls at nitrogen by ethyls considerably increases the stability of ammonium ions, which results in a change in the ratio of the ionized forms in favor of the latter (from 49 to 88%). The following fact deserves attention: in this situation the contribution to pK_a is independent of the nature of the substituents at C_3 and the heteroatom and amounts on an average to 1.24 log units[3,6].

In contrast to 3,3-dimethylsubstituted ions [3], the transition from phthalylium ions to thiophthalylium ones involves, in addition to stabilization of carbocations, inconsiderable destabilization of ammonium ions.

Finally it should be noted that regardless of the fact that the substituents at position 3 are considerably removed from a nitrogen atom, they essentially affect the stability of ammonium ions: the substitution of methyls for phenyls results in a decrease in their stability. This effect is independent of the nature of alkyl groups at nitrogen and amounts to $\sim$1.6 log units for thiophthalylium ions (see Tables 1 and [3]) and to $\sim$1.3 log units for phthalylium ions[7].

Thiophthalylium ions I-VII absorb in the visible region (Table 1). The position of long wave maximum is governed by the character of the substituents at C_1 and C_3 and by the nature of the hetero atom. However, the extent of the contribution of these structural fragments to the overall chromophore system is different. The nature of substituents at the ion carbenium center exerts the most pronounced effect: the long wave absorption band is bathochromically shifted with the increase in the electron-donating capacity of the substituents at the para-position of 1-aryl. For example, on substitititing $Ar=C_6H_5$ by $Ar=(CH_3)_2NC_6H_4$ $\Delta\lambda$ amounts to 192 nm. A similar effect is also observed in a series of 3,3-dimethyl-1-arylthiophthalylium ions ($\Delta\lambda$=194 nm) [3], whereas with the oxygen analogs, phthalylium ions, the electron-donating substituents show a less pronounced effect ($\Delta\lambda_{av}$=156nm)[3,4,9]. It should be noted that in the series of thiophthalylium ions studied the wave numbers which correspond to λ_{max} correlate with the σ^+-constants for the para-substituents in 1-aryl $[p = (4.90 \pm 0.51)\cdot 10^3,\ r = 0.984,\ n = 5]$.

As with the oxygen analogs [3,4], the transition from 3,3-dimethylsubstituted [3] to 3,3-diphenylsubstituted thiophthalylium ions induces a bathochromic shift in λ_{max} on an average by 13 nm.

The substitution of oxygen by sulfur in the five-member ring also produces a bathochromic shift in the long-wave absorption maximum, the hetero atom effect being more pronounced for 3,3-diphenylsubstituted cations ($\Delta\lambda \sim 41$ nm) in comparison with 3,3-dimethylsubstituted cations ($\Delta\lambda \sim 31$ nm)[3].

In the series of thiophthalylium ions discussed, the intensity of the long wave absorption maximum enhances as the electron-donating capacity of substituents in 1-aryl increases (Table 1). In this situation, a satisfactory linear correlation has been found between the light absorption values and the electrophilic constants for the substituents irrespectively of the position of the latter in aryl $[p = (-1.05 \pm 0.08)\cdot 10^4,\ r = 0.989,\ n = 6]$.

EXPERIMENTAL

Electronic spectra were obtained in HCOOH at 18 °C using a spectrophotometer Specord UV-Vis. The method for determination of pK_{R^+} values is described in Ref.[9]. With perchlorates II,III,VI,VII formic acid solutions were used, whereas in the case of perchlorates IV and V - 0.1 M citrate buffer solutions[10]. The H_R values for HCOOH solution were taken from Ref.[11]. The experimental data were processed by the least squares method.

3,3-Diphenyl-1-arylthiophthalylium perchlorates (II,III, V-VII) were obtained from 6.5 mol diphenyl thiophthalide[5] and the corresponding aryl magnesium bromides by magnesium organic synthesis. The reaction was carried out in medium of

Table 2

Characterization of Perchlorates

Compd.	Yield,%	M.p. °C	Found, %				Empirical formula	Calculated, %			
			C	H	Cl	S		C	H	Cl	S
II	18	165-8	67.8	4.4	7.2	6.4	$C_{27}H_{21}ClO_4S$	68.0	4.4	7.4	6.7
III	45	182-5	65.4	4.4	7.0	6.2	$C_{27}H_{21}ClO_5S$	65.8	4.4	7.2	6.5
V	47	215-7	67.3	5.5	6.3	5.9	$C_{30}H_{28}ClNO_4S$	67.5	5.3	6.6	6.0
VI	21	150-2	67.7	4.6	7.3	6.5	$C_{27}H_{21}ClO_4S$	68.0	4.4	7.4	6.7
VII	17	176-7	64.6	4.0	7.2	6.6	$C_{26}H_{18}FClO_4S$	64.9	3.8	7.4	6.7

anhydrous THF under N_2 at 3-fold excess of Gringard reagent. The reaction mixture was decomposed by diluted (1:4) hydrochloric acid (in producing perchlorate V a saturated NH_4Cl solution was used), treated with ester. After removal of the solvent, the oil reaction products were dissolved in 10 ml of glacial acetic acid (II,III,VI,VII) or 50 ml of ester (V) and 2 ml of 57% $HClO_4$ was added. The crystalline perchlorates formed during long-term standing were filtered off and recrystallized twice from acetic acid.

The yields, melting points and the elementary analysis data of perchlorates II,III,V-VII are listed in Table 2.

The perchlorate IV synthesis was described earlier[12].

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REACTIONS OF IMIDE ACIDS' DERIVATIVES WITH NUCLEOPHILIC REAGENTS. KINETICS AND INTERACTION MECHANISM OF CYCLIC IMIDOYL CHLORIDES WITH ARYLAMINES IN ACETONITRILE

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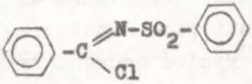
Interaction of cyanuric chloride and Ψ-saccharin chloride with arylamines at 25°C can be characterized as having the first order of reagents in each case. The ρ-Hammett constant value of the amine structure for the processes studied (ρ = -3.4) is closest to the analogous parameters observed in case of the earlier studied reactions of nucleophilic aromatic substitution in activated benzene halides.

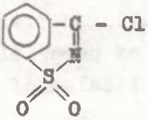
It has been shown[1-3] that the interaction of the N-substituted benzimidoyl chlorides $R^1C_6H_4C(Cl)=NR^2$ with arylamines proceeds according to various mechanisms in protoinert media. Thus, in case of electron-donor substituents at the nitrogen R^2 atom, a preliminary substrate inonization is observed. The pecularities of the process on the example of the N-methylbenzimidochloride have been discussed in[2]. For the aminolysis reactions of the N-phenylsulfonyl benzimidoyl chloride aminolysis reactions $C_6H_5C(Cl)=NSO_2C_6H_5$(I), containing an electron-acceptor substituent in case of the nitrogen atom, most probably the addition-separation mechanism functions via the tetrahedral medium product whose decomposition is determined by the rate of the limiting step[3].

In the present research we have investigated the interaction kinetics of ψ-saccharin chloride (II) and cyanuric chloride (III) with arylamines R^3ArNH_2(R^3=3-NO_2-4-CH_3; 3-NO_2 3-NO_2-4-Br; 3-NO_2-5-$COOCH_3$; 3,5-$(NO_2)_2$ in acetonitrile at 25°C. Compound II can be taken as a N-phenyl-sulfonylbenzimidoyl chloride cyclic analog, although there is no literature data on the mechanism of its reaction with nucleophilic agents. Cyanuric chloride is a heteroaromatic imidoyl halogenide whose reactions with arylamines are of remarkable practical interest, since they enable us to obtain semiproducts for dyes, herbicides, thermostable polymers, etc.

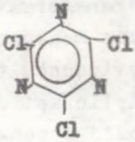
Several reports given in the list of references deal with the rate of interaction of cyanuric chloride with nucleophilic reagents[4-7]. The reaction with aromatic amines was studied[4] in benzene and it was established that besides the bimolecular route it includes the catalytic ones connected with the participation of the second amine molecule and with the precipitating hydrocloride. There is no data about the reactivity of some other imidoylhalogenides, concerning aryl-amines in benzene. As in the polar media the bimolecular mechanisms are realized in the way that is not complicated by the catalysis or the autocatalysis, but the existence of ionization mechanisms can be proved more easily than in the non-polar media[1,2], we studied the arylaminolysis of II and III imidoylchlorides in acetonitrile. Our aim was to compare the substitution mechanisms in the cyclic (II, III) and acyclic I[3] imidoyl chlorides.



I

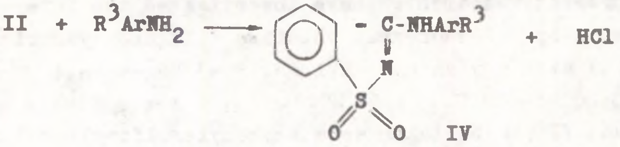


II



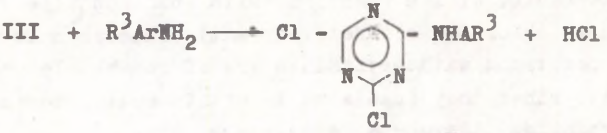
III

Imidoylchloride I reacts with arylamines in the proto-inert media quantitatively with formation of the corresponding amidines[3]. It was established that compounds II, III in acetonitrile with the studied amines give also qualitatively and irreversibly corresponding aminoderivatives IV, V:



IV

(1)



V

(2)

The processes (1,2) were monitored by two methods: a) spectrophotometrically according to the loss of the dyed amines; b) conductometrically according to the hydrogen chloride accumulation in the solution. In the case of the pseudomonomolecularity (for spectral measurements) $[II], [III] \gg [R^3ArNH_2]$ and conductometric measurements $[R^3ArNH_2] \gg [II], [III]$) the rate constants of pseudofirst order k_H^I remain stable during the process depending linearly on the concentration of the reagent which is in excess. Their values in case of various concentrations are given in Tables 1, 2. Here are also given the second order rate constants k_H^{II} calculated from linear dependences " k_H^I $[R^3ArNH_2]$" or " k_H^I - [I], [II]".

Excellent coincidence of the k_H^{II} constants obtained in case of transformation of the pseudomolecular conditions of the kinetic measurements employing different rate monitoring methods evidences the absence of parallel routes caused by the catalytic action of the molecules of the reagents.

We could suppose that in the case of conductometric measurements (a large amine excess in comparison with III), the following halogen substitution in product V would proceed at a commensurable rate. Studying the rate of the obtained earlier product V aminolysis with arylamine shows that it is

Table 1

Pseudofirst $k_H^I(s^{-1})$ and Secord Order $k_H^{II}(l \cdot mol^{-1} . s^{-1})$ Rate Constants of ψ-Saccharin Chloride (II) and Cyanuric Chloride (III) Reactions with Arylamines (H_2NArR^3) in Acetonitrile at 25°(Measured Spectrophotometrically).

Substrate	R^3	$[substrate] \cdot 10^2$, $mol \cdot l^{-1}$	$k_H^I \cdot 10^4, s^{-1}$
1	2	3	4
II	$3\text{-}NO_2\text{-}4\text{-}CH_3$	0.526	64.7
		0.530	89.6
		1.91	254
		3.21	465
		$k_H^{II} = 1.43 \pm 0.20$	
	$3\text{-}NO_2$	3.21	126
		9.89	342
		$k_H^{II} = (3.69 \pm 0.23) \cdot 10^{-1}$	
	$3\text{-}NO_2\text{-}4\text{-}Br$	1.91	8.88
		3.00	14.9
		5.60	40.0
		10.7	47.4
		22.7	109
		$k_H^{II} = (4.88 \pm 0.50) \cdot 10^{-2}$	
	$3\text{-}NO_2\text{-}5\text{-}COOCH_3$	3.21	9.21
		5.60	18.0
		9.89	26.1
		10.7	38.0
		$k_H^{II} = (3.07 \pm 0.3) \cdot 10^{-2}$	

Table 1 continued

1	2	3	4
	3,5-$(NO_2)_2$	5.60	0.739
		10.7	1.53
		22.7	3.02
		$K_H^{II} = (1.36 \pm 0.05) \cdot 10^{-3}$	
III	3-NO_2-4-CH_3	0.28	26.0
		0.55	50.5
		1.11	91.4
		2.22	225
		$k_H^{II} = (7.79 \pm 0.46) \cdot 10^{-1}$	
	3-NO_2	0.188	4.05
		0.375	7.71
		0.750	14.9
		1.20	25.8
		1.50	32.1
		3.00	63.0
		$k_H^{II} = (2.11 \pm 0.11) \cdot 10^{-1}$	
	3-NO_2-5-$COOCH_3$	0.375	0.83
		0.750	1.64
		1.50	3.33
		2.40	5.25
		3.00	6.14
		$k_H^{II} = (2.06 \pm 0.07) \cdot 10^{-2}$	
	3,5-$(NO_2)_2$	1.28	0.12
		2.04	0.18
		2.56	0.22
		4.10	0.35
		5.11	0.42
		$k_H^{II} = (7.94 \pm 0.10) \cdot 10^{-4}$	

Table 2.

Pseudofirst $k_H^I(s^{-1})$ and Second Order $k_H^{II}(l\cdot mol^{-1}\cdot s^{-1})$ Rate Constants of ψ-Saccharin Chloride (II) and Cyanuric Chloride (III) Reactions with Arylamines (H_2NArR^3) in Acetonitrile at 25°(Measured Conductometrically)

Substrate	R^3	(Nucleophile)·10^2, mol·l^{-1}	$k_H^I\cdot 10, s^{-1}$
III	$3\text{-}NO_2\text{-}4\text{-}CH_3$	0.125	1.75
		0.250	3.10
		0.500	4.92
		1.00	8.19
		2,00	17.5
		2.60	19.9
		$k_H^{II} = (7.53 \pm 0.37)\cdot 10^{-1}$	
II	$3\text{-}NO_2$	4.73	18.3
		4.73	16.8
		$k_H^{II} = (3.70 \pm 0.20)\cdot 10^{-1}$	

negligible if compared to the substitution rate of the first atom of chlorine in III. This is in agreement with the data obtained in[6] on the reactivity of cyanuric chloride and dichlorotriazine derivatives similar to V, as regards the other nucleophilic reagents.

The rate constants of the bimolecular interaction of compounds II and III with arylamines (R^3ArNH_2) obey the Hammett equation:

$$\text{(II)}\quad \log k_H^{II} = (1.74 \pm 0.07) - (3.38 \pm 0.07)\sum\sigma_{R^3} \qquad (3)$$

$s_o = 0.050$; $r = 0.999$; $N = 4$

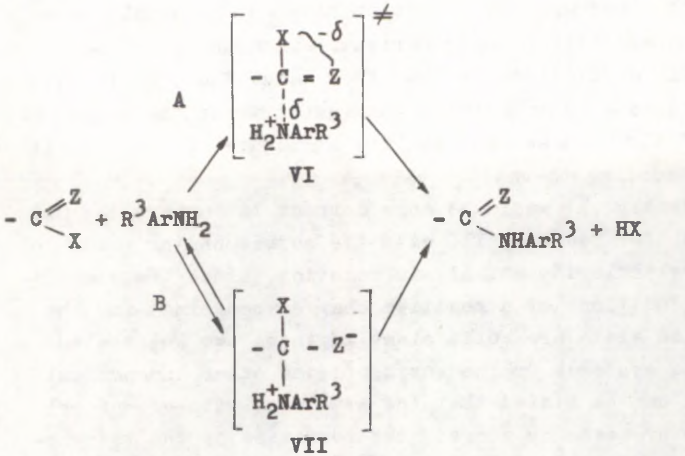
$$\text{(III)}\quad \log k_H^{II} = (1.99 \pm 0.07) - (3.43 \pm 0.07)\sum\sigma_{R^3} \qquad (4)$$

$s_o = 0.050$; $r = 0.999$; $N = 5$.

It follows from Eqs. (3) and (4) that the reactions with participation of imidoylhalogenides II and III are practically equally sensitive to the arylamine structure. Consequently, the substitution of chlorine atoms under the action of nucleophilic reagents proceeds here according to one and the same mechanism, although there are significant differences in the structure of the initial substrates.

It is the S_N2(IP) route that should be excluded first in case of these systems. The formation of nitrile cations (ion pairs or a free cation) in case of cyclic imidoylhalogenides is not beneficial because of the nonlinearity of the $-\overset{+}{\widehat{C{=}N}}-$ fragment in the hypothetical cation which should be extremely unstable in comparison with its linear analog formed during ionization with acyclic imidoylhalogenides. It can also be confirmed by comparing the ρ values in case of the N-methylbenzimidoyl chloride ($C_6H_5C(Cl){=}NCH_3$) reaction with arylamine in acetonitrile (ρ_R[3]$= -2.2 \pm 0.1$), whose ion-pair substitution type[2] has been firmly proved with the corresponding ρ_R[3] parameters for the reactions with participation of II and III (see Eqs. (3) and (4)). A series of data concerning the kinetics of the nucleophilic substitution reactions in cyanuric chloride is not in keeping with the S_N2(IP) mechanism of the aminolysis of cyclic imidoylchlorides. It concerns especially the substantial effects of the bifunctional catalysis in the arylaminolysis of cyanuric chloride as well as the other heteroaromatic imidoylhalogenides discovered by Zollinger[5].

There are two basic kinetically identical mechanisms discussed in literature (scheme 5) for the bimolecular nucleophilic substitution of the halogen atom at the sp^2-hybridized centers, involving also the studied imidoyl compounds II,III: A - concerted substitution via the single transition state VI (the S_N2(S) mechanism), B- substitution by stages via the tetrahedral intermediate of type VII (the S_N2(TI) mechanism). The former is more preferable in case of the arylaminolysis in the proton-inert media if acylchlorides[8] are employed;the latter in the case of the activated noncyclic imidoylhalogenides of type I[3] and polynitrohalogenbenzenes[9].



(5)

Z = O; NR^2; CH-

The constants of sensitivity to the structural effect of the ρ_R3 arylamine of a number of the most typical reactions are presented in Table 3.

Table 3.

Hammett Parameters ρ_R3 In Case of Reactions of Unsaturated Halogen Derivatives with Arylamines (R^3ArNH_2) in Protoinert Media

No	Substrate	Medium	log k_o	ρ_R3	Reference
1.	Benzoyl chloride	Nitrobenzene, 25°C	0.025	-2.6±0.1	8
2.	Saccharin chloride	Acetonitrile, 25°C	1.74	-3.38±0.07	This report
3.	Cyanuric chloride	Acetonitrile, 25°C	1.99	-3.43±0.07	This report
4.	N-phenylsulfonylbenzimidoyl chloride	Acetonitrile, 25°C	2.50	-4.1 ±0.2	3
5.	Picryl chloride	Acetonitrile, 25°C	-0.75	-3.7 ±0.1	10

All processes of bimolecular substitution of the halogen atom at the unsaturated centers have close and rather high ρ_R3 values. Besides, the cyclic imidoylchlorides II, III occupy the intermediate positions between the acyclic analog I and aromatic halogen derivatives on one hand, and carbonylic derivatives on the other hand. Thus, it is difficult to come to a definite conclusion about the stage character of the process and the fine structure of the transition state according to the ρ_R3 value.

Evidently, it would be more correct to compare the ρ_R3 parameter for reaction III with the corresponding value of the picryl chloride aminolysis reaction, since the stabilization conditions of a negative charge appearing in the transition state are quite close in these two substrates (aromatic system). On the basis of some other independent data, it can be stated that the arylaminolysis of picryl chloride proceeds by stages, the formation of the tetrahedral intermediate[9] being the rate determining stage. Consequently, the similarity of the values obtained in the above mentioned reactions and those studied by us with participation of II and III refers to the analogous way of transition (see B in Scheme (5).

Experimental

Saccharin chloride was obtained from saccharin and the pentachloride of phosphor and it was recrystallized from hexane three times, the melting point being 142°C (melting point given in literature is 141-144° [11]). Crude cyanuric chloride was twice recrystallized from heptane at melting point of 146°C (melting point given in literature is 146°C[12]). Employed arylamines were obtained and purified as described in[1], their melting points coincided with the literature data. Acetonitrile was purified according to the known methods[13].

In order to isolate the reaction yield, the solutions of equimolar quantities of imidoyl chloride and arylamine in acetonitrile were boiled until the hydrogen chloride percipitation stopped.After the solvent distillation in the vaccuum of a water-jet pump, the precipitate was dryed at 100°C (≈5 mm Torr).

2,4-Dichloro-6-(3-nitrophenylamino)-S-triazin yield

94.2%; melting point 202-203.5°C (in literature 200-201°C[14]).

3-(3-Nitrophenylamino)-benz(d)-isothiazol-1,1-dioxide. Yield 99.7%, melting point 332-336°C. % found: C 51.44; N 13.62;S 10.65.$C_{13}H_9NO_4S$. % calculated: C 51.48; N 13.85; S 10.57; NMR (dimethylamide, δ ppm: 11.5 (C 1H), 9.0÷ 7.6 (M 8H).

Methods of kinetic measurements have been described in[1-3]. In order to avoid the hydrolysis of imidoylchlorides, their solutions were prepared in a box dryed with phosphorus pentoxide. The error of determining rate constants in an individual experiment did not exceed 2%.

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PHOTOELECTRON SPECTRA OF MOLECULES
7. ALDEHYDES.

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Photoelectron spectra of aldehydes have been analyzed applying the non-empirical (the Gaussian-80 system, the STO-3G, 3-21G, 4-31G, 6-31G basis sets) and semiempirical (HAM/3, CNDO/2) quantum-chemical calculation. A relatively general linear relationship between the consecutive experimental ionization potentials IP_i from the photoelectron spectra and the corresponding calculated MO energies ($-\varepsilon_i$) has been established in case of the given class of compounds as well as for the individual molecules:

$$IP_i = a\,\varepsilon_i + b,$$

where a and b are constants. The most

adequate reproduction of experimental spectra was observed in terms of the HAM/3 method.

In the experimental section, the PE spectra of CF_3CHO and CCl_3CHO were recorded.

In the previous contributions of the present series we have analyzed the PE spectra of derivatives of alcohols[1], aliphatic ethers[2], nitriles[3], amines[4], halides[5] and pyridines[6]. As to the interpretation of the PE spectra of complex molecules without almost any symmetry elements and having a strong overlapping of bonds, the PES only give relatively limited information. A complex approach turned out to be more efficient in this case (for rewiev see[7]). Therefore alongside with studying the empirical relationships between the ionization potentials (IP) and the other energetic parameters (the proton affinities (PA), the binding energy of the inner shell electrons, the shifts of the OH-stretching frequencies of phenol in case of complex formation with a base in CCl_4 solution, the IP values of similar compounds, etc.), we have also analyzed the PES by means of quantum-chemical calculation methods.

The compounds discussed in our previous papers, can be characterized by the fact that there is always a lone electron pair located on a definite atom, i.e. on the ionization center. In the present and in the following papers an attempt has been made to expand this approach also to the compounds containing the C=O group (aldehydes, ketones, amides, carboxylic acids, esters, halide anhydrides)[*]. As in previous cases, in order to reach a more general approach to the problem of the substituent effect on the ionization center in the gas phase, a special attention will be given to the compounds with electronegative substituents. The other aspects of the substituent effects on the ionization potentials of organic compounds were studied in a separate series of pa-

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[*] For preliminary reports see [8-11].

pers using either the substituent constants[11] or the internal substituent[12] scales.

Experimental

The methods of determining the IP and the instrumentation were described in the first paper of the series[1]. The vertical IP-s have been determined at the locations of the maximum of the bands in the PES, while the adiabatic ones (IP_a) refer to the beginning of the band, the half-width of the argon line being added. It enabled us to measure the IP_a being in good agreement with the values obtained for a number of molecules by means of photoionization.

Gaseous CF_3CHO and CCl_3CHO were obtained at a moderate heating of the $CF_3CHO \cdot H_2O$ and $CCl_3CHO \cdot H_2O$ in the presence of P_2O_5 directly in the inlet ampoule of a PE spectrometer, the spectrum was taken right after the synthesis. Before recording the spectrum, the compounds were subjected to several freeze-pump-thaw cycles to remove gaseous impurities.

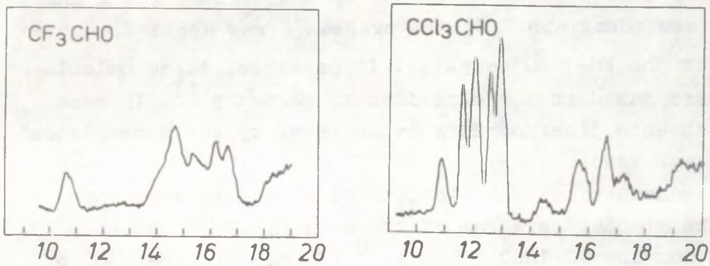

Fig. 1. PE spectra of CF_3CHO and CCl_3CHO.

The PES of CF_3CHO and CCl_3CHO presented in Fig. 1, are the averaged representation of the results of the repeated scanning of the spectrum. The IP values found according to the spectra as well as those determined by another researchers are given in Table 1. This Table includes the literature data of the successive IP, used in the present paper for the purposes of comparison. In Table 1 are given also the IP values calculated by the quantum-chemical methods according to the Koopmans' theorem (the total energy of a molecule is also indicated. The MO symmetry and the approximate localization character of MO were marked as it is generally accepted.

The semiempirical CNDO/2 calculations (see[10;13]) were performed according to the original parametrization[14],using the standard program of Pople. Since the latter does not include the optimization of the geometry of the molecule,the "optimum" bond lengths B were used. In aldehydes were applied CO = 1.22Å, CH = 1.09Å, $C_{sp^2}C_{sp^3}$ = 1.55Å , CF = 1.332Å, CCl = 1.76Å (the latter value was found by the authors of the paper). The carbon atom of the carbonyl group was assumed to have the sp^2 hybridization with the valence angle of 120°. All valence angles in the methyl group and in its fluoro- and chloro-substituted derivatives were considered tetrahedral.

In the calculations performed by the semiempirical HAM/3 method (see monograph [15a]) the program[16] was applied,adapted by us for the EC-1060 computer. If possible, these calculations were based on the experimental geometry [17]. In case of its absence, the geometry established by the nonempirical methods was used.

The nonempirical calculations of molecules were done using the standard program of the Gaussian-80[18] system, adapted for the EC-1060 computer[20]. To compare the PES of the molecules having similar structures and to find out the substituent effect on the order of the orbitals, the calculations for all the molecules were conducted on the same standard bases. In order to check the applicability of the split-valence 3-21G basis set which has been used rather seldom in predicting the PES of molecules, calculations of a series of compounds were carried out also using this basis set. The nonempirical calculations were performed with a complete optimization of the geometry by the method of gradients, or in some cases by the Sargent-Murtagh or Fletcher-Powell[18] techniques.

The quantum-chemical calculations were performed on a computer EC-1060 of the Tartu State University Computing Center.

Discussion

It is reasonable to start the analysis of the PES with the formaldehyde and acetaldehyde spectra, which have been repeatedly interpreted on different levels of the quantum-chemical approach. In his book[19] Kimura and his coworkers give the results of calculation of the PES of these molecules, making use of the extended 6-31G basis set. They also present the calculation of the ionic state energies of the molecules, applying CI method. The most stable conformation in case of any calculation method coincides with the experimental[17] symmetry, but some discrepancies appear in the succession of the MO energies. Here holds the well-known rule which says that the number of bands in a PE spectrum must, according to the spin valence scheme be equal to a half of number of electrons localized at the bonds or existing in the form of lone pairs.

Table 1

Ionization Potentials, Determined from PES and Calculated by Quantum-Chemical Methods.

1. H_2CO

IP_v^a	CNDO/2 [b]		HAM/3 [c]		STO-3G [d]		3-21G [e]	
	$-\varepsilon_i$	MO	$-\varepsilon_i$	MO	$-\varepsilon_i$	MO	$-\varepsilon_i$	MO
10.86	14.82	$2b_2$ n_O	10.71	$2b_2$ n_O	9.64	$2b_2$ n_O	11.78	$2b_2$ n_O
14.4	17.86	$1b_1$ π_{CO}	14.77	$1b_1$ π_{CO}	12.06	$1b_1$ π_{CO}	14.33	$1b_1$ π_{CO}
16.0	20.11	$3a_1$ σ_{CO}	16.41	$5a_1$ σ_{CO}	14.84	$5a_1$ $\bar{n}_O,\sigma_{CO}$	17.32	$5a_1$ $\bar{n}_O,\sigma_{CO}$
16.9	24.67	$1b_2$ π_{CH_2},n_O	17.35	$1b_2$ π_{CH_2},n_O	17.22	$1b_2$ π_{CH_2}	19.04	$1b_2$ π_{CH_2},n_O
21	28.53	$2a_1$ π_{CH_2}	21.50	$2a_1$	21.97	$4a_1$	26.37	$4a_1$ σ_{CH}

a - see[19]

b - E_{tot}= -26.8373 a.u., see also[10]

c - this report, experimental geometry[17], see also[15c,21]

d - E_{tot}= -112.3544 a.u., this report; see also[19,22]

e - E_{tot}= -113.2218 a.u., this report, see also[19,22], report[19] contains the 4-31G and 6-31G calculations.

2. CH_3CHO Table 1 continued

IP_v^a	CNDO/2[b]		HAM/3[c]		STO-3G[d]		3-21G[e]	
	$-\varepsilon_i$	MO	$-\varepsilon_i$	MO	$-\varepsilon_i$	MO	$-\varepsilon_i$	MO
10.26	13.91	$7a'$ n_O	10.26	$7a'$ n_O	9.15	$10a'$ n_O	11.30	$10a'$ n_O
13.24	15.41	$2a''$ π_{CO}, π_{CH_3}	13.22	$2a''$ π_{CO}, π_{CH_3}	11.32	$2a''$ π_{CO}	13.46	$2a''$ π_{CO}
14.15	17.14	$6a'$ σ_{CO}, π_{CH_3}	14.07	$6a'$ π_{CH_3}	13.64	$9a'$ $\bar{n}_O, \sigma_{CO}, \pi_{CH_3}$	15.18	$9a'$ π_{CH_3}
15.34	20.76	$5a'$ $\bar{n}_O, \pi_{CH_3}$	14.74	$5a'$ σ_{CO}	14.77	$8a'$ σ_{CO}, π_{CH_3}	16.53	$1a''$ π_{CH_3}
(15.6)	23.17	$1a''$ π_{CH_3}, π_{CO}	15.24	$1a''$ π_{CH_3}, π_{CO}	15.25	$1a''$ π_{CH_3}	16.81	$8a'$ σ_{CO}
16.47	23.60	$4a'$ σ_{CH}, σ_{CC}	15.96	$4a'$ $\bar{n}_O, \sigma_{CH}$	16.50	$7a'$ σ_{CC}	18.33	$7a'$ $\sigma_{CC}, \bar{n}_O$

a - see [19]

b - E_{tot} = -35.5505 a.u., this report, see also [10,13]

c - this report, experimental geometry [17]

d - E_{tot} = -150.9460 a.u., this report, cis - conformation; for trans-conformation E_{tot} = -150.9442 a.u., see also [20,22].

e - E_{tot} = -152.0552 a.u., this report, cis-conformation; see also [20,22], report[19] contains the 4-31G and 6-31G calculations.

3. FCHO

Table 1 continued

IP_v [a]	CNDO/2 [b]			HAM/3 [c]			STO-3G [d]			3-21G [e]		
	$-\varepsilon_i$	MO		$-\varepsilon_i$	MO		$-\varepsilon_i$	MO		$-\varepsilon_i$	MO	
12.55	16.05	$7a'$	n_O n_O	11.82	$7a'$	n_O	10.44	$10a'$	n_O, n_F	13.63	$10a'$	n_O
14.54	16.96	$2a''$	π_{CO}, n_F	14.31	$2a''$	π_{CO}, n_F	11.13	$2a''$	π_{CO}, n_F	14.77	$2a''$	π_{CO}, n_F
15.45	18.94	$6a'$	$\bar{n}_O, n_F$	15.78	$6a'$	$n_F, \bar{n}_O$	12.92	$9a'$	$n_F, \bar{n}_O$	16.89	$9a'$	$n_F, \bar{n}_O$
17.74	22.85	$5a'$	$n_F, \bar{n}_O$	17.44	$5a'$	$\bar{n}_O, n_F$	15.88	$1a''$	n_F, π_{CO}	19.28	$8a'$	$\bar{n}_O, n_F$
(18.6) [b]	23.93	$1a''$	n_F, π_{CO}	18.27	$1a''$	n_F, π_{CO}	15.97	$8a'$	$\bar{n}_O, n_F$	21.25	$1a''$	n_F, π_{CO}

a - see[23]

b - the value, given in the present report

c - E_{tot}= -53.8414 a.u., this report, see also[10,13]

d - this report, experimental geometry

e - E_{tot}= -209.8308 a.u., this report, see also[20,22]

f - E_{tot}= -211.5704 a.u., this report, see also[20,22]

4. CF_3CHO Table 1 continued

IP_v^a	CNDO/2^b		HAM/3^c		STO-$3G^d$		3-$21G^e$	
	$-\varepsilon_i$	MO	$-\varepsilon_i$	MO	$-\varepsilon_i$	MO	$-\varepsilon_i$	MO
11.66	15.09	12a′ n_O	11.16	12a′ n_O	9.65	17a′ n_O	13.11	17a′ n_O
15.27	18.19	6a″ π_{CO}	14.82	6a″ π_{CO}	12.68	7a″ π_{CO}	15.65	7a″ π_{CO}
15.65	19.19	11a′ n_F,σ_{CO}	15.58	11a′ $n_F,\bar{n}_O$	12.89	16a′ n_F	17.59	16a′ $\bar{n}_O,n_F$
(16.1)	19.91	10a′ n_F	15.68	5a″ n_F	12.93	6a″ n_F	17.86	6a″ n_F
16.34	20.24	5a″ n_F	15.90	10a′ n_F	13.44	5a″ n_F	18.10	5a″ n_F
(16.8)	21.52	9a′ $n_F,\bar{n}_O$	16.29	4a″ n_F	13.52	15a′ $\bar{n}_O,n_F$	18.11	15a′ n_F
17.10	21.56	4a″ n_F	16.75	3a″ $\bar{n}_O,n_F$	14.12	14a′ n_F	18.85	14a′ $n_F,\bar{n}_O$
17.58	22.49	3a″ n_F	16.89	9a′ n_F	14.34	4a″ n_F	19.31	4a″ n_F
	22.63	8a′ n_F	17.15	8a′ n_F			19.52	13a′ n_F
19.46	25.65	7a′	19.00	7a′ σ_{CH}	15.94	13a′ σ_{CO}	21.71	12a′

a - this report, $IP^{(1)} = 11.35$, $IP^{(2)} = 14.80$, see also [9,10,11]

b - $E_{tot} = -116.5077$ a.u., this report; c - this report, the optimum 3-21G geometry;

d - $E_{tot} = -443.3200$ a.u., this report, see also [20], cis-conformation; in case of a perpendicular conformation $E_{tot} = -443.3198$ a.u.; in case of a trans-conformation $E_{tot} = -443.3196$ a.u.; e - $E_{tot} = -447.0233$ a.u., this report, the optimum geometry: CO=1.199Å, CC=1.507Å, CF_1=1.336Å, CF=1.349Å, HC=1.077Å, ∠CCO=122.75°, ∠FCC=112.29°, ∠HCO=124.65°, ∠FCF=107.26°, cis-conformation; in case of a perpendicular conformation $E_{tot} = -447.0223$ a.u.

5. CCl_3CHO Table 1 continued

IP_v [a]	IP_v [b]	CNDO/2 [c]		STO-3G [d]		3-21G [e]		4-31G [f]	
		$-\varepsilon_i$	MO	$-\varepsilon_i$	MO	$-\varepsilon_i$	MO	$-\varepsilon_i$	MO
10.89	10.88	13.54	n_O, n_{Cl}	10.60 24a′	n_O, n_{Cl}	12.69 24a′	n_O, n_{Cl}	12.55 24a′	n_O
11.63	11.62	14.13	n_{Cl}	11.47 12a″	n_{Cl}	12.88 12a″	n_{Cl}	12.68 12a″	n_{Cl}
		14.14	n_{Cl}						
12.06	12.07	14.85	n_{Cl}	11.53 23a′	n_{Cl}	13.03 23a′	n_{Cl}	12.90 11a″	n_{Cl}
				11.54 11a″	n_{Cl}	13.18 11a″	n_{Cl}	12.93 23a′	n_{Cl}
12.64	12.68	15.58	n_{Cl}	12.28 10a″	n_{Cl}	13.89 22a′	n_{Cl}	13.70 10a″	n_{Cl}
		15.59	n_{Cl}						
13.00	13.03	16.25	n_{Cl}, n_O	12.33 22a′	n_{Cl}	14.01 10a″	n_{Cl}	14.00 22a′	n_{Cl}
				12.66 21a′	n_{Cl}, n_O	14.43 21a′	n_{Cl}, n_O	14.28 21a′	n_{Cl}, n_O
14.62	14.47	17.93	π_{CO}, n_{Cl}	13.48 9a″	π_{CO}, n_{Cl}	15.46 9a″	π_{CO}	15.38 9a″	π_{CO}
15.7	15.62	18.44	n_{Cl}	15.10 20a′	σ_{CCl}	16.79 20a′	σ_{CCl}	17.00 20a′	σ_{CCl}
16.75	16.65	21.46	σ_{CO}	16.00 8a″	n_{Cl}, π_{CO}	17.87 8a″	σ_{CCl}	17.90 8a″	σ_{CCl}
17.37	17.27	22.15	π_{CO}	16.69 19a′	$\bar{n}_O$	18.94 19a′	σ_{CO}	18.71 19a′	σ_{CO}
	(17.6)	22.42		17.94 18a′		19.87 18a	$\bar{n}_O$	19.85 18a	$\bar{n}_O$

a - this report, $IP_a^{(1)} = 10.70$, $IP_a^{(2)} = 11.59$

b - see [24]; c - $E_{tot} = -81.7609$ a.u., see also [10]; d - $E_{tot} = -1512.9163$ a.u., this work, cis-conformation; for transformation $E_{tot} = -1512.9139$ a.u., see also [20].

e - $E_{tot} = -1522.1623$ a.u., this report, the optimum geometry: CO= 1.195Å, CCl_1=1.820 Å, CCl = 1.838 Å, CH=1.080Å, ∠CCO= 124.05°, ∠ClCC=108.04°, ∠Cl_1CC=111.07°, ∠HCO=124.40°, Cis-conformation, f - $E_{tot} = -1527.8513$ a.u., see [19].

Table 1 continued

6. CNCHO

HAM/3[a]		STO-3G[b]		3-21G[c]	
$-\varepsilon_i$	MO	$-\varepsilon_i$	MO	$-\varepsilon_i$	MO
11.39	8a' n_O	11.07	12a' n_O	13.46	12a' n_O, π_{CO}
13.59	2a'' π_{CN}, π_{CO}	11.36	2a'' π_{CN}, π_{CO}	13.59	2a'' π_{CN}, π_{CO}
13.95	7a' π_{CN}	11.96	11a' π_{CN}, σ_{CC}	14.08	11a' π_{CN}
14.40	6a' n_N	13.81	10a' n_N	16.23	10a' n_N
15.44	1a'' π_{CO}, π_{CN}	14.25	1a'' π_{CO}, π_{CN}	16.43	1a'' π_{CO}, π_{CN}
16.55	5a' $\bar{n}_O$, σ_{CO}	16.44	9a' $\bar{n}_O$, σ_{CO}	18.93	9a' $\bar{n}_O$
18.44	4a' σ_{CH}	19.26	8a' σ_{CH}, n_O	21.34	8a' σ_{CH}, n_O

a - this report, the optimum 3-21G geometry

b - E_{tot} = -202.9024 a.u., this report

c - E_{tot} = -204.4323 a.u., this report, the optimum geometry: CO=1.205Å, HC= 1.078Å, CC=1.452Å, NC= 1.138Å, ∠HCO=122.76°, ∠CCO=123.53°

In case of both the STO-3G basis set and the 3-21G and 6-31G basis sets , the $5a_1$ orbital of the formaldehyde molecule is a combination of the σ_{CO} and $\bar{n}_O$ orbitals (the MO of a lone pair, directed along the C=O bond axis). If the semiempirical CNDO/2 and HAM/3 methods are used, it corresponds to the σ_{CO} bond of strong polarity, the electron density being shifted towards the oxygen atom.

The results of semiempirical (HAM/3 and CNDO/2) and nonempirical (3-21G) calculations reveal that in case of substitution of fluorine for a hydrogen atom, a remarkable mixing of the π_{CO} and $\bar{n}_O$ orbitals of the carbonyl group with the n_F orbital (see Table 1, No 3) can be observed*. The n_O-nature of the first band in the PES is quite evident, but proceeding from the aforesaid, it should be admitted that the identification of the band/bands of the corresponding π_{CO} orbital is more complicated a problem. It is possible that the value 14.54 corresponding to the 2nd band of the PES should be replaced by the arithmetic mean of the IP_v values, corresponding to the 2nd (2a") and the 5th (1a") MO, i.e. by value (14.54 + 18.6)/2 = 16.5.

In the spectrum of the acetaldehyde molecule the CNDO/2 predicts mixing of the π_{CO} with the π_{CH_2} orbital in the 2a" and 1a" orbitals, which fully corresponds to the calculations by the HAM/3 technique. In case of calculations performed using the STO-3G basis set, such kind of mixing is not observed (2a" is purely π_{CO} and 1a" purely π_{CH_2}) , while in the 3-21G and b-31G the degree of mixing is quite negligible. As to the succession of the $\bar{n}_O$ and σ_{CO} orbitals, there is no entirely common stand on it yet. According to the CNDO/2 method, the mixture of the σ_{CO} and π_{CH_3} orbitals correspond to 6a'; that of $\bar{n}_O$ and π_{CH_3} orbitals corresponds to 5a' . But according to the HAM/3 method these orbitals are situated much deeper (at 5a' and 4a' , respectively) thus not being mixed with the π_{CH_3} orbital. Calculations using the STO-3G basis set lead to the mixing mentioned above, but in a reverse succession of the orbitals. If the calculations are conducted using the more extensive basis set such a mixing will not be observed and the degree of mixing of the σ_{CO} orbital is increasing with the extension of the basis set, reaching the 7a orbital at the 6-31G level.

In a molecule of trifluoroacetic aldehyde, the CNDO/2 refers to the mixing of the σ_{CO} and $\bar{n}_O$ orbitals with the n_F orbital. According to the more advanced semiempirical HAM/3 method and non empirical calculations, at the STO-3G and 3-21G basis set level only the $\bar{n}_O$ and n_F orbitals are mixing, the σ_{CO} orbital being situated much deeper.

In Figs. 2 and 3 are given the correlation diagrams of the MO energy of aldehydes, calculated using the STO-3G and 3-21G basis sets. The figures show that the nonempirical calculations confirm the appearance of the"perfluoro alkyl effect"[1, 7, 25] established empirically, which means that in case of the CF_3-group substitution for the methyl group all MO of the fixed part of the molecule undergo an approximately parallel shift without changes in their succession or their type of symmetry. It is also worth mentioning that the analogous regularity holds in the spectrum of the MO energies of CCl_3CHO.

At any level of calculations, mixing of the n_O and n_{Cl} orbitals can be detected in the CCl_3CHO spectrum. Calculations with the STO-3G basis set lead to a remarkable stabilization of all MO of the molecule in comparison with the CF_3CHO molecule. These results contradict to the experimental data obtained from the PE spectra. Taking into account a relatively good agreement of the calculations of PES of molecules at this level[19], such a result is quite unexpected. Besides, a tendency of the semiempirical CNDO/2 method to change the IP in case of the substitution should be considered correct. The split-valence 3-21G basis set also characterizes in correct proportions the changing of energy of the highest MO during substitution. The nonempirical calculations at the 4-31G level are generally in agreement with[19] our calculations using the 3-21G basis set. In the work of Kimura, the trans-conformation of the C_s symmetry for the CCl_3CHO molecule has been used. Our calculations revealed that at the STO-3G level, the cis-conformation of the molecule is by 1.5 kcal/mol more stable than the trans-form. The analogous conformation has been observed also in the initial state in case of acetaldehyde and CF_3CHO, the difference in the energies of their cis-and trans- forms being 1.1 kcal/mol and 0.3 kcal/mol, respectively.

Somewhat surprisingly, in the case of CF_3CHO molecule (see Table 1, No 4) the energy of the perpendicular conformation (COH group is turned by 90° relative to the "upper" F- atom of the CF_3 group) is practically equal to the energies of cis- and trans forms. Within the present work, we have also carried out the calculations of the NCCHO molecule whose PES is unknown. The results of different calculations are in good agreement, referring to the mixing of the π_{CN} and π_{CO} orbitals. In case of empirical calculations the role of mixing of orbitals is expressed more clearly than when using the semiempirical HAM/3 technique. The 1st IP of this molecule calculated by the HAM/3 seems to be a bit lowered. Unfortunately the experimental geometry of the molecule is not known either and the HAM/3 calculations were performed applying the optimum geometry, calculated in the 3-21G basis set. It is known[18] that the calculations at 3-21G level excellently reproduce the experimentally established geometry, but in our case the calculation of the $(CN)_2CO$ molecule at this level leads to a too short C≡N bond (1.1375 Å instead of the experimental 1.165 Å).

In our previous reports[7,10,26] as well as in that of Kimura et al[19] it has been shown that in case of a rather good approximation of the successive IP molecule values determined from the PE spectra and the calculated energies of the corresponding MO within the applicability range of the Koopmans' theorem, exists the following linear dependence:

$$IP = a\,\varepsilon_i + b, \qquad (1)$$

where a and b are constants.

Holding of these dependences has been checked in case of the whole set of the molecules studied (see, e.g. Fig.4).

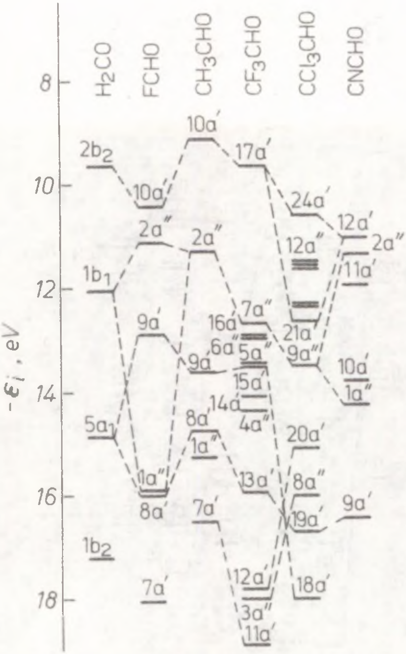

Fig. 2. Correlation diagram of the MO($-\varepsilon_i$) energies of some aldehydes, calculated at the minimal STO-3G level.

The results of their statistical treatment are given in Table 2. The results indicate that although the IP calculated by the Koopmans' method sometimes differ in their absolute values by a few eV compared with the experimental ones, the given relationship is statistically quite well obeyed.

In a number of cases such correlations [7,19] enable us to find in the PE spectra the bands difficult to measure because of the band overlapping.

It can be seen in Table 2 that transition from the semiempirical calculation according to the CNDO/2 method to the nonempirical calculations (even in case of the minimal basis) set) generally gives a spectrum of eigenvalues being in a better correlation with the experimental PES (the slope is

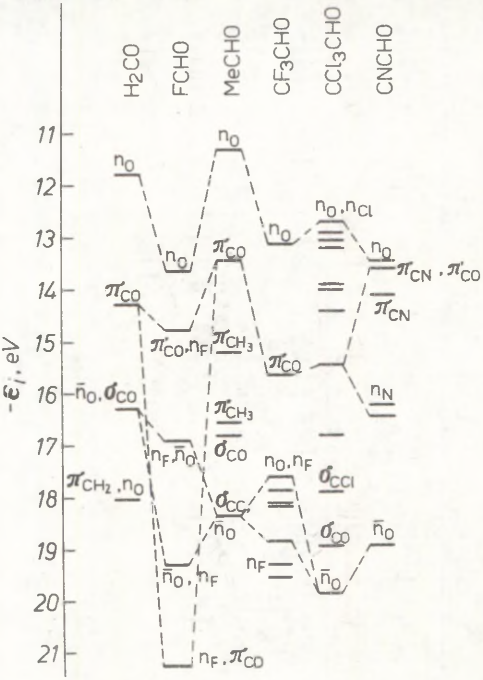

Fig. 3. Correlation diagram of the MO ($-\varepsilon_i$) energies of some aldehydes. Calculated with the split-valence 3-21G basis set.

closer to unity, the intercept and the errors of these parameters are decreasing, but the mean-square deviation does not still give a satisfactory result). Basis set extension in case of the nonempirical calculation of the PES in the framework of the Koopmans' theorem does not improve the situation within the theorem, the split valence 3-21G bases set is close to the 6-31G bases set, as to its accuracy of the PES description. With the nonempirical calculations, progress can be made exceeding the limits of the **Hartree-Fock technique, using either the traditional** CI method as it has been done by Kimura et al[19] or by some

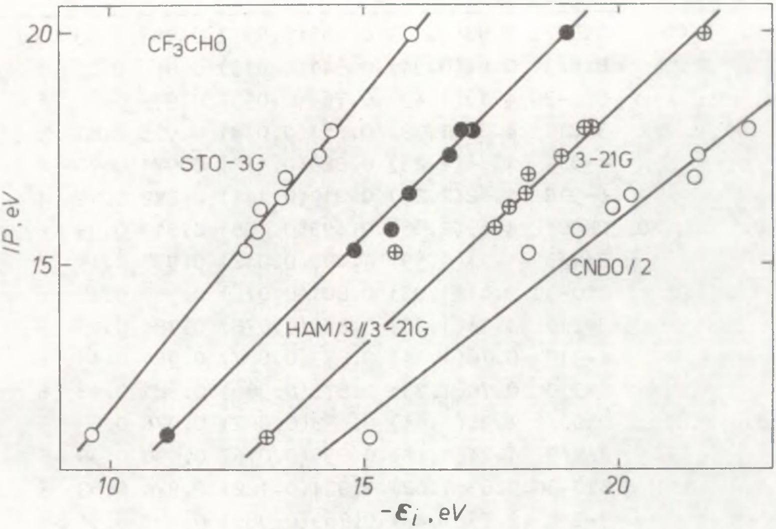

Fig. 4. Comparison of experimental IP_i and the MO($-\varepsilon_i$) energies for CF_3CHO predicted according to various quantum-chemical methods (see Table 2, No 4).

other methods.

Table 2 again confirms a clear prevalence of the HAM/3 technique, specially parametrized for calculation of the PE spectra, not only over the simple semiempirical CNDO/2 method but also over any other nonempirical HF calculations at minimal or split-valence basis set (STO-3G, 3-21G, 6-31G) level applied in the present research. Under other equal conditions, the adequacy of the results of calculation of the PES of small molecules and even anions according to the HAM/3 successfully compete[15,16] with those obtained in calculations using the post-Hartee-Fock approaches.

Table 2

Results of Regression Analysis of Calculated Spectra of the Eigenvalues $(-\varepsilon_i)$ of Various Molecules According to Eq.(1)[*]

No	Molecule	Calculation methods	b	-a	r	s	n
1.	H_2CO	CNDO/2	1.93(2.12)	0.655(0.099)	0.967	1.09	5
		HAM/3	0.64(0.31)	0.941(0.019)	0.999	0.15	5
		STO-3G	4.19(1.43)	0.769(0.095)	0.978	0.91	5
		3-21G	4.26(1.39)	0.651(0.078)	0.979	0.87	5
		4-31G	1.64(2.23)	0.820(0.141)	0.971	0.78	4
		6-31G	1.62(2.23)	0.819(0.141)	0.972	0.77	4
2.	CH_3CHO	CNDO/2	4.69(2.06)	0.499(0.108)	0.917	0.99	6
		HAM/3	-1.11(0.59)	1.098(0.042)	0.997	0.19	6
		STO-3G	3.41(1.03)	0.801(0.076)	0.982	0.47	6
		3-21G	1.16(1.20)	0.850(0.078)	0.984	0.45	6
		4-31G	0.76(1.34)	0.873(0.087)	0.981	0.49	6
		6-31G	0.70(1.33)	0.875(0.086)	0.981	0.48	6
3.	FCHO	CNDO/2	2.38(1.64)	0.678(0.082)	0.978	0.58	5
		HAM/3	1.24(1.18)	0.935(0.076)	0.990	0.39	5
		STO-3G	3.63(1.62)	0.914(0.122)	0.974	0.63	5
		3-21G	2.73(1.48)	0.759(0.085)	0.981	0.54	5
4.	CF_3CHO	CNDO/2	4.82(0.41)	0.566(0.019)	0.996	0.12	9
		HAM/3	0.44(0.41)	0.998(0.025)	0.998	0.15	9
		STO-3G	-0.29(0.55)	1.243(0.041)	0.996	0.20	9
		3-21G	0.84(1.18)	0.862(0.065)	0.980	0.45	9
5.	CCl_3CHO	CNDO/2	0.55(1.07)	0.776(0.063)	0.987	0.44	10
		STO-3G	0.71(0.73)	0.983(0.053)	0.989	0.40	10
		3-21G	-0.33(0.80)	0.934(0.051)	0.988	0.41	10
		4-31G	0.05(0.75)	0.915(0.048)	0.989	0.39	10

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[*] a and b are the regression coefficients of Eq.(1), in parentheses are given their statistic deviations; r is the correlation coefficient; s denotes standard deviation (in eV), n is the number of points in the sample.

Various approximations and basis sets of quantum-chemical calculation have in some cases led to the non-coinciding succession of MO. The calculated distributions of charge densities in a molecule, in the present paper given as the orbital characters, also tend to differ. But if the analysis includes the results obtained by several methods at different theoretical levels, it will not be difficult to trace some general regularities. The comparative complex analysis[7] of the results of such calculations permits to more reliably determine the characters of the MO localization.

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Ab initio LCAO MO CALCULATIONS OF MOLECULES.
V. COMPLEX FORMATION OF ALUMINIUM MONOCATION WITH CARBONYL CONTAINING BASES

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Nonempirical quantum chemical calculation of complex formation energy of aluminium monooation with a number of oxygen-containing bases (aldehydes, ketones) has been carried out applying the Gaussian 80 and Gaussian 82 system of programs (STO-3G, 3-21G and 3-21G*). It is shown that in case of a split-valence 3-21G* polarization basis set, the changes of experimental and predicted relative energies of complex formation between the base and the aluminium monocation practically coincide.

According to the definition, the gas phase basicity (GB) of any neutral base B to the proton is equal to the standard free energy ΔG^o (taken with an opposite sign) of the following reaction:

$$B + H^+ \xrightarrow[\Delta H^o]{\Delta G^o} BH^+ , \qquad (1)$$

where $GB(B) = - \Delta G^o$.

The corresponding value of standard enthalpy (with an opposite sign) of the same reaction is called the proton affinity PA of the same base: $PA(B) = - \Delta H^o$.

The interaction of the Lewis base B (B has a basicity center and it can be either a neutral molecule or a charged particle) with a generalized electrophile E^+(E^+ has a vacant MO) proceeds according to the scheme:

$$B + E^+ \xrightarrow[\Delta H^o]{\Delta G^o} BE^+ \qquad (2)$$

where $GB(B,E^+) = -\Delta G^o$ and $PE(B,E^+) = -\Delta H^o$ (analogous to the proton affinity, the $PE(B, E^+)$ value can be called an electrophile E^+ affinity (e.g., CH_3^+, Al^+, Cu^+, Ni^+ , etc.).

Up to now, the gas phase basicities and/or the proton affinities of approximately 1000 neutral and anionic bases have been determined (see[1-3] for a review). As to the gas phase basicity of the other electrophiles, it is known[4-11] for a rather limited number of bases.

According to the concept of hard and soft acids and bases[12,13], the intensity of interaction between the Lewis bases and acids (see Eq. (2)) can be determined by two characteristics, the "hardness" and "softness" of both partners*. Naturally, the ratio between the hard and soft components for the latter can vary a lot, depending on their chemical nature. But this is equivalent to the change of a formal interaction mechanism of the given acid (base) with bases (acids) of different nature. Therefore, it can hardly be expected that the affinity or the gas phase basicity of bases to the electrophiles having different chemical structures, and consequently, also different hardness and softness, interchange symbatically or even linearly. The same holds also in case of comparison of the affinity and gas phase basicity towards the proton, which is one of the most typical hard Lewis' acids with the affinity or basicity[4-11] towards the electrophiles which are characterized by a contribution of close or even dominating softness of the components into a total energy of the donor-acceptor interaction. Thus, in general, the following linear dependence

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* - The "hard" interaction is often identified with the electrostatic one and the "soft" effect with the covalent interaction.

$$GB(B,E^+) = a + b\ GB(B,H^+) \qquad (3)$$

where a and b are constants.

should be observed only for some limited series of structurally related bases, characterized by the approximately constant relative contributions of hard and soft components in a total variation of the free energy or enthalpy of the donor-acceptor interaction according to Scheme (2).

Table 1.

Comparison of Relative Gas Phase Basicity of Bases to Proton with their Basicity towards Al^+ in the Framework of Eq.(3)[*]

No	Series	a	-b	r	s	n
1.	All points of Fig. 1	10.43 (0.19)	0.675 (0.021)	0.980	1.4	43
2.	Aldehydes, ketones, ethers, nitriles.	9.68 (0.21)	0.650 (0.024)	0.982	1.3	29
3.	Aldehydes, ketones, ethers.	9.6 (0.2)	0.629 (0.029)	0.980	1.4	21
4.	Nitriles	10.6 (0.3)	0.738 (0.027)	0.996	0.6	8
5.	Carboxylic acids, amides, esters	11.98 (0.13)	0.725 (0.014)	0.997	0.6	14

[*] a and b are the regression coefficients from Eq. (3). Their confidence intervals are given in parenthesis. r is the correlation coefficient, s - standard deviation (kcal/mol), n is the number of points.

The aforesaid is illustrated by Figs. 1 and 2 which visualize the dependences between the relative basicity of a number of bases to the hard proton acid[1-3,14] on the relative gas phase basicity to the Al^+ monocation as a relatively hard electrophile on one hand[10,11] (see Table 1) and on the affinity towards clearly expressed soft acid (addition of two ligands to Ni^+), on the other hand.[8]

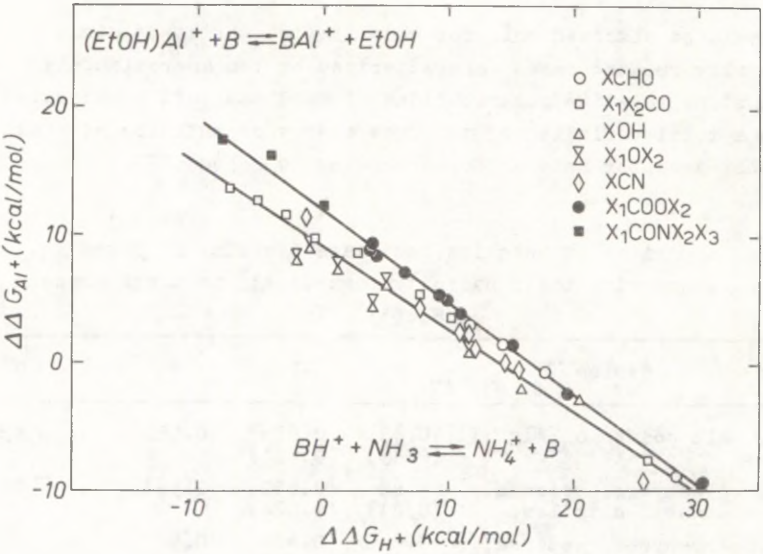

Fig. 1. Dependence of affinities of some oxygen-containing bases to Al$^+$ on their corresponding proton affinities.

In case of a relatively harder Al$^+$ monocation, having the $1s^2 2s^2 2p^6 3s^2$ (^1S_o) configuration,a remarkably more pronounced parallelism between the compared values is observed . According to the correlation statistics of Table 1, the majority of points are concentrated by the two main practically parallel straight lines I and II (see Fig.(1) and Eqs. (2) and (5) of Table 1), shifted relative to each other along the ordinate axis by ≈ 2 kcal/mol.

It should be noted that the situation formally resembles an analogous case when comparing the PA and IP values for oxygen-containing compounds[15]. In both cases the carbonylic

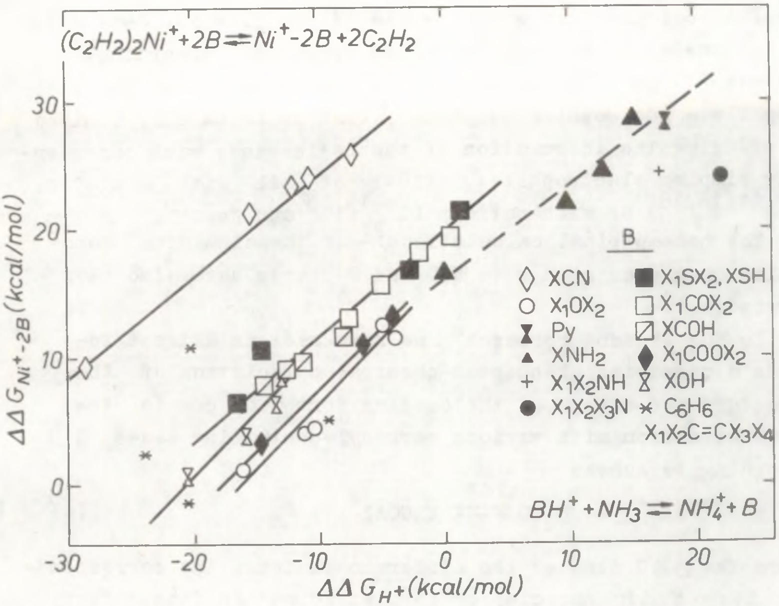

Fig. 2. Dependence of affinities of some bases to Ni^+ (two ligand addition) on their proton affinities.

compounds having the NR_1R_2, OH or OR electron-donor group in the vicinity of the C=O group deviate from the straight line corresponding to ketones, aldehydes, ethers and alcohols.

As to the comparison of the basicity of various bases to the typical soft Ni^+ electrophile, whose basic state has the $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$ (^2D) configuration, with the gas phase basicity to the hard electrophile-proton (Fig. 2), it can be seen that there is no general linear dependence between the compared values but also numerous inversions of "ordinary" series of the gas phase Brønsted basicities of organic bases are observed (see also[8]).

At a high enough level, the modern nonempirical quantum chemical calculations with the aim of quantitative estimation of the energy of complex formation processes according to schemes (1) and (2),and of finding the structure of the electrophile - nucleophile complexes, tend to be usually limited to studying the interaction of the Lewis bases with considerably simpler electrophiles, first of all with a proton (see[14,16,18]) or with cations Li^+ [19,20] and Na^+ [20].

The nonempirical calculations[21] of the aluminium monocation complexes with some N,O and F- bases have also been carried out.

In the present research[*] we have made an attempt towards a nonempirical quantum-chemical calculation of the structure and energy of the complex formation due to the Al^+ interaction with various carbonyl-containing bases B according to scheme

$$BAl^+ + H_2CO \overset{\Delta\Delta E}{\rightleftarrows} H_2COAl^+ + B, \qquad (4)$$

where the $\Delta\Delta E$ denotes the difference between the corresponding ΔE and ΔE^0 energies of complex formation (the entropy term is negligible) of the given (B) and the standard (H_2CO) bases with the aluminium monocation.

The calculations were performed applying the Gaussian 80[22] and Gaussian 82[16,23] program systems. A full optimization of the species geometry was done according to the method of gradients.

The energetics of the process is reflected in Table 2, where for the purposes of comparison with our results, are included also some results of Jorgensen's calculations[21]. Total energies of various molecules and complexes and the basic features of their geometry are presented in Table 3.

It can be seen in Fig. 3 that in case of all bases used, the calculated relative energies of the Al^+ complex formation with the observed bases are in rather good correlation with the corresponding experimental values, measured in the

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[*] A number of preliminary results have been cited in ref.[11].

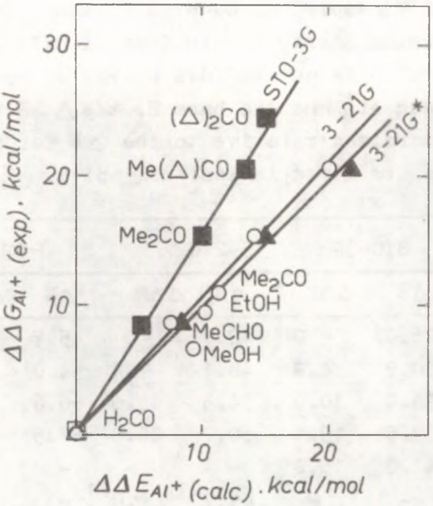

Fig.3. Comparison of experimental free energies of Al^+ complex formation with some bases (standard base H_2CO) and relative complex formation energies calculated by nonempirical methods (the Gaussian-82 system).

basis ■- STO-3G
set: ○- 3-21G
▲- $3\text{-}21G^*$

gas phase by means of the ICR spectroscopy.

The slopes of the corresponding straight lines in the $\Delta\Delta E_{calc}-\Delta\Delta G_{exp}$ coordinates are as follows: STO-3G basis set...0.64;3-21G basis set...0.926, $3\text{-}21G^*$ basis set...1.0.

Consequently, the calculations at the minimal basis set level clearly underestimate the structural effect on the relative stability of the Al^+ complexes with the studied basis, thus leading to the excessively reduced complex formation energy changes resulting from the substitution of the hydrogen atoms in the H_2CO molecule for the alkyl or cycloalkyl radicals.

Table 2

Results of Nonempirical Quantum Chemical Calculations of Equilibrium Energy (4) in Case of Different Bases. The ΔE value is an absolute energy of complex formation between Al^+ and the base B, the $\Delta\Delta E$ value has been standardized relative to the ΔE for formaldehyde. All values are given in kcal/mol units.

Basis set	STO-3G		3-21G		$3\text{-}21G^*$		Experimental
	ΔE	$\Delta\Delta E$	ΔE	$\Delta\Delta E$	ΔE	$\Delta\Delta E$	$\Delta\Delta G$[7,11]
H_2CO	26.0	0	40.7	0	45.7	0	0
MeCHO	30.9	4.9	48.1	7.4	54.0	8.3	8.7
Me_2CO	36.0	10.0	54.3	13.6	60.6	14.9	15.3
cy-Pr_2COMe	39.5	13.5	60.7	20.0	67.5	21.8	21.4
cy-Pr_2CO	41.0	15.0	-	-	-	-	24.4
MeOH	-	-	49.7[21]	9.0[21]	-	-	
Me_2O	-	-	52.0[21]	11.3[21]	-	-	
EtOH	-	-	50.9[21]	10.2[21]	-	-	

A substantial improvement of the agreement between the experiment and the theory was observed if the split-valence 3-21G basis set was employed. A practically absolute coincidence of the experimentally obtained and theoretically predicted structural effects can still be achieved in case of application of the $3\text{-}21G^*$ polarization basis set[16]. The latter is constructed from the previous one adding to the second-row elements six primitive Gaussian functions of d-symmetry.

Transition to a theoretically higher level remarkably influences the above mentioned geometry of the base complex with Al^+. Thus, in case of complex formation with carbonyl containing compounds, the STO-3G basis set predicts that the $\angle COAl$ angle will be ≈ 145°, while in case of the 3-21G and $3\text{-}21G^*$ basis sets this angle is already practically equal to 180°. The Al^+ complexes with carbonylic bases differ by the highly ionic nature of the OAl bond and relatively moderate charge transfer between the interacting components. Thus,

Table 3

Nonempirical Calculation of Structure of Al^+ Cation Complexes with a Number of Carbonyl-Containing Compounds

	System	$-E_{tot}$ (a.e.)			Notes
		STO-3G	3-21G	3-21G*	
1	2	3	4	5	6
1.	a) H_2COAl^+	351.2754	353.6349[a]	353.6760	STO-3G: OAl=2.035Å, CO=1.23Å, CH=1.106Å ∠HCO=121.3÷÷ 122.6°, ∠COAl=144.8° q_{Al}=0.836 a.u., q_{O}^{*} - 0.269 a.u., 3-21G: OAl=1.928Å, CH= 1.077Å,CO=1.234Å, ∠COAl=179.9°, ∠HCO=120.8°, 3-21G*: OAl=1.90Å, ∠COAl=178.9°
	b) H_2CO	112.3544[b]	113.2218[b]		
2.	a) $Me(H)COAl^+$	389.8754	392.4803[a]	392.5227	STO-3G: OAl=1.98Å, CC=1.53Å, CO=1.23Å CH(Me)=1.089Å, CH=1,109Å, ∠COAl=146.6°, ∠CCO=125.3°, ∠CCH=115.7°,q_{Al}=0.810 a.u. 3-21G:OAl=1.89Å, CO=1.245Å, CC=1.475Å, CH(Me)=1.078Å, CH=1.089Å, ∠COAl=178.2°, ∠CCO=124.6°, ∠CCH=117.0°, 3-21G*:OAl=1.86Å, CO=1.248Å,

Table 3 continued

1	2	3	4	5	6
					CC=1.475Å, CH(Me)=1.077Å, CH=1.088Å, ∠COAl=178.9°, ∠CCO=124.4°, ∠CCH=117.7°
	b) MeCHO		152.0553^b		
3.	a) Me_2COAl^+	428.4736	431.3220	431.3651	STO-3G: OAl=1.95Å, CO=1.239Å, CH=1.087Å, ∠CCH=110.9°, ∠CCC=117.3°, ∠CCO=120.3°, ∠COAl=145.1°, q_{Al}=0.7913 a.u., q_O= =-0.324 a.u. $3\text{-}21G^*$: OAl=1.83Å, CO=1.257Å, =1.08~~::~~–1.09Å, CC=1.49Å, ∠CCC=118.6°, ∠COAl=179.6°, ∠CCO=120.7°, ∠CCH=111.6°
	b) Me_2CO	189.5360^b	190.8872^b		
4.	a) cy-Pr(Me)$COAl^+$	504.4230	507.6743	507.7698	STO-3G: OAl=1.92Å, CO=1.23Å, CH=1.08Å, ∠COAl=145.0°, 3-21G: OAl=1.89Å, CO=1.245Å, CC=1.51Å, ∠COAl=177.0° $3\text{-}21G^*$: OAl=1.81Å, CO=1.250Å, CH=1.07Å, ∠CCO=122.2°, ∠COAl=175.4°
	b) cy-PrCOMe	265.4800	267.3260		STO-3G: CO=1.223Å, q_O=-0.233 a.u. 3-21G: CO=1.213Å, q_O=-0.5875 a.u.

Table 3 continued

1	2	3	4	5	6
5.	a) cy-Pr$_2$COAl$^+$	580.3700	-	-	STO-3G: OAl=1.92Å, CH=1.08Å,CO=1.25Å, CC=1.52Å,∠CCO=117.5°, ∠COAl=144.6°, q_{AI}=0.774 a.u., q_O= -0.355 a.u.
	b) cy-Pr$_2$CO	341.4237	-	-	STO-3G CO=1.22Å, C(cy-Pr) C(CO)=1.53Å, CC(cy-Pr)=1.513Å, CH=1.08Å, ∠C(cy-Pr)CO=121.1°, q_O= -0.236 a.u., μ=1.97D.
6.	a) CO$_2$Al$^+$	423.9730	-	-	STO-3G: OAl=2.055Å, CO=1.17Å, ∠COAl= =146.9°, q_{AI}= 0.840 a.u.,q_O=-0.302 a.u.
	b) CO$_2$	185.0681[b]	-	-	
7.	Al$^+$	238.8801	240.3483[a]	240.3814	

a - See also [21]

b - See also [14,17,18]

the average formal charge at the aluminium atom (3G-basis set) in the complexes with H_2CO, Me_2CO, $(\triangle)_2CO$ is ≈ 0.8 electron charge units, but in protonated forms of the latter[18], the positive charge at the hydrogen atom bonded with the oxygen atom is more than twice smaller. The C-O bond in the Al^+-complexes of aldehydes and ketones (1.23-1.25Å) is also only slightly longer than in free bases (1.21-1.22Å), while in case of protonation, our calculations proved it to be ≈ 1.3Å.

It should be said in conclusion that in comparison with studying the proton transfer reaction in the gas phase, both the experimental and especially, the theoretical investigation of the analogous, rather important from the practical and theoretical viewpoints reactions of electrophile transfer (2), has still advanced undeservedly slowly.

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