

All of the conclusions presented in this paper are consistent not only with the present data but with that available in the preceding paper of this series.<sup>3</sup>

**Acknowledgment.**—This work was aided by a grant from the Research Corporation which per-

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC COMPANY]

### Molecular Compounds. III. The Effect of Molecular Compound Formation on the Rates of Reaction of Aniline with 2,4-Dinitrochlorobenzene

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The rate of reaction of aniline with 2,4-dinitrochlorobenzene has been measured in ethanol, 50% ethanol-50% ethyl acetate and ethyl acetate. In both ethanol and 50% ethanol-50% ethyl acetate at constant 2,4-dinitrochlorobenzene concentration the bimolecular rate constant decreases with increasing aniline concentration. It is shown by both kinetic analysis and spectroscopic measurements that the observed decreases in rate are attributable to molecular compound formation between aniline and 2,4-dinitrochlorobenzene. In ethyl acetate the rate constant is unchanged by increasing the aniline concentration, and in this solvent complex formation occurs, at most, to only a minor extent.

The rate of reaction of aniline with 2,4-dinitrochlorobenzene in ethanol has been measured by Rheinlander<sup>1</sup> and Singh and Peacock.<sup>2</sup> In both instances it was observed that, although individual runs gave satisfactorily linear second-order plots, the derived rate constants were not independent of the initial concentrations of aniline and 2,4-dinitrochlorobenzene. In every experiment where one reactant was kept constant and the concentration of the second reactant was increased, a lower velocity constant resulted. Singh and Peacock pointed out this anomalous effect but did not comment on it. Rheinlander noticed further that when aniline and 2,4-dinitrochlorobenzene were mixed in ethanol the solution became colored, but argued that the concentration of colored complex was not sufficient to have any observable effect on the reaction rate. In contrast to these results, Brady and Cropper,<sup>3</sup> who measured the rates of reaction of 2,4-dinitrochlorobenzene with a series of aliphatic amines, found that the bimolecular rate constant was independent of the initial concentrations within the accuracy of their measurements.

On the basis of current theories of molecular compound formation,<sup>4</sup> one would expect appreciable complex formation between 2,4-dinitrochlorobenzene and aniline but not between the former and aliphatic amines. Moreover, although color formation is an indication of molecular compound formation of the charge-transfer type, other non-colored complexes or associations, capable of affecting a reaction rate, can exist in solution.<sup>5</sup> Because of these considerations, we have investigated the rate of reaction of 2,4-dinitrochlorobenzene and aniline in ethanol, ethyl acetate and 50% ethanol-50% ethyl acetate at 24.4 ± 0.1° and focused our attention on the previously observed anomalies.

(1) A. H. Rheinlander, *J. Chem. Soc.*, 3099 (1923).

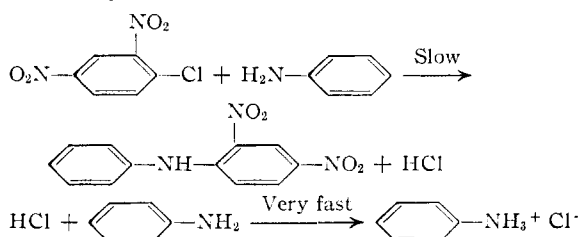
(2) A. Singh and D. H. Peacock, *ibid.*, 1410, 1411 (1935); *J. Phys. Chem.*, **40**, 669 (1936).

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

(4) (a) J. Weiss, *ibid.*, 245 (1942); (b) R. B. Woodward, *THIS JOURNAL*, **64**, 3058 (1942); (c) W. Brackmann, *Rec. trav. chim.*, **68**, 147 (1949); (d) R. S. Mulliken, *THIS JOURNAL*, **72**, 600 (1950); **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).

(5) S. D. Ross, M. Bassin, M. Finkelstein and W. A. Leach, *THIS JOURNAL*, **76**, 69 (1954).

**Reaction Rate Studies.**—Aniline reacts with 2,4-dinitrochlorobenzene to form 2,4-dinitrodiphenylamine and hydrochloric acid. The latter product reacts rapidly with another mole of aniline to give aniline hydrochloride.



The differential equation for the above reaction sequence is given by

$$dx/dt = k^*(a - 2x)(b - x) \quad (1)$$

where  $a$  is the initial concentration of aniline,  $b$  the initial concentration of 2,4-dinitrochlorobenzene and  $x$  is the concentration of 2,4-dinitrodiphenylamine at any time,  $t$ . For the case where  $a$  is greater than  $2b$ , the integrated form of this equation is

$$k^*t = \frac{2.303}{a - 2b} \cdot \log \frac{b(a - 2x)}{a(b - x)} \quad (2)$$

We have measured the rate of this reaction in absolute ethanol at 24.4 ± 0.1°, maintaining the dinitrochlorobenzene concentration at 0.050-0.052  $M$  and varying the aniline concentration from 0.2 to 1.0  $M$ . As is apparent from Fig. 1, the individual runs give satisfactory second-order plots. The results, summarized in Table I, however, clearly demonstrate that the differential expression (1) does not represent an adequate mechanism for the

TABLE I

RATES OF REACTION OF 2,4-DINITROCHLOROBENZENE AND ANILINE IN ETHANOL

2,4-Dinitrochlorobenzene, mole/l.	Aniline, moles/l.	$k^*$ , $l. \times \text{mole}^{-1} \times \text{hr.}^{-1}$
0.04993	0.2004	0.262
.05210	.5009	.232
.05230	.6737	.221
.04980	1.0106	.192

reaction. In going from 0.2 *M* to 1.0 *M* aniline the obtained rate constant,  $k^*$ , changes by 27%, and this is far too great a change to be attributable to experimental error.

The results of two measurements of the rate of reaction of 2,4-dinitrochlorobenzene with di-*n*-butylamine in the same solvent and at the same temperature are given in Table II. Changing the amine concentration from 0.28 *M* to 1.0 *M* changes the rate constant by less than 7%. This difference is within the expected experimental error for measurements of this type. Moreover, similar results have been reported by Brady and Cropper<sup>3</sup> for other aliphatic amines. For 2,4-dinitrochlorobenzene and the aliphatic amines equation 1 is, therefore, an adequate rate expression.

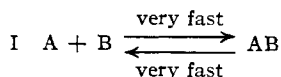
TABLE II

RATES OF REACTION OF 2,4-DINITROCHLOROBENZENE AND DI-*n*-BUTYLAMINE IN ETHANOL

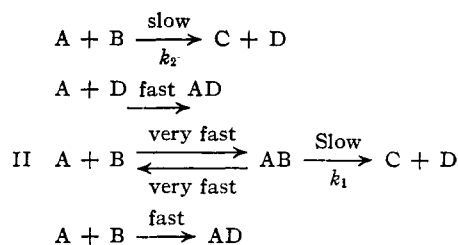
2,4-Dinitrochlorobenzene, mole/l.	Di- <i>n</i> -butylamine, moles/l.	$k^*$ , $l. \times \text{mole}^{-1} \times \text{hr.}^{-1}$
0.05279	0.2755	0.92
.05468	1.0109	.98

Although the final products of the reaction between 2,4-dinitrochlorobenzene and aniline are 2,4-dinitrodiphenylamine and aniline hydrochloride, as previously indicated, it is clear that there is an additional factor present which operates to affect the reaction rate. That this additional factor may be molecular compound formation is suggested by the facts that aniline and 2,4-dinitrochlorobenzene generate color (the change is from almost colorless to deep yellow) when mixed in solution and that increasing the aniline concentration causes a decrease in the measured second-order rate constant. Aniline is a donor molecule and 2,4-dinitrochlorobenzene is an acceptor molecule. Molecular complex formation is to be expected when the two are mixed in solution.<sup>4d</sup> Moreover, Landauer and McConnell<sup>6</sup> have shown that aniline forms a measurable amount of complex in chloroform solution with *m*-d nitrobenzene, *p*-dinitrobenzene and *s*-trinitrobenzene, and Pickett, McClure and Jacob<sup>7</sup> have measured the stability of the aniline-*m*-dinitrobenzene complex in ethanol.

If molecular compound formation is the perturbing factor responsible for the anomalous rate results with aniline and 2,4-dinitrochlorobenzene, there are two mechanisms which must be considered. In the first, aniline A and 2,4-dinitrochlorobenzene B are in equilibrium with the molecular compound AB. Simultaneously, A and B react in a rate-determining step to form 2,4-dinitrodiphenylamine C and hydrogen chloride D. The hydrogen chloride then reacts rapidly with aniline to form aniline hydrochloride. Alternatively, the products, C and D, may result from the decomposition, in a rate determining step, of the molecular adduct, AB. We may represent the two possibilities as



(6) J. Landauer and H. McConnell, *THIS JOURNAL*, **74**, 1221 (1952).  
 (7) L. W. Pickett, H. M. McClure and M. A. Jacobs, ONR report under contract N8onr-74100 with Mount Holyoke College (Oct. 1, 1949-June 30, 1951).



If we now let

$A_0$  = the initial concentration of A  
 $B_0$  = the initial concentration of B  
 $y$  = the concentration of AB at any time  $t$   
 $x$  = the concentration of C at any time  $t$

we can write the following differential expression for mechanism I.

$$dx/dt = k_2(A_0 - y - 2x)(B_0 - y - x) \quad (3)$$

For the equilibrium constant we may write

$$K = \frac{y}{(A_0 - y - 2x)(B_0 - y - x)} \quad (4)$$

Similarly for mechanism II we may write

$$dx/dt = k_1y = k_1K(A_0 - 2x - y)(B_0 - x - y) \quad (5)$$

The expression for the equilibrium constant is identical for mechanisms I and II and given by 4.

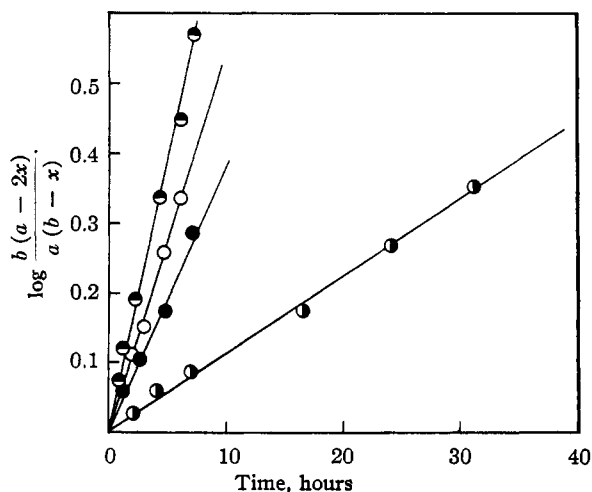


Fig. 1.—Second-order plots for the rate of reaction of aniline and 2,4-dinitrochlorobenzene in absolute ethanol at  $24.4 \pm 0.1^\circ$ :  $\ominus$ ,  $A_0 = 1.0106 M$ ,  $B_0 = 0.04980 M$ ;  $\circ$ ,  $A_0 = 0.6737 M$ ,  $B_0 = 0.05230 M$ ;  $\bullet$ ,  $A_0 = 0.5009 M$ ,  $B_0 = 0.05210 M$ ;  $\ominus$ ,  $A_0 = 0.2004 M$ ,  $B_0 = 0.04993 M$ .

It is apparent from these equations that, for either mechanism, the system can be completely defined in terms of two constants, an equilibrium constant  $K$  and a rate constant  $k_1$  or  $k_2$ . Moreover, the differential expressions for the two mechanisms differ only in the substitution of  $k_1K$ , in mechanism II, for  $k_2$ . Let us for the moment, therefore, consider the system in terms of  $K$  and a constant  $k_x$  and hold in abeyance the question of whether  $k_x = k_2$  or  $k_1K$ . If our rate results can be adequately encompassed by the two constants  $K$  and  $k_x$ , it will lend support to the hypothesis that molecular compound formation is the perturbing factor.

Let us focus our attention on the reaction at

zero time, for at this time we can quantitatively define a sufficient number of the concentrations to permit a determination of  $K$  and  $k_x$ . Since  $A$  and  $B$  are in instantaneous equilibrium with complex  $y$ , we must distinguish between free  $A$ ,  $A_t$  and  $A_0$ , and between free  $B$ ,  $B_t$ , and  $B_0$  even at zero time. We, therefore, define the concentrations at zero time as

$$\begin{aligned} A_t &= A_0 - y \cong A_0 \\ B_t &= B_0 - y \end{aligned}$$

From equation 3 or 5 it follows that

$$dx/dt_{t=0} = k_x(A_0 - y)(B_0 - y) \quad (6)$$

and, for  $t = 0$ , equation 4 becomes

$$K = \frac{y}{(A_0 - y)(B_0 - y)} \quad (7)$$

From equation 1, we obtain an alternate expression for  $dx/dt_{t=0}$

$$dx/dt_{t=0} = k^*A_0B_0 \quad (8)$$

Combining equations 6, 7 and 8 and using the definitions above, it may be shown that<sup>8</sup>

$$\frac{1}{k^*} = \frac{1}{k_x} + \frac{K}{k_x}A_0 \quad (9)$$

In equation 9 both  $k^*$  and  $A_0$  are known for each experiment. A plot of  $k^*$  vs.  $A_0$  for our experiment should result in a straight line with the intercept equal to  $1/k_x$  and the slope equal to  $K/k_x$ . Figure 2 shows our data plotted in this manner. The straight line drawn through the experimental points was determined by the method of least squares. From the slope and intercept of this line  $k_x$  was found to be equal to  $0.29 \pm 0.03$  l. mole<sup>-1</sup> hr.<sup>-1</sup> and  $K$  was found to equal  $0.49 \pm 0.05$  l. mole<sup>-1</sup>. The uncertainties in  $k_x$  and  $K$  were determined from the prob-

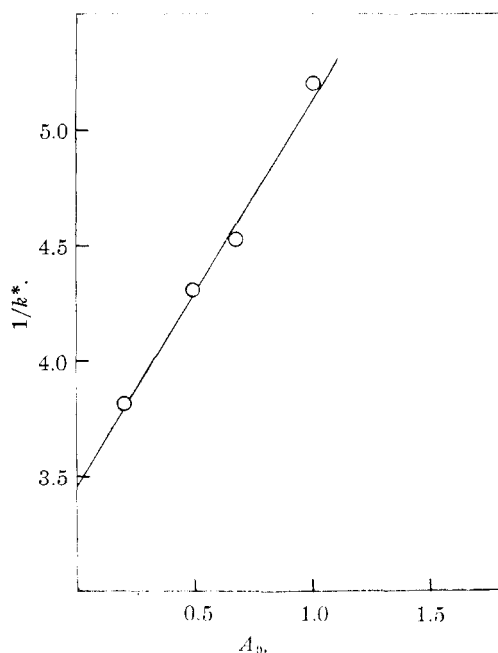


Fig. 2.—A plot of  $1/k^*$  vs. the initial aniline concentration,  $A_0$ , in absolute ethanol.

(8) We are indebted to the referee for pointing out this simplified method for obtaining  $k_x$  and  $K$ . We had previously used a more laborious procedure for evaluating these constants.

able errors in the slope and in the intercept as calculated according to Worthing and Geffner.<sup>9</sup>

We now turn to measurements of the rate of reaction of aniline and 2,4-dinitrochlorobenzene in ethyl acetate. The results are summarized in Table III. The rate constants were calculated using the integrated form of equation 1. In this solvent the rate constant is clearly independent of the aniline concentration within the accuracy of our measurements. We conclude that in this solvent complexing is either absent or its extent is too small to perturb the rate measurements.

TABLE III  
RATES OF REACTION OF 2,4-DINITROCHLOROBENZENE AND ANILINE IN ETHYL ACETATE

2,4-Dinitrochlorobenzene, mole/l.	Aniline, moles/l.	$k^*$ , l. $\times$ mole <sup>-1</sup> $\times$ hr. <sup>-1</sup>
0.05027	0.5018	0.0153
.05005	0.7500	.0158
.04998	1.002	.0157
.05003	1.251	.0152

The reaction rates in 50% ethanol-50% ethyl acetate by volume are given in Table IV. As before the rate constants were calculated using equation 2. In this solvent system, too, there is a definite decrease in the rate constant as the aniline concentration is increased. The decrease, however, is not as large as that observed in ethanol. In going from 0.20  $M$  to 1.5  $M$  aniline the rate constant decreases by 17.5%, an amount which is well in excess of our experimental error.

TABLE IV  
RATES OF REACTION OF 2,4-DINITROCHLOROBENZENE AND ANILINE IN 50% ETHANOL-50% ETHYL ACETATE BY VOLUME

2,4-Dinitrochlorobenzene, mole/l.	Aniline, moles/l.	$k^*$
0.05020	0.2000	0.0860
.05008	0.3516	.0850
.05017	1.003	.0777
.05019	1.498	.0710

The values of  $K$  and  $k_x$  in this solvent system were determined by the method used to determine these constants in absolute ethanol. Figure 3 shows a plot of  $1/k^*$  vs.  $A_0$ . Again the straight line drawn through the experimental points was determined by the method of least squares. The resultant values are  $0.090 \pm 0.002$  l. mole<sup>-1</sup> hr.<sup>-1</sup> for  $k_x$  and  $0.170 \pm 0.004$  l. mole<sup>-1</sup> for  $K$ .

**Absorption Spectra Studies.**—Our reaction rate studies support but do not definitely establish the hypothesis that molecular compound formation is the perturbing factor in the aniline-2,4-dinitrochlorobenzene rate measurements. A complete demonstration of this proposition requires an independent measurement, by some method not involving reaction rates, of the extent of complexing in this system. In a previous study<sup>5</sup> we have shown that more than one type of interaction may affect a reaction rate in solution and that the amount of complexing found is dependent on the measurement method chosen. However, in the aniline-

(9) A. G. Worthing and J. Geffner, "Treatment of Experimental Data," John Wiley and Sons, Inc., New York, N. Y., 1943, Chap. XI.

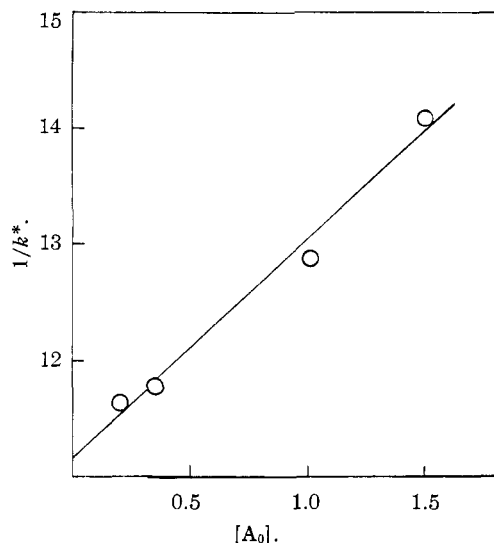


Fig. 3.—A plot of  $1/k^*$  vs. the initial aniline concentration,  $A_0$ , in 50% ethanol-50% ethyl acetate.

2,4-dinitrochlorobenzene system, the observed color phenomena suggest that the complex is, at least in part, of the charge-transfer type.<sup>4d</sup> We, therefore, chose the spectroscopic method for the measurements.

Determination of the spectroscopic equilibrium constants in this system is complicated by the fact that aniline and 2,4-dinitrochlorobenzene react to form 2,4-dinitrodiphenylamine and aniline hydrochloride. A further complication stems from the fact that both 2,4-dinitrodiphenylamine and 2,4-dinitrochlorobenzene absorb in the visible, as does the molecular addition compound. The concentration of 2,4-dinitrodiphenylamine increases as the reaction proceeds, whereas the concentration of 2,4-dinitrochlorobenzene decreases with time.

These difficulties were overcome by measuring optical densities as a function of time and extrapolating to get the optical density at zero time. At zero time the system contains only three components, aniline, 2,4-dinitrochlorobenzene and the molecular addition compound, and the optical densities at zero time may be used, in the usual manner, to calculate the equilibrium constants. We are assuming that complex formation is so rapid that it may be considered instantaneous for our purpose. The justification for this assumption has been given in the first paper of this series.<sup>5</sup> Some typical extrapolations are shown in Fig. 4. In every instance plots of optical density vs. time were linear, and this both makes the extrapolation facile and improves its reliability. As a partial explanation of this linearity, we would cite the fact that if values of the concentration of 2,4-dinitrodiphenylamine are calculated from the rate data for the same time period and plotted against time, a straight line is again obtained.

The spectroscopic data are given in Table V. In determining the equilibrium constants we used the treatment of Keefer and Andrews.<sup>10</sup> The optical

(10) R. M. Keefer and L. J. Andrews, *THIS JOURNAL*, **74**, 1891 (1952). For an alternate treatment see R. S. Stearns and G. W. Wheland, *ibid.*, **69**, 2025 (1947).

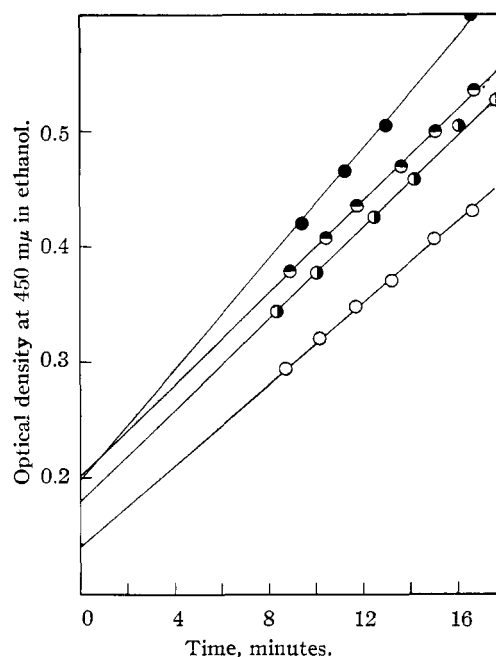


Fig. 4.—Extrapolations of optical density in ethanol at 450  $m\mu$  for aniline-2,4-dinitrochlorobenzene systems: ●,  $A_0 = 4.270 M$ ,  $B_0 = 0.001436 M$ ; ●,  $A_0 = 4.456 M$ ,  $B_0 = 0.001267 M$ ; ●,  $A_0 = 4.685 M$ ,  $B_0 = 0.001148 M$ ; ○,  $A_0 = 4.006 M$ ,  $B_0 = 0.001055 M$ .

density,  $d$ , is given by

$$\log \frac{I_0}{I} = d = A\epsilon_A + B\epsilon_B + AB\epsilon_{AB}$$

where  $A$ ,  $B$  and  $AB$  are the molar concentrations of aniline, 2,4-dinitrochlorobenzene and the complex,

TABLE V  
OPTICAL DENSITIES, EXTRAPOLATED TO ZERO TIME, IN THREE SOLVENTS

Init. aniline concn., moles/l.	Init. 2,4-dinitrochlorobenzene concn., moles/l.	Solvent	Wave length, $\mu$	Optical density extrap. to zero time
3.959	0.002040	Ethyl acetate	444	0.303
4.473	.001204	Ethyl acetate	444	.200
4.323	.002407	Ethyl acetate	444	.388
5.041	.000981	Ethyl acetate	444	.186
4.398	.001963	Ethyl acetate	444	.330
4.090	.001024	50% EtAc-50% EtOH	450	.144
5.054	.002048	50% EtAc-50% EtOH	450	.336
4.369	.000819	50% EtAc-50% EtOH	450	.123
4.374	.001191	50% EtAc-50% EtOH	450	.176
4.762	.001191	50% EtAc-50% EtOH	450	.186
5.303	.000992	50% EtAc-50% EtOH	450	.163
4.270	.001436	Ethanol	444	.230
4.270	.001436	Ethanol	450	.196
4.685	.001148	Ethanol	444	.192
4.685	.001148	Ethanol	450	.166
4.006	.001055	Ethanol	444	.161
4.006	.001055	Ethanol	450	.140
4.456	.001267	Ethanol	444	.200
4.456	.001267	Ethanol	450	.189
4.775	.002111	Ethanol	444	.347
4.775	.002111	Ethanol	450	.292
4.782	.002871	Ethanol	444	.461
4.782	.002871	Ethanol	450	.400

respectively, and the  $\epsilon$ 's are the appropriate molar extinction coefficients. The equation is written for the one-cm. cells employed in the investigation. The optical density due to the complex,  $d_{AB}$ , is

$$d_{AB} = d - A\epsilon_A - B\epsilon_B = AB\epsilon_{AB}$$

It may be shown that

$$\frac{A^*}{d_{AB}} = \frac{1}{K\epsilon_{AB}} \cdot B^* + \frac{1}{\epsilon_{AB}}$$

where

$$A^* = \frac{(A_0)(B_0)}{A_0 + B_0 - AB} \text{ and } B^* = \frac{1}{A_0 + B_0 - AB}$$

and the subscript, 0, refers to initial concentrations.

Using the initial concentrations of aniline and halide and the extrapolated values of the optical density, tentative values of  $d_{AB}$ ,  $A^*$  and  $B^*$  were obtained.

Treatment of  $A^*/d_{AB}$  vs.  $B^*$  plots by the method of least squares gave tentative values of  $K$  and  $\epsilon_{AB}$ . Corrected values of  $d_{AB}$  were now determined and  $K$  and  $\epsilon_{AB}$  were recalculated. The corrections were insignificant in all cases. The probable error in the slope and intercept,  $P_a$  and  $P_b$ , were determined by the procedure described by Worthing and Geffner,<sup>9</sup> considering all points of equal weight. The probable error in  $\epsilon_{AB}$  was taken as the probable error in the intercept. The probable error in  $K$ ,  $P_k$ , was taken as  $P_k = \sqrt{Pa^2 + Pb^2}$ .

The results are summarized in Table VI. The reported uncertainties in the spectroscopic  $K$ 's are based on the probable error calculations. For comparison purposes we have included the equilibrium constants determined by the reaction rate treatment. The uncertainties in the values of the spectroscopic equilibrium constants are admittedly large. Some improvement in the precision of the measurements could be achieved by using absorption cells with different light paths. Unfortunately these were not available to us at the time these measurements were made. However, it is clear that the values obtained are of the same order of magnitude as those obtained from our rate studies, in spite of the fact that the spectroscopic measurements were made with aniline and 2,4-dinitrochlorobenzene concentrations very much different from those used in the rate studies. Moreover, the agreement is sufficient to completely establish the hypothesis that molecular compound formation is the perturbing factor in the aniline-2,4-dinitrochlorobenzene rate studies.

TABLE VI

EQUILIBRIUM CONSTANTS FOR MOLECULAR COMPOUND FORMATION BETWEEN ANILINE AND 2,4-DINITROCHLOROBENZENE

Solvent	Wave length, m $\mu$	$\epsilon_{AB}$	$K$ at	$K$ at
			23.8 $\pm$ 0.1 $^\circ$ spectro- scopic, l. mole $^{-1}$	24.4 $\pm$ 0.1 $^\circ$ rate studies, l. moles $^{-1}$
Ethanol	444	277 $\pm$ 75	0.29 $\pm$ 0.13	0.49 $\pm$ 0.05
Ethanol	450	223 $\pm$ 54	.34 $\pm$ .15	
EtOH-50% EtAc	450	423 $\pm$ 140	.12 $\pm$ .05	0.170 $\pm$ 0.004
Ethyl acetate	444	1111 $\pm$ 1033	.05 $\pm$ .04	Not measurable

### Experimental

**Materials.**—Absolute ethanol was used as obtained from the U. S. Industrial Chemicals Company. One batch of alcohol sufficed for all our experiments and had  $n_D^{20}$  1.3599 and  $d_4^{20}$

0.78553. Rimbach and Wintgen<sup>11</sup> report  $n_D^{20}$  1.3599 for 100% ethanol.

**Ethyl Acetate.**—Eastman Kodak Co. white label, anhydrous grade ethyl acetate was distilled through a Todd column and a middle fraction of b.p. 76 $^\circ$  was used;  $n_D^{20}$  1.3704.

**50% Ethyl Acetate-50% Ethanol.**—This solvent mixture was prepared by mixing equal volumes of the above two solvents.

**Aniline.**—Eastman Kodak white label aniline was distilled from zinc dust immediately before use, and a middle fraction of b.p. 63 $^\circ$  at 8 mm. was used.

2,4-Dinitrochlorobenzene was crystallized from ethanol until the m.p. was constant at 50.5–51.5 $^\circ$ .

**Rate Measurements.**—Determinate solutions of aniline and 2,4-dinitrochlorobenzene were made up in the appropriate solvents and brought to temperature in the thermostat. Aliquots (5 cc.) of each solution were added to individual tubes, and the time of mixing was recorded. At appropriate time intervals tubes were withdrawn, and the reaction was quenched by pouring the contents into 25 cc. of 4.5 *N* nitric acid contained in a separatory funnel. Benzene (25 cc.) was added, and, after shaking, the aqueous layer was separated. The benzene layer was extracted two additional times with water, and the combined aqueous layers were analyzed for chloride ion by the usual Volhard procedure.

**Spectroscopic Measurements.**—A solution of 2,4-dinitrochlorobenzene in the appropriate solvent was prepared by filling a volumetric flask into which a sample of the halide had been weighed directly. A sample of aniline was weighed directly into a small volumetric flask and placed in a thermostat at 23.8  $\pm$  0.1 $^\circ$ . A portion of the halide stock solution, which had been similarly placed in a thermostat, was pipetted into the flask containing the aniline; the stop watch was started when the pipet had half drained. The flask was then filled quickly to the mark with solvent and placed in the thermostat for five minutes. A portion of the aniline-halide solution was then transferred to a one-cm. cell in a cell housing maintained at constant temperature by water circulated from the thermostat. The optical density as a function of time was determined with a Beckman model DU spectrophotometer. The time of each reading was carefully noted.

### Discussion

Our results establish the fact that molecular compound formation is responsible for the anomalies observed in the rate of reaction between aniline and 2,4-dinitrochlorobenzene. However, our results do not permit us to make a choice between mechanism I and mechanism II; *i.e.*, there still remains the question of whether the final products arise from a bimolecular reaction between aniline and 2,4-dinitrochlorobenzene or from a decomposition of the complex. There is, of course, the additional possibility that product may be formed *via* both paths simultaneously. We shall, therefore, continue to discuss our results in terms of  $K$  and  $k_x$ .

Singh and Peacock<sup>2</sup> have measured the rate of the aniline-2,4-dinitrochlorobenzene reaction in absolute ethanol at 35 $^\circ$  and 45 $^\circ$ . Since they report data at two aniline concentrations, we can calculate  $K$  and  $k_x$  at these temperatures.<sup>12</sup> The results,

(11) E. Rimbach and R. Wintgen, *Z. physik. Chem.*, **74**, 233 (1910).

(12) For these calculations, we combined equations 6 and 8 to give

$$k^*(A_0)(B_0) = k_x(A_0 - y)(B_0 - y) \quad (9)$$

In equation 9 only  $k_x$  and  $y$  are unknown. We then assumed values for  $k_x$  and calculated corresponding values of  $y$ . The values assumed for  $k_x$  must, in each case, be greater than the experimentally determined value of  $k^*$ . The values of  $y$  were then used to calculate values of  $K$ , using equation 7. In each case a plot of  $K$  vs.  $k_x$  gave a straight line. We then converted the calculated values of  $K$  and  $k_x$  for each run into the form of an equation of a straight line, and solved the two equations, corresponding to the two aniline concentrations, simultaneously to obtain  $K$  and  $k_x$ .

Singh and Peacock have also reported data for 2,5-dinitrochlorobenzene and a series of *ortho*, *meta* and *para* substituted anilines. We have calculated  $K$ 's and  $k_x$ 's for these data, too, and will report the results in connection with studies of our own on the effect of substitution on complexing.

along with our results at 24.4°, are given in Table VII.

TABLE VII

RATES AND EQUILIBRIA FOR THE ANILINE-2,4-DINITROCHLOROBENZENE REACTION IN ABSOLUTE ETHANOL

Temp., °C.	$k_2$ , l. mole <sup>-1</sup> hr. <sup>-1</sup>	$K$ , l. mole <sup>-1</sup>
24.4	0.29	0.45
35.0	.46	.19
45.0	.77	.10

From the slope of a plot of  $\ln K$  vs.  $1/T$ , we can estimate  $\Delta H^\circ$  for the equilibrium between the complex and aniline and 2,4-dinitrochlorobenzene. Using the expressions  $\Delta F^\circ = -RT \ln K$  and  $\Delta H^\circ =$

TABLE VIII

ENTROPY, FREE ENERGY AND HEAT CONTENT OF THE ANILINE-2,4-DINITROCHLOROBENZENE MOLECULAR COMPLEX EQUILIBRIUM

Temp., °C.	$\Delta H^\circ$ , kcal. mole <sup>-1</sup>	$\Delta F^\circ$ , cal. mole <sup>-1</sup>	$\Delta S^\circ$ , cal. mole <sup>-1</sup>
24.4	-13.1	+ 472	-45.8
35.0	-13.1	+1020	-46.0
45.0	-13.1	+1460	-45.9

$\Delta F^\circ - T\Delta S^\circ$ , we can estimate  $\Delta F^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  for this equilibrium. The results are presented in Table VIII.<sup>13</sup>

The data of Table VI permit us to draw some conclusions as to the effect of solvent on the extent of complexing between aniline and 2,4-dinitrochlorobenzene. Complexing is most extensive in the most polar solvent, ethanol, and is either absent or occurs to only a slight extent in the least polar solvent, ethyl acetate. In a mixture of these two solvents, the equilibrium constant has the expected intermediate value. The observed effect is that predicted by both Weiss<sup>4a</sup> and Mulliken<sup>4d</sup> for complexing of the charge-transfer type and lends support to their theories.

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(13) It is also possible to plot both  $\ln k_2$  and  $\ln k_1$  vs.  $1/T$  and then to calculate the heat, entropy and free energy of activation for both  $k_1$  and  $k_2$ .

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## Mechanisms of Elimination Reactions. XI. Alkaline Dehydrobromination of Isomers of $\beta$ -Bromostyrene and of *p*-Nitro- $\beta$ -bromostyrene<sup>1,2</sup>

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Reaction-rate constants and quantities of activation for the dehydrobromination of the *cis* and *trans* isomers of  $\beta$ -bromostyrene and of *p*-nitro- $\beta$ -bromostyrene with sodium hydroxide in isopropyl alcohol have been measured. The effect of the *p*-nitro substituent was found to be significantly greater in elimination of *cis* elements of hydrogen bromide than elimination of *trans* groups. The data are discussed in terms of a concerted process for *trans* elimination and a multiple-stage, carbanion-intermediate process for *cis* elimination.

It has been previously proposed<sup>2-4</sup> that at least two mechanisms exist for base-promoted dehydrohalogenation of alkyl halides (and in general, for bimolecular elimination reactions). One of these has been described as a concerted process in which the removal of the proton by base is believed to be synchronous with the formation of the multiple bond and loss of halide ion. The second process has been termed "multiple-stage" and is presumed to involve a rate-determining removal of a proton by base yielding a carbanion, which then loses a halide ion to give the olefinic product. Elimination of *trans* groups has been assumed to use the concerted process, whereas *cis* elimination has been assumed to involve the multiple-stage process. Isotopic evidence that a carbanion intermediate is involved in elimination from  $\beta$ -benzene hexachloride has been described recently.<sup>2</sup>

A consequence of this dual mechanistic scheme

(see below for extended discussion) is that the appropriate placing of electron-attracting or electron-withdrawing groups on the  $\beta$ -carbon atoms should have a greater effect upon the multiple-stage process, where the carbanion is being formed, than on the concerted process, where much of the negative charge is being dispersed to the departing halogen rather than to the  $\beta$ -carbon atom. Accordingly data on elimination from the *cis* and *trans* isomers of  $\beta$ -bromostyrene and *p*-nitro- $\beta$ -bromostyrene should be a test of this theory.

**Product Study.**—As ethanol was found to be an unsuitable solvent for the alkaline dehydrobromination of *trans-p*-nitro- $\beta$ -bromostyrene, due to the formation of the ethyl acetal of *p*-nitrobenzaldehyde rather than the *p*-nitrophenylacetylene desired,<sup>5</sup> the first problem was to find a solvent in which one could prove that elimination occurred. As sodium *t*-butoxide in *t*-butyl alcohol ordinarily is sluggish in addition to multiple bonds,<sup>6</sup> this was first studied. It was found that *trans-p*-nitro- $\beta$ -bromostyrene (the slower eliminating isomer) gave an 88% yield of *p*-nitrophenylacetylene upon

(1) This paper was presented in part before the Division of Organic Chemistry at the Spring 1953 meeting of the American Chemical Society in Los Angeles, California.

(2) Previous paper in series: S. J. Cristol and D. D. Fix, *THIS JOURNAL*, **75**, 2647 (1953).

(3) (a) S. J. Cristol, *ibid.*, **69**, 338 (1947); (b) S. J. Cristol, N. L. Hause and J. S. Meek, *ibid.*, **73**, 674 (1951); (c) S. J. Cristol and A. Begoon, *ibid.*, **74**, 5025 (1952).

(4) S. I. Miller and R. M. Noyes, *ibid.*, **74**, 629 (1952).

(5) S. J. Cristol, A. Begoon, W. P. Norris and P. S. Ramey, unpublished work.

(6) F. Beyerstadt and S. M. McElvain, *THIS JOURNAL*, **58**, 529 (1936); **59**, 2266 (1937).