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REACTIVITY OF THE SIMPLEST RADICAL - THE HYDROGEN ATOM: QUANTUM-CHEMICAL ASPECTS

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The present-day situation and prospects of the quantum-chemical studies of the mechanisms of radical reactions have been discussed on the example of the reactions of hydrogen atom with organic compounds.

I. Introduction

The reactions of the hydrogen atom belong to the simplest prototypes of the radical processes, bordering on several fields of the present-day chemistry. Especially keen interest in them can on one hand, be explained by a monohydrogen simple configuration and wide variation range of the energetic spectrum, and, on the other hand, by the possibility of contrasting of various isotopic versions of the same reactions in order to better understand the mechanism of the processes[1,2].

Quantum chemical studies of these reaction mechanisms are based on the classical works by Heitler, Eyring et al[3,4]. Nevertheless, more reliable and interesting results have been obtained in the last 10-15 years, thanks to a better qualitative level of the experiments, which is connected

with the progress in the field of computing systems and with development of the quantum chemical methods. In the present review, an attempt has been made to illustrate the present-day achievements of quantum chemical studies of the mecha - nism of monohydrogen reaction with organic substrates from detailed calculations of the potential energy surfaces of simple standard systems up to the semiquantitative and qualitative methods of the reactivity indices (RI).

Recently, a tendency towards a more intense application of nonempirical calculation schemes has been observed, latter are well controllable and do not contain any elements of arbitrariness, otherwise characteristic to the semiempirical methods. Still, composing the potential energy surfaces by means of these methods is connected with a number of technical difficulties. First, it is 1-2 times more labor-consuming than the calculations of the geometry of separate molecules: in order to find saddle point of the transition state (TS), it would be expedient to pass the way of the minimal energy between the local energy minimums, corresponding to the equilibrium states of the reagents and reac - tion yield, and/or then to minimize the gradient norm in the vicinity of the suggested saddle point. The procedure will be rather labor-consuming if non empirical calcula - tions are used, needing a lot of computer time and hence it can be justified when solving small problems only. Another complication is the fact that the TS energy can be reliably assessed only if the correlations of electrons are taken into consideration in real ab inito calculations, the saddle point geometry is first found using the minimum basis set after which the geometric and energetic parameters of the TS are specified by broadening the basis set and/or by including correlational effects. A detailed analysis of such calculations, applied to simple organic and inorganic sys - tems e.g. $H + CH_4$, $H + F_2$, $H + NH_3$, $H + NO$, $H + CH_3NH_2$, etc. being very significant from the point of view of modelling of complex chemical and biological reactions, studying of which on the same level is rather difficult, was carried out.

In practice, more economical but less-reliable semiem -

pirical methods are applied, therefore the analysis of their applicability in the case of the problems discussed has also been included. Above all, special attention has been paid to the latest achievements of the index approach, since simple qualitative approaches are more suitable for every-day chemistry practice.

II. Calculation Methods of Radical Systems

The Hartree-Fock[5] approximation is usually used when calculating the electron characteristics of radicals. The multielectronic wave function Ψ of the system, including the ($N = N^{\alpha} + N^{\beta}$) electrons with the α and β spins is approximated with the antisymmetrized product of mono-electron functions φ_i^{α}, φ_j^{β} of molecular spin-orbitals (MO)

$$\Psi = A \det \left| \varphi_I^{\beta} \dots \varphi_i^{\beta} \varphi_I^{\alpha} \dots \varphi_j^{\alpha} \right| \qquad (1)$$

The value of the coefficient A is determined by normaliza - tion of it to a unity.

The molecular orbitals φ_i are to be seeked as the linear combination of the atomic orbitals of χ_{μ} - LCAO

$$\varphi_i^{\varkappa} = \sum C_{\mu_i}^{\varkappa} \chi_{\mu} \quad ; \quad \varkappa = \alpha, \beta$$

where C_i are the coefficients to be found. The basis for their calculation is the variation principle with minimizing the total electronic energy E, thus finally leading to solution of the Hartree-Fock-Roothan[6] equation.

$$\sum_{\mu} (F_{\mu\nu}^{\varkappa} - \varepsilon_i S_{\mu\nu}) C_{\mu_i}^{\varkappa} = 0; \quad i = 1, 2 \cdots N \qquad (2)$$

Solution of the nonlinear algebraic equation (2) applying the iteration method (the method of self-consistent field SCF) yields a set of single-electron MO of ε_i. The $S_{\mu\nu}$ is the overlap matrix of the atomic orbitals of χ_{μ} and χ_{ν}.

For calculation of the systems with open electronic shell, a single-determinant wave function is often applied where different spacial elements for the spin orbitals of φ_i^{α} and φ_i^{β} are often used. Free variation of the orbitals by solving the system of equations (2) with $\varkappa = \alpha$ and β leads to the approximation of the unrestricted Hartree-Fock method (UHF).

Alongside with the UHF, the symmetry-restricted Hartree-Fock (RHF) method and the semielectronic Dewar[8] method have been widely used for calculation of free radicals. Within these methods, the occupied MO fall into two groups corresponding to the closed (twice filled) and open electronic shells. In the case of the calculations by the RHF methods, the equations of type (2) include nondiagonal Lagrangian products connecting the closed and open shells, which complicates their solution and brings about the difficulties characterizing the SCF prooess (see, e.g.[9]). In the semielectronic Dewar method, the molecular orbitals are selected by minimizing expression $E + I/4(\mu\mu|\mu\mu)$, where $(\mu\mu|\mu\mu)$ is the Coulomb integral for single occupied MO. The calculations for definite radical and triplet systems have shown[10,11] that the UHF and the semielectronic methods yield close results.

The major problem determining the computing time necessery for the calculations and, thus, also the calculation cost, is connected with calculation of the multicenter integrals $(\mu\nu \mid \lambda\sigma)$. Their total number depends on the size of the basis set N being $\sim N^4/4$. The problems connected with selection of the optimum basis set have been discussed in reports[12-15].

The above-mentioned (nonempirical or ab initio) methods quite well reflect the properties of molecules depending on the charge distribution, i.e. the equilibrium distances , dipole and quadrupole moments, etc. Nevertheless, being a single-particle approximation, the Hartree-Fock method does not adequately convey the energetic characteristics of the systems. Although the relative error in calculation of the total energy is rather insignificant, its value is close to

that of the bond dissociation energy in a molecule. Evident neglection of the Coulomb interactions of electrons with oppositely directed spins leads to the so called "correlation" errors. To the time being, a large number of various methods for estimation of the electronic correlation energy have been created; their review can be found in[13, 15-18].

During the nonempirical calculations of the monohydrogen reactions, configurational interaction (CI) is usually taken into consideration. A full wave function appears to be in the form of a linear combination of antisymmetrized products of the Slater determinants

$$\Phi = \sum_k C_k \Psi(k) \qquad (3)$$

The solutions of Eqs. (2) have usually been employed as the wave functions $\Psi(k)$ for the virtual orbitals. Since the configuration series is a convergent one the calculations are the more accurate, the larger the number of configurations taken into consideration. Convergence is perceptibely improved in the case of simultaneous variation of orbitals and the C_k coefficients in the configuration series (3), the method of multiconfigurational SCF is used.

There are different ways of selection of more essential configurations using the methods of configurational interactions[19-24] since the double correlations constitute the major part of the correlation energy of electrons[21], it would in some cases be sensible to form the multiple-electron wave function from two-electron functions - geminales. In Ref.[22], grouped paired configurational functions (PAIR ... CI) have been used, any of which includes rearrangements in a definite pair of occupied spin-orbitals. The coefficients of the determinants are fixed at the values found on the basis of the perturbation theory. This theory has also been used for estimation of the contributions of various configurations[19,20]. Together with the above-mentioned version of the CI method, the approximation of the connected electron pairs, applying the paired natural or -

bitals of the PNO-sulfur[25-27] has also been used for studying the reactions of hydrogen atom . A review concerning the theory of the electron pairs employed for calculation of correlation energy can be found in[28]. In a number of cases, the CI calculations are based on the orbitals obtained in the framework of the generalized method of strictly orthogonalized valence bonds (POL-CI(SOGVB)[29,30]. The nature of the latter is quite close to the MO method, its advantage being in considering the intra-pair correlation which enables us to correctly treat the atomic hydrogen reactions.

In order to study the reactivity of practically significant chemical and biological systems, approximate semiempirical methods, most often that of zero differential overlap have been widely used; see, e.g.[31-34]. Without dwelling upon the details of these methods, it should be mentioned that they mainly differ in their degree of consideration of the interaction integrals and in the way of introduction of the empirical parameters. The methods of complete neglect of differential overlap take into account the integrals of type $(\mu\mu/\nu\nu)$, while those with partial neglect of differential overlap include additional single-center integrals $(\mu_A \nu_A/ \lambda_A\sigma_A)$, thus making it possible to take into consideration the spin polarization of electrons, which is inevitable for studying radical systems.

To investigate the potential energy surfaces, in particular those for the radical reactions, the MNDO[35-37] methods and MPNDO[36,38] worked out by Dewar et. al have been widely used. In these cases, parametrization has been aimed at as accurate as possible calculation of the largest number of physical properties. Thus, these methods have found wide recognition in finding the formation heats, ionization potentials, stability of free radicals and reaction heats.

III. Studies of Potential Energy Surfaces

I. Investigation Methods of Potential Energy Surfaces

Before analyzing the results of our research in the field of the mono-hydrogen reactions of potential energy surfaces, one should give a short review of the situation concerning the methods of calculation of stationary points of multidimentional surfaces of potential energy.

The potential energy surface $V(q_i)$ is the function of the 3N-nuclear coordinates or (3N-6) the degrees of freedom. The initial compounds and the reaction products correspond to the local minimums of the function. Furthermore, the local minimums of this function can correspond to the intermediates and to the products forming in the case of other reaction routes. The more stable configuration corresponds to the global minimum.

It is characteristic to the local minimums on the potential energy surfaces that the first energy derivatives from all inner coordinates are equal to zero, while the curviture of the surface $F_{ij} = (\delta^2 E/\delta x \delta y)$ is positive in any direction. The saddle point, in whose case the minimax condition is satisfied, corresponds to the transition state on the potential energy surface. For finding the stationary points on the potential energy surface the methods of variable metrics[39-41] were more often used. These methods allow to find the enhanced geometry of X^{n+1} according to the data on the initial system X^n by means of the recurrent relationship.

$$X^{n+1} = X^n - \alpha_n A^n g^n ,$$

where g^n is the energy gradient. The methods of variable metrics differ from each other by determining the scalar value α_n and the symmetrical matrix A^n. The authors of report[41] have formulated a series of conditions which must be satified by point q, corresponding to the transition

state. They have also worked out an algorithm enabling rather precisely to locate the saddle point position, simultaneously determining, whether it corresponds to the transition state or if it is a local minimum .

As the expected coordinate, the authors[41] suggested to use either the length of the breaking bond or the angle variation, characteristic to the present reaction. Another method has been suggested in[42,43]. These are the so called "linear internal coordinate ways", determined by a set of internal coordinates

$$q(\lambda) = q^{p} - \lambda(q^{np} - q^{p})$$

In the case of changing the linear parameter λ from zero to one, the coordinates undergo changes from q^{p} (characterizes the reagent) to q^{np} (characterizes the product). The energy and the limit of its gradient δ, should be studied both from the point of view of the minimum and maximum values. The state of double minimum for δ when the value is equal to zero simultaneously in the case of transition from the reagent and from the product, is used for the initial estimation of the geometry in the minimization according to the least squares method. This idea has been developed by Lipscomb et al[44] who used the Cartesian coordinates, avoiding the calculation of the gradients. In[45], a pseudokinetic way of the reaction coordinates determination using the least motion method has been suggested . In this case not the breaking bond length but the distance between the gravity centers of the fragments has been taken for the reaction coordinate. The authors of Ref.[46] have suggested an algorithm for search of the stationary points of the PES. It is based on the parabolic approximations of the surface sections with calculation of the gradient and the Hessian. An analytical procedure has been realized in[47] for the ab initio calculations. Analytical calculations of the MC SCF force constants has been carried out by the authors of[48].

These procedures can mainly be used in the case of the

semiempirical calculation methods. In connection with that a number of methodological problems have arisen, which will be discussed in the next part. We should like only to draw attention to certain difficulties arising during the selection of the open shell calculation method. Remember that in the "half electron" formalism the molecular orbitals are selected by minimization of the $E + 1/4(\mu\mu|\mu\mu)$ value and not of the total electron energy E[7]. The molecular orbitals found are not identical with those obtained at the minimization of E, thus not being invariant to slight geometrical changes. As a result, complete self-consistent field calculations for each point of the potential must be carried out, which needs more computer time. To avoid it, the formalism of the UHF method (see, e.g.[49-51]) enabling to calculate the energy derivatives could have been emp - loyed. Nevertheless, in this case the calculation time would extend even more thanks to the doubling of the diagonali - zing matrixes (for the α and β electrons). In addition to that, the wave function of the UHF method does not ap - pear to be the eigenfunction of the square of the full spin S^2. Application of the projection operators enabling one to eliminate from the UHF the additional compounds having somewhat higher multiplicity is quite labor-consuming, demand - ing a lot of computer time. Thus, in several cases these two methods can be successfully combined. Numerous calculations conducted according to the semielectronic method have shown that finding the formation heat for the radicals is in keeping with the experiment (see[10,11]).

2. Basic Mechanisms of Monohydrogen Reactions

The reactions of monohydrogen (T) with polyfunctional organic compounds can be described by means of the follow - ing basic schemes:

1. Breaking reaction of the functional group X or atom H.

$$RX + T \longrightarrow R + XT \qquad (4)$$

2. Substitution of the group by either the configu - ration inversion or by maintaing the symmetry of the attacking center:

$$RX + T \longrightarrow RT + X \qquad (5)$$

3. Addition to the unsaturated bond

A. Reactions of Removal of H atom

The reaction $T + CH_4$ is the best studied organic system from both the theoretical and experimental points of view, thus enabling us to compare not only the adequacy of various quantum-chemical approaches but it also serves as a good example of stereochemical realization of transition states having different structures. Therefore, this example deserves to be studied in a more detailed way.

The system contains a reversible reaction

$$CH_4 + T \rightleftharpoons TH + CH_3 \qquad (6)$$

and the exchange reaction

$$CH_4 + T \longrightarrow CH_3T + H \qquad (7)$$

In accordance with the experimental data, reaction (6) is an exothermic one ($\Delta Q = -0.3$ kcal/mole), proceeding at the activation energy E_a, whose value belongs to the range of 4.5-12 kcal/mol, depending on the conditions of an experiment[52-54].

A thermoneutral exchange reaction proceeds in the presence of the so called "hot" atoms. The threshold of the reactions of the photolytically generated "hot" tritium atoms equals 35-40 kcal/mole[55] in the $T + CD_4$ system.

The results of the potential energy surface calcula - tions of reaction (6) applying various semiempirical and

nonempirical methods have been collected in Tables 1 and 2. In all papers we have discussed similar models of axial attack (a) (see Fig.), first used by Eyring et al.[4].

Supposedly, the hydrogen atom (T) is drawing colinearly nearer to one of the C-H bonds of methane, the C_3 symmetry being retained during the reaction. It can be seen from the data of the Tables that nearly all semiempirical methods predict that the potential energy minimum is situated on the potential energy surface, while numerous ab initio calculations refer that on the potential energy surface there exists a single saddle point which corresponds to the transition state of the reaction. In this case the transition state is localized in the output channel of the surface and its geometric structure does not that much depend on a selected basis set and on the consideration of correlation effects than the barrier value. Thus, for instance, inclusion of even a limited configurational interaction (692 configurations) leads in the case of the symmetrical RHF method[60] to a steep, almost double, decrease of the barrier height. If there are no restrictions concerning the spin (the UHF method[61])(they were removed because of a partial estimation of correlation), the height of the barrier decreases by 9 kcal/mol compared with the symmetrical RHF method calculations in the same basis set[60]. Taking into account the polarization functions of hydrogen - 2p and carbon - 3d does not improve the results either (the difference is 0.8 kcal/mol only; see Table 2). It it interesting to mention that the calculations conducted by the PAIR-CI method with inclusion of polarization functions, making use of 18271 excited configurations[62] reveal an unexpectedly small change of calculation results by means of the RHF and CI method[60]. Evidently, the spin-polarization effects, which have been directly considered as well as the approximations of the UHF method can also be described by means of the RHF and CI methods with once and twice excited configurations. Table 2 shows that the calculations[30] based on the application of the generalized method of valence schemes, and taking into account the polarization functions and correlation of electrons POL-CI (SOGVB) agree

the best with the experiment. A fairly flexible basis set was used in the present study (see Table 2). The internal correlation has also been taken into consideration, thus ensuring the correctness of the obtained results. The error of the POL-CI method for the CH_5 system from its comparison with the reference reaction $H + H_2$, which was studied within the limits of the Hartree-Fock base was found to be about 2.4 kcal/mol.

Table 1

Characteristics of Stationary Points of the Potential Energy Surface of Reaction (6). Semiempirical Calculations*

Method	E** kcal/mol	Structural parameters R_{tH} Å	R_{CH} Å	R_{CH_3} Å	θ degree	Q kcal/mol	Ref.
the Eyring method	9.5	1.40	1.17	1.09	105.0	-7.4	4
	-7.6	0.95	1.22	-	-	-	
	6.0	0.80	1.55	-	-	-	
the modified Eyring method***	8.1	1.40	1.20	-	109.5	-5.3	53
	-4.0	0.80	1.30	-	-	-	
CNDO/BW-UHF	-13.0	0.50	1.10	1.09	109.47	-	59
PNDO-UHF	75.0	0.91	1.56	1.09	109.47	-15.7	59
CNDO/2	-12.3	0.70	1.13	1.12	109.9	-44.0	57
MPNDO/3	2.25	1.40	1.12	1.10	108.7	-2.4	56
	-2.21	0.87	1.22	1.10	106.98		
	-0.2	0.76	1.69	1.09	101.15		
PNDO-UHF****	-8.3	1.2	1.11	1.10	108.5		56
CNDO/2-UHF****	-8.7	-	-	-	-		56

* - for symbols see Fig., a.

** - E - relative energies of stationary points. Negative barrier refers to a stable intermediate.

*** - the method similar to finding the parameters D in the Morse equation was used.

**** - recalculation of the minimal energetic way (MEW) obtained by means of the modified partial differential overlap/3 method[56].

Table 2

Characteristics of Stationary Points of Potential Energy Surface of Reaction (6). Nonempirical Calculations

Method, basis set	Structural parameters					ΔQ kcal/mol	Ref.
	ΔE kcal mol	R_{tH} Å	R_{CH} Å	R_{CH_3} Å	θ degree		
1	2	3	4	5	6	7	8
RHF-STO-3G	37,5	0.87	1.37	1.08	109.5	14.0	60
RHF-STO-4-31G	35.2	0.86	1.42	-	-	6.71	60
RHF-STO-4-31G+CI	18.0	0.95	1.48	-	-	2.11	60
UHF-STO-4-31G	25.0	0.93	1.38	1.077	103.6	4.5	61
UHF-STO-4-31G+$2p_x^H$ +3	24.2	0.83	1.22	1.10	-	3.2	61
UHF-$3G^X$	25.8	0.87	1.22	1.10	106.9	-	56
UHF-STO-4-$31G^X$	26.6	-	-	-	-	4.5	56
UHF-STO-6-$31G^X$	26.6	-	-	-	-	3.3	56
PAIR-CI	17.7	0.90	1.38	-	103.5	3.3	52
UHF-$(NO^S5p1^d/5^S1p)/5^S1p)/5^S2p1^d/2^S1p$+CI	17.7	-	-	-	-	3.1	62
UHF-STO-6-31G	24.74	0.934	1.363	1.077	104.3	3.32	66
UHF-CI(CIPSI-INO)	16.19	-	-	-	-	-0.10	66
POL-CI$(9^S5p/4^S)3^S2p/2^S$	18.7	0.92	1.48	1.08	102.8	6.8	30

Table 2 continued

1	2	3	4	5	6	7	8
(SOGVB) $(9^s5p1^d/8^s1p)/3^s2p1d/2^s1p)$	16.2	0.92	1.47	-	102.4	5.3	30
$(11^s6p2^d/5^s1p)/4^s3p2^d/3^s3p$	15.9	-	-	-	-	5.2	30
Empirical[xx]	16.9	0.91	1.84				63
Modif. LEPS[xx]	5.6	0.74	1.60				64

[x] - recalculation of EPM obtained by means of MPNDO/3

[xx] - dynamical calculations using potential energy surfaces

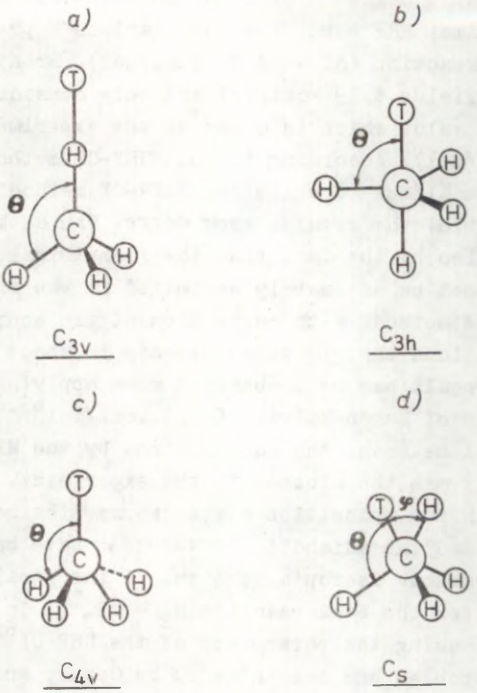


Fig. Geometry of the CH_4T complexes:
a - model of axial break of the H atom;
b - transition state of the reactions with inversion;
c - transition state of pseudorotation;
d - transition state of the reaction maintaining the configuration.

As to the calculated energies of the isolated reagents, determining the values of thermodynamic parameters, they to a considerable degree depend on the basis set quality. Thus, in the minimal RHF base, the calculations[60] predict an endothermic reaction (ΔQ = 14.01 kcal/mol). Broadening of the basis set yields 6.79 kcal/mol and only consideration of the CI gives a value which is close to the experimental one (2.11 kcal/mol). According to the HUHF-CI method, this value is 3.1 kcal/mol[62], while the PAIR-CI method yields 3.3 kcal/mol, i.e. the results grow worse. The authors of[62] explain it also by the fact that the geometrical parameters of CH_3 cannot be adequately estimated in the framework of the applied method. With correction of the energies of the zero-deviations the ΔQ value amounts to about 1.5 kcal/mol. The best result has been obtained when applying the iterative scheme of Huron-Malrieu (-0.1 kcal/mol[65,66]). Among semiempirical methods, the calculations by the MPNDO/3 (-2.4 kcal/mol[56]) are the closest to the experiment.

Within the transition state theory, the reaction rate constants and the adiabatic thresholds have been calculated both for various isotopic versions of the straight line H + CH_4[67] and for the back reaction H_2 + CH_3[70]. On the nonempirical level, using the parameters of the UHF-CI[62] saddle point the same problem has been studied by Čarsky and Zahradnik[68]. Force constants were calculated according to the UHF method in the 4-31G basis set. The distribution functions of the reagents and activated complex were determined according to the statistical weight of the basic states of these systems. This was proved by the fact that the lowest excited state of the structure C_{3V} - the transition state reaction (5), found by means of the CNDO/C[68] method has a rather high energy as regards the basic state. The theoretically and experimentally found rate constants of reaction (6) agreed quite well with each other in a large temperature range.

The trajectory calculations on various PES have been carried out in [63,64]. The analysis of these data and the results of direct calculations of the reaction rate constants for the PES POL-CI (SOGVB) have been given in [70].

If at high temperature values the rate constant found in [68] agrees with the experiment, at room temperature it is overestimated 30 times. Taking into account the tunnel correction[71], according to the Yakubets method[72], their difference decreases about 5 times. The author of [71] considers that in the UHF-CI calculations, overestimation of E_a by 1-2 kcal/mol explains the remaining disagreement. In the case of calculation of the pre-exponential factor in[70], the frequencies of normal vibrations were found in harmonic approximation, the tunnel corrections were made according to Wigner[73]. Comparison of the temperature dependencies of the calculated rate constants with the experiment leads to the conclusion that the optimum E_a value ensuring the best agreement with the experiment is 12.5 kcal/mol.

The studies of various isotopic versions of reaction (6) have shown that the H-separation prevails over the D-break in the reactions H + CH_3D and H + CH_2D_2[70]; but in the case of the H + CHD_3 reaction, at 700°K the corresponding rate constants K_H and K_D are equal, while at temperatures lower than 700°K $K_H > K_D$, and higher than 700° K - $K_H < K_D$.

Some progress has also been made in studying the monohydrogen reaction with more complex organic compounds. A tendency to change the transition state characteristics in a series of substituted methane has been studied in papers[56, 74-76]. The semiempirical MPNDO/3 method with a full optimization of geometrical parameters together with a limited number of nonempirical UHF calculations using various basis sets have been employed for studying the PES. Similarly to the ab initio calculations, the MPNDO/3 method predicts the existence of a single saddle point corresponding to the transition state for the H-separation reactions in all cases studied, the H + CH_4 system excluded (see Tables 3, 4). The data of the tables refer to the agreement between the methods, concerning the transition state localization. In both cases the transition states have been localized in the input channel of the reaction. This conclusion also fits the empirical principle of Hammond[77], which says that the barrier of the exothermal reaction has been shifted to-

Table 3

Transition State Characteristics of Reactions RH + T ⟶ R + HT, Calculated by MPNDO/3 Method[76]

R	E kcal/ mol	ΔQ kcal/ mol	Δr_{AH} Å	Δr_{TH} Å	q_A e	q_H e	q_T e
CH_3	2.25	2.4	0.03	0.73	0.046	0.030	0.070
$HOOC-CH_2$	4.92	11.4	0.04	0.63	0.063	0.073	-0.072
H_2N-CH_2	5.24	28.5	0.06	0.71	0.199	-0.002	-0.112
$H_2N \diagdown CH$ $HOOC \diagup$	9.27	41.6	0.09	0.59	0.075	0.048	-0.120
$H_3N^+ \diagdown CH$ $OOC^- \diagup$	9.44	27.6	0.05	0.66	-0.091	0.059	-0.134
H_3C-NH	7.09	10.8	0.02	0.56	-0.124	0.108	-0.116
H_3C-COO	25.03	-11.1	0.44	0.06	-0.481	0.111	-0.052

$x - r_{AH} = r^{nc}_{AH} - r^{o}_{AH}$, where A is the central atom, connected with the reacting hydrogen atom. Charges are marked by symbols q_A, q_H and q_T.

Table 4

Transition State Characteristics of H Break-off, Calculated Nonempirically Using the Minimum Energy Way, Obtained by MPNDO/3 Method[76]

R	ΔE kcal/ mol	ΔQ kcal/ mol	r_{AH} Å	r_{TH} Å	q_A e	q_H e	q_T e
CH_3^{*}	26.9	-3.2	0.12	0.12	-0.494	-0.037	-0.011
$H_2N-CH_2^{*}$	8.6	-3.6	0.06	0.02	-0.070	0.310	-0.003
$HOOC-CH_2$	49.0	-19.1	0.03	0.02	0.060	0.006	0.025

* - the STO-4-31G basis set

** - the STO-3G basis set

wards reagents along the coordinate. Thus, the parametrization errors of the MPNDO/3 method (in particular, the affinity of the electron is usually overestimated in the case of this method) can usually be observed only for "small" systems of the $H + CH_4$[56] and $H^- + CH_4$[78] types. Nevertheless, the errors become less remarkable at transition to more complicated systems (a kind of basis extension), excessive stationary points at the PES disappear[74,78]. According to the analysis of the change of the electron structure of the reaction centers in the substituted methane series, there is no correlation with the ΔQ values[76]. As it was expected, the electronic characteristics do not belong to the intermediate ones in the case of these systems. This is caused by the appearance of the transition state polarization effects, especially remarkably expressed for the reactions of aminoderivatives. The polarity increase of the transition state which is to ensure the appearance of the long-range Coulomb force brings about the barrier lowering and the transition state shift towards the reagents. The characteristics of the molecular and zwitter-ionic forms of glycine[76] calculated according to the MPNDO methods do not significantly differ (Table 3). This conclusion is rather important, since it forms the basis for the transfer of the transition state structure from the calculation of the molecular model systems to the more complicated bipolar significant systems, particularly so when calculating the dynamical reactivity indices[79] (see part U of this review).

It should be mentioned that the MPNDO method conveys quite well the energy profiles of the reaction of the break-off of the H-atoms, directly connected with hetero-atoms (N-H, O-H). The high barrier of the H-break-off of the carboxylic group (25 kcal/mol[76]) refers to the low reaction rate in comparison with the separation of the H-atom of the CH_3 group. It is worth mentioning that the transition state geometry stands closer to the results of the nonempirical calculations[56] of the H-break-off reactions in methane (Tables 2,3). But, in the case of a similar amino group reaction, a considerably lower activation barrier (7.09

kcal/mol[74]) must be surpassed. The average E_a value for the break-off of the hydrogen atoms of the methyl and amino groups are in good agreement with the experiment (5.3 kcal/mol[80], 9.1±0.8 kcal/mol[81]). In the recent nonempirical calculations[82], the value of an analogous barrier in the reaction H + NH_3 within the POL-CI/6-31G method has been estimated to equal 13.6 kcal/mol. This corresponds to the semiempirical data[74] for methyl amine, all the more that the transition state structures are very close. See Table 5, which gives also the structural parameters of the transition states of the reactions H + H_2, CH_4 + H, NH_3 + H, PH_3 + H[82]. The barrier values of the reactions H + SiH_4 and H + PH_3, obtained by means of the above-mentioned nonempirical method equal 5.3 and 1.6 kcal/mol, respectively.

B. Substitution in Model System H + CH_4

From the stereochemical point of view, another peculiarity of the H + CH_4 system is the fact that the transition states having principally different high symmetry structures corresponding to various reaction channels, can be realized within it. This side of the problem has been thoroughly studied in several works both from the experimental[83] and theoretical[30,56,60-62] standpoints. The more general stereochemical conclusion, based on the experiments with substituted methane[83] says that in the reaction

$$T + CH_4 \longrightarrow TCH_3 + H$$

the tetrahedral configuration is prevalently maintained, thus, it does not proceed according to the Walden inversion as in the reactions of nucleophilic substitution[84].

Probable stationary points of reaction (7) are the CH_5 structures of the D_{3h} symmetry (the mechanism of the Walden inversion), C_{4v} (mechanism of configuration maintenance funtions via pseudo-rotation, see above) and C_s (configuration maintenance in the course of direct displacement), presented in Fig., b-d.

The D_{3h} structure which is realized during the tritium attack from the rear side at the C-H bond of methane has been already studied by Eyring in the framework of the semiempirical method[4] suggested by him. The estimated barrier height is 37 kcal/mol, thus being in agreement with the later obtained experimental threshold value of this reaction (35-40 kcal/mol)[55]. As it has already been mentioned, the exchange reaction usually proceeds with configuration maintenance. Therefore, afterwords were calculated the above-mentioned structures, the expected saddle points of the PES, chosen analogously to the CH_5^+ and CH_5^- calculations[85-89]. The results of the calculations obtained by means of various methods are given in Table 6. Detailed nonempirical calculations show that all symmetrical CH_5 structures have much higher energy level than the reagents, while in all cases the D_{3h} structure is by 20 kcal/mol more preferable, i.e., most probably, it is the Walden inversion that contradicts the above experiment. This conclusion is also supported by the analysis of normal shifts of the optimized D_{3h} struture calculated by the UHF method[61]. Thus, all force constants, except those, corresponding to the shifts being in interaction bacause of the inversion, have positive values, while the vibrations are imaginary, as it was actually expected if the transition state of the D_{3h} symmetry were the local maximum.

As to the two other structures (C_{4v} and C_s), within the UHF[61] method the energy of the conformers is approximately equal to the C_4, being by ≈3 kcal/mol more stable in contrast to the results obtained using the RHF method[60], in the case of which the C_s structure is reported to have a better stability (Table 6). The data of Table 6 also reveal certain indifference of the saddle points geometry to the basis chosen. At the same time, as in the case of reaction (6), the barrier height is sensitive both to the basis set and to the way of consideration of electron correlation. It is interesting to mention that the RHF-CI[60] and UHF-CI[62] methods yield rather close inversion barrier values, while without the CI, the difference is 9 kcal/mol.

Table 5

Transition State Characteristics of $XH_{n+1} + H \longrightarrow XH_n + H_2$. The E values are calculated by POL-CI/6-31G + $p^{x\ 82}$ method

XH	ΔE kcal/mol	R_{HH} Å	R_{XH} Å	Notes
H_2	13.2	0.930	0.930	
CH_4	17.6	0.924	1.362	θ = 104.2 , R_{CH_3} = 1.079
SiH_4	5.3	1.041	1.685	
NH_3	13.6	0.967	1.232	NHH = 162°, HNH = 102.6°
PH_3	1.6	1.534	1.178	PHH = 172°, HPH = 93.5°

x - polarization functions

Table 6

Characteristics of Stationary Points of the PES of Reaction (7). Structure of the D_{3h}^{x} Symmetry

Method	R_{TC} Å	R_{CH} Å	ΔE kcal/mol	References
RHF-STO-3IG	1.320	1.094	82.6	60
RHF-STO-4-31G	1.349	1.086	63.7	60
RHF-CI	-	-	41.7	60
RHF-STO-4-31G	1.452	1.074	54.6	61
+ $2p^H$	1.401	1.077	54.3	61
+ $3d^C$	-	-	54.9	61
RHF-CI	1.360	1.100	42.8	62
PNO-CEPA	1.360	1.090	41.6	26
POL-CI(9s5p/4d)/3s2p/2s	1.440	1.080	41.5	30
(9s5p1d/4s1p)/3s2p1d/2s1p	1.410	1.080	37.6	30
(11s6p2d/5s1p)/4s3d2d/3s3p	-	-	36.9	30
CNDO/2	1.119	1.140	-31.5	57
MPNDO/3	1.170	1.120	0.6	56

Table 6 continued

The C_s and C_{4V} Symmetry Structures

Method	R_{TC} Å	R_{CH} Å	Θ^x degree	γ^x degree	ΔE kcal/mol	Ref.
			C_s structure			
RHF-STO-3G	1.322	1.088	109.47	72.4	109.2	60
RHF-STO-4-31G	1.322	-	-	-	86.6	60
RHF-CI	1.360	-	-	71.2	64.2	60
UHF-STO-4-31G	1.378	1.092	105.1	72.6	77.1	61
+ $2p^H$	1.317	1.100	104.1	73.7	74.6	61
MPNDO/3	1.851	1.859	103.2	23.0	1.6	56
CNDO/2	1.210	1.138	105.1	67.7	-28.7	57
			C_{4V} structure			
RHF-STO-3G	1.088	1.090	103.0	-	112.0	60
UHF-STO-4-31G	1.198	1.081	86.2	-	74.7	61
+ $2p^H$	1.187	1.083	86.0	-	71.8	61
MPNDO/3	1.110	1.151	108.6	-	0.7	56
CNDO/2	1.125	1.172	83.6	-	-31.4	57

x - see figure for symbols

The authors of[62] connect it with the significance of consideration of the spin polarization effects in the case of calculation of such structures. Inclusion of the 2p- and 3d-polarization functions on the H and C atoms into the UHF wave function does not practically affect the energy of the D_{3h} and CH_4 symmetry structures; the energy of the structures of the C_{4V} and C_s symmetry drops by ≈ 3 kcal/mol:

$$|\Delta E(C_{4V})| \approx |\Delta E(C_s)| > |\Delta E(D_{3h})| \approx |\Delta E(CH_4)|$$

i.e. the inclusion of these parameters mainly stabilises the systems with low symmetry.

In contrast to the results of nonempirical calculations[25,60-62], the results obtained via the CNDO/2 method, using the Wiberg parametrization[57] show that the studied structures appear to be the local minimums. Nevertheless, the calculations enable us to derive the correct relative stability of the D_{3h} conformer.

$$E(D_{3h}) < E(C_{4V}) < E(C_s)$$

The authors of report[57] have also studied the process of maintaining configuration using the Berry[90] pseudo-rotation, which is actually similar to that of the five-coordinate trigonal-bipyramidal complexes (for a few assessments concerning the level of liability to pseudorotation, see[91, 92]). Among other things, a conclusion has been drawn about the possibility of the configuration inversion by means of two pseudorotations of the same type. Nevertheless, according to[93], the structure C_{4V} can function as the transition state only in the case of pseudorotation of two D_{3h} structures (having the smallest energies), which in their turn, are the transition states of the process of inversion. In report[57] the energy minimum does not correspond to the symmetrical D_{3h} structure, but to the C_{3V}, where $\Theta = 115.5^{\circ}$ (see Fig., b).

The analysis of the eigenvalues and eigen-vectors of the matrices of force constants within the MPNDO/3 method with optimization of all internal variables[56] shows that the D_{3h} structure, whose energy exceeds that of the reagent by 0.6 kcal/mol, should be considered a local minimum in the pseudorotation $D_{3h} \rightarrow C_{4V} \rightarrow D_{3h}$.

Thus, the ab initio (Table 6) calculations refer to the favorable inversion mechanism. Maintenance of the configuration by the carbon center that has been observed experimentally, is usually connected with prevalence of certain dynamic factors in the course of the reaction[63,64]. In the trajectory calculations, on the semiempirical PES, the barrier is supposed to be ~40 kcal/mol[63], while on the semiempirical level its estimated value is 50 kcal/mol[64].

In calculation of the exchange reaction constants, the D_{3h}[69] structure was used. The adiabatic threshold of the reaction calculated for the surface found by means of the POL-CI (SOGVB)[70] method agrees excellently with that of experiment (34.5 kcal/mol).

C. Substitution of Functional Groups.

The substitution of group X can basically proceed according to two mechanisms:

the direct removal (elimination) reaction

$$RX + T \longrightarrow R + XT \qquad (8)$$

and the displacement reaction

$$RX + T \longrightarrow RT + X \qquad (9)$$

Various ways of deamination and decarboxylation in systems T + (CH_3NH_2, CH_3COOH, NH_2CH_2COOH, $NH_3^+CH_2COO^-$) have been discussed in works[74,76,94]. According to these data, the displacement reaction (9) can be realized as a result of the Walden rotation of the carbon center. Both the MPNDO/3 and the nonempirical UHF approaches refer to the existence of high activation barriers, the transition states have the structure of the distorted trigonal bipyramidal inverting center. These structures are according to the nonempirical calculations[74,76] strongly polarized, notwithstanding the MPNDO/3 method data. According to the data of the latter method, the comparison of the E_a in a series of model systems refers to a larger probability of the carboxyl group displacement (E_a = 19 kcal/mol) if compared with that of the NH_2 group (E_a = 30 kcal/mol). It shoul also be noted that at the transition from the simple model systems of type T + CH_3NH_2, T + CH_3COOH to glycine, the obtained E_a values do not significantly change[76], i.e., the inclusion of an additional "hard" substituent in the vicinity of the carbon center does not bring about any remarkable improvement of the inversion barrier.

The data of[76] show that the inversion of the carboxylic group in the T + CH_3COOH system goes via the transition states of the distorted tetrahedron structure and thus, calls for surpassing the high activation barrier (already within the MPNDO/3 method its value was estimated to be 25 kcal/mol). Proceeding from that, the authors of[74,76] have reached the conclusion that in the case of thermal hydrogen atoms there are no conditions for proceeding of the process, while the "hot" T-atoms can undergo the Walden rotation of the attacking center.

It has also been shown in[74] that the energy profile of the approximation of the T atom to the hetero-atom (the mechanism of reaction (4) is supposed to hold) is not correctly reflected by the semiempirical MPNDO/3 method. A possibility of realization of the stable CH_3NH_3 structure, which actually contradicts the ab initio[94] calculation and the experiment[80] has also been predicted. The authors of[94] have shown in the framework of the UHF method and in the extended 4-31G basis set that at the PES the reactions of the direct break of the amino group in the T + CH_3NH_2 system are carried out by a single saddle point, the energy exceeding the total energy of reagents by 57.7 kcal/mol. The found barrier is localized in the output channel of the reaction $R_{CN} = R^{nc}_{CN} - R_{CN} = 0.24$ A, $R_{TN} = R^{nc}_{TN} - R^{o}_{TN} = 0.18$ A. The exothermal reaction constitutes 27.8 kcal/mol, which is quite close to the experimental value (24.4 kcal/mol)[80]. The analysis of the population density of AO along the reaction coordinate revealed[94] that in the PES, the spin population $\varrho_{CH_3} \approx \varrho_T \approx 0.5$, while in the case of the maximum absolute value, ϱ_N. Nevertheless, no charge transfer from the T atom onto the substrate has been observed. Equal distribution of the spin density between reagents in the transition state can, perhaps, be rather a rule than an exception, since the same situation was traced also in the UHF-PNDO calculations of the H + CH_4[59] system (in the transition state region, calculated by the nonempirical RHF-CI[60] method). Thus, according to the nonempirical calculation data[94] the process of the amino group direct break-off is highly probable to

proceed according to the mechanism of conserving the non-planar NH_2 configuration.

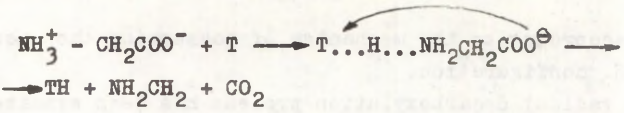
The radical decarboxylation process has been examined in works[95,76]. The direct break-off of the carboxylic group in the case of monohydrogen attack at various oxygen atoms cannot proceed without surpassing high activation barriers[76]. In report[95], it has been shown by the CI method that in a completely symmetrical state of the ^2A radical of CH_3COOH, a potential which corresponds to the C-2C bond stretch is not deep. Therefore, we can draw a conclusion that the radical mentioned is very liable to the decomposition by means of its decarboxylation. Such a phenomenon could also be met in the T + CH_3COOH system, although with a lower probability. The H break-off of the carboxylic group[76] acts as the limiting step of this way of decarboxylation, since in the latter case a barrier of 28 kcal/mol should be surpassed (see Table 3).

Using the molecular model prototypes[74,94], it is difficult to explain the substitution mechanism of functional groups in amino acids and proteins, found experimentally in the case of the interaction of the latter with the thermal atoms of tritium[1, 79]. The deviation is connected with the existence of some additional solvation factors which are present in the condensed phase[76]. The analysis of the energy characteristics of the PES has yielded the following substitution mechanisms of functional groups of the reactions of the zwitter-ionic glycine existing in the solution: deamination takes most probably place at the initial addition of the atom T, depending on the charged COO^- group and on the $C(sp^3)$-NH_3^+ bond breaking

$$NH_3^+ - CH_2 - COO^- + T \longrightarrow NH_3 \ldots CH_2COO^{\ominus} \ldots T \longrightarrow$$

$$NH_3 + CH_2COOT.$$

In the case of decarboxylation, first takes place the axial separation of the H atom of the charged amino group with the NH_2CH_2COO radical formation, which in its turn, spontaneously decomposed into CO_2 and the NH_2CH_2 radical.



Interaction of the H atoms with the CO, N_2 and NO molecules, taking into consideration the CI, has been discussed by the authors of[96]. The barrier was detected in the region R_{HC} = 1.59 A (system HCO), and R_{HN} = 1.43 A (system HN_2). In adiabatic approximation the approach to the positively charged parts of these molecules has turned out to be more preferable. Thus, the HCO formation is more favorable than that of HOC, since on the potential HCO curve, the minimum lies somewhat lower than the total energy of reagents. The best energy stability concerning the reagents has also been established for the HN_2 system. The application of the Walsh correlation diagram for the calculation of the discussed isolated (HOC, HCO) system yields 120° for θ, while the calculations predict that the angle θ = 117° (the HOC system), 130° (the HCO), and 120° (the HNN system).

Within the PNDO-UHF-CI method, a shallow minimum was found[97] for the ground state of the H_2CO + H system if R_{HO} = = 1.2 A, whose existence must yet be proved by the nonempirical calculations.

Correlation effects play a decisive role in the monohydrogen reactions with halogens[98]. In a single-determinant approximation, in the case of the H + F_2 system, the barrier height, -12.2 kcal/mol, is overestimated (the experimental value -1.2 kcal/mol)[99] and the exothermic nature of the reaction, -132.4 kcal/mol (the experimental value -88 kcal/mol) has also been strongly overestimated, while consideration of 555 ^2A configurations in the CI method yields that E_a = 1 kcal/mol and Q = 102.5 kcal/mol, being quite close to the experimental values. The saddle point has got a linear structure, where R_{HF} = 2.05 A and R_{FF} = 1.57 A Consequently, the F-F bond has been extended only by 0.03 A in comparison with the equilibrium. The transition state linearity is in keeping with the LEPS model and with the experiment[99], according to which the coordinate of the H + Cl_2

reaction is linear (H···Cl...Cl), that of H + Br_2^- slightly linear and of the H + I_2 remarkably deviates from the linearity.

E. Addition to the Unsaturated Bond.

The simplest examples of this class are the reactions

$$T + CH_2 = CH_2 \rightarrow CH_2T - CH_2 \qquad (10)$$

$$T + CH \equiv CH \rightarrow CHT = CH \qquad (11)$$

These reactions have been sufficiently studied both experimentally[100-102] and theoretically[103-108]. It has been established that the double bond appears to have a good reactivity to the radical addition. It has been found for the corresponding rate constants[100,101] that $k_1 \approx 10^{11}$ and $k_2 \approx 10^{10}$ $cm^3 \cdot mol^{-1} \cdot s^{-1}$. If at room temperature holds the relationship k_1/k_2 8.6, then at low temperatures (77°K), it is equal to $6 \cdot 10^3$ [102]. It is also known[109] that the anionic addition is probable in the case of the triple bond, while the olefinic bond is connected with the cationic and radical addition.

In[104-108] have been conducted nonempirical calculations for reactions (10) and (11) in various basis sets. In the 4-31G basis set the barrier of reaction (10) is estimated to equal 2.2 kcal/mol[107] which is in good keeping with the experimental data in different temperature ranges: 198 - 320° K (E_a = 1.5 kcal/mol[111]). Analogous calculations[104] for reaction (11) predict that E_a = 6.2 kcal/mol. In the both cases the saddle points found are localized in the input channel of the reaction (in the former case, R_{CT} = = 2.015 A, in the latter case - 1.930 A). Similar transition state localization has been observed also in the reactions of addition of the other radicals to the unsaturated bond, in particular in the case of method[51, 112-114] and ethyl[115] radicals' addition to ethylene as well as at that of phenyl radical to benzene[115].

High reactivity of the olefinic bond is maintained al-

so in the T + CH_2 = CH - C = CH[107] system. In the UHF formalism, the following results were obtained for the barrier height of the single-hydrogen addition to different carboxylic centers of vinylacetylene[107]: 1.4, 4.9, 7.3, 3.9 kcal/mol, respectively, for atoms 1-4 (numbering starts from olefinic bond). In order to explain the nature of the phenomenon, the interaction energy decomposition into various components has been carried out. It has been proved that[107] both in the case of ethylene and vinylacetylene reactions, the decisive role in selection of the reaction direction play the highest order members of the intermolecular interaction, the so-called superpositional members (see the next chapter). These are the exchange components that have an essential role in destabilization, but in this case, the interaction with charge transfer is not a prevailing factor, as it was actually expected on the basis of a simple comparison of the ionization potentials of ethylene and acetylene (10.5 and 11.4 eV, respectively). The conclusion is supported by a recent theoretical study concerning the reactivity of alkenes and alkynes in the reactions of anionic additions[115]. Although the HBMO/NVMO energy of acetylene exceeds that of ethylene, its molecule deformation taking place at interaction with H^- makes it drop drastically thus promoting its interaction with the charge transfer, and leads to a better reactivity of alkynes. A more substantial study of the H^- - C_2H_4 system can be found in[117].

The basic difference between the H and H^- addition reactions to ethylene lies in the fact that for the cationic addition, the probability of the formation of the bridge- and δ-intermediate is equal, their stabilities being rather close[118, 119], while in the case of radical addition the version with the C_{2V} symmetry is less favorable[120, 121].

A number of problems concerning the stereoselectivity of addition of mono hydrogen (as that of H^+ and H^-) to the asymmetrically substituted unsaturated molecules has been discussed in[122]. The conclusions have been drawn on the basis of the nonempirical calculation of the model transition state, depending on the rotation angle of the propene CH_2

group.

IV. Nature of Mono-Hydrogen and Substrate Interaction with the Closed Electron Shell. Decomposition of Interaction Energy into Components

Qualitative aspects of studying the chemical mechanisms of especially the radical reactions are connected with investigation of the nature of the intermolecular forces, starting with those belonging to the region of small electron overlapping up to the vicinity of the transition states. The nature of these forces has been studied in a large number of works, using the methods of the perturbation theory and configurational interaction (see, e.g. [123-127]). There are several ways for the decomposition of the intermolecular interaction energy into physically interpreted components. These were often simple mono-hydrogen reactions[106, 107,128,131,133,134], which served as suitable model objects for chemical processes. Being radical in character, they are less influenced by the medium effects than the ion ones, thus they are controlled by the forces which function between isolated reagents more strictly. In a number of works[106,107,128], the interaction energy decomposition scheme suggested by Morokuma and Kitaura[129,130] has been applied. In this case the intermolecular interactions have been studied by means of the CI methods as a variational problem. The existing solutions of the equation of Schroedinger for isolated subsystems have been used. In particular, the energy values and the individual contributions into the total interaction energy are determined as

$$\Delta E_i = E_i - (E_A^o + E_B^o), \quad E_i = \int \psi_i^* H \psi_i d$$

where E_A^o and E_B^o denote energies; ψ_i - the normed initial probe wave functions of isolated molecules, obtained by various methods: a) from a simple product of the wave func-

tions of isolated molecules, obtained by various methods: a) from a simple product of the wave functions of the SCF of isolated subsystems Ψ_A^o and Ψ_B^o; b) from the antisymmetrized products of these functions; c) from a simple product of two wave functions, optimized separately in the electrostatic field of the second subsystem; from an ordinary antisymmetrized and optimized SCF wave function of the whole complex. By means of the E_i set found, various contributions into the total interaction energy have been described in[125,129]: E_{es}, $E_{exch.}$, $E_{pol.}$, $E_{etr.}$, corresponding to the electrostatic, exchange, polarizational and the charge transfer energies. A combination of this approach with consideration of the CI has also been suggested[130]. In this case, the eigen values should be calculated, diagonalizing the matrices of configurational interaction indices. The energy decomposition results from a systematic neglection of certain nondiagonal elements of the matrix, as well as that of electron exchange operators. A further decomposition of the charge transfer energy into the "real" E_{ctr}, the exchange-polarization $E_{exch.-pol.}$ energies as well as into an additional member (sometimes called superpositional member), which can be determined by various types of matrix elements - $E_{shift.}$.

The energy barrier of decomposition (6) and substitution (7) reactions in the $T + CH_4$ system, as well as the additions of single hydrogen to C_2H_4 and C_2H_3F have been presented by the authors of[128] as the total of relative energies of isolated subsystems with the geometry of transition state (the intramolecular deformation energy) and the intermolecular interaction energy, which has been decomposed according to the above-mentioned method[129,130]. In the increase of the stability of the intermediate of radical addition, the molecular deformation plays a more significant role than in the case of cationic (protonic) addition, which has also been discussed in[128]. The most important component of intermolecular interaction is the interaction with charge transfer, while in the case of cationic addition, alongside with the E_{ctr}, the polariza-

tion term is of considerable significance. It is noteworthy that the E_{es} for the cationic intermediate makes a desta - bilizing contribution into the total energy, mainly owing to the absence of the electron ($E_{ch} = 0$) to be changed. At the final stage of the reaction, it brings about the forma- tion of destabilizing E_{es} owing to a short-range interac - tion of the proton with the ethylene nuclei.

The authors of[128] have also studied the reactions of break-off and substitution (6), (7) for the transition states of the C_3 symmetry, borrowed from[61], as well as the D_{3h} and C_s structures. It has been established that accor- ding to the data of intermolecular components and that of E_{def} the axial break-off is more favorable. In all models used, the ΔE is formed exclusively thanks to the defor - mation energy. The destabilization, caused by the latter, is partially neutralized by electrostatic and polarizational interactions, and by charge transfer. In substitution models, exchange repulsion tends to prevail unlike the reaction of break-off. Thus, the transition state of reaction (6) ap - pears to be favorable both sterically (on the expense of $E_{exch.}$) and from the point of view of electron-transfer (on the expense of E_{ctr}).

The nature of exchange interaction in reaction $T + CH_4$ (the D_{3h}) model has been studied more thoroughly in[131]. For this purpose, the exchange density ρ_k can be presented by two components - by the term characterizing the repulsion owing to the intermolecular overlapping of molecular orbi - tals of interacting systems of "repulsive overlapping" ρ_k^R

$$\rho_k^R(1) \simeq 2\sum^{occ}\left\{\sum^{occ}(S_{ik}\phi_i^2(1) - \phi_i(1)\psi_k(1)S_{ki}\right\} + \\ + 2\sum^{occ}\left\{\sum^{occ}(S_{ki}\psi_k^2(1) - \psi_k(1)\phi_i(1))S_{ik}\right\} \qquad (12)$$

and by the term characterizing the overlapping of orbitals - ρ_k^M

$$\rho_k^M(1) \simeq \sum_k^{occ}\sum_l^{occ}\sum_{i=i}^{occ}(\phi_i(1)\phi_i(1) + \phi_i(1)\phi_i(1))S_{ik}S_{ik} +$$

$$+ \sum_{i}^{occ} \sum_{k}^{occ} \sum_{k=k}^{occ} (\psi_k(1)\psi_k(1) + \psi_k(1)\psi_k(1))S_{ki}S_{ki} \quad (13)$$

where $S_{ik} = \int \phi_i(1)\psi_k(1)dv$, the double occupied MO_i belong to the A system, the ψ_k to system B. The nature of the phenomenon lies in the fact that the density of overlapping orbitals between these systems has the same order ($\phi_i \psi_k S_{ki} + \psi_k \phi_i S_{ik}$) both for the electrons with α - and for those with β-spins. Intergration within the whole space yields the $4S_{ik}^2$ value. It means that the interaction of two sys - tems with double occupied MO brings about a decrease in the electron density in the intermolecular region. An additio - nal electron density is accumulating on the MO of ϕ_i and ψ_k, taking values $2S_{ik}\phi_i^2$ and $2S_{ik}\psi_k^2$ for systems A and B. Thus, such overlapping should hinder the reaction . The same phenomenon has been called in[131] the "repulsive overlapping", which can be found according to Eq.(10). In Eq.(11) has been given another term of exchange interaction i.e. the mixing of the ϕ_i and ϕ_i' orbitals of system A (or those of ψ_k and ψ_k' of system B) thanks to the over- lapping with MO of ψ_k (or ϕ_i). This term reproduces the redistribution of electron density within subsystems, i.e. its accumulation in the vicinity of reaction centers. Thus, the forming forces favor the reaction. It has been shown[131] on the basis of the single-hydrogen exchange reaction with methane (an early stage of the Walden inversion model - C_{3v}) that the rehybridization of the reaction center is caused by cooperation of these two effects. The population overlap between the atoms of methane and the approaching atom is negative for the electrons having α-spin and positive for those with β-spin. Since the 1 AO of hydrogen efficiently overlap with the occupied molecular orbitals of methane, the arising overlap appears to be highly repulsive. The ρ_k^R leads to the appearance of the forces, supporting the inversion of the carbon center, while the mixing of orbitals favors the conservation of the configuration of the reaction cen- ter.

According to the data[106,107] in the systems $T + C_2H_2$ and $T + C_2H_4$, the reaction route is determined mostly by

means of exchange interactions. At the same time, the direction of addition to the unsaturated bond is determined by a superpositional member. These conclusions were drawn after comparing various ΔE in the mono-hydrogen reaction with ethylene, acetylene and vinyl acetylene.

In[128], the reaction of asymmetrically substituted ethylene ($CH_2 = CHF$) has been studied. It was known that the radical attack tends to take place at the unsubstituted end of olefinic bond[132]. Although according to E_{es} and E_{ctr}, the intermediate CH_3CHF is more favorable in comparison with CH_3CH_2, the gain in energy is compensated by deformation interaction. As a result, the ΔE values are close.

Among numerous work on the application of perturbation theory for solving the problem of intermolecular interactions (see, e.g.[125,134-140]), should be mentioned[135-137], dealing with the systems including open shells. To the problems analyzed in the present paper stand closer the calculations carried out by Kaneti[136], who has discussed in particular, the $CH_3 + H_2$ system according to the C_{3V} model. If the application of the perturbation theory of the first order leads to the classical Coulomb interaction, in the case of the second order stabilization[138,139] on the expense of the CI of locally excited AB^X and A^XB, twice excited A^XB^X states and those with charge transfer A^-B^+ and A^+B^-, mixed with the basic AB state have been observed. Considering only the single-electron excitations, using the formulae, obtained for the systems with a closed shell[139], and rearranging them taking into account the existence of an unpaired elector, the authors of[136] have also predicted a slightly dispersing atteraction at the distances of 3.5-4.0 Å, no energetic minimum was found within the range of 2-6 Å. It should be mentioned that the SCF calculation in the minimum basis set at $R = 3.2$ Å[141] refer to the existence of a shallow minimum of potential energy. Fukui et al.[140] have analyzed the components of the potential energy gradient along the coordinate of the inversion reaction in the system $T + CH_4$. The analysis of

the coefficients of the corresponding configurations have led to the conclusion that in the initial stage of the reaction, the contribution of the configurations, corresponding to the electron transfer (delocalization term) and to the electronic exsitations (polarizational term) is rather small. In the course of the reaction their contribution is increasing. The gradient analysis along the reaction coordinate, found by means of preliminary UHF-STO 4-31 calculations has proved that the exchange term usually tends to increase the gradient, while the term of mixing of electron transfer configurations leads generally to its decrease. The mixing of excited configurations with the ground state can be characterized as repulsive action. The effect of individual con - tributions of delocalization and polarization is insignificant.

Division of electronic population into components made the authors of[140] show that if R_{TH} = 1.6 A, (the intermediate stage of reaction (7)) the exchange term leads to the non-bonding population in the intermolecular region, referring, consequently to the repulsion between the orbitals, while the terms connected with configurational mixing form binding components. This agrees with the results of the above mentioned report[137] saying that the contribution of the β-electron transfer starts to dominate in the forma - tion of a new bond, since the contribution of α-electronic transfer is balanced by the exchange repulsion. The contribution of overlapping of polarization configurations with the ground state (for the Walden inversion model) makes the hydridization of carbon atom change and favors the exchange interactions. The latter are of intermolecular nature, while the polarization interaction is basically intramolecular , which actually causes inversion. The mixing of the configurations of transfer from methane to tritium, in the case of ground state, leads to the formation of a binding component between tritium and neighboring hydrogen atom.

V. Application of Reactivity Indices

The presented data show that in the case of a simplified quantum-chemical analysis of the reactivity of reacting molecules, should first of all be analyzed the character of the boundary MO; their changes during the reaction can be assessed from the data according to the E_{nz}. This yields a widely used delocalization index, introduced by Fukui et al[142-144] and its simplified version - the index of boundary density of electrons $f(R) = (C_r^{HOMO})^2 + (C_r^{LUMO})^2$, where r is the hydrogen atom studied. Its applicability range is limited to the relative reactivity of various positions in a single molecule[144]. The indices calculated by means of simple LCAO-MO[142] methods are in a satisfactory correlation with the activation energies of reaction the H-break-off of the hydrocarbors by halogen atoms and with the CH_3 and CF_3 radicals. The authors of[145] have based their calculations on the characteristics of wave functions, found according to the MINDO/3 method, thus establishing a good agreement with the values for alkanes. In the presence of polar substituent, it was found that the calculation data did not correlate with the experimental ones as it had actually been expected.

In papers[146,147] was discussed a possibility of using the reactivity indices for the description of a relative reactivity of the atoms of the hydrogen of amino acids in the reactions with the atomic tritium. In addition to these indices, in[147] were also used the relative stability values of the intermediate radicals of break-off; E_r, and the spin densities of reaction centers, r, calculated by means of the UHF-CNDO/2 method. There exists an intramolecular correlation between the E_r and r, evidencing about their interchangeability. There is also correlation with the boundary electron densities of carbon atoms f_r^c, calculated as

$$f_r^c = i(C_{ri}^{HOMO})^2 - (C_{ri}^{LUMO})^2 ,$$

where the sum including all valence orbitals of the atoms concerned. The latter correlation suggests[147] that it would be possible to get some information about the stability of the resultant radicals of the OH break-off by calculating the f_r^C of molecules.

Certain qualitative concepts concerning monohydrogen reactions have been given by Herndon[148] who has suggested to use within the VMO method as reactivity indices the coefficient values which do not bind the MO the r of forming radicals. In this case, the values of the Coulomb and the exchange integrals act as calculation parameters. The exchange integrals of the bonds $C(sp^3)$ - $C(sp^3)$ and $C(sp)^3$ - H(s) are taken as being equal to each other. The σ-orbital system is presented as a graph, whose tops correspond to the orbitals and the linear regions to the orbital interactions. The obtained r values correlate with the activation energies of the activation reactions of the hydrocarbon H break-off. An anomalous situation has been traced in the case of the H break-off reaction by the chlorine atoms.

The index approach has also been applied when studying the poly-conjugated regions in radical polymerization reactions[154] the spin densities of model active centers, forming at the monohydrogen addition to the terminal carbon atom of the olefine bond of monomer should be used as the reactivity indices. In the case of polar substituents, the process is controlled by electrostatic interaction. In all cases, holds the linear correlation with dipole moment values. Proceeding from that, the authors of[154] propose to use them as the reactivity indices in the reactions of the radical polymerization of the bound system of such a type.

As the reactivity indices of the break reaction of the hydrogen atom, the authors of[155] have used a number of traditional characteristics of reacting systems calculated by the PNDO-UHF method: the dissociation energy of loosening R-H and forming X-H bonds; the resonance stabilization of forming radicals; substituent effect on the polarization of transition state. As it was expected, the abnormality

can be observed with the molecules containing a hetero atom: which the authors tend to connect with the polarization of transition states (see also[76]).

Since the dispersion forces, aiming at the radical interaction with the substrate promote the reaction proceeding, there should be a certain correlation between the polarizability of substrate α_{AB} and the activation energy of H-break[156]. It is noteworthy that the C/α_{AB} correlation, where the C-constant is well presented both in the alkene reactions but also in those of H-break-off of polar molecules hydrogen halides .

The above-given indices were based on the approximation of isolated molecules. Therefore, their application range was limited to the hydrocarbon reactions with an equal charge distribution, in the case of which either the stability of transition state geometry in reaction series or the weakness of the reagents interaction in transition states was expected. These conditions are rather satisfactorily maintained in the case of radical reactions of alkanes but if the polar substituents are involved, their fulfilling cannot be ensured (see e.g.[149]). In a series of papers[79,150-152] the dynamic reactivity indices obtained from calculation of a limited set of structures, selected either on the bases of a priori approaches or from the results of the PES calculations of model reactions were used.

The coordination of the attacking monohydrogen leads in several functional groups of polar molecules (e.g. zwitter-ionic amino acids) to the loosening of a group of bonds and to simplification of the others, thus reflecting the probable ways of substitutions of these groups. In connection with that, the authors of[79] have chosen the following dynamic reactivity indices within the CNDO/2 method.

$$W_{AB} = \frac{W_{AB} - W_{AB}}{W_{AB}} \cdot 100\% ;$$

$$E_{AB} = \frac{E_{AB} - E_{AB}}{E_{AB}} \cdot 100\%$$

where W_{AB} and E_{AB} are the Wiberg indices and two-centered components of the full energy of isolated amino acids showing the strength of the A-B bond; W_{AB} and E_{AB} denote their values in the case of coordination. The analysis of electronic and energetic characteristics alongside with the calculated reactivity indices of the W_{AB} and ΔE_{AB} values which mainly correlate with each other enabled the authors of[79] to discuss various break-off mechanisms of functional groups of zwitterionic amino acids by atomic tritium. Using the mentioned reactivity indices, has also been studied[76,152] the dependence of the reactivity of functional groups of amino acids on its form of existence in solutions (e.g. on the ionization of the system if the medium's pH is changed) on the example of the reactions of polyfunctional model system of the α, γ-diamino butyric acid (α, γ - DABA) with atomic tritium. The maximal effect of deamination can be predicted for the zwitter-ionic form of the α, γ - DABA, which is also in keeping with the experiment (if pH = 8-10)[152].

In the stereoselective addition of monohydrogen to various carbon atoms of some substituted dienes, the overlapping populations of the coordinating H...C bonds (R = 3.0 A[153]) have been applied as the dynamic reactivity indices.

Thus, in order to study the reactions of monohydrogen, the dynamic reactivity indices directly considering the interaction of reagents in a pre-reaction complex happen to be the most promising reactivity indices. Their application is not limited to the hydrocarbon reactions which has been traced in the case of static reactivity indices. Thus, they can be used for studying the reactions of significant multiple-atom systems.

Depending on a definite task it is necessary to com - bine the dynamic reactivity indices with the estimation of the characteristics of wave functions of isolated reagents, calculated in one and the same approximation. Improvement of these indices is particularly connected with advances in

studying of the PES of model systems and, consequently, also with understanding the mechanisms of the processes going on in model prototypes.

x x x

The data discussed shows that in the case of the simplest monohydrogen reactions, can actually be studied the general form of the PES; the quantitative estimation of kinetic and thermodynamic characteristics can also be given within strict ab initio methods. Nevertheless, analysing of more complicated reactions, especially those proceeding in the condensed stage demand either model calculations or the application of some more accessible semiempirical methods. Application of the latter needs certain precaution, especially when discussing direct interaction in the region of small intermolecular overlap of single hydrogen with the heteroatom having unshared electron pairs. There is a possibility for cropping up wrong stationary points on the PES here. Such a phenomenon is connected with neglect of a series of integrals in the ZDO[157] method, as well as with the incorrect approximation of the exchange interactions of the core repulsion potential of in the MINDO/3 method (see, e.g.[31,40]).

Further progress in the application of these methods seems to be connected with elimination of these drawbacks, it concerns, especially, using the corrections for the core interactions. Evidently, the inclusion of empirical correlation into their interaction potential can be one possible way of such a correction. It was conducted by the authors of[158] in the calculation scheme by the MPNDO. In practice, one can confine himself either to the nonempirical check calculations of the extremums found, or to the recalculation of minimal energy ways. In the ab initio calculations of the energetic characteristics of monohydrogen reactions, it is necessary to correctly assess the effect of the basis set, especially, the mistakes of superposition[157,159] and electron correlation, while the transition state geometry can

well enough be described in the minimal Slater basis.

Soon a considerable progress will probably be achieved in studying the mechanisms of radical reactions, particu - larly, the reactions of atomic hydrogen, which is first of all connected with developing and application of novel ef- fecient methods of analytical calculation of energy deriva- tives, which by now hampers the analysis of multidimen - sional PES. Remarkable success has been gained in this field during recent years, see e.g. the review[60] and[48,161]. Ac - cessible calculation methods have been worked out not only for the UHF wave functions[47,162] but also for the wave functions of the multiple-configurational UHF[160].

Broad application of the multiple-configurational UHF method which is connected with calculation difficulties can in the nearest future lead to the compiling of universal , simple program packets used in practical experimental work.

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ON THE REACTIVITY OF THE CONJUGATED MONOMERS IN THE PROCESS OF FORMATION OF THE POLYMER COMPLEXES WITH IODINE

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The π-polarizabilities of some derivatives of pyridine within the PPP approximation of the coupled Hartree-Fock perturbation theory have been calculated. Linear correlation between these values and the yields of the polymer complexes (PC), which are the products of the thermic interaction of monomers with iodine have been obtained. The qualitative agreement between the conductivities of PC and the spin densities on donor centers of cation-radical forms of monomers, which was calcu - lated by the CNDO/2-UHF method has also been showed.

Recently, it was reported[1,2], that the thermic inter - action of molecular iodine with aromatic and heteroaromatic compounds leads to the formation of polymer complexes (PC), having semiconducting properties. Unlike another electroactive halogen doped materials, in this case, iodine is not only a doping agent, but a catalyst of the polymerization process. Consequently, it would be reasonable to carry out a detailed theoretical study of their reactivity towards the conjugated monomers. As an experimental criterion of the reactivity of monomers, the resulting yields of PC, ob-

tained at the optimal concentrations of reactants, temperature and reaction times, have been given.

It is well known that at low temperatures iodine interaction with such compounds leads to the formation of stable charge-transfer complexes (CTC)[3]. For the explanation of the thermic experiment, we first of all estimate the easiness of the formation of CTC and some of their properties for the series of methyl derivatives of pyridine within the semiempirical methods of SCF-MO-LCAO. Preliminary calculations of any theoretical characteristics, such as the ionization potentials, dipole moments, electron densities of the σ-donor and the spin densities at the radical centers of the molecular and ionized form of monomers were carried out.

Although these parameters explain the combined experimental data on the formation and any properties of low-molecular CTC, they do not obey the regularities of the high temperature complex formation.

On the other hand, it is reasonable to suppose, that under the thermic interaction of conjugated systems the essential role will be played by the induction component of the total interaction energy between the reactants. Excep - tionally, in this case the induction energy of neutral mo - lecules is small, however for long molecules with conjuga - ted bonds their contributions are considerable[4]. That is why for the characteristic, describing the "response" of the system to the external perturbation, has been taken the polarizability of the monomers (α_M). These parameters have been calculated within the π-electron coupled Hartree-Fock perturbation theory[3]. The parameters for the heteroatom were taken from[6]. The geometric parameters are: $R_{C-C}=R_{C-N}=1.39\text{Å}$, R_{C-H} = 1.08 A, R_{C-CH_3} = 1.52 A, all the valence angles were taken 120°.

In the figure are plotted the yields of PC vs. α_M^{π}. One can see a satisfactory agreement between the mentioned parameters.

From the data of Table 1, one can see that the above-mentioned parameters correlate in the series of polyaroma -

tic compounds, too, thus testifying about the universal nature of dominant factors in the process of thermic polymerization of the conjugated monomers with iodine.

Thus, the polarizability plays a significant role in the limiting stage of the formation of the PC, leading to the activation of any bonds under the generation of active centers of the polymerization process. Perhaps this behavior can be explained with the stabilization of the PC with the I_3^--like anions.

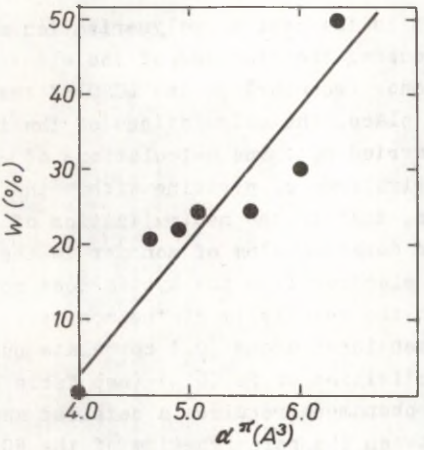

Fig. Experimental yields of the PC vs. π-polarizability of methyl derivatives of monomers.

A more detailed discussion of these phenomena requires numerical estimations of different contributions of intermolecular interaction energy[4]. The explanation of the elementary mechanism of the process of active center generations requires at least the calculation of simple dynamic indices of reactivity (see for example[8]) with the explicit estimation of the interactions between the reactants.

Table 1

The Yields of PC (W) and the Total Polarizability (α_M) of Some Polyaromatic Systems

Monomer	W, %[1]	α_M^*, A^3
Benzene	1	9.73
Naphthalene	70	18.64
Anthracene	73	28.64
Phenanthrene	84	32.36

Assuming that in the case of polymerization at the first stage of process, the transfer of the electron from the HOMH of the donor (monomer) to the LUMO of the acceptor (iodine) can take place, the calculations of the ionized forms have been carried out. The calculations of cation radicals of some derivatives of pyridine within the CNDO/2-UHF method[9] have shown, that in the neutralization of the negative charge of the donating atom of monomer in the case of extraction of one electron from the system does not proceed in accordance with the reactivity of the monomer, the spin densities of the mentioned atoms (ρ_N) correlate qualitatively with the conductivities of PC (σ_{PC}) (see Table 2). Understanding of these phenomena requires a detailed analysis of the connection between the paramagnetism of the PC and the nature of the charge carriers in such electroactive materials.

* The calculated values of the total polarizability within the modified ACF method was given in[7].

Table 2

Electrical Conductivities of PC (σ_{PC}), the Calculated Electron (q_N) and Spin (ρ_N) Densities for Donor Atoms in the Cation-Radicals of Some Methyl Derivatives of Pyridine

Monomer	σ, S/sm	ρ_N, e	q_N, e
Pyridine	10^{-4}	0.664	0.061
2.5-lutidine	10^{-7}	0.631	0.015
2.6-lutidine	10^{-8}	0.623	-0.022
2.3-lutidine	10^{-9}	0.621	0.017
2.4-lutidine	-	0.620	0.007
2.4.6-collidine	10^{-10}	0.602	-0.043

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CHEMICAL SHIFTS OF ^{1}H, ^{79}Br, ^{17}O, ^{13}C, AND ^{14}N IN AQUEOUS SOLUTION OF Bu_4NBr

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NMR method was used for the study of aqueous solutions of n-C_4H_9NBr(Bu_4NBr). The spectra of ^{1}H, ^{13}C, ^{79}Br, ^{14}N, and ^{17}O were monitored. Despite the wide-spread viewpoint that Bu_4NBr strengthens the structure of water it was noticed that the increase of the concentration of this electrolyte in water leads to the shift of the resonance signal of ^{1}H of water molecule towards the higher field which usually accompanies the destruction of the structure of bulk water. In its turn, the increase of the concentration of Bu_4NBr in water leads to the downfield shift of the signal of ^{17}O nucleus in water which, on the contrary, does agree with the hypothesis about the structure-making role of this electrolyte in aqueous solution.

In their turn, chemical shifts of ^{13}C and ^{14}N nuclei evidence that the partial chemical shifts of Bu_4N^+ ion practically do not depend on the concentration of Bu_4NBr.

Chemical shifts of the resonance of ^{79}Br were

compared in aqueous solutions of two electrolytes, Bu_4NBr and NH_4Br. It was shown that in the case of Bu_4NBr (as compared with NH_4Br) very significant (more than 200 ppm) downfield chemical shifts of the ^{79}Br signal occurred. The increase of the concentration of Bu_4NBr in the aqueous solution is accompanied by a very large (up to 40 kHz) broadening of the ^{79}Br resonance line.

It was concluded that only on the basis of measurement of chemical shifts of various nuclei one cannot draw unambigous inference about the physical nature of interactions between separate ions of electrolytes and water molecules in the studied systems. It was suggested that the chemical shifts of the signals from the above mentioned nuclei could be connected with the process of formation of ion pairs.

In literature (See Ref. 1-3 for review) the ideas about the significant influence of chemical nature and concentration of various electrolytes on the structure of water are rather widespread. It is, e.g., believed that the additions of most 1 : 1 electrolytes to water break the structure of the latter, whereas, on the contrary, some alkylammonium halides act as structure-makers. After the determination of the gross-polarity of aqueous solutions the addition of Bu_4NBr to water reduces its gross-polarity E_T down close to the respective quantity for dipolar aprotic solvent - DMSO. At the same time the 1 : 1 electrolytes LiCl, KBr, NaCl, and $NaClO_4$ increase the electrophilic solvation ability and the gross-polarity of water. Also, the study of the kinetics of hydrolysis of substituted benzoates[5] shows that Bu_4NBr reduces the electrophilicity of medium whereas the additions of NaCl and $NaClO_4$ change it in the opposite direction. The structure-making nature of Bu_4NBr was also deduced from the measurements of density and viscosity of its aqueous solutions, from conductometric measurements[9], from measurements of enthalpies of aqueous solutions[10, 11], from solubitities

of Bu_4NBr in alcohol[12,13], and from measurements of relaxtion times of ^{17}O in aqueous solution of Bu_4NBr[14,15].

Experimental

The ^1H spectra were recorded on a TESLA BS 478 B NMR spectrometer at the working frequency 80 MHz (internal standard - t-BuOH), ^{13}C spectra were recorded on a BRUKER WH-90 spectrometer (external standard - TMS). NMR spectra of ^{14}N, ^{17}O, and ^{79}Br were measured on BRUKER AM-500 spectrometer. For measurements of ^{14}N and ^{79}Br resonances the 4.9 M solution of NH_4Br was used as an external standard whereas the ^{17}O spectra were recorded relative to water as an external standard. Due to the low natural abundance of ^{17}O and also because of the broadening of its signal the upper limit for the determination of this isotope in aqueous solutions of Bu_4NBr was 2.0 M solution.

The results of measurements of chemical shifts of resonances from various elements are given in Tables 1-3. Besides that, in Tables 2 and 3 for nuclei ^{14}N, ^{17}O, and ^{79}Br also the widths of the resonance lines at their half heights ($\Delta\nu_{1/2}$) are given.

Discussion

On can see from Fig. 1 that the additions of $NaClO_4$ and Bu_4NBr induce the upfield shift of the resonance signal of protons of OH-group of water molecule, whereas Bu_4NOH leads to the downfield shift of the ^1H signal.

In the case of aqueous solution of NH_4Br the ^1H chemical shift does not practically depend on the concentration of this salt. One can see that those 1 : 1 type electrolytes which are believed to be structure-breakers (e.g., perchlorates and halides) lead [1-3] to the upfield shift of the resonance of protons of the OH-group. It agrees with the hypothesis[1-3] that the breakdown of the structure of water shifts the ^1H NMR signal of hydroxylic group towards the higher magnetic field. The latter suggestion is evidently

Table 1

The Relative NMR Chemical Shifts ($\Delta\delta$) of ^{1}H Nuclei of Water Molecules in Aqueous Solution of Bu_4NBr and Bu_4NOH (internal standard - t-BuOH). Molar Concentration (M) of the Salt is Given

Bu_4NBr		Bu_4NOH	
M	- $\Delta\delta$(ppm)	M	$\Delta\delta$(ppm)
0	0	0	0
0.46	0.05	0.10	0.01
0.74	0.09	0.14	0.01
1.06	0.08	0.224	0.03
1.58	0.30	0.37	0.06
1.87	0.33	0.56	0.09
2.32	0.61		
2.50	0.79		
2.65	0.88		
2.70	0.91		

Table 2

The Relative NMR Chemical Shifts ($\Delta\delta$) and Line Widths at Half Height for ^{14}N Signal in Aqueous Solution of Bu_4NBr. 4.9 M Aqueous Solution of NH_4Br Served as External Standard

M	$\Delta\delta$ (ppm)	Line Width (in Hz)
0.42	39.7	70
0.94	39.8	77
1.2	40.1	84
1.5	40.2	100
2.0	40.4	115
2.52	40.6	130
2.9	41.1	148

Table 3

The NMR Chemical Shifts ($\Delta\delta$) and Linewidths (at Half Height) for ^{17}O and ^{79}Br Nuclei in Aqueous Solutions of Bu_4NBr and NH_4Br. Water Served as External Standard for ^{17}O Resonance Whereas 4.9 M Aqueous Solution of NH_4Br Was Used as External Reference for ^{79}Br Spectra

Bu_4NBr					NH_4Br		
M	^{79}Br $\Delta\delta$(ppm)	^{79}Br Line Width (in KHz)	^{17}O $\Delta\delta$(ppm)	^{17}O Line Width (Hz)	M	^{79}Br $\Delta\delta$(ppm)	^{79}Br Line Width (KHz)
0	-	-	0	115	0.079	-24.3	0.81
0.16	-15.6	3.37	0.4	123	0.318	-23.8	0.83
0.45	3	10.6	1.1	168	0.448	-22.4	0.79
0.94	48	25	1.8	218	0.838	-18.5	0.80
1.23	117	28	2.3	256	1.38	-16.9	0.82
1.58	115	42.5	2.9	287	1.89	-14.6	0.79
2.00	162	44.8	3.5	340	4.00	+0.3	0.84
2.58	196	44					
2.86	210	43.5					

supported by the facts that the increase of the temperature of the sample or its dilution by the inert solvent both cause the upfield shifts of the resonance signal of the hydroxylic proton[16-19].

Shoolery and Alder showed already in 1955 that the small polyvalent ions induce the downfield shifts of the ^1H resonance, whereas the large 1 : 1 electrolytes which are capable to break the structure of water initiate the upfield shifts of the resonance signal from the protons of the hydroxylic group.

However, according to our data (see Table 1 and Fig. 1), Bu_4NBr which is believed to be a "classical" water structure maker leads to the upfield shift of the ^1H resonance of the hydroxylic protons of water. The comparison of the proton chemical shifts of OH group in aqueous solutions of Bu_4NBr

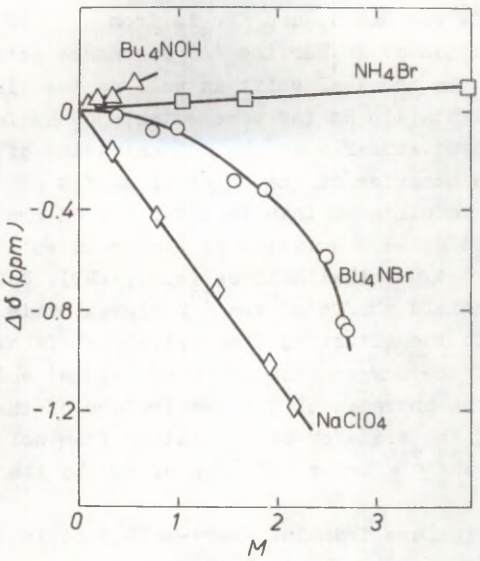

Fig. 1. The dependence of relative NMR chemical shifts of the signal from protons of the OH-group of H_2O (internal standard - t-BuOH) on concentration of various electrolytes in aqueous solution.

and NH_4Br shows that Bu_4N^+ ion is characterized by the shift of the ^1H resonance towards the higher field than in the case of NH_4^+-ion. Analogous upfield shifts of the ^1H resonance were noticed also in some other solutions of Bu_4NBr[14] and for aqueous solutions of alcohols and carboxylic acids with increasing length of the carbon chain[18]. The upfield shifts were recorded[21] also in aqueous solutions of $ROSO_3Na$ (where R = Et, Bu, Oct), whereas the shifts are increasing with the increase of the number of carbon atoms in the alkyl radical R.

Fig. 2 reflects the dependence of the relative chemical

NMR shifts of the signal of ^{17}O nuclei of water on the concentration of various electrolytes in their aqueous solution (the data for $NaClO_4$ and KBr is from Ref. 22). In the aqueous solution of Bu_4NBr the ^{17}O resonance shifts downfield , whereas the chemical shift as well as the linewidth at the half height (115 Hz for pure water, 340 Hz for 2M solution) both depend linearly on the concentration of Bu_4NBr.It seems that the behavior of the chemical shifts of ^{17}O resonance is more complicated than that for the OH-proton chemical shifts in aqueous solution of electrolytes (vide supra). So, the 1 : 1 type alkalihalides (e.g., KBr), $NaClO_4$, etc. cause the downfield shifts of the ^{17}O signal. This is just the opposite to the situation (the upfield shift of the ^{17}O resonance of the oxygen atom of water occurs) which takes place due to the increase of the temperature of the sample[22], because of the transfer of the latter from solution to the gas phase[23,24] or on dilution of H_2O by the organic solvents[22] .

It follows from the above-said that in the case of data on ^{1}H and ^{17}O chemical shifts of the signals belonging to the atoms, in a water molecule one must exercize great care while interpreting the results of the study of the influence of the chemical nature and concentration of various electrolytes on the structure of water.

In the aqueous solution of electrolytes the water molecule can occupy three different positions:

a) in the (immediate) vicinity of cation
b) in the (immediate) vicinity of anion
c) in the neighborhood of the other water molecules.

As far as experimentally only one resonance signal could be recorded then the observed quantity seems to be the superposition from the ^{17}O chemical shifts characteristic of three different environments. According to Hindman[26], one can distinguish the following contributions into the observed proton chemical shifts in aqueous solutions of electrolytes:

1) Upfield shifts - the break-down of hydrogen bonds

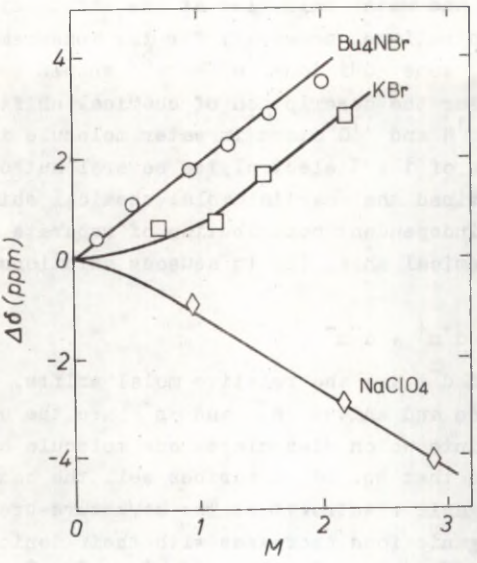

Fig. 2. The dependence of relative chemical shifts of the signal of ^{17}O atom of water molecule (external standard-water) on the concentration of some electrolytes in their aqueous solution.

in the process of reorientation of water molecules; the additional rupture of hydrogen bonds in the vicinity of ions.

2) Downfield shifts - the introduction of the ion generates more structured system than in pure water ; ionic (electrostatic) field influences the electro - nic distribution around the proton; nonelectrostatic interactions between cation and anion with water molecule.

Those factors should be responsible for the interactions between ions and water molecules at the infite dilution. At higher concentrations, necessary for the measurement of chemical shifts, some additional effects[25] should be taken into account. For the description of chemical shifts of the resonance of ^{1}H and ^{17}O atoms in water molecule in the aqueous solutions of 1 : 1 electrolytes several authors[20,22,26-28] determined the partial molal chemical shifts which reflect the independent contribution of separate ions into the gross chemical shift (d) in aqueous solutions of elec - trolytes:

$$d = d^{+}n^{+} + d^{-}n^{-} , \qquad (1)$$

where d^{+} and d^{-} are the relative molal shifts, caused by cations and anions n^{+} and n^{-} are the number of ions into which dissociates one molecule of salt.

It is belived that Eq. (1) describes well the behavior of several inorganic electrolytes. The structure-breaking ability of inorganic ions increases with their ionic radius[26]. In the rows F^{-}, Cl^{-}, Br^{-}, I^{-}, and Li^{+}, Na^{+}, K^{+}, Rb^{+}, Cs^{+} the linear relationships between ionic molal chemical shifts of ^{1}H and ^{17}O on one hand and the crystallographic ionic radii of the anions and cations, on the other hand, were found to hold[3,8,26] .

The calculation from our data of the corresponding molal chemical shifts for Bu_4NBr shows that practically the whole gross chemical shift of protons of the hydroxylic group of water is determined by Br^{-} -ions. The molal chemical shifts of the other alkylammonium ions as calculated from data[3] for R_4NBr(R = Me, Et, Pr) are also rather small.

On the basis of molal chemical shifts of the signal of ^{17}O atom from water[22,28], one can conclude that all halide ions cause a downfield shift which increases when passing from F^{-} to I^{-}. Monovalent cations, which initiate rather modest positive chemical shifts are ordered as follows : $Li^{+} > Na^{+} > K^{+} > Cs^{+} > Me_4N^{+}$. Br^{-} -ions display more signifi - cant response which markedly (4 times for Me_4NBr and 1.8 times for Bu_4NBr) exceeds the influence of R_4N^{+} ions.

Several authors[3,22,28-30] have suggested that the breakdown of the water structure does not make the decisive contribution into the observed chemical shifts which are supposed to be determined by the solvent-solute interac - tions in the system anion-medium (water), in particular, by the electrophilic solvation power of the solvent. In order to check that hypothesis one should turn to Fig. 3 and 4 which show that the chemical shifts of ^{79}Br and ^{17}O in aqueous solutions of Bu_4NBr as well as the linewidths of the signals from the same nuclei in these conditions depend , within their error limits, linearly on the gross-polarity E_T parameters of these salt solutions[4].

As far as the E_T values for the aqueous solutions of Bu_4NBr are practically linearly connected with the electro- philicity parameters of the same medium then at least for- mally, both figures seem to evidence that the chemical shifts of ^{79}Br and ^{17}O decrease (upfield shift) with the in - crease of the electrophilic solvation power of the aqueous solution of Bu_4NBr. However, this behavior does not agree with the results[31, 32] of nonempirical quantum chemical cal- culations (supermolecular approach), which predict that the electrophilic hydration of anions (F^-, HO^-, etc.) should result in a decrease of the population of the negative charge on the anion. Simultaneously, the negative charge transfer to water molecule and the increase of the population of the negative density on the oxygen atom should take place.

Assuming that with the decrease of the population of the negative charge around the given nucleus the shielding of the latter also decreases, one might expect that the stronger electrophilic solvation of Br^- -anion should lead to the downfield shift of the resonance of the latter and to the upfield shift of the resonance of ^{17}O nucleus of water molecules. The results of the present work do not agree with either of these simplified predictions. Therefore, it is clear that experimental results could not be adequate- ly interpreted only in terms of above-mentioned primitive model based on the concept of specific electrophilic solva- tion of anion by water molecules and on acceptance of assump-

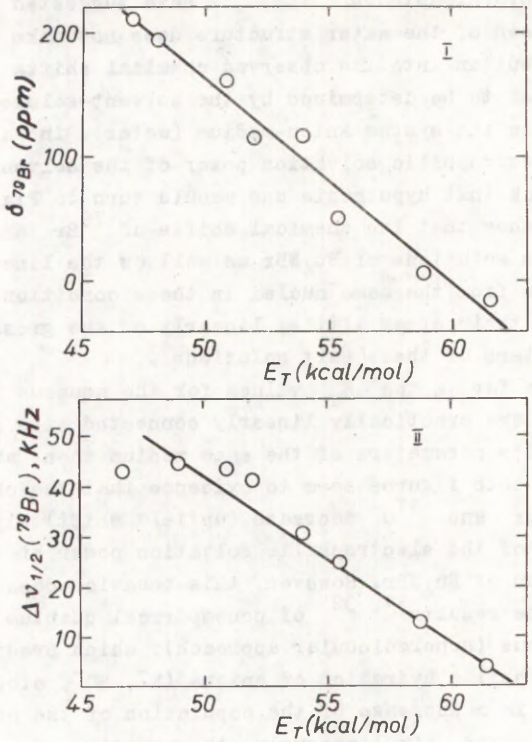

Fig. 3. Comparison of chemical shifts (I) of the resonance of ^{79}Br and the linewidth (II) of that signal at half height ($\Delta\nu_{1/2}$) in the aqueous solution of Bu_4NBr with the E_T gross polarity parameters of the latter system.

tion about the existence of direct linear relationship between the chemical shift of the signal of the given nucleus, on one hand, and the calculated Mulliken charge density on the latter, on the other hand.

NMR spectra of Bu_4N^+ ion evidence that the corresponding

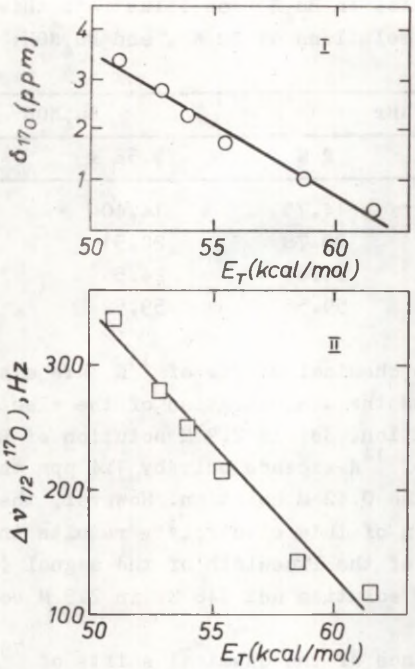

Fig. 4. Comparison of chemical shifts δ (I) of the resonance of the ^{17}O atom of water and the linewidth (II) of that signal at half height in aqueous solution of Bu_4NBr with the E_T gross polarity parameters of the latter system.

carbon chemical shifts practically does not depend either on the concentration of the salt or on the nature of the anion. The following data on chemical shifts (in ppm) of the resonance of ^{13}C nuclei in Bu_4N^+ ion illustrate this conclusion for the aqueous solutions of Bu_4NBr and Bu_4NOH:

	Bu_4NBr		Bu_4NOH	
	0.42 M	2 M	0.56 M	0.37 M
C_1	14.30	14.73	14.40	14.30
C_2	20.48	20.78	20.51	20.51
C_3	24.48	24.80	24.55	24.45
C_4	59.45	59.58	59.52	53.45

Analogously, the chemical shifts of ^{14}N are also rather insensitive towards the concentration of the electrolyte in its aqueous solution. So, in 2.9 M solution of Bu_4NBr the chemical shift of ^{14}N exceeds only by 1.4 ppm the corresponding value for the 0.42 M solution. However, the increase of the concentration of this electrolyte results in a nearly linear increase of the linewidth of the signal from ^{14}N (70 Hz in 0.42 M solution and 148 Hz in 2.9 M solution of Bu_4NBr).

The dependence of the chemical shifts of ^{79}Br and the linewidth of this signal at half height on concentration of Bu_4NBr (aqueous solution, see also Table 3) is shown in Figs. 5 and 6. The cause of the significant broadening of resonance lines is, probably, due to the circumstances, that the ^{79}Br nuclei are characterized by the distribution of nuclear charge which does not have the spherical symmetry.

At the same time it was noticed[26,33-35] that in the case of the Br-anions (as compared with covalently bonded bromine atom) still narrower lineshapes of the signals were recorded. It is reasonable to assume that if the nucleus which has the quadrupolar moment is in an environment which is characterized by a high degree of symmetry, then the gradient of the quadrupolar electric field in the location of

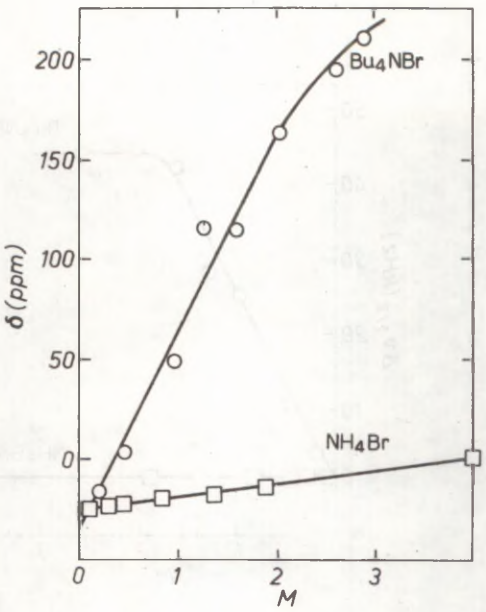

Fig. 5. The dependence of chemical shifts of ^{79}Br (external reference - 4.9 M (aqueous solution of NH_4Br) on the concentration of electrolyte in aqueous solutions of Bu_4NBr and NH_4Br.

that nucleus should decrease. It is possible that such a situation holds for NH_4^+ and Br^- ions in aqueous solutions, at conditions where the line-broadening is not yet significant.

On the grounds of the above-said it seems unreasonable to explain the dependences of chemical shifts of the resonance of ^{79}Br in aqueous solutions of Bu_4NBr and NH_4Br on

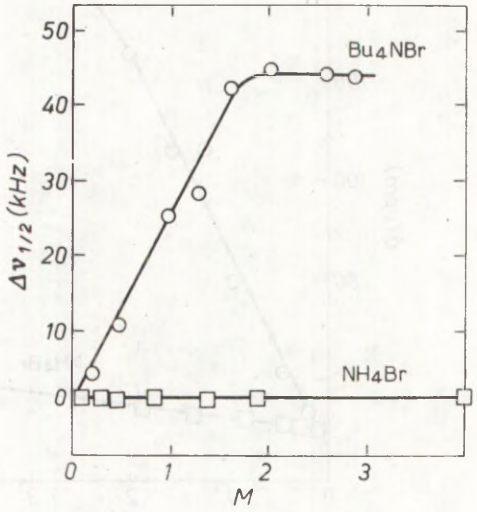

Fig. 6. The dependence of the line width at the half height ($\Delta\nu_{1/2}$) of the signal of ^{79}Br on the concentration in aqueous solutions of Bu_4NBr and NH_4Br.

their concentration in terms of structure-making effect of Bu_4N^+ ion and that of specific solvent-solute interaction between Br^- anions and water molecules.

A hypothesis could be suggested that the significant chemical shift of ^{79}Br ions and the very strong broadening of the resonance line in case of the aqueous solutions of Bu_4NBr might be explained by the formation of the "intimate" or contact ion pairs between Bu_4N^+ and Br^- in a more concentrated solutions of the electrolyte. Differently

from the Bu_4N^+ ion the NH_4^+ cation is specifically solvated by the molecules of water which might hinder the formation of its ion pairs with Br^- -ions.

At the relatively low concentrations of Bu_4NBr the following equilibrium must be operative:

$$Br^-\text{-ion in hydration shell} \rightleftharpoons Br^-\text{-ion in the "intimate" ion pair, not separated by water molecules} \qquad (2)$$

In the hydration shell the resonance line of ^{79}Br is relatively narrow ($\sim$800 Hz) and is located in a relatively high magnetic field. The further increase of the concentration of Bu_4NBr shifts the equilibrium (2) towards the formation of intimate ion pairs consisting of the Bu_4N^+ cations and Br^- anions, not separated by the water molecules. In the latter the spherical and symmetric distribution of the nuclear charge should be perturbed. The formation of the above-said ion pairs could be considered also as the complex formation between the electrophile (cation) and nucleophile (anion) which should result in the decrease of the electron density on the Br^- ion and, consequently, in deshielding of the given (^{79}Br) nucleus. As an overall result of the perturbation of the spherical nuclear charge distribution and because of the deshielding of the ^{79}Br nucleus the significant line broadening of the signals from ^{79}Br and ^{14}N nuclei as well as the shift of the resonance signal of the ^{79}Br nucleus towards the lower magnetic fields are expected. The same situation is observed also in practice. However, the magnitudes of variation of chemical shifts and line widths for the ^{79}Br and ^{14}N nuclei differ from each other rather significantly.

So the changes of the corresponding chemical shifts and line widths which characterize these two nuclei while going from the dilute solution into the 2M solution of Bu_4NBr

Chemical Shifts (Hz)		Line Widths (Hz)	
^{79}Br	^{14}N	^{79}Br	^{14}N
24.000	40	44.200	63

evidence that the chemical shifts of the ^{79}Br are 600 times larger and the line widths more than 700 times larger than those of the ^{14}N nucleus in the same conditions. It could be expected that in the highly concentrated ($M \geqslant 2$) solutions of Bu_4NBr the equilibrium (2) is completely shifted towards the formation of contact ion pairs which should be reflected by the practical constancy of the line widths of the signal. It is instructive to remember that in highly concentrated ($M \geqslant 2$) aqueous solutions of Bu_4NBr the E_T-parameters of the solvent gross polarity already are practically independent of the temperature[4]. At the same time the calculated electrophilicity parameters for such concentrated solutions almost reach their possible minimum value, characteristic of the pure Bu_4NBr as a melted salt (see also Fig. 3 and 4). In highly concentrated solutions of Bu_4NBr the chemical shifts of ^{79}Br have a similar saturation effect and further only a rather small downfield shift was observed. The hypothesis about the formation of the contact ion pairs is not overridden either by the fact that[37] the solution of bromides in organic solvent leads to the downfield shifts of the signal from ^{79}Br. So, in 0.2 M aqueous solutions of LiBr, KBr, NaBr and Me_4NBr, i.e. in conditions Br^- ions are hydrated the chemical shifts of ^{79}Br for all those compouns are equal. However, the transfer of these bromides into an organic solvent leads to the downfield shift of the signal from ^{79}Br. Simultaneously, the chemical shifts depend both on the nature of the solvent as well as of that of cation. This is the case while studying the chemical shifts of the signals from the ^{79}Br nucleus for some electrolytes in DMSO where the corresponding values of chemical shifts (in ppm) decrease in the following order:

LiBr	NaBr	KBr	Me_4NBr
170	167	167	104

The analogous effect was noticed[35] also in some other solvents (DMF, MeCN) during the study of chemical shifts of ^{35}Cl and ^{127}I nuclei.

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ACIDITY OF SOME CARBOXYLIC ACIDS IN DMSO

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pK_a values of several carboxylic acids XCOOH, where X = H(pK_a = 10.45), Me(12.4), t-Bu(12.9), CHF_2(6.51), CF_3(3.6), CF_3CF_2(3.2), $CF_3CF_2CF_2$(3.2), CH_2CN(8.2), $CHCl_2$(6.32), $HC{\equiv}C$(7.0), $CH_2{=}CHCH_2$(11.3), CH_2Ph(11.6), CH_2OMe(10.5), 1-AdCH_2(13.0), $CH_2NMe_3^+$ (6.2),  (12.2),  (12.9),  (12.4), $C{\equiv}CCO_2^-$(9.4), COOH(6.32), CO_2^-(14.97), 3-$CF_3C_6H_4$(9.7), 3,5-$(CF_3)_2C_6H_3$(8.0) were measured by potentiometric titration with Bu_4NOH in dimethylsulfoxide (DMSO).

These results and literature data for DMSO were compared with the acidity of corresponding aliphatic carboxylic acids in the gas phase and aqueous solution. It was shown that the transfer of this reaction series from water into DMSO enhances its susceptibility towards substituent effects ~1.7 times, whereas the transfer from DMSO into gas phase is characterized by only slightly higher (1.8 times) increase of the solvent attenuation factor of substituent effects.

The statistical analysis revealed that unlike the gas phase results, the acidity of carboxylic acids in DMSO and aqueous solution does not practically depend on the polarizability of the substituent.

First of all, the influence of structure of aliphatic and alicyclic carboxylic acids on their acidity has been most thoroughly studied in water and in its mixtures with various organic solvents[1].

Recently, the series of studies on the gas phase acidity of these classes of compounds were completed[2-10]. As a result it was found[5-9,11,12] that in the case of aliphatic carboxylic acids (substituted acetic acids), alongside with the other structural factors, the acidity of these acids also depends on the polarizability of the substituent, whereas the acidity of 4-substituted bicyclo [2.2.2] -octane-1-COOH and 4-substituted bicyclo [2.2.2] -octene-1-COOH, by analogy with substituted benzoic acids and phenols, does not depend on that type of substituent effects[7-9,12].

The first studies[13-16] on determination of pK_a values of aliphatic carboxylic acids in DMSO were performed already about 20 years ago. Nevertheless, one cannot consider the data bank of the pK_a values for these compounds as sufficiently complete and representative (see Ref. 1 for further references and Refs. 17-22).

The above-mentioned holds also for the study of acidity of alicyclic acids in DMSO for which only the pK_a values of the series of 2,3 or 4-substituted adamantane-1-carboxylic acids (AdCOOH) were measured[23]. Analogously with the two series of the above-mentioned alicyclic carboxylic acids in gas phase it was found[23] that the acidity of those derivatives of AdCOOH in DMSO also does not depend on the polarizability of the substituent in the adamantane ring.

In the present work the pK_a values of acidic dissociation of the majority of aliphatic carboxylic acids, as well as some alicyclic carboxylic acids (4-substituted bicyclo [2.2.2] -octane-1-COOH (OctCOOH), 4-substituted [2.2.2] -octene-1-COOH (OcteCOOH), and 4-substituted-cubane-1-COOH (CubCOOH))[x] were measured in DMSO solution.

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[x] pK_a values of the derivatives of the acids of these classes will be given in a separate publication.

Experimental

Reagents. DMSO was purified as described earlier[23]. The purification of benzene and i-PrOH was described also in Ref. 23. The solution of Bu_4NOH in the mixture of benzene and i-PrOH (4 : 1) was prepared according to Denesh[24] from Bu_4NI and silver oxide in i-PrOH. It was purified by passing it through the column filled up with anionite amberlite IRA-400 (Serva).

In most cases the commercial, additionally purified acids were used. The derivatives of bicyclo [2.2.2] octane-1-COOH, bicyclo [2.2.2] octene-1-COOH and cubane-1-COOH were delivered by Prof. R.W. Taft (University of California, Irvine), $(CF_3)_2CHCOOH$ was from the laboratory of academician I.L. Knunyants (Institute of Elementoorganic Compounds, Academy of Sciences, Moscow). For the determination of pK_a of betaine its hydrochloride was used. For X = C ≡ CCO_2^- the sodium salt was used.

Potentiometric measurements

For the determination of the pK_a value, the potentiometric titration of the given acid with the solution of Bu_4NOH in the mixture (4.1) of benzene and i-PrOH was used. Detailed description of the technique is given in Refs. 23, 25.

The calibration of the glass electrode (filled with mercury) was done using for the reference points the pK_a values for the benzoic acid (11.0)[1], 2.6-$(NO_2)_2C_6H_3OH$(4.9)[1] and phenol (17.1)[1].

Within the experimental errors the slope of the calibration plot in coordinates p_aH vs. log a_{H^+} does not differ from the theoretical value.

Every day, before and after the series of experiments the check of the proper functioning of the electrode system was undertaken by the repeated titration of the standard substance, benzoic acid.

As a rule, the titration of the overwhelming majority of acids obeys the necessary stoichiometry which is charac-

Table 1

The Acidity of some Carboxylic Acids XCOOH in DMSO Water and Gas Phase[+]

	X	pK_a (DMSO)		$pK_a(H_2O)$[1]	$-\delta\Delta G$ (gas phase), kcal/mol[6-10]
		This work	Literature		
1	2	3	4	5	6
1.	H	10.4 ±0.1	-	3.75	2.7
2.	Me	12.4 ±0.1	11.6[14], 11.41[19] 11.4[13], 12.6[16]	4.75	0
3.	i-Pr	-	-	4.86	1.8
4.	t-Bu	12.9 ±0.05	12.39[19]	5.05	3.5
5.	$CHCl_2$	6.32±0.05	6.36[20]	1.3	19.9
6.	CHF_2	6.22±0.02	-	1.3	16.9
7.	CH_2CN	8.20±0.08	8.5[20]	2.46	16.0
8.	CH_2Ph	11.6 ±0.1	11.6[16]	4.3	6.9
9.	CH_2OH	-	10.2[20]	3.82	-
10.	CH_2CH_2OH	-	11.47[20]	4.51	-
11.	1-Ad	13.1[23]	-	-	4.4
12.	1-AdCH_2	13.0 ±0.1	-	-	-
13.		12.9 ±0.1	-	-	3.8

Table 1 continued

1	2	3	4	5	6
14.		12.4 ±0.1	-	-	5.0
15.		12.2 ±0.1	-	-	5.0
16.	CH_2OMe	10.5 ±0.1	-	3.53	6.0
17.	HC ≡ C-	7.0 ±0.1	-	1.84	-
18.	CH_2=CH-CH_2	11.30±0.05	-	4.35	-
19.	CF_3	3.6 ±0.1	-	-0.3 $\overset{\cdot\cdot}{\cdot\cdot}$ 0.5	23.8
20.	CF_3CF_2	3.2 ±0.1	-	-	-
21.	$CF_3CF_2CF_2$	3.2 ±0.1	-	0.16	-
22.	CF_3CH_2	-	-	3.04	13.2
23.	$(CF_3)_2CH$	-	-	2.35[26]	-
24.	C≡CCO_2^-	9.4 ±0.2	-	-	-
25.	$Me_3\overset{+}{N}CH_2$	6.2 ±0.2	-	1.83	-
26.	CH_2Cl	-	8.9[16]	2.85	12.6
27.	COOH	6.32±0.05	6.2[16]	1.27	-
28.	COO^-	14,97±0.07	14.9[16]	4.3	-
29.	CH_2COOH	-	7.2[20]	2.8	-
30.	CH_2COO^-	-	18.55[20]	5.7	-
31.	CMe_2Ph	-	11.1[19]	-	-
32.	$CMePh_2$	-	10.0[19]	-	-

Table 1 continued

1	2	3	4	5	6
33.	CPh_3	-	9.29[19]	3.96	-
34.	$GeMe_3$	-	11.13[19]	-	-
35.	$CH(OH)COOH$	-	6.8[20]	-	-
36.	$CH(Br)CH_2Br$	-	7.13[20]	-	-
37.	$CH(OH)COO^-$	-	16.7[20]	-	-
38.	Ph	11.0	11.0[1]	4.20	6.8
39.	$3\text{-}CF_3C_6H_4$	9.70 ± 0.05	-	3.79	8.4
40.	$3,5\text{-}(CF_3)_2C_6H_3$	8.0 ± 0.1	-	-	23.3
41.	$3,5\text{-}(NO_2)_2C_6H_3$	-	7.4	2.8	
42.	$2,4\text{-}(NO_2)_2C_6H_3$	-	6.52	1.42	
43.	$4\text{-}NO_2C_6H_4$	-	8.9	3.4	
44.	$2\text{-}NO_2C_6H_4$	-	8.18	2.17	
45.	$4\text{-}NH_2C_6H_4$	-	12.7	4.87	

+ In the last column are reported the relative free energies $\delta\Delta G$ (reference compound-acetic acid) which characterize the intrinsic acidity of the corresponding acids in gas phase.

x This paper.

teristic to the removal of one or two ($(COOH)_2$) protons from the carboxylic group of the acid. Different behavior is present in the case of $(CF_3)_2CHCOOH$ which evidently decomposes in DMSO (white fume emerges after the contact with this solvent). On the titration curve of this acid (one equivalent of Bu_4NOH was added) two "jumps" of the electrode potential appeared in the region of pH = 10 ÷ 12 and pH = 16 ÷ 19, either of which evidently does not correspond to the removal of the proton from the carboxylic group of $(CF_3)_2CHCOOH$. In aqueous solution, however, this acid seems to behave normally and only one "jump" appears on the titration curve after addition of one equivalent of Bu_4NOH (pK_a = 2.1 ± 0.1 was determined at 25°C (compare with pK_a = 2.35[26])).

The procedure of calculation of pK_a values was earlier described in detail in Refs. 23, 25. For each acid the titration was usually repeated 3-5 times. From the mean values of the individual runs the arithmetic mean pK_a values were calculated. The latter, alongside with their reliability intervals and the corresponding literature pK_a values, are listed in Table 1.

If available, the acidities of the same acids in aqueous solution[1] and in the gas phase[6-10] were also included in Table 1. For the comparison with the aliphatic acids, some data for substituted benzoic acids is also given.

Discussion

The transfer of some reaction series from the gas phase into solution is accompanied by the nonspecific and (almost always) specific solvation of the initial reagents and the final products on the reaction path[27]. Those above-mentioned solvent-solute interactions can lead to very significant changes in the structure and reactivity of reagents[7,8,12,27-30]. The reaction series of dissociation of carboxylic acids is by no means exceptional and its sensitivity towards substituent effects decreases drastically with the transfer from the gas phase into aqueous solution[7-9,29,30].

As regards the nonspecific solution then in this case the

transfer from the gas phase into solution should lead to the relative stabilization of ionic (anionic) final state as compared with the neutral dipolar initial state.

Specific nucleophilic solvation of the neutral acid by the water molecules should stabilize the initial state (decrease of the acidity of the acid), whereas the specific electrophilic solvation should stabilize the anionic form (i.e. deprotonized acid), which, in its turn, is expected to increase the acidity of the acid. At the same time, the relative importance and intensity of the electrophilic solvation of anion, as a rule, dominates[7-9,27-31] over the contribution of the nucleophilic stabilization of the neutral form of the acid.

The gross contributions of specific and nonspecific solvent-solute interactions both influence in the same direction. As far as usually the solvent-induced stabilization of the ionic final state significantly dominates over the solvation stabilization of the neutral form of the acid then, as a final outcome, it results in contraction (compression) of the absolute gas phase acidity scale. Simultaneously it also leads to the decrease of the susceptibility of the reaction series towards structural effects[7-9,27-31]. As a rule, the transfer from the gas phase into dipolar aprotic solvent DMSO (it has higher polarizability[27] (n_D^{25}(DMSO)=1.4773, $n_D^{25}(H_2O)$ = 1.3325) and lower polarity[27] (dielectric permittivity ε^{25}(DMSO) = 46.4, $\varepsilon^{25}(H_2O)$ = 78.2) than water, in its turn the nucleophilicity[27] of DMSO (B(DMSO) = 369) is much higher than that of water (B(H_2O) = 158), whereas the latter exceeds significantly DMSO by its eletrophilic solvation ability (E(H_2O) = 21.8, E(DMSO) = 3.2)) leads, as compared with the aqueous solution, to the relative destabilization of the final (anionic) state and to the less intensive stabilization of the initial state*. As a result of

* It is possible that, by the analogy with the complex formation between DMSO and small hard anions[12,29], DMSO is also able to stabilize carboxylate-anions via the electrophilic solvation of the latter by the positive end of its dipole (S-atom).

that, one might expect that the substitution of water or some other aqueous-organic solvent for DMSO should lead to the increase of pK_a values (decrease of the acidity of the acid) as well as to the change (increase) of the susceptibility of the given reaction series towards substituent effects.

The straightforward comparison of the pK_a values (Table 1) for the reaction series of acidic dissociation of carboxylic acids in DMSO and aqueous solution on one hand (Fig. 1), and for H_2O and DMSO with the gase phase results, on the other hand (Fig. 2), fully confirms the above-mentioned conclusions. One can see from Fig. 1 that in the case of the 1st pair of solvents a satisfactory linear relationship between the $pK_{a(DMSO)}$ and $pK_{a(H_2O)}$ values holds (slope = 1.66 ± 0.04). Probably by chance, some points for substituted benzoic acids also fit this straight line, whereas the points for the 1st and 2nd steps of dissociation of malonic acid and that of the 2nd step of dissociation of oxalic acid deviate from it.

In the case of malonic acid the formation of intramolecular H-bond is sometimes believed[17,18,33] to play an important role by stabilizing the monoanionic form of the acid (the increase of the acid strength at the 1st step of dissociation and the decrease of it at the 2nd step of dissociation of the acid). One has also to remember that in the case of the 2nd steps of dissociation of oxalic and malonic acids their acidity $pK_{a(2)}$ should be somewhat decreased by the electrostatic destabilization[33] of the final dianionic state which in aqueous solution is for $(CO_2^-)_2$ ~1 pK_a unit and amounts for $CH_2(CO_2^-)_2$ to 0.8 pK_a units[33]. In DMSO solution the corresponding contributions should be 1.7 (i.e. $\varepsilon(H_2O)/\varepsilon(DMSO) = 78/46$) times larger, i.e. - 1.7 and - 1.3 units of pK_a*. However,

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* The negative sign of this correction means that its introduction makes the acid stronger (lower pK_a values).

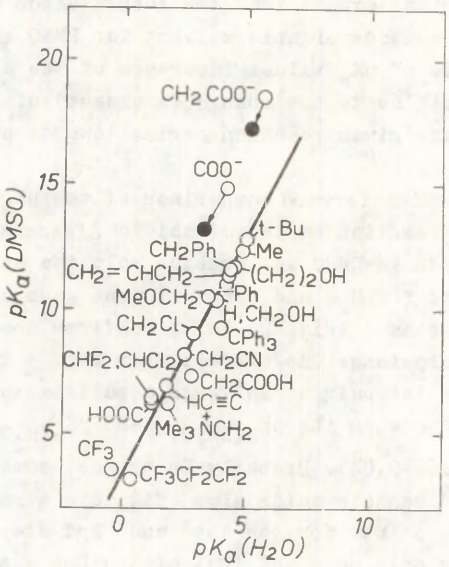

Fig. 1. Comparison of the pK_a values for the acidic dissociation of aliphatic carboxylic acids in DMSO and H_2O.

○ - electrostatic correction is not included

● - electrostatic correction for the destabilization of the dianionic form of the acid or for the stabilization of the zwitter-ionic form of betaine was included

even the introduction of these corrections into the experimental pK_a values (see Fig. 1) of these acids does not remove the deviation (by ca 4.2 units of pK_a) of the point for $pK_{a(2)}$ for the oxalic acid from the general straight line in Fig. 1.

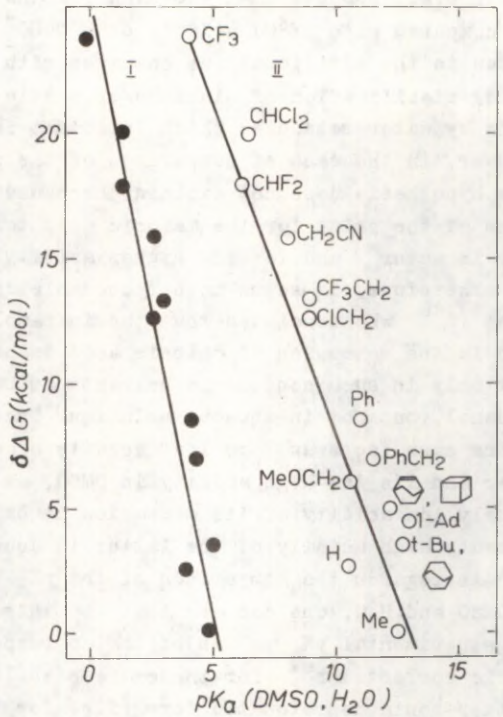

Fig. 2. Comparison of relative acidity of some carboxylic acids in the gas phase with the corresponding pK_a values of these acids in H_2O (I) and DMSO (II).

In the case of the $pK_{a(2)}$ value for malonic acid this correction does not either change the situation drastically: the deviation of the point for the 1st step of dissociation of this acid from the straight line with the slope 1.66 in coordinates $pK_{a(DMSO)}$ vs. $pK_{a(H_2O)}$ is more than twice less than the deviation of the point for $pK_{a(2)}$ values for $HOOCCH_2CO_2^-$ from the same straight line in Fig. 1. The reasons of these deviations are hard to explain. One

might, e.g., suppose that too high for the aqueous solution (as compared with DMSO) acidity of $HOOCCO_2^-$ and $HOOCCH_2CO_2^-$ is due to the additional (as compared with the monobasic acids) stabilization of dianions of oxalic and malonic acids by water molecules which is absent in DMSO solution. However, in the case of comparison of the $pK_{a(1)}$ values this hypothesis does not explain the cause of the deviations of the point for the malonic acid towards lower acidity in water* and towards higher acidity in DMSO.

Therefore, it seems more reasonable to follow Kolthoff et al[17,18] who concluded that the intramolecular hydrogen bond in the monoanion of malonic acid is practically present only in such nonaqueous solvents as DMSO, MeCN, and methanol, but not in aqueous solution. That suggestion explains such facts as "too low" acidity of malonic acid in water and its too high acidity in DMSO, as well as the anomalously low acidity of its monoanion in DMSO and the unexpectedly high acidity of the latter in aqueous solution.

As regards the comparison of the pK_a values of betaine in DMSO and H_2O, one can see that the introduction into the experimental pK_a values of the corresponding electrostatic corrections** for the extra-stabilization of its zwitter-ionic deprotonated form (i.e. for the betaine itself) decreases the deviation of this point from the general straight line (see Fig. 1) in coordinates $pK_{a(DMSO)}$ vs. $pK_{a(H_2O)}$.

As compared with the transfer from water into the dipolar aprotic solvent DMSO the transfer from water into an aqueous-organic mixture (e.g., aqueous alcohol) or a protonodonating solvent ($HCONH_2$, $HO(CH_2)_2OH$, etc.) is characterized by a relative constancy of solvation characteris -

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* In this case, in the 1st step of dissociation of this acid the intramolecular H-bond should increase the acidity of malonic acid.

** For the aqueous solution this correction is[33] +0.88 units of pK_a, whereas for DMSO it equals +1.5 units of pK_a.

tics of solvents[27]. In its turn, it also should lead to the solvent attenuation factors which are rather close to those for aqueous solutions. Indeed, as it was shown[7,8,11,30-33] this is, e.g., evidenced by Taft's ρ^{*} constants observed for the solvents-hydrogen bond donors.

As it was already demonstrated, the transfer from water into DMSO increases the susceptibility of the reaction series of the acidic dissociation of aliphatic carboxylic acids towards substituent effects 1.66 times.

Statistical analysis shows (see also Fig. 2) that only slightly more, 1.80 ± 0.07 times, increases the susceptibility of the same reaction series towards structural effects when transfer from DMSO into the gas phase occurs. At the same time one can see (see Fig. 2) that this change of solvent results in several inversions of the acidity order which is characteristic of aqueous solution or DMSO. So due to the significant contribution of the polarizational interactions into the gross substituent effect, in the gas phase some acids (pivalic acid (Piv), bicyclo [2.2.2] oc - tane-1-COOH(Oct), bicyclo [2.2.2] octene-1-COOH(Octe) adamantane-1-COOH(Ad), cubane-1-COOH(Cub) etc.) which contain bulky, highly polarizable substituents are more acidic than the formic and acetic acid (AcOH)[+].

Indeed, earlier[7,8,11,12,32], in terms of the approach which is based on the multiparametric equation

$$A = a_0 + a_1\sum\sigma^{*} + a_2\sum\Delta R + a_3\sum\sigma_R^{o} + a_4 n_1 + a_5\Delta n_2, \quad (1)$$

where A is the measurable quantity (gas phase basicity or acidity, ionization potential, pK_a, etc.), a_0, a_1, a_2, a_3, a_4 and a_5 are constants of the

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[+] In the aqueous ethanol[1] and in DMSO (Ref. 1 and Table 1) the acidity dereases as follows: AcOH > Cub > Piv > Oct Octe > Ad whereas in the gas phase[7-10] the acidity order is: Cub ≈ Octe > Ad > Piv > Oct > AcOH.

reaction series, $\sum\sigma^*$ and $\sum\sigma_R^o$ - the sums of inductive and resonance constants of substituents attached to the reaction center, $\Delta R = MR - MR_{(methyl)}$ where MR is the calculated additive molecular refraction of the substituents (this quantity is believed to serve[7,8,11,12] as an approximate quantitative measure of the polarizability of the substituent); n_1 and $\Delta n_2 = n_2 - n_{methyl}$ - are the numbers of H-atoms attached directly (n_1) or in the α-position to the reaction center.

it was shown that in the gas phase the gross substituent effect of alkyl-substituents is first of all determined by their polarizability characteristics.

This conclusion was recently confirmed also in the framework of another approach[5,9] which is based on separation of gross structural effects into field, polarizational and resonance contributions as reflected by Eq (2):

$$\delta\Delta G = a + b\sigma_F + c\sigma_\alpha + d\sigma_R \quad , \qquad (2)$$

where $\delta\Delta G$ - is the relative measured quantity (e.g., gas phase basicity or acidity), a, b, c, d - are the constants, characterizing the reaction series, σ_F, σ_α, and σ_R are the substituent constants which characterize, correspondingly, the contributions of substituent's field, polarizational and resonance effects.

The statistical treatment of the data shows (See Table 2 and[7,8,11,12]) that Eq. (1) and its partial variants are applicable also for the reaction series of the acidic dissociation of carboxylic acids. One has, however, to admit (See Table 2), that the contribution of the polarizability effect for this reaction series in aqueous solution is very much lower than in the gas phase, whereas in DMSO it is statistically negligible.

As expected, the a_1 value also decreases significantly

Table 2

The Results of Regression Analysis of Acidity of Carboxylic Acids in DMSO and H_2O (pK_a values) and in the Gas Phase (ΔG values) in Terms of Eq.(1) and Its Special Variants[+].

Medium		a_0	a_1	a_2	a_3	a_4	a_5	R	s	D_{max}	n
1	2 3	4	5	6	7	8	9	10	11	12	13
1. Gas Phase	a	0.9 (0.7)	9.26 (0.69)	0.208 (0.041)	-10.53 (6.45)	0	0	0.975	1.5	23.8	18
	b	1.1 (0.8)	8.56 (0.52)	0.194 (0.045)	-	-	-	0.975	1.7	23.8	19
	c	4.5 (0.5)	7.19 (0.50)	-	-	-	-	0.966	1.9	23.8	17
2. DMSO	a	12.20 (0.16)	-2.85 (0.12)	0	-1.12 (1.06)	0	0.202 (0.070)	0.993	0.30	9.5	20
	b	11.96 (0.17)	-2.97 (0.12)	0	-	-	-	0.987	0.42	9.5	21
	c	11.78 (0.10)	-2.91 (0.09)	-	-	-	-	0.991	0.35	9.5	20

Table 2 continued

1	2	3	4	5	6	7	8	9	10	11	12	13
3.	H_2O	a	4.75 (0.08)	-1.68 (0.06)	0.010 (0.003)	0	0.299 (0.197)	0.144 (0.05)	0.993	0.16	5.4	20
		b	4.65 (0.09)	-1.77 (0.07)	0.008 (0.003)	-	-	-	0.988	0.23	5.4	21
		c	4.67 (0.05)	-1.83 (0.04)	-	-	-	-	0.995	0.14	5.4	17

* For a_0, a_1, a_2, a_3, a_4 and a_5 see the text. In Table, under the regression coefficients a_i are given their reliability limits. R - correlation coefficient, s - standard deviation, D_{max} - maximum range of variation of measured quantity, n - the number of points. The zero value of a_i means its statistical negligibility, the dash in the Table shows that this factor was not included into the statistical treatment from the very beginning. For the gas phase throughout this Table the kcal/mol units are used, whereas for DMSO and H_2O the pK_a units are used. δ^* and δ^o_R constants are from[28,33-35]. For the fluorinated substituents (CF_3, CF_3CF_2, F_2CH etc.) the non-additive ("experimental") δ^* - values were used (compare with Ref. 7,8,11,12). The regression analysis program written by Prof. V.A. Palm (See Ref. 36 for the general features of the program) was used. The quantities A (pK_a and $\delta\Delta G$) to be correlated were taken from Table 1 of the present work.

with the transfer from the gas phase into solution. However, the inductive effect seems to be the major structural factor which determines the acidity of aliphatic carboxylic acids in DMSO and water.

Earlier it was shown[12,29] that such a decrease of a_1 and a_2 values with the transfer from gas phase into solution does not contradict the simple model considerations which visualize the substituent inductive effect through ion-dipole or dipole-dipole interactions and the substituent polarization effect via the charge-induced dipole interactions.

In conclusion it seems reasonable to make an attempt to estimate the pK_a value for perfluoropivalic acid $(CF_3)_3CCOOH$ which as such has never been liberated from its derivatives because of the easy decomposition of the free acid via the ejection of carbon dioxide. In connection with that problem it is also interesting to discuss some regularities which are characteristic to the effect of introduction of fluorine atoms or CF_3-groups into the immediate vicinity of the acidity center in the case of some reaction series (acidic dissociation of aliphatic carboxylic acids, CH-acids and alcohols). So, on the basis of the data on the successive substitution of hydrogen atoms in acetic acid for the CF_3 group and F-atoms one can see (Tables 3 and 4) that these substituent effects are non-additive, whereas the largest change of the pK_a or $\triangle G$ values takes place when the 1st substituent is introduced instead of the H-atom. In its turn (Tables 3-5) the effects of the further (2nd and third) introduction of F-atom or CF_3-group instead of H-atoms are roughly equal and their contribution is 60-70% of the increment which is characteristic to the substitution of the 1st H-atom for the substituent.

On the basis of the above-said and the data from Tables 3-5 one can make a rough estimation of the pK_a value for $(CF_3)_3CCOOH$ in water in the range between 1.2 and

Table 3

The Effect of Successive Substitution of Hydrogen Atoms of Methyl Group in CH_3COOH for Fluorine Atoms for Reaction Series of Acidic Dissociation of Aliphatic Carboxylic Acids in Gas Phase ($\delta\Delta G$), DMSO and Water (ΔpK_a)[a]

Medium		CH_3COOH	→	FCH_2COOH	→	$F_2CHCOOH$	→	CF_3COOH
Gas Phase	ΔG	341.1		331.3		323.8		316.3
	$\delta\Delta G$		9.8		7.5		6.5	
DMSO	pK_a	12.4		(8.9)[b]		6.2		3.6
	ΔpK_a		3.5		2.7		2.6	
H_2O	pK_a	4.75		2.6		1.2		0.$\pm$0.4
	ΔpK_a		2.15		1.4		1.2	

a - The gas phase acidities ΔG (kcal/mol) are taken from Refs. 6-10, pK_a values are from Table 1 or from Refs. 1, 37.

b - pK_a value for $ClCH_2COOH$ was used.

Table 4

Effects of Successive Substitution of H-atoms in Methyl Group of CH_3COOH for CF_3-group for Reaction Series of Acidic Dissociation of Aliphatic Carboxylic Acids in Gas Phase ($\delta\Delta G$) and Water (ΔpK_a)[a]

Medium		CH_3COOH	⟶	CF_3CH_2COOH	⟶	$(CF_3)_2CHCOOH$	⟶	$(CF_3)_3CCOOH$
H_2O	pK_a	4.75		3.00		2.35[26] 2.1[b]		(1.4 ± 0.2)[c]
	ΔpK_a		1.75		0.8 ± 0.1		(0.8)[b]	
Gas Phase	ΔG	341.1		327.7		-		-
	$\delta\Delta G$		13.4		-		-	

a - The gas phase acidities ΔG (kcal/mol) are from Refs. 6-10, pK_a values are from Ref. 1.

b - This work.

c - Rough estimate, this work. For the pK_a value of $(CF_3)_2CHCOOH$ the arithmetic mean value (2.2 ± 0.2) was used. The increment ΔpK_a was taken to equal 0.8 pK_a units.

Table 5

The Effects of Successive Substitution of CH_3-Groups in $(CH_3CO)_2CH_2$ for CF_3-Groups for Reaction Series of Acidic Dissociation of Derivatives of Acetylacetone in H_2O, DMSO (ΔpK_a) and Gas Phase ($\delta\Delta G$)[a]

Medium		$(CH_3CO)_2CH_2$	⟶	$CH_3COCH_2COCF_3$	⟶	$(CF_3CO)_2CH_2$
H_2O	pK_a	9.0		6.8		5.4
	ΔpK_a		2.2		1.4	
DMSO	pK_a	13.0		6.3[b]		2.2[b]
	ΔpK_a		6.7		4.1	
Gas Phase	ΔG	336.7		322.0		-
	$\delta\Delta G$		14.1		-	

a - Gas phase acidity ΔG (kcal/mol) is from Ref. 6-10, pK_a values for H_2O and DMSO from Ref. 37.

b - This work. The detailed description of the results will be given in a separate publication.

Table 6

The Effects of Successive Substitution of H-atoms in Methyl Group of CH_3OH for CF_3-Groups in Gas Phase ($\delta\Delta G$), DMSO and H_2O (ΔpK_a) for the Reaction Series of Acidic Dissociation of Aliphatic Alcohols[a]

Medium		CH_3OH	⟶	CF_3CH_2OH	⟶	$(CF_3)_2CHOH$	⟶	$(CF_3)_3COH$
Gas Phase	ΔG	374.0		354.1		338.3		324.0
	$\delta\Delta G$		19.9[10] 15.9[28]		15.8		14.3	
DMSO	pK_a	28.9		22.8		16.0[7]		10.4
	ΔpK_a		6.1		6.8		5.6	
H_2O	pK_a	15.5		12.3		9.2		5.4
	ΔpK_a		3.2		2.9		3.8	

a - Gas phase acidities ΔG (kcal/mol) are from Refs.[6-10], pK_a values for DMSO and H_2O from Refs. 1, 7, 35.

1.6 (See Table 4)[+] . Inspite of somewhat contradictory nature of the corresponding data, it is reasonable to assume that in the case of acidic dissociation of aliphatic fluoro-substituted alcohols (See Table 6) the substituent effects are most probably not far from being additive (See also Refs.7, 28, 34, 39).

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CHEMICAL SHIFTS OF HYDROXYLIC PROTON IN BINARY MIXTURES OF ACETONITRILE WITH ALCOHOLS

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Chemical shifts of hydroxylic proton of the OH-group of alcohol in binary mixtures of aceto - nitrile-ROH (R = Me, Et, i-Pr, t-Bu, $(CF_3)_2CH$, $(CF_3)_3C$) were measured at the alcohols mole fraction $0.1 \leq N_{ROH} \leq 1.0$. It was found that the in - crease of the concentration of alkyl-substituted alcohols leads to the downfield shifts of the ^1H resonance. In all systems the chemical shift of the hydroxylic proton changes monotonously with the composition of the binary solvent. Deviations of the chemical shifts from the values predicted on the basis of their mole fractional additivity were also studied. It was found that for the system MeCN-ROH the maximum deviations from the additivity occur at $N_{ROH} \approx 0.4 \div 0.5$.

Unlike the behavior of the alkyl-substituted alcohols, the alcohols with the strongly electronegative substituents induce the shift of the ^1H resonance towards the higher magnetic field.

Earlier, studying the solvent effects of the binary mixtures of dipolar aprotic solvents with hydroxylic components (alcohols) on some chemical (e.g., log k of the solvolysis of alkyl halides) and spectroscopic (E_T parameters of Dimroth and Reichardt) characteristics of the solute it was demonstrated[1,2] that sometimes, the relationships between the solute property and the composition of the binary mixture are characterized by clearly pronounced extremums.

On the other hand, differently from the aforesaid the direct study of concentrational dependence of such a solvent property as the chemical shift of hydroxylic proton of alcohols in their binary mixtures with some aprotic solvents (DMSO, aceton, etc.) shows[3,4] that the extremums on the plots, measured property-solvent composition, are mostly quite rare exceptions rather than a widespread rule.

For the further study of that problem in the present work the dependence of the chemical shifts of the protons of the OH-group of alcohols on the molar fraction of the latter in their binary mixtures with acetonitrile has been studied. In order to study the influence of the electronic structure of the alcohol on the chemical shifts of proton of the alcohol's OH-group alongside with the alkyl-substituted alcohols some mixtures of fluorinated alcohols, $(CF_3)_2CHOH$ and $(CF_3)_3COH$ with the acetonitrile were also included.

Experimental

Acetonitrile and aliphatic alcohols were purified and dehydrated according to the standard procedures[5,6]. $(CF_3)_2CHOH$ (Aldrich) and $(CF_3)_3COH$(PCR) were used without any further purification. Proton NMR spectra were measured at room temperature on a TESLA BS 487 B spectrometer at 80 MHz. The TMS was used as internal reference. The results of the measurements are recorded in Tables 1 and 2.

Table 1

Chemical Shifts δ_{OH}(ppm) of Hydroxylic Proton of Alcohol in Its Binary Mixtures with Acetonitrile

MeOH		EtOH		i-PrOH		t-BuOH	
N_{ROH}	δ_{OH}	N_{ROH}	δ_{OH}	N_{ROH}	δ_{OH}	N_{ROH}	δ_{OH}
0.113	2.64	0.096	2.89	0.118	2.98	0.099	2.74
0.204	3.03	0.189	3.31	0.189	3.26	0.203	3.06
0.301	3.33	0.279	3.61	0.329	3.71	0.315	3.34
0.434	3.75	0.401	4.01	0.407	3.93	0.518	3.78
0.535	3.99	0.481	4.21	0.517	4.21	0.581	3.91
0.616	4.16	0.606	4.50	0.720	4.63	0.655	4.06
0.682	4.31	0.678	4.66	0.838	4.85	0.776	4.31
0.801	4.54	0.773	4.88	0.908	5.01	0.883	4.53
0.888	4.71	0.871	5.08	1.0	5.26	1.0	4.73
1.0	4.85	1.0	5.38				

Table 2

Chemical Shifts δ_{OH}(ppm) and Line Width at Half Height $\Delta\nu_{1/2}$(Hz) of Hydroxylic Proton of Fluorinated Alcohols in Their Mixtures with Acetonitrile

$(CF_3)_2CHOH$			$(CF_3)_3COH$		
N_{ROH}	δ_{OH}	$\Delta\nu_{1/2}$	N_{ROH}	δ_{OH}	$\Delta\nu_{1/2}$
0.18	5.45	55	0.1	8.2	-
0.324	5.24	44	1.0	4.18	42
1.0	4.76	15			

Discussion

In Fig. 1 the concentrational relationship between the proton chemical shift of OH-group of the alkyl-substituted or fluorinated alcohols and the molar fraction of the latter

in their binary mixtures with acetonitrile is shown. One can see that for all alkyl-substituted alcohols the chemical shifts of the hydroxylic proton change (decrease) monotonously with the increase of the content of MeCN in the binary mixture - i.e. the downfield shift was monitored. These facts support the conclusion[3] that the heteroassociation between the aliphatic alkyl-substituted alcohol and the basic solvent causes the upfield chemical shift of the hydroxylic proton of the alcohol whereas the selfassociation of the latter initiates the shift of the proton resonance signal in the opposite direction.

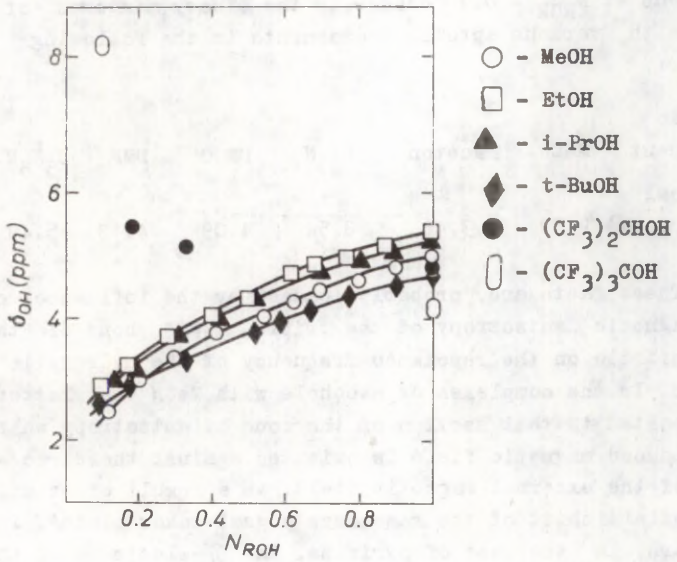

Fig. 1. The dependence of the chemical shifts δ_{OH} of the hydroxylic proton in the binary mixtures of alcohol-acetonitrile on the molar fraction of alcohol, N_{ROH}.

In the all earlier[3] studied binary systems (aprotic component - DMSO, acetone, Et_3N, DMF or pyridin) as well as in the mixtures of alcohols with MeCN the chemical shifts of the hydroxylic proton at a fixed molar fraction N_{ROH} = 0.1 increase in the following order $\delta_{MeOH} < \delta_{t\text{-}BuOH} < \delta_{i\text{-}PrOH} < \delta_{EtOH}$. The comparison of the chemical shifts of the hydroxylic proton in the various binary mixtures at a fixed N_{ROH} = 0.1 shows that for the presently studied system MeCN - ROH the ^1H resonance signal is located at a higher magnetic field than in the case of the above-mentioned systems.

So, the chemical shifts of the proton of the methanol's OH-group at N_{ROH} = 0.1 change in the binary mixtures of MeOH with various aprotic components in the following manner:

Aprotic component	MeCN	aceton	Et_3N	DMSO	DMF	C_5H_5N
Chemical shift (ppm)	2.59	3.46	3.54	4.09	4.13	5.49

These facts are, probably, caused by the influence of the magnetic anisotropy of the triple C ≡ N bond of the acetonitrile on the resonance frequency of the hydroxylic proton. In the complexes of alcohols with MeCN the latter are located in that section of the cone of anisotropy where the induced magnetic field is oriented against the direction of the external magnetic field. As a result of that the upfield shift of the resonance signal takes place[7]. In its turn, in the case of pyridine, the π-electrons of the latter induce the local magnetic field which shifts the signal of the hydroxylic proton towards the lower magnetic field as compared with the other solvents.

The study of the deviations ($\Delta\delta_{OH}$) of chemical shifts of the signal of the hydroxylic proton from the values predicted on the basis of the hypothesis about their mole fractional additivity shows (see Fig. 2) that in this respect the binary systems alcohol-acetonitrile are characte-

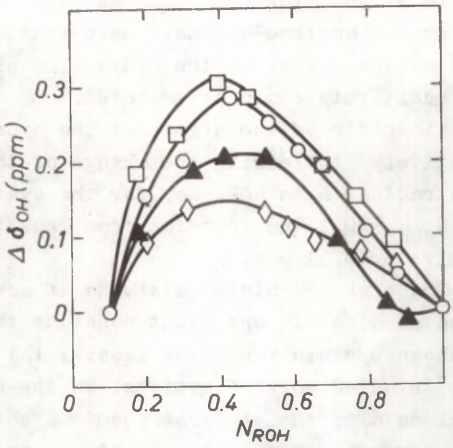

Fig. 2. Deviations of chemical shifts $\Delta\delta_{OH}$ of alcohol's hydroxylic proton from the mole fractional additivity for the binary mixtures alcohol-acetonitrile. See Fig. 1 for notation of points.

rized by relatively small deviations from the additivity. At the same time, one can see that for these systems the maximum deviations refer to $N_{ROH} \approx 0.4 \div 0.5$.

The results about the maximum deviations of the chemical shifts of the resonance of the hydroxylic proton from mole fractional additivity could be used to classify the binary systems studied by us into two main categories. So, in the case of the binary systems[3] consisting from alcohols and DMSO or DMF the maximum deviations from the additivity refer to the 2 : 1 ratio of the hydroxylic and aprotic components of the binary mixture.

Differently from these systems, for the binary mixtures of alcohols with Et_3N[3], pyridin[3] and acetonitrile

the maximum deviations of the resonance of the hydroxylic proton from its mole fractional additivity occur at the equimolar ratio of the hydroxylic and aprotic components whereas for the system acetone-alcohol[3] no deviation of the chemical shift of the signal of the hydroxylic proton from mole fractional additivity could be detected.

Chemical shifts of the signal of the hydroxylic proton change relatively little with the change of the chemical nature of the radical R in ROH. So, for the system acetonitrile-alcohol at N_{ROH} = 0.1 the transfer from MeOH to EtOH changes the δ_{OH} only by 0.31 ppm.

In the case of the binary mixtures of acetonitrile with the fluorinated alcohols one might conclude that the behavior of these systems resembles closely the situation for the earlier[4] studied solvent systems. On the basis of our experimental data on the study of chemical shifts of the signals of hydroxylic proton in the binary systems alcohol-aprotic component the behavior of the systems containing fluorinated alcohols could be summed up as follows:

a) the binary mixtures which involve fluorinated alcohols on one hand, and alkyl-substituted alcohols, on the other hand, have rather different dependences of the chemical shifts δ_{OH} on the mole fraction N_{ROH} of the hydroxylic component. In other words, the increase of the concentration of the latter leads to the downfield shift of the signal from the proton of the OH-group of the fluorinated alcohol. The opposite is true for the systems which include the alkyl-substituted alcohols;

b) the increase of the electronegativity of the radical R in ROH leads to the significant increase of the chemical shift of the signal from the hydroxylic proton at the lower mole fractions of the alcohol in their binary mixtures with the aprotic component;

c) the resonance line which refers to the signal of the proton of the OH-group of the fluorinated alcohol broadens with the change of N_{ROH} (see Table 2). The linewidth $\Delta\nu_{1/2}$ reaches its maximum value at comparable concentra -

tions of the H-bonded complex and free molecules of alcohol. It probably means that the linewidth is determined by the processes of the repeated rupture and formation[8] of the H-bonded complex between the hydroxylic and aprotic components of the binary mixture.

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THE EFFECT OF THE SOLVENTS OF THE THERMAL DECOMPOSITION RATE OF THE PERPROPIONIC ACID

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The rate constants of the thermal decomposition reaction of perpropionic acid in some solvents in a temperature range of 313-353K are estimated. It is shown that the decomposition rate of peroxide is described well by two-parametric regression equation taking into account the basicity and polarizability of the medium.

Perpropionic acid, as other organic peroxides, is characterized by thermal instability, decreasing with its participation the selectivity of liquid-phase reactions. It is known[1] that the decomposition rate of peracids depends upon a number of factors: nucleophility of medium, reactor material, initial concentration etc. To choose the optimal alternative of the solvent and to estimate the losses of active oxygen on account of spontaneous decomposition of perpropionic acid, the kinetic data on the process rate are required.

The experiments were carried out in the temperature range of 313-353 K in the most frequently used solvents - chlorine derivatives of methane, aromatic hydrocarbons and ethylacetate. The decomposition reaction of perpropionic acid was conducted in sealed pyrex ampoules with thermostatic con-

trol. Peracid solutions were prepared using the method[2] and its concentration was varied in the range of 0.1-1.1 mol/l. The solutions were purified by known procedures[3]. The decomposition reaction of perpropionic acid was followed by its concentration change; the latter was determined by the iodometric titration[4]. The linear regression equation was solved on a computer.

The thermal decomposition of perpropionic acid proceeds at measured rate at temperature above 313 K and the curves of its expenditure obey the equation of the first-order reaction. Numerical values of rate constants in the investigated temperature range and the activation process parameters are listed in the Table. The accuracy of the rate constant measurements is on the average $\pm$ 10%. Relatively low activation energy and preexponential factor indicate that the measured experimental rate constants of the perpropionic acid decomposition reaction are effective and the process itself appears to prooeed by a complex chain-radical mechanism. This is particularly evident from the fact of inhibition of peracids decomposition reaction by insignificant additives of phenols, hydroquinone, picolinic acid[5].

From the kinetic data it is obvious that the decomposition reaction rate of perpropionic acid depends on a solvent and increases in the series CCl_4-$CH_3COOC_2H_5$ by more than one order. For the quantitative determination of the reaction sensivity to the properties of the medium we attempted to establish the relationship between the factor taking into account both nonspecific (polarity Y, polarizability P) and specific (total acidity E and basicity B) solvation by the solvent. Calculation was performed by the four-parametric correlation method[6] of Palm and Koppel.

For making the calculation the rate constants of the perpropionic acid decomposition were taken at 293 K, since all the solvent constants are given at this temperature. Numerical values of solvent features (Y, P, B) are presented in the monography[7]. For lack of the data on acidity value of each studied solvent the effect of this factor

KINETIC PARAMETERS OF THE THERMAL DECOMPOSITION REACTION OF THE PERPROPIONIC ACID IN DIFFERENT SOLVENTS

NN:	Solvent	T,K	$k \cdot 10^5$, sec^{-1}	E, kj/mol	log A
1.	Tetrachloride carbon	313	0.10		
		323	0.23		
		333	0.45	61.9±2.9	4.3±0.4
		343	0.96		
		353	1.56		
2.	Dichloromethane	313	0.22		
		323	0.47		
		333	0.67	55.2±2.5	3.6±0.4
		343	1.44		
		353	2.56		
3.	Chlorobenzene	313	0.36		
		323	0.72		
		333	1.49	61.1±1.2	4.7±0.2
		343	2.83		
		353	4.95		
4.	Benzene	313	0.39		
		323	0.79		
		333	1.60	59.8±0.8	4.6±0.1
		343	2.90		
		353	5.35		
5.	p-Xylene	313	1.08		
		323	2.23		
		333	4.20	60.7±2.9	5.1±0.5
		343	9.02		
		353	14.58		
6.	Ethylacetate	313	2.97		
		323	5.66		
		333	7.88	51.5±2.9	4.0±0.5
		343	14.9		
		353	24.6		

was not taken into consideration. The performed calculations indicate that the overall correlation is 0.976 and the three-parametric regression equation is as follows:

$$\log k \cdot 10^5 = -2.936 + 0.1964(Y) + 3.6387(P) + 0.0095(B)$$

$$R = 0.976; \qquad S = 0.29$$

Since the regression coefficients do not permit to estimate the significance of the individual parameters of the obtained equation their sequential elimination to determine the particular correlation coefficients has been made[8].

$\log k = f(Y, P)$ $\quad R = 0.478$
$\log k = f(Y, B)$ $\quad R = 0.963$
$\log k = f(P, B)$ $\quad R = 0.975$

The obtained values point to the practical insignifi - cance of the polarity parameter. This confirms the conclu - sion that due to the homolytical decomposition mechanism of organic peroxides the medium polarity does not play an important role in this process[9].

Thus, the effect of the medium on the rate of the studied reaction can be described with a sufficient accuracy by the two-parametric linear equation taking into account the polarizability and the basicity of the solvent:

$$\log k \cdot 10^5 = -2.7768 + 3.3687(P) + 0.00954(B)$$

$$R = 0.975 \qquad S = 0.29$$

The analysis of this equation shows that the basicity affects mainly the rate constant value (paired correlation coefficient $\bar{r} = 0.96$). However, the factor of nonspecific solvation plays an important role in moleclar activation. A considerable decrease in the coefficient R, while elimina - ting it, and a comparatively high value of the paired correlation coefficient of polarizability $\bar{r} = 0.48$ comfirm the above mentioned statement. The corresponding relationship

$2.777 + \log k \cdot 10^5 - 3.369(P) = f(B)$ is shown in the fig - ure.

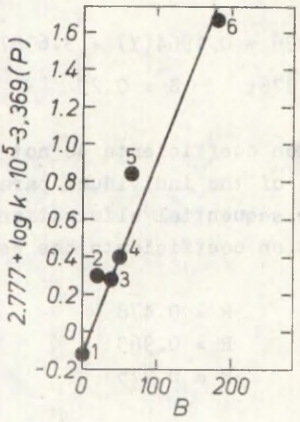

Fig. 1. Two-parametric correlation of the reaction rate of perpropionic acid thermal decomposition in different solvents. (Numerals correspond to the ordinal number in the Table).

Point 5 falls to some extent out from the above rela - tionship (p-xylene) in which the decomposition rate is higher than the calculated one. The elimination of this solvent permits to increase the correlation coefficient R to 0.992 which corresponds to the "perfect" correlation[7]. Positive values of regression coefficients with parameters P and B indicate the relative stabilization of the activated state of the peroxide molecule due to its solvation by the solvent.

The obtained results permit to predict the rate of the side decomposition reaction of perpropionic acid in the solvents with the known values of polarizability and basicity parameters.

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THE GRIGNARD REAGENT CATALYZED GRIGNARD REACTION

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The reaction between alkylhalides and magnesium is catalyzed by the monosolvated Grignard reagent. The activity of the catalyst depends on its structure, while the chlorides are more active compared with the bromides. The process can be described by the first-order kinetics if the reagent and the alkylhalide from which the catalyst is prepared, coincide. Otherwise, either self-catalytic behavior or aperiodic oscillation in the product formation rate can be observed. The oscillation-phenomenon in the Grignard reaction has been discovered first. It is the first example of an heterogeneous oscillating system where the catalyst is dissolved and the solid surface is a reagent.

Recently[1-3] we found that in the presence of small additions of organic bases (less than one mole to a mole of the halide) the organomagnesium compound formatiom in inert media proceeds in two steps. In the first rapid stage, a monosolvated Grignard reagent is formed, the yield of the latter corresponding to the amount of the base in the reaction mixture. After the rapid stage, a slow completion of the reaction occurs, which is apparently catalyzed by the solvated Grignard reagent. This stage of reaction was of

zero kinetic order.

Investigation of the slow step of the reaction is of certain interest in connection with application of the bases in catalytic amounts in industrial organomagnesium synthesis, especially because during this stage a considerable amount of the products is formed. Besides, due to the uncomplicated kinetics and accessibility of investigation, the slow stage may become a versatile tool of investigation of Grignard reaction mechanism.

In oder to verify our assumptions concerning the catalysis, the kinetics of some alkylmagnesium bromides and chlorides formation in the presence of various equimolecular complexes of alkylmagnesium halides with ethyl ether has been studied.

Experimental

Reagents and solvents were purified as described earlier[1]. Magnesium metal was used in the form of beads, 1.0 - 1.6 mm in diameter.

The reaction flask (a 35 ml Erlenmeyer flask) was capped with a teflon stopper which was equipped with a silicon rubber disk. The reaction flesk was placed into a glass vessel, whose temperature was kept at $30\pm0.1^{\circ}C$. The reaction mixture was stirred by means of a magnetic stirring bar.

Before the kinetic runs 6 ± 0.05 g of magnesium (0.25 g atom, total surface about 160 cm^2) was placed into the flask. Toluene and ethyl ether (altogether 20.0 ml in each run) were introduced into the flask by calibrated syrenges. After switching on the stirrer an appropriate amount of alkylhalide (the molar ratio of ether and alkylhalide was 1 : 1) was introduced. After completion of the exothermic reaction a monosolvated alkylmagnesium halide, as a catalyst , was formed. The concentration of the latter was mostly 0.51 M (about 0.012 g mole in the reaction mixture). When the system had reached a constant temperature ($30^{\circ}C$), about 0.016 g mole of the corresponding alkyl halide was introduced. At that moment also started the time accounting. During the

reaction at appropriate moments of time aliquots of 1.0 ml were withdrawn and analyzed acidimetrically for the content of basic magnesium. In the same aliquots the amount of halide was determined by the Volhard method.

The kinetic curves were produced by plotting the yield vs time.

Results and discussion

In our earlier investigations[1-3] the corresponding entire amount of alkyl halide was introduced into the reaction mixture. The rapid stage of the reaction was followed by the slow one, the kinetics of this stage was of zero-order. The values of rate constants show a quadratic dependence on the ether content in the reaction mixture at the constant initial concentration of the halide.

In this study the two stages of reaction were separated. Preliminarily, the catalyst (the monosolvated Grignard reagent) was prepared and then another portion of alkyl halide was added. In this way the reaction between alkyl halides and magnesium was investigated in the presence of the chosen catalyst.

In the first experimental series the reactions of n-butylbromide and -chloride were investigated in the presence of various amounts of the catalysts of the same nature, i.e., of the complexes of n-butylmagnesium bromide and -chloride with Et_2O, correspondingly. As it was expected[1] the rate constants of the zero-order reaction for n-butylbromide were in a square dependence on the concentration of the corresponding catalyst (Fig. 1). However, the reaction system, where bromine is replaced by chlorine behaver differently. The rate constants linearly depend on the concentration of the catalyst at the large range of its concentration. Besides, the chloride-system essentially reacts more rapidly than that of bromides. The latter circumstance appears to be somewhat surprising while in pure Et_2O the chlorides compared with bromides have markedly lower reactivity[4].

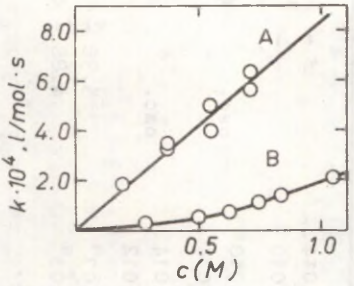

Fig. 1. Dependence of reaction rate on concentration of the catalyst. A - n-butyl chloride, B - n-butyl bromide.

Further the reagents as well as the catalysts were varied. All the kinetic measurements were carried out at the fixed concentration of catalyst (0.51 M).

It was discovered that in our experimental conditions in the case of the coincidence of the reagent and alkyl - halide from which the catalyst was prepared the reaction proceeds normally by the zero-oder kinetics. Lacking of such kind of coincidence causes irregular oscillation in the rate of product-formation. In the case of an insignificant difference in alkyl groups and halogen the amplitude of oscillation remains within the limits of an experimental error, and the relationship the yield vs time can be approximated by a straight line corresponding to the zero-order kinetics (Table). However, the oscillation achieves markedly greater amplitudes while the reagents differ from each other by halides or at least one of the alkyl groups is branched. A typical example of a such kind of process is presented in Fig. 2. To the oscillation in the rate of alkylmagnesium halide formation always strictly corresponds the oscillation in the rate of magnesium halide

Table

Rate Constants of Formation of Alkylmagnesium Halides, $k \cdot 10^4$ mole.sec^{-1}

Reagent	Catalyst			
	EtMgBr · Et_2O	nBuMgBr · Et_2O	iBuMgBr · Et_2O	nBuMgCl · Et_2O
EtBr	1.10 ± 0.04	0.410 ± 0.012	0.108 ± 0.014	-
	1.02 ± 0.08	0.506 ± 0.022	0.146 ± 0.010	-
nBuBr	0.77 ± 0.08	0.486 ± 0.016	0.258 ± 0.010	osc. 4.0[a]
		0.492 ± 0.026	0.316 ± 0.014	
iBuBr	0.60 ± 0.04	0.248 ± 0.034	0.138 ± 0.014	osc. 4.5[a]
		0.226 ± 0.012	0.156 ± 0.012	
nBuCl	0.15 ± 0.02[a]	0.22 ± 0.03[a]	0.25 ± 0.03[a]	5.98 ± 0.08
	0.22 ± 0.04[a]	0.24 ± 0.04[a]	0.24 ± 0.03[a]	4.88 ± 0.19
	self-catal.	self-catal.	self-catal.	
iBuCl	oscillations	oscillations	oscillations	0.74 ± 0.07[a]
				0.88 ± 0.04[a]
				self-catal.

[a] Initial rate.

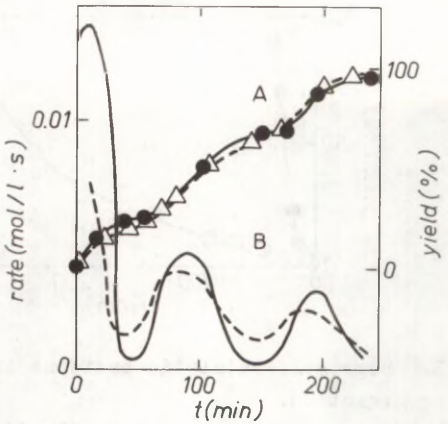

Fig. 2. An example of the self-catalytic process. Catalyst: ethylmagnesium bromide-ethyl ether (0.51 M). Reagent: isobutyl chloride.
A - dependence of the yield of isobutyl - magnesium chloride vs. time.
B - dependence of the reaction rate vs. time.

formation. If the experimental conditions are kept constant the oscillations are reproducible (Fig. 2.). Alteration of the amount of catalyst in the reaction mixture causes the alteration of the character of oscillations, however, we could not reveal any regularities in the concentration effect of the catalyst.

Sometimes, for example, in the case of n-butylchloride and bromide-catalysts or in the case of isobutyl chloride and n-butylmagnesium chloride catalyst, a self-catalytic pattern pf process was observed instead of oscillations. It is not excluded that one could observe a transition to the oscillating process by a greater initial concentration of the reagent. In order to characterize such kind of process

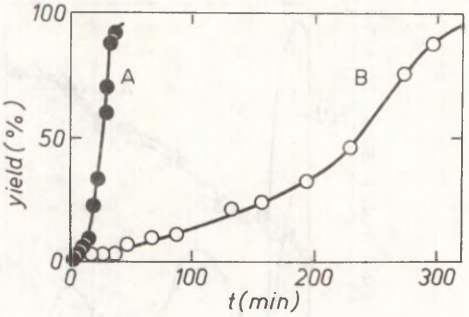

Fig. 3. Some self-catalytic patterns of the reaction.
A - n-butylmagnesium chloride-ethyl ether (catalyst) and isobutyl chloride.
B - n-butylmagnesium bromide-ethyl ether (catalyst) and n-butyl chloride.

the initial rates of reaction were determined (Table I).

It follows from the data in this table that the rate of reaction is determined mainly by the nature of catalyst. Both the bromides and the chlorides in the case of bromide-catalyst react relatively slowly. The activity of bromide catalysts at least for alkylbromides decreases in order : ethyl > n-butyl > iso-butyl. At the same time bromides and chlorides react rapidly in the presence of chloride cata - lyst.

To our mind the above mentioned experimental material confirms well the hypothesis about the catalysis by the solvated organomagnesium compounds. If the catalysis was car - ried out by uncomplexed ether then with an increase of the concentration of the organomagnesium compound should occur the decrease in the equilibrium concentration of the uncomplexed ether in the reaction mixture. These circumstances do not permit to explain the linear or self-catalytic pat - tern of the reaction. Moreower, alkylmagnesium chlorides are more effective Lewis' acids compared with the corres-

ponding bromides and therefore can more strongly bind the ether and thereby lower the reaction rate. However, the alkylmagnesium chlorides appeared to be very effective catalysts.

An essential role in the structure of catalyst performs the hydrocarbon group. A specially synthesised and investigated system of $MgBr_2 \cdot Et_2O$ revealed no catalytic activity neither for alkyl bromides nor for chlorides. Entirely unexpected was the self-oscillation of the process under certain conditions. By the way, the number of the reactions accompanied by oscillation speedily increases[6].

We found a novel self-oscillating reaction - the well-known Grignard reaction carried out under certain condition.

So far as the subject of investigation appears to be very complicated, due to its heterogenity and as the details of Grignard's reagent formation mechanism are not completely known, there are many alternative possibilities to explain the oscillations in this reaction. Let us consider two of them.

First, in order to guarantee the development of the process, it is necessary to remove the reaction products from the surface of magnesium metal. This causes the presence of two states of reaction centres on the magnesium surface. That may cause the self-oscillations analogically to the catalytic reactions with solid catalysts.

Second. We found that different monosolvated Grignard reagents have different catalytic activity. We also found that by our experimental conditions both the catalyst and the products of the reaction were present in the solution[x]. Consequently the unsolvated product of the reaction is complexed with solvated alkylmagnesium halide. Thus, during the reaction there is a permanently changing system of complicated complexes or associates in the reaction mixture.

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[x] E. g., according to our estimations, the solubility of ethyl ether complexes with n-butylmagnesium chloride and bromide in toluene is nearly 1.5 M.

The distribution of the organic base between those particles may not reach an equilibrium during the reaction and so can cause the oscillations in the reaction rate. We consider the latter explanation most likely to hold in the case of a long period oscillation (Fig. 2.), although the contribution of the former is not excluded.

The above-mentioned case happens to be the first example of such kind of an oscillating system where the catalyst is dissolved but the reagent is a solid surface. Our preliminary experiments indicate that an analogical phenomenon occurs when tetrahydrofurane is used as an organic base.

The mechanism of catalysis by monosolvated alkylmagnesium halides remains still obscure.

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C O N T E N T S

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