The Influence of the Solvent on Reaction Velocity

XXVI. The Reaction between Triethylamine and Ethyl Iodide in Dimethyl Sulphoxide-Benzene Mixtures

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The reaction between triethylamine and ethyl iodide has been investigated in benzene, dimethyl sulphoxide and various dimethyl-sulphoxide-benzene mixtures at four temperatures. The reaction rate increases with increasing dimethyl sulphoxide concentration in the solvent. In general, changes in the activation entropy are more important than changes in the activation energy. The solvent effect is discussed. The results are compared with those previously obtained for the reaction in acetone-benzene mixtures.

The kinetics of the reaction between triethylamine and ethyl iodide,

$$(C_2H_5)_3N + C_2H_5I \rightarrow (C_2H_5)_4NI$$
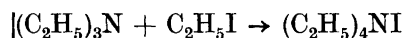
have been investigated under various conditions. The work described in this paper is an extension of the kinetic studies of different reactions in mixtures containing dimethyl sulphoxide (DMSO) that have been carried out in this laboratory.[1-5] It is also a continuation of two earlier papers in which the kinetics of the reaction between triethylamine and ethyl iodide in different acetone-benzene,[6] acetone-dioxan [6] and acetone-tetrahydrofuran mixtures [7] were studied.

EXPERIMENTAL

Reactants. Commercial products of high purity were distilled before use, triethylamine after drying with potassium hydroxide pellets and ethyl iodide after shaking with sodium thiosulphate crystals to remove the small quantity of free iodine it contained.

Solvents. Thiophene-free benzene was stored over sodium for one night, refluxed with sodium for 3 h, and distilled. The dimethyl sulphoxide (Nitroglycerin AB, Gyttorp, Sweden) was purified by distillation at reduced pressure and repeated fractional crystallization from the melt until the melting point of the product was at least 18.50°C.

Solvent mixtures for the kinetic experiments were prepared by pipetting the required volume of benzene into a 200-ml volumetric flask and making up to volume with DMSO. The compositions of the mixtures in weight per cent were obtained from the data given by Kenttämaa, Lindberg and Nissema.[8]

Kinetic measurements. The method was that described in the previous paper.[6] 3-ml volumes of a 0.2 M triethylamine solution and a 0.2 M ethyl iodide solution were pipetted into approximately 8-ml reaction tubes of Pyrex glass, the tubes were sealed by fusion and immersed in electrically regulated thermostats, the temperatures of which remained constant within $\pm$ 0.02°. The exact concentrations of the reactants at this moment were determined on a sample as described below. Tubes were withdrawn after suitable times and chilled rapidly in ice-water. The contents were washed into an excess of 0.02 HCl and shaken vigorously. The acid was back-titrated with 0.02 N Ba(OH)$_2$ with methyl red as the indicator. The end point of titration was very sharp. In solvents which contained 70 % or more benzene, crystals of the quaternary ammonium salt appeared in the tubes after some time, but this did not seem to affect the rate. The reaction is very rapid in solvents which contain 92 % or more DMSO and therefore the experiments were carried out in two-compartment reaction vessels. Small amounts of free iodine were liberated from ethyl iodide in solvents rich in DMSO, but this did not occur when short reaction times were used. The thermometers were checked against a thermometer calibrated by the National Bureau of Standards (U.S.A.).

Satisfactory rate constants were obtained by applying the ordinary second order formula. The number of separate determinations in each run was seven or eight. All rate constants (means of the runs) were corrected for the thermal expansion of the solvent; the temperature expansion coefficients (Table 1) were obtained from the measurements of Lindberg *et al.*[8],[9]

RESULTS AND DISCUSSION

The results of the kinetic measurements are summarized in Table 2. The activation energies, E, and frequency factors, A (in 1 mole^{-1} sec^{-1}), were calculated by the method of least squares from the rate constants at four temperatures, the plots of log k against $1/T$ being linear in all cases. The entropy of activation, ΔS^*, was computed for 25° from the formula $A = e(kT/h)$ exp $\Delta S^*/R$, and the free enthalpy of activation, ΔG^*, from the equation $\Delta G^* = E - RT - T\Delta S^*$.

It is observed from the table that like acetone,[6] dimethyl sulphoxide increases the reaction rate, when it is added to benzene, but the accelerating effect of DMSO is much greater than that of acetone. The values of the ratio k/k_B (k_B is the rate constant in pure benzene) for benzene-DMSO mixtures are plotted in Fig. 1.

Table 1. Temperature expansion coefficients of DMSO-benzene mixtures.

Benzene, ml/l	20°	30°	40°	50°
1000	1.000	1.006	1.025	1.036
900	1.000	1.006	1.025	1.036
800	1.000	1.006	1.023	1.033
700	1.000	1.006	1.022	1.032
600	1.000	1.006	1.022	1.032
500	1.000	1.005	1.021	1.031
400	1.000	1.005	1.021	1.031
300	1.000	1.005	1.021	1.030
200	1.000	1.004	1.020	1.030
100	1.000	1.004	1.018	1.028
0	1.000	1.004	1.020	1.029

Table 2. The reaction $Et_3N + EtI \rightarrow Et_4NI$ in various DMSO-benzene mixtures.

B ml/l	DMSO wt.%	x_{DMSO}	$10^5 k$ l mole^{-1} sec^{-1}				E cal	log A	ΔS^* E.U.	ΔG^* cal
			20.00°	25.00°	40.00°	50.00°				
1000	0	0	0.395	0.584	1.53	2.78	12 190	3.691	−43.6	24 600
950	6.0	0.060	1.35	1.92	4.97	8.72	11 740	3.883	−42.7	23 890
900	12.4	0.124	2.67	3.95	9.68	17.7	11 720	4.169	−41.4	23 480
800	24.2	0.242	6.26	8.82	22.6	40.6	11 740	4.544	−39.7	22 990
700	35.1	0.351	9.29	13.8	35.5	66.4	12 190	5.063	−37.3	22 690
600	45.7	0.457	14.0	19.9	54.1	96.2	12 130	5.194	−36.7	22 490
500	55.8	0.558	19.7	28.0	78.9	147	12 660	5.733	−34.1	22 260
400	65.2	0.652	25.5	38.0	105	201	12 870	6.009	−33.0	22 120
200	83.8	0.838	36.6	55.5	163	320	13 540	6.670	−30.0	21 890
100	91.8	0.918	49.5	69.5	227	439	13 900	7.047	−28.3	21 740
0	100	1.000	62.0	87.3	290	597	14 360	7.487	−26.3	21 600

As in general for quaternary ammonium salt formation,[10,11] the activation energies and especially the frequency factors are low in value, *i.e.* the activation entropies very negative. Fig. 2 plots the quantities E, log A and ΔG^* as functions of the composition of the solvent ($\Delta H^* = E - RT$ or $E - 590$ cal at 25°). As in benzene-acetone mixtures,[6] E passes through a minimum at high benzene concentrations, but then continuously increases with increasing DMSO content. It is conspicuous that log A, or $T\Delta S^*$, is very accurately a linear function of the mole fraction of DMSO over nearly the whole range of mixtures; only in the neighbourhood of pure DMSO does there seem to be a slight deviation from linearity. At mole fractions of DMSO between 0.3 and
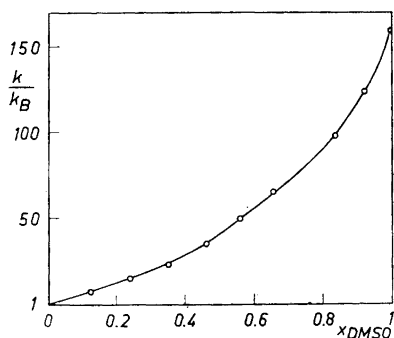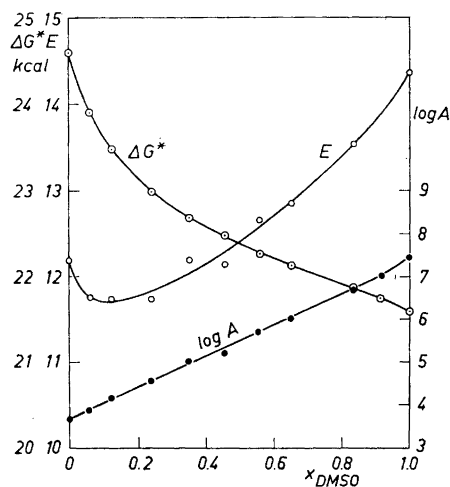

Fig. 1. Plot of k/k_B against the mole fraction of DMSO. Temperature 25°.

Fig. 2. Variation of the kinetic quantities with the mole fraction of DMSO.

0.55 there probably are some irregularities in the E curve, similar to those previously found for acetone-dioxan mixtures.[6] It is seen from Table 2 and Fig. 2 that after the minimum of E the enhancement in the reaction rate caused by addition of DMSO is entirely due to the increase in the frequency factor, the effect of which overweighs the opposite effect of the change in the activation energy.

In the previous paper [6] it was suggested that the low values of the frequency factor A are due to restrictions in the energy transitions involved in the formation of the transition state. The transition complex is highly polar: in fact it undoubtedly resembles the quaternary ammonium salt formed as product.[12] Directed solute-solvent interactions have been demonstrated also in benzene solution [13] and these may be more powerful with respect to the transition state than with respect to the less polar reactants. Accordingly, the large negative activation entropy may also be partly explained by the loss of entropy when the solvent molecules become frozen in the polar transition state.[6] In many cases the solvent effect can be explained by changes in the solvation of the reactants and the transition state.[12] However, this is not the case here. Ethyl iodide and triethylamine are miscible with benzene in all proportions, ethyl iodide also with DMSO. There is no marked heat effect on mixing, which indicates that the forces between the solute and solvent are weak and that the solvation of the solute particles is minimal. A special determination showed that triethylamine dissolves in DMSO to give only an about 0.5 M solution at 25°, and that the reaction product, tetraethylammonium iodide, is practically insoluble in benzene. Its solubility in DMSO at 25° is about 0.25 mole/l. Thus the solvation of the reactants decreases, but that of the transition state increases with increasing DMSO concentration. The latter change tends to lower the potential energy of the transition state and the former tends to raise the potential energy of the initial state, and thus the activation energy, which is the difference between these two energies, should decrease as the DMSO concentration is increased. At the same time the entropy of activation should become more negative as a result of these changes in the solvation. It is therefore rather surprising that according to Table 2 the frequency factor increases over the whole range and that also the activation energy increases in the range from $x_{DMSO} = 0.1$ to pure DMSO. Various factors, such as changes in the internal structure of the solvent and the ability of the solvent to prevent reversion of the transition state into the initial state, can be invoked to explain such effects.[6] The solvation of cations is similar in DMSO and water, but anions are solvated only to a limited extend in DMSO.[14,15] However, the iodide ion is much more solvated in DMSO than, e.g., the chloride ion or hydroxide ion.[14] Thus DMSO probably tends to split the transition complex into the ions of the quaternary ammonium salt. It is further known that DMSO forms with methyl iodide a stable addition compound, $Me_4SO^+I^-$, which can be isolated in crystalline form,[16,17] and it is reasonable to assume that also ethyl iodide has an attraction for DMSO, although the addition product has not been isolated. This attraction between ethyl iodide and DMSO for its part should cause E and A to increase with increasing DMSO concentration.

An interesting empirical relation, first proposed by Venkataraman and Hinshelwood,[18] is shown in Fig. 3, where log $k_{25°}$ and log $k_{40°}$ are plotted against
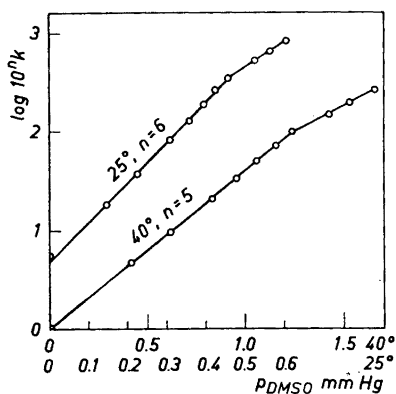
Fig. 3. Plot of log k against the partial vapour pressure of DMSO.
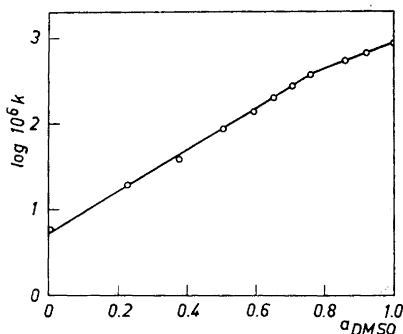
Fig. 4. Plot of log k against the activity of DMSO at 25°.

the partial pressure [19] of the polar component, *i.e.* DMSO. It is seen that the plot consists of two linear parts, one in the region from pure benzene to $x_{DMSO} = 0.65$, and the other in the region from $x_{DMSO} = 0.65$ to pure DMSO. The plot against the activity [19] of DMSO are similar (Fig. 4). According to the mentioned authors, this partial vapour pressure is a measure of the tendency for the polar component to escape from the bulk medium and may be related to the ease with which its molecules can be disengaged to arrange themselves around the reactants and the transition complex as a solvation sphere, and thus affect the reaction rate. The linar relation between the partial pressure or the activity of DMSO and log k is interesting as is also the fact that the slope of the plot changes at the point where the relative numbers of DMSO and benzene molecules in the solvent are 2:1. No similar behaviour has been observed at this composition in other curves which characterise kinetic or thermodynamic [8],[9],[19] properties of the system. This problem is obviously not a very tractable one.[18]

According to electrostatic theory, log k should vary linearly with the reciprocal of the dielectric constant of the solvent. This is in fact the case for the
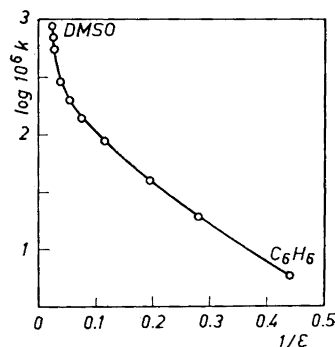

Fig. 5. Plot of log k against the reciprocal of the dielectric constant, 25°.

reaction between triethylamine and ethyl iodide in benzene-acetone, dioxan-acetone and tetrahydrofuran-acetone mixtures.[20] For the reaction in benzene-DMSO mixtures, the plot of log k against the reciprocal of the dielectric constant [21] is not linear (Fig. 5). However, the reaction rate does increase with increasing dielectric constant of the solvent.

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