Kinetic and Mechanistic Studies of Reactions of Aniline and Substituted Anilines with Chloramine T

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Rates of reactions of aniline and substituted anilines with chloramine T (CAT) to form *N*-chloroanilines have been measured. Each reaction showed first-order dependence on CAT and fractional order dependence on the amine. The latter observation indicates that the reaction involves formation of a complex in a fast equilibrium step followed by slow decomposition of the complex. The equilibrium constant (K) for the formation of the complex and its decomposition rate constant (k_2) in each case have been calculated from the plot of $1/k_{obs}$ *versus* 1/[amine]. In addition, the reaction constant (ρ −0.976, obtained from a Hammett plot) and thermodynamic parameters have been evaluated, and mechanisms are proposed.

THERE have been a number of studies on the reactions between amines and halogenating agents.[1-10] The reactions of primary and secondary amines with hypohalites produce *N*-halogeno-amines.[1-4,6,8] However, no study has yet appeared on the reactions of amines with chloramine T (CAT), a well known oxidant [11-20] and chlorinating [21-24] agent. The present investigation deals with the kinetics and mechanism of formation of *N*-chloroanilines in reactions of aniline and substituted anilines with CAT.

RESULTS AND DISCUSSION

Dependence of the Reaction Rate on [CAT].—Reactions were carried out in buffered (pH 7.4) ethanol (50% v/v) medium with the amine in large excess. The order of reaction with respect to CAT was unity, from a linear plot of log [CAT] *versus* time up to at least 60% completion of the reaction in each case. The constancy of k_{obs} for different initial concentrations of CAT calculated from the integrated first-order rate equation (Table 1)

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[1] (*a*) F. D. Chattaway and K. J. P. Orton, *J. Chem. Soc.*, 1901, **79**, 461; (*b*) K. J. P. Orton and W. J. Jones, *ibid.*, 1909, **95**, 1456.

[2] D. R. Pryde and F. G. Soper, *J. Chem. Soc.*, 1931, 1510.

[3] I. Weil and J. C. Morris, *J. Amer. Chem. Soc.*, 1949, **71**, 1664.

[4] W. E. Bachmann, M. P. Cava, and A. S. Dreiding, *J. Amer. Chem. Soc.*, 1954, **76**, 5554.

[5] S. Dunstan and H. B. Henbest, *J. Chem. Soc.*, 1957, 4905.

[6] T. Higuchi, U.S. Dept. Commerce Office Technical Rev. AD, 1962, No. 412,343 (*Chem. Abs.*, 1964, **60**, 9115g).

[7] T. Higuchi and J. Hasegawa, *J. Phys. Chem.*, 1965, **69**, 796.

[8] P. Haberfield and D. Paul, *J. Amer. Chem. Soc.*, 1965, **87**, 5502.

[9] D. G. Lee and R. Srinivasan, *Canad. J. Chem.*, 1973, **51**, 2546.

[10] Y. Ogata and K. Nagura, *J.C.S. Perkin II*, 1974, 1089.

[11] D. S. Mahadevappa and H. M. K. Naidu, *Talanta*, 1973, **20**, 349.

[12] S. Pinzauti, V. D. Piaz, and E. LaPorta, *J. Pharm. Sci.*, 1974, **63**, 1446.

[13] V. M. Sadagopa Ramanujam and N. M. Trieff, *Analyst*, 1975, **100**, 655, and references cited therein.

[14] J. Coull, H. B. Hope, and B. Gouguell, *J. Amer. Chem. Soc.*, 1935, **57**, 1489.

[15] M. C. Agrawal and S. P. Mushran, *J. Phys. Chem.*, 1971, **75**, 838.

[16] S. P. Mushran, M. C. Agrawal, and B. Prasad, *J. Chem. Soc.*, 1971, 1712.

[17] M. C. Agrawal and S. P. Mushran, *J. Chem. Soc.*, 1973, 762.

[18] D. S. Mahadevappa and H. M. K. Naidu, *Austral. J. Chem.*, 1974, **27**, 1203.

[19] F. Ruff and A. Kucksman, *J.C.S. Perkin II*, 1975, 509.

[20] M. M. Natarajan and V. Thiagarajan, *J.C.S. Perkin II*, 1975, 1590.

[21] F. G. Soper and G. F. Smith, *J. Chem. Soc.*, 1926, 1582.

[22] T. Higuchi and A. Hussain, *J. Chem. Soc.* (*B*), 1967, 549.

[23] J. M. Antelo, J. M. Cachaza, J. Casado, and M. A. Herraez, *Anales de Quim.*, 1974, **70**, 461.

[24] V. Balasubramanian and V. Thiagarajan, *Internat. J. Chem. Kinetics*, 1975, **7**, 605.

gave further evidence for the first-order dependence on CAT.

Dependence on [Amine].—The dependence of the rate on the concentrations of the various anilines is summarised in Table 1 (amine concentrations in the range 0.01—0.05M). An increase in [amine] without change in [CAT] increases the rate of the reaction. However, the linearity of a plot of log k_{obs} *versus* log [amine] shows that the order with respect to the amine is fractional and less than one, for each amine studied (Table 1), indicating a complex dependence of rate on [amine]. The data also yield a linear plot of $1/k_{obs}$ against 1/[amine] (Figure 1). This suggests a rate law (derived by applying the steady-state principle[25]) of the form (1), when [amine] is large

$$-d[\mathrm{CAT}]/dt = k_2K[\mathrm{amine}][\mathrm{CAT}]/(1 + K[\mathrm{amine}]) \quad (1)$$

in comparison with [CAT]. This behaviour is typical of a reaction proceeding through some intermediate complex prior to the rate-limiting step.[26-29] This hypothesis is strengthened by the fact that changes of colour were observed prior to the formation of products. The absorption maximum for the coloured intermediate was at 530 nm.

TABLE 1

Rate data ($10^4k_{obs}/s^{-1}$) for the reactions of aniline and substituted anilines with CAT; temp. 30 °C; solvent 50% ethanol (v/v); pH 7.4; [CAT] 0.002M

	[amine]/M						Order *
Aniline	0.01	0.015	0.020	0.030	0.040	0.050	w.r.t. amine
Unsubst. (1)	4.03	5.24	6.15	7.41	8.33 (8.48,[a] 8.38[b])	8.93	0.56
p-Chloro (2)	2.11	2.79	3.32	4.08	4.65 (4.82,[a] 4.62[b])	5.06	0.60
p-Bromo (3)	1.79	2.42	2.88	3.61	4.08	4.50	0.64
p-Iodo (4)	2.82	3.66	4.32	5.21	5.88	6.29	0.56
p-Cyano (5)	0.917	1.21	1.38	1.70	1.89 (1.84,[a] 1.87[b])	2.04	0.48
p-Nitro (6)	0.763	0.980	1.15	1.38	1.60 (1.67,[a] 1.64[b])		0.57
p-Methyl (7)	4.43	5.95	7.14	8.93	10.2 (10.3,[a] 10.0[b])	11.1	0.64
p-Methoxy (8)	6.10	8.00	9.62	11.8	13.7 (13.5,[a] 13.9[b])	14.9	0.56
m-Chloro (9)	1.67	2.16	2.54	3.18	3.45	3.77	0.51
m-Bromo (10)	1.56	2.00	2.44	2.90	3.23 (3.20,[a] 3.25[b])	3.57	0.52
m-Iodo (11)	1.75	2.33	2.69	3.45	3.70	4.08	0.51
m-Cyano (12)	1.28	1.67	1.96	2.38	2.65 (2.60,[a] 2.68[b])	2.84	0.49
m-Nitro (13)	0.833	1.09	1.25	1.40	1.53 (1.50,[a] 1.52[b])		0.42
m-Methyl (14)	3.92	5.26	6.33	7.69	8.92	9.52	0.56
p-Sulphamoyl (15)	1.32	1.64	1.91	2.19	2.42 (2.38,[a] 2.45[b])		0.43

* Determined from the plot of log k_{obs} *versus* log [amine]. [a] [CAT] 0.004M. [b] [CAT] 0.006M.

From the intercept (equal to $1/k_2$) and slope of the double reciprocal plot in Figure 1, k_2, the decomposition constant, and K, the equilibrium constant for formation of the complex, were calculated in each case (Table 2). For all further discussion, only the decomposition constant values will be taken into consideration, since there is little variation in K for the various amines.

Effect of Changing the Solvent Composition.—The reaction rate is considerably affected by the solvent composition; *e.g.* increasing the proportion of ethanol in ethanol–water decreases the rate.

According to Landskroener and Laidler,[30] for a bimolecular reaction the general equation relating the effect of dielectric constant (D) to reaction velocity is (2),

$$\ln k' = \ln k'_0 + \frac{e^2}{2\kappa T}\left(\frac{1}{D} - 1\right)\left[\frac{Z_A^2}{b_A} + \frac{Z_B^2}{b_B} - \frac{(Z_A + Z_B)^2}{b_\ddagger}\right] + \frac{3e^2}{8\kappa T}\left(\frac{2}{D} - 1\right)\left[\frac{G_A}{b_A^3} + \frac{G_B}{b_B^3} - \frac{G_\ddagger}{b_\ddagger^3}\right] \quad (2)$$

where k' is the observed specific velocity constant, k_0' is the specific velocity constant at the reference dielectric constant ($D = 1$); Z_A and Z_B are the valences of the reactants A and B; b_A, b_B, and $b_\ddagger$ are the effective radii and G_A, G_B, and $G_\ddagger$ the complex functions of the charges and structures of the reactants A and B and intermediate, respectively; and κ is the Boltzmann constant.

TABLE 2

Decomposition constant (k_2) values for aniline and substituted anilines in the temperature range 25—50 °C with equilibrium constant (K) data at 30 °C; solvent 50% ethanol (v/v)

	$10^4k_2/s^{-1}$					
Aniline	25 °C	30 °C	40 °C	50 °C	σ	K/ l mol^{-1}
Unsubst. (1)	10.8	12.8	20.4	30.2	0	45.4
p-Chloro (2)	6.17	7.87	12.4	19.1	+0.227	36.6
p-Bromo (3)	5.63	7.19	11.8	17.8	+0.232	34.8
p-Iodo (4)	7.50	9.09	15.0	21.9	+0.180	44.9
p-Cyano (5)	2.22	2.89	5.37	9.08	+0.660	46.8
p-Nitro (6)	1.68	2.33	4.27	7.42	+0.778	48.8
p-Methyl (7)	15.3	18.2	26.9	37.2	−0.170	33.1
p-Methoxy (8)	21.1	24.6	34.7	45.2	−0.268	31.7
m-Chloro (9)	4.22	5.63	9.55	15.3	+0.373	41.5
m-Bromo (10)	3.81	5.13	8.88	14.5	+0.391	43.7
m-Iodo (11)	4.74	6.17	10.5	16.2	+0.352	39.9
m-Cyano (12)	3.02	4.08	7.08	11.9	+0.560	46.0
m-Nitro (13)	1.88	2.58	4.70	7.95	+0.710	46.9
m-Methyl (14)	13.5	15.5	23.2	33.2	−0.069	34.5
p-Sulphamoyl (15)	2.14	3.39	6.31	12.0	+0.570	64.3

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[25] A. A. Frost and R. G. Pearson, ' Kinetics and Mechanism,' Wiley, New York, 1956, pp. 95—99, 179—183.

[26] F. R. Duke, *J. Amer. Chem. Soc.*, 1947, **69**, 2885, 3054.

[27] M. Ardon, *J. Chem. Soc.*, 1957, 1811.

[28] D. Paquette and M. Zador, *Canad. J. Chem.*, 1968, **46**, 3507.

[29] T. R. Balasubramanian and N. Venkatasubramanian, *Indian J. Chem.*, 1971, **9**, 36.

[30] P. A. Landskroener and K. J. La dler, *Trans. Faraday Soc.*, 1956, **52**, 200.

For a reaction between two dipoles having no net charge, the solvent effect is given entirely by the last term. This equation predicts a linear dependence of ln k' on $1/D$,

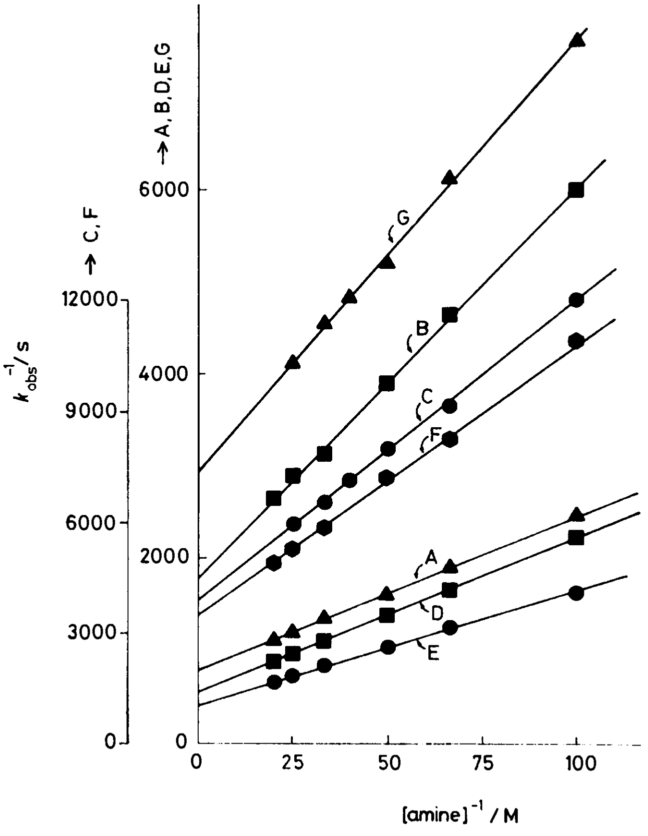

FIGURE 1 Plots of $1/k_{obs}$ *versus* 1/[amine]: A, aniline; B, *m*-chloroaniline; C, *m*-nitroaniline; D, *p*-toluidine; E, *p*-anisidine; F, *p*-aminobenzonitrile; G, *p*-aminobenzenesulphonamide (temp. 30 °C; solvent 50% ethanol; pH 7.4)

giving an explicit expression for the slope in terms of the charges, radii, and dipole moment.

For the limiting case of zero angle of approach between two dipoles, Amis [31,32] has derived expression (3) for the

$$\ln k'_D = \ln k'_{D=\infty} - 2\mu_1\mu_2/D\kappa Tr^3 \qquad (3)$$

velocity constant k'_D as a function of dielectric constant, where μ_1 and μ_2 are the dipole moments of the reactants. This equation also predicts a linear relation between ln k'_D and $1/D$; the slope of the line should be negative for the reaction between two dipolar molecules, whereas the corresponding equations for ion–dipole reactions give a positive slope. From the slope of such a plot, r ($= r_A + r_B$), the distance of approach for the two dipoles, can be calculated.

In the present investigation, the plot of log k_{obs} *versus* $1/D$ (dielectric constant values are taken from the literature [33,34]) is linear with a negative slope in each case (Figure 2), suggesting that CAT is reacting in a neutral and not an ionic form. Detailed quantitative aspects of this solvent influence, obtained by the application of the equations of Landskroener and Laidler [30] and of Amis [31,32] to the present system, will be reported elsewhere.

Effects of Substituents.—The decomposition constant data in Table 2 indicate that electron-releasing substituents (such as Me) on the benzene ring of the aniline accelerate the decomposition of the complex, whereas electron-withdrawing substituents (such as CN and NO_2) retard it. Hammett treatment (Figure 3) of the present data, using σ constants (taken from the literature [35,36]) yields a ρ value of -0.976 (r 0.997, S_a 0.031 8) at 30 °C. The σ values used for *p*-CN and *p*-$SO_2{\cdot}NH_2$ are the ordinary benzoic acid values and not the σ^- values normally associated with aniline reactions. The significance of the conformity of such substituents to the Hammett plot is discussed below.

Temperature Dependence and Thermodynamic Parameters.—Temperature dependence in the range 25—50 °C is shown in Table 2. From the Arrhenius plots (log k_2 *versus* $1/T$), all of which are linear, the activation energies (E_a) and the heats ($\Delta H^‡$) and entropies ($\Delta S^‡$) of activation have been evaluated (Table 3).

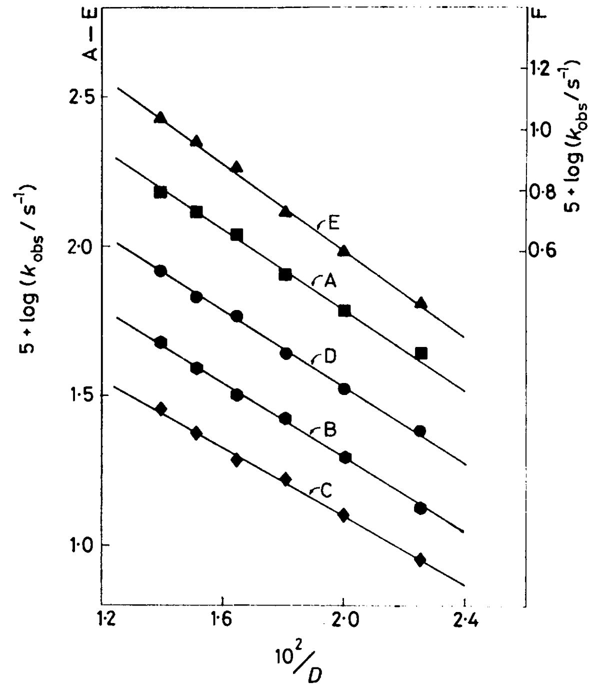

FIGURE 2 Plots of log k_{obs} *versus* $1/D$ in ethanol–water: A, aniline; B, *m*-aminobenzonitrile; C, *m*-nitroaniline; D, *p*-chloroaniline; E, *p*-anisidine; F, *p*-toluidine (temp. 30 °C; pH 7.4; [amine] 0.02M; [CAT] 0.002M)

Mechanism.—Chloramine T (*N*-chloro-*N*-sodiotoluene-*p*-sulphonamide trihydrate) acts as a two-electron oxidizing agent, giving toluene-*p*-sulphonamide (TSA).

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[31] E. S. Amis, *J. Chem. Educ.*, 1953, **30**, 351.

[32] E. S. Amis, *Analyt. Chem.*, 1955, **27**, 1672.

[33] G. Akerlof, *J. Amer. Chem. Soc.*, 1932, **54**, 4125.

[34] M. Balakrishnan, G. Venkoba Rao, and N. Venkatasubramanian, *Proc. Indian Acad. Sci.*, 1974, **80A**, 50.

[35] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.

[36] J. Hine, ' Physical Organic Chemistry,' McGraw-Hill, New York, 1962, p. 87.

The oxidation potential of the CAT–TSA system decreases with increase in pH of the medium.[37] Chlorination of phenols has been studied by several workers [21-24] in acid medium (pH 4—6.75); according to these authors

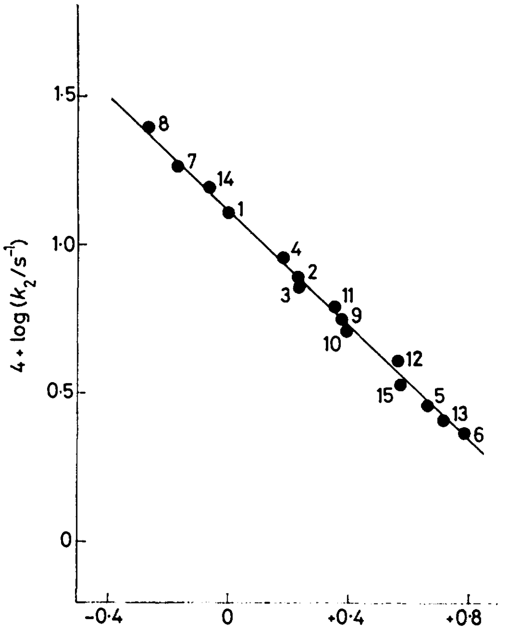
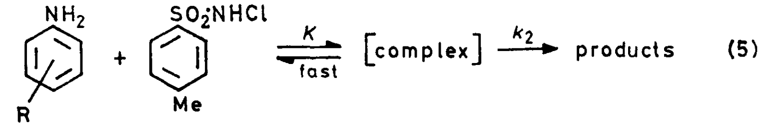


FIGURE 3 Correlation of decomposition constants with Hammett σ constants for *m*- and *p*-substituted anilines at 30 °C (numbering as in Table 2)

the effective chlorinating agent may be HOCl, dichloramine T (DCAT), or protonated *N*-chlorotoluene-*p*-sulphonamide. The disproportionation of *N*-chlorotoluene-*p*-sulphonamide (ClTSA) into DCAT and TSA has been studied by Higuchi *et al.*,[38] who observed that ClTSA does not disproportionate at higher pH values, so that in alkaline solution DCAT is not present.

To determine the actual species present in the aniline–CAT systems, we hoped to make comparable kinetic studies on the amine–HOCl and amine–DCAT systems, and compare the results with those for the amine–CAT system. However the kinetics of such reactions could not be followed since HOCl and DCAT are easily decomposed under the experimental conditions of this investigation (50% ethanol; pH 7.4) and the rates (k_{obs}) of such decompositions are similar to those of the reaction between amine and CAT. If either HOCl or DCAT were formed during these reactions, then the kinetics of the amine–CAT system would have been affected. That the reaction between amine and CAT is clean, giving highly reproducible rate constants in each case, shows clearly that neither HOCl nor DCAT is produced under the present conditions. Also, very little decomposition (1—2%) of CAT was observed over 30 h at 50 °C under the experimental conditions. Hence, one can conclude that the effective chlorinating species is ClTSA.



An observation supporting this proposal is the absence of reaction between CAT and acetanilide (containing an electron-withdrawing *N*-acetyl group) under the same conditions. This observation can be explained in terms of the equilibrium (4). The reverse

$$PhNHAc + p\text{-}MeC_6H_4{\cdot}SO_2{\cdot}NHCl \rightleftharpoons PhNClAc + p\text{-}MeC_6H_4{\cdot}SO_2{\cdot}NH_2 \quad (4)$$

reaction of equation (4) has already been observed by Pryde and Soper,[39] and must therefore be fast in comparison with the forward reaction.

TABLE 3

Thermodynamic parameters

Aniline	E_a/ kJ mol^{-1}	$\Delta H^\ddagger$/ kJ mol^{-1}	$-\Delta S^\ddagger$/ J mol^{-1} K^{-1}	$\Delta G^\ddagger$/ kJ mol^{-1}
Unsubst. (1)	31.4	28.9	197.2	88.7
p-Chloro (2)	36.8	34.3	183.3	90.0
p-Bromo (3)	39.3	36.8	175.8	90.0
p-Iodo (4)	35.6	33.1	186.3	89.6
p-Cyano (5)	45.6	43.1	162.8	92.5
p-Nitro (6)	47.7	45.2	157.4	92.9
p-Methyl (7)	28.9	26.4	202.6	87.9
p-Methoxy (8)	26.0	23.5	209.7	87.1
m-Chloro (9)	41.0	38.5	172.0	90.8
m-Bromo (10)	41.9	39.4	170.4	90.8
m-Iodo (11)	40.2	37.7	174.1	90.4
m-Cyano (12)	43.1	40.6	167.9	91.7
m-Nitro (13)	46.0	43.5	162.0	92.5
m-Methyl (14)	30.1	27.6	199.7	88.3
p-Sulphamoyl (15)	54.0	51.5	133.6	92.1

To summarize the conclusions from our study: (*a*) the reaction involves a 1 : 1 stoicheiometry ([amine] : [CAT]) (see Experimental section for details); (*b*) fractional order dependence on amine, indicating the formation of an intermediate complex; (*c*) a small negative ρ value; and (*d*) a decrease in rate with decreasing dielectric constant of the medium, suggesting a dipole–dipole interaction (CAT reacting in neutral form). The general mechanism (5) can thus be postulated. The intermediate complex and the subsequent movements of electrons may then be represented in detail as in Scheme 1 or 2. Possibly the intermediate complex involves some kind of loose association (probably electrostatic) between the slightly positive chlorine of the ClTSA molecule and the lone pair of electrons on the aniline nitrogen. This association should be strong enough to prevent delocalisation of the nitrogen lone pair into the ring, so

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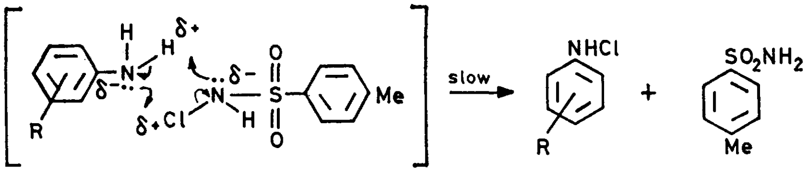
[37] A. R. V. Murthy and B. S. Rao, *Proc. Indian Acad. Sci.*, 1952, **35A**, 69.

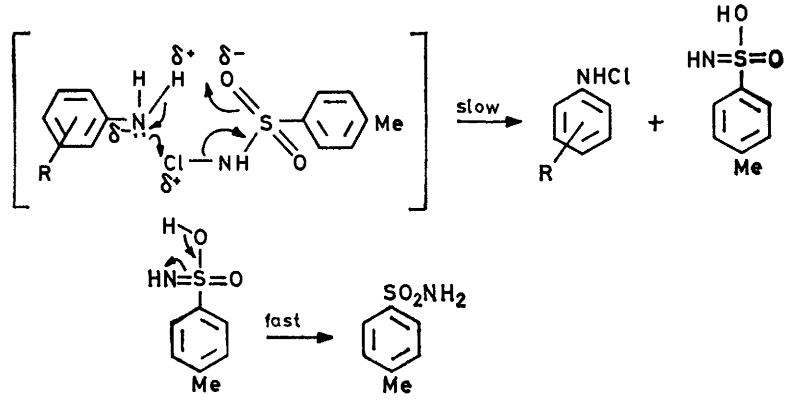
[38] T. Higuchi, K. Ikeda, and A. Hussain, *J. Chem. Soc.* (*B*), 1967, 546.

[39] D. R. Pryde and F. G. Soper, *J. Chem. Soc.*, 1931, 1514.

that subsequent passage to the transition state for decomposition to products does not give substituents such as p-NO_2, p-CN, and p-$SO_2{\cdot}NH_2$ any opportunity to exhibit substantial resonance effects. Passage to the transition state involves synchronous N–Cl bond making and N–H bond breaking in the aniline molecule, and *vice versa* in the ClTSA molecule. This mechanism is in accord with the small negative ρ value (slight dominance of N–Cl bond making in aniline). Also, the substantial negative entropies of activation and strongly positive free energy of activation suggest the important role of bond breaking in attaining the activated transition state complex (Table 3). Table 3 indicates that, while there is substantial variation in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ among the compounds studied, the values of $\Delta G^{\ddagger}$ are virtually constant, reflecting a constancy in K. In the absence of definitive evidence, a choice between Schemes 1 and 2 (involving four- and six-membered intermediates, respectively) can be only speculative.



SCHEME 1



SCHEME 2

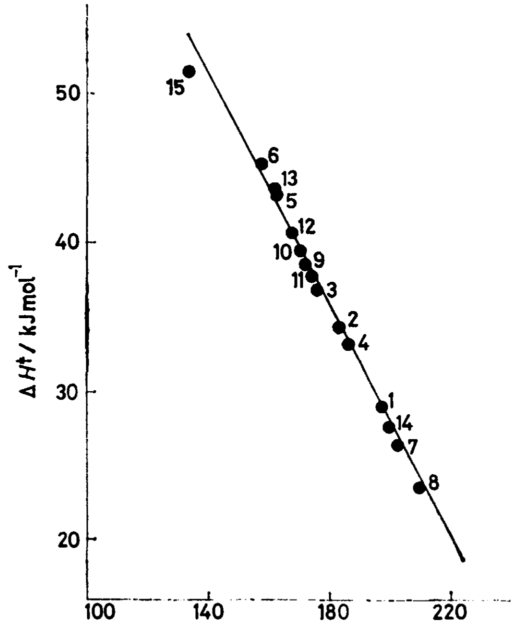


FIGURE 4 $\Delta H^{\ddagger}$ *versus* $-\Delta S^{\ddagger}$ for *m*- and *p*-substituted anilines (numbering as in Table 3)

Energy–Entropy Relationship.—With regard to heats and entropies of activation, it has been pointed out by Leffler [40] that these two variables are related by equation (6), where β is the isokinetic temperature. Figure 4

$$\Delta H^{\ddagger} = \Delta H_0^{\ddagger} + \beta \Delta S^{\ddagger} \qquad (6)$$

gives the least mean square (r 0.994) isokinetic plot ($\Delta H^{\ddagger}$ *versus* $-\Delta S^{\ddagger}$) for the reaction of aniline and its derivatives with CAT. The isokinetic temperature for this series is 115 °C. The fact that the isokinetic temperature is 65—90 °C apart from the experimental temperatures (25—50 °C) makes the isokinetic relationship valid [40] for this series. The correlation was found genuine by applying Exner's criteria.[41] However, current views [42-44] do not attach much physical meaning to the isokinetic temperature, since a linear correlation in equation (6) is usually a necessary condition for the validity of the Hammett equation.

EXPERIMENTAL

Materials.—Aniline and its derivatives (except p-iodoaniline) were all of analytical reagent grade (Eastman

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[40] J. E. Leffler, *J. Org. Chem.*, 1955, **20**, 1202.

[41] O. Exner, *Coll. Czech. Chem. Comm.*, 1964, **29**, 1094.

[42] J. E. Leffler, *J. Org. Chem.*, 1966, **31**, 533.

[43] O. Exner, *Coll. Czech. Chem. Comm.*, 1972, **37**, 1425.

[44] O. Exner and V. Beranek, *Coll. Czech. Chem. Comm.*, 1973, **38**, 781.

Kodak or Aldrich). *p*-Iodoaniline was prepared by iodination of aniline [45] and crystallized from light petroleum as needles, m.p. 62—63 °C.

CAT (Eastman Kodak) was freed from possible dichloro-contaminants by washing several times with carbon tetrachloride and dried in a vacuum desiccator ($CaCl_2$).

Kinetic Measurements.—All experiments were carried out under pseudo-first-order conditions by keeping [amine] large in comparison with [CAT]. The amine was accurately weighed out and transferred to a well stoppered flask. Ethanol (25 ml) and $NaOH-KH_2PO_4$ buffer [46] (pH 7.4; 25 ml) were added and the mixture was maintained at the required temperature. The solution of CAT (twice the initial concentration required) was prepared by taking the requisite amount in a 100 ml volumetric flask containing ethanol (50 ml) and $NaOH-KH_2PO_4$ buffer (pH 7.4; 50 ml) and maintained at the same temperature. The CAT solution (50 ml) was transferred quickly to the amine solution. The reaction was then followed by withdrawing samples (5 ml) and quenching in freshly prepared potassium iodide solution (5%; 5 ml). To the quenched solution, 5N-sulphuric acid (10 ml) was added and the liberated iodine was estimated with standard sodium thiosulphate in order to determine the concentration of unchanged CAT. A blank experiment was performed under identical conditions without the amine: negligible decomposition (1—2%) of CAT was noticed after 30 h at 50 °C.

The first-order rate constants (k_{obs}) were obtained from the slopes of the plots of log $(b - x)$ *versus* (t/s), where b is the initial concentration of CAT and x its concentration at time t. Since the first-order rate equation is (7), $k_{obs} = -\text{slope} \times 2.303$.

$$\log (b/b - x) = k_{obs}t/2.303 \qquad (7)$$

Stoicheiometry.—Reaction mixtures containing slight excess of CAT in comparison with amine were kept at 50 °C under the conditions described earlier. Estimation of the unchanged CAT after 24 h showed that one mole of the amine reacted with one mole of CAT.

Product Analysis.—We took *p*-aminobenzenesulphonamide as a typical example. The initial product (m.p. >250 °C) isolated (88%) from reaction with CAT was identified as *p*-(chloroamino)benzenesulphonamide; $\nu_{max.}$ (Perkin-Elmer 337 grating spectrometer; Nujol) 3 370, 3 280, 1 380, and 1 155 cm^{-1} (SO_2NH_2) (comparison with *p*-aminobenzenesulphonamide showed the absence of free *p*-NH_2) [Found: Cl, 17.3 (by combustion), 17.1 (volumetric; *cf.* procedure for *N*-chloroacetanilides [47]). $C_6H_7ClN_2O_2S$ requires Cl, 17.15%].

The corresponding *N*-chloroanilines were also isolated from the reactions of other substituted anilines [*p*-NO_2 (42%), *p*-Br (62%), *p*-Cl (58%), and *m*-CN (68%)]. The chlorine content determined volumetrically was in close agreement with that required in each case.

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[45] R. Q. Brewster, *Org. Synth.*, Coll. Vol. II, 1943, p. 347.

[46] N. A. Lange and G. M. Forker, ' Handbook of Chemistry,' Handbook Publishers Inc., Sandusky, Ohio, 1956, p. 952.

[47] F. D. Chattaway and K. J. P. Orton, *J. Chem. Soc.*, 1901, **79**, 816.