Title	KINETICS OF CHEMICAL REACTIONS IN POLAR LIQUIDS : II : Comparison with Experiment
Author(s)	GERMAN, E. D.; DOGONADZE, R. R.; KUZNETSOV, A. M. et al.
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 19(2), 115-125
Issue Date	1971-08
Doc URL	https://hdl.handle.net/2115/24926
Type	departmental bulletin paper
File Information	19(2)_P115-125.pdf

J. Res. Inst. Catalysis. Hokkaido Univ., Vol. 19, No. 2, p. 115 to 125 (1971)

KINETICS OF CHEMICAL REACTIONS IN POLAR LIQUIDS

II: Comparison with Experiment

By

E. D. GERMAN*), R. R. DOGONADZE*), A. M. KUZNETSOV*),
V. G. LEVICH*) and YU. I. KHARKATS*)

(Received February 23, 1971)

Abstract

Experimental data (reaction rate constants, reaction heats) for some proton transfer reactions are discussed on the base of quantum theory of chemical reaction kinetics in polar media. It is shown that the solvent reorganization energy E_s is different for reactions of primary, secondary and tertiary amines. This is because primary, secondary and tertiary amines must form different reaction series. The theoretical dependences of reaction rate constant on the equilibria constant were plotted using the calculated values of E_s for ionization reactions of nitrocompounds in water. These curves were compaired with the experimental data.

In the preceding paper1) the main results of a general quantum-statistical theory of chemical reactions in a polar medium were presented. In the present paper some results of the theory are compared with the experimental data for proton transfer reactions.

Study of proton transfer reactions in polar medium is of interest in itself as well as of great importance for the treatment of more complex processes. For instance, in the case of catalysis by acids and bases, one of the intermediate steps, which is often the limiting step, is the proton transfer from substrate to base, or from acid to substrate.2,3)

It was shown in an experimental study of the kinetics of this type of reactions catalyzed by acids3) that the observed reaction rate constants are related to the dissociation constants of acids by the Brönsted relation

$$\log k_0 = G_{AH} + \alpha \log K_{AH} \qquad (1)$$

where k_0 is the observed rate constant of catalytic reaction, K_{AH}-the equilib-

---

*) Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow, USSR.

rium dissociation constant of the acid, α-the Brösted coefficient, G_{AH}-a constant.

The quantities α and G_{AH} characterize a given series of acids and depend on the reaction type, solvent and temperature. A similar relationship was found for the case of catalysis by bases

$$\log k_0 = G_{BH} + \beta \log K_{BH} \tag{1 a}$$

For a reaction series with varying acid AH or base B, relation (1) is often written in an equivalent form

$$\log k_0 = \text{const} - \alpha (pK), \qquad (2)$$
$$pK \equiv pK_{AH} - pK_{BH} = -\log (K_{AH}/K_{BH})$$

where K is the equilibrium constant of the reaction

$$AH + B \rightleftarrows A^- + BH^+$$

In terms of the absolute reaction rates theory formula (2) is interpreted as a linear relation between the free energy of activation ($\Delta F^{\#}$) and the free energy of reaction (ΔF)[4,5)]

$$\Delta F^{\#} = \text{const} + \alpha \, \Delta F \tag{2 a}$$

in which the Brönsted coefficient α for a reaction series is a constant, the values of α for different series ranging from zero to unity.

In some studies[2,6,8)], however, it was pointed out that the coefficient α can vary within this range even for a single reaction series. The first attempt to explain the limiting values of α lying close to zero and to unity was made by Eigen[6)], who considered the limiting values of α to be associated with the diffusion limitations for the direct and the back reactions, respectively. This explanation, however, is not adequate for slow proton transfer reactions, when the diffusion limitations are known to be absent.

In the theory set forth in Part 1 it was established that in the general case for reactions carried out in the solution a correlation should be expected to exist between the activation energy and the reaction heat rather than between the free energies of activation and reaction:

$$\alpha(\Delta J) = \frac{d(E_a)}{d(\Delta J)}, \qquad E_a = \text{const} + \int \alpha(\Delta J)\, d(\Delta J) \tag{3}$$

If, however, within a reaction series, the reaction entropy ΔS and the preexponential factor are approximately constant, along with the correlation between the activation energy and the reaction heat, there should exist also a correlation between the logarithms of the reaction rate constant and equilibrium constant Moreover, even in the absence of diffusion limitations, the Brönsted coefficient in formula (3) is not a constant within one reaction series and, generally speaking, ranges from zero to unity, which can be readily seen when considering the dependence of E_a on ΔJ shown in Fig. 3 in Part 1.

Now we shall pass to the discussion of the experimental data for proton transfer reactions in polar medium.

1. Protonation of amines.

Since the protonation of amines, like other reactions to be considered below, is a purely proton transfer process, the relevant activation energy, as shown in Part 1, can be written as :

$$E_a = \frac{(E_s + \Delta J)^2}{4E_s}, \quad |\Delta J| < E_s \tag{4}$$

It follows from (4) that in this case the coefficient α is equal to

$$\alpha = \frac{d(E_a)}{d(\Delta J)} = \frac{1}{2} + \frac{\Delta J}{2E_s} \tag{5}$$

The physical significance of the quantities ΔJ and E_s contained in (4) was discussed in detail in Part 1. Here we shall only say that for the reactions under consideration $(-\Delta J)$ practically coincides with the reaction heat and E_s is the energy of the solvent repolarization in the course of reaction, which depends on the charge redistribution in the reactants and reaction products.

In the case of the reaction series obtained by introducing substituents into the reacting molecules, the charge redistribution in the course of reaction can be expected to be the same, which should lead to the constancy of the parameter E_s within this series. The constancy of E_s is most likely to be observed for the reaction series in which substituents are introduced at a large distance from the reaction centre, When substituents are introduced near the reaction centre, their effect on the charge redistribution should be greater and it is possible that the reorganization energy will not be a constant.

Let us consider the reaction of interaction of methylamines and pyridine with nitroethane. Substituting into (4) the experimental values of the activation energies E_a and the reaction heats $(-\Delta J)$ we find the corresponding values of E_s :

$$E_s = 2E_a - \Delta J + \sqrt{(2E_a - \Delta J)^2 - \Delta J} \qquad (6)$$

The values of E_s calculated by means of formula (6) are given in Talbe 1.

TABLE 1.

n	B	E_a kcal/mole	$-\Delta J$ kcal/mole	E_s kcal/mole	$\Delta E_s = E_{sn} - E_{s1}$ kcal/mole	References
1	CH_3NH_2	15.6	10.5	81.5	0.0	(9)
2	$(CH_3)_2NH$	16.5	8.9	82.7	~0.0	(9)
3	$(CH_3)_3N$	16.4	5.4	76.0	−5.5	(9)
4	pyridine	16.6	3.2	72.5	−9.0	(10, 11)

It is clear from Table 1 that the values of E_s in the reaction of $C_2H_5NO_2$ with pyridine and $(CH_3)_3N$ differ markedly from E_s in the reaction of $C_2H_5NO_2$ with $CH_3N\ H_2$ (coincidence of E_s in the case of CH_3NH_2 and $(CH_3)_2NH$ can be due, in particular, to experimental error). This difference in the solvent reorganization energy for different kinds of amines, due apparently to the group CH_3 substituting hydrogen in primary amines being introduced near the reaction atom, accounts for the fact well-known from other reactions that primary, secondary and tetriary amines do not form a single reaction series$^{2)}$. For instance, the catalytic rate constants of N-methylaniline and N-dimethylaniline in the decomposition reaction of nitramide in H_2O and their pK_{BH} do not agree with the Brönsted relation for N-unsubstituted anilines$^{2)}$. It should be noted that since in the series of amines of the same type the reaction entropy seems to change little, correlation should be considered to exist not only between $\log k_0$ and ΔJ, but also between $\log k_0$ and pK. Thus, each type of amines (primary, secondary, tertiary) forms its own reaction series, in which the interaction of the proton donor with these amines involves an identical redistribution of electron density. In the decomposition reaction of nitramide in anisole catalyzed by aromatic amines, the $\log k_0 - pK_{BH}$ plots, where k_0 is the observed catalytic constant and K_{BH}-the dissociation constant of protonated amines in H_2O, are four parallel lines (2).

Primary aromatic amines	$\log k_0 = -5.39 + 0.64\,pK_{BH}$
Secondary aromatic amines	$\log k_0 = -5.04 + 0.64\,pK_{BH}$
Tertiary aromatic amines	$\log k_0 = -4.42 + 0.64\,pK_{BH}$
Tertiary heterocyclic amines	$\log k_0 = -3.49 + 0.64\,pK_{BH}$

This indicates that tertiary heterocyclic amines are nearly 100 times as effective as primary aromatic amines*). We could not calculate E_s directly by means of formula (6) because we had no exprimental data on the activation energies and reaction heats at our disposal. Nevertheless, it is possible to estimate the change of E_s when passing from one type of amines to another. Assuming the preexponetial factors for these compounds to be approximately the same, as is for example true for adiabatic reactions, and neglecting the quadratic term in (4), we obtain for the change of E_s when passing from one series of reactions to another:

$$\Delta E_s = E_{s_n} - E_{s_r} = \left[4(\log k_1 - \log k_n) + 2(pK_1 - pK_n)\right] 2.3\, kT \qquad (8)$$

The values of E_s thus calculated are listed in Table 2.

TABLE 2.

No.	B	ΔE_s kcal/mole
1	Primary aromatic amines	0.0
2	Secondary aromatic amines	~0.0
3	Tertiary aromatic amines	−5.0
4	Heterocyclic amines	−10.0

As it follows from Table 2, the repolarization energy in the decomposition reaction of nitramide in anisole catalyzed by aromatic amines as well as in the reaction of amines with nitroethane change in a similar manner when passing from primary to tertiary compounds.

2. Ionization of nitrocompounds

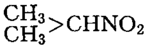
Let us consider ionization in water of nitroethane, nitromethane and 2-nitropropane. In the case of these compounds the breaking of the C–H bond leads to a subsequent shift of electron density from carbon to oxygen. The ensuing change in the frequencies of normal vibrations[27] and a possible alternation of the geometric structure of molecules dees not make any contribution to the activation energy since the above reorganization is associated with the change in the quantum degrees of freedom.

---

*) According to BELL[2], the difference in the properties of the amines being considered in this type of reactions is due to the different nature of the interaction of their protonated forms with the solvent inasmuch as the degree of hydrogen bonding with the solvent depends upon the number of hydrogen atoms in the ammonium ion. However, this interpretation does not clear up the problem at all.

Using formulae (4) and (6), we can calculate the reorganization energy of the solvent in this type of reaction. The results of calculations are listed in Table 3.

TABLE 3.

No.	AH	E_a kcal/mole	$-\Delta J$ kcal/mole	E_s kcal/mole	ΔE_s kcal/mole	References
1	CH_3NO_2	~23.0	6.8	78.0	0.0	(12, 13)
2	$CH_3CH_2NO_2$	~23.0	1.7	87.5	9.5	(13, 14)
3	 $\begin{matrix}CH_3\\CH_3\end{matrix}\!>CHNO_2$	20.0	3.2	74.0	−4.0	(13, 15)

The three nitrocompounds have different values of E_s and in accordance with the theory presented Part 1 should not form a single reaction series, which is in agreement with the data on $\log k_0$ and pK available for these compounds. Particularly different are E_s for 2-nitropropane containing a secondary H atom and for nitroethane with primary H atom.

In the case when it is possible to estimate E_s and the reaction heats are known, it is not difficult to calculate theoretically using formula (4) the corresponding activation energies. Thus, *e.g.* for the reaction of pyridine with nitroethane the value $E_s=72.5$ kcal/mole was found (see Table 1). Assuming the value of E_s for the reactions of substituted pyridines with nitroethane to be the same as for unsubstituted pyridine (the charge redistribution for the compounds in question being apparently the same), it was possible from the known values of the reaction heats $(-\Delta J)$[17] to calculate the activation energies of these reactions. The calculated values of E_a^{theor} for a series of methyl- and dimethylpyridines lie in the range of 15.5 kcal/mole–16.5 kcal/mole.

Similarly were calculated the activation energies of the reaction of nitroethane with acetate-ion $(E_a^{\text{theor}}=19.1)$[18,19], with ethylamine $(E_a^{\text{theor}}=14.9)$[18] and with diethylamine $(E_a^{\text{theor}}=15.5)$.[18]

On the other hand, using the calculated values of E_s, it is possible to compare with experimental data the theoretical dependence of the reaction rate constant on the equilibrium constant determined by formula (4). The theoretical curve and the experimental data on the interaction reaction of nitroethane with some bases are given in Fig. 1. The point corresponding to the reaction for which from the reaction heat and the activation energy was calculated the value of $E_s=80.0$ kcal/mole used in plotting the curve is marked with a cross. It is clear from the plot that the theoretical curve agrees well with experiment.

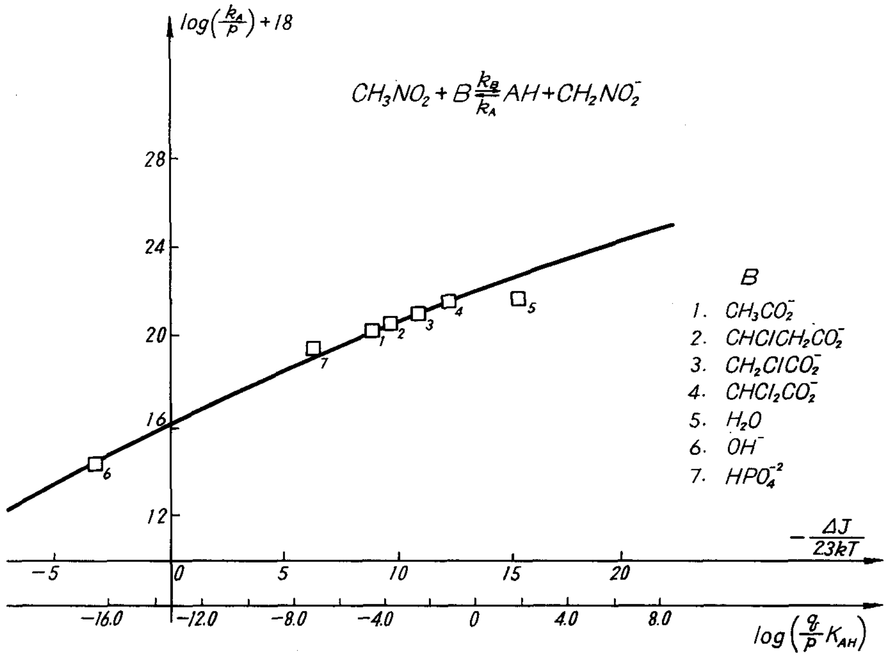

$\log\left(\frac{k_A}{p}\right)+18$
$CH_3NO_2 + B \underset{k_A}{\overset{k_B}{\rightleftharpoons}} AH + CH_2NO_2^-$
28
24
20
16
12
1
2
3
4
5
6
7
B
1. $CH_3CO_2^-$
2. $CHClCH_2CO_2^-$
3. $CH_2ClCO_2^-$
4. $CHCl_2CO_2^-$
5. H_2O
6. OH^-
7. HPO_4^{-2}
$-\frac{\Delta J}{2.3kT}$
−5
0
5
10
15
20
−16.0
−12.0
−8.0
−4.0
0
4.0
8.0
$\log\left(\frac{q}{p}K_{AH}\right)$

Fig. 1.

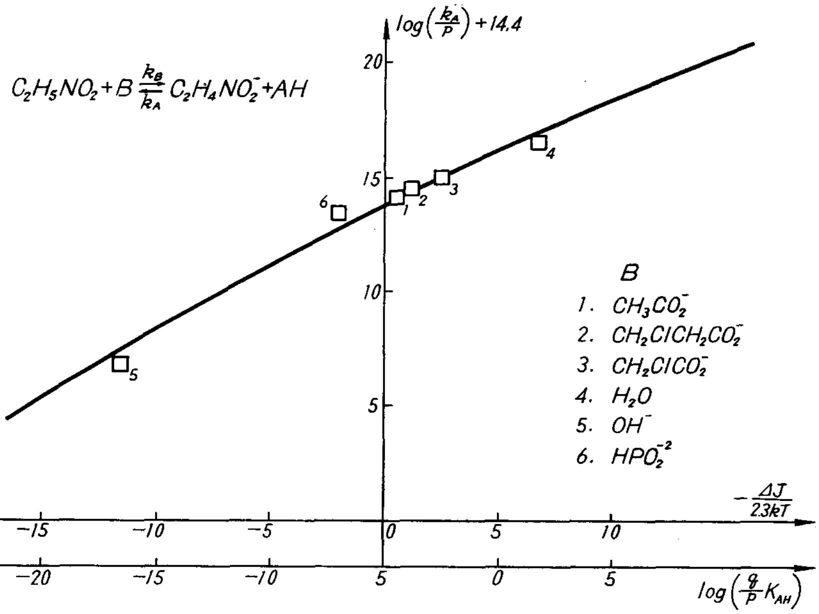

$\log\left(\frac{k_A}{p}\right)+14.4$
$C_2H_5NO_2 + B \underset{k_A}{\overset{k_B}{\rightleftharpoons}} C_2H_4NO_2^- + AH$
20
15
10
5
1
2
3
4
5
6
B
1. $CH_3CO_2^-$
2. $CH_2ClCH_2CO_2^-$
3. $CH_2ClCO_2^-$
4. H_2O
5. OH^-
6. HPO_2^{-2}
$-\frac{\Delta J}{2.3kT}$
−15
−10
−5
0
5
10
−20
−15
−10
5
0
5
$\log\left(\frac{q}{p}K_{AH}\right)$

Fig. 2.

It should be noted that along with the carboxylate-ions of the same type, MARON and La MEER[12], included into this reaction series also the nonisostructural bases H_2O, OH^-, HPO_4^{-2}, the points corresponding to these bases proving to lie near the theoretical $\log k_0 - pK$ curve (Fig. 1). This fact can be explained as follows. First, accidentally the values of E_s for these bases can be the same as in the reaction of CH_3NO_2 with carboxylate-ions. A situation is also possible when the values of E_s corresponding to the bases under consideration differ from those for carboxylate-ions, but the preexponential in the expression for the rate constant compensates for the change of E_s. As regards H_2O, in this case we know both the value of E_s (see Table 3) and the preexponential A.[12] Since E_s and A for H_2O have other values than for carboxylate-ions H_2O does not belong to the reaction series under consideration in the sense assumed in Part 1. For lack of the relevant data, for OH^- and HPO_4^{-2} no definite conclusions can be drawn.

For the reaction of these bases with nitroethane the comparison of theory with experiment was made in a similar manner. The experimental points and the theoretical curve for this case are given in Fig. 2.

3. Ionization of Ketones

The ionization of ketones in water under the action of bases was studied by Bell *et al.*[2,20-23] and by Pearson *et al.*[24] using the halogenation method.

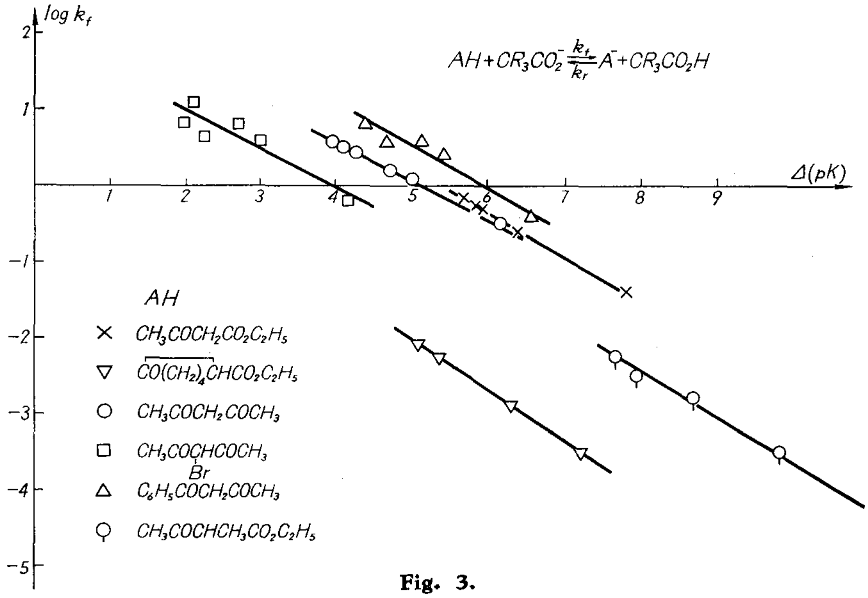


Fig. 3.

Now it is an established fact that the limiting step in the halogenation of ketones in alkaline medium is the breaking of the C–H bond.[2,16]

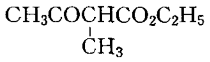
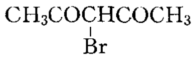
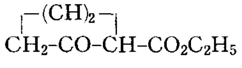
Unfortunately, we did not have at our disposal the values of E_a and ΔJ for this group of reactions (we know only E_A for the ionization of methylacetylacetone[24] and α-ethyl acetoacetate.[24] Nevertheless, in this case the repolarization energy can be found from the analysis of the correlations $\log k_0 - pK$ if we determine the range of $\Delta(pK)$ in which α changes from 0 to 1. Such an approach was used in paper by Levich *et al.*[25] (Fig. 5). In the range of $\Delta(pK)$ studied the coefficient α varied from ~ 0.2 to ~ 0.7. Since a complete change of α from 0 to 1 occurs in the range $\Delta(pK) = 2E_s$ (see Part 1) the corresponding value of E_s is about 1 ev. It should be noted that this reaction series includes bases of various kinds. It is quite possible that the points on the plot given by LEVICH *et al.*[25] actually correspond to several correlations with different values of E_s. However, in order to obtain more accurate results it is necessary to calculate E_s from E_a and ΔJ for each particular interacting pair AH and B.

Some other correlations $\log k_0 - pK$ characterizing the interaction of various diketones with the same carboxylate-ions are shown in Fig. 3. In these cases it is impossible to determine E_s with sufficient accuracy owing to the smallness of the range of $\Delta(pK)$. The values listed in Table 4 are only approximate. For ethyl-α-methylacetotoacetate we calculated E_s from the equation for the rate constant

$$\log k_0 = \left(\log A - \frac{E_s/4}{2.3\,kT}\right) + \frac{1}{2}\Delta J - \frac{(\Delta J)^2}{4E_s\,12.3\,kT}$$

and for other compounds we estimated E_s with respect to this diketone.

TABLE 4.

n	AH	$\Delta E_S = E_{Sn} - E_{S1}$ kcal/mole	E_S kcal/mole	References
1	 $CH_3CO\underset{\substack{\vert \\ CH_3}}{C}HCO_2C_2H_5$	0.0	55.5	(22, 23)
2	 $CH_3CO\underset{\substack{\vert \\ Br}}{C}HCOCH_3$	~0.0	55.0	(20)
3	$CH_3COCH_2COC_2H_5$	−4.6	50.9	(20)
4	$CH_3COCH_2COC_6H_5$	−6.9	48.6	(20)
5	$CH_3COCH_2COCH_3$	−4.6	50.9	(20)
6	 $\overset{\ulcorner (CH)_2 \urcorner}{CH_2\text{-}CO\text{-}CH}\text{-}CO_2C_2H_5$	−4.6	50.9	(21)

From the data in Table 4 it can be concluded that the substitution at the carbon atom bound with the reacting proton leads to a marked increase of E_s, *i.e.*, to a significant charge redistribution. The values of E_s are less sensitive to the substitution far from the reacting proton and the corresponding substituted ketones must form a reaction series (ketones 3–5 in table 4). However, for a more detailed analysis it is necessary to know the activation energies and the corresponding reaction heats.

In considering the experimentnl data we confined ourselves to three groups of reactions, since we had no data for other cases. Thus, in the investigation of catalytic hydration of some phenylacetylenes it was established[26] that the limiting step of the process is the proton transfer from acid to substrate with formation of vinyl cation. This involved the determination of the activation energy of the protonation reaction. However, owing to the absence of the data on the heats of the protonation reaction and the correlation $\log k_0 - pK$ it was impossible to calculate the values of E_s for this group of compounds and thus to compare the charge density distribution in vinyl cations.

Recently the correlations $\log k_0 - pK$ for the ionization reaction of hydrocarbons (fluorene and its derivatives) in methanol and in dimethylsulfooxide (DMSO) (Fig. 4) were reported by Ritchie and Ushold[8]. They

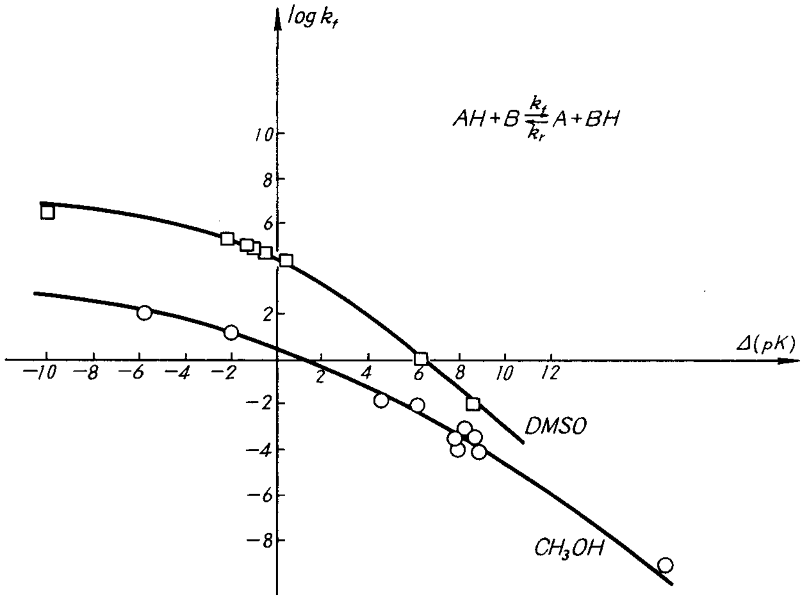


Fig. 4.

draw the conclusion that the effect of the solvent on the reaction rate manifests itself in different solvent reorganization energies, which for DMSO is less. Quantitative estimates cannot be obtained in this case either owing to a low accuracy of experiments (20% in the determination of the rate constancts). In spite of the fact that the authors extrapolated the plots to the range of $\alpha \approx 0$ and $\alpha \approx 1$ quite arbitrarily, it is possible to find from the experimental points that a larger E_s corresponds to the reaction in methanol than to the reaction in DMSO. It would be of great interest to determine E_s in the ionization reaction of such C–H acids.

We wish to express our thanks to Dr. M. N. VARGAFTIC and Dr. O. N. TEMKIN for usefull discussion.

References

1) E. D. GERMAN, R. R. DOGONADZE, A. M. KUZNETSOV, V. G. LEVICH and YU. I. KHARKATS, This Journal, **19**, 99 (1971).
2) R. BELL, *Proton in Chemistry*, N. Y., 1959.
3) J. N. BRÖNSTED, Chem. Rev., **5**, 231 (1928).
4) V. A. PALM, *Osnovy kolichestvennoy teorii khimicheskih reaktziy*, Leningrad, 1967.
5) J. LEFLER and E. GRUNWALD, *Rates and equilibria of organic reactions*, N. Y., 1963.
6) M. EIGEN, Disc. Farad. Soc., **39**, 10 (1965); Angew. Chem. Int. Ed. **3**, 1, 1964.
7) E. F. CALDIN, *Fast Reactions in Solutions*, Oxford 1964.
8) C. RITCHIE and R. USHOLD, J. Am. Chem. Soc., **90**, 3415 (1968).
9) R. PEARSON, J. Am. Chem. Soc., **70**, 204 (1948).
10) E. LEWIS and L. FUNDERBRUK, J. Am. Chem. Soc., **89**, 2322 (1967).
11) R. PEARSON and F. WILLIAMS, J. Am. Chem. Soc., **75**, 3073 (1953).
12) S. MARON and V. LA MEER, **61**, 2018 (1939).
13) D. TURNBULL and S. MARSON, J. Am. Chem. Soc., **65**, 212 (1943).
14) R. PEARSON and R. DILLON, J. Am. Chem. Soc., **72**, 3574 (1950).
15) S. MARON and V. LA MEER, J. Am. Chem. Soc., **60**, 2588 (1938).
16) S. W. BENSON, *The Foundations of Chemical Kinetics*, McGrow-Hill Book Co, Inc. New York, Toronto, London, 1960.
17) L. SACCONI, *et. al.*, J. Am. Chem. Soc., **82**, 3831 (1960).
18) M. GREGORI and T. BRUICE, J. Am. Chem. Soc., **89**, 2327 (1967).
19) A. PIHL and A. TIMOTHEUS, *Reaktzionnaya Sposobnost Organicheskih Soedineniy*, **3**, No. 4, 7 (1966), ed. Tartu University.
20) R. BELL, F. GELLES and E. MØLLER, Proc. Roy. Soc., **A 198**, 308 (1949).
21) R. BELL, R. SMIT and L. WUDWORD, Proc. Roy. Soc., **A 192**, 479 (1948).
22) R. BELL and D. GOODAL, Proc. Roy. Soc., **A 294**, 273 (1966).
23) R. BELL, Disc. Farad. Soc., **39**, 18 (1965).
24) R. PEARSON and J. MILLS, J. Am. Chem. Soc., **72**, 1692 (1950).
25) V. G. LEVICH, E. D. GERMAN, R. R. DOGONADZE, A. M. KUZNETSOV and YU. I. KHARKATS Electrochimica Acta, **15**, 353 (1970)
26) D. NOYCE and M. SHIAVELLI, J. Am. Chem. Soc., **90**, 1020 (1968).