# A STUDY OF EFFECT OF TEMPERATURE ON THE INFLUENCE OF MEDIUM ON THE REACTION OF TRIETHYLAMINE WITH ETHYL IODIDE

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The rate constants of the reaction of triethylamine with ethyl iodide have been measured in 15 solvents at the temperatures of 293, 313, 333 and 373 K. The solvent characteristics by Kamlet and Taft and those by Pytela have been found to be excellently applicable to evaluation of influence of medium on this reaction at all the temperatures mentioned. However, these methods give different results with regard to the proton-donor effects of solvents on the reaction.

For as long as 100 years, i.e. since the original papers by Menshutkin[1-3], quaternization reactions of amines with alkyl halogenides belong to the most favourite reactions for both experimental and theoretical studies of solvent effects on the reaction rate (see e.g. refs[4-6]). The popularity of these reactions in studies of solvent effects is due to two facts: these reactions show a distinct dependence on medium and are easily monitored experimentally. The large number of quaternization reactions for which solvent effects were studied is documented in several recent reviews[7,8] which adopt the rate constants of quaternization reactions to adjust the solvent characteristics by means of statistical methods.

Little attention, however, has been paid until now to the interdependence of solvent effects and temperature. Out of the large number of empirical solvent characteristics so far suggested, only the $E_T(30)$ parameters were studied with respect to their temperature dependences[9]. This gap in knowledge exists in spite of the fact that the theory of dielectric, which – by the way – has been applied to the interpretation of solvent effects most frequently, states that the effects of medium should depend on temperature (due to different temperature dependences of relative permittivity and refractive index of solvents).

The aim of the present work was to carry out a study of the effect of medium for a set of different solvents (hydrocarbons, aromatics, alcohols) used in the reaction of triethylamine with ethyl iodide at four temperatures within the range of 293 – 373 K and to evaluate the reaction rates measured by means of the methods by Kamlet and Taft[10] and Pytela[11]; the results should show the applicability of these methods to evaluation of solvent effects within the given temperature range.

## EXPERIMENTAL

Triethylamine and ethyl iodide were purified by means of distillation before the preparation of solutions for kinetic experiments. Except for dibromomethane, which was used without purification, the solvents were dried and rectified. The kinetic experiments were carried out in the same way as in our previous studies[12], the temperature of reaction mixtures was kept with the accuracy of ±0·1 K.

## RESULTS AND DISCUSSION

Table I presents the rate constants obtained for the reaction studied along with the respective calculated activation parameters. The available papers[4,6] about the effect of medium on the quaternization reaction of amines show that this reaction is affected only by polarity and polarizability of medium and by proton-donor ability of medium. In the sense of the rules by Hughes and Ingold[4] the polarity of medium has a positive effect on the rate of these reactions (separation of opposite charges in the transition state). An analysis of effects of a set of solvents very much differing in polarity (characterized by relative permittivity) and polarizability (characterized by refractive index of medium) showed[13] that also the polarizability of medium has a positive effect on the rate of these reactions, this effect being of comparable magni-

TABLE I

Effects of temperature and medium on the rate constants $k$ ($dm^3 mol^{-1} s^{-1}$) of the reaction $(C_2H_5)_3N + C_2H_5I = (C_2H_5)_4N^+ + I^-$ and the activation parameters of this reaction

| Solvent | $k$ for | | | | $\Delta H^{\ddagger}$ kJ mol$^{-1}$ | $\Delta S^{\ddagger}$ J mol$^{-1}$ . K$^{-1}$ |
|---|---|---|---|---|---|---|
| | 293·1 K | 313·1 K | 333·1 K | 373·1 K | | |
| Hexane | 1·00 . $10^{-8}$ | 5·00 . $10^{-8}$ | 2·30 . $10^{-7}$ | 2·40 . $10^{-6}$ | 60·0 | 193 |
| Cyclohexane | 3·00 . $10^{-8}$ | 1·00 . $10^{-7}$ | 3·60 . $10^{-7}$ | 5·20 . $10^{-6}$ | 56·5 | 198 |
| Dibutyl ether | 1·21 . $10^{-7}$ | 5·69 . $10^{-7}$ | 2·31 . $10^{-6}$ | 5·72 . $10^{-5}$ | 67·5 | 149 |
| Ethyl acetate | 7·41 . $10^{-6}$ | 3·46 . $10^{-5}$ | 1·11 . $10^{-4}$ | 1·04 . $10^{-3}$ | 53·4 | 161 |
| Acetone | 4·55 . $10^{-5}$ | 1·60 . $10^{-4}$ | 4·92 . $10^{-4}$ | 4·67 . $10^{-3}$ | 50·2 | 158 |
| 1,2-Dichloroethane | 9·65 . $10^{-5}$ | 3·10 . $10^{-4}$ | 1·08 . $10^{-3}$ | 4·79 . $10^{-3}$ | 42·4 | 177 |
| Acetonitrile | 1·72 . $10^{-4}$ | 5·43 . $10^{-4}$ | 1·90 . $10^{-3}$ | 1·55 . $10^{-2}$ | 49·1 | 150 |
| Dibromomethane | 3·76 . $10^{-4}$ | 1·61 . $10^{-3}$ | 4·66 . $10^{-3}$ | 3·53 . $10^{-2}$ | 48·7 | 144 |
| Methanol | 2·51 . $10^{-6}$ | 1·77 . $10^{-5}$ | 1·18 . $10^{-4}$ | 3·22 . $10^{-3}$ | 79·2 | 83 |
| Ethanol | 1·82 . $10^{-6}$ | 1·39 . $10^{-5}$ | 8·70 . $10^{-5}$ | 2·33 . $10^{-3}$ | 78·9 | 86 |
| 1-Propanol | 1·50 . $10^{-6}$ | 1·33 . $10^{-5}$ | 7·60 . $10^{-5}$ | 1·75 . $10^{-3}$ | 77·5 | 92 |
| 1-Butanol | 1·21 . $10^{-6}$ | 1·09 . $10^{-5}$ | 6·54 . $10^{-5}$ | 1·41 . $10^{-3}$ | 77·5 | 93 |
| Benzene | 3·72 . $10^{-6}$ | 1·15 . $10^{-5}$ | 4·28 . $10^{-5}$ | 4·94 . $10^{-4}$ | 53·6 | 167 |
| Chlorobenzene | 2·08 . $10^{-5}$ | 7·40 . $10^{-5}$ | 1·78 . $10^{-4}$ | 1·21 . $10^{-3}$ | 43·3 | 187 |
| Nitrobenzene | 2·07 . $10^{-4}$ | 6·56 . $10^{-4}$ | 1·91 . $10^{-3}$ | 1·53 . $10^{-2}$ | 46·5 | 157 |

tude with that of polarity. The proton-donor ability of medium has a negative effect on these reactions, which is ascribed to formation of hydrogen bond between the proton of solvent and electron pair at nitrogen atom of the reacting amine whose ability of formation of the precursor of the activated complex with alkyl halogenide is thereby diminished. Moreover, the papers[4,6,13] showed that solvent basicity has no effect on these reactions.

Two empirical methods (which appear to be the most suitable at present[11]) were used for evaluation of the effect of medium, viz. that by Kamlet and Taft[10] and that by Pytela[11]. The Kamlet–Taft equation was used in the following form:

$$\log k = \log k_0 + s(\pi^* + d\delta) + a\alpha\,, \tag{1}$$

where $k$ and $k_0$ are the rate constants found in a given medium and in cyclohexane (the standard medium), respectively, $\pi^*$, $\delta$, and $\alpha$ are the characteristics of polarity–polarizability, the polarizability correction factor for aromatic and polychlorinated solvents, and the characteristic of proton-donor ability of solvent, respectively. The regression coefficients $s$, $d$, and $a$ reflect the sensitivity of the rate constant to the individual solvent characteristics. The equation by Pytela was used in the following form:

$$\log k = \log k_0 + aPA + bPB + pPP\,, \tag{2}$$

where $PA$, $PB$, and $PP$ are the parameters of polarity–acidity, polarity–basicity, and polarity–polarizability, respectively (they were obtained by the method of conjugate deviations on the basis of analysis of 378 data sets about solvent effects[11]). Tables II and III give the results of correlation analysis of our experimental data (given in Table I) using the two equations. From the standpoint of the correlation characteristics, i.e. the correlation coefficient $R$ and the standard deviation $\sigma'$, both the methods appear to be very suitable for the evaluation of effect of medium on the reaction studied within the temperature range of 293–373 K. Interestingly, the efficiency of both the methods even increases with increasing temperature in spite of the distinct decrease in sensitivity of the reaction rate to the solvent effects with increasing temperature. For the set investigated Eq. (*2*) seems to be more successful. As far as the effects of the individual solvents are concerned Table II shows that their effect decreases with increasing temperature, the reaction rate being less affected by both polarity–polarizability and acidity at higher temperatures. According to expectation this decrease is faster in the case of the acidity effect, which is connected with the fact that the disturbance of mutual orientation of solute and/or activated complex with the solvent molecules with increasing temperature has a greater impact on the interactions realized by hydrogen bonds. In both the methods discrepancies are encountered in the case of the proton-donor ability of solvent. It is generally accepted that a medium acting as a proton donor in hydrogen bonds retards these quaternization reactions by binding the electron pair at the amine nitrogen atom by hydrogen bond whereby the ability of the amine to form the precursor of the activated complex with alkyl halogenide is decreased (because this precursor involves just this electron pair of amine nitrogen). Within this concept the negative effect of protondonocity of medium on the reaction rate should decrease with temperature, and it can be expected that this effect should be negligible at a certain temperature. However, only the method by Pytela agrees with this idea. The effect of acidity characterized by the regression coefficient a decreases, and it is negligible at 373 K. In the Kamlet–Taft approach the absolute value of the regression coefficient a also decreases and becomes negligible at 333 K, but at 373 K it already assumes a significant positive value. This finding evokes an idea of at least two effects of protondonocity of medium on this reaction rate: (i) the negative effect due to the interaction of solvent with the nitrogen electron pair by hydrogen bond and (ii) the positive effect (which predominates at higher temperature) which could result from the interaction of solvent with the leaving group. Similar discrepancy in the effect of protondonocity of medium show the two methods in the case of solvent effect on the reaction rate

TABLE II

Results of regression analysis of experimental data by means of Eq. (*1*)

| $T$, K | $\log k_0$ | $s$ | $d$ | $a$ | $R$ | $\sigma'$ |
|---|---|---|---|---|---|---|
| 293 | −7·68 ± 0·15 | 4·82 ± 0·26 | −0·129 | −0·706 ± 0·21 | 0·987 | 0·26 |
| 313 | −7·19 ± 0·12 | 4·89 ± 0·21 | −0·134 | −0·300 ± 0·17 | 0·991 | 0·21 |
| 333 | −6·41 ± 0·10 | 4·50 ± 0·18 | −0·143 | −0·051 ± 0·15 | 0·992 | 0·18 |
| 373 | −5·24 ± 0·06 | 4·13 ± 0·10 | −0·154 | 0·453 ± 0·08 | 0·997 | 0·10 |

TABLE III

Results of regression analysis of experimental data by means of Eq. (*2*)

| $T$, K | $\log k_0$ | $a$ | $b$ | $p$ | $R$ | $\sigma'$ |
|---|---|---|---|---|---|---|
| 293 | −7·85 ± 0·09 | −2·41 ± 0·32 | −0·03 ± 0·34 | 6·34 ± 0·29 | 0·996 | 0·14 |
| 313 | −7·42 ± 0·09 | −1·68 ± 0·30 | 0·32 ± 0·32 | 6·06 ± 0·27 | 0·996 | 0·14 |
| 333 | −6·67 ± 0·07 | −1·04 ± 0·25 | 0·38 ± 0·26 | 5·36 ± 0·22 | 0·997 | 0·11 |
| 373 | −5·53 ± 0·05 | −0·26 ± 0·16 | 0·95 ± 0·17 | 4·23 ± 0·14 | 0·998 | 0·07 |

of 1,4-diazabicyclo[2,2,2]octane (DABCO) with (2-chloroethyl)benzene, (2-bromoethyl)benzene, and (2-iodoethyl)benzene at 54·5°C. We carried out a regression analysis of an extensive data set published by Auriel and Hoffmann[14] using Eq. (*1*) (25 dates for each halogen) and Eq. (*2*) (23 dates for each halogen). The results of this regression analysis are given in Tables IV and V. Both methods reveal a decreasing effect of polarity–polarizability of medium on the reaction rate in the order from the chloro to the iodo derivative (whereas the reaction rate increases in the order of the Cl, Br, I derivatives). However, as far as the effect of protondonocity of medium is concerned the results of the two methods again are contradictory. According to the method by Pytela the effect of polarity–acidity is negative, being significant only with the iodo and bromo derivative and insignificant with the chloro derivative. On the other hand, the method by Kamlet and Taft finds a negative effect of the proton-donor ability of medium only for the iodo and bromo derivatives, whereas with the chloro derivative the effects is positive. Also interesting is the finding of the method by Pytela concerning the positive effect of basicity of medium on these reactions of various halogeno derivatives.

TABLE IV

Results of regression analysis of the dependence of rate constants of reactions of 1,4-diazabicyclo[2,2,2]octane (DABCO) with (2-chloroethyl)benzene (CEB), (2-bromoethyl)benzene (BEB), and (2-iodoethyl)benzene (IEB) on reaction medium by application of Eq. (*1*)

| Reaction | log $k_0$ | $s$ | $d$ | $a$ | $R$ | $\sigma'$ |
|---|---|---|---|---|---|---|
| DABCO + CEB | −6·18 ± 0·28 | 4·28 ± 0·36 | −0·13 | 0·42 ± 0·20 | 0·946 | 0·25 |
| DABCO + BEB | −3·89 ± 0·16 | 4·10 ± 0·22 | −0·15 | −0·22 ± 0·15 | 0·974 | 0·20 |
| DABCO + IEB | −3·14 ± 0·15 | 3·97 ± 0·21 | −0·16 | −0·80 ± 0·14 | 0·979 | 0·19 |

TABLE V

Results of regression analysis of the dependence of rate constants of reactions of 1,4-diazabicyclo[2,2,2]octane (DABCO) with (2-chloroethyl)benzene (CEB), (2-bromoethyl)benzene (BEB), and (2-iodoethyl)benzene (IEB) on reaction medium by application of Eq. (*2*)

| Reaction | log $k_0$ | $a$ | $b$ | $p$ | $R$ | $\sigma'$ |
|---|---|---|---|---|---|---|
| DABCO + CEB | −6·55 ± 0·13 | −0·47 ± 0·19 | 0·85 ± 0·18 | 4·71 ± 0·26 | 0·989 | 0·11 |
| DABCO + BEB | −4·20 ± 0·08 | −1·70 ± 0·15 | 0·85 ± 0·14 | 4·76 ± 0·18 | 0·995 | 0·09 |
| DABCO + IEB | −3·42 ± 0·12 | −2·85 ± 0·22 | 0·86 ± 0·21 | 4·88 ± 0·26 | 0·990 | 0·14 |

Out of the effects of medium on the activation parameters of this reaction those on the reaction entropy appear to predominate (Table I). The low activation entropy found in alcohols could be regarded to be a certain confirmation of the interpretation concerning the two effects of protondonocity of medium.

In conclusion we would like to point out the satisfactory relations between the parameters $PP$ by Pytela and $(A^* + d\delta)$ by Kamlet and Taft and our[15] empirical parameters $W_B$. The mutual correlation equations (all 51 parameters by Pytela being taken into account) have the following form:

$$PP = (0{\cdot}006 \pm 0{\cdot}017) + 0{\cdot}803(\pi^* - 0{\cdot}11\delta) \qquad (3)$$

$$R = 0{\cdot}978\,, \quad \sigma' = 0{\cdot}049$$

$$PP = (-0{\cdot}658 \pm 0{\cdot}030) + (2{\cdot}845 \pm 0{\cdot}069)\, W f(n^2) \qquad (4)$$

$$R = 0{\cdot}987\,, \quad \sigma' = 0{\cdot}038$$

Both equations can serve for estimates of one type of parameters from another set of parameters and, moreover, Eq. (*4*) offers a possibility of estimate of the $PP$ parameter by Pytela for gas phase ($-0{\cdot}658$) when $W$ (by definition) and the Born function of refractive index $f(n^2) = (n^2 - 1)/n^2$ are equal to zero.

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