

The Influence of the Solvent on Reaction Velocity

VII*. The Reaction between Triethylamine and Ethyl Iodide in Acetone-Benzene and Acetone-Dioxan Mixtures

EERO TOMMILA and PENTTI KAURANEN

Institute of Chemistry, University of Helsinki, Helsinki, Finland

In all of the cases studied in the previous investigations of this series the solvent or one of its components takes part in the reaction. According to the results of these investigations, a common feature of all solvolytic reactions in mixed solvents seems to be that the parameters of the Arrhenius equation are greatly influenced by the medium; the plots of the activation energy and the frequency factor against the composition of the solvent are usually characterized by more or less pronounced maxima and minima. Their occurrence is, partly at least, accounted for by changes in the solvation of the reactants and the transition state¹. In connexion with these observations it was found advisable to study a reaction in which the solvent does not take part, in mixed solvents in which the proportion of the components is continuously altered. As such a process the reaction between triethylamine and ethyl iodide was chosen:



The reaction is excellent for a kinetic study. It is quantitative, it proceeds at a conveniently measurable rate, and the amount of the amine present in the reaction mixture may be readily determined. To avoid every solvolysis of ethyl iodide, acetone-benzene and acetone-dioxan mixtures were chosen as solvents. In the former mixtures one of the components (acetone) is strongly polar, the other (benzene) non-polar; in the latter, the dipole moment of dioxan is practically zero, but in reality the dioxan molecule has two equal moments acting in opposite senses.

Menschutkin in his classical work² on the reaction between triethylamine and ethyl iodide measured its velocity in 22 different solvents, but at one temperature only, *viz.* at 100° C. He found that its velocity is greatly dependent on the solvent. Following the increasing order of the reaction velocity the

* VI. *Suomen Kemistilehti* B 26 (1953) 79.

solvents can be arranged in the following row: hydrocarbons < ethers < esters < alcohols < ketones. The two last-mentioned must be written rather in the opposite order. The relative rate constants in some of the various solvents were: hexane 1, heptane 1.3, ethyl ether 4.2, xylene 15.9, benzene 38 . . . ethyl alcohol 211, acetone 352, benzyl alcohol 769. Thus the rate constant increased almost 800-fold in passing from hexane to benzyl alcohol. The reaction is always faster in an aromatic solvent than in the corresponding aliphatic solvent. The parameters of the Arrhenius equation for the reaction were determined by Grimm, Ruf, and Wolff³ in a number of pure solvents. According to their results, the general effect of changing the solvent is to bring about a change in both activation energy and frequency factor, in some cases the change in E , in some cases that in A being more important⁴. Moelwyn-Hughes and Hinshelwood⁵ found that in gaseous phase the reaction takes place, at least partly, on the surface of the glass. They studied the reaction also in hexane. No information on this reaction in various mixtures of two liquids is available, but the reaction between triethylamine and ethyl bromide⁶ has been investigated in various acetone-benzene mixtures and the results have been discussed^{7,11}. Some other quaternary ammonium salt formation reactions have also been studied in mixed solvents, *viz.* the reactions of triethylamine and pyridine with benzyl bromide in benzene-nitrobenzene mixtures⁸, and the formation of methylpyridinium iodide in various pure liquids⁹ and binary mixtures¹⁰. The kinetics of the quaternary ammonium salt formation has been studied by many other investigators and it has been extensively discussed^{2, 3, 4, 11}.

EXPERIMENTAL

Chemicals. All the substances used were commercial products of high purity. Triethylamine and ethyl iodide were fractionated to correct and constant boiling point, triethylamine after drying over potassium hydroxide. Merck's acetone 'pro analysi' was found to be dry enough and to require no further purification. The dioxan was purified by the method of Hess and Frahm¹². Triphen-free benzene was refluxed several hours with sodium and distilled.

Preparation of the solvent mixtures. A quantity of the component the proportion of which in the mixture will be less than 50 % was measured with a pipette into a volumetric flask and made up to volume with the other component. The volume per cents given in the tables refer to these values. The proportion of the constituents in the solvent was measured also by weight. Each mixture was prepared in a quantity sufficient for all experiments in this solvent.

Equal volumes of 0.2 *M* solutions of triethylamine and ethyl iodide were mixed, so that the initial concentration of each was 0.1 *M*. From this mixture samples of 5 ml were pipetted into approximately 6 ml reaction tubes of Pyrex glass, the tubes sealed and immersed in the thermostats the temperature of which could be held constant to within about 0.02°. The exact concentration of the reactants at this moment was determined analytically as given below, for which purpose two or three of the tubes were used. After the reaction had proceeded for the desired length of time, the tubes were rapidly chilled in ice-water and the contents titrated with 0.02 *N* HCl, methyl red being used as indicator. The end-point of the titration was very sharp. No appreciable hydrolysis of ethyl iodide takes place during titration. In the case of the acetone-benzene mixtures, the contents of the tubes were washed into excess of 0.02 *N* HCl, vigorously shaken, and back-titrated with 0.1 *N* NaOH, a micro-burette being used in these titrations. Since the reaction times were fairly long (over one hour), the contents of the tubes small, and all operations could be carried out very quickly, correction for the time required for heating

up and analysing the mixtures could be neglected. — All thermometers were checked against a thermometer calibrated by the National Bureau of Standards (U.S.A.).

Satisfactory constants were obtained by applying the ordinary bimolecular formula, as exemplified by the following two runs:

1. Solvent: Acetone 7.28 % + dioxan 92.18 % by weight. $a = 0.0988$. 75.00°C.

t mins.	166	241	300	430	486	648	906	954	990
change, %	29.2	37.6	42.2	51.4	55.0	61.5	69.2	70.3	70.7
$10^6 k$ l mole ⁻¹ sec. ⁻¹	41.9	41.4	41.0	41.5	42.4	41.5	41.9	41.8	41.2

2. Solvent: Acetone 37.56 % + benzene 62.44 % by weight. $a = 0.0998$. 75.00°.

t mins.	145	202	256	323	390
change, %	34.5	42.9	49.2	55.0	59.5
$10^6 k$ l mole ⁻¹ sec. ⁻¹	61.7	62.1	63.2	63.3	62.8

All rate constants (means of the runs) were corrected for the thermal expansion of the solvents.

Since the object of the experiments was to measure small changes in activation energy and frequency factor as accurately as possible, the preparation of the solvent and all other operations were carefully standardised and the determination of the rate constants was carried out always at four temperatures. All the measurements were made by one of the writers (P.K.) in order to eliminate personal factors as much as possible.

RESULTS

Tables 1 and 2 summarise the values found for the rate constants, activation energies, frequency factors, and activation entropies. The activation energies and frequency factors were calculated by the method of least squares from the variation of $\log k$ with $1/T$. The entropy of activation, ΔS^* , was calculated from the frequency factor A by means of the equation¹¹

$$A = e (kT/h) e^{\Delta S^*/R}$$

The Arrhenius equation is obeyed within the experimental error in all cases.

Estimated from the errors in the rate constants, the probable error in the activation energies is in the acetone-dioxan series ± 40 to ± 50 cal., in the acetone-benzene series ± 70 to ± 100 cal., and that in $\log A$ in the former series ± 0.040 to ± 0.050 , and ± 0.050 to ± 0.070 in the latter, the probable error in the entropies of activation in the two series being thus ± 0.1 to ± 0.2 and ± 0.2 to ± 0.3 entropy units, respectively. In view of this the variations of E and ΔS^* (or $\log A$), to be discussed in the next section, are fully significant with respect to the experimental uncertainty, all the more if we take into account the fact that relative values of A and E are more accurate than their absolute values.

DISCUSSION

Our values for the pure acetone solution are in good agreement with those of Grimm, Ruf and Wolff (E 11.9 kcal., $\log A$ 4.4). The small difference is probably essentially due to the correction for the thermal expansion of the solvent, made by us. In benzene solution our values for E and A are much

Table 1. Acetone-dioxan mixtures.

D vol. %	D wt. %	x_D	10^5k liter mole ⁻¹ sec. ⁻¹				E cal.	log A	ΔS^* E.U.
			40.00°	50.00°	60.00°	75.00°			
0	0	0	17.72	32.84	58.29	126.9	12 190	4.756	-38.8
5	6.40	0.0431	18.18	33.19	58.07	125.6	11 960	4.609	-39.4
10	12.72	0.0877	18.14	32.70	56.05	121.7	11 770	4.470	-40.0
12.5	15.74	0.1097	18.19	33.18	58.12	125.9	11 980	4.618	-39.4
15	18.74	0.1320	17.82	32.44	57.81	125.6	12 060	4.674	-39.1
20	24.62	0.1771	17.63	32.14	56.64	123.5	12 050	4.659	-39.2
30	35.84	0.2691	17.13	31.20	54.68	118.7	11 980	4.597	-39.5
45	51.58	0.4126	16.07	29.38	50.79	110.2	11 900	4.513	-39.9
55	61.54	0.5176	14.68	26.29	46.36	101.0	11 960	4.510	-39.9
60	66.36	0.5625	13.73	24.93	43.80	94.56	11 950	4.479	-40.0
65	70.79	0.6150	12.75	23.03	40.34	86.52	11 860	4.384	-40.5
70	75.26	0.6673	11.66	21.14	36.77	78.82	11 830	4.322	-40.8
75	79.71	0.7209	10.58	18.93	33.03	70.29	11 740	4.215	-41.2
80	83.97	0.7754	8.996	16.57	28.95	62.44	11 980	4.320	-40.8
80II	83.96	0.7753	9.089	16.53	29.23	63.11	12 010	4.340	-40.9
85	88.11	0.8301	7.731	14.11	24.93	54.36	12 080	4.319	-40.8
90	92.18	0.8860	6.225	11.45	20.08	44.41	12 160	4.281	-40.9
94.7	95.86	0.9386	4.978	9.220	16.39	36.63	12 350	4.316	-40.8
100	100	1.0000	3.343	6.318	11.52	25.88	12 680	4.374	-40.5

higher than those of these authors (E 11.4 kcal., log A 3.3). We are unable to explain this discrepancy. A possible explanation would be that Grimm, Ruf and Wolff carried out their experiments at higher temperatures than we did and that E and A are somewhat dependent on temperature. The reaction might also be very sensitive for impurities. In dioxan, where the reaction has not been previously investigated, its velocity is less than in acetone, but greater than in benzene. The value of the energy of activation is about the same as in benzene. On passing from acetone to benzene, or to dioxan, the reduction in reaction velocity is caused partly by an increase in E and partly by a

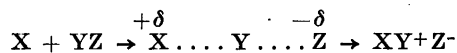
Table 2. Acetone-benzene mixtures.

B vol. %	B wt. %	x_B	10^5k liter mole ⁻¹ sec. ⁻¹				E cal.	log A	ΔS^* E.U.
			40.00°	50.00°	60.00°	75.00°			
0	0	0	17.72	32.84	58.29	126.9	12 190	4.756	-38.8
10	10.99	0.0841	18.81	34.48	61.12	133.9	12 160	4.758	-38.8
20	21.85	0.1721	17.13	31.04	55.13	121.1	12 120	4.692	-39.1
40	42.66	0.3561	14.28	25.46	45.36	98.96	12 020	4.540	-39.8
60	62.44	0.5528	10.30	18.21	31.88	68.07	11 720	4.187	-41.4
80	81.61	0.7674	5.920	10.60	18.37	39.41	11 740	3.964	-42.4
90	90.93	0.8817	3.572	6.404	11.43	24.41	11 930	3.880	-43.8
95	95.48	0.9402	2.413	4.428	7.771	17.04	12 090	3.823	-43.0
100	100	1.0000	1.478	2.773	5.025	11.50	12 700	4.034	-42.1

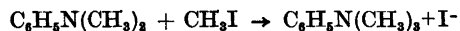
decrease in A . The difference in reaction velocity between benzene and dioxan solutions is accounted for solely by changes in A .

The values of E and A are very low in all the three solvents, but this applies also to many other media ⁴. For the low value of A the following explanation can be given ¹¹. In the reaction where the reactants are diatomic and for polyatomic molecules the formation of the transition complex is accompanied by the disappearance of three translational and three rotational degrees of freedom, and the formation of five new vibrational degrees of freedom and one along the reaction coordinate. The low values of A or the large negative values of the entropy of activation are clearly due to the restrictions in the energy transitions involved in the formation of the transition state. There is a considerable rearrangement of energy among the various degrees of freedom to accompany the formation of the transition state, *i.e.*, a small probability of formation of the transition state, and, therefore, the entropy of activation is negative the more elaborate the mechanical reorganization which the reaction involves. Two molecules possessing the necessary energy for reaction may approach but unless the energy can be transferred to the appropriate degrees of freedom the transition state cannot form. According to the statistical theory, the probability factor P in the equation $A = PZ$ (Z is the calculated collision frequency) is, for a reaction between two polyatomic molecules, $P = (f_V/f_R)^5$, where f_V and f_R denote the contributions of vibrational and rotational degrees of freedom to the total partition function. At ordinary temperatures, f_V is generally of the order of unity, while f_R is of the order of 10 to 100, and so the ratio f_V/f_R is 10^{-1} to 10^{-2} and $(f_V/f_R)^5$ approximately 10^{-5} to 10^{-10} . However, that is so only for gas reactions; for the reactions in solution the presence of the solvent modifies the partition functions in a way which is not accurately known, and thus the calculations are more uncertain. The collision frequency Z is, also for the reactions in solution ⁴, about 2.8×10^{11} . The experimental values for P are thus 0.4×10^{-7} (benzene), 1.0×10^{-7} (dioxan), and 2.0×10^{-7} (acetone).

In the formation of quaternary ammonium salts the lone pair of electrons of the nitrogen atom in the amine is shared with carbon under splitting off the halogen. The product is a highly polar substance and also the transition state is highly polar. The process can be represented by



On the ground of the entropy data available ¹³ it has been shown ¹¹ that for the reaction



the transition complex is very similar in structure to the quaternary ammonium salt obtained as product, and there is little doubt that this is the case also in the reaction between triethylamine and ethyl iodide.

In cases where the products are more polar than the reactants, there is a general tendency for A to be greater in a more polar solvent than in a less polar solvent ¹⁴. It probably depends partly on an actual increase in Z with a change to a more polar solvent, and partly on an action of the latter in stabi-

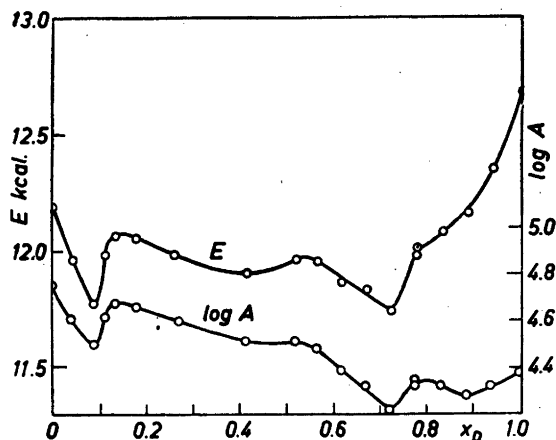


Fig. 1. Plots of E and $\log A$ against the mole fraction of dioxan in acetone-dioxan mixtures.

zing the products of the reaction. The increase in Z would be due to a kind of extrusion of solute molecules from the structural pattern of the solvent, as has been shown probable by the use of a mechanical model^{15,16} and also inferred on the basis of chemical experiments¹⁶. According to Hinshelwood¹⁴, "The stabilizing effect will only be in evidence in reactions, such as the formation of quaternary ammonium salts, where the product is a highly polar substance, and where the transition complex will have a great tendency to relapse into its original components unless a polar environment is provided to prevent it. If much reversion occurs, P will be small. Hence the increase of P with polarity of solvent." The same suggestion has been made by Soper and co-workers, who postulated that the solvent tends to disrupt the critical complex into those substances for which the solvent has the greater affinity¹⁷. From the standpoint of the theory of absolute reaction rates this means that the transmission coefficient, κ , in the reaction rate equation

$$k = \kappa \frac{kT}{h} e^{-\Delta G^*/RT}$$

is affected by the solvents.

However, there are also solvent effects of another kind, as can be estimated on the basis of activation energies. As highly polar, the transition complex no doubt is more solvated than the reactants and, accordingly, the large negative activation entropies found almost certainly are partly due to the entropy lost by solvent molecules frozen around the partially ionic transition states. Since this effect is the stronger the more polar the solvent, it operates contrary to that discussed above. The increase of solvation accompanied the formation of the transition complex decreases the value of the parameter A of the Arrhenius equation, but it also reduces the energy of activation. The former effect retards, the latter accelerates the reaction. Since a change from a less polar to a more polar solvent increases the organisation of the solvent molecules

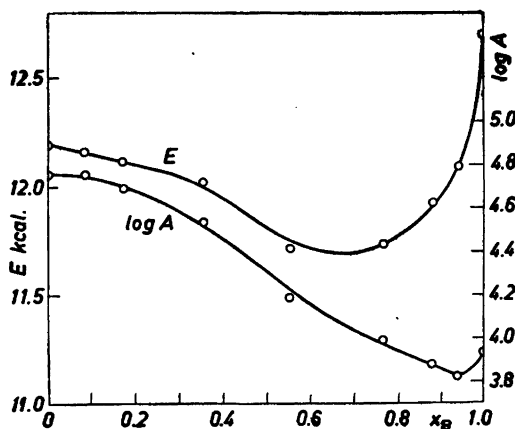


Fig. 2. Plots of E and $\log A$ against the mole fraction of benzene in acetone-benzene mixtures.

around the partially ionic transition complex more than around the less polar reactants, it will decrease the energy of activation and also decrease the frequency factor; the experimental result that a more polar solvent accelerates the reaction indicates that the energy change dominates the rate change. The solvation especially of the transition complex in a polar solvent is without any further consideration clear. Wynne-Jones, in a recent investigation¹⁸, has assumed that also the benzene molecules are powerfully oriented by the strongly polar compounds and related his results to the mechanism of the Menschutkin reaction. Attention has also been focussed¹⁹ to the fact that reactions in which the transition state is more highly polar, and hence more extensively solvated, than the initial state, are greatly accelerated by pressure, while those in which the transition state is less ionic than the initial state are retarded by pressure²⁰.

When we pass through a series of mixed solvents, the degree of the solvation in general will be changed, and hence it follows that E and A will be changed. The curves representing E and A as functions of the composition of the solvent may vary greatly from case to case. The experimental activation energies and frequency factors given in Tables 1 and 2, and related to the composition of the solvent in Figs. 1 and 2, show that for the reaction between triethylamine and ethyl iodide the state of affairs is simpler in acetone-benzene than in acetone-dioxan mixtures. The behaviour of E and A may highly probably principally be attributed to changes in the solvation of the transition state, and it is reasonable to assume that the solvation changes with the composition of the solvent more regularly in the case of acetone-benzene than in the case of acetone-dioxan.

The minima in E and A correspond to domains where the solvation of the transition state is particularly powerful; in the case of acetone-dioxan there are three such minima, two sharp and one flat; in the case of acetone-benzene there is only one minimum. It is obvious that in the regions of the minima the

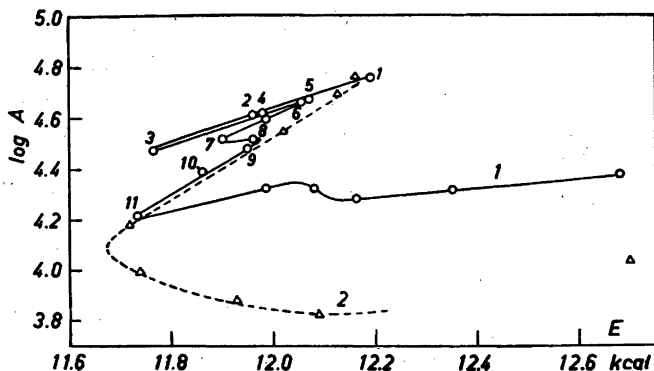


Fig. 3. Plot $\log A$ against E . 1. Acetone-dioxan mixtures, 2. Acetone-benzene mixtures.

relative proportion of the components of the mixed solvent is suitable, so that both of them can profitably take part in the formation of the solvation layer. Other factors, such as the internal structure of the solvent and the ability of the solvent to prevent the relapse of the transition complex into its original components, may also play a part in the matter. Especially the curves for acetone-dioxan mixtures show how important it is in the study of solvent effects in mixed solvents that a sufficient number of observations has been taken. In contrast to the behaviour of E and A the plots for the rate constants against the composition of the solvent are much simpler, certain deviations which are scarcely noticeable correspond to the irregularities in the E and $\log A$ curves.

In acetone-dioxan solvents the E and $\log A$ curves are close similar in form until the mixture contains 80 % of dioxan, and in acetone-benzene mixtures until the percentage of benzene is 70, after which A continuously decreases although there is a powerful rise in E . Fig 3, in which are given plots of $\log A$ against E for the both mixtures, shows linear relationships for all the regions between the different turning points in the curves in Figs. 1 and 2. Linear relationships between E and $\log A$ have been found in many other reactions, and various attempts to justify them have been made^{1,10}.

Much attention has been paid to the relationship between the dielectric constant of the medium and the rate of reaction. Unfortunately the dielectric constants of the mixtures used by us as solvent have not been measured.

In recent years, attention has been paid also to the discussion of the Arrhenius equation⁴, and cases are known where the energy of activation changes with rise in temperature. Since our data at least for acetone-dioxan mixtures may be assumed to be of considerable accuracy, we have calculated the values of E for the temperature intervals 40—50°, 50—60°, and 60—75°. For the reaction in pure acetone the values are 12 400, 12 300, and 11 950 calories, respectively, but in the mixed solvents and in pure dioxan and in pure benzene the differences are too small to allow any definite conclusions. To save space the single values are not given here.

SUMMARY

The reaction between triethylamine and ethyl iodide has been investigated in various acetone-benzene and acetone-dioxan mixtures. The plot of \bar{E} and $\log A$ against the composition of the solvent shows in the former case a minimum, in the latter one flat and two sharp minima. Between the turning points of the curves there exist linear relationships between $\log A$ and \bar{E} . The results are discussed.

REFERENCES

1. Tommila, E., Koivisto, A., Lyyra, J. P., Antell, K. and Heimo, S. *Ann. Acad. Sci. Fennicae A II* (1952) No. 47.
2. Menschutkin, N. *Z. physik. Chem.* **6** (1890) 41.
3. Grimm, H. G., Ruf, H. and Wolff, H. *Z. physik. Chem.* **B 13** (1931) 301.
4. Moelwyn-Hughes, E. A. *The Kinetics of Reactions in Solutions*, 2nd Ed. Oxford 1947, p. 56, 70, 210.
5. Moelwyn-Hughes, E. A. and Hinshelwood, C. N. *J. Chem. Soc.* **1932** 230.
6. v. Hemptinne, A. and Bekaert, A. *Z. physik. Chem.* **28** (1895) 225.
7. Wynne-Jones, W. F. K. and Eyring, H. *J. Chem. Phys.* **3** (1935) 493.
8. Muchin, G. E., Ginsberg, R. and Moissejeva, Kh. *Ukrain. Chem. J.* **2** (1926) 136; *Chem. Zentr.* **1926 II** 2376.
9. Pickles, N. J. T. and Hinshelwood, C. N. *J. Chem. Soc.* **1936** 1353.
10. Fairclough, R. A. and Hinshelwood, C. N. *J. Chem. Soc.* **1937** 538, 1573; Raine, H. C. and Hinshelwood, C. N. *Ibid.* **1939** 1378.
11. Glasstone, S., Laidler, K. J. and Eyring, H. *The Theory of Rate Processes*, New York 1941, p. 17, 417, 418.
12. Hess, K. and Frahm, H. *Ber.* **71** (1938) 2627.
13. Essex, H. and Gelormini, O. *J. Am. Chem. Soc.* **48** (1926) 882.
14. Hinshelwood, C. N. *The Kinetics of Chemical Change*, Oxford 1942, p. 250.
15. Rabinowitch, E. and Wood W. C. *Trans. Faraday Soc.* **32** (1936) 1381; Rabinowitch, E. *Ibid.* **33** (1937) 1225.
16. Fairclough, R. A. and Hinshelwood, C. N. *J. Chem. Soc.* **1939** 593.
17. Soper, F. G. and Richardson, M. *J. Chem. Soc.* **1929** 1873; Soper, F. G. and Williams, E. *Ibid.* **1931** 2297; *Proc. Roy. Soc. A* **140** (1933) 59.
18. Greenwood, N. N. *Nature* **172** (1953) 150.
19. Buchanan, J. and Hamann, S. D. *Trans. Faraday Soc.* **49** (1953) 1425.
20. Perrin, M. W. *Trans. Faraday Soc.* **34** (1938) 144.

Received April 2, 1954.