
**SIGNIFICANCE TEST OF REFRACTIVE INDEX OF SOLVENT
IN EVALUATION OF EFFECT OF MEDIUM ON RATES
OF QUATERNIZATION REACTIONS OF METHYL IODIDE WITH
AMINES**

Taťjana NEVĚČNÁ and Vojtěch BEKÁREK

*Department of Inorganic and Physical Chemistry,
Palacký University, 771 46 Olomouc*

Received February 20, 1989

Accepted March 3, 1989

Dedicated to Professor Otto Exner on the occasion of his 65th birthday.

The rate constants have been measured of the reactions of methyl iodide with triethylamine (*I*) and tributylamine (*III*) at 293 K in twelve aprotic solvents, methyl iodide with tripropylamine (*II*) at 293, 313, 323, and 333 K in fifteen solvents differing greatly in their dipole moments, relative permittivities, and refractive indexes, and diiodomethane with tripropylamine in diiodomethane at 293 K ($k_1 = 2.1 \cdot 10^{-5} \text{ s}^{-1}$). The aprotic solvents predominantly affect the activation entropy which for the reaction of *II* varies from $-200 \text{ J mol}^{-1} \text{ s}^{-1}$ (in cyclohexane) to $-108 \text{ J mol}^{-1} \text{ s}^{-1}$ (in diiodomethane). The activation enthalpy of the reaction of methyl iodide with tripropylamine (*II*) is only little affected by aprotic solvents, a significant increase in activation enthalpy has been observed in the case of amphiprotic solvents. The evaluation of effect of medium on the rate constants of the above-mentioned reactions by means of the Kirkwood functions of relative permittivity and refractive index has shown a significant contribution of the refractive index of solvent which is comparable with the effect of relative permittivity.

In the past the reactions of alkyl halides with amines were often studied in the context of solvent effects (see e.g. refs¹⁻¹⁰), and they can be said to have a non-substitutable position in the studies of solvent effects on chemical properties and processes. This is confirmed e.g. by the fact that Menshutkin¹¹ studied the effect of medium on the reaction rate of triethylamine with ethyl iodide as early as 100 years ago, and $\log k_2$ of some of these reactions became the basis of the empirical solvent characteristics φ (refs¹⁻³).

In the discussions of the problem of the solvent properties which have the main effect on the rate of these reactions most often considered was the relative permittivity in the sense of the Kirkwood equation¹ (this equation was also used to estimate the dipole moment of the transition state of some of these reactions⁴), and the deviations observed with some solvents were qualitatively interpreted as a consequence of the effect of refractive index of these solvents¹.

The aim of this present report was to measure the rate constants of reactions of methyl iodide with triethylamine (*I*), tripropylamine (*II*), and tributylamine (*III*) in

a set of solvents mutually differing in both the relative permittivity and refractive index and their ratio. Using the Kirkwood functions of relative permittivity and refractive index we tried to estimate quantitatively the contributions of these two properties of solvent to the overall effect of medium on the rate of the reactions studied.

EXPERIMENTAL

Trialkylamines and methyl iodide were redistilled before the preparation of solutions for kinetic measurements. The solvents used were purified by rectifications except for carbon disulfide, dibromomethane, and diiodomethane which were used without purification, viz. the carbon disulfide and dibromomethane as chemically pure (Merck) and diiodomethane pure with min. content of 99% (Jansen Chimica). The kinetic measurements were carried out as in our previous studies^{12,13}, the below-given temperatures of the reaction mixtures being maintained with the accuracy of 0.1 K. The reaction of methyl iodide with tripropylamine was studied at 293, 313, 323, and 333 K in all the solvents except diethyl ether and carbon disulfide in which the measurements were carried out only at 280, 285, 293, and 303 K.

RESULTS AND DISCUSSION

Table I summarizes the rate constants of the reactions studied at 293 K along with the activation enthalpy and entropy of the reaction of methyl iodide with tripropylamine and the dipole moment and the Kirkwood functions of relative permittivity (ϵ) and refractive index (n) of the solvents used. The role of refractive index of solvent played in the overall solvent effect was tested by means of Eq. (1).

$$\log k = A + B(\epsilon - 1)/(2\epsilon + 1) + C(n^2 - 1)/(2n^2 + 1) \quad (1)$$

The terms $(\epsilon - 1)/(2\epsilon + 1) = f(\epsilon)$ and $(n^2 - 1)/(2n^2 + 1) = f(n^2)$ are the Kirkwood functions of relative permittivity and of refractive index of solvent. In this study we have used aliphatic solvents whose relative permittivities and refractive indexes markedly varied, and the ϵ/n^2 ratios were also different. These solvents include the first 12 solvents in Table I. Within this set the functions $f(\epsilon)$ and $f(n^2)$ show no linear dependence (the correlation coefficient of the dependence of $f(\epsilon)$ on $f(n^2)$ is 0.339 for these solvents).

The general equation (1) for $\log k$ of the three reactions studied in these twelve solvents has the form of Eqs (2)–(4).

Methyl iodide + triethylamine

$$\log k = -13.16 + 16.81f(\epsilon) + 20.12f(n^2) \quad (2)$$

$$R = 0.989, \quad \sigma = 0.21, \quad r = 0.868$$

TABLE I

Medium effect on the rate constants of the S_N2 reaction of iodomethane with triethylamine (I), tripropylamine (II), and tributylamine (III) as well as on the activation parameters for the reaction of iodomethane with tripropylamine (II)

Solvent	$\bar{\mu} \cdot 10^{30}$ C m	$f(\epsilon)$	$f(n^2)$	$k \cdot 10^4, \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$			ΔH^\ddagger kJ mol $^{-1}$	$-\Delta S^\ddagger$ J mol $^{-1} \text{K}^{-1}$
				I	II	III		
Cyclohexane	0	0.203	0.204	0.025	0.011	0.016	44.8	200
Diethyl ether	4.3	0.345	0.178	1.06	0.20	0.26	43.6	182
Carbon disulphide	0	0.261	0.260	1.94	0.42	1.25	41.4	181
Ethyl acetate	6.0	0.385	0.185	13.4	3.59	7.90	37.7	180
1,2-Dimethoxyethane	5.7	0.400	0.188	31.5	4.46	9.65	39.9	172
Acetone	9.5	0.465	0.180	1.28	28.0	40.0	38.4	163
1,2-Dichloroethane	6.2	0.431	0.200	201	58.8	90.5	45.0	142
Acetonitrile	11.5	0.480	0.174	363	70.8	110	43.1	137
Dibromomethane	4.8	0.403	0.239	370	93.0	160	44.9	129
Nitromethane	11.9	0.481	0.188	762	249	452	44.4	124
Dimethyl sulfoxide	13.0	0.486	0.220	910	500	570	44.1	119
Diiodomethane	3.6	0.371	0.287	1 010	750	670	44.8	108
Methanol	5.7	0.477	0.168		2.3		53.6	130
Ethanol	5.8	0.470	0.181		1.8		57.2	121
Propanol	5.5	0.464	0.198		1.4		60.3	114

Methyl iodide + tripropylamine

$$\log k = -14.54 + 17.15f(\epsilon) + 23.51f(n^2) \quad (3)$$

$$R = 0.985, \quad \sigma = 0.25, \quad r = 0.829$$

Methyl iodide + tributylamine

$$\log k = -13.93 + 16.65f(\epsilon) + 22.52f(n^2) \quad (4)$$

$$R = 0.985, \quad \sigma = 0.25, \quad r = 0.833$$

R means the overall correlation coefficient, σ is the standard deviation, and r means the partial correlation coefficient between $\log k$ and $f(\epsilon)$. From the magnitude of regression coefficients of the correlations (2)–(4) it follows that the refractive index of medium affects the rate of these reactions even more markedly than the relative permittivity does. In the sense of the Hughes–Ingold principle¹ the observed effect of $f(\epsilon)$ and $f(n^2)$ is interpreted as being due to higher polarity of the transition state compared to the reactants, the difference in the extent of interactions by dispersion forces and dipole–induced dipole interactions between the activated complex and the reactants being greater than this difference in the extent of dipole–dipole interactions. In terms of the concepts by Entelis and Tiger⁵ this high contribution of the function of refractive index of medium indicates a considerably non-equilibrium solvation of the activated complex in the course of these reactions, i.e. the life-time of the activated complex is shorter than the time necessary for orientational polarization of solvent molecules. According to Burgos and Bertrán¹⁴ the term with relative permittivity function indicates that a precursor of the transition state of these reactions is more polar than the reactants, and the term with refractive index function indicates that the transition state itself is more polar than this precursor in these reactions and that the life-time of the transition state is shorter than 10^{-12} s.

In the set of the results obtained the highest rate constant value is that found in diiodomethane, which could arise suspicion with regard to the commonly adopted evaluation of the effect of medium on rates of chemical reactions based only on the functions of relative permittivity¹. One possible interpretation is that amines react not only with methyl iodide but also with diiodomethane, and the higher rate constants result from the fact that the rates of these reactions are obtained from the consumption of amine^{12,13}. Therefore we measured the rate constant of reaction of tripropylamine with diiodomethane in diiodomethane at 293 K. The rate constant of this reaction (the reaction was considered as pseudomonomolecular (cryptobimolecular) with respect to tripropylamine), $k_1 = 2.1 \cdot 10^{-5} \text{ s}^{-1}$, is by three orders lower than the rate constants of reactions of methyl iodide with the trialkylamines studied. Hence there is no risk of affecting the rate constants of the reactions studied in diiodomethane solution by this reaction.

In the case of reaction of methyl iodide with tripropylamine the rate constants and activation parameters were also determined in three amphiprotic solvents. Although even textbooks (see e.g. ref.¹⁵), directly quoting Menshutkin, state that these reactions are very fast in alcohols (faster than e.g. in acetone and aromatic hydrocarbons), we have found in accordance with Jungers⁶ that the rate of these reactions is smaller in aliphatic alcohols than in ketones or benzene. According to Eq. (3) the rate of reaction of methyl iodide with tripropylamine should be 1 order higher in the case of methanol or even 2 orders higher in the case of 1-propanol. Nevertheless, the activation entropies (from Table I it can be seen that the reaction rate is entropy-controlled) are high just in the case of alcoholic solutions, hence the discrepancy observed in the medium effect of alcohols on this reaction is caused by the high activation enthalpy of these reactions in alcohols. This finding, of course, agrees well with the qualitative idea of a hydrogen bond between trialkylamines and alcoholic hydroxyl group. This hydrogen bond is split during the reaction, hence the rate of these reactions carried out in alcohols is more deeply affected by temperature.

The authors are indebted to Professor Ch. Reichardt for his making available the diiodomethane and his kind interest in this our study.

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Translated by J. Panchartek.