

167. *The Activation Energy of Organic Reactions. Part II. The Formation of Quaternary Ammonium Salts.*

By K. J. LAIDLER and C. N. HINSHELWOOD.

The activation energies have been determined for the reactions of each of two amines with two alkyl iodides. The results are closely parallel for two solvents of different polarity, benzene and nitrobenzene. They are explained in terms of the theory discussed in Part I, changes in the importance of the repulsive energy term being postulated. The variations of $\log PZ$, and the solvent influence on the parameters of the Arrhenius equation are also considered.

In the usual Arrhenius equation ($k = PZe^{-E/RT}$), the factor P varies over a very wide range, but it has now been shown that for reactions belonging to one series its variation is not considerable when compared with that of E , and when it occurs it can often be explained as due either to a functional relation with E (Fairclough and Hinshelwood, J., 1937, 538), or, in those cases in which the changes of structure are not very small, to ordinary geometrical effects. The variation of P and E in quaternary salt formation has already been studied by Winkler and Hinshelwood (J., 1935, 1147). The object of the present investigation was to determine, in greater detail than was done in that paper, the change

in E with changes in the amine and the halide, and to see how far these can be explained by correlating the modern analysis of activation energy with the theory of electron displacements in organic compounds (see preceding paper).

For this purpose it was decided to study the reactions of two amines of quite different strengths, *viz.*, triethylamine and pyridine, with two iodides in which the carbon-iodine bond strengths differed considerably, *viz.*, methyl and isopropyl iodides. In addition, since it was expected that the influence of any electrostatic forces concerned would vary with the solvent, the four reactions were measured in two solvents of widely differing polarity, *viz.*, benzene and nitrobenzene.

Nitrobenzene was purified by distillation, and, in order that no errors should arise from the use of specimens of different purity, was prepared in large quantities at a time; when different specimens were used, these were tested against one another by measuring a given reaction rate in them at two temperatures. "AnalaR" Benzene was used. The reacting substances were fractionated to correct and constant b. p. in an all-glass apparatus; pyridine was dried for some time over potassium hydroxide.

All activation energies were determined from measurements of velocity constants at four temperatures. From 15° to 80° electrically controlled thermostats, constant to less than 0.1°, were used, from 100° to 150° specially constructed boiling-liquid thermostats, and for 5° a Dewar vessel containing melting benzene. Thermometers were compared with N.P.L. standards. With the exception to be mentioned below, the experimental method was to seal up 2 c.c. of each of the reactants, $N/5$ before mixing, in small glass tubes, immerse them in the thermostats for known times, correcting when necessary for the time required for heating up, and then to analyse the mixtures by washing them into excess of $N/50$ -acid and back-titrating with baryta. The indicators used were methyl-red for triethylamine, and for pyridine a mixture of equal volumes of aqueous 0.1% methyl-orange and 0.02% methylene-blue (Fawcett and Gibson, J., 1934, 396). Glassware was standardised, and all velocity constants were corrected for change of concentration due to expansion of solvent.

Results.—Except with one reaction which showed autocatalysis, and with one which went to an equilibrium, satisfactory constants were obtained by applying the ordinary bimolecular formula. Velocity determinations were also made with the reactants diluted five times; within the limits of experimental error no change in constant was found, except in the reaction between triethylamine and isopropyl iodide in nitrobenzene, where an increase with dilution was observed. In all cases end-point determinations were made.

The following reactions presented special features.

Triethylamine and isopropyl iodide in benzene. Here, pronounced autocatalysis was observed, the bimolecular constant rising considerably as the reaction proceeded, this rise being greater at higher temperatures. This is explained by the fact that the reaction only proceeds conveniently in a temperature range in which the salt produced remains partly dissolved in the benzene, making the solvent more polar. The true constant was obtained by plotting that given by the ordinary formula against the corresponding percentage, and extrapolating to zero percentage.

Triethylamine and methyl iodide in nitrobenzene. Owing to the high velocity of this reaction, it was necessary to work at a higher dilution, $N/25$ -solutions of each of the reactants being mixed. At 5° this was done with pipettes, at 15° and 25° by breaking a bulb containing one of the reactants inside a tube containing the other, the whole having been immersed in the thermostat for some time, and at 40°, where this method could not be used owing to the high volatility of the methyl iodide, a special mixer was used. The essential feature of this was that the methyl iodide was prevented from escaping by means of a stopper which could be removed when the reaction was to be started. The ordinary method of stopping the reaction was here too slow, the acid being immiscible with nitrobenzene; the method used was to pour in a solution of hydrochloric acid in aqueous acetone, with 50 c.c. of which the nitrobenzene solutions were completely miscible.

Pyridine and isopropyl iodide in nitrobenzene. This reaction proceeds to an equilibrium. The equilibrium constants at the four temperatures of the reaction were determined, and from them the velocity constants of the forward reaction were calculated from the integrated form of the expression $dx/dt = k_1(a-x)^2 - k_2x$, which is $k_1 = \frac{1}{2at} \log_e \left[\frac{x - (\beta + \alpha)}{x - (\beta - \alpha)} \cdot \frac{(\beta - \alpha)}{(\beta + \alpha)} \right]$ where $\alpha = \sqrt{aK + K^2}/4$, $\beta = a + K/2$, and $K = k_2/k_1$. The values so obtained were com-

pared with those obtained by the extrapolation to zero reaction of the ordinary bimolecular constants, satisfactory agreement being found (see Table II).

Triethylamine and isopropyl iodide in nitrobenzene. With this reaction a pronounced increase in velocity constant was found on dilution, the effect being repeated at several temperatures (Table III). We ascribe it to the high sensitivity of the reactions to the solvent, which may in this case be made more polar by the dissolution of the quaternary salt formed. The bimolecular constants obtained were satisfactory; E was measured for a constant dilution.

All of the other cases were straightforward. The numbers in Table I illustrate the type of constant obtained; α is the percentage change, a the initial concentration of amine and iodide,

TABLE I.

NEt ₃ and MeI in Ph·NO ₂ at 39·3°; $a = 0\cdot02$.			NEt ₃ and Pr ^{β} I in Ph·NO ₂ at 60·1°; $a = 0\cdot1$.			C ₅ H ₅ N and MeI in C ₆ H ₆ at 99·3°; $a = 0\cdot1$.		
t (secs.).	α .	$k \times 10^2$.	t (mins.).	α .	$k \times 10^5$.	t (mins.).	α .	$k \times 10^3$.
325	31·4	7·06	1,580	15·7	1·97	58	26·75	1·050
1124	60·1	6·75	4,490	33·8	1·91	80	32·75	1·005
1295	64·9	7·14	7,508	45·35	1·85	88	35·3	1·035
1530	68·8	7·20	10,036	52·9	1·88	231	58·5	1·020
1975	73·7	7·19	14,298	61·7	1·89	244	59·75	1·014
2405	76·3	6·72	17,637	66·5	1·88	315	65·68	1·013
						340	67·7	1·028

TABLE II.

Details of the reaction between pyridine and isopropyl iodide in nitrobenzene ($a = 0\cdot1$).

[k' is the value obtained from the ordinary bimolecular formula, k that obtained by the use of the equilibrium formula given in the text.]

At 60·0°.				At 121·0°.			
t (mins.).	α .	$k' \times 10^5$.	$k \times 10^5$.	t (mins.).	α .	$k' \times 10^3$.	$k \times 10^3$.
2,202	24·3	2·430	2·655	50	26·0	1·168	1·216
3,700	34·45	2·425	2·650	62	30·0	1·152	1·208
5,518	43·5	2·320	2·680	101	40·6	1·129	1·213
8,760	53·55	2·197	2·580	175	52·3	1·043	1·210
12,780	61·2	2·055	2·432	215·5	56·8	1·018	1·242
15,450	65·2	1·960	2·415	304	63·0	0·978	1·300
Average value of $k = 2\cdot57 \times 10^{-5}$.				Average value of $k = 1\cdot231 \times 10^{-3}$.			
Extrapolated value of $k' = 2\cdot59 \times 10^{-5}$.				Extrapolated value of $k' = 1\cdot225 \times 10^{-3}$.			

TABLE III.

The effect of dilution on the constants—typical results.

Solvent.	Reaction.	Temp.	Constant* at $a =$		
			0·1.	0·04.	0·02.
C ₆ H ₆	NEt ₃ + MeI	39·75°	$31\cdot11 \times 10^{-4}$	—	$30\cdot54 \times 10^{-4}$
C ₆ H ₆	C ₅ H ₅ N + MeI	99·3	$102\cdot4 \times 10^{-5}$	—	$102\cdot5 \times 10^{-5}$
Ph·NO ₂	NEt ₃ + Pr ^{β} I	79·9	$7\cdot83 \times 10^{-5}$	$9\cdot47 \times 10^{-5}$	—
		100·2	$26\cdot34 \times 10^{-5}$	$30\cdot8 \times 10^{-5}$	—
		121·1	$78\cdot0 \times 10^{-5}$	$90\cdot0 \times 10^{-5}$	$110\cdot4 \times 10^{-5}$

* The constants are uncorrected for solvent expansion.

TABLE IV.

NEt ₃ and MeI.		NEt ₃ and Pr ^{β} I.		C ₅ H ₅ N and MeI.		C ₅ H ₅ N and Pr ^{β} I.	
Temp.	$k \times 10^4$.	Temp.	$k \times 10^6$.	Temp.	$k \times 10^5$.	Temp.	$k \times 10^6$.
<i>In benzene.</i>							
4·8°	4·40	99·6°	1·777	39·8°	3·893	99·7°	10·37
15·0	8·05	120·4	6·370	60·0	14·60	121·0	39·00
24·9	14·20	137·5	15·27	80·1	52·40	138·0	109·2
39·75	31·65	152·4	27·28	99·3	112·4	149·8	196·2
<i>In nitrobenzene.</i>							
4·1	93·5	60·1	19·50	24·8	31·76	60·0	26·45
15·0	181·0	79·9	82·05	39·9	98·20	80·1	112·8
24·8	309·5	100·2	280·5	60·0	349·0	100·2	428·0
39·9	708·5	121·1	845·5	80·3	1182·0	112·0	1333·0

TABLE V.

Solvent : Benzene.					Solvent : Nitrobenzene.				
Amine.	Iodide.	$\log (k_{100^\circ} \times 10^6)$.	E .	$\log PZ$.	Amine.	Iodide.	$\log (k_{100^\circ} \times 10^6)$.	E .	$\log PZ$.
NET ₃	MeI	4.59	9,700	4.29	NET ₃	MeI	5.94	9,700	5.65
"	Pr ^{β} I	0.248	17,100	4.29	"	Pr ^{β} I	2.44	16,000	5.86
C ₅ H ₅ N	MeI	3.17	14,300	5.59	C ₅ H ₅ N	MeI	4.50	13,600	6.50
"	Pr ^{β} I	1.03	18,000	5.62	"	Pr ^{β} I	2.62	16,700	6.43

TABLE VI.

Activation energy differences.

	C ₅ H ₅ N-NEt ₃ .		Pr ^{β} I-MeI.			C ₆ H ₆ -Ph·NO ₂ .	
	MeI.	Pr ^{β} I.	NEt ₃ .	C ₅ H ₅ N.		MeI.	Pr ^{β} I.
C ₆ H ₆	4600	900	7400	3700	NET ₃	0	1100
Ph·NO ₂	3900	700	6300	3100	C ₅ H ₅ N	700	1300

and k the bimolecular constant in (l. g.-mol.⁻¹ secs.⁻¹), uncorrected for solvent expansion. Table IV gives the velocity constants obtained at the various temperatures, corrected for solvent expansion; in each case the Arrhenius equation is satisfactorily obeyed. The final values of \bar{E} , $\log_{10} PZ$, and $\log_{10} (k_{100^\circ} \times 10^6)$ are given in Table V; E is always calculated both from the slope of the line obtained by plotting $\log_{10} k$ against $1/T$, and by the method of least squares, agreement being found in each case.

DISCUSSION OF RESULTS.

It is seen from the figures in Table V that the most important factor determining the changes in velocity is the energy of activation; for instance, whereas $\log_{10} k_{100^\circ}$ varies by about 5.7, the maximum variation of $\log PZ$ is only about 2.2. For small changes in velocity, however, a change in PZ may be of importance; e.g., with *isopropyl iodide*, on changing the base, the change of PZ is seen, in both solvents, to outweigh the change of E .

The changes in the energy of activation will be considered first. It is seen from Table VI, which shows the differences between the activation energies for the various changes, that (1) the changes in E on changing the base and on changing the iodide are of the same order in the two solvents; (2) a rise in E is found on passing from triethylamine to pyridine and also (3) on passing from methyl iodide to *isopropyl iodide*; (4) the change of base causes a smaller change in the energy of activation in the reactions with *isopropyl iodide* than in those with methyl iodide; and similarly, (5) the change in E on varying the iodide is less in the reactions with pyridine than in those with triethylamine.

Points (2)—(5) are shown in both solvents, the results illustrating (2) and (3) four times, and (4) and (5) twice each.

(6) With regard to change of solvent, on passing from benzene to nitrobenzene, E falls, except in the case of the triethylamine-methyl iodide reaction, where it remains constant. Moreover, the changes in E on changing one of the reactants are somewhat smaller in nitrobenzene than they are in benzene.

In view of the widely differing polarities of the solvents, (1) is of some significance, since it shows that the results are not seriously distorted by slight deviations from the Arrhenius equation due to the variation of the dielectric constant with the temperature. In addition, since the products of the reactions were in all cases soluble in nitrobenzene but very sparingly soluble in benzene, we may conclude that rate of crystallisation does not affect the observed rate of the change.

Facts (2)—(5) can be explained in terms of the theory explained in the preceding paper. Phenomena (2) and (3) are due to the decreases in e_A and e_B respectively. The former is due to the inductive effect of the methyl groups added to the central carbon atom. The lower e_A for pyridine is connected with its weaker basicity. Facts (4) and (5) are due to a displacement of the relative importance of bond energy and repulsive energy in E , an increase in the importance of bond energy being associated with an increase of E itself.

The influence of the solvent is more difficult to interpret. An increased dielectric constant will diminish repulsion energies, and make changes in them less important; and it will also have some effect in decreasing the bond strength. A more important effect still is that solvents of high dielectric constant will tend to solvate the polar salt, in this way stabilising the product, and, in accordance with the principles explained in the preceding paper, lowering the activation energy. These influences compensate for one another to a considerable extent. Since, further, the dielectric constant in the immediate vicinity of the reacting molecules must, for polar and non-polar solvents alike, be less than the average value for a continuous phase, we are probably justified in expecting the solvents to influence the variations in E to a much smaller extent than would be calculated from the influence of dielectric constant on electrostatic forces alone. The one case in which the full polarity of the solvent might be expected to come into play is in the solvation of the polar product; this would explain why the activation energies in nitrobenzene are on the whole slightly lower than those in benzene.

With regard to the changes in $\log PZ$, it is found that there is (1) very little change with change of iodide, (2) an increase on passing from triethylamine to pyridine, and (3) an increase on passing from benzene to nitrobenzene.

(1) requires no comment. In (2) the change happens to be in the same direction as the increase in E itself, and might be an example of the correlation of P and E frequently found, although in this case it is perhaps more likely to be a geometrical effect (cf. Winkler and Hinshelwood, *loc. cit.*). (3) is an example of the general influence of polar solvents in increasing PZ in reactions of this type (Fairclough and Hinshelwood, J., 1937, 1573; this vol., p. 236).

OXFORD UNIVERSITY.

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