633. *The Decomposition of Hydrogen Peroxide by Ceric Salts. Part I. The Action of Ceric Sulphate.*

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In the pH range of 0—1·4 the reaction between solutions of ceric sulphate and hydrogen peroxide can be represented by two processes :

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

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

without consideration of the actual state of the reacting entities in the solution. It is shown that reoxidation of the Ce^{3+} formed does not occur at all and that the reaction $H_2O_2 + HO_2 \longrightarrow H_2O + O_2 + OH$ does not take place at an appreciable rate; OH radicals are proved to be absent from the system, which thus serves as a source of HO_2 radicals alone. Some experiments using ceric perchlorate solutions are described which indicate that the formation of a stable peroxide complex in this case modifies the reaction with hydrogen peroxide.

THE decomposition of hydrogen peroxide by various metal ions and particularly by those of iron has been the subject of many recent investigations (for reviews, see, *e.g.*, Uri, *Chem.*

Reviews, 1952, **50**, 375; Baxendale, *Adv. Catalysis*, 1952, **4**, 31; Weiss, *ibid.*, p. 343). Although the detailed mechanism of these processes is not completely elucidated, it seems to be established that a reversible change between the valencies of Fe^{2+} and Fe^{3+}, leading to the formation of transient entities such as the radicals OH and HO_2 and their dissociation products, plays an important part. It is because of the simultaneous formation of several different transient entities that the exact rôle of each of them is so difficult to elucidate in processes where, as, *e.g.*, in the oxidation of organic substrates with Fenton's reagent, this system is employed.

It therefore seemed useful to propound a system wherein the number of labile intermediates simultaneously existing is a minimum, and the reactions of the remaining ones can be clearly demonstrated. Such might be the case with a metal ion which reacts with hydrogen peroxide to form an ion of lower valency, if the latter ion is itself incapable of decomposing hydrogen peroxide and is not itself reoxidised by any of the labile intermediates occurring in the reaction. If, moreover, the intermediates do not attack hydrogen peroxide, a further simplification of the reaction mechanism can be obtained. It is now shown that the reaction between solutions of ceric sulphate and hydrogen peroxide appears to have these characteristics. This system has been used for the determination of hydrogen peroxide (Hart and Matheson, *Discuss. Faraday Soc.*, 1952, **12**, 169). Treadwell and Hall (" Analytical Chemistry," Wiley, New York, 8th Edn., Vol. II, p. 752) describe this reaction as suitable for the determination of Ce^{4+} if a large excess of hydrogen peroxide is avoided. It will be shown that any such implied deviation from the stoicheiometric ratio is not due to any reaction of cerium ions but to impurities present in the materials normally used.

EXPERIMENTAL

Experiments were carried out in a vessel of approx. 200 ml. capacity, fitted with mercury-sealed stirrer, gas burette, and burette for the addition of liquids, all *via* ground-glass joints. The temperature of the thermostat containing the vessel was regulated to $\pm 0{\cdot}1°$, the whole of the gas phase being immersed. A 15% solution of sodium chloride was used as the confining liquid in the gas burette. The well-known reactions between hydrogen peroxide and (*a*) excess of ferrous sulphate (no gas evolved) or (*b*) ferric sulphate solution containing traces of ferrous sulphate (oxygen evolved according to: $2H_2O_2 \longrightarrow 2H_2O + O_2$) were used to calibrate the apparatus. Most experiments were carried out at $27° \pm 0{\cdot}1°$. The variables measured were (*a*) amount of oxygen evolved, (*b*) amount of hydrogen peroxide decomposed, and (*c*) amount of ceric ion reduced. Two of these are sufficient to fix all relations, and these were chosen according to the relative concentrations.

Ce^{4+} was determined by addition of excess of ferrous sulphate, freshly standardised against potassium dichromate, which was used also for determination of the excess. No interaction with Ce^{3+} was observed. Diphenylamine was used as indicator. Hydrogen peroxide was determined (i) by potassium permanganate solution standardised against arsenious oxide (Ce^{3+} did not interfere in the cold), or (ii) by adding it to excess of ferrous sulphate, the excess being determined by dichromate with diphenylamine as indicator.

The water used in preparing all solutions was triply distilled (redistillations from alkaline permanganate and dilute phosphoric acid). Ordinary distilled water leads to faulty results.

Ceric sulphate solutions were prepared from " AnalaR " ceric ammonium nitrate *via* the hydroxide, precipitated by ammonia (Baker's " Analysed "). The precipitate was washed several times with triply distilled water, and dissolved in dilute sulphuric acid (" AnalaR "). Ceric perchlorate solutions were prepared similarly, " AnalaR " perchloric acid being used in the last step. In certain experiments ceric sulphate and ceric perchlorate solutions were prepared from ceric oxide (spectroscopically pure; Messrs. Johnson, Matthey and Co.). The hydrogen peroxide and the iron salts were of " AnalaR " quality.

RESULTS AND DISCUSSION

Experiments with ceric sulphate solutions in excess, to which hydrogen peroxide solutions were added, at various pH values, are recorded in Table 1. An instantaneous reaction occurs which leads to the complete decomposition of the peroxide, unlike the decomposition of hydrogen peroxide by ferric sulphate which is slow, as is to be expected from the respective reduction potentials. It will be seen from Table 1 that the quantitative results agree exactly with a mechanism according to which the relative quantities of oxygen evolved, hydrogen peroxide decomposed, and ceric ion reduced are related by the sum of the two reactions (1) and (2) (p. 3176). Within the experimental error it is shown, that Ce^{3+} ions are not reoxidised under these conditions and also that other processes involving an attack on hydrogen peroxides are absent. However, such processes are not favoured by the conditions employed for the work reported in Table 1. The use of high concentrations of hydrogen peroxide in excess, to which ceric sulphate solutions are added, would favour the occurrence of processes such as

TABLE 1. *Reaction between excess of ceric sulphate solutions (from " AnalaR " material) and added hydrogen peroxide.*

Ce^{4+} solution:		H_2O_2 solution:				
10^{-2}N	quantity, 10^{-4} equiv.	10^{-2}N	quantity, 10^{-5} equiv.	pH	O_2 evolved, 10^{-4} mole	Ce^{4+} reduced, 10^{-5} equiv.
5·00	10·00	5·10	25·4	0·75	1·27	—
5·00	10·00	5·10	25·4	0·75	1·28	—
0·86	3·44	1·67	3·19	0·5	—	3·18
1·04	4·16	2·02	3·01	0·1	—	3·01
1·04	4·16	2·02	3·02	0·1	—	3·04
1·00	6·00	8·04	4·02	0·1	—	4·02

$$(3)\ H_2O_2 + HO_2 \longrightarrow H_2O + O_2 + OH$$

leading to the formation of other radicals and the consequent decomposition of hydrogen peroxide in quantities not in agreement with the above simple scheme. Under these conditions, and with " AnalaR "-quality ceric sulphate, the results shown in Tables 2*a* and 2*b* were obtained, and it appears that additional reactions are occurring.

TABLE 2*a*. *Reaction between excess of hydrogen peroxide solution (40 ml.) and ceric sulphate solution (from " AnalaR " material).*

			$Ce(SO_4)_2$ solution:			
No.	H_2O_2, N	pH	normality, 10^{-1}N	ml.	Ce^{4+} reduced, 10^{-4} mole	O_2 evolved, 10^{-4} mole
1	1·92	1·4	1·00	4·00	4·00	2·21
2	1·91	1·35	1·04	4·07	4·28	2·39
3	1·96	1·3	1·00	4·00	4·00	2·23
4	1·87	1·1	1·00	4·00	4·00	2·18
5	1·76	1·1	1·00	4·00	4·00	2·17

TABLE 2*b*. *Showing rate of production of oxygen in experiments of Table 2a.*

Time, min., after addition of Ce^{4+}	Gas burette reading, ml., in Expt. 1	2	3	4	5	Time, min., after addition of Ce^{4+}	Gas burette reading, ml., in Expt. 1	2	3	4	5
5	11·00	11·45	10·95	11·10	11·35	15	11·25	11·70	11·40	11·40	11·65
10	11·15	11·65	11·25	11·35	11·55	20	—	11·73	11·50	—	—

However, on repeating these experiments with ceric sulphate solutions prepared from spectroscopically pure material, it was shown (Tables 3*a* and 3*b*) that there were no reactions in addition to those required by (1) and (2) even in the presence of high concentrations of hydrogen peroxide. The results with the less pure salt are presumably due to traces of impurities which decompose the peroxide catalytically, a process apparently not initiated by pure cerium salts under these conditions.

It appears therefore that HO_2 radicals, if they are in fact formed as postulated in this reaction mechanism, are incapable of reoxidising cerous ions. This is in agreement with the known thermodynamic data (Uri, *loc. cit.*). It appears also that under these conditions HO_2 radicals do not attack hydrogen peroxide molecules. This confirms previous indirect postulates (Uri, *loc. cit.*; Ebert and Boag, *Discuss. Faraday Soc.*, 1952, **12**, 189), and indicates that, when such attack does occur, it is the anion related to the radical, namely O_2^-, which is responsible for it. Under the conditions employed, the HO_2 radical will be only inappreciably dissociated ($K_{HO_2} \sim 10^{-12}$).

In using ceric sulphate solutions there is no evidence that the HO_2 radicals do not appear as such in the course of the reaction, but remain implicit in a complex; such evidence seems to appear when ceric perchlorate solutions are used to decompose hydrogen peroxide. In spite of the fact that the oxidation–reduction potential of these solutions is higher than in the case of the sulphate solutions, no instantaneous decomposition of the peroxide takes place, but a deep red complex is formed, yielding a precipitate under suitable conditions even in strongly acid solutions. The slow evolution of oxygen from the solution is a function of the pH.

TABLE 3*a*. *Reaction between excess of hydrogen peroxide solution* (40 *ml.*) *and ceric sulphate solution* (*from spectroscopically pure material*).

No.	H_2O_2, N	pH	$6·4 \times 10^{-2}$N-$Ce(SO_4)_2$ solution ml.	Ce^{4+} reduced, 10^{-4} mole	O_2 evolved, 10^{-4} mole
1	0·50	1·4	4·5	2·88	1·40
2	1·00	1·3	4·5	2·88	1·43
3	2·00	1·3	4·5	2·88	1·43
4	5·00	1·2	4·5	2·88	1·43

TABLE 3*b*. *Showing rate of production of oxygen in experiments in Table* 3*a*.

Time, min. after addition of Ce^{4+}	Gas burette reading, ml., in Expt. 1	2	3	4
10	9·20	9·32	9·30	9·33
20	9·20	9·30	9·30	9·30

Experiments are now in progress to determine the composition of the complex and the kinetics of its decomposition. Although in solutions containing sulphate the ceric ion is mainly present as the complex $Ce(SO_4)_3^{2-}$ under the conditions employed (Hardwick and Robertson, *Canadian J. Chem.*, 1951, **29**, 828), yet it appears that in perchlorate solutions such as we used, the complex with perchlorate anion plays only a very minor rôle, and the ions mainly present are Ce^{4+} and $Ce(OH)^{3+}$. The complex with hydrogen peroxide obtained here is clearly related to that discussed by Evans, George, and Uri (*Trans. Faraday Soc.*, 1949, **45**, 230) for ferric perchlorate solutions, which they identify as $Fe(HO_2)^{2+}$. However, at least in the case of ceric ions, preliminary results indicate that in the formation of the complex two ceric ions are involved per molecule of peroxide complex.

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