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The Production of Hydrogen Peroxide in the Mercury Sensitized Hydrogen–Oxygen Reaction

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In spite of a large number of investigations there still seems to exist considerable doubt as to the mechanism whereby oxygen reacts with hydrogen atoms produced by different methods.[1] Still more striking is the fact that there is no agreement among the various workers as to the primary products of the reaction. Bates and Taylor[2] reported that in the mercury sensitized reaction, which is generally conceded to go through the intermediate stage of atomic hydrogen, they were able to show hydrogen peroxide to be the sole product. This fact was in complete agreement with the mechanism originally suggested by Taylor and Marshall, which may be written

$$\begin{aligned} Hg' + H_2 &\longrightarrow Hg + 2H && (1)\\ H + O_2 &\longrightarrow HO_2 && (2)\\ HO_2 + H_2 &\longrightarrow H_2O_2 + H && (3)\\ H + H &\longrightarrow H_2 && (4) \end{aligned}$$

This mechanism has chain characteristics and, therefore, can have a quantum yield of hydrogen peroxide of any magnitude, depending upon the relative efficiency of the processes involving oxidation compared with the recombination of hydrogen atoms. Thus if (2) and (3) are relatively rapid and (4) is slow, we might have chains much greater than unity, while if the reverse were true, yields of unity or less might be expected.

Another possible mechanism was postulated by Bonhoeffer and Haber[3]

$$\begin{aligned} H + O_2 &\longrightarrow HO_2 && (2)\\ HO_2 + H_2 &\longrightarrow H_2O + OH && (3a)\\ OH + H_2 &\longrightarrow H_2O + H && (4a)\\ OH + OH &\longrightarrow H_2O_2 && (5a) \end{aligned}$$

We see that the initial process is the formation according to (3a) of water and an hydroxyl group. The latter may react according to (4a), giving water and hydrogen atom, again a chain process. If, however, the latter process required a large activation, it would occur so seldom as to allow practically all of the hydroxyls to form hydrogen peroxide according to (5a). If the latter condition exists, the quantum yield of hydrogen peroxide formation is unity, and. what is most important, there are formed

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(1) Taylor. THIS JOURNAL. **48.** 2840 (1926), contains references up to this date; Marshall, *J. Phys. Chem.*, **30.** **34.** 1078 (1926); THIS JOURNAL. **49.** 2763 (1927); Haber and von Schweinitz. *Sitzb. preuss. Akad. Wiss.*, **30.** 499 (1928); Farkas. Haber and Goldfinger, *Naturwissenschaften*, **17.** 674 (1929); **18.** 266 (1930); Haber, *ibid.*, **18.** 917 (1930); Farkas, Haber and Harteck, *ibid.*, **18.** 266, 443 (1930); *Z. Elektrochem.*. **36.** 711 (1930); Frankenburger and Klinkhardt, *Z. physik. Chem.*, **8B.** 138 (1930); **15B.** 421 (1932); *Trans. Faraday Soc.*, **27.** 431 (1931).

(2) Bates and Taylor, THIS JOURNAL, **49.** 2438 (1927).

(3) Bonhoeffer and Haber, *Z. physik. Chem.*, **137A.** 263 (1928); *Z. angew. Chem.*, **42.** 475 (1929); see also Farkas. Haber and Harteck, *Naturwissenschaften*. **18**, 266 (1930).

simultaneously at least two molecules of water. There must appear, therefore, at least 51.4 weight per cent. of water in the products. This mechanism has received general recognition, in spite of the work of Bates and Taylor already cited, and of Bonhoeffer and Boehm,[4] who found 75% of hydrogen peroxide in the products of the reaction of molecular oxygen with hydrogen atoms produced by a discharge.

Another possible point of divergence is the quantum yield of hydrogen peroxide. If this were of a magnitude greater than unity the Haber mechanism would be ruled out. A yield, however, of unity or less would be entirely inconclusive. Marshall's measurements of the quantum yield[4a] gave a value of 6.6. More recently Frankenburger and Klinkhardt have redetermined this magnitude and find a value near unity, which they advance as strong proof of the Haber mechanism. Since, however, they find that in fifteen out of twenty-three experiments recorded the value was somewhat greater than unity, these authors have introduced an alternative reaction to (3a)

$$HO_2 + H_2O \longrightarrow H_2O_2 + OH \qquad (6a)$$

This would lead to a quantum yield of three, and they then explain their high values by suggesting that both (3a) and (6a) take place, giving a value intermediate between 1 and 3. This supposition rules out the later work of Marshall[5] as a basis for distinguishing between the two mechanisms, because he used moist gases in obtaining 100% hydrogen peroxide formation.

It immediately appears that considerably more importance is to be attached to the early work, which showed hydrogen peroxide as the sole product in dry gases, than was supposed at that time. This work has, therefore, been repeated with great care with a view to settling this point and thereby differentiating between the two postulated mechanisms. The great frequency with which the Haber mechanism has been introduced into various reaction kinetics during the past years makes this simple yet crucial experiment seem of great importance.[6]

The effect of water vapor on the production of hydrogen peroxide has also been studied in an effort to test the validity of reaction (6a).

Experimental

Tank hydrogen and tank oxygen were used without purification, since the possible impurities, nitrogen. etc.. have been shown by Marshall to be without effect on the reaction.

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(4) Bonhoeffer and Boehm, *Z. physik. Chem..* **119.** 385 (1926); Bonhoeffer and Loeb, *ibid..* **119.** 474 (1926).

(4a) In a note published since this article was written. Marshall has revised this value to 2.5 [THIS JOURNAL. **54.** 4460 (1932)].

(5) Marshall. THIS JOURNAL. **49.** 2763 (1927).

(6) Bodenstein, *Trans. Faraday Soc.*, **27.** 413 (1931): von Elbe and Lewis. THIS JOURNAL. **54,** 552 (1932); Lewis. *Chem. Rev.*, **10.** 49 (1932): Norrish, *Trans. Faraday Soc..* **27,** 461 (1931): *Proc. Roy. Soc..* (London) **A135.** 332 (1932); Alyea. THIS JOURNAL, **53.** 1324 (1931): Kassel, "Kinetics of Gas Reactions." Am. Chem. Soc. Monograph No. 57, p. 121.

In all the experiments a flow system was used. The rate of flow was measured by flowmeters previously calibrated against a standard gasometer. The gases. before entering the reaction zone. were separately bubbled through wash bottles containing mercury. and. after the streams of hydrogen and oxygen were united. they were once more bubbled through mercury to ensure saturation and complete mixing. The gas mixture was then either dried over phosphorus pentoxide, or else passed through a medium which regulated the water vapor pressure to a desired amount. On leaving the illuminated zone. the gases were led into a trap or traps immersed in liquid air. Quartz to Pyrex seals and ungreased ground glass joints were used to prevent as much as possible any decomposition of the peroxide which might occur from contact with rubber or other foreign materials.

Two methods of illumination were employed. In the first. an ordinary vertical arc of the Cooper–Hewitt type was immersed in a water-bath maintained at 14°. Surrounding this. and also under water, was a quartz spiral of 4.5 cm. diameter. made of 140 cm. of 5-mm. bore quartz tubing. The arc burned at 6 amperes and 21 volts. The second method of illumination made use of the special type of mercury arc described in detail by Bates and Taylor.[3] The reaction tube is surrounded by the arc. and the gases flow through in a straight line. In our set-up. the reaction tube was of quartz. 8 mm. in bore and 40 cm. long.

Procedure

In making a run. the arc was first started and allowed to come to a constant condition. The gases were turned on. and their rates of flow adjusted to the desired values: they were not permitted to flow through the reaction zone until a moment before a run was started. in order to avoid as much as possible the formation and deposition of mercuric oxide at the outlet from the reaction zone. since it was found that an accumulation of this yellow oxide materially reduced the yield of hydrogen peroxide. When all was ready. the gases were passed through the reaction zone for one minute. and the trap, previously weighed and now immersed in liquid air. was attached by the ground glass joint to the outlet. In order that frost should not form at the outlet and later melt and run back into the trap. the off-gases were led out through a length of rubber tube attached to the trap. After the reaction had been permitted to proceed for the desired time (usually ten minutes). the trap was removed from the liquid air. warmed up to room temperature and weighed. The reaction products were then rinsed out with distilled water. and titrated for hydrogen peroxide with 0.1 *N* potassium permanganate. The operations of weighing and titration were carried out as expeditiously as possible in order to minimize the amount of peroxide decomposed during the time. From the total weight of the product. and the amount of hydrogen peroxide as determined in the titration. the percentage yield of the hydrogen peroxide could be calculated.

Experimental Results

Dry Gases.—It has been stated previously that the gases were dried in the experiments by passing them over phosphorus pentoxide. In order to indicate the efficiency of this process several blank runs were made at various times during the investigation, and in no instance was any weighable moisture frozen out in the traps.

The results with the quartz spiral and small mercury lamp are recorded in Table I. experiments 1 to 7. Various rates of flow and different ratios of hydrogen to oxygen were tried. It was observed that mercury oxide was deposited on the last coil of the spiral and that it considerably decreased the peroxide yield from any subsequent run. Consequently, the practice was adopted for the later experiments of cleaning out the spiral with dilute nitric acid before each test. The data show that in all except the first two experiments. the weight per cent. of hydrogen peroxide in the product was greater than the 50% yield to be expected according to Frankenburger. In one instance it was as high as 75%.

Using the special type of mercury arc, more experiments were carried out with dry gases. A rate of flow of about 135 liters per hour and an eight to one hydrogen to oxygen mixture gave the best results. Here as with the other set-up an accumulation of mercury oxide at the outlet of the reaction zone cut down the peroxide yield. The results are shown in Table I. experiments 12 to 21.

TABLE I

RUNS WITH DRY GASES

No.	Rate of flow liters/hr. O_2	H_2	Ratio $H_2:O_2$	Time of run, min.	Total product, mg.	H_2O_2, mg.	H_2O_2 %
1	20	105	5:1	5	11.5	4.4	38.5
2	20	102	5:1	5	17.7	5.4	30.7
6	25	120	5:1	10	8.5	5.6	65.5
3	14	130	9:1	20	23.6	16.1	68.5
4	12	129	11:1	20	19.1	10.3	54.0
5	12	127	11:1	10	9.8	7.3	74.9
7	8	140	17:1	11	10.1	7.3	72.6
12	29	117	4:1	5	5.8	3.4	58.0
13	20	118	6:1	10	16.8	13.6	81.0
14	20	118	6:1	10	12.5	9.7	77.2
24	22	151	7:1	10	11.3	7.7	67.9
17	10	73	7:1	10	10.2	7.4	72.5
15	15	118	8:1	10	9.2	7.5	82.0
16	15	118	8:1	10	11.3	9.1	80.5
22	14	120	8.5:1	10	10.5	5.5	52.0
23	14	119	8.5:1	10	11.0	7.5	68.1
11	12	118	10:1	5	7.8	4.4	57.0
21	12	130	11:1	10	14.0	10.2	73.2

Experiments 1 to 7 with quartz spiral; experiments 12 to 21 with special arc.

They indicate that again more than 50% by weight of peroxide could be obtained, and that in fact a yield of over 80% was found in two cases.

It seemed possible that in the freezing-out process hydrogen peroxide might be trapped more easily than water, thereby leading to high peroxide yields. It was not expected that a preferential condensation of the peroxide could be occurring by reason of a difference in vapor pressure of the two substances for at liquid air temperatures the vapor pressures of both must be negligibly small. Nevertheless, a purely mechanical separation might be effected, for while the peroxide might be trapped out completely, the water might be caught only partially, since it is known that water tends to be carried through a liquid air trap in the form of a mist or "snowstorm."

Consequently, a second trap (Trap No. 2) of the ordinary type was attached in series with the first (Trap No. 1) by means of a ground glass joint, and more experiments were made. These showed that a considerable quantity of the product was carried through the first trap and caught in the second. But what is more to the point, the water was as readily trapped out as the peroxide, for the percentage of the latter was the same in both traps. Table II, experiments 2 to 23, contains a résumé of these results. In this set of experiments, peroxide yields as high as 88% were obtained, while the average of seven tests was 82.5%.

Inasmuch as all the product might not be caught even in two traps, the second was replaced by another trap of a different type. This consisted of a series of five U-tubes made from a single long length of 6-mm. Pyrex tubing. The bends were made sharply so that all five could be put into one Dewar flask containing the liquid air. This multiple trap was attached to the first by a ground glass joint, so that in reality there were six traps in series. During a run, the top bends of the multiple trap were kept warm by a blast of hot air. Thus any "snowstorm" of water or peroxide must have been melted during its passage from one U to the next, thereby ensuring a more complete condensation of the product.

In accordance with expectations, experiments showed that a large portion of the total amount of the substance was frozen out in this multiple trap. Liquid was condensed in progressively smaller amounts on each down tube of the successive U's. On the fourth down tube, the amount condensed was just visible, while on the last, little or no product was observable. The conclusion was reached that with this device essentially complete recovery of the product was accomplished. As in the previous work with the double trap the percentage of hydrogen peroxide was the same in the multiple as

TABLE II

RUNS WITH DRY GASES AND SPECIAL ARC

Total rate of flow. 136 liters/hr. Ratio $H_2:O_2 = 8:1$

No.	Time of run, min.	Total product, mg. Trap No. 1	Total product, mg. Trap No. 2	Ratio $\frac{\text{Mg. in No. 1}}{\text{Mg. in No. 2}}$	H_2O_2, mg. Trap No. 1	H_2O_2, mg. Trap No. 2	Ratio $\frac{H_2O_2 \text{ in No. 1}}{H_2O_2 \text{ in No. 2}}$	H_2O_2, % Trap No. 1	H_2O_2, % Trap No. 2
1	10	14.1	6.0	2.35	10.6	4.1	2.46	75.0	68.0
2	10	12.6	5.6	2.25	11.0	4.5	2.56	86.5	79.0
8	10	12.1	5.4	2.24	9.0	4.1	2.40	80.6	72.5
11	10	12.2	5.3	2.30	10.8	4.7	2.32	87.8	87.5
14	10	11.3	5.2	2.17	9.6	4.6	2.12	85.5	87.4
21	10	11.9	5.5	2.16	10.0	4.7	2.11	83.5	85.6
23	10	12.4	6.1	2.03	11.0	5.3	2.06	88.5	87.0
29	10	14.5	12.0	1.21	10.1	6.5	1.56	70.0	54.5
31	10	13.5	10.0	1.35	11.3	8.1	1.40	83.3	80.5
32	10	13.8	10.0	1.38	11.3	8.3	1.40	82.2	82.6
33	10	15.0	9.4	1.60	13.4	7.9	1.70	89.0	83.5
41	10	12.1	7.9	1.53	10.3	6.8	1.51	84.8	86.0

Double trap, runs 2 to 23: multiple trap, runs 29 to 41.

in the first trap, indicating again that the peroxide was not preferentially condensed. The data are tabulated in Table II, experiments 29 to 41.

The results of all the preceding experiments with dry gases demonstrate conclusively that 85% by weight of hydrogen peroxide can be obtained easily in the condensable product from the mercury sensitized hydrogen-oxygen reaction.

Moist Gases.—In the first experiments to determine how moisture in the gases influences the hydrogen peroxide yields, only the total amount of peroxide appearing in the product was ascertained. Alternate runs were made, using first dry and then moist gases, in order to bracket and check the results. To regulate the moisture in the gases, they were by-passed either through a long tube containing granular calcium chloride, or through a trap containing cracked ice, the trap itself being maintained in an ice-bath. These two environments ensured a partial pressure of water in the gases of about 0.4 mm. and 4 mm., respectively. When using ice to maintain the water vapor pressure, the ice trap was put in the gas train before the mercury saturators in order that the mercury pressure in the gases might not be altered.

The observations obtained using the special type of mercury arc as a source of illumination are recorded in Table III, experiments 18a to 18f indicating the results with 0.4 mm. of water, experiments 19a to 20c with 4 mm. of water.

TABLE III

RUNS WITH MOIST GASES AND SPECIAL ARC

No.	Condition of gases	Rate of flow liters/hr. O_2	H_2	Ratio H_2/O_2	Time of run, min.	H_2O_2, mg.
18a	Dry	15	118	8:1	10	8.3
18b	Wet	15	119	8:1	10	9.5
18c	Dry	15	120	8:1	10	5.6
18d	Wet	15	118	8:1	10	9.3
18e	Dry	15	120	8:1	10	9.6
18f	Wet	15	120	8:1	10	12.0

Gases dried over phosphorus pentoxide. Gases wet over calcium chloride.

19a	Dry	15	120	8:1	10	9.9
19b	Wet	15	120	8:1	10	5.9
19c	Dry	15	120	8:1	10	7.5
19d	Wet	15	120	8:1	10	8.0
19e	Dry	12	120	8:1	10	7.0
20a	Dry	12	130	11:1	10	9.0
20b	Wet	12	130	11:1	10	8.7
20c	Dry	12	130	11:1	10	8.7

Gases dried over phosphorus pentoxide. Gases wet over ice.

An examination of the results apparently indicates that when the lower pressure of water was used, the peroxide yield was very slightly increased over that obtained with dry gases. However, but little trust is to be placed in this conclusion, since the magnitude of the observed differences between the yields with wet and dry gases may be within the experimental error. Certainly with the higher concentration of water, no differences between the wet and dry runs are to be found, since the amounts of peroxide procured in the alternate runs agree well within the experimental deviation.

A number of runs, in which two traps were placed in series to catch the products, were conducted using moist gases. In these experiments, only calcium chloride was used as a means for regulating the moisture content of the gas mixture. The amount of water which could be recovered from the moist gases was ascertained by making several blank runs. Such a determination was accomplished by weighing the water caught in the two traps, and also by observing the increase in weight of a small phosphorus pentoxide tube attached directly to the outlet from the reaction zone. The phosphorus pentoxide tube caught about 1 mg. more moisture than the total amount found in the two traps. This was not surprising in view of the fact. already shown, that two traps cannot catch all the product. The amount of water recovered was about that to be expected if 0.3 to 0.4 mm. partial pressure of water existed in the gases. The results given in Table IV, experiments 12 to 22, are to be compared with those of Table II, experiments 1 to 23, for the runs with the moist gases were alternated with those of the dry gases recorded in that table. In Table IV, the amounts of moisture collected in the blank runs are also recorded. experiments 4 to 24.

These results indicate very definitely that with 0.4 mm. of water vapor in the gases, the total hydrogen peroxide yield is not altered to an observable extent. Moreover, since the ratio H_2O_2 in No. 1/H_2O_2 in No. 2, is the same whether the gases be originally wet or dry, it is apparent that the presence of water does not affect the relative amounts of hydrogen peroxide caught in the two traps. This conclusion is also warranted by the fact that the percentage yields of hydrogen peroxide recorded in Table IV are identical for both traps.

Finally, the work was repeated using the multiple trap. Here again, a study of the data of Table IV, experiments 36 to 43, together with those of Table II, experiments 29 to 41, shows that moisture in the gases does not increase the yield of hydrogen peroxide nor alter the relative amounts of product caught in the respective traps.

Using ice as the medium to supply the moisture some experiments were carried out with the quartz spiral set-up. Alternate runs with wet and dry gases were made, only the total amount of hydrogen peroxide formed being determined. It appeared that with this particular experimental arrangement, the total amount of peroxide was actually reduced more than 40% by the presence of 4 mm. of water in the gases. We have no explanation for this result, but present it as further evidence that hydrogen peroxide is decomposed during the course of the reaction.

TABLE IV

RUNS WITH MOIST GASES AND SPECIAL ARC

Total rate of flow, 136 liters/hr. Ratio $H_2 : O_2 = 8 : 1$. Time of run, 10 min.

	Total condensate, mg.		Ratio	H_2O_2, mg.		Ratio	H_2O_2, %		Average H_2O in incident gases, mg.		Products of reaction Total, mg.			
No.	Trap No. 1	Trap No. 2	Mg. in No. 1 / Mg. in No. 2	Trap No. 1	Trap No. 2	H_2O_2 in No. 1 / H_2O_2 in No. 2	Trap No. 1	Trap No. 2	Trap No. 1	Trap No. 2	Trap No. 1	Trap No. 2	H_2O_2, % No. 1	No. 2
12	17.9	7.2	2.49	10.8	4.5	2.40	59.8	62.0	6.3	1.6	11.6	5.6	93	80
13	18.0	7.8	2.31	10.3	4.7	2.19	57.3	60.0	6.3	1.6	11.7	6.1	88	78
20	18.5	7.2	2.57	10.5	4.3	2.44	56.4	59.5	6.3	1.6	12.2	5.6	86	78
22	19.1	8.5	2.24	11.5	5.0	2.30	59.5	58.4	6.3	1.6	12.8	6.9	90	73
	Blank runs (arc off)													
4	6.0	1.3	4.6											
5	6.0	1.1	5.3											
10	5.2	1.6	3.7											
15	6.8	1.8	3.8											
16	6.8	1.6	4.2											
18	6.6	1.7	3.9											
24	6.3	1.9	3.3											
36	16.0	12.5	1.3	9.1	6.5	1.4	56.8	52.1	4.6	3.3	11.4	9.2	80	71
37	18.7	13.4	1.4	10.5	7.0	1.5	56.0	52.0	4.6	3.3	14.1	10.1	75	70
42	19.0	14.3	1.3	..	7.4	..	..	53.0	4.6	3.3	14.4	11.0	..	72
43	18.3	13.6	1.3	9.8	7.6	1.3	51.5	54.0	4.6	3.3	13.7	10.3	67	69
	Blank runs (arc off)													
34	4.0	3.2	1.3											
35	5.1	3.4	1.5											

Double trap, experiments 4 to 24; multiple trap, experiments 34 to 43.

Discussion of Results

It is quite obvious that the original Haber mechanism is not capable of accounting for percentage yields of hydrogen peroxide of the order of 85%. Thus we can rule this out as giving a complete description of the processes occurring in the reaction. It should be emphasized that the values of the percentage composition of peroxide in the products are minimum values. All experimental errors would tend to decrease it. For example, in weighing the trap in which the products are condensed after drying at room temperature or above. then immersing it in liquid air and again weighing after allowing it to warm up and drying with a towel, it would perhaps be expected that the weight in the latter case might be higher than the former due to condensation of moisture from the atmosphere. This would result in an apparent increased total weight of products and consequently a smaller observed percentage of peroxide.

Any objection to these results based upon the supposition that the peroxide is caught preferentially and water allowed to go through the trap is ruled out by the facts that the same percentage of peroxide is found in subsequent traps as in the first and also that in moist gases the water is caught as well or better than peroxide.

It is to be observed that, since we have been able to show the products of the reaction to consist of from 85–100% hydrogen peroxide, as compared with the smaller percentage reported by Frankenburger and Klinkhardt, their quantum yield must have been higher than their calculations show. Most or all of the water reported by these authors in their products must result from subsequent decomposition of peroxide. This would mean that their quantum yield of peroxide is in reality at least 3 molecules per quantum. These authors did not report the water formed in their individual experiments. If, therefore, the two to one ratio of water to hydrogen peroxide, which they claim to be present in some runs, persisted in all their runs, then in reality they were obtaining average values of 3.6 and maximum values up to 6 molecules per quantum. Such values would be in good agreement with those reported by Marshall. Furthermore, mercury is known to bring about decomposition of hydrogen peroxide.[7] Indeed, we have actual proof that this occurs to some extent. When the products in the trap are first observed mercury appears as a black deposit. After warming and weighing this can be seen to have changed to the characteristic yellow of mercuric oxide. Due to these facts, together with the possibility of decomposition in the reaction zone, of which there is evidence in the appearance of mercuric oxide, the authors are inclined to the view that hydrogen peroxide is the sole primary product of the reaction.

However, the suggestion of Frankenburger and Klinkhardt that the reaction

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(7) Elder and Rideal, *Trans. Faraday Soc.*, **23**, 550 (1927).

$$HO_2 + H_2O \longrightarrow H_2O_2 + OH \qquad (6a)$$

might play a part in the reaction must be considered in some detail in order to see if this process will account for the high peroxide yields, even in dry gases. This suggestion may be formulated

$$K_1 \quad HO_2 + H_2 \longrightarrow H_2O + OH \qquad (3a)$$
$$K_2 \quad HO_2 + H_2O \longrightarrow H_2O_2 + OH \qquad (6a)$$

Reaction (3a) gives rise to one molecule of water and one-half molecule of peroxide; reaction (6a) to three-halves molecules of peroxide. We may then write

$$\mathrm{d}\,\frac{[H_2O_2]}{\mathrm{d}t} = \frac{[HO_2]\,[H_2]}{2}\,K_1 + \frac{3[HO_2]\,[H_2O]}{2}\,K_2$$
$$\mathrm{d}\,\frac{[H_2O]}{\mathrm{d}t} = [HO_2]\,[H_2]\,K_1 - [HO_2]\,[H_2O]\,K_2$$

dividing, we obtain

$$\frac{\mathrm{d}[H_2O_2]}{\mathrm{d}[H_2O]} = 1/2\,\frac{([H_2]\,K_1 + 3[H_2O]\,K_2)}{[H_2]\,K_1 - [H_2O]K_2}$$
$$2[H_2O_2] = \int_{[H_2O_0]}^{[H_2O_E]} \frac{[H_2]\,K_1 + 3[H_2O]\,K_2}{[H_2]\,K_1 - [H_2O]\,K_2}\,\mathrm{d}[H_2O]$$

where $[H_2O_0]$ is the initial water concentration, and $[H_2O_E]$ the final. Integrating, and taking the limits, we obtain

$$2[H_2O_2] + 3([H_2O_E] - [H_2O_0]) = 4K \ln \frac{K - [H_2O_0]}{K - [H_2O_E]} \qquad \text{(A)}$$

where $K = K_1[H_2]/K_2$, and $[H_2]$ is considered constant.

If now we take the average values for $[H_2O_2]$, $[H_2O]$, and $[H_2]$ as found from the data in Table II, runs 2–23, and express them in mm., we find $[H_2O_0] = 0$, $[H_2O_E] = 0.122$ mm., $[H_2O_2] = 0.359$ mm., $[H_2] = 675$ mm. These substituted in equation (A) give $K = 0.144$, or $K_2/K_1 = 4700$, which means that HO_2 would react at least 4700 times as fast with H_2O as with H_2, or that the activation energy of reaction (3a) would be some 5.0 Cal. greater than reaction (6a), which is not at all an impossible result, in spite of the fact that process (3a) is some 80 cal. more exothermic than (6a).

However, if we now take the data from Table IV (runs 12–22) in which moist gases were studied and find the pressures of the reactants and resultants, we find $[H_2O_0] = 0.360$ mm., $[H_2O_E] = 0.482$ mm., and $[H_2O_2] = 0.371$ mm. as the average values. These give a $K = 0.76$, over five times the value determined in the dry gases, a difference which is much larger than the experimental error, and indicates that water has no effect on the reaction. The above data used in the calculations of K_2/K_1 are those of our results which present the most favorable case for the Frankenburger mechanism. However, only about 75% of the total product was caught using the double trap, so the value of the partial pressure of H_2O_2 and H_2O used in the above calculations should be increased some 25%. This does not change to any great extent the value of K_2/K_1 calculated for the dry gases, but makes the discrepancy between the constants in the dry and moist gases even more marked. This is shown by taking the data from Table II, runs 31–41, and Table III, runs 36 to 43, where, for the dry gases $[H_2O_2] = 0.465$ mm., $[H_2O_0] = 0$, $[H_2O_E] = 0.164$, whence $K = 0.195$: for the moist gases, $[H_2O_2] = 0.405$ mm.. $[H_2O_0] = 0.360$ mm., $[H_2O_E] = 0.665$, where $K = 1.75$. Thus K for the wet gases is some 9 times greater than K for the dry, which is somewhat greater than that obtained above. This can also be indicated from the fact that the amounts of hydrogen peroxide and water produced in the moist gases are practically the same as those in dry gases, in spite of the increase in water concentration, thus 0.371 mm. as against 0.359 mm., and $0.482 - 0.360 = 0.122$ mm. According to the value of K obtained from the dry gases, we should expect, if this were the true mechanism, that the water concentrations should have actually decreased in the moist gases experiments. This can be seen from the fact that at equilibrium

$$[H_2]\,K_1 = [H_2O]\,K_2$$
$$[H_2O] = [K_1]\,[H_2]/K_2 = K = 0.144$$

Therefore, starting with $[H_2O_0] = 0.360$, we should expect $[H_2O_E]$ to lie between 0.360 and 0.144, instead of being greater than 0.360. Thus we can find no support for the Haber mechanism as modified by Frankenburger and Klinkhardt.

The mechanism of Marshall and Taylor has been criticized by Frankenburger and Klinkhardt for two reasons. First, they object because it postulates the necessity of an association reaction

$$H + O_2 \longrightarrow HO_2 \qquad (2)$$

But this actually has no basis, since the other mechanisms have the same assumption. The three-body reaction is in reality two consecutive bimolecular reactions, with the additional requirement that collision of the quasi-molecular association with its next reaction partner must come within its life-time, whatever that may be. The second criticism is that, if we assume that the two hydrogen atoms which add to oxygen each result in 69 cal. of energy, the reaction

$$HO_2 + H_2 \longrightarrow H_2O_2 + H - 31 \qquad (3)$$

would be 31 calories endothermic. On the same basis the reaction

$$HO_2 + H_2O \longrightarrow H_2O_2 + OH - 42 \qquad (6a)$$

would be 42 calories endothermic.

A further objection that reaction (3) would never take place, because the hydrogen atom would react with the hydrogen peroxide to give the more exothermic result

$$HO_2 + H_2 \longrightarrow H_2O + OH + 33 \qquad (3a)$$

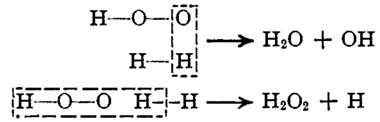
or

$$H + O_2 + H_2 \longrightarrow H_2O + OH + 112$$

instead of

$$H + O_2 + H_2 \longrightarrow H_2O_2 + H + 38$$

is not justified. Reaction (3a) most probably requires a higher activation energy than reaction (3), because in general the activation energies of processes involving a mutual interchange of partners and the breaking of two bonds are greater than those of simple replacement



$$\begin{matrix} H{-}O{-}O \\ H{-}H \end{matrix} \longrightarrow H_2O + OH$$

$$H{-}O{-}O\ \ H{-}H \longrightarrow H_2O_2 + H$$

The calculation of the activation energy of the reaction $OH + H_2 \longrightarrow H_2O + H$ from Frankenburger and Klinkhardt's data, used by them to support the validity of their assumptions. is of no value for two reasons. First. we have shown that it is possible to obtain very high peroxide percentages which would invalidate their results and second the value of this energy obtained from the data of Farkas, Haber and Harteck, and with which they found agreement, is now recognized as not being characteristic of this process at all.[8] The present authors see no necessary connection between reactions in the gas phase and the cathodic formation of hydrogen peroxide at a rate of one mole per mole of hydrogen ions liberated, which Frankenburger and Klinkhardt advance as support for their mechanism. However, even granting a correspondence between the cathodic and gas phase reactions, we can see no discrepancies between this equivalence and the mechanism postulated on page 110.

The original mechanism of Taylor and Marshall meets with none of these difficulties and the authors are inclined to believe it to be the true one. Since this reaction scheme has chain characteristics, why are the quantum yields of both Marshall, and Frankenburger and Klinkhardt so low? This difficulty can be met by a slightly modified mechanism. The heat of formation of hydrogen peroxide from $H + H + O_2$ is 138 kilocalories. Assuming that this energy is divided equally between the two steps (2) and (3), the complex HO_2 is endowed with 69 calories at the instant of its formation. It is, therefore, an activated molecule, and may have an appreciable life. If its first collision after formation is with a hydrogen molecule, the reaction to give H_2O_2 and H can easily take place, since the internal energy of the complex can overcome the endothermicity of the reaction step.

A series of possible processes could be

$$H + O_2 \longrightarrow HO_2' \tag{2b}$$
$$HO_2' + H_2 \longrightarrow H_2O_2 + H \tag{3b}$$
$$HO_2' + O_2 \longrightarrow HO_2 + O_2' \tag{6}$$
$$\text{or } HO_2' + O_2 \longrightarrow H + 2O_2 \tag{7}$$
$$\text{or } HO_2' \longrightarrow H + O_2 \tag{8}$$
$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2 \tag{9}$$
$$H + H \longrightarrow H_2 \tag{4}$$

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[8] Haber and Oppenheimer, *Z. physik. Chem.*, **16B**, 443 (1932); unpublished work in this Laboratory; see Taylor and Salley, THIS JOURNAL, **55**, 96 (1933).

Such a mechanism involving activated complexes can explain the shortness of the chains at room temperature. Steps (6) and (8) indicate how the complex might be deactivated or disrupted; either process tends to give (9) and (4) more chance to take place. Step (9) might very possibly occur predominantly as a wall reaction. since this reaction is neither exothermic nor endothermic. but may require an activation energy. Any part of the reaction which goes through step (9) gives rise to one molecule of peroxide per quantum. If hydrogen atoms recombine according to (4) there is no yield of peroxide. Both of these reactions would. therefore. tend to lower the observed quantum yield.

These considerations have been based on the assumption of Frankenburger and Klinkhardt. that both hydrogen atoms adding to oxygen give the same energy. If, however. as is possible, the second hydrogen gives rise to a greater energy liberation, the endothermicity of reaction (3) is decreased. If the first hydrogen–oxygen bond were 38 cal. and the second 100 cal.. reaction (3) would have no heat of reaction. This reaction would then occur on every collision if there were no activation energy involved. Considerations of this type, however, will lead us nowhere with our present lack of knowledge of the relative magnitude of these hydrogen–oxygen linkages.

It must not be forgotten that in the mercury sensitized reaction, mercury hydride, HgH, may be playing a role. A possible mechanism would be as follows

$$\begin{array}{rcll}
Hg' + H_2 & \longrightarrow & HgH + H & \quad (1a) \\
HgH + O_2 & \longrightarrow & HgO + OH & \quad (11) \\
H + O_2 & \longrightarrow & HO_2 & \quad (2) \\
HO_2 + H_2 & \longrightarrow & H_2O + OH & \quad (3a) \\
OH + OH & \longrightarrow & H_2O_2 & \quad (5a) \\
H + H & \longrightarrow & H_2 & \quad (4)
\end{array}$$

For every quantum of light absorbed, one hydrogen peroxide molecule and one water molecule would be formed, leading to a yield of 65% by weight of peroxide. However, even this is lower than the observed 85% yield, and so cannot account completely for the observed results. If some hydrogen atoms recombined, the peroxide percentage might be increased. This, however. would give rise to a quantum yield even less than unity. Further, mercury atoms are known to absorb many quanta of light in passing through the reaction zone, which would be improbable if mercuric oxide were formed in the process. For several reasons, then, we can eliminate such a mechanism.

The authors wish to thank Professor Hugh S. Taylor for his interest and valuable assistance in this work.

Summary

1. The yield of hydrogen peroxide from the mercury sensitized hydrogen–oxygen reaction is greater than 85%. The water formed is ascribed in

the main to secondary peroxide decomposition. It is concluded that hydrogen peroxide is the sole product of the reaction significant as regards reaction mechanism.

2. The yield of hydrogen peroxide is unaltered by the presence of water vapor in the gases. As a consequence, the reaction step $H + O_2 + H_2O = H_2O_2 + OH$ cannot be of any importance.

3. The Haber mechanism for the reaction of hydrogen atoms with oxygen molecules does not represent the only course of the reaction at ordinary temperatures. Peroxide formation must occur not only by combination of OH radicals but also by some other reaction.

4. Possible reaction mechanisms consistent with the results have been discussed.

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Effect of Particle Size upon Intensity in x-Ray Spectroscopic Analysis

BY GORDON R. FONDA

In a limited number of elements,[1] a lower intensity of the $L\alpha$ doublet has been observed when the element was in the form of a metallic powder rather than in that of a polished metallic plate or even in that of an oxide. It persisted whether the crystal in the spectroscope was sodium chloride or aluminum oxide. No such difference was observed for the $K\alpha$ doublet. As such irregularities are liable to introduce serious errors in applications of x-ray spectroscopy to quantitative analysis, the subject has been studied further. The conclusion is that they are a consequence of too large particle size which brings about an abnormal absorption of the x-radiation emitted, particularly when it is in the longer wave length range. It is for this reason that it was first noticed in L radiation. The effect has been found to be present likewise in K radiation, though to a much less extent. It occurs under the experimental condition which generally holds—namely, that the emitted x-ray beam be examined at a different angle from that made by the exciting beam of electrons.

x-Radiation is excited throughout a certain depth of material, depending on the penetration of the electrons, and consequently encounters in its emission a corresponding amount of absorption by the material itself. If there are any irregular protrusions in the surface which lie in the path of the beam which is under observation, then the radiation is subjected to additional absorption as it passes through them. Such an effect should

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[1] Fonda, THIS JOURNAL, 54, 115 (1932).