330. *The Factors determining the Velocity of Reactions in Solution. The Formation of Quaternary Ammonium Salts.*

By Keith J. Laidler.

The parameters of the Arrhenius equation have been determined for the reactions between substituted dimethylanilines and pyridines and methyl iodide in nitrobenzene solution. In each of the two series of reactions PZ is found to be approximately constant, changes in velocity being due to changes in E. The order of activation energies is shown to be that which would be predicted from a consideration of the electronic effects of the substituent groups, on the assumption that a low energy is associated with a high density of electrons on the nitrogen atom. α-Picoline is an exception to this, since E is abnormally high owing to steric hindrance, which, however, is not reflected in a low value of PZ. The reverse reactions, the decompositions of the quaternary salts, are also briefly discussed.

As pointed out by Hinshelwood, Laidler, and Timm (this vol., p. 848), reaction series in which substituents are separated from the reacting centre by a benzene ring fall into one of two classes, according to whether P remains constant or increases functionally with E. The factors which determine into which class a reaction falls are not known, largely owing to insufficiency of experimental data; and the present paper contributes additional examples. An investigation has been made of the effect of changing the base by introducing substituents into dimethylaniline and pyridine in their reactions with methyl iodide in nitrobenzene solution. In order that geometrical effects should not intervene, *p*-substituted compounds were used in the dimethylaniline series, and a β-substituted pyridine compound was used. In addition, however, in order to find out something more about the nature of "steric hindrance," measurements were made with α-picoline.

EXPERIMENTAL.

Nitrobenzene and methyl iodide were purified by distillation, the latter in an all-glass apparatus. Dimethyl-*p*-anisidine and -*p*-toluidine, and *p*-chloro- and *p*-bromo-dimethylanilines were made by first preparing the *p*-substituted anilines by the usual methods, and methylating these by refluxing them with methyl iodide under the correct conditions of alkalinity. *m*-Nitrodimethylaniline was prepared by heating *m*-nitroaniline with methyl sulphate in a sealed tube at 150°. The above amines were purified by heating them with acetic anhydride, extraction with ether in order to remove any monomethyl compound, and finally either by repeated crystallisation from aqueous alcohol or by fractionation in an all-glass apparatus. Unsubstituted dimethylaniline was purified in the same manner. Nicotinic ester was prepared by esterification of the acid by ethyl alcohol, and it and α-picoline were purified by fractionation. The m. p.'s or b. p.'s of all of these compounds were carefully determined, and found to agree with the values recorded in the literature.

The general procedure was similar to that described by Laidler and Hinshelwood (this vol., p. 858), with, however, certain differences. The reacting solutions were made up to be exactly N/10 before mixing, 2 c.c. of each being mixed in the tubes. Owing to the weakness of some of the bases used, they could not be titrated by acids, and the method of analysis was always to wash out the tubes into excess of N/100-silver nitrate solution, filter off the precipitated silver chloride, and estimate the silver nitrate remaining by Volhard's method, using an N/100-solution of ammonium thiocyanate with ferric alum as indicator. The faster reactions had to be stopped by washing out the tubes into dilute acid.

In only a few cases were the constants obtained from the simple bimolecular formula satisfactory, for a fall was usually found as the reaction proceeded, indicating that the reaction went to an equilibrium. End-point determinations were therefore made for all of the reactions at four temperatures, with a view to finding the equilibrium constants; in each case the temperatures were 60°, 80°, 100°, and 120°, since precipitation of the products occurred at the lower temperatures. With α-picoline the determinations showed that the reaction went practically to completion, and the simple bimolecular formula gave satisfactory constants; this was also the case for several of the other reactions at the lower temperatures.

In order to discover whether the reverse reactions are kinetically of the first or second order in nitrobenzene, equilibrium determinations were made in some cases with the solutions of the reactants diluted six times. It was found that a pronounced change of the simple equilibrium constant $k = [\text{amine}][\text{iodide}]/[\text{salt}]$ took place on dilution, indicating that a second-order back reaction also plays a part, as may be expected if the salt is appreciably ionised. Strictly, this would invalidate the use of the equilibrium formula employed in the previous paper, but on trial it was found that this formula sometimes gave satisfactory constants, and at other times values which showed a much smaller drift than the constants from the ordinary bimolecular formula. The method adopted for obtaining the true value of the forward velocity constant was therefore as follows. If the equilibrium determinations showed that the reaction went almost or entirely to completion, the constant obtained from the ordinary bimolecular formula was accepted; if not, the equilibrium formula was also applied, and if a constant was obtained this was accepted, and confirmed by extrapolating the simple bimolecular constants to zero reaction. If both formulæ gave drifting constants, however, the final value was obtained by extrapolating both sets to zero reaction. In every case good agreement was obtained, showing that the empirical procedure had correctly allowed for the influence of the back reaction on the velocity constant of the forward reaction which was being studied. These methods are illustrated in the examples given in Table I, in which t is the time in minutes, and x the change %; the initial concentration was always 0·05N.

m-Nitrodimethylaniline did not react at all over a wide range of temperatures, owing presumably to an unfavourable equilibrium. An attempt was also made to study the decomposition of the salt formed with methyl iodide, but it was found that the rate could not be followed, since the salt was only very sparingly soluble in nitrobenzene, and decomposed as fast as it dissolved.

The velocity constants obtained at the various temperatures, corrected for solvent expansion, are given in Table II; in each case the Arrhenius law is satisfactorily obeyed. The final values of E, $\log_{10}(k_{100} \times 10^6)$, and $\log_{10}PZ$ are also given in Table II; E is always calculated from the slope of the line obtained by plotting log k against $1/T$, and by the method of least squares, agreement being found in each case. The values obtained for pyridine in the previous paper are included.

TABLE I.

Velocity constants for reaction with methyl iodide.

(k' is the value obtained from the ordinary bimolecular formula, k that obtained by the use of the equilibrium formula. The constants are uncorrected for solvent expansion.)

Dimethyl-p-*anisidine* : T = 40·1°.

t.	x.	$k' \times 10^3$.
61	24·5	1·773
105	36·6	1·829
105·5	36·25	1·798
151	45·0	1·804
187	50·2	1·796
244	57·65	1·871
324	63·05	1·752

Nicotinic ester : T = 40·0°.

t.	x.	$k' \times 10^4$.
466	18·25	1·593
680	25·2	1·650
1488	42·8	1·678
2520	53·95	1·550
4098	67·1	1·660
4366	66·7	1·530

a-Picoline : T = 40·0°.

t.	x.	$k' \times 10^4$.
132	15·0	4·44
224	23·05	4·44
365	33·05	4·51
627	44·9	4·33
651	46·55	4·46
1142	60·9	4·53

p-*Chlorodimethylaniline* : T = 60·0°.
K = 0·1838.

t.	x.	$k' \times 10^4$.	$k \times 10^4$.
110·5	7·05	2·265	2·740
154·0	9·1	2·160	2·840
199·5	11·0	2·070	2·865
276·0	13·25	1·834	3·040
296·5	14·0	1·832	3·120
391·5	15·75	1·591	3·275

Both k and k' extrapolate to $2·49 \times 10^{-4}$.

Dimethyl-p-*toluidine* : T = 80·1°.
$K = 1·444 \times 10^{-2}$.

t.	x.	$k' \times 10^3$.	$k \times 10^3$.
10·2	17·5	7·22	7·22
16·5	25·2	6·82	7·66
26·5	34·3	6·57	7·14
36·0	40·2	6·30	7·22
55·0	47·05	5·38	7·03
78·0	52·3	4·68	7·06
100·0	55·6	4·17	7·47
		Mean	7·26

$k' \times 10^3$ (extrapolated) = 7·52.

TABLE II.

$k \times 10^5$, corr. for solvent expansion.

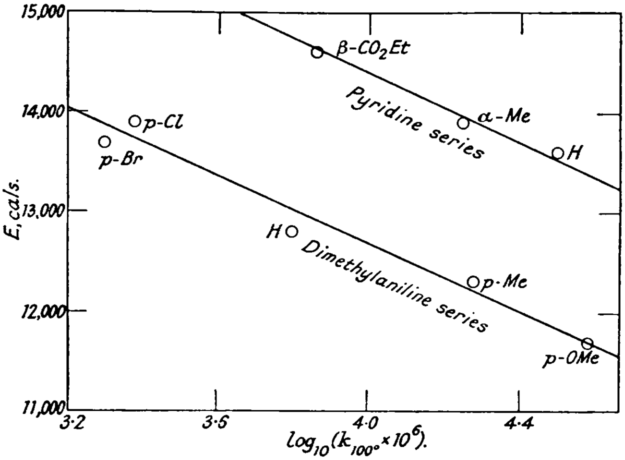
	Temp.						log	log
Amine.	15·0°.	24·8°.	40·1°.	60·0°.	80·1°.	E.	$(k \times 10^6)$.	PZ.
Dimethyl-*p*-anisidine	34·65	71·92	182·8	560·0	—	11,700	4·58	5·45
Dimethyl-*p*-toluidine	—	28·44	79·58	252·8	758·5	12,300	4·28	5·52
Dimethylaniline	—	8·39	20·98	77·20	238·3	12,800	3·80	5·34
p-Chlorodimethylaniline	0·9265	2·110	5·970	25·61	—	13,900	3·38	5·59
p-Bromodimethylaniline	0·8240	1·800	5·545	21·30	—	13,700	3·30	5·35
Pyridine	—	—	—	—	—	13,600	4·50	6·50
	15·8°.	24·9°.	40·0°.	60·0°.	80·0°.			
a-Picoline	7·05	14·65	45·1	177·3	—	13,900	4·25	6·42
Nicotinic ester	—	4·857	16·30	62·30	234·0	14,600	3·86	6·44

DISCUSSION.

It is to be seen from Table II and the accompanying figure that for each of the two series of reactions the changes in velocity are almost entirely due to the changes in the energy of activation, P being approximately constant; in the figure the lines are of the slope $- 2·303\boldsymbol{R}T$, corresponding to constant P. In giving a probability factor which is constant, this class of reaction therefore resembles the alkaline hydrolysis of esters, the benzoylation of amines, and a number of other reactions.

The order of activation energies found in the two series is practically the same as that found by other workers for other types of reactions (*e.g.*, the acid and alkaline hydrolysis of esters, the benzoylation of amines, and the hydrolysis of acyl and triarylmethyl chlorides), and is the order which would be predicted from a knowledge of the electronic effects of the groups based upon physical measurements such as the dipole-moment measurements of Sutton (*Proc. Roy. Soc.*, 1931, **133**, *A*, 668), on the assumption that a lower energy of activation is associated with a higher density of electrons on the nitrogen atom of the base; thus halogen atoms, by withdrawing electrons from the nitrogen atom, raise the energy. In these particular series of reactions it is likely that the order of dipole moments would be found to be identical with the order of energies, although this is neither expected nor found when the molecules are not of about the same size and shape.

The case of α-picoline is an exception to these simple generalisations, since in spite of the positive inductive effect of the methyl group the activation energy is higher than it is with pyridine. This effect must be due to the so-called steric hindrance, which is now known in certain cases to be mainly energetic rather that geometrical in character (Hinshelwood and Legard, J., 1935, 587). It is interesting to observe that here there is no decrease of *P* associated with the hindrance, as was also found by Hinshelwood and Legard, although with some reactions, *e.g.*, the acid and the alkaline hydrolysis of benzoic esters (Timm and Hinshelwood, this vol., p. 862; Evans, Gordon, and Watson, J., 1937, 1430), a fall is brought about by the introduction of ortho-substituents. A high *E* associated with steric hindrance appears, however, to be usual.



It was originally intended to make a complete study of the kinetics of the forward and back reactions by making use of the equilibrium data; but this could not be done owing to the change of equilibrium constant on dilution. Since the forward reactions are truly bimolecular, as is shown in those cases in which the reactions went to completion (Table I), this change must be due to the composite nature of the back reactions (due to the ionisation of the quaternary salts in the solvent), which cannot therefore be easily studied. Certain quantitative remarks can, however, be made in connection with the dimethylaniline series. The temperature coefficients of the equilibrium constants vary widely from reaction to reaction, and in such a manner as to indicate that the activation energies of the decomposition reactions *decrease* in the direction: dimethyl-*p*-anisidine to *p*-halogenodimethylaniline. It is thus clear that the influence of substituents on the velocity of decomposition of quaternary ammonium salts is the opposite to what it is on the velocity of their formation.

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