OXYGEN INDUCED ELECTROREDUCTION OF HYDROGEN PEROXIDE AT THE ROTATED PLATINUM ELECTRODE

Sir:

Based upon the following considerations the effect of hydrogen peroxide upon the diffusion current of oxygen has been investigated. It is assumed that the electroreduction of oxygen to hydrogen peroxide occurs in two steps

$$O_2 + e^- \longrightarrow O_2^- \quad (1)$$
$$O_2^- + e^- \longrightarrow O_2^{=} \quad (2)$$

At the surface of the electrode the O_2^-—or its corresponding acid HO_2—may react according to the Haber–Weiss[1] mechanism with hydrogen peroxide

$$O_2^- + H_2O_2 \longrightarrow OH^- + OH\cdot + O_2 \quad (3)$$
$$HO_2 + H_2O_2 \longrightarrow H_2O + OH\cdot + O_2 \quad (3a)$$
$$OH\cdot + H_2O_2 \longrightarrow HO_2 + HO_2 \quad (4)$$

Reactions (1) and (3) account for an exalted oxygen wave in the presence of hydrogen peroxide. Reactions (1), (3) and (4) also account for the same effect.

Terminators of the above chains are reaction (2) and

$$OH\cdot + e^- \longrightarrow OH^- \quad (5)$$

No information on the rate of electroreduction of $OH\cdot$ and HO_2 under the experimental conditions being available, the effect of hydrogen peroxide upon the oxygen reduction was studied empirically. Experimentally it was found that hydrogen peroxide causes a very large increase in the limiting current of oxygen at the rotated platinum electrode. Figure 1 illustrates the effect in 0.1 M sodium perchlorate solution. The oxygen concentration of the original solution was less than 10^{-6} M and the solution yielded a diffusion current of the order of 0.2 microampere at 25°. In the presence of 3.2×10^{-4} M hydrogen peroxide the limiting current became 2 μ and in 16×10^{-4} M hydrogen peroxide, 10 μ. Under the experimental conditions the exaltation was proportional to the hydrogen peroxide concentration. Analytical application of this exaltation for the determination of traces of oxygen is now being made.

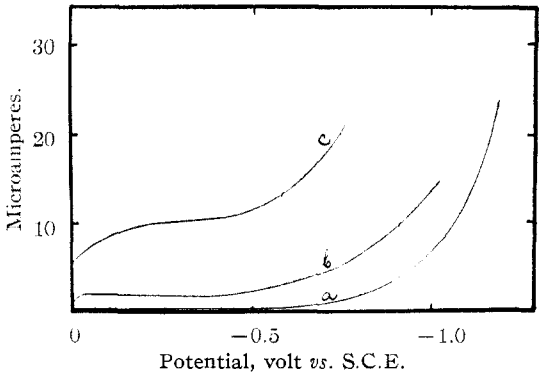

Fig. 1.—Current–voltage curves in 0.1 M sodium perchlorate: $[O_2] < 10^{-6} M$; (a) no H_2O_2, (b) $3.2 \times 10^{-4} M$ H_2O_2, (c) $16 \times 10^{-4} M$ H_2O_2.

(1) F. Haber and J. Weiss, *Naturwiss*, **20**, 948 (1932); *Proc. Roy. Soc. (London)*, **A147**, 332 (1934).

The effect was also observed at the stationary platinum electrode. However, at the dropping mercury electrode the exaltation was obscured by maxima.

Substances which react very rapidly with $OH\cdot$, like acrylonitrile, allyl acetate, and other monomers did not affect the exaltation at the rotated electrode. From this it was concluded[2] that reaction (4) does not occur to a measurable extent and that reaction (5) is the main terminating reaction. Thus the electroreduction of oxygen induces the electroreduction of hydrogen peroxide, at potentials at which hydrogen peroxide is not (or very slowly) reduced, according to the over-all reaction

$$H_2O_2 + 2e^- \longrightarrow 2OH^-$$

This was confirmed by electrolysis experiments with a large platinum cathode in which the decrease of the hydrogen peroxide concentration during the electrolysis was determined.

The effect of various factors, such as pH, kind of supporting electrolyte, concentration of oxygen and hydrogen peroxide and of the temperature are now being investigated. A detailed account will be given at a later date.

(2) See I. M. Kolthoff and E. P. Parry, THIS JOURNAL, **73**, 3718 (1951).

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CRYSTALLINE PYRIDOXAMINE PHOSPHATE

Sir:

Phosphorylated derivatives of vitamin B_6 are believed to play an important role in a number of enzyme systems, including transaminases, amino acid decarboxylases, and tryptophanase. It appears probable that pyridoxamine phosphate (2-methyl - 3 - hydroxy - 4 - aminomethyl - 5 - pyridylmethylphosphoric acid,[1,2] which has been reported to occur naturally,[3,4] is involved in biological transamination. Although this system has received considerable attention, the cofactors have thus far been available only in impure condition and the mechanisms of their action have not been established. Very recently, Viscontini, *et al.*,[5] have reported the preparation of calcium pyridoxal phosphate of high purity. We report at this time the preparation of crystalline pyridoxamine phosphate which gives theoretical analytical values and a very high order of activity.

Commercial pyridoxamine dihydrochloride was converted to the free amine and purified by recrystallization from 50% ethanol. To the colorless amine was added 10 times its weight of anhydrous phosphoric acid (1 part P_2O_5 to 2.5 parts 85% H_3PO_4)[6] and the mixture was heated at 100° for

(1) D. Heyl, E. Luz, S. A. Harris and K. Folkers, THIS JOURNAL, **73**, 3436 (1951).

(2) A. N. Wilson and S. A. Harris, *ibid.*, **73**, 4693 (1951).

(3) J. C. Rabinowitz and E. E. Snell, *J. Biol. Chem.*, **169**, 643 (1947).

(4) W. S. McNutt and E. E. Snell, *ibid.*, **173**, 801 (1948).

(5) von M. Viscontini, C. Ebnöther and P. Karrer, *Helv. chim. acta*, **34**, 1834 (1951).

(6) R. H. A. Plimmer and W. J. N. Burch, *Biochem. J.*, **31**, 308 (1937).