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Catalytic Decomposition of Hypochlorite Solution by Iridium Compounds. I. The *p*H–Time Relationship[1,2]

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A study has been made of the change in *p*H accompanying the decomposition of sodium hypochlorite solution, catalyzed by iridium compounds. For a given concentration of hypochlorite, solutions of high initial *p*H (about 10) showed negligible change in *p*H during reaction, which produced oxygen as product. When the initial *p*H was in the range 7 to 8, the *p*H decreased slowly during the first part of the reaction, then decreased sharply to the region of 3 to 4 and stayed constant during the remainder of the reaction; some chlorine appeared as a reaction product simultaneously with the rapid drop in *p*H. Solutions of initial *p*H about 9 showed a gradual decrease in *p*H during the first part of the reaction, then an increase in *p*H. For solutions of the same initial *p*H in the 7 to 8 range, the sharp decrease in *p*H during reaction was shown only by the higher concentrations of hypochlorite; the lower the initial *p*H, the more rapid was the drop in *p*H. The various possible reactions of hypochlorite have been interpreted to give a qualitative explanation of the observed changes in *p*H and in reaction products.

While studying interfering agents in the spectrophotometric determination of rhodium with hypochlorite[3] it was observed that iridium(IV) solutions caused rapid decomposition of the hypochlorite solution, with evolution of oxygen; solutions of the other platinum metals were without effect, but cobalt(II) solutions slowly decomposed the hypochlorite solution. The catalytic decomposition of hypochlorite solution has been the subject of various studies for more than a century; in the past few decades, comprehensive studies have been made by Howell,[4] Chirnoaga,[5] Lewis,[6] Fink,[7] Lister,[8] and others. In these studies, catalysis was effected by metals such as iron, cobalt, nickel and copper, or their oxides or peroxides. Skrabal[9] examined different methods of analysis of chlorine bleaching solutions for chloride and chlorate, and determined the ionization constant of hypochlorous acid; his kinetic studies did not involve the use of catalysts, and no mention was made of oxygen as a reaction product. Reports as to the reaction order have varied considerably. In some studies, it has not been clear whether cognizance was taken of the influence of *p*H, or of possible photochemical action. Hoffman and Ritter[10] stated that the oxides of cobalt, nickel, and iridium exerted about equal effects on hypochlorite solutions, while salts of ruthenium and rhodium had little effect. A comprehensive study of the catalytic decomposition of hypochlorite solution by iridium compounds appears not to have been made previously.

A later paper will give the results of kinetic studies; the present report concerns the *p*H–time relationship in the catalytic decomposition of hypochlorite solutions by iridium compounds. The approach was similar to that used by Sorum, *et al.*,[11] in studying the *p*H–time relation in the Landolt reaction. Owing to the complexity of the hypochlorite system, it was impossible to study the proposed reactions separately; however, an explanation is proposed which accounts qualitatively for the observed effects.

Experimental

Reagents.—Iridium metal powder, obtained from A. D. Mackay, Inc., was examined spectrographically and found to contain only traces of platinum, rhodium, copper, silver, magnesium and calcium as impurities. A weighed amount of iridium powder was mixed with excess sodium chloride, which had been finely ground and previously ignited; the mixture, in a porcelain boat, was heated in a combustion

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[2] Presented at the Eighth Southwest Regional Meeting of the American Chemical Society, Little Rock, Ark., December 5, 1952.

[3] G. H. Ayres and F. Young, *Anal. Chem.*, **24**, 165 (1952).

[4] O. R. Howell, *Proc. Royal Soc.* (*London*), **104A**, 134 (1923).

[5] E. Chirnoaga, *J. Chem. Soc.*, 1693 (1926^2).

[6] J. R. Lewis, *J. Phys. Chem*, **32**, 243, 1808 (1928); **35**, 915 (1931).

[7] C. G. Fink, *Trans. Electrochem. Soc.*, **71**, 487 (1937).

[8] M. W. Lister, *Can. J. Chem.*, **30**, 879 (1952).

[9] A. Skrabal, *Monatsh.*, **71**, 251 (1937–1938); **72**, 200 (1938); **73**, 269 (1941).

[10] K. A. Hoffman and K. Ritter, *Ber.*, **47**, 2233 (1914).

[11] C. H. Sorum, F. S. Charlton, J. A. Neptune and J. O. Anderson, THIS JOURNAL, **74**, 219 (1952).

furnace at 730° while moist chlorine gas was passed at the rate of 500 ml. per min. for 3 hours. The product was dissolved in water containing a small amount of hydrochloric acid, and diluted to known volume. The solution, containing sodium hexachloroiridate(IV), was analyzed for iridium content both gravimetrically[12] and spectrophotometrically.[13]

Sodium hypochlorite solutions were prepared by the method described by Lewis.[6]

Analytical Methods.—Hypochlorite was determined by treatment with excess potassium iodide, acidification with 1:10 acetic acid, and titration with standard sodium thiosulfate solution, using starch indicator. Hypochlorite and chlorate were determined together by treatment of the sample solution with excess potassium iodide, acidification with hydrochloric acid to give a solution 8 *M* in acid, dilution with water to make the solution about 1 *M* in acid, and titration with standard sodium thiosulfate solution; the entire operation was conducted in carbon dioxide atmosphere. Chlorate was obtained by difference from the two titrations.

Chlorine gas in the decomposition products was analyzed by absorption in sodium hydroxide solution, followed by iodometric determination. Oxygen was determined gasometrically by absorption in alkaline pyrogallol.

Measurements of *p*H were made with a Beckman Model H-2 *p*H meter, using a glass indicator electrode and a calomel reference electrode.

Procedure.—To a known amount of sodium hypochlorite solution, sodium chloride was added to make the solution 2 *M* (to provide a solution of approximately constant ionic strength). One hundred ml. of this solution was placed in the reaction flask and a measured amount of iridium catalyst solution was added. Immediately the *p*H of the solution was adjusted to the desired initial value by addition of sodium hydroxide or hydrochloric acid as required; adjustment of the *p*H usually required about 30 sec. Timing was started, and *p*H readings were recorded at regular intervals for the duration of the reaction; magnetic stirring was used. Gaseous products were collected and analyzed, and the reaction solution was analyzed, from time to time, for hypochlorite and chlorate. The effects of initial *p*H and of initial hypochlorite concentration were studied. Some difficulty was experienced in obtaining good reproducibility of a given experimental point (in time or in *p*H), but multiplicate runs for identical conditions always gave *p*H–time curves of the same shape.

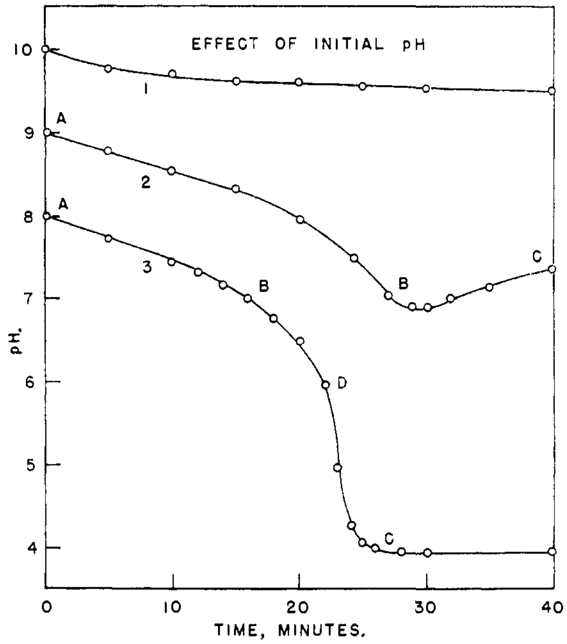

Fig. 1.—Effect of initial *p*H on rate of change of *p*H during catalytic decomposition of sodium hypochlorite; NaOCl = 0.136 *N*.

Results and Discussion

Typical results are shown in Fig. 1; each solution was 0.136 *N* in sodium hypochlorite and 2 *M* in sodium chloride, and contained catalyst solution equivalent to 2.0 mg. of iridium in a volume of 110 ml.; the samples differed only in initial *p*H. Explanations are offered below to account for the general shape of the *p*H–time curves, and are substantiated by chemical analysis of the reaction products. The possible reactions in this system and their standard potentials[14] are

$$2OCl^- \longrightarrow O_2 + 2Cl^- \qquad E^0 = +0.49 \text{ v.} \quad (1)$$

$$3OCl^- \longrightarrow ClO_3^- + 2Cl^- \qquad E^0 = +0.39 \text{ v.} \quad (2)$$

$$2HOCl \longrightarrow O_2 + 2Cl^- + 2H^+ \qquad E^0 = +0.26 \text{ v.} \quad (3)$$

$$3HOCl \longrightarrow ClO_3^- + 2Cl^- + 3H^+ \qquad E^0 = +0.06 \text{ v.} \quad (4)$$

$$HOCl + Cl^- + H^+ \longrightarrow Cl_2 + H_2O \qquad E^0 = +0.13 \text{ v.} \quad (5)$$

The nearly constant *p*H shown in curve 1 indicates that the decomposition is proceeding by reactions (1) and (2); analysis of products showed that reaction (1) accounted for about 28%, and reaction (2) accounted for about 72% of the original hypochlorite. The slight decrease in *p*H may have been caused by absorption of carbon dioxide by the alkaline solution.

In the reaction represented by curve 2, the products were oxygen 70%, and chlorate 30%, in terms of original hypochlorite; in the reaction represented by curve 3, the products were oxygen 73%, chlorate 25%, and chlorine, 2%. For purposes of explanation, curves 2 and 3 are divided into two portions, designated AB and BC. In the initial stages of reaction (AB portion) there is very rapid evolution of oxygen, *i.e.*, reactions (1) and (3) predominate; high *p*H (OCl^- solution) favors reaction (1), and lower *p*H (HOCl solution) favors reaction (3). However, reactions (2) and (4) are also taking place, forming chlorate. Reactions (3) and (4), in which hydrogen ion is formed, account for the decrease in *p*H as reaction progresses. Hypochlorous acid is slightly ionized ($K_a = 3.2 \times 10^{-8}$); as reaction proceeds, the concentration of hypochlorite ion and its buffer action decrease. As the *p*H decreases, the concentration of OCl^- decreases and the concentration of HOCl increases by displacement of the ionization equilibrium of hypochlorous acid. Reactions (1) and (2) therefore decrease, and reactions (3) and (4) increase, the latter serving to decrease the *p*H still further.

An explanation of the BC portion of curves 2 and 3 involves also reaction (5), in which hydrogen ion is consumed and chlorine is formed. In the reaction represented by curve 2, no chlorine was detected in the gaseous products. It is assumed that the amount of chlorine formed is less than its solubility limit in the solution; calculations based on reaction (5) and the observed *p*H change show this to be the case. Such calculations are only approximate, because reaction (3) is still in progress and it opposes the *p*H change produced by reaction (5).

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[12] R. Gilchrist and E. Wichers, THIS JOURNAL, **57**, 2565 (1935).

[13] G. H. Ayres and Q. Quick, *Anal. Chem.*, **22**, 1403 (1950).

[14] W. M. Latimer, "Oxidation States of the Elements and Their Potentials in Aqueous Solution," 2nd ed., Prentice-Hall, Inc., New York, N. Y., 1952, pp. 54–57.

In the vicinity of point B, *p*H near 7, the hypochlorite ion concentration is small, and the solute exists principally as undissociated hypochlorous acid. The slight increase in *p*H in the BC portion of curve 2 (during which oxygen evolution continues) may be explained by assuming that reactions (3) and (5) predominate. If it be assumed also that the rate constants for these reactions are of the same order of magnitude, reaction (5), having a first power dependence on hypochlorous acid concentration, would consume hydrogen ions faster than they are produced by reaction (3) which has a second power dependence on hypochlorous acid concentration.

Figure 2 shows the *p*H–time curves for different hypochlorite concentrations when the initial conditions of *p*H are similar to those that exist at points B, curves 2 and 3 of Fig. 1; whether the *p*H shows a slight increase or a sudden decrease depends upon the hypochlorite concentration. It appears, therefore, that at point B, curve 3 (Fig. 1), the hypochlorite (hypochlorous acid) concentration is greater than at a similar point in curve 2. At point D in curve 3, chlorine was first detected in the gaseous products, and this occurred simultaneously with the rapid decrease of *p*H. It seems likely that as the hydrogen ion concentration increases, the HOCl concentration increases at the expense of OCl^- in the solution, thus increasing the rates of reactions (3) and (4), which produce hydrogen ions faster than they are consumed by reaction (5) which produces the chlorine.

It must be emphasized that the system is very complex, involving not only reactions (1) to (5), but also the ionization equilibrium of hypochlorous acid and the hydrolysis of hypochlorite ion. The observed changes are undoubtedly the resultants of several competing reactions of widely different reaction rates. The explanations are suggested only for qualitative interpretation of the general shape of the *p*H–time curves.

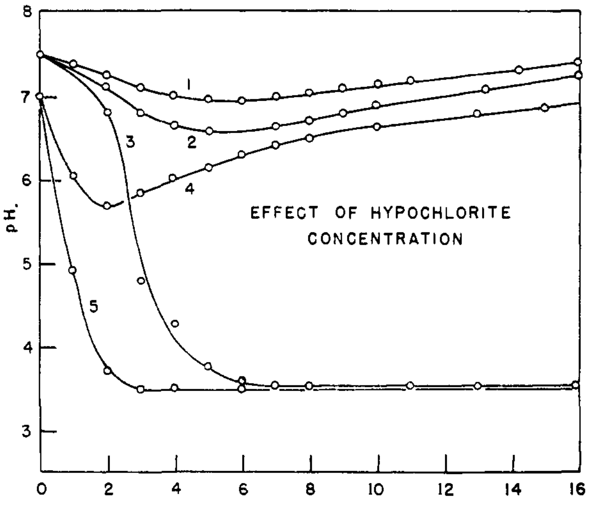

Fig. 2.—Effect of hypochlorite concentration on rate of change of *p*H during catalytic decomposition. Normalities of NaOCl: 1, 0.0014; 2, 0.0028; 3, 0.0070; 4, 0.0014; 5, 0.0056.

The catalyst solution consisted of sodium hexachloroiridate(IV); at the initial *p*H (above 7) of the hypochlorite solutions, conditions were suitable for the formation of hydrous iridium dioxide. During the decomposition of the hypochlorite solutions, marked color changes were observed. When the initial *p*H was 9 or less, the color changed, as the *p*H of the solution decreased during reaction, from yellow through various shades of green, blue, and purple, to black, then later changed to red and finally, in most cases, to light yellow. The final yellow product contained iridium both in colloidal and in solution form; the colloidal material was very stable, showing no visible coagulation in several days. When the initial *p*H was 10 to 11, or when the initial hypochlorite concentration was less than about 0.08 *N*, blue colloidal systems were formed, which coagulated rapidly, leaving a colorless supernatant solution. A more complete discussion of the catalyst will be given in a subsequent paper.[15]

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[15] G. H. Ayres and M. H. Booth, THIS JOURNAL, **77**, 828 (1955).