The Reaction of Hydrogen and Oxygen through a Silent Electric Discharge. II. The Effect of Packings on a Peroxide Formation

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The formation of ozone in a discharge tube containing various fillings has been previously reported[1]. To complement this report, similar investigations were carried out on the hydrogen-oxygen reaction. The hydrogen-oxygen reaction is generally known to be influenced by the chemical composition and the nature of the material constituting the surface of the reaction vessel[2-5]. Further, it is conceivable that the reaction through silent discharge may be considerably affected by the composition of the fillings employed in the discharge gap. The results were satisfactory from the viewpoint of confirming this hypothesis.

Experimental

The apparatus used and the procedures followed, were similar to the previously reported work[6]; however, the packing fill of the discharge tube was varied. The reactant gas, consisting of 4.5% oxygen by volume, was sent from a reservoir through the discharge tube after passing through the drying column. After passing through the discharge tube, the reactant gas was immediately cooled in a condensation trap, where the hydrogen peroxide and water produced were caught by freezing. The packing materials consisted of several kinds of ceramics containing titanium(IV) oxide, soda glass, boric oxide and orthoboric acid. Except for boric acid, the granular size of the packing materials was 0.7~1.0 mm. sieve mesh, while for boric acid it was between 0.5~0.85 mm. Thus, the void of the packed discharge tube was 45% in the former case and 38% in the latter case. The discharge tube made of hard glass (Hario glass) had a gap length and electrode area of 2 mm. and 200 cm^2 respectively. The electric source frequency for the silent discharge was 1000 c./sec. and the pulse current was measured in a way similar to that of the previous work[1].

Results

In every discharge tube the experiment was carried out under a constant flow rate so that the resident time was between 3.9 to 4.1 sec. Table I shows the peroxide concentration and the overall conversion rate of the reactant oxygen gas to peroxide and water at a certain fixed pulse current of 100 μ amp.

TABLE I.

No.	Composition of the packings	Dielectric constant	Peroxide concn. %	Overall conversion rate, %
1	Blank	1	46.0	2.4
2	Soda glass	6	4.5	3.7
3	$2\,MgO/TiO_2$	20	1.2	3.3
4	TiO_2	100	1.7	3.6
5	$BaTiO_3$	1200	2.5	3.5
6	$95\,BaTiO_3/5\,SnO_2$	5500~6000	0.7	3.2
7	B_2O_3		45.5	3.1
8	H_3BO_3		42.1	2.5

Discharge tube: Hario glass, $A=200\,cm^2$, $d=2$ mm.
Pulse current: 100 μ amp.
Residence time: 3.9~4.1 sec.

When the packing consisted of soda glass, and especially when the packing consisted of ceramics, the peroxide concentration was appreciably lowered. However, when the packing consisted of boric oxide or boric acid, the peroxide concentration was nearly the same as that resulting from a void discharge tube. The overall conversion rate to peroxide and water is larger when the discharge tube has a packing fill than when the tube is empty. This partly agrees with the finding of the investigation of ozone formation in a packed discharge tube[1].

Concerning the boric oxide packing, a kind of aging phenomena was observed. That is, the fresh boric oxide packing initially gave a high concentration of peroxide and a low conversion rate. After repeated use, the above values approached saturation values. In Fig. 1, the results of the aging phenomena are shown. Each point represents the concentration of the conversion rate of the product in one hour of continuous dicharge. Both the concentration and the conversion rate seem to settle to steady values after a few hours of discharge.

Discussion

In an ordinary discharge tube without packing fill, the overall conversion rate to peroxide and

1) K. Morinaga and M. Suzuki, This Bulletin, 35, 429 (1962).
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5) R. R. Baldwin et al., ibid., 56, 80, 93, 103 (1960).
6) K. Morinaga, This Bulletin, 35, 345 (1962).

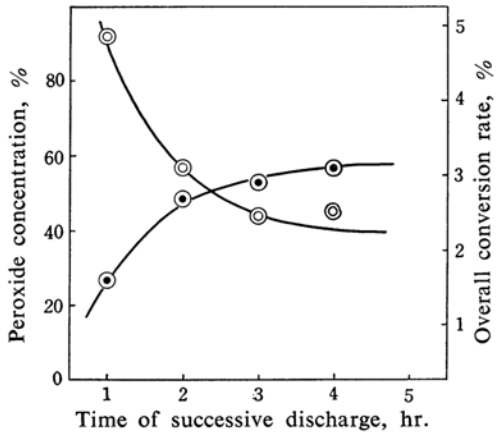

Fig. 1. The peroxide concentration and the overall conversion rate against time of successive dischage.
◎ Peroxide concentration
⊙ Overall conversion rate

water was larger when a smaller gap length was used[6]. This agrees with the results obtained in the investigation of the ozone formation[7]. In a silent discharge with a packing-filled discharge tube, the ozone formation rate and ozone concentration were improved appreciably[1]. This was ascribed to the fact that the shortening of the gap length, which was due to the packing fill, will improve the ozone yield.

In this experiment, however, though the overall conversion rate to peroxide and water was larger in the packing-filled discharge tube, the final product of the reaction was greatly affected by the packing materials employed in the discharge gap. This was not the case in the previously studied formation of ozone. The difference in the peroxide concentration can be seen in Table I. These differences can be ascribed to the effect of the surface of the filling material on the reaction, similar to the case pointed out in the previous paper[6].

Hinshelwood et al.[2] suggested that, in the second explosion limit of hydrogen and oxygen gas, the surface destruction of the HO_2 radical was dominant in halide-coated or in silica vessels. On the other hand, the boric acid-coated vessel does not provide enough reaction for the surface destruction of both HO_2 and H_2O_2; thus, the HO_2 radicals form H_2O_2 either by the surface or the gas phase process. Baldwin et al.[5] showed that the gas phase binary reaction of HO_2 to form H_2O_2 and O_2 was more predominant than the surface process of HO_2 to form $1/2\,H_2O_2$ and $1/2\,O_2$. In the reports[5] it was also concluded that the formation of peroxide from HO_2 and H_2 was preponderant over the formation of water from the same species.

7) K. Morinaga and M. Suzuki, ibid., **34**, 157 (1961).

The peroxide formation resulting from a silent discharge is first assumed to be a gas phase reaction accompanied by the other elementary process of water formation. In the course of the catalytic decomposition of H_2O_2 on the surface of the discharge tube or the packing granules, the quantity of water increased, consequently lowering the peroxide concentration in the product. This tendency will be more preponderant when there is a shorter gap length or when a discharge tube with other than boric oxide and boric acid fillings is used.

Walsh[8] has evidence which has lead him to believe that the anti-knock effect of lead tetra-ethyl is due to the destruction of HO_2 and H_2O_2 on the lead(II) oxide surfaces. In the present case, the ceramics which contained titanium(IV) oxide and other metallic oxides will behave similarly to those described above. Soda glass may be similar to the halide-coated or silica surfaces. On the surface of boric oxide and boric acid, the destruction of HO_2 and H_2O_2 will be suppressed and the concentration of peroxide will be increased.

The overall conversion rate in the packing-filled discharge tube will be increased with the improvement of the discharge efficiency which arises from the packing fill[1,7].

In the case of boric oxide fillings, the water molecules will reside on the fresh surfaces of the granules. After the saturation-like adsorption of water molecules, the surface activity seems to be lowered.

Summary

By applying several packings in the discharge gap space, the peroxide formation through a silent discharge was studied. The peroxide concentration was higher in a void discharge tube or in a boric acid (boric oxide) packing-filled discharge tube and lower in the case of the soda glass and the ceramic packing containing titanium(IV) oxide. This was explained by the insufficient destruction of HO_2 and H_2O_2 on the boric acid surface, and by the great destruction on the surface of the packing consisting of soda glass and ceramics. A kind of aging phenomena observed in the boric oxide packing was tentatively explained.

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8) A. D. Walsh et al., *Proc. Roy. Soc.*, **A215**, 175, 454 (1952).