The Reduction of Oxygen to Hydrogen Peroxide by the Irradiation of Its Aqueous Solution with XRays

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The Reduction of Oxygen to Hydrogen Peroxide by the Irradiation of Its Aqueous Solution with X-Rays*

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(Received June 11, 1934)

Irradiation with x-rays produces no chemical change in air-free water. With oxygen present, hydrogen peroxide is formed due to a primary activation of the water. The initial production of hydrogen peroxide is independent of the oxygen pressure, from 4 to 70 cm Hg and is dependent on the hydrogen ion concentration according to:

$$\frac{H_2O_2}{1000r \times 1000 \text{ cc}} = \left[2.2 + 2.2\left[\frac{10^{9.6-pH}}{1+10^{9.6-pH}}\right]\right]10^{-6}N.$$

IRRADIATION with x-rays produces no chemical change in air-free water.[1] With oxygen present, hydrogen peroxide is formed due to a primary production of activated water molecules.[2] This reaction has been studied at a temperature of 30°C. The effect of variation of x-ray dosage, oxygen pressure and hydrogen ion concentration has been determined.

The analysis for hydrogen peroxide was carried out by adding a surplus of acid potassium bichromate to the irradiated solution and titrating back with ferrous sulfate. A high degree of purity of the water, particularly with respect to organic matter is essential. The water was purified by distillations from basic permanganate and acid bichromate solutions, in an all-Pyrex system, and thereafter the vapor mixed with air was passed through a quartz tube heated to 900°C. The water was next transferred to a de-aerator, saturated with oxygen at the desired pressure, and passed into the irradiation cells. The cells and de-aerator could be heated to 500°C for the purpose of removing possible traces of organic material.

Irradiation of the gas-free water gives a convenient test for the presence of organic impurities which are thereby decomposed with the formation of carbon dioxide and hydrogen. Even with the precautions used, the order of one micro-mol/liter of these gases was produced in the water. This value may be increased several times by less exacting means of purification and handling.

All solutions irradiated have been tested for organic impurities by this method. Its general usefulness will be obvious.

The oxygen pressure has been varied over the range of 4 to 70 cm of mercury, for water and for sodium hydroxide at pH = 13. The initial production of hydrogen peroxide is independent of the oxygen pressure. The results for water are shown in Fig. 1. The x-ray dosage was determined by irradiation of ferrous sulfate solutions in

[1] H. Fricke and E. R. Brownscombe, Phys. Rev. **44**, 240 (1933).

[2] H. Fricke and E. R. Brownscombe, J. Am. Chem. Soc. **55**, 2358 (1933).
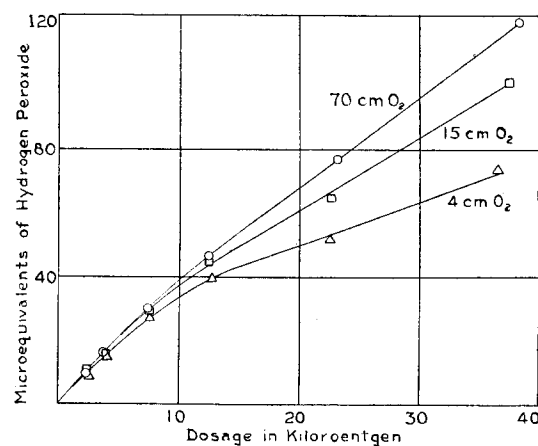
Fig. 1. The production of hydrogen peroxide as a function of the x-ray dosage for different values of the oxygen pressure.

0.8N sulfuric acid.[2] The deviation of the dosage curves from a straight line is accounted for by the decomposition of the hydrogen peroxide by the rays, as was established by the irradiation of solutions to which hydrogen peroxide had been added.

The dependence on the hydrogen ion concentration has been studied in the range pH = 3 to 13. The results are shown in Fig. 2 where the
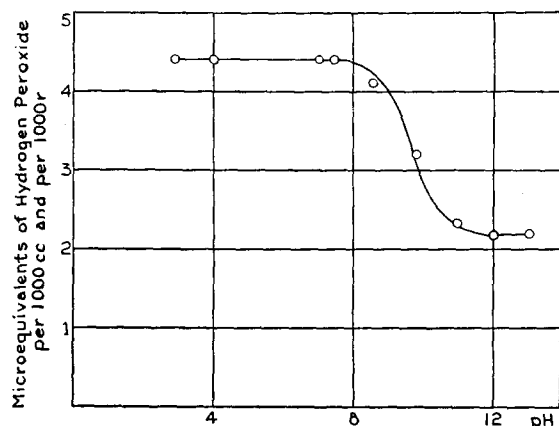

FIG. 2. The production of hydrogen peroxide as a function of the hydrogen ion concentration.

numbers of microequivalents of hydrogen peroxide produced per 1000 cc of solution and per 1000 r of dosage are plotted as a function of the hydrogen ion concentration of the irradiated solution. The values given represent the initial formation of hydrogen peroxide and are determined by taking the tangent of the dosage curve at the origin. The experimental accuracy may be placed at ±5 percent. Representative dosage curves are shown in Fig. 3.

The value given at pH = 7 refers to water. In the acid range sulfuric and phosphoric acids were used and no difference in the results was found. Hydrochloric and nitric acids exert a specific influence. For alkaline solutions, sodium hydroxide was used from pH = 11 to 13 and the results checked at pH = 11 and 12, with calcium hydroxide and with potassium hydroxide. From pH = 7.5 to 9.6 sodium phosphate and borate buffers were used. For each particular value of the pH the concentration of the buffer was changed from 0.5 to 5.0 millimolar with no variation in the results, indicating that the

anions exerted no influence in the reaction. The concentration of chemicals used in all solutions was so low that the x-ray absorption was not appreciably different from that of pure water.

The curve shown in Fig. 2 is calculated from the function

$$\frac{H_2O_2}{1000\ cc \times 1000r} = \left[2.2 + 2.2\frac{10^{9.6-pH}}{1+10^{9.6-pH}}\right]10^{-6}N. \quad (1)$$

The deviations of the experimental points from the theoretical curve may be within the limits of experimental error.

The change in hydrogen peroxide production which takes place between pH = 7.5 and 11.5 is linked with a change in the form of the dosage curve which becomes more nearly a straight line as the pH increases. For the higher dosages the curves appear to have the same slope.

The results indicate that the two terms in (1) are associated with two different reactions which in acid solution contribute equally to the production of hydrogen peroxide. One of these reactions is independent of the hydrogen ion concentration and only slightly interfered with
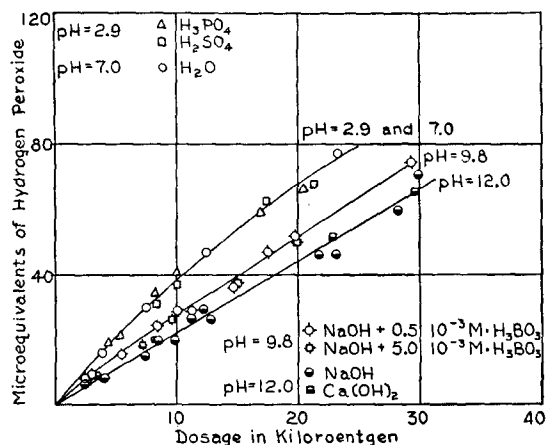

FIG. 3. The production of hydrogen peroxide as a function of the x-ray dosage for different values of the hydrogen ion concentration.

by the presence of hydrogen peroxide. The other reaction is inhibited by hydrogen peroxide in low concentration and its dependence on the hydrogen ion concentration indicates that its course involves the reversible combination of an intermediate (activated) product with the hydrogen ion.