395. *Nucleophilic Aromatic Substitution. Kinetics of the Reaction between 1-Chloro-2 : 4-dinitrobenzene and Aromatic Amines in Aqueous Dioxan.*

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The reaction between 1-chloro-2 : 4-dinitrobenzene and *p*-toluidine has been studied in aqueous dioxan as a function of solvent composition. The reaction is faster in the more polar media. There is no simple correlation with dielectric constant but the increase is related to the Grunwald–Winstein factor *Y*,[1] which is a measure of the solvating power of the medium. Addition of salts also increases the rate. Further measurements in pure dioxan with aniline as nucleophil are reported.

MOST nucleophilic aromatic substitutions are bimolecular, except for the S_N1 decomposition of diazonium cations.[2] Two views are held on the mechanism. These differ in whether the intermediate stage is a true transition state [3] or a stable addition complex in equilibrium with the reactants,[4] the distinction being shown by the potential-energy diagram.[5,6] Many data for these reactions, as in the present case, can be interpreted to favour either view.[5-11]

Most workers have obtained second-order kinetics.[2] A more refined analysis of the kinetics of the chlorodinitrobenzene–aliphatic amine reaction by Ross and his co-workers [12,13] has suggested participation of a bimolecular and a termolecular reaction, two amine molecules reacting in the second process. The acceleration observed by Bunnett and Randall [14] when *N*-methylaniline reacts with fluorodinitrobenzene in presence of a base (potassium acetate or sodium hydroxide) is also consistent with a termolecular process.

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[1] See Fainberg and Winstein, *J. Amer. Chem. Soc.*, 1956, **78**, 2770.
[2] Bunnett, *Quart. Rev.*, 1938, **12**, 1.
[3] Chapman and Russell-Hill, *J.*, 1956, 1563.
[4] Bunnett and Zahler, *Chem. Revs.*, 1951, **49**, 273.
[5] Bunnett, Garbisch, and Pruitt, *J. Amer. Chem. Soc.*, 1957, **79**, 385.
[6] Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 334.
[7] Ainscough and Caldin, *J.*, 1956, 2528.
[8] Bunnett and Merritt, *J. Amer. Chem. Soc.*, 1957, **79**, 5967.
[9] Cooper and Hughes, *J.*, 1937, 1183.
[10] Hammond and Parks, *J. Amer. Chem. Soc.*, 1955, **77**, 340.
[11] (*a*) Cortier, Fierens, and Halleux, *Bull. Soc. chim. belges*, 1955, **64**, 709; (*b*) Fierens and Halleux, *ibid.*, p. 717.
[12] (*a*) Ross and Finkelstein, *J. Amer. Chem. Soc.*, 1957, **79**, 6547; (*b*) Ross and Petersen, *ibid.*, 1958, **80**, 2447.
[13] Ross, *ibid.*, 1958, **80**, 5319.
[14] Bunnett and Randall, *J. Amer. Chem. Soc.*, 1958, **80**, 6020.

The authors interpret their data in terms of the intermediate-complex mechanism in which the second step is accelerated by base and the first step becomes rate-determining.

The present example of nucleophilic substitution has been studied as a function of solvent composition. The results confirm the usual second-order kinetics. The reaction between chlorodinitrobenzene and *p*-toluidine was carried out in media containing 0—50% of water by volume. The kinetics in both limiting media were complicated by separation of a second phase. In pure dioxan the separation of amine hydrochloride after 30% of reaction introduced the possibility of heterogeneous catalysis; in 50% dioxan the second phase was a red liquid, probably a saturated solution of dinitrodiphenylamine in dioxan. Reaction of aniline with chlorodinitrobenzene in pure dioxan was also rendered heterogeneous by separation of crystals of amine hydrochloride. Isolation reactions in pure dioxan containing a large excess of amine or chlorodinitrobenzene were studied, and were homogeneous.

EXPERIMENTAL

Materials.—Aniline was fractionally distilled, b. p. 184°, from zinc dust. *p*-Toluidine was recrystallised, m. p. 43°, from light petroleum (b. p. 40—60°). Dioxan was purified by Rische and Milas's method.[15] All salts were " AnalaR."

Kinetic Measurements.—Several samples were made up for each run, in stoppered test tubes, from stock solutions prepared at reaction temperature. Reactions were timed from the addition of chlorodinitrobenzene solution. Samples were analysed for halide by Volhard's method after partition between 15 ml. of benzene, 10 ml. of water, 5 ml. of 4N-nitric acid, and excess of 0·1N-silver nitrate in a separating funnel. The aqueous layer and 2 × 15 ml. washings were titrated with 0·01N-ammonium thiocyanate.

Isolation of Products.—50% *Dioxan.* 40 ml. of reaction solution at infinite time was poured into 100 ml. of distilled water containing 5 ml. of concentrated nitric acid. The red crystals were filtered off, dried, and weighed. The filtrate was neutralised. Its benzene extract on evaporation was combined with the first crystals; yield 94%, m. p. 135·5—136·5° (lit. 137 [16]) raised to 136·8—137·5° after recrystallisation from ethanol.

60% *Dioxan containing* 0·18M-*potassium acetate.* Yield 97%, m. p. 135·5—136·5°.

DISCUSSION

The reaction in pure dioxan obeyed the kinetic equation

$$dx/dt = k_2(a - 2x)(b - x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where *x* is the concentration of *p*-toluidine hydrochloride at time *t*, *a* is the initial concentration of amine and *b* of chlorodinitrobenzene. Plots of log $(a - 2x)/(b - x)$ against time were linear to at least 60% reaction. Runs with excess of either component gave excellent first-order plots. The results are shown in Table 1. From the corresponding data at 45° and 25°, the Arrhenius activation energy for the chlorodinitrobenzene–*p*-toluidine reaction was estimated at 10·9 ± 0·5 kcal. mole⁻¹ (Singh and Peacock [17] report

TABLE 1. *Rate constants in pure dioxan.*

p-Toluidine (M)	0·25	0·42	0·25	0·39	5·2	0·025	0·099
$Cl{\cdot}C_6H_3(NO_2)_2$	0·05	0·05	0·10	0·10	0·10	1·05	1·05
Temp.	45°	45°	45°	45°	45°	45°	45°
10^3k_2 (l. mole^{-1} min.$^{-1}$)	1·33	1·35	1·33	1·37	1·36 [h]	1·35 [h]	1·37 [h]
p-Toluidine (M)	0·123	0·248	0·246				
Aniline (M)				0·28	2·75	2·75	5·5
$Cl{\cdot}C_6H_3(NO_2)_2$ (M)	1·05	0·10	0·101	0·05	0·016	0·10	0·10
Temp.	45°	25°	25°	45°	45°	45°	45°
10^3k_2 (l. mole^{-1} min.$^{-1}$)	1·38	0·430	0·408	0·389	0·430 [h]	0·434 [h]	0·628 [h]

[h] Run was homogeneous throughout.

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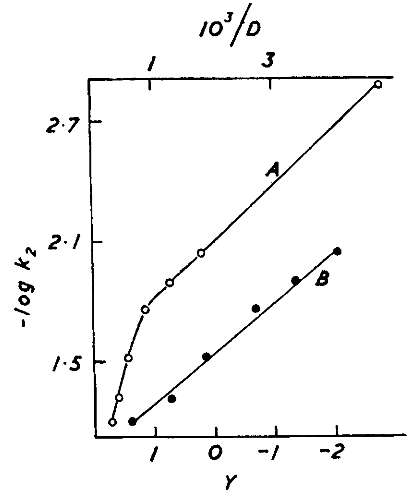
[15] See Weissberger, " Technique of Organic Chemistry. Vol. VII, Organic Solvents," Interscience Publishers Inc., New York, 1955, p. 372.

[16] Kabachnik and Zitser, *J. Gen. Chem. U.S.S.R.*, 1937, **7**, 162.

[17] Singh and Peacock, *J. Phys. Chem.*, 1936, **40**, 669.

10·06 ± 0·3 for reactions of 0·4M-*p*-toluidine and 10·81 ± 0·3 kcal. mole^{-1} for 0·8M-*p*-toluidine in ethanol).

Solvent Effects.—The second-order rate constant for *p*-toluidine in Table 1 shows only a slight increase with increasing amine concentration, even when the solvent is approximately 50% dioxan by volume (5·2M-*p*-toluidine). Similarly when the chlorodinitrobenzene concentration is increased to approximately 25% by volume (1·05M) the rate increase is only a few units per cent. The trend of rate constant with increasing aniline concentration is more definite. When the aniline concentration is increased tenfold to 25% by volume (2·75M), k_2 is increased by 10%; when it is increased to 50% by volume (5·5M) the rate is almost doubled. The latter variation of k_2 may be qualitatively explained by a medium effect since aniline–dioxan solvents should be more polar than the corresponding *p*-toluidine–dioxan or chlorodinitrobenzene–dioxan mixtures.



A, Variation of log k_2 with $1/D$.
B, Variation of log k_2 with Y.

In Table 2 are collected data for reactions in aqueous dioxan solvents at 45°. Eqn. (1) was again obeyed but plots of log $(a - 2x)/(b - x)$ against time showed slight deviation after 60—70% of reaction, possibly owing to the gradually increasing ionic strength of the solution as amine hydrochloride accumulated. The transition state or metastable intermediate would be more polar than the reactants. The reaction rate obviously increases with solvent polarity, as expected for such cases. It has been predicted that for such a reaction log k should be linear in $1/D$ where D is the dielectric constant of the medium.[18,1] Such relationships are frequently found for reactions in a binary solvent pair in which the dielectric constant can be suitably varied. However, a plot of log k_2 from Table 2 against $1/D$ is a continuous curve (Figure), indicating that the dielectric constant is not an adequate measure of the solvent's rôle in this reaction.

TABLE 2. *Variation in k_2 with change of medium at 45°.*

Dioxan (% v/v)	90	90	85	79	79	70	70	60	60	50	50
p-Toluidine (M)	0·250	0·125	0·250	0·248	0·124	0·124	0·123	0·123	0·122	0·124	0·122
$Cl\cdot C_6H_3(NO_2)_2$ (M)	0·05	0·05	0·05	0·05	0·05	0·05	0·05	0·05	0·05	0·05	0·05
10^2k_2 (l. mole^{-1} min.$^{-1}$)	0·899	0·875	1·29	1·77	1·74	2·72	2·97	4·71	4·71	6·32[n]	6·44[n]

[n] Run heterogeneous after 25% reaction.

The various properties which contribute to the ability of a solvent to solvate ions can be measured by the quantity Y,[1] termed the "ionising power" of the solvent, which is a function of solute–solvent interaction defined by the relation:

$$\log k = \log k_0 + mY \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

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[18] Laidler and Eyring, *Ann. N.Y. Acad. Sci.*, 1940, **39**, 303.

The standard values for Y have been measured in many solvents for the S_N1 solvolysis of *tert.*-butyl chloride at 25°. In 80% ethanol Y is arbitrarily taken as zero and $k = k_0$. The parameter m measures the susceptibility of a reaction to Y relative to that of *tert.*-butyl chloride. The correlation of solvolysis rates by this empirical method [1] is better in many cases than by the method involving dielectric constant. The scope and limitation of eqn. (2) have been investigated.[19-21]

In the current case the Y function has provided a close description of rate variation. A straight-line graph of log k_2 *versus* Y is shown in the Figure. The slope $m = 0{\cdot}250$ and the closeness of fit of eqn. (2) is $\pm 0{\cdot}0472$. An extrapolation of the line to the k_2 value for pure dioxan yields a Y value of $-5{\cdot}34$ for that solvent. Nucleophilic aromatic substitution may thus provide another measure of solvating power in non-hydroxylic media, analogous to Kosower's Z values.[22] A relation of k_2 with Y could be predicted from either the S_N2 or the intermediate-complex viewpoint and this finding does not differentiate between the two.

Salt Effects.—The effect on rate of the salt formed in the reaction (*p*-toluidine hydrochloride which is also an acid), common-ion salt, neutral salts, and potassium acetate was briefly investigated and the results are shown in Table 3. Addition of salt seems to accelerate the reaction slightly, but the results differ slightly for different salts so the effect cannot merely be that of increased ionic strength. Ion pairs and higher aggregates may be important in all the media considered, as the reagent concentrations were high for media of such low polarity. The product, *p*-toluidine hydrochloride, produces roughly a 10% increment on rate when half a mole is present in relation to one mole of chlorodinitrobenzene. Neutral salts in equimolar proportion to chlorodinitrobenzene produce a 6—7% increase, the chloride salt a 10% increase, and potassium acetate a very slight increase. Any specificity of the salt effects is probably accentuated by the low polarity of the medium.

An increase in rate with increase in ionic strength may be predicted for both mechanisms as the transition states will be more polar in each case than the reactants.

TABLE 3. *Salt effects on k_2 in various media at 45°.*

Dioxan (% v/v)	90	90	79	79	70	50	50
p-Toluidine (M)	0·125	0·249	0·124	0·126	0·126	0·124	0·126
$Cl{\cdot}C_6H_3(NO_2)_2$ (M)	0·05	0·05	0·05	0·05	0·05	0·05	0·05
Salt [a]	PTH	PTH	PTH	PTH	PTH	PTH	PTH
(M)	0·0133	0·0133	0·005	0·0133	0·0133	0·0133	0·0269
10^2k_2 (l. mole^{-1} min.$^{-1}$)	0·904	0·902	1·85	1·97	3·13	6·89 [n]	7·27 [n]

Dioxan (% v/v)	60	60	60	60	60	60
p-Toluidine (M)	0·123	0·123	0·123	0·123	0·123	0·123
$Cl{\cdot}C_6H_3(NO_2)_2$ (M)	0·05	0·05	0·05	0·05	0·05	0·05
Salt	KNO_3	$NaClO_4$	KCl	$CH_3{\cdot}CO_2K$	$CH_3{\cdot}CO_2K$	$CH_3{\cdot}CO_2K$
(M)	0·0509	0·0503	0·0509	0·0726	0·185	0·251
10^2k_2 (l. mole^{-1} min.$^{-1}$)	5·09	5·03	5·60	4·76 [b]	5·04 [b]	5·07 [b]

[a] PTH is *p*-toluidine hydrochloride. [b] Values calculated from the kinetic equation, $dx/dt = k(a - x)(b - x)$ because potassium acetate reacts with amine hydrochloride to give free amine and acetic acid, and so only one amine molecule is used up in the reaction. A plot of log $(a - 2x)/(b - x)$ against time curves strongly for the last two runs, although log $(a - x)/(b - x)$ gives a straight line to 80% reaction for the last three runs.

[n] Run heterogeneous after 25% reaction.

The effect of acid (*p*-toluidine hydrochloride) is of the magnitude of a salt effect, and there is no apparent catalysis by the base potassium acetate.

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[19] Wilputte-Steinert and Fierens, *Bull. Soc. chim. belges*, 1955, **64**, 308.

[20] Winstein, Fainberg, and Grunwald, *J. Amer. Chem. Soc.*, 1957, **79**, 4146.

[21] Hudson and Saville, *J.*, 1955, 4114.

[22] Kosower, *J. Amer. Chem. Soc.*, 1958, **80**, 3253, 3261, 3267.