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

By DAVID P. EVANS.

[Reprint Order No. 4114.]

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

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 since been further investigated by several workers. With the exception of those of 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), the data are not suitable for analysis on the basis of the kinetic equation $k = PZ \, . \, e^{-E_a/RT}$, which affords useful indications of the effects of the substituents upon reactivity. As an

---

* Part VI, preceding paper.

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.

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 accepted temperature: Me$_2$, 95°/30 mm.; Et$_2$, 96°/13 mm.; Pr$^n_2$ 122°/14 mm.; MeEt, 89·5°/15 mm.; MePr^n 96·5°/10 mm.; EtPr^n, 111°/13 mm.

Measurements.—The reactions were carried out at three temperatures in absolute methyl alcohol in exactly the same manner as described by Evans, Watson, and Williams (*loc. cit.*). Satisfactory velocity constants were obtained by applying the simple bimolecular formula in the case of dimethyl-, ethylmethyl-, 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. mole^{-1} sec.$^{-1}$.

Ethylmethylaniline and methyl iodide at 65°.

$a = 0·09754$ mole/l.

Time (min.)	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
$k \times 10^4$	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.

NPhMe$_2$

Temp.	10^4k
25°	0·562
35·5	1·31
65	11·9

$E = 15,200$
log $PZ = 6·9$

NPhMeEt

Temp.	10^4k
44·85°	1·97
65	8·50
84·2	29·0

$E = 15,400$
log $PZ = 6·9$

NPhMePr^n

Temp.	10^4k
44·8°	1·12
65·25	4·94
84·9	17·5

$E = 15,430$
log $PZ = 6·7$

NPhEt$_2$

Temp.	10^4k
65°	1·24
85·5	5·69
99·4	14·9

$E = 18,000$
log $PZ = 7·7$

NPhEtPr^n

Temp.	10^4k
65°	0·775
84·3	3·54
99·8	11·0

$E = 19,030$
log $PZ = 8·2$

NPhPr$^n_2$

Temp.	10^4k
65·2°	0·548
84·7	2·52
100	7·72

$E = 19,060$
log $PZ = 8·1$

NPhBu$^n_2$

Temp.	10^4k
85°	2·83
100	8·66
65	0·683

$E = 19,000$
log $PZ = 8·1$

DISCUSSION

The velocity constants at 65° decrease in the order

$$\text{Me}_2 > \text{MeEt} > \text{MePr}^n > \text{Et}_2 > \text{EtPr}^n > \text{Pr}^n_2 \simeq \text{Bu}^n_2;$$

indicating an approximately constant value for the di-*n*-propyl, the di-*n*-butyl, and presumably the higher di-*n*-alkyl compounds. The velocity coefficients at 65° referred to that of dimethylaniline as unity are given in the second line below:

Aniline	Me$_2$	MeEt	MePr^n	Et$_2$	Pr$_2$
k_{R_2}/k_{Me_2}	1·0	0·71	0·41	0·10	0·046
k_{R_2}/k_{Me_2}	1·0	0·66	0·44	0·07	—

and are in close accord with the same ratios (line 3) 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 by approximately 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.

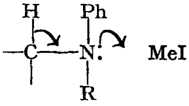
The formation of quaternary ammonium salts is facilitated by electron accession to the nitrogen atom (cf. Davies and Lewis, *J.*, 1934, 1599; Evans, Watson, and Williams, *loc. cit.*), the increase in velocity due to an electron-repulsive *meta-* or *para*-nuclear substituent being caused entirely by the decrease in activation energy. Hinshelwood, Laidler, and Timm (*J.*, 1938, 848) suggested that, since both the base strength and the energy of activation for quaternary salt formation appear to be governed by the reactivity of the unshared electron of the nitrogen, then for a given alkyl halide the activation energy should increase with decreasing strength of the tertiary base. They quoted several instances where the above 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 calories, respectively. In the dialkylanilines the slight increase in the inductive effect of the substituents as the alkyl series is ascended might be expected to cause a decrease in the activation energy; experiment, however, proves that this is not the case.

The results in the main Table show that, whenever the tertiary base contains two groups higher than methyl linked to nitrogen, the velocity coefficient is lower than that for the alkylmethylanilines.

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 groups	Me_2	MeEt	Et_2	MePr	EtPr	Pr_2
pK_h	5·06	5·98	6·56	5·64	6·34	5·57
E, cal.	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 cal., approx.) instead of decreasing as expected on Hinshelwood, Laidler, and Timm's suggestion, whilst for the alkylmethylanilines which vary appreciably in strength, the activation energies are approximately constant. Baker (*Trans. Faraday Soc.*, 1941, **37**, 647) suggested that the increase in activation energy in the diethyl- and higher dialkyl-anilines may be due to the decreased electron release according to the mechanism inset. 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. Moreover, the alkyl groups are linked through nitrogen to the conjugate phenyl nucleus, which enhances the hyperconjugation of methyl. This large hyperconjugate electron release operates most strongly in dimethylaniline, and is reduced in ethylmethylaniline, as indicated by change in pK_h. Brown and Fried's observation (*loc. cit.*) that steric hindrance occurred in the reaction of methyl iodide with $\overline{C_6H_4\cdot[CH_2]_n\cdot N}Me$ when *n* changed from 3 to 4, with a sudden rise in activation energy of approximately 5000 cal., is similar to some of the present results where large increases in E occur between successive members of homologous series, *viz.*,



$$Me,Et\text{–}Et_2,\ \Delta E = 2600 \text{ cal.};\quad Me,Pr\text{–}Et,Pr,\ \Delta E = 3600 \text{ cal.}$$

Moreover, the smaller difference in E values between diethyl- and ethyl-*n*-propyl- (1030 cal.), and the negligible difference between ethyl-*n*-propyl- and di-*n*-propyl-aniline, seems to point to a " saturation " value being reached. In the diethyl- and higher dialkyl-anilines, therefore, it is likely that steric effects of the type described by Brown and Fried (*loc. cit.*) come into play in addition to electronic influences and it is difficult to separate the effects.

I thank Dr. R. Williams for experimental assistance.

GLAMORGAN TECHNICAL COLLEGE, TREFOREST. [*Received, February* 19*th*, 1953.]