JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY

VOLUME 56 MAY 5, 1934 NUMBER 5

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, PEIPING UNION MEDICAL COLLEGE]

Mechanism of Oxidation Promoted by Ultrasonic Radiation

BY SZU-CHIH LIU AND HSIEN WU

Oxidations promoted by ultrasonic radiations were recently observed[1] and several reactions involving the liberation of iodine from iodide have been studied. The mechanism of the oxidation, however, is not yet clear. The formation of hydrogen peroxide from water and oxygen under radiation naturally suggests itself, and Schmitt, Johnson and Olson[1] obtained indeed positive tests for hydrogen peroxide with titanium sulfate in the majority of trials. However, "the depth of color produced by a three-minute period of radiation of potassium iodide solution is of the same order of magnitude as that produced by one part in a million of hydrogen peroxide," while "a mixture of equal volumes of a 3% solution of hydrogen peroxide and of the aqueous solution of hydrogen sulfide produced opalescence at a much slower rate than that observed under the influence of ultrasonic radiation." In our study[2] of the effect of radiation on indicators it was observed that addition of 1 cc. of 2% hydrogen peroxide to 15 cc. of a dilute indicator solution did not produce any observable effect while ultrasonic radiation destroyed the color of the indicator permanently. It is clear from these observations that the production of hydrogen peroxide requires confirmation and that it plays, if at all, only an insignificant part in ultrasonic oxidation.

Another possibility is the formation of ozone. Schmitt, Johnson and Olson failed to detect this substance with manganous sulfate, although they did not consider their result conclusive. A third possibility is the direct activation of oxygen by radiation. This was discussed by Schmitt, Johnson and Olson in connection with the effect of pressure on oxidation, but no definite conclusion was reached.

The present communication extends the observations of Schmitt, Johnson and Olson and the experimental results seem to indicate that oxygen is directly activated under the influence of radiation.

Experimental

The oscillating circuit was described in our previous paper[2] and the quartz plate was adjusted to vibrate at the rate of 1.4×10^6 times per second. Solutions to be radiated were placed in a small thin test-tube 15 mm. in diameter. The tube was clamped so that its bottom was buried in the mount of the vibrating dielectric, vigorous vibration and cavitation being set up inside the tube.

The intensity of radiation was found to vary with the thickness, the shape and the position of the test-tube even though the power input was kept constant. The results selected for comparison were, therefore, made by using the same test-tube at a fixed position. Temperature was kept between 25–30° by means of a cooling coil described in our previous paper.

1. Necessity of Oxygen and Cavitation.—Schmitt, Johnson and Olson demonstrated the oxidation of a number of substances in the presence of oxygen and water by subjecting them to ultrasonic radiation under such conditions that gas bubbles might be formed in the liquid. They did not exclude, however, the possibility of oxidation without cavitation, which they did indeed observe in a solution of potassium iodide containing very small amounts of dissolved air. Iodine was liberated although

---

[1] Schmitt, Johnson and Olson, THIS JOURNAL, **51**, 370 (1929).

[2] Liu and Wu, *ibid.*, **54**, 791 (1932).

no bubbles were seen. We have made some observations which leave no doubt that both oxygen and cavitation are essential.

A carbon tetrachloride–water–potassium iodide–starch mixture was boiled in a long tube to free it from air. The tube was then sealed[3] and radiated. Neither cavitation nor liberation of iodine occurred. The tube was then opened, shaken with air and again radiated. Cavitation and blue color appeared immediately.

To show the necessity of cavitation, silicic acid sol and gel (saturated with air before setting) containing potassium iodide and starch were radiated. The sol showed cavitation and slight coloration, while in the gel neither cavitation nor coloration occurred. To show that cavitation alone cannot cause ultrasonic oxidation, a carbon tetrachloride–water–potassium iodide–starch mixture, made gas free by boiling, was saturated with hydrogen or carbon dioxide after cooling. With carbon dioxide neither cavitation nor liberation of iodine occurred; while with hydrogen, potassium iodide was not oxidized even though vigorous cavitation took place.

The necessity of oxygen is shown further by the following experiment. Seven cc. of water, 1 cc. of 1% starch and 1 cc. of 1% potassium iodide were mixed in the small test-tube and radiated for different lengths of time. After exposure the amount of iodine liberated was determined by titration. The content of the tube was transferred to a 50-cc. flask and rinsed with 10 cc. of water; 1 cc. of 1 *N* hydrochloric acid was added before titrating with 0.002 *N* thiosulfate. The amount of iodine was found to increase with the time of radiation very rapidly during the first six minutes and became practically constant after eight minutes. This is probably due to the fact that most of the dissolved oxygen was either consumed or expelled during the first seven or eight minutes of radiation. To prove the correctness of this explanation, potassium iodide–starch mixture was radiated for seven minutes, when cavitation almost ceased. A fine stream of oxygen was bubbled slowly through the mixture, while the radiation was continued. The amount of iodine liberated under these conditions was found to increase steadily. The result of a typical experiment is shown in Table I.

Schmitt, Johnson and Olson found that bubbling oxygen in a fine stream during radiation through an aqueous solution of potassium iodide–starch which was originally gas free did not give rise to color. They suggested as an explanation that "apparently none of the oxygen dissolved." This seems unlikely in the light of our findings.

TABLE I

AMOUNT OF IODINE LIBERATED AND DURATION OF RADIATION

7 cc. H_2O + 1 cc. 1% Starch + 1 cc. 1% KI

Time of radiation, min.	Iodine liberated, mg.		
2	0.02		
3	.04		
4	.06		
5	.08		
6	.09		
7	.10		
8	.10	0.12	oxygen introduced
9	.12	.14	
10	.11	.16	
12	.11	.20	

2. **Formation of Peroxide.**—To confirm the presence of hydrogen peroxide, we exposed a dilute solution of potassium permanganate (about 0.002 *N*) to radiation. The permanganate was decolorized. Addition of potassium permanganate to water which has been radiated showed the same result. Since hydrogen peroxide is the only substance which can be formed from oxygen and water and is capable of decolorizing potassium permanganate, we regard our observation as a conclusive proof of the production of hydrogen peroxide under the influence of radiation.

The amount of hydrogen peroxide formed in 8 cc. of water after seven minutes' radiation was found by titration with 0.002 *N* potassium permanganate to be about 0.006 mg. Taking the amount of oxygen dissolved in water from air to be 6 cc. per liter, 0.15 mg. of hydrogen peroxide should be produced if all the oxygen dissolved in 8 cc. of water is converted into hydrogen peroxide by radiation. Hence only about 4% of the oxygen is converted into hydrogen peroxide under the conditions of our experiment.

We have also studied the effect of electrolytes upon the production of hydrogen peroxide. In acid (*N*/10 HCl, H_2SO_4 or H_3PO_4) solutions the amount of hydrogen peroxide formed in eight minutes of radiation is about five times as much as in distilled water, salt or alkaline solutions of the same concentration.

3. **Reaction with Chloroform and Carbon Tetrachloride.**—Schmitt, Johnson and Olson found that when carbon tetrachloride was added to potassium iodide and starch solution, an intense blue color developed immediately upon radiation. We have shown that chloroform is just as effective. To test whether the formation of hydrogen peroxide can account for such a reaction, a solution of 3% hydrogen peroxide was added to chloroform–potassium iodide–starch mixture without exposing to radiation. No immediate development of color was observed, even when a large amount of hydrogen peroxide was added. This proves that peroxide formation cannot account for this reaction.

Addition of potassium iodide–starch to a mixture of chloroform or carbon tetrachloride and water after radiation also gives the iodine reaction immediately. Addition of silver nitrate gives a positive test for chloride, while a mixture of 3% hydrogen peroxide and carbon tetrachloride or chloroform without radiation gives a negative test. It is clear from these observations that chloroform or carbon tetrachloride does not act catalytically in the oxidation of potassium iodide, but is itself decomposed, giving rise to some free chlorine.

4. **Absence of Ozone.**—Potassium iodide reacts with ozone and hydrogen peroxide while potassium permanganate reacts with hydrogen peroxide but not with ozone.

---

(3) Sealing of the tube containing carbon tetrachloride–water–potassium iodide–starch after boiling involved some experimental difficulty. Carbon tetrachloride vapor remaining in the tube was readily decomposed when the tube was heated to a high temperature during sealing. The decomposition product liberated iodine from iodide to give a blue color. To avoid this difficulty, the water layer was heated first almost to boiling. The carbon tetrachloride was then boiled and the vapor in the tube was finally driven out completely by heating the aqueous layer to vigorous boiling for about ten minutes. Only steam remained in the upper part of the tube after such boiling.

If there is any ozone present, iodine titration should indicate more oxidizing power than potassium permanganate titration. We therefore compared iodine titration with potassium permanganate titration. Several portions of radiated water were mixed and divided into two portions. One was titrated immediately with potassium permanganate and to the other potassium iodide was added. After standing for one hour, the iodine liberated was titrated with 0.002 *N* thiosulfate. The amounts of oxidizing power calculated from the two titration values were identical within the limit of experimental error (about 5%). If there is any ozone produced by radiation, the amount cannot be more than one part in 20 million. Such a small amount of ozone certainly cannot account for any of the oxidation observed.

Summary

Since it has been shown that oxygen is necessary for ultrasonic oxidation, and that the amount of hydrogen peroxide, the only oxidizing agent formed during radiation, cannot account for all the reaction observed, we are forced to conclude that oxygen is directly activated under the influence of ultrasonic radiation. Cavitation being essential, it is clear that only the oxygen molecules on the surface of the bubbles are active *during radiation*. As soon as radiation ceases, the activity of the oxygen disappears. The active oxygen can liberate iodine from iodide or react with water to form hydrogen peroxide. When carbon tetrachloride or chloroform is present, it reacts with the active oxygen to give free chlorine.

PEIPING, CHINA

RECEIVED JUNE 12, 1933

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Dissociation of Some Inorganic Acids, Bases and Salts in Glacial Acetic Acid as Solvent.[1] I

BY I. M. KOLTHOFF AND A. WILLMAN

The pioneer work of Conant and Hall[2] has opened the field of acidity and basicity in acetic acid as a solvent. These authors mainly concentrated on the measurement of the proton activity of various systems and were thus able to compare the acidity and basicity of different compounds. They were well aware of the fact that no quantitative conclusions could be drawn from their work with regard to the degree of dissociation of various electrolytes. In the present work this problem was approached by measuring the electrical conductivities of some acids, bases and salts and by studying the influence of small amounts of water upon the conductance of electrolyte solutions in glacial acetic acid.

Primarily the dissociation of an acid AH is determined by the tendency of the substance to split off protons and the affinity of acetic acid for protons

$$AH + CH_3COOH \rightleftharpoons CH_3COOHH^+ + A^- \tag{1}$$

If the acid is weak, reaction (1) will be incomplete and much AH as such is left in the solution. If the acid is strong, the dissociation according to (1) has a tendency to go to completion. It should be realized, however, that acetic acid has a small dielectric constant and therefore it can be expected that part of the ions may combine to form ion pairs

$$CH_3COOHH^+ + A^- \rightleftharpoons CH_3C(OH)_2A \tag{2}$$

Such ion pairs are comparable to the "acetacidium" compounds of Hantzsch and Voigt[3] and Hantzsch and Langbein,[4] and the hydronium perchlorate, H_3OClO_4. It is quite possible that the weak acids can also associate with the solvent with the formation of addition compounds; the latter, however, will behave as non-electrolytes. This distinction between the character of the undissociated parts of strong and weak acids as "ion pairs" and un-ionized, respectively, is quite helpful in a qualitative interpretation of the effect of small amounts of water upon the electrical conductivity of solutions of acids in glacial acetic acid. Water is a much stronger base than acetic acid. Therefore it is to be expected that water will promote the dissociation of a weak acid AH. If on the other hand the acid is so strong that all of it is present in the form of ions and "ion-pairs," the effect of a trace of water will

---

[1] From the experimental part of a thesis submitted by A. Willman to the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy. 1933.

[2] (a) N. F. Hall and J. B. Conant, THIS JOURNAL, **49**, 3047 (1927); (b) Conant and Hall, *ibid.*, **49**, 3062 (1927); (c) Hall and T. H. Werner, *ibid.*, **50**, 2367 (1928); (d) Conant and Werner, *ibid.*, **52**, 4436 (1930); (e) Hall, *ibid.*, **52**, 5115 (1930); for a complete review of the literature see (f) Hall, *Chem. Rev.*, **8**, 191 (1931).

[3] A. Hantzsch and W. Voigt, *Ber.*, **62**, 975 (1929).

[4] A. Hantzsch and V. Langbein, *Z. anorg. allgem. Chem.*, **204**, 193 (1932).