34. *Kinetics of the Bromination of Some Aromatic Amines.*

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Measurement of redox potentials has been used to follow the rate of bromination of *NN*-dialkylanilines in strongly acid solution, bromine concentrations in the range 10^{-3}—10^{-7}M being used. The observed rates decrease rapidly with increasing acid concentration, and by using the acidity functions of these solutions it is possible to evaluate second-order velocity constants for the reaction between bromine and the amine molecules: these lie in the range 10^6—10^{10} l. mole^{-1} sec.$^{-1}$. In some instances complications arise from complex formation between bromine and the amine cations.

Aromatic amines react very rapidly with aqueous bromine, and no reliable measurements have been made on the kinetics of this reaction. Francis [1] reported values for the relative rates of bromination of various anilines and phenols, based on competition experiments, but no attempt was made to control the acidity of the reaction mixture. Since it would be expected (and is borne out by our results) that an anilinium ion will react very much more slowly than an aniline molecule, little meaning can be attached even to his relative rates. Robertson and his co-workers [2] assessed the activity effect of the dimethylamino-group on the benzene ring at 5×10^{18}, a strongly deactivating group being used to obtain rates slow enough to be measured, but they give few kinetic results.

The present paper describes measurements of the rate of bromination of some *NN*-dialkylanilines. The second-order velocity constants obtained were in the range 10^{+6}—10^{+10} l. mole^{-1} sec.$^{-1}$, and two devices were used to obtain measurable rates. In the first place bromination was studied in concentrated aqueous acids (mostly 1—8M-sulphuric acid) in which only one part in 10^5—10^{10} of the amine is present as the reactive undissociated species. By adjusting the acid concentration, convenient rates can be obtained with a wide range of amines. In the second place the disappearance of bromine was followed by observing the redox potential of the solution, thus making it possible to use low initial concentrations and to follow a rapid change of bromine concentration through several powers of ten (normally in the range 10^{-3}—10^{-7}M).

Experimental

The amines were B.D.H. products, redistilled before use. All the inorganic reagents were of AnalaR grade, and the concentration of the acid solutions was checked by titration with standard alkali. Reactions were carried out at 25° ± 0·01° in a 150-c.c. beaker closed by a rubber stopper and fitted with a stirrer rotating at 1500 r.p.m. The beaker contained amine dissolved in acid, together with some potassium bromide, and the reaction was started by breaking a bulb containing 1 c.c. of a bromide–bromate solution. The bromide concentration was the same in the two solutions, and the usual initial concentrations were $[Br_2] = 0{\cdot}003$M, [amine] = 0·005—0·03M. In the strongly acid conditions used in our experiments the formation of bromine from bromate is almost instantaneous,[3] and identical results were obtained if the bulb contained bromine water or chloramine-T in place of bromate. Blank experiments

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[1] Francis, *J. Amer. Chem. Soc.*, 1925, **47**, 2340.

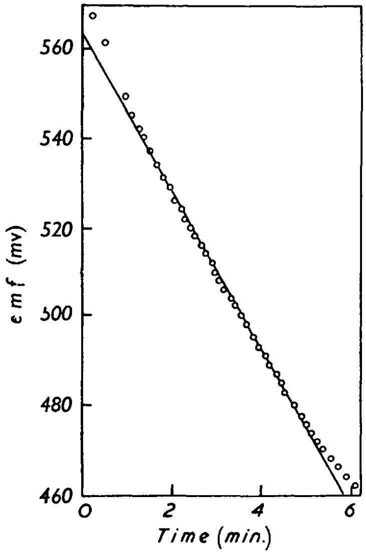
[2] Robertson, de la Mare, and Swedlund, *J.*, 1953, 782.

[3] See " Tables of Chemical Kinetics," N.B.S. Circular 510, 1951, p. 669.

showed that loss of bromine by evaporation is negligible during the short times involved, and the results were not affected by the exclusion of light.

The redox potential of the solution was followed by a platinum gauze electrode, which was periodically cleaned by heating it in concentrated nitric acid. Ideally the comparison electrode should be chosen so as to avoid a liquid junction and various forms of silver–silver bromide and mercury–mercurous bromide electrodes were tried. However, these were not sufficiently stable under our conditions of high acidity and violent stirring, and the final measurements were made with a calomel half-cell having a side-arm dipping in the reaction solution and drawn to a fine point. This gave stable potentials during the duration of an experiment (2—30 min.), and the uncertain junction potential is no disadvantage since we are concerned only with the change in e.m.f. and not with its absolute value. The e.m.f. was measured by a Tinsley potentiometer, and all leads had earthed shields.

The Figure shows the course of a typical experiment. After an initial curved portion the e.m.f. varies linearly with time over a range of 60 mv, corresponding to a hundredfold variation in the bromine concentration. The concentration of bromide is effectively constant during each reaction, so that the e.m.f. is given by $E = E_0 + \frac{\boldsymbol{RT}}{\boldsymbol{2F}} \ln \frac{[\mathrm{Br_2}]}{[\mathrm{Br^-}]^2} = E_0{}^1 + 0{\cdot}0295 \log [\mathrm{Br_2}]$: hence the linearity of the plot of E against t shows that the reaction is kinetically of the first order with respect to bromine. The initial curvature of this plot corresponds to a decrease in the amine concentration, but since 90% of the initial bromine has disappeared when the initial e.m.f. has fallen by 30 mv, the amine concentration is effectively constant beyond this point. Finally, when the bromine concentration has fallen below about 10^{-6}—10^{-7}M the e.m.f. begins to change more slowly, and eventually becomes constant. This is no doubt because the bromine concentration is no longer sufficient to poison the electrode, whose potential will begin to be controlled by some other system, for example the organic redox system represented by $\mathrm{RH} + \mathrm{Br^-} \rightleftharpoons \mathrm{RBr} + \mathrm{H^+} + 2e$. Other possibilities are that dissolved oxygen is affecting the potential, or that there is an oxide layer on the platinum causing it to behave as a hydrogen-ion electrode. The point at which the linearity ceased varied from one experiment to another, and was not always reproduced on repeating an experiment: however, a linear portion corresponding to a variation of several powers of ten in bromine concentration was almost always present, and its failure to appear indicated that the electrode needed cleaning.



The analytical concentration of bromine in the solution can be written as $[\mathrm{Br_2}]_a = [\mathrm{Br_2}] + [\mathrm{Br_3}^-] = [\mathrm{Br_2}]\{1 + K[\mathrm{Br^-}]\}$, where the equilibrium constant $K = 17{\cdot}8$ at 25°.[4] In a given experiment we can define an observed first-order velocity constant k_1 by

$$k_1 = \mathrm{d} \ln [\mathrm{Br_2}]_a/\mathrm{d}t = \mathrm{d} \ln [\mathrm{Br_2}]/\mathrm{d}t = 0{\cdot}0782\ \mathrm{d}E/\mathrm{d}t \quad . \quad . \quad . \quad . \quad . \quad (1)$$

with E in mv. For a given amine k_1 will depend on the amine concentration c, the acidity of the medium, and the bromide concentration. Dependence on the two last factors will be controlled by the relative reactivities of the various species present, but *ceteris paribus* k_1 should be directly proportional to c. If n molecules of bromine react with one of amine, the value of c appropriate to the linear portion of the E against t curve is $c_0 - \frac{1}{n}[\mathrm{Br_2}]_a{}^0$, c_0 and $[\mathrm{Br_2}]_a{}^0$ representing initial concentrations. For all the reactions studied here $n = 1$. This was established by isolating the monobromo-derivatives (with the bromine atom *para* to the amino-group) in larger-scale experiments, and also by kinetic experiments in which one molecule of bromine was first allowed to react: when a second molecule of bromine was added the e.m.f.

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[4] Griffith, McKeown, and Winn, *Trans. Faraday Soc.*, 1932, **28**, 101.

did not change faster than could be accounted for by evaporation. Plots of k_1 against $c_0 - [Br_2]_a^0$ were in fact linear, and the slope of these plots was used to obtain an apparent second-order constant k_2*, defined by

$$k_2^* = \frac{k_1}{c} = \frac{0{\cdot}0782\ \mathrm{d}E/\mathrm{d}t}{c_0 - [\mathrm{Br}_2]_a^0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The observed values of k_2* are tabulated in the following sections.

Our interpretation of the kinetic measurements depends on the assumption that the equilibria $Br_3^- \rightleftharpoons Br_2 + Br^-$ and $AH^+ + H_2O \rightleftharpoons A + H_3O^+$ (A = amine) are re-established rapidly compared with the bromination reactions being studied. While there is no direct evidence to support this assumption, it seems extremely probable. Both of these reactions are endothermic, but only to the extent of a few kcal./mole, and it is unlikely that their activation energies exceed this value.

In addition to the kinetic measurements, optical measurements were made in order to study the initial interaction between bromine and the amine solutions. These were carried out at room temperature, a Unicam spectrophotometer model S.P. 500 being used with 1-cm. quartz cells.

RESULTS

Complex Formation between Bromine and Amines.—This subject will be dealt with here only in so far as it represents a complicating factor in the kinetic measurements, and a fuller study will be reported later. In an attempt to study spectrophotometrically the slow reaction between bromine and *p*-bromo-*NN*-dimethylaniline in 0·5M-sulphuric acid, it was found that the usual bromine peak at 3950 Å was gradually replaced by one at 4650 Å, which then slowly disappeared as bromination progressed. This suggests that most of the bromine reacts with amine to form a complex, with the result that the normal bromination reaction is greatly retarded. The effect is diminished by an increase of bromide concentration, but is almost independent of acid concentration in the range 0·5—6M-sulphuric acid, suggesting that the amine cation is involved. There are many examples of the formation of solid addition complexes between bromine and aromatic amines, *e.g.*, by pyridine and quinoline, respectively[5] $(C_5H_5N)_2HBr,Br_4$ and C_7H_7N,Br_4. Higher concentrations of *p*-bromo-*NN*-dimethylaniline and bromine produced a red precipitate which decomposed without melting at 85° and contained two molecules of bromine per molecule of amine. It liberated iodine from potassium iodide, and reacted with sodium hydrogen sulphite to re-form the original amine. It is interesting to note that the absorption spectrum of aqueous bromine is not modified by acid solutions of pyridine, quinoline, tetramethylammonium bromide, or trimethylphenylammonium bromide, although all these substances form solid addition compounds with bromine.

We shall not discuss here the probable structures of these complexes, as solids or in solution, but shall summarise briefly the results of spectrophotometric observations on various amine solutions immediately after adding 0·003M-bromine. The bromide concentration was 0·025M throughout, and the medium 6M-sulphuric acid. The *NN*-dialkyltoluidines gave no evidence of complex formation at amine concentrations of 0·01M, though they did so at 0·1M. *NN*-Dimethylaniline exhibited some complex formation even at 0·01M, but this disappeared as soon as the amine concentration had been reduced considerably by the normal bromination reaction. *NN*-Diethylaniline showed a strong peak attributable to complex formation, and this disappeared very slowly even with more dilute amine solutions: for this reason it has not proved possible to obtain a reliable value for the rate of bromination of this compound. The very slow rate observed either potentiometrically or spectrophotometrically may be due to the low concentration of free bromine present, or it may represent a slow reaction between the complex and an amine molecule. In any event it cannot be compared directly with the rates observed with the other amines which, on the above evidence, should not be materially affected by complex formation.

Measurements were also made to compare the absorption spectrum of bromine in water and in 6M-sulphuric acid: no difference was found. Similar experiments in hydrochloric acid gave evidence of the equilibrium $Br_2 + Cl^- \rightleftharpoons Br_2Cl^-$, with an equilibrium constant of about 0·6, which is less than the value 1·4 derived from partition measurements.[6] Most of the kinetic

[5] Grimaux, *Bull. Soc. chim. France*, 1882, **38**, 124.

[6] Dancaster, *J.*, 1924, 2039; Ray and Sarkar, *J.*, 1922, 1453.

experiments were therefore carried out in sulphuric acid to avoid complications due to formation of halide complex. The equilibrium $Br_2 + Br^- \rightleftharpoons Br_3^-$ was also studied spectrophotometrically in 6M-sulphuric acid, giving an equilibrium constant of about 13. This is appreciably lower than 17·8, the value for dilute aqueous solutions, but since we have no information about its variation with acid concentration we have preferred to use $K = 17{\cdot}8$ in the subsequent discussion.

Kinetic Results.—Most of the kinetic experiments were done with a bromide concentration of either 0·025M or 0·5M, and a range of acid concentrations. At each acid concentration several amine concentrations in the range 0·005—0·03M were usually investigated, but when complex formation was suspected only concentrations below 0·01M were used, and in a few instances the velocity constant is based on experiments at 0·01M only. The initial bromine concentration was normally 0·003M. The results for sulphuric acid solutions are given in Table 1, the values of the acidity function H_0 being interpolated from the results of Hammett and Paul.[7]

TABLE 1. *Bromination in sulphuric acid solution.*

a = acid concentration, moles/l. of solution. k_2^* = apparent second-order velocity constant, mole^{-1} sec.$^{-1}$ (cf. eqn. 2). A, [Br$^-$] = 0·025; B, [Br$^-$] = 0·5.

NN-*Dimethylaniline*

	A						*B*				
a	4·96	5·73	5·94	6·24	6·31	6·76	4·88	5·44	6·09	6·09	7·13
$-H_0$	2·11	2·47	2·57	2·74	2·78	3·02	2·08	2·33	2·66	2·66	3·22
k_2^*	30·9	11·6	9·12	5·32	2·57	2·22	16·8	6·83	2·32	2·76	0·48

NN-*Dimethyl*-o-*toluidine*

	A				*B*			
a	1·45	1·96	2·55	3·07	1·04	1·40	1·40	2·10
$-H_0$	0·37	0·66	0·99	1·24	0·13	0·35	0·35	0·76
k_2^*	3·16	2·76	1·18	0·66	3·77	2·15	2·61	0·82

NN-*Dimethyl*-m-*toluidine*

	A				*B*					
a	6·25	6·69	7·07	8·35	5·53	5·90	6·27	6·53	6·53	6·91
$-H_0$	2·74	2·99	3·20	3·90	2·38	2·55	2·76	2·90	2·90	3·12
k_2^*	6·59	3·42	2·82	0·32	13·7	7·50	3·20	3·11	3·36	1·69

NN-*Dimethyl*-p-*toluidine*

	A				*B*			
a	4·89	5·64	6·30	6·30	4·03	4·89	5·92	6·70
$-H_0$	2·08	2·44	2·77	2·77	1·67	2·08	2·57	2·99
k_2^*	6·57	2·48	0·77	0·85	20·4	4·13	0·76	0·12

NN-*Diethyl*-o-*toluidine*

	A					*B*		
a	0·255	0·510	1·05	1·44	1·99	1·03	1·51	1·88
$-H_0$	−0·56	−0·23	0·13	0·37	0·69	0·12	0·41	0·63
k_2^*	0·821	0·361	0·102	0·056	0·023	0·073	0·035	0·020

NN-*Diethyl*-m-*toluidine*

	A						*B*			
a	2·56	3·11	3·95	3·95	4·89	5·72	1·91	1·91	3·12	4·89
$-H_0$	0·99	1·24	1·61	1·61	2·09	2·47	0·64	0·64	1·44	2·09
k_2^*	110	35·2	8·75	10·6	2·13	0·59	89·8	87·0	14·3	1·04

NN-*Diethyl*-p-*toluidine*

	A			*B*			
a	3·05	3·55	3·95	1·82	2·26	2·77	3·16
$-H_0$	1·22	1·44	1·64	0·59	0·84	1·09	1·30
k_2^*	6·58	3·36	1·78	18·7	6·50	4·07	2·45

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[7] Hammett and Paul, *J. Amer. Chem. Soc.*, 1934, **56**, 827.

DISCUSSION

All the results in Table 1 show that the reaction velocity decreases sharply with increasing acidity, as would be expected if the only reacting species were the amine molecule. Since the amines were present mainly as cations in all the solutions used, this implies on the simplest view that for a given amine and bromide concentration a plot of $\log_{10} k_2^*$ against H_0 should give a straight line of unit slope. These plots are all approximately linear, but their slopes are appreciably greater than unity, the average value being 1·20.

Slopes of greater than unity have been frequently found in logarithmic correlations between acidity functions and the rates of acid-catalysed reactions,[8] and have been reasonably attributed to the limitations of the arguments on which such correlations are based, notably the differences in chemical type between the reacting molecule and the indicators used in measuring the acidity functions. However, this explanation cannot apply here, since both the kinetic work and the measurements of acidity functions involve aromatic amines. Moreover, in the bromination reactions the acidity is not directly concerned in the reaction kinetics, but serves to reduce the concentration of reactive species by way of a pre-equilibrium so that a slope of unity seems particularly likely. A tertiary amine has not so far been used for measuring H_0, but measurements in this laboratory [9] with *NN*-dimethyl-2 : 4-dinitroaniline in sulphuric acid between 2M and 5M gave acidities parallel with those obtained by using *o*-nitroaniline or 4-chloro-2-nitroaniline: thus the usual acidity functions should apply to the tertiary amines used in our experiments.

If it is assumed that the concentration of undissociated amine is in fact inversely proportional to h_0 ($H_0 = -\log h_0$), then the exponent of 1·2 can only be attributed to a medium effect on the velocity constant of the bromination reaction. This interpretation is quite reasonable in view of the high concentrations of acid involved, and is confirmed by kinetic experiments in solutions of perchloric and phosphoric acids, where the medium effect is likely to be different. The rates in these solutions were in fact 25—100% higher than in sulphuric acid of the same acidity, the actual value depending upon the acid concentration and the nature of the amine.

In using our kinetic data as a direct measure of the reactivity of the amines it is necessary to assume that the amine cations are not brominated at an appreciable rate. Bromination experiments with trimethylphenylammonium bromide showed a rate of disappearance of bromine not significantly greater than the loss by evaporation in a blank experiment. Although the concentration of cations in our experiments is of the order of 10^6 greater than that of the undissociated amine, it would be surprising if it made a measurable contribution to the bromination rate. Robertson [2] has estimated the activating effect of the dimethylamino-group in the benzene ring as 5×10^{18}, and in the dimethylphenylammonium ion this activating effect is replaced by a powerful deactivation. It may be noted that any measurable bromination of cations would decrease the slopes of the plots of $\log k_2^*$ against H_0, and could not account for the observed slopes of greater than unity.

To obtain comparable values for the reactivities of the different amines we have used values of k_2^* at $H_0 = -1{\cdot}43$ (3·5M-sulphuric acid) interpolated or extrapolated from the data in Table 1, a slope of 1·20 being used throughout for the plot of $\log k_2^*$ against H_0. These values, $(k_2^*)_{1\cdot43}$, are given in the second and the third column of Table 2. The second-order velocity constants k_2 for the bromination of the amine in 3·5M-sulphuric acid are then given by the relation $\log k_2 = \log (k_2^*)_{1\cdot43} + \mathrm{p}K_a + 1{\cdot}43$, where $\mathrm{p}K_a$ refers to the acid dissociation of the amine cation. These velocity constants are given in the last

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[8] *E.g.*, Bell and Brown, *J.*, 1954, 774; Bell, Bascombe, and McCoubrey, *J.*, 1956, 1286; Gold and Hilton, *J.*, 1955, 843; Gold and Satchell, *J.*, 1955, 2622; 1956, 1635; Long and McIntyre, *J. Amer. Chem. Soc.*, 1954, **76**, 3240.

[9] Bell and Bascombe, to be published.

two columns of Table 2. The pK_a values are taken from the work of Hall and Sprinkle,[10] except that for *NN*-diethyl-*m*-toluidine, which was determined by measuring the optical density of the base in acid solution, in alkaline solution, and in phosphate buffer solutions of pH 6·47, 6·81, and 7·17. The measurements were made with a Unicam S.P. 500 spectrophotometer, at 2550 Å, which corresponds to a peak in the absorption curve of the undissociated amine.

TABLE 2.

Amine	pK_a	log $(k_2^*)_{1\cdot43}$		log k_2	
	$[Br^-]$ =	0·025	0·5	0·025	0·05
NN-Dimethylaniline	5·06	2·29	1·95	8·84	8·50
NN-Dimethyl-*o*-toluidine	5·86	−0·50	−0·96	6·87	6·39
NN-Dimethyl-*m*-toluidine	5·24	2·48	2·29	9·21	9·02
NN-Dimethyl-*p*-toluidine	5·50	1·56	1·31	8·55	8·30
NN-Diethyl-*o*-toluidine	7·18	−2·54	−2·69	6·13	5·98
NN-Diethyl-*m*-toluidine	7·12	1·19	1·02	9·80	9·63
NN-Diethyl-*p*-toluidine	7·09	0·56	0·24	9·12	8·80

The velocity constants k_2 in Table 2 refer to the total bromine in the solution, which is present almost exclusively as Br_2 or Br_3^-. The concentrations of HOBr (a less active brominating agent) are very small, and it can easily be shown that H_2OBr^+ cannot be present in kinetically significant amounts. If k_2' and k_2'' are the second-order velocity constants for the reaction of Br_2 and Br_3^- with the amine, then k_2 is given by

$$k_2 = (k_2' + k_2''K[Br^-])/(1 + K[Br^-]) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $K = [Br_3^-]/[Br_2][Br^-] = 17{\cdot}8$. It should be possible to test this equation by measurements over a wide range of bromide concentrations. However, as shown by Table 2, the effect of bromide concentration is not large, and extensive and accurate measurements would be required: moreover, the interpretation would be complicated by salt effects, uncertainty as to the value of K in the sulphuric acid media, and also the possibility of small effects due to formation of complex between bromine and the amine. We have therefore confined ourselves to measurements at the two bromide concentrations 0·025M and 0·5M, and Table 2 shows that the ratio of the velocities in these two solutions has the average value 1·8 : 1. Inserting this in eqn. 3 gives $k_2'/k_2'' \simeq 3$: this is similar to the ratios found by Bell and Spiro [11] for the reaction of Br_2 and Br_3^- with the enol and the anion of ethyl malonate. In our experiments in 0·025M-bromide, k_2 will be about 80% of k_2', and these values of k_2 are thus a good measure of both the absolute and the relative rates of reaction between Br_2 and the amine molecules.

The values of k_2 are all in the range 10^6—10^{10} l. mole^{-1} sec.$^{-1}$ and thus represent extremely rapid reactions. By comparison with the rate of bromination of aromatic hydrocarbons [12] we can assess the activating power of the diethylamino- and dimethylamino-groups on the aromatic ring as about 10^{16}—10^{17}, though the comparison is not strictly valid, since the measurements refer to different solvents. This figure may be compared with 5×10^{18} estimated by Robertson [2] indirectly.

Several of the velocity constants in Table 2 are close to the values which would be expected in a collision reaction having zero activation energy. Solution reactions in this class would normally be regarded as diffusion-controlled, since the reaction rate is high enough to disturb the random spatial distribution of the reactants. However, these considerations do not apply here, since the reacting amine molecules are in dynamic equilibrium with a much larger concentration of amine cations, and the normal distribution of collisions will not be appreciably disturbed by the reaction.

NN-Dimethyl-*m*-toluidine reacts about twice as fast as *NN*-dimethylaniline, which

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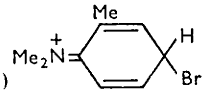
[10] Hall and Sprinkle, *J. Amer. Chem. Soc.*, 1932, **54**, 3469.

[11] Bell and Spiro, *J.*, 1953, 429.

[12] Data collected by Robertson *et al.*, ref. 2.

may be attributed to the presence of a methyl group *ortho* to the point of substitution. In *NN*-dimethyl-*p*-toluidine the methyl group blocks the normal point of attack, and the lower velocity refers to substitution in the less reactive *ortho*-position, weakly activated by the methyl group. *NN*-Dimethyl-*o*-toluidine reacts about 100 times more slowly than the other dimethylanilines: this is presumably because the methyl group hinders the attainment of a planar configuration in a transition state such as (X). The same effect is apparent, though to a smaller extent, in the higher pK_a value of dimethyl-*o*-toluidine, where steric hindrance will diminish the resonance stabilisation of the amine molecule.



(X)

NN-Diethyl-*m*-toluidine and *NN*-diethyl-*p*-toluidine are more reactive than the corresponding dimethyl-compounds, though the differences are not so great as in the pK_a values. On the other hand, *NN*-diethyl-*o*-toluidine reacts about four times more slowly than the dimethyl-compound, presumably because of the greater steric effect of the ethyl groups.

We thank the Department of Scientific and Industrial Research for a maintenance grant and the Royal Society for the award of a Jaffé Studentship to one of us (E. N. R.).

PHYSICAL CHEMISTRY LABORATORY, OXFORD. [*Received, August 7th,* 1957.]