

THE ROLE OF SOLVENT IN CHEMICAL REACTIONS

Part I. The Reaction between Pyridine and Methyl Iodide *

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THE role of solvents on the course of chemical reactions is still far from clear, even though a good deal of work has been published. Menshutkin¹³ classified solvents according as they accelerated or retarded a reaction and, from an analysis of rate constants, concluded that there was specific solvent solute interaction. Van't Hoff¹⁹ analysed the effect into two parts: a catalytic one depending on the physical properties and another related to the solubility of the components, but his analysis of von Halban's work and of the Menshutkin reaction failed to give any conclusive results. Dimroth's refinement of the picture did not improve the situation but both Hawkins⁷ and Lewis¹² noticed a rough correlation between the rate and the dielectric constant. Hinshelwood and his associates^{8, 9} have made an extensive study of the reaction noticing distinct correlation between the two Arrhenius parameters. The work reported here deals with the reaction in 95 per cent. alcohol and in acetone.

EXPERIMENTAL

Pyridine, B.D.H. Analar, was dried over sticks of potassium hydroxide, and distilled, large head and tail fractions being rejected b.p. 115° C./760 mm.

Methyl Iodide.—May and Baker L.R., was freed from elementary iodine by repeated washing with sodium carbonate solution, then washed with water, dried over anhydrous calcium chloride for several days in the dark and then fractionated in the dark, the middle fraction being collected, b.p. 42° C./760 mm.

Acetone was purified by the method of Norris and Prentiss,¹⁷ the solvent being kept in contact with potassium permanganate with repeated shaking for several days (not less than 14 days were generally used), freed from precipitated manganese dioxide, and distilled. The distillate was dried over Merck's Extra Pure Anhydrous potassium carbonate for a week and then fractionated, b.p. 56° C./760 mm.

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Rectified spirit was fractionated twice, rejecting large head and tail fractions each time, fresh products being used each time. The solvent was found to be free from aldehydes, homologues and higher boiling fractions.

Benzene, crystallisable, for molecular weight determinations, was freshly distilled and used for extractions.

The reactions were carried out in an electrical thermostat, the thermal fluctuations being within 0.005°C . at 40°C ., 0.01° at 50°C . and 0.02° at 60°C . Solutions of the amine and of methyl iodide were separately prepared and 5 ml. of each were mixed in a drawn-out 'Borosil' tube kept in a freezing mixture and then sealed off. The sealed tubes were then immersed in the thermostat, the time of immersion being taken as zero time (less than 1 minute was found to be needed for the tubes to reach the temperature of the thermostat and no great error was found to be introduced by this procedure). At suitable intervals, the tubes were taken out, cooled rapidly in

TABLE I
The Reaction in Acetone Solution

		Temperature $^{\circ}\text{C}$.						
		40		50		60		
Strength of silver nitrate solution		0.02352 N		0.02496 N		0.02475 N		
Initial concentration of pyridine (a) gm. mol./l. ..		0.09727		0.09792		0.08459		
Initial concentration of methyl iodide (b) gm. mol./l. equivalent ..		0.08280		0.08549		0.07920		
Volume equivalent of amine in terms of silver nitrate (V_a) ..		41.35		39.22		34.18		
Volume equivalent of methyl iodide in terms of silver nitrate (V_b) ..		35.25		34.25		32.00		
		A		B		C		
A	Time (min.)..	89.5	139.8	190.5	343.8	427.3		
	Volume (titre)	8.25	11.70	14.30	19.80	22.10		
B	Time (min.)..	120.0	150.0	182.0	210.0	240.0	285.0	
	Volume (titre)	15.60	17.73	19.40	20.85	21.95	23.55	
C	Time (min.)..	50.0	80.0	110.0	141.0	170.0	200.0	260.0
	Volume (titre)	10.60	14.15	16.95	18.85	20.20	21.70	23.45

TABLE II
The Reaction in 95 per cent. Ethyl Alcohol

		Temperature °C.					
		40		50		60	
Strength of silver nitrate solutions		0.02352 N		0.02504 N		0.02475 N	
(a)	gm. mol./l. ..	0.09480		0.09893		0.09194	
(b)	gm. mol./l. ..	0.08563		0.08539		0.07698	
V _a	ml. ..	40.33		39.51		37.15	
V _b	ml. ..	36.40		34.10		31.10	
		D		E		F	

D	Time (min.)	411.2	598.0	718.8	909.0	1282.0	1880.0	
	Volume (titre)	5.90	8.10	9.50	11.25	14.00	17.80	
E	Time (min.)	240.0	300.0	420.0	720.0	960.0	1200.0	1440.0
	Volume (titre)	7.85	9.40	11.83	16.25	19.30	21.38	23.00
F	Time (min.)	39.0	90.0	150.0	210.0	300.0	420.0	
	Volume (titre)	2.50	6.10	9.30	11.55	14.30	17.30	

freezing mixture, the tips broken off and the contents poured into a mixture of 30 ml. of ice-cold 2 N acetic acid and 30 ml. well-cooled benzene. The inside of the tubes were thoroughly washed out with ice-cold water. Five or six drops of eosin solution were added and the solution titrated rapidly against silver nitrate solution. The end-point was indicated by the aqueous layer turning pink through the adsorption of the indicator by the silver iodide solution. Benzene is used to help in keeping the unreacted amine and alkyl halide out of the aqueous layer. Acidimetric methods have been used for these estimations^{1, 4} but we found that with pyridine, the end-points under the conditions of our experiment were not sharp and argentimetric methods gave more consistent results. The silver nitrate solutions were invariably standardised by gravimetric methods. Typical runs, in the two solvents used, are presented in Tables I and II above.

DISCUSSION OF RESULTS

The results presented here are for a completely homogeneous reaction and there was no separation of solid phase at any stage of the reaction.

They serve to some extent to supplement earlier observations of others.^{9a, b, c} One difficulty in comparing earlier work should be mentioned here. The initial concentrations employed are such that separation of some of the product of the reaction should have taken place though the details provided give no indication on this point. Especially with non-polar solvents, homogeneous conditions may not prevail. Edwards³ first drew attention to this aspect of the problem when he noticed that the dominant influence on the course of the reaction was the rate of crystallisation of the product. Davies and Cox² restricted their observations to the region up to which homogeneous conditions prevail. Neither of these, however, dealt with the pyridine-methyl iodide reaction. The rate constants and the Arrhenius parameters are convenient data for comparative studies and these are given in Table III.

TABLE III

Solvent	Rate Constant mol./l. sec. ⁻¹ × 10 ⁵ .			E K. cal.	Log ₁₀ PZ
	40° C.	50° C.	60° C.		
Acetone ..	58.43	111.4	193.5	11.280	4.70
95% Alcohol ..	8.367	20.95	48.35	17.820	8.41

From the trend of the logarithm of the rate constant in relation to the dielectric constant of the solvent, it has generally been held that the reaction studied is one of the dipole-dipole type.^{5, 14b} Kinetically, the alternatives are for a unimolecular and a bimolecular mechanism. The present studies, as well as the earlier published work, give consistently satisfactory second order rate constants over a considerable range of concentrations and ionisation of the alkyl halide may not be the rate-determining step. Essentially, the reaction is a three centre one, with simultaneous approach of the base and removal of the iodide ion. The driving force of the reaction is the availability of the unshared pair of electrons for co-ordination, while the inertia is provided by the polarisation of the C-I bond. The activation energy will involve the C-N and C-I bond energies and the repulsion energies of the reactants and products, while the entropy of activation or frequency factor arises from the need for the transition state in which the encounter between pyridine and the alkyl halide has to be in the region of the unshared electron pair and the alkyl group. All these factors are subject to environmental influence. However, since the products are ions, the coulombic attraction may more than offset the repulsion energy.

In analysing solvent influences, it will be convenient to take the data provided by other workers in other solvents and where these are not available, evaluating these parameters from the data provided. These are presented in Tables IV and V.

TABLE IV
The Pyridine-Methyl Iodide Reaction

Solvent	E K. cal.	Log ₁₀ PZ	Reference
60% alcohol-water ..	18.200	9.05	9(b)
95% alcohol-water ..	17.820	8.41	Present work
100% alcohol ..	18.000	8.32	9(b)
78.3% alcohol-benzene ..	17.200	7.86	do
47.5% do ..	15.900	6.99	do
15.5% do ..	14.900	6.28	do
100% benzene ..	14.400	5.55	do

TABLE V

Solvent	Reaction	E K. cal.	Log ₁₀ PZ	Reference
Ethyl alcohol ..	Pyridine-allyl bromide	15.100	10.9	7
100% alcohol ..	Pyridine-benzyl bromide	14.360	8.63	15
10% benzene alcohol ..	do	14.170	8.47	do
25% do ..	do	14.180	8.43	do
50% do ..	do	14.110	8.27	do
75% do ..	do	16.060	9.438	do
90% do ..	do	16.250	9.267	do
100% benzene ..	do	13.150	6.394	do
100% alcohol ..	Triethylamine-benzyl bromide	14.120	8.81	do
10% benzene alcohol ..	do	13.420	8.33	do
25% do ..	do	13.150	8.13	do
50% do ..	do	13.490	8.30	do
75% do ..	do	14.110	8.58	do
90% do ..	do	13.300	7.75	do
100% benzene ..	do	10.500	5.39	do
Alcohol ..	Dimethylaniline-benzyl bromide	13.200	8.78	10(a)

More work and a wider range of solvent compositions are needed before one can draw any conclusion in the case of alcohol-water mixtures. The activation energy, within the range studied, appears to be more or less constant but the frequency factor shows differences beyond the limits of experimental error.

The breakdown of any direct correlation between the Arrhenius parameters or the logarithm of the rate constant and dielectric constant is clearly

brought out by the results with benzene-alcohol mixtures. The figures in Table V have been obtained from the rate constant data reported by the Russian authors. In every one of the reactions, it will be noticed that benzene requires a lower activation energy than ethyl alcohol or mixtures of alcohol with benzene. Whether one considers the solvation of the complex in the transition state or the polarisation of the C-Hal. bond, a higher dielectric constant of the solvent may be expected to favour the process and lead to a corresponding reduction of the activation energy. The abnormal result can be partly accounted for in two ways. The Frank-Rabinowitch cage effect has been invoked by Norrish¹⁶ in dealing with solvent influences. This involves a quasi-crystalline structure of liquids, demanding a fairly rigorous orientation of molecules and strong dipolar forces in solution. In mixed solvents, one may visualise the reactant molecules in an ordered (?) environment in which the solvent molecules of only one type are largely present and at a critical composition which may vary with temperature, a change similar to phase reversal in colloidal systems takes place. Further, if crystallisation takes place during the reaction, as seems likely in all the reported cases except in the present work and in alcoholic solutions of higher alcohol content, one has to reckon not only the rate of the reaction but also the rate of crystallisation and in computing true activation energies, one has to take into account the heat of crystallisation also. With such a picture, the macroscopic dielectric constant may differ considerably from the local value in the region of the reaction and a deviation from the $\log k - 1/D$ or $\log k - D-1/2D + 1$ relationship for a dipole-dipole reaction is only to be expected.

The need for considering a possible solvation of the transition state complex is also shown by the trend in E values in Table V with the different tertiary amines and the same alkyl halide in 100 per cent. alcohol. The low P values generally noticed for these reactions is also consistent with this picture that reaction is through the solvated reactant.

An analysis of all the results reveals one distinct feature. Both Arrhenius parameters are high in alcohol and the addition of alcohol or of water tends to increase both these. The difference noticed between acetone and alcohol is not peculiar to the reaction under investigation alone, as may be seen from the values of E for different reactions presented in Table VI.

Frequency factors also show a similar trend towards lower values in acetone. The reaction is, however, faster in acetone than in alcohol, indicating that the dominant factor affecting rate is the activation energy.

TABLE VI

Reaction	E in alcohol	Reference	E in acetone	Reference
Pyridine-methyl iodide ..	17.820	Present work	11.280	Present work
Pyridine-allyl bromide ..	15.100	7	13.490	10 (b)
Dimethyl aniline-benzyl bromide ..	13.200	10 (a)	9.747	10 (a)
Diethyl sulphide-methyl iodide ..	17.240	6	12.150	18

The abnormal features noticed can arise either through the ionisation of the base or the solvolysis of the alkyl halide. Even with isopropyl halides, Hughes¹¹ has shown that ether formation through S_N2 mechanism occurs to only 4 per cent. and in methyl halides may be expected to be less. As for hydrolysis, Moelwyn-Hughes has reported that the rate constant even at 100° C. is only 4.47×10^{-4} ,^{14a}. Formation of pyridinium ion is possible in alcohol as well as in water and the addition of either of these to an organic solvent naturally leads to an increase in the formation of this reactant. This will tend to introduce the repulsion energy between the positive pyridinium ions and the positive pole of the alkyl halide. The net result is thus an increase in the activation energy. On the other hand the lowering of the activation energy in acetone can be traced to the strong attractive forces between the polarised alkyl halide and the carbonyl group of the solvent.

SUMMARY

The reaction between pyridine and methyl iodide has been studied in 95 per cent. ethyl alcohol and in acetone. The reaction is faster in the latter solvent at the three temperatures studied. The Arrhenius parameters have been evaluated and the variations discussed in relation to solvent influences.

REFERENCES

1. Baker, J. W. and Nathan, W. S. .. *J.C.S.*, 1935, 519.
2. Davies, W. C. and Cox, R. G. .. *Ibid.*, 1937, 614.
3. Edwards, G. E. .. *Trans. Farad. Soc.*, 1937, 33, 1294.
4. Fawcett, E. W. and Gibson, R. O. .. *J.C.S.*, 1934, 396.
5. Glasstone, S., Laidler, K. J. and Eyring, H. .. *Theory of Rate Processes* (Mcgraw-Hill), 1941.
6. Gladishev, A. and Syrkin, Y. .. *Chem. Zentr.*, 1938, 2, 841.
7. Hawkins, J. A. .. *J.C.S.*, 1922, 121, 1170.
8. Hinshelwood, C. N. .. *Kinetics of Chemical Change* (O.U.P.), 1943.
9. ——— and co-workers .. (a) *J.C.S.*, 1936, 371, &c; (b) *Ibid.*, 1937, 538, &c; (c) *Ibid.*, 1938, 848, &c.

10. Holt'sshmidt and co-workers .. (a) *Chem. Abstracts*, 1937, **31**, 5662; (b) *Ibid.*, 1942, **36**, 6068.
11. Hughes, E. D. .. *J.C.S.*, 1935, 255; *Trans. Farad. Soc.*, 1941, **37**, 603.
12. Lewis, W. C. Mc. .. *Ibid.*, 1918, **113**, 471.
13. Menshutkin, N. .. *Z. Phys. Chem.*, 1887, **1**, 611; 1890, **5**, 589; 1890, **6**, 41.
14. Moelwyn-Hughes, E. A. .. (a) *Proc. Roy. Soc.*, 1938, **164A**, 295; (b) *Kinetics of Reactions in Solution*. (O.U.P.), 1947.
15. Muchin and co-workers .. *Ukrain Chem. Jour.*, 1926, &c; *Chem. Zentr.*, 1926, **2**, 2376.
16. Norrish, R. G. W. .. *Tran. Farad. Soc.*, 1937, **33**, 1521.
17. Norris, L. F. and Prentiss, S. W. .. *J.A.C.S.*, 1928, **50**, 3042.
18. Syrkin, Y. and Gladishev, A. .. *Chem. Abstracts*, 1935, **29**, 7768.
19. Van't Hoff, J. H. .. *Lectures on Theoretic! and Physical Chemistry*, (Arnold, London), 1898.