

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

A Laboratory Ozonizer for Liquid Air Temperatures

BY A. C. BYRNS

It has been known for many years^{1,2,3} that oxygen can be converted almost completely into ozone in the electric discharge at liquid air temperatures, but no practical application seems to have been made of this fact. The ozonizer shown in the accompanying sketch (Fig. 1) has been designed as a convenient method of preparation of small quantities of pure ozone.

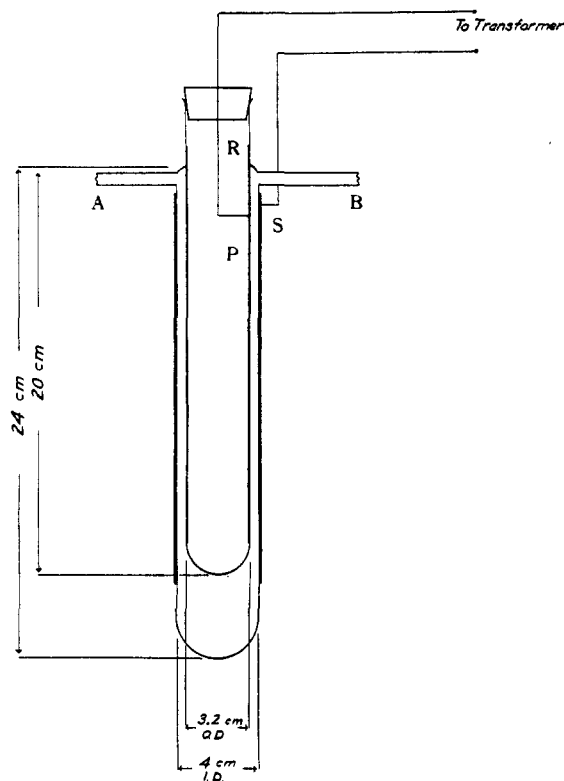


Fig. 1.

As shown by the pressure *vs.* time curves of Fig. 2, it is possible to obtain more than 99% conversion of oxygen into ozone in a single operation with this apparatus.

In principle it is essentially a Siemen's tube, employing a silent discharge. Efficient designs have been determined⁴ for ozonizers operating at atmospheric pressure and temperature, and from this work an annular spacing of 4 mm. was chosen. Pyrex glass is used throughout. The

- (1) Briner and Durand, *Compt. rend.*, **145**, 1272 (1907).
- (2) Goldstein, *Ber.*, **36**, 3042 (1903).
- (3) Brewer and Westhaver, *J. Phys. Chem.*, **34**, 1280 (1930).
- (4) Henne, *THIS JOURNAL*, **51**, 2676 (1929).

source of current has been a 10,000 volt, 1 kw. Thordarson transformer with 10 ohms in series with the primary. The tubes A, B, are sealed to the oxygen purifying and storage line, and to the pumping system. The inner electrode contact, P, is a snugly fitting tin foil cylinder; the connecting wire, R, is run through a rubber stopper in the top to prevent condensation of moisture on the inner wall of the cold ozonizer. The outer electrode connection, S, is made by closely winding copper wire (no. 20) on the external glass tube in the form of a cylinder; this may be kept in place with a thin film of solder down the side. Wire is preferable to foil for this contact, since it may be wound tightly enough at room temperature so that it will shrink to a perfect fit at the lower temperature, thus preventing excessive strain on the glass, and foaming of liquid air between the glass and metal surfaces.

The manipulation is quite simple; it is only necessary to admit oxygen into the evacuated ozonizer, cool with a bath of liquid air, and then turn on the current. If a larger amount of oxygen is desired than can be held by the ozonizer at one time, the storage bulb may be left open and oxygen condensed in with the liquid air. Due to

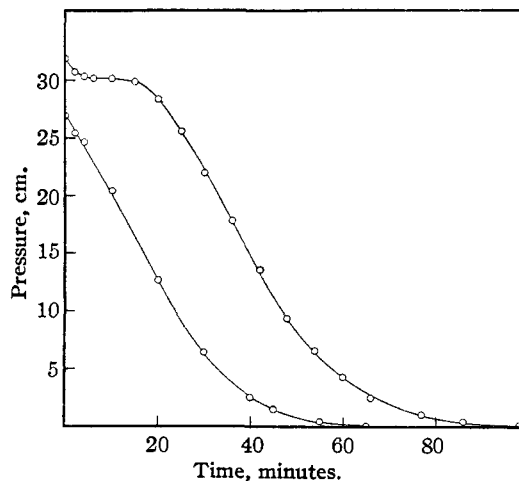


Fig. 2.

its low vapor pressure at liquid air temperatures (< 0.1 mm.), the ozone formed in the discharge condenses on the walls, runs to the bottom of the vessel and is thus removed from the reaction zone.

When sufficient ozone has been formed, the residual oxygen is pumped off after shutting off the transformer, the liquid air removed, and the ozone condensed with liquid air into that part of the system in which it is to be used. This is done while the ozonizer is warming up from the lower temperature, thus keeping the vapor pressure fairly low, and serves three purposes: there is less danger of explosion on vaporization, less decomposition while going through any stopcocks in the line and by closing the stopcock next to the ozonizer before the last bit of liquid ozone has evaporated, impurities such as traces of water or nitrogen pentoxide are retained in the ozonizer (to be thoroughly pumped out later).

Repeated distillation is unnecessary to obtain quite pure ozone, for any oxygen formed may be pumped off before vaporization in the system where it is to be used. It should be strongly em-

phasized that the essential precaution in avoiding explosions in handling liquid ozone is to prevent any mechanical agitation and bubble formation during vaporization. This is done by always keeping the pressure low, so that vaporization takes place principally from the surface. It has been observed by several workers that the greatest danger of explosion is incurred when the liquid reaches its boiling point and bubbles form in the body of the liquid. If a few per cent. of oxygen, due to decomposition while going through greased stopcocks in the line, are permissible, a convenient method is to vaporize the liquid into an evacuated bulb of such size that the pressure never becomes greater than about a half atmosphere. It can then be transferred to the rest of the system as needed, and the oxygen pumped off as before.

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The Photochemical Decomposition of Phosgene

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At the beginning of the present program of work on the photochemical reactions of phosgene, it was thought likely that a knowledge of the kinetics of the phosgene decomposition reaction would be necessary for interpreting completely the results of the other reactions. Furthermore, it was believed that the decomposition might enter as a primary reaction, in the oxidation, the reaction with hydrogen and in the phosgene-sensitized oxidation of carbon monoxide. The results already published^{1,2,3} indicate, however, that, in the case of these latter three reactions, the decomposition may be considered negligible in so far as we are concerned with the stoichiometry and mechanisms of these reactions. The results of the present research, therefore, do not alter any of the conclusions or explanations arrived at in the preceding work, but rather constitute additional confirmatory evidence for the correctness of the mechanisms already postulated.

(1) G. K. Rollefson and C. W. Montgomery, *THIS JOURNAL*, **55**, 142 (1933).

(2) C. W. Montgomery and G. K. Rollefson, *ibid.*, **55**, 4025 (1933).

(3) G. K. Rollefson and C. W. Montgomery, *ibid.*, **55**, 4036 (1933).

Experimental

Most of the experimental details have already been described. The reaction vessel, a clear fused quartz spherical bulb of approximately 200-cc. capacity, was mounted in a small tank having a clear fused quartz window. This tank was filled with water and, before recording pressure measurements, the water temperature was always adjusted to 20°. A 200-volt quartz mercury arc was used in conjunction with a short focal length cylindrical quartz lens. For part of the work, a quartz chlorine-bromine light filter was used. This was made from a cell about 6 cm. thick with detachable plane parallel end plates and was filled with chlorine bubbled through liquid bromine at a total pressure somewhat greater than atmospheric. Photographs of the mercury arc spectrum showed that the transmission of the filter for the prominent lines in the region of the chlorine absorption maximum (3300-3400 Å.) was negligibly small. A sulfuric acid (sp. gr. 1.84) manometer was used to follow the course of the reaction.

Results

In Table I are recorded the results of a series of initial rate experiments in which the phosgene