[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC CO.]

Nucleophilic Displacement Reactions in Aromatic Systems. IV. Rates of Reaction of 1-Halo-2,4-dinitrobenzene with *n*-Butylamine in Chloroform and with *n*-Butylamine and *t*-Butylamine in Dimethylformamide

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The rates of reactions of 2,4-dinitrobromobenzene and 2,4-dinitroiodobenzene with *n*-butylamine have been measured in chloroform at 24.8 ± 0.1°. The rates of the reactions of *t*-butylamine with chloro-, bromo- and iododinitrobenzene and of *n*-butylamine with 2,4-dinitroiodobenzene have been measured in dimethylformamide at the same temperature. The reaction path involving two amine molecules is either small in magnitude or completely absent in dimethylformamide. The results are discussed in terms of the intermediate complex mechanism.

Previous reports from this Laboratory[1] have shown that a third-order term, involving one halide molecule and two amine molecules, is necessary to describe fully the reactions of 2,4-dinitrochlorobenzene with primary and secondary amines. The need for such a term is certain and has been demonstrated in three solvents and for four different amines. In the present paper it is shown, in addition, that this need is equally true for the reactions of both 2,4-dinitrobromobenzene and 2,4-dinitroiodobenzene with *n*-butylamine in chloroform, for in both of these systems the measured second-order rate constants increase with increasing initial amine concentrations. Nevertheless, it seemed to us probable that there might be experimental conditions under which this third-order term would be either completely absent or negligible in magnitude. In an effort to define one set of such conditions we have studied the rates of reaction of three 1-halo-2,4-dinitrobenzenes with *t*-butylamine, and in one case with *n*-butylamine, in dimethylformamide.

Experimental

Materials.—Baker and Adamson Reagent Grade chloroform, Lot No. N070N059, was used without purification. This solvent contains 0.75% ethanol as stabilizer. Du Pont Technical Grade dimethylformamide was purified by method I described in Thomas and Rochow.[2] The solvent used had a final resistivity of 5 × 10⁶ ohm-cm. 2,4-Dinitrochlorobenzene and *n*-butylamine were purified as before.[1a] Eastman Kodak Co. white label *t*-butylamine was twice distilled from calcium hydride, and a middle fraction, b.p. 42°, was used. Eastman Kodak Co. white label 2,4-dinitrobromobenzene was crystallized from absolute ethanol; m.p. 75°. 2,4-Dinitroiodobenzene was prepared by a standard procedure[3] and crystallized from ligroin; m.p. 88.5–89.5°.

Rate Measurements.—The procedure for the rate measurements has been described.[1] Where dimethylformamide was the solvent, aliquots were quenched by adding them directly to 25 ml. of 4 *N* nitric acid and analyzed for halide ion by the Volhard method.

Isolation of Products. N-*t*-Butyl-2,4-dinitroaniline.—*t*-Butylamine (20 ml.) was added to a solution of 2,4-dinitrobromobenzene (2.47 g., 0.01 mole) in dimethylformamide (200 ml.). The solution was permitted to stand for 24 hours at room temperature and then poured into 4 *N* nitric acid (400 ml.). The product was filtered and dried; m.p. 151–153°, yield 2.3 g. (96%). After crystallization from ethanol the yield was 2.0 g. (84%), m.p. 151–153°.

Anal. Calcd. for $C_{10}H_{13}N_3O_4$: C, 50.20; H, 5.48; N, 17.57. Found: C, 50.24; H, 5.29; N, 16.99.

This product has been prepared previously by Brady and Cropper[4] who reported a melting point of 119°. We can offer no explanation for the discrepancy in the melting points.

The same reaction with 2,4-dinitroiodobenzene again resulted in a 96% yield of crude product and an 84% yield of recrystallized product, m.p. 151–153°. The reaction time in this case was 120 hours.

N-*n*-Butyl-2,4-dinitroaniline.—A solution of *n*-butylamine (20 ml.) and 2,4-dinitroiodobenzene (2.94 g., 0.01 mole) in dimethylformamide (200 ml.) was left standing 6 hours at room temperature and then poured into 4 *N* nitric acid (400 ml.). The product was filtered and dried; yield 2.25 g. (93%), m.p. 89–90°.

Results and Discussion

Data on the rates of reaction of both 2,4-dinitrobromobenzene and 2,4-dinitroiodobenzene with *n*-butylamine in chloroform at 24.8 ± 0.1° are given in Table I. With both halides the measured, second-order rate constants increase markedly with increasing initial amine concentration, and, as in the case of the chloride,[1a] plots of the rate constants *vs.* the initial amine concentrations are linear (Fig. 1). From the intercepts and slopes of these lines it is possible to obtain values for the constants k_1 and k_3, respectively, in the rate equation

$$\text{d product}/\text{d}t = k_1(\text{A})(\text{B}) + k_3(\text{A})(\text{B})^2 \qquad (1)$$

where A is the halide and B the amine, and the measured rate constant, k_2, can be equated to

$$k_2 = k_1 + k_3(\text{B}_0) \qquad (2)$$

where the subscript indicates an initial concentration. More reliable values of k_1 and k_3 may be obtained by using equation 1 in its integrated form.[1b,c] The values for the rate constants, calculated in this way, are summarized in Table II. The previously reported values for 2,4-dinitrochlorobenzene[1b] are included for comparison.

The order of mobility of the halogens, as indicated by the magnitudes of k_1 and k_3, is Br > Cl > I, or perhaps more realistically stated, Br ~ Cl > I. This order of reactivity in activated nucleophilic substitution reactions has been observed earlier in the reactions of the 2,4-dinitrohalobenzenes with aniline, N-methylaniline and substituted anilines,[5] in the reaction of α-halo-β-nitronaphthalenes and β-halo-α-nitronaphthalenes with piperidine[6] and in the reactions *o*- and *p*-nitrohalobenzenes with piperidine,[7] and the order F > Cl > Br > I or F >

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[1] (a) S. D. Ross and M. Finkelstein, THIS JOURNAL, **79**, 6547 (1957); (b) S. D. Ross and R. C. Petersen, *ibid.*, **80**, 2447 (1958); (c) S. D. Ross, *ibid.*, **80**, 5319 (1958).

[2] A. B. Thomas and E. G. Rochow, *ibid.*, **79**, 1843 (1957).

[3] G. M. Bennett and I. H. Vernon, *J. Chem. Soc.*, 1783 (1938).

[4] O. L. Brady and F. R. Cropper, *ibid.*, 507 (1950).

[5] A. Rheinlander, *ibid.*, 3099 (1923); N. B. Chapman and R. E. Parker, *ibid.*, 3301 (1951).

[6] E. Berliner, M. J. Quinn and P. J. Edgerton, THIS JOURNAL, **72**, 5305 (1950).

[7] N. B. Chapman, R. E. Parker and P. W. Soames, *J. Chem. Soc.*, 2109 (1954).

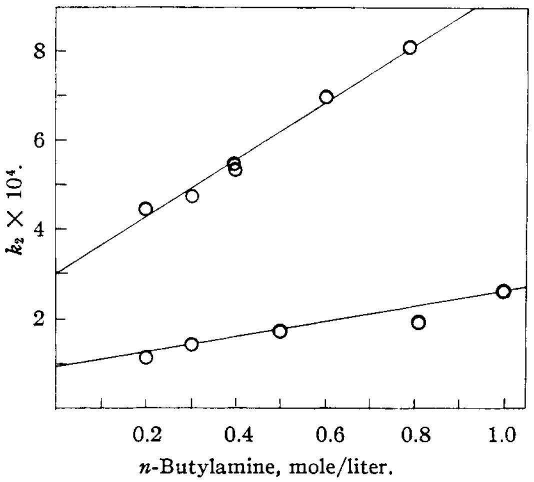


Fig. 1.—Second-order rate constants *vs.* initial *n*-butylamine concentrations for the reactions of 2,4-dinitrobromobenzene (upper line) and 2,4-dinitroiodobenzene (lower line) with *n*-butylamine in chloroform at 24.8 ± 0.1°.

Cl ~ Br > I has been reported for the reactions of the *p*-nitrohalobenzenes with ethoxide ion[8] and the reactions of the 2,4-dinitrohalobenzenes with methoxide ion and with *p*-nitrophenolate ion.[9]

This is to be contrasted with the order of mobility of the halogens, I > Br > Cl > F, found in displacement reactions at saturated carbon atoms for both S_N2 and S_N1 mechanisms,[10] and Berliner[6] and Bunnett[11] have cited this as evidence for a two-stage mechanism, involving an intermediate complex, in activated nucleophilic substitution reactions. Hammond[12] and Fierens[13] have pointed out that this sequence of rates is equally consistent with a one-step mechanism in which bond-breaking has made little or no progress in the transition state. They have found experimentally that the order characteristic of substitution at a saturated carbon atom, Br > Cl > F, is shown by the reactions of the 2,4-dinitrohalobenzenes with N-methylaniline[12] and with iodide ion.[13] We prefer to discuss the present results in terms of the intermediate complex hypothesis, since this mechanism can accommodate both the third-order terms, which we have found necessary in these reactions and which suggest that bond-breaking is involved in the rate-determining steps, and the observed order of reactivity of the halogens, which for a one-step mechanism demands that bond-breaking had made little progress at the rate-determining transition step.

TABLE I

RATES OF REACTION OF 1-HALO-2,4-DINITROBENZENES WITH *n*-BUTYLAMINE IN CHLOROFORM AT 24.8 ± 0.1°

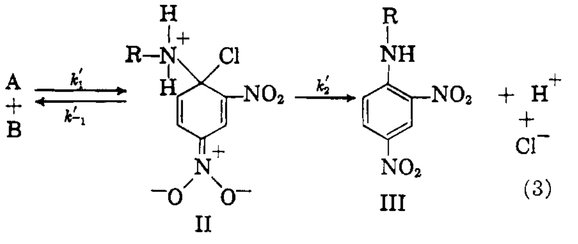
Halogen	Halide, mole/l.	*n*-Butylamine, mole/l.	$k_2 \times 10^4$, l. mole^{-1} sec.$^{-1}$
Bromine	0.04918	0.1981	4.47
	.04908	.3010	4.75
	.04966	.3961	5.46
	.04999	.3965	5.35
	.05092	.6016	7.01
	.04956	.7917	8.11
Iodine	.05113	.2004	1.13
	.05174	.3000	1.43
	.05182	.4989	1.74
	.05217	.8073	1.97
	.05095	.9987	2.66

TABLE II

RATES OF REACTION OF 1-HALO-2,4-DINITROBENZENES WITH *n*-BUTYLAMINE IN CHLOROFORM AT 24.8 ± 0.1°

Halogen	$k_1 \times 10^4$, l. mole^{-1} sec.$^{-1}$	$k_3 \times 10^4$, l.^{2} mole^{-2} sec.$^{-1}$	k_3/k_1, l. mole^{-1}
Chlorine	2.2	5.4	2.45
Bromine	3.0	7.0	2.33
Iodine	0.94	1.7	1.81

In the present case the intermediate complex mechanism may be formulated as:



(3)

$$\mathrm{II} + \mathrm{B} \xrightarrow{k_3'} \mathrm{III} + \mathrm{BH}^+ + \mathrm{Cl}^- \qquad (4)$$

The rate equation is given by

$$\frac{d\mathrm{III}}{dt} = \frac{k_1'}{k_{-1}' + k_2' + k_3'(\mathrm{B})}\,[k_2'(\mathrm{A})(\mathrm{B}) + k_3'(\mathrm{A})(\mathrm{B})^2] \qquad (5)$$

The special conditions under which this mechanism results in a rate expression of the form of equation 1 have been described.[1b] The two product-forming steps, with rate constants k_2' and k_3', have been written as if they involved a concerted process with simultaneous breaking of a carbon–chlorine and a nitrogen–hydrogen bond. Alternatively, they might have been written in two steps, one for the breaking of each bond, with either or both steps reversible. Since the product III and amine hydrochloride do not revert to starting materials and since the reaction is not retarded by initially added chloride ion,[1a] only the simpler formulation shown above will be considered. In any case, our experiments offer no hope of distinguishing between these particular possibilities.

As indicated by equation 5, the relative importance of the third-order term will depend, at any given amine concentration, only on the ratio, k_3'/k_2'. In the last column of Table II we have given experimental values of k_3/k_1 for the reactions of the 1-halo-2,4-dinitrobenzenes with *n*-butylamine. If the postulated mechanism is correct, these values are identical with values of k_3'/k_2'. These values decrease in the order, Cl > Br > I, and this can be rationalized as being due to an increase in the relative magnitude of k_2' in going from the chloride to

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[8] C. W. L. Bevan, *J. Chem. Soc.*, 2340 (1951).

[9] A. L. Beckwith, J. Miller and G. D. Leahy, *ibid.*, 3552 (1952).

[10] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 338.

[11] J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 273 (1951); J. F. Bunnett, E. W. Garbisch, Jr., and K. M. Pruitt, THIS JOURNAL, **79**, 385 (1957).

[12] G. S. Hammond and L. R. Parks, *ibid.*, **77**, 340 (1955).

[13] J. Cortier, P. J. C. Fierens, M. Gilon and A. Halleux, *Bull. soc. chim. Belg.*, **64**, 709 (1955); P. J. C. Fierens and A. Halleux, *ibid.*, **64**, 717 (1955).

the bromide to the iodide. This reaction, with rate constant k_2', should have the characteristics of a displacement at a saturated carbon atom and should obey the rate sequence, I > Br > Cl.[10]

As might be expected, the ratio k_3/k_1 is strongly sensitive to solvent changes. Data are available on the reaction of 2,4-dinitrochlorobenzene and *n*-butylamine in chloroform, absolute ethanol and 50% dioxane–50% water. The ratios are 2.45 in chloroform, 0.744 in the more polar solvent ethanol, and 0.285 in the still more polar dioxane–water mixture. Finally, a change from *n*-butylamine to an amine with a larger steric requirement, *t*-butylamine, might be expected to favor k_2' over k_3'. The rate constant k_2' might be expected to increase due to steric acceleration of the rate resulting from the decrease in strain in going from the intermediate complex to the product, when the amine is *t*-butylamine. The rate constant k_3' might be expected to decrease because access to the reaction site is sterically inhibited by the bulkier *t*-butylamine.

TABLE III

RATES OF REACTION OF 1-HALO-2,4-DINITROBENZENES WITH AMINES IN DIMETHYLFORMAMIDE AT 24. 8 ± 0.1°

Halogen	Amine	Halide, mole/l.	Amine, mole/l.	$k_2 \times 10^5$, l. mole^{-1} sec.$^{-1}$
Chlorine	*t*-BuNH$_2$	0.05037	0.1820	23.8
		.04984	.3682	23.2
		.04922	.5570	24.2
		.05021	.7408	25.2
		.04890	.9316	25.4
Bromine	*t*-BuNH$_2$	.04851	.1816	16.4
		.04979	.3663	16.0
		.05022	.5540	16.7
		.04835	.7383	17.2
		.04842	.9332	17.4
Iodine	*t*-BuNH$_2$	.05140	.1818	2.38
		.05192	.3682	2.21
		.05179	.5530	2.33
		.05146	.7313	2.22
		.05197	.9340	2.20
Iodine	*n*-BuNH$_2$	.05170	.1686	923
		.05112	.1979	927
		.05163	.2992	897
		.05137	.3975	932

The foregoing considerations led to the study of the rates of the reactions of the 1-halo-2,4-dinitrobenzenes with *t*-butylamine in dimethylformamide at 24.8 ± 0.1° shown in Table III. All of the reactions in Table III are bimolecular within experimental error. However, with the chloride and the bromide there are distinct trends in the results, with the rate constants increasing with increasing initial amine concentrations. For the chloride, the average bimolecular rate constant is 2.44×10^{-4} l. mole^{-1} sec.$^{-1}$. The maximum deviation from this average value is 4.1%, and the average deviation is 3.3%. Nevertheless, a plot of k_2 *vs.* (B_0) is linear, and a least squares treatment of the data results in values of 2.28×10^{-4} l. mole^{-1} sec.$^{-1}$ for k_1 and 0.28×10^{-4} l^2. mole^{-2} sec.$^{-1}$ for k_3. The resultant value for k_3/k_1 is 0.123 l. mole^{-1}. The results with the bromide are similar. The average value for k_2 is 1.67×10^{-4} l. mole^{-1} sec.$^{-1}$. The maximum deviation is 4.2%, and the average deviation is 2.6%. Treating the data as above results in estimates of 1.58×10^{-4} l. mole^{-1} sec.$^{-1}$ for k_1, 0.17×10^{-4} l.^{2}. mole^{-2} sec.$^{-1}$ for k_3 and 0.108 l. mole^{-1} for the ratio k_3/k_1.

With the iodide there is no discernible trend in the rates as the initial amine concentrations are increased. This reaction is clearly bimolecular. The average of the rate constants is 2.27×10^{-5} l. mole^{-1} sec.$^{-1}$. The maximum deviation from this average value is 4.8%, and the average deviation is 3.1%. The experimental results are thus in accord with our predictions and suggest that the rationalization which led to these experiments may have some validity.

The measurements with 2,4-dinitroiodobenzene and *n*-butylamine in dimethylformamide are suggestive and have, therefore, been included in Table III. The reaction with *n*-butylamine is almost 500 times faster than the reaction with *t*-butylamine. As a result the reaction was studied over a more limited range of amine concentrations. In this series of measurements there is no pronounced tendency for the measured rate constants to increase as the amine increases in concentration. This suggests that, of the three influences on the ratio k_3/k_1, the influence of the solvent may be the predominant one. This is also indicated by the large drop in k_3/k_1 in going from chloroform to ethanol as solvent and the further drop in going from ethanol to 50% dioxane–50% water.[1a,c] This is understandable if we assume that solvent is involved in solvating the hydrogen ion and chloride ion in the product-forming step. When the solvent is only partially effective in performing this function for either of the leaving ions, an additional reactant molecule may take over this function and become involved in the transition state of the product-forming step.

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