114. *The Influence of Alkyl Groups upon Reaction Velocities in Solution. Part V. The Formation of Phenyltrialkylammonium Iodides in Methyl Alcohol.*

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A study of the reactions between several dialkylanilines and methyl iodide has shown that in passing from methylalkylanilines to diethyl-, ethylpropyl-, dipropyl-, or dibutyl-aniline there is a large increase in activation energy accompanied by a rise in the factor PZ of the kinetic equation. The observations have been interpreted as being due mainly to a steric effect of the terminal methyl groups coupled with the possible formation of a hydrogen bond.

THE reaction between tertiary amines and alkyl halides, first studied by Menschutkin (*Z. physikal. Chem.*, 1890, **6**, 41; *Ber.*, 1895, **28**, 1399, and later papers), has often been further investigated, but only Winkler and

Hinshelwood (*J.*, 1935, 1147), Laidler (*J.*, 1938, 1786), Evans, Watson, and Williams (*J.*, 1939, 1345, 1348), and Brown and Fried (*J. Amer. Chem. Soc.*, 1943, **65**, 1841) have provided data suitable for analysis on the basis of the kinetic equation $k = PZe^{-E/\mathbf{R}T}$, which affords useful indications of the effects of the substituents upon reactivity. As an extension of the problem indicated in the title, the reaction between methyl iodide and several dialkylanilines has been studied at various temperatures in methyl alcohol as solvent. Some of the preliminary results have been quoted elsewhere (*Trans. Faraday Soc.*, 1941, **37**, 645) but now circumstances make it desirable to record the results and conclusions to date.

EXPERIMENTAL.

Materials.—The dialkylanilines were prepared by Hickinbottom's methods (*J.*, 1930, 992) and in all cases were freed from traces of primary and secondary bases by treatment with acetic anhydride and subsequent steam distillation. The liquids boiled within 0·1° of the temperatures recorded : Me$_2$, 95°/30 mm.; Et$_2$, 96°/13 mm.; Pr$^a{}_2$, 122°/14 mm.; *n*-Bu$_2$, 130°/7 mm.; MeEt, 89·5°/15 mm.; MePr^a 96·5°/10 mm.; EtPr^a, 111°/13 mm.

Measurements.—The reactions were carried out at three temperatures in absolute methyl alcohol exactly as described by Evans, Watson, and Williams. Satisfactory velocity constants were obtained by applying the simple bimolecular formula in the case of dimethyl-, methylethyl-, methylpropyl-, and dibutyl-anilines, but the other compounds showed slight autocatalysis. In these cases the slope of the tangent at zero time to the curve obtained on plotting $1/(a - x)$ against time gave constants which fell on the Arrhenius line. The tangents always passed through the first one or two points recorded and extrapolation of the plot of k against percentage change also gave the same values of the velocity coefficients. A typical set of results is recorded below, where a = initial concentration of amine and iodide, x = concentration of the quaternary salt, and k is the velocity coefficient in l. g.-mol.$^{-1}$ sec.$^{-1}$.
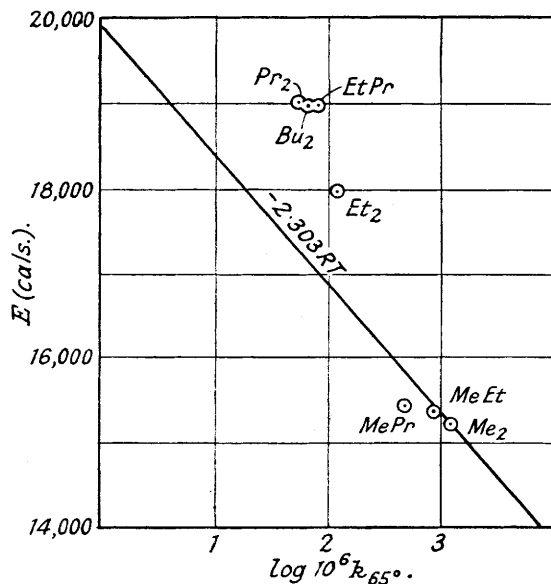
Methylethylaniline and methyl iodide at 44·85°.

$a = 0.09754$ g.-mol. per litre.

Time (mins.)	125	255	390	565	890	990	1140	1320
Titre, c.c. of 0·01131N-AgNO$_3$	4·49	7·94	10·9	13·85	17·75	18·75	19·80	21·30
$10^4 k$	2·00	1·95	1·96	1·96	1·96	1·96	1·93	1·98

The following table records the results for the velocity coefficients at various temperatures, together with the calculated values of the energies of activation and of log PZ.

Dimethylaniline.		Methylethylaniline.		Methyl-*n*-propylaniline.		Diethylaniline.	
Temp.	$10^4 k$.	Temp.	$10^4 k$.	Temp.	$10^4 k$.	Temp.	$10^4 k$.
25°	0·562	44·85°	1·97	44·8°	1·12	65°	1·24
35·5	1·31	65	8·50	65·25	4·94	85·5	5·69
65	11·9	84·2	29·0	84·9	17·5	99·4	14·9

$E = 15{,}200$ $E = 15{,}400$ $E = 15{,}430$ $E = 18{,}000$
log $PZ = 6·9$ log $PZ = 6·9$ log $PZ = 6·7$ log $PZ = 7·7$

Ethyl-*n*-propylaniline.		Di-*n*-propylaniline.		Di-*n*-butylaniline.	
65	0·775	65·2	0·548	65	0·68
84·3	3·54	84·7	2·52	85	2·83
99·8	11·0	100	7·72	100	8·66

$E = 19{,}030$ $E = 19{,}060$ $E = 19{,}000$
log $PZ = 8·2$ log $PZ = 8·1$ log $PZ = 8·1$

DISCUSSION.

The velocity coefficients at 65° decrease in the order Me$_2$ > MeEt > MePr > Et$_2$ > EtPr > Pr$_2$; an approximately constant value being attained in the dipropyl compound. The velocity coefficients at 65° referred to that of dimethylaniline as unity are given in the second line below :

	Aniline.	Me$_2$.	MeEt.	MePr.	Et$_2$.	Pr$_2$.
$k_{\mathrm{R}_2}/k_{\mathrm{Me}_2}${	Present work	1·0	0·71	0·41	0·10	0·046
	Thomas	1·0	0·66	0·44	0·07	—

and are in close accord with the same ratios (third line) calculated from Thomas's results (*J.*, 1913, **103**, 594) for the reaction of these bases with allyl bromide at 40° in ethyl alcohol. The similarity appears to indicate that, although the absolute values of the coefficients in the two reactions differ in the ratio of *ca.* 10^3, the variation in velocity from base to base is independent of the alkyl halide and is governed by the nature of the alkyl groups in the base.

The formation of quaternary ammonium salts is facilitated by electron accession at the nitrogen atom (cf. Davies and Lewis, J., 1934, 1599; Evans, Watson, and Williams, *loc. cit.*); the increase in velocity due to an electron-repulsive *m*- or *p*-nuclear substituent being caused entirely by the decrease in activation energy. Hinshelwood, Laidler, and Timm (J., 1938, 848) have suggested that, since both the basic strength and the energy of activation for quaternary salt formation appear to be governed by the reactivity of the unshared electrons of the nitrogen, then for a given alkyl halide the activation energy should increase with decreasing strength of the tertiary base. Several instances were quoted by these workers where this rule was obeyed; *e.g.*, for the addition of methyl iodide to pyridine and triethylamine (in benzene) the activation energies are 14,300 and 9700 cals., respectively. In the dialkylanilines the slight increase in the inductive effect of the substituents as the alkyl series is ascended might be expected (in the absence of any other complicating effects) to cause a decrease in the activation energy; experiment, however, proves that this is not the case.

The detailed results (p. 423) show that, whenever the tertiary base contains two groups higher than methyl linked to nitrogen, the velocity coefficient is lower than that for the methylalkylanilines. This would be expected on the conventional steric hindrance effect. When the energies of activation are plotted against $\log k_{65°}$ (see fig.), however, in agreement with most recent work it is found that the decrease in velocity is due mainly to a rise in the energy of activation and not to a fall in the non-exponential factor of the kinetic equation; in fact, there is a general increase in P with E as the alkyl chain lengthens. A possible reason for this rise in P has been suggested by Davies and Evans (J., 1940, 339) and Evans, Watson, and Williams (*loc. cit.*).

The present observations show that the slight increase in the normal inductive effect of the alkyl groups is offset by some very powerful effect which is present in all the bases containing two groups higher than methyl. A comparison of the energies of activation and the base strengths is instructive. The relevant data are given below, the values of pK_H being due to Hall and Sprinkle (*J. Amer. Chem. Soc.*, 1932, **54**, 3469).

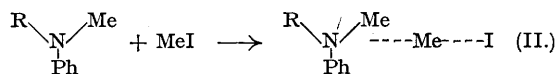| Alkyl subst.	Me$_2$.	MeEt.	Et$_2$.	MePr.	EtPr.	Pr$_2$.
pK_H	5·06	5·98	6·56	5·64	6·34	5·57
E, cals.	15,200	15,400	18,000	15,430	19,030	19,060

Even in the base strengths the influence of the inductive effect of the alkyl groups does not offer a complete interpretation, since the ethyl substituent has a definite enhancing influence not present in methyl or *n*-propyl. On passing from dimethylaniline to the stronger bases diethyl-, dipropyl-, or ethylpropyl-aniline, the activation energies for the addition of methyl iodide *increase* by a considerable amount (3000 cals. approx.) instead of decreasing as expected on the suggestion of Hinshelwood, Laidler, and Timm, whilst for the methylalkyl-anilines, which vary appreciably in strength, the activation energies are practically constant. It follows that in the present case there must be an important factor other than the availability of the unshared electrons on the nitrogen atom. The actual nature of this effect, which becomes sharply evident in the diethyl member, is not easy to determine and the following are possible interpretations. Baker (*Trans. Faraday Soc.*, 1941, **37**, 647) has suggested that the increase in activation energy in the diethyl and higher dialkylanilines may be due to the decreased electron release according to the mechanism (I) occurring in the transition complex.
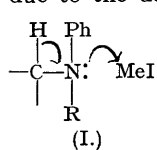
Since the alkyl group is so close to the seat of the reaction, such an effect might have a large influence on the activation energy. It is difficult, however, to understand why it is essential to have substitution in both the methyl groups of dimethylaniline before the influence is felt.

Brown and Fried (*loc. cit.*) have recently put forward an interesting suggestion regarding the influence of retarding ortho-substituents in the Menschutkin reaction, which closely resembles a postulate of Hughes (*Trans. Faraday Soc.*, 1941, **37**, 620) in connection with the bimolecular hydrolysis of *neo*pentyl bromide. Brown and Fried suggest that in quaternary salt formation " the alkyl group approaches the exposed face of the nitrogen atom along a line at right angles to the plane of the three groups to which it is attached. In hindered amines the nitrogen atom is shielded from approach along a normal line." The sudden large increase in activation energy (approx. 5000 cals.) in passing from $n = 3$ to $n = 4$ in $C_6H_4 \cdot [CH_2]_n \cdot NMe$ supports this view. The similar sudden large increase in E found in the present work when both groups attached to nitrogen are larger than methyl, points to the possibility of a similar explanation. In dimethyl- and the methylalkyl-anilines the approach of methyl iodide can apparently take place unhindered (II), but in the diethyl and higher alkyl bases the longer alkyl chain offers a serious obstruction to the approach-

ing methyl. Here we have an almost pure bulk effect which appears similar to that observed in the bimolecular hydrolysis of *neo*pentyl bromide (Hughes, *loc. cit.*), the sudden rise in E being expected because of the steep rise in the potential-energy curves when the distance between the terminal methyl groups of the substituents and the attacking reagent falls below a critical value.

The third possible explanation of the rise in activation energy observed here is an extension of the suggestion given in previous parts of this series, *viz.*, the possibility of hydrogen-bond formation in the transition complex between the alkyl group and the reactive centre of the molecule. In diethylaniline, ring formation of the type

indicated in (III) would involve formation of a 4-membered " ring " which might exist in the transition state of the reaction with methyl iodide. The constraint thus placed on the nitrogen lone pair would possibly account for the rise in activation energy in passing from dimethyl- to diethyl-aniline. The further rise in E for dipropyl-, ethylpropyl-, and dibutyl-anilines may be accounted for by the formation of more stable five- and six-membered rings by hydrogen-bond formation between the terminal methyl and the nitrogen, which involves greater restraint on the unshared electrons.

C_2H_5
Ph N CH_2 CH_2
H
(III.)

Which of these interpretations is nearest the truth it is difficult to decide. In any reaction each effect may come into play simultaneously with one preponderating over the other two. The author regards the second interpretation as the most likely in the present case, with the possible intervention of the hydrogen bond as a supporting effect. It would be interesting to discover whether, on increasing the size of the entering group, the steric influence due to repulsion as suggested by Hughes and by Brown and Fried would be felt in methyl-propyl- or even methylethyl-aniline.

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