390. *Studies in Electrolytic Oxidation. Part V. The Formation of Hydrogen Peroxide by Electrolysis with a Glow-discharge Anode.*

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IN the previous parts of this series (J., 1932, 2345, 2800; 1933, 829; this vol., p. 10) it has been suggested that certain electrolytic oxidation reactions in aqueous solution involve the primary formation of hydrogen peroxide by the irreversible union in pairs of discharged hydroxyl ions. Detection of the hydrogen peroxide by analytical methods is not usually possible, and in the few cases in which it has been found it may have arisen by secondary chemical reactions; the only unequivocal result seems to be that of Riesenfeld and Reinhold (*Ber.*, 1909, **42**, 2977), who obtained the peroxide by the electrolysis of potassium hydroxide solution at low temperature. In Part I the difficulty of detecting the peroxide was attributed to its formation at high concentration in contact with a large surface of metal, probably locally heated, which is a good catalyst for its decomposition. If this is so, it should be possible to identify the peroxide, provided an electrolysis could be carried out without any electrode material being in contact with the electrolyte. In this connexion it is of interest that Rodebush and Wahl (*J. Chem. Physics*, **1933**, **1**, 696) obtained large quantities of hydrogen peroxide by passing an electrodeless discharge through water vapour at reduced pressure; it was not obtained, however, if metals were introduced into the vapour. By elimination of various mechanisms, these authors concluded that the peroxide was formed directly by the union of discharged hydroxyl ions, a view identical with that put forward previously by us for aqueous solutions.

It appeared probable that a glow-discharge anode would provide the necessary conditions for our purpose, and, in fact, the observations of Makowetsky (*Z. Elektrochem.*, 1911, **17**, 217) and of Haber and Klemenc (*ibid.*, 1914, **20**, 485) indicate that, with such an anode placed above the surface of an electrolyte, the peroxide is formed in certain circumstances. We have now made a series of experiments with such an anode, using a number of very dilute electrolytes, and in all cases the formation of hydrogen peroxide, in amounts approximating to those required by Faraday's laws, has been observed.

EXPERIMENTAL.

The electrolytic vessel consisted of a small filter flask, forming the anode compartment, into which was inserted through a rubber stopper the cathode vessel consisting of a wide tube, closed at the bottom with a tight plug of filter paper, and fitted with a side arm. The anode and cathode were made of nickel wire (S.W.G. 18), the position of the anode being such that its lower end was about 3 mm. above the surface of the liquid. 100 C.c. of anolyte were used in each experiment, and sufficient electrolyte was introduced into the cathode vessel to make good contact with the electrode. The side tubes of anode and cathode compartments were connected through a Y-tube to a manometer and water-pump; a pressure of about 15 mm. of mercury was maintained in the apparatus during the electrolyses. The electrolytes used were boiled out before electrolysis in order to remove dissolved air. Direct current at a pressure of about 700 volts was supplied from a rectifier working on the A.C. mains, and led to the apparatus through a calibrated milliammeter and a variable resistance. The discharge was started by tilting the apparatus so that the anode came momentarily into contact with the surface of the electrolyte; a steady current could then be maintained with only occasional adjustment of the rheostat. During the electrolyses the cell was cooled in ice.

Results.—In a preliminary experiment, 0·05*N*-sulphuric acid was electrolysed for 30 minutes with a current of 0·075 amp. The resulting solution liberated iodine slowly from potassium iodide, gave a strong yellow coloration with titanium sulphate, produced a blue colour with chromic acid and ether, and decolorised permanganate immediately. On rendering it alkaline with caustic soda and boiling for one minute, effervescence was observed and the solution lost its oxidising power completely. Powdered manganese dioxide, cobalt sesquioxide, and precipitated silver also decomposed the solution with effervescence, so it is evident that it contained hydrogen peroxide.

For the quantitative experiments, various electrolytes were used, the solutions being as dilute as it was possible to employ for the necessary current to flow; in each case a current of 0·05 amp. was passed for 965 secs., giving 0·0005 faraday. After electrolysis, the presence of hydrogen peroxide was established by the reaction with titanium sulphate solution, and then measured portions of the electrolyte were titrated with 0·01*N*-permanganate. The following results for the current efficiencies (%) of hydrogen peroxide formation were in general reproducible to within 1—2%: 0·05*N*-H_2SO_4, 75; 0·05*N*-$HClO_4$, 52; 0·10*N*-H_3PO_4, 69; 0·10*N*-NaF, 79; 0·05*N*-K_2SO_4, 98; 0·10*N*-KH_2PO_4, 93; 0·10*N*-$Na_2S_2O_6$, 100. The salt solutions, which were initially neutral, were acid after the electrolysis, showing that hydroxyl ions had been discharged.

Discussion.—The results show that in all the electrolyses hydrogen peroxide is formed in quantity, and it is probable that it arises by the union of hydroxyl radicals formed at the electrolyte surface by the discharge of hydroxyl ions. Since the peroxide is not formed in direct contact with a metal, it is not decomposed but persists in the electrolyte. It might be considered that the peroxide is formed by the action of the electrical discharge on the water vapour, although it does not appear probable that any peroxide formed in this way could exist for more than a very short period in the vicinity of the hot electrode (see Rodebush and Wahl, *loc. cit.*), nor would it be likely to enter the solution under the conditions of constant evacuation. Nevertheless, the possibility was tested and excluded by electrolysing 0·05*N*-sulphuric acid with the gas-discharge electrode as cathode, for under these conditions no trace of hydrogen peroxide was detected. The possibility that hydrogen peroxide arises by secondary reactions in all the solutions used appears too remote to merit further consideration.

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