[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

THE EFFECT OF AIR IN THE JONES REDUCTOR

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The formation of hydrogen peroxide during the slow oxidation of zinc in the presence of water was reported by Traube.[1] The hydrogen peroxide was shown to be an intermediate product subsequently destroyed by further action with the zinc: $Zn + 2H_2O + O_2 = Zn(OH)_2 + H_2O_2$; $H_2O_2 + Zn = Zn(OH)_2$.

It was soon after this report that authors of analytical textbooks, in discussing the Jones reductor, introduced the precaution that air must not be permitted to enter the reductor. The hydrogen peroxide formed would react with the permanganate and vitiate results. Later reports by Dunstan,[2] Smith[3] and Barnes,[4] confirmed Traube and gave credence to the belief that the precaution mentioned above is really necessary.

The present work was undertaken to find out whether hydrogen peroxide is actually formed in a Jones reductor and, if so, to measure its effect in the subsequent titrations.

The reducing substance in the reductor is nascent hydrogen. It might be expected that any traces of hydrogen peroxide formed would immediately react with the excess of hydrogen. If, however, some peroxide may have escaped into the reduced iron solution it would certainly react to reoxidize the iron and would not react with the permanganate solution. Experiments have justified these conclusions. Several cubic centimeters of fresh hydrogen peroxide solution have been run through the reductor with the iron solution. In no case has there been any measurable effect on the subsequent titrations.

Experiments were performed using an open reductor in which the column of amalgamated zinc was washed several times with dil. sulfuric acid. This was allowed to drain completely several times, and free access of air thereby permitted. The filtrates gave no test for hydrogen peroxide with titanium sulfate. Similar results were obtained with both hot and cold water. These results indicate that air introduced into a reductor, as ordinarily used, has no effect on the titrations with permanganate. The following experiments show that there is no change in results when air is permitted to enter the reductor.

An iron solution was standardized by passing portions through a closed reductor kept entirely free from air. Five different titrations with 0.1 *N*

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[1] Traube, *Ber.*, **26,** 1471 (1893).

[2] Dunstan, *J. Chem. Soc.*, **87,** 1548 (1905).

[3] Smith, *ibid.*, **89,** 481 (1906).

[4] Barnes, *J. Phys. Chem.*, **12,** 468 (1908).

potassium permanganate solution gave concordant results within two-tenths of one per cent. The funnel was then removed and iron solutions passed through the open reductor. At no time was the liquid allowed to drain below the top of the zinc column. Five determinations showed the following results.

Anal. Subs. (Fe): 0.2140, 0.2137, 0.2136, 0.2137, 0.1424. Found: Fe, 0.2136, 0.2135, 0.2136, 0.2136, 0.1424.

Five determinations were carried out in which the solutions were permitted to drain below the top of the zinc column.

Anal. Subs. (Fe): 0.2136, 0.2136, 0.2136, 0.2136, 0.1424. Found: Fe, 0.2132, 0.2135, 0.2138, 0.2135, 0.1425.

Five tests were made where the solutions were allowed to drain completely several times.

Anal. Subs. (Fe): 0.1424 in each test. Found: Fe, 0.1426, 0.1422, 0.1424, 0.1421, 0.1424.

The maximum error in these determinations is about 0.2%. Such agreement is quite satisfactory in any ordinary analytical work. The checks are as accurate as can be secured with a closed reductor. During the last year open reductors have been used in this Laboratory. Results have been fully as satisfactory as previously obtained with closed reductors. In fact, there is less danger of spattering when the funnel is left off.

Since no hydrogen peroxide had been found in the experiments described above, tests were made to find the conditions under which it might be formed and in what quantities. A rapid stream of air was passed through the column of amalgamated zinc for a period of one minute. When the zinc was covered with dil. sulfuric acid or with hot water the results were negative. With water at room temperature a faint test for hydrogen peroxide was obtained. Five-minute treatments again gave negative results with dilute acid and with hot water. With water at 20° enough hydrogen peroxide[5] was formed to decolorize 0.5 cc. of 0.1 *N* permanganate solution. Using pure oxygen in place of air negative results were obtained with both dilute acid and hot water. With water at 20° five-minute treatments with oxygen gave from 0.0092–0.0220 g. of hydrogen peroxide, depending on the rate at which the oxygen was bubbled through the column. Continued treatment with oxygen over a period of two hours showed, with water at 20°, only about 0.0080 g. of peroxide. The appearance of a white precipitate indicated the formation of zinc hydroxide as reported by Traube.[1]

Similar experiments with columns of unamalgamated zinc have shown only very faint traces of hydrogen peroxide even with cold water. This

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[5] It is assumed that the reducing agent here is hydrogen peroxide, since faint traces of it were evident even in the final washings. Frequent tests were made with titanium sulfate in these experiments.

would indicate that the mercury plays a very important part in the formation of the peroxide.

Summary

Under the ordinary conditions of analysis no hydrogen peroxide is formed in a Jones reductor. It has been proved that the entrance of air does not vitiate results. Hydrogen peroxide solutions introduced into reduced iron solutions cannot then react with permanganate solutions.

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THE KINETICS OF THE OXIDATION OF TRIVALENT TITANIUM BY IODINE

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Introduction

The oxidation-reduction reactions involving iodine admit of the following rough but useful classification: (1) those in which iodide ion is oxidized to iodine by an oxygen acid; (2) those in which iodide ion is oxidized to iodine by an oxidizing agent not containing oxygen; (3) those in which iodine is reduced by a reducing agent which takes up oxygen; (4) those in which iodine is reduced by a reducing agent which loses an electron but does not add oxygen to form an oxygen acid.

The reactions of Class 1 were studied by Bray,[1] who showed that their mechanism consists in the slow formation of hypo-iodous acid which then reacts with iodide ion to give iodine; for example, $HBrO_3 + HI = HIO + HBrO_2$, followed by $HIO + HI = I_2 + H_2O$.

The reactions of Class 2 do not conform to this mechanism, but in their case the slow step consists in direct oxidation (or, according to the ideas of Brönsted,[2] it consists in the formation of an addition product whose charge is the algebraic sum of the two reacting ions); the reaction $Fe^{+++} + I^- = Fe^{++} + \frac{1}{2}I_2$ is the best example of this class.

The various reactions of Class 3 differ from one another in their mechanisms. Thus the rate of the reaction, $I_2 + H_3AsO_3 + H_2O = 2HI + H_3AsO_4$, has been shown by Roebuck[3] to depend on the concentration of hypo-iodous acid which arises from the hydrolysis of iodine.[4] On the other hand, the reaction between phosphorous acid and iodine does not admit of

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[1] Bray, *Z. physik. Chem.*, **54**, 463 (1906).

[2] Brönsted, *ibid.*, **102**, 169 (1922).

[3] Roebuck, *J. Phys. Chem.*, **6**, 365 (1902).

[4] Noyes, *Z. physik. Chem.*, **47**, 121 (1904).