

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

Nucleophilic Displacement Reactions in Aromatic Systems. II.¹ Catalysis of the Reaction of 2,4-Dinitrochlorobenzene and *n*-Butylamine by Triethylamine in Chloroform

BY SIDNEY D. ROSS AND RAYMOND C. PETERSEN

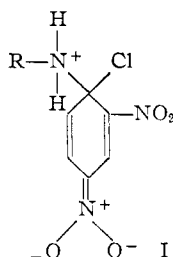
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It is shown that, in the presence of triethylamine, the over-all rate equation for the reaction of 2,4-dinitrochlorobenzene and *n*-butylamine is given by $d \text{ product}/dt = k_1(\text{RCI})(n\text{-BuNH}_2) + k_2(\text{RCI})(n\text{-BuNH}_2)^2 + k_3(\text{RCI})(n\text{-BuNH}_2)(\text{Et}_3\text{N})$. All three of these rate constants have been evaluated, and the mechanism has been discussed.

In a previous report from this Laboratory¹ it was shown that the correct rate expression for the reaction of 2,4-dinitrochlorobenzene and *n*-butylamine is

$$d \text{ Product}/dt = k_1(\text{RCI})(n\text{-BuNH}_2) + k_3(\text{RCI})(n\text{-BuNH}_2)^2 \quad (1)$$

It was suggested that the function of the second amine molecule in the third-order term of equation 1 was to facilitate product formation by removal of a proton from an intermediate of the type I



Such a mechanism had been proposed previously² to account for the fact that triethylamine, which does not react to an appreciable extent with 2,4-dinitrochlorobenzene, nevertheless increases the rate of reaction of this chloride with methylamine in alcohol. The reaction of 2,4-dinitrochlorobenzene with *n*-butylamine in chloroform represents a favorable system for a quantitative study of the catalysis by triethylamine, since, in this reaction, the third-order term makes a relatively large contribution to the total product formation and since triethylamine does not react with the chloride in this solvent to a measurable extent.

Experimental

Materials.—Baker and Adamson Reagent Grade chloroform, Lot No. N070N059, was used without purification. This solvent contains 0.75% ethanol as a stabilizer. Eastman Kodak Co. white label *n*-butylamine and triethylamine were distilled twice from calcium hydride, and middle fractions were distilled from b.p. 77 and 89°, respectively, were used. 2,4-Dinitrochlorobenzene, Eastman Kodak Co. white label, was crystallized two times from absolute ethanol; m.p. 51°.

Rate Measurements.—Separate, determinate solutions of 2,4-dinitrochlorobenzene and the two amines in chloroform were made up at the temperature of the measurements, 24.8 ± 0.1°. The solutions were mixed at zero time, and aliquots were withdrawn at appropriate time intervals. The aliquots were quenched by partitioning them between benzene (50 ml.) and 4 *N* nitric acid (25 ml.) and extracting the benzene solution two additional times with water. They were then analyzed for chloride ion by the Volhard method.

(1) For the first paper in this series see S. D. Ross and M. Finkelstein, *THIS JOURNAL*, **79**, 8547 (1957).

(2) O. L. Brady and F. R. Cropper, *J. Chem. Soc.*, 507 (1950).

Results and Discussion

If a triethylamine molecule can perform the same function as the second *n*-butylamine molecule in the third-order term of equation 1, the over-all rate, V , will be given by

$$V = k_1(\text{RCI})(n\text{-BuNH}_2) + k_3(\text{RCI})(n\text{-BuNH}_2)^2 + k_4(\text{RCI})(n\text{-BuNH}_2)(\text{Et}_3\text{N}) \quad (2)$$

and the expression for the specific rate is

$$k_2 = k_1 + k_3(n\text{-BuNH}_2) + k_4(\text{Et}_3\text{N}) \quad (3)$$

The k_2 in equation 3 is the second-order rate constant for an individual run. If we make a series of measurements at constant initial 2,4-dinitrochlorobenzene and *n*-butylamine concentrations and vary the initial triethylamine concentrations and plot the k_2 's vs. the initial triethylamine concentrations, we should obtain a straight line with the slope equal to k_4 and the intercept equal to $k_1 + k_3(n\text{-BuNH}_2)$. Similarly, for a plot of k_2 's vs. initial *n*-butylamine concentrations for a series of measurements at constant chloride and triethylamine concentrations and varying *n*-butylamine concentrations, the resultant straight line should have a slope equal to k_3 and an intercept equal to $k_1 + k_4(\text{Et}_3\text{N})$. Thus, from the two series of measurements it should be possible to evaluate all three of the constants, k_1 , k_3 and k_4 .

There is, however, a complication in determining the k_2 's. The products in this reaction are 2,4-dinitro-*N-n*-butylaniline and hydrogen chloride, which combines rapidly with a second amine molecule to form the amine hydrochloride. In the absence of triethylamine, the hydrogen chloride reacts with a second *n*-butylamine molecule, and the correct second-order rate equation is

$$k_2t = \frac{2.303}{B_0 - 2A_0} \log \frac{A_0(B_0 - 2D)}{B_0(A_0 - D)} \quad (4)$$

where A_0 is the initial 2,4-dinitrochlorobenzene concentration, B_0 is the initial *n*-butylamine concentration and D is the product, chloride ion or 2,4-dinitro-*N-n*-butylaniline. In the presence of triethylamine, equation 4 is correct only in the limiting case that all the hydrogen chloride is bound by *n*-butylamine. The alternate limiting case is the one where all the hydrogen chloride formed reacts with triethylamine, and the corresponding rate expression is

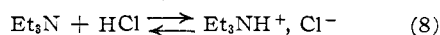
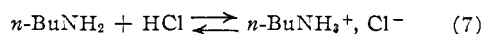
$$k_2t = \frac{2.303}{B_0 - A_0} \log \frac{A_0(B_0 - D)}{B_0(A_0 - D)} \quad (5)$$

In actual fact neither of these limiting equations is appropriate, since *n*-butylamine and triethylamine are bases of comparable strength. In water *n*-

butylamine has a pK_a of 10.48 and triethylamine has a pK_a of 10.65.³ The concentration of *n*-butylamine at any time, *t*, is given by

$$B = B_0 - f(D) \quad (6)$$

where $f(D)$ is a complicated function involving not only D but also the equilibrium constants for the reactions



This difficulty can be obviated by plotting measured values of $\Delta D/\Delta t$ vs. t for each run and extrapolating to zero time to obtain values of $(dD/dt)_{t=0}$. The second-order rate constant is then given by

$$k_2 = \frac{1}{A_0 B_0} \left(\frac{dD}{dt} \right)_{t=0} \quad (9)$$

In Table I we have compiled the rate constants for six runs at constant *n*-butylamine concentration and varying triethylamine concentration and for two sets of three runs at constant triethylamine concentration and varying *n*-butylamine concentrations. The most reliable values for the rate constants are those calculated from equation 9 and given in the last column of Table I. The application of either equation 4 or equation 5 to our data results in a satisfactory linear plot in every case, and the rate constants obtained with these two equations have been included in Table I for purposes of comparison. Some pertinent, previously reported¹ runs, in the absence of triethylamine, are also given in Table I, and the rate constants have been recalculated using equation 9.

TABLE I

RATES OF REACTION OF 2,4-DINITROCHLOROBENZENE AND *n*-BUTYLAMINE IN THE PRESENCE AND ABSENCE OF TRIETHYLAMINE IN CHLOROFORM CONTAINING 0.75% ETHANOL AS STABILIZER AT $24.8 \pm 0.1^\circ$

| 2,4-Di-nitro-chloro-benzene, mole l. ⁻¹ | <i>n</i> -Butyl-amine, mole l. ⁻¹ | Triethyl-amine, mole l. ⁻¹ | $k_2 \times 10^4$ | $k_2 \times 10^4$ | $k_2 \times 10^4$ |
|--|--|---------------------------------------|--|--|--|
| | | | from eq. 4, l. mole ⁻¹ sec. ⁻¹ | from eq. 5, l. mole ⁻¹ sec. ⁻¹ | from eq. 9, l. mole ⁻¹ sec. ⁻¹ |
| 0.05097 | 0.2003 | 0.0420 | 3.29 | 2.94 | 3.58 |
| .05060 | .1978 | .1422 | 3.91 | 3.57 | 4.08 |
| .05026 | .1993 | .2141 | 4.14 | 3.69 | 4.16 |
| .05113 | .1987 | .3529 | 4.60 | 4.19 | 4.59 |
| .05111 | .1980 | .3565 | 4.65 | 4.14 | 4.58 |
| .05056 | .2000 | .5653 | 5.10 | 4.60 | 5.14 |
| .04975 | .3977 | .1420 | 4.07 | 4.48 | 5.14 |
| .05119 | .5018 | .1426 | 5.08 | 4.87 | 5.66 |
| .05016 | .2998 | .5712 | 5.20 | 4.92 | 5.43 |
| .05265 | .3986 | .5711 | 5.53 | 5.27 | 5.92 |
| .05165 | .1038 | | 2.47 | | 2.75 |
| .05141 | .1866 | | 3.25 | | 3.63 |
| .05111 | .1985 | | 3.07 | | 3.53 |
| .05061 | .4961 | | 4.37 | | 5.34 |
| .05168 | .8018 | | 6.22 | | 7.12 |
| .05108 | .9997 | | 7.45 | | 7.90 |

Figure 1 presents a plot of k_2 vs. the initial triethylamine concentrations for the measurements at constant *n*-butylamine concentration. The least squares value for the slope, k_4 , is 2.86×10^{-4} l.² mole⁻² sec.⁻¹ and for the intercept, $k_1 + k_3(n\text{-BuNH}_2)_0$, the resultant value is 3.56×10^{-4} l.

(3) H. K. Hall, Jr., THIS JOURNAL, 79, 5441 (1957).

mole⁻¹ sec.⁻¹. In Fig. 2, k_2 is plotted against initial *n*-butylamine concentration for the two sets of data at constant initial triethylamine concentration. For the upper line, the initial triethylamine concentration is approximately constant at 0.57 *M*; for the lower line the triethylamine concentration is 0.142 *M*. In drawing the upper line we have intentionally favored the two points at the higher initial *n*-butylamine concentrations, since our data for the run at 0.2000 *M* *n*-butylamine proved difficult to extrapolate. For the data at 0.57 *M* triethylamine, the slope, k_3 , is equal to 4.86×10^{-4} l.² mole⁻² sec.⁻¹, and the intercept, $k_1 + k_4(\text{Et}_3\text{N})_0$, is equal to 3.98×10^{-4} l. mole⁻¹ sec.⁻¹. For the data at 0.142 *M* triethylamine, the slope, k_3 , is equal to 5.22×10^{-4} l.² mole⁻² sec.⁻¹, and the intercept, $k_1 + k_4(\text{Et}_3\text{N})_0$, is equal to 3.05×10^{-4} l. mole⁻¹ sec.⁻¹. Combining and averaging these three sets of data, the following values are obtained for the three rate constants: $k_1 = 2.5 \times 10^{-4}$ l. mole⁻¹ sec.⁻¹; $k_3 = 5.0 \times 10^{-4}$ l.² mole⁻² sec.⁻¹; $k_4 = 2.9 \times 10^{-4}$ l.² mole⁻² sec.⁻¹.

These values of k_1 and k_3 are to be compared with our previously reported¹ values for these two constants. The earlier measurements, made without triethylamine present in the system, gave values of 2.0×10^{-4} l. mole⁻¹ sec.⁻¹ for k_1 and 5.3×10^{-4} l.² mole⁻² sec.⁻¹ for k_3 . The agreement is reasonable. Nevertheless, it is of interest to determine whether or not the use of equation 4 to calculate the second-order rate constants at zero time introduces a significant error even when triethylamine is absent. The rate constants have, therefore, been recalculated using equation 9. The resultant values are given in Table I. A plot of k_2 vs. the initial *n*-butylamine concentration is again linear. The least squares values are 2.4×10^{-4} l. mole⁻¹ sec.⁻¹ for the intercept k_1 and 5.7×10^{-4} l.² mole⁻² sec.⁻¹ for the slope k_3 .

It is now pertinent to ask which set of values for k_1 and k_3 is the most reliable. When no triethylamine is present, the rate equation is

$$dD/dt = k_1(A_0 - D)(B_0 - 2D) + k_3(A_0 - D)(B_0 - 2D)^2 \quad (10)$$

This equation can be integrated to give

$$\frac{1}{B_0 - 2A_0} \ln \frac{A_0 B}{A B_0} - \frac{k_3}{k_1} \left[\ln \frac{B_0}{B} - \ln \frac{B_0 + \frac{k_1}{k_3}}{B + \frac{k_1}{k_3}} \right] = k_1 t + k_3 t (B_0 - 2A_0) \quad (11)$$

The second term on the left in equation 11 will normally be small and insensitive to the values of k_1 and k_3 . Hence it can be ignored in the first approximation. In using 11, D was first obtained as a function of t for all six of the runs without triethylamine. The first term on the left was then plotted against $(B_0 - 2A_0)$ for points from each run at a fixed time. The time was so chosen that the points represented less than 10% reaction at one extreme and more than 90% reaction at the other extreme. Values of k_1 and k_3 were then obtained from the intercept and slope, respectively, of the straight line plot obtained. Using these initial values of k_1 and k_3 the second term on the left of equation 11

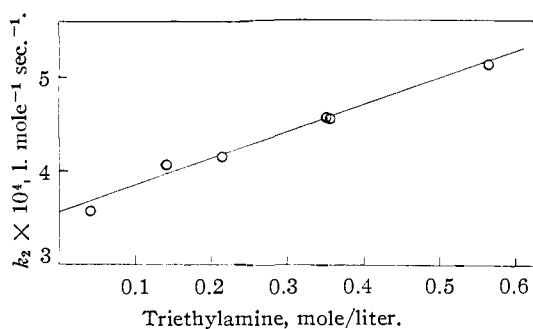


Fig. 1.—A plot of k_2 vs. the initial triethylamine concentration.

was calculated, and the procedure was repeated until the values of k_1 and k_3 became constant. This treatment resulted finally in values of 2.2×10^{-4} l. mole $^{-1}$ sec. $^{-1}$ for k_1 and 5.4×10^{-4} l. 2 mole $^{-2}$ sec. $^{-1}$ for k_3 . These calculations involve neither an assumption about the rate at zero time nor an extrapolation to zero time. They include experiments with an almost tenfold variation in the initial *n*-butylamine concentration and reaction percentages of less than 10% and more than 90%. These, therefore, are the most reliable single values for k_1 and k_3 . It is, moreover, encouraging that we can include all of our values, even those determined in the presence of triethylamine, and still set limits of $2.25 \pm 0.25 \times 10^{-4}$ l. mole $^{-1}$ sec. $^{-1}$ for k_1 and $5.35 \pm 0.35 \times 10^{-4}$ l. 2 mole $^{-2}$ sec. $^{-1}$ for k_3 .

Our results, in the presence of triethylamine, are thus consistent with the rate equation

$$dD/dt = k_1(A)(B) + k_3(A)(B)^2 + k_4(A)(B)(E) \quad (12)$$

where E is triethylamine. This equation can be derived either by assuming an equilibrium between A, B and an intermediate, I, or by assuming a steady state concentration of I. For the latter assumption, the steady state concentration of I is given by

$$I = \frac{k_1'(A)(B)}{k'_{-1} + k'_2 + k'_3(B) + k'_4(E)} \quad (13)$$

where the rate constants correspond to the reactions

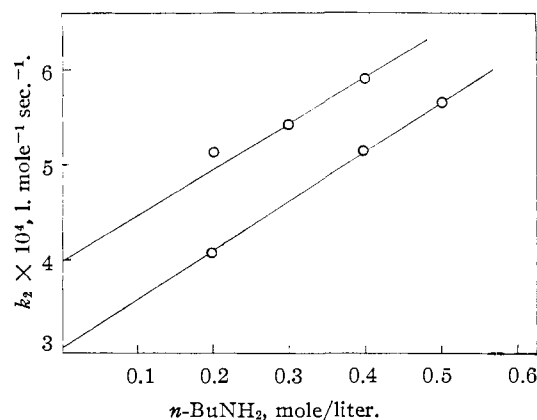
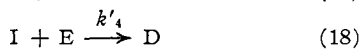
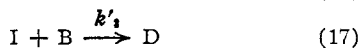
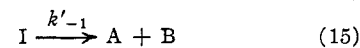
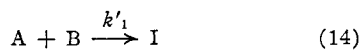


Fig. 2.—Plots of k_2 vs. the initial *n*-butylamine concentration. For the upper line the initial triethylamine concentrations are 0.57 *M*; for the lower line the initial triethylamine concentrations are 0.142 *M*.

The rate equation resulting from a combination of equations 13 through 18 is

$$\frac{dD}{dt} = k'_1(A)(B) \left(\frac{k'_2 + k'_3(B) + k'_4(E)}{k'_{-1} + k'_2 + k'_3(B) + k'_4(E)} \right) \quad (19)$$

An equation of the form 12 can then be obtained by applying the assumption

$$k'_{-1} \gg k'_2 + k'_3(B) + k'_4(E) \quad (20)$$

which is equivalent to assuming an equilibrium among A, B and I, or by applying to the denominator of the term in parentheses of equation 19 either of the assumptions

$$k'_2 \gg k'_{-1} + k'_3(B) + k'_4(E) \quad (21)$$

$$k'_{-1} + k'_2 \gg k'_3(B) + k'_4(E) \quad (22)$$

It should be noted that if $k'_{-1} > k'_2$, assumption 22 is identical to 20. Otherwise it should be noted that the application of 21 or 22 to the numerator of equation 19 as well as to the denominator leads to the simple second-order rate expression

$$dD/dt = k(A)(B) \quad (23)$$

in contradiction to the experimental facts. This is not sufficient reason to discard these two possibilities, since the numerator of the term in parentheses of equation 19 is more sensitive to variations in B and E than is the denominator. Thus our experiments do not permit any choice among these assumptions.

NORTH ADAMS, MASS.