[Contribution from the Chemical Laboratory of the University of California]

THE REARRANGEMENT OF ACETYLCHLORO-AMINOBENZENE

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The properties of acetylchloro-aminobenzene have been under investigation, intermittently, for more than forty years[1] but the mechanism whereby it is converted into *o*- and *p*-chloro-acetanilide has not yet been definitely established. The plan outlined by Orton and his associates has been generally accepted but it fails to account for some of our observations. As envisaged by Orton and others, the first step in the process is a reversible reaction between acetylchloro-aminobenzene and hydrogen chloride which gives rise to acetanilide and chlorine. This is followed by an irreversible chlorination of acetanilide.

$$C_6H_5NAcCl + HCl \rightleftharpoons C_6H_5NAcH + Cl_2 \qquad (A)$$

$$C_6H_5NAcH + Cl_2 \longrightarrow ClC_6H_4NAcH + HCl \qquad (B)$$

When acetanilide is added to an acetic acid solution of acetylchloro-aminobenzene and hydrogen chloride, the rate of the reaction increases but reaches a maximum after a certain definite concentration of acetanilide has been added.[2] This is explained by Soper as being due to the fact that "in the mixture of chloro-amine and hydrochloric acid, the chlorine when formed undergoes two main and simultaneous reactions, (a) with the acetanilide forming *o*- and *p*-chloro-anilides and (b) with the chloro-anilides, which are present at a much higher concentration than acetanilide, forming chloro-amines. These chloro-amines of the chloro-anilides are formed progressively and since they contribute to the iodine titer, the observed rate of fall of iodine titer is less than that of the formation of chlorine in reaction A. When excess of some readily C-chlorinatable substance is present, competition for the chlorine reduces the N-chlorination of the chloro-anilides to a negligible amount and the rate of fall of titer increases to a constant value equal to that of the formation of chlorine."[3]

If this mechanism were correct the addition of chlorine should produce a change in the rate of disappearance of active chlorine similar to that caused by the addition of acetanilide, for this would insure the removal of the acetanilide as fast as formed in Equation A. We found the effect of chlorine to be entirely different from that of acetanilide. Moreover, on

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[1] Bender, *Ber.*, 19, 2272 (1886); Slosson, *ibid.*, 28, 3265 (1895); Chattaway and Orton, *J. Chem. Soc.*, **75**, 1046 (1899); Armstrong, *ibid.*, **77**, 1047 (1900); Mathews and Williamson, This Journal, **45**, 2574 (1923); Blanksma, *Rec. trav. chim.*, 21, 290 (1902); Acree and Johnson, *Am. Chem. J.*, 38, 258 (1907); Porter and Wilbur, This Journal, **49**, 2145 (1927); Orton, Soper and Williams, *J. Chem. Soc.*, 998 (1928); Richardson and Soper, *ibid.*, 1873 (1929); Williams, *ibid.*, 37 (1930); Belton, *ibid.*, 116 (1930).

[2] Orton and Jones, *British Assocn. Advancement Sci. Repts.*, 1910, p. 86.

[3] Soper, *J. Phys. Chem.*, 31, 1193 (1927).

the basis of the above explanation, the maximum rate obtainable by adding acetanilide should not be exceeded by the substitution of any other amide. We have found that the use of β-acetnaphthalide causes the disappearance of the chloro-amine at a rate exceeding the maximum rate attainable with acetanilide.

The rearrangement of acetylchloro-aminobenzene is catalyzed by hydrogen chloride and since side reactions result in the accumulation of hydrogen chloride the reaction appears to be autocatalytic. In order to maintain constant hydrogen-ion and chloride-ion concentrations, sodium acetate and sodium chloride were used as buffers. The solubility of sodium chloride in a 0.05 *M* solution of sodium acetate in glacial acetic acid is 0.015 mole per liter at 40°. In 0.02 *M* sodium acetate solution the solubility of sodium chloride is 0.017 mole per liter at 40°. With solid sodium chloride present a constant concentration of chloride ion was maintained. With sodium acetate present the hydrogen-ion concentration was held at a constant value. The solvent used in every experiment was glacial acetic acid.

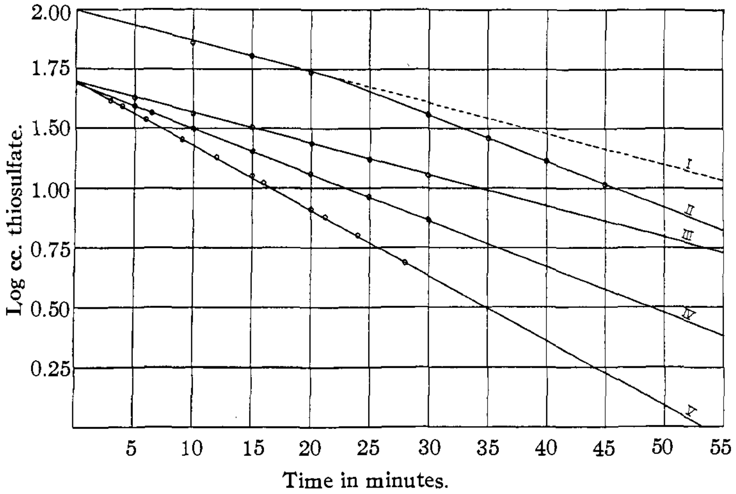

Fig. 1.—Each curve represents a rate of disappearance of active chlorine. In each case the acetylchloro-aminobenzene was dissolved in glacial acetic acid containing sodium acetate (0.05 *M*) and saturated with sodium chloride. The temperature was 40°. Curve I, 0.1 *M* acetylchloro-aminobenzene alone. Curve II, same as I at the beginning but twenty-five minutes later acetanilide was added in sufficient quantity to produce the maximum rate attainable with this reagent. Curve III, 0.05 *M* acetylchloro-aminobenzene (same as I but with one-half as much chloro-amine). Curve IV, 0.05 *M* acetylchloro-aminobenzene and 0.05 *M* acetanilide. Curve V, 0.05 *M* acetylchloro-aminobenzene and 0.05 *M* β-acetnaphthalide.

The rates of the reaction in the presence of varying quantities of acetanilide and of other amides are shown graphically in Fig. 1. The slope of Curve I represents the uncatalyzed rate. Curve III also represents this rate. Different concentrations of the chloro-amine were used in the two cases but it will be observed that the lines are parallel. Curve IV and the last half of Curve II show the maximum rate attainable with acetanilide added, and Curve V shows the maximum rate obtainable by adding β-acetnaphthalide. The slope of Curve V is steeper than that of IV. We believe that these anilides are chlorinated directly by acetylchloro-aminobenzene and that the formation of free chlorine is not a necessary antecedent. This, however, fails to explain the fact that maximum rates are reached with various chlorine acceptors.

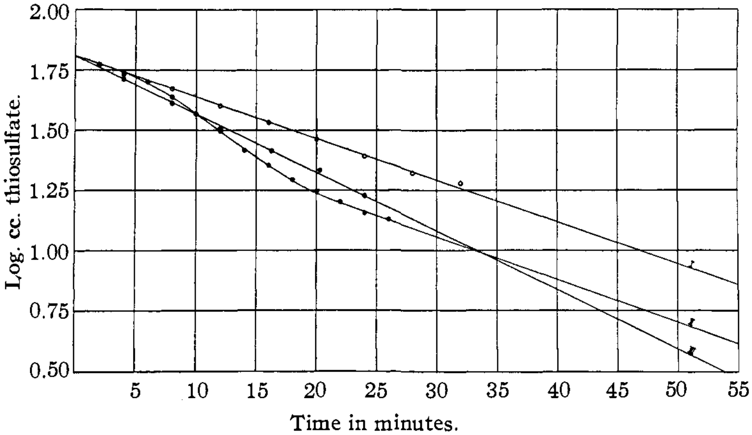

Fig. 2.—The solvent in each case was glacial acetic acid saturated with sodium chloride and 0.02 *M* with respect to sodium acetate. The temperature was 40°. Curve I, 0.06 *M* acetylchloro-aminobenzene alone. Curve II, 0.05 *M* acetylchloro-aminobenzene and enough chlorine added to make the initial titration approximately equal to that of a 0.06 *M* solution of the chloro-amine. Curve III, 0.06 acetylchloro-aminobenzene and an excess of acetanilide.

The addition of chlorine instead of acetanilide does not increase the rate of disappearance of chlorine at once. For a short time the normal products of the rearrangement are formed at the uncatalyzed rate. This is followed by a rapid reaction in which the chlorine is used and finally the rate falls to that of the original uncatalyzed reaction. The course of the reaction with chlorine added is shown by Curve II in Fig. 2. We assume that free chlorine acts rapidly upon acetanilide and upon *o*- and *p*-chloro-acetanilide but very slowly or not at all upon an N-chlorinated anilide. The added free chlorine, therefore, has no appreciable influence until acetanilide or a rearrangement product of acetylchloro-aminobenzene appears. It acts rapidly upon these compounds, substituting chlorine in the ring. When the added chlorine has been removed the rate returns to the uncatalyzed value. The slope of the curve during the period when the chlorine is being removed exceeds that of the maximum rate produced by the addition of acetanilide.

We are unable to harmonize the effects shown in Figs. 1 and 2 with the current theory of the rearrangement. On the other hand, we have no thoroughly satisfactory mechanism to offer as a substitute.

Summary

In glacial acetic acid containing sodium chloride and sodium acetate as buffers, the rearrangement of acetylchloro-aminobenzene is a first-order reaction. The rate of disappearance of the chloro-amine is accelerated by the addition of acetanilide or β-acetnaphthalide. In each case a maximum rate can be secured but the maximum rates produced by the two amides are not identical.

The addition of chlorine and of acetanilide have entirely different effects upon the rate of the reaction. These results are not in harmony with the view that the first step, and the slowest one, is the reversible production of chlorine and acetanilide from the chloro-amine and hydrochloric acid.

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TETRACYCLOHEXYLDIPHENYLETHANE

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In recent years it has been shown that the cyclohexyl group is effective in promoting the dissociation of hexa-substituted ethanes. Ziegler and Schnell[1] have prepared dicyclohexyltetraphenylethane and found that it forms a peroxide in the air. Conant and his students[2] have observed that dicyclohexyldixanthyl is dissociated into the free radical cyclohexylxanthyl to a considerable extent. These facts make it desirable to know the properties of ethanes which have more than two cyclohexyl groups in the molecule.

Some time ago Gray with Marvel[3] reported the preparation of a hydrocarbon, which they believed to be tetracyclohexyldiphenylethane, by the action of silver on a boiling toluene solution of dicyclohexylphenylchloromethane. Later Conant, Small and Sloan[2b] showed that this hydrocarbon was in reality phenylcyclohexylidinecyclohexylmethane. In view

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[1] Ziegler and Schnell, *Ann.*, **437**, 252 (1924).

[2] (a) Conant and Small, THIS JOURNAL, **47**, 3068 (1925); (b) Conant, Small and Sloan, *ibid.*, **48**, 1743 (1926).

[3] Gray with Marvel, *ibid.*, **47**, 2796 (1925).