A STUDY OF EFFECTS OF TEMPERATURE AND MEDIUM ON REACTION OF TRIETHYLAMINE WITH ETHYL BROMIDE

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The rate constants of reaction of triethylamine with ethyl bromide have been measured in 13 solvents at the temperatures of 293, 313, 333, and 373 K. The activation entropies in the individual solvents increase when going from nonpolar to dipolar aprotic and polar protic solvents, which is explained by dominant solvation of the basic triethylamine and by formation of highly ordered associates without solvent in the activated complex in nonpolar solvent media. No isokinetic relationship has been found between the activation entropy and activation enthalpy, which indicates different solvent effects on the two quantities. The activation enthalpy and entropy of the reaction investigated are close to those of the reaction of triethylamine with ethyl iodide. Three methods have been used to evaluate the effect of medium at all the temperatures, their success being decreased in the order: Pytela's method – Kamlet–Taft – Koppel–Palm. Irrespective of the temperature, all the methods indicate that the reaction is accelerated by the solvent polarity, the significance of other effects being reflected differently depending on the temperature and the correlation equation used. A complex evaluation involving also the interpretation of the entropy and enthalpy components by means of empiric solvent parameters has shown that the resulting Gibbs energy represents a superposition of different effects of solvents on the two thermodynamic quantities, the solvent effect upon the activation entropy being predominant at the higher temperatures.

The quaternization reaction of amines with halides has been attracting attention of both experimental and theoretical chemists since the original Menshutkin papers[1,2] at the end of last century (for a survey see e.g. refs[3–6]). The popularity of these reactions in the field of studies of effects of medium has two main reasons. The rate of these reactions shows a distinct dependence upon the medium, the kinetic monitoring being, at the same time, not experimentally laborious. In the area of the so-called empirical methods for evaluation of effect of medium, two of these methods were suggested and accepted as scales of polarity of medium[7,8], and owing to the high number of the data published about the effect of medium upon these two reactions, the rate constant data were extensively adopted in deriving the solvent parameters by statistical treatment of experimental data.

The aim of the present paper is to study the effect of medium upon the rate of reaction of triethylamine with ethyl bromide at several temperatures and to interpret the activation parameters as functions of solvent effects, to compare the application successfulness of the three correlation methods for evaluation of effect of medium on the rate constants of the process investigated, and thus to obtain a more detailed idea about the role of solvent in the individual reaction phases. A partial aim is – in the context with the earlier papers – to compare the effect of halogen in the alkyl halide upon the activation parameters of quaternization reactions in various media, which has not been published yet.

EXPERIMENTAL

Triethylamine and ethyl bromide were purified by distillation before use for preparing the solutions for kinetic measurements. The solvents used were pre-dried and rectified. The kinetic experiments were similar to those in the previous studies[9], the temperature of reaction mixtures was maintained with the accuracy of ±0.3 K. The mathematical-statistical treatment of data was carried out on a PC using our own programs.

RESULTS AND DISCUSSION

The second order rate constants of the reaction of triethylamine with ethyl bromide at four temperature values in 13 solvents are given in Table I.

TABLE I
Effect of temperature upon rate constants k of reaction of $(C_2H_5)_3N + C_2H_5Br$ and activation parameters of the reaction

Solvent	k, dm^{-3} mol^{-1} s^{-1}				$\Delta H^{\neq}$ kJ mol^{-1}	$-\Delta S^{\neq}$ J mol^{-1} K^{-1}
	293 K	313 K	333 K	373 K		
Cyclohexane	$9.83 . 10^{-9}$	$4.00 . 10^{-8}$	$1.05 . 10^{-7}$	$8.97 . 10^{-7}$	48.0 ± 1.7	234 ± 5
1,2-Dimethoxyethane	$8.71 . 10^{-7}$	$3.08 . 10^{-6}$	$1.62 . 10^{-5}$	$1.45 . 10^{-4}$	56.4 ± 2.7	168 ± 8
Ethyl acetate	$9.83 . 10^{-7}$	$5.56 . 10^{-6}$	$1.72 . 10^{-5}$	$1.35 . 10^{-4}$	52.5 ± 2.3	180 ± 7
1,2-Dichloroethane	$1.60 . 10^{-5}$	$5.38 . 10^{-5}$	$1.47 . 10^{-4}$	$1.10 . 10^{-3}$	45.3 ± 1.3	183 ± 4
Acetone	$6.86 . 10^{-6}$	$2.65 . 10^{-5}$	$7.89 . 10^{-5}$	$7.71 . 10^{-4}$	51.0 ± 1.8	171 ± 5
Acetonitrile	$3.03 . 10^{-5}$	$1.32 . 10^{-4}$	$4.39 . 10^{-4}$	$3.55 . 10^{-3}$	51.3 ± 0.5	156 ± 1
Nitromethane	$1.49 . 10^{-4}$	$4.68 . 10^{-4}$	$1.36 . 10^{-3}$	$9.27 . 10^{-3}$	44.4 ± 1.0	167 ± 3
Benzene	$4.78 . 10^{-7}$	$2.11 . 10^{-6}$	$8.80 . 10^{-6}$	$1.04 . 10^{-4}$	58.7 ± 1.2	166 ± 4
Chlorobenzene	$1.81 . 10^{-6}$	$7.08 . 10^{-6}$	$2.45 . 10^{-5}$	$1.84 . 10^{-4}$	49.9 ± 0.2	185 ± 1
Nitrobenzene	$2.26 . 10^{-5}$	$9.44 . 10^{-5}$	$2.97 . 10^{-4}$	$2.05 . 10^{-3}$	48.4 ± 0.9	168 ± 3
Methanol	$1.20 . 10^{-6}$	$9.52 . 10^{-6}$	$6.11 . 10^{-5}$	$1.31 . 10^{-3}$	76.9 ± 0.3	96 ± 1
Ethanol	$8.63 . 10^{-7}$	$6.60 . 10^{-6}$	$4.03 . 10^{-5}$	$9.64 . 10^{-4}$	77.0 ± 0.7	98 ± 2
1-Propanol	$4.50 . 10^{-7}$	$2.96 . 10^{-6}$	$2.19 . 10^{-5}$	$4.92 . 10^{-4}$	77.4 ± 1.8	103 ± 5

Evaluation and Interpretation of Activation Parameters

The activation enthalpy and activation entropy were evaluated by linear regression using the known relationship

$$\ln (k/T) = [\ln (\mathbf{k/h}) + \Delta S^{\neq}/\mathbf{R}] - [\Delta H^{\neq}/\mathbf{R}]/T. \tag{1}$$

The activation parameters obtained are presented in Table I along with the corresponding standard deviations. As it can be seen from the data given the effect of activation entropy upon the rate constant is comparable with that of the activation enthalpy. Distinct differences between the activation entropy values in the individual solvents also indicate that the large negative value of activation entropy does not result only from the bimolecularity of process, but the solvation must play a marked role, too. Among the given set of solvents, cyclohexane represents one in which all types of solvation mechanisms make themselves felt to the least extent, and – at the same time – the reaction studied has a negative value of activation entropy in it. Paradoxically, the decrease in absolute value of this quantity when going to dipolar aprotic solvents indicates a decrease in demands for order of the solvated activated complex as compared with cyclohexane medium. As any greater specific solvation of educts (compared with the more highly polar activated complex) cannot be presumed in dipolar aprotic solvents, the result observed may be a consequence of the highly organized associates involving the activated complex and polar educts and products without participation of solvent in cyclohexane and the less organized associates with better stabilizing solvent molecules in dipolar aprotic solvents. When going to polar protic solvents, we can see another distinct decrease in the activation entropy, which can only be interpreted by formation of hydrogen bonds between the solvent and very basic triethylamine. Upon formation of the activated complex, there occurs a partial desolvation, which is demonstrated by increasing activation enthalpy and decreasing activation entropy as compared with the solvents which do not form hydrogen bonds with educts. This process is probably dominant in polar protic solvents, since otherwise we would expect a stabilization of the polar activated complex connected with a decrease in activation entropy due to greater polarity of solvent. Similar conclusions were made in the case of the reaction of triethylamine with ethyl iodide[10], the combination of reactants probably having a less polar activated complex (less similar to products) in this case than in the case of the reaction with ethyl bromide.

Using the rate constants from Table I we also examined the validity of isokinetic relation for the given solvent set. In the way described elsewhere[11] we determined the values of $s_0 = 0.459$, $s_{\infty} = 0.0937$, and isokinetic temperature $\beta = 781 \pm 1\,236$ K. The value of test criterion of the hypothesis $s_0 = s_{\infty}$ is 24.0, i.e. much more than the critical value of $F_{0.95}(37,26) = 1.86$. Quite obviously, the isokinetic relation is not fulfilled,

moreover the found value of isokinetic temperature is characteristic of an isoentropic process, which obviously contradicts the above-discussed fact. This result shows that the two activation parameters, for the process and solvent set studied, are affected by solvent more or less independently.

Evaluation and Interpretation of Solvent Effects by Correlation Equations

For evaluation of effect of medium on the rate of reaction of triethylamine with ethyl bromide we adopted the equations suggested by Kamlet and Taft[12] (Eq. (*2*)), Pytela[13] (Eq. (*3*)), and Koppel and Palm[14] (Eq. (*4*)).

$$\log k = \log k_0 + s(\pi^* + d\,\delta) + a\,\alpha \tag{2}$$

$$\log k = \log k_0 + a\,\text{PA} + b\,\text{PB} + p\,\text{PP} \tag{3}$$

$$\log k = \log k_0 + y\,Y + e\,E + p\,P + b\,B \tag{4}$$

In Eqs (*2*) – (*4*) k and k_0 denote the reaction rate constants in the measured and in standard media, respectively, π^* is the polarity–polarizability parameter by Kamlet–Taft, δ is a characteristic of aromatic polychlorinated solvents, α is an acidity parameter, PA, PB, and PP are the parameters of polarity–acidity, polarity–basicity, and polarity–polarizability by Pytela, respectively, $Y = (\varepsilon_r - 1)/(\varepsilon_r + 2)$ (where ε_r is relative permittivity), $P = (n^2 - 1)/(n^2 + 2)$ (where n means refractive index), E and B are parameters describing the acidity and basicity of medium, respectively. The symbols s, d, a, b, y, p, e are regression coefficients characterizing the sensitivity of logarithm of reaction rate constant to the property described by the corresponding solvent parameters. The statistically significant regression coefficients in Eqs (*2*) through (*4*) are given in Tables II through IV along with the corresponding standard deviations, coefficients of multiple correlation R, and standard deviations s. A comparison of the standard deviations indicates that the fit of correlation decreases in the order of Eqs (*3*), (*2*), (*4*), the successfulness of the equations being increased with temperature of the corresponding kinetic measurements. On the basis of analysis of residua, the fit of correlations is decreased by the deviating points: for Eq. (*2*) these are the measurements in acetonitrile and nitromethane, for Eq. (*3*) in cyclohexane, and for Eq. (*4*) in benzene. The effect of medium is indicated by the methods used in different ways, the only agreement being in the positive effect of polarity on rate constant. According to Kamlet and Taft (Eq. (*2*), Table II) basicity shows a negative effect at lower temperatures and, on the other hand, acidity shows a positive effect at higher temperatures. A negative

effect of basicity at lower temperatures is also indicated by equation of Koppel and Palm (Eg. (*4*), Table IV). On the other hand, the equation by Pytela (Eq. (*3*), Table III) indicates an effect of specific solvation only at higher temperatures, this effect being positive. The effects of deformation polarizability of medium is not indicated by the equation by Koppel and Palm, whereas the other methods evaluate it as positive. Addi-

TABLE II
Results of regression analysis of data by Kamlet–Taft method (Eq. (*2*)), d(293 K) = 0.21, d(313 K) = 0.11, d(333 K) = 0.13, d(373 K) = 0.12

T, K	$-\log k_0$	s	a	b	R	s
293	8.05 ± 0.13	4.75 ± 0.25	–	−0.959 ± 0.249	0.992	0.152
313	7.62 ± 0.20	4.55 ± 0.33	–	–	0.975	0.249
333	6.99 ± 0.17	4.51 ± 0.28	–	–	0.981	0.213
373	6.03 ± 0.16	4.24 ± 0.25	0.775 ± 0.167	–	0.986	0.188

TABLE III
Results of regression analysis of data by Pytela method (Eq. (*3*))

T, K	$-\log k_0$	a	b	p	R	s
293	8.61 ± 0.30	–	–	5.30 ± 0.53	0.964	0.319
313	7.88 ± 0.22	–	–	5.19 ± 0.35	0.980	0.231
333	7.37 ± 0.12	–	0.659 ± 0.218	4.70 ± 0.27	0.994	0.133
373	6.37 ± 0.12	0.685 ± 0.287	0.811 ± 0.246	4.20 ± 0.25	0.995	0.124

TABLE IV
Results of regression analysis of data by Koppel–Palm method (Eq. (*4*))

T, K	$-\log k_0$	y	b	R	s
293	9.68 ± 0.80	12.0 ± 2.2	$-(6.43 ± 2.61) \cdot 10^{-3}$	0.885	0.591
313	8.54 ± 0.83	8.97 ± 1.98	–	0.834	0.634
333	8.11 ± 0.76	9.26 ± 1.81	–	0.862	0.581
373	7.19 ± 0.68	9.46 ± 1.61	–	0.890	0.518

tional effects of aromatic solvents (the symbol δ in Eq. (*2*)) somewhat decrease with increasing temperature, whereas the opposite was true for the reaction of triethylamine with ethyl iodide[10]. Except for these opposite temperature effects on δ, the influence on the reaction studied and that on the reaction of triethylamine and ethyl iodide are similar. The observed changes in the effect of specific solvation by medium which are due to temperature show that the entropy and enthalpy components of the Gibbs activation energy are probably affected in different ways.

Complex Evaluation and Interpretation of Effects of Temperature and Solvent

From the above-mentioned analysis it follows that the effect of a solvent on the process taking place therein is temperature-dependent, and any separate evaluation of the two factors is difficult. Therefore the data of Table I were interpreted by a more general correlation equation starting from Eq. (*1*) in which the respective activation parameters were replaced by linear combination of solvent parameters according to Eqs (*2*) – (*4*). The evaluation according to the combination of Eqs (*1*) and (*2*) gave the relation (*5*) and analogously the combination of Eqs (*1*) and (*3*) gave Eq. (*6*) and that of Eqs (*1*) and (*4*) gave the relation (*7*):

$$\ln (k/T) = -(22.1 \pm 0.3) + (27.0 \pm 3.1) \, \pi^* + (1.19 \pm 0.49) \, \alpha + (21.4 \pm 5.0) \, \beta - (5.38 \pm 0.99) \cdot 10^3 \, (\pi^* + 0.12 \, \delta)/T - (7.54 \pm 1.60) \cdot 10^3 \beta/T,$$

$$n = 52, \, s = 0.726, \, R = 0.972 \tag{5}$$

$$\ln (k/T) = -(23.1 \pm 0.3) + (29.5 \pm 7.3) \, PA + (1.70 \pm 0.67) \, PB + (26.7 \pm 4.2) \, PP - (1.00 \pm 0.24) \cdot 10^4 PA/T - (5.10 \pm 1.34) \cdot 10^3 \, PB/T,$$

$$n = 52, \, s = 0.676, \, R = 0.978 \tag{6}$$

$$\ln (k/T) = -(25.4 \pm 2.5) + (70.1 \pm 10.5) \, P + (1.37 \pm 0.42) \, E + (8.56 \pm 0.78) \cdot 10^3 \, Y/T - (2.31 \pm 0.27) \cdot 10^3 \, P/T - (4.55 \pm 1.36) \cdot 10^3 \, E/T - (3.12 \pm 1.33) \, B/T,$$

$$n = 52, \, s = 1.205, \, R = 0.934. \tag{7}$$

As it can be seen from the equations given, the correlation fit is comparable for the equations by Kamlet–Taft (6 explaining variables) and by Pytela (5 explaining variables), giving roughly twice as bad standard deviation for the parameters by Koppel

and Palm (6 explaining variables). According to Eq. (*5*) all properties of solvent influence the entropy component of the Gibbs activation energy, whereas the regression coefficients of Eq. (*6*) indicate a dominant effect of acidity and polarity and a smaller effect of basicity, and according to Eq. (*7*) only acidity and polarizability dominate. From the results given it may be stated – in analogy to the analysis of the activation parameters of the reaction in individual solvents – that the activation entropy increases with increasing solvent's specific solvation ability. A likely reason may lie in preferable formation of hydrogen bonds between the basic triethylamine and a protic solvent. To a lesser extent this can obviously be due to the replacement of the highly ordered associates in the activated complex in little polar solvents by looser – in polar medium more stable – associates with solvent. In the interpretation of enthalpy component of the Gibbs activation energy the results of Eqs (*5*) – (*7*) somewhat differ. Using the parameters by Kamlet and Taft we arrive at the conclusion that this component, expressed similarly as the enthalpy in Eq. (*1*), increases with increasing polarity and basicity of solvent. Nevertheless, the positive dependence on polarity is unexpected; it can be explained by stabilization of polar adducts between triethylamine and protic solvent, but the explanation of positive dependence upon basicity is difficult. The correlation with Pytela's parameters indicates a dominant effect of polarity–acidity and about a half effect of polarity–polarizability. Again the positive dependence on acidity indicates a significant role of specific solvation of triethylamine connected with desolvation during the nucleophilic attack on the substrate. It is also difficult to explain the solvent effect on the enthalpy component of the Gibbs activation energy by means of Eq. (*7*) as all the corresponding regression coefficients are statistically significant and, moreover, the dependence upon solvent polarity is opposite to that of the remaining parameter sets. When comparing Tables II, III, and IV with the Eqs (*5*) – (*7*), one can see that the resulting Gibbs activation energy (or the logarithm of rate constant) represents a superposition of different effects of the individual factors of solvents upon the activation enthalpy and activation entropy, the effects of activation entropy being manifested to a larger extent at higher temperatures.

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