349. *The Reactivities and Basic Strengths of the* p-*Alkyldimethylanilines.*

By W. Cule Davies.

The basic dissociation constants of a series of *p*-alkyldimethylanilines and their velocities of reaction at several temperatures with methyl iodide have been determined. The Hammett relation between the equilibrium constants and the rate constants holds with fair accuracy. The sequence Me $>$ Pr$^{\beta}$ $>$ *tert.*-Bu, Et $>$ Bu^{a} $>$ Pr^{a} $>$ H $\sim$ *iso*Bu for the relative influence of the *p*-alkyl groups on the measurements is discussed in relation to the electronic effects of alkyl groups. For the reaction of the bases with methyl iodide the factors *E* and *P* in the Arrhenius equation have been calculated; *E* is practically constant, and the velocity changes depend mainly on changes in *P*.

EXPLANATIONS of the influences of substituent alkyl groups on the reactions of organic compounds have recently been offered, notably by Baker and Nathan (J., 1935, 1844), Evans (J., 1936, 785), and Ayling (this vol., p. 1014). The last worker divides the available data into two classes: (*a*) where the alkyl group participates in the reaction and the normal sequence for the inductive effect (+ *I*) is observed, *viz.*,

$$\mathrm{Me} < \mathrm{Et} < \mathrm{Pr}^{\alpha} < \mathrm{Bu}^{\alpha},\ \mathrm{Pr}^{\alpha} < \mathrm{Pr}^{\beta},$$

etc., and (*b*) where the group only exerts a modifying influence and the uniform sequence is displaced. Baker and Nathan suggested an additional electronic effect which gave the methyl group in the requisite system an increased capacity for electron release. This effect follows the sequence Me > Et > Pr^{β} > *tert.*-Bu (see also Baker, Dippy, and Page, J., 1937, 1774). Ayling pointed out that the greatest abnormality often occurs when the *n*-propyl group is the substituent, and offered an explanation based on the operation of a field effect, which from geometrical considerations would be greatest with the *n*-propyl group, in addition to the normal inductive effect. The present work records data for a further series of alkyl compounds, where the substituent group is isolated from the point of reaction.

Details of the preparation and purification of the *p*-alkyldimethylanilines used herein are given by Davies and Hulbert (*J. Soc. Chem. Ind.*, 1938, **57**, 349). After treatment with acetic anhydride and steam-distillation to remove primary and secondary amines, the base was repeatedly fractionally distilled at reduced pressure, until a sample gave constant velocity coefficients over at least 70% of the whole of the reaction with methyl iodide in solution in aqueous acetone. A sample of *p*-*iso*propyldimethylaniline prepared from *p*-dimethylaminobenzaldehyde (Sachs and Sachs, *Ber.*, 1905, **38**, 517) gave, after two distillations, satisfactorily constant bimolecular velocity coefficients at 35° of mean value 5·9 (100*k*, l. g.-mol.$^{-1}$ min.$^{-1}$). Another sample, prepared from *iso*propylbenzene, gave coefficients ranging from 3·6 to 2·8 after two distillations. However, after six distillations the coefficients became reasonably constant at a mean value of 6·1.

Dissociation constants at 20° of the *p*-alkyldimethylanilines were determined by the method described by Davies and Addis (J., 1937, 1622). A solution of the base in 50% alcohol (50 vols. of absolute ethyl alcohol diluted to 100 vols. with water) was titrated electrometrically with N/50-hydrochloric acid in 50% alcohol, a glass electrode being used with a saturated potassium chloride–calomel half cell as reference electrode. The dissociation constant given in Table I is a mean value of $p_K = p_H + \log C_{\text{salt}}/C_{\text{base}}$ (where necessary the form corrected for hydrolysis was used) obtained with 5 or 6 determinations of p_H with successive additions of hydrochloric acid in a titration of the base.

TABLE I.

Dissociation Constants of Bases $\mathrm{R{\cdot}C_6H_4{\cdot}NMe_2}$ *at* 20°.

Solvent: 50% alcohol. Titrant: *N*/50-hydrochloric acid.

R.	G. of base/ 100 c.c.	Mean p_K.	Mean variation from mean p_K.	R.	G. of base/ 100 c.c.	Mean p_K.	Mean variation from mean p_K.
(H)	0·2045	4·22 *	±0·025	Pr^{β}	0·2126	4·77 §	±0·02
Me	0·2106	4·77 †	0·05	Bu^{α}	0·1973	4·62	0·03
Et	0·1972	4·69	0·01	*sec.*-Bu	0·2022	4·62	0·01
Pr^{α}	0·2034	4·43	0·02	*iso*Bu	0·2178	4·19	0·01
Pr^{β}	0·2004	4·78 ‡	0·025	*tert.*-Bu	0·2134	4·65	0·02

* Davies and Addis (*loc. cit.*) gave 4·21. † Davies and Addis gave 4·77.

‡ Base prepared from *iso*propylbenzene § Base prepared from *p*-dimethylaminobenzaldehyde.

Table II summarises the results obtained for measurements of reaction velocity between methyl iodide and the *p*-alkyldimethylanilines in aqueous acetone solution. The bimolecular velocity coefficient *k* is in l. g.-mol.$^{-1}$ min.$^{-1}$, and the values of $\log_{10}PZ$ and of *E* are derived from the Arrhenius equation *k* (time in secs.) $= PZe^{-E/RT}$. At 35° and 45° the reaction vessel method of Davies and Lewis (J., 1934, 1599) was employed for the experimental work: no corrections for solvent thermal expansion or initial time of mixing are necessary with this method. The initial concentration of each reactant was 0·1 g.-mol./l. in the mixture at 35° or 45°. For the reaction at 55°, solutions of the reactants were prepared at room temperature,

TABLE II.

Reaction between Methyl Iodide and p-*Alkyldimethylanilines*, $R{\cdot}C_6H_4{\cdot}NMe_2$.

Solvent: aqueous acetone (10 vols. of water diluted to 100 vols. with acetone).

R.	100*k* (l. g.-mol.$^{-1}$ min.$^{-1}$). 35°.	45°.	55°.	*E*.	$\log_{10} PZ$.
(H)	2·67	5·06	8·54	11,670	4·94
Me	6·99	12·3	22·5	11,710	5·38
Et	5·41	—	17·3	11,660	5·23
Pr^α	3·49	6·46	11·0	11,520	4·95
Pr^β	6·08	—	19·5	11,690	5·31
Bu^α	5·26	—	—	—	—
sec.-Bu	4·92	—	—	—	—
*iso*Bu	2·58	—	8·35	11,790	5·00
tert.-Bu	5·47	—	17·4	11,610	5·20

TABLE III.

p-*iso*Propyldimethylaniline and methyl iodide at 35°.

$[\text{Base}]_{35^\circ} = [\text{MeI}]_{35^\circ} = 0{\cdot}1$.

3·63 C.c. (measured at 35°) of reaction mixture titrated with N/40-silver nitrate.

t, mins.	$AgNO_3$, c.c.	100*k*.	*t*, mins.	$AgNO_3$, c.c.	100*k*.
92	5·2	6·06	280	9·15	6·08
131	6·45	6·10	363	10·0	6·09
197	7·9	6·06	402	10·3	6·07
239	8·6	6·08	Mean 100*k* = 6·08		

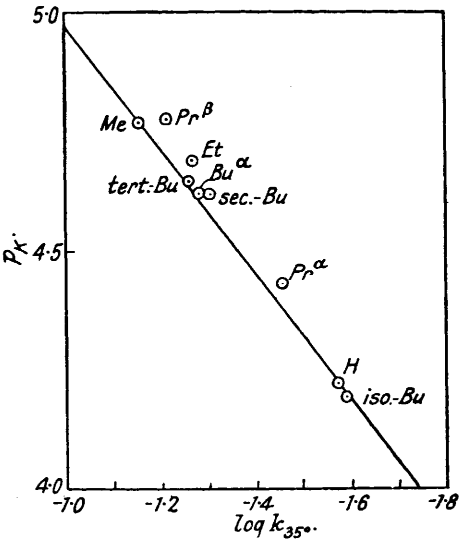
p-*tert.*-Butyldimethylaniline and methyl iodide at 55°.

$[\text{Base}]_{55^\circ} = [\text{MeI}]_{55^\circ} = 0{\cdot}0946$.

6·08 C.c. (contents of a sealed tube, volume corrected to that at 65°) titrated with N/40-silver nitrate.

t, mins. (corr.).	$AgNO_3$, c.c.	100*k*.	*t*, mins. (corr.).	$AgNO_3$, c.c.	100*k*.
12·5	3·95	17·5	42	9·4	17·4
17	5·1	17·7	55·5	11·0	17·5
25	6·8	17·7	80	13·1	17·5
33	8·1	17·4	Mean 100*k* = 17·5		

mixed, and aliquot portions of the mixture measured into tubes which were then sealed and placed in the thermostat. Actual concentrations at 55° were calculated from a knowledge of the thermal expansion of the solvent, and the true zero time was obtained graphically from the time–concentration curve of quaternary salt measurements. The initial concentration of base and halide at 55° in the mixture was 0·0946 g.-mol./l. Determination of the quaternary salt formed was carried out as described by Davies and Lewis. Detailed examples are given in Table III.



Dissociation constants and velocity coefficients of reaction with methyl iodide of p-*alkyldimethylanilines.*

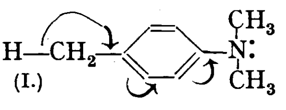
Relation between the Equilibrium and Rate Constants.—Hammett and Pfluger (*J. Amer. Chem. Soc.*, 1933, **55**, 4079) showed that a simple relationship exists between the rate constants of one series of reactions and the equilibrium constants of another distinct, though related, series. Hammett (*Chem. Reviews*, 1935, **17**, 125; *J. Amer. Chem. Soc.*, 1937, **59**, 96; *Trans. Faraday Soc.*, 1938, **34**, 156) later included several other reaction series, and pointed out limits to the range of structural variation permissible. Davies and Addis (*loc. cit.*) showed that a linear relation held between the p_K of dimethylaniline (in 50% alcohol) and its *p*-substituted derivatives (MeO, Me, H, Hal.) and the logarithm of the bimolecular velocity coefficient of the reaction between the base and methyl iodide (in 90% acetone). The figure shows that the points corresponding with the present measurements with the various *p*-alkyldimethylanilines are grouped around the line drawn through the points for the measurements of Davies and Addis : departures from linearity are quite small. It is concluded that the polar effect of the alkyl groups is similar for the two reactions (salt formation and basic hydroxide formation).

Sequence of Alkyl Groups.—Since alkyl groups are feebly electron-repelling, it would be expected that the reactivity of dimethylaniline towards methyl iodide should be enhanced by the substitution of *p*-alkyl groups. Basic strength should likewise be increased.* The one exception is *p*-*iso*butyldimethylaniline, which has practically the same reactivity and basic strength as the unsubstituted base.

Considering the relative effects of the different alkyl groups the sequence is Me > Pr^{β} > *tert.*-Bu, Et > Bu^{a} > Pr^{a} > H $\sim$ *iso*Bu, which is not the order expected if the sole electronic effect of the alkyl groups is the inductive effect. Steric effects are not considered to be of importance, since the substituent is so far isolated from the point of reaction. It must be concluded that in this reaction there is an additional effect associated with the alkyl groups which tends to give methyl a large positive effect. Baker and Nathan (*loc. cit.*) obtained the following order for the effect of the substituent on the velocity of the reaction between *p*-alkylbenzyl bromides and pyridine :

Me > Et > Pr^{β} > *tert.*-Bu > H.

They suggested that, when a methyl group occurs in the requisite conjugated system, there operates a type of tautomeric effect ($+T$) in addition to the normal inductive effect of the group. The effect decreases with the higher radicals. The abnormal sequences obtained may be due therefore to a superimposition of the two electronic effects. For dimethyl-*p*-toluidine the additional effect would be represented as in (I). It should be made clear that the differences in reactivity are, in general, very small, since the electronic effects of alkyl groups are small, and further, we are tracing them at a distant point. We can only be certain of the general trend of the results and of some cases where the differences are large.


(I.)

The present results strikingly resemble those obtained by Baker, Dippy, and Page (*loc. cit.*) for the dissociation constants of the *p*-alkylbenzoic acids. The order is, as expected, the reverse of the present order, except in the one case of the *tert.*-butyl substituent.

The *n*-propyl substituent, when compared with the ethyl and the *n*-butyl substituent of the present series, appears to have a smaller positive effect than expected. This is probably a further example of the abnormality associated with the *n*-propyl group which was pointed out by Ayling (*loc. cit.*). His explanation that there operates a field effect, which because of geometrical considerations is greatest with the *n*-propyl group, can be applied satisfactorily here. The terminal carbon atom and its attached hydrogen atoms of the *p*-*n*-propyl group are actually closest in proximity to the benzene nucleus without appreciable overlapping of the attached hydrogen atoms and the nucleus. The terminal carbon atom of the butyl group substantially overlaps, and that of the ethyl group is relatively distant from the nucleus. A reversed field effect was attributed to the methyl group by Bennett and Mosses (J., 1930, 2366). Baddeley and Bennett's views (J., 1933, 265) on the reversed field effect of the halogen atom operating at the *p*-position and being transmitted through the benzene nucleus are now applied to the alkyl substituent.

An *iso*butyl substituent frequently causes a marked decrease in the reactivity of a substance (see, *e.g.*, Menschutkin, *Z. physikal. Chem.*, 1890, **5**, 589 ; Bennett and Reynolds, J., 1935, 131 ; Hardwick, J., 1935, 141), but in other cases the group has a normal effect (Olsson, *Z. physikal. Chem.*, 1925, **118**, 99; Norris, *J. Amer. Chem. Soc.*, 1925, **47**, 837; 1927, **49**, 2640). *p*-*iso*Butyldimethylaniline is now seen to be of similar reactivity to dimethylaniline, which is much less reactive than the *n*- and the *sec.*-butyl-compound. An explanation following Baker and Nathan's views shows that the capacity for electron release of the *sec.*-butyl group is greater than that for the *iso*butyl group, but seems inadequate to account for the large difference in reactivity.

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* On account of the relation mentioned in the previous section, the subsequent discussion refers to the effect of the substituent group on reactivity towards methyl iodide and on basic strength.

Energy of Activation and Probability Factor.—It is generally agreed that in the reactions of a series of *p*-substituted benzene derivatives, the velocity changes are due almost entirely to changes in the energy of activation, *E*, and not to changes in the probability factor, *P*. Where the range of velocities with a series of *p*-substituted compounds is small, it has been pointed out that the Arrhenius equation is really inadequate, and that care should be taken in these cases before ascribing significance to changes in *P*. In the present series of reactions, the range of velocities is small, *viz.*, about 1 : 2·5. The energy of activation remains almost constant, and the velocity changes are governed mainly by the probability factor. For instance, in introducing the *p*-methyl group into dimethylaniline the greatest change in velocity is obtained : there is a slight increase in *E*. Since dimethyl-*p*-toluidine is a stronger base than dimethylaniline, we might expect a considerable decrease in *E*. The increase in *P* in this case is sufficient to account for the whole of the velocity increase.

These results should be compared with those of Baker and Nathan (*loc. cit.*), which they resemble very strikingly. The similarity of these two sets of results suggests that we are dealing with real departures from the generalisation mentioned above, and that changes in *P* may occur in cases where the substituent is at a point isolated from the centre of the reaction.

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