80. *The Reaction between Hydrogen Peroxide and Cerous Hydroxide.*

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It is known (Pissarjewsky, *Z. anorg. Chem.*, 1902, **31**, 359) that hydrogen peroxide reacts quantitatively with excess of cerous hydroxide in suspension to give a precipitate of ceric hydroperoxide $Ce(OH)_3O{\cdot}OH$, but the quantitative determination of the latter (Wieland and Rosenfeld, *Annalen*, 1930, **477**, 72) has caused considerable difficulty. From the work of Schwartz and Giese (*Z. anorg. Chem.*, 1928, **176**, 217), it appeared that the determination might be made by measurement of the oxygen evolved on adding acidified potassium permanganate solution; also, Macrae (*J. Biol. Chem.*, 1933, **27**, 1248) dissolved the hydroperoxide in acetic acid and titrated the resulting solution iodometrically either directly or after decomposition of the peroxide with catalase (Macrae and Wieland, *Annalen*, 1930, **483**, 229). Tests with known small amounts of hydrogen peroxide, however, gave low results by the above methods, so we re-examined the reaction.

The addition of hydrogen peroxide to a suspension of cerous hydroxide at p_H 5·8—9·0 gives, almost immediately, a bright yellow colour, the peroxide being rapidly absorbed. The mixture does not take up or evolve appreciable amounts of oxygen over a period of 10 hours. After 24 hours, however, a slight evolution of oxygen takes place. On treatment with dilute sulphuric acid, a freshly prepared mixture becomes colourless, but a mixture which has been kept for some time gives a yellow solution; oxygen is evolved in both cases.

On acidification of the mixture, peroxidic oxygen and ceric salt react according to the equation

$$2Ce(SO_4)_2 + H_2O_2 = Ce_2(SO_4)_3 + O_2 + H_2SO_4 \quad . \quad . \quad . \quad . \quad (1)$$

and, unless the two reactants happen to be present in this proportion, one or the other remains in solution. From measurement of the oxygen evolved and determination of excess peroxide or ceric salt, it was possible to calculate the amounts of each of the latter present in the suspension, and it was found that, if $[H_2O_2]_0$ represents the amount of hydrogen peroxide added originally, then with increase of time : (i) the oxygen evolved rises to a maximum corresponding to $\frac{1}{2}[H_2O_2]_0$ and then falls; (ii) the amount of peroxide in the precipitate falls steadily from an initial value (determined by extrapolation) equivalent to $\frac{2}{3}[H_2O_2]_0$; (iii) the amount of ceric salt in the precipitate rises from an initial value equivalent to $\frac{2}{3}[H_2O_2]_0$; (iv) the peroxide content of the acidified solution gradually falls to zero, and ceric salt then appears and increases with increasing age of the suspension.

The above results are in agreement with the view that the following reactions take place in the precipitate :

$$2Ce(OH)_3 + 3H_2O_2 = 2Ce(OH)_3O{\cdot}OH + 2H_2O \quad . \quad . \quad . \quad . \quad (2)$$

$$Ce(OH)_3O{\cdot}OH + 2Ce(OH)_3 + H_2O = 3Ce(OH)_4 \quad . \quad . \quad . \quad . \quad (3)$$

and on this basis the originally added hydrogen peroxide was always accounted for within an error of $\pm$ 3%.

The maximum in the oxygen evolution arises as follows. The relation between peroxidic oxygen and ceric salt in the precipitate is given by

$$2H^{\cdot} + 2Ce^{III} + H_2O_2 = 2Ce^{IV} + 2H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

so, if 1 g.-mol. of hydrogen peroxide is added originally and a fraction x has been consumed in the oxidation of cerous salt, then $[H_2O_2] = 1 - x$ and $[Ce^{IV}] = 2x$. On acidification [equation (1)] the oxygen evolved is equivalent to $1 - x$ or to x g.-mols. according as ceric salt or peroxide is in excess, and when neither is in excess, $1 - x = x$, or $x = \frac{1}{2}$, so the oxygen evolution is equivalent to $\frac{1}{2}[H_2O_2]_0$.

The peroxide content of the precipitate can also be determined directly by measurement of the oxygen evolved on treatment with acidified potassium permanganate solution.

In order to follow the reaction during the first 9 mins., it was necessary to use a titrimetric method (see p. 364) instead of a gasometric method for determining the oxygen evolved on acidification, and this led to evidence for the formation of cerous hydroperoxide, $Ce(OH)_2O{\cdot}OH$, during these early stages. From equations (1) and (2), it is seen that the loss of peroxide in the precipitate should be equal to half the loss on acidification, but even after 9 mins. its value had not fallen to that required by (2) (loss of $\frac{1}{3}[H_2O_2]_0$) and extrapolation to zero time gave an initial peroxide value greater than $\frac{2}{3}[H_2O_2]_0$. It would appear, therefore, that cerous hydroperoxide is first formed according to

$$Ce(OH)_3 + H_2O_2 = Ce(OH)_2O{\cdot}OH + H_2O \quad . \quad . \quad . \quad . \quad . \quad (5)$$

which causes no loss in available peroxide.

The course of the whole reaction would then be successively :

(a) (5)—fast, giving complete absorption of H_2O_2 within 3 mins.;
(b) $3Ce(OH)_2O{\cdot}OH + H_2O = 2Ce(OH)_3O{\cdot}OH + Ce(OH)_3$—fast, complete within 15 mins.;
(c) (3)—comparatively slow;

the net reaction being $2Ce(OH)_3 + H_2O_2 = 2Ce(OH)_4$.

It will be seen from the above that any method for the determination of hydrogen peroxide by cerous hydroxide at p_H 5·8—9·0 must take into account the fact that, although the whole of the oxidising power of the peroxide remains in the solution, it is distributed between ceric salt and a peroxide, the former continually increasing, and the latter correspondingly decreasing, with time.

Hydrogen peroxide may be determined by cerous hydroxide by measuring the oxygen evolved on acidification of the precipitate and the residual ceric salt or hydrogen peroxide present after acidification. Such a method yields good results for amounts of hydrogen peroxide of the order of 2—8 × 10^{-5} g.-mol. provided not more than about 6 hours elapse before acidification.

EXPERIMENTAL.

Stability of the Cerous Hydroxide–Hydrogen Peroxide Complex.—To verify that no autoxidation of the cerous hydroxide suspension occurred, 2 c.c. each of 0·027*N*-cerous sulphate and 0·1*M*-borax

(p_H of mixture found to be 7·0) were placed in separate limbs of a modified Barcroft apparatus in a thermostat at 25°. They were then mixed, and during 24 hours no appreciable gas evolution or absorption took place. To verify that the peroxide precipitate underwent no loss in oxidising power, 2 c.c. of 0·027*N*-cerous sulphate and 0·8 c.c. of 0·1*M*-borax (p_H 6·2) were placed in one compartment of the Barcroft apparatus, and 1·0 c.c. of 0·048*N*-hydrogen peroxide in the other. Again, on mixing, no appreciable gas evolution or absorption took place within 10 hrs., but after 24 hrs., slight evolution of oxygen was observed.

Change of Composition of Complex with Time.—Determination of total peroxide content. (1) After short time intervals (before acidification). Expt. 1. 15 C.c. of 0·027*N*-cerous sulphate and 10 c.c. of 0·1*M*-borax were mixed, and 10 c.c. of 0·02475*N*-hydrogen peroxide added (p_H 6·4), the time being noted. All reagents were maintained at 25° before and after mixing. 5 C.c. portions (= $35·3 \times 10^{-6}$ g.-mol. H_2O_2) were added to dilute sulphuric acid at noted times (with acetic acid the reaction, though taking place, was too slow for convenience; cf. Macrae and Wieland, *loc. cit.*), and the hydrogen peroxide in the resulting solution determined by adding a known excess of 0·1*N*-potassium permanganate and back titrating iodometrically. (This method is independent of any reaction between the permanganate and cerium, since they both react with iodide to give iodine.)

Expt. 2. The above procedure was repeated but with 25 c.c. of 0·0236*M*-hydrogen peroxide (p_H 6·2); 5 c.c. of the mixture therefore contained originally $59·0 \times 10^{-6}$ g.-mol. H_2O_2.

TABLE I.

Expt.	Time, mins.	Free H_2O_2 after acidification.	Loss in H_2O_2 after acidification.	Loss in ppt.=$\frac{1}{2}$ × (loss on acidification).	H_2O_2 left in ppt.
1	0·75	21·8	13·5	6·7	28·5
	2·0	19·1	16·2	8·1	27·2
	3·0	17·4	17·9	8·9	26·3
	4·0	17·4	17·9	8·9	26·3
	5·0	16·3	19·0	9·5	25·8
	6·0	15·2	20·1	10·0	25·25
2	1·0	35·3	23·7	11·8	47·1
	2·0	32·8	26·2	13·1	45·9
	3·0	30·5	28·5	14·2	44·7
	4·0	28·0	31·0	15·5	43·5
	5·0	27·8	31·2	15·6	43·4
	6·0	26·7	32·2	16·1	42·9
	7·0	25·7	33·3	16·65	42·35
	8·0	25·0	34·0	17·0	42·0
	9·0	23·7	35·3	17·65	41·35

From the results in Table I (in which all weights are expressed as g.-mol. × 10^6) it will be seen that at the end of the run the peroxide content has not fallen to two-thirds of the original amount added.

(2) After long time intervals (before acidification). 25 C.c. each of 0·024*M*-hydrogen peroxide, 0·0135*N*-cerous sulphate, and 0·16*M*-borax (p_H 8·8) were mixed at 25°. From time to time, 5 c.c. portions were removed and placed in the Barcroft apparatus, 1 c.c. each of dilute sulphuric acid and 0·1*N*-permanganate being added together, and the oxygen evolution measured.

TABLE II.

Time, mins.	Total peroxide.	Time, mins.	Total peroxide.	Time, mins.	Total peroxide.	Time, mins.	Total peroxide.
16	25·4	51	21·4	129	17·8	256	16·8
34	22·4	86	18·8	160	17·5	405	15·7

From the results (Table II) it will be seen that the total peroxide decreases with time. Extrapolation to zero time gives a value for total peroxide equal to approximately two-thirds of the original amount added.

Determination of total peroxide and cerium. Expt. 1. 25 C.c. of 0·028*M*-hydrogen peroxide, 25 c.c. of 0·03*N*-cerous sulphate, and 20 c.c. of 0·1*M*-borax (p_H 6·1) were mixed. From time to time, 5 c.c. portions (equal to $50·8 \times 10^{-6}$ g.-mol. H_2O_2 originally) were treated with dilute sulphuric acid and the oxygen evolution measured as above. The residual peroxide or ceric salt in the acidified solution was determined, the former titrimetrically as above, and the latter iodometrically.

Expt. 2. 25 C.c. of 0·0244*M*-hydrogen peroxide, 50 c.c. of 0·027*N*-cerous sulphate, and 20 c.c. of 0·1*M*-borax (p_{H} 6·3) were treated as in Expt. 1, 5 c.c. of solution being originally equivalent to 32·1 × 10^{-6} g.-mol. H_2O_2. The results are given in Table III, whence it will be seen that the oxygen evolution rises to a maximum and then falls, and that the maximum corresponds to half the peroxide originally added, *i.e.*, half of this has reacted to give ceric salt. Extrapolation to zero time gives an oxygen evolution approximately equal to that obtainable from $Ce(OH)_3O{\cdot}OH$. Further, the total peroxide decreases and total ceric salt increases with time (see fig.). Extrapolation of both to zero time, the former by means of an empirical relation involving its square, gives values for ·OOH approximately equal to those obtainable from $Ce(OH)_3O{\cdot}OH$.

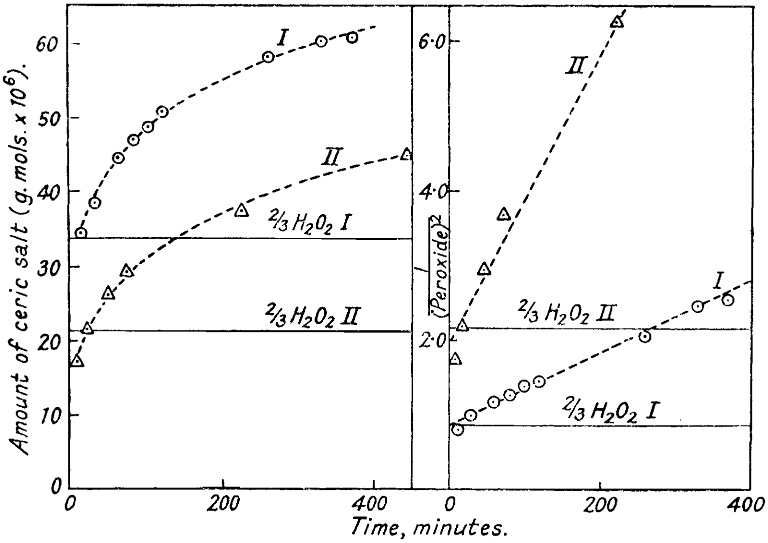

Table III.

Expt.	Time, mins.	O_2 evoln.	H_2O_2 after acidification.	Ce^{IV} after acidification.	Total OOH.	Total Ce^{IV}.	$\frac{1}{[\cdot OOH]^2}$. *	Orig. H_2O_2 (calc.).	Error, %.
I	12	17·2	17·6	—	34·8	34·4	0·824	52·0	+2·4
	29	19·3	12·1	—	31·4	38·6	1·015	50·7	−0·2
	60	22·2	6·7	—	28·9	44·5	1·195	51·2	+0·8
	79	23·5	4·4	—	27·9	47·0	1·285	51·4	+1·2
	100	24·4	2·2	—	26·6	48·8	1·415	51·0	+0·4
	119	25·4	0·7	—	26·1	50·8	1·469	51·5	+1·4
	260	22·0	—	14·3	22·0	58·3	2·060	51·1	+0·6
	329	20·1	—	20·2	20·1	60·4	2·480	50·3	−1·0
	372	19·8	—	21·2	19·8	60·8	2·550	50·2	−1·2
	506	17·4	—	29·2	17·4	64·0	3·310	49·4	−2·8
II	7·5	8·6	15·4	—	24·0	17·2	1·740	32·6	+1·6
	20	10·9	10·3	—	21·2	21·7	2·22	32·0	−0·3
	49	13·1	5·3	—	18·4	26·2	2·95	31·5	−1·9
	73	14·7	1·9	—	16·5	29·4	3·67	31·2	−2·8
	224	12·7	—	12·1	12·6	37·4	6·30	31·3	−2·5
	446	10·5	—	24·1	10·5	45·1	9·02	33·0	+2·8
	1334	6·6	—	36·8	6·6	49·9	22·90	31·5	−1·9

* The values in this column are expressed in g.-mol. × 10^{-9}.

From results in Table III the original amount of peroxide (col. 9) present was calculated as indicated on p. 363, the maximum error being ± 3%.

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