The Chemical Reaction in Silent Electric Discharge. II. The Frequency Effect on Ozone Formation

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Numerous accounts have been published on silent discharge[1-11], the majority dealing with the electric characteristics of the ozonizer[1-6]. In the oscillographic study of the discharge[1-4] that was originated by Klemenc et al.[1], the rapid impulse with a "fringe"[2] structure was noticed, and the relation between the pulse and the discharge spot that appeared on the photographic plate in the gap space was investigated[3]. Fillipov et al. derived a equation[5,6] for the effective current in an ozonizer from a knowledge of the static and dynamic characteristics of discharge, and recently[7] they have combined this equation

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4) K. Honda and Y. Naito, *J. Phys. Soc. Japan*, **10**, 1007 (1955).
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11) K. Morinaga and M. Suzuki, This Bulletin, **34**, 157 (1961).

with the intensity of the formation and decomposition of ozone in an ozonizer. Lunt has pointed out[10] the gaps in knowledge which hinder the identification of the reaction mechanism.

In the previous paper the ozone formation through silent discharge (50 c/sec.) was studied with its relation to the pulse current, the gap length and the discharge electrode area. The results showed that the ozone yield is proportional to the pulse current and that the ozone formation rate per unit pulse current has a linear relationship with A/d, where A is the effective discharge area and d, the discharge gap distance.

In the case of the 50 c/sec. electric source of the previous work[11], the pulse current was restricted up to 200 μ amp. on account of possible damage to the discharge tube due to electrical breakdown. Furthermore, upon increasing the pulse current beyond the above value, the wave form of the secondary current became more irregular, making rather ambiguous the measurement of the pulse current by means of pulse heights.

In the present work, a relatively high and variable frequency electric source is applied. Accordingly, the pulse current range, upon applying a relatively high frequency current, could be extended up to 0～1300 μamp. The frequency dependence of the ozone formation that clarifies the effect of the pulse current on ozone formation was also pursued.

Experimental

All experiments were performed in an atmospheric flow system. The equipment and procedure were similar in principle to those described in the previous work. The glass discharge tubes had a discharge area of 50～200 cm^2 and a gap of 1～3 mm. respectively. The variable frequency electric source was supplied by a high frequency generator of 32 poles. The number of cycles could be adjusted from 500 to 2000 c/sec. by changing the number of revolutions of the armature. The output voltage could be regulated between 50 and 100 V. The applied high tension to the discharge tube was obtained from a core type transformer which had been designed in order to diminish the core loss of the current. The wave form of the output current remained steady, even with frequencies up to 2000 c/sec.

The frequency measurement of the source current was performed by both the tachometer and oscillographic methods. The frequency deviation in each run was controlled within a limit of ±3% by regulating the field current of the driving D. C. motor. The procedure for taking measurements of the pulse current was the same as in the previous work. The time constant of the leakage resistance and the integral condenser of the oscillogram circuit was 2.7×10^{-6} sec.

The ozone, after leaving the discharge tube, was led into a neutral potassium iodide solution and then analyzed in the usual method.

Results

The Effect of the Frequency.—In the course of the research for the frequency effect on ozone formation, the experiments were carried out with the value of variables as follows: the pulse current covering 0～1300 μamp., resident time 0.3～10 sec., and the total discharge current 0～16 mamp. using a discharge tube with an effective discharge area of 100 cm^2 (in one electrode side) and a gap length of 1 mm. This resulted in almost identical curves of ozone concentration vs. resident time τ in the various frequencies. The asymptotes on the curves of ozone concentration vs. resident time at $\tau=0$ give the value of the initial ozone formation rate. In Fig. 1, the ozone formation rates at

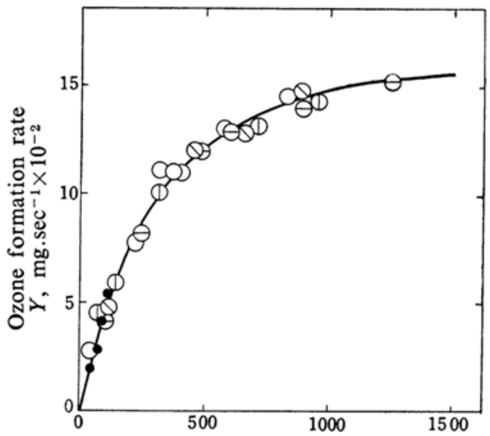

Fig. 1. Ozone formation rates at various frequencies electric source against pulse current. Discharge are a 100 cm^2, Discharge gap length 1 mm.

⊖ 2000, ○ 1000, ● 50, ⦶ 1500, ⊘ 500 sec.

various frequencies against pulse current are given. The ozone formation rate is expressed in one diagram independent of the frequencies of the current. If the above rates are plotted against other parameters, such as total discharge current, secondary voltage etc., then the diagram does not show any unified form but rather appears as separate curves according to the frequency used.

In the previous report[11] the same ozone formation rate at 50 c/sec. current, under otherwise identical conditions, varied linearly with the pulse current, whereas in the present case the diagram starts at first linearly, then with the increase of the pulse current, bends gradually downwards until it approaches a certain definite value. It should be noted that in the former case a high value of pulse current was precluded because of the reasons described elsewhere above, while in the present case the high frequency current enables a more intense flow of the pulse current.

In a discharge of a low pulse current the linear relationship will validly hold no matter how the frequency alters, but in the region of a high discharge current the rate value will be smaller than is anticipated from a linear relationship unaffected by a change of the frequency.

The Effect of Discharge Area and Gap Length.—Figures. 2, 3 and 4 show a relationship similar to that given in Fig. 1 for a certain current frequency (1000 c/sec.) and for various electrode areas, in which each diagram corresponds to values of a certain gap length. The operational specifications are the same as for the foregoing series, but the areas are changed 50, 100 and 200 cm^2 and the gap lengths are changed 1, 2, 3 mm. respectively. The whole aspect of the diagrams somewhat resembles that of Fig. 1.

The region where the curves leave the linear property depends upon the discharge area, and the values of the corresponding pulse current are around or less than 200 μamp.

To compare these results with those in the previous work, the authors denoted as before the ozone formation rates per unit pulse

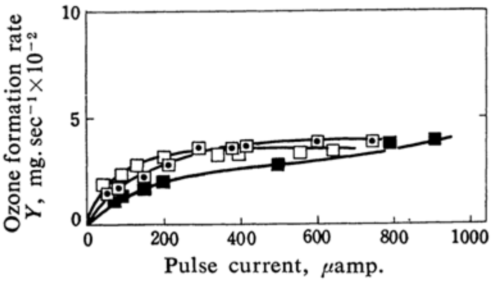

Fig. 2. Ozone formation rates against pulse current. Frequency 1000 c/sec., Discharge area 50 cm^2, Discharge gap lengths 1, 2, 3 mm.

■ Gap 1 mm., area 50 cm^2
⊡ Gap 2 mm., area 50 cm^2
□ Gap 3 mm., area 50 cm^2

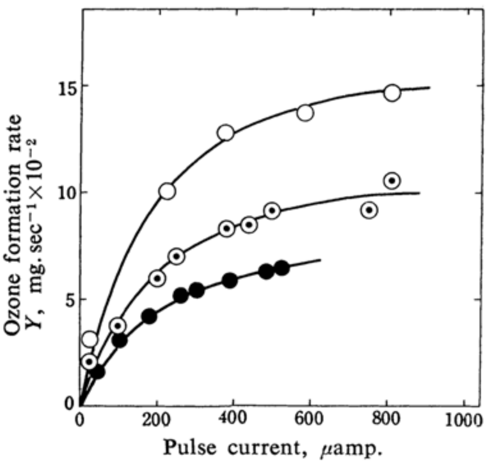

Fig. 3. Ozon formation rates against pulse current. Frequency 1000 c/sec., Discharge gap length 1, 2, 3 mm.

● Gap 1 mm., area 100 cm^2
⊙ Gap 2 mm., area 100 cm^2
○ Gap 3 mm., area 100 cm^2

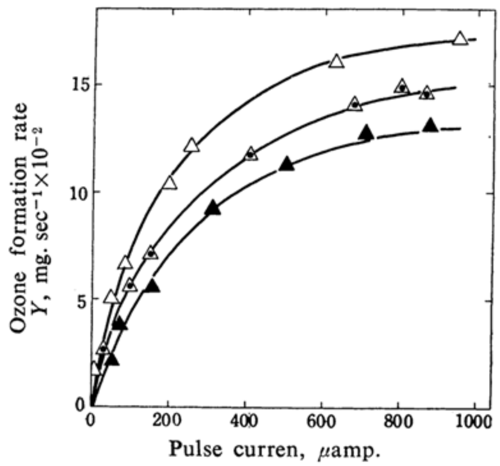

Fig. 4. Ozone formation rate against pulse current. Frequency 1000 c/sec., Discharge area 200 cm^2, Discharge gap length 1, 2, 3 mm.

▲ Gap 1 mm., area 200 cm^2
◬ Gap 2 mm., area 200 cm^2
△ Gap 3 mm., area 200 cm^2

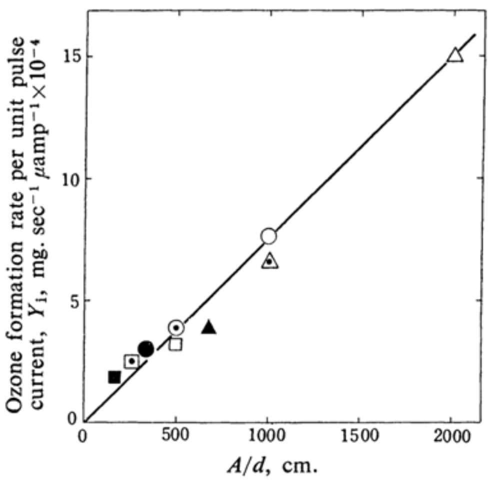

Fig. 5. Ozone formation rate per unit pulse current Y_1 against A/d. The plots represents as in Figs, 2, 3 and 4.

current at a low pulse current region as Y_i. The relation between Y_i and A/d is shown in Fig. 5. The linear feature, independent of the value of frequency, appears here again as in the previous case of a 50 c/sec. current discharge. This linear relationship seemed to be valid for the frequency up to 200 c/sec. The slope was found to be 7.5×10^{-7} mg. sec^{-1} μamp^{-1} cm^{-1} whereas the corresponding value in the previous paper is 7.0×10^{-7} mg. sec^{-1} μamp^{-1} cm^{-1}; they therefore seem essentially equal.

Discussion

In the high frequency silent discharge, pulses were not noticeable up to a certain value of the total discharge current, and as long as the pulses were not observed, there was no gain of ozone. The above discharge region of missing pulses had hardly been noticed in the previous work of 50 c/sec. electric source frequency.

It seems that the electric source frequencies of the present studies would not be concerned with the ozone formation or with appropriate representation of the extent of silent discharge by the pulse current. Thus, as shown in Fig. 1, the ozone formation rates are solely dependent on the value of the pulse current and independent of the electric source frequencies used here.

The relationship between pulse current and initial ozone formation rate, which was reported in the previous paper[11], was revealed to be essentially consistent even in the high frequency discharge area studied here, i. e. 500∼2000 c/sec., and with the pulse current up to 200 μamp. The ozone formation rate per unit pulse current Y_i at a low pulse current region changes along with the value of A/d linearly.

There have been observed, nevertheless, some discrepancies from the previous work. As is shown in Fig. 1, the linear relationship between the initial ozone formation rate Y and pulse current I_p holds up to a certain value of I_p independent of the frequency value. As is shown in Figs. 2, 3 and 4, however, the linear relationship is not valid from a certain current value upwards. The values where this linearity does not hold remain appreciably unaffected by the change of value of the discharge area. With an increasing discharge area, the pulse current region at which the curve departs from the linear relationship between Y and I_p, comes to assume a higher value.

Concerning the spot number, it was seemingly conceivable, as was discussed in the previous work[11], that the increase of discharge area led to the increase in spot number, because the increase of the discharge area implies that the spots are distributed more sporadically, thus offering more chance for the generation of new spot sites. As long as the number of the electrons ejected from a spot does not exceed the number of molecules just in front of the spot and as for as the more the generation of spots with an increasing pulse current is permitted, the formation of ozone may possibly be proportional to the number of electrons or, further, to the pulse current. The larger the area of the discharge electrodes is, the larger the region of the pulse current where are fulfilled the above conditions. Consequently, with an increase in the discharge area, the deviation from the linear relations tends to appear in a higher pulse current region than is the case in a smaller discharge area.

Concerning a lower pulse current region than the above discussion, the ozone formation rates per unit pulse current in high frequency discharge showed the same behavior as in the previous work, and the dependence on A/d was explainable in the same manner as in the previous paper.

The results which have been obtained in the present work are explainable by the above discussion, and the discussion also evidently supports the discussion of the previous paper.

Summary

1. The ozone formation in the silent electric discharge was investigated with a current of higher frequency. The rate is independent of the electric source frequency but dependent solely upon the value of the pulse current, and the rate per pulse current is linear in relation to the electrode area divided by the gap length. The above findings are similar to those in the case of 50 c/sec.

2. At a higher value of pulse current, the ozone formation rate is no longer linear to the pulse current and shows a type of saturation curve.

3. Some relations at a high frequency discharge among pulse current, electrode area and gap length have been discussed.

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