

found by Smith and Menzies as a fourth fixed point for thermometer calibration. In addition these authors have calculated the vapor pressure of mercury from thermal measurements on the liquid and estimates of the second virial coefficient of the vapor. Their results are given by their equation 35.

Epstein and Powers⁷ obtained an expression for the vapor pressure of mercury utilizing all available thermodynamic measurements which is intended to be valid from the triple point to the critical point.

Beattie, Blaisdell and Kaminsky³ measured the vapor pressure of mercury very accurately in the range 660 to 860 mm. and with these measurements fixed the boiling point as 356.580°.

The vapor pressures calculated from the expressions of the five investigators mentioned have been tabulated for rounded values of temperature from 250 to 360° in Table II. The values of Smith and Menzies are for the corrected temperature given by Douglas, Ball and Ginnings.⁶

It is seen that the agreement between various investigators is quite good. All expressions must of course give the same value at the normal boiling

(7) L. F. Epstein and M. D. Powers, AECU-1640, Sept. 1951.

TABLE II

THE VAPOR PRESSURE OF MERCURY IN MM. AT ROUNDED TEMPERATURES ACCORDING TO VARIOUS INVESTIGATORS

| t (°C.) | S and D. | B., B. and K. | S. and M. | D., B. and G. | E. and P. |
|------------|----------|------------------|-----------|------------------|-----------|
| 250 | 74.41 | | 74.49 | 74.50 | 74.35 |
| 260 | 96.40 | | 96.47 | 96.48 | 96.30 |
| 270 | 123.66 | | 123.73 | 123.73 | 123.52 |
| 280 | 157.17 | | 157.23 | 157.23 | 156.97 |
| 290 | 198.02 | | 198.05 | 198.05 | 197.76 |
| 300 | 247.41 | | 247.41 | 247.41 | 247.08 |
| 310 | 306.68 | | 306.66 | 306.65 | 306.32 |
| 320 | 377.32 | | 377.28 | 377.27 | 376.93 |
| 330 | 460.94 | | 460.89 | 460.87 | 460.56 |
| 340 | 559.30 | | 559.25 | 559.22 | 558.98 |
| 350 | 674.28 | 674.26 | 674.26 | 674.24 | 674.12 |
| 360 | 870.95 | 808.00 | 807.97 | 807.99 | 808.03 |

point. The very close agreement of Douglas, Ball and Ginnings with the data of Smith and Menzies is due in part to the fact that the value chosen for the second virial coefficient of the vapor in the former calculations was adopted partly because of the close agreement with measured vapor pressures. The differences generally are too small to be ascribed any significance.

KINETICS OF THE REACTION BETWEEN *o*-CHLORONITROBENZENE AND ETHANOLAMINE

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The reaction between *o*-chloronitrobenzene and ethanolamine has been studied. The high rate of reaction, the more negative ΔS^\ddagger and the smaller E_a compared with the lower rates, less negative ΔS^\ddagger and the larger E_a for *n*-butylamine are evidence for a cyclic mechanism. In accord with this mechanism also is the fact that a mixture of ethylamine and ethanol—in which the functional groups are on separate molecules—reacts more slowly than ethanolamine. Thus, the reaction with ethanolamine is depicted as going through a cyclic transition state in which the amino group is attacking the carbon holding chlorine while simultaneously the hydroxyl group is solvating the chlorine atom. At low concentrations phenol accelerates the reaction; at higher concentration it decelerates the reaction. This effect is that expected for a substance more electrophilic than the alcohol, but which can effectively remove amine from solution by neutralization.

Introduction

During the investigation of a number of organic bases as dehydrochlorinating agents for polymeric materials, such as polyvinylidene chloride and polyvinyl chloride, it was observed that ethanolamine was uniquely effective.⁴ In fact, its efficiency was ultimately exploited by the development of an analytical procedure for chlorine in copolymers of vinylidene chloride.⁴ Tests on a number of aromatic molecules with reactive halogens demonstrated that among these, also, ethanolamine was an effective reagent for displacing the halogen. It thus became the purpose of this investigation to determine the cause of the effectiveness of ethanolamine in displacing chloride from aromatic molecules.

(1) Taken from the Dissertation presented to the Graduate Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1953.

(2) Dow Chemical Company, Midland, Michigan.

(3) To whom inquiries concerning this publication should be sent.

(4) P. L. Gordon and G. Dolgin, M.S. theses, Polytechnic Institute of Brooklyn, 1948.

The reaction selected for study was that between ethanolamine and *o*-chloronitrobenzene. The product, *N*-(2'-nitrophenyl)-ethanolamine had already been characterized.⁵⁻⁷ Using larger excesses of ethanolamine and a temperature range of 57–82°, the described product could be obtained in 95% yield, indicating the suitability of these conditions for the kinetic study. The course of this investigation was patterned after Swain's study of the displacement reaction of trityl chloride in which kinetic evidence for the termolecular mechanism was established.⁸

Experimental

Starting Materials.—*o*-Chloronitrobenzene (E. K. White Label grade) was recrystallized from petroleum ether twice to a pale yellow solid, m.p. 31.5°. Ethanolamine, ethylamine, *n*-butylamine, pyridine, methanol, ethanol, isopropyl alcohol, *n*-hexanol, 2-butoxyethanol and *n*-butyl ether were

(5) P. Karrer, E. Schlittler, K. Pfaelder and F. Benz, *Helv. Chim. Acta*, **17**, 1516 (1934).

(6) C. B. Kremer, *J. Am. Chem. Soc.*, **59**, 1681 (1937).

(7) C. B. Kremer, *ibid.*, **61**, 1223 (1939).

(8) C. G. Swain, *ibid.*, **70**, 1119 (1948).

highest purity, commercially available compounds, which were dried and distilled before use taking heart cuts which were checked to agree with the literature values. Dioxane was a specially purified, anhydrous material, m.p. 10.5°. Phenol was recrystallized from petroleum ether, m.p. 43.0°. β -Methoxyethylamine was obtained from a 70% aqueous solution by azeotropic removal of the water with benzene and twice distilling the amine. The heart cut, b.p. 94°, was used for the experiments.

Procedure.—The reactions were run in a Precision Scientific Company constant temperature bath with a rated and measured accuracy of $\pm 0.05^\circ$. The first run was made using 2.0 g. of *o*-chloronitrobenzene and 98 g. of ethanolamine. The reactants were weighed into a 500-ml. erlenmeyer flask with a ground glass stopper. After allowing the flask containing the ethanolamine to come to 57.0° in the constant temperature bath, the *o*-chloronitrobenzene was added. The stopper was sealed with tape and the contents were swirled in the bath to effect rapid solution. The mixture was maintained at 57.0° for eight hours. Ten-gram samples were pipetted at timed intervals into 150 ml. of cold water. After acidification, the chloride content was determined gravimetrically as silver chloride.

In order to determine whether the reaction rate was affected by possible traces of moisture in the reagents or solvents, the reaction was repeated using 0.5, 1.0 and 2.0% of water based on the weight of ethanolamine. No significant difference in rate was observed for any of these concentrations.

The kinetic determinations using varying concentrations of 2-butoxyethanol were performed in the same manner. In the case of the methanol series, the use of ground glass stoppered flasks was unsatisfactory due to the volatility of the methanol. For this series sealed test-tubes were simultaneously placed in the bath and individually withdrawn at timed intervals. Cooling the tubes in ice and water served to stop the reaction before opening them. The same analytical procedure was used. This method was used for all subsequent kinetic studies.

Results and Discussion

In all cases the reaction was found to be first order in *o*-chloronitrobenzene by standard techniques,⁹ as was to be expected with one of the reactants in large excess. For the reaction using varying quantities of 2-butoxyethanol the data

TABLE I

TABULATION OF RATE CONSTANTS FOR THE REACTION BETWEEN *o*-CHLORONITROBENZENE AND ETHANOLAMINE IN VARYING CONCENTRATIONS OF 2-BUTOXYETHANOL AT 57.0°

| <i>o</i> -Chloronitrobenzene, mole/l. | Ethanolamine, mole/l. | 2-Butoxyethanol, mole/l. | Rate constants, $k \times 10^7$ |
|---------------------------------------|-----------------------|--------------------------|---------------------------------|
| 0.0636 | 16.28 | ... | 675.0 |
| .0636 | 8.2 | 3.72 | 146.1 |
| .0636 | 4.1 | 5.61 | 38.0 |
| .0636 | 2.05 | 6.55 | 16.25 |
| .1272 | 1.02 | 7.00 | 6.09 |
| .1272 | 0.515 | 7.25 | 2.96 |

TABLE II

TABULATION OF RATE CONSTANTS FOR THE REACTION BETWEEN *o*-CHLORONITROBENZENE AND ETHANOLAMINE IN VARYING CONCENTRATIONS OF METHANOL AT 57.0°

| <i>o</i> -Chloronitrobenzene, mole/l. | Ethanolamine, mole/l. | Methanol, mole/l. | Rate constants, $k \times 10^7$ |
|---------------------------------------|-----------------------|-------------------|---------------------------------|
| 0.0636 | 16.25 | ... | 675.0 |
| .0636 | 12.27 | 6.0 | 166.0 |
| .0636 | 8.20 | 12.24 | 40.2 |
| .0636 | 4.10 | 18.0 | 10.3 |
| .1272 | 2.05 | 21.6 | 2.87 |
| .1272 | 1.008 | 22.85 | 1.66 |

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

are shown in Table I; for the methanol series in Table II; for the additional series of solvents in Table III.

TABLE III

TABULATION OF RATE CONSTANTS FOR THE REACTION BETWEEN *o*-CHLORONITROBENZENE AND ETHANOLAMINE IN VARIOUS SOLVENTS AT 57.0°
o-Chloronitrobenzene, 0.1272 mole/l.; ethanolamine, 2.05 mole/l.

| Solvent | Concn., mole/l. | Rate constant, $k \times 10^7$ |
|-----------------------|-----------------|--------------------------------|
| Methanol | 21.6 | 2.87 |
| Ethanol | 14.82 | 6.22 |
| Isopropyl alcohol | 11.7 | 9.24 |
| 2-Butoxyethanol | 6.55 | 16.25 |
| Methanol | 10.8 | 8.6 |
| 2-Butoxyethanol | 3.36 | |
| Hexanol | 3.5 | 13.7 |
| 2-Butoxyethanol | 3.36 | |
| Dioxane | 10.26 | 42.8 |
| Dioxane | 5.13 | 21.2 |
| 2-Butoxyethanol | 3.36 | |
| <i>n</i> -Butyl ether | 2.94 | 18.4 |
| 2-Butoxyethanol | 3.36 | |
| Pyridine | 10.84 | 32.6 |

Comparison of the data of Tables I and II shows that at fixed concentrations of *o*-chloronitrobenzene and ethanolamine, the rate is slower with the larger molar concentration of methanol. This is taken to mean that the larger concentration of added hydroxyl groups has slowed the reaction. That this decrease in rate is probably not due to the ether function of 2-butoxyethanol is shown by comparison with the reaction in dioxane (Table III) in which the rate is faster than for the hydroxylic solvents. With these facts as a guide, an empirical equation was devised which took into account the concentration of ethanolamine and also the inhibiting effect of the hydroxylic solvents.

$$k = \frac{[\text{Ethanolamine}]}{a + b [\text{Solvent}]^2} \quad (1)$$

where

k = experimental first-order rate constant in sec.⁻¹

[] = concentrations in mole l.⁻¹

a = constant for no solvent in mole sec. l.⁻¹

b = constant for the solvent in l. sec. mole⁻¹

The constants were determined as follows: with no solvent Equation 1 becomes

$$k = \frac{[\text{Ethanolamine}]}{a} \quad (2)$$

thus permitting the evaluation of a directly from the experimental data. Using the value of a so obtained, 2.42×10^{-5} mole/sec. l.⁻¹. Equation 1 was then used for evaluating b in each experiment in the 2-butoxyethanol series and in the methanol series. The results are given in Table IV. The small average deviations, about 6%, validate equation 1 for these series.

It is now possible to examine a mechanism for the reaction. The reaction is first order in *o*-chloronitrobenzene, the reactant in minimum quantity, and depends to an inverse second power

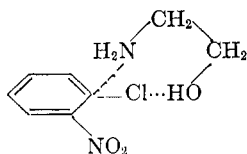
TABLE IV

| Measured values, $k = 10^7$ | $b \times 10^{-1}$ | Calcd. values for $k \times 10^7$ using av. value for $b = 2.61 \times 10^4$ | | % |
|---------------------------------|--------------------|--|--|-----|
| | | | | |
| 2-Butoxyethanol series | | | | |
| 146 | 2.28 | 137 | | 6.0 |
| 38 | 2.68 | 38.7 | | 1.8 |
| 16.25 | 2.42 | 15.2 | | 6.4 |
| 6.09 | 2.87 | 6.4 | | 6.5 |
| 2.97 | 2.83 | 3.18 | | 7.0 |
| Av. dev. for this series = 5.8% | | | | |
| Methanol series ^a | | | | |
| 166 | 1.38 | 174 | | 4.6 |
| 40.2 | 1.20 | 38.9 | | 3.3 |
| 10.3 | 1.17 | 9.52 | | 7.5 |
| 2.87 | 1.48 | 3.24 | | 9.6 |
| 1.50 | 1.26 | 1.45 | | 3.3 |

Av. dev. for this series = 5.66%

^a Calculated values for $k \times 10^7$ using average value for $b = 1.28 \times 10^4$.

on the concentration of solvent. Of a number of mechanisms consistent with these facts is the following: One molecule of ethanolamine reacts with one molecule of *o*-chloronitrobenzene. As the nucleophilic group ($-\text{NH}_2$) attacks the carbon to which the chlorine is attached, there is a simultaneous solvating attack on the chlorine by the electrophilic group ($-\text{OH}$). The accompanying diagram depicts the cyclic transition inferred.



This treatment is, thus, a cyclic adaptation of the termolecular, or concerted, displacement mechanism of Swain¹⁰ and corresponds to his Type D reaction in his illustrations for the different possibilities for concerted displacements.

The introduction of a hydroxylic solvent, such as methanol or 2-butoxyethanol, inhibits the reaction. Hydrogen bonding to both the chlorine atom and to the ethanolamine is consistent with the inverse square dependence on the concentration of solvent. The inhibition results from disturbance of the favorable juxtaposition of groups in the cyclic transition state. The effect of added alcohols may be found in their probable different acidities or in their different structures which may interfere with hydrogen bonding. Swain and Brown^{11a} have previously put forth a cyclic mechanism to account for the unique effectiveness of 2-hydroxypyridine on the mutarotation of tetramethylglucose in benzene.

With equation 1 as a guide, an interpretation of the significance of a and b may be made. The constant a is a function of the ethanolamine, which in this case is also the electrophilic reagent. The value for this constant is unaffected by the solvent used in the reaction, and if the interpretation of the

(10) C. G. Swain, *J. Am. Chem. Soc.*, **72**, 4578 (1950).

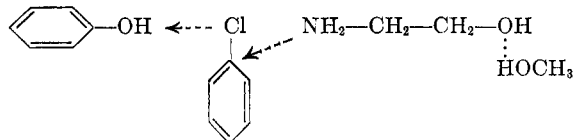
(11) (a) C. G. Swain and J. F. Brown, Jr., *ibid.*, **74**, 2534 (1952); (b) **74**, 2538 (1952).

mechanism is feasible, can be used as a relative value for the inhibiting effect of the solvent. From the equation the value of b is directly proportional to the inhibiting effect of the polar solvent.

The series of kinetic runs made with the different solvents gave results which fitted this hypothesis. Based on the interpretation above it would be predicted that for longer carbon chains attached to the OH group in an alcohol, *i.e.*, the lower the molar concentration of OH, there would be less inhibition and a higher rate for a comparable mixture of reactants. The data of Table III bear out this contention.

The use of ether-type solvents, such as dioxane or *n*-butyl ether, instead of alcohols, also resulted in higher reaction rates between *o*-chloronitrobenzene and ethanolamine. When solvent mixtures were used, the rates were roughly equal to the average of the values for the two solvents taken separately.

The next portion of this investigation was concerned with the effect of phenol on the reaction rate. On the basis of the postulated mechanism for the present reaction, and Swain's work on the effect of phenol on the solvolysis of trityl chloride in methanol, it was possible to predict the behavior of phenol when added to a mixture of *o*-chloronitrobenzene and ethanolamine in methanol. Swain⁸ had shown that phenol solvates halogen more efficiently than carbon and also that the complexing tendency between phenol and methanol is negligible. Therefore, the addition of phenol to the reaction mixture should set up a concerted displacement according to the following diagram. Analogously, for the reaction of *o*-chloronitro-



benzene and ethanolamine the initial effect of phenol should be an acceleration of the rate of reaction. As the concentration is increased, the acid-base reaction between the phenol and ethanolamine should effectively reduce the concentration of ethanolamine, and beyond some optimum point, the rate of reaction should decrease.

The results of the series of kinetic studies on the effect of phenol on the reaction between *o*-chloronitrobenzene and ethanolamine, substantiated these predictions. The data are given in Table V, and

TABLE V

TABULATION OF RATE CONSTANTS FOR THE REACTION BETWEEN *o*-CHLORONITROBENZENE AND ETHANOLAMINE IN METHANOL WITH VARYING CONCENTRATIONS OF PHENOL *o*-chloronitrobenzene, 0.1272 mole/l.; ethanolamine, 2.05 mole/l.

| Phenol, mole/l. | Methanol, mole/l. | Rate constant, $k \times 10^7$ |
|-----------------|-------------------|--------------------------------|
| ... | 21.60 | 2.87 |
| 0.0695 | 21.55 | 4.67 |
| 0.1390 | 21.48 | 7.58 |
| 0.2770 | 21.35 | 8.95 |
| 0.5560 | 21.18 | 5.71 |
| 1.1100 | 20.62 | 1.85 |

the plot of rate constants against concentration of phenol in Fig. 1 clearly shows a maximum of $k = 8.9 \times 10^{-7}$ sec.⁻¹ with 0.255 molar phenol.

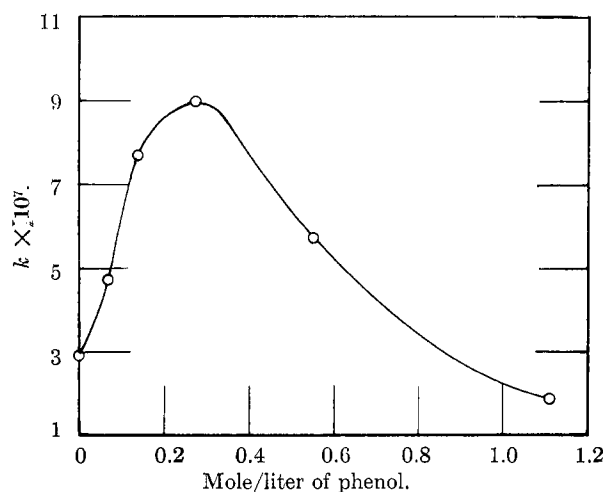


Fig. 1.—Effect of concentration of phenol on the rate constant for the reaction between *o*-chloronitrobenzene and ethanolamine at 57°.

This reaction would be expected to be first order in *o*-chloronitrobenzene, first order in phenol, and first order in the complex formed by ethanolamine and methanol. However, since the complexing reaction is undoubtedly reversible, a simple termolecular rate equation would not suffice in this case. An attempt was made here to fit an equation to the data.

A further test for a cyclic mechanism is based on the absolute rate equation 3 of Eyring. In this treatment the entropy of activation is examined. A high negative value for ΔS^\ddagger indicates the loss of a number of degrees of freedom in proceeding from the reactants to the transition state, which is consistent with a cyclic transition state. A recent example of this reasoning is that of Foster, *et al.*,¹² in their investigation of the energy of activation and the entropy of activation in the rearrangement of three-carbon systems.

In order to apply this treatment, it was necessary to obtain the activation energy for the reaction between *o*-chloronitrobenzene and ethanolamine, and also for the reaction between *o*-chloronitrobenzene and *n*-butylamine. Since a cyclic intermediate could not be involved in the case of *n*-butylamine, a sizeably larger ΔS^\ddagger for the ethanolamine reaction over that for the *n*-butylamine reaction should indicate a cyclic intermediate for the ethanolamine case.

The activation energies for the two reactions were obtained from the slopes of the plots of $\log k$ versus $1/T \times 10^3$ from the data in Tables VIII and IX. The values of k at various temperatures were determined from the data in Tables VI and VII. For the reaction with ethanolamine $E_a = 9.41$ kcal. mole⁻¹; for the reaction with *n*-butylamine, $E_a = 18.0$ kcal. mole⁻¹. The low activation energy for the ethanolamine reaction is another point in favor of the termolecular mechanism of Swain.⁸

The entropies of activation, ΔS^\ddagger , were calcu-

(12) G. E. Foster, A. C. Cope and F. Daniels, *J. Am. Chem. Soc.*, **69**, 1893 (1947).

TABLE VI

EFFECT OF THE VARIATION OF TEMPERATURE ON THE RATE OF REACTION BETWEEN *o*-CHLORONITROBENZENE AND ETHANOLAMINE

o-Chloronitrobenzene (a), 0.0636 mole/l.; ethanolamine 16.25 mole/l.

| Reaction time, hr. | Chlorine removed, % | Reaction time, hr. | Chlorine removed, % | Reaction time, hr. | Chlorine removed, % |
|---------------------------|---------------------|---------------------------|---------------------|---------------------------|---------------------|
| Temp., 57° | | Temp., 76° | | Temp., 82° | |
| 0.5 | 12.85 | 0.75 | 36.8 | 0.75 | 56.3 |
| 2.0 | 41.1 | 1.5 | 68.0 | 1.0 | 67.7 |
| 2.75 | 49.5 | 2.0 | 71.5 | 1.5 | 76.1 |
| 3.5 | 58.8 | 2.5 | 79.6 | 2.5 | 93.0 |
| 4.5 | 67.7 | 2.75 | 82.5 | 3.12 | 94.1 |
| 5.5 | 75.1 | 3.5 | 89.0 | | |
| $k = 6.75 \times 10^{-5}$ | | $k = 17.2 \times 10^{-5}$ | | $k = 21.8 \times 10^{-5}$ | |

TABLE VII

EFFECT OF THE VARIATION OF TEMPERATURE ON THE RATE OF REACTION BETWEEN *o*-CHLORONITROBENZENE AND *n*-BUTYLAMINE

o-Chloronitrobenzene (a), 0.0636, mole/l.; *n*-butylamine 10.02 mole/l.

| Reaction time, hr. | Chlorine removed, % | Reaction time, hr. | Chlorine removed, % | Reaction time, hr. | Chlorine removed, % |
|---------------------------|---------------------|---------------------------|---------------------|---------------------------|---------------------|
| Temp., 57° | | Temp., 68° | | Temp., 76° | |
| 3.0 | 22.1 | 1.0 | 20.5 | 1.0 | 40.2 |
| 5.0 | 33.6 | 3.0 | 45.4 | 2.0 | 59.3 |
| 8.5 | 49.9 | 5.0 | 64.3 | 3.0 | 69.0 |
| 10.0 | 54.6 | 8.0 | 78.0 | 4.5 | 82.6 |
| 13.5 | 66.1 | 16.0 | 98.6 | 8.0 | 95.2 |
| 16.0 | 71.8 | | | | |
| $k = 2.27 \times 10^{-5}$ | | $k = 5.26 \times 10^{-5}$ | | $k = 9.18 \times 10^{-5}$ | |

TABLE VIII

TABULATION OF RATE CONSTANTS FOR THE REACTION BETWEEN *o*-CHLORONITROBENZENE AND ETHANOLAMINE AT VARYING TEMPERATURES

| Temp., °K. | $1/T \times 10^3$ | Rate constant, $k \times 10^5$ | $\log k$ |
|------------|-------------------|--------------------------------|----------|
| 330.2 | 302.8 | 6.75 | -4.171 |
| 349.2 | 216.4 | 17.2 | -3.765 |
| 355.2 | 281.5 | 21.8 | -3.662 |

TABLE IX

TABULATION OF RATE CONSTANTS FOR THE REACTION BETWEEN *o*-CHLORONITROBENZENE AND *n*-BUTYLAMINE AT VARYING TEMPERATURES

| Temp., °K. | $1/T \times 10^3$ | Rate constant, $k \times 10^5$ | $\log k$ |
|------------|-------------------|--------------------------------|----------|
| 330.2 | 302.8 | 2.27 | -4.645 |
| 341.2 | 293.1 | 5.26 | -4.280 |
| 349.2 | 286.4 | 9.18 | -4.037 |

^a T is absolute temperature.

lated from the Eyring rate equation, assuming κ (κ) to be unity

$$k = \frac{\kappa k T}{h} e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT} \quad (3)$$

- κ = transmission coefficient, assumed to be unity
- k = first-order reaction rate constant
- k = Boltzmann constant, 1.3805×10^{-16} erg deg.⁻¹
- T = temperature in °K.
- h = Planck's constant, 6.626×10^{-27} erg sec.
- ΔH^\ddagger = heat of activation
- S^\ddagger = entropy of activation

Thus, for the ethanolamine reaction, in which $\Delta H^\ddagger = 8.75$ kcal./mole⁻¹, $\Delta S^\ddagger = -51.3$ e.u. and for the reaction with *n*-butylamine, $\Delta S^\ddagger = -27.5$ e.u.

These results definitely show a greater loss of degrees of freedom on going to the transition state for the reaction between *o*-chloronitrobenzene and ethanolamine as against the reaction with *n*-butylamine. This loss of additional degrees of freedom for an analogous reaction is strong evidence for a cyclic transition state.

In order to provide further evidence for the cyclic transition state, a study was made in which the ordinary type of termolecular reaction would take place, that is, a reaction in which the nucleophilic and electrophilic groups were in different molecules. This was accomplished by using ethylamine and ethanol in equimolecular proportions and adding *o*-chloronitrobenzene in dioxane at 57.0°. The rate constants for this series are given in Table X. The rate constant for this reaction was found to be 12.87×10^{-7} sec.⁻¹, approximately one-third the rate for a comparable reaction with ethanolamine. A more rapid rate would be expected for the cyclic mechanism, since each time the nucleophilic group attacked, the electrophilic group would be in position to aid in the reaction. β -Methoxyethylamine was treated with *o*-chloronitrobenzene in dioxane at 57.0°. The data for these runs are presented in Table XI. The rate constant for this reaction was found to be 7.82×10^{-7} sec.⁻¹ as against 42.8×10^{-7} sec.⁻¹ for the reaction between ethanolamine and *o*-chloronitrobenzene in dioxane, using the same molar proportions. This demonstrated that when the actively functioning hydroxyl group in ethanolamine is converted to a relatively inac-

tive ether, the compound acts like a monofunctional reagent.

Conclusions

(1) The reaction between ethanolamine and *o*-chloronitrobenzene is of the nucleophilic displacement type, and the product is an almost quantitative yield of *N*-(2'-nitrophenyl)-ethanolamine, when the reaction is run at temperatures between 57 and 82° in a large excess of ethanolamine.

(2) The reaction is inhibited by alcohols and ethers.

(3) For the concentration of reactants used in these determinations, the over-all reaction rate was first order in all cases.

(4) The mechanism of the reaction between ethanolamine and *o*-chloronitrobenzene was interpreted as involving a cyclic intermediate in which the amino group of the ethanolamine is the nucleophilic group and the hydroxyl group of the same molecule is the electrophilic group.

(5) In hydroxylic solvents, the reaction was found to be first order in *o*-chloronitrobenzene and first order in ethanolamine, with an inverse second order dependence on solvent, in accordance with the rate equation

$$k = \frac{[\text{Ethanolamine}]}{a + b [\text{Solvent}]^2}$$

The inhibiting action of the solvent was tentatively related to its hydrogen-bonding capacity.

(6) The addition of phenol to the reaction mixture of ethanolamine, *o*-chloronitrobenzene and methanol was found to increase the rate of reaction initially and then to decrease it when the effective concentration of ethanolamine was reduced by acid-base reaction with the phenol.

(7) The energy of activation for the reaction between *o*-chloronitrobenzene and ethanolamine was found to be 9.4 kcal. mole⁻¹ and for the reaction with *n*-butylamine it was 18.0 kcal. mole⁻¹. The entropy of activation for the ethanolamine reaction was -51.3 and -27.5 e.u. for the *n*-butylamine reaction. These figures are in accord with the argument for a cyclic transition state complex.

(8) With a mixture of ethylamine and ethanol in place of ethanolamine in the reaction with *o*-chloronitrobenzene the rate was one-third as fast as that obtained with ethanolamine, providing further evidence for the cyclic mechanism. When the hydroxyl group of the ethanolamine was replaced by methoxyl, the rate of reaction dropped to approximately one-sixtieth of a comparable ethanolamine reaction.

Acknowledgment.—The authors wish here to express their deep appreciation to Professor J. Steigman for a number of critical discussions and to the American Waterproofing Corporation in whose laboratories this work was carried out.

TABLE X

RATE OF REACTION BETWEEN *o*-CHLORONITROBENZENE AND ETHYLAMINE IN ETHANOL AND DIOXANE AT 57.0°

o-Chloronitrobenzene, 0.1272 mole/l.; ethylamine, 2.05; ethanol, 2.05; dioxane, 8.04.

| Reaction time, hr. | Chlorine removed, % | Reaction time, hr. | Chlorine removed, % |
|--------------------|---------------------|--------------------|---------------------|
| 8 | 4.9 | 34 | 16.4 |
| 15 | 8.1 | 48 | 22.0 |
| 22 | 11.5 | 54 | 23.7 |

$$k = 12.82 \times 10^{-7} \text{ sec.}^{-1}$$

TABLE XI

RATE OF REACTION BETWEEN *o*-CHLORONITROBENZENE AND β -METHOXYETHYLAMINE IN DIOXANE AT 57.0°

o-Chloronitrobenzene, 0.1272 mole/l.; β -methoxyethylamine, 2.05; dioxane, 10.49.

| Reaction time, hr. | Chlorine removed, % | Reaction time, hr. | Chlorine removed, % |
|--------------------|---------------------|--------------------|---------------------|
| 8 | 3.4 | 34 | 10.4 |
| 15 | 5.8 | 48 | 13.3 |
| 22 | 7.5 | 54 | 14.4 |

$$k = 7.82 \times 10^{-7}$$