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

The Rearrangement of N-Chloroacetanilide

BY A. R. OLSON, R. S. HALFORD AND J. C. HORNEL[1]

The kinetics and the mechanism by which N-chloroacetanilide rearranges to form the *o*- and *p*-chloroacetanilides has been the subject of many investigations. In one of the most recent of these, Olson, Porter, Long and Halford,[2] using radioactive hydrochloric acid as a catalyst, compared the rate of loss of oxidizing power with the rate of disappearance of radioactive chloride ion from solution. They showed that the chloroamine disappeared by at least two paths and so they assumed that this implied that the chloroacetanilides likewise were formed by at least two paths. This appeared to be justified since previous investigators had shown that under experimental conditions which were somewhat different, side reactions were of negligible importance.

Olson, Porter, Long and Halford further showed that if one of these paths involved a chlorine intermediate, not more than about 60% of the reaction could proceed by this path since the chlorine attained to complete radioactive equilibrium with the chloride ion before reaction with acetanilide. This meant that no radioactive chloride ion could be removed from solution in the 40% going by the other path. The intramolecular mechanism advanced by Porter from his studies of the rearrangement of the solid phase conformed with this condition.

In the present article we will show that a side reaction, by which chloride ion is produced, instead of being of negligible importance, is a major factor under our experimental conditions and that this alters the interpretation of the radioactive results of Olson, Porter, Long and Halford.

Experimental

All experiments were performed at 40°.

In general our procedure was as follows: 0.04 mole of N-chloroacetanilide (prepared by the method of Barnes and Porter[3]) and 0.04 mole of sodium chloride were dissolved in 1 liter of 20% ethyl alcohol to which enough sulfuric acid had been added to make it 1.43 *N* with respect to hydrogen ion. At stated intervals 70 cc. was withdrawn from the reaction flask. Five cc. of this was used to follow the change in oxidizing power by the usual iodometric titration. The results are shown in Table I and plotted in Fig. 1.

TABLE I

Time, min.	Chloride ion as % of initial N-chloroacetanilide	*p*-Chloroacetanilide as % of initial N-chloroacetanilide	% of oxidizing power remaining in solution
0	0	0	100
2.5	6.1	...	...
3.0	...	...	91.8
7.5	8.6	...	...
10.0	...	5.9	...
10.3	...	...	79.5
14.5	10.0	...	...
20.0	...	11.5	65.0
24.75	13.5	...	...
30.0	...	16.6	...
32.0	...	...	49.5
35.75	15.0	...	...
40.0	...	20.8	...
49.5	17.8	...	35.5
60.0	...	25.8	...
65.6	20.6	...	27.25
80.3	...	27.1	21.25

Determination of Chloride Ion.—The remaining 65 cc. of the sample was extracted with 30 cc. of cold benzene. Fifty cc. of the filtered aqueous phase was used for the determination of chloride ion by the usual methods. The results of a typical run are shown in Table I and plotted in Fig. 1.

Production of *p*-Chloroacetanilide.—One liter of reacting solution was made up as in the previous section, and poured into 100-cc. flasks. At specified times a flask was withdrawn from the solution, cooled in ice, and the precipitate filtered off, washed with a small quantity of benzene, dried and weighed.

The melting points of the precipitates were determined. They were found to vary from 169.5 to 171.5°. On the same equipment pure *p*-chloroacetanilide was found to melt at 172.5°. We assumed, therefore, that the precipitates were, within the limits of error required for this discussion, pure *p*-chloroacetanilide.

In order to get an estimate of the solubility of *p*-chloroacetanilide in our stock solvent, the

---

(1) Commonwealth Fund Fellow.

(2) Olson, Porter, Long and Halford, THIS JOURNAL, **58**, 2467 (1936).

(3) Barnes and Porter, *ibid.*, **52**, 1721 (1930). In a verbal communication Professor Porter has pointed out that in the preparation of solution B, the volume is not restricted to 150 cc. A suitable quantity of water may be added as long as the quantity of chlorine is calculated per cc. of 1.0 *M* sodium carbonate.

following experiment was performed: 0.4 g. of *p*-chloroacetanilide was dissolved in 10 cc. of ethyl alcohol; 0.2 cc. of this solution was added to 10 cc. of stock solvent which had been cooled in an ice-bath. Finely divided crystals of *p*-chloroacetanilide appeared almost immediately. Another 10 cc. of cold solvent was added, the mixture shaken and allowed to stand. This was repeated until 90 cc. of solvent had been used. Some crystals still remained. This corresponds to a solubility of 0.1 g. per liter of solvent and so the weights of the *p*-chloroacetanilide precipitates (in Table I) have been corrected for this solubility. The data are plotted in Fig. 1.

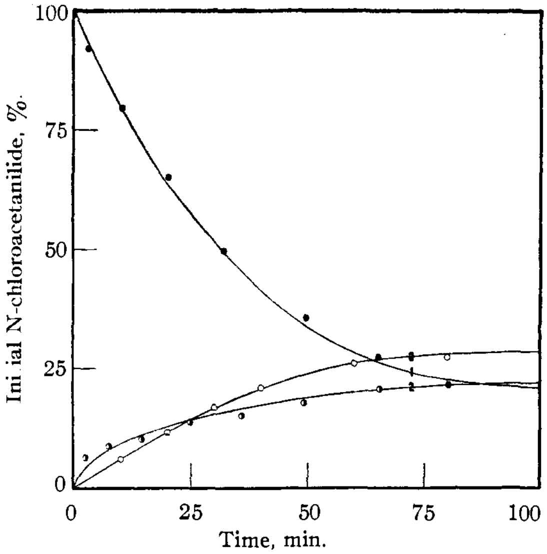

Fig. 1.—Filled circles refer to experimentally determined oxidizing power; half filled circles refer to experimentally determined increase of chloride ion; and open circles to experimental *p*-chloroacetanilide. The ordinates of curve 1 have been calculated by subtracting from 100, the sum of the ordinate of curve 2 plus twice the ordinate of curve 3.

Production of *o*- and *p*-Chloroacetanilides from Chlorine and Acetanilide.—A saturated solution of acetanilide in our stock solvent was prepared and chlorine passed through slowly with continuous shaking. The amount of chlorine used was about one-fifth that required for complete chlorination calculated as monochloride. After cooling in ice the precipitate was filtered off, washed, dried and weighed. The filtrate was neutralized and titrated with silver nitrate to determine the actual amount of chlorine used. On the basis of the chloride ion found the yield of *p*-chloroacetanilide was 50 ± 1% of the chlorinated products.

We conclude, therefore, that in the reaction between chlorine and acetanilide *o*- and *p*-chloroacetanilides are formed in equal amounts in our solvent.

Determination of the Radioactivity of Chloride Ion in Solution.—The procedure was largely that described by Olson, Porter, Long and Halford.[2] However, instead of precipitating the chloride ion as silver chloride and weighing out a given amount, the following procedure was adopted to correct for the changing amount of chloride ion. At the times stated (Table I) 125 cc. of the reaction mixture was removed, extracted with benzene and filtered as described above. To 100 cc. of the aqueous phase, excess silver nitrate was added. All of the silver chloride from this sample was collected, washed and then dissolved in 150 cc. of dilute ammonium hydroxide.

The dilution method of Olson, Libby, Long and Halford,[4] in which a counter was replaced by an electroscope, was used. By precipitating all of the chloride ion in the given volume of our solution we eliminate the effect of changing the total amount of chloride ion, insofar as it concerns the amount of radioactive chloride ion in solution.

The results of these determinations are shown in Table II and Fig. 2.

TABLE II

Time, min.	Radioactive chloride ion remaining in solution, %
0	100
10	87.2
25	72.2
50	61.7
80	57.5

Discussion of Results

Curve 1 in Fig. 1 shows the loss of oxidizing power which we have calculated on the basis of the two following assumptions: first, that in the reaction *o*- and *p*-chloroacetanilides are formed in equal amounts; second, that there is a loss of two equivalents of oxidizing power for every mole of chloroacetanilide or every mole of chloride ion produced. These quantities are taken from the smoothed out curves 2 and 3 in Fig. 1. The points on curve 1 represent the experimentally observed losses of oxidizing power. While we present the data for a single run, our conclusions are based on a number of runs in which the material balance is preserved to within 1 or 2%. This material

---

(4) Olson, Libby, Long and Halford, THIS JOURNAL, 58, 1313 (1936).

balance is in accordance with the assumption that all of the chloroacetanilide is produced through the chlorine intermediate mechanism, but does not exclude the possibility that some chloroamine rearranges intramolecularly provided that this path also produces *o*- and *p*-chloroacetanilides in equal amounts. Therefore so far as the chemical evidence alone is concerned the possibility of an intramolecular mechanism is not excluded.

Fortunately our curve showing how the radioactivity of the chloride ion in solution changes as the reaction progresses does permit us to make this distinction. An intramolecular rearrangement could affect the radioactivity of the chloride ion in solution if, and only if, the chlorine exchange on the nitrogen of the chloroamine were fast. This possibility has been excluded by Olson, Porter, Long and Halford.[2]

The curve in Fig. 2 has been calculated from the rate of formation of chloroacetanilide, assuming that the chlorine which entered into the ring had come into complete radioactive equilibrium with the chloride ion in solution. That this assumption is justified in the case of a chlorine intermediate was shown by Long and Olson.[5]

In this calculation allowance was made for the dilution effect of the chloride ion produced. If any chloroacetanilide had been produced by an intramolecular rearrangement, the curve would lie above the one shown. Since we get complete agreement between our experimentally observed points and our calculated curve, we conclude that if any intramolecular rearrangement takes place it must be to a negligible extent.

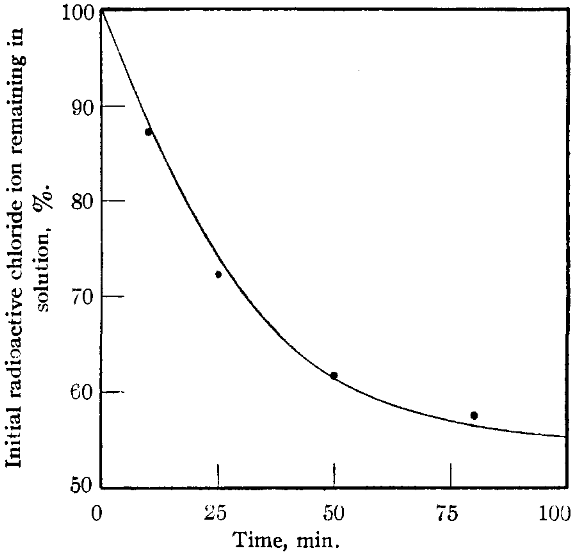

Fig. 2.

Summary

We have reinvestigated the rearrangement of N-chloroacetanilide using radioactive chloride ion as a catalyst. The solvent was aqueous alcohol which contained enough sulfuric acid to make it 1.43 N with respect to hydrogen ion.

Under our experimental conditions we find that some of the chloroamine produces chloride ion and a substance as yet unidentified. The balance of the chloroamine produces *o*- and *p*-chloroacetanilide in equal amounts. We have shown that the change in the concentration of radioactive chloride ion can be completely accounted for by assuming that all of the chloroacetanilides are produced by the chlorine intermediate mechanism.

BERKELEY, CALIF.

RECEIVED JUNE 28, 1937

---

(5) Long and Olson, THIS JOURNAL, **58**, 2214 (1936).