The Reaction of Hydrogen and Oxygen through a Silent Electric Discharge. I. The Formation of Hydrogen Peroxide

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The formation of hydrogen peroxide from a hydrogen-oxygen gas mixture through a high frequency silent discharge has been investigated with the intention of obtaining a reaction pattern in connection with an accompanying pulse current. The features of the peroxide formation more resembles that of ozone formation in a silent discharge[1,2] than that of both gases in a low pressure glow discharge.

Experimental

All the measurements were carried out under atmospheric pressure using the flow method.

The reaction mixture of hydrogen and oxygen gas (4.5% vol. O_2) was held in a gas holder of ca. 1 m^3. The gas mixture was dried by passing it through a 4 m. glass tube filled with calcium chloride and silica gel and then was served for use. The humidity of the gas on the final issue was about -20°C.

The electric circuit was similar to that which had been used in the previous work[2]. The high frequency electric current was provided by a 32 pole generator with the R. P. M. selected so as to obtain an output frequency of from 500 c./sec. to 2000 c./sec.

The discharge tubes were of the Siemens type, made of Telex glass, with a length and diameter of 40 and 4 cm. respectively. The gap length was varied between 1, 2 and 3 mm., and the discharge area could be varied by applying an adequate expansion of a tin foil patch on the outside of the glass tube.

After being exposed to the electric discharge, the reactant gas was cooled in a condensation trap where the hydrogen peroxide and water were caught by freezing. The cooling agents of the condensation trap were a salt-ice mixture or liquid air. The former was used mainly for the constant flow system, and the latter for the variable rapid flow system. The condensate was weighed and analyzed by iodometry, using ammonium molybdate as a decomposition catalyst for the hydrogen peroxide.

Results

1) The effect of the change of frequencies of the discharge current on the formation of peroxide is shown in Fig. 1, where the pulse current is scaled on the abscissa and the rate of conversion of reactant oxygen gas to hydrogen peroxide, on the ordinate. The flow rate, or the time (τ) of the residence in the discharge tube, is the same throughout the runs — 5.0 sec. for each run. The measurements were conducted up to the high frequency pulse current value of 600 μamp., this being the safety limit to prevent damage to the discharge tube. The area of the electrode and the gap length have values of 233 cm^2 and 3 mm. respectively.

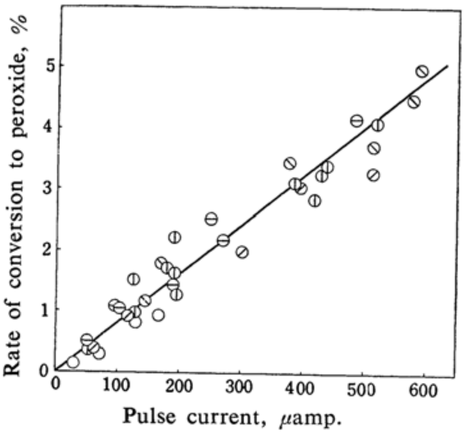

Fig. 1. The rate of conversion to the peroxide under the discharge of various frequencies against pulse current.
$A=233$ cm^2 ; $d=3$ mm.
○ 50 c./sec. ⊖ 500 c./sec. ⦶ 1000 c./sec.
⊘ 1500 c./sec. ⦸ 2000 c./sec.

As shown in Fig. 1, the above rate, plotted against the pulse current, shows as a straight line and is independent of the frequency of the discharge current. The exclusive products of the reaction were water and hydrogen peroxide. The concentration of the hydrogen peroxide in the product solution was about 60% by wt., which percentage does not vary extensively in accordance with the different values of frequencies.

2) The rate of peroxide formation in various shaped discharge tubes was measured with respect to the pulse current. The values of the time of residence ($\tau=5.0$ sec.) and the frequency of discharge current (1000 c./sec.) were kept constant.

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1) K. Morinaga and M. Suzuki, This Bulletin, 34, 157 (1961).

2) K. Morinaga and M. Suzuki, ibid., 35, 204 (1962).

In Fig. 2, the concentration of the hydrogen peroxide in the condensate is plotted against the pulse current per unit electrode area. The concentration does not depend on the pulse current, or on the electrode area, but rather depends on the gap length of the discharge tube. In Figs. 3, 4 and 5, the pulse current per unit electrode area is plotted on the abscissa. The conversion rate of the peroxide and water are increased linearly with respect to the pulse current per unit electrode area but does not depend on the electrode area. In these figures, one gap length corresponds to

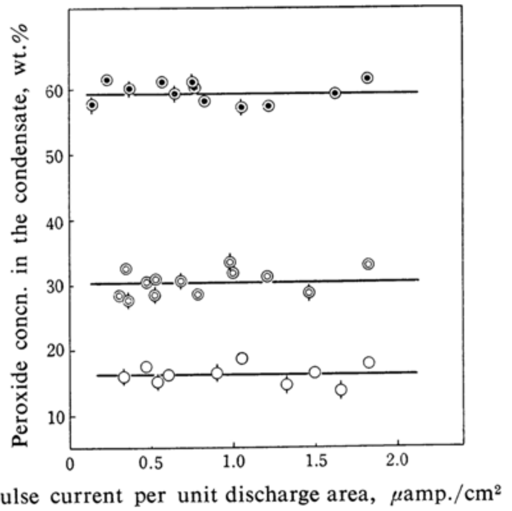

Fig. 2. The peroxide concentration in the condensate against the pulse current per unit discharge area. A and d varies.

○ $d=1$ mm., $A=120$ cm²
◎ $d=2$ mm., $A=120$ cm²
⊙ $d=3$ mm., $A=120$ cm²
○ $d=1$ mm., $A=250$ cm²
◎ $d=2$ mm., $A=250$ cm²
⊙ $d=3$ mm., $A=250$ cm²

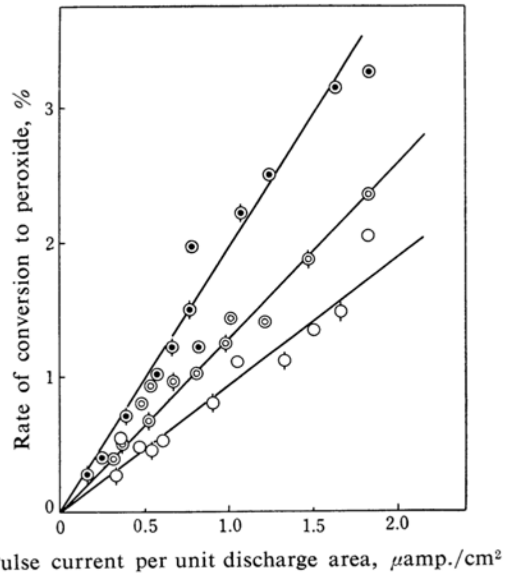

Fig. 3. The rate of conversion to the peroxide against the pulse current per unit discharge area. A and d are varied. Each of the plots represents such the discharge tube as is noted in Fig. 2.

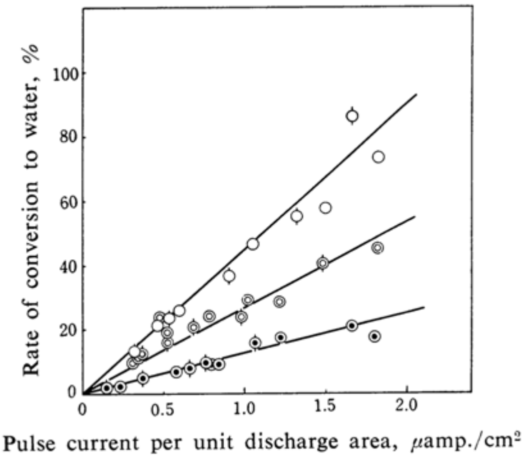

Fig. 4. The rate of conversion to water against pulse current per unit discharge area. A and d are varied. Each of the plots represents such the discharge tube as is noted in Fig. 2.

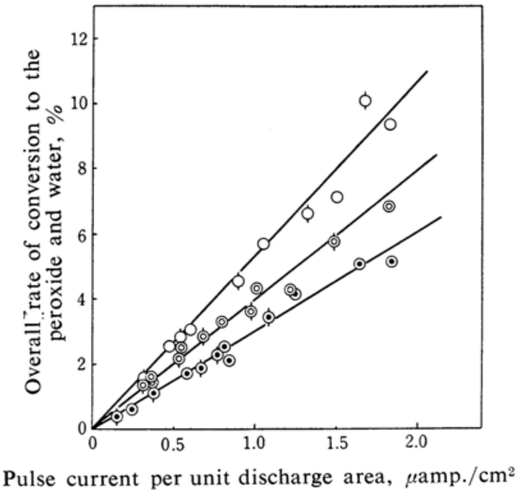

Fig. 5. The overall conversion rate to the peroxide and water, against pulse current per unit discharge area. A and d are varied. Each of the plots represents such the discharge tube as is noted in Fig. 2.

one straight line. The rate of conversion of the peroxide is larger with the larger gap length, while, on the other hand, that of water is larger in the shorter gap length. In Fig. 5, the overall conversion rate is summarized. So far as the constant resident time (ca. 5 sec.) is concerned, the results obtained using both liquid air or salt-ice coolants were entirely identical.

3) In the following experiments, the results of which are shown in Figs. 6, 7 and 8, the gap length of the discharge tubes were 1, 2 and 3 mm. and the discharge area was 250 cm^2. In these figures, the peroxide concentration and the rate of conversion of peroxide and water are plotted against the time of residence, the pulse current per area being ca. 0.85 μamp./cm^2. For each case, a run corresponding to a certain gap length is represented by a curve. In the runs where the flow velocities vary, that is, when the time of residence is occasionally very short, the condensate product was trapped by liquid air freezing. The peroxide concentration in the condensate decreases with increasing resident time, as is shown in Fig. 6, and the conversion rate to the peroxide plotted in Fig. 7, showed a kind of saturation-like behavior against the resident time. On the other hand, the conversion rate to water shows a different behavior than Fig. 7.

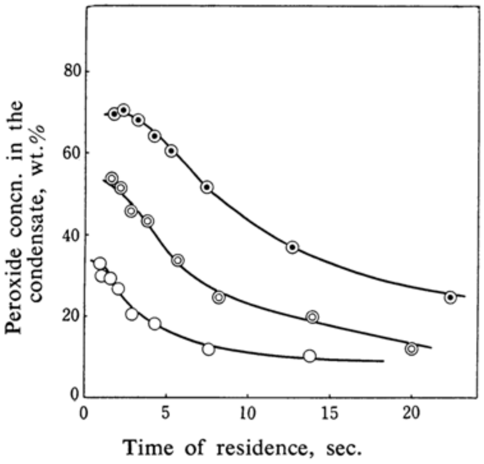

Fig. 6. Peroxide concentration in the condensate against time of residence. d is varied.

○ $d=1$ mm., $A=250$ cm^2

◎ $d=2$ mm., $A=250$ cm^2

⊙ $d=3$ mm., $A=250$ cm^2

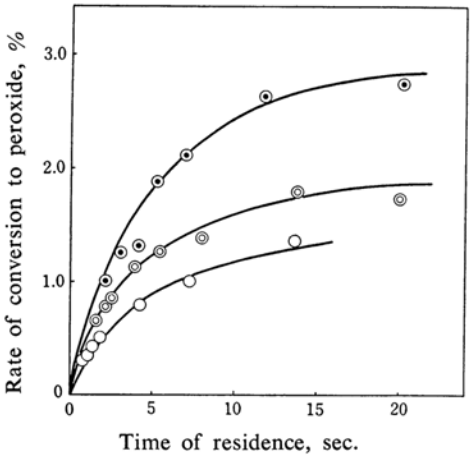

Fig. 7. Rate of conversion to peroxide against time of residence. d is varied. Each of the plots represents such the discharge tube as is noted in Fig. 6.

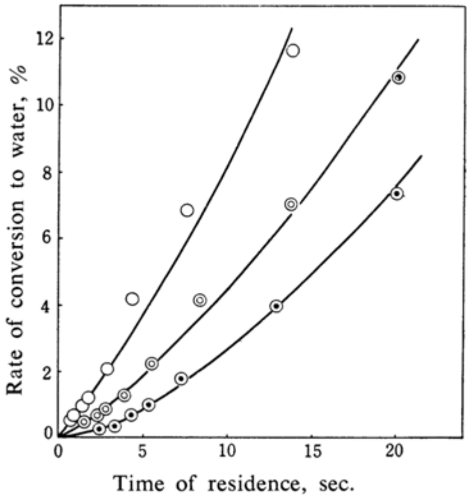

Fig. 8. Rate of conversion to water against time of residence. d is varied. Each of the plots represents such the discharge tube as is noted in Fig. 6.

Discussion

From Fig. 1, one may conclude that the mechanism of the rate of formation of hydrogen peroxide is the same for all reactions, regardless of the output frequency (between 50 c./sec. and 2000 c./sec.). The same applies to the formation of water under identical conditions, for the rate of water formation versus pulse current has about the same characteristics as those of peroxide formation.

The whole pattern which is apparent in the above-mentioned figures is very much like those of ozone formation. In the reaction between hydrogen and oxygen, the elementary processes which govern the rate of formation of the entire series would be, then, the one wherein an electron participates.

According to the generally accepted mechanism[3-8], the simplest reaction scheme to explain these essential features may be written as follows:

$$H_2+e=2H+e \quad (1)$$

$$O_2+e=2O+e \quad (2)$$

$$H+O_2=OH+O \quad (3)$$

$$O+H_2=OH+H \quad (4)$$

$$OH+H_2=H_2O+H \quad (5)$$

$$OH+OH=H_2O_2 \quad (6)$$

$$H_2O_2+H=H_2O+OH \quad (7)$$

The reaction involving H atoms and the OH radical may be of importance here. If the pressure under which the reaction proceeds is rather high, then the concentration of the H atom is not likely to be high; on the other hand, if the amount of oxygen in the starting mixture is small, then the number of oxygen atoms will also be small. Because reactions 3 and 4 are fast, an equilibrium concentration for the OH radical may be established which will govern the overall reaction rate and, simultaneously, be governed by the molecular entities of the collision product with electrons.

It seems to be irrelevant to go into more detail in each of these elementary processes; it will suffice to explore the obtained results from the postulate concerning the behavior of issued electrons and their first-step elementary act. Therefore, in this pattern of reaction mechanism, the overall rate of formation should keep a linear relationship with the quantity of electrons carried through the discharge zone or the pulse current which is in accord with Figs. 3, 4 and 5.

The fact that, in Fig. 2, the concentration of the produced hydrogen peroxide remains constant, independent of the value of the pulse current, agrees with the features of the diagrams in Figs. 3, 4 and 5. The reaction rate at a certain flow velocity ($\tau=5.0$ sec.), and under a certain frequency of discharge current, is again proportional to the pulse current. In conclusion, the ratio of produced hydrogen peroxide to the whole reaction product should remain constant regardless of the pulse current per unit area.

Each straight line in Figs. 3, 4 and 5 is assigned to a certain value of gap length because the rate of reaction should receive considerable influence from the gap length between the electrodes.

The curves for the relationship between concentration and flow velocities (Figs. 6, 7 and 8) are those usually known for such cases. As the flow rate becomes smaller, the composition of the product tends to approach a limiting value which is expected to be an equilibrium value between formation and destruction at an approximately static state.

As has been pointed out in the ozone formation process[1], the initiation of the reaction is started in a small column by an individual discharge lasting half the period of every discharge frequency. The remaining space in the whole discharge zone serves partly as a destruction area for the hydrogen peroxide which is the result of the sequence of processes in the discharge column. The larger the gap length is, then, the more the small discharge column will be expanded; in other words, the field of formation is relatively larger than that of destruction. The postulate is then concordant with the results.

The elucidation of the detailed behavior of the reacting molecular species in connection with the accepted elementary processes is not yet fully feasible because of the lack of detailed knowledge of the discharge phenomena which accompany chemical reactions.

Summary

1) The reaction between hydrogen and oxygen in a silent electric discharge of high frequency was investigated. The product, in the course of reaction, is solely hydrogen peroxide and water.

2) The linear relationship, independent of the frequency of the current, between the rate of formation of hydrogen peroxide or of water and the pulse current was established.

3) The composition of the hydrogen peroxide-water solution is constant so long as the gap length is constant.

4) The flow rate and the said composition relation were measured.

5) The reaction pattern in the discharge zone was briefly discussed.

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