292. *The Influence of Solvents on Reaction Velocity. The Interaction of Pyridine and Methyl Iodide and the Benzoylation of* m-*Nitroaniline.*

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Systematic investigation of series of reactions is yielding information about the relative importance of changes in the factors P and E in the expression for the reaction rate, $PZe^{-E/RT}$, in passing from one reaction to another. The influence of polar substituents, sterically hindering groups, catalysts and reaction type has been studied in this way. The object of this paper is to extend existing knowledge in a direction making possible general statements about the influence of change of solvent on these two factors.

EXPERIMENTAL.

Two reactions have been chosen for investigation : first, the combination of pyridine and methyl iodide, the data for which will be comparable with those of Grimm, Ruf, and Wolff (*Z. physikal. Chem.*, **1931**, *B*, **13**, 299) for triethylamine and ethyl iodide; and secondly, the benzoylation of *m*-nitroaniline. Both are bimolecular with rates conveniently measurable in a wide range of solvents at accessible temperatures. The rate of the first was measured by a modification of Menschutkin's method (Winkler and Hinshelwood, J., **1935**, 1147), and the second as described by Grant and Hinshelwood (J., **1933**, 1351). A special device was used for rapid reactions, which were started by breaking a bulb of one reactant in a flask containing the other, preheated to the reaction temperature; and stopped by liberal dilution with a cold inert solvent, usually benzene. Timing was by stop-watch.

The solvents were dried and distilled in all-glass apparatus. Methyl iodide was redistilled, pyridine dried over potassium hydroxide and fractionated, benzoyl chloride vacuum distilled, and *m*-nitroaniline recrystallised from water and dried at 100°. Temperatures were measured with N.P.L. thermometers. For each solvent the reaction rate was measured at five temperatures over a range of about 75°, as is always desirable if reliable results are to be obtained for the activation energies. All velocity constants recorded are corrected for the expansion of the solvent. In general the initial concentrations were $M/10$ for the Menschutkin reaction; and for the benzoylation reaction, benzoyl chloride $M/100$, *m*-nitroaniline $M/50$. Except where explicitly stated, bimolecular constants (l./g.-mol.-sec.) were satisfactory, and the Arrhenius equation was followed exactly, as illustrated by the following examples.

Pyridine and methyl iodide in chlorobenzene at 25·0°.

Mins.	% Change.	$k \times 10^5$.
300	6·32	3·73
1,515	24·8	3·63
1,911	28·8	3·53
3,180	40·0	3·50
4,995	50·6	3·42
11,595	70·3	3·40

Benzoyl chloride and m-*nitroaniline in nitrobenzene at 60·0°.*

Secs.	% Change.	$k \times 10^2$.
120	23·3	6·33
210	35·6	6·58
300	45·0	6·81
420	53·0	6·72
		(uncorr. for expansion)

Pyridine and methyl iodide in anisole at 60·0°.

Mins.	% Change.	$k \times 10^4$.
67	25·3	8·42
103	33·3	8·08
194	49·1	8·29
240	54·7	8·39
1001	83·2	8·25
		(uncorr. for expansion)

Pyridine and methyl iodide in benzonitrile.

Temp.	0·0°		25·0°		39·9°		60·0°		80·0°
$k \times 10^5$	3·59		30·4		91·8		340		1120
E		13,800		13,700		13,500		13,900	

In this table the values of E are calculated from each successive interval of temperature, which exaggerates the errors. In practice E was found graphically from the best plot of log k and $1/T$.

Where comparisons of individual velocity constants with previous work have been possible, the agreement is usually satisfactory (Winkler and Hinshelwood, *loc. cit.*; Thompson and Blandon, J., **1933**, 1237; Newling, Staveley, and Hinshelwood, *Trans. Faraday Soc.*, **1934**, **30**, 597).

Departures from normal behaviour were observed in some solvents. In hexane and in *cyclo*hexane the pyridine–methyl iodide reaction showed so marked an autocatalysis as the solid reaction product was formed, that reliable constants could not be obtained; *e.g.*, at 100° in *cyclo*hexane the following numbers were found :

Minutes	185	252	1074	1272	1410
% Change	3·7	7·4	61·2	69·0	72·5

With so pronounced an acceleration any extrapolation would be doubtful. In *iso*propyl ether the same effect was observed, but in a much smaller degree, and constants could be obtained by extrapolation to zero time. With the benzoylation reaction in carbon tetrachloride there are departures from the bimolecular law at higher temperatures. For example, at 80°, starting with $M/100$-amine and $M/200$-acid chloride, the constant fell from an initial value of $1{\cdot}07 \times 10^{-3}$ to $0{\cdot}79 \times 10^{-3}$ at 50% change. When the initial concentrations were halved, the constant rose from an initial value of $0{\cdot}50 \times 10^{-3}$ to $0{\cdot}66 \times 10^{-3}$ over the same range. These effects can be explained by assuming that the reaction between the acid chloride and the amine requires the presence of a polar molecule. In an active solvent the polar molecules are those of the solvent itself, but in an inert medium like carbon tetrachloride the rôle must be taken over either by molecules of one of the reactants (which virtually increases the order of the reaction from two to three and accounts for the fall of the bimolecular constants on dilution), or by the polar solid product which acts as a heterogeneous autocatalyst. The latter effect accounts for an increase of the constant as the reaction proceeds. At the higher initial concentration the removal of reactants as time goes on has an effect outweighing the autocatalysis, but at the lower initial concentration the latter is relatively the greater. Analogous observations were made by Grant and Hinshelwood for the benzoylation of aniline.

The pyridine–methyl iodide reaction gave erratic constants at the higher temperatures, and iodine was liberated. Consequently, the activation energy had to be determined from measurements at three temperatures only, and is less accurate. The benzoylation reaction in carbon tetrachloride and in *iso*propyl ether follows the Arrhenius equation at higher temperatures, but in the lower range gives constants greater than those required by the equation, as though some different reaction mechanism were coming into relative prominence. The activation energy was therefore calculated from the measurements at the higher temperatures only (60—100° for carbon tetrachloride; 25—80° for *iso*propyl ether). This and all other values for cases which were in any way anomalous are marked with an asterisk in the table.

TABLE I.

Reaction between pyridine and methyl iodide.

Solvent.	$\log_{10} (k_{100^\circ} \times 10^5)$.	E.	Dipole moment of solvent.
*iso*Propyl ether	1·195	13,800	1·0
Carbon tetrachloride	1·65	18,700 *	0
Mesitylene	1·94	14,900	0
Toluene	2·07	14,500	0·4
Benzene	2·15	14,100	0
Chloroform	2·525	13,200	1·18
Chlorobenzene	2·60	13,900	1·56
Dioxan	2·61	13,600	0·45
Bromobenzene	2·70	13 700	1·53
Anisole	2·83	13,200	1·23
Iodobenzene	3·06	13,800	1·25
Benzonitrile	3·50	13,700	3·93
Nitrobenzene	3·57	13,700	4·24

TABLE II.

Benzoylation of m-*nitroaniline.*

Solvent.	$\log_{10} (k_{100^\circ} \times 10^4)$.	E.	Solvent.	$\log_{10} (k_{100^\circ} \times 10^4)$.	E.
Carbon tetrachloride	1·530	13,600 *	Bromobenzene	2·259	10,600
*iso*Propyl ether	2·060	10,900 *	Toluene	2·297	9,700
Benzene	2·162	10,300	Nitrobenzene	3·492	9,400
Chlorobenzene	2·230	11,350	Benzonitrile	4·540	10,100

DISCUSSION.

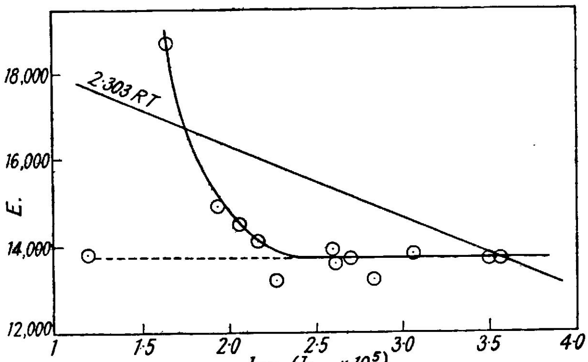
In Figs. 1 and 2 the activation energy is plotted against log k. If changes in E from one solvent to another were solely responsible for the changes in rate, the points would lie on a line of slope $- 2{\cdot}303RT$: if changes in P were alone concerned the line would be horizontal. It is evident that changes in P play an important part. This fact stands in contrast to what is found when the rate is modified by the introduction of polar substituents which cause changes principally in the activation energy. With the pyridine–methyl iodide reaction the value of E remains almost constant for the more active solvents, P alone varying. What happens in the inert solvents does not appear unambiguously; E rises steeply for carbon tetrachloride, and the rise appears already to be slightly in evidence with toluene and mesitylene, but is completely absent with *iso*propyl ether. If the results of Grimm, Ruf, and Wolff for the reaction between triethylamine and ethyl iodide are plotted in the same way, the points relating to the active solvents vary rather less regularly, but here also, E remains fairly constant. For the inert solvents hexane and *cyclo*hexane, a pronounced rise in E appears, corresponding to what we find with carbon tetrachloride.

In the benzoylation reaction the changes in P are again in evidence, but are accompanied by rather greater variations in E. In the most inert solvents E shows the same steep increase found in the other two examples.

Taking the results as a whole, we may draw the following conclusions : (1) In quaternary ammonium salt formation and in benzoylation, change of solvent produces important changes in the factor P. In certain cases these may account for almost the whole difference in reaction velocity, as, for example, with the pyridine-methyl iodide reaction in a series of benzene derivatives as solvents. In general, however, E varies at the same time.

Fig. 1.

Reaction between pyridine and methyl iodide.



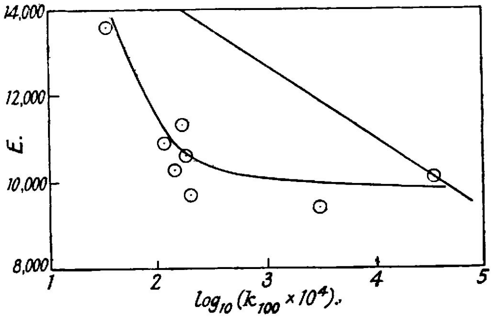
From left to right the points on the diagram are in the order of the corresponding values in Table I.

(2) Where P alone changes, it increases in a rough parallelism with the dipole moment of the solvent, though no exact relation exists (or is to be expected).

(3) Although there is no reason why plotting E against log k for a series of solvents should give a definite curve, Figs. 1 and 2 show that there is a tendency for most of the points to group themselves about such a curve. The interesting possibility presents itself that the general trend may be as represented in Fig. 1, E remaining nearly constant for the active solvents and rising sharply for the least active. This suggestion must be made with a certain reserve, since investigation of the inert solvents is rendered difficult by disturbing factors such as the catalytic action of the solid products, or even of the reactants themselves, as described above. Individual results for this range of the curve might therefore be challenged, yet taken together they give a strong indication that a curve of the form shown may possess general significance.

Fig. 2.

Reaction between benzoyl chloride and m-*nitroaniline.*



From left to right the points on the diagram are in the order of the corresponding values in Table II.

Theories of the manner in which solvents affect the velocity of reactions must account for these rough generalisations. The changes in the activation energy are to be expected. Polar substituents in the reactants exert a profound influence on it (for benzoylation reaction see Williams and Hinshelwood, J., 1934, 1079), and therefore, even apart from any question of solvation, the external field of the solvent molecules can very well exert a similar though probably smaller effect.*

The variations in P are less simple, and no specific theory of them is here advanced. The following observations, however, may contribute to their elucidation. (1) It must first be remembered that the value of Z, the collision number, is derived from a formula for gaseous systems the extension of which to solutes depends partly upon approximations and partly upon empirical verification for special solvents. In the present examples it may

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* If the reaction rate is thought to depend upon solvent–solute collisions, the question of applying Jowett's correction to E arises. This has not been done in the table, but if it is, then the conclusions stated above are in no way altered, and the general trend of the results is much the same as before (see Moelwyn-Hughes, " Kinetics of Reactions in Solution," p. 18).

be only roughly true; and although any errors introduced by its use would certainly not explain away values of P as small as 10^{-6} to 10^{-8}, in which region most of the present values lie, these errors might distort the ratio of the values for widely different solvents. We do not consider it at all likely that the general relations discussed above could be explained as changes in Z rather than changes in P. An improved theory of collisions in solution which could explain away on this basis the observed apparent changes in P would certainly have great claims to consideration. In the meantime, however, we shall assume that the variations observed are actually those in P itself.

(2) There is a suggestive similarity between the increase in P with the polarity of the solvent, and that which occurs when we pass in catalytic reactions from an uncharged to a charged catalyst. It may be connected with a favourable influence of the solvent on the orientation of the reacting molecules, increasing with the polarity of the solvent (J., 1935, 1112).

(3) It is conceivable that in some cases one function of the solvent is to remove energy from the intermediate activated complex and so prevent the latter from reverting into the reactants. In such a case P would be a direct measure of the efficiency with which the solvent molecules fulfilled this function, and, where the product is a polar salt, might be expected to increase in a rough parallelism with the polarity of the solvent (cf. *Trans. Faraday Soc.*, 1936, **32**, 970). Further investigations with different types of reaction are, however, necessary before this question can profitably be discussed further.

Whatever be the nature of the variations in P, to account for the shape of the curve drawn in Fig. 1 no very specialised hypotheses would be necessary. We know that foreign molecules can reduce the activation energy, presumably by a direct modification of the potential-energy curves of the reacting molecules. This is, in fact, one of the primary factors in all catalytic action. It is only necessary to assume a saturation limit to the reduction which can be brought about in this way to account for the observed trend of E, and if the more active solvents are still capable of affecting P after E has been reduced to the limit, then the form of the curve would be explained.

SUMMARY.

Two reactions, the combination of pyridine and methyl iodide and the benzoylation of *m*-nitroaniline, have been studied in a wide variety of solvents, and certain general conclusions about the influence of the solvents upon the factors P and E of the equation, reaction rate $= PZe^{-E/RT}$, have been drawn.

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