—10° fine, red crystals of selenium tetrabromide separate from the solution but the liquid has no definite melting point. It is significant that $SeO_2.2HBr$ can be dehydrated by selenium dioxide. An excess of dry selenium dioxide introduced into the liquid gives a crop of yellow, needle-shaped crystals that melt at approximately 40°, dissolve in chloroform and on analysis conform to the formula $SeOBr_2$. The action of concd. sulfuric acid or of phosphoric acid is to precipitate selenium tetrabromide from $SeO_2.2HBr$, but owing to the unstability of the selenium oxybromide, they cannot be used for its preparation from $SeO_2.2HBr$.

The existence of the compound $SeO_2.4HBr$ reported by Ditte has been verified, but no evidence could be obtained of the existence of the compound $SeO_2.5HBr$.

Summary

The compounds $SeO_2.2HCl$ and $SeO_2.2HBr$ have been shown to be identical with the hydrates $SeOCl_2.H_2O$ and $SeOBr_2.H_2O$.

A new method is given by which selenium oxychloride can be produced from $SeO_2.2HCl$ and as well from hydrated selenium oxychloride.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

A LABORATORY OZONIZER YIELDING HIGH CONCENTRATIONS OF OZONE

BY LEE IRVIN SMITH

RECEIVED FEBRUARY 12, 1925 PUBLISHED JULY 3, 1925

The researches of Harries and his pupils[1] upon the properties of ozone have shown that this substance is an excellent reagent for purposes of oxidation and structure determination of unsaturated organic compounds. Indeed, Harries has characterized it as a reagent "par excellence," and if this statement be true, ozone has not become nearly as common a reagent as it should be. This is, no doubt, because rather high concentrations of ozone are usually required for the formation of ozonides, and it is not possible to purchase in this country apparatus capable of producing ozone of high concentrations, while such apparatus purchased abroad is rather expensive. The construction of a satisfactory ozonizer also offers difficulties, for although many directions are available for making ozonizers capable of giving low concentrations of ozone, Harries,[2] and recently Briner, Patry and deLuserna,[3] are the only ones who have published anything concerning high-concentration ozonizers. Moreover, in his paper describing his ozonizer,[2] Harries did not give dimensions and anyone

[1] Harries, "Untersuchungen uber das Ozon," Springer, Berlin, 1916.

[2] Harries, *Ann.*, **343**, 311 (1905).

[3] Briner, Patry and deLuserna, *Helvetica Chim. Acta*, **7**, 62 (1924).

building such an apparatus had to trust largely to chance and later experiment, a method which increases the cost considerably.

The present paper describes a laboratory ozonizer which will give an ozonized oxygen containing about 15% of ozone, a concentration which is ample for most purposes, and with a capacity of over 4 g. of ozone per hour. The dimensions of the Berthelot tubes in this apparatus are the same as those of the tubes used by Briner, Patry and deLuserna[3] but the apparatus differs from theirs in being more flexible and in avoiding the necessity of plating the outside of the tubes.

The Parts of the Ozonizer

The ozonizer proper is composed of three modified Berthelot tubes, connected in series and mounted on graphite bases in a large battery jar. All connections which come in contact with ozone are made through mercury seals. The battery jar is supplied with a wooden top in which are suitable holes for the Berthelot tubes, and the inlet and outlet tubes of the cooling coil. All glass parts are made of soft glass, 0.8–1.0 mm. in thickness.

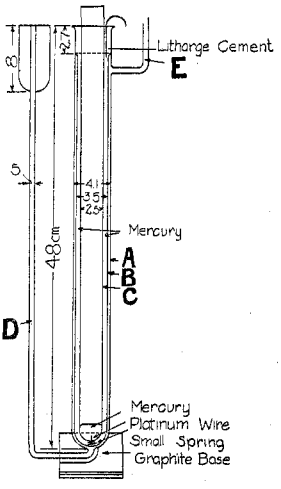

Fig. 1.—Berthelot tube.

The Mercury Seals.—These are of the conventional design, consisting of two parts, one fitting into the other, and about 9 cm. long. In the following discussion, the larger part will be called the "outside seal" and the smaller part, the "inside seal."

The Berthelot Tubes.—Fig. 1.—Each complete Berthelot tube consists of an outside tube A, 41 mm. in diameter and 48 cm. long, carrying an inlet tube D and exit tube E. Into Tube A is sealed a second tube B, 35 mm. in diameter and 45 cm. long, in such a way that the annular space between the two tubes is always 3 mm. across. Tube B is supplied with a core C, a glass tube 25 mm. in diameter and about 52 cm. long. Tube C is closed at one end and a small piece of rather heavy platinum wire is sealed through the bottom to act as a conductor. The inlet tube D ends with an "outside seal" and the top of this seal is about 2 cm. above the top of Tube A. The exit tube E ends with an "inside seal," but this is not welded to the exit tube E until the generator has been assembled.

The Graphite Bases.—These are cylindrical pieces of graphite, cupped to form a support for the Berthelot tubes, and with a groove channeled through them in order that no weight shall be borne by the lower part of the inlet tubes D. The lower surfaces of these graphite bases are under-

cut with a number of grooves, so that the whole base may be more securely cemented to the glass surface of the battery jar container.

The Battery Jar.—This is a commercial product, 21 × 31 × 42.5 cm. ($8^1/_2 \times 12^3/_8 \times 17$ inches) Type F-9, obtained from the Exide Battery Company. It is equipped with a wooden top through which project the Berthelot tubes. The top serves to hold these tubes in place, but does not in any way support them. The entire weight of the tubes is born by the graphite bases. Holes are also bored in the top for the inlet and outlet tubes of the cooling coil, and for the purpose of adding or removing liquid from the battery jar.

The Cooling Coil.—This consists of 9 mm. ($^3/_8$ in.) No. 20 B. and S. copper tubing, bent into the form of a flat, rectangular coil. It rests in grooves upon two small graphite bases cemented to the bottom of the battery jar, and is held in place by projecting through the holes made for it in the wooden top. This cooling coil also serves as one of the electrodes.

The Transformer and Other Electrical Parts.—The transformer is one which was supplied with a commercial ozonizer, operating upon a 110 v., 60-cycle primary current. The voltage in the secondary is 7500 to 8000, and the capacity of the transformer is 0.055 kva. An ammeter and a voltmeter in the primary circuit complete the electrical equipment.

Assembling the Apparatus

The bottom of the battery jar is thoroughly cleaned and dried, and then the three graphite bases for the Berthelot tubes and the two to hold the cooling coil are cemented into place, using a glycerol-litharge cement or a thick shellac. The bases for the Berthelot tubes are set so that when the tubes are in place, the inlet tubes D will be toward the back and the exit tubes E toward the front, and they should be about 8 cm. apart, from center to center. After the cement has set, the Berthelot tubes are ready for assembling.

The cooling coil is put into place, the wooden top is fitted to the battery jar, and the Berthelot tubes are carefully lowered into position. The battery jar containing the tubes is then placed in a frame of boards about 15 cm. wide, so constructed that the top of the frame is about 10 cm. above the tops of the tubes. A small coil of brass wire, about 0.5 cm. high, is dropped into each of the tubes, and then the core C is carefully lowered into place, while care is taken that the piece of platinum wire emerging from the bottom of the tube C is encircled by the small brass coil. This brass coil acts as a spring buffer and prevents puncturing of the tube B by the piece of platinum wire. The core C is carefully centered so that the annular space between B and C is as uniform as possible, and is held in place by wedges between the top of C and the top of the wooden frame. After the cores C have been adjusted and fixed in position, the annular

spaces between B and C are filled with mercury, and care is taken that no air bubbles are entrapped. The top of the mercury column is adjusted to stand about 2.7 cm. from the top of the tube A. A small capillary tube bent in the form of a hook, and reaching down to the mercury, is dropped into place, and then the remaining space between the tubes is filled with glycerol-litharge cement. The apparatus is allowed to stand for 24 hours to be sure that the cement has set, and then the wooden frame is removed.

The inside seals are now ready to be welded to the exit tubes E. A small amount of mercury is put into each of the outside seals on the tubes D; the inside seals are then clamped into position so that when the joints are welded the Berthelot tubes will be connected in series. The welding of these joints completes the ozonizer proper.

The construction is such that the tubes may be removed as often as is desired, and if a tube is damaged it can be replaced by another standard tube without breaking any glass joints anywhere. The apparatus can be used as a one-, two- or three-tube ozonizer, and when more than three tubes are desired, two of these units can be connected together in series.

The ozonizer is placed where it is to be used, and the electrical connections are made. One wire from the secondary of the transformer is run directly above the tubes, and leads from this wire dip into a small amount of mercury in the tubes C. Thus the entire annular layer of mercury between B and C serves as one electrode. The battery jar is filled with distilled water, and the other wire from the secondary of the transformer is connected to the copper cooling coil; the water surrounding the tubes thus serves as the other electrode. At the high voltage used, the resistance of the distilled water is negligible and there is almost no heating effect.

In making the electrical connections, the wire connected to the cooling coil is grounded, and then the other wire is run in such a way that the danger of contact with it is minimized.

The primary of the transformer is connected in the usual way to the 110 v. alternating current, with an ammeter and a voltmeter in the circuit.

Operation of the Apparatus

In these experiments, oxygen from a cylinder was ozonized. Since air always gives a lower concentration of ozone than oxygen, and the purpose of the investigation was to build an ozonizer giving as high a concentration of ozone as possible, no experiments were made with air.

The gas is passed through sulfuric acid and phosphorus pentoxide before entering the ozonizer. It is absolutely essential that ozonizing space and surfaces of the tubes A and B bounding the ozonizing space be dry, for the slightest trace of moisture causes sparking to take place between the surfaces of the tubes. After passing through the apparatus, the ozonized

oxygen is led through glass tubing to a work table. All pieces of apparatus are equipped with outside seals on the inlet and exit tubes, and connections between pieces of apparatus are made by sealing together two inside tubes in the form of a U. By making the arms of these U-tubes of various lengths and distances apart, it is possible to have a variety of connecting tubes so that any two pieces of apparatus may be quickly joined, thus giving great flexibility to the whole set-up. See Fig. 2.

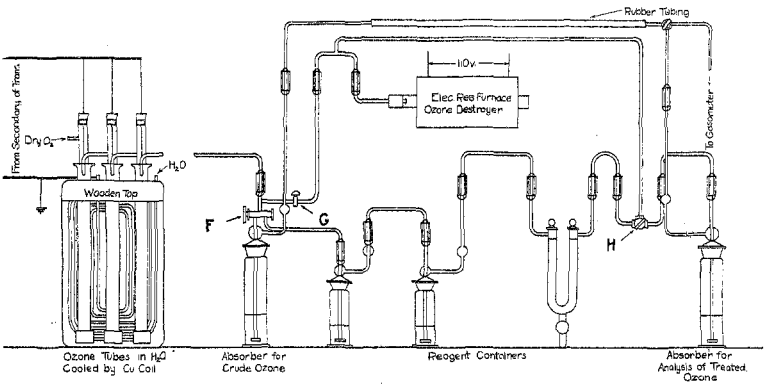

Fig. 2.

The glass line carrying the ozonized oxygen terminates in a two-way stopcock F, so that the ozone may be sent through a series of apparatus or directly through the analysis bottle by simply turning the stopcock. Above this two-way stopcock is a side tube with a one-way stopcock G. This side is for the purpose of connecting the line with an "ozone destroyer," a tube filled with granular manganese dioxide and heated to about 250° in an electric furnace. This "destroyer" is used to remove ozone from the exit gases of the apparatus, because in subjecting the ozone to the action of reagents the analyses are not made at once, but some time is allowed for reactions to come to equilibrium, for sweeping out the apparatus, etc., and the unused ozone must not be allowed to escape into the laboratory air. The whole set-up is arranged so that the ozone, after passing through a series of apparatus, may be sent through the destroyer, or by turning the three-way stopcock H, through an analysis bottle and then to the gas meter.

The analysis of the ozonized oxygen mixture is made by passing a known volume of the gas through neutral potassium iodide solution, after which the solution is acidified with sulfuric acid and the liberated iodine titrated with standard thiosulfate solution. A gas-washing bottle is used for the absorption of the ozone.

Since there is no change in volume on absorption, the sample may be metered either before or after passing through the potassium iodide. A

wet meter was used in these experiments, and to avoid corrosion of the meter by the ozone, the sample was measured after passing through the potassium iodide solution.[4] The time for the sample to pass through was taken by means of a stopwatch, and from this the rate in liters per hour was calculated.

The reaction, $O_3 + 2KI + H_2O \longrightarrow I_2 + 2KOH + O_2$, is very rapid and complete; using two potassium iodide bottles in series, and running the gas through at the rate of 45 liters per hour, only a trace of ozone reaches the second bottle, enough to require one or two drops of 0.5 *N* thiosulfate solution after acidification, while the reagent in the first bottle will require several cubic centimeters of the thiosulfate solution.

The procedure used in making the analyses was as follows. Seventy-five cc. of 5% potassium iodide solution was placed in the analysis bottle, 200 cc. of distilled water added and the bottle connected to the ozone line by means of the mercury seals. A sample of 1416 cc. (this volume was chosen because of convenience; it was 0.05 cu. ft. = $^1/_2$ revolution of the large hand of the meter used) was passed through and the time taken by means of a stopwatch. After the sample had passed through, the contents of the bottle were washed into a flask, acidified with 35 cc. of 5% sulfuric acid, and the liberated iodine was titrated with 0.5 *N* thiosulfate solution in the usual way. The temperature and pressure were noted, the observed volume of the sample was reduced to standard conditions, and the percentage of ozone by volume calculated directly. The percentage of ozone by weight was obtained from a table.[5]

Results

The results given in Table I are typical of some 75 similar runs, and serve to show, in a general way, the performance of the ozonizer. All the analyses were made as described above, and the samples were all of 1416 cc. measured under laboratory conditions. The voltage of the primary was measured in the first few experiments and found to be practically constant at 114–116 v. The amperage varied from 0.6 to 0.8 in the different runs. The temperature of the ozonizing tubes varied between 17° and 25° in

TABLE I
RESULTS

Standard vol. of sample Cc.	Rate, liters per hr.	% of O_3 by vol.	% of O_3 by wt.	Wt. of O_3 per hr. G.
1215	0.38	8.9	12.8	0.06
1226	4.0	10.1	14.4	.76
1268	10.5	9.7	13.9	1.51
1225	17.0	7.5	10.8	2.37
1251	20.0	5.75	8.4	3.68
1235	100	2.50	3.70	4.68

[4] It should be remembered that the sample to be analyzed must be taken after the whole apparatus has become filled with the ozonized oxygen. Due to the contraction in volume which takes place when ozone is formed from oxygen, a considerable error results if the zero reading of the meter is taken the moment the current is turned on, and the final reading taken the moment the current is turned off, even though the whole apparatus is swept out afterwards, and the "sweepings" are passed through the analysis bottle.

[5] Max Moeller, "Das Ozon," Vieweg u. Sohn, Braunschweig, **1921**, p. 149.

the different runs, but during individual runs it never varied more than 1°, even when the ozonizer ran continuously for several hours.

It will be seen from the table that the concentration of ozone increases slowly with the rate at which the gas passes through the apparatus. This continues until a maximum of about 15% is reached at a rate of about 5 liters per hour. Then the concentration gradually decreases with increasing rate. The total amount of ozone produced in an hour, however, increases steadily with the rate, reaching 4.68 g. when the rate is 100 liters per hour.

Summary

This paper contains a description of a flexible, relatively inexpensive ozonizer for laboratory work, capable of producing concentrations of ozone in ozonized oxygen of about 15%, or of making over 4 g. of ozone per hour, depending upon the rate at which the gas is passed through the apparatus.

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THE ACTION OF CERTAIN REAGENTS UPON OZONE

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RECEIVED FEBRUARY 12, 1925 PUBLISHED JULY 3, 1925

Preliminary to some work upon organic ozonides, it was desired to know the effect of various reagents upon the decomposition of ozone when ozonized oxygen was passed through them at various rates. Many qualitative statements dealing with this subject are to be found in the literature, but the quantitative data are comparatively rare. This paper reports the results of a series of investigations undertaken to obtain such quantitative data.

Apparatus and Method of Attack

The ozonizer used in these experiments is described in the preceding paper.[1] The oxygen was obtained from a cylinder, and was passed through sulfuric acid and phosphorus pentoxide before it was ozonized. The apparatus for containing the liquid reagents consisted of three types. (*a*) Ordinary gas washing bottles each with a small bulb blown on the end of the inlet tube and this bulb perforated several times. These were of two sizes, 500 cc. and 125 cc. (*b*) The same as (*a*), but with an "apron" over the small perforated bulb, and with a capacity of 125 cc. (*c*) Emmerling towers filled with glass pearls. These towers were made of soft glass and were 4 × 45 cm. in size.

Solid reagents were placed in U-tubes, each arm of the tube approximately 3 × 30 cm. and terminating in a stopcock. All pieces of apparatus

[1] Smith, THIS JOURNAL, **47**, 1844 (1925).