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Ozone in Silent Electric Discharge

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Ozone is produced in silent discharges in air by collisions intermediate between ionizing energies and attaching energies, due to the dissociation of oxygen molecules into atoms by electrons. A more detailed mechanism for the silent discharge is given.

THE rate of production of ozone has been measured for several forms of the silent electric discharge. The results of these measurements shed further light on the detailed processes of this form of discharge which has been receiving increased attention recently.[1]

The measurements of ozone generating rates were made using electrodes of either a straight wire form like that shown in Fig. 1(a) or in the form of segments of a wire arranged in a row as in Fig. 1(b), so that each segment discharged from an exposed end while the other end was attached firmly to a connecting wire bus. The discharge electrode was arranged to discharge towards the space between the two target electrodes whose cross sections were approximately air foil in shape, as shown in Fig. 2. This arrangement of electrodes was used in order that the electric wind produced by the discharge would produce air movement inside the enclosure where the discharge took place and thoroughly mix the ozone-laden air.

The enclosure used was constructed of galvanized iron and had a volume of 18 cubic feet. A formica disk six inches in diameter was fastened into a hole in the top of the tank, closing the hole. A copper tubing connection for high voltage extended through the disk into the tank for application of potential to the discharge device. Air at any desired humidity was admitted to that tank through a train which removed sulphur dioxide and dust, and the humidity was adjusted by passing the air through a suitable solution. For making a measurement, a 0.0369 cu. ft. sample of air was drawn off from the tank and bubbled slowly through potassium iodide solution. The solution was titrated with sodium arsenite.

Early in the investigation, it was found that paper and similar materials had a strong tendency to absorb ozone and that the rate of such absorption was proportional to the ozone concentration present. By removing all such materials from inside the tank, it was found that the rate of disappearance of ozone decreased greatly and also became proportional to the square of the ozone concentration present rather than proportional to concentration, indicating that ozone can disappear, at least at concentrations of 50 to 100 parts per million, by a bimolecular reaction at the galvanized surface. All the measurements here reported were made at much lower concentrations than those at which the

[1] A recent review appears in *Fundamental Processes of Electrical Discharge in Gases* by Loeb (John Wiley, 1939), pp. 514–536.

above supposed bimolecular reaction produces an appreciable effect. The procedure used was to operate the discharge under accurately controlled electrical conditions and to measure the ozone concentration hourly. About every 24 hours, the discharge was stopped, the air inside the tank was completely changed, and a new series of measurements begun in order to observe whether the discharge electrode had reached an

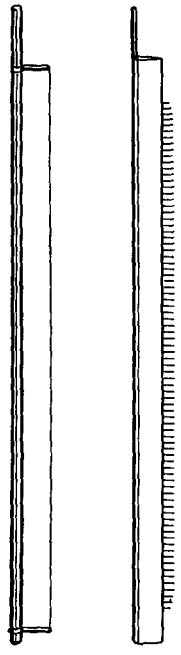

FIG. 1.

equilibrium condition. As will be observed later from the pictures, this is a significant precaution.

Three kinds of discharge electrodes were used. One electrode consisted of a straight 0.005-inch tungsten wire fastened to a $\frac{1}{4}$-inch brass rod support, as shown in Fig. 1(a). Another discharge electrode, of the kind shown in Fig. 1(b), used segments of 0.001-inch tungsten wire. A third electrode used segments of a 0.001-inch wire made by electroplating rhodium metal on 0.0009-inch nickel alloy wire. The a.c. used either for a.c. operation of the discharge or for supply to the rectifier circuit for the d.c. operations was drawn from a voltage regulator which remained steady to within less than $\frac{1}{2}$ percent. The current supplied to the discharge electrode was measured with a 150-volt electrostatic voltmeter connected across 1 megohm of resistance through which the discharge current passed, and the applied voltage in all cases was adjusted so that the discharge current was always just 0.120 milliampere. When the discharge was operated on a.c. a condenser with 0.1 microfarad capacity was put in series with the discharge circuit in order that any tendency of the discharge to pass a larger current with the discharge electrode negative than the current with the discharge electrode positive would be exactly compensated automatically by a d.c. bias accumulated on the interposed condenser. The discharge was passed until the rate of generation of ozone did not detectably increase between two successive days, in each instance.

OBSERVATIONS

In Table I are shown the rates of generation of ozone in milligrams per second per ampere. (See also Figs. 3(a), (b) and (c).) The pictures are representative of the respective discharge surfaces at equilibrium in each instance with the exception that the 5-mil straight wire appears to continue to etch indefinitely so that, after several months steady operation, the wire would etch through. The discharge from the 0.005-inch straight wire on negative d.c. and on a.c. is localized in spots so that the pictures are taken of these spots. There are four principal trends to be noticed in the data. (1) The smaller the radius of the curvature of the discharge surface,

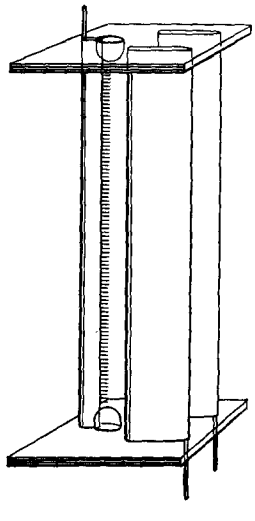

FIG. 2.

(*a*) 0.001″ rhodium on nickel. (*b*) 0.001″ tungsten. (*c*) 0.005″ tungsten.

FIG. 3.

the smaller is the rate of generation of ozone. (2) The action of the rhodium coating is to reduce the formation of the oxide coat at the tip of the point and thereby to reduce the equilibrium radius of curvature. (3) The generation rate is greater on negative than on positive (the rate on a.c. is the average of the negative value and the positive value). (4) The excess for negative over positive is greater for the larger wire than for the smaller wire.

If each electron produced one molecule of ozone, the rate would be 48,000 mg per second amp. so that for the maximum rate shown, only about one electron in 16,500 produced a molecule of ozone.

If a sharp projection was deliberately put on a target electrode to induce the formation of streamers, the rate of generation of ozone could be increased to at least ten times the highest value shown in the table.

Discharge electrodes of several other metals were tried. Steel becomes covered with more of a growth of oxide than does tungsten, and the coating on steel is rust-colored. Platinum acquires a dense black coat at the region of the discharge. These coatings appear on either the negative or positive polarity. The greater the growth in every case, the greater was the rate of generation of ozone. It is quite possible that the oxide coats acted as insulating layers whose frequent breakdown resulted in local streamer formation, although any such effect was not particularly outstanding and, as seen later, could be explained on the basis of the increase of radius of curvature caused by the oxide coat.

TABLE I. *Generation rates of ozone in milligrams per second per ampere.*

DISCHARGE	0.001″ RHODIUM ON NICKEL	0.001″ TUNGSTEN	0.005″ TUNGSTEN
d.c.+	1.05	1.20	1.95
a.c.	2.85	5.70	16.5
d.c.+	1.13	1.58	2.40
d.c.−	5.25	7.80	29.1
d.c.+	1.13	1.65	2.48

DISCUSSION

The explanation of the silent electric discharge in air when the discharge electrode is negative is as follows. The electric field near the emitting surface, due to the applied voltage, is distorted by the electrical charges produced by ionization near the point in general, and the discharge is pulsating in nature.[2] The pulsations are set off by a few electrons arising at or near the surface of the point. As these charges move away from the discharge point under the action of the field, they cause an avalanche-like accumulation of electronic charge. This cloud of electrons increases to a quantity of charge of about 10^{-10} coulomb. Most of this 10^{-10} coulomb is produced by ionization occurring in the last few free paths of the electrons so that most of the electrical charge in the pulse originates at a rather definite distance away from the tip of the point. This region of ionizing collisions will be referred to hereafter as the "ionizing sheath." As these electrons try to move on from the positive ions from which they have just been separated, they are retarded by these positive ions so that,

[2] A. F. Kip, Phys. Rev. **54**, 139 (1938); L. W. Trichel, Phys. Rev. **54**, 1078 (1938); Leonard B. Loeb and A. F. Kip, J. App. Phys. **10**, 142 (1939).

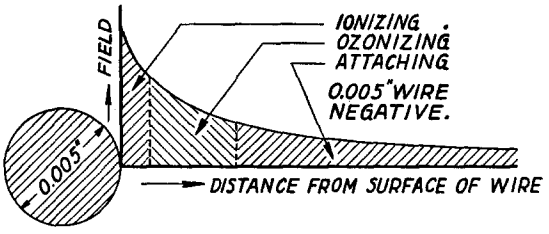

FIG. 4.

locally, the electric field is reduced below the field which would be there due to the applied voltage in the absence of such space charges. The magnitude of the pulse is limited by the ability of the positive ion charge to hold back on the electronic charges sufficiently to prevent the electrons from producing any more ionizations. Beyond the ionizing sheath, essentially all the electrons make collisions at energies less than the ionization potential 12.5 ev. The electrons can dissociate O_2 molecules to atoms resulting in the formation of ozone:

$$O+O_2 \rightarrow O_3$$

at energies down to 5.09 ev, and such ozone-producing collisions can occur in a sheath extending essentially from the ionizing sheath to a distance further from the tip of the point where the collisions occur at less than the dissociation potential. This will be referred to as the "ozoning sheath." Beyond the ozoning sheath, the electrons enter a region where their usual energy of collision is suitable for exciting molecular oxygen by collisions at a little more than 1.62 ev and in so doing, lose energy and attach to form stable negative molecular oxygen ions, after the method of Bradbury.[3] This last sheath will be referred to as the "attachment sheath." The negative ions tend to shield the region near the tip of the point and they must move away from the region near the tip of the point before the field can return to a sufficient intensity to support a new pulse.

The processes occurring when the discharge electrode is positive may be explained as follows. One or a few negative ions drift toward the region of intense field near the tip of the point. As soon as they make collisions at sufficient energy to liberate the attached electrons, the electrons initiate an avalanche-like accumulation of electronic charge. Most of the ionizations in this avalanche occur within a sheath around the tip of the point which is only a few ionization distances thick. The electrons go directly to the discharge point to be absorbed, and are not allowed much time in the gas for making the kind of collisions which result in dissociation of molecules into atoms. In this way, it is seen that much less ozone is produced when the discharge point is positive than when it is negative. Since the sheath in which ozone can be produced is so much thinner when the point is positive than when it is negative, it might be supposed that much less ozone should be generated on positive than that reported in the table of data above. There are two factors which can prevent such an extreme distinction from obtaining.

First, there is a persistent density of positive ions around the small positive discharge point under the relatively steady conditions of discharge at the value of current used here. This positive ion density partially shields the discharge point increasing the effective radius, and considerably reducing the proportion of collisions below that which would obtain in the absence of the positive ions. In this way, the positive ions increase the thickness of the sheath in which an electron can make its last few ionizations before arriving at the surface of the discharge point, and the distance in which an electron can dissociate molecules and produce ozone is correspondingly increased.

Second, excitation in excess of the dissociation energy can give rise to ultraviolet radiation

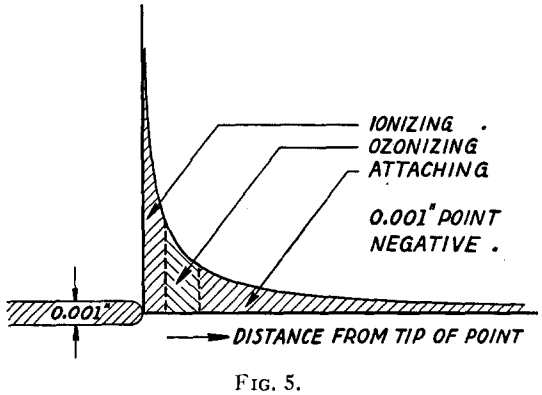

FIG. 5.

[3] N. E. Bradbury, Phys. Rev. **44**, 883 (1933). See also Loeb, reference 1, pp. 276–296.

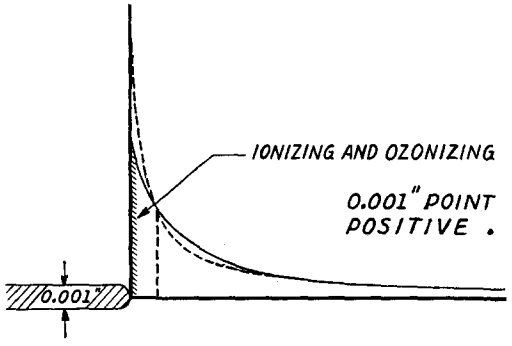

FIG. 6.

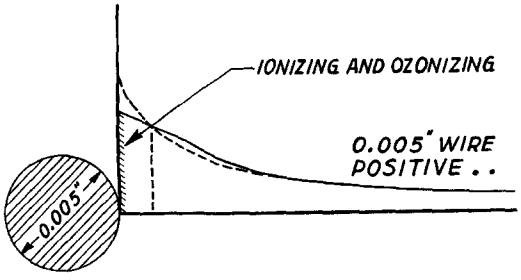

FIG. 7.

which in turn can dissociate molecules farther from the discharge point than the region of intense ionization.

The effect of the reduction of radius of curvature of the discharge electrode to reduce the rate of generation of ozone can be understood with Figs. 4–7. In Fig. 4 is represented the field as a function of distance from a straight 0.005-inch wire and the three sheaths are approximately located for the case when the discharge is negative. In Fig. 5 the field at the end of a 0.001-inch wire is shown assuming that the wire end is an approximation to a hyperboloid for regions near the tip.[4]

It is seen that the smaller radius of curvature causes a shorter range in which dissociating collisions are likely to occur. Figures 6 and 7 show the field around a 0.005-inch straight wire and a 0.001-inch wire end, respectively, on positive as the field is affected by the persistent positive ion space charge. It is seen that the electric field next adjacent and electrode surface, where most of the electrons are, is much more intense for the 0.001-inch wire end than for the 0.005-inch straight wire so that the proportion of collisions which can dissociate molecules is less for the 0.001-inch than for the 0.005-inch electrode.

[4] Eyring, Mackeown and Millikan, Phys. Rev. **31**, 900 (1928).

CONCLUSIONS

Ozone is produced in the silent electric discharge principally by collisions between electrons and oxygen molecules at energies suitable for molecular dissociation. When the discharge electrode is negative, collisions occur at dissociation energies principally in the region outside the ionizing sheath but well inside the sheath where the electrons excite the first critical potential in oxygen and attach to oxygen molecules. When the electrode is positive, collisions at dissociation energies occur in a thin sheath adjacent to the electrode surface, and dissociations also occur due to ultraviolet radiation of high energy.