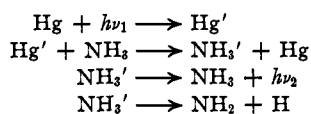


same course in both cases. The present experiments show that this assumption must be viewed with suspicion. The safe plan is to perform the experiments leading to a deduction of reaction mechanism under the same conditions as the quantum yield experiments, or better still to combine them in the same experiments.

The mercury-sensitized decomposition differs from the photochemical decomposition in the nature of the primary processes and by the fact that marked fluorescence was observed.<sup>3</sup>



The low quantum yield for the photosensitized decomposition may be attributed to fluorescence and suggests that the quantum of  $\lambda 2537 \text{ \AA}$ .

(approximately 112,000 cal. per mole) is barely sufficient to produce decomposition.

### Summary

The photochemical and mercury photosensitized decompositions of ammonia have been investigated in the region of very small amounts of decomposition. In contrast to the results obtained with large amounts of decomposition, namely, a quantum yield of 0.25 and gaseous products consisting of 75% hydrogen and 25% nitrogen, with small amounts of decomposition the quantum yield approaches unity and the gaseous products approach pure hydrogen, in the case of the photochemical decomposition. For the photosensitized decomposition a quantum yield of 0.12 was obtained.

PASADENA, CALIF.

RECEIVED OCTOBER 6, 1936

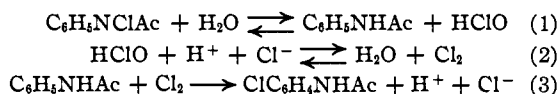
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

## The Rearrangement of Acetylchloroaminobenzene in the Presence of Radioactive Hydrochloric Acid

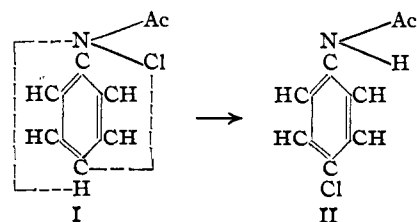
BY A. R. OLSON, C. W. PORTER, F. A. LONG AND R. S. HALFORD

The mechanism of the Hofmann rearrangement of N-substituted aromatic amines has been under investigation, intermittently, over a period of sixty years. As early as 1881 Michael<sup>1</sup> advanced the theory that in the rearrangement of methyl-aniline hydrochloride into the hydrochloride of *p*-toluidine, the first step is a dissociation into methyl chloride and aniline. The methyl chloride is then supposed to act upon the aniline, substituting the methyl group for the para hydrogen atom. In 1920 Michael<sup>2</sup> reaffirmed this conclusion and referred to the dissociation mechanism as a "self-evident explanation."

Orton and his colleagues<sup>3</sup> outlined a mechanism for the rearrangement of acetylchloroaminobenzene which has become almost universally accepted. They envisage the reaction as proceeding in three steps: (1) the hydrolysis of the chloroamine; (2) the production of chlorine from hydrochloric and hypochlorous acids; (3) the chlorination of acetanilide.



At the Richmond meeting of the American Chemical Society (1927) one of us presented the view that the arrangement is intramolecular.<sup>4</sup> It was postulated that a bond is formed between the chlorine atom and the para carbon atom while the chlorine is still attached to the nitrogen. Similarly it was assumed a bond is formed between the nitrogen atom and the para hydrogen atom in advance of any dissociation process. These weak bonds are represented by dotted lines in formula I. When molecules in state I become



sufficiently activated the bonds represented by dotted lines become full valence bonds and the rearrangement is accomplished. In the Richmond

(4) C. W. Porter, paper read at the April meeting, 1927.

(1) A. Michael, *Ber.*, **14**, 2105 (1881).

(2) A. Michael, *THIS JOURNAL*, **42**, 787 (1920).

(3) F. O. Chattaway and K. J. P. Orton, *Proc. Chem. Soc.*, **18**, 200 (1902); K. J. P. Orton and W. J. Jones, *Brit. Assn. Adv. Sci. Repts.*, 1910, p. 85; F. S. Kipping, *et. al.*, *Chem. News*, **108**, 155 (1913).

meeting this mechanism was referred to, derisively, as the "flip-flop theory."

The discovery of methods for producing artificial radioactivity has furnished a new tool for investigating problems of this type. Thus in this rearrangement, if we use ordinary acetylchloroaminobenzene and radioactive hydrochloric acid as a catalyst, we can determine the distribution of radioactivity among the products as the reaction progresses. This distribution will depend on the following factors: (1) the reaction mechanism or mechanisms; (2) the amount of exchange between radioactive chloride ion and chlorine (a) on the nitrogen of the chloroaminobenzene, (b) on the carbon of the chloroacetanilide and (c) of the molecular chlorine or hypochlorous acid in solution.

Of these factors 2b and 2c need no further investigation. Olson and Long<sup>5</sup> have shown that the exchange between chloride ion and chlorine on an aliphatic carbon is very slow. The exchange on an aromatic carbon is probably even slower and so it can be neglected in the present investigation. Also Long and Olson<sup>6</sup> have just shown that the equilibrium between chlorine and chloride ion is completely established before the chlorine can react with acetanilide. The remaining factors are considered in the present work.

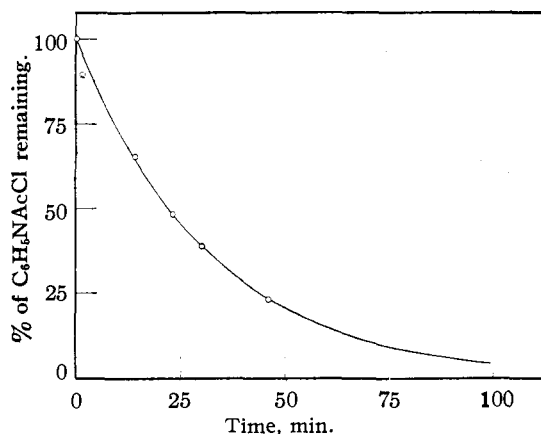


Fig. 1.—The circles are the experimental results for the chemical rate as taken from Table I. The solid line has been calculated from a unimolecular rate constant,  $k_1 = 0.0316 \text{ min.}^{-1}$ .

### Experimental

The acetylchloroaminobenzene was prepared by the method of Barnes and Porter.<sup>7</sup>

The radioactive chlorine was prepared in Professor E. O. Lawrence's radiation laboratory, by bombarding solid sodium chloride with deuterons.

The concentrations of the reagents and the temperature were chosen so that the half-life of the reaction was somewhat shorter than the half-life of the radioactive chlorine. The solvent was aqueous alcohol (20% alcohol by volume).

In making a run, the acetylchloroaminobenzene was dissolved in the aqueous alcohol solution to which enough sulfuric acid had been added to make it 1 *N* with respect to hydrogen ion. The radioactive sodium chloride was dissolved separately in a predetermined volume of the same solvent, so that after a portion of the solution had been used for the initial radioactive analysis, the remaining portion, when mixed with the chloroamine, would produce a solution 0.04 molar with respect to both acetylchloroaminobenzene and radioactive sodium chloride. The solutions were brought to the temperature of the thermostat before mixing and the time of mixing was taken as the zero time for the reaction.

At times shown in Table I, 5-cc. samples were withdrawn and analyzed in the usual manner by adding excess potassium iodide solution and titrating the liberated iodine with standard thiosulfate. The results are given in Table I and plotted in Fig. 1. The solid line in this figure has been calculated using a unimolecular rate constant,  $k_1 = 0.0316$ .

TABLE I  
DATA FOR CHEMICAL RATE

Time, min.	Thio used, cc.	% $C_6H_5NAcCl$ unreacted
0	3.90	100
1.5	3.50	89.8
14	2.55	65.4
23	1.90	48.7
30	1.50	38.5
46	0.90	23.0

In addition to following the rate of rearrangement in the usual chemical way, we determined the rate of change with time of the radioactivity of the chloride ion in solution. This change was due not only to the natural radioactive decay but also to the fact that some radioactive chloride ions were used in the reaction and were replaced by non-radioactive chloride ions. At regular intervals 100-cc. samples were withdrawn from the reaction vessel, silver nitrate solution was added and the silver chloride was filtered off, washed and dried. A weighed amount of this silver chloride was then dissolved in a known volume of ammonium hydroxide and the radioactivity of the chloride ion was determined by the method outlined by Olson, Libby, Long and Halford.<sup>8</sup>

In addition to these measurements, two determinations of a different type were made. In the first of these the radioactivity of the rearranged product, *p*-chloroacetanilide, was obtained. This was done by taking a somewhat larger sample than usual, destroying the chloroamine with iodide ion, reducing the liberated iodine with thiosulfate, then extracting the rearranged product with benzene. After evaporating the benzene, the chloroacetanilide was fused with potassium hydroxide, dissolved in water and

(5) A. R. Olson and F. A. Long, *THIS JOURNAL*, **56**, 1294 (1934).

(6) F. A. Long and A. R. Olson, *ibid.*, **58**, 2214 (1936).

(7) C. D. Barnes and C. W. Porter, *ibid.*, **52**, 1721 (1930).

(8) A. R. Olson, W. F. Libby, F. A. Long and R. S. Halford, *ibid.*, **58**, 1313 (1936).

acidified with nitric acid. Excess silver nitrate was then added, the silver chloride filtered off, dried and examined for radioactivity in the usual manner. Two sources of inaccuracy entered into this determination. First, the silver chloride was quite dark, indicating the presence of some silver sulfide. Second, the amount of silver chloride obtained from this experiment was only one-fifth as much as we otherwise used for a radioactive determination.

The second experiment was devised to determine the rate with which radioactive chlorine replaces the non-radioactive chlorine on the nitrogen of the acetylchloroaminobenzene. After the reaction was about one-fourth over, a sample of the reaction mixture was removed and sufficient sodium carbonate was added to make the solution somewhat alkaline. This was done to convert any slight amount of chlorine into hypochlorite and chloride ions. The chloroamine and chloroanilide were then extracted with benzene. This benzene extract was shaken thoroughly with an aqueous solution of sodium sulfite which reduced the chloroamine to chloride ion and acetanilide. The aqueous solution was acidified, the chloride precipitated as silver chloride and its radioactivity determined.

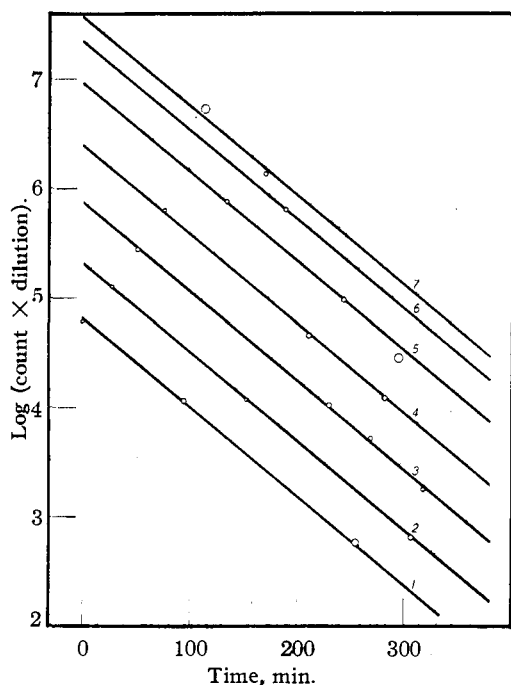


Fig. 2.—The numbers of the curves refer to the correspondingly numbered samples in Table II. The curves have been displaced upward by 0.6 unit from the preceding curve with the exception of Curve 6 which has been displaced twice this amount.

In Fig. 2 we have plotted the time of counting against the logarithm of the product of the net count times the dilution for all these silver chloride samples. In every case the slope of the line corresponds to the known half-life of radioactive chlorine. If we call the radioactivity of the control sample 100%, then, from the intercepts of these lines on the  $t = 0$  axis, we can calculate immediately

No. of corresp. curve in Fig. 2	Source of AgCl	Time, min.	% radioactivity compared to control sample
1	Solution	0	100
2	Solution	6.67	79.2
3	Solution	20	72.7
4	Solution	44	60.2
5	Solution	81.2	55.7
6	Chloroacetanilide	30	40.5
7	Chloroamine	11.16	4.09

the percentages of radioactivity in each of these samples as compared with the control. The results of these calculations are given in Table II, and the data for the chloride ion in solution have been plotted in Fig. 3.

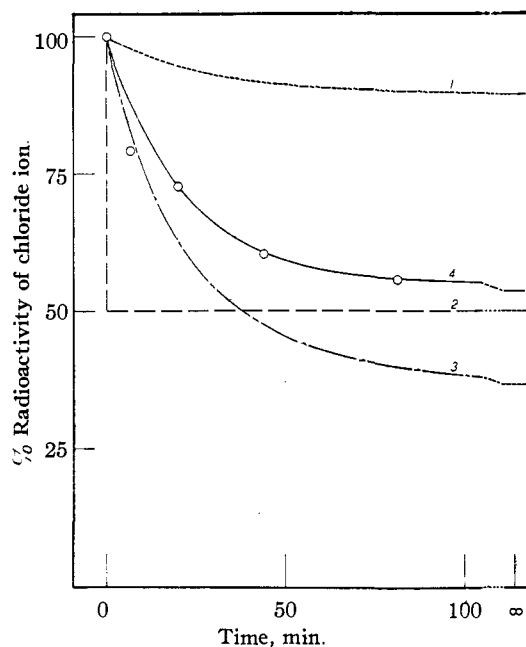
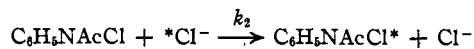


Fig. 3.—Graphic representation of the results for various mechanisms. Curve 1 is for intramolecular rearrangement with exchange on the nitrogen. Curves 2 and 3 give the upper and lower limits for the chlorine intermediate path. Curve 4 is for the two mechanisms proceeding simultaneously. The circles are the experimental results as shown in Table II.

With the datum given in Table II it is possible to calculate the specific rate of the exchange reaction



with an accuracy sufficient for our purpose, by assuming that the concentration of radioactive chloride ion is, over this short time interval, constant and equal to its initial value. Table II shows that approximately 4% of the chlorine of the acetylchloroaminobenzene is radioactive after 11.16 minutes. This corresponds to a

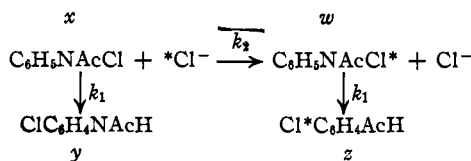
specific rate constant for this reaction of  $k_2 = 0.094 \text{ mole}^{-1} \text{ min.}^{-1}$ .

In addition to the data given above several preliminary runs were made. The data for these runs are not included here, for, while the results are in accord with this run, they are not sufficiently accurate to merit inclusion.

### Detailed Consideration of Possible Mechanisms

(1) Intramolecular rearrangement without exchange on the nitrogen of the chloroamine: This mechanism alone cannot possibly account for the experimental facts since, then, there would be no decrease of the radioactivity of the chloride ion in solution as the reaction progressed.

(2) Intramolecular rearrangement, allowing for exchange on the nitrogen: Schematically this mechanism can be represented by



The specific rate of interchange of chlorine on the nitrogen of the chloroamine is given by  $k_2$  and the specific rate of the rearrangement is given by  $k_1$ .

To obtain the rate expression for this mechanism, let  $x$ ,  $y$ ,  $w$  and  $z$  be the concentrations of  $\text{C}_6\text{H}_5\text{NAcCl}$ ,  $\text{ClC}_6\text{H}_4\text{NAcH}$ ,  $\text{C}_6\text{H}_5\text{NAcCl*}$  and  $\text{Cl*C}_6\text{H}_4\text{AcH}$ , respectively, at time,  $t$ . In addition, let  $a$  be the initial concentration of  $\text{C}_6\text{H}_5\text{NAcCl}$  and  $b$  be the initial concentration of radioactive chloride ion.

We can therefore write

$$\begin{aligned}
 dx/dt &= -k_1x - k_2(b - w - z)x \\
 dw/dt &= k_2(b - w - z)x - k_1w \\
 dy/dt &= +k_1x \\
 dz/dt &= +k_1w
 \end{aligned}$$

Since the hydrogen ion and the total chloride ion concentrations do not change during a run (except very slowly due to side reactions) we have included the magnitude of these factors in  $k_1$ , the chemically determined rate constant. The equations then represent the fact that under these conditions the chemical rate is unimolecular, depending only on  $x + w$ , the total concentration of chloroamine. The rate at which chloroamine is converted into the radioactive variety depends not only on the concentration of the inactive chloroamine, but also upon  $b - w - z$ , the

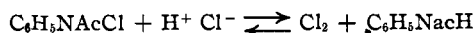
concentration of the radioactive chloride ion, since this, as distinguished from  $b$ , the total chloride ion concentration, is a function of the time.

This set of equations can be solved conveniently by a series of approximations. In the first approximation we set the radioactive chloride ion concentration,  $\text{*Cl}^-$ , equal to  $b$ . Integration with this assumption gives

$$\begin{aligned}
 x &= ae^{-(k_1 + k_2b)t} \\
 w &= a[e^{-k_1t} - e^{-(k_1 + k_2b)t}] \\
 z &= a \left[ \frac{k_2b}{k_1 + k_2b} + \left( 1 - \frac{k_2b}{k_1 + k_2b} \right) e^{-(k_1 + k_2b)t} - e^{-k_1t} \right] \\
 y &= a - (x + w + z)
 \end{aligned}$$

Making use of the values  $k_1 = 0.0316$  and  $k_2b = 0.00376$ , as given in earlier paragraphs, we can calculate the concentrations of radioactive chloride ion which should be present at any time  $t$  according to this mechanism. This we have done. The dotted line, labeled 1, in Fig. 3 shows the results of these calculations. The very large discrepancy between the calculated and observed percentages cannot be accounted for by the approximation which we have introduced in order to simplify the calculations, for  $k_2b$  would need to be almost ten times as large as the value found, in order to obtain an agreement between the observed and calculated values. It is obvious, therefore, that this mechanism by itself cannot account for the data observed under these experimental conditions.

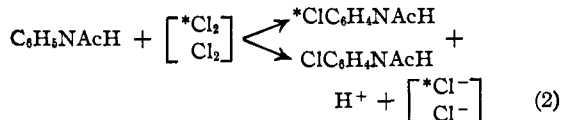
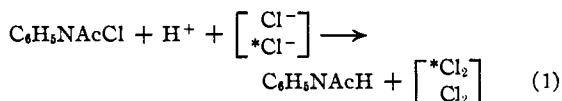
(3) The reaction proceeds through the intermediate formation of chlorine: (a) The concentration of chlorine is large. All of the chemical evidence is against this assumption. However, it may not be amiss to point out that if all the chloroamine reacted to give chlorine before any of the final product were formed, then the radioactivity of the chloride ion in solution would drop to 50% of its original value and thereafter remain constant. The assumption of a large concentration of chlorine is equivalent mathematically, so far as the distribution of radioactivity in the products is concerned, to assuming that the equilibrium



is established rapidly. Therefore any mechanism which depends upon such a *rapid* reversible reaction must be wrong.

(b) The concentration of chlorine is small. In order to get the limiting value under this assumption we shall assume that the concentration of chlorine is infinitesimal and that no exchange on

the nitrogen occurs. We can represent the mechanism as



where  $\left[ \begin{array}{c} * \text{Cl}_2 \\ \text{Cl}_2 \end{array} \right]$  includes all the varieties of chlorine molecules. We do not wish to commit ourselves to any particular mechanism by which molecular chlorine may be formed from the chloroamine, but wish to assume merely that molecular chlorine is an intermediate.

Since the concentration of chlorine remains small, the total rate of production of the chloroanilide must be equal to the rate of disappearance of chloroamine, and therefore equal to the chemical rate.

Designating, as before, the concentrations at time  $t$ , of  $\text{C}_6\text{H}_5\text{NacCl}$ ,  $\text{ClC}_6\text{H}_4\text{NacH}$  and  $*\text{ClC}_6\text{H}_4\text{NacH}$  as  $x$ ,  $y$  and  $z$ , respectively, we obtain

$$-dx/dt = +k_1bx = dy/dt + dz/dt$$

where, for convenience, we have replaced  $k_1$  of a former section by  $k_1b$ . The ratio  $(dz/dt)/(dy/dt)$  is equal to the ratio of the probability that a chlorine atom in molecular chlorine is radioactive, to the probability that it is inactive. Since we have shown that there is a very rapid interchange between chloride ion and chlorine, this ratio of probabilities is merely the ratio of the concentrations of radioactive chloride ion to inactive chloride ion, which in turn is  $(b-z)/z$ .

Our rate equations are then

$$\begin{aligned} dx/dt &= -k_1bx \\ dz/dt &= +k_1(b-z)x \\ dy/dt &= +k_1zx \end{aligned}$$

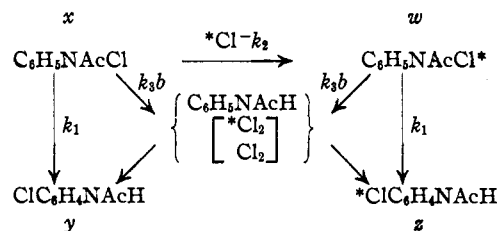
The integrated expressions are

$$\begin{aligned} x &= ae^{-k_1bt} \\ b-z &= be^{-(1-e^{-k_1bt})} = (*\text{Cl}^-) \\ y &= a-x-z \end{aligned}$$

Curve 3 in Fig. 3 represents the values for the percentages of radioactive chloride ion in solution calculated under this assumption. Curve 2 is a plot of the percentages of radioactive chloride ion under the assumptions of paragraph (a) or the equivalent assumption that the exchange on the nitrogen is very fast. Any assumption

with respect to the concentration of chlorine or with respect to the speed of the exchange on the nitrogen, but which retains the chlorine intermediate as the sole path of the reaction, must give a curve which lies intermediate between curve 3 and curve 2. Since our experimental curve lies outside of these limits, we can conclude that the reaction cannot go solely by a chlorine intermediate. It is thus evident that no single mechanism so far proposed is sufficient to explain the experimental facts which we have observed.

(4) Intramolecular rearrangement and the chlorine intermediate mechanism acting simultaneously: We can represent such a combination of these two mechanisms schematically as



As before, since chlorine does not accumulate in the solution, the chemical rate of disappearance of the chloroamine,  $-(dx/dt + dw/dt)$ , must be equal to the rate at which chloroacetanilide is formed by all paths, *i. e.*,  $dy/dt + dz/dt$ . According to this mechanism it also will be equal to  $(k_1 + k_3b)(x + w)$ . If we set  $dy/dt = dy'/dt + dy''/dt$  and  $dz/dt = dz'/dt + dz''/dt$  where  $dy''/dt$  and  $dz''/dt$  are the contributions of the chlorine intermediate mechanism to the rates, we see that  $(dz''/dt)/(dy''/dt)$  must as before be equal to  $(*\text{Cl}^-)/(\text{Cl}^-)$  which now becomes  $(b-w-z)/(w+z)$ .

The differential equations, with the same symbols as used originally, are

$$\begin{aligned} dx/dt &= -k_1x - k_2x(b-w-z) - k_3bx \\ dw/dt &= +k_2x(b-w-z) - k_1w - k_3bw \\ dz/dt &= +k_1z + k_3(x+w)(b-w-z) \\ dy/dt &= +k_1x + k_3(x+w)(w+z) \end{aligned}$$

Assuming that the concentration of radioactive chloride ion is constant and equal to the initial value, the following approximate expressions for  $x$  and  $w$ , as functions of time, are obtained.

$$\begin{aligned} x &= ae^{-(k_1+k_2b+k_3b)t} \\ w &= a[e^{-(k_1+k_3b)t} - e^{-(k_1+k_2b+k_3b)t}] \end{aligned}$$

Substituting these expressions in the equation for  $dz/dt$ , we get an expression to integrate which contains an exponential to an exponential. Expanding one exponential by a series and integrating, we finally obtain

$$z = ae^{+(k_3a/m)e^{-mt}} \left[ (1 - e^{-mt}) - \frac{k_3a}{m} (1 - e^{-2mt}) + \frac{k_3^2a^2}{2m^2} (1 - e^{-3mt}) - \frac{k_3^3a^3}{6m^3} (1 - e^{-4mt}) + \dots - \frac{k_1}{m+n} (1 - e^{-(m+n)t}) + \frac{k_3a}{2m+n} \left( 1 + \frac{k_1}{m} \right) (1 - e^{-(2m+n)t}) - \frac{k_3^2a^2}{m(3m+n)} \left( 1 + \frac{k_1}{2m} \right) (1 - e^{-(3m+n)t}) + \dots \right]$$

where  $m = k_1 + k_3b$  and  $n = k_2b$ . The specific chemical rate is given by  $k_1 + k_3b$ .  $k_2$  has been evaluated from the experiment on the exchange of the chlorine on the nitrogen of the chloroamine.

The fraction of chloride ion in solution which is radioactive is given by  $[b - (w + z)]/b$ . This obviously depends upon the values chosen for  $k_1$  and  $k_3$ . If we choose  $k_1 = 0.0136$  and  $k_3b = 0.0180$  we get curve 4 in Fig. 3 which agrees well with the experimental data. The values of the rate constants chosen above correspond to 43% of the acetylchloroaminobenzene rearranging *intramolecularly* and 57% disappearing through the *chlorine intermediate* path. It is quite likely that changes in the experimental conditions would change not only the actual values of these three rate constants but also the relative amounts going by the two paths.

By calculating, according to the combined mechanisms of the preceding paragraph,  $z/(y + z)$  for  $t = 30$  minutes we obtain the value, 48.2%. The experimental value of this quantity, taken

from Table II, is 40.5%. Considering the inaccuracies of this particular determination we feel that the check is sufficiently close.

In all of this work we must not overlook the fact that we are placing a heavy burden on the single determination of  $k_2$ . However, calculations show that a 100% change in the value of this rate constant will not affect our conclusions materially.

### Summary

The rearrangement of ordinary acetylchloroaminobenzene has been induced by the action of radioactive hydrochloric acid.

The time rates of change of the percentages of radioactivity in the products have been measured. The rate with which the chlorine on the nitrogen of acetylchloroaminobenzene interchanges with the chloride ion in solution also has been measured.

For these measurements it has been shown that under the conditions of this experiment the rearrangement of acetylchloroaminobenzene does not proceed exclusively either by an intramolecular rearrangement or by a chlorine intermediate.

A combination of these two mechanisms, with 43% of the reaction going by direct rearrangement, and 57% through a chlorine intermediate, will explain all our results.

BERKELEY, CALIF.

RECEIVED AUGUST 24, 1936

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, OHIO STATE UNIVERSITY]

## Vapor Pressures of Saturated Solutions

BY ALFRED E. HIRSCHLER

Roehl<sup>1</sup> has pointed out the interesting fact that when all the scanty available data on vapor pressures of saturated aqueous salt solutions are plotted as  $\log P$  against  $1/T$ , straight lines are obtained which are all parallel to the water curve. He was unable to offer an explanation for this "unexpected" result.

While this fact does seem somewhat surprising at first sight, it is the purpose of this paper to show that a closer scrutiny reveals that this is just what would be expected from the magnitudes of the heat effects involved.

The change in fugacity of water from a continu-

ously saturated solution of a solid solute as the temperature rises is given by the equation<sup>2a</sup>

$$d \ln f_1/dT = (H_1^* - \bar{H}_1)/RT^2 + N_2(H_2' - \bar{H}_2)/N_1RT^2 \quad (1)$$

where  $f_1$  is the fugacity of water from the solution,  $H_1^*$  the molal heat content of attenuated water vapor,  $H_2'$  the molal heat content of the solid salt,  $\bar{H}_1$ ,  $N_1$  and  $\bar{H}_2$ ,  $N_2$  the partial molal heat contents and mole fractions of water and solute, respectively. In this equation and those to follow, constant pressure is assumed. We may choose pure liquid water, and an infinitely dilute

(2) (a) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw Hill Book Co., New York, 1923, p. 220; (b) p. 222; (c) p. 201; (d) p. 92; (e) p. 477.

(1) Roehl, THIS JOURNAL, 58, 1291 (1936).