286. *A Kinetic Study of the Formation of Aryltrimethylammonium Iodides in Methyl-alcoholic Solution.*

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Substituents in the *p*- or *m*-position in dimethylaniline influence the speed of the reaction with methyl iodide in methyl-alcoholic solution by changing the energy of activation. A similar result has been reported by Laidler for the same reaction in nitrobenzene. The change of solvent from nitrobenzene to methyl alcohol leads to a change in both the energy of activation and the non-exponential term of the Arrhenius equation. Other comparisons are made with recorded data for related changes.

Numerous investigations of the reactions of alkyl halides with tertiary bases, $NR_3 + AlkX \longrightarrow [NR_3Alk]X$, are on record; they include studies of the effects of variations in the medium, the hydrostatic pressure, the halogen X, the group Alk, and the base NR_3.

Following Menschutkin, solvent effects have been examined by Hawkins (J., 1922, **121**, 1170), Essex and Gelormini (*J. Amer. Chem. Soc.*, 1926, **48**, 882), Grimm, Ruf, and Wolff (*Z. physikal. Chem.*, 1931, **13**, 301), and others. Hinshelwood and his collaborators (Pickles and Hinshelwood, J., 1936, 1353; Fairclough and Hinshelwood, J., 1937, 538, 1573; 1938, 236), analysing their data on the basis of the equation $k = PZe^{-E/RT}$, find that E and PZ increase together for a series of solvents of about the same polarity, whereas an independent rise in PZ occurs when more highly polar media are employed (compare Hinshelwood, *Trans. Faraday Soc.*, 1938, **34**, 138). Our results for solutions in methyl alcohol, when compared with those of Laidler (J., 1938, 1786) for the same reactions in nitrobenzene, confirm the simultaneous variation of E and PZ. Gibson, Fawcett, and Perrin (*Proc. Roy. Soc.*, 1935, *A*, **150**, 223; compare Perrin, *Trans. Faraday Soc.*, 1938, **34**, 144) have found that E and PZ also rise together when the hydrostatic pressure on the medium is increased. Variations in the alkyl halide have been studied by a number of workers (*e.g.*, Menschutkin, *Ber.*, 1895, **28**, 1398; Clarke, J., 1910, **97**, 416; Preston and Jones, J., 1912, **101**, 1930; Long, J., 1911, **99**, 2164; Winkler and Hinshelwood, J., 1935, 1147; Laidler and Hinshelwood, J., 1938, 858); we have employed methyl iodide throughout our experiments.

Menschutkin, Long (*locc. cit.*), and Thomas (J., 1913, **103**, 594) have also examined the effect of changes in the base, and variations in both E and PZ have been observed in passing from one base to another (Winkler and Hinshelwood; Laidler and Hinshelwood; *locc. cit.*). The order of velocities for the reactions of a series of nuclear-substituted dimethylanilines is that normally associated with a reaction which is favoured by accession of electrons to the seat of reaction (Davies and Lewis, J., 1934, 1599): this is also the order of basic strengths (Davies and Addis, J., 1937, 1622).

The present kinetic study of the reactions of a number of substituted dimethylanilines with methyl iodide was undertaken with the object of determining the effects of substituents upon the parameters of the Arrhenius equation. The results, summarised in Table I, indicate that groups in the *p*- or *m*-positions influence the reaction velocity by changing the energy of activation, variations in the PZ term being unimportant. When our work was nearing completion, Laidler (*loc. cit.*) published his investigation of the reactions of certain nuclear-substituted dimethylanilines with methyl iodide in nitrobenzene; he, too, finds that the influence of the group is manifested in variations of E, PZ remaining practically constant.

TABLE I.

Values of E *and log* PZ *for the reaction of* MeI *with* $C_6H_4X{\cdot}NMe_2$.

X	H	*p*-Me	*m*-Me	*p*-OMe	*p*-OPh	*p*-Ph	*p*-F	*p*-Cl
E(cals.)...	15,200	14,500	14,900	14,300	15,100	15,400	15,500	16,200
log *PZ* ...	6·9	6·8	6·8	6·9	6·9	7·0	7·0	7·0

(Mean value of log *PZ* = 6·9.)

Laidler has also studied the reaction of pyridine with methyl iodide, and a comparison of our results with his, and with Hawkins's observations (*loc. cit.*) upon the reaction of pyridine with allyl bromide in nitrobenzene and in ethyl alcohol, is instructive. The relevant figures are given in Table II.

TABLE II.

Values of E *and log* PZ *for reactions of alkyl halides with tertiary bases.*

	In nitrobenzene.			In alcohol.	
	C_5H_5N and C_3H_5Br.*	C_5H_5N and CH_3I.†	$PhNMe_2$ and CH_3I.†	C_5H_5N and C_3H_5Br.‡	$PhNMe_2$ and CH_3I.§
E(cals.).........	13,300	13,600	12,800	15,100	15,200
log *PZ*	7·8	6·5	5·3	8·4	6·9

* Hawkins. † Laidler. ‡ Hawkins (ethyl alcohol). § Present paper (methyl alcohol).

The following facts emerge from the comparison : (1) For a given solvent, the value of *E* does not change very greatly when pyridine is replaced by dimethylaniline; this is not surprising in view of the similarity of the strengths of the two bases. Actually, the introduction of *p*-OMe or *p*-Cl into dimethylaniline leads to a greater change in *E* than does the change from dimethylaniline to pyridine. Also, the replacement of allyl bromide by methyl iodide has but little effect upon *E*.

(2) The value of *PZ* falls appreciably in passing from pyridine to dimethylaniline and from allyl bromide to methyl iodide.

(3) A change of solvent from nitrobenzene to methyl or ethyl alcohol leads to a simultaneous increase in *E* and *PZ*. In the dimethylanilines for which data are available there is an increase in *E* averaging 2,400 calories, and at the same time *PZ* increases by a factor of 40. Other observations of a similar character have already been referred to. The rise in *P* may in this case be due in part to an increase of the ratio (average life of transition complex)/(average life of transition complex + time required for stabilisation of the ionic product) as suggested by Norrish (*Trans. Faraday Soc.*, 1937, **33**, 1521).

EXPERIMENTAL.

The solvent employed was absolute methyl alcohol, prepared as follows. Commercial methyl alcohol (1 l.) was treated with iodine (25 g.), and the solution poured into N-sodium hydroxide (500 c.c.). In order to precipitate the iodoform, it was sometimes necessary to add a further 100 c.c. of water. After standing overnight, the mixture was filtered, and heated under a reflux until the odour of iodoform was absent (2—3 hours) (compare Bates, Mullaly, and Hartley, J., 1923, **123**, 401). The liquid was then distilled in an apparatus in which all corks were covered with tinfoil. By repeated fractionation through a modified evaporator column (Young, " Distillation Principles and Processes," London, 1922, p. 134) the major portion of the alcohol was then separated, b. p. 65°. On treatment with magnesium powder (Bjerrum and Zechmeister, *Ber.*, 1923, **56**, 894), the metal readily reacted, and a final distillation yielded absolute methyl alcohol, b. p. 64·75°/770 mm., $d_{4°}^{25°}$ 0·7866.

Methyl iodide was washed successively with dilute sodium thiosulphate, water, dilute sodium carbonate, and water, dried over calcium chloride, and distilled, passing over as a clear, colourless liquid, b. p. 42·8°, which was stored over mercury.

Dimethyl-aniline and -*m*- and -*p*-toluidines were distilled, refluxed with acetic anhydride, and again fractionated. The distillates were dried over potassium hydroxide, and on redistillation under reduced pressure yielded colourless liquids, b. p.'s 95°/30 mm., 108·5°/30 mm., and 80°/6 mm. respectively. The pure dimethylaniline gave no coloured compounds with methyl iodide (compare Edwards, *Trans. Faraday Soc.*, 1937, **33**, 1294). All the other dimethylanilines were prepared by methylation of the corresponding primary amines by van Duin's method (*Rec. Trav. chim.*, 1932, **51**, 878) modified in certain instances (see Evans and Williams, this vol., p. 1199). In each case primary and secondary amines were removed by heating with acetic anhydride, and fractionating or steam-distilling the mixture with or without addition of sodium hydroxide. The white solids had the following m. p.'s. :

Dimethylaniline.	M. p.	Dimethylaniline.	M. p.
p-Fluoro-	35·2° (35°) *	*p*-Methoxy-	47° (48°) *
p-Chloro-	32·8 (35·5) *	*p*-Phenyl-	122 (123; † 119—120 ‡)
p-Nitro-	165 (162) *	*p*-Phenoxy-	34

* Davies and Cox (J., 1937, 615), Davies (*Bull. Soc. chim.*, 1935, **2**, 295). † Bell and Kenyon (J., 1926, 2705). ‡ Banús and Tomás (*Anal. Fís. Quím.*, 1921, **19**, 293).

Kinetic Measurements.—0·2M-Stock solutions of methyl iodide and of tertiary amine (freshly distilled or crystallised) were made in methyl alcohol at 25°. For temperatures below 55°, 10 c.c. of each solution were mixed in a stoppered flask immersed in a thermostat, and the reaction was followed by withdrawing 2 c.c. of solution at suitable intervals, pouring it into 25 c.c. of light petroleum, and extracting three times with 10 c.c. portions of distilled water. During the extraction process the tip of the separating funnel was washed out with water each time before shaking. The aqueous extract was then rendered slightly acid by addition of five drops of dilute acetic acid, and titrated with N/100-silver nitrate, eosin or dimethyldi-iodofluorescein being used as indicator. A 10-c.c. N.P.L.-standardised burette, graduated in 0·02 c.c., was employed. For temperatures of 55° and above, the reactions were carried out in sealed tubes. 2 C.c. of M/5-methyl iodide solution and 2 c.c. of M/5-amine solution were mixed in a test-tube, which was then sealed. A number (usually 8) of these tubes were inserted in the thermostat, zero time being the moment of immersion in the bath. At suitable intervals a tube was removed, washed, and the contents transferred to a funnel containing 25 c.c. of light petroleum. The solution was extracted, and the aqueous extract titrated as described above. The initial concentrations of the reagents were corrected for solvent expansion in the usual manner. Owing to the sparing solubility of 4-dimethylaminodiphenyl and of *p*-nitrodimethylaniline in methyl alcohol, the initial concentrations of these substances used were 0·02M and 0·01M respectively.

The thermostats were electrically controlled. For temperatures below 65° the control consisted of a toluene regulator in conjunction with a Sun Vic vacuum tube switch; the temperatures were constant to ±0·02°. The higher temperatures were obtained in a copper bath (12″ × 12″ × 12″) filled with heavy oil and maintained within 0·1° of any desired temperature up to 150° by lamp heaters one of which was controlled by means of a Sun Vic bimetallic thermoregulator Type T.3, in conjunction with a vacuum tube switch.

The reactions were kinetically bimolecular, and in all cases the equation $dx/dt = k(a - x)^2$ was followed accurately over at least the first 50% of the change. The following table gives two typical runs.

Dimethyl-*p*-anisidine at 55° (sealed tubes).
$a = 0\cdot09627$ g.-mol./l.

t (mins.).	10^5x.	10^3k.	t (mins.).	10^5x.	10^3k.
8	937	2·33	45	3621	2·32
12	1352	2·36	50	3893	2·35
16	1713	2·34	55	4099	2·33
22	2214	2·35	60	4340	2·37
30	2790	2·36	65	4470	2·31
35	3049	2·29	70	4712	2·37
40	3393	2·36		Mean	2·36

Dimethyl-*p*-toluidine at 25° (stoppered flasks).
$a = 0\cdot1$ g.-mol./l.

t (mins.).	10^5x.	10^4k.	t (mins.).	10^5x.	10^4k.
555	3144	1·38	2805	7057	1·43
870	4226	1·40	2858	7098	1·43
1380	5405	1·42	3420	7442	1·42
1420	5441	1·40	3651	7590	1·44
1980	6292	1·43	4213	7854	1·45
2220	6555	1·43		Mean	1·42

The velocity coefficients (in l. g.-mol.$^{-1}$ sec.$^{-1}$) at the various temperatures are summarised below.

X in $C_6H_4X\cdot NMe_2$.	10^5k_{25}.	10^4k_{35}.	10^4k_{45}.	10^4k_{55}.	10^3k_{65}.	10^3k_{75}.
H	5·62	1·31 [2]	—	4·15 [1]	1·19	—
p-CH_3	14·2	3·20	—	9·39 [1]	2·55	—
m-CH_3	—	1·75	3·74	7·56	1·50	—
p-F	—	1·06	2·32	4·96	9·63	—
p-Cl	—	—	0·787	1·70	0·360	0·728
p-OCH_3	2·53	5·72	11·4	23·4	(4·47) *	—
p-C_6H_5	—	—	49·6 [3]	92·94	(1·04) *	2·38 [5]
p-OC_6H_5	—	1·71	3·51	7·66	1·50	—

[1] Temp. = 50°; [2] temp. = 35·5°; [3] temp. = 89·3°; [4] temp. = 100·5°; [5] temp. = 78°.
* = Calculated.

In experiments with *p*-nitrodimethylaniline, little or no change was found after 24 hours at 100°. These results are similar to those of Laidler (*loc. cit.*) where, owing to the unfavourable position of the equilibrium, *m*-nitrodimethylaniline did not react with methyl iodide.

We thank Messrs. Imperial Chemical Industries Ltd. for grants.

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[*Received, June* 17*th,* 1939.]