The Chemical Reaction in Silent Electric Discharge. I

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In a series of reports[1-3], it was proposed that in regard to the chemical processes in silent electric discharge, more significance should be put on the high frequency pulse current which accompanies the discharge, rather than on the basic current, usually 50 c/s, which sustains the whole discharge process.

In the present work some electrical, as well as geometrical conditions contributing significantly to the ozone formation process, were studied in more detail. This seems to have been helpful in realizing the actual feature of the reaction.

Experimental

The discharge tube used was of the Siemens type with two concentric glass cylinders which served as dielectric electrodes. The whole length and diameter of the discharge tube was 35 cm. and 4 cm. respectively. The outer surface of the outer cylinder was patched with tin foil and the inner tube was filled with brine. The area covered by the foil patches varied from 50 to 200 cm^2 for the purpose of having the desired electrode area. To change the gap distance, several ozonizers of the same type with different gap distance of 1~3 mm. were used. The electrical system was a usual circuit. The current of 50 c/s city source was sent through a voltage regulator to a leakage transformer where the voltage was stepped up to the required value. The discharge current was side circuited by a cathode ray oscillograph (Toshiba ST-1651) for the observation of basic 50 c/s, as well as the high frequency pulse current.

The whole system of the circuit is shown diagrammatically in Fig. 1. A series of shots of each oscillogram were taken using the single sweep system. The time constant of the oscillogram circuit was 5.4×10^{-6} sec.

1) M. Suzuki, *Proc. Japan Acad.*, **26**, 21 (1950).
2) M. Suzuki and Y. Naito, ibid., **28**, 429 (1951).
3) M. Suzuki, S. Okazaki and T. Yamamoto, *J. Am. Chem. Soc., Adv. Chem. Ser.*, **No. 26**, 331 (1957).

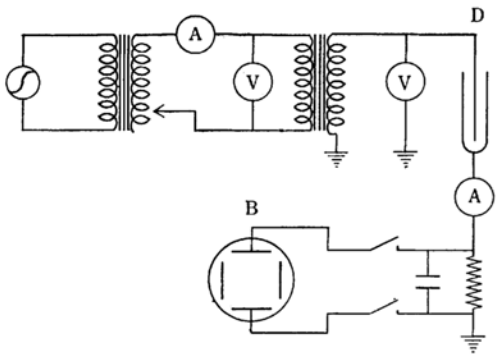

Fig. 1. The circuit system.
D, ozonizer; B, oscillograph

The sum of the height of each pulse current which appears as hairs on the base current diagram in an oscillogram, is due to the total electricity carried through the electric discharge during a cycle of base current which is simply noted here as pulse current[2]. The value of the sum in every run is an arithmetic mean of several successive shots of the oscillogram.

To obtain the yield of ozone in each run the leading glass tube distance from the discharge tube to the ozone absorption bulb was shortened as much as possible. The gas mixture submitted to the discharge was led through the neutral potassium iodide solution in the absorption bulb which was later analyzed by the usual known process. The oxygen, which served as a reactant, was taken from a cylinder and used after drying with calcium chloride.

Results

Variation in ozone concentration in the oxygen gas after leaving the discharge vessel with apparent residence time τ, is shown in Fig. 2. The ozone concentration increases at first linearly as the time of residence increases, until finally it reaches a saturation value. At a saturation state the rates of the ozone formation and of the ozone destruction by any of the chemical entities existing there have equal values. This leads to the stationary ozone concentration in the exit gas.

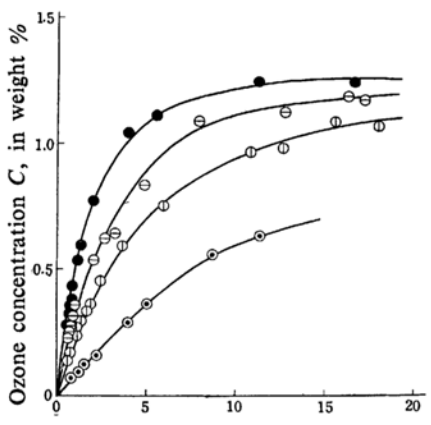

Fig. 2. The relation between the ozone concentration C and the residence time τ. Gap distance 2 mm. electrode area 100 cm².
● Pulse current 184~199 μamp.
⊖ 148~155 μamp.
◐ 87~92 μamp.
⊙ 28~30 μamp.

The rate value of ozone formation Y (mg./sec.) at $\tau=0$ where presumably hardly any destruction reaction takes place is referred to further in the results. This consideration will simplify the discussion to some extent, because the reaction, in that case, will be restricted simply to the formation of ozone.

The numerical value of the pulse current is obtainable from the comparison of the sum of length of a certain pulse current with an adequate standard current. In Fig. 3, the value of Y (mg./sec. at $\tau=0$) is plotted against the pulse current in μamp. which was obtained through the above procedure. These curves manifest themselves again as a group of straight lines of which the inclination depends solely upon the physical conditions under which the experiments were carried out.

The dependence of ozone yield per unit pulse current Y_1 (mg./sec. μamp.) on A/d, where A (cm²) is the area of the electrode,

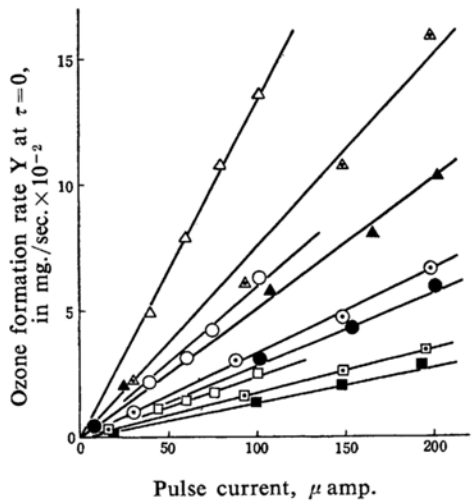

Fig. 3. The relation between the rate of ozone formation at $\tau=0$ in the various shape of ozonizers and the pulse current.
△ Area 200 cm². Gap 1 mm.
○ Area 100 cm². Gap 1 mm.
□ Area 50 cm². Gap 1 mm.
◬ Area 200 cm². Gap 2 mm.
⊙ Area 100 cm². Gap 2 mm.
▣ Area 50 cm². Gap 2 mm.
▲ Area 200 cm². Gap 3 mm.
● Area 100 cm². Gap 3 mm.
■ Area 50 cm². Gap 3 mm.

and d (mm.) is the gap distance between electrodes, is shown in Fig. 4. Y_i values increase linearly with A/d, no matter how the individual value of A or d varies respectively, nor does it depend upon the total value of the current through the discharge vessel. The inclination of the straight lines has the value of 7.0×10^{-7} (mg./sec. μamp. cm.).

In Figs. 5, 6 and 7, ozone concentration (weight %) at steady state was plotted against pulse current. It will be seen from the figures that the ozone concentration is the highest at a certain optimum value of electrode area, and above or under this value the ozone concentration becomes lower.

Discussion

The behavior of the diagram which manifests itself in Fig. 4 seems to require some explanation from the chemical as well as the electrical viewpoint.

To begin with, under the experimental conditions during which the measurements were made, Paschen's law is applicable with virtual validity[4]. Then, as the pressure throughout the measurements is atmospheric and therefore constant, the sparking potential E_s, which initiates each individual small discharge at certain points on the electrode surface, depends solely on the gap distance d[2]. Further, E_s should increase proportionally with d within our experimental conditions[2].

With increasing E_s, the leaving of electrons from the electrode surface will be more difficult where on the oscillogram the hairs will shift to the upper part of the basic wave form and its placement will be more dense. Keeping ones sight on a certain definite number of electrons from the electrode, and taking into consideration the fact that the spots are distributed fairly uniformly and that the number of electrons issuing from each spot are virtually equal[2], the number of spots from which the individual small discharge starts will accordingly be less and the decrease of the number of spots in a unit area shows that the spots are located more sporadically. Or in our experimental conditions the greater the gap distance is, the greater the sparking potential, the less the number of spots in a unit area where the individual small discharge starts and finally the more the number of electrons which leave each spot, so long as one definite number of electrons which come into reactions are dealt with.

Now electrons leaving the electrode will collide with surrounding chemical molecules initiating some chemical change which leads to a chemical reaction.

Collisions which would cause some chemical reaction would seem to prevail as long the electrons travel along the spark gap distance. But actually the electrons, just after leaving the electrode, only then have sufficient energy to provoke a chemical effect such as dissociation. With the first collision, electron energy is virtually lost. Normally, the electron would regain energy in the electrical field; but, because of the very short mean free path, which is in the order of 10^{-6} cm. at atmospheric pressure[5], the electrons can not acquire sufficient energy to be able to react further chemically. Thus, further collisions between electron and molecule will hardly contribute to the initiation of the ozone formation. Accordingly, after the first collision, the distance traveled by the electron through gap distance may be disregarded in this discussion.

As far the change of Townsend's first coefficient α in relation to the gap distance; α/P is known to be the function of X/P where X is field strength. In this experiment the pressure is constant, α therefore, depends solely on X. As $X=E_s/d$ and E_s increases proportionally with d, the X value is independent of d. Thus the behavior of α along with change of d can likely be neglected in this present case.

In Fig. 4 Y_i is shown to be proportional to the electrode area A and inversely proportional to the gap distance d. The increase of A, keeping the total electron number constant, leads to the increase of the total spot number in a whole discharge tube, because the increase

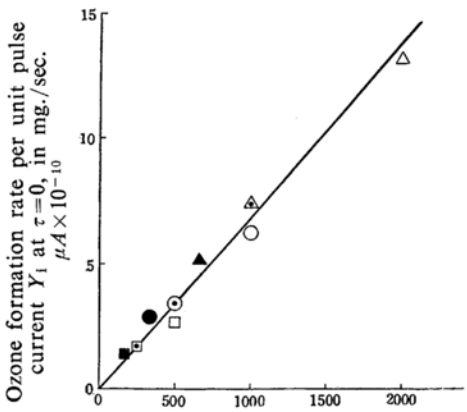

Fig. 4. The rate Y_i of ozone formation per unit pulse current at various value of A/d.

4) K. S. Fitzsimons, *Phys. Rev.*, **58**, 197 (1940); W. R. Haseltine, ibid., **72**, 423 (1947).

5) R. H. Healey and J. W. Reed, "The Behaviour of Slow Electrons", Amalgamated Wireless Press, Sydney (1941).

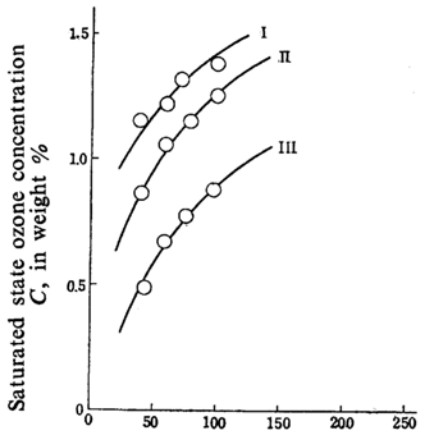

Fig. 5. Saturation ozone concentration against pulse current (Gap distance 1 mm.).
I Electrode area $A=100\,cm^2$; II $A=200\,cm^2$; III $A=50\,cm^2$

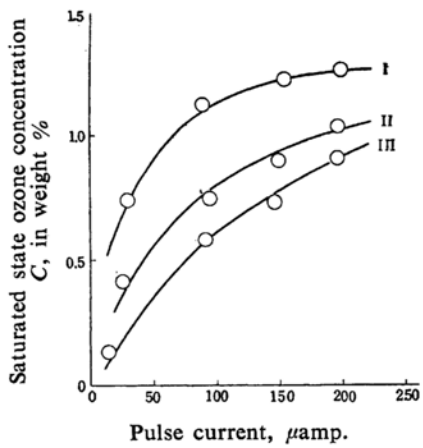

Fig. 6. Saturation ozone concentration against pulse current (Gap distance 2 mm.).
I Electrode area $A=100\,cm^2$; II $A=200\,cm^2$; III $A=50\,cm^2$

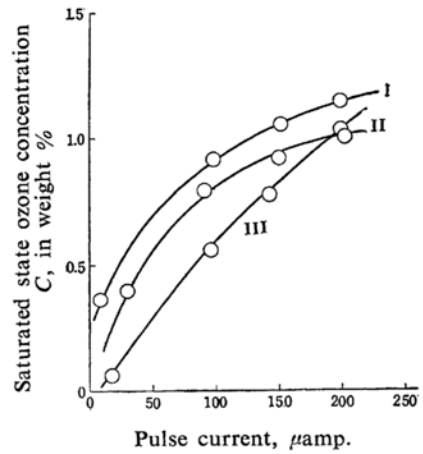

Fig. 7. Saturation ozone concentration against pulse current (Gap distance 3 mm.).
I Electrode area $A=100\,cm^2$; II $A=200\,cm^2$; III $A=50\,cm^2$

of the discharge area implies that the spots come to be distributed more sporadically and more chances are offered for the generation of more new spots. This corresponds to the effect of decreasing gap distance as just stated above. It might be conceivable if Y_1 be inversely proportional to d; then it should be proportional to A.

A tentative explanation of this phenomena is proposed as follows: In the experiment the average value of the pulse current is about 100 μamp., and the number of hairs on the half wave of 50 c/s base current from city source, in an oscillogram, is virtually 30~50. The number of spots involved in a hair, i. e. in one shot of pulse current, is about $10\sim10^{2}$ [2], thus the number of electrons ejected from a spot has the order of 10^{10}. On the other hand, the area of each spot is $10^{-2}\sim10^{-4}\,cm^2$ [2], and the number of molecules just in front of this area is about 10^{10} or a little less, which means that the above number of gas molecules has almost the same number or a little fewer than those of ejected electrons from a spot.

Now the velocity of electrons, just after they leave the electrode, is estimated at $10^{8}\sim10^{9}$ cm./sec.[6] which features, because of the virtually instantaneous time of travel up to the first collision, that the electron beam from each spot might seem to suffer hardly any appreciable conical diversion and hit the molecule target covering almost the same dimension as the spot area.

In this pattern of collision, the more sporadically the spots are located, the more packed is the ejected stream electrons, which lead to the increase of the ineffective collision. The rate of the ineffectiveness will essentially be regarded to be linear to the rate of congestion of the electron stream. Thus the effective collision number for a definite number of electrons of Y_1 is proportional to the number of spots, or in other words, to the electrode area and the reciprocal of the gap distance.

The postulate appears qualitatively to make sense, but from the quantitative point of view further and more detailed investigation may be required.

6) N. E. Bradbury and R. A. Nielson, *Phys. Rev.*, **49**, 338 (1936); **51**, 69 (1937).

Summary

1. The ozone yield Y from oxygen gas in the silent electric discharge in a Siemens ozonizer is proportional to the pulse current which was measured from an oscillogram where Y is referred to $\tau=0$ value. The proportionality is valid independent of the gap distance d between electrodes and the effective area A of electrodes.

2. The above ozone yield Y_1 which is referred to $\tau=0$ and further to unit pulse current is proportional to A/d.

3. The reason of the above relationship is briefly discussed.

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