290. *The Mechanism of Bimolecular Reactions in Solution. The Addition of Methyl Iodide to Pyridine in Several Solvents.*

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The success of the "collision theory" in explaining the rates of thermal homogeneous gas reactions has made it desirable to discover whether it is also applicable to reactions occurring in solution. Bimolecular reactions in solution appear to fall into two classes. On the one hand there are processes the rates of which are given by the simple formula $z \, . \, e^{E/RT}$, z being the collision frequency, and E the energy of activation; and on the other, there are many reactions the measured rate of which is considerably lower than this calculated value (Grant and Hinshelwood, this vol., p. 258). A comparison of the rates and energies of activation of the same "abnormally slow" reaction when occurring in different solvents suggests that the slowness of the reaction does not arise as a result of solvent deactivation, and there are other experiments which confirm this view (Moelwyn-Hughes and Hinshelwood, J., 1932, 230). It appears that the difference in the rate in different solvents is due to catalytic action on the part of the solvents. Moelwyn-Hughes has summarised the relevant data and theories on the subject (*Chem. Rev.*, 1932, **10**, 241): one generalisation is that reactions between neutral molecules are usually "slow," and those between a neutral molecule and an ion are "normal."

It is clear that further information regarding bimolecular reactions in solution is needed. The present paper summarises measurements on the addition of methyl iodide to pyridine in several solvents. The reaction is bimolecular, and the measured rate is some powers of ten lower than that of the hypothetical gas reaction occurring at the same temperatures with the energy of activation measured for the solvent reaction. Comparison of the rate in any two solvents shows that it is higher the higher the energy of activation.

The velocity of addition of methyl iodide to pyridine in acetylene tetrachloride was measured by Essex and Gelormini (*J. Amer. Chem. Soc.*, 1926, **48**, 882). Over the range 0—40° the Arrhenius energy of activation was 13,200 cals. At 60° the bimolecular velocity constant was $1{\cdot}82 \times 10^{-3}$. Norris and Prentiss (*ibid.*, 1928, **50**, 3042) compared the rate of addition of ethyl iodide to pyridine in different solvents; and Kerr (J., 1929, 239) and also Muchin and Ginsburg (*A.*, 1931, 315, 316) made similar measurements with allyl bromide. Another closely-related reaction, the addition of ethyl iodide to triethylamine, has recently been reinvestigated by Moelwyn-Hughes and Hinshelwood (J., 1932, 230), and also by Grimm, Ruf, and Wolff (*Z. physikal. Chem.*, 1931, *B*, **13**, 301). The rate at which this reaction proceeds in carbon tetrachloride is about 10^8 times smaller than that of the hypothetical gas reaction with the observed energy of activation.

Experimental.

The solvents used were supplied as pure by Messrs. Harrington, and were redistilled from calcium chloride. The methyl iodide was washed with potassium iodide solution, then with water, dried, and redistilled; the final product was quite colourless. The pyridine was distilled twice after drying with calcium chloride, and the final fraction boiled within 0·5°.

Solutions of the reactants were made up separately and introduced in the required proportion into clean test-tubes, which were then sealed off and placed in the thermostat. After suitable intervals, a tube was removed, broken at the tip, and the contents poured into 50 c.c. of cold distilled water, which checked the reaction. The quaternary iodide present was then titrated with $N/100$-silver nitrate with eosin as indicator.

Results.—In the tables, some typical results are set out in detail, and the remainder summarised; a and b are the concentrations (g.-mols./l.) of methyl iodide and pyridine respectively, t the time in minutes, x the concentration of quaternary iodide estimated, and k the bimolecular velocity constant; the temperature is also given. With initial concentrations of approximately the same value, k was determined from the expression $x/a(a - x)t$; with unlike initial concentrations the expression $1/(a - b)t \, . \, \log_e b(a - x)/a(b - x)$ was employed. Corrections were made where necessary for the time of heating of the solutions immediately after immersion in the thermostat.

Chloroform.

At 60°; a = 0·0322; b = 0·3013.

t.	10x.	$k \times 10^4$.	Mean.
57·5	0·282	4·28	4·34
89·5	0·401	4·32	
135·5	0·536	4·33	
182·5	0·648	4·39	
228·5	0·721	4·40	

At 42·6°; a = 0·0796; b = 0·0790.

t.	10x.	$k \times 10^4$.	Mean.
625	0·213	1·28	1·30
840	0·270	1·28	
1149	0·335	1·34	
1438	0·375	1·31	
2107	0·453	1·33	
2647	0·453	1·28	

Temp.	a.	b.	$k \times 10^4$ (mean).	Temp.	a.	b.	$k \times 10^4$ (mean).	Temp.	a.	b.	$k \times 10^4$ (mean).
60°	0·0322	0·3103	4·39	50°	0·1454	0·1502	2·38	42·6°	0·0273	0·0271	1·27
60	0·2418	0·0610	4·31	50	0·0703	0·2243	2·28	42·6	0·0762	0·0796	1·44
60	0·1177	0·1212	4·34	42·6	0·0594	0·0658	1·28	42·6	0·1044	0·1095	1·31
50	0·1406	0·1163	2·23								

These results are collated in the following table, T being the absolute temperature.

Temp.	T.	$10^3/T$.	$k \times 10^4$.	$\log_{10}k$.
60°	333°	3·003	4·34	$\bar{4}$·6375
50	323	3·096	2·30	$\bar{4}$·3617
42·6	315·6	3·169	1·30	$\bar{4}$·1139

By plotting $\log_{10}k$ against $1/T$, a good straight line is obtained, giving the energy of activation E = 14,200 cals. The constants are well represented by $k = 5 \times 10^4\sqrt{T} . e^{-14,200/RT}$.

Anisole.

Temp.	a.	b.	$k \times 10^4$ (mean).	Temp.	a.	b.	$k \times 10^4$ (mean).	Temp.	a.	b.	$k \times 10^4$ (mean).
60°	0·1269	0·1266	8·99	50°	0·1480	0·1478	4·46	42·5°	0·1696	0·1715	2·63
60	0·1558	0·1566	8·78	50	0·1515	0·1578	4·46	42·5	0·1385	0·1275	2·64
60	0·1108	0·1124	8·82	42·5	0·1305	0·1248	2·66				

The plot of $\log_{10}k$ against $1/T$, from the following results, is linear, giving E = 14,300 cals., and the results agree with $k = 1·3 \times 10^5 . \sqrt{T} . e^{-14,300/RT}$.

Temp.	T.	$10^3/T$.	$k \times 10^4$.	$\log_{10}k$.
60°	333°	3·003	8·86	$\bar{4}$·9474
50	323	3·096	4·46	$\bar{4}$·6493
42·5	315·5	3·170	2·64	$\bar{4}$·4216

Nitrobenzene.

Temp.	a.	b.	$k \times 10^3$ (mean).	Temp.	a.	b.	$k \times 10^3$ (mean).	Temp.	a.	b.	$k \times 10^3$ (mean).
60°	0·08	0·1095	4·85	60°	0·0998	0·0889	4·73	50°	0·0795	0·08	2·38

The velocity constants from these data are $k_{50^\circ} = 2·38 \times 10^{-3}$ and $k_{60^\circ} = 4·8 \times 10^{-3}$, giving an energy of activation of 15,000 cals., and the general expression $k = 1·85 \times 10^6 . \sqrt{T} . e^{-15,000/RT}$.

Carbon Tetrachloride.

This, the first solvent employed, is regarded as " normal " in the sense that some reactions proceed in it at the same rate as they would if occurring in the gas phase at the same temperature; and also in the sense that reactions are usually " slow " in this solvent as compared with others.

In the Series I, at 60°, the mean value of k was $2·53 \times 10^{-5}$. In a later series (II) it increased somewhat to $2·62 \times 10^{-5}$, though this was probably an under-estimated mean. In Series III there was a noticeable increase to $3·35 \times 10^{-5}$, and it became clear that some factor, possibly gradual absorption of water vapour by the solvent, was producing a steady increase in the rate Accordingly, a fresh sample of the solvent was carefully dried and a new series carried out The constants were somewhat irregular, but noticeably lower (Series IV), whereas later, Series V, they increased slightly.

Series.	*a.*	*b.*	*t.*	10*x.*	$k \times 10^5$ and mean.	
I	0·1948	0·1935	945	0·399	2·34	2·53
			1015	0·447	2·51	
			1060	0·482	2·67	
			1370	0·551	2·47	
			1440	0·598	2·64	
II	0·1968	0·1969	1240	0·570	2·77	2·62
			1300	0·619	2·89	
			1360	0·603	2·75	
			1670	0·621	2·34	
			2680	0·832	2·34	

Series.	*a.*	*b.*	*t.*	10*x.*	$k \times 10^5$ and mean.	
III	0·2273	0·2694	1300	0·954	3·17	3·35
			1400	1·038	2·84	
			1760	1·218	3·74	
			2705	1·374	3·14	
			3090	1·544	3·97	
IV	0·2285	0·2280	1136	0·525	1·92	2·06
			1500	0·676	2·05	
			2500	0·980	2·20	
			3890	1·069	(1·65)	
V	0·2088	0·2619	2340	1·87	2·50	2·44
			2770	1·226	2·28	
			3760	1·491	2·53	

It is therefore clear that in carbon tetrachloride k_{60° is approximately $2{\cdot}0 \times 10^{-5}$, but may increase in some peculiar manner. In another series at 50°, k_{50° had the value $1{\cdot}0 \times 10^{-5}$. From these values for k, the energy of activation would be 14,800 cals., and the rate is expressed by $k = 6{\cdot}3 \times 10^3\sqrt{T}\,.\,e^{-14,800/RT}$.

DISCUSSION.

The velocity constant of a bimolecular reaction is expressed in terms of the collision theory by

$$k = 5{\cdot}71 \times 10^{25}\sqrt{T}\sqrt{\frac{M_1 + M_2}{M_1 M_2}}\left(\frac{\sigma_1 + \sigma_2}{2}\right)^2 e^{-E/RT}$$

where M_1 and M_2 are the respective molecular weights of the reacting molecules, σ_1 and σ_2 their molecular diameters, and k is expressed in litres per g.-mol. per sec.

Values of the molecular diameters of methyl iodide and pyridine are not available. According to Landolt–Börnstein $\sigma_{C_6H_6} = 4{\cdot}1 \times 10^{-8}$ and $\sigma_{CH_3Cl} = 3{\cdot}4 \times 10^{-8}$. The values assumed are $\sigma_{C_5H_5N} = 4 \times 10^{-8}$ and $\sigma_{CH_3I} = 3{\cdot}5 \times 10^{-8}$ cm.; whence $k_{calc.} = 1{\cdot}124 \times 10^{10}\sqrt{T}\,.\,e^{-E/RT}$.

In chloroform the ratio $k_{calc.}/k_{obs.} = 2{\cdot}2 \times 10^5$, *i.e.*, the reaction proceeds about 10^5 times as slowly as the hypothetical gas reaction with the same energy of activation. In anisole the discrepancy is 9×10^4, and in nitrobenzene 6×10^3. In carbon tetrachloride the measured rate is $1{\cdot}8 \times 10^6$ times smaller than that calculated, but the data here are less trustworthy.

The reaction between pyridine and methyl iodide in different solvents, therefore, provides another instance in which the reaction in solution proceeds much more slowly than the corresponding hypothetical gas reaction with the same energy of activation. The relative velocities in different solvents are in agreement with what is usually found. The following table indicates how the present measurements fall well into line with previous ones (cf. Moelwyn-Hughes, *Chem. Rev.*, *loc. cit.*). It can be seen that the quantity $E + 10^3 \log k_{calc.}/k_{obs.}$ is approximately constant for the series of reactions given.

Reaction.	Solvent.	*E.*	$k_{calc.}/k_{obs.}$	$E + 10^3 \log k_{calc.}/k_{obs.}$
$(C_2H_5)_3N + C_2H_5Br$	C_6H_6	11,190	$1{\cdot}9 \times 10^9$	20,500
$C_6H_5{\cdot}N(CH_3)_2 + CH_3I$	$C_2H_2Cl_4$	11,680	$2{\cdot}1 \times 10^7$	19,000
$(C_2H_5)_3N + C_2H_5Br$	$(CH_3)_2CO$	11,710	$6{\cdot}2 \times 10^7$	19,500
$C_6H_5{\cdot}N(CH_3)_2 + CH_3I$	$C_6H_5{\cdot}NO_2$	13,020	$1{\cdot}9 \times 10^7$	20,300
$C_5H_5N + CH_3I$	$C_2H_2Cl_4$	13,220	5×10^5	18,900
$C_6H_5{\cdot}N(CH_3)_2 + C_2H_5I$	$(CH_3)_2CO$	13,680	$1{\cdot}6 \times 10^7$	21,000
*$C_5H_5N + CH_3I$	$CHCl_3$	14,200	$2{\cdot}2 \times 10^5$	19,500
*$C_5H_5N + CH_3I$	$C_6H_5{\cdot}OCH_3$	14,300	9×10^4	19,300
$C_6H_5{\cdot}N(CH_3)_2 + CH_3I$	$C_6H_5{\cdot}CH_2OH$	14,400	6×10^4	19,200
$(CH_3)_2NH + C_3H_5I$	$C_2H_5{\cdot}OH$	14,740	4×10^4	19,300
*$C_5H_5N + CH_3I$	$C_6H_5{\cdot}NO_2$	15,000	6×10^3	19,000

Once again the result emerges that the disparity between the calculated and the observed rate is least when the energy of activation is highest; so that deactivation by solvent molecules cannot be responsible for the low rate and for the difference in rate in different solvents.

It is not possible to discuss the applicability of any of the various hypotheses which have been suggested to explain the abnormally small reaction rate. It seems hardly likely that the "orientation" factor or the "phase" factor could lead to the discrepancy found. On the other hand, the influence of careful drying of the solvent, found to be so important with carbon tetrachloride, may indicate that ionisation phenomena play a part in the mechanism.

The Reaction between Methyl Iodide and Pyridine in the Gas Phase.—No previous measurements have been made on this process. In the addition of ethyl iodide to triethylamine, an analogous reaction, Moelwyn-Hughes and Hinshelwood (*loc. cit.*) found that the rate in the gas phase is of the same low order of magnitude as in carbon tetrachloride or hexane, *i.e.*, the calculated velocity constant for a gas reaction having the energy of activation of the reaction in solution is 10^8 times higher than that observed.

Weighed amounts of pyridine were sealed in small glass capillaries, and introduced into dry cylindrical glass tubes of known volume (*ca.* 50 c.c.). Methyl iodide vapour was introduced to the required pressure, the tubes sealed off, and the capillaries broken by shaking. The tubes were then immersed in an oil-thermostat maintained at the required temperature, and on removal after suitable intervals the progress of the reaction was estimated as already described, the quaternary iodide formed being washed out with water.

A difficulty arises in that some reaction of the methyl iodide vapour appears to occur with the liquid pyridine at room temperature before the latter becomes vaporised at the temperature of the bath.

Measurements of the temperature coefficient were made, but since the reaction is in itself erratic, they are not significant. The process is almost certainly predominantly a surface reaction. Nevertheless, one important result emerges. The measured bimolecular velocity constant of the reaction at 215° is approximately 0·25 l./g.-mol./sec. (three values were 0·22, 0·28, and 0·24). The velocity constant of the reaction in chloroform at this temperature would be about 0·45. It is therefore clear, despite catalysis by the vessel walls, that the gas reaction has approximately the same rate as the reaction in chloroform, and may be slower than that in nitrobenzene. Thus the "slowness" in the solvents cannot be due to deactivation by the solvent molecules. The relationships are essentially the same as those found by Moelwyn-Hughes in the other reactions mentioned above.

SUMMARY.

The kinetics of the addition of methyl iodide to pyridine in several solvents has been investigated. Some measurements on the reaction in the gas phase were also made. The rate at which the reaction proceeds in the solvents is some powers of ten lower than that of the hypothetical gas reaction having the same energy of activation. The discrepancy is not due to solvent deactivation, for the reaction in the gas phase is also "slow" and of about the same velocity as in the solvents. In the solvents studied, the rate is lowest in carbon tetrachloride and highest in nitrobenzene, the energy of activation being greatest in the latter solvent. Careful drying affects the rate noticeably in carbon tetrachloride; ionisation may be important in the mechanism.

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