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Nucleophilic Displacement Reactions in Aromatic Systems. V. The Mechanism of the Reaction of 2,4-Dinitrochlorobenzene with Primary Amines in Chloroform

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The reaction of 2,4-dinitrochlorobenzene and allylamine in chloroform is catalyzed by aromatic nitro groups as well as by the amine. This necessitates the more complex rate expression shown below, $dD/dt = k_1(A)(B) + k_2(A)(B)^2 + k_4(A)^2(B) + k_5(A)(B)(D) + k_3(A)(B)(C)$, where A is the chloride, B the amine, C *m*-dinitrobenzene and D the product. It is shown that this equation fits the reaction, and all of the rate constants involved have been determined. Rate studies with N,N-dideuterio-*n*-butylamine and 2,4-dinitrochlorobenzene show no deuterium isotope effect. A reaction mechanism consistent with these results is proposed.

In previous reports from this Laboratory,¹ it was shown that rate measurements in chloroform on the reaction of 2,4-dinitrochlorobenzene and primary or secondary amines, with the chloride concentration held constant and the amine concentrations varied, require the rate expression 1

$$dD/dt = k_1(A)(B) + k_2(A)(B)^2 \quad (1)$$

where D is the product, an N-alkyl-2,4-dinitroaniline, A is the chloride and B is the amine. The significance of the third-order term of equation 1 for the mechanism of the reaction has yet to be established with certainty. At least two explanations for this phase of the total reaction are possible. The third-order term may be attributable to a base catalysis in which the second amine molecule facilitates the over-all reaction by assisting in the removal of a proton, or it may be necessitated by a general undefined medium effect, linear with the amine concentration. The experiments to be described herein were originally designed to permit a decision between these alternatives.

Equation 1 may be integrated and, for the present purpose, the integrated form is best written as 2

$$t = \frac{1}{k_1 + k_2(B_0 - 2A_0)} \left[\frac{1}{B_0 - 2A_0} \ln \frac{A_0 B}{A B_0} - \frac{k_2}{k_1} \left(\ln \frac{B_0}{B} - \ln \frac{B_0 + (k_1/k_2)}{B + (k_1/k_2)} \right) \right] \quad (2)$$

where the subscripts, 0 indicate initial concentrations. In principle, equation 2 permits a choice between a third-order kinetic term and a medium effect. This requires a series of experiments with B_0 large and constant and A_0 small and varying. By selecting a time from each of several runs such that B is the same for all runs, k_1 and k_2 can be evaluated by equation 2. If k_2 results from a medium effect, its value, as determined in this manner, will be zero, since the media are all essentially the same. On the other hand, if the k_2 term is really necessary in the rate expression, the value of k_2 obtained will be essentially that value obtained from the previous experiments^{1a,b} with A_0 constant and B_0 varying. The success of this treatment depends on k_2 being much larger than k_1 .

Experiments of the type described above were performed with *n*-butylamine and with allylamine, for the latter of which the ratio, k_2/k_1 , is larger and a higher order of precision of measurement is possible. In neither case could the results ob-

tained be accommodated adequately either by a bimolecular rate expression, with accompanying general medium effect, or by equation 1 with its two terms.

This led to the detailed rate studies which follow. Included are determinations of the effects of varying both the amine and halide concentrations with both *n*-butylamine and allylamine, the rates with N,N-dideuterio-*n*-butylamine and the effects of added *m*-dinitrobenzene on the rate of reaction of 2,4-dinitrochlorobenzene and allylamine, all in chloroform, containing 0.75% ethanol as stabilizer, at $24.8 \pm 0.1^\circ$.

Results

The rates of reaction of 2,4-dinitrochlorobenzene and allylamine in chloroform containing 0.75% ethanol at $24.8 \pm 0.1^\circ$ are given in Table I. This

TABLE I
RATES OF REACTION OF 2,4-DINITROCHLORO-BENZENE AND ALLYLAMINE IN CHLOROFORM CONTAINING 0.75% ETHANOL AT $24.8 \pm 0.1^\circ$

Chloride, mole l. ⁻¹	Amine, mole l. ⁻¹	Intercept	Slope $\times 10^3$	$k_2 \times 10^4$, l. mole ⁻¹ sec. ⁻¹
0.04995	0.2010	0.0070	0.3042	0.617
.05106	.2048	.0090	.2712	.608
.05081	.1946	.0050	.2622	.649
.04954	.4050	.0050	1.1167	.841
.05010	.4142	.0062	1.1767	.863
.04978	.5994	.0070	2.3500	1.08
.05023	.7426	.0050	3.5667	1.28
.04988	1.0550	.0120	1.1067	1.71
.05022	0.5968	.0060	2.3722	1.10
.10095	.5951	.0030	1.9259	1.13
.15029	.6018	.0020	1.5167	1.16
.20008	.5951	.0010	1.0217	1.21
.05016	.7887	.0050	3.9667	1.33
.10024	.7904	.0040	3.5167	1.37
.15023	.7892	.0020	3.1333	1.48
.20036	.7908	.0030	2.5500	1.51
.25117	.7904	.0025	1.9167	1.53
.29992	.7905	.0005	1.2967	1.57
.35050	.7878	.0015	1.1083	1.77

table contains three sets of results: one with the chloride constant at 0.05 *M* and the amine concentrations varied; one with amine constant at 0.60 *M* and the chloride concentrations varied; one with the amine constant at 0.79 *M* and the chloride concentrations again varied. For all of the runs, the total variation in chloride concentration is more than 7-fold, and the total variation in amine con-

(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).

centration is more than 5-fold. The slopes and intercepts given in the tables are from plots of $\log A_0(B_0 - 2D)/B_0(A_0 - D)$, vs. t , in seconds, and the tabulated bimolecular rate constants are obtained from these plots. Since all of the experimental data fall almost exactly on such linear plots, this abbreviated presentation will permit a reconstruction of the data. In all cases the reactions were followed to at least 60% of completion and in many cases to beyond 80% of completion.

The results of experiments with the amine and chloride concentrations constant and varying concentrations of added *m*-dinitrobenzene are shown in Table II. The bimolecular rate constants, shown in this and the other tables in this paper to permit comparison with other results in the literature, are of minor significance. In this case, however, they do indicate the striking effect on the rate which results from the addition of *m*-dinitrobenzene, for in the presence of approximately 0.42 *M* *m*-dinitrobenzene, the reaction rate is increased by more than 60%.

TABLE II

EFFECT OF *m*-DINITROBENZENE ON THE RATES OF REACTION OF 2,4-DINITROCHLOROBENZENE AND ALLYLAMINE IN CHLOROFORM CONTAINING 0.75% ETHANOL AT $24.8 \pm 0.1^\circ$

Chloride, mole l. ⁻¹	Amine, mole l. ⁻¹	<i>m</i> -Dinitrobenzene, mole l. ⁻¹	Intercept	Slope $\times 10^5$	$k_2 \times 10^4$, l. mole ⁻¹ sec. ⁻¹
0.05048	0.2011	0.1213	0.0070	0.2858	0.658
.05010	.2014	.1853	.0092	.3425	.779
.05147	.2281	.2060	.0090	.4445	.818
.05076	.2066	.3407	.0050	.4000	.877
.05146	.1995	.4196	.0040	.4175	.996

All of the results with *n*-butylamine are summarized in Table III. There are two sets of determi-

TABLE III

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

Chloride, mole l. ⁻¹	Amine, mole l. ⁻¹	Intercept	Slope $\times 10^6$	$k_2 \times 10^4$, l. mole ⁻¹ sec. ⁻¹
0.05165	0.1038	0	0.0054	2.47
.05141	.1866	0	1.18	3.25
.05111	.1985	0	1.28	3.07
.05061	.4961	0	7.50	4.37
.05168	.8018	0	18.89	6.22
.05108	.9997	0	29.00	7.45
.05196	1.0090	0	27.50	7.81
.02449	0.9945	0	31.39	7.63
.01339	.4009	0.0200	6.28	3.87
.02543	.4005	.0100	5.92	3.90
.05136	.3995	.0070	5.18	4.02
.07578	.3991	.0060	4.37	4.06
.08885	.3967	.0070	3.77	3.96
.10004	.3985	.0030	3.50	4.06
.12445	.3968	.0040	2.58	4.01
.14882	.3993	.0023	1.75	3.97

nations here. The measurements with the chloride constant at approximately 0.05 *M* and the amine concentrations varied have been reported previously^{1a,b} and are repeated here for the sake of convenience. The second set of experiments is with the amine held constant at 0.4 *M* and the chloride

concentrations varied. The total variation represented in these rate measurements is about 10-fold for both the chloride and amine concentrations.

The results of three measurements of the rate of reaction of N,N-dideuterio-*n*-butylamine with 2,4-dinitrochlorobenzene in chloroform at $24.8 \pm 0.1^\circ$ are shown in Table IV. Although a direct com-

TABLE IV

RATES OF REACTION OF 2,4-DINITROCHLOROBENZENE AND N,N-DIDEUTERIO-*n*-BUTYLAMINE IN CHLOROFORM CONTAINING 0.75% ETHANOL AT $24.8 \pm 0.1^\circ$

Chloride, mole l. ⁻¹	Amine, mole l. ⁻¹	Intercept	Slope $\times 10^5$	$k_2 \times 10^4$, l. mole ⁻¹ sec. ⁻¹
0.05433	0.2040	0.0080	1.233	2.98
.05189	.4108	.0020	5.462	4.10
.05230	.6108	.0060	11.182	5.09

parison with runs at the same concentrations in Table III is not possible, it will, nevertheless, be possible to show that deuterium substitution in the amine is without effect on the reaction rate.

Experimental

Materials.—Baker and Adamson Reagent Grade chloroform was used without purification. This solvent contains 0.75% ethanol as a stabilizer. Eastman Kodak Co. white label *n*-butylamine was distilled twice from calcium hydride, and a middle fraction of b.p. 77° was used. Allylamine, from the Shell Chemical Corp., was twice distilled from calcium hydride; b.p. 53° . Eastman Kodak Co. white label 2,4-dinitrochlorobenzene and *m*-dinitrobenzene were both twice recrystallized from ethanol and had m.p.'s 51° and $89-89.5^\circ$, respectively.

Rate Measurements.—The procedure for the rate measurements has been described.¹ In most of the present experiments it was found more convenient to quench the aliquots by adding them to 25 ml. of 50% concentrated nitric acid-50% glacial acetic acid. The solutions were then diluted with water and analyzed as before.

N,N-Dideuterio-*n*-butylamine.—The exchange was effected by a procedure described by Hawthorne.² *n*-Butylamine (50 ml.) was added to 20 ml. of 99.8% deuterium oxide to which had previously been added 1 g. of phosphorus pentoxide. The solution was refluxed 3 hours; the amine was distilled from the reaction mixture and then redistilled from 3 g. of barium oxide. These exchange and drying procedures were repeated two additional times. The final product was then distilled three more times from 3-g. portions of barium oxide. The yield was 26 g., b.p. $74-76^\circ$. The infrared absorption spectrum of this compound, obtained in the form of the pure liquid, was compared with the spectrum of *n*-butylamine. In the deuterated amine the bands at 2.95 and 6.2 μ , due to NH stretching and NH deformation,³ respectively, are almost completely absent. In addition, new bands appear at 3.95, 4.1 and 8.4 μ . From the relative intensities of these bands it is estimated that the deuterated amine contains at least 78% of N,N-dideuterio-*n*-butylamine.

N-Allyl-2,4-dinitroaniline.—A solution of 2,4-dinitrochlorobenzene (4.04 g., 0.0002 mole) and allylamine (10 ml.) in chloroform (90 ml.) was left standing overnight at room temperature. The solution was taken up in benzene and washed two times with 1 *N* hydrochloric acid. The solution was dried over anhydrous magnesium sulfate, and the solvent was removed. The crude product was crystallized from ethanol; yield 3.39 g. (74%), m.p. $75-76^\circ$. A sample for analysis crystallized two additional times from ethanol had m.p. $75.5-76^\circ$.

Anal. Calcd. for $C_9H_9N_2O_4$: C, 48.43; H, 4.06; N, 18.83. Found: C, 48.91; H, 4.26; N, 18.82.

(2) M. F. Hawthorne, *THIS JOURNAL*, **76**, 8358 (1954).

(3) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, Chap. 14.

Discussion

It has already been indicated that the present results cannot be accommodated either by equation 1 or a bimolecular formulation accompanied by a general medium effect, linear with the amine concentration. The latter hypothesis is untenable, since the application of equation 2 to points selected such that B is constant for every point and the A_0 's and B_0 's vary does not result in $k_3 = 0$.

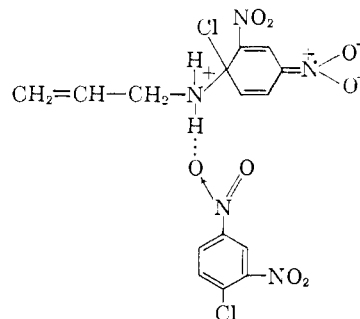
The former hypothesis, in which product results from competing bimolecular and termolecular reactions according to equation 1, is also inadequate. This can be shown by considering the experiments with varying concentrations of allylamine and 2,4-dinitrochlorobenzene (Table I). The fit of the experimental data to equation 2 can be tested in greater detail than we have previously attempted.^{1b,c} This can be done by performing a least squares treatment, using the I. B. M. 650 computer, on values of t for the purpose of determining the best values of k_1 and k_3 . This makes it possible to include in the calculation all of the actual experimental points rather than points selected from a plot of D vs. t . When such a treatment is applied to the ten experiments in Table I with the initial chloride concentrations constant at approximately 0.05 M and the initial amine concentrations variable, the values of k_1 and k_3 that result are 5.15×10^{-5} l.mole⁻¹ sec.⁻¹ and 1.10×10^{-4} l.²mole⁻²sec.⁻¹, respectively. If the same treatment is applied to all nineteen runs in Table I (more than 150 experimental points), the values obtained for k_1 and k_3 are 4.99×10^{-5} l.mole⁻¹ sec.⁻¹ and 1.20×10^{-4} l.²mole⁻²sec.⁻¹, respectively.

In spite of this excellent agreement there are two compelling reasons for rejecting this hypothesis. The first is that if this same treatment is applied to either set of measurements with A_0 variable and B_0 constant, much larger values for k_1 and much smaller values for k_3 are obtained. Even more important, if theoretical D vs. t plots are calculated for either pair of rate constants above and compared with the experimental D vs. t plots, very poor fits result, particularly for the two sets of experiments with B_0 constant. We conclude, therefore, that neither of these hypotheses adequately explains the experimental data.

One cause of the difficulty is suggested by the results in Table I. It is to be noted that in both sets of measurements with the initial amine concentrations constant, the second-order rate constants increase regularly with increasing initial 2,4-dinitrochlorobenzene concentrations. For the experiments at 0.79 M allylamine, a 7-fold increase in the chloride concentration results in more than 30% increase in the rate constant. This suggests that perhaps the rate expression for this reaction should contain a term which is first-order in amine and second-order in the halide.

This is the equivalent of saying that one path leading to final product is characterized by a transition state which involves two 2,4-dinitrochlorobenzene molecules and one allylamine molecule. Such a transition state, whatever its probability, is certainly not impossible. One possible

structure is



Here the function of the second 2,4-dinitrochlorobenzene molecule is to form a hydrogen bond from hydrogen on nitrogen to the oxygen of a nitro group, thus facilitating the over-all reaction by weakening the nitrogen-hydrogen bond. Since the ability of the aromatic nitro group to form hydrogen bonds both intermolecularly⁴ and intramolecularly with appropriate adjacent substituents⁵ has been demonstrated, this hypothesis merits consideration.

It is to be noted that, in accordance with this hypothesis, the effectiveness of the second 2,4-dinitrochlorobenzene molecule in promoting the reaction is entirely resident in the nitro substituents. This permits an experimental test, since other aromatic nitro compounds should also be capable of accelerating the reaction. The measurements summarized in Table II were designed to serve this purpose. In these experiments the initial amine and chloride concentrations were kept low and constant, and the concentrations of initially added *m*-dinitrobenzene were varied. The results are unequivocal. The addition of 0.4196 M *m*-dinitrobenzene raises the bimolecular rate constant from 6.1×10^{-5} to 10×10^{-5} l.mole⁻¹sec.⁻¹, an increase of more than 60%. We conclude that the aromatic nitro group does catalyze the reaction in chloroform.⁶

Once the accelerating effect of the aromatic nitro group has been demonstrated and is accepted, it becomes obvious that the rate expression for this reaction must include a term for each of the nitro compounds present in the system. Nitro substituents are present in the starting material, 2,4-dinitrochlorobenzene, A; the product, N-allyl-2,4-dinitroaniline, D; and *m*-dinitrobenzene, C, when it is added to the system. In experiments with low A_0 , the product D is of minor importance, since its concentration, initially zero, is low throughout the reaction. However, in runs with A_0 large, appreciable concentrations of D are present,

(4) G. C. Pimentel and C. H. Sederholm, *J. Chem. Phys.*, **24**, 639 (1956).

(5) A. W. Baker and A. T. Shulgin, *THIS JOURNAL*, **80**, 5358 (1958).

(6) Since *m*-dinitrobenzene has a large dipole moment ($\mu = 3.81 \times 10^{-18}$ debye at 25°)⁷ and, as a result, a high dielectric constant, it might be argued that the catalytic effect observed with *m*-dinitrobenzene is really a solvent effect. Such an argument can be rejected, since, on a molar basis, *sym*-trinitrobenzene which has a low dipole moment ($\mu = 0.8 \times 10^{-18}$ debye at 25°)⁸ has an even larger catalytic effect than does *m*-dinitrobenzene. In one experiment with 0.05010 M 2,4-dinitrochlorobenzene, 0.2006 M allylamine and 0.2919 M *sym*-trinitrobenzene in chloroform at 24.8 ± 0.1°, the bimolecular rate constant was 8.5×10^{-5} l. mole⁻¹ sec.⁻¹.

(7) J. W. Williams and C. H. Schwigel, *THIS JOURNAL*, **50**, 366 (1928).

(8) J. W. Williams, *ibid.*, **50**, 2350 (1928).

particularly at high % reactions and, as will be shown, a term in D becomes necessary to obtain good fits at high conversions.

When these terms are included, the rate expression becomes

$$dD/dt = k_1(A)(B) + k_3(A)(B)^2 + k_4(A)^2(B) + k_5(A)(B)(D) + k_6(A)(B)(C) \quad (3)$$

where

$$A = A_0 - D \quad (4)$$

and

$$B = B_0 - 2D \quad (5)$$

since a second amine molecule reacts with the hydrogen chloride produced in the reaction, and C, which is not consumed in the reaction, is independent of both t and D . Equation 3 may be integrated to give

$$t = \frac{1}{\beta + \gamma A_0} \left[\frac{1}{(B_0 - 2A_0)} \ln \frac{A_0(B_0 - 2D)}{B_0(A_0 - D)} + \frac{\gamma}{2\beta + \gamma B_0} \ln \frac{B_0(\beta + \gamma D)}{(B_0 - 2D)\beta} \right] \quad (6)$$

where

$$\beta = k_1 + k_3 B_0 + k_4 A_0 + k_6 C \quad (7)$$

and

$$\gamma = k_5 - 2k_3 - k_4 \quad (8)$$

Equation 6 permits the calculation of theoretical D vs. t curves for any given set of values for the five rate constants in equation 3. Such calculations were carried out with the aid of an I.B.M. 650 computer. The comparison of such theoretical D vs. t curves with the experimental D vs. t curves permits a test of the significance of equation 3 for the mechanism of this reaction. If equation 3 is a valid rate expression for this reaction, then there must be at least one set of values for the rate constants which will adequately fit all of the runs of Tables I and II.

Fortunately, the selection of values for these constants is not a purely trial and error process. Preliminary estimates may be obtained from approximate equations. Equation 3 may be rewritten as

$$\frac{1}{A_0 B_0} \frac{dD}{dt} = k_2 = k_1 + k_3(B_0) + k_4(A_0) + k_6(C) \quad (9)$$

where k_2 is the experimental second-order rate constant extrapolated to zero time. The k_5 term becomes zero, since at $t = 0$, $D = 0$. By applying equation 9 only to runs with C absent, it may be simplified further to

$$k_2 = k_1 + k_3(B_0) + k_4(A_0) \quad (10)$$

If we first take the runs with A_0 constant and B_0 variable and plot k_2 vs. B_0 , the slope of the resulting straight line is equal to k_3 , and the intercept is equal to $k_1 + k_4(A_0)$. Similarly, from the linear plot of k_2 vs. A_0 for runs with B_0 constant and A_0 variable, one obtains an intercept equal to $k_1 + k_3(B_0)$ and a slope equal to k_4 . From the combination of these four values preliminary values are obtained for k_1 , k_3 and k_4 . Although there are minor differences between the extrapolated values of the second-order rate constants and the k_2 's presented in Table I,^{1b} the actual values listed on Table I are adequate for the above purpose.

A first value for k_6 may be obtained from the data of Table II and the relationship

$$k_2^* - k_2 = k_6(C) \quad (11)$$

where k_2^* is the rate constant given in Table II for a particular experiment and k_2 is the rate constant (from Table I) for the same A_0 and B_0 but with C absent. These considerations afforded estimates of four of the five rate constants. The fifth constant, k_5 , was assumed to be similar in magnitude to k_4 and k_6 in the early calculations, and the values of all five constants were then adjusted by essentially a trial and error process to obtain optimum coincidence of experimental and theoretical D vs. t curves.

The approximate procedure which has just been described gave the following preliminary values for the rate constants: $k_1 = 3.8 \times 10^{-5}$ l.mole⁻¹.sec.⁻¹, $k_3 = 1.1 \times 10^{-4}$ l.²mole⁻².sec.⁻¹, $k_4 = 1.2 \times 10^{-4}$ l.²mole⁻².sec.⁻¹, $k_5 = 1.0 \times 10^{-4}$ l.²mole⁻².sec.⁻¹, $k_6 = 8 \times 10^{-5}$ l.²mole⁻².sec.⁻¹, k_5 being taken as an average of k_4 and k_6 . If the rate equation which has been postulated is correct, these approximate procedures should give values for the rate constants which are reasonably close to those finally obtained by a careful fitting of experimental and calculated D vs. t curves. This expectation proved to be correct, for the constants which finally resulted were: $k_1 = 3.00 \times 10^{-5}$ l.mole⁻¹.sec.⁻¹, $k_3 = k_4 = k_5 = 1.38 \times 10^{-4}$ l.²mole⁻².sec.⁻¹, $k_6 = 1.12 \times 10^{-4}$ l.²mole⁻².sec.⁻¹.

It remains now to consider how good a fit is obtained to the experimental data by combination of the rate constants above and equation 3. One qualitative criterion is to take the arithmetic sum of the deviations of the experimental D 's from the theoretical D vs. t curve times one hundred for each run, divide this by the sum of the experimental D 's and consider this figure as a "percentage deviation." When this is done for the 24 runs in Tables I and II, 10 have percentage deviations between 0 and 1, 8 have percentage deviations between 1 and 3, 5 have percentage deviations between 3 and 5 and 1 has a percentage deviation slightly above 8. Though this indicates a very good fit, it is an arbitrary procedure which favors those runs which have more of the experimental points at higher percentage reactions. The most valid criterion is the actual comparison of the experimental and calculated D vs. t curves. Such comparisons are shown in Figs. 1-4. In preparing these figures an effort was made to select the representative rather than the best-fitting runs. Figure 1 shows three curves for runs with A_0 constant and B_0 variable. Figures 2 and 3 show three curves each for the two sets of runs with A_0 variable and B_0 constant and Fig. 4 shows curves for experiments with initially added *m*-dinitrobenzene. In all of these figures the solid lines represent the calculated D vs. t relationships, and the circles are the experimental points.

A change of even a few per cent. in any single constant will result in some obviously poor fits. Simultaneous variation of two or more of the rate constants can be made to yield a new set of values which will give satisfactory fits, but even in this case the values are fixed within rather narrow

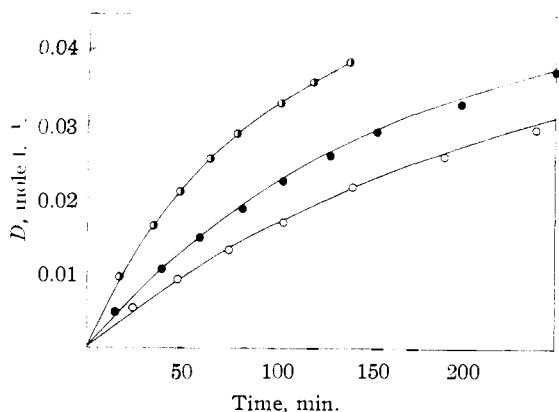


Fig. 1.— D vs. t curves for the reaction of 2,4-dinitrochlorobenzene and allylamine in chloroform containing 0.75% ethanol at $24.8 \pm 0.1^\circ$: \circ , $A_0 = 0.04988 M$, $B_0 = 1.0550 M$; \bullet , $A_0 = 0.05023 M$, $B_0 = 0.7426 M$; \circ , $A_0 = 0.04978 M$, $B_0 = 0.5994 M$.

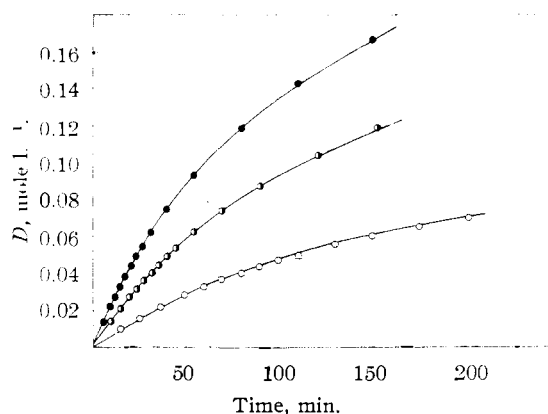


Fig. 3.— D vs. t curves for the reaction of 2,4-dinitrochlorobenzene and allylamine in chloroform containing 0.75% ethanol at $24.8 \pm 0.1^\circ$: \bullet , $A_0 = 0.2999 M$, $B_0 = 0.7905 M$; \circ , $A_0 = 0.2004 M$, $B_0 = 0.7908 M$; \circ , $A_0 = 0.1002 M$, $B_0 = 0.7904 M$.

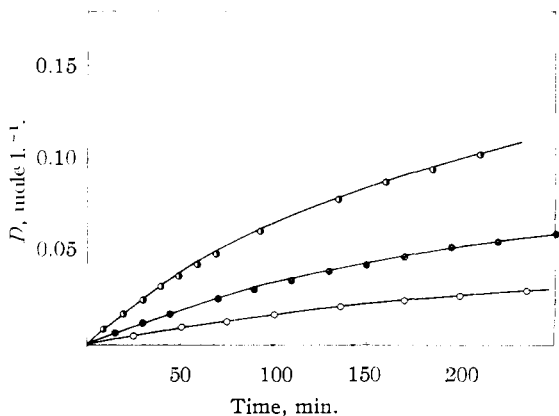


Fig. 2.— D vs. t curves for the reaction of 2,4-dinitrochlorobenzene and allylamine in chloroform containing 0.75% ethanol at $24.8 \pm 0.1^\circ$: \circ , $A_0 = 0.2001 M$, $B_0 = 0.5951 M$; \bullet , $A_0 = 0.1010 M$, $B_0 = 0.5951 M$; \circ , $A_0 = 0.05022 M$, $B_0 = 0.5968 M$.

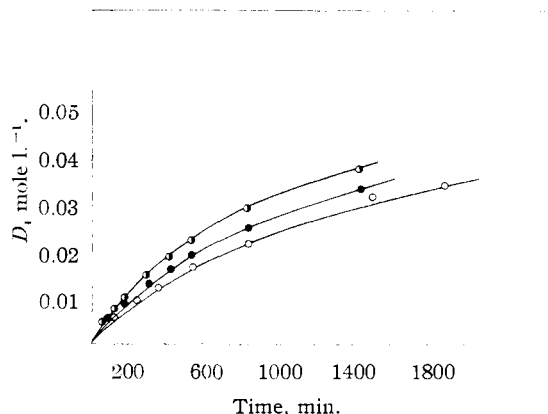


Fig. 4.— D vs. t curves for the reaction of 2,4-dinitrochlorobenzene and allylamine in chloroform containing 0.75% ethanol at $24.8 \pm 0.1^\circ$: \circ , $A_0 = 0.05146 M$, $B_0 = 0.1995 M$, $C_0 = 0.4196 M$; \bullet , $A_0 = 0.05010 M$, $B_0 = 0.2014 M$, $C_0 = 0.1853 M$; \circ , $A_0 = 0.05106 M$, $B_0 = 0.2048 M$, $C_0 = 0$.

limits. Experience in fitting values of the constants to the experimental data suggests limits of about 10% for k_1 , k_3 and k_4 and slightly wider limits for k_5 and k_6 . These surprisingly narrow limits result from the wide concentration ranges employed.

Allylamine is not unique in requiring equation 3 to fit satisfactorily the rate measurements. An almost identical situation obtains for the reaction of *n*-butylamine and 2,4-dinitrochlorobenzene. The data of Table III contain two sets of measurements, one with A_0 constant and B_0 variable and one with A_0 variable and B_0 constant. Since in this case there are no experiments with an added nitro compound, the term in k_6 in equation 3 is not involved. In all other respects, the procedures used with *n*-butylamine were identical. The rate constants which finally resulted are: $k_1 = 2.00 \times 10^{-4} \text{ l.mole}^{-1}\text{sec.}^{-1}$, $k_3 = 5.17 \times 10^{-4} \text{ l.}^2\text{mole}^{-2}\text{sec.}^{-1}$, $k_4 = k_5 = 4.67 \times 10^{-4} \text{ l.}^2\text{mole}^{-2}\text{sec.}^{-1}$. With these four constants excellent fits, shown for four representative runs in Fig. 5, were obtained for all sixteen runs of Table III.

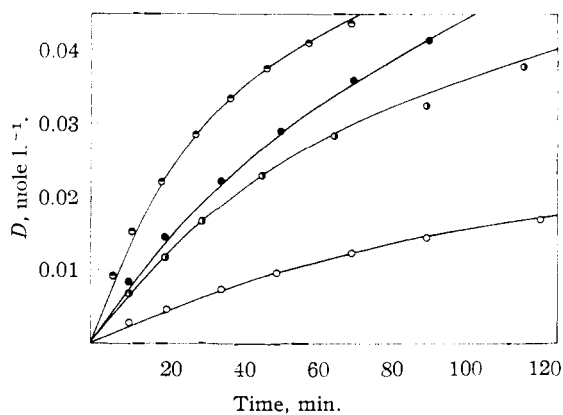
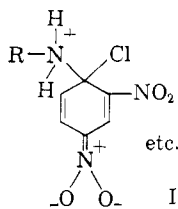


Fig. 5.— D vs. t curves for the reaction of 2,4-dinitrochlorobenzene and *n*-butylamine in chloroform containing 0.75% ethanol at $24.8 \pm 0.1^\circ$: \circ , $A_0 = 0.05168 M$, $B_0 = 0.8018 M$; \bullet , $A_0 = 0.07579 M$, $B_0 = 0.3991 M$; \circ , $A_0 = 0.05061 M$, $B_0 = 0.4961 M$; \circ , $A_0 = 0.02543 M$, $B_0 = 0.4005 M$.

The results of experiments with N,N-dideuterio-*n*-butylamine are shown in Table IV. Within experimental error, this reaction shows no deuterium isotope effect. This can be best demonstrated by reference to Fig. 6. The straight line is a plot of the second-order rate constants for the reactions of 2,4-dinitrochlorobenzene and *n*-butylamine *vs.* the initial amine concentrations (the data of Table III). The circles are for the three measurements with N,N-dideuterio-*n*-butylamine. Since all three points fall on the line, there is no discernible distinction between the rates with *n*-butylamine and the rates with N,N-dideuterio-*n*-butylamine.

Thus far it has been shown that the reaction of 2,4-dinitrochlorobenzene with a primary amine in chloroform involves a large number of separate and distinguishable product-forming steps. In the reaction with allylamine in the presence of *m*-dinitrobenzene, it has been demonstrated that there are five such reactions. Four of the five appear in the kinetic equation as third-order terms and seem to show the characteristics of a base catalysis, since the involvement of the third species is best rationalized as being due to an attack, usually *via* hydrogen bonding, on hydrogen bonded to nitrogen. The function of this third species, in every case, appears to be to facilitate the over-all reaction by assisting in the removal of a proton. Nevertheless, the reaction shows no measurable deuterium isotope effect. It is in the light of this seeming contradiction that the pertinence of the present results to the mechanism of this reaction must be explored.

The facts that there are a number of product-forming steps and that they all involve at least one amine molecule and one chloride molecule suggest that a single intermediate is common to all of the reactions. This hypothesis is further supported by the improbability that three or more truly termolecular reactions are involved. It seems far more reasonable that each third-order term in the rate equation results from either an equilibrium or steady state concentration of some intermediate formed from the interaction of two of the three species. An intermediate of the type shown below, I, has been proposed for nucleophilic aromatic substitution reactions,⁹ and there now exists a



large body of experimental evidence in support of this hypothesis.¹⁰ The present results lend further support to this point of view.

(9) (a) E. Bamberger and J. Müller, *Ber.*, **33**, 102 (1900); (b) E. Berliner, M. J. Quinn and P. J. Edgerton, *This Journal*, **72**, 5305 (1950); (c) J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 344 (1951).

(10) For a good summary of this evidence see, J. F. Bunnett, *Quart. Revs.*, **12**, 1 (1958). For individual papers of particular importance see (a) J. B. Ainscough and E. F. Caldin, *J. Chem. Soc.*, 2528 (1956); (b) J. F. Bunnett, E. W. Garbisch, Jr., and K. M. Pruitt, *This Journal*, **79**, 385 (1957); (c) J. F. Bunnett and J. J. Randall, *ibid.*, **80**, 6020 (1958).

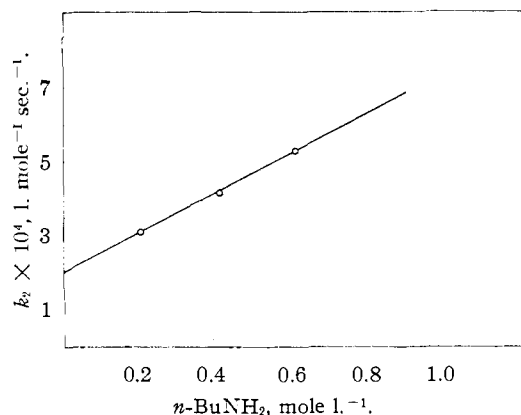
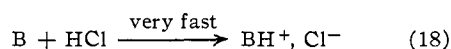
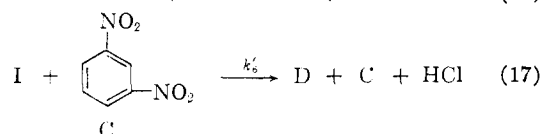
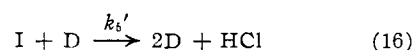
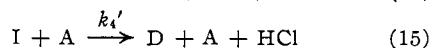
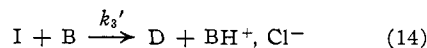
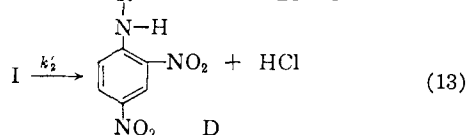
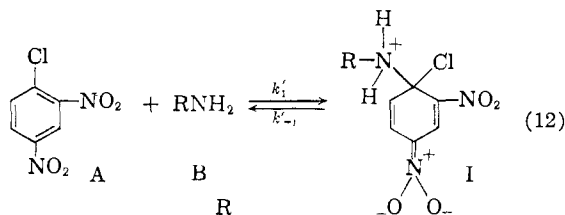


Fig. 6.—Bimolecular rate constants *vs.* B_0 for the reaction of *n*-butylamine and 2,4-dinitrochlorobenzene in chloroform containing 0.75% ethanol at $24.8 \pm 0.1^\circ$. The solid line is for the reaction with *n*-butylamine. The three points are for reactions with N,N-dideuterio-*n*-butylamine.

If the intermediate complex hypothesis is accepted, the reactions involved may be formulated as



Reaction 13 is a first-order decomposition of the intermediate to give the final products. Reactions 14–17 are all considered to have transition states of the form shown previously for *m*-dinitrobenzene; *i.e.*, they all involve hydrogen bonding from an amino hydrogen of I to some species that can act as an acceptor. It is possible and perhaps even probable that a solvent molecule performs this function in reaction 13. Assuming an equilibrium among A, B and I, the rate equation that results is

$$\frac{dD}{dt} = K(A)(B)[k_2' + k_3'(B) + k_4'(A) + k_5'(D) + k_6'(C)] \quad (19)$$

where $K = k_1'/k_{-1}'$. This equation is identical in form with equation 3, and the rate measurements

are fully consistent with the reaction sequence proposed above.¹¹

The transformation of the intermediate I to the final product, an N-alkyl-2,4-dinitroaniline, involves the breaking of both a carbon-chlorine bond and a nitrogen-hydrogen bond. This may take place in two consecutive steps or in a single, concerted process. The results with the dideuterioamine are directly pertinent to this question. A mechanism for this reaction must be consistent with the absence of a measurable deuterium isotope effect and the fact that the observed rates are affected by the process in which the nitrogen-hydrogen bond is broken.

If the rate-determining step involves simply a breaking or weakening of the N-H bond, a large isotope effect (possibly as much as a factor of 8 or 9 in rate) is to be expected.¹² Since no isotope effect is found, it is proper to conclude that the rate-determining step is not merely a breaking or weakening of the N-H bond. It may, however, involve breaking or partial breaking of the N-H bond accompanied by a simultaneous forming or partial forming of another bond to the same hydrogen. If such a single step of bond breaking-bond forming were to occur, it might well exhibit no isotope effect. An interesting parallel to the present situation, suggesting an alternate explanation, is provided by Hammond's discussion of isotope effects in aromatic electrophilic substitution.¹³

Still another explanation lies in the possibility that the rate-determining step is a concerted process including breaking or partial breaking of the N-H bond together with breaking of the C-Cl bond, and that the energy of the process is essentially that required to break the C-Cl bond. In this case, of course, the isotope effect would be masked.

Further speculation is neither warranted nor justified. Suffice it to say that the rate-determining step, at least for k_3 , k_4 , k_5 and k_6 , apparently involves hydrogen-bonded complexes, and involves

(11) If the steady state assumption is made, the concentration of I is given by

$$(I) = \frac{k_1'(A)(B)}{k_{-1}' + k_2' + k_3'(B) + k_4'(A) + k_5'(D) + k_6'(C)}$$

and the rate equation becomes

$$\frac{dD}{dt} = k_1'(A)(B)$$

$$\left[\frac{k_2' + k_3'(B) + k_4'(A) + k_5'(D) + k_6'(C)}{k_{-1}' + k_2' + k_3'(B) + k_4'(A) + k_5'(D) + k_6'(C)} \right]$$

The conditions under which an equation of this form becomes equivalent in form to equation 3 have been discussed previously.^{1b} It should, however, be pointed out here that this equation becomes identical with equation 19 if $k_{-1}' \gg k_2' + k_3'(B) + k_4'(A) + k_5'(D) + k_6'(C)$.

(12) K. Wiberg, *Chem. Revs.*, **55**, 713 (1955). It is perhaps appropriate to note that Wiberg, in his summary, urges caution in the use of the isotope effect to decide whether or not a bond to hydrogen is cleaved in the rate-determining step, citing examples of cases in which conclusions based on isotope effects are apparently faulty.

(13) G. S. Hammond, *THIS JOURNAL*, **77**, 334 (1955).

something more than a simple breaking of the N-H bond.

These results bear some resemblances to previous studies of nucleophilic substitution reactions at a saturated carbon atom in media of low ionizing power.¹⁴ In the present studies the solvent was chloroform whereas in Swain's experiments the solvent was benzene, but we would expect very similar results in pure benzene.¹⁵ In particular, both studies are characterized by termolecular processes, and, in both cases, these high-order reactions manifest themselves when the solvent is inefficient in electrophilic and/or nucleophilic solvation. In dimethylformamide, which presumably can both solvate the chloride ion and compete efficiently with other species as an acceptor for hydrogen bond formation, the third-order terms in the kinetic equation are no longer present for some nucleophilic aromatic substitution reactions.¹⁶ Yet, in some relatively polar solvents, ethanol^{1a} and 50% dioxane-50% water,^{1c} these termolecular processes still manifest themselves, albeit to a diminished extent. In this reaction there is no sharp distinction to be drawn between the bimolecular mechanism and the mechanisms of higher molecularity. Both mechanisms involve the same intermediate, and they differ only in whether it is a solvent molecule or some other species which assists in the electrophilic solvation of the proton.

Acknowledgment.—We are indebted to Mr. Kurt Schoeni and Mr. Bernard Friedman for their aid in the computations, and to Dr. Robert F. Fellows for the infrared spectra.

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(14) C. G. Swain, *ibid.*, **70**, 1119 (1948); C. G. Swain and R. W. Eddy, *ibid.*, **70**, 2989 (1948); C. G. Swain and W. P. Langsdorf, Jr., *ibid.*, **73**, 2813 (1951); C. G. Swain and J. F. Brown, Jr., *ibid.*, **74**, 2534 (1952); C. G. Swain and M. M. Kreevoy, *ibid.*, **77**, 1122 (1955); C. G. Swain and E. E. Peques, *ibid.*, **80**, 812 (1958). For an alternate interpretation see, E. D. Hughes, C. K. Ingold, S. F. Mok, S. Patai and Y. Pocker, *J. Chem. Soc.*, 1265 (1957), and subsequent papers.

(15) It was not possible to conduct experiments in pure benzene because of the insolubility of allylamine hydrochloride, but as shown in the table below, the results in 50% benzene-50% chloroform are very similar to the results in chloroform, suggesting that comparable results would again be obtained in pure benzene.

RATES OF REACTION OF 2,4-DINITROCHLOROBENZENE AND ALLYLAMINE IN 50% BENZENE-50% CHLOROFORM CONTAINING 0.75% ETHANOL AT 24.8 ± 0.1°

Chloride, mole l. ⁻¹	Amine, mole l. ⁻¹	Intercept	Slope × 10 ⁵	$k_2 \times 10^4$, l. mole ⁻¹ sec. ⁻¹
0.04973	0.1971	0.0040	0.339	0.799
.05085	.2984	.0040	0.808	0.946
.05036	.6062	.0040	3.167	1.44
.05076	.7367	.0080	4.517	1.64
.05031	.8921	.0120	6.600	1.92

(16) S. D. Ross, *THIS JOURNAL*, **81**, 2113 (1959).