21. *The Decomposition of Hydrogen Peroxide by Ceric Salts. Part II.* The Action of Ceric Perchlorate.*

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Ceric perchlorate solutions above pH 0·7 may contain a part of the Ce(IV) in the form of a colloidal polymer. Once formed, this polymeric form remains stable in cold 2N-perchloric acid. Solutions containing the polymer yield a coloured complex with hydrogen peroxide which is decomposed only slowly. Such solutions are very much less active photochemically than those containing only $Ce^{4+}_{aq.}$ and its simple products of hydrolysis.

IN Part I * it was shown that the reaction between very pure ceric sulphate and hydrogen peroxide in the pH range 0—1·4 was very fast and can be described entirely by the two processes :

$$H_2O_2 + Ce^{4+} \longrightarrow HO_2 + H^+ + Ce^{3+} \quad . \ . \ . \ . \ . \ . \ . \ . \quad (1)$$

$$HO_2 + Ce^{4+} \longrightarrow O_2 + H^+ + Ce^{3+} \quad . \ . \ . \ . \ . \ . \ . \ . \quad (2)$$

Complex formation was not observed. Even if present in large excess and at a high concentration hydrogen peroxide was not attacked by HO_2, and chain reactions did not appear. In these solutions the ceric form is present as sulphate complexes (Moore and Anderson, *J. Amer. Chem. Soc.*, 1945, **67**, 167). It was observed that in ceric perchlorate solutions, where complex formation is small and the cerium is present as the $Ce^{4+}_{aq.}$ ion and its products of hydrolysis (Hardwick and Robertson, *Canad. J. Chem.*, 1951, **29**, 818), the reaction with hydrogen peroxide became slow and a coloured complex was formed. In view of the importance of ceric perchlorate solutions in, *e.g.*, photochemical processes, we have now investigated the reaction in perchlorate and nitrate solutions.

EXPERIMENTAL

Solutions were prepared in triply distilled water. The hydrogen peroxide used was of "AnalaR" quality. The ceric solutions were prepared from "AnalaR" quality ceric ammonium nitrate by two methods : (*A*) precipitating ceric hydroxide by ammonia, washing it free from ammonium and nitrate ions, and dissolving it in 2N-perchloric or -nitric acid ("AnalaR") on a water-bath; (*B*) as in (*A*), followed by reduction of the ceric solution thus obtained with hydrogen peroxide and electrolytic reoxidation of the cerous solution. This oxidation was carried out according to Smith, Frank, and Kott (*Ind. Eng. Chem., Anal.*, 1940, **12**, 268) without a diaphragm.

Dialysis was carried out with regenerated viscose cellulose membranes. Optical density was measured with a Beckman DU spectrophotometer, pH with a Cambridge pH indicator, and redox potentials by means of a Fisher bridge and bright platinum electrodes. Ultraviolet irradiations were by an unfiltered Hanovia S220 lamp as the source.

Results.—When ceric perchlorate solution (0·05—0·1N) prepared according to procedure (*A*) reacted at pH 0—2·0 with hydrogen peroxide solutions, the solution became orange and decomposition of the peroxide was only slow. Fig. 1 shows the absorption spectrum of such a solution and that of the ceric perchlorate solution alone, at the same pH and concentration. The decomposition of the complex may be followed by measuring the optical density at 400 or 425 mμ where the complex has a considerable absorption whilst neither the ceric nor the resulting cerous perchlorate absorbs strongly. As Fig. 2 shows, in one typical experiment, after the initial part where the formation of the complex takes place at a measurable rate, the decomposition is of approximately second order during most of the reaction.

In order to gain information regarding the composition of the complex, measurements by Job's method (Fallab and Erlenmeyer, *Helv. Chim. Acta*, 1953, **36**, 6) were carried out. Although not entirely satisfactory, owing to the decomposition's taking place during measurements, the results (Fig. 3) indicate a possible simple ratio of $H_2O_2 : Ce^{4+} = 1 : 2$.

When solutions of ceric perchlorate prepared by method (*A*) and capable of giving the complex with hydrogen peroxide were dialysed in a stationary system, it was found that the ceric ions were present mainly in a form which did not pass the membrane. The membrane

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* Part I, Baer and Stein, *J.*, 1953, 3176.

FIG. 1.

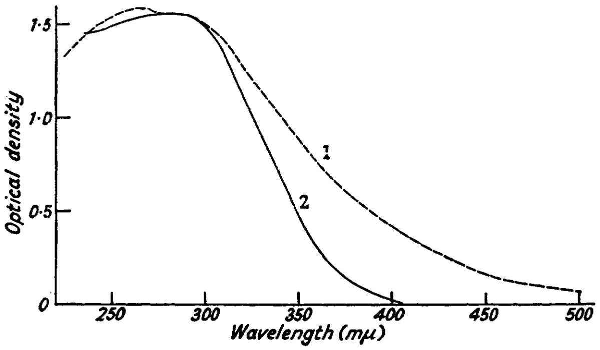

FIG. 2.

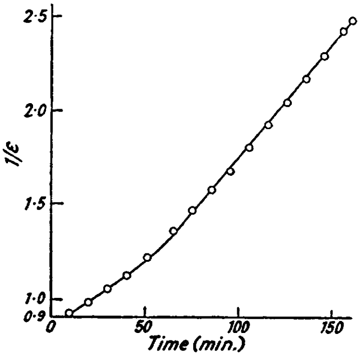

FIG. 1. *Absorption spectrum of ceric perchlorate solution prepared by method (A); (1) in the presence and (2) in the absence of hydrogen peroxide. Both solutions at* pH = 2 *and having*$[\mathrm{Ce}^{\mathrm{IV}}] = 5 \times 10^{-4}$M, $[H_2O_2] = 0{\cdot}05$M.

FIG. 2. *Decomposition of the complex formed in ceric perchlorate solution [method (A)] on addition of hydrogen peroxide:* 25°, pH = 1·0, $[\mathrm{Ce}^{\mathrm{IV}}] = 25 \times 10^{-4}$M, $[H_2O_2] = 5 \times 10^{-2}$M.

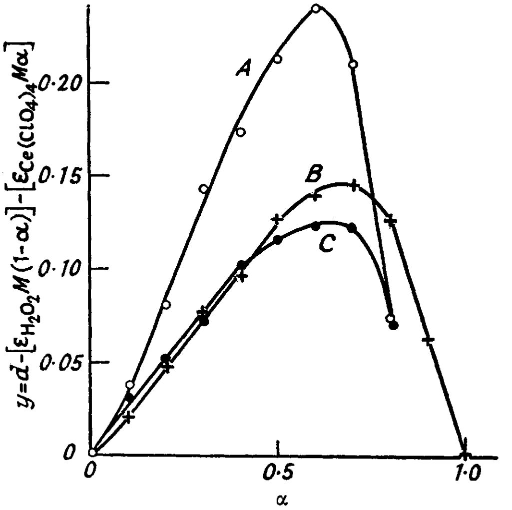

FIG. 3. *Results of using Job's method for the complex between ceric perchlorate [prepared by method (A)] and hydrogen peroxide. Curve A:* M = 1×10^{-3}, $[H^+] = 2 \times 10^{-2}$. *Curve B:* M = $0{\cdot}5 \times 10^{-3}$, $[H^+] = 1 \times 10^{-2}$. *Curve C:* M = $0{\cdot}5 \times 10^{-3}$, $[H^+] = 2 \times 10^{-2}$.

α = mole fraction of ceric ion.

FIG. 4.

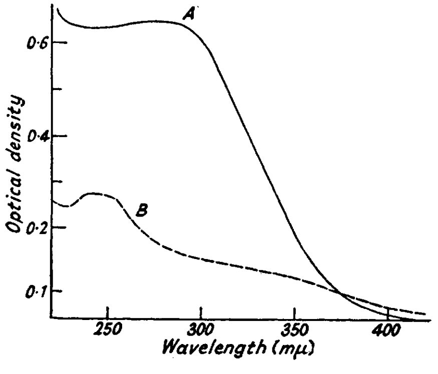

FIG. 5.

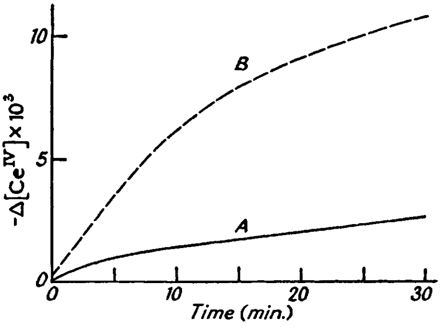

FIG. 4. *Absorption spectra of solutions prepared by methods (A) and (B), obtained with experimental solutions of* 2×10^{-4}*M-concentration in both cases, in* N-$HClO_4$ *solution.*

FIG. 5. *Ultraviolet irradiation of soluiions prepared by methods (A) and (B).* Ceric solutions $1{\cdot}5 \times 10^{-4}$M in N-$HClO_4$. Decrease in ceric concentration as function of time of irradiation in minutes.

was slightly attacked chemically and the solution remaining in it gave the reaction with hydrogen peroxide. Solutions prepared by method (*A*) were thermally stable for very long periods.

When the ceric perchlorate solutions were prepared by method (*B*), it was found that in, *e.g.*, 0·1N-Ce^{IV} solutions in the range of pH 0—0·7, they did not give any complex with hydrogen peroxide and the decomposition of the latter was very fast. Above pH 0·7, however, a solution so prepared is metastable and passes into one of the type given by method (*A*) at a rate increasing with increasing pH and increasing [Ce^{IV}]. Reconversion into a solution as obtained by method (*B*) by addition of perchloric acid is possible only for a short time and after some ageing of the solution obtained by method (*A*) [formed either from the solution obtained by method (*B*) above pH 0·7, or directly] it remains stable even in 2N-perchloric acid. The absorption spectra of the two types of solution are compared in Fig. 4 at the same pH. Dialysis experiments with a solution prepared by method (*B*) were unsuccessful since it attacks the membrane strongly, till all the Ce^{IV} is used up; also it decomposes water in a thermal reaction at a measurable rate.

Measurements of potential difference between the two types of solution were made by means of a concentration cell, with agar bridges. Concentrations of total Ce^{IV} (*a*) and of total cerium including cerous (*b*) were determined in both half-cells by (*a*) potentiometric titration with Fe^{2+} in excess of sulphuric acid and (*b*) oxidation with ammonium persulphate followed by potentiometric titration with Fe^{2+} in excess of sulphuric acid. The results showed that the ratio ${Ce^{4+}}_A : {Ce^{4+}}_B$ is not greater than 0·05 when both solutions are in 1N-perchloric acid each containing 0·1N-Ce^{IV} and where Ce^{4+} denotes the species of free hydrated ceric ions with respect to which the electrodes are reversible.

The photochemical stability of the two types of solution is shown in Fig. 5.

Discussion.—The results indicate that in solution (*B*) the ceric ions are present in those forms described by Sherrill, King, and Spooner (*J. Amer. Chem. Soc.*, 1943, **65**, 170). These solutions do not give a complex with hydrogen peroxide, appear to have a higher oxidation potential, and decompose water in thermal and photochemical processes; they are metastable even at relatively low pH values with respect to solution (*A*). The latter appears to contain the ceric ions mainly in the form of a colloidal polymer, apparently related to the dimer $[Ce\text{–}O\text{–}Ce]^{6+}$ discussed by Hardwick and Robertson (*loc. cit.*). The formation of such polymers has been assumed by King and Pandow (*J. Amer. Chem. Soc.*, 1952, **74**, 1966). The colloid observed by us gives a well-defined coloured complex with hydrogen peroxide. Once formed and aged the colloidal polymer remains stable even in 2N-perchloric or -nitric acid and strongly influences the chemical properties of such solutions.

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