



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

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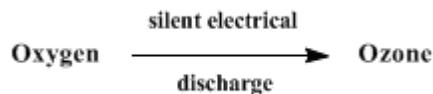
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 3, p.673 (1955); Vol. 26, p.63 (1946).*

## OZONE

### [A laboratory ozonizer]



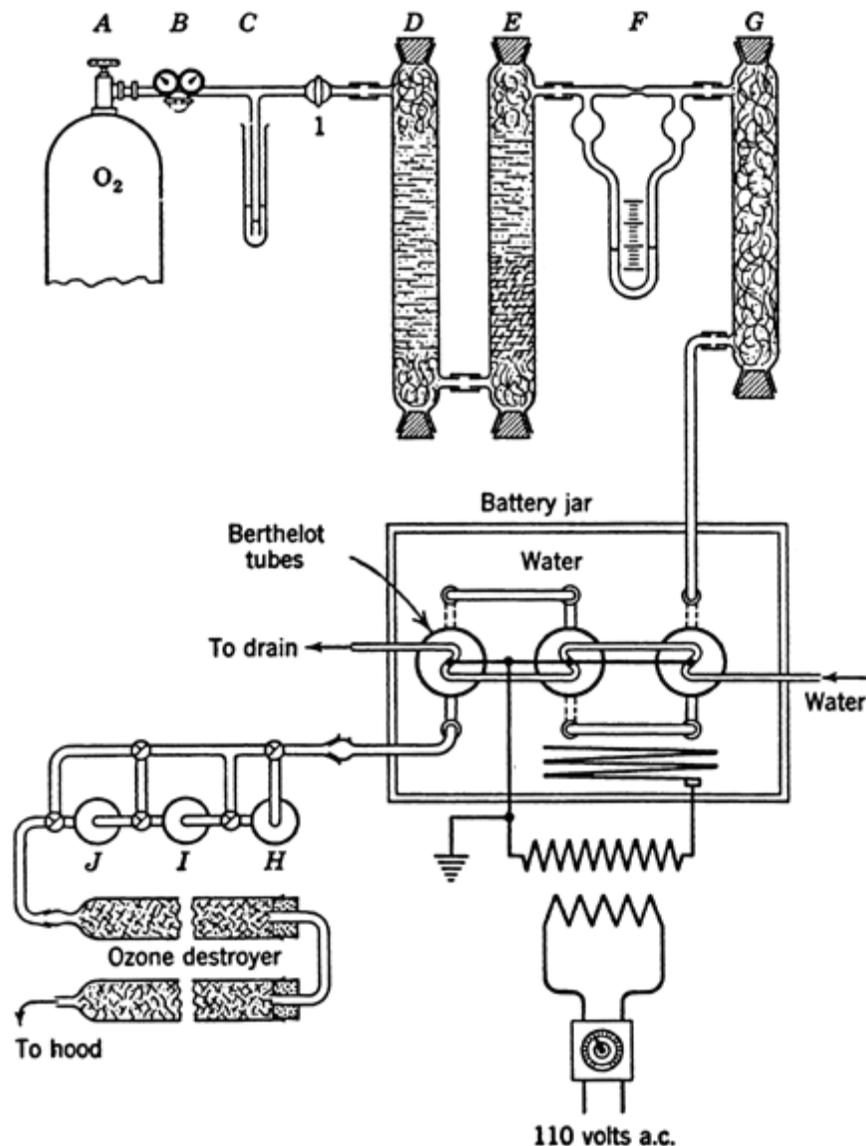
Submitted by L. I. Smith, F. L. Greenwood, and O. Hudrlik.  
Checked by R. L. Shriner, C. E. Kaslow, and R. D. Stayner.

### 1. Procedure

*Caution! Ozone is extremely toxic and can react explosively with certain oxidizable substances. Ozone also reacts with some compounds to form explosive and shock-sensitive products. Ozone should only be handled by individuals trained in its proper and safe use and all operations should be carried out in a well-ventilated fume hood behind a protective safety shield. [Note added September 2009].*

A diagrammatic sketch of the complete apparatus for the laboratory production and use of ozone in organic reactions is shown in Fig. 21.

**Fig. 21.**



A. *Purification train.* Oxygen from a cylinder (A) fitted with a reducing valve (B) is led to a pressure release tube (C). This is a T-tube, the long arm of which dips into a test tube of mercury. The height of the mercury column should be about 2 to 3 cm. The release tube is connected through a stopcock (1) to a 40-cm. condenser jacket (D). This is filled with 4-mesh anhydrous calcium chloride held in place by plugs of glass wool at the ends. A second condenser jacket (E) is filled about halfway with 4-mesh soda lime, then a 4- to 6-in. layer of anhydrous calcium chloride, and the remainder of the tube is packed with glass wool. The ends of the condensers are closed with rubber stoppers. Part F is a flowmeter, the U-tube of which should be about 20 cm. long. The bore of the capillary should be about 0.5 mm. in diameter. The flowmeter tube is filled about half full with Hyvac pump oil. Part G is a condenser jacket (40 cm.) loosely packed with glass wool.

All parts up to the ozonizer may be connected with heavy rubber tubing or, preferably, Tygon tubing. If rubber tubing is used, it is desirable to place this purification train several feet from the ozonizer proper in order to prolong the life of the rubber connectors (Note 1). The sizes of parts C through G are not critical. After this part of the apparatus has been assembled, a very rapid stream of oxygen should be passed through it for 30 minutes in order to blow out all dust particles.

B. *Ozonizer.* The conversion of oxygen to ozone is accomplished by means of three Berthelot tubes constructed of soft lime glass (Note 2) with the dimensions shown in Fig. 22. It is important that the glass be thoroughly cleaned and that the annular space through which the gases pass be as uniform as possible. Each tube has a cooling coil (Note 3) consisting of a long U-shaped piece of 6-mm. Pyrex glass tubing which fits into the innermost space of the Berthelot tube and reaches nearly to the bottom. The top of the Berthelot tube is closed by a cork with three holes, two for the cooling tubes and one for the inner electrode. The last is a stainless steel rod about 2–4 mm. in diameter. This electrode should extend to about 1 cm. of the bottom of the inner tube. The Berthelot tubes (Fig. 22) are connected by means of mercury-cup seals as shown in Fig. 23 (Note 4). The third Berthelot tube is connected to the reaction vessels by means of either mercury-cup seals or ground-glass joints. No rubber connectors can be used for gases containing ozone.

Fig. 22.

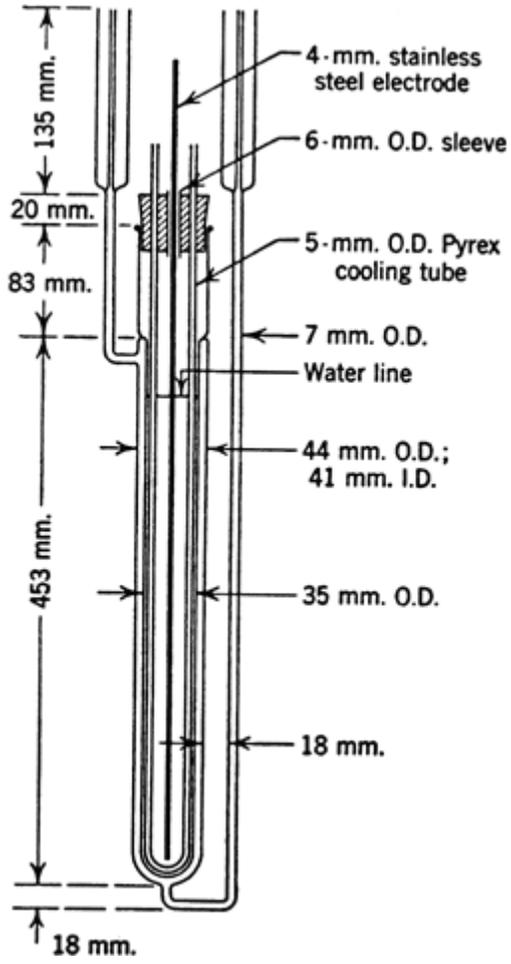
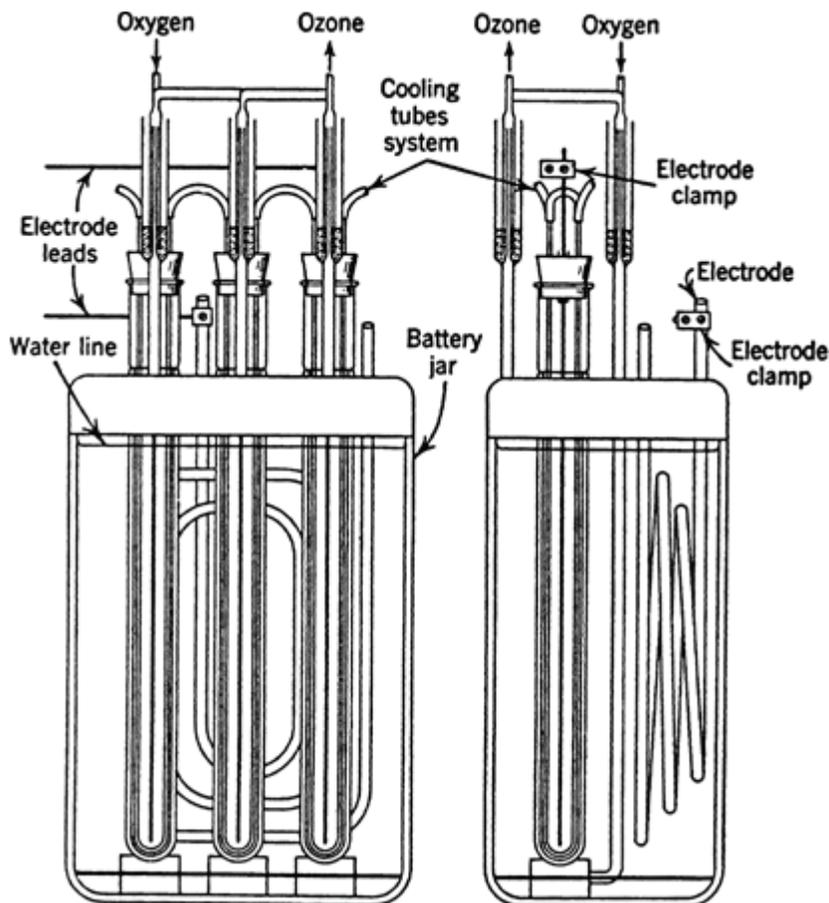


Fig. 23.



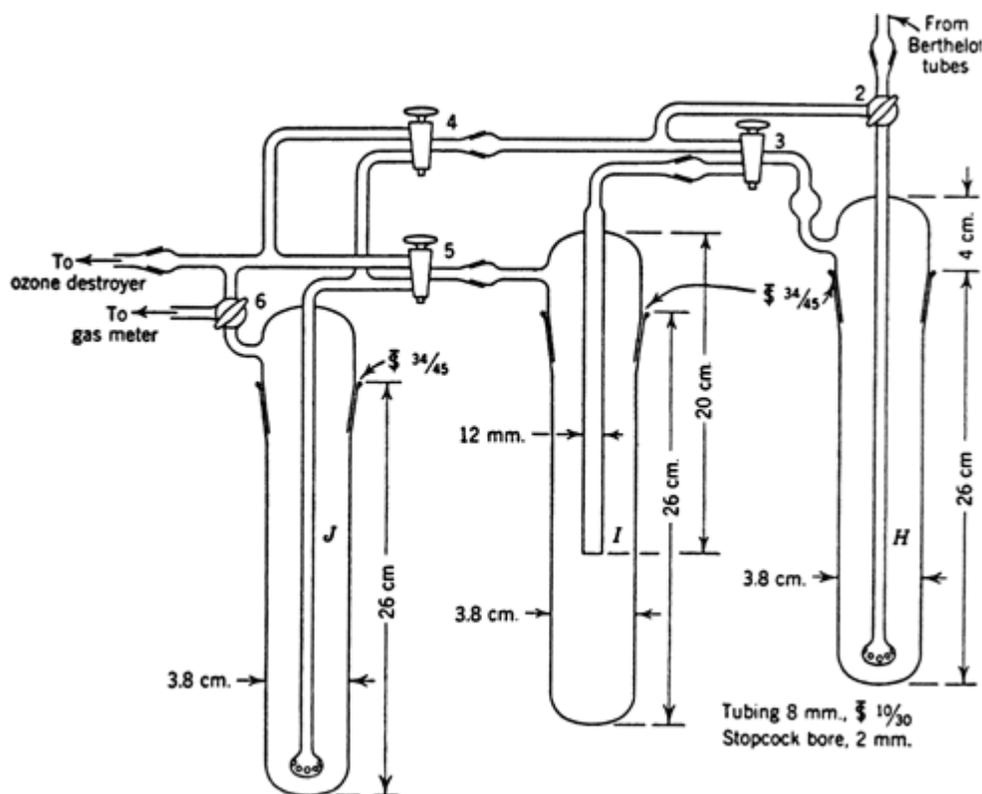
The three Berthelot tubes are mounted vertically in a large battery jar about 13 in. by 9 in. by 18 in. (Note 5). They are held in place by a wooden top (see Fig. 23) which has holes and slots cut to fit the tubes. A second wooden block with holes and slots to fit the bottom of the Berthelot tubes (Fig. 22) is placed in the bottom of the battery jar. It should be weighted with a few pieces of lead. Both the top and the bottom blocks should be soaked in hot molten paraffin wax. The holes in the top should be directly above those in the bottom so that the Berthelot tubes will be as nearly vertical as possible to facilitate making good connections (Note 6). However, a slight slant of the tubes does not affect the operation of the ozonizer.

*C. Electrical equipment.* A transformer operating on 110 volts alternating current having a secondary capable of producing about 8000–15,000 volts and a capacity of about 400 watts or more is suitable. It is important that provision be made for varying the secondary voltage. This may be done by purchasing a transformer provided with taps on the primary windings or by inserting a variable transformer in series with the primary (Note 7). During the initial test runs for calibration it is desirable to connect an ammeter in the primary circuit in order to make certain the transformer is not overloaded.

The inner electrodes of the Berthelot tubes are connected to one of the secondary terminals of the transformer. *This wire must be grounded* (Note 8); otherwise the cooling tube inside the Berthelot tube will act as a conductor to the water line and the laboratory water line would be charged. The other wire from the secondary is connected to the electrode in the battery jar. This outer electrode consists of a grid of stainless-steel wire (No. 8 or 10 B. and S. gauge). Connecting the inner electrode to the ground results in a charge on the battery jar. *Precautions* must be taken so that the jar is not touched while the current is passing. Also the battery jar must be kept away from any of the plumbing so that it will not be grounded. It is best to arrange a wooden shield so that the operator cannot come in contact with any of the high-voltage connections of the secondary.

*D. Ozone absorption assembly.* One useful combination of reaction flasks is shown in Fig. 24. It is best that the parts be connected by ground-glass joints. Tube *H* is the main reaction flask (Note 9), *I* is a condensing tube surrounded by acetone and Dry Ice to trap any volatile compounds, and *J* is an auxiliary analyzing tube for determining the amount of ozone not absorbed by the compound in tube *H*. The tubes should be assembled and clamped high enough above the desk for cooling baths to be placed around tubes *H* and *I* in order that ozonizations may be carried out at temperatures below that of the surroundings.

Fig. 24.



E. *Ozone destroyer.* *Ozone* is a powerful irritant. The maximum possible working concentration has been reported to be 0.15 to 1.0 part per million of air.<sup>1</sup> It is necessary to destroy any excess *ozone* and to see that the exit tube from the above absorption assembly is connected to a good hood. It is safer to incorporate an *ozone* destroyer in the set-up. One such destroyer consists of two tall towers (30 in.) filled with broken glass moistened with 5% aqueous *sodium hydroxide* and connected in series (Note 10). The room in which an ozonizer is used should be well ventilated.

F. *Analysis for ozone.* The analysis is made by passing a definite amount of *oxygen* through the ozonizer at a selected secondary voltage and then through a neutral 2% solution of *potassium iodide*. *Iodine* is liberated, and the resulting solution is acidified with 10% *sulfuric acid* (about 15 ml.) and titrated with a previously standardized 0.1 N *sodium thiosulfate* solution using soluble starch as the indicator.

G. *Procedure and calibration of apparatus.* For satisfactory use of an ozonizer it is desirable to obtain data relating rate of flow and secondary voltage with the amount of *ozone* produced.

A wet-type gas meter (Note 11) is connected to the tube *J* as indicated in Fig. 24. Enough 2% *potassium iodide* solution (about 70 ml.) is added to absorption tubes *H* and *J* to fill them to a depth of about one-third to one-half their height, and the tubes are marked at this level (Note 12). The reducing valve of the *oxygen* tank is opened far enough to show a pressure of 3–4 lb. per sq. in.; stopcocks 2, 3, 4, 5, and 6 are turned so as to by-pass *H*, *I*, and *J* and direct the gases through the *ozone* destroyer. Stopcock 1 is opened far enough to give a flowmeter reading of about 2–3 mm.; the transformer is turned on and adjusted to a definite voltage (Note 13). After the apparatus has been swept out for 5 minutes, the stopcocks are turned so as to pass the ozonized *oxygen* successively through tubes *H*, *I*, *J*, and the gas meter. The ozonized *oxygen* is passed through the *potassium iodide* solution for 5 minutes (stopwatch), and notes are made of the exact flowmeter reading and the volume of gas passing through the wet meter. At the end of 5 minutes the stopcocks are turned so as to by-pass tubes *H*, *I*, *J*, and the gas meter; and the ozonized *oxygen* stream is directed through the *ozone* destroyer. (Caution: do not pass the *ozone* through the wet gas meter.) The solutions in *H* and *J* are then combined, acidified, and titrated as described in paragraph F above. Practically all the *ozone* is absorbed in tube *H*. The second tube *J* is to prevent any damage to the wet gas meter.

The procedure is then repeated, the secondary voltage being kept constant but the rate of flow of *oxygen* being increased so that the flowmeter readings are about 5 mm. and 10 mm. The voltage is then changed so that the general range of 7000–12,000 volts in steps of about 1000 volts is obtained (Note 13). Determinations of *ozone* produced are made for each voltage and each rate of flow. These data may be plotted on coordinate paper in order to determine the performance of the ozonizer. A portion of such data is summarized in Table I, which represents the results from two different ozonizers

constructed by different workers in different laboratories.

**TABLE I VARIATION IN PERCENTAGE (BY VOLUME) OF OZONE (FROM OXYGEN) WITH RATE OF FLOW AND SECONDARY VOLTAGE**

Flowmeter Reading, mm.	Rate of Flow, l./hr.	Secondary Voltage					
		7000	8000	9000	10,000	11,000	12,000
Ozonizer 1							
2.0	5.6	1.3%	3.1%	4.5%	6.0%	...	...
6.0	10.6	0.9	2.1	4.2	5.6	...	...
12.0	15.4	0.5	1.7	3.6	4.9	...	...
Ozonizer 2							
2.0	5.7	6.7%	7.0%	7.1%	7.3%	7.2%	7.1%
5.0	9.8	6.0	6.5	6.7	7.2	6.9	6.8
10.0	14.4	5.5	6.2	6.5	6.7	6.8	6.9

For practical use in ozonolysis of compounds it is convenient to recalculate these data to show the time required to produce 0.1 mole of ozone at a specified rate of flow and voltage. This is illustrated by Table II.

**TABLE II HOURS REQUIRED TO PRODUCE 0.1 MOLE OZONE FROM OXYGEN**

Flowmeter, mm.	Rate of Flow, l./hr.	Secondary Voltage					
		7000	8000	9000	10,000	11,000	12,000
		hr.	hr.	hr.	hr.	hr.	hr.
2.0	5.7	5.97	5.55	5.55	5.48	5.48	5.48
5.0	9.8	3.60	3.55	3.42	3.32	3.33	3.33
10.0	14.4	2.90	2.57	2.43	2.32	2.29	2.26

All ozonizers have individual characteristics since it is difficult if not impossible to build two absolutely identical ozonizers. Variations in the composition of the glass and the annular space in the Berthelot tubes cause considerable changes in the amount of ozone produced, as shown by Table I. Hence the performances indicated by the data in Table I would be duplicated only under very fortuitous circumstances. The production of ozone from the same ozonizer may vary from time to time; hence it is desirable to check the percentage of ozone occasionally. If the production of ozone drops markedly, the Berthelot tubes should be carefully cleaned with hot nitric acid, thoroughly rinsed, and dried. Higher percentages of ozone may be obtained by having more Berthelot tubes. With six tubes, concentrations of 9–11% may be obtained.

H. *Ozonization of organic compounds.* The ozonization of each unsaturated organic compound is more or less an individual problem, but some general comments may be made. *Organic ozonides are highly explosive*, and hence it is safest to carry out the ozonization in a solvent which dissolves both the original compound and the ozonide. *In all cases, a shatter proof screen* of laminated safety glass should be placed between the operator and the tubes *H, I, and J*. A second screen should be placed back of the tubes to protect other pieces of the apparatus.

The general procedure consists in dissolving a weighed amount of the compound in a suitable solvent such as glacial acetic acid, methyl chloride, ethyl chloride, or carbon tetrachloride. The solution is placed in tube *H*, and such an amount is used that the same hydrostatic head is obtained as when the 2% potassium iodide solution was used in both tubes *H* and *J*. Usually both tubes *H* and *I* are surrounded by cooling baths. The ozonizer is started and the gases by-passed through the destroyer for about 5 minutes while the apparatus is attaining equilibrium. The ozonized oxygen is then passed through the solution of the compound for the calculated time. Since all organic compounds do not absorb ozone rapidly enough for a quantitative absorption it is frequently necessary to run the ozonization longer. The presence of unsaturation may often be detected by testing a small portion of the reaction mixture with a dilute solution of bromine in carbon tetrachloride. The ozonization is continued until the test with the bromine solution is negative.

It is also possible to place a solution of the compound in tube *H* to the proper height and use a 2% potassium iodide solution in tube *J*. At the end of the calculated time the contents of tube *J* are titrated in order to determine the amount of ozone that failed to react with the compound. From these data the additional time necessary to complete the ozonization is

calculated and the apparatus operated accordingly (Note 14) and (Note 15).

The procedures for the decomposition of the ozonide and separation of the reaction products will vary according to the nature of the compounds and must be designed and selected accordingly.

Selective ozonization of compounds containing different types of unsaturated linkages is possible by choosing a proper concentration of ozone and by stopping the ozonization at the right time. It is for this reason that the calibration described above is carried out, since for certain ozonizations it is important to have the correct concentration for best results.

1. *Use of air in place of oxygen.* When air is the source of oxygen the exit gases from the Berthelot tubes contain lower percentages of ozone than when pure oxygen is used. The gases also contain small amounts of nitric anhydride,<sup>2</sup> the presence of which may cause some side reactions to occur. However, a considerable number of compounds may be satisfactorily ozonized with air as the source of oxygen. The above apparatus will operate satisfactorily with compressed air. It is essential to bubble the compressed air through three 5-l. flasks half filled with concentrated sulfuric acid before passing the air into the purification train B, C, D, E, F, G. Some data on the production of ozone from air at a secondary potential of 10,000 volts are given in Table III.

TABLE III PRODUCTION OF OZONE FROM AIR AT  
SECONDARY VOLTAGE OF 10,000

	Rate of Flow	
	15.3 l./hr.	21.8 l./hr.
Ozone, % by volume	3.0	2.9
Hours for production of 0.1 mole ozone	4.8	3.4
N <sub>2</sub> O <sub>5</sub> , % by volume	0.13	0.08
Moles HNO <sub>3</sub> formed per 0.1 mole ozone	0.009	0.006

At higher secondary voltages the percentage of nitrogen pentoxide rises. A decrease in the rate of flow also increases the amount of nitrogen pentoxide. It is obvious from the data in Table III that the amounts of nitrogen pentoxide are very small and need to be considered only when examining a reaction mixture for small amounts of by-products or when the presence of this oxide of nitrogen would act as a catalyst for the oxidation of the organic compounds by oxygen or ozone.

## 2. Notes

1. If necessary, the rubber connecting tubes in the purification train may be protected by painting them with molten paraffin wax.

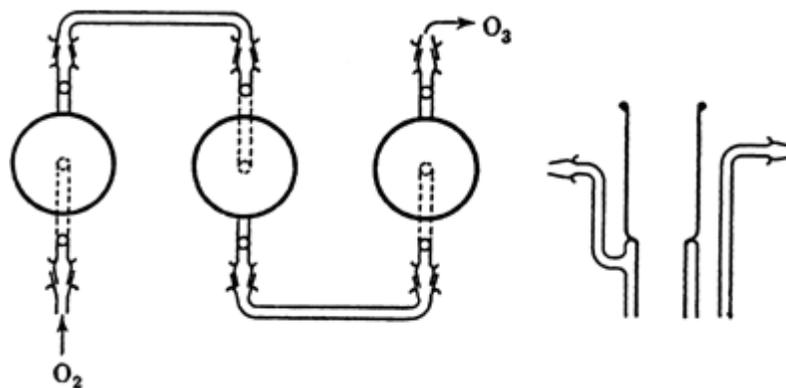
2. Berthelot tubes constructed of Pyrex may fail to produce ozone or may give a low yield.<sup>3</sup> However, Henne and Perilstein<sup>4</sup> have described a satisfactory ozonizer constructed of Pyrex glass.

With Pyrex tubes, voltages of 14,000–18,000 volts are needed. The power consumption is 15–25 watts per tube. The gap should be 1.5–2.00 mm.; this may be obtained through the use of 22-mm. o.d. and 28-mm. o.d. Pyrex tubing. The transformer which is recommended (E. O. Brimm and G. A. Cook, private communication) for use with Pyrex equipment is catalog No. 969-001-395, 15,000 volts, 30 M.A., of the Jefferson Electric Company.

3. Some form of cooling is necessary. The equipment described here involves the use of a cooling coil in the inner tubes. It is also possible to cool the entire unit by means of a copper cooling coil inserted in the outer bath. When the latter method is used, the inner tubes are not cooled and the outer bath is grounded. This is reported to be a less hazardous method of operation (E. O. Brimm and G. A. Cook).

4. Mercury cup seals have been recommended in the past, but satisfactory results have been obtained with ground joints lubricated with a very small amount of 85% phosphoric acid. It is also possible to use Tygon connections with the tube ends butted together. If ground-glass connections are used the inlet and outlet tubes should be bent to facilitate union. Figure 25 shows top and side views of such Berthelot tubes. The holes in the wooden supports should be large enough to permit the tubes to fit loosely.

Fig. 25.



5. Any large commercial laboratory battery jar is suitable. The Exide types F-9 or F-11 are satisfactory.

6. The dimensions of these wooden supports will be determined by the battery jar. The position of the holes and slots should be arranged so that the tubes may be spaced at convenient distances as shown in Fig. 23.

7. The submitters used a transformer purchased from the Franklin Transformer Company, Minneapolis, Minnesota. It was provided with taps so that secondary voltages of 5500, 6600, 7700, 8800, 9900, and 11,000 could be obtained. These transformers do not always deliver the rated voltage and hence should be calibrated by actual measurement. The checkers used a luminous tube transformer obtained from the Jefferson Electric Company, Bellwood, Illinois, catalog No. 721-411. Cap. 825 V.A. Primary 115 V.A.C. 60 cycles. Secondary 15,000 volts, 60 M.A. The variable transformer used to regulate the voltage should be rated at 7.5 amperes.

8. It may make a difference which side of the transformer is grounded, depending on the construction of the transformer; the maker of the transformer should be queried on this point.

9. The reaction flask *H* can be made of different sizes depending on the amount of solution being ozonized. The dimensions of the parts in Fig. 24 are not critical; any tubes and stopcocks of convenient size are suitable.

10. Many reagents act as contact catalysts for the destruction of ozone; a study of some of them has been made.<sup>5</sup>

11. A wet gas meter such as No. S-39465, E. H. Sargent and Company, is satisfactory. This meter need not be a permanent part of the apparatus. It is used only to calibrate the flowmeter.

12. In order that the flowmeter may be used during an ozonization when tube *J* is empty it is necessary to mark the heights of liquid on both tubes. The same liquid head (height  $\times$  density) must be present in the absorption tubes during calibration and ozonization. For very accurate work a pressure regulator should be incorporated in the oxygen train and a gas meter made part of the set-up. For ordinary preparative work, however, these are not necessary.

13. If a transformer with taps is used the voltage chosen is determined by each tap. With a luminous tube transformer and Variac, a voltmeter is connected across the primary of the transformer. Since these transformers have a fixed ratio of primary to secondary windings, the secondary voltage will be nearly proportional to the impressed primary voltage. Thus a transformer designed to deliver 15,000 volts with a primary voltage of 115 volts will deliver approximately 12,000 volts when the primary voltage is  $\frac{4}{5}$  of 115 or 92 volts.

14. It is evident that for ordinary preparative work the careful calibration given in section G is not essential. It is only necessary to adjust the voltage of the transformer to about 10,000 to 11,000 volts and turn on the flow of oxygen to as rapid a rate as the absorption tubes will handle when surrounded by cooling baths. The amount of ozone produced in 5 minutes at the observed flowmeter reading is determined as in section F. By operating the ozonizer at this rate of flow and voltage the ozonization of organic compounds can be carried out.

15. The ozonizer may be operated at higher rates of flow of oxygen than shown in Tables I and II, provided that the organic compound reacts with ozone at a reasonably rapid rate. Some data on high rates of flow are given in Table IV.

**TABLE IV PRODUCTION OF OZONE FROM OXYGEN AT HIGH RATES OF FLOW AND SECONDARY VOLTAGE OF 10,000**

<i>Rate, l./hr. % Ozone (by volume) Hours to Produce 0.1 Mole Ozone</i>		
27	4.7	1.76
32	4.5	1.55
45	4.1	1.23

16. A laboratory ozonizer is manufactured by the Welsbach Corporation, Philadelphia, Pennsylvania.

### 3. Discussion

Ozone for laboratory use has always been prepared by the action of a silent electric discharge upon a stream of air or oxygen. Although dielectrics other than glass are used in commercial ozonizers, they do not give a percentage of ozone high enough for laboratory use, and practically all laboratory ozonizers employ the Berthelot tube and are modeled after the one originally constructed by Harries.<sup>6</sup> Good ozonizers of this type have been described by Briner, Patry, and de Luserna,<sup>7</sup> and by Church, Whitmore, and McGrew.<sup>8</sup> The ozonizer described above is a modification of the one described by Smith,<sup>9</sup> as improved by Henne,<sup>10</sup> and by Smith and Ullyot<sup>3</sup> and Greenwood.<sup>11</sup> Henne and Perilstein<sup>4</sup> described a modification of their ozonizer in which the inner electrode is a tube filled with mercury; the outer electrode is water-cooled. More recently a 4% concentration of ozone has been prepared using a compressed-air-cooled inner electrode.<sup>12</sup> Ozone has also been produced in good concentrations (over 12%) by electrolysis methods.<sup>13</sup>

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 8, 403](#)

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### References and Notes

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13. Boer, *Rec. trav. chim.*, **67**, 217 (1948).

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### Appendix

#### Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

soda lime

oxide of nitrogen

[calcium chloride](#) (10043-52-4)

[sulfuric acid](#) (7664-93-9)

[acetic acid](#) (64-19-7)

[sodium hydroxide](#) (1310-73-2)

[nitric acid](#) (7697-37-2)

[lead](#) (7439-92-1)

[bromine](#) (7726-95-6)

[oxygen](#) (7782-44-7)

[carbon tetrachloride](#) (56-23-5)

[potassium iodide](#) (7681-11-0)

[sodium thiosulfate](#) (7772-98-7)

[mercury](#) (7439-97-6)

[methyl chloride](#) (74-87-3)

[iodine](#) (7553-56-2)

[acetone](#) (67-64-1)

[phosphoric acid](#) (7664-38-2)

ozone (10028-15-6)

nitric anhydride,  
nitrogen pentoxide

ethyl chloride (75-00-3)

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