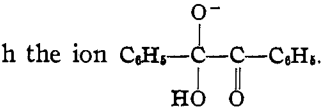
Acknowledgment.—The author owes an especial debt of gratitude to Professor L. P. Hammett for his advice and assistance. He wishes also to thank Professor J. J. Beaver for the use of his conductivity apparatus.

Summary

1. The rate of the rearrangement of benzil to benzilic acid has been measured in solutions of hydroxyl ion and in phenol–phenolate and *o*-chlorophenol–*o*-chlorophenolate ion buffers, all in 32% alcohol at 100%. The reaction is strictly bimolecular.

2. The hydrolysis constants of phenolate and of *o*-chlorophenolate ions have been measured, in 32% alcohol at 100°, by conductivity.

3 The conclusion is drawn that the rearrangement proceeds through the ion  $C_6H_5—\overset{O^-}{\underset{HO}{C}}—\underset{O}{\overset{}{C}}—C_6H_5$.

NEW YORK, N. Y. RECEIVED JULY 27, 1936

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

The Rate of Exchange between Chloride Ion and Chlorine in Aqueous Solution

BY F. A. LONG AND A. R. OLSON

Two investigations dealing with the rate of exchange between halide ions and halogens have been published recently. Grosse and Agruss[1] studied the exchange between bromine and bromide ion and Hull, Shiflett and Lind[2] that between iodine and iodide ion. Both of these investigations employed radioactive indicators to follow the reactions. We can conclude from the results of these investigators that considerable interchange takes place during the course of several minutes, but no attempt was made in either investigation to ascertain the order of magnitude of the rate of the interchange reaction.

In studying the mechanism of the rearrangement of chloroacetylaminobenzene, Olson, Porter, Long and Halford[3] found that it was necessary to know whether such an interchange was fast or slow compared to the rate at which chlorine reacts with acetanilide in aqueous solution. Since this latter reaction is itself extremely fast, it is obvious that we could draw no inferences from the published investigations which would be valid in this work. We have therefore determined the relative speed of these two fast reactions by passing non-radioactive chlorine into an aqueous solution of acetanilide and radioactive chloride ion, followed by an examination of the distribution of the radioactivity in the products of the reaction. Radioactivity in the resulting chloroacetanilide will thus indicate that the chlorine has interchanged with the chloride ions before chlorinating the acetanilide. Even though the chlorination of acetanilide is immeasurably fast, we found the exchange reaction to be complete within the limits of experimental error.

Experimental

0.033 Mole of acetanilide was dissolved in 35 cc. of 95% alcohol, 515 cc. of 1 *N* sulfuric acid added and 0.0825 mole of radioactive sodium chloride was dissolved in this mixture. The concentrations in the resulting 550 cc. of solution were thus 0.06 *M* acetanilide and 0.15 *M* chloride ion. Fifty cc. of this solution was withdrawn for radioactive analysis and, to the remaining 500 cc., 0.00617 mole of chlorine was added with vigorous shaking. The chlorine disappeared rapidly and a precipitate of chloroacetanilide appeared almost immediately. The organic matter, chloroacetanilide and unreacted acetanilide, was then extracted with two portions of ether, the ethereal solution evaporated to dryness and the solid material fused with potassium hydroxide in a nickel crucible. The resulting fused mass was dissolved in water and acidified with nitric acid. To this solution, containing chloride ion from the chloroacetanilide only, and to the 50-cc. initial sample, excess silver nitrate solution was added. Weighed amounts of the dried silver chloride precipitates were dissolved in ammonium hydroxide and radioactive determinations were then made by the method described by Olson, Libby, Long and Halford.[4] The control sample was made by using 0.4 g. of silver chloride. From the fusion we were able to obtain only 0.33 g. of silver chloride and so 0.07 g. of non-radioactive silver chloride was added. In comparing the radioactive analyses this factor must be taken into account.

In Fig. 1 we have plotted the time against the logarithm of the net count times the dilution. The circles represent the observed data and the straight lines have been drawn with a slope corresponding to the known half-life of radioactive chlorine (thirty-seven minutes). Our radioactive material exhibited some gamma radiation but

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[1] A. V. Grosse and M. S. Agruss, THIS JOURNAL, **57**, 591 (1935).

[2] D. E. Hull, C. H. Shiflett and S. C. Lind, *ibid.*, **58**, 535 (1936).

[3] A. R. Olson, C. W. Porter, F. A. Long and R. S. Halford, to be published soon.

[4] A. R. Olson, W. F. Libby, F. A. Long and R. S. Halford, THIS JOURNAL, **58**, 1313 (1936).

any contribution due to this was ignored in calculating our results. During the run the counting apparatus developed some instability as was shown by a variation of the background count and so the accuracy is not as great as we could have expected for this type of experiment. However, the errors are not large enough to throw any doubt on our conclusions.

Figure 1 shows immediately that considerable interchange must take place since the chlorine in the final product is highly radioactive. A comparison of the readings for the two samples at any given time shows that the activity of the silver chloride from the chloroacetanilide is about 79% of that of the control sample.

Discussion and Calculations

The particular concentrations that we used were chosen, first, so that the ratio of chloride ion to acetanilide would be small enough so that the chlorine would not have too great a chance of interchanging before colliding with an acetanilide molecule, and second, with the ratio of radioactive chloride ion to the amount of chlorine rather large so as to permit simplification in calculating the results. Every molecule of chlorine that reacts with acetanilide forms one molecule of chloroacetanilide and sets free one chloride ion. Thus, if a is the initial amount of radioactive chloride ion and x is the amount of chlorine introduced at any time, then, since all chlorine that goes into solution reacts almost immediately, the total amount of chloride ion, radioactive or non-radioactive, is $a + x$. If all of the chlorine becomes radioactive before reacting with the acetanilide, the amount of radioactive chloride ion in solution would be $a - x$. To correct for the fact that as the reaction progresses the chlorine has a decreasing probability of becoming radioactive, we must alter the above amount to $a - x\,(a - x)/(a + x)$. As the reaction progresses the probability that the chlorine will become radioactive decreases for two reasons: first, because the total amount of chloride ion increases and, second, because the amount of radioactive chloride ion decreases. Thus the probability that a chlorine molecule will become radioactive is equal to $[a - x\,(a - x)/(a + x)]/(a + x)$. Then the decrease in radioactivity of the chloride ion in solution will be very nearly equal to the integral from zero to x of $\frac{a - x(a - x)/(a + x)}{a + x}\,dx$. This, of course, will also be the total amount of radioactivity to be found in the chloroacetanilide. In our experiment the ratio of x to a is 1 to 13.35. Putting these values into the above integral we find that the radioactivity of the chlorine in the chloroacetanilide should be 93% of the original radioactive chloride ion. When we apply the further correction of 33/40 due to the undersized sample we find that the radioactivity of the silver chloride from the chloroacetanilide should be about 77% of that for the control sample, assuming complete interchange between chlorine and chloride ion. This agrees very well with our experimental value of 79%. Therefore we can conclude that the establishment of the equilibrium between chlorine and chloride ions in an acidified aqueous solution is extremely rapid.

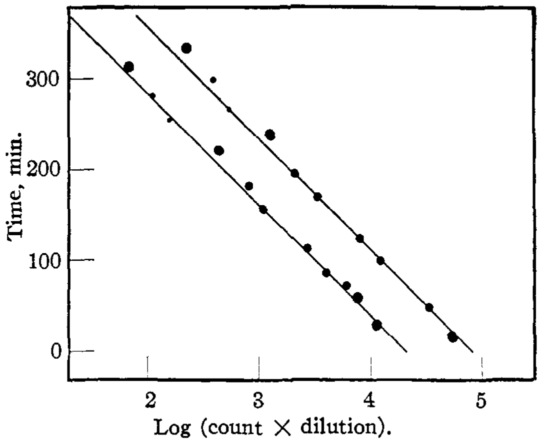

Fig. 1.—The upper curve, which is for the control sample, has been displaced to the right by one-half a unit.

In conclusion we express our indebtedness to Professor E. O. Lawrence and his colleagues for supplying us with the radioactive sodium chloride.

BERKELEY, CALIF.

RECEIVED AUGUST 19, 1936