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OZONE CHEMISTRY AND TECHNOLOGY

This book presents sixty papers constituting the Proceedings of the International Ozone Conference held in Chicago, November 1956. A group of international authors presents many facets of the science, technology, and application of this versatile form of oxygen.

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Introduction

Ozone has been an important reagent of the organic chemist almost from the time of its discovery by Schönbein in 1840. With the discovery of the ozone layer in the upper atmosphere, and its all-important role as an ultraviolet shield, the properties and reactions of ozone became of intense interest in an entirely different field of science.

Ten years ago there would have been little to gain in bringing together the diverse interests represented by these two aspects of ozone chemistry. The recent establishment of transient ozone formation in urban atmospheres—resulting from research on the Los Angeles air pollution problem—came from contributions by meteorologists, photochemists, organic and analytical chemists, and perhaps foremost, by a plant physiologist utilizing all these disciplines, A. J. Haagen-Smit.

The International Ozone Conference, held in Chicago, November 28 to 30, 1956, succeeded in providing a medium for current contributions concerning ozone as it affects science and technology. The participants in the conference differed widely in the reasons for their interest in ozone. But the high level and enthusiastic response from 300 registrants, which vastly exceeded our expectations, attested to an effective interchange of ozone knowledge.

We had hoped to receive a sufficient number of papers to occupy three days of single sessions. But so many worth-while papers were submitted—over 60—that the conference was scheduled in triple concurrent sessions.

The event marked the first occasion for an international exchange of information concerning ozone in both science and technology. We think it marked an important step forward for ozone research.

Many individuals and groups who did much for the success of the conference deserve great appreciation for giving of their time and talent. Among them especially were the sponsors of the conference—namely:

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Photochemical Production of Ozone

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The problem of photochemical production of ozone still has many indeterminate points. The upper limit of the wave length of active radiations has been found to be in the spectral region of 2000 to 2100 A. This limit has been taken into account in the interpretation of ozone formation by solar radiation (atmospheric ozone) or by mercury lamps. The energy yield measured during ozone formation by mercury lamps is much inferior to that obtained by silent discharge or by electrolysis.

The photochemical production of ozone is of limited industrial interest because the practical yield is much lower than that produced by silent electric discharge. However, there are a number of scientific problems connected with photochemical ozone production which have not yet been solved, and the number continually increases, because of the important role which ozone plays in the atmosphere. As a constituent of the atmosphere (about 100 millionth parts thereof at the earth's surface), ozone forms a protective screen because it absorbs radiations of wave lengths below 3000 A. which are deleterious to life. Furthermore, the heat liberated by such absorption and by the exothermic decomposition of ozone creates in the higher atmosphere (at approximately 40 km.) a warm layer which helps to establish thermal equilibrium on our planet.

The principal object of this research was to answer the questions: What is the effective spectral range for the production of ozone? What are the energy yields in the production of ozone?

Spectral Range for Ozone Production

The spectral range which is active in ozone production is one of the points requiring further study. Knowledge concerning it has both practical and theoretical importance, inasmuch as it can furnish evidence about the photochemical process of ozone formation. In fact, the problem posed by investigators reduces to this: Is there a limiting wave length above which radiations do not produce ozone, and, if so, where is that limit? On these questions opinions are very divergent. A critical bibliography on this subject is available (*2*, *3*).

Experimental Procedure. As source of ultraviolet light the author used sparks between zinc electrodes, the hydrogen lamp (which gives a continuous spectrum), or mercury lamps of differing model and power, fed by alternating or by direct current; all the mercury lamps emit an arc spectrum. The spectra from these sources were determined by a spectrograph with quartz optics or a diffraction spectrograph with a fluorite window.

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The author has used three filters with special advantage: WG 7, 8, and 10, for which the transmittances, based on the hydrogen lamp, are indicated in Figure 1.

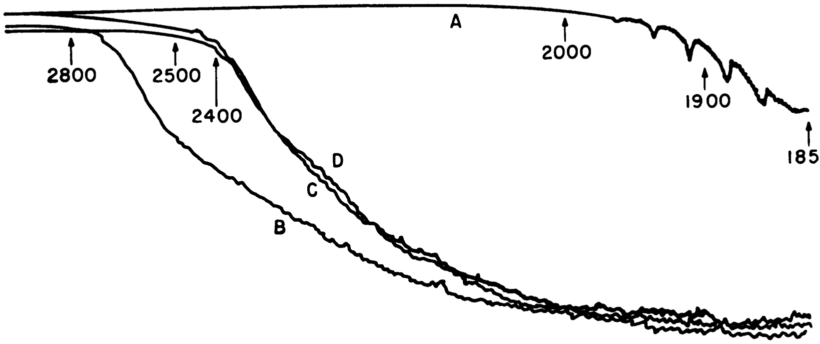

Figure 1. Transmittances of filters WG 7, WG 8, and WG 10

A. Hydrogen lamp, no filter
B. Filter WG 7
C. Filter WG 8
D. Filter WG 10

Curve *A*, which refers to that of the hydrogen lamp alone, shows a complete transmittance starting from the long waves down to those of 2100 A.; below 2000 A. the Schumann-Runge absorption bands due to molecular oxygen are distinctly observed. Interposition of the filter WG 7 resulted in curve *B*; transmittance is diminished, at first slowly then more rapidly. In the region of 2500 A., close to the resonance line of mercury (2535.6 A.), the transmittance was still 50%, the absorption was almost complete below 2100 A. The transmittances of WG 8 (C) and WG 10 (D) were close together. They decreased slowly so that in the 2500 A. region the transmittances were still 90%, but towards 2100 to 2000 A., these filters were only slightly transparent, WG 10 rather more than WG 8.

Oxygen was used at ordinary pressure and also at pressures as high as 60 atm., which improves the absorption. In many experiments the measurements were made on liquid oxygen, which had not previously been systematically employed. In the latter case, absorption increased strongly, made evident by a large continuous band extending over the whole of the ultraviolet region below 2600 A.; in fact, the oxygen concentration is 800 times that of oxygen gas at atmospheric pressure. An additional advantage results from working at a constant temperature of —183° C.—namely, that the ozone, dissolved in liquid oxygen, is thereby protected from thermal decomposition; this makes possible the use of powerful lamps, evolving much heat. But this advantage is diminished by the ultraviolet absorption of the two quartz walls of the Dewar container. In addition, as ozone dissolves in oxygen, the transparency of the system for ultraviolet rays progressively decreases.

Using the WG 8 filter with a mercury vapor lamp, direct current, and oxygen circulating at 40 atm. in a quartz tube, less than one hundredth of the ozone obtained without the filter was formed. Similar results were obtained by using sparks from zinc electrodes as the light source or by working with liquid oxygen. From this it was concluded that ozone was formed under the action of radiations of $\lambda < 2200$ A.

With a weak mercury lamp (15 watts) acting upon oxygen at ordinary pressure inside a quartz tube, the production of ozone was completely prohibited by interposition of a WG 7 filter. Use of the WG 8 filter reduced the ozone production to one hundredth of the value obtained without such a filter, and the WG 10 filter cut it down to one fifteenth of this value.

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If the most powerful radiation of a mercury lamp, 2536.5 A., were active in ozone formation, the bulk of ozone formation would have to be attributed to this one radiation and ozone formation would also be obtained after inserting the filters. Keeping in mind the behavior of these three filters towards ultraviolet light, the small amount of ozone formed on interposing the filters WG 8 and WG 10 may be attributed to radiations below 2100 A., for which WG 8 and especially WG 10 are slightly transparent. Using liquid oxygen and a powerful mercury lamp (440 watts) the results were similar to those just described.

With the hydrogen lamp, as radiations pass through only a little quartz window, the ozone produced was much smaller in quantity and was completely arrested by interposition of the filters WG 7 and WG 8.

To summarize, there does exist an upper limit for the wave lengths effective in ozone formation. The limit is in the region of 2000 to 2100 A.; the filters used were insufficiently selective for making a more precise statement.

One must, however, envisage the existence of a special zone effective in the production of ozone at $\lambda \leqslant 1750$ A., of which there is question in the bibliography cited. But this cannot enter into account in the experiments with mercury arc lamps, as the only wave length to be considered would be that at 1648.9 A. (*13*), for which the quartz walls and the air to be traversed would be completely opaque. Hence it is the radiations between 1750 and 2000 to 2100 A. which are completely responsible for the ozone formation. They are shown (Figure 2) in the spectrum registered when a weak mercury lamp is used and correspond to the wave lengths 1850, 1940, 1970, and 2000 A. Here the conditions of absorption are realized by the bands of oxygen (Schumann-Runge and others); they widen under the effect of pressure and, when operating in liquid oxygen, form the strong continuous band referred to.

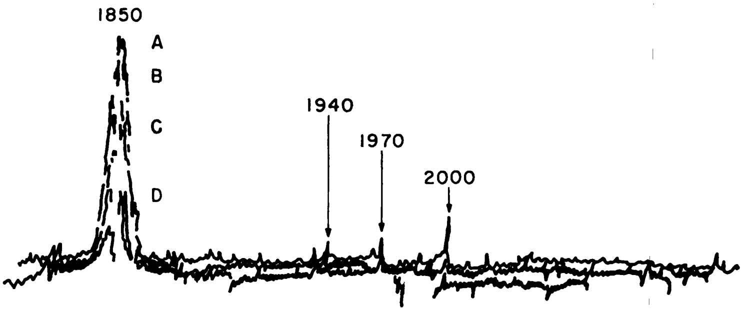

Figure 2. Spectra of ozone produced by a mercury lamp

But radiations below 1750 A. will act upon oxygen with great efficiency if they are able to penetrate. The absorption conditions in this region are rather favorable, because of a very strong, continuous band, which starts at 1750 A. and extends to 1150 A. It is so intense that high absorption can be attained even if the oxygen is at very low pressures. These conditions had been realized earlier by using fluorite windows (*17*) or exceedingly thin quartz walls (*8*). Such conditions are realized also in the higher layers of the atmosphere above 40 to 50 km., where the solar radiations of exceedingly short wave length penetrate, to which the production of atmospheric ozone must in fact be attributed.

With regard to the mechanism of this photochemical production, two different mechanisms must be postulated, one for radiations below 1750 A. and one for those from 1750 to 2000 or 2100 A.

In the first case the initial photochemical reaction is the dissociation of oxygen into two oxygen atoms, one in the normal state, the other in an activated, the *D* state.

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Its energy, E, per gram mole of oxygen, calculated for the wave length 1750 A. by means of the expression $E = 284000/\lambda$ (deduced from the Einstein principle of photochemical equivalence) has the value 163.8 kcal., of which the activation energy of the one oxygen atom accounts for 45.7 kcal. As each atom combines with 1 mole of oxygen, 2 moles of ozone are formed per quantum absorbed, corresponding to $\lambda =$ 1750 A. This is, in effect the quanta yield obtained by Vaughan and Noyes (*17*).

But it is difficult to explain the efficiency of radiation between 2000 and 2100 A. From the energetic point of view, Warburg's theory, that the initial photochemical reaction is the dissociation of oxygen into two normal oxygen atoms, is untenable, as that requires an energy of only 117 kcal. corresponding to the quantum of $\lambda = 2427$ A. The same holds for the alternative theories which consider the initial photochemical reaction as the activation of the oxygen molecule; for unless one brings into play higher energy levels, the energy quantum E necessary corresponds to still higher wave lengths.

The author believes that his experimental findings can be explained by the photochemical action brought about by radiations (*9, 10, 20*) upon double oxygen molecules, $(O_2)_2$, according to:

$$(O_2)_2 + h\mu = O_3 + O$$

$$O + O_2 = O_3$$

yielding two molecules of ozone per quantum absorbed.

It is particularly worthy of attention in regard to experimental results on liquid oxygen. The latter contains ca. 50% (*12*) of $(O_2)_2$, so that their participation in the initial reaction is very probable. The strong absorption bands found in liquid oxygen have already been interpreted as being due to $(O_2)_2$. The better yields produced with oxygen under pressure may also easily be interpreted as being due to the increased proportion of double molecules (*16*).

The energy to be furnished, however, is found by calculation to be $E = 92.7$ kcal. (*2*), corresponding to a wave length of 3075 A. The latter is too high, but if one supposes that the atom of oxygen liberated is in the active state, as in the photochemical dissociation of O_2, the supplementary energy of 45.7 kcal. which is needed brings the value of E to 138.4 kcal.; this indeed corresponds to a wave length of 2075 A., agreeing well with the values observed as the upper limit of activation. In the absence of experimental data concerning the action of radiations on double oxygen molecules, this interpretation is only tentative.

Energy Yields in Ozone Production

This work throws light on some of the numerous points needing investigation with regard to the energetic yield in ozone formation. This yield can be considered in the first place from a theoretical point of view, applying the Einstein equilibrium principle to the initial step in ozone production. If, for example, this first step is the photochemical dissociation of oxygen, the energy will be $E = 163.8$ kcal., as explained above. For a (hypothetical) monochromatic light source, not evolving heat, the energetic yield would be 508 grams of ozone per kilowatt-hour. But this value is much higher than that practically attainable; indeed, for the light sources used, only a very small proportion of radiations $\lambda \leqslant 1750$ A., is emitted. Calculating in the same way the yield for radiation at 2000 A., one obtains a theoretical yield of 559 grams of ozone per kilowatt-hour.

In the following, the experimental values for energetic yields of ozone, until now very little studied, are considered. These results have been obtained with rectilinear type mercury vapor lamps of different powers.

In one series oxygen gas was circulated through a quartz sleeve which surrounded the lamp for its full length; hence the radiation had to pass through the lamp walls

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and through the sleeve. As the thermal destruction of the ozone was an important source of loss, it was better to use low-power lamps. Table I gives the results for a 7-watt lamp.

Table I. Ozone Produced by 7-Watt Lamp

Oxygen Fed, Liters/Hour	Ozone Obtained, Mg.	Ozone Concentration	Energy Yield, Mg. Ozone/Kw.-Hr.
7.5	2.13	1.33×10^{-4}	304
15.0	2.26	7.03×10^{-5}	323
22.5	2.50	5.20×10^{-5}	358
30.0	2.57	4.00×10^{-5}	367
37.5	2.75	3.42×10^{-5}	393
45.0	2.88	2.98×10^{-5}	412
60.0	3.08	2.40×10^{-5}	440

These results show the favorable effect produced by increased rate of flow; the ozone formed is more effectively removed from the destructive thermal or photochemical action, the more the flow rate is increased. These experimental conditions are unsuitable for powerful lamps where thermal decomposition is great; but, on the other hand, when liquid oxygen is used the yields are considerably improved by using 350- or 450-watt lamps. The arrangement used is shown schematically in Figure 3.

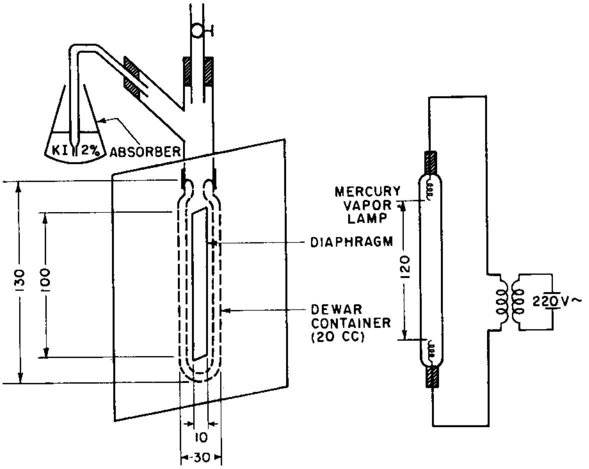

Figure 3. Apparatus used for production of ozone in liquid oxygen

For the energy yield calculations, the lamp is considered as the main axis of a cylinder, the radius of which is equal to the distance between the lamp and the Dewar vessel of transparent quartz. If the radiation losses at the top and at the bottom of the lamp are ignored, approximately all of the energy from the lamp is received by the internal surface of the cylinder. The diaphragm in front of the Dewar cuts out a small arc segment. It can be replaced by a rectangle made up from the width (10 mm.) of the diaphragm times its height (100 mm.). Thus the energy fraction received by the surface of the rectangle can be calculated and, as the energy furnished by the lamp is known, also the yield of ozone per kilowatt-hour.

Table II. Ozone Produced by a 450-Watt Lamp

Distance, Mm.	Ozone Produced, Mg./Hour	Ozone Calculated for Total Circumference, Mg.	Energy Yields, Mg. Ozone/Kw.-Hr.
20	63.5	211	1820
100	9.25	554	1230
240	3.26	417	926
480	0.284	235	522
820	0.043	22.5	50

Table II shows the results with a 450-watt lamp. When liquid oxygen is used, the greatly increased amounts of ozone formed, due to the high concentration of oxygen and intense absorption, suffer relatively very small loss by photochemical or thermal decomposition. The best yield obtained was 1.82 grams of ozone per kilowatt-hour.

Moreover by recovering all of the ozone formed and taking all the necessary precautions when evaporating liquid oxygen and then liquid ozone, approximately 3 grams of ozone per kilowatt-hour were obtained, which constitutes a noticeable improvement over experiments with gaseous oxygen.

The photochemical method of ozone production gives rather low energy yields in comparison to the two methods used industrially—viz., by silent electric discharge or by electrolysis of sulfuric acid solutions.

The silent discharge process is by far the better and is the one used by large firms. By silent discharge through oxygen at ordinary temperatures, ozone in yields of 100 to 150 grams per kilowatt-hour is obtained. Under the most favorable conditions—i.e., the silent discharge unit immersed in liquid oxygen at —183° C., at optimum values of frequency, of current intensity, and of the oxygen gas pressure—yields close to 300 grams per kilowatt-hour have been obtained (*4, 5, 15*). There again the ozone was protected against destructive action by its condensation in the liquid oxygen.

Electrolysis yields only low amounts of ozone, 4 to 7 grams per kilowatt-hour, because the high current densities needed at the anode cause heavy losses of ozone by thermal destruction. Here, too, the yields can be improved by lowering the temperature. Thus, using sufficiently concentrated sulfuric acid solutions, it is possible to electrolyze at temperatures slightly above the eutectic point (—75° C.) of the sulfuric acid–water system, and so obtain yields close to 12 grams per kilowatt-hour (*1, 6*).

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Oxyluminescence of a Few Fluorescent Compounds of Ozone

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Numerous oxyluminescences, which can be obtained in organic chemistry by rising ozone, open new possibilities for ozone assay, and preliminary results show that a suitable method may be found. Numerical values show the sensitivity of this technique. Small paper disks about the size of confetti and containing no more than 1 γ of luminol permit measurements which take only a few minutes. Relatively simple electronic devices permit translation of these luminescence phenomena into doses (percentages).

Attempts to classify the chemiluminescence reactions (*4*, *6*) have shown that the oxidants capable of producing oxyluminescence are but few in number and that ozone plays an outstanding role in the excitation of organic compounds.

As photometric methods have been improved recently by the introduction of photocounters and photomultipliers, it is now possible to study such phenomena quantitatively. By the use of such equipment chemiluminescence becomes a new physical method for the study of certain chemical reactions. Thus, certain chemical factors can be expressed as a spontaneous luminescence which can be recorded.

In the experiments described the authors have tried to find out whether it is possible to determine ozone quantitatively by a method based upon organic oxyluminescence phenomena.

Chemiluminescence Brought about by Ozone

Pure Ozone. Luminosity may be obtained simply by the thermal decomposition of ozone. Schuller (*24*) noted that ozonized water emitted a weak light, and Meyer (*19*) expressed the opinion that this phenomenon really was responsible for the light emission by phosphorus. Beger (*3*) by working at 350° C. was able to show that the luminescence could be attributed to the transformation of ozone into oxygen. This was the conclusion which Dewar (*13*) also drew from his vacuum experiments.

Stuchtey (*28*) studied the phenomenon by means of spectral analysis at 400° to 450° C., and noted that the spectral composition of the light varied with different concentrations of nitrogen and water vapor.

On the basis of work done by Wulf (*32*), Barbier, Chalonge, and Masriera (*2*) recently studied oxygen and air containing ozone and plotted the continuous spectrum from 3850 to 6500 A. (the sensitivity limit of their plates); this spectrum proved to be similar to that of active oxygen discovered by Lord Rayleigh [according to Strutt (*27*)].

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In this spectrum Stoddart (*25*) discerned the bands which Kondratjew (*18*) had obtained by thermal excitation of nitrogen dioxide; thus there is definitely a discrepancy between these results and those obtained by Stuchtey, which is obviously due to the different experimental techniques.

Ozone in Presence of Mineral Compounds. With the metalloids, Baker and Strutt (*1*) have reported an orange oxyluminescence with iodine and with sulfur (which shows a continuous spectrum from 2300 to 4800 A., with a band spectrum from 2300 to 2600), the ultraviolet spectrum here having been studied by Zabiezynski and Orlowski (*33*).

According to Chappuis (*12*), phosphorus glows in oxygen under atmospheric pressures, as soon as some ozone is introduced. These results have been corroborated by Centnerszwer (*11*).

Among the metals, Baker and Strutt (*1*) investigated the emission spectrum from sodium and thallium produced by the action of ozone.

Chemiluminescence is also shown with a few simple mineral compounds. Otto (*21*) expressed the opinion that, if ozone causes a luminescence in the presence of water, it acts upon impurities therein. Hydrogen sulfide gives rise to an ultraviolet chemiluminescence with ozone (Zabiezynski and Orlowski, *33*). Several oxygen compounds of nitrogen, especially nitric oxide, show, under the action of ozone, a spectrum different from that of active nitrogen [Morren (*20*), Sarrasin (*23*), Strutt (*26*), Knauss and Murrey (*17*)]. Solid phosphorus trixode becomes luminescent [Thorpe and Tutton (*29*)]; and so do carbon monoxide, carbonyl sulfide, and carbonyl chloride at 200° C. The first of these furnishes a band spectrum of 4000 to 5000 A. which corresponds to a bimolecular process [Trautz and Seidel (*31*) and Trautz and Haller (*30*)]. Siloxane too shows oxyluminescence [Kautsky and Zocher (*16*)] under the influence of ozone.

Finally the phosphorescent zinc sulfide under the influence of ozone emits a diffuse light with scintillations [Richarz and Schenck (*22*)].

Ozone in Presence of Organic Compounds. Numerous oxyluminescences produced by the action of ozone are brought about with hydrocarbons or their heterocyclic analogs, such as benzene and thiophene [Otto (*21*)]; ethyl alcohol [Otto (*21*)]; polyphenols in aqueous or organic solutions, such as resorcinol, hydroquinone, pyrogallol, pyrocatechol, and phloroglucinol; even a glucoside, aesculin; and certain dyes and chlorophyll [Biswas and Dhar (*8*)]. All show oxyluminescence under the action of ozone.

The chemiluminescent hydrazides, especially luminol, produce beautiful luminescence in alkaline solution with ozone [Harvey (*15*); Briner (*9, 10*); Druckrey and Richter (*14*)].

Finally certain naturally occurring liquids, such as impure water, urine, milk, and sea water, under the action of ozone may all become luminous.

The majority of the experiments cited thus far are qualitative and rather old. It is not possible to study them critically. The luminescence was rather weak, and the experimental techniques used were not suitable for establishing any theories based upon the experimental findings. Comparative study of chemiluminescence and fluorescence spectra has become possible in recent years owing to the progress in optics, especially electron optics. The authors repeated certain experiments with such improved devices for the purpose of obtaining a rapid quantitive analysis for ozone by means of chemiluminescence.

Oxyluminescence Experiments with Paper

Certain experiments by Biswas and Dhar (*8*) were successfully repeated by bubbling ozonized air into water or ethyl alcohol solutions of dyes, euchrosin, and riboflavin.

As this experimental technique was not suitable for furnishing a regular lumi-

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nescence, the authors used chromatographic papers impregnated with solutions and in contact with a gas stream. To get an even distribution of the material under investigation on the paper it was dipped into solution, the excess of moisture was allowed to run off, and the paper was dried vertically by means of rays from an infrared lamp. The edges of the paper were then cut off with scissors, and a fluorescence check under a Wood light confirmed the impregnation. The paper was then cut into round sheets of constant weight, which were rolled together and inserted into a tube through which ozone was passed.

The luminescence was measured by aid of a Lallemand photomultiplier which registered directly on a galvanometer. The ozone was produced by a small generator used for medical purposes which operates at a high-frequency current.

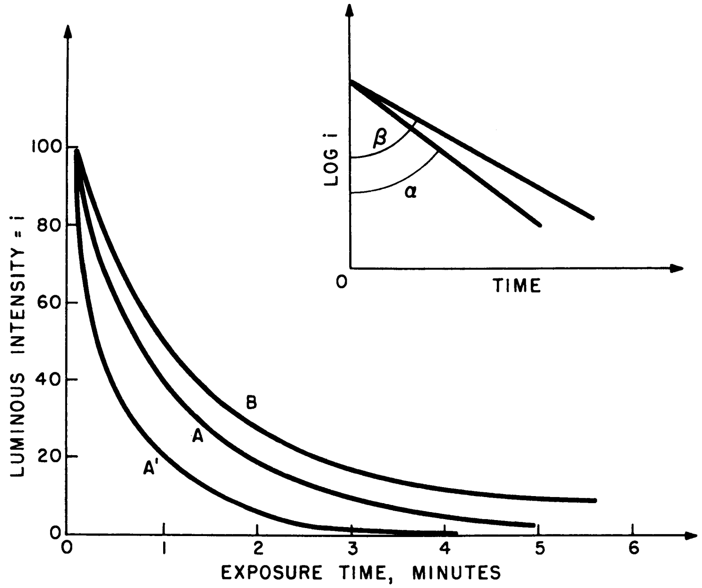

Figure 1. Luminous intensity produced by paper disks treated with luminol and exposed to ozone

A. High ozone concentration
A'. High wet ozone concentration
B. Low ozone concentration
Inset. Action of ozone on dry paper disks

For the measurement only two materials were selected: rhodamine B, which shows a beautiful orange luminescence, and luminol—i.e., 3-aminophthalhydrazide or 2,3-phthalazdione. Luminol was preferred because the yield seemed to be higher and its emission spectrum corresponded better to the spectral sensitivity curve of the photomultiplier. The rhodamine type of compound—i.e., the compound without any substitution—prepared in the authors' laboratory, was not found suitable.

Experiment for Instantaneous Dosage of Ozone. The paper disk became luminescent as soon as ozone was introduced into the air stream circulating in the tube. The luminescence reached its maximum in a few seconds; then the brightness decreased in accordance with an exponential time function (Figure 1).

When the paper was wetted at the moment of use, the reaction went much faster than with dry paper. If the paper was rendered hydrophobic by processes which have been used previously for the observation of organic compound phosphorescence on

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paper (*7*), the luminescence did not appear. This shows that humidity is essential. The luminescence is visible to an eye which has become accommodated to darkness. During the first minutes the color of the light may even be noted.

Thus luminous intensity may be expressed by

$$B = B_0 e^{-Kt} \tag{1}$$

where B is the brightness of the paper at the time t, B_0 is the starting brightness (a function of the ozone concentration and of the paper preparation), and K is a constant which is also a function of the ozone concentration and paper preparation.

By plotting log B along the ordinate, a straight line is obtained

$$\ln B = \ln B_0 - Kt \tag{2}$$

Its slope is proportional to the ozone concentration for any reactive paper which is used under similar conditions:

$$K \cong a[O_3] \tag{3}$$

Thus for a given setup the slope must permit an evaluation of ozone concentration, either by simple proportionality or with the aid of a calibration curve, if necessary. Two measurements in a given time interval will furnish the atmospheric ozone assay by the difference of the logarithms of the instrument deflections. A less precise method would be the determination of the luminosity at a given instant after the introduction of the paper.

Attempt to Measure Total Quantity of Ozone Produced. In an earlier paper (*5*) the change of the total amount of light emitted by the oxidation of a certain quantity of luminol by sodium hypochlorite was studied as a function of the pH. For a pH of approximately 10, the reaction is complete and almost instantaneous. The authors attempted to make a dosage with luminol as it was oxidized by ozone after a paper disk was treated with an excess of sodium hypochlorite solution and to measure the light by means of a photometric setup, including a ballistic galvanometer.

But, in contrast to what was expected, the paper which had been subjected for some time to the action of ozone emitted more light under the action of sodium hypochlorite than paper which had not been exposed to ozone. Figure 2 shows this

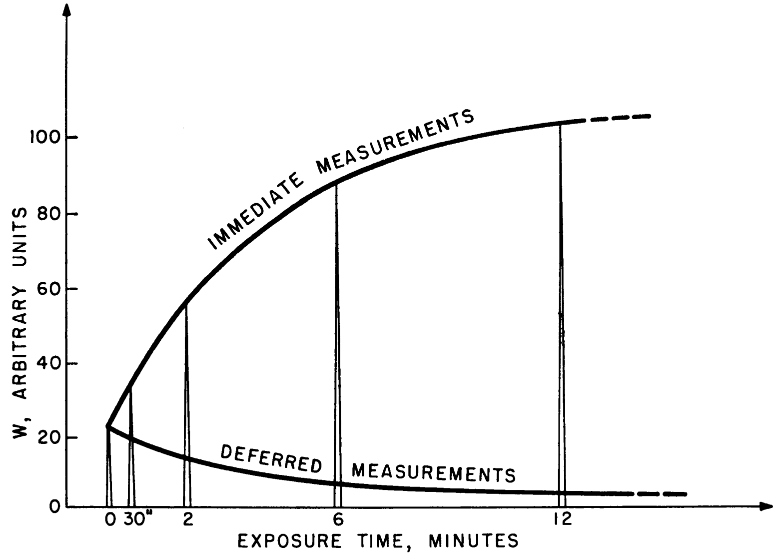

Figure 2. Amount of total light, W, produced by dry paper disks treated with luminol and sodium hypochlorite and exposed to ozone

superactivation, which increases up to a certain limit as a function of the time of passage of ozone. After a sufficiently long exposure the paper ceases to be luminescent under the action of sodium hypochlorite.

The effect of this superactivation disappeared with time, and papers treated with sodium hypochlorite 8 hours after exposure to ozone definitely show amounts of light which decrease when the exposure to ozone has been too great (Figure 2, lower curve).

The reactions occurring during the chemiluminescence of luminol are still not too well known. Several theories have been proposed, but the difficulty of identifying the intermediate products has thus far made it impossible to draw definite conclusions (*5*). Drew suggested that peroxides and ozonides are the intermediate products, but it is also possible that cellulose, which has always been looked upon as an inert carrier, takes an active part in the reaction. Thus the phenomenon in this form cannot be used as a basis for measurements, because one is never interested in a method, which, in order to furnish good results, must be extended over several hours.

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Experimental Data

Photometric Assembly. The photometric assembly (*5*) consists of a Lallemand 18-step photomultiplier—i.e., 18 amplification steps (calcium on oxidized silver)—feeding directly into a galvanometer which moves in steps up to 110 volts. Its sensitivity is about ten times higher than that of the IP 21 RCA which operates with the same voltage. The window of the photomultiplier is 6 cm. from the light source.

Preparation of Papers. The solution used contained 100 mg. of Kodak luminol (or rhodamine B), 50 cc. of 21.2 grams of sodium carbonate in 1 liter of water, and enough distilled water to make 100 ml. of solution; it had a pH of about 9.7.

The paper used was washed, chromatography, No. 302, purchased at the Papeteries d'Arches; 10 sq. dm. has a dry weight of 1.052 grams. When a paper 10 sq. dm. was dipped into the solution and the excess allowed to run off, it retained 2.220 grams of water. The rectangles used first, 9 × 11 × 1 cm., were discarded. The final disks weighed 3.20 ± 0.5 mg.

Ozone Generator. The generator used was an IXU apparatus fed by a blower having an air output of 1.35 liters per minute (air). When the generator was fully active, its ozone assay was 1.5 mg. per liter. The internal diameter of the experimental tube was 5 mm.

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Laboratory Techniques for Handling High-Concentration Liquid Ozone

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Because of the unstable nature of ozone, the usual techniques for determination of physical properties can rarely be applied. Contact with many materials generally used in experimental work, such as rubber tubing, organic stopcock grease, and mercury, must be avoided. The quantity of pure liquid ozone must be kept small in the interests of safety. Even 1 ml. of undiluted liquid ozone can cause a disastrous explosion unless suitable precautions are taken to protect the experimenter.

The production of dilute liquid ozone and its concentration on a laboratory scale are relatively simple. Pure oxygen is passed through a series of three or four glass Berthelot tubes (Figure 1) immersed in a water bath. The central portion of each tube is filled with slightly acidified water and contains a metal rod. The center rods of the tubes are all wired in parallel and connected to the high voltage terminal of a 15,000-volt transformer. The outer bath (Figure 2) is grounded.

Oxygen is passed through the 2-mm. annular space between the inner and outer tubes of the ozonizer, and the ozone-oxygen mixture produced in the Berthelot tubes is condensed in a glass bulb immersed in liquid oxygen. The ozone content of the mixture varies from 1 to 5 mole %, depending upon rate of flow and temperature. Because of the great difference in vapor pressures between liquid oxygen and liquid ozone, oxygen gas can be pumped off the mixture while it is at the normal boiling point (−183° C.) of liquid oxygen. At this temperature liquid ozone has a vapor pressure of only 0.1 mm. of mercury, and its purity can easily be checked by a vapor pressure measurement. Dilution by even 0.1 mole % of oxygen increases the vapor pressure from 0.1 to 6.5 mm. of mercury (Figure 3). On a sulfuric acid manometer, 99.99 mole % ozone would give a reading of 6 mm., compared with less than 1 mm. for pure ozone.

In the laboratory at Tonawanda, N. Y., the liquid ozone-oxygen mixture has always been concentrated by the method of Lainé (Figure 2). Lainé (*8*) used two glass bulbs, each flushed out with nitrogen gas, evacuated, and filled with the vapor from the mixture. This series of operations is conducted alternately in the two bulbs. Lainé's system avoids passing oxygen and traces of ozone through the pumping system. Direct pumping on the liquid ozone is used only in the final stage of concentrating the ozone. From the concentrating system, liquid ozone is vaporized as needed and recondensed in the apparatus to be used for making the physical measurements. The

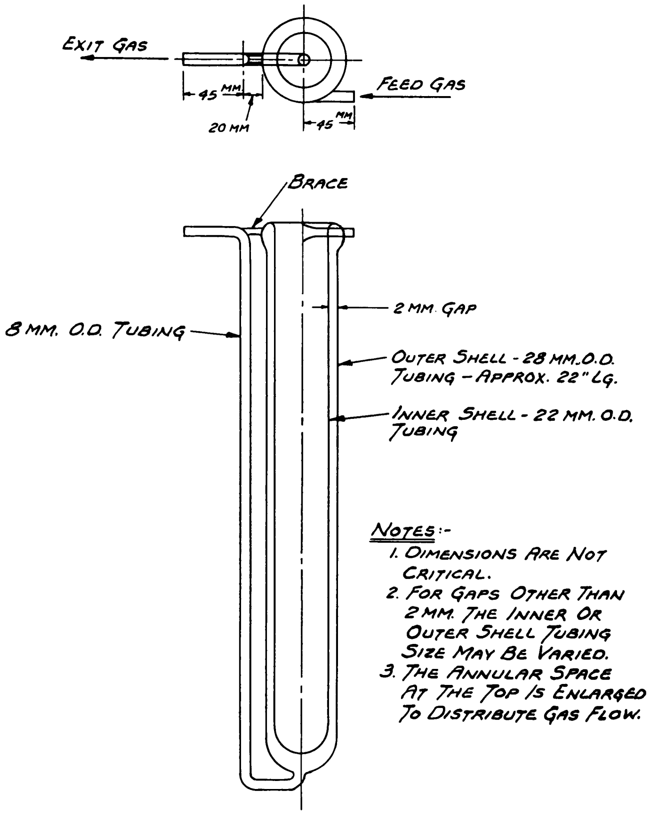

Figure 1. Berthelot ozonizer tube

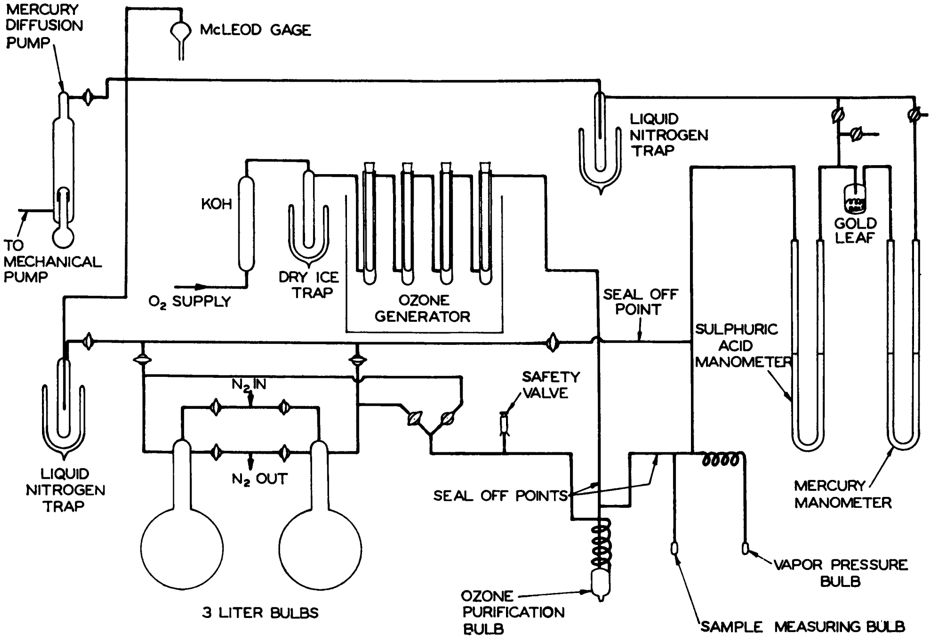

Figure 2. Flow diagram of vapor pressure apparatus

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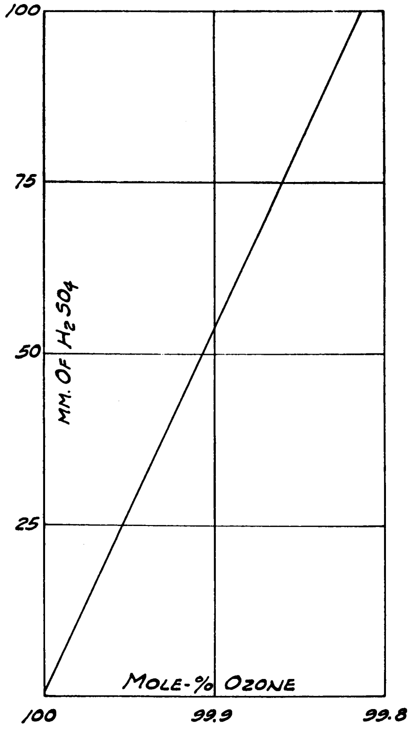

Figure 3. Vapor pressure of ozone-oxygen mixtures at −183° C.

ozone is then subjected to additional pumping to remove any traces of oxygen introduced by decomposition during the transfer, and its concentration is checked by vapor pressure measurement. By making, concentrating, and using the ozone all in the same closed system, contamination is avoided.

One of the questions which arise when pure liquid ozone is used, is how to dispose of the sample when the measurements are completed. The ozone is usually vaporized and then dissolved in a large volume of liquid oxygen in a 2-liter Dewar flask. The very dilute ozone-oxygen mixture is then taken outdoors and poured on the ground over a large area. The apparatus should be well flushed with pure oxygen gas to remove all ozone vapor. The necessity for doing this was discovered when an explosion occurred in a piece of apparatus from which the ozone had been vaporized, and which had been left open to the air over a week end. As this vessel was being removed for alterations on Monday morning, it exploded violently. Evidently much of the ozone had remained in the vessel during this 64-hour period.

Safety Precautions

Every possible precaution must be taken to protect the experimenter in case an explosion occurs. Shields of ¼-inch Plexiglas offer suitable protection against flying glass. Goggles, face shields, leather gloves, and leather aprons should be worn. Dewar flasks can be raised or lowered by modified automobile jacks (Figure 4). Stopcocks can be turned by means of lazy rods inserted through holes in the Plexiglas shields.

Inhalation of ozone should be avoided. A threshold limit value of 0.1 p.p.m. of ozone in air has been adopted by the American Conference of Governmental Industrial Hygienists. This represents the concentration of ozone in air considered safe for an

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch003

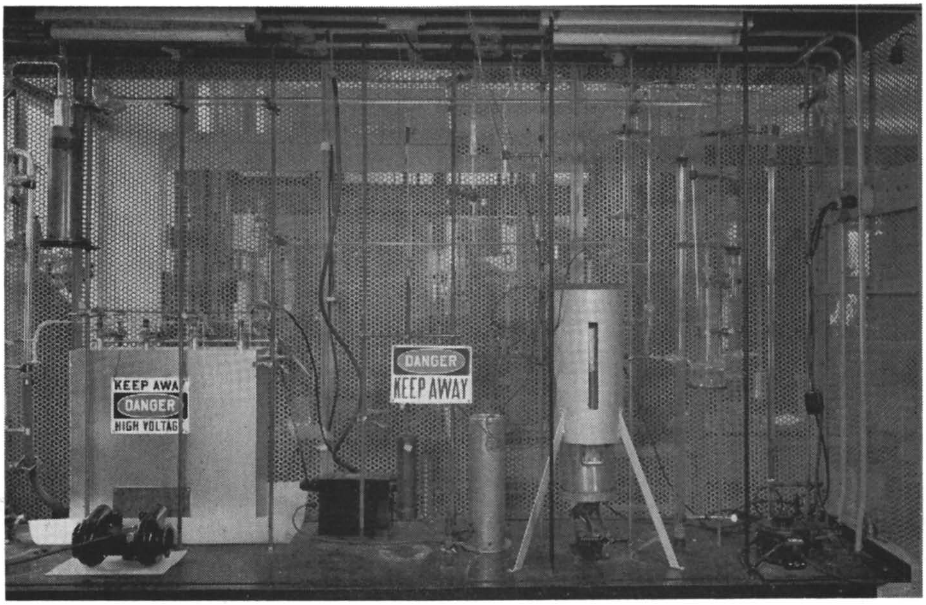

Figure 4. Ozone system

8-hour exposure. A few parts per million may be inhaled without harm for short periods of time. In handling pure ozone, much higher concentrations may accidentally be encountered if suitable precautions are not taken. When it is necessary to purge the apparatus into the air of the laboratory, a gas stream containing a low concentration of ozone may be passed over a catalyst to decompose the ozone. Linde Molecular Sieve Type 13X, used at room temperature, is very effective for this purpose.

Materials of Construction for Laboratory Apparatus

Experience has shown that the most satisfactory material for the construction of small laboratory apparatus is glass. Use of stockcock grease should be avoided if possible, but for some purposes Fluorolube LG (polymer of trifluorovinyl chloride, Hooker Electrochemical Co., Niagara Falls, N. Y.) has been used, stiffened by mixing with colloidal silica such as Santocel. To avoid the use of stopcocks requiring lubrication, glass break seals are sometimes used. Diaphragm- or bellows-type stainless steel valves may be joined to glass by Kovar seals. Concentrated sulfuric acid does not react with ozone and is satisfactory as a manometric liquid. All glassware should be cleaned before use; a sulfuric acid–potassium dichromate solution has been used for this purpose, followed by thorough rinsing with distilled water.

There seems to be considerable evidence that the purity of the oxygen used to make ozone is a factor in ozone stability. After a supply of specially prepared high purity oxygen, 99.995% pure, was obtained, explosions were much less frequent. A part of the improvement may, however, have been due to more experience in handling ozone, and to unknown factors.

One Explosion and Its Probable Cause

In spite of all precautions, explosions may occur. Pure liquid ozone at temperatures near its normal boiling point is particularly dangerous. At this temperature the slightest jar or vibration may cause an explosion. The most disastrous explosion, however, occurred when about 1 ml. of pure liquid ozone was in a glass tube immersed in 2 liters of liquid nitrogen. At this temperature liquid ozone had been thought fairly safe.

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch003

The experiment involved measurement of liquid densities, and spectroscopically pure helium had been used to apply pressure to the ozone column. As preparations were being made to dispose of the ozone, a slight but sudden change in pressure occurred and an explosion took place (Figure 5). The liquid nitrogen was instantly vaporized and the Dewar flask was pulverized. This was the first explosion in more than 18 months of work. Fortunately, there was no serious injury.

At first a Fluorolube oil used as a manometric fluid was suspected as the cause of the explosion. However, two more explosions occurred in the same type of apparatus when sulfuric acid was used as a manometric fluid. It may be that a small but sudden change in pressure caused these explosions by the adiabatic compression of small gas bubbles in the liquid The energy produced by this sudden compression is probably sufficient to start a chain reaction, and the whole mass of ozone is then decomposed. This has been demonstrated with other materials by Bowden and Yoffe (*2*).

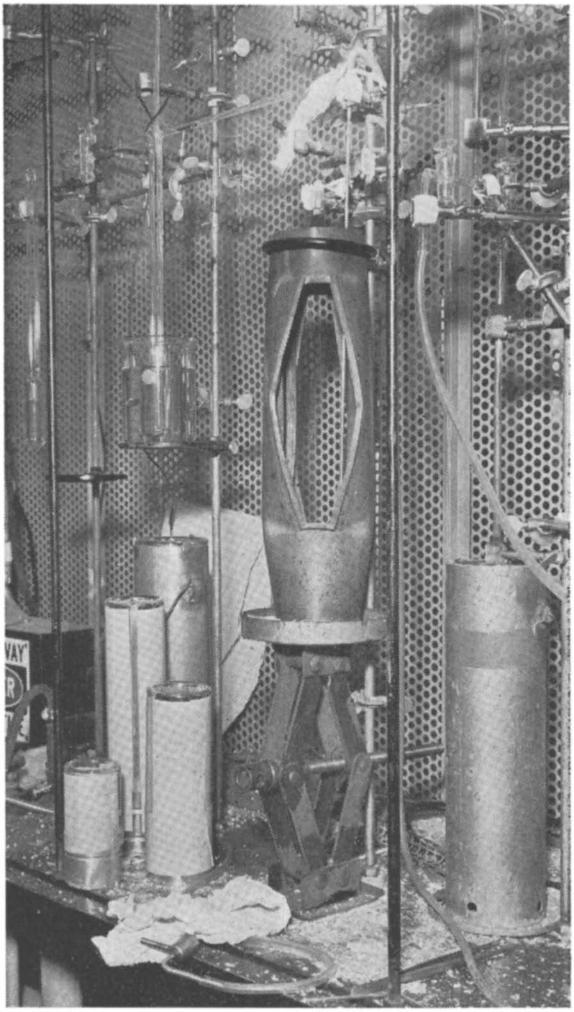
Figure 5. Apparatus after explosion

The author's experiences confirm those of Riesenfeld and Schwab (*9*), who in 1922 wrote, "By avoiding even the slightest traces of ozone decomposition catalysts, (ether, for example), rapid increases in pressure, or warming, we have so far never had an explosion of liquid ozone."

Measuring Physical Properties of Liquid Ozone on Small Samples

For vapor pressure measurements a copper block was used, $1\frac{3}{8}$ inches in diameter and 8 inches long, with a central drilled well for the vapor pressure bulb, and a thermocouple well (Figure 6). The copper block was provided with an external copper cooling coil and a heating coil. The block was suspended from a Transite top in an otherwise empty Dewar flask. The copper block was cooled by passing liquid nitrogen or cold gaseous nitrogen through the coil, and the temperature was

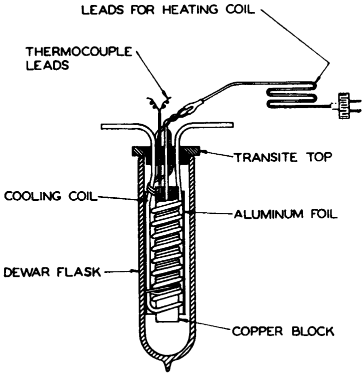

Figure 6. Copper block cryostat for vapor pressure measurements

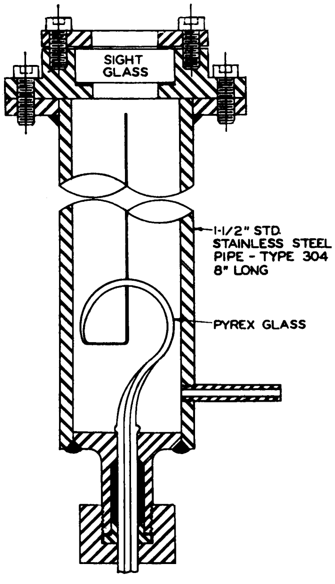

Figure 7. Sickle gage assembly for high range vapor pressure measurements

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controlled by means of the heating coil. Vapor pressures above 1 atm. were measured with the help of a glass sickle gage (Figure 7) attached to the vapor pressure bulb and used as a null pressure device. The internal pressure was balanced by external nitrogen pressure which was measured on a calibrated test gage.

Determination of the curve of boiling point *vs.* time (Figure 8) presented another problem in apparatus construction. This experiment was carried out to prove that there is no azeotropic mixture of ozone and oxygen boiling at −105° C., as reported by Schumacher in 1953 (*10*). If Schumacher were correct, a freely boiling ozone-oxygen mixture would stop becoming richer in ozone when it reaches a temperature of −105° C. At this point, liquid and vapor would have the same composition, 87 mole % ozone, and the mixture would boil at this temperature and maintain constant composition until depleted. The experiment showed that no such maximum in the boiling curve exists and that the mixture keeps getting richer in ozone until it reaches the boiling point of pure ozone, −111.9° C.

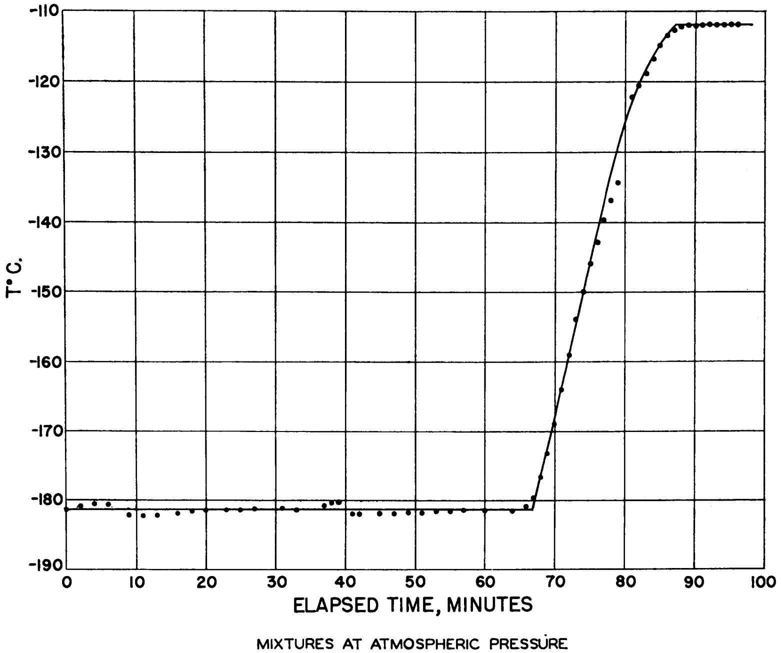

Figure 8. Boiling point *vs.* time curve for ozone-oxygen mixtures

The chief experimental problem was to measure correctly the temperature of the mixture down to the last 0.5 ml. of liquid. For this purpose the apparatus shown in Figure 9 was devised.

The lower part of the inner vessel had a capacity of about 0.7 ml. It had a small re-entrant tube extending upward about half-way. A 30-gage copper-constantan thermocouple was wound (in several turns) around the outside and the junction inserted in the re-entrant tube, which was then filled with wax to provide thermal contact. The inner vessel was filled with about 25 ml. of the ozone-oxygen mixture and the outer vessel was evacuated to reduce the boiling rate. The liquid nitrogen bath (not shown), was removed, and the mixture allowed to evaporate at atmospheric pressure. The apparatus was tested first with liquid oxygen and gave the correct boiling point down to the last 0.5 ml. of liquid.

A somewhat similar arrangement was used to determine the melting point of pure ozone (Figure 10). Here it was necessary to measure accurately the temperature of a small sample.

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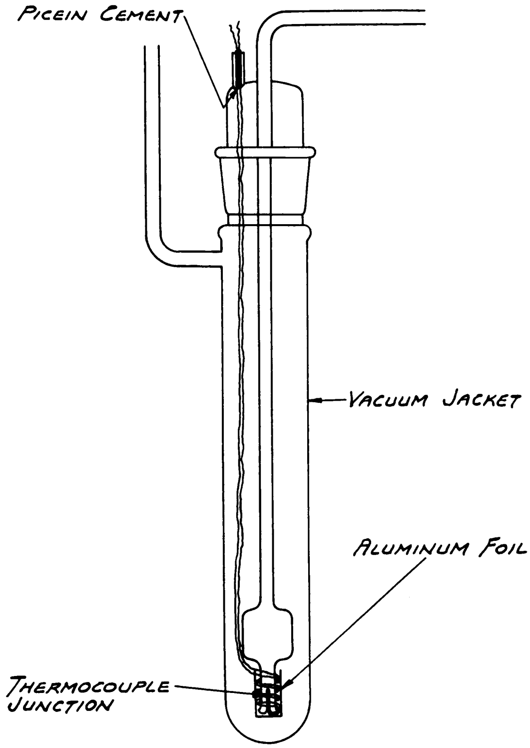

Figure 9. Boiling point apparatus

Helium was admitted to the space surrounding the innermost tube to increase the rate of thermal conduction. The temperature of the liquid air in the liquid air space was lowered by pumping on it. Somewhere below —200° C., the pure ozone in the inner container froze. Pumping on the liquid air was then stopped and it was allowed to warm up to its normal boiling point. At the same time the helium was pumped out of the space surrounding the sample tube. Temperatures of the ozone were recorded against time and the melting curves shown in Figure 11 obtained. Satisfactory freezing point curves were not obtained with this apparatus, because ozone supercools readily. By the time the ozone froze, the liquid air was 20° to 30° below the equilibrium freezing point of ozone.

For about 30 years the melting point value given in handbooks has been —251° C., a value reported by Riesenfeld and Schwab in 1922. The true figure is —192.5° C.

The experimental techniques described are only a few of the methods used (*1, 3, 7*).

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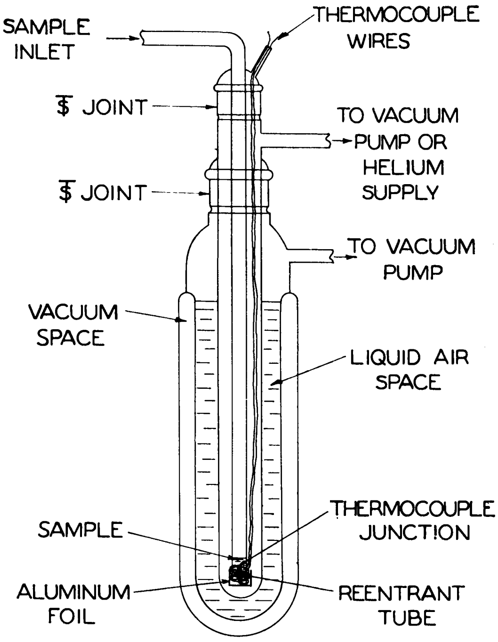

Figure 10. Melting point apparatus

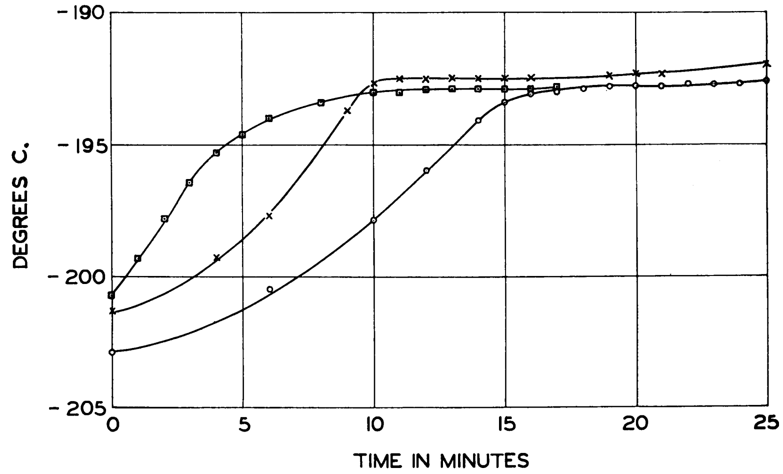

Figure 11. Melting point curves for pure ozone

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Physical Properties of Liquid Ozone-Oxygen Mixtures: Density, Viscosity, and Surface Tension

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By the use of measured volumes of liquid ozone at low temperature, liquid ozone-oxygen mixtures are prepared without ozone decomposition. Techniques for the preparation, mixing, disposal, and measurement of the physical properties of these mixtures are described at the liquid phase boundaries at −183° and −195.5° C., the specific volume of ozone-oxygen mixtures is additive within experimental error (0.005 gram per cc). The viscosity of solutions at −183° C. (on a log scale) varied linearly with the composition from 0.189 cp. for 100% oxygen to 1.57 cp. for 100% ozone. At −195.5° C., the viscosity of supercooled liquid ozone is 4.20 cp. Single phase liquid ozone-oxygen mixtures are Newtonian fluids. The surface tension of liquid ozone is 43.8 and 38.4 dynes per cm. at −195.5° and −183° C., respectively. The parachor of liquid ozone is 76.5.

The decomposition of ozone at ordinary temperatures complicates the preparation of mixtures of known composition. At liquid air temperatures, thermal decomposition is negligible and, with precautions to avoid sensitized decomposition, stable liquid mixtures may be prepared. The density of liquid ozone has been reported (*3*) with a margin of error of ±0.25%, permitting volumetric preparation of mixtures with comparable accuracy.

The mutual solubility of ozone and oxygen at −183° and −195.5° C. has been determined by measuring the magnetic susceptibility and vapor pressure (*4*) of solutions, and a critical solution temperature of −180° C is indicated. The vapor pressure-composition data, combined with vapor pressure data for liquid ozone (*1*), were used to interpret the phase diagram of the system (*2*). Measurements of the density and viscosity of solutions and the surface tension of liquid ozone are reported.

Handling of Liquid Ozone

Liquid ozone-oxygen mixtures of known compositions were prepared in borosilicate glass apparatus (Figure 1). Before assembly, all components of the apparatus were

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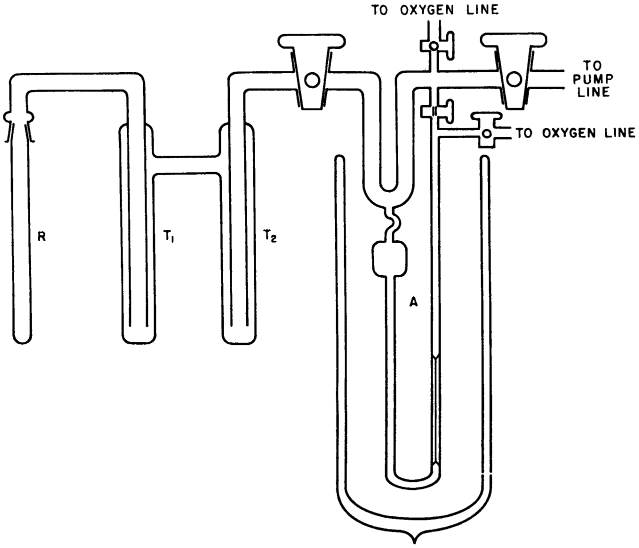

Figure 1. Apparatus for determination of physical properties of liquid ozone-oxygen mixtures

cleaned with chromic acid and rinsed with distilled water. Stopcocks and the taper joint at *R* were lubricated with a low vapor pressure halocarbon grease applied with a clean glass rod. After assembly, and before each run, the apparatus was flushed with oxygen while the portions which were to receive liquid ozone were flamed vigorously with a Bunsen burner.

Oxygen was drawn from a reservoir of liquefied oxygen condensed from a gaseous stream which had flowed over copper oxide at 700° C. Commercial electrolytic oxygen was used after traces of hydrogen and nitrogen had been removed by pumping off a portion of the condensed liquid. A gas buret in the oxygen line was used to measure the pressure and volume of oxygen admitted. Concentrated sulfuric acid was the confining liquid in the gas buret (*4*) and the gas pressure was read on an absolute mercury manometer. Gas in the buret was separated from the manometer by a U-tube filled with sulfuric acid to avoid contamination. The pump line was trapped with a cold trap (liquid oxygen) to condense pump vapors and a hot trap (400° C.) to decompose ozone vapor.

Ozone (approximately 1 ml.) was prepared by corona discharge in a laboratory ozonizer and condensed in the receiver tube, *R*. Tube *R* was then attached to the apparatus, T_1, which was cooled in liquid nitrogen. The system was evacuated, and ozone was distilled successively into T_1, T_2, and the U-tube section of the apparatus, *A*, with the system open to the pump. The multiple distillation ensured removal of oxygen. Results indicate that oxygen is easily removed from liquid ozone and that a single distillation through a re-entrant trap is sufficient.

Before the apparatus was assembled, the volume of the U-tube was determined as a function of the distance from a reference mark at the bottom of the tube. The volume of liquid ozone collected was then determined by reading the liquid level with a cathetometer. The liquid level was viewed through an unsilvered strip in the Dewar flask and the boiling liquid oxygen (or nitrogen) which was used as a refrigerant. The distortions inherent in these readings limited the accuracy, but the compositions at the liquid phase boundaries were reproducible within 0.5%.

Metered quantities of oxygen were admitted from the gas buret into the right arm of the U-tube. With a vacuum applied to the left arm, oxygen bubbled through the liquid violently, showing that ozone at low temperature can withstand considerable agitation without detonation. However, several samples exploded when attempts were made to stir the liquid magnetically with a glass-enclosed iron pellet. Solutions were mixed by using the sulfuric acid in the gas buret as a piston, alternately increasing the

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pressure on the right arm of the U-tube and decreasing the pressure on the left arm. Constant vapor pressure was attained in a few cycles, and the dissolved oxygen was given by the difference between the total oxygen admitted and that in the vapor phase. The volume of gas in the vapor phase was determined without ozone in the system. The liquid oxygen (or nitrogen) temperature bath was stirred with a stream of gas of the same composition and close control of both the bath level and its rate of evaporation was needed to maintain a constant volume of vapor. Bath temperatures were read with an oxygen vapor pressure thermometer.

The portion of the apparatus shown in Figure 1 was enclosed in a ventilated hood behind a safety glass window. Operators wore safety glasses and welding face masks and gloves when exposed directly to liquid ozone. At the end of a run, oxygen was admitted to atmospheric pressure, and tube *R* was removed. A flow of oxygen was bubbled through the mixture in the U-tube, while the Dewar flask was lowered slowly until liquid ozone evaporated.

Density

Liquid ozone solutions were prepared in a U-tube similar to that shown in Figure 1 but without the capillary section. A second U-tube, connected in parallel and filled with a low vapor pressure fluorocarbon oil (Kel F No. 10; density, 1.933 grams per cc. at 27.4° C.), permitted comparison of the hydrostatic heads of the two liquids when a fixed pressure was applied across the manometers. For 100% ozone (*3*), the fixed pressure was applied by admitting helium to one arm of each U-tube. With oxygen solutions, oxygen condensed when helium was admitted and a fixed pressure differential was more easily obtained by removing a small volume of oxygen from one arm. The rate of evaporation of oxygen from ozone-rich solutions was sufficiently slow to permit readings of the liquid levels. In oxygen-rich solutions, evaporation was too rapid for reliable readings.

The density of the saturated solutions at −183° and −195° C. was determined. Oxygen was admitted until a small amount of the oxygen-rich phase appeared. In the mixing procedure described, this was transferred entirely to the left arm of the U-tube. A pressure differential was produced by removing a small quantity of oxygen from the right arm of the U-tube, and the density of the ozone-rich phase was determined by comparing the hydrostatic heads of the solution and the fluorocarbon oil. Excess oxygen was admitted to form a substantial quantity of the oxygen-rich light phase which was transferred largely to the left arm of the U-tube in mixing. The ratio of the densities of the two phases was determined from the hydrostatic balance without a pressure differential in the vapor phase.

In Table I, the results are compared with the densities calculated from the sum of the volumes of liquid ozone and oxygen in the mixtures:

Table I. Density of Liquid Ozone and Oxygen and of Saturated Liquid Mixtures

At −195.5° C.				At −183° C.			
Ozone		Density, G./Cc.		Ozone		Density, G./Cc.	
Wt. %	Mole %	Exptl.	Eq. 3	Wt. %	Mole %	Exptl.	Eq. 2
0	0	1.200 (*6*)	...	0	0	1.146 (*6*)	...
9.0	6.2	1.230 ± 0.004	1.229	29.8	22.1	1.245 ± 0.003	1.245
90.8	86.8	1.563 ± 0.005	1.566	72.4	63.6	1.426 ± 0.004	1.422
100.0	100.0	1.614 (*3*)	...	100.0	100.0	1.571 (*3*)	...

$$1/\rho_s = 1/\rho_{O_2}(1 - W) + 1/\rho_{O_3} W \qquad (1)$$

where

ρ_s = density of the solution

ρ_{O_2} = density of liquid oxygen

ρ_{O_3} = density of liquid ozone

W = weight fraction of ozone

The deviation from additive volumes is less than the experimental error for the four solutions measured. The density of the solutions may be calculated to ±0.3% from the sum of the volumes of liquid ozone and oxygen:

At $$-183^\circ \text{C.},\ 1/\rho_s = 0.833 - 0.213\,W \tag{2}$$

and at $$-195.5^\circ \text{C.},\ 1/\rho_s = 0.888 - 0.238\,W \tag{3}$$

Viscosity

The viscosity of ozone-oxygen mixtures was determined in a modified Ostwald viscometer, which was used with a variable volume of liquid. The viscometer, shown in section *A* of Figure 1, was made from precision-bore glass tubing (4-mm. bore) with a capillary section 0.28 mm. in diameter and 10 cm. long.

Liquid was forced to a convenient height above the capillary section by helium pressure, or by withdrawal of oxygen in the case of ozone-oxygen solutions. Then the stopcock isolating the two arms of the viscometer was opened and readings of the height, *h*, of liquid as it fell through the capillary were taken as a function of time. The driving pressure was proportional to the difference between the liquid and the equilibrium levels $(h - h_e)$ and, in uniform bore tubing, the rate of flow was proportional to dh/dt. Hence, for liquids following Poiseuille's law, $\log(h - h_e)$ should be proportional to the time of flow. In every case, a linear relation between $\log(h - h_e)$ and time was obtained, which shows that ozone-oxygen solutions are Newtonian fluids. Typical plots are given in Figure 2.

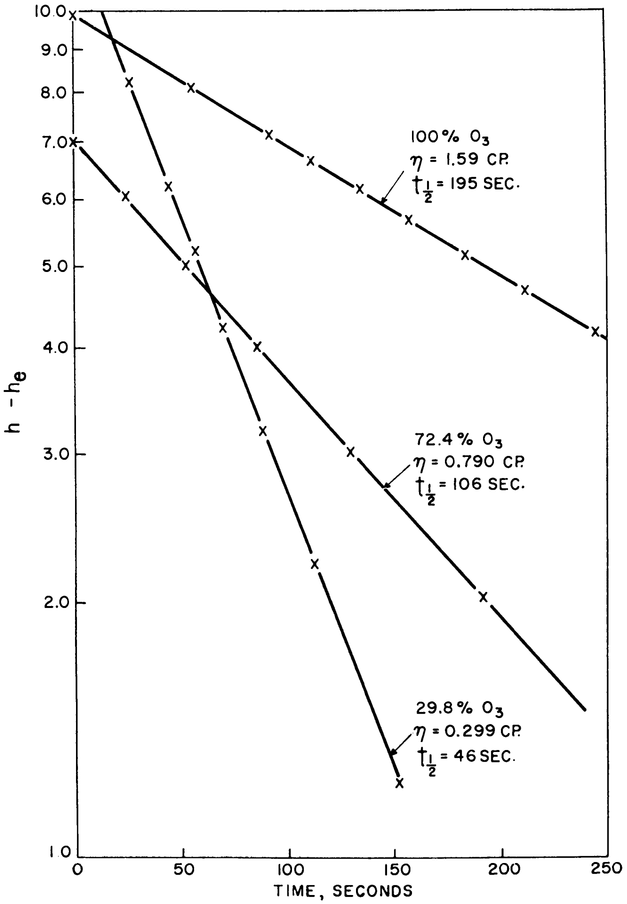

Figure 2. Typical flow curves for ozone and ozone-oxygen mixtures at −183° C.

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For convenience, the half time, $(t_{1/2})$, which is the time required for the liquid to fall one half the distance from the initial level to the equilibrium level, was determined from the plots. The viscosity was calculated from the equation:

$$\eta = c\, t_{1/2}\, \rho$$

where η = viscosity

ρ = the density of the fluid

c = an apparatus constant determined with liquids of known viscosity.

Good agreement was obtained in the relative viscosities of water (1.00 cp.) and ethylene glycol (16.1 cp.) at 20° C. and liquid oxygen (0.189 cp.) at —183° C. which gave a value of 5.25×10^{-5} cp./cc.-sec. gram for the apparatus constant, c.

The results (Table II) represent at least two independent measurements for each viscosity reported. Viscosities at —183° C., plotted in Figure 3 on a semilog scale against mole fraction, show a nearly linear relation common to solutions of nonassociated liquids (*5*). The viscosity determination of 100% ozone at —195.5° C. was made with liquid supercooled more than 2° C., because the melting point of solid ozone is —193° (*2*).

Table II. Viscosity of Ozone-Oxygen Mixtures

Ozone		Viscosity, Cp.	
Wt. %	Mole %	−195.5° C.	−183° C.
100.0	100.0	4.20 ± 0.01	1.57 ± 0.02
72.4	63.6	...	0.79 ± 0.01
29.8	22.1	...	0.31 ± 0.01
26.0	19.0	...	0.27 ± 0.01
9.0	6.2	0.34 ± 0.01	...
0	0	...	0.189

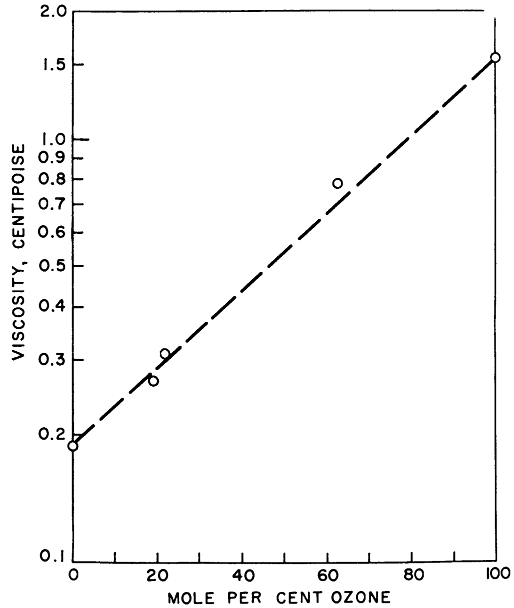

Figure 3. Viscosity of liquid ozone-oxygen mixtures as a function of composition at —183° C.

Surface Tension

The surface tension of pure ozone was determined by the capillary rise method in the apparatus used for viscosity measurements. The ratio of the capillary rise of liquid ozone to that of water at 20° C. was measured and zero contact angle was assumed. Results at —183° and —195.5° C. are given in Table III. The parachor for ozone, calculated from the surface tension data, is 76.5 cgs units.

Table III. Surface Tension of Ozone and Oxygen

Composition, Wt. %		Surface Tension, Dynes/Cm.	
O_3	O_2	−195.5° C.	−183° C.
100	0	43.8 ± 0.1	38.4 ± 0.7
0	100	15.7	13.2

Summary

A striking physical property of liquid ozone-oxygen mixtures is their partial miscibility at temperatures below —180° C. A corollary of this is a high vapor pressure of oxygen over solutions even at low oxygen concentrations. Other physical properties are consistent with solutions of nonassociated liquids. Ozone is not paramagnetic, and the magnetic susceptibility of solutions with oxygen is nearly proportional to the oxygen content. The specific volume of mixtures is additive within the present accuracy of ± 0.3%. Liquid ozone is more than eight times more viscous than oxygen at —183° C., but even liquid ozone supercooled at —195.5° C. flows readily (4.20 cp.). The viscosity of solutions decreases rapidly as oxygen is added, and a semilog relation is approximated when viscosity is plotted against composition at —183° C. The surface tension of ozone is approximately three times that of oxygen.

Acknowledgment

The writers are grateful to coworkers at Armour Research Foundation for many helpful suggestions on the handling of liquid ozone, especially to C. E. Thorp, L. C. Kinney, R. F. Remaly, and G. M. Platz. Thanks are also given to S. Jones, now of General Mills, Inc., for his help with the design of the viscometer.

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Detonation Properties of Ozone

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High concentrations of ozone can explode in a most violent and, usually, unexpected way. The initial ozone pressure affects detonation properties. A notable feature of the ozone system is the wide range of detonation properties in the detonatable region of composition, compared to the hydrogen-oxygen system.

The decomposition of ozone has been of great interest to those concerned with combustion, because of the apparent simplicity of the reaction and the fact that there is only one product gas, oxygen. Lewis and von Elbe (*13*) developed a theory of flame propagation in ozone-oxygen mixtures on the basis of their burning velocity studies. They (*12*) derived high-temperature specific heat values for oxygen from their explosion data.

Preparation and Analysis of Ozone-Oxygen Mixtures

Concentrated ozone was prepared by a method similar to that of Karrer and Wulf (*9*). A schematic diagram of the apparatus is shown in Figure 1.

A stream of ozonized oxygen from a Siemens-type ozonizer (about 3 mole % ozone) was condensed in the trap. The lower part of the trap was encased in a copper sheath to reduce temperature gradients. A heater coil was wound on the surface of the copper. Temperature at the base of the trap was indicated by a copper-constantan couple inserted in a thermocouple well. The thermocouple was attached to a recording potentiometer.

When a sufficient quantity of the liquid mixture had collected in *A*, the ozonizer stream was shut off. The ozone content of the liquid was then enriched by evaporating the oxygen, by opening (slightly) the valve to the vacuum pump. (The pump was protected from ozone by a soda-lime tube.) When the oxygen had been removed, the pump was shut off, and the stopcock to the evacuated storage tank, *D*, was opened. The heater was then turned on and the temperature raised slowly, causing the ozone to boil and collect in *D*. (The liquid-air level in the Dewar was below the bottom of the trap during this operation. A nice control of temperature was possible.) The pressure was followed on a stainless steel Bourdon gage. Accurate pressure measurements were made on a mercury manometer protected by a sulfuric acid buffer manometer.

For analysis, the ozone mixture was admitted into the evacuated analysis bulb, *B* (Figure 1), to a pressure of 10 to 50 mm. of mercury. The gas was diluted with oxygen to a pressure of 1 atm., and bubbled through a potassium iodide solution in *J*. The liberated iodine was titrated with sodium thiosulfate.

Freshly prepared ozone was found to be 95% pure. (Oxygen made up the remainder of the gas.) After standing for 1 day in the storage flask, the concentration of ozone dropped to about 80%, and after about 1 week to 50%.

In OZONE CHEMISTRY AND TECHNOLOGY;
Advances in Chemistry; American Chemical Society: Washington, DC, 1959.

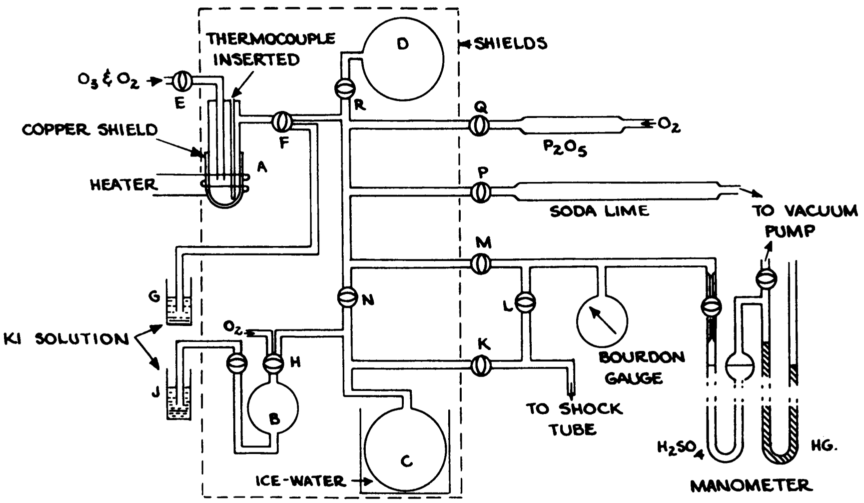

Figure 1. Apparatus for preparation of gaseous mixtures of ozone and oxygen

A. Ozone condenser
B. Ozone analysis bulb
C. Mixing flask
D. Ozone gas storage flask

Ozone-oxygen mixtures of the desired concentration were made up in the mixing flask, *C*, and analyzed just before use. The mixture was finally transferred from the mixing flask to the detonation tube.

Detonation Apparatus

Detonation Tube. The detonation tube assembly is shown in Figure 2.

The detonation tube proper was of stainless steel, 2.54 cm. in inside diameter and 4.9 meters long. Four piezoelectric gages were spaced along the tube at intervals.

Attached by a standard pipe union to the front of the detonation tube was an "initiator" section of equal diameter and 1.9 meters long. For experiments with rich ozone mixtures, which would ignite by a spark and develop a detonation wave, the whole tube, including the initiator section, was filled with the ozone-oxygen mixture. For experiments with more dilute mixtures, where detonation would not build up, it was necessary to start the detonation with a strong shock wave. In order to produce the shock, a cellophane diaphragm was clamped in the pipe union, and the initiator section was filled with a stoichiometric mixture of hydrogen and oxygen (knallgas). The knallgas detonated when it was ignited by a spark, producing a powerful shock wave. Detonation started immediately when the shock wave advanced into the ozone mixture.

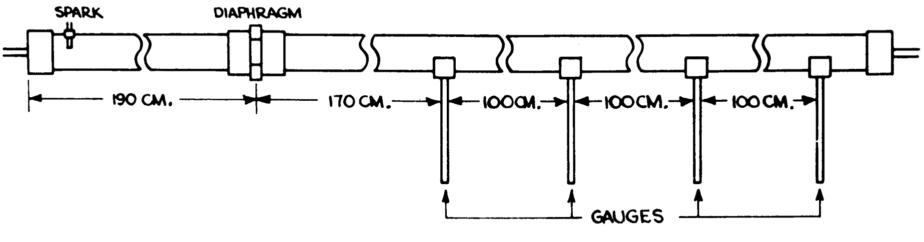

Figure 2. Detonation tube

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Piezoelectric Gages. The gage construction (Figure 3) was similar to that used previously by Gordon (7).

The crystal element consisted of a sandwich of four tourmaline disks mounted on a steel shank. (Crystal elements of this type are available from Crystal Research, Inc., 40 Concord Lane, Cambridge, Mass.) This element, supported by an axial shaft, was held in a 6-inch length of ¼-inch diameter brass tube (standard ⅛-inch pipe). The upper edge of the element was about 1 mm. below the rim of the tube. The tube was filled under vacuum with a warm mixture of medicinal mineral oil and petroleum jelly, which set into a soft gel on cooling. The gage unit was fastened by a threaded joint in the wall of the detonation tube, with the rim of the gage tube flush with the inside of the detonation tube.

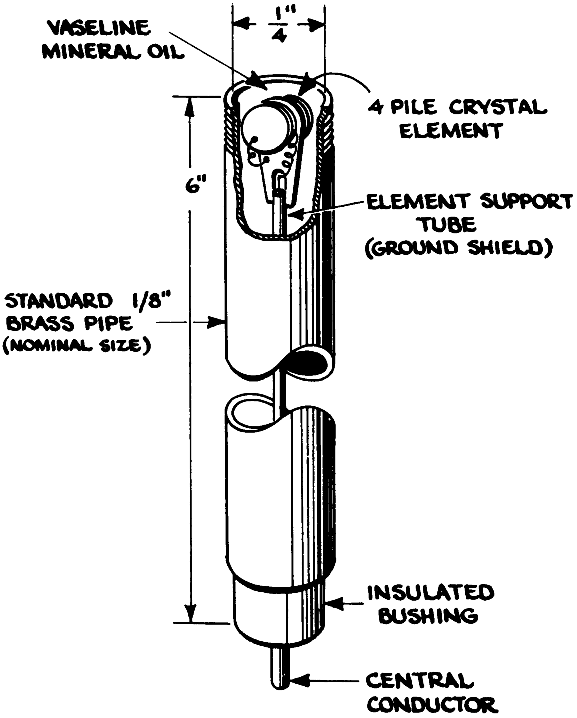

Figure 3. Piezoelectric gage

Calibration. Calibration by three independent methods gave good agreement. The first calibration was made by the manufacturer of the crystal elements, by measuring the electric charge produced when the pressure on the element was suddenly reduced. A similar "static" calibration was made on the complete gage units.

The third method of calibration was more significant for the detonation wave measurements. The gages were mounted in position in the detonation tube. The initiator section of the tube was filled with knallgas and the gage section with air. Upon detonation of the knallgas, a shock wave was produced in the gage section. The shock wave had a contour similar to that of the ozone detonation wave. Therefore, the same dynamic characteristics of the gages were brought into play by the shock wave as by the detonation wave.

For the calibration, the pressure in the shock wave was computed from the velocity through the Hugoniot relation. The velocity (and pressure) of the shock wave produced in this way decays rapidly as the wave progresses down the tube. The

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch005

instantaneous velocity of the wave at each gage was computed by an empirical formula from the average velocities measured in the three intervals between the gage (*8*).

Recording System. A schematic diagram of the recording system is shown in Figure 4.

The amplified signals from the crystals—the four gages were connected in parallel—were impressed on the horizontal-deflection plates of the cathode-ray tube. The screen of the tube was photographed with a rotating-drum camera. The drum ran at a uniform speed and, therefore, the time base was linear. Time calibration was obtained by means of a flashing neon "crater" tube (Sylvania, Type R1130B) which was activated by a 1000-cycle tuning-fork oscillator. The crater tube was in the field of the camera and was photographed simultaneously with the trace on the cathode-ray screen.

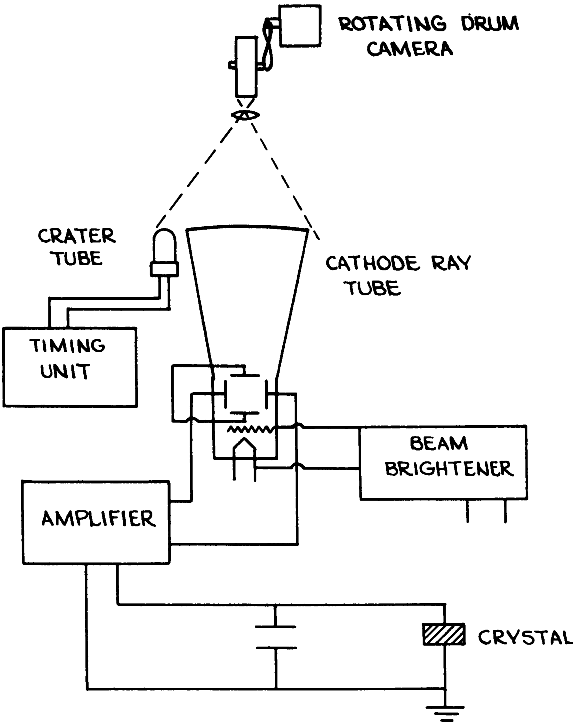

Figure 4. Recording system

Oscillograph Records. The four piezoelectric gages were used to obtain the velocity as well as the pressure of the detonation wave. By reading from the record the time of arrival of the detonation front at successive gages, the average speed of the front in the interval between gages was obtained.

Figure 5 shows typical records for three different concentrations of ozone. The middle record (for 17.3% ozone) is typical of a nonspinning detonation. The vibrations in the other two records are associated with spin.

To measure pressure, an enlarged tracing of the record was made and a smooth median line drawn through the vibrations. The intersection of this median line with the rise line (not visible in Figure 5 because of low intensity) was taken as the detonation pressure.

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch005

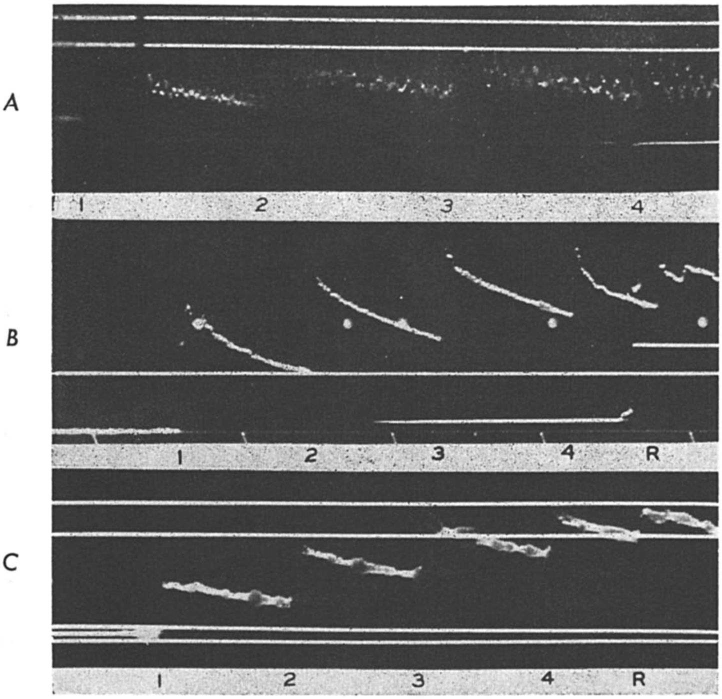

Figure 5. Oscillograph records for various ozone-oxygen mixtures

A. 10.5% ozone
B. 17.3% ozone
C. 77% ozone

Calculated Detonation Properties

The calculated Chapman-Jouget detonation properties for ozone are given in Table I. The methods of calculation are described in several places—for example, by Lewis and von Elbe (*11*).

Table I. Theoretical Detonation Properties of Ozone-Oxygen Mixtures

Ozone, Mole %	Initial Pressure, Atm.	Detonation Temp. ° K.	Product Dissociation, %	Detonation Pressure Ratio	Detonation Velocity, M./Sec.
100	0.100	4018	5.45	29.48	1836
80.0	0.147	3555	3.29	25.75	1781
80.0	0.100	3545	3.54	25.46	1771
75.0	0.132	3426	2.90	24.54	1755
70.0	0.132	3291	2.35	23.52	1736
64.0	0.175	3123	1.71	22.24	1710
45.4	0.172	2533	0.38	17.50	1577
36.8	0.138	2218	0.11	14.88	1481
25.0	...	1733	...	10.98	1302
17.3	...	1373	...	8.26	1144
10.5	...	1019	...	5.77	964
9.2	...	945	...	5.28	921

The initial pressure of the ozone mixture affects the detonation properties through the influence of pressure on the degree of dissociation of the product gases—in this case just oxygen. Therefore initial pressure values were chosen for calculations in Table I to correspond to conditions in the experiments. For low ozone concentrations,

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dissociation is negligible (because of the low detonation temperature), and, therefore, the detonation properties are independent of pressure.

A notable feature of the ozone system is the wide range of the detonation properties in the detonatable region of composition, as compared, for example, with the hydrogen-oxygen system. For this reason, the ozone system provides a good test of the Chapman-Jouget theory.

Detonation Velocity. The detonation wave in ozone mixtures, in common with all systems, reaches a steady state only after traveling some distance in the tube, irrespective of the means of initiation, whether by spark or shock wave. In the beginning, the wave is usually "overinitiated" (*14*), having both a higher pressure and velocity than in the steady state. For the shock-wave initiated mixtures (below 60% ozone), the degree of overinitiation could be reduced by putting a buffer zone of air ahead of the knallgas mixture in the initiator section. The shock wave was thereby attenuated before it reached the ozone mixture. When the average velocities in the last two gage intervals agreed within 1% or better, it was assumed that a steady state had been reached.

Table II. Experimental Detonation Velocities

Ozone, Mole %	Initial Pressure, Mm. Hg	Velocity, M./Sec. Obsd.	Velocity, M./Sec. Calcd.	Deviation, %
77	110	1733	1765	−1.8
77	112	1727	1765	−2.2
73	99	1720	1747	−1.6
64	133	1691	1710	−1.2
64	109	1691	1708	−1.0
45.4	130	1498	1577	−5.0
36.8	105	1406	1481	−5.1
25.0	275	1273	1302	−2.2
17.3	399	1140	1144	−0.4
10.5	486	932	964	−3.3
9.2	497	879	921	−4.6

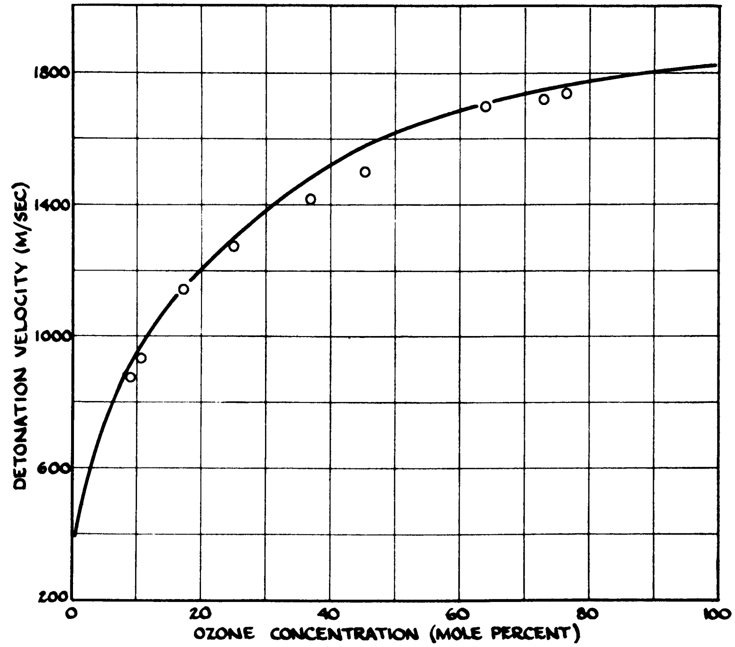

Figure 6. Detonation velocity of ozone-oxygen mixtures

The velocity results are given in Table II. The experimental values (generally slightly lower than theoretical) are also plotted in Figure 6 for comparison with the theoretical curve. Such a result is also found for hydrogen-oxygen mixtures (*15*), and is explained by two factors, heat losses and spin effects. Both effects are greatest in dilute mixtures and at low pressures.

Detonation Pressures. The interpretation of the piezoelectric gage records was not unambiguous. In the first place, many of the records showed large vibrations, especially for the very low ozone concentrations. These vibrations are known to be associated with a spinning detonation wave. Secondly, the records for the 17 and 25% ozone mixtures had the so-called von Neuman "spike" at the wave front. (The sharp pressure peaks are barely discernible in the record for the discernible 17.3% mixture in Figure 5, but they were evident in the original negative.)

A consistent procedure was followed in measuring the records: A median line was drawn through the oscillograph trace, starting at a point well beyond the wave front, and extending back up toward the peak to the point where it crossed the rise line. In this procedure, the contour of the expansion wave is extrapolated back to the shock front. The value obtained in this manner should be closely comparable to the Chapman-Jouget pressure.

Because of overinitiation, the pressure, like the velocity, usually was high on the first gage and dropped off and leveled out on gages 3 and 4. The pressure values from these last two gages agreed within experimental error, the average difference between them being about 7%. In Table III are listed the average pressure values from gages 3 and 4 for several ozone-oxygen mixtures. These points are also plotted in Figure 7 for comparison with the theoretical curve.

Table III. Experimental Detonation Pressures

Ozone, Mole %	Initial Pressure, Mm. Hg	Pressure Ratio		Deviation, %
		Obsd.	Calcd.	
77	110	23.5	25.0	−6.0
77	112	22.6	25.0	−9.6
73	99	21.3	24.1	−11.5
64	133	21.0	22.2	−5.4
64	109	20.2	22.2	−9.0
45.4	130	16.2	17.5	−7.4
36.8	105	13.6	14.9	−8.7
25.0	275	10.4	11.0	−5.4
25.0	181	10.2	11.0	−7.3
17.3	399	7.8	8.3	−6.0
17.3	263	8.2	8.3	−0.1
10.5	486	4.2	5.8	−27.5
10.5	321	4.7	5.8	−19.0
9.2	497	4.5	5.3	−15.0

The experimental pressures are generally several per cent lower than the theoretical values. However, the variation of pressure with ozone concentration is closely in accord with theory. Since energy losses would be expected to lower the pressure by a percentage two to three times as great as that for the velocity, pressure and velocity results are mutually consistent.

Spin

In experiments preceding those on ozone detonations, the effect of sending shock waves from a shock tube into mixtures of ozone, nitrogen pentoxide, and oxygen was investigated. The pressure records from these experiments had oscillations of very high amplitude, hard to explain. On observing in a darkened room the propagation of a shock wave into a glass tube filled with the mixture, it was noticed that the pink

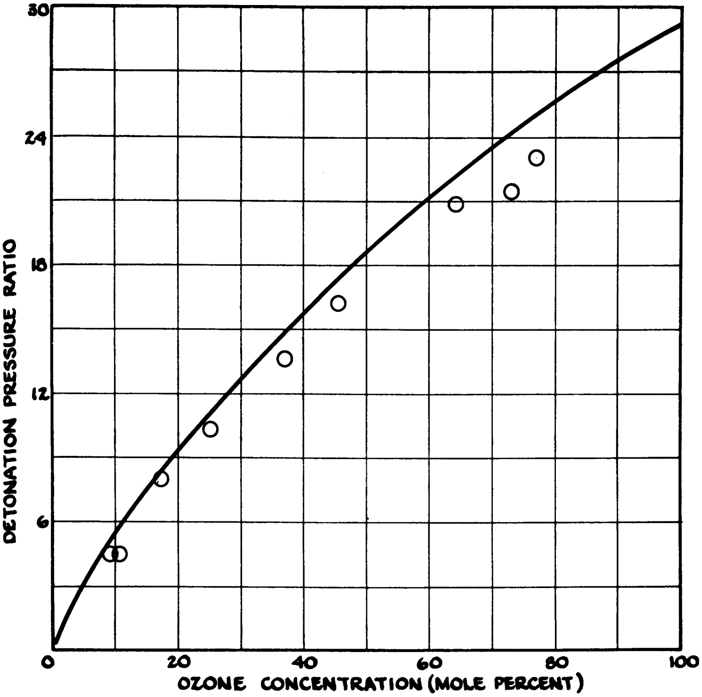

Figure 7. Detonation pressure of ozone-oxygen mixtures

Figure 8. Spinning detonation in a mixture of ozone, nitrogen pentoxide, and oxygen

flame had a "banded" appearance. Figure 8 was taken with an open-shutter camera. Figure 9 is the pressure record of the shock wave from a similar experiment.

A spiraling zone of luminescence (Figure 8) was first observed in detonations by Campbell and Woodhead (*4*), and referred to by them as "spin." Many photographic

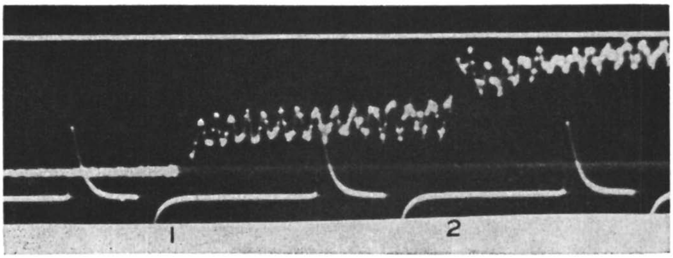

Figure 9. Pressure record of spinning detonation in Figure 8

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investigations of the phenomenon (*1–3*), have since shown that a highly luminous zone, traveling with the wave front, describes a helical path near the surface of the tube. The pitch of the helix was usually about three times the tube diameter.

Clearly, the pressure oscillations in Figure 9 are associated with the spin, for, when the frequency of the oscillations is divided into the shock wave velocity, the "wave length" so obtained is just equal to the pitch of the helix as measured from the photograph (Figure 8). Subsequently, vibrations of this type have been observed in pressure records from many detonations (*14*).

A theory for spinning detonation has been put forth by Fay (*6*). He shows that spin is a self-excited transverse vibratory motion in the burned gas, akin to a standing sound wave, but with helical symmetry. The possible modes of vibration can be calculated from the properties of the gas. The fundamental mode always has a pitch equal to about three tube diameters; higher modes have an apparent pitch smaller than this. Several different modes have been observed and good correlations are found with Fay's theory.

The oscillograph records in Figure 5 illustrate the spin effects found in ozone detonations. For high ozone concentrations, there was a high-frequency (high modal number), relatively low-amplitude spin; in the middle concentration range, there was no spin; and at lower concentrations, a fundamental spin mode developed, which increased in amplitude as the concentration was dropped. The behavior of hydrogen mixtures is very similar to this (*15*).

Many interesting questions remain to be answered about spinning detonation. Why does spin always appear at low concentrations near the detonation limit? What determines the stable mode and amplitude of the spin? What effect, if any, does spin have on the stability of detonations?

Other Features of Ozone Detonations

According to the theory advanced independently by von Neuman (*16*), Doring (*5*), and Zeldovich (*17*), the detonation front is simply a shock wave in the as yet unreacted gas. The reaction is started by the sudden increase of temperature and pressure associated with the shock front, and proceeds in the zone which follows immediately behind it. As the gas reacts, the pressure drops. At the so-called "Chapman-Jouget plane" where the reaction is complete, the pressure has dropped to about one half the value at the shock front. Beyond this point, the pressure decreased more slowly in the normal Riemann expansion wave (*11*).

Until recently, there has been little experimental evidence to support the von Neuman theory. However, Kistiakowsky and Kydd (*10*) have now detected a narrow dense region at the wave front in certain detonations by x-ray flash photography, which appears to be the von Neuman spike (high-pressure reaction zone in front of the Chapman-Jouget plane). The pressure records for stoichiometric hydrogen-oxygen mixtures do not reveal this high pressure region (*7*), but a faint high peak was observed (*8*) in certain dilute hydrogen mixtures.

The von Neuman spike was clearly present in the pressure records of 17 and 25% ozone mixtures. The value at the peak, which according to theory should be about twice as high as the Chapman-Jouget pressure, was only about 25% higher than the latter. However, because of the physical size of the gage and the limited frequency response of the amplifiers, it is not to be expected that a very narrow high-pressure region would be faithfully recorded. Neither the richer nor the weaker ozone mixtures showed the spike phenomenon. The reaction zone may be too narrow to be observed in the richer mixtures. On the other hand, the spike might be obscured in the weak mixtures by the spin effects. Alternatively, spinning detonation actually is perhaps a different mode of propagation from the von Neuman mechanism, and both in rich and weak mixtures where spin is present, there is no von Neuman spike.

Another feature of interest is the low value of the concentration limit for detonation, about 9% ozone. The energy of this mixture is much lower than that of hydrogen-oxygen mixtures at the limit (*15*). The calculated temperature at the shock front (von Neuman theory) for 9% ozone is only 670° K. The corresponding temperature in limit hydrogen mixtures is about 1100° K. These facts may be expressed in another way by saying that ozone is much more sensitive toward detonation than hydrogen-oxygen mixtures.

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Pure Ozone Flame and the Combustion of Various Fuel Gases in Pure Ozone

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The interest in studies of pure ozone, solid or liquid, in explosives lies not only in the momentary production of high temperatures, but primarily in the possibility of determining experimentally the parameters for equations of state for simple molecules in a region of pressures (about 100,000 atm.) and temperatures (5000° to over 10,000° K.) far outside of that which can be investigated by any ordinary method.

In the last few years this institute has been particularly interested in the production of high temperatures by chemical methods. The two prerequisites for producing high temperatures are: a reaction with a high heat release, and thermal stability of the reaction products.

Carbon monoxide and nitrogen are thermally the most stable molecules known. By burning cyanogen with oxygen to these products at 1 atm. a temperature of 4800° K. was produced (*2*). By carrying out the same combustion under pressure 5050° K. has been attained (*1*). By using a more endothermic compound, such as carbon subnitride, or C_4N_2, a temperature of 5260° K. has been reached (*5*). By combining the above endothermic fuels with an endothermic oxidizer, still higher temperatures should be attainable. Because ozone is an obvious substitute for oxygen, combustions with ozone were studied.

Ozone is one of the most sensitive compounds known and at high concentrations is prone to explosions or detonations. For this reason the decomposition or "combustion" flame of ozone to oxygen was first studied. The heat of combustion of ozone to molecular oxygen or $\Delta H°_f$ at 291° K. $= -33.92$ kcal. per mole. In view of this high heat liberation it was expected that pure ozone could be burned to oxygen in a visible flame, if its explosion or detonation could be avoided. Ozone-oxygen mixtures and even pure ozone can be burned in a regular flame to oxygen without mishap, if the ozone used is pure and free from sensitizers. The ozone was purified by the method first described by Thorp, Armour Research Foundation (*7*). The experimental procedure has been described in detail by Streng and Grosse (*6*).

Pure ozone burns to oxygen with a blue flame with a typical pink cast. The luminosity of the flame is low, although its temperature is 2677° K. for 100% ozone at 1-atm. pressure and 300° K. initial temperature. The experimentally determined burning velocity under the same conditions is 475 cm. per second.

The pure ozone flame is of particular theoretical interest, because it represents the simplest flame imaginable. The only possible intermediates between the initial and final products are oxygen atoms. T. von Karman, J. O. Hirschfelder, and their

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associates and R. Sandri have developed the theory of laminar flame propagation. Recently this theory was applied by von Karman when calculating the theoretical flame velocity for 100% ozone. His results (*8*) are essentially in agreement with the authors' experimental results. The theories give a detailed insight into the mechanism and kinetics of the flame propagation.

Temperature Effect on Burning Velocity of Ozone

Subsequent to the Yale presentation (*6*), the burning velocity of pure ozone was also determined at —78° C. and found to equal 270 cm. per second. In first approximation the burning velocity of ozone is a straight-line function of temperature.

Extrapolated Velocities

°C.	°K.	Cm./Sec.
0	273	420
−50	233	325
−112[a]	161	205

[a] Boiling point of ozone.

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch006

Diffusion Flames of Pure Ozone with Fuel Gases

Pure ozone was successfully burned, in a diffusion flame, with hydrogen, carbon monoxide, cyanogen, methane, and ethylene. The ozone was admitted at the rate of ≃ 6 cc. per second through the inner tube of an aluminum burner (tip area 0.34 sq. mm.), while the fuel gases were admitted through an annulus with an area of 1.42 sq. mm., usually in quantities sufficient for complete combustion. Details of the burning tip are given in Figure 1. Comparative runs were made with the same amount of oxygen.

Ozone burns in hydrogen similarly to oxygen, the only difference being that the ozone flame is slightly brighter. The ozone was admitted first and hydrogen added subsequently.

In carbon monoxide ozone burns with a much brighter flame than oxygen. The carbon monoxide was ignited first, then ozone was admitted. Photographs of this flame are shown in Figure 2, compared with the carbon monoxide–oxygen and pure ozone flame.

Ozone burns in cyanogen with the brightest flame produced so far in these laboratories (Figure 3). The flame temperature is calculated to be 5200° K.—i.e., practically identical to that of the C_4N_2–O_2 flame (*3*). In this case the ozone flame was established first and then the cyanogen was added.

Methane and ethylene, respectively, were ignited first and then ozone was added. Both flames were again brighter than the corresponding oxygen flames.

Self-Igniting Properties of Ozone—Fuel Gas Mixtures

Special tests were made to determine the self-igniting characteristics of the fuel gas–ozone mixtures.

At atmospheric pressure, when the mixture was admitted through the aluminum tip, no ignition took place with hydrogen, cyanogen, and methane (ozone rate 6 cc. per second). Carbon monoxide and ethylene, however, ignited spontaneously and burned normally afterwards without initiating an explosion or detonation in the ozone line.

Static Behavior of 100% Ozone—Fuel Gas Mixtures

The preceding results indicated that mixing 100% ozone with hydrogen, cyanogen, and methane is possible, even if for a very short time. This led to tests of mixing 100% ozone with hydrogen, cyanogen, and methane, respectively. The mixed gases

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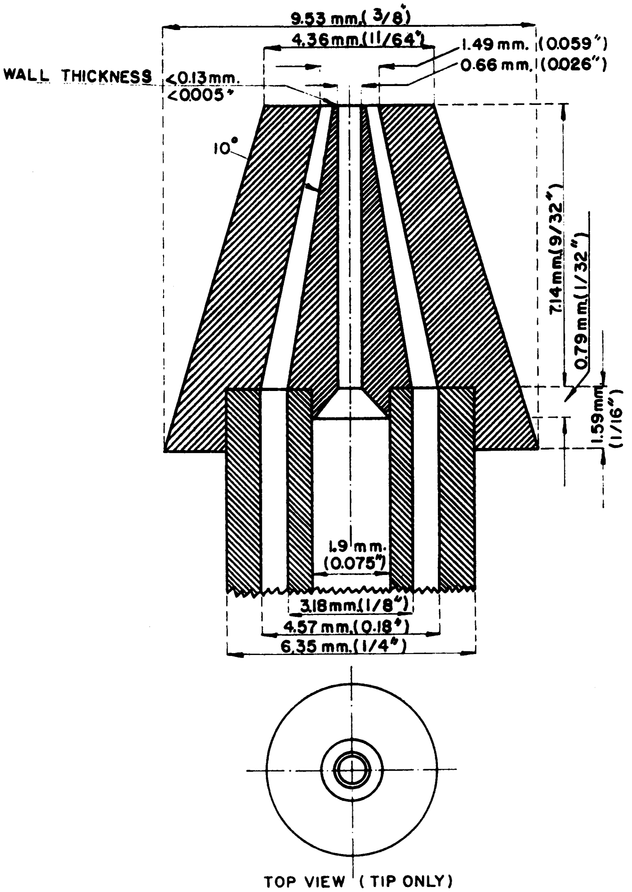

Figure 1. Burner tip for ozone diffusion flames

were allowed to stand in borosilicate glass tubes (Pyrex brand No. 7740) of about 10 cc. volume. The conditions used and observations made are given in Table I.

Table I. Behavior of Various Fuel Gases with Pure Ozone

Mixture	Total Pressure, Mm. Hg	Temp., °C.	Time of Standing, Hours	Results
$4H_2 + O_3$	504	−78	19	No change in pressure. No visible reaction
$4H_2 + O_3$	504	+21	4.0	
$1.5C_2N_2 + O_3$	774	0	2.0	
$1.5C_2N_2 + O_3$	551	+23	18	Pressure increased 6 mm.
$1.5CH_4 + 2O_3$	778	−78	1.0	No change in pressure.
$1.5CH_4 + 2O_3$	804	+21	1.0	Pressure increased 26 mm.

All three mixtures are stable for hours, at least at dry ice temperatures. Methane reacts noticeably at room temperature, while hydrogen and cyanogen cause no change in pressure. The blue color of ozone could be observed after all these tests. On immersing the cyanogen-ozone tube in liquid oxygen, solid cyanogen and blue liquid ozone condensed after the test; on immersing the same tube in a dry ice bath, the unreacted cyanogen was solidified and the unreacted ozone gas pumped off.

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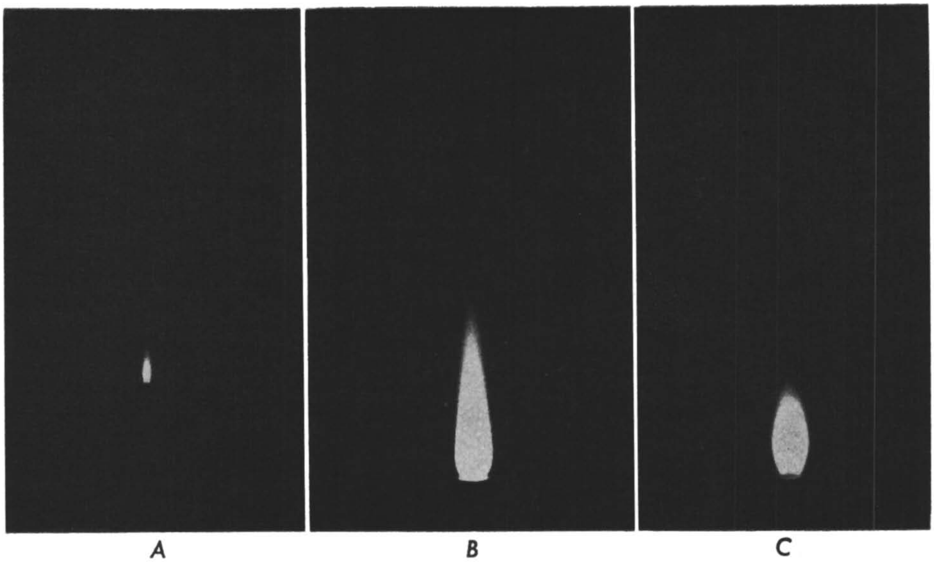

Figure 2. Ozone flames burning at 6 cc. per second

A. Combustion of 100% ozone, 6 cc. per second, to oxygen
B. Combustion of 100% ozone, 6 cc. per second, in excess of carbon monoxide
C. Combustion of pure oxygen, 6 cc. per second, in excess of carbon monoxide

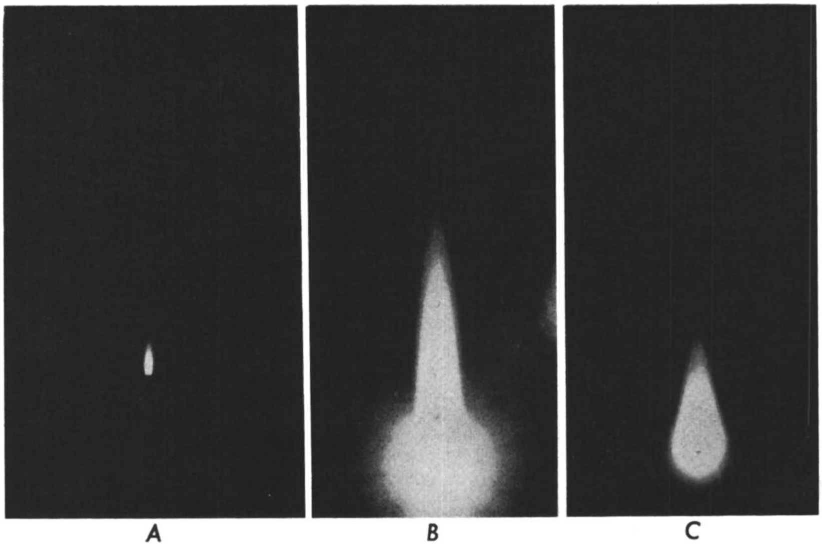

Figure 3. Ozone flames burning at 6 cc. per second

A. Combustion of 100% ozone, 6 cc. per second, to oxygen
B. Combustion of 100% ozone, 6 cc. per second, in excess of cyanogen (temperature of flame 5200°K.)
C. Combustion of pure oxygen, 6 cc. per second, in excess of cyanogen

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Premixed Cyanogen-Ozone Flames

In view of the surprizing stability of cyanogen-ozone mixtures, the gases were burned in long tubes 1.6 mm. in inside diameter, without detonation, at room temperature and atmospheric pressure. In wider tubes, as expected, the mixtures exploded, shattering the tubes completely.

The stoichiometric cyanogen-ozone mixture ($1.5\ C_2N_2 + O_3$) burns very rapidly with a very bright flame but without explosion or detonation. The corresponding mixture of cyanogen and oxygen burns rapidly under the same conditions, although more slowly, and the flame is definitely less bright than the flame with ozone. Pure ozone under the same conditions burns with a fallow flame, again without explosion or detonation. In view of the fact that the same mixtures of cyanogen-oxygen and pure ozone itself can be burned from burner tips at a steady flame at a constant rate, it is likely that ozone-cyanogen mixtures can also be successfully burned in the same manner.

Production of Instantaneous High Temperatures

The demonstrated possibility of premixing various fuels with pure ozone opens up new opportunities for using pure ozone in the study of explosives.

In connection with the above investigation, it has been found that liquid ozone is stable in the presence of cyanogen powder at 90° K. By evaporating liquid ozone in a vacuum it can be solidified in the form of ozone crystals on crystals of cyanogen without explosion.

Careful handling should make it possible to study the detonation of various mixtures of solid cyanogen powder with either liquid ozone or solid ozone powder at various loading densities. Whereas in the gaseous cyanogen-ozone system the highest temperatures are produced when the products of combustion are carbon monoxide and nitrogen, simple application of the hydrodynamic theory of detonation shows that higher temperatures—i.e., up to and even above 10,000° K.—would be reached for the stoichiometric equation:

$$(CN)_2 + 4/3\ O_3 \rightarrow 2CO_2 + N_2$$

because at the very high pressures of a detonation wave in a condensed explosive (of the order of 100,000 atm.) the dissociation of the carbon dioxide molecule is negligible as compared to atmospheric pressure.

Thus detonations of solid cyanogen or carbon monoxide mixtures with solid ozone (or solid oxygen) would give data for the carbon dioxide and nitrogen molecules. Detonations of solid ozone alone would give data on the oxygen molecule, etc. Techniques for handling and studying the solid cyanogen-liquid oxygen system have been developed (*4*).

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Separation of Ozone from Oxygen by a Sorption Process

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Ozone is separated from oxygen by adsorption on refrigerated silica gel, followed by desorption, either in pure form at reduced pressure, or diluted by air, nitrogen, argon, or other gas not strongly adsorbed on silica gel. This is a practical method, free from hazard when correctly performed.

There are several reasons why it might be desirable to separate ozone from oxygen. Because ozone is usually produced in concentrations of only 1 to 4 mole % in a stream of air or oxygen, anyone wishing to use more concentrated ozone, or ozone in the absence of oxygen, must separate the two gases. In a large plant it is more economical to produce ozone from oxygen than from air, if the unconverted oxygen can be separated cheaply enough from the ozone and recycled to the ozone generator.

The separation may be accomplished in several ways. One way is condensing the ozone out as a liquid at a low temperature and then pumping off any oxygen that condensed along with the ozone; this presents the hazards of handling concentrated liquid ozone, a touchy and brisant explosive.

Another possibility is to pass the gas stream through a solvent which will dissolve the ozone while letting most of the oxygen pass through. Early in 1948 the authors discovered that cold, liquid dichlorodifluoromethane (CF_2Cl_2), chlorotrifluoromethane (CF_3Cl), or mixtures of the two, could be used for this purpose. Evaporating ozone gas from one of these solvents entails a loss of solvent and is somewhat hazardous; it should be done only with suitable precautions, preferably at low partial pressure of ozone. A safer way of recovering the ozone is to blow it out with a stream of some gas, such as nitrogen or air, that is not appreciably soluble in the halogenated methane solvent.

Another way of separating oxygen from ozone is to pass the mixture through a vessel containing material that will react with the ozone. The oxygen that passes through the vessel is purified, if necessary, and recycled to the ozone generator. This method is satisfactory if the presence of oxygen in the ozone reaction vessel is not harmful.

A method which is free of hazard if performed correctly, and represents a practical way of separating ozone from oxygen, consists of adsorbing ozone on refrigerated silica gel and then desorbing it, either in pure form at reduced pressure, or diluted by air, nitrogen, argon, or other gas not strongly adsorbed on silica gel.

In OZONE CHEMISTRY AND TECHNOLOGY;
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Adsorption of Ozone on Silica Gel

In 1950 extensive measurements were made of the adsorption of ozone in the presence of oxygen on commercial Grade 40 and PA 100 silica gel purchased from Davison Chemical Corp. The technique used in measuring the adsorption was simple. A stream of dry oxygen at atmospheric pressure and containing a known concentration of ozone was passed through a vessel immersed in a bath kept at a constant, known temperature. The vessel contained a known weight of silica gel fresh from Davison, and not treated in any way before being used. The dilute stream of ozone in oxygen was passed through the bed of silica gel until the concentration of ozone in the off-gas was equal to that in the entering gas. The ozone-oxygen flow was then stopped and a stream of pure, dry oxygen was passed through the silica gel and into a solution of potassium iodide in water. When all the ozone had been desorbed, the liberated iodine was titrated with standard sodium thiosulfate solution (*1*).

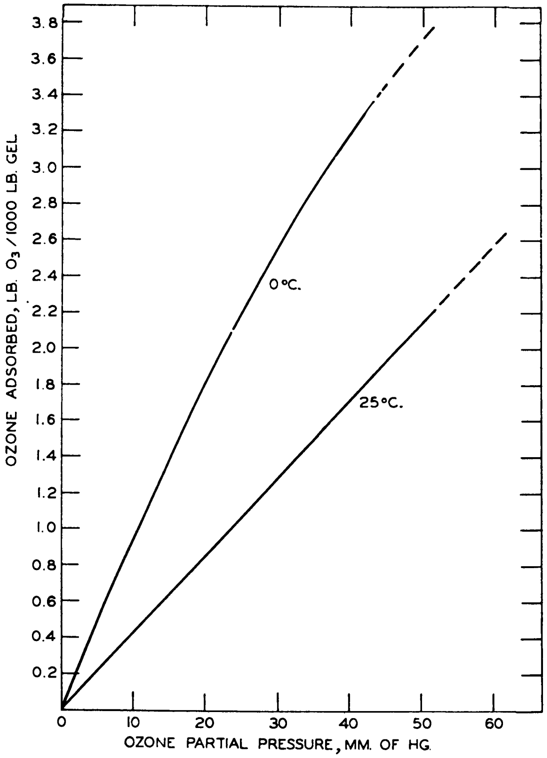

Figure 1. Adsorption isotherms at 0° and 25° C. for ozone in oxygen on Davison silica gel

Total pressure 1 atm.

The isotherms obtained for 0° and 25° C. are shown in Figure 1, and for lower temperatures in Figure 2. The adsorption at 0° C. was very much less than that at —78° C. and below. (The units for the ordinate in Figure 1 are in pounds of ozone per 1000 pounds of gel; in Figure 2, in pounds of ozone per 100 pounds of gel.)

Information from Davison indicated that the two grades of silica gel differed only in particle size, Grade 40 being 6 to 12 mesh, and PA 100 being 14 to 20 mesh. Differences in ozone adsorption between the two grades were within experimental error.

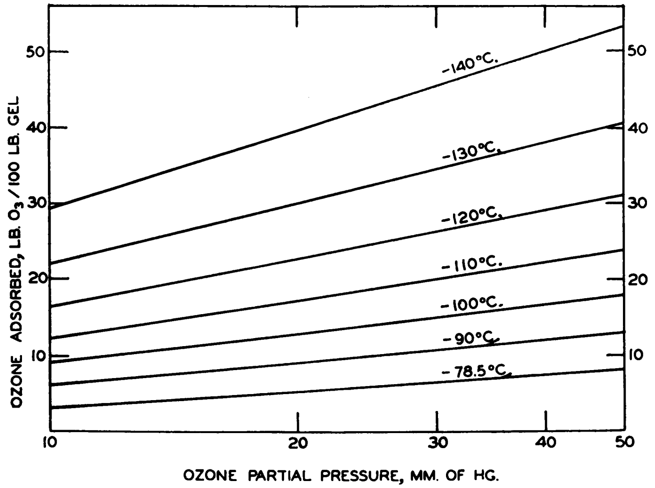

Figure 2. Smoothed adsorption isotherms for ozone in oxygen on Davison silica gel at temperatures ranging from −78.5° to −140° C.

Total pressure 1 atm.

Adsorption of oxygen, argon, and nitrogen on silica gel was measured and found to be very small compared to the adsorption of ozone.

The heat of adsorption of ozone on silica gel was calculated for various conditions with the help of the Clausius-Clapeyron equation (Figure 3). In the region of temperature and ozone concentration of most interest, the heat of adsorption is about 5400 cal. per gram-mole of ozone.

Only two papers give data for ozone adsorption on silica gel. The results reported by Magnus and Grähling (*3*) appear to be in good agreement with the present work, although their method of reporting is somewhat ambiguous. Briner and Lachmann (*2*) made only six isolated experimental measurements. The results of three of these are

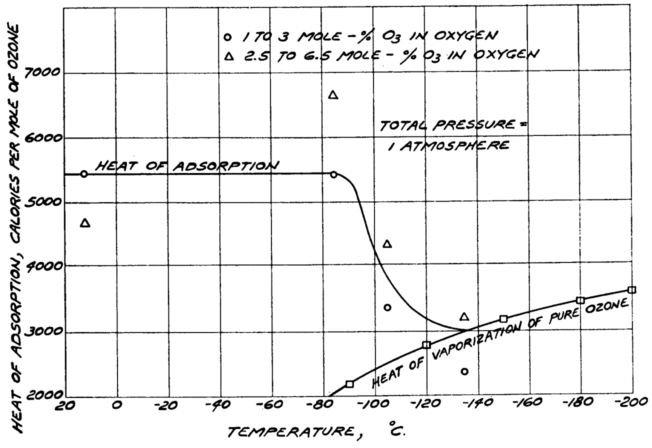

Figure 3. Estimated heat of adsorption of ozone on Davison silica gel

in fair agreement with the authors' data; the other three differ by an order of magnitude. The cause of this discrepancy is not known.

Safety Tests

Both small and larger scale safety tests were made on silica gel loaded with adsorbed ozone. By using in each case a few grams of ozone-containing gel in the laboratory, the following experiments were carried out.

An electric spark was passed between two tungsten electrodes within the gel bed. No explosions took place at −105° C. with loadings as high as 21 grams of ozone per 100 grams of gel.

A piece of fine iron wire was placed in the bed of gel and ignited by passing an electric current through it. With a loading of 9 grams of ozone per 100 grams of gel, a test was made at −78° C. After ignition of the wire, a glow in the vessel was observed, but no explosion took place. With a loading of 20 grams of ozone per 100 grams of gel at −105° C., a dull pop was heard when the wire was ignited, most of the ozone changed to oxygen, and the gel was extensively pulverized. The glass container was broken but not shattered.

Safety tests were also made on 0.2 cu. foot (over 5 liters) of silica gel loaded with ozone. The main conclusion from these tests was that, at loadings up to 10 pounds of ozone per 100 pounds of gel, if the temperature is kept below −78° C. so that the vapor pressure of the ozone in the gas phase of the vessel is low, an explosion will not take place when a hot wire buried in the gel is ignited. At higher temperatures explosions, apparently initiated in the gas phase, took place, but their force was greatly damped by the presence of the gel.

Even up to a loading of 30 pounds of ozone per 100 pounds of gel, explosions were successfully contained in the 0.2-cu. foot test vessel, which was made of 8-inch extra-heavy stainless steel pipe and pipe caps, welded together. The 700 p.s.i. bursting disk on the vessel was, however, ruptured by the explosion at this high ozone loading.

Turpentine, gasoline, kerosine, and linseed oil at room temperature were ignited when particles of silica gel holding 26 grams of ozone per 100 grams of gel were dropped in.

Four-Stage Ozone Transfer Cycle

In 1950–51 a pilot plant was erected at this laboratory and operated successfully to demonstrate the removal of ozone from oxygen and its transfer to other gases, such as air or nitrogen. A four-stage cycle was used.

1. Adsorption of ozone from a stream of oxygen by refrigerated silica gel until breakthrough of the ozone takes place.
2. Partial evacuation of the silica gel vessel to recover most of the gaseous oxygen left in the space between silica gel particles.
3. Desorption of the ozone into a dry stream of air, oxygen, nitrogen, argon, or other carrier gas.
4. Partial evacuation to remove the carrier gas which would otherwise contaminate the oxygen flowing through in the next step.

Figure 4 shows a simplified flow diagram of the pilot plant. The central feature is a group of three towers, made of 6-inch aluminum pipes, each filled to a height of about 15 feet with silica gel, about 125 pounds of gel for each tower. The three towers were all connected in parallel and supplied with automatically timed and operated electric motor-driven valves.

The pilot plant had three main fluid streams: the dilute ozone-oxygen mixture from the Welsbach ozone generator, the vacuum system, and the carrier gas supply system. (The carrier gas actually used was dry air.)

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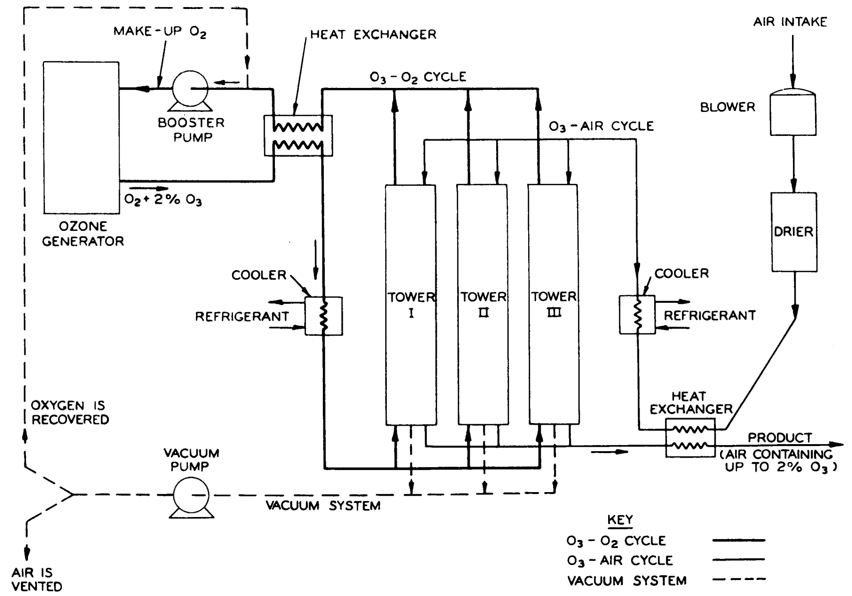

Figure 4. Simplified flow diagram for four-stage transfer process

The timing of the four stages or steps that took place in each tower per cycle is shown in Figure 5. Starting with Tower I, the ozone adsorption step takes one third of a cycle, the oxygen evacuation step one sixth, the ozone desorption one third, and the air evacuation one sixth. This arrangement made it possible to operate the three towers concurrently to give smoothly integrated flows of gas streams.

Results of Pilot Plant Study

In the pilot plant, a stream of oxygen containing 2 weight % ozone left the ozone generator, was cooled, and was fed to the silica gel beds. Evacuation and

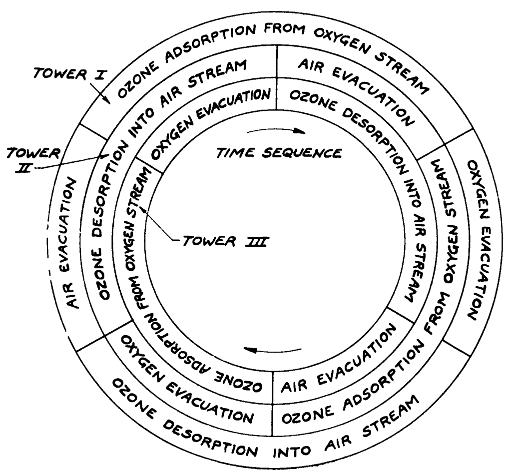

Figure 5. Time cycle for four-stage transfer process

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desorption were then carried out. The over-all recovery of ozone with the silica gel beds at −10° C. was about 90%—i.e., 90% of the ozone originally produced in the ozonizer found its way into the air stream serving as carrier gas. The other 10% of the ozone was lost by decomposition in the vacuum pump and in other ways. The concentration of ozone in the air (carrier gas) was 2 weight % about half of the time, and gradually fell to 0.5% during the second half of the desorption step.

During 200 hours of operation the capacity of silica gel for ozone was reduced to about half of that for new gel. However, the gel was readily regenerated to its original state by heating in a vacuum, and it is therefore concluded that the loss in ozone capacity was caused by adsorption of a small amount of water vapor during each cycle from the gases passing over the gel. Occasional regeneration of the gel, perhaps by blowing hot air through it, might therefore be required in plant operations.

Most of the oxygen originally fed to the ozonizer was recovered and recycled, as shown above, but some of it, about 0.4 pound of oxygen per pound of useful ozone recovered in the new carrier gas, was lost. Total oxygen consumption to produce each pound of usable ozone was therefore about 1.4 pounds of oxygen.

Possible Modifications of Cycle. At lower temperatures the quantity of ozone adsorbed on silica gel greatly increases, other conditions being equal. Thus, for a gas containing 2 weight % ozone, 100 pounds of silica gel adsorbs the weights of ozone shown in Table I. The partial pressure of ozone is 10.3 mm. of mercury when the ozone-oxygen mixture is at atmospheric pressure and 15.9 mm. of mercury when the gas mixture is at 8 p.s.i.g.; the latter is the usual pressure at which commercial Welsbach ozone generators are operated.

Table I. Ozone on Silica Gel

	Lb. O_3/100 Lb. Gel	
Temp., ° C.	10.3 mm. Hg	15.9 mm. Hg
25	0.042	0.068
0	0.092	0.146
−10	0.13	0.21
−40	0.45	0.72
−78.5	3.0	4.5
−90	6.0	8.0

The values for −10° and −40° C. were obtained by interpolation, with the help of the logarithmic curves shown in Figure 6.

The tests described above showed that any of these concentrations of ozone could be handled safely with suitable precautions.

The chief disadvantage of operating at a temperature lower than −10° C. is the higher cost of the refrigeration and heat exchangers. The advantages are:

The size of the silica gel towers and the investment in silica gel can be greatly reduced.

The two evacuation steps in the four-step cycle can be eliminated, thus eliminating investment in the vacuum pump, reducing oxygen losses, and simplifying the entire plant. The higher the concentration of ozone adsorbed on the gel, the smaller the relative amount of unadsorbed oxygen (or air) left in the spaces between the particles of silica gel.

It becomes possible, then, to choose between two simplified methods of operation.

Method I (Figure 7). [Step 1—Start]. Adsorb ozone on silica gel from the stream of oxygen plus ozone.

Step 2. Desorb ozone in a stream of carrier gas, letting the relatively small amount of oxygen blown out initially from the silica gel bed contaminate the carrier gas.

Step 1. Adsorb ozone on silica gel from the stream of oxygen plus ozone, letting the relatively small amount of carrier gas blown out initially from the silica gel bed contaminate the oxygen recycled to the ozonizer.

Step 2. Same as above, etc.

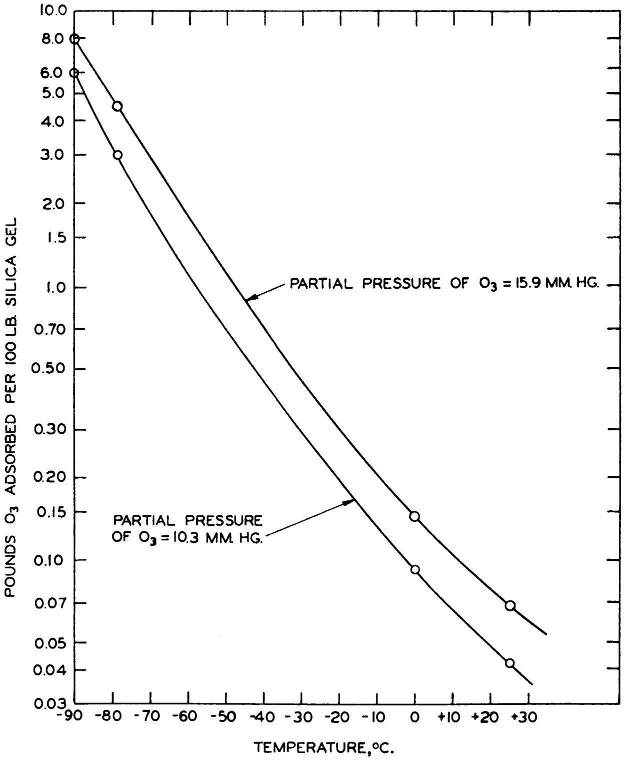

Figure 6. Adsorption of ozone on silica gel at a concentration of 2 weight % in oxygen

Total pressure 1 atm.

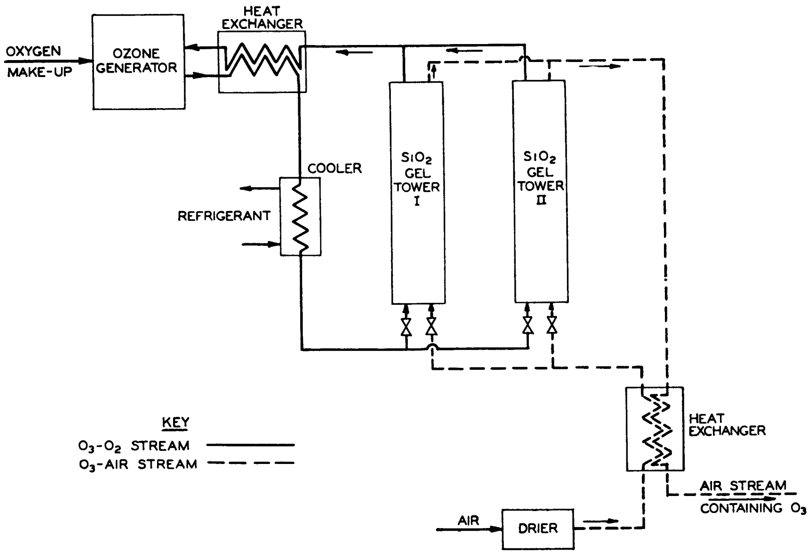

Figure 7. Simplified flow diagram for two-stage transfer process

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Method II. [Step 1—Start]. Adsorb ozone on silica gel from the stream of ozone plus oxygen.

Step 2. Desorb ozone in a stream of carrier gas, first directing the relatively small amount of oxygen blown out initially from the silica gel bed back to the ozonizer.

Step 1. Adsorb ozone on silica gel from the stream of oxygen plus ozone, first purging the relatively small amount of carrier gas blown out initially from the silica gel bed through an ozone decomposition catalyst to the atmosphere (or to a gas holder if the carrier gas is valuable), then recycling the oxygen back to the ozonizer.

Step 2. Same as above, etc.

Method I is slightly simpler than Method II, and for most purposes would probably be satisfactory. In either method the oxygen consumption could probably be reduced to 1.1 pounds per pound of ozone.

These two-stage methods were not tried in the pilot plant. The main purpose of the pilot plant was to demonstrate that ozone could readily be transferred on a large scale from oxygen to some other carrier gas, and this purpose was amply fulfilled.

The optimum operating temperature for the silica gel beds would have to be selected after a cost study for each individual case.

Advantages of Ozone Transfer Process

Cost. The transfer process is one of the ways by which oxygen may be used economically instead of air to make ozone. When oxygen is used, about twice as much ozone can be produced per hour from a given ozonizer and from a given amount of electrical energy as when air is used. Thus the use of oxygen halves the power consumption per pound of ozone made, halves the investment in ozone generators, and doubles the concentration of ozone in the product gas. Use of oxygen greatly reduces the concentration of, or eliminates entirely, oxides of nitrogen produced in the ozonizer. Against these advantages would have to be placed the investment and operating cost for the silica gel transfer plant and the cost of the oxygen used. Without some method of recycling the oxygen, the cost for oxygen would be very large, as an ozone generator usually converts only 1 to 4% of the entering oxygen to ozone. The transfer process makes it possible to recycle most of the oxygen to the ozone generator.

Safety. If the ozone is to be allowed to react with organic matter, it is safer to have it in a stream of nitrogen, or even air, than in oxygen.

Selectivity of Reaction with Organic Compounds. Degradation by reaction with oxygen is an undesirable side reaction of the ozonation of double bonds, which may be avoided if the ozone is in an inert carrier gas.

Undiluted ozone at a pressure somewhat below atmospheric (depending on the silica gel loading) may be obtained by pumping ozone off the silica gel. By keeping the ozone gas at a low pressure, gas phase explosions may be avoided. If the ozone is to be used in a chemical reaction, the reactor might be placed between the silica gel beds and the vacuum pump.

Ozone can be removed from oxygen at a low concentration—e.g., 2 weight %—and added to a carrier gas at a higher concentration, by desorbing the ozone at a higher temperature than is used to adsorb it. Changing the temperature of the silica gel beds, however, is a slow process, and complicates the cycle. An easier way of accomplishing the same purpose would be to desorb the ozone at subatmospheric pressure, sweeping it off the gel with a carrier gas in the desired ratio of carrier gas to ozone, and then compress the mixture to any desired pressure. For example, ozone at a pressure of 10 mm. of mercury mixed with nitrogen at 90 mm. of mercury would give a 10 mole % mixture of ozone, which could safely be compressed to atmospheric pressure. The Nash Hytor-type water-sealed vacuum pump would seem to be suitable for this purpose in applications where water vapor would do no harm, as the heat of compression in such a pump is largely absorbed by the water. (Experiments in this laboratory indicate that water does not catalyze the decomposition of ozone.)

Storing and Shipping of Ozone

Studies of the adsorption of ozone on silica gel and the safety tests made on the gel with adsorbed ozone indicate that ozone may be shipped safely if adsorbed on silica gel to a concentration of about 10 pounds of ozone per 100 pounds of gel and if the gel is suitably refrigerated. Refrigeration with dry ice is fairly satisfactory, but leaves some ozone in the gas phase. This gaseous ozone slowly decomposes, leading to a gradual loss of ozone. In storage tests at —78° C. lasting for 2 weeks and with ozone loadings of about 18 grams per 100 grams of gel, loss by decomposition in a glass container with glass wool as retaining material was about 9% ozone, and the loss was about 25% in the presence of stainless steel and aluminum wools.

At liquid oxygen or nitrogen temperatures there would be substantially no ozone in the vapor phase and no ozone decomposition losses would be expected. As silica gel will extract ozone from even a dilute solution of ozone in liquid oxygen, and liquid oxygen poured over silica gel loaded to 32% of its weight with ozone extracts no ozone from the gel, there would appear to be no danger of liquid ozone's forming in a vessel filled with silica gel loaded with ozone up to only about 10% of its weight.

One problem with these adsorption methods of transporting ozone is safe disposal of the desorbed ozone gas, if refrigeration fails en route. One way might be to equip the ozone transport vessel with an electrically driven pump operated from a storage battery. If the refrigeration fails and the temperature in the vessel starts rising, the pump can blow outside air into the vessel and sweep the ozone out through a chamber filled with an ozone-decomposing catalyst.

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Transfer of Ozone from Oxygen to a Carrier Gas

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A method is presented for converting oxygen to ozone. The ozone is condensed, separated from the oxygen carrier gas which is to be recycled, and then revaporized. Operating cost and results are given. This method overcomes handling difficulties and lowers production costs.

Since ozone was first produced as a highly concentrated gas or liquid, it has been known as instable, perhaps because its character is not fully understood.

In spite of its instability, handling difficulties, and production cost, ozone has been used as an industrial chemical. Ozone would have greater application if its handling and production problems could be solved.

In the present commercial ozone-producing system, the ozonator itself is important in the over-all cost of ozone. If oxygen is used as raw material, an ozonator will produce twice as much ozone as when operated with air. The savings in ozonator investment more than offset the cost of the oxygen feed and ozone can be produced more economically, if the unconverted oxygen can be recycled.

Recycling presents a problem if the oxygen is contaminated in the ozone utilization step. Transfer of the ozone from the oxygen stream leaving the ozonator to a carrier gas would, if economically practicable, permit recycle of the oxygen without contamination regardless of the environment in which the transferred ozone is utilized.

If oxygen-free ozone is desired, an effective method of transferring ozone from oxygen to a carrier gas is required.

Process Description

A system for separating ozone from oxygen being recycled through the ozonator is shown in Figure 1 (*1*). It consists of selective condensation of the ozone, separation of the condensate from the recycle gas, and then revaporization of the condensate.

Substantially complete condensation can be accomplished by cooling the oxygen stream to just above the boiling point of oxygen. At that low temperature, the vapor pressure of pure ozone is of the order of only a few hundredths of a millimeter of mercury. It, therefore, can be condensed from an oxygen stream without condensing a large amount of oxygen. This step is not easy because the ozone concentration in the oxygen stream may be only 2% by weight. To condense 1 pound of ozone under these circumstances, roughly 50 times as much oxygen needs to be cooled to the lowest temperature in the system. There must be efficient heat exchange between the oxygen gas entering the separator and the oxygen recycled; otherwise the refrigerant required to maintain operation would be excessive.

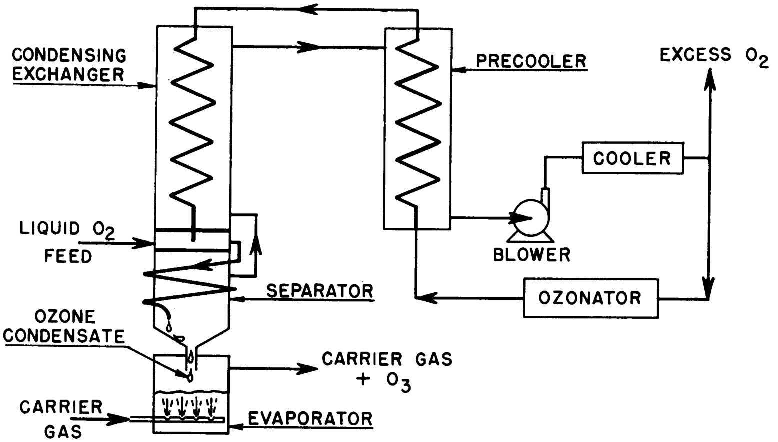

Figure 1. Diagram of system for producing oxygen-free ozone in a carrier gas

The refrigeration required to operate this transfer system is determined by the volume of the recycle gas, the heat losses from the exchanger, and the thermal properties of the materials being handled.

Much of the required refrigeration can be supplied by feeding the oxygen needed for ozone production into the system as liquid. If the latent heat of ozone were substantially lower than that of oxygen, the refrigeration from the make-up oxygen would be sufficient. However, the heat evolved when 1 pound of ozone is condensed in the system will vaporize 1.5 pounds of oxygen. As a result, oxygen in excess of that converted to ozone will be vaporized and must be withdrawn from the system as a gas. If this excess cannot be used elsewhere, it must be reconverted to liquid or charged to the process as raw material.

After condensation and separation of ozone from the oxygen stream, the condensate is led to an evaporator. As evaporation of ozone by boiling with indirect heat at atmospheric pressure sometimes leads to explosions, the ozone is evaporated by direct contact with a high boiling liquid such as water. The gaseous ozone joins a stream of carrier gas of selected composition and volume.

Heat Exchanger

In the first section of the heat exchanger the oxygen-ozone mixture is cooled to just above the point of initial ozone condensation. Because liquid ozone will not be formed in this section of the interchanger, it can be constructed and operated with little regard to ozone hazard.

In the second section of the exchanger where condensation occurs, accumulation of appreciable liquid ozone must be prevented. The ozone-containing gas passes through narrow pipes, and the velocity of the gas stream is increased so that the condensed ozone is swept from the condensing surfaces. Only a thin film of liquid is present in the exchanger at any time. This section of the exchanger is mounted in a vertical position to avoid traps in which liquid might collect.

Refrigerant Introduction

Refrigeration is supplied by introducing liquid oxygen directly into the stream of gaseous oxygen and condensate leaving the cold end of the second section of the exchanger. The liquid oxygen flows concurrently with the main stream through an

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elongated pipe to the separator. In this pipe, heat is exchanged by direct contact between the liquid oxygen and the gas. Oxygen is evaporated and heat is withdrawn from the gas, producing the lowest temperature in the system, and ozone condensation is completed.

The mixture of gaseous oxygen and liquid ozone is led to a refrigerated vessel in which the heavy liquid is separated from the gas by combined centrifugal and gravitational action. The gas containing very little ozone is recycled.

Evaporator

The condensate is led to a vessel containing an appropriate liquid which is agitated by introducing the carrier gas through a sparger submerged in the liquid. The heavy ozone is dispersed throughout the body of the liquid in the form of small droplets and evaporates without appreciable decomposition. The heat for evaporating the condensate may be supplied by preheating the carrier gas.

Operation

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Results. Equipment based on Figure 1 was designed and operated to produce 1 pound of ozone per hour using a Welsbach C-34 ozonator.

Many early runs terminated in explosions. When liquid ozone collected on warm solid surfaces, evaporation and spontaneous decomposition occurred. After the equipment was modified to prevent premature evaporation, seven runs were made without incident.

Although a high concentration of ozone in the condensate was not sought, concentrations up to 90% should be obtained with ozone recovery in the range from 95 to 98%. As heat losses in a small unit are disproportionately large, reliable data on the liquid oxygen feed required per pound of ozone transferred were not obtainable. Calculated values, assuming a 5° F. difference in the exchanger, range from about 2.3 to 1.9 pounds of liquid oxygen per pound of ozone. This range corresponds to ozonator effluent concentrations from 2.0 to 5.0% by weight of ozone, respectively. This ozone transfer method requires on the order of 1 pound of oxygen per pound of ozone in excess of that consumed in the formation of the ozone.

The scale of this operation, although admittedly small, represents the farthest known advance beyond the test tube stage. These solutions of operational problems encourage further scaling up.

Costs. The basic cost of ozone to be separated from the oxygen stream depends on the cost of the raw material, the equipment (the ozonator representing the principal item), power, labor, and overhead. In this study, attention was not paid to the basic cost of ozone production.

The incremental cost of the ozone transfer depends on the volume of oxygen recycled per pound of ozone produced, which is inversely proportional to the ozone concentration in the ozonator effluent. This, in turn, affects the heat transfer surface required for exchanger efficiency.

Table I gives estimates of the incremental equipment costs, the corresponding fixed charges, and the incremental power requirements for transferring ozone to a carrier gas in a system designed for oxygen recycle. The operating cost does not

Table I. Incremental Cost of Ozone Transfer Equipment and Power

(Based on a production scale of 700,000 pounds per year)

O_3 concn. in ozonator effluent, % by wt.	1.5	2.0	3.0	4.0	5.0
Equipment cost, $	115,000	100,000	80,000	70,000	65,000
Annual fixed charges at 16%, $	18,000	15,000	12,000	11,300	10,000
Annual power charge at 1¢/kw.-hr., $[a]	7,000	5,600	3,850	2,800	2,400
Operating cost, ¢/lb. of ozone[b]	3.6	2.9	2.3	2.0	1.8

[a] Includes only incremental power to overcome a pressure drop of 4 p.s.i. through exchangers.
[b] Does not include charge for oxygen fed to system.

include that of the liquid oxygen used as refrigerant. The oxygen feed which later appears as ozone is charged to the basic cost of the ozone produced. Only the excess oxygen purged from the system represents expense in the ozone transfer operation. This expense can be determined if costs and credits can be taken into account.

From the standpoint of cost of ozone transfer, it would be desirable to increase ozone concentration in the effluent as far as possible. However, as the effluent ozone concentration increases, the basic cost also increases. A compromise between increasing basic cost and decreasing incremental cost must be effected to obtain minimum over-all cost.

To evaluate the process described fully, it should be compared with alternative methods of transfer such as selective adsorption or extraction, taking into account complex process requirements and economic factors.

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Application of Ozone from Sterilamp in Control of Mold, Bacteria, and Odors

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In using a Sterilamp for the tenderization and preservation of meat and the preservation of other types of foods, a controlled amount of ozone is generated by the lamp to destroy or suppress growth of mold and bacteria in the unirradiated areas. Minute amounts of ozone are also used to destroy odors in both commercial and domestic refrigerators and in air-conditioning systems.

A low-pressure mercury lamp sold by Westinghouse under the trade-mark, Sterilamp, was placed on the market in 1936. The lamp was primarily designed to emit a copious amount of bactericidal ultraviolet radiation with a minimum amount of radiation below 2000 A. The latter radiation is responsible for the photochemical production of ozone from oxygen of the air. The effectiveness of the lamp in destroying bacteria (*25*) and mold (*21*) on Petri plates, in operating rooms (*17*, *18*), bacteriological laboratories (*32*), and air-conditioning systems (*22*, *24*) has been amply demonstrated.

In some applications of the lamp, it was soon discovered that a controlled amount of ozone, together with the bactericidal radiation, resulted in a more effective method of destroying microorganisms. Ozone also oxidized many of the odors. The present survey describes only those applications of the Sterilamp tube which utilize lamps generating a controlled amount of ozone to destroy mold, bacteria, and odors.

Tenderay Process

One of the first applications of the germicidal lamp was in the tenderizing of meat (*1*, *19*). Fresh beef sides which have been partially chilled in a cooler are held for 42 to 44 hours at 68° F. at a relative humidity of about 85%. Increase in tenderness of meat during storage results from the digestive action of naturally contained enzymes upon the muscular and connective tissues in the meat. The increased temperature greatly accelerates this enzyme action, so that the degree of tenderness is equivalent to beef hung for 20 days at 40° F. However, the increase of temperature also provides a more favorable environment for the growth of mold and bacteria. The purpose of the Sterilamp ultraviolet tubes is to destroy these surface organisms. Figure 1 is a typical installation of this process. Approximately 170,000,000 pounds of beef per year are tenderized by this method.

Results of tests during the development of this process showed that a controlled amount of ozone was necessary to destroy mold or bacteria on portions of meat not

In OZONE CHEMISTRY AND TECHNOLOGY;
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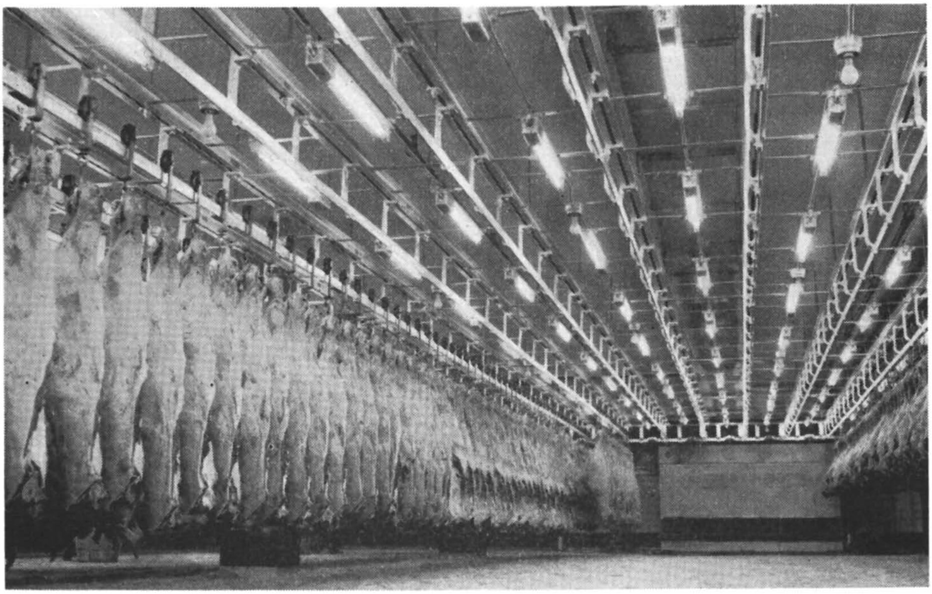

Figure 1. Typical Tenderay process room, showing method of installing Sterilamp tube

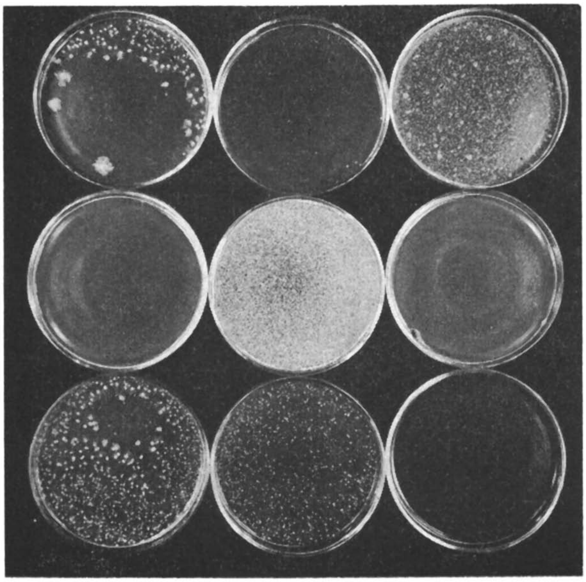

Figure 2. Slime-forming organisms exposed in meat box

Top shelf	**Ozone, 24 hours**	**Ozone, 48 hours**	**Control**
	Ultraviolet, top, 24 hours	**Control**	**Ultraviolet, bottom, 24 hours**
Bottom shelf	**Ozone, 24 hours**	**Ozone, 48 hours**	**Ozone, 72 hours**

directly irradiated by the lamps. Quantitative determinations of the effectiveness of ozone were made by bacteria counts taken from the surface of the meat and by exposing Petri plates seeded with bacteria and mold taken from infected meat. Figure 2 is an example of organisms on Petri plates exposed to direct radiation plus ozone and some to ozone alone. The latter Petri plates were inverted and placed in various positions in the refrigerator. Figure 2 shows that about 72 hours are necessary before all of the organisms are destroyed.

The concentration of ozone in such tenderizing rooms, according to Ewell (*11, 12*), is of the order of 0.1 p.p.m. by volume. Elford and Van den Ende (*6*) have shown that ozone as low as 0.04 p.p.m. can destroy bacteria if the relative humidity is 60 to 90%. Mallmann and Churchill (*20*), experimenting with naturally contaminated beef, also showed that 0.1 p.p.m. by volume of ozone would retard the growth of the organisms.

Both bactericidal radiation and ozone can destroy only the surface organisms. Heavy growth of mold and bacteria will not be destroyed by these small amounts of ozone. The length of time necessary to destroy all of the organisms seeded on a Petri plate would be a function of the concentration of ozone. Ewell (*7*) has shown that the reciprocity law, which requires that the per cent killing be proportional to the concentration times duration of ozone, holds for a limited concentration. At low concentrations of ozone and very long times corresponding to the number of life cycles of the organism, the total amount of ozone (*23*) or ultraviolet energy (*25*) is much less for the same per cent of destruction of the organisms. These results would indicate that, at one stage of their life cycle, mold and bacteria are very sensitive to minute amounts of these lethal agents.

The concentration of ozone in the tenderizing room is controlled by the number and type of ultraviolet lamps. Most of the lamps in such a room emit predominantly bactericidal radiation. A certain percentage of the lamps are of a special type that emit a controlled amount of radiation below 2000 A. This radiation is active in the photochemical production of ozone from oxygen of the air. Some of the ozone is decomposed by 2537-A. radiation (*9, 10*) before it can be utilized in the destruction of mold and bacteria or the oxidation of odors. The half life of the ozone molecule under the present conditions of humidity and temperatures is probably of the order of 3 minutes (*9*). Thus, an accumulation of ozone in such a room is impossible. Measurement of the concentration of ozone soon after the introduction of meat into a tenderizing room shows a marked reduction in the amount of this gas. This can be attributed to the oxidation of odors associated with fresh meat.

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Meat Storage Rooms and Walk-In Coolers

Meat taken from the room where the Tenderay process is carried out is immediately cooled below 40° F. to inhibit the enzyme action responsible for the tenderization.

The rate of growth of bacteria and mold is greatly reduced at these low temperatures. The half life of the ozone molecule (*9*) has been extended to over 6 minutes because of the lower temperature and marked reduction in the absolute humidity as well as a reduction in the odor level. Under these conditions the number of ultraviolet lamps necessary is decreased to about one half of that used in the room where the Tenderay process is carried out. However, the ratio of the bactericidal lamps to the ultraviolet lamps also producing a controlled amount of ozone is kept constant. The concentration of ozone in such a refrigerator has been stated by Ewell (*8, 10*) to be approximately 0.1 p.p.m. by volume. Tests using Petri plates seeded with bacteria taken from infected meat show results similar to those seen in Figure 2.

A typical walk-in cooler is shown in Figure 3. If the temperature in walk-in coolers is approximately 40° F., the number and type of ultraviolet lamps used for a given area will be the same as for the meat storage refrigerators. At temperatures

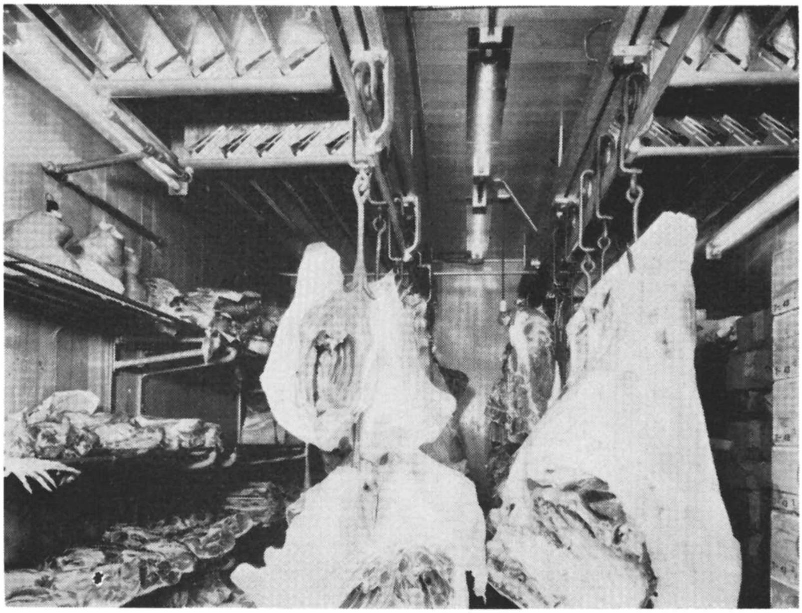

Figure 3. Typical walk-in cooler with Sterilamp tubes on ceiling

between 32° and 35° F. ambient, the ultraviolet output of most mercury lamps is too small to be practical unless steps are taken to increase the temperature of the lamp. The design of the Sterilamp tube permits operation at these temperatures.

Domestic Refrigerators

Considerable research was done on the application of an ozone-producing lamp for domestic refrigerators. It was necessary to find a balance between the amount of ultraviolet radiation and ozone so that mold and bacteria on the food and refrigerator wall would be destroyed, while the level of food odors and the transfer of food odors to other foods would be greatly reduced without causing reactions in certain sensitive foods.

Two refrigerators were loaded with food as shown in Figure 4. One of the boxes contained an ultraviolet lamp which operated only on the on cycle, while the other box was the control. Daily observations of the foods showed that the odor level in the box with the lamp as well as the transfer of odors from one food to another can be reduced to a large degree. Bacteria and mold on food and on the walls of a high humidity box are destroyed by the minute amounts of ozone generated by the lamp. The average concentration of ozone is approximately 0.1 p.p.m. by volume (*10, 11*).

Figure 5 shows that more than 48 hours of exposure to the ozone is necessary before all of the organisms are destroyed on seeded Petri plates. Higher concentrations of ozone will destroy the organisms in a shorter time; however, rancidity would be produced in some foods. Concentrations of ozone which would necessitate longer exposures of the Petri plates before all of the organisms were destroyed would not be so effective in oxidizing the odors. Thus, the rate of destruction of organisms is a measure of the amount of ozone in the box. This method can also be used to determine the circulation of air containing ozone in a refrigerator.

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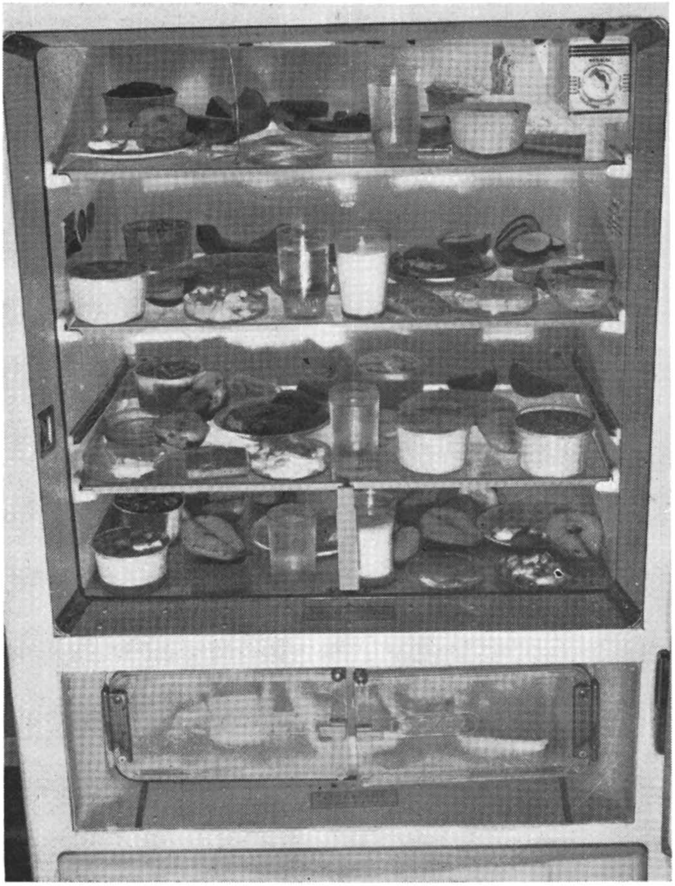

Figure 4. Domestic refrigerator used to study effect of ultraviolet radiation on various foods and bacteria

Cheese Ripening and Storage

The Sterilamp ultraviolet tube producing a minute amount of ozone has been used to destroy mold on Cheddar cheese during ripening (*13, 14*). Ewell (*11*) has reported that less than 0.2 p.p.m. by volume will extend the holding time by 11 weeks at 59° F. and 80 to 85% relative humidity before the appearance of visible mold on the cheese. The ozone also oxidized the odor in the room.

Apple Storage

The use of ozone in control of surface mold on packages and walls in apple storage and maintenance of a pleasant odor has been reported by a number of investigators (*12, 16, 28, 31*). Ozone has also been used to retard ripening of fruits. Ethylene gas liberated by fruit stimulates the ripening. The gas is readily oxidized by ozone (*2, 14*). The Sterilamp tube has been used to provide a controlled amount of ozone to oxidize this gas and other odors as well as to destroy microorganisms in apple storage rooms.

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch009

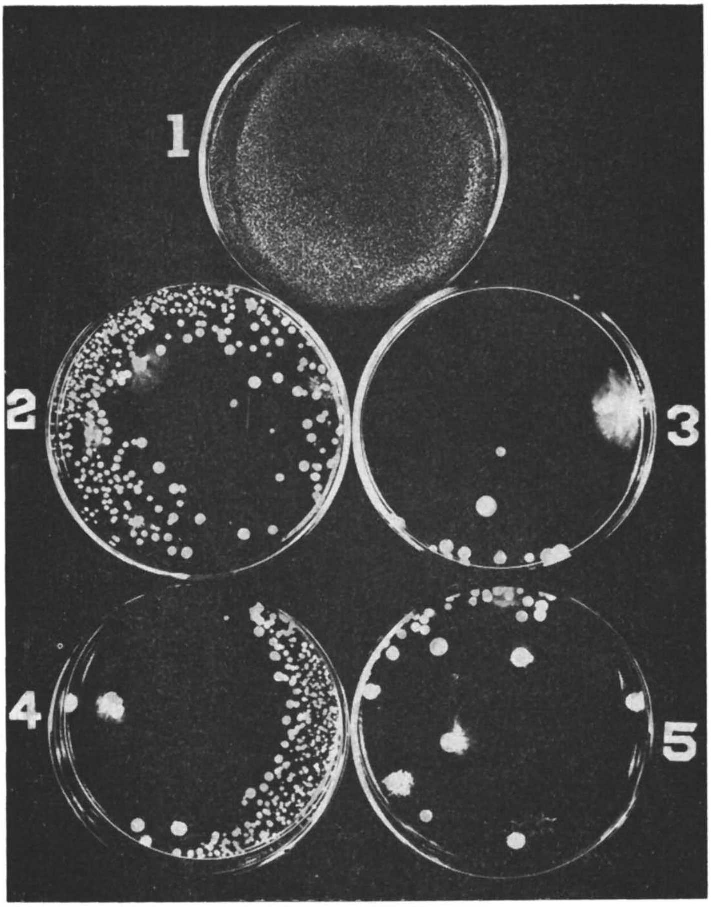

Figure 5. Slime-forming organisms exposed to ozone in domestic refrigerator

1. Control
2. Top left, indirect, 24 hours
3. Top left, indirect, 48 hours
4. Top right, indirect, 24 hours
5. Top right, indirect, 48 hours

Air Conditioning

The primary purpose of the Sterilamp tube in air-conditioning systems has been to destroy microorganisms (*22*). Tests on the effect of 1 to 2 p.p.m. by volume of ozone on *E. coli* sprayed into an air duct revealed that the organisms were not destroyed. This would confirm the data of Elford and Van den Ende (*6*) that ozone is a poor disinfectant of air at low relative humidity. At high relative humidity these authors found that as low as 0.04 p.p.m. by volume destroyed bacteria dispersed in an aerosol. This would also agree with the results reported here, that organisms on surfaces and seeded on Petri plates can be destroyed by minute amounts of ozone.

With the introduction of a Sterilamp tube producing a comtrolled amount of ozone, there has been an increasing number of installations for the purpose of oxidizing body, smoke, or cooking odors. The lamps have been installed in the air ducts of large office

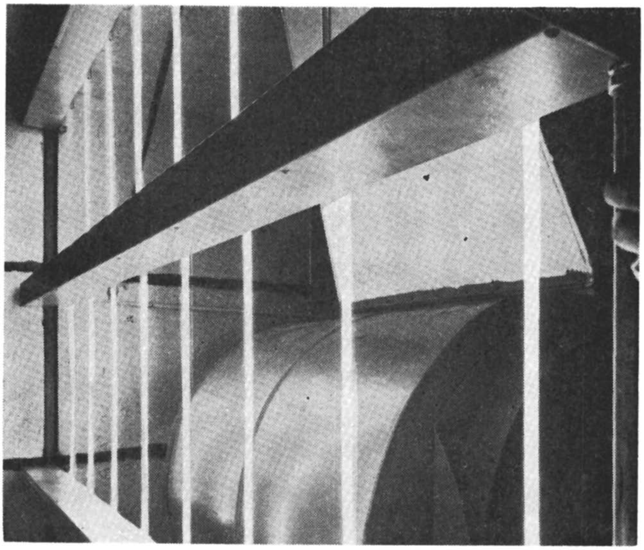

Figure 6. Installation of Sterilamp tubes in large air duct

buildings, hospitals, and cooking establishments (Figure 6). Smaller units have been used in the hot air heating systems of homes and still smaller units for offices or individual rooms.

Tests on a number of these small units revealed that the ozone concentration in the room was less than 0.01 p.p.m. by weight. There is ample evidence that various food odors, such as from fish, onions, acrolin from burnt fat, and tobacco as well as body odors can be oxidized by ozone. This is substantiated by many reports in the literature (*4, 13–15, 30, 31*). Tests made in the laboratory with various unsaturated organic compounds such as indole and skatole (fecal odor), allyl sulfide (garlic odor), and methyl thiocyanate (unpleasant odor of almonds) showed them to be readily oxidized, as evidenced by lack of odor. Saturated compounds such as butyric and valeric acids were not oxidized under the same conditions. Special fixures with ultraviolet lamps producing a controlled amount of ozone are used in animal hospitals and kennels for prevention of cross infection and for the oxidation of animal and fecal odors.

Determination of Ozone

Information on the amount of ozone generated by the lamp under various conditions is of interest to the research scientist, application engineer, and health officer. Many of the divergent views on the bactericidal effect and toxicity of ozone can be attributed to the methods of determination used by the authors as well as the purity of their gas. As an example, oxides of nitrogen were produced as a by-product by some of the early ozone generators. These oxides react with some of the reagents used for the measurement of ozone; they have also been shown to be toxic (*5, 26*). Ultraviolet lamps do not produce oxides of nitrogen.

The concentration of ozone in Tenderay process rooms and refrigerators has been determined by Ewell (*9*) using calibrated potassium iodide-starch paper. This method is not applicable for concentrations lower than 0.4 p.p.m. by volume. Measurement of concentrations below 0.1 p.p.m. by volume involved installing a large number of known lamps in a refrigerator and then dividing the reading to obtain a value for a box with a normal number of lamps. The potassium iodide–starch paper was later compared with the Crabtree and Kemp (*3*) atomized neutral potassium iodide method and

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also with the modified ultraviolet absorption method of Stair (*29*). The results of all three methods were in good agreement at a concentration of about 1 p.p.m. by weight. The alkaline potassium iodide method of Smith and Diamond (*27*) consistently gave low results.

The method used to determine the relative amounts of ozone from various types of Sterilamp tubes shown in Table I was that of Crabtree and Kemp (*3*). The lamps were hung in about the geometrical center of a small vacant room of 1780 cubic feet. The relative humidity was between 20 and 30% at 70° to 75° F. Figure 7 shows that,

Table I. Concentration of Ozone from Average Sterilamp Operated at Optimum Conditions

Sterilamp	Application Examples	Wattage	Ozone per 1000 Cu. Ft., P.P.M. by Wt.
794-H (Odorout)	Room, office	3.5	0.05
794	Domestic refrigerator	3.5	0.02
782-H-30	Large refrigerators	17.0	0.42
782-H-10	Hot air furnaces	12.0	0.15
G36 T6-H[a]	Air-conditioning ducts	39.0	2.10

[a] L type of Sterilamp transmits about one tenth to one fiftieth of the 1849-A. radiation as the H type.

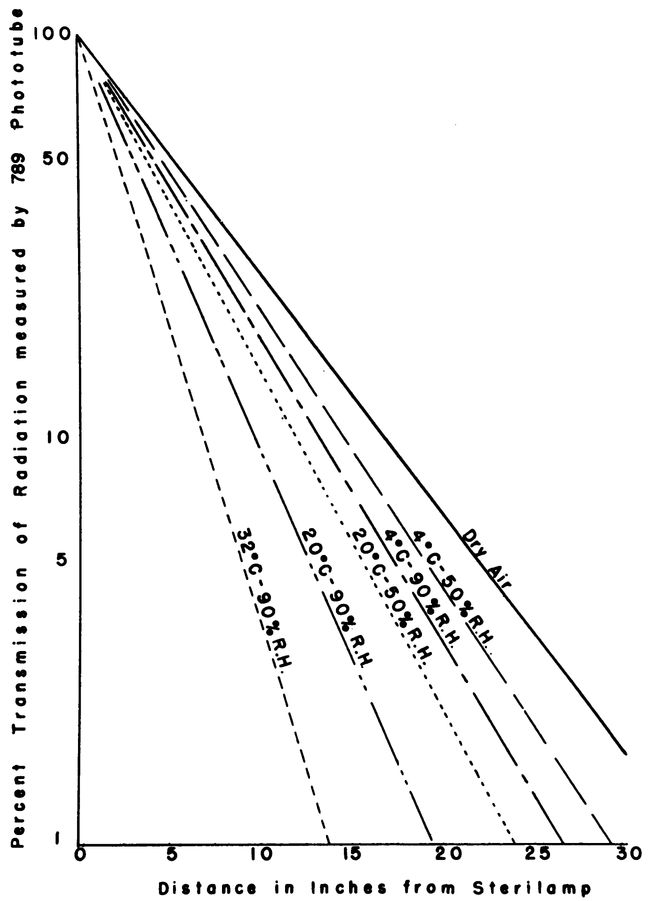

Figure 7. Transmittance of radiation below 2000 A. through air at various relative humidities

with the available ray length and humidity, nearly all of the 1849-A. radiation generated by the lamp was absorbed by the oxygen of the air, and the maximum amount of ozone would be expected. Operating these lamps in enclosed fixtures, air ducts, at lower temperatures, or at higher humidity will decrease the amount of ozone generated. In actual installations only about one tenth of the concentration given in Table I will be found. Table I is a measure of the relative proportion of ozone generated by the various lamps.

The relative amount of ozone generated by various ultraviolet lamps can be ascertained by the measurement of the radiation emitted below 2000 A. A 789 phototube, which will respond only to these short radiations, has been used for such comparisons and for control of the quality of glass in the production of the lamps.

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Ozone Oxidation of Aqueous Cyanide Waste Solutions in Stirred Batch Reactors and Packed Towers

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The use of ozone as an oxidant for industrial wastes containing cyanides and other reducible toxic substances appears worthy of careful investigation. The oxidation of simple cyanides by ozone is rapid and complete. Mass transfer controls the absorption. The use of packed towers or sieve plate towers is indicated, and the maintenance of a pH of at least 9.0 is recommended. The destruction of cyanates and cyanide complexes is slower than the cyanide oxidation. These substances are destroyed if sufficient contact time and proper pH control are maintained so that these slower reactions can take place. The use of redox potential to control the degree of oxidation appears promising. Proper interpretation of the redox potential of the treated waste will give an excellent indication of the effectiveness of the treatment and the degree of removal of cyanide and cyanate.

The destruction of toxic cyanides in industrial waste waters is a problem of mounting importance because of accelerating industrial development and decreasing availability of water supplies. The scarcity of dilution water for reducing the concentrations of toxic wastes has required many manufacturers to take a longer look at the waste-disposal operations which must accompany their manufacturing processes. Industries particularly affected by cyanide disposal problems are the metal finishing, electroplating, metallurgical, and refining industries. The need for further development in the treatment of cyanide wastes is best demonstrated by a review of methods that have been commonly employed, all of which show some disadvantages in terms of cost, efficiency, degree of effectiveness, and hazards (*18*).

Cyanides are commonly treated by chemical or biological oxidation. Of lesser importance is the precipitation of cyanide ion as complex iron cyanide, or by the direct atmospheric release of hydrogen cyanide by acidification and aeration. The oxidation methods, however, have found widest acceptance; chemical oxidation is preferred for all but the more dilute cyanides free from other toxics, which may be diluted or treated biologically. Biological treatment of cyanides offers the possibility

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of good removal where relatively stable conditions exist for ponding or ditching, and special strains of organisms can be developed.

Gurnham (*9*) has described the use of trickling filters for biological oxidation of cyanides, and shows that the greater bulk of simple cyanides may be quickly and economically removed by this method. Further work in progress in this field should be of great value in defining the limits of such biological treatment.

Chemical oxidations using chlorine, hypochlorite, hydrogen peroxide, lead oxide, and ozone have been used in some cases, and chlorine in one or another of its forms has been the commonly accepted chemical oxidation procedure. Tyler (*22*) presented data on the oxidation of cyanides utilizing ozone; the advantages of ozone are such that further investigation was made. Foulke and Ledford (*5*) and, earlier, Dodge and Cams (*4*) reviewed the literature of cyanide waste disposal thoroughly, including the use of ozone.

The use of chlorine has several disadvantages.

Chlorine must be used in considerable excess—about 8 pounds per pound of cyanide. Destruction of 100 p.p.m. of cyanide is accomplished with an increase of 800 p.p.m. of chloride ion. This value of chloride ion may not be acceptable to public health authorities, because the re-use of such effluents farther downstream is highly questionable. Ozone leaves no toxic or deleterious substance in the finished waste.

Excess chlorine may have a residual free chlorine which may be toxic to biologic life in the receiving stream and must be removed or controlled. Ozone leaves no harmful residual.

Chlorine may be expensive, depending upon the location of the plant and its size, the cost varying from 15 to 3 cents per pound. Freight and handling charges and the quantities to be purchased all determine the final cost. Ozone costs vary directly with the cost of purchased electric power, and are about 13 cents per pound (based on 1 cent power); no freight, delivery, or handling costs are necessary (*11*).

Against the high costs of ozone equipment must be balanced the comparable costs of chlorine equipment, loading equipment, feeders, dechlorination equipment, retention tanks, railroad spurs, storage rooms, injectors, and similar items. Ozone is produced by outdoor installed generators having negligible maintenance.

Chlorine oxidation requires large detention tanks or basins. Ozone oxidation may be done in a continuous flow packed tower, the oxidation of cyanide to cyanate being practically instantaneous. Cyanogen chloride cannot form when ozone is used, and the treatment facilities do not require inside space.

Ozone is a more efficient oxidant than chlorine. It lends itself to oxidations where phenols, sulfites, and other reducible substances are present (*17*).

Some proposed treatment systems for ozone are presented in Figure 1.

Chemistry of Ozonation of Cyanides and Cyanates

The ozonation of cyanides involves two separate chemical steps, oxidation of cyanide to cyanate and oxidation or hydrolysis of cyanate to nitrogen and ammonia. Ideally, cyanide nitrogen should be released as nitrogen gas.

$$2CN^- + 4(O) \rightarrow 2CO_2\uparrow + N_2\uparrow \qquad (1)$$

This reaction would be ideal in the sense that two nontoxic gases are the sole products of the destruction of a toxic ion, and no dissolved solids build-up in the waste has occurred. Comparison of cyanides to cyanates shows that the former compounds are relatively stable; the cyanates either hydrolyze to ammonium carbonate (*1*, *19*) or rearrange to urea (*1*, *16*, *24*):

$$OCN^- + 2H^+ + H_2O \rightleftharpoons CO_2\uparrow + NH_4^+ \qquad (2)$$

$$OCN^- + NH_4^+ \rightleftharpoons NH_2CONH_2 \ (8,\ 21) \qquad (3)$$

The ozonation of cyanides is marked by extremely rapid absorption of ozone in cyanide solutions:

$$CN^- + O_3 \rightarrow CNO^- + O_2\uparrow \qquad (4)$$

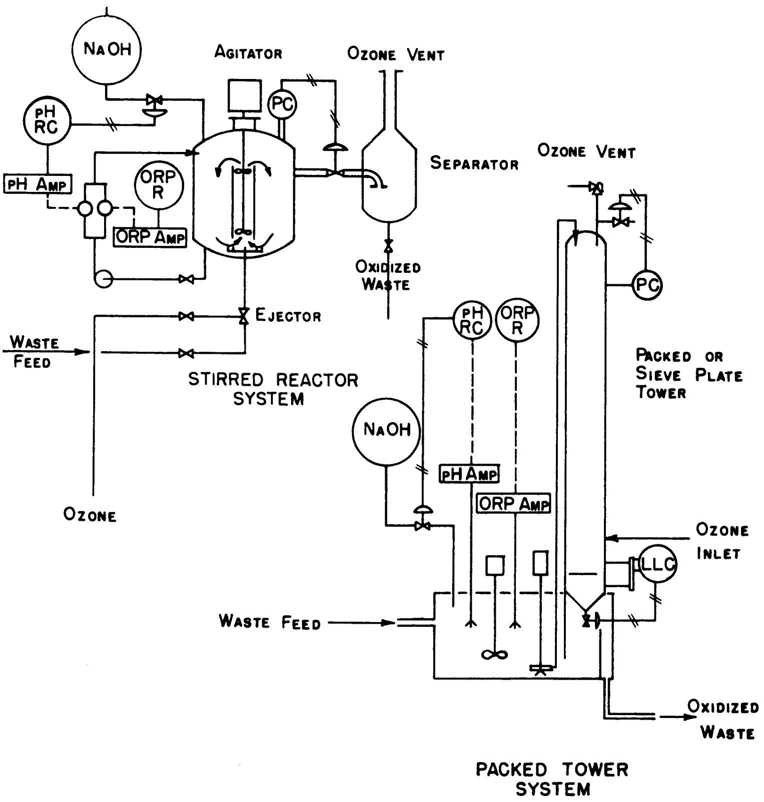

Figure 1. Schematic diagram of continuous flow oxidation systems utilizing ozone for cyanide wastes

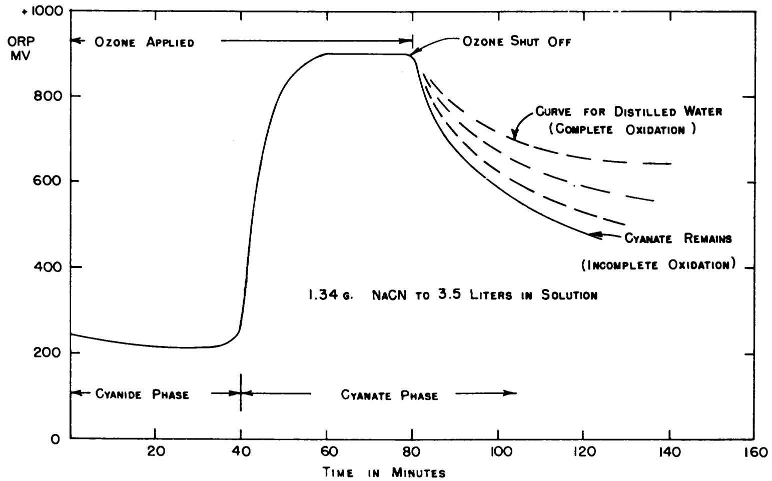

Figure 2. Redox potential history of cyanide and cyanate oxidation by ozone

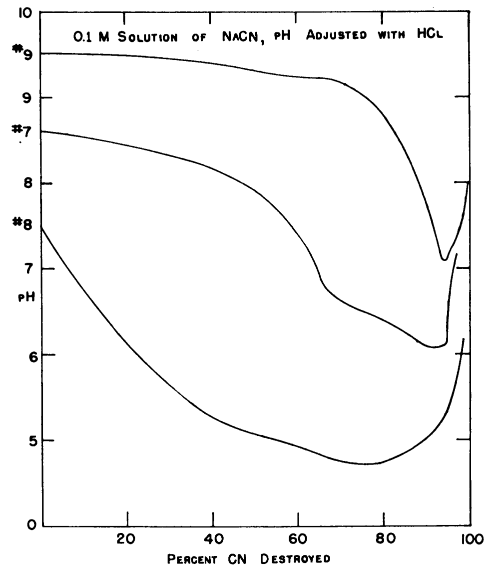

Figure 3. Effect of pH on ozonation of cyanides

The solution of cyanide ion contains no ozone in solution during this cyanide phase, as may be determined by the oxidation potential of the solution. The redox potential will remain at a low value, rising slowly and gradually as the cyanide is consumed (Figure 2). When the cyanide ion practically has all been oxidized, an immediate and sudden rise in potential is experienced, at which point the solution is an oxidizing one and releases iodine from potassium iodide solutions.

The oxidation of cyanides lowers pH in a manner illustrated by Figures 3 and 4. Chamberlin and Snyder (*3*) have presented the relationship existing between hydrocyanic acid and cyanide at various pH values, and show that as the pH falls, because

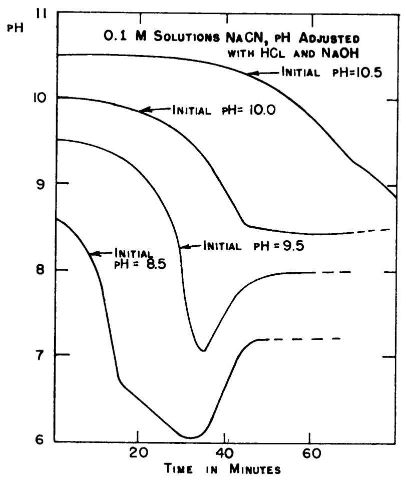

Figure 4. Effect of ozone on pH of cyanide solutions

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cyanic acid is a stronger acid than is hydrocyanic acid, the amount of free cyanide ion must decrease very rapidly, and at or near the termination of the ozonation the cyanide is almost entirely present as hydrocyanic acid where the pH has fallen to the neutral point.

Ozone is more soluble in acid solutions than in alkaline solutions (*10*), and dissolves in dilute acid with a rapid pH rise. This solution holds the dissolved ozone in solution longer than is possible in higher pH solutions, where hydroxyl ion catalyzes the decomposition. As the ozone decomposes, pH falls back to the original value. Figure 5 shows these effects, which are presented to compare them with the absorption of ozone in cyanide solutions. In all cases where ozone dissolves in water containing no oxidizable materials, the pH rises, provided it is initially below pH 10.5. The addition of ozone to cyanide and cyanate solutions results in definite pH effects opposite the ordinary solution of the gas in water; this indicates that a chemical reaction must be taking place.

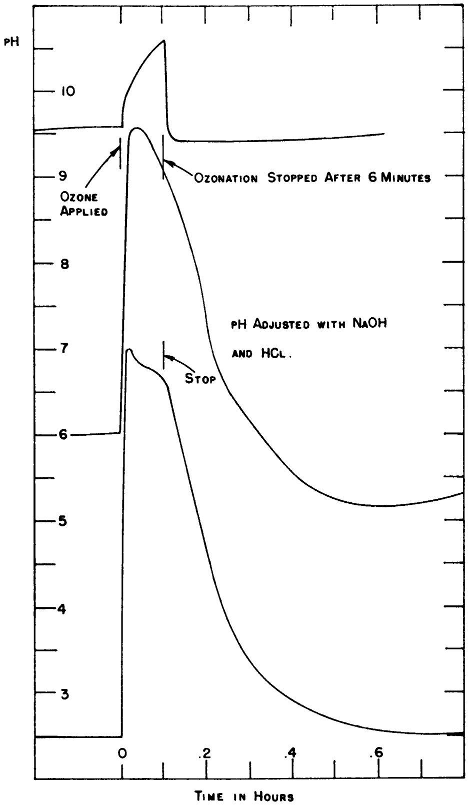

Figure 5. Effect of ozonation on water

Proposed Reaction of Ozone with Water:

$O_3 + H_2O \rightarrow HO_3^+ + OH^-$ (slow)

$HO_3^+ + OH^- \rightleftharpoons 2\ HO_2$ (maintained)

$O_3 + HO_2 \rightarrow HO + 2\ O_2$ (slow)

$HO + HO_2 \rightarrow O_2 + H_2O$

The pH fall from that of a cyanide solution to that of a cyanate solution when ozone is added is to be expected; this may be seen from Figure 6, where both cyanide and cyanate solutions of equal molarity are ozonated at the same rate.

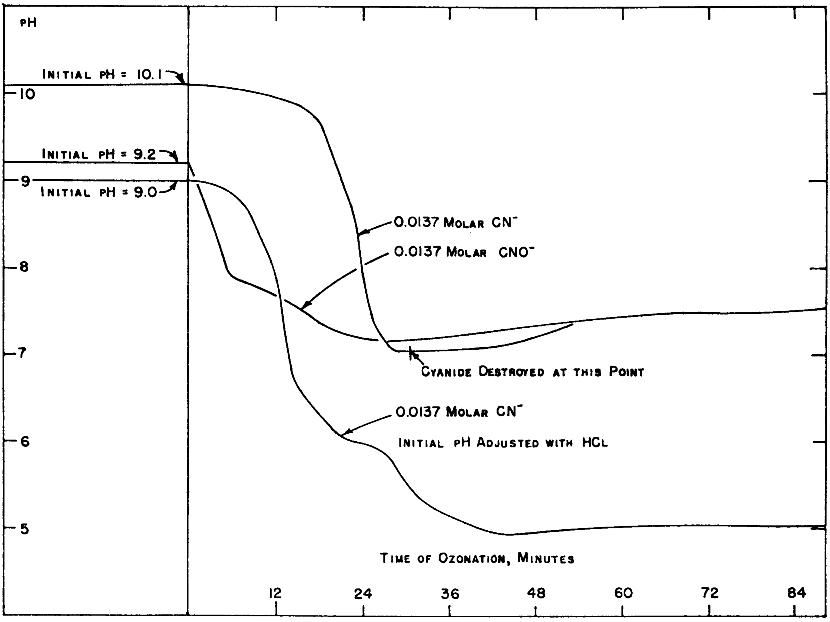

Figure 6. Effect of ozonation on pH of cyanide and cyanate solutions

The absorption of ozone by cyanide solutions in stirred reactors is complicated by mass transfer considerations. The presence of ozone gas in the exhaust from such a reactor does not indicate that equilibrium has been obtained between ozone gas bubbles and ozone in solution, but rather that the mass transfer through the individual bubbles is not complete, because of the resistance on the gas side. In other words, mass transfer controls the reaction, as the ozone will react almost instantaneously with the cyanide ion in solution. The presence of some metals, particularly copper, appears to speed up the absorption by acting as oxygen carriers. A solution of ozone in dilute acid decomposes somewhat more quickly when a trace of cupric ion is added. The presence of these metal catalysts, if this be their function, does not appear to be a necessary condition to ozone oxidation. What is important is that adequate mass transfer time and surface be available, as would be found in a countercurrent packed tower.

The stoichiometry of this reaction has been studied by Walker and Zabban (*23*), who indicate that the actual cyanide requirements are between 1 and 0.33 mole of ozone per mole of cyanide.

Any dilute solution of soluble cyanates is undergoing Reactions 2 and 3. At room temperatures the equilibrium

$$NH_4^+ + CNO^- \rightleftharpoons NH_2CONH_2 \qquad (5)$$

is almost completely to the right side of the equation (*6, 8, 20, 21*). Presence of the enzyme urease reverses the reaction to form ammonium carbonate (*13, 15, 16, 24*):

$$2H_2O + NH_2CONH_2 \xrightarrow{\text{Urease}} (NH_4)_2CO_3 \qquad (6)$$

Thiourea will hydrolyze in a similar manner to the ammonium and thiocyanate ions in an equilibrium essentially independent of pH, but the equilibrium will lie far to the thiocyanate side (*21*).

Kolthoff and Stenger (*14*) list the strongly alkaline hydrolysis of cyanates as a possible method of estimation of cyanates:

$$CNO^- + OH^- + HOH \rightarrow CO_3^{--} + NH_3 \qquad (7)$$

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch010

The standard method of analysis of cyanates involves the acid hydrolysis (*6, 19*), the kinetics of which have been studied by Amell (*1*):

$$CNO^- + 2H_2O + H^+ \rightarrow NH_4^+ + HCO_3^- \qquad (8)$$

Further, Tyler (*22*) and some subsequent workers (*5*) postulate a cyanate oxidation to the release of carbon dioxide and nitrogen:

$$2CNO^- + H_2O + 3O_2 \rightarrow 2HCO_3^- + 3O_2\uparrow + N_2\uparrow \qquad (9)$$

Thus the mechanism of destruction of the cyanate ion is not well understood, as in all likelihood Equations 5, 7, and 9 may all be occurring to some extent, dependent upon the conditions. Experimental difficulties experienced in attempting to follow accurately the course of the cyanate disappearance and measuring the products formed make selection of the predominant mechanism uncertain. The cyanate solution becomes saturated with ozone, and this may be monitored by its redox potential, using platinum or gold–S.C.E. electrodes. When the cyanide has disappeared, the redox potential quickly rises to a high value, which slowly increases as the reaction of oxidation or catalyzed hydrolysis proceeds, as shown by Figure 2. If the ozone flow is stopped, the potential falls almost immediately, and the degree and rate of fall with time depend upon the amount of cyanate remaining.

A tracing from an e.m.f. recorder is shown as Figure 7. A 0.033*M* cyanate solution was ozonated, the flow of oxidant stopped, and curves *A*, *B*, and *C* were recorded

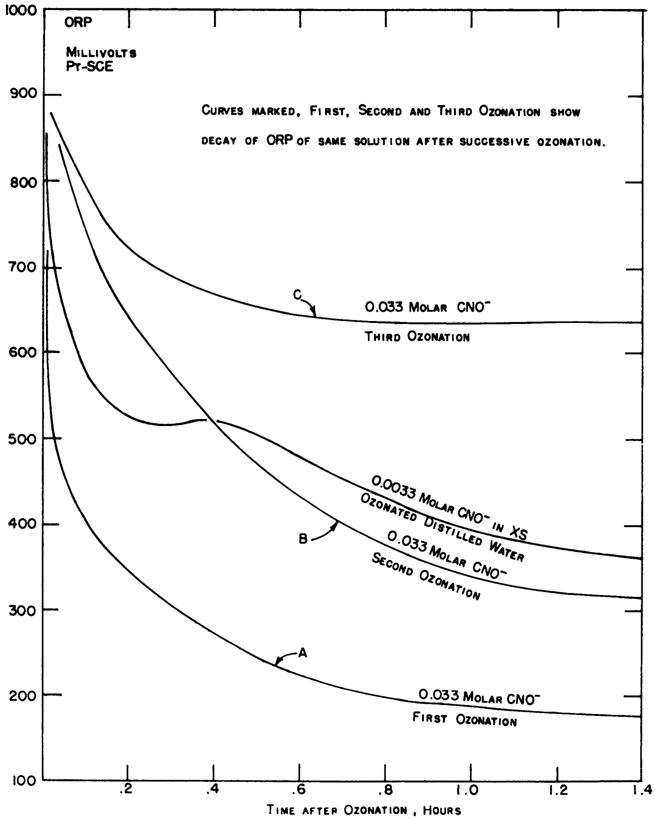

Figure 7. Effects of ozone on redox potential of solutions of cyanate ion

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch010

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch010

after successive ozonations. As the cyanate was consumed, the redox potential values become higher at any given time.

Then 0.01 mole of potassium cyanate was dissolved in a small amount of water and added to a saturated solution of ozone in 3100 ml. of neutral distilled water, which was agitated thoroughly. The redox potential fell to a minimum point, rose slightly, and then fell off in a normal decay curve. The raising of the pH which would follow upon addition of cyanate could catalyze the decomposition of ozone, but would not account for the minimum in the curve. Cyanate solutions will, therefore, exercise an ozone demand, whether through hydrolysis or oxidation, and ozone will be consumed until the demand is satisfied.

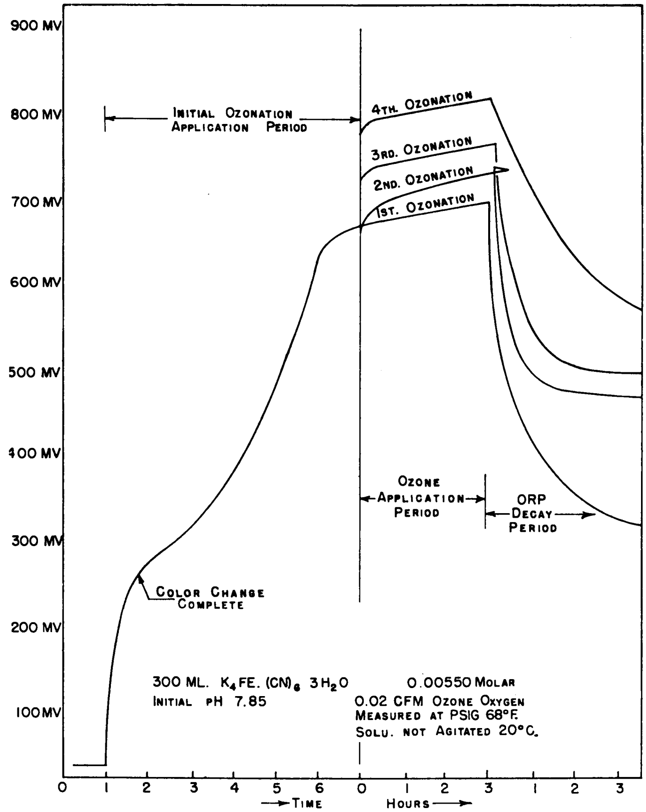

Figure 8. History of ozonation of ferrocyanide solutions

It has been reported that ozone will not decompose ferrocyanides or ferricyanides (*23*). In this work it was found that ozone oxidizes ferrocyanides first to ferricyanides and then to ferric hydroxide sols. The first effect noted in the ozonation of ferrocyanides was rapid change of color (see Figure 8). As ozonation proceeded, the solution became turbid with the ferric hydroxide sol, some of which later settled on the bottom of the absorption bottle and was identified as $Fe(OH)_3$. The ferricyanide was not completely consumed in any of the runs; traces remained even after prolonged ozonation. As soon as the ozone was admitted to the bottle, the pH of the solution rose very quickly and ran off the recorder chart. Acid was added to drop the pH to 4.2 on three occasions to keep the pH under 11.0. The third addition of acid held the pH at 10.4, which then slowly dropped off to neutrality. Tests of such ozonated solutions with

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch010

thiocyanate show the presence of ferric ion after the ozonation has been concluded. The addition of ferrous ions, with subsequent formation of the dark blue complex, showed that under the conditions studied some ferrocyanide ions still remained. Material balances on the ozone show that 39% of the total flow was absorbed, the remainder passing to the ozone trap. A ratio of 7.25 to 1 moles of ozone absorbed per mole of $K_4Fe(CN)_6 \cdot 3H_2O$ was found, but this ratio would include the ozone decomposed by catalysis due to hydroxyl ion and other causes.

Figure 8 shows the effect of ozone on the redox potential of ferrocyanide solutions. Successive additions of ozone show a decreased ozone demand in the solution.

Use of Redox Potential for Control of Ozone Addition

The use of oxidation-reduction measurements made on the waste solutions for control of the oxidation process appears to be a logical part of the design of such systems. The Gold–S.C.E. electrodes indicate the positive ozone content of an aqueous solution with good reliability. Gold electrodes appear to be more resistant to strong oxidants than do platinum electrodes. Gold is more susceptible to attack from free cyanides. The effects of agitation on the response of platinum–S.C.E. electrodes are shown in Figure 9. Better response appears to result when the solutions are thoroughly agitated. The redox potential of ozonized distilled water decays at a rate that is approximately linear on a plot of millivolts *vs.* log time as shown by Figure 10. In solutions containing ozone demand, such as cyanates, the decay is much faster, and is roughly proportional to the amounts of such ozone demand. Redox potential systems

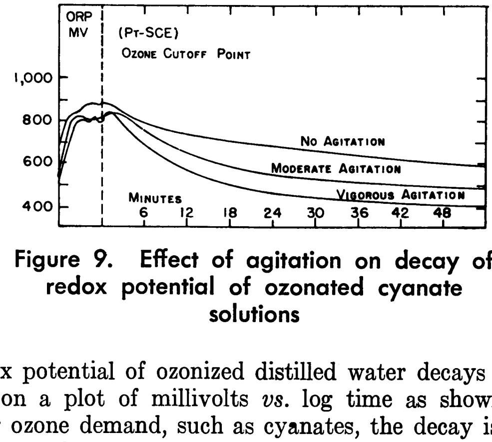

Figure 9. Effect of agitation on decay of redox potential of ozonated cyanate solutions

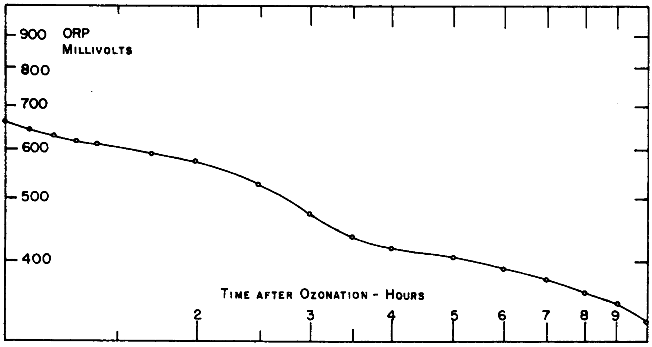

Figure 10. Decay of redox potential of saturated calomel electrode–platinum electrodes in agitation of ozonized distilled water at 25° C.

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch010

should be of the flow type, and the use of special ozone-resistant materials is indicated for wiring and the like. All rubber materials used should be fabricated from Hypalon or a poly(vinyl chloride) material, and stainless steel, aluminum, and ceramics should be used as materials of construction where ozone is present.

Treatment of Cyanide Solutions by Absorption in Packed Towers

The absorption of ozone by unagitated batch cyanide solutions at atmospheric pressure involves the sequence of initially complete absorption, followed by a period when ozone appears in the exhaust gas and cyanides are still present in the batch reactor. A countercurrent absorption tower was indicated to provide more intimate contact and better mass transfer where the last traces of ozone in the carrier gas would come in contact with the fresh solution at the top of the tower, and the weakest solution leaving at the bottom of the tower would come in contact with gas of the highest ozone content entering at that point. To investigate the characteristics of such a system, an all-glass absorption tower was constructed to study the effects of gas and liquid rates, tower height, and pH. Some of the data from these tests are presented in Tables I, II, and III.

Table I. Oxidation of Cyanides by Ozone

Tower pressure = 1 atm.

Feed solution. 80.5 p.p.m. of cyanide ion at pH 8.50 and 28° to 30° C.

Ozonator. 8 p.s.i.g., 112 volts alternating current; feeding 0.12 cu. foot per minute of ozonized oxygen at 70° F. and 8 p.s.i.g.

Absorption towei. Heat-resistant glass; inside diameter, 4.094 inches; 4 feet long. Column cross section, 0.09152 sq. foot. Packed with 1/4-inch Intalox saddles

Tower Feed Rates			Bottoms Product			
	Lb./sq. ft.-hr.			CN⁻ residuals		
Gal./ min.	Liquid rate	CN⁻	pH	P.p.m.	Lb./sq. ft.-hr.	CN destroyed lb./sq. ft.-hr.,
0.20	1,092	0.0879	7.80	14.7	0.01605	0.0718
0.30	1,638	0.1319	7.85	21.8	0.03571	0.0962
0.40	2,184	0.1758	7.82	43.6	0.09522	0.0806
0.45	2,457	0.1978	7.90	48.0	0.1179	0.0799
0.50	2,731	0.2198	7.90	52.5	0.1434	0.0764
0.60	3,277	0.2638	7.42	55.1	0.1806	0.0832
0.70	3,823	0.3078	8.17	60.0	0.2294	0.0784
0.80	4,369	0.3517		63.0	0.2752	0.0765
0.90	4,915	0.3957	8.28	65.5	0.3219	0.0738
1.00	5,461	0.4396	8.30	66.5	0.3632	0.0764
1.10	6,007	0.4835	8.34	67.0	0.4025	0.0810
1.40	7,646	0.6155	8.38	68.9	0.5268	0.0887
1.60	8,738	0.7034	8.40	67.5	0.5898	0.1136
2.00	10,922	0.7922	8.48	65.2	0.7121	0.0801

Table II. Oxidation of Cyanide by Ozone

Feed solution. 82.5 p.p.m. of cyanide ion at pH 7.40 and 29.5° C.

Ozonator. 8 p.s.i.g., 112 volts alternating current; feeding 0.10 cu. foot per minute at 8 p.s.i.g. and 70° F.

Absorption tower. As described in Table I.

Tower Feed Rates			Bottoms Product			
	Lb./sq. ft.-hr.			CN⁻ residuals		
Gal./ min.	Liquid rate	CN⁻	pH	P.p.m.	Lb./sq. ft.-hr.	CN destroyed, lb./sq. ft.-hr.
No ozone			7.50	82.5		0.0
0.20	1,092	0.09009	7.70	6.5	0.007098	0.0830
0.30	1,638	0.1351	7.60	11.2	0.01835	0.1167
0.40	2,184	0.1802	7.46	26.0	0.05678	0.1234
0.50	2,731	0.2253	7.45	36.3	0.09914	0.1262
0.60	3,277	0.2704	7.47	46.4	0.1521	0.1183
0.80	4,369	0.3604	7.45	59.0	0.2578	0.1026
1.00	5,461	0.4505	7.43	66.0	0.3604	0.0901
1.20	6,553	0.5406	7.47	72.4	0.4744	0.0662
1.40	7,646	0.6308	7.46	74.0	0.5532	0.0776
1.60	8,738	0.7209	7.45	77.4	0.6763	0.0446
1.80	9,830	0.8110	7.50	78.3	0.7697	0.0413
2.00	10,922	0.9011	7.46	78.3	0.8552	0.0459

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Table III. Oxidation of Cyanides by Ozone at Atmospheric Pressure

Feed solution. 44.5 p.p.m. of cyanide ion at pH 8.80 and 28° to 30° C.

Ozonator. 8 p.s.i.g., 112 volts alternating current; feeding 0.10 cu. foot per minute of ozone (1.78% by weight) at 8 p.s.i.g. and 70° F.

Absorption tower. As described in Table I.

Tower Feed Rates			Bottoms Product			
	Lb./sq. ft.-hr.			CN^- residuals		
Gal./min.	Liquid rate	CN^-	pH	P.p.m.	Lb./sq. ft.-hr.	CN destroyed, lb./sq. ft.-hr.
0.20	1,092	0.04859	7.82	0.90	0.00983	0.0476
0.30	1,638	0.07289	7.70	2.80	0.00458	0.0683
0.40	2,184	0.09719	7.68	8.70	0.01900	0.0782
0.60	3,277	0.1458	7.82	18.2	0.05964	0.0862
0.80	4,369	0.1944	8.15	27.3	0.1193	0.0751
1.00	5,461	0.2430	8.17	30.4	0.1660	0.0770
1.20	6,553	0.2916	8.20	32.3	0.2117	0.0799
1.40	7,646	0.3402	8.20	35.3	0.2699	0.0703
1.60	8,738	0.3888	8.27	36.4	0.3181	0.0707
1.80	9,830	0.4374	8.28	37.0	0.3637	0.0737
2.00	10,922	0.4860	8.31	39.0	0.4260	0.0600

The tower was operated through a range of liquid rates with constant-composition feed solutions and feed gas, and the effects on cyanide content and pH were noted. The tower was operated, in most cases, at cyanide feed rates considerably in excess of the ozone-generating capacity of the laboratory ozonator, to facilitate the analytical determination of cyanides. Flow data taken on the ozone content of the feed were discarded in the first runs because of experimental errors, but the bottoms product shows a relatively constant cyanide removal throughout the various flow ranges studied. The flow rates were increased to as high as 30,000 pounds per sq. foot per hour without flooding. In Table III the ozone was determined by analysis to be 1.78% by weight, and the gas flow was metered through a rotameter. The ozone produced during this run was less than two thirds of that required to accomplish the cyanide oxidation which was found by analysis; this indicates that ozone may react on the basis of 0.33 mole of ozone per mole of cyanide as suggested by Walker and Zabban (*23*).

The reasons for variation in the amount of cyanide destroyed at various flows are not clear. Each flow was held at least 15 minutes to establish equilibrium in the tower. The data being incomplete, it is believed that further work in progress will establish these effects more clearly.

Further runs were made with more dilute cyanide solutions in a 6-inch diameter ceramic tower with a 9-foot packed section, using the same packing; similar results were obtained.

The presence of heavy metals not complexed with cyanide offers no interference, and may be of some value in catalyzing the oxidation (*11*). If trivalent chromium is present in alkaline or neutral solution as the precipitated hydroxide, ozone will effect oxidation to the sexivalent stage. For this reason wastes containing both chromium and cyanides should be first oxidized, then acidified and reduced with sulfur dioxide or other reducing agent. The heavy metal should be precipitated and the reducing agent removed with excess ozone from the cyanide oxidation, leaving an oxidized effluent free from heavy metals.

Experimental Procedure

Ozone was generated for this study by a Welsbach T23 laboratory ozonator fed with oxygen. The samples were ozonated at atmospheric pressure in a 3.5-liter ceramic vessel containing a variable speed, all-glass turbine agitator, glass electrode, saturated calomel reference electrode, platinum or gold electrode, thermometer, and fritted glass diffusing bulb located at the bottom of the vessel. Redox potential and pH were measured by a Beckman H2 pH instrument, which was connected to a Fisher recorder to record these values directly. The recorder was provided with a zero shifter mechanism and was standardized against standard buffer solutions. Cyanides were determined by the A.P.H.A. standard method using dimethylaminobenzalrhodanine indicator (*2*), and cyanates by hydrolysis in acid solution to ammonia, with colorimetric analysis using Nessler's reagent (*19*).

Packed tower studies were made with a borosilicate glass column 4 inches in inside diameter packed with ¼-inch ceramic Intalox saddles. The feed was metered through a rotameter from a constant-head tank, and distributed through the tower with a perforated aluminum plate. Aluminum tubing and polyethylene pipe were used to connect the ozone generator to the tower. A continuous sample was withdrawn from the tower bottom for analysis, and exit gas from the top of the tower was conducted to a wet-test meter for volume measurements. Ozone was absorbed in 5% potassium iodide solutions and titrated with thiosulfate to a starch end point.

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Kinetics of Ozonation of Cyanides

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Rates of oxidation of aqueous cyanide solutions by ozonized oxygen have been determined under a variety of controlled conditions. The reaction rate constant is more than doubled when copper(II) ions are added as a catalyst, but increasing copper(II) concentration does not markedly affect the reaction rate. The rate is not affected by copper sulfate, nitrate, acetate, or sulfide, or by temperatures from 13° to 30° C.

The first waste cyanide solutions of any significance were produced in the gold and silver mining industries, where cyanides were used to dissolve the metals from their ores. Since that time the use of cyanides has expanded significantly into the field of electroplating and case hardening of steel parts.

The problem of the disposal of cyanide waste has become increasingly important because sewage disposal regulations in many communities require the removal of wastes that are toxic to plant and animal life.

Various methods for treating cyanide containing industrial wastes have been used. Dodge and Reams (*3*) have written an extensive literature review on this subject for the American Electroplaters' Society. These methods have been classified into two general groups: physical methods and chemical methods.

One important chemical treatment of such waste is treatment with gaseous ozone. This method has not received adequate attention. Ozone has become important in recent years as an industrial raw material for the chemical industry. It is now available in tonnage quantities at a competitive cost for use as an oxidizing agent and as a chemical raw material. An excellent compilation of history, generation, and properties of ozone has been prepared by Hann and Manley (*5*).

Studies of ozone and cyanide reactions have been published by Neuwirth (*7*), Tyler and coworkers (*8*), and Walker and Zabban (*9*). The chief results of these investigations were material balances which simply related the simultaneous disappearance of ozone and cyanide under various conditions (*6*).

Theoretical Considerations

A gaseous mixture of oxygen and ozone is bubbled through a vessel containing an aqueous solution of cyanide ion. The ozone dissolves in the liquid and then reacts with the cyanide ions. If the reaction in the liquid solution can be represented by the following equation:

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$$n\mathrm{CN}^- + m\mathrm{O}_3 + (xs)\mathrm{H_2O} \rightarrow n\mathrm{CNO}^- + (xs)\mathrm{H_2O} + \text{products}$$

the rate of cyanide disappearance can be expressed as:

$$-\frac{d[\mathrm{CN}^-]}{d\theta} = k'[\mathrm{O}_3]^m[\mathrm{CN}^-]^n$$

It was assumed in correlating the data that the ozone concentration in the liquid remains substantially constant after the first minute or two of the start of the reaction, because:

The concentration of ozone in the gas phase was maintained fairly constant and ranged from 70 to 90 mg. of ozone per liter of oxygen.

In most of the data reported here, the rate of ozone application was 20 to 25 mg. per minute.

The solubility of ozone, in water at 20° C., is low (25 mg. per liter of water).

The rate constants presented are fairly consistent when based on this assumption, which seems plausible. However, the observed reaction rate may deviate somewhat from a calculated rate during the first minute or two of the reaction time. Consequently, on the assumption that the ozone concentration in the solution is constant, the rate equation can be simplified by combining the constants,

$$K = k'[\mathrm{O}_3]^m$$

Thus, the new rate equation becomes:

$$-\frac{d[\mathrm{CN}^-]}{d\theta} = K[\mathrm{CN}^-]^n$$

Apparatus

A Welsbach T-23 Model laboratory ozonator was utilized to produce ozonized oxygen from cylinder oxygen which had been scrubbed to remove carbon dioxide. Figure 1 shows the general features of the experimental equipment, with the 1500-ml. borosilicate glass reactor used for batch reactions. The 1500-ml. absorption tower packed with borosilicate glass rings and equipped with a pump to recycle the solution from the bottom to the top of the tower is not shown.

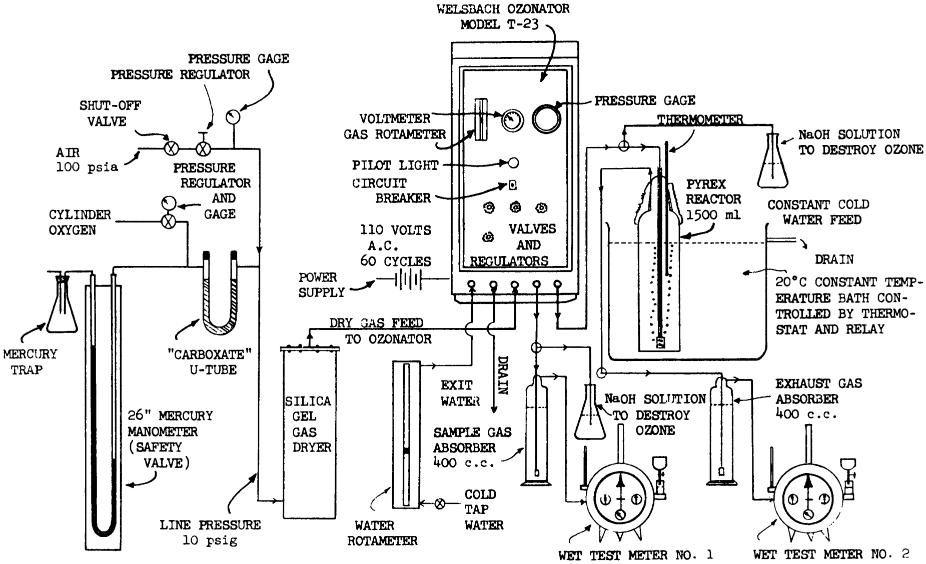

Figure 1. Flow diagram of apparatus for ozonation of cyanides

Analytical Procedures

The iodometric method for the determination of ozone concentration in oxygen consists of absorbing the sample containing ozone in a 2% solution of potassium iodide. The iodine produced is titrated with standard potassium thiosulfate solution, using starch as an indicator.

The pyridine-benzidine colorimetric method (*1, 2*) was used for determination of the cyanide in solution.

The 1500-ml. sample of 100 p.p.m. of potassium cyanide as CN^- (cyanide ions) aqueous solution, with potassium hydroxide added to raise the pH, was introduced into the reactor (bottle type or absorption column). The desired catalytic solution was added by means of a pipet. The ozonized oxygen was passed into the reactor and the exhaust gas was measured by a wet-test meter, after the excess ozone had been scrubbed out by a potassium iodide solution. At the same time a separate sample of exit gas was analyzed by using potassium iodide solution and measuring the gas with a gas meter. The gas stream to the reactor was led into another gas absorption bottle with potassium iodide solution at definite intervals, so that samples of the residual cyanide solution could be withdrawn.

The concentration of ozone in the oxygen was calculated as milligrams of ozone per liter of oxygen. The amount of ozone to be applied to the cyanide solution was determined from this. The cyanide concentration as a function of time was calculated from the periodic cyanide analyses.

Variables Studied. Effect of copper(II) concentration from copper sulfate on the reaction rate.

Effect on the reaction of copper(II) from salts—cupric chloride, nitrate, acetate, and sulfate.

Effect on the reaction rate due to the physical manner in which ozone and cyanide interact, in a reactor bottle or a packed column.

Effect on the reaction rate due to cations of copper(II), nickel(II), manganese(II), and cadmium(II) sulfate.

Effect of solution temperature on reaction rate over the range 13° to 30° C.

Discussion of Results

A series of runs was made to study the ozonation of cyanide under a variety of conditions. Figures 2 to 5 are graphical representations of results from runs 55 to 83.

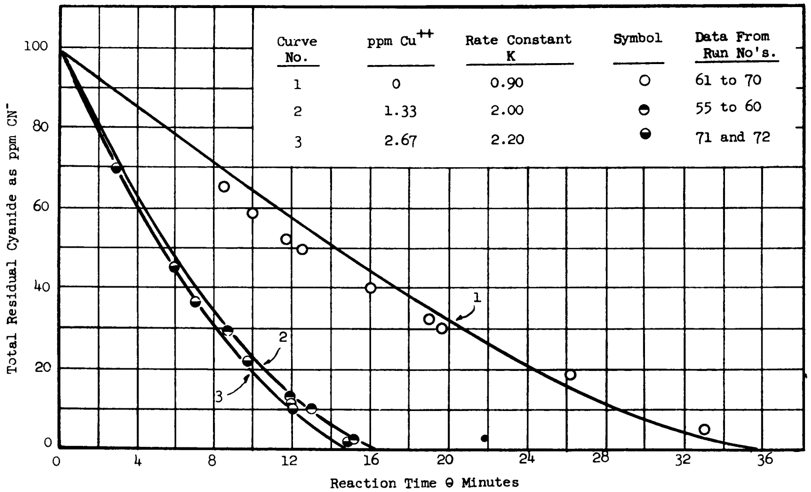

Figure 2. Effect of copper(II) sulfate on ozonation rate of potassium cyanide in water solution

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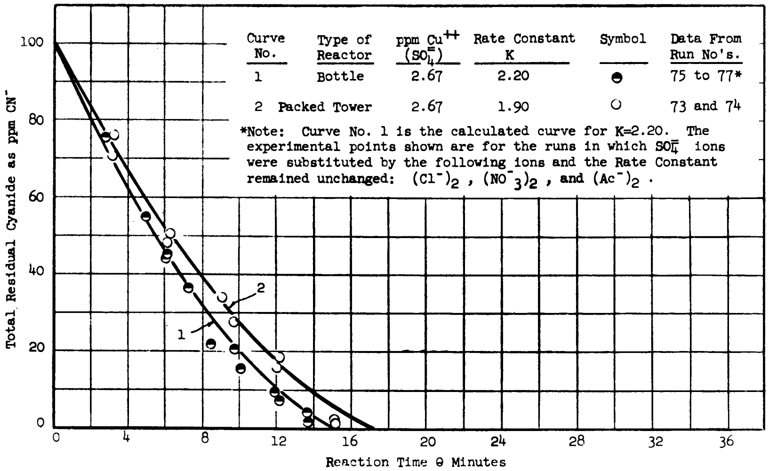
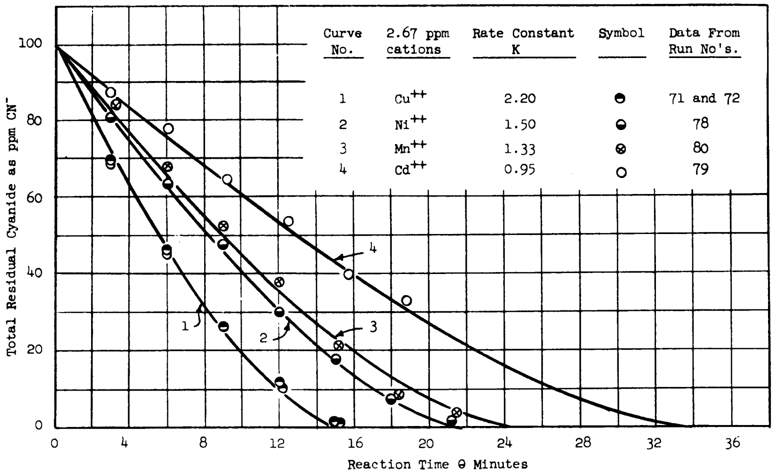


Curve No.	Type of Reactor	ppm Cu^{++} ($SO_4^=$)	Rate Constant K	Symbol	Data From Run No's.
1	Bottle	2.67	2.20	●	75 to 77*
2	Packed Tower	2.67	1.90	○	73 and 74

*Note: Curve No. 1 is the calculated curve for K=2.20. The experimental points shown are for the runs in which $SO_4^=$ ions were substituted by the following ions and the Rate Constant remained unchanged: $(Cl^-)_2$, $(NO^-_3)_2$, and $(Ac^-)_2$.

Figure 3. Effect of type of reactor used and different anions of copper salts on ozonation rate of potassium cyanide in water solution



Curve No.	2.67 ppm cations	Rate Constant K	Symbol	Data From Run No's.
1	Cu^{++}	2.20	●	71 and 72
2	Ni^{++}	1.50	◒	78
3	Mn^{++}	1.33	⊗	80
4	Cd^{++}	0.95	○	79

Figure 4. Metal sulfates used as catalysts on ozonation rate of potassium cyanide in water solution

All runs were conducted at 20° C., with the exception of runs 81, 82, and 83. The pH was maintained at 11.3 ± 0.5 in order to hold this variable constant. These runs were all conducted in the bottle-type reactor, with the exception of 73 and 74, which were conducted in the packed absorption tower.

In Figure 6 typical data are plotted as residual cyanide in solution *vs.* reaction time.

$$\text{Rate of KCN disappearance} = r = -\frac{d[\text{KCN}]}{d\theta} = -\frac{d[\text{CN}^-]}{d\theta}$$

where r = slope of curve in Figure 6.

Now, $r = K[\text{CN}^-]^n$

where n is the order of reaction with respect to the cyanide concentration.

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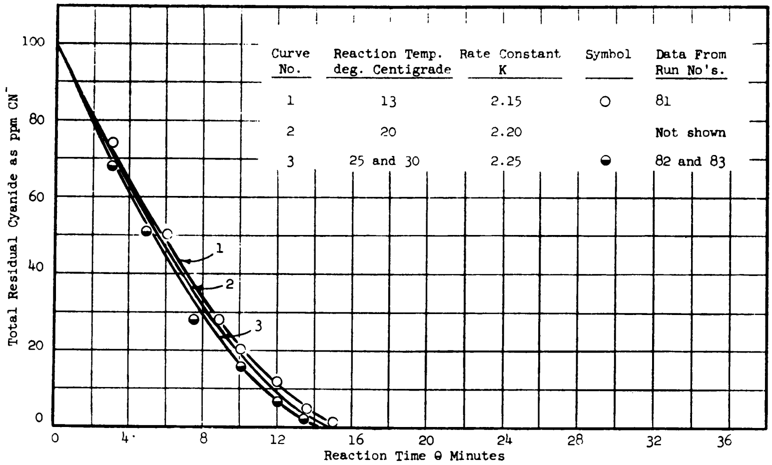


Figure 5. Effect of temperature on ozonation rate of potassium cyanide in water solution

2.67 p.p.m. $Cu(SO_4)$ used as catalyst

To find n, the following simplification is conducted:

$$\log r = n \log [CN^-] + \log K$$

Figure 7 shows the plot of residual potassium cyanide as parts per million of cyanide *vs.* reaction rate r. The slope of these lines is constant and is expressed as:

$$\text{Slope} = n = \frac{\Delta(\log r)}{\Delta(\log CN^-)}$$

Curve 4 in Figure 7 is the calculated result of data shown in Figure 6. Curves similar to Figure 6 were obtained for all the data and calculations of slope r at various

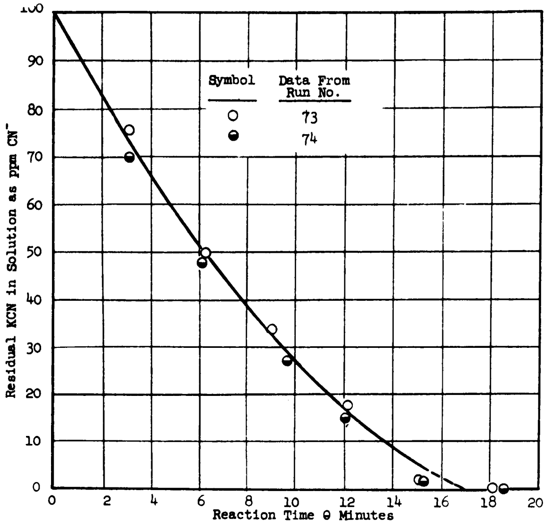
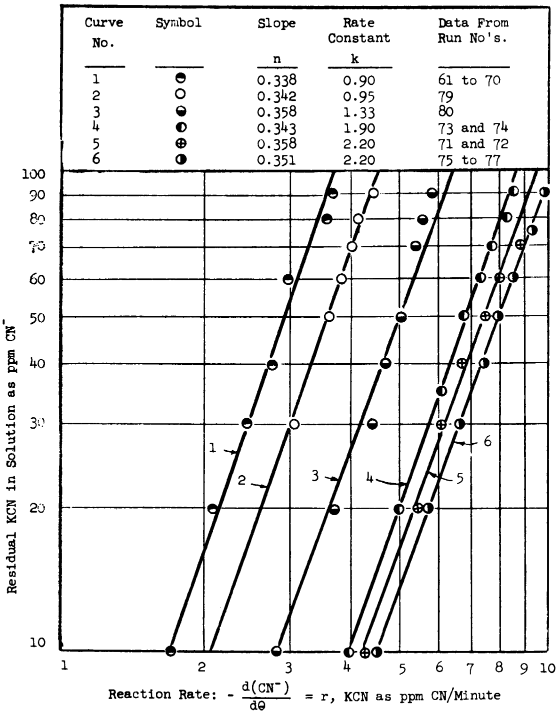


Figure 6. Rate of ozonation of potassium cyanide



Curve No.	Symbol	Slope n	Rate Constant k	Data From Run No's.
1	◓	0.338	0.90	61 to 70
2	○	0.342	0.95	79
3	◒	0.358	1.33	80
4	◐	0.343	1.90	73 and 74
5	⊕	0.358	2.20	71 and 72
6	◑	0.351	2.20	75 to 77

Figure 7. Calculation of order of reaction of potassium cyanide and ozone with respect to cyanide concentration

potassium cyanide concentrations. These data were plotted, as shown in Figure 7, for several runs.

Calculated Values of *n* and *K*

Run No.[a]	*n*	*K*
55 to 60	0.339	2.00
61 to 70	0.338	0.90
71 to 72	0.358	2.20
73 to 74	0.343	1.90
75 to 77	0.351	2.20
78	0.345	1.50
79	0.342	0.95
80	0.358	1.33
81	0.362	2.15
82	0.352	2.25
83	0.362	2.25

[a] Runs 1 to 54 are not reported here. These are available in (*6*).

The fractional value for *n*—i.e., the apparent order of reaction—is probably due to the complex nature of the competing reactions and the instability of the intermediates. In other words, the mechanism and the kinetics of ozone decomposition in aqueous solution and the possible intermediate unstable ozonide-ring leading from cyanide to cyanate will affect the apparent order of reaction.

Thus:

$$-\frac{d[CN^-]}{d\theta} = K[CN^-]^{1/3}$$

or

$$-\int_{CN^- = 100}^{CN^-} \frac{d[CN^-]}{[CN^-]^{1/3}} = K \int_{\theta=0}^{\theta} d\theta$$

Integrating,

$$-([CN^-]^{2/3}_{\theta_2} - [CN^-]^{2/3}_{\theta_1}) = (2/3)K(\theta_2 - \theta_1)$$

At the start of the reaction in this investigation on all runs,

$$\theta_1 = 0 \text{ and } [CN^-]_{\theta_1} = 100 \text{ p.p.m. } CN^-$$

Substituting these values and simplifying, one gets

$$[CN^-] = [21.6 - 2/3K\theta]^{3/2}$$

where $[CN^-]_\theta$ is CN^- concentration in parts per million after θ minutes of reaction.

To calculate the value of K, the rate constant with respect to cyanide concentration, several values of $[CN^-]$ and θ were taken from the type of graph shown in Figure 6, and K was calculated from the above equation.

For the data shown in Figure 6, the following values of K were calculated:

θ Minutes	CN^-, P.P.M.	K
1	91.0	1.95
2	82.5	1.95
5	59.0	1.92
7	45.5	1.87
10	27.5	1.87

The modified rate constant, K, was calculated for all the variable conditions studied (Figures 2 to 5). All the curves on these figures are based on calculated values from the rate equation and the calculated values of K.

Figure 2 shows the ozonation of cyanide in the absence of any catalyst and with different concentrations of copper(II) ions from copper sulfate. The addition of copper(II) ions more than doubles the rate of ozonation of cyanide. However, doubling the copper(II) concentration did not markedly increase the rate of ozonation. The calculated values of K are tabulated on Figure 2 as a function of copper(II) concentration.

Figure 3 shows the ozonation for two different types of reactors: the 1500-ml. bottle reactor and the 1500-ml. packed tower reactor. There is no marked difference in the reaction rate constants, although the packed tower has a slightly lower rate constant than the bottle. If mass transfer were controlling in the reaction, the great deal of agitation in the packed tower would be expected to increase the value of K. The results, however, do not indicate this. It can be concluded that the ozonation does not need to be conducted in a packed tower type of reactor, and that the rate of solution of ozone is very fast compared to the rate of its reaction with cyanide, and that the rate of reaction is controlling.

The experimental points shown for curve 1 are those for runs in which the sulfate anions of copper(II) cations were replaced by $(Cl^-)_2$, $(NO_3^-)_2$, and $(Ac^-)_2$ anions, in order to observe the anion effect on the value of K. It is apparent that no such effect exists, as the experimental points followed the calculated curve for the sulfate anions. It is concluded that the critical ion of the catalyst is the cation, and that the anions do not affect the reaction rate.

In Figure 4, the results are shown for studies on the use of cations of the sulfate salts of copper(II), nickel(II), and cadmium(II) on the value of K. Copper(II) gave the highest rate constant and then nickel(II), manganese(II), and cadmium(II) in decreasing order. $K = 0.95$ for cadmium(II) ions, while the uncatalyzed reaction (see Figure 2) gave a value of $K = 0.90$. These values are substantially identical for the purposes of this investigation. It can be concluded that copper(II) ions gave the highest value of K among the cations studied and that the presence of any cation studied did not prevent the ozonation of cyanide.

Values for Single Electrode Potentials *(4)*

Ion	Electrode Potential	K^a
Mn^{++}	1.10	1.33
Cd^{++}	0.401	0.95
Ni^{++}	0.231	1.50
Cu^{++}	−0.344	2.20
Ag^{+}	−0.7978	—
Hg^{++}	−0.7986	—
Pb^{++++}	−0.80	—

[a] Calculated from this investigation.

The order of increasing *K* values for cadmium(II), nickel(II), and copper(II) is the order in which these metals appear in the electromotive force series, except for manganese(II) ions. It is generally understood that as the electrode potential of metals decreases, their oxides become more and more unstable. Thus, the oxide of copper is the most unstable among the cations studied. This leads to the belief that the mechanism of catalysis of the cations is by forming an oxide with the ozone and the cation is regenerated by reaction of the oxide with cyanide. In order to investigate this concept further and to reach a definite conclusion, work should be conducted using silver(I), mercury(II), and lead(IV) as cations. If this concept is valid, these cations will give an increasing value of *K* in the order as listed.

This leads to some speculation as to the role of manganese(II) ions in the reaction. When manganese(II) was used as a catalyst, a slight turbidity was observed in the solution. The manganese(II) could have formed a hydroxide in the alkaline solution. Thus, the possibility exists of its giving poor catalysis in the reaction.

Results are compared in Figure 5 for the ozonation of cyanide at 13°, 20°, 25°, and 30° C. Although the value of *K* increases slightly with increase in temperature, it can only be concluded that the temperature coefficient of the reaction rate constant is small. Thus, the rate of ozonation of cyanide does not depend, for practical purposes, on the temperature in the range of 13° to 30° C. It would be highly interesting to study the temperature effect of this reaction in the light of the rate of ozone decomposition and ozone solubility in solution.

It is obvious that ozonation of cyanide can be used for treatment of effluent containing cyanides. The reaction is not affected, for practical purposes, by the temperature of effluents to be ozonated.

For all practical purposes the oxidation of cyanide by ozone stops at cyanate. Cyanates are reported to be a thousand times less toxic than cyanides. In practice, cyanate has been reported to be readily hydrolyzed to the relatively nontoxic products of ammonium carbonate and urea.

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Conclusions

The following rate equation correlates the data from the ozonation of cyanide based on cyanide disappearance:

$$-\frac{d[CN^-]}{d\theta} = K[CN^-]^{1/3}$$

where $[CN^-]$ = concentration

θ = reaction time

K = reaction rate constant

Apparent order of the reaction = 1/3

The reaction rate constant is more than doubled when copper(II) ions are added as a catalyst. Increasing the copper(II) concentration does not markedly increase the reaction rate.

The rate constant for ozonation of cyanide increases in the following order with the sulfate salts of the cations; cadmium(II), manganese(II) nickel(II), and copper(II). The rate constant for cadmium(II) is practically the same as for the uncatalyzed reaction.

The rate constant is not affected by the following anions of copper salts: sulfate, nitrate, acetate, and chloride.

Temperatures in the range of 13° to 30° C. do not substantially affect the value of the rate constant.

Acknowledgment

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Catalytic Atmospheric Ozone Analyzer

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With the catalytic ozone analyzer described, ozone concentration can be measured by the temperature differential between two thermistors placed in the gas stream. One of the thermistors is coated with a catalyst promoting the decomposition of ozone; the other is uncoated and is used as reference to the temperature of the gas. The two thermistors are part of a bridge circuit, the output of which is fed directly to a recorder. The instrument is not affected by the presence of water vapor, carbon monoxide, chlorine, nitrogen dioxide, sulfur dioxide, organic peroxides, hydrocarbon vapors, and combustion smokes at their usual concentrations in polluted atmospheres.

The problem of controlling atmospheric pollution in industrial areas has become acute. This pollution is characterized by decreased visibility, eye and nose irritation, deterioration of rubber articles, and damage to vegetation. In extreme cases it may even affect human life.

Atmospheric pollution cannot be controlled so long as the nature and the mechanism of formation of its deleterious constituents remain unknown. While many chemical constituents of polluted atmospheres have been identified, their presence or concentration does not seem to follow a regular pattern. On the other hand, ozone is always present in polluted outdoor atmospheres. Its concentration consistently rises from a normal value of a few parts per hundred million to many times this value during periods of severe contamination. Whether ozone is the primary cause of pollution or is a secondary effect of the reaction of other substances is not entirely clear, but it appears to be an important link in the chain of chemical reactions which produce atmospheric pollution. Very likely, a knowledge of the variations of ozone concentration in atmospheres would permit a study of the influence of the various parameters, and this knowledge may eventually furnish a lead to an explanation of the mechanism of formation and the effects of pollutants.

Recently, a number of municipalities have become so concerned with the problem that they have installed automatic ozone recorders at strategic locations. Some of these instruments are based on the chemical determination of ozone by oxidation of potassium iodide, and colorimetric or electrometric measurement of the extent of the reaction. Others are spectrophotometric instruments; a few are based on rubber cracking. The value of the chemical determinations of ozone in the presence of the oxidizing or reducing substances present in polluted atmospheres is questionable. Spectrophotometric methods require a light path of a few hundred feet and cannot be moved easily from one location to another. Determination by rubber cracking is

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not specific and does not provide continuous indications, and its interpretation is subjective.

The Armour Research Foundation has developed an atmospheric ozone analyzer which is not subject to the drawbacks of the different kinds of apparatus mentioned.

Principle of Operation

The principle of the instrument is illustrated in Figure 1. The gas to be analyzed is circulated through a chamber containing two thermistors. One of these is coated with a catalyst to promote decomposition of ozone. The two thermistors are part of a bridge circuit, which is schematically shown in Figure 2. Any increase in the temperature of the coated thermistor is reflected by a decrease in its resistance. The unbalance of the bridge causes a potential to appear between points *A* and *B*. This is fed to the chopper and amplifier of a Brown Elektronik recorder, and causes the balancing motor to rotate. The rotation of this motor is transmitted to the cursor of the potentiometer, *P*, which re-establishes the balance in the circuit.

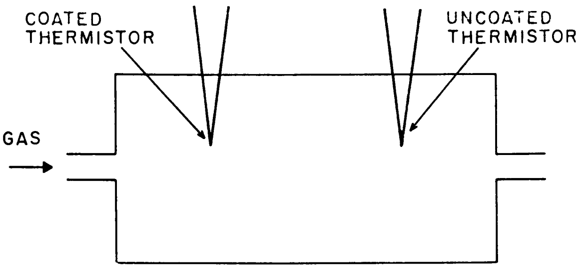

Figure 1. Principle of the ozone analyzer

The current from the battery flows continuously through the thermistors in such a way that their temperature is slightly higher than that of the surrounding gas. If

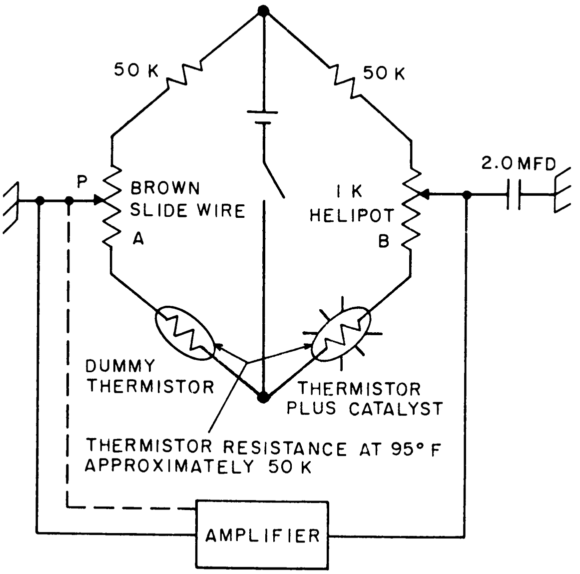

Figure 2. The bridge circuit

the gas flowing past the thermistors contains ozone, a certain number of molecules of ozone will strike the catalyst and decompose, generating a small amount of heat. The rate at which the heat is liberated may be assumed to be proportional to the molal ozone concentration in the gas. Because the rise in temperature of the coated thermistor is approximately proportional to the ozone concentration, the temperature differential between the two thermistors, and, therefore, the output signal, is also approximately proportional to the ozone concentration.

In this method no attempt is made to decompose all the ozone present in the sample. The cross section of the thermistors is purposely kept small in relation to the chamber in order to minimize adiabatic heat effects due to changes in velocity of the gas.

The thermistors (Model 101A1, Victory Engineering Corp.) are about 1/32 inch in diameter. They have a nominal resistance of 10^5 ohms at room temperature. The catalyst is applied by coating the thermistor with an adhesive and dipping into the pulverized catalyst. In this setup, the output of the bridge when the air stream contains 1 p.p.m. of ozone is about 0.001 volt, which corresponds to a decrease of 5 ohms in the resistance of the coated thermistor. This, in turn, corresponds to a temperature differential of about 0.001° C. per 1 p.p.m. of ozone between the thermistors.

The mechanical inertia of the recorder filters out all the noise from the circuit. The speed of response is such that the recorder pen traverses the full width of the scale in about 10 to 20 minutes when the ozone concentration is varied from 0 to 1 p.p.m. or from 1 to 0 p.p.m. This slow response may not be objectionable in following the variations of concentration in atmospheric ozone.

Hopcalite, manufactured by the Mine Safety Appliances Co., has been found to be an excellent catalyst for this purpose; it is a mixture of sintered metallic oxides. In a preliminary series of experiments, the catalyst qualitatively decomposed 90 p.p.m. of ozone in an air stream, and its activity remained unchanged after 100 hours of operation, when the experiment was discontinued.

Operation of Analyzer

If the two thermistors were perfectly matched in respect to their resistances, temperature coefficients of resistance, and heat dissipation characteristics, the analyzer could be operated without regard to variations in the temperature of the chamber or of the gas or in the rate of flow of the gas. In practice, the characteristics of a pair of thermistors differ appreciably. Thus, if the temperature of the chamber or of the gas is increased, the operating temperature of both thermistors also increases, but an undesirable differential occurs between the temperature of the two thermistors. Transient effects also appear when the temperature or rate of flow is abruptly changed. These are due to momentary differences between the rate of heating or cooling of the two thermistors. Such effects can be eliminated by enclosing the chamber containing the thermistors in a constant temperature bath and by regulating the air flow.

In the prototype the thermistors were enclosed in a massive aluminum block immersed in a water bath. The temperature of the latter was controlled to within 0.2° C. by the usual system of thermostat and heaters. Possible effects of cyclic variations of temperature within this range were not observable on the records or were less than those corresponding to 1 p.p.h.m. of ozone. It is possible that a temperature control as coarse as 1° or 2° C. might be adequate. The temperature of the gas was controlled by passing it through 4 or 5 feet of glass or aluminum tubing placed in the bath. From a theoretical standpoint the sensitivity of the analyzer is increased by maintaining the bath at a low temperature. Practically, the requirements for refrigeration, for more efficient heat exchange between the gas and the bath, and for prevention of moisture condensation in the chamber or on the thermistors make this solution unattractive. In the prototype the temperature of the bath was maintained at 32° C.—that is, slightly above room temperature.

When the rate at which the gas is passed over the catalyst is increased, the temperature of the thermistors is lowered, and if the two thermistors are not matched, a signal appears across the bridge. This difficulty was eliminated by circulating the gas by means of a small mechanical vacuum pump placed on the outlet of the chamber and by controlling the flow by means of a critical orifice between pump and chamber. The sensitivity of the analyzer is a complex function of the flow rate of the gas. In a low flow rate a small number of ozone molecules strike the catalyst per unit time. At a high flow rate the rate of heat dissipation from the thermistors is high. Thus, at both low and high flow rates the sensitivity is low. It is maximum for a flow rate corresponding to about 100 cc. per minute; this optimum flow rate is obtained by adjusting the critical orifice.

The sensitivity of the analyzer was determined by circulating synthetic mixtures of air and ozone prepared from 100% ozone with successive dilutions with air; these mixtures were prepared by members of the Ozone Technology Group.

An analyzer with a range of 0.1 to 10 p.p.m. of ozone is being used in the Biochemistry Research Section of the foundation. Another prototype with a range of 0.01 to 1 p.p.m. was found to be subject to drift. The drift was traced to temperature differentials between the various elements of the bridge circuit and leakages due to superficial condensation of atmospheric moisture. An improved instrument is being assembled in which all the elements of the circuit, except the balancing potentiometer, are enclosed in the thermostatically controlled bath.

The value of an atmospheric ozone analyzer is determined almost entirely by its specificity toward ozone. Chemical analytical methods are influenced by the presence of such reducing or oxidizing agents as chlorine, sulfur dioxide, nitrogen dioxide, and peroxides, which are all present in polluted atmospheres.

The influence of these agents on the catalytic analyzer was investigated by introducing measured concentrations of them into the air stream passing over the thermistors. The dilution apparatus is represented in Figure 3.

The influence of the pollutant was observed when air alone or ozone-air mixtures were passed over the thermistors. This procedure was repeated several times over a period of several hours in order not only to observe the influence of the pollutant on the zero position of the recorder pointer but also to ensure that the presence of

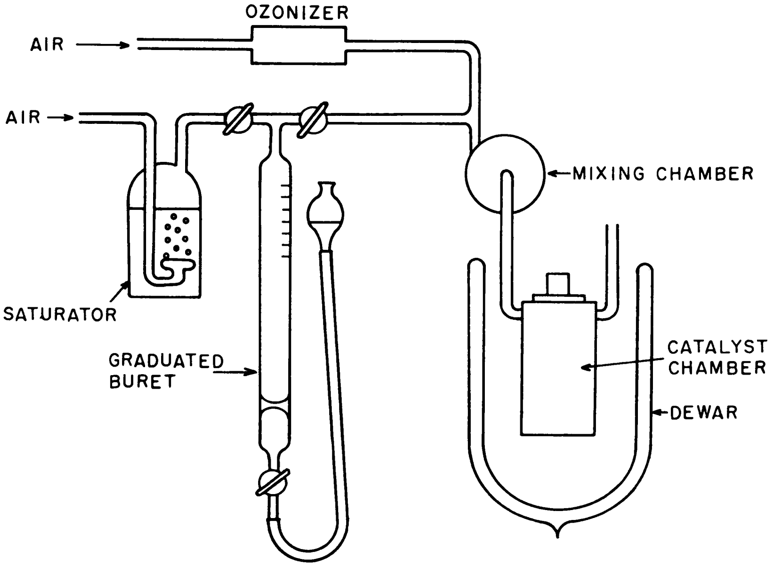

Figure 3. Diagram of the dilution apparatus

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the impurity had no effect on the sensitivity of the catalyst toward ozone. This effect would have been shown by a progressive change in magnitude of the deflection of the pointer when identical amounts of ozone were introduced in the gas stream.

Carbon Monoxide. It was found that 20 p.p.m. of carbon monoxide do not interfere with the operation or sensitivity of the analyzer. This result is surprising, because the catalyst used in this study (Hopcalite) is also used to detect carbon monoxide in a device manufactured by the Mine Safety Appliances Co. However, the catalyst must be carefully dried prior to use in order to decompose any carbon monoxide present. The inertness of the ozone detector to carbon monoxide in these experiments may be attributed to the poisoning of the catalyst by the water vapor normally present in the atmosphere.

Chlorine and Nitrogen Dioxide. Chlorine in concentrations to 20 p.p.m. does not affect the ozone analyzer.

Concentrations of nitrogen dioxide up to 10 p.p.m. have no perceptible effect. With 10 to 20 p.p.m. of nitrogen dioxide some slight irregularities were observed on the recorded trace. These irregularities are not reproducible and cannot be unambiguously attributed to nitrogen dioxide. As the atmospheric concentration of nitrogen dioxide in air seldom exceeds 3 p.p.m., the effect of this gas is probably negligible, even in measuring very low concentrations of ozone.

Water. A switch from substantially dry air to air of about 90% relative humidity does not perceptibly affect the analyzer. However, if liquid water collects over a thermistor, the bridge is thrown out of balance. The thermistor must then be dried by circulation of dry air for considerable periods of time before the operation of the bridge returns to normal.

Hydrocarbons and Smokes. Illuminating gas, benzene vapors, and cigar smoke did not appreciably affect the operation of the analyzer. No effort was made to measure the concentrations of these pollutants; however, the concentrations must have been much larger than those occurring in normal atmospheres. In particular, some of the transient effects observed with illuminating gas are believed to be due to excessive concentrations of this gas and to drastic changes in the heat transfer coefficient of the atmosphere surrounding the thermistors.

Peroxides. Even rather small concentrations of some peroxides affect the operation of the analyzer noticeably; the magnitude of the possible error in apparent ozone concentration due to peroxide contamination depends upon the particular peroxide or peroxides present. The analyzer differs widely in its response toward the various peroxides; the variations may be due either to the differences between the heats of decomposition of the compounds or to differences between rates of decomposition upon the catalyst. Uncertainty as to the chemical decomposition mechanism of the peroxides makes it difficult to calculate the heats of decomposition, so at the present time it has not been possible to determine exactly what causes the variations.

For instance, *tert*-butyl hydroperoxide at a concentration of 14 p.p.m. produces a deflection of 20 divisions on the recorder, or 1.4 divisions per 1 p.p.m. of peroxide. At volume concentrations equal to that of the ozone present, *tert*-butyl peroxide thus introduces an error of slightly over 2%.

At a concentration of 3.6 p.p.m. of cumene peroxide, the deflection is 3 divisions; the error is 1.2%. At a concentration of 120 p.p.m. of di-*tert*-butyl peroxide, the deflection is only 14 divisions, corresponding to an error of 0.18%.

Equal volumetric concentrations of ozone and some common peroxides produce the following relative deflections on the galvanometer:

Ozone	100
Hydrogen peroxide	7
tert-Butyl hydroperoxide	2
Cumene hydroperoxide	1.2
Di-*tert*-butyl peroxide	0.2

The data presented in the Technical Reports of Stanford Research Institute indicate that the concentration of peroxides or precursors in the atmosphere does not exceed one third or one half that of ozone. If only half of these peroxides are in the form of hydroperoxides of low molecular weight, similar to *tert*-butyl hydroperoxide, the error due to the presence of these interfering agents should not exceed 1% of the readings due to the presence of ozone alone.

In order to determine whether the activity of the catalyst might be affected by prolonged exposure to any one or a combination of some of the many compounds present in polluted atmosphere, some of the catalyst was shipped to the Stanford Laboratories and exposed to Los Angeles atmosphere for 100 hours during a period of smog. No significant difference was observed in the performance of the exposed catalyst as compared to that of fresh material. Thus, it appears that the normal atmospheric constituents of polluted atmospheres do not affect the sensitivity of Hopcalite toward decomposing ozone.

Admittedly, this experiment might not be conclusive; longer field trials in various polluted atmospheres will be required to measure the resistance of the catalyst to poisoning. Even in an unfavorable case, however, the catalyst-coated thermistor could be replaced in a few minutes.

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Determination of Ozone in Air by Neutral and Alkaline Iodide Procedures

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One per cent potassium iodide in neutral buffered or alkali solutions is more stable and useful than 20% potassium iodide in bubblers for collection and determination of ozone in air. Either 1% solution may be used to determine low concentrations of ozone; however, there is a difference in their stoichiometry. Over the range of 0.01 to 30 p.p.m. (v./v.) results by the alkaline procedure should be multiplied by 1.54 to correct for stoichiometry. The neutral reagent does not require acidification and has more nearly uniform stoichiometry. The alkaline procedure is preferable when final analysis may be delayed. Experiments with boric acid for acidification of samples in the alkaline reagent show that some mechanism other than oxidation of iodide to iodate or periodate is involved, possibly formation of hypoiodite. Preliminary experiments with gas phase titrations of nitrogen dioxide and nitric oxide against ozone confirm the stoichiometry of the neutral reagent as 1 mole of iodine released for each mole of ozone.

The determination of concentrations of ozone in air in the range of a few parts per million has become increasingly important as a result of current toxicological and air pollution studies. Toxic concentrations of ozone may be encountered in high altitude flights, as well as in rocket work and in inert gas-shielded arc welding. Ozone also appears to play a key role in certain smog-forming processes, as well as in the generation of eye irritants and plant-damaging substances. Although a great many methods for ozone determinations have been employed (*6*, *10*), the uncertain stoichiometry and the lack of specificity continue to be serious problems. The iodide chemical methods appeared to be among the most promising, and were selected for investigation.

Many workers have used iodometric methods for the determination of concentrations of ozone in the range of several per cent by volume and higher. They have investigated the stoichiometry by comparison of the amounts of iodine liberated with the amounts of ozone determined by physical measurements of gas density or pressure change. Thus Lechner (*5*) found that both neutral and alkaline ($0.2N$ potassium hydroxide) potassium iodide ($0.2M$) absorbed ozone efficiently and yielded the same amount of iodine, equivalent to one oxygen atom in the ozone molecule. This stoichiometry was confirmed by Boelter, Putnam, and Lash (*2*) for 4 to 20% ozone by weight absorbed in 0.2*M* potassium iodide buffered to various pH values from 2.3 to 12.3. In another recent study by Birdsall, Jenkins, and Spadinger (*1*), similar results were obtained for 1 to 25 mole % ozone (1.7 to 41 weight %) absorbed in 2% unbuffered potassium iodide, but results with boric acid-buffered solutions were high. The discrepancy between Birdsall's findings and those of Boelter was explained by the difference in sampling equipment: Boelter obtained good results with acid solutions because he used an absorption bulb in which the surface reactions could cause local alkalinity at the point at which ozone was absorbed. Birdsall used a bubbler in which absorption proceeded at the acid pH of the bulk of the solution. Although there are also contrary reports in the literature, the use of both neutral and alkaline iodide solutions for determination of high concentrations of ozone seems to be established.

Similar procedures have been applied to the determination of low concentrations of ozone in the parts per million range. Renzetti and Romanovsky (*6*) reported that in Los Angeles air the neutral method gives apparently low results (perhaps due to reducing pollutants) in the early and late hours of the day, and high results (perhaps due to other oxidizing pollutants) during the peak smog time of day, both as compared to ultraviolet spectrophotometric determinations of ozone. Smith and Diamond (*9*) recommended a reagent consisting of 1% potassium iodide in 1*N* sodium hydroxide, acidified after sampling with 1/5 volume of 36% phosphoric acid to release the iodine for spectrophotometric estimation. This was modified by Byers, Saltzman, and Hyslop (*3*), who found that the interference from nitrogen dioxide could be greatly reduced, and the colors stabilized, if the acid were saturated with sulfamic acid, which destroys nitrite. The specificity was investigated by Effenberger (*4*), who used 0.01*N* potassium iodide buffered to various pH values. The amounts of iodine liberated by ozone varied from 90% at pH 9 to 113% at pH 1, as compared to that at pH 7. For nitrogen dioxide the variation was much greater, the corresponding figures being 70 and 340%. Thus the two could be distinguished by simultaneous analyses at two different pH values. Saltzman (*8*) believed the 1% potassium iodide in 1*N* sodium hydroxide reagent more specific than the neutral reagents in the presence of oxidized hexene, and he also reported 62 to 70% stoichiometry for 3 to 27 p.p.m. (v./v.) ozone (as compared to the iodine released in a neutral reagent). The validity of the application of neutral and alkaline iodide reagents to the determination of low concentrations of ozone was therefore investigated.

The preparation of known low concentrations of ozone has always been a major difficulty in this type of investigation. A flow system was set up in which a stream of ozone from a dielectric-type ozonizer could be diluted with air purified by scrubbing with dichromate in concentrated sulfuric acid, followed by calcium chloride and silica gel. Flows were measured with rotameters and could be adjusted to give known dilution ratios. The reagents were used for wide ranges of undiluted and diluted ozone concentrations, and samples of widely varying sizes were collected. The assumption was made that the high concentration analyses were likely to be correct, and the deviations resulting from varying the sample sizes and from the dilution were studied.

Ozone Procedures

Reagents. Three reagents were tested extensively: reagent I, 20% potassium iodide in 0.1*M* potassium dihydrogen phosphate–0.1*M* disodium hydrogen phosphate; reagent II, 1% potassium iodide in the same neutral phosphate buffer medium; and reagent III, 1% potassium iodide in 1*N* sodium hydroxide, acidified after sampling with 1/5 volume of 36% phosphoric acid saturated with sulfamic acid. Reagent I was prepared fresh and used within several hours. Reagents II and III were allowed to stand for several days before being used. This stabilized the blank. With each reagent it was necessary to determine the reagent blank and to deduct it from all standardizations and determinations. Only the highest grade analytical reagents were used.

Reagent I is commonly used in oxidant recorders (*6*), but was too unstable and

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photosensitive for the usual manual procedures. Reagent II yielded almost as much iodine as reagent I with much superior stability. Reagent III proved the most suitable for field studies where hours or days might elapse between collecting and analyzing the samples.

Sampling. Samples were collected in 10 ml. of reagent in midget impingers using air-flow rates of 1 to 3 liters per minute. Other simple bubblers may be used; however, the midget impinger is most convenient and effective. Sampling of high concentrations by evacuated flasks was tried and found unsuitable.

Measurements. Iodine liberated by the ozone was measured photometrically or titrimetrically. The iodine absorbance at 352-mμ wave length was measured by a Beckman DU spectrophotometer. Test tubes of 2-cm. light path and matched to 0.5% transmittance were used in a special holder. Distilled water was used in the reference tube.

Titrations were made with 0.005*N* sodium thiosulfate in a semimicroburet and using a visual end point with starch indicator.

Procedures and standardization. Reagents I and II. After collection, the samples were transferred immediately to photometer tubes and the absorbances determined.

Standard graphs of absorbance *vs.* iodine (or ozone) were plotted from readings from a series of prepared standards. Standard 0.0100*N* iodine solution was freshly diluted with reagent solution to various strengths from zero to 0.00004*N* (5.08 γ of iodine per ml.) and the absorbances were determined. The ozone equivalent was calculated on the basis of $O_3 \Bumpeq I_2$ (1 ml. of $0.01N\ I_2 \Bumpeq 240\ \gamma$ of O_3).

Reagent III. The phosphoric acid reagent for use with the alkaline reagent was prepared as follows:

Several grams of reagent quality sulfamic acid were dissolved in 150 ml. of warm distilled water, then 126 ml. of 90% phosphoric acid were added and the mixture was made to 300-ml. volume with distilled water. After cooling, the precipitated sulfamic acid was removed by decantation (or centrifugation) and saved for preparation of future batches of reagent.

Samples in 10 ml. of the alkaline iodide reagent were rapidly acidified and mixed with 2.0 ml. of phosphoric acid reagent. The mixture (in a stoppered container) was cooled to room temperature in a water bath, and the absorbance determined 5 to 10 minutes after acidification.

A strong stock solution of potassium iodate (0.2973 gram per liter) was diluted 1 to 10 with distilled water to give a dilute standard, 1 ml. of which was equivalent to 105.8 γ of iodine. Aliquots of 0.1 to 0.5 ml. of this dilute standard were diluted to 10 ml. with reagent III and acidified and the absorbances read. Calculations were originally made on the basis of $3O_3 \Bumpeq KIO_3$ (1 ml. of dilute stock $KIO_3 \Bumpeq 20\ \gamma$ of O_3). The work showed the need for a correction factor of 1.54 which would make 1 ml. of dilute stock $KIO_3 \Bumpeq 30.8\ \gamma$ of O_3.

Calculation. The following relationship may be used rather than graphs for calculation of ozone concentrations:

$$\text{P.p.m. } O_3 = K\,A/V$$

where A is the absorbance corrected for the blank, V is the volume in liters of air sampled (corrected to 25° C. and 760 mm. of mercury), and K is the standardization factor. For 2-cm. tubes K was 4.61 for reagent I, 4.88 for reagent II, and 9.13 for reagent III. The last figure is higher because it incorporates the correction factor and because the corresponding absorbances are lowered by the dilution of the sample to 12 ml. by the acidification.

Effects of Sample Size

The undiluted ozone concentrations ranged from 300 to 5000 p.p.m., depending upon the flow rate and oxygen content of the gas passing through the ozonator, and

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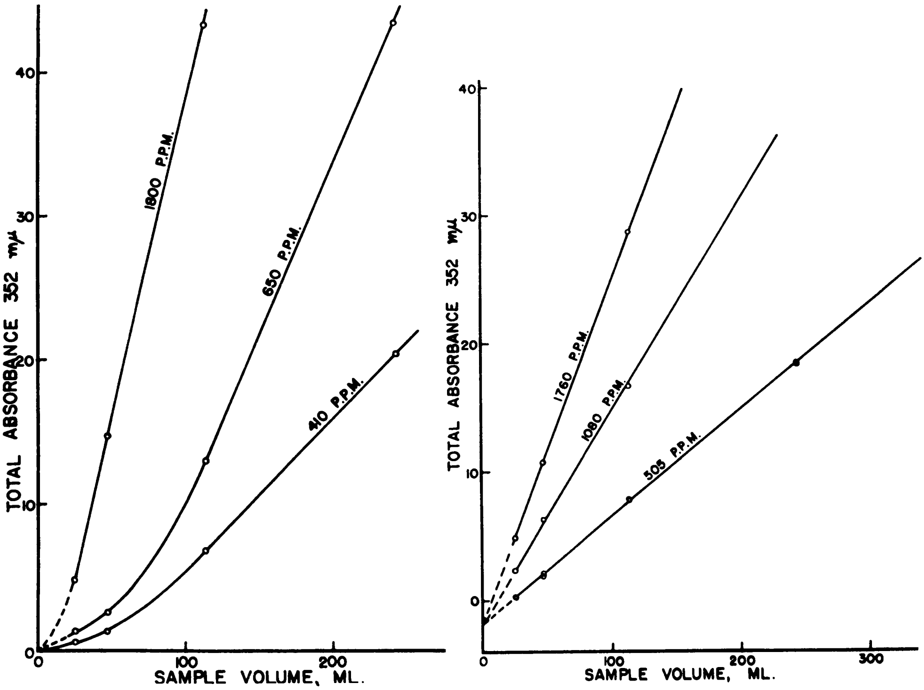

Figure 1. Effect of sample size on photometric determinations of high concentrations of ozone

Left. Neutral 20% KI reagent
Right. Alkaline KI reagent

the voltage applied. The photometric determination of these levels using reagents I and III had (*8*) been found unsatisfactory because of the extreme dilutions required to permit readings in the photometer and of a nonlinear relationship between the amounts of iodine and sample sizes as shown in Figure 1. This figure gives the data obtained by simultaneously sampling with calibrated evacuated bottles of various sizes, containing these reagents. The amounts of iodine were estimated photometrically, and some of the higher amounts were checked by titration. The plots show the total absorbance (the measured absorbance, corrected for the blank, multiplied by the dilution factor) for 2-cm. cells *vs.* sample size.

The neutral method with 20% potassium iodide (reagent I) gave curved lines in the useful photometric region, which approached straight lines only at absorbances requiring extreme dilutions. The values indicated for ozone were assigned on the basis of the limiting slopes of the curves at high values. The alkaline method (reagent III) gave almost straight lines, which seemed to converge to a negative absorbance at zero sample volume. This negative absorbance intercept may be regarded as the "ozone demand" of the reagent, and was found for both evacuated bottle and impinger samples at high concentrations. The ozone demand appeared to increase with the age of the reagent, and was reduced somewhat by the addition of iodate to the sampling reagent to produce artificially an appreciable positive iodine blank. This ozone demand was fairly constant through a small range of ozone concentrations, but increased somewhat at much higher absorbances and ozone concentrations. The reasons for these discrepancies are not known.

Subsequently high concentrations of ozone were determined by titrimetric procedures. Effects of errors due to sample size were thus minimized by liberation of larger amounts of iodine.

Reagents II and III were used successfully for photometric determination of low concentrations of ozone, as only slight discrepancies resulted from variations of sample size. This is shown in Figure 2, which also shows a difference in stoichiometry. The midget impinger with 10 ml. of reagent was used at sampling flow rates of 1, 2, and 3 liters of air per minute. The differences in flow rates had little or no effect except as they determined the volume sampled. Both reagents show good linear relationships of absorbance and sample size for ozone concentrations in the 0.1 to 20 p.p.m. (v./v.) range. The results by the alkaline procedure are consistently lower, with a tendency to an increasing proportion of iodine for very large samples.

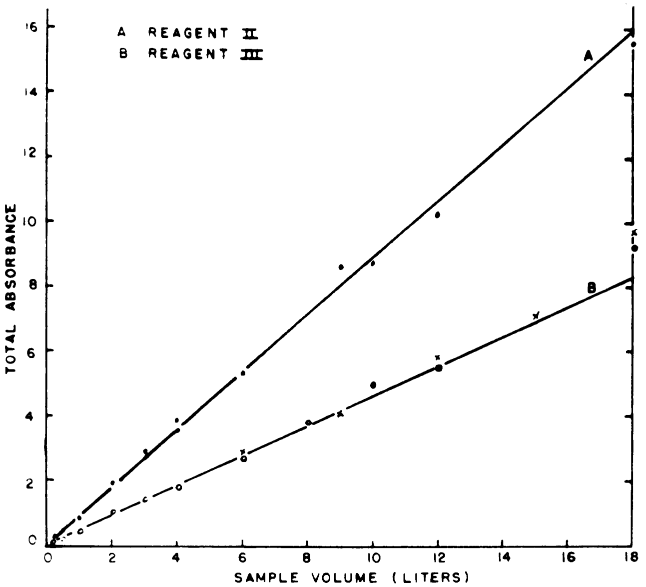

Figure 2. Effect of sample size on photometric determinations of low concentration (4.25 p.p.m.) of ozone with neutral and alkaline 1% potassium iodide reagents

Effects of Ozone Concentration

Analyses with reagents II and III were compared at both high and low concentrations. Low concentrations were obtained by accurately diluting high concentration ozone 1 to 99 with purified air. Simultaneous samples were collected and analyzed, with the results given in Table I. The two methods give fair agreement at concentrations of several thousand parts per million, but diverge at lower concentrations, the results by the alkaline procedure being consistently lower. Measurements of the diluted ozone by the neutral reagent gave about 85% of the calculated value with little variation, while the alkaline reagent gave much lower and more erratic results. Inasmuch as paired samples were collected simultaneously, the differences could not be due to fluctuations in ozone concentrations. Subsequent tests revealed a 6% loss of ozone in the system between the point of sampling the high concentration and the point of dilution. It appears that the stoichiometry of reagent II is more nearly constant with such changes of concentration.

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Table I. Simultaneous Determinations of Undiluted and Diluted Ozone Concentrations by Reagents II and III (Neutral and Alkaline)

Reagent II, P.P.M.		Reagent III, P.P.M.	
Undiluted	Diluted 1/100	Undiluted	Diluted 1/100
5350		4760	
5050		5400	
4310		4250	
3510		4360	
3030	25.1	3045	14.4
1895	15.9	1650	11.4
1413	14.4	1262	9.72
1280	11.5	1125	8.19
980	8.13	808	4.06
791	6.70	636	3.67
547	4.92	600	3.69
473	3.56	379	2.73
453	3.78	394	2.56
439		374	
437		375	
433		384	
425	3.81	353	2.53

Relative Values by Neutral and Alkaline Reagents

In Figure 3 the relationship between analyses by the neutral and alkaline reagents I, II, and III is shown for corresponding samples collected simultaneously or at very close intervals over a wide range of ozone concentrations. Because of the extreme range of concentrations a log-log plot is used. Concentrations above 100 p.p.m. (v./v.) were determined titrimetrically; below this, photometrically.

The differences between alkaline and neutral analyses cannot be explained by differences in absorption efficiencies, as they were high with all three reagents. When two impingers were used in series, the second never showed more than a few per cent of the amount of iodine released in the first impinger. Very little ozone was destroyed by the water, alkali, or sampling apparatus. When 1*N* sodium hydroxide (reagent III without potassium iodide) was used in the first of two impingers in series, 85 to 90% of the ozone passed into the second impinger. The apparently lost ozone was dissolved in the alkali, and by the addition of potassium iodide and acid it released iodine

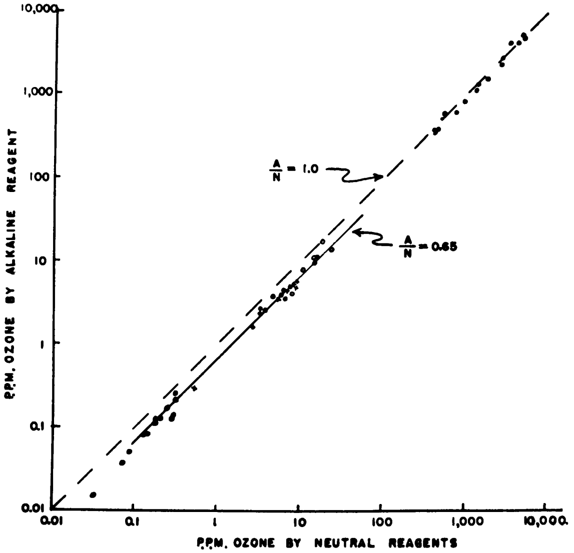

Figure 3. Determination of ozone in duplicate samples with neutral and alkaline reagents

for its determination. Thus it seemed likely that the absence of iodine in a second sampler was significant, and that the absorption efficiencies were high.

Differences likewise cannot be explained on the basis of standardization. The neutral reagents were standardized by adding dilute iodine solutions, and the alkaline reagent by adding standard potassium iodate. The iodine extinction coefficients in units of absorption (to logarithmic base 10) per centimeter per gram per liter were: (I) 104, (II) 99, (III) 97. The slightly higher coefficient for reagent I may be explained by the higher iodide concentration, which intensifies the iodine color. The slightly low coefficient for reagent III may be due to losses of iodine in the acidification procedure.

Assuming that the relationship in Figure 3 would be a straight line, or nearly so, the best fit was determined by the method of least squares. The photometrically determined points gave a line with a slope of 1.016, and all points shown gave a line with a slope of 1.045. Calculated relationships of results at several concentrations according to the best fit of photometric determinations are:

O_3 concentration, p.p.m.	0.01	0.1	1.0	10	100
Alkaline/neutral, %	60	62	64	66	69

When the data for both photometric and titrimetric results are fitted, the corresponding values by alkaline determinations range from 50 to 80% of the neutral reagent result.

The scatter of results shown by Figure 3 is such that the relationship of alkaline to neutral analyses of 65%, as indicated by the line $A/N = 0.65$ can be applied over the range of 0.01 to 30 p.p.m. and perhaps beyond at either end while staying within the probable experimental error. Because the neutral analyses are presumed to be more nearly correct, results of alkaline analyses should be multiplied by a correction factor of 1.54.

Stoichiometry

It thus seems that the actual reaction between the ozone and the iodide must have a different stoichiometry in alkaline solution. The reaction between ozone and iodide is commonly given as:

$$O_3 + 2H^+ + 2I^- \rightarrow O_2 + H_2O + I_2 \qquad (1)$$

In weak alkali, the equivalent reactions for the same stoichiometry are commonly given as:

$$3O_3 + I^- \rightarrow 3O_2 + IO_3^- \qquad (2)$$

followed upon acidification by:

$$IO_3^- + 6H^+ + 5I^- \rightarrow 3I_2 + 3H_2O \qquad (3)$$

Experimental evidence indicates that in strong alkali this pattern is not followed. When portions of samples in reagent III were acidified to pH 6.2 with solid boric acid, the iodine released was approximately 50% of that resulting from the usual acidification to pH 2. No iodine was obtained from reagent III with added iodate, upon acidification with boric acid. With added periodate, such acidification yielded 14 to 20% of the iodine obtained at pH 2. This compares with 25% reported for periodate by Willard and Merritt (*11*). A reasonable explanation of these data would appear to be the formation of hypoiodite by the following reaction:

$$I^- + O_3 \rightarrow IO^- + O_2 \qquad (4)$$

The dismutation of hypoiodite to give iodate appears to occur over a period of many hours. Another possible explanation could be the formation of iodite.

The stoichiometry is being confirmed in an independent way by gas titrations. A stream of ozone is mixed with either nitric oxide or nitrogen dioxide, and enough

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flow time is allowed for complete reaction, after which ozone and nitrogen dioxide are determined. In the former case, the ozone is converted to an equivalent amount of nitrogen dioxide:

$$O_3 + NO \rightarrow O_2 + NO_2 \qquad (5)$$

In the latter case, the following reaction occurs:

$$O_3 + 2NO_2 \rightarrow O_2 + N_2O_5 \qquad (6)$$

As Reaction 5 is 260 times as fast as 6, in the presence of excess nitric oxide, no appreciable quantities of nitrogen pentoxide need be expected. Linear relationships are found between the amounts of ozone and the amounts of nitrogen dioxide generated or consumed, the latter determined with Saltzman reagent (7). These systems appear to change very sluggishly when the reactant concentrations are changed, perhaps because of surface effects, and the systems are not yet completely satisfactory.

The data for one run in which nitrogen dioxide was titrated with ozone are given in Figure 4. A dynamic system was used in which the gases were mixed at high concentrations, allowed to react, then diluted into a large chamber with purified air. The nitrogen dioxide input was held constant and the ozone input was varied. The ozone input to the chamber was calculated from calibrating runs without nitrogen dioxide. Ozone was determined with reagent III, corrected for stoichiometry by the factor 1.54. Ozone analyses to the left of the end point (line *D*) represent the interference of excess nitrogen dioxide, or nitrogen pentoxide, with the analytical method. Line *C* shows the much higher interference of NO_2 when sulfamic acid is not added to the phosphoric acid reagent. A sharp end point is not obtained, but can be extrapolated with approximately the correct stoichiometry. Line *B* shows the consumption of nitrogen dioxide, and line *A* shows the accumulation of excess ozone.

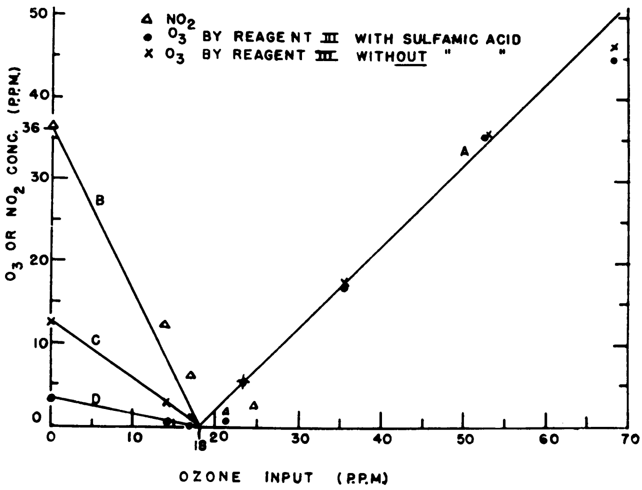

Figure 4. Dynamic gas phase titration of NO_2 with Ozone

NO_2 input held constant at 36 p.p.m. as O_3 input was increased

Comparison of Procedures

Either neutral or alkaline iodide procedures may be applied for determination of ozone in air; the latter procedure requires use of a correction factor for stoichiometry.

One of the advantages of the alkaline procedure is the relative stability of the exposed reagent prior to acidification. This permits collection of samples in the field, and completion of the analyses in the laboratory. In one test, aliquots of a pooled alkaline sample were acidified and read at intervals for 3 days after sampling. Most of the loss of 10 to 20% which was observed occurred in the first day, so that even older samples were practicable. Some lots of sampling reagent behaved better than others in this respect. A special reagent in which the sodium hydroxide was ozonized, then boiled before addition of potassium iodide, did not give significantly higher results.

The reproducibility of both methods for replicate samples of ozone was not as precise as could be expected from the experimental conditions. Reagent II seemed to be the best. It showed maximum differences up to 5%, while reagent III showed maximum differences up to 10%, and average differences of about 5%. Apparently the latter variations occurred during the ozone sampling step, as much closer agreement with reagent III was obtained by acidifying aliquots of a large pooled sample.

Reagent III required rapid acidification; upon very slow acidification with either ozone or iodate added, iodine losses have been observed. Similar losses occur upon addition of standard iodine to the alkaline reagent before acidification, regardless of the rate of acidification, but not when iodine is added after acidification. Apparently in the former cases iodine is released at the surface of acid drops and absorbed into the surrounding alkali, where the loss occurs. With rapid acidification of samples the iodine extinction coefficient for reagent III agrees well with expected values.

A limited amount of work has been carried out on the effect of pollutants. Sulfur dioxide decreased the amount of iodine liberated from all reagents; the difference between reagents II and III was small. Nitrogen dioxide yielded 8 to 11% interference with reagent III, and about the same with II. Five tests with 500 p.p.m. of nitric acid vapor showed an average interference of 0.5 p.p.m. of ozone with reagent III. Interferences from other smog constituents have not been completely evaluated.

Comparative analyses by the two methods of natural and synthetic (ozone-hexene) smogs gave a different pattern of results than for ozone-air mixtures. In some cases, analyses by the alkaline procedure gave results higher than those by the neutral procedure.

Acknowledgment

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Determining Ozone in Solution

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Stable ozone solutions have been analyzed by various techniques recommended in the literature, and results are compared and interpreted. Data are presented to correlate the quantity of the by-product oxygen from the ozone reaction with the apparent amount of original ozone.

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The determination of ozone in water solution is complicated by the instability of the ozone in solution. Alder and Hill (*1*) and Stumm (*12*) showed that ozone in solution is much more stable at low pH values and at temperatures near the freezing point of water, using the absorbance of an ozone solution at 258 to 260 mμ. The authors repeated the work of Alder and Hill (*1*) and Kilpatrick, Herrick, and Kilpatrick (*8*) at pH 2.0 and 1° C. and found the ozone solution completely stable, with no change in absorbance after 8 hours. Under these conditions, an extinction coefficient of 2600 was obtained as compared with 3000 (*8*) and 1000 (*1*).

In the classical equation,

$$O_3 + 2H^+ + 2I^- \rightleftarrows O_2 + I_2 + H_2O \qquad (1)$$

equimolar amounts of oxygen and iodine are liberated. By using the Winkler technique (*2*) to determine the dissolved oxygen before and after the liberation of iodine by ozone, the ratio of the molecules of oxygen to iodine liberated should be determined. Both Alder and Hill (*1*) and Kilpatrick, Herrick, and Kilpatrick (*8*) indicated that either some compound of oxygen or molecular oxygen interferes with the ozone iodine titration in acid solution.

As indicated by Equation 1, a standard procedure for ozone recommends the addition of iodide ions and the titration of the liberated iodine. There is a serious problem in interpreting the results of the iodide reaction: The quantity of iodine liberated is pH dependent. Inglis (*6*) reported that acid solutions gave more than one molecule of iodine per molecule of ozone. He tried bromide in normal nitric acid but obtained decreasing amounts of bromine from aliquots of the original ozone solution with time, while the iodine liberated from iodide remained constant. He concluded that the bromide-bromine reaction was unsatisfactory. Alder and Hill (*1*) found that ozone decomposes, according to its ultraviolet spectrum, faster than the decreasing ability of the same solution to liberate iodine from iodide. They concluded that a decomposition product of ozone, the hydroperoxyl ion, liberates iodine from iodide in the absence of ozone.

Boelter, Putnam, and Lash (*4*) concluded that potassium iodide absorbants in the pH range from 2.3 to 12.3 give results for concentration of ozone up to 20 weight %, if the solution is acidified with strong acid before titration with sodium thiosulfate;

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strongly acidified potassium iodide absorbants give high results; and the concentration of acid affects the degree of error. Birdsall, Jenkins, and Spadinger (*3*) concluded that in the concentration range from 1 to 25 mole % the use of a 2% unbuffered aqueous solution of potassium iodide for the analytical determination of ozone gives precise results, accurate to 2%, compared with a physical method. Thorpe (*14*), who published a summary of his work along with a discussion of the literature, indicates that a solution of potassium iodide at pH 5.5 to 6.0 gives a proper value for the amount of ozone absorbed. These three reports are based on the absorption of the ozone in a solution containing the reductant during absorption. The authors used a stable pure ozone solution, except for sulfuric acid to control pH at 1° C.

Luther and Inglis (*10*) used the ferrous-ferric system to measure ozone at pH 2.0. An excess of ferrous ion is added to the ozone solution and the excess ferrous ion is titrated with permanganate. The author found this technique, also used by David (*5*) and Kawamura (*7*), to be highly precise and to give values for the ozone which agree with the equation

$$O_3 + 2FeSO_4 + H_2SO_4 \rightleftarrows Fe_2(SO_4)_3 + O_2 + H_2O \qquad (2)$$

Thorpe (*15*), however, states that this method gives results that are lower than the correct value for the ozone.

Manley (*11*) and Zehender and Stumm (*17*) published a technique in which the ozone oxidizes added manganous ion. The oxidized manganous ion is then determined with *o*-tolidine.

Methods

The ozone is generated in an ozone generator (laboratory model, The Welsbach Corp., Philadelphia, Pa.) from pure (commercial) oxygen gas. The generator and the oxygen itself are cooled to 1° C., and the cooling water is maintained at this temperature by circulation from a large tank stored in the same room. The ozone is collected in an air scrubber with the solution of 0.01*N* sulfuric acid at 1° C. Measurement of the absorbance of this solution at 258 mμ indicates that the ozone is completely stable for an 8-hour period.

The 300 ml. of ozone solution from the scrubber is divided and analyzed in various ways. When crystals of iodide are added to an aliquot of the ozone solution at pH 2.0, much more iodine is liberated than when a second aliquot of the solution is first adjusted to pH 7.0 and iodide is added. Also, more iodine is produced at pH 7.0 than at pH 9.0. The solution with iodide at pH 9.0 liberated an amount of iodine equivalent to the amount of ferrous ion oxidized to the ferric ion at pH 2.0. This agrees with the observations of Manley (*11*). Observation of the ozone and iodide equation indicated that the newly liberated oxygen or some intermediary substance might be responsible for the increasing iodine as the hydrogen ion concentration increases. An experiment was designed to determine the difference in the concentration of dissolved oxygen after the reaction of ozone with iodide at pH 2.0 and 9.0

The outline of the experiment is shown in Figure 1. The 50-ml. samples of liquid saturated with gas at 1° C. were transferred into 8-ounce glass-stoppered reagent bottles containing approximately 200 ml. of a buffer solution unsaturated with respect to oxygen. These bottles were immediately filled to the neck with buffer solution and stoppered. The solutions were analyzed as indicated. The dissolved oxygen (DO) in those labeled *A* was determined by the conventional Winkler technique (*2*): oxidation of manganese sulfate in an alkaline solution containing potassium iodide, followed by acidification and determination of the iodine liberated with sodium thiosulfate. Potassium iodide was added to solutions labeled *B*, the solutions were acidified if necessary, and the iodine was determined with sodium thiosulfate. Potassium iodide was added to solutions *C*, followed by the conventional Winkler technique for dissolved oxygen. The iodine liberated from this solution represents the sum of that from the ozone and the dissolved oxygen. The entire experiment except the final titration for iodine was conducted in a room thermostated to 1° C. with solutions equilibrated to that temperature.

The results are shown in Table I. Each experiment represents the average of

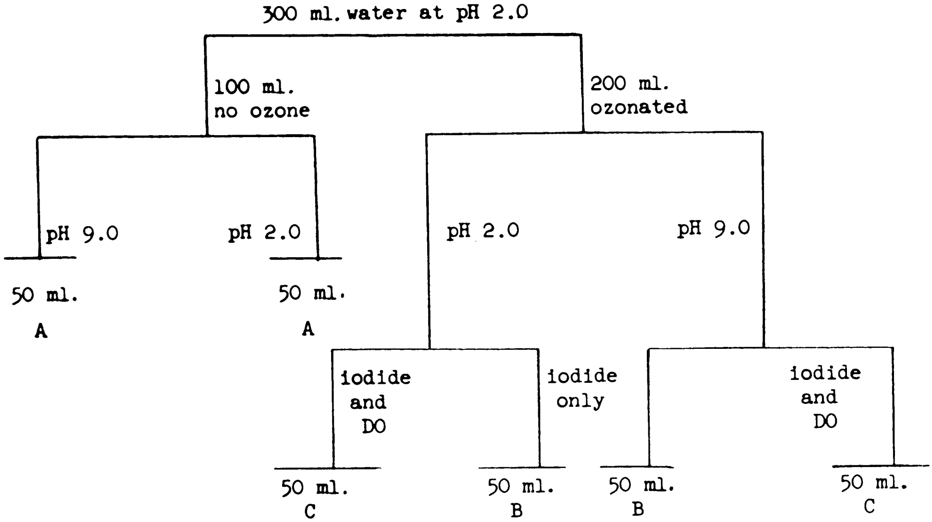

Figure 1. Scheme for analyzing ozone solutions with iodide to determine the ratio between the products of iodine and oxygen at two pH values

A, B, and C refer to column headings in Table I

Table I. Relationship between Iodine Liberated by Ozone and Oxygen at Two Different pH Values

		Meq./Liter			By-Product		
Example	pH	*A*, DO with no ozone	*B*, ozone	*C*, total DO plus ozone	Oxygen,[a] meq./l.	Theoret. produced, %[b]	Apparent Ozone, Mg./L.
1	2.0	2.38	0.75	3.40	0.27	18	18.0
2	2.0	2.62	0.60	3.30	0.08	7	14.5
1	9.0	2.14	0.36	3.31	0.81	112	8.7
2	9.0	2.27	0.25	2.86	0.34	68	6.0

[a] $O_2 = C - (A + B)$.

[b] Based on $O_3 + 2I^- + 2H^+ = O_2 + I_2 + H_2O$ and ratio between generated oxygen and iodine, with iodine from oxygen as base.

two determinations; the two experiments were run on different days. More than twice as much iodine is liberated at pH 2 as at pH 9. Very little oxygen is liberated into the solution at pH 2, while a much closer approach to the theoretical yield occurs at pH 9. The total oxidizing strength of the solution computed as the sum of the ozone (*8*) and the by-product oxygen is within the limits of experimental uncertainty, the same at pH 2 as at pH 9. Hence, either the reaction goes by two different paths, one of which is acid-catalyzed (*16*), or the oxygen liberated in the reaction of ozone with the halide ion is in some form which can further oxidize iodide ion in acid solutions.

Theoretical considerations, the reference of Inglis (*6*), and the recommendations of Manley (*11*) suggested that the reaction of ozone with bromide at pH 2.0 be studied. The analytical scheme using bromide ion is based on the addition of potassium bromide to ozonated solutions at pH 2 followed by the addition of potassium iodide to reduce the bromine liberated by the ozone.

Table II summarizes the data obtained by three analytical methods: oxidation of iodide ion at pH 9, bromide ion at pH 2, and ferrous ion at pH 2. Data are reported for seven experiments conducted over a period of several days. Six aliquots were taken from each ozone solution, so that each value reported in the first three

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Table II. Comparison of Three Techniques for Determination of Ozone in Seven Different Solutions

	Technique, Mg./Liter					
Expt. No.	Iodide pH 9	Bromide pH 2	Ferrous pH 2	$\bar{X}$,[a] Mg./L.	Standard Deviation, Mg./L.	V[b]
1	37	39	39	38	1.2	3.2
2	52	55	53	54	1.7	3.2
3	26	27	26	26	0.7	2.7
4	46	54	48	49	4.2	8.6
5	25	24	24	24	0.7	2.9
6	28	28	26	27	1.2	4.3
7	27	30	26	28	2.1	7.5
Av.[c]	34	37	34			

[a] Mean value of ozone concentrations.
[b] Coefficient of variability (Pearson).
[c] Comparative values of the three techniques.

columns is the average of two individual titrations. The amount of bromine liberated at pH 2.0 agrees approximately with the amount of iodine liberated at pH 9.0 and the amount of ferrous ion oxidized to ferric ion at pH 2.0.

Theoretical

The reaction between ozone and the halides may be represented by the following equation:

$$O_3 + 2H^+ + 2X^- \rightleftarrows O_2 + X_2 + H_2O \qquad (3)$$

To determine the driving force of the ozone at equilibrium which will liberate the free halogen at a given hydrogen ion concentration, the following equation must be examined.

$$E = E^0{}_{X_2} + E^0{}_{O_3} - \frac{RT}{2.3 \times 2 \times F} \log \frac{C_{X_2} P_{O_2}}{C^2{}_{X^-} P_{O_3} C^2{}_{H^+}} \qquad (4)$$

The $E^0{}_{O_3}$ is given by Latimer (*9*) to be +2.07 volts while the $E^0{}_{X_2}$ is given for iodine as −0.54 volt, for bromine as −1.09 volts, and for chlorine as −1.40 volts. The resultant sum of the component reaction voltages is given in the second column of Table III. Equation 4, changed to give a separate pH factor, becomes

Table III. Relative Potentials with Various Reductants for Determining Ozone and Oxygen

	Ozone Potentials			Oxygen Potentials		
		Driving			Driving	
Reductant	Standard, volts	At pH	Volts	Standard, volt	At pH	Volt
Iodide	1.53	9.0	0.93	0.69	9.0	0.18
	1.53	2.0	1.38	0.69	2.0	0.57
Bromide	0.98	2.0	0.83	0.14	2.0	0.02
Chloride	0.66	2.0	0.54	−0.16	2.0	−0.28
	0.66	0.0	0.66	−0.16	0.0	−0.16
Manganous	0.56					
Ferrous	1.30					

$$E = E^0 - 0.03 \log \frac{C_{X_2} P_{O_2}}{C^2{}_{X^-} P_{O_3}} - 0.06 \text{ pH at } 25° \text{ C.} \qquad (5)$$

When it is assumed that the pressure of the oxygen equals 1 atm., the pressure of the ozone equals 0.05 atm., the concentration of the free halogen is millimolar, and the halide is 0.1*M*, the factor with these components becomes

$$\frac{C_{X_2} P_{O_2}}{C^2{}_{X^-} P_{O_3}} = \frac{0.001 \times 1}{0.01 \times 0.05} \qquad (6)$$

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Substituting this, Equation 5 becomes

$$E = E^0 - 0.01 - 0.06\,\text{pH} \tag{7}$$

The data for the three halogens in this equation for specific pH values are given in Table III. The potential needed for ozone to liberate bromine from bromide at pH 2 is about the same as that required to liberate iodine from iodide at pH 9. The high driving potential apparently required for this reaction may indicate that the ozone could liberate iodine quantitatively at a pH higher than 9.0 if the ozone did not decompose too rapidly at the higher pH and if reactions leading to other oxidation states such as iodate did not interfere. Thus, even pH 9.0 may be a compromise between the rate of decomposition of the ozone, the side reactions to other oxidation states, and the liberation of iodine by the by-product oxygen.

When similar computations are made for the reactions between oxygen and halides, the results in Table III are obtained. There is a large driving potential for oxygen to liberate iodine from iodide at pH 2.0. Because little interference by molecular oxygen is encountered at pH 2.0, the mechanism of the reaction involving molecular oxygen is such that there is a very low rate for the reaction. The products formed in the decomposition of ozone as discussed by Alder and Hill (*1*) and Kilpatrick, Herrick, and Kilpatrick (*8*) may allow this reaction to proceed.

Discussion

If the driving potential for the ozone against bromide at pH 2.0 is inadequate or more time is needed for the reaction, a slight excess of ozone may be present when the iodide is added for the titration. When chloride is added to the ozone solution at pH 2.0, the ozone odor persists in a closed reaction vessel for an hour, as discussed by Yeatts and Taube (*16*). After the chloride has been added at pH 0.0, there is a greater excess of iodine than that calculated from the ferrous-ferric system; ozone may have been present at the time of the iodine addition.

The use of the manganous ion as the reductant for determining ozone has been recommended by Zehender and Stumm (*17*) and Manley (*11*). This technique was considered by the authors after the work on the halides had been completed. The amount of oxidation of bromide and manganous ions was the same. However, the color developed from the manganic ion with *o*-tolidine is stable, while the color from *o*-tolidine with the bromine or chlorine liberated from ozone is unstable. The presence of an ozone odor after the reaction of ozone with chloride at pH 2.0 may explain the development and subsequent loss in *o*-tolidine color. The production of a higher state of oxidation of the *o*-tolidine from an excess of chlorine would produce a red precipitate. The loss of *o*-tolidine color in the presence of bromine where the reaction between ozone and bromide is thought to be complete (*13*) means that some decomposition products (*8*) of ozone do not liberate bromine, but can destroy *o*-tolidine. This also may be true of the chloride and ozone.

Conclusions

One molecule of ozone liberates one molecule of iodine and one molecule of oxygen when the pH of the medium is 9.0. The value obtained with ozone and iodide at pH 9.0 is a compromise between the rate of decomposition of the ozone and the oxidation of iodide by different reaction paths leading to stoichiometry different from that assumed. At pH 2, more iodine is liberated which may be ascribed to either oxidation by the by-product oxygen liberated in the reaction even though normal molecular oxygen generally does not cause this reaction, or to a second reaction path which is acid-catalyzed.

The manganous ion is readily oxidized to the manganic ion at pH 2.0 by ozone to the equivalent extent of the iodine liberated by ozone at pH 9.0. The amount of ferric ion produced from the ferrous ion by ozone at pH 2.0 is comparable to the amount of iodine liberated from iodide at pH 9.0. The concentration of ozone determined by oxidation of bromide at pH 2.0 agrees with that obtained by the ferrous-ferric and manganous-manganic systems.

For stability of color with *o*-tolidine, the manganous system is recommended for low ozone concentrations. For an easy titration procedure, the titration of excess ferrous ions with permanganate is suggested.

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Ozone Concentration Meters

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Three meters were designed and built to measure the concentration of ozone in an ozonized-oxygen stream. They were used in both laboratory and large-scale ozonolyses. Their construction and operation are described.

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In performing carefully controlled ozonolysis experiments for kinetic studies, it was convenient to have a means for continuously assaying the ozonized oxygen stream. In this way, gradual drifts in the ozone concentration could be compensated for by a change in the applied voltage on the ozone generator. Thus, the ozone concentration and also the rate of ozone addition could be held constant. Instruments which were designed and constructed for this purpose have also been incorporated in production-size installations. They offer a convenient and accurate means for measuring the total amount of ozone used in a chemical reaction and are readily adapted to automatic recording operation.

Because ozonolysis reactions are becoming increasingly important in the chemical industry, these instruments should be of interest to many engineers and designers. This paper, therefore, describes the construction and operation of three such instruments. The first is rather simple in construction, yet very satisfactory. The second and third models incorporate certain refinements which improve the stability and ease of operation but also increase the cost of construction. The third, or most elegant, instrument was constructed at a cost of less than $1000.

Method of Measurement

Of the various methods available for the determination of ozone in gaseous mixtures (*4*), the spectrophotometric methods, particularly the ultraviolet, appeared to be most suited for the purpose. These methods are all based on the strong absorption maximum for ozone in the ultraviolet at 254 $m\mu$. Thus, one can determine ozone concentration with a Beckman spectrophotometer by the usual procedure. Several other instruments (*1*, *3*, *6*) have been specifically designed to measure ozone concentrations by this photometric method. The meters constructed by the authors also operate on this principle. The total ozone stream, or an aliquot of known proportion, is passed through the meter and the per cent transmittance at 253.7 $m\mu$ is read from the dial. The ozone concentration at this temperature and pressure is then either determined from a calibration curve (Figure 1), constructed from titration data (the dial could be calibrated directly in concentration units), or calculated (*2*) using Beer's law:

$$\mathrm{Log}_{10} \frac{I}{I_0} = \alpha - d$$

where α is 149 (*5*).

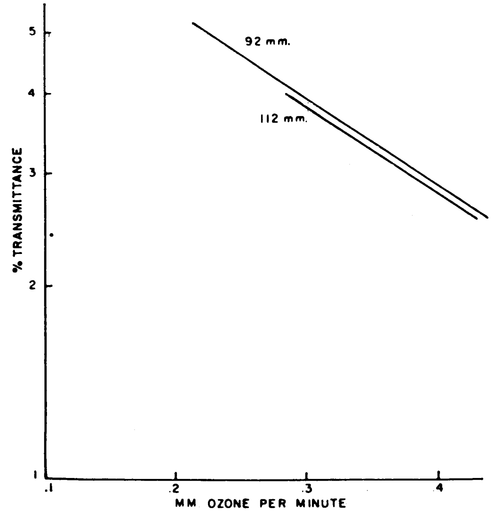

Figure 1. Calibration curve for Model 2 ozone meter at two pressures

The effect of the ultraviolet light on the ozone concentration was determined by titrating samples collected with and without the meter in operation. At a pressure of 112 mm. of mercury, a flow of 0.3 liter per minute, and a temperature of 20°, the ozone concentration of the effluent from the meter was about 94% of that delivered to the meter.

Construction of Meters

All these meters utilize the high absorbance of ozone at 254 $m\mu$. Fortunately, this absorption peak corresponds almost exactly with the powerful mercury line at 253.7 $m\mu$. With the aid of suitable filters, a General Electric germicidal lamp is used as a nearly monochromatic light source. The GE 4W germicidal lamp generates only a small amount of light both above and below the main peak at 2537 A. The lamp is masked to use radiation just above the dark space at the cathode end. (The anode end has a high-frequency flicker.) This light is allowed to fall on two photocells, on one directly, generating a reference current, and on the other via the absorption cell, generating a sample current.

The currents from these two photocells, modified so as to contain large alternating current components, are compared in a calibrated, adjustable resistance network. The difference current is fed to an amplifier which drives a small two-phase servo-motor. This motor is coupled back through a gear train to this calibrated adjustable resistance network. Thus, when light reaching the sample photocell is reduced by the presence of ozone in the absorption cell, the difference output is fed to the amplifier, which causes the servo-motor to rotate in the appropriate direction, to cause the resistance network to insert in the reference photocell circuit an attenuation equal to the reduction of the light falling upon the sample photocell. When the balance has been reached, the motor stops and the per cent transmittance can be read from the dial of the calibrated resistance network. Means are provided for adjusting the dial to zero concentration, or 100% transmittance, with no ozone present.

Two methods are employed to obtain from these photocells output currents with large alternating current components. In Model 1 a 60-cps. alternating current polarizing voltage is applied to the cells, while Models 2 and 3 use a rotating-disk chopper

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comprised of alternating segments of two different glass filters which were chosen so that the 2537 A. light is chopped at 60 cps. The rotating-disk chopper also minimizes the effects of light from the germicidal lamp of higher and lower wave length than 2537 A. In Model 1 the effect of this light is minimized by means of a movable filter of Corning 9700 glass. The instrument is adjusted to zero transmittance with the filter in front of the sample cell.

Rotating Disk Chopper. Although most of the energy of the mercury vapor lamp is at 2537 A. it is desirable to reduce to a minimum the effect of radiation at other wave lengths. Unfortunately, the number of band-pass filters for the ultraviolet region is very limited. The combined effect of a band-pass filter and an optical chopper was achieved through the use of a rotating disk composed of segments of two different ultraviolet-transmitting glass filters. The rotating-disk device (Figure 2) consists of four 90° segments of about 1½-inch radius held together by an arbor and rotated at 1800 r.p.m. by a synchronous motor. The segments of the disk are composed of pieces of Corning 9700 and 7910 glass 2 mm. thick, arranged alternately. In the wave length region longer than 350 mμ, these glasses transmit equally well. In the region between 240 and 280 mμ, the 7910 glass transmits well; the 9700 glass transmits hardly at all. Thus, the rotating disk modulates or "chops" at 60 cps. light whose wave length lies within these limits. As the cutoff of these glasses is not extremely sharp, the chopping effect is extended in lesser degree from 220 to 320 mμ.

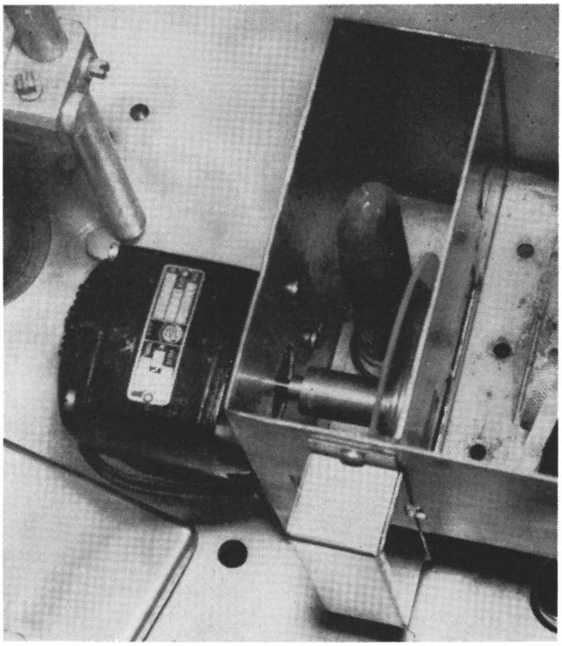


Figure 2. Rotating disk construction

Absorption Cells. The absorption cells for Model 1 and 2 ozone meters (Figures 3 and 4) are constructed of stainless steel and have Corning 7910 Vycor circular windows exactly 1.0 mm. apart. The design was improved in Model 3 to permit the cell thickness to be more precisely maintained (Figure 4). This cell is constructed of anodized aluminum.

Optical Systems and Circuits. Additional details of construction are shown in Figures 5 through 16.

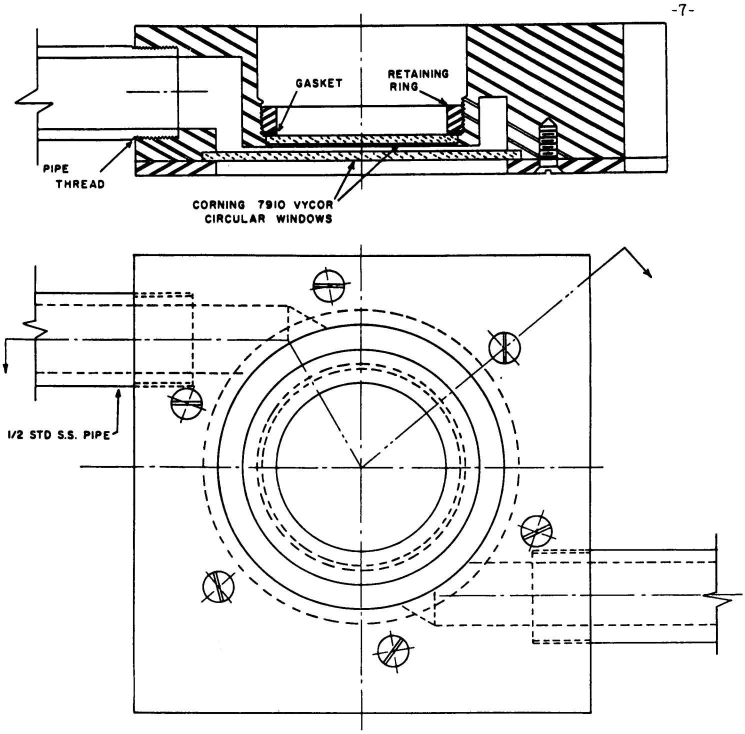


Figure 3. Absorption cell, Model 1 and Model 2 ozone meters

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch015

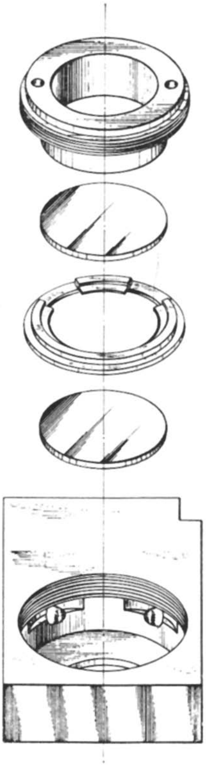


Figure 4. Absorption cell, Model 3 ozone meter

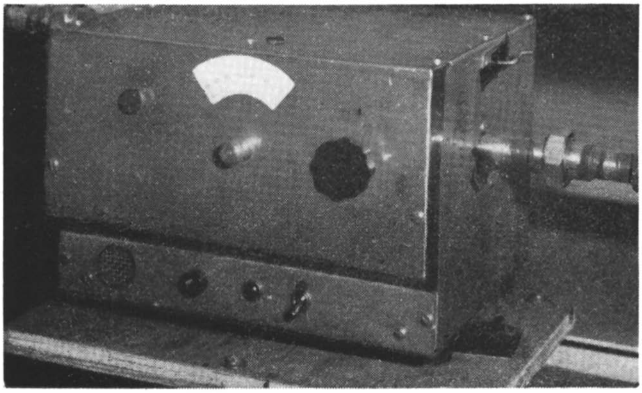
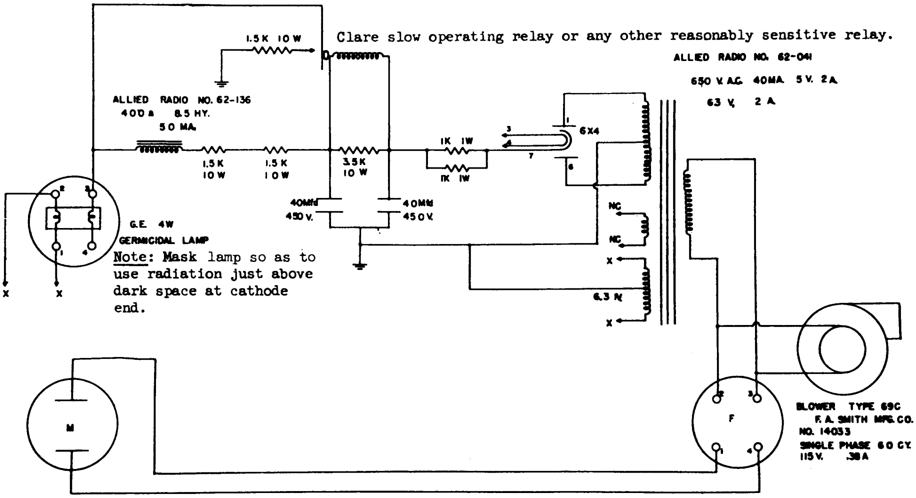


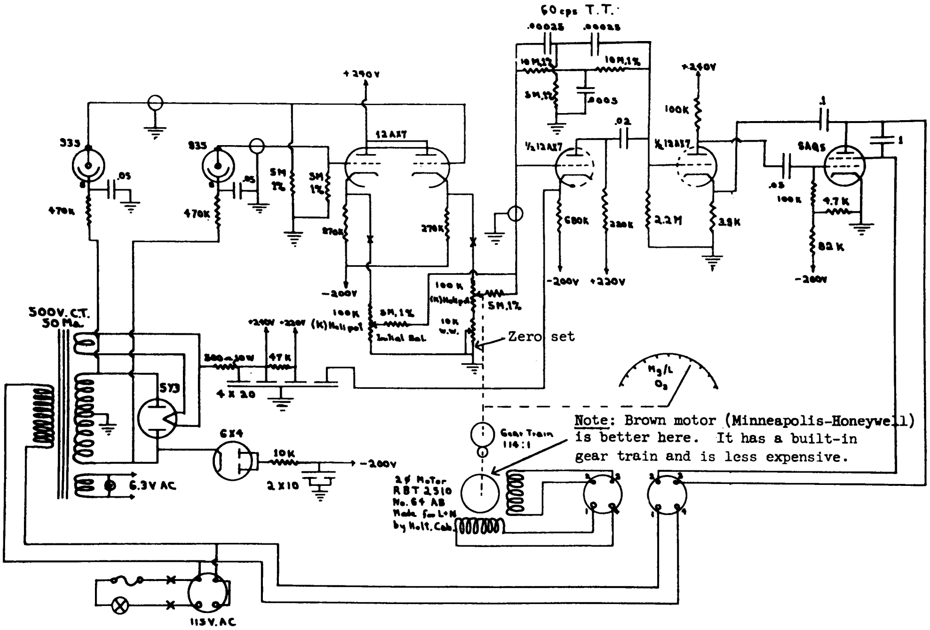
Figure 5. Model 1 ozone meter



Clare slow operating relay or any other reasonably sensitive relay.

Note: Mask lamp so as to use radiation just above dark space at cathode end.

Figure 6. Mercury lamp circuit, Model 1 ozone meter



Note: Brown motor (Minneapolis-Honeywell) is better here. It has a built-in gear train and is less expensive.

Figure 7. Circuit, Model 1 ozone meter

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch015

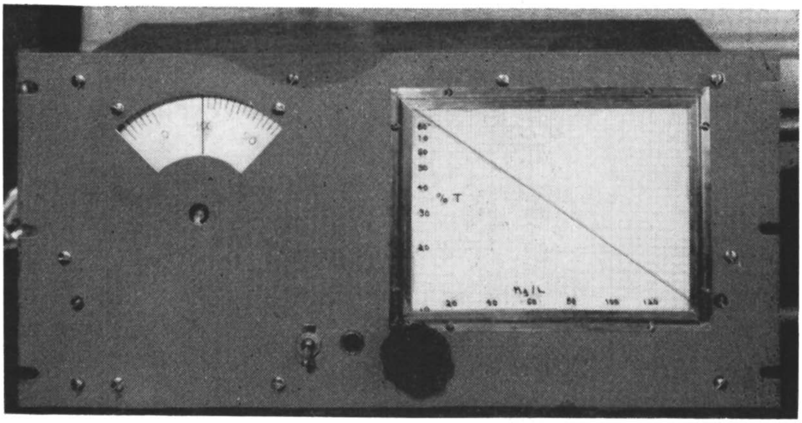


Figure 8. Model 2 ozone meter

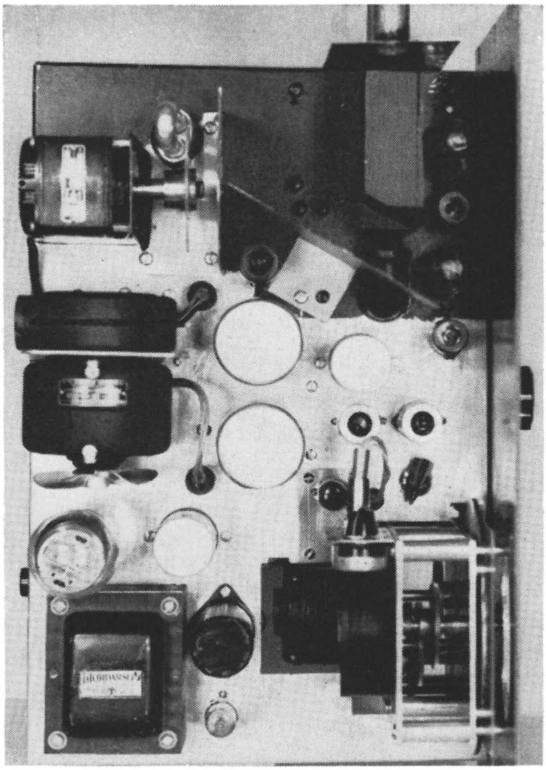


Figure 9. Top view, Model 2 ozone meter

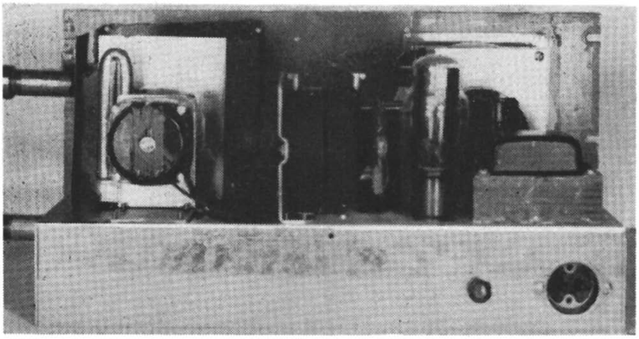


Figure 10. Back view, Model 2 ozone meter

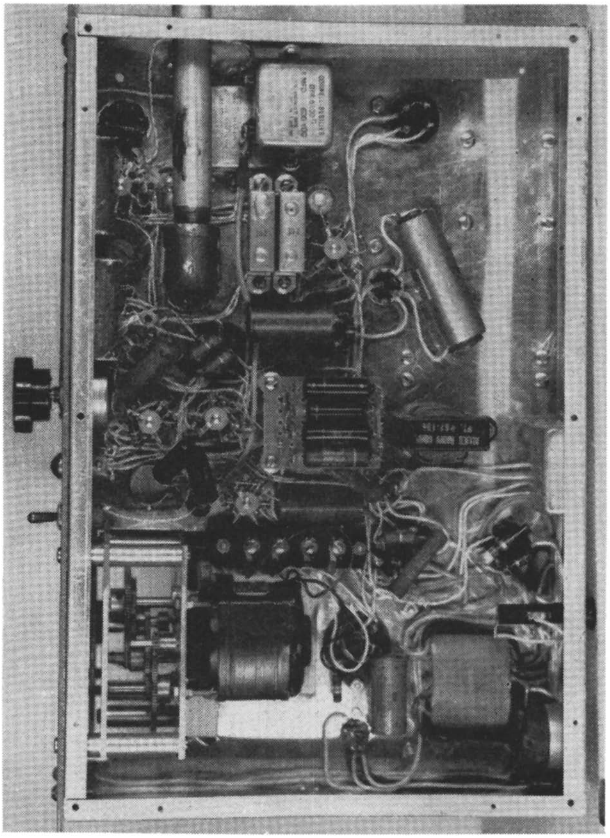


Figure 11. Bottom view, Model 2 ozone meter

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch015

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch015

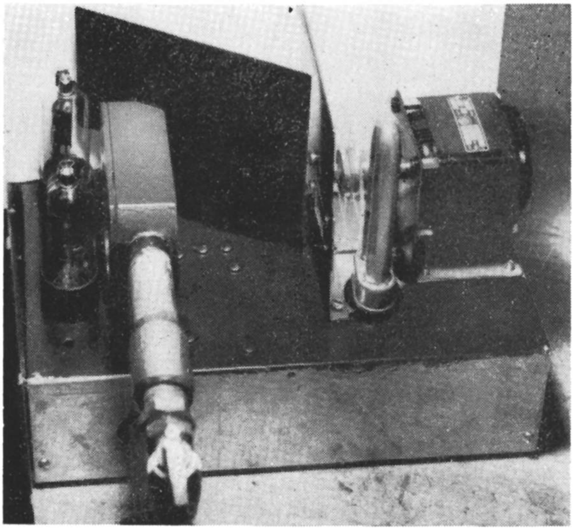


Figure 12. Optical system, Model 2 ozone meter

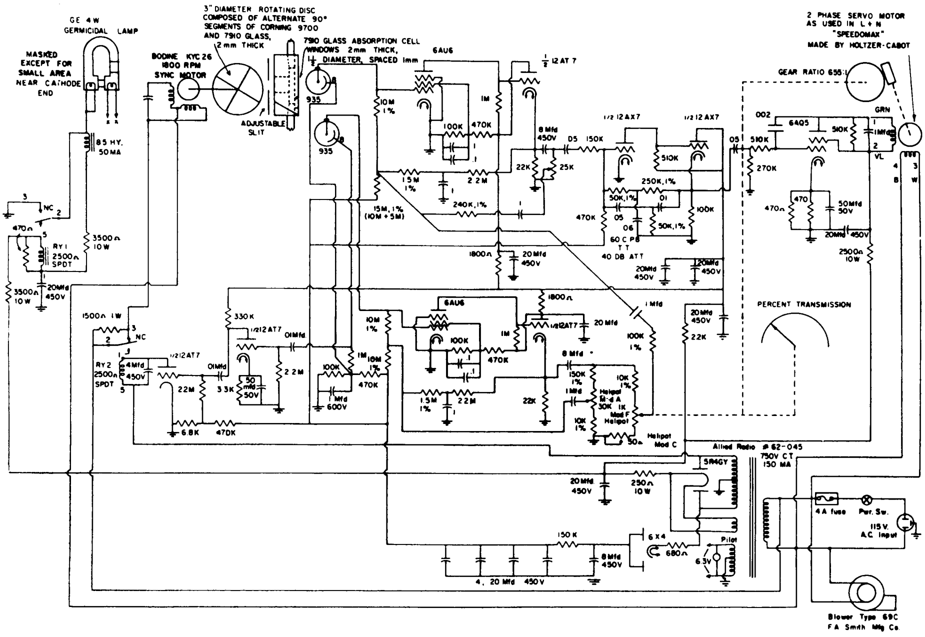


Figure 13. Circuit, Model 3 ozone meter

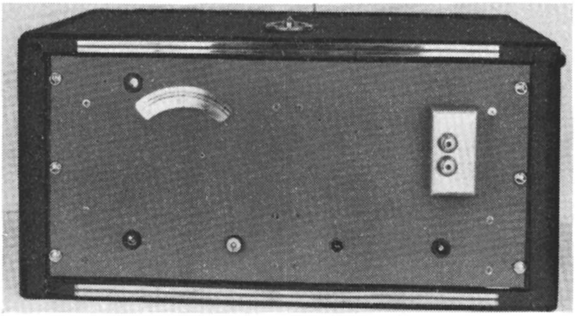


Figure 14. Model 3 ozone meter

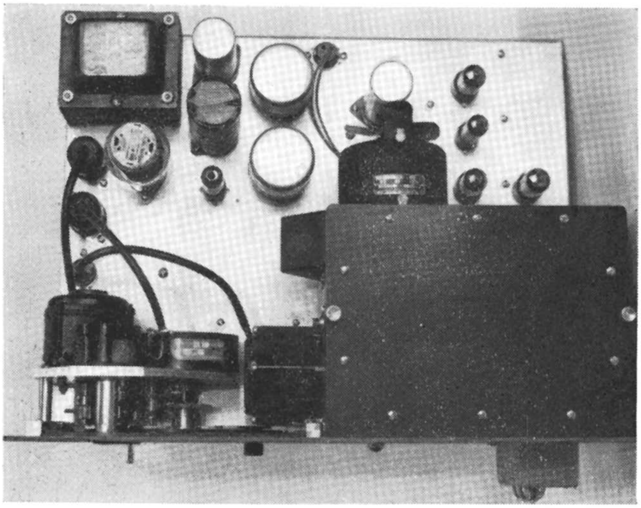


Figure 15. Top view, Model 3 ozone meter

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch015

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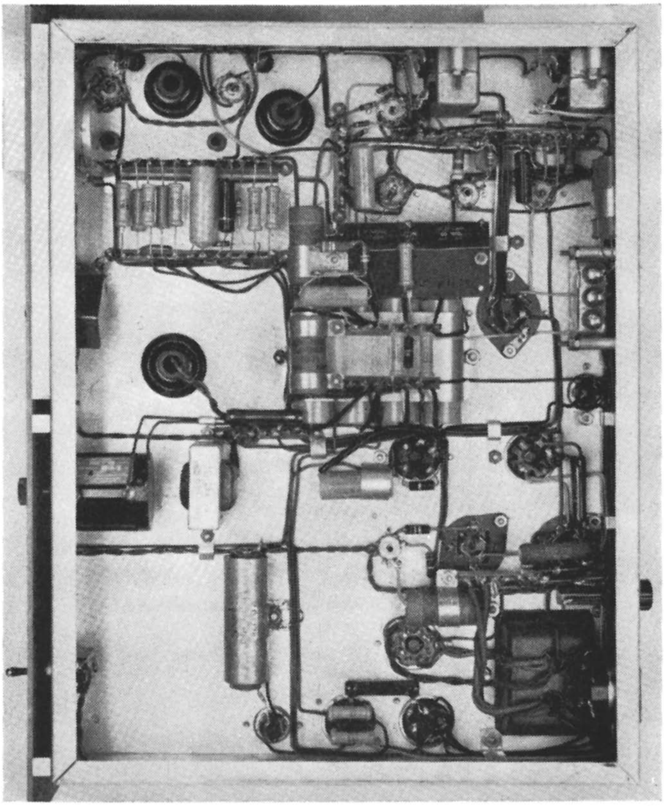

Figure 16. Bottom view, Model 3 ozone meter

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Nonaqueous Colorimetric Method for Determination of Ozone

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A new colorimetric procedure has been developed for the quantitative measurement of atmospheric ozone. The specific, sensitive, and reproducible nonaqueous method utilizes the rate of color produced on ozonization of o-dichlorobenzene solutions of N-phenyl-2-naphthylamine. The color reaction conforms to Beer's law and has a practical sensitivity of ±1.8 × 10^{-3} mg. of ozone. Oxygen and oxides of nitrogen, in concentrations greater than those normally occurring in the atmosphere, do not interfere with the chromogenic reaction.

Investigation of the degradative effects of ozone on elastomeric materials has necessitated developing techniques to measure ozone concentration precisely. The literature (*2–4, 7, 9, 10, 13*) has presented the efforts of several workers. However, the techniques used costly equipment such as infrared and ultraviolet spectrophotometers, aqueous colorimetric methods involving the formation or destruction of fluorescence or dyes, and iodometric procedures.

Aqueous colorimetric methods give erratic results, because trace amounts of such oxidizing agents as oxides of nitrogen interfere. In the iodometric procedures (*2–4*), the reaction of ozone with potassium iodide is significantly affected by the pH of the reacting medium and is truly quantitative only in neutral solution. During the analysis of air containing high ozone concentrations, for example, the potassium iodide solutions tend to increase in alkalinity resulting from the formation of potassium hydroxide, and the results become more inaccurate with increasing absorption time. However, the iodometric procedure agrees over an ozone concentration range from 24 to 160 mg. per liter (*2, 3, 8*), with absolute methods based on gas density measurements. It is accurate to 0.06 mg. per liter if precautions are taken to control pH and avoid loss of iodine by vaporization.

The authors investigated by viscometric techniques (*5, 6*) the potential suitability of several commercially available chemicals as inhibitors of ozone-induced polymer chain scission. Color changes were observed during the ozonization of elastomer solutions containing such protectant chemicals as *N,N'*-di-*sec*-butyl-*p*-phenylenediamine, nickel dibutyldithiocarbamate, and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline, respectively. The chromogenic reactions of these and other chemicals indicated that the color change varied with ozone concentration, and of the chemicals examined, *N*-phenyl-2-naphthylamine exhibited superior behavior. This paper reports its use as a colorimetric reagent for determining ozone concentrations.

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Advances in Chemistry; American Chemical Society: Washington, DC, 1959.

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Reagents and Apparatus

Colorimetry. A 0.01*M* solution of *N*-phenyl-2-naphthylamine is prepared by dissolving 0.439 gram of chemical, Eastman Kodak No. 2767 or equivalent, in 200 ml. of redistilled *o*-dichlorobenzene.

Iodometric Calibration. Potassium iodide (crystalline powder, reagent grade), 0.002*N* sodium thiosulfate, 0.025*N* potassium dihydrogen phosphate, 0.025*N* disodium hydrogen phosphate, 0.002*N* iodine, 50% sulfuric acid (by volume), and 2% soluble starch (by weight) are required.

Oxides of Nitrogen. To determine their concentration, 0.01*N* potassium permanganate and sulfuric acid (specific gravity 1.84 at 15.6° C.) are required. A 0.005*N* sodium carbonate solution containing 0.1 mole of potassium permanganate (*11*) is used as an absorbant for oxides of nitrogen.

Ozonization. The apparatus used to ozonize all solutions has been described in detail (*6*).

Colorimetry Measurements. A Klett-Summerson photoelectric colorimeter, Model M3896, equipped with a No. 42 filter having an approximate spectral range from 400 to 465 mμ, was used for colorimetric measurements.

Experimental

An investigation of the effects of reagent concentration on the intensity of color produced during the chromogenic reaction between ozone and *N*-phenyl-2-naphthylamine in *o*-dichlorobenzene indicated that the optimum solution concentration was 0.01*M*.

Reaction Rate. The intensity of color produced during ozonization of *N*-phenyl-2-naphthylamine in *o*-dichlorobenzene solution was determined. A stream of ozonized air or ozonized oxygen, flowing at a rate of 0.05, 0.10, 0.15, and 0.20 cubic meter per hour, respectively, was bubbled through 200 ml. of a solution containing 0.01 mole of reagent at room temperature and atmospheric pressure. Aliquots of the ozonized solutions were removed at preselected time intervals for colorimetric measurement. The results obtained for each of the flow rates were identical for the respective ozonized gases. The data are plotted in Figure 1. The results of the chromogenic reaction vary with the concentration of ozone in accordance with Beer's law.

Calibration. The ozone equivalency of colorimeter scale readings, in terms of milligrams of ozone, was calculated from iodometric measurements (*12*) of ozone

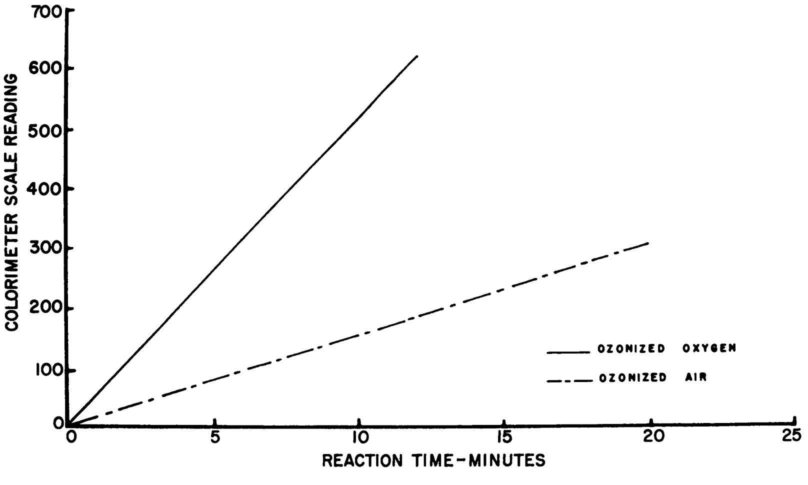

Figure 1. Rate of color formation

concentration. The ozonized gas was passed through a solution containing 20 grams of potassium iodide and 50 ml. each of $0.002N$ sodium thiosulfate, $0.025N$ potassium dihydrogen phosphate, and $0.025N$ disodium hydrogen phosphate for predetermined time intervals at room temperature and atmospheric pressure. The unreacted sodium thiosulfate was titrated with a standardized $0.002N$ iodine solution, using freshly prepared soluble starch solution as the indicator. The volume of effluent gas was corrected for temperature and pressure to 25° C. and 760 mm. The ozone concentration was calculated as follows:

$$\text{Ozone concentration, mg. per liter} = \frac{\text{ml. of iodine (blank} - \text{sample)} \times N \text{ of iodine} \times 24}{\text{corrected volume}} \qquad (1)$$

A plot of colorimeter scale readings against milligrams of ozone gave a straight-line curve.

Figure 2 presents the ozone concentration measurements of ozonized air and ozonized oxygen. The ozone concentration was inversely proportional to the rate of flow of effluent gas. In addition, the quantity of ozone produced by the generator remains relatively constant for each of the gases studied.

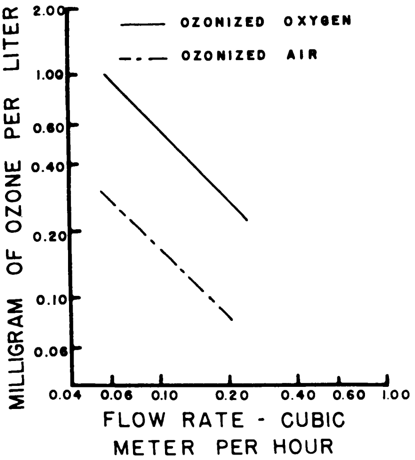

Figure 2. Ozone concentration by iodometry

The calibration relationship, colorimeter scale reading *vs.* milligrams of ozone, may be used to determine the ozone concentration of unknown specimens.

$$\text{Ozone concentration (mg. per liter)} = \frac{\text{colorimeter scale reading} \times \text{mg. of ozone equiv.}}{\text{corrected volume}} \qquad (2)$$

Effects of Oxygen. The effects of oxygen alone on *o*-dichlorobenzene solutions of *N*-phenyl-2-naphthylamine were determined by repeating the procedure with unozonized oxygen. As no significant color change was observed in the reagent solution after 6 hours, oxygen alone has no effect on the chromogenic reaction.

Effects of Oxides of Nitrogen. To determine the effects of oxides of nitrogen on the chromogenic reaction investigated, the ozonization procedure was repeated after passing the ozonized air through approximately 20 ml. of potassium permanganate absorbant.

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The results were identical with those for ozonized air (Figure 1). Therefore, the oxides of nitrogen are completely removed by this absorbant without affecting the ozone concentration.

The concentration of oxides of nitrogen in ozonized air was determined by bubbling a stream of gas, flowing at 0.05, 0.10, 0.15, and 0.20 cubic meter per hour, respectively, through 50 ml. of concentrated sulfuric acid for 2 hours at room temperature and atmospheric pressure. The acid containing the absorbed oxides of nitrogen was added slowly to 50 ml. of distilled water in an ice bath, so as to form two layers. The chilled liquid was then titrated with 0.01*N* potassium permanganate solution, with gradual stirring to mix the two layers slowly, until a faint pink color persisted for 1 minute. The volume of ozonized air was corrected for temperature and pressure to 25° C. and 760 mm. The value of oxides of nitrogen, determined as nitrogen dioxide, were calculated.

Concentration of oxides of nitrogen (mg. per liter) =

$$\frac{\text{ml. of } KMnO_4 \times N \text{ of } KMnO_4 \times 46}{\text{corrected volume}} \qquad (3)$$

Results of these measurements are presented in Figure 3. These concentrations of oxides of nitrogen, greater even than the 0.7×10^{-3} mg. per liter encountered in air samples during smog in Los Angeles (*1*), have no effect on the intensity of color produced in the reagent solution during ozonization.

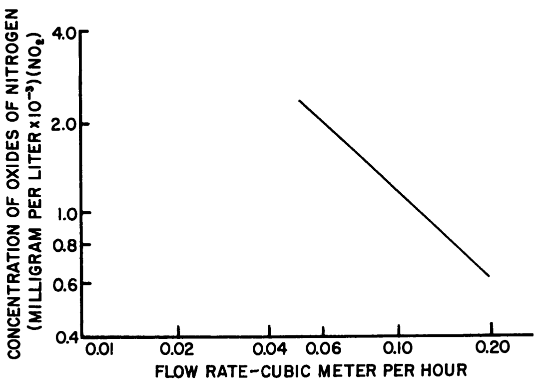

Figure 3. Concentration of oxides of nitrogen in ozonized air

Applicability of Method. The potential suitability of the colorimetric technique, for use in measuring atmospheric ozone concentration, was determined by repeating the ozonization procedure with unozonized air flowing at 0.40 cubic meter per hour. Iodometric measurements of atmospheric ozone concentration were made simultaneously.

The results of colorimetric measurements are given in Figure 4. The ozone concentration of this air specimen was, using Equation 2, approximately 1.8×10^{-4} mg. per liter. This value is equivalent to 9 p.p.h.m. (by volume), which is identical with that determined iodometrically.

Recommended Procedure

As the chromogenic reaction presented follows Beer's law, the recommended procedure is as follows:

Bubble a stream of air through the reagent solution until a color change is observed. Make a single colorimetric measurement of the ozonized reagent. Determine the volume of effluent gas used, correcting for temperature and pressure. Calculate the ozone concentration, using Equation 2.

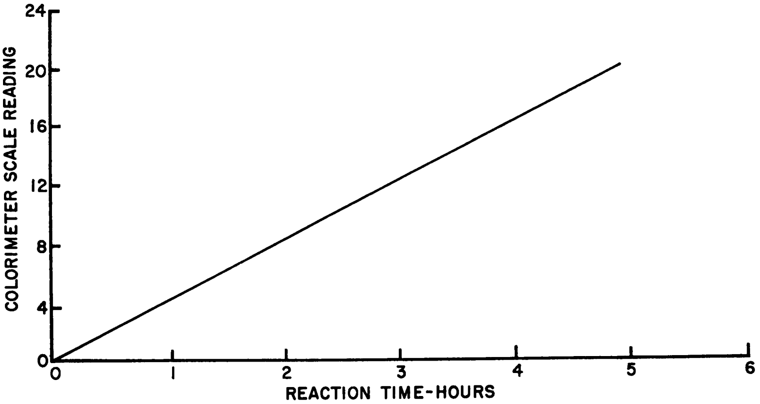

Figure 4. Rate of color formation by atmospheric ozone

Precision of Method

Because the precision of measurement is approximately 0.1 division at the midpoint of the colorimeter scale, in the working range used, the sensitivity of the colorimetric technique is equivalent to approximately $\pm 1.8 \times 10^{-3}$ mg. of ozone.

Acknowledgment

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Automatic Chemical Determination of Atmospheric Ozone

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An automatic recorder of atmospheric ozone has been developed which gives direct and absolute measure of ozone in the atmosphere in the form of a direct-reading curve. The fact that ozone dissociates at 300° C. is used to prevent interference from other atmospheric components.

The need for an automatic recorder of atmospheric ozone, which would discriminate against other oxidants in the atmosphere and would trace a direct-reading curve, led to the development of the instrument described.

The principle of the method is shown in Figure 1.

Outside air enters at the bottom and divides in equal parts to the right and left. The air may be heated to a temperature of about 300° C. by each of the electric ovens. At this temperature ozone is dissociated, and this specific property of ozone is used here to discriminate against other atmospheric components which may affect the chemical reaction. If one heater is on and the other off, the heated air stream is free of ozone. After bubbling through the reaction chambers, the air is removed through the outlet shown at the top of Figure 1. At present, a flow rate of 7 liters of air per minute through each chamber is used.

The reaction chambers are supplied with distilled water directly from a glass distilling apparatus and simultaneously with a solution containing essentially potassium iodide and sodium thiosulfate. The solution accumulates in a standpipe (upper half of Figure 1) and is divided into two exactly equal parts by two capillaries before entering the reaction chambers. It drains eventually through overflow tubes. The rate of flow of the solution gives it a mean life of about 30 minutes in the reaction chamber.

The chemical reaction is of the iodide-iodine type; the ozone produces iodine quantitatively from the potassium iodide solution. Addition of sodium thiosulfate to the potassium iodide solution prevents volatilization of the iodine (*5*) and allows accurate amperometric detection of the end point by means of a pair of sensing electrodes (*2–4*).

The quantity of sodium thiosulfate in each chamber is titrated by a coulometric production of iodine from the iodide solution with a current which passes through a separate pair of production electrodes. This method of determining sodium thiosulfate has been used for some time by Ehmert (*2*) in a manual method for ozone determination.

Both the sensing and the production electrodes are mounted in a separate tube (Figure 1), through which the solution flows at a fast rate due to the pumping action of the air stream which passes through the reaction chamber. The arrows in Figure 1 indicate the direction of this circulation.

To render this process automatic the current flowing through the sensing electrodes due to the appearance of iodine is used to control the concentration of iodine by

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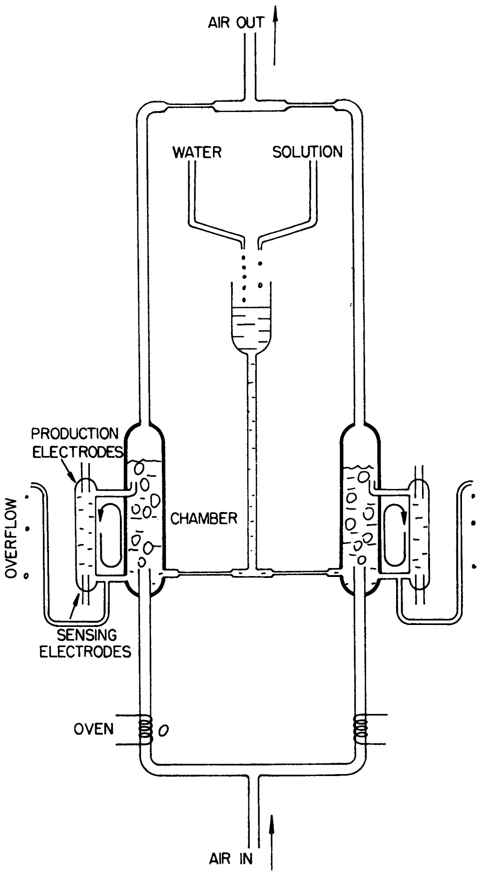

Figure 1. Simplified schematic diagram of differential method of recording atmospheric ozone

means of a servo system. The servo loop consists of a commercial direct current amplifier, which employs a chopper at the input and operates directly into a servo motor. This motor adjusts the position of a potentiometer to increase the current through the production electrodes when the iodine concentration is low and decrease it when the iodine concentration is high. The servo system is adjusted to maintain the current through the sensing electrodes at 10^{-7} ampere.

Each of the two chambers has its own servo amplifier. The iodine-producing current is thus for each chamber a measure of the amount of sodium thiosulfate which enters per unit time and has not reacted with iodine from other sources. If both ovens are in operation, the air flowing through the two chambers is alike in every respect and the two iodine-producing currents are equal. However, when one of the ovens is turned off, one chamber is supplied with ozone, which produces iodine from the iodide.

The difference of the two production currents which now develops is a direct and absolute measure of the amount of ozone reacting per unit time in the chamber supplied with ozone. This difference in the two production currents is recorded on a strip chart recorder.

The differential method of measuring ozone has the added convenience that the indication of the instrument does not depend on the strength of the solution. A dilute

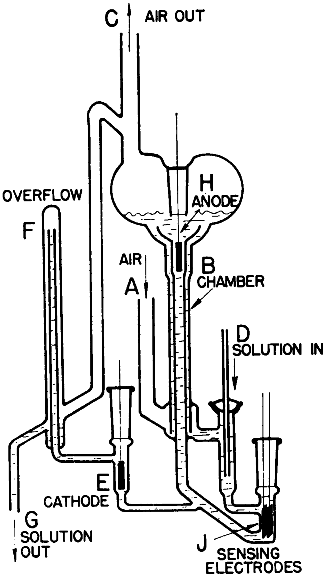

Figure 2. Schematic diagram of reaction chamber

solution of sodium thiosulfate does not stay constant for several days unless special precautions are taken (*1*).

Figure 2 shows the actual construction of one of the chambers.

The air stream enters at *A*, rises in the narrow space between the inside tube and the outside tube of chamber *B*, and leaves at *C*. The solution enters through the capillary at *D*; it leaves eventually through the overflow, *F*, and then through a trap connected to *G*. The anode for iodine production is at *H*; the cathode is recessed into the overflow tube at *E* to avoid reduction of iodine. The sensing electrodes are at *J*. The pumping action of the air makes the solution complete the closed paths from the anode *H* down through the center tube past the sensing electrodes, *J*, and then up through chamber *B* within a few seconds. Thus the sensing electrodes perceive a change in the iodine concentration with no appreciable delay.

The strength of the solution is adjusted to give a no-ozone production current of about 150 μa. A normal atmospheric ozone concentration of about 2.5×10^{-3} cm. per km. reduces this current in the "active" chamber to 130 μa. The response time of the instrument to a sudden change in ozone concentration is on the order of 1 minute.

Figure 3 shows a typical ozone record for one day at Albuquerque.

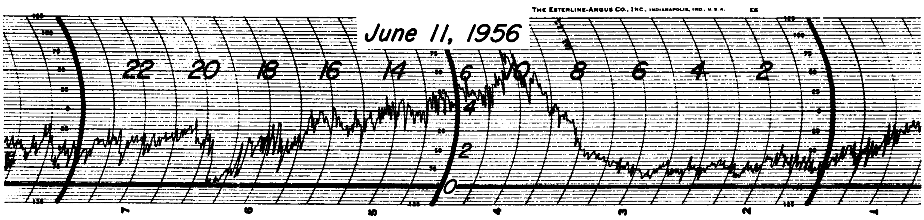

Figure 3. Record of concentration of atmospheric ozone at the earth's surface for one day at Albuquerque, N. M.

Acknowledgment

The author acknowledges the participation of John R. Green, John W. McLean, and Alan Peterson in the construction of this device. Five units were built at the University of New Mexico for the United States Weather Bureau under Contract Cwb 8811.

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Chemical Ozone Measurement

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A simple method for measuring ozone concentration semiautomatically is presented. The amount of sodium thiosulfate equivalent to the ozone present is measured by electrolysis with an iodinemeter. Although smoke interferes, the true ozone content can be measured by difference at higher temperatures. The consistency of measurements with this method is demonstrated.

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A well known reaction for measuring ozone is the oxidation of potassium iodide in neutral solution:

$$2KI + O_3 + H_2O \rightarrow O_2 + 2KOH + I_2 \qquad (1)$$

In the method of Cauer (*2*) the free iodine, formed mostly as I_3^-, is blown out with the air which brings in the ozone. The remaining potassium iodide is oxidized with nitric acid. This method is difficult, and the solution needs buffering. Furthermore, it is difficult to make the reaction go to completion, as the potassium iodide concentration must be very low if small ozone concentrations are to be measured.

Best results are obtained by using sodium thiosulfate in a more concentrated neutral solution of potassium iodide. By the quick secondary reaction

$$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6 \qquad (2)$$

the active free iodine is immediately brought into the nonactive ionic form. The loss of sodium thiosulfate is measured by titration or coulometry.

Methods for determining ozone were developed by Regener (*10*) and Ehmert (*7*). Recording methods were constructed by Gluckauf, Heal, Martin, and Paneth (*9*) and Bowen and Regener (*1*). They added fixed amounts of sodium thiosulfate automatically and recorded the volume of air containing the equivalent amount of ozone.

The author developed a simple method for semiautomatically measuring ozone concentration (*5*, *7*).

The reaction vessel (Figure 1), required special glasses such as Jenaer Geräte-Glas which had no influence on the solution even when it was in the iodinemeter for 2 days. Care was used to prevent light from entering the solution. Exactly 3 ml. of a neutral 2% potassium iodide solution (1 ml. of 0.01*N* sodium thiosulfate in 750 ml. of solution) is pipetted into bottle 4. The bottle is attached to the apparatus. If air is taken through joint 3 by a pump or a connected evacuated vessel, the air entering at the right side forces the solution through the sintered-glass filter at the lower end of tube 1 into the bottle. The air which follows bubbles through the solution. At a rate of 2 liters per minute, full reaction occurs and no solution leaves by joint 3 with the air. From 5 to 10 liters of air is used. After the reaction, bottle 4 is detached and

In OZONE CHEMISTRY AND TECHNOLOGY;
Advances in Chemistry; American Chemical Society: Washington, DC, 1959.

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch018

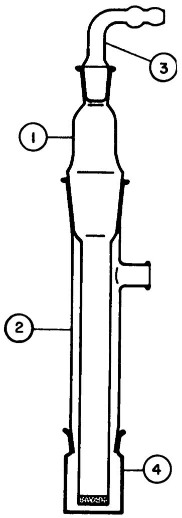

Figure 1. Reaction vessel

lowered by about 1 cm., and the solution is blown back into this bottle. After 2 ml. of water is poured in at the upper point, all of the solution is collected again in bottle 4. The residual content of sodium thiosulfate in this bottle is measured and compared with that of a blank.

This measurement is simple and rapid with an iodinemeter [Colora GMBH (14a) Lorch, Germany], whose circuit scheme is shown in Figure 2. Four platinum electrodes are brought into the solution in bottle 4, and the solution is moved against these electrodes. Two of them are connected to an electric potential of 0.18 volt (the value is not critical). At this voltage, polarization prevents electrolysis. By its depolarizing action, free iodine causes an electric current directly proportional to its concentration, but potassium iodide produces no current. As long as there is sodium thiosulfate in the solution, no electric current can flow. The sensitivity is high enough to allow measurement with small amounts of air.

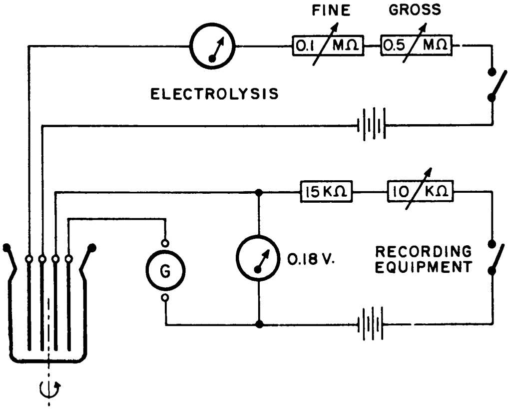

Figure 2. Iodinemeter

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Free iodine is produced in the solution when the potassium iodide is electrolyzed by the two other electrodes with a suitable current. When all of the sodium thiosulfate has reacted with iodine, a current flows through the indicating electrodes, which is linear with time (Figure 3).

From Faraday's constant, 1 γ of iodine (1 $\gamma = 10^{-6}$ gram) is obtained for an electrolysis current of 38 μa. in 20 seconds. This coulometric method does not need calibrated solutions. The sensitivity is high enough to detect the equivalent with an accuracy to 10^{-7} gram of iodine in 10 ml. of solution. Higher accuracy is possible.

Measurements away from industry and cities gave comparable values (*5*), but large errors arose from smoke and industrial contamination. These components, brought into the solution with the air, reduce iodine. As their reaction is not distinguishable from the action of sodium thiosulfate, the ozone content calculated is low. With severe contamination by smoke, "negative" ozone values are found.

As these contaminants withstand a brief heating to 150° C. while ozone undergoes decay, the true ozone content can be measured by difference. Such measurements, originally undertaken to detect nitrogen oxides by the negative effect, brought out the effect of chimney smoke in high dilution. Changes of wind direction are accompanied by apparent changes in ozone concentration, the greater part resulting from contamination.

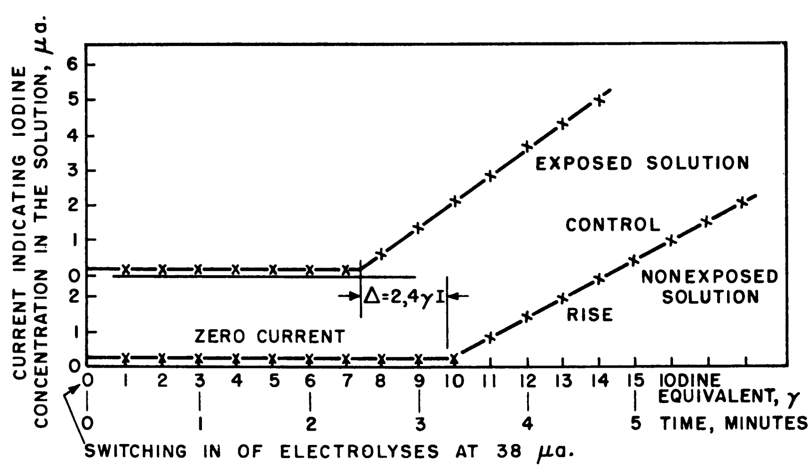

Figure 3. Typical current measurement

The consistency of measurements with this method is demonstrated by examples from earlier publications. Figure 4 shows tropospheric ozone distribution (*3*, *4*). The relation of ozone to air is independent of height for a well-mixed air mass. The temperature gradients indicate the boundaries of the air mass with constant relation.

Figure 5 shows the variation of ozone density at 1880 (Arosa) and 400 meters (Tübingen) above ground (*5*). The stations are 200 km. apart. During the day thermal convection is high and both reach the same ozone content. A new air mass arriving with a warm front on August 11 brought lower ozone concentrations at both stations. The values at Arosa are reduced for the air pressure at Tübingen.

Figure 6 shows two independent measurements (*6*), 1.5 and 21.5 meters above ground. At several hundred meters, daily variation due to convection does not exist (*8*). Near the ground, wind conditions have severe influence, and ozone destruction occurs when air convection ceases.

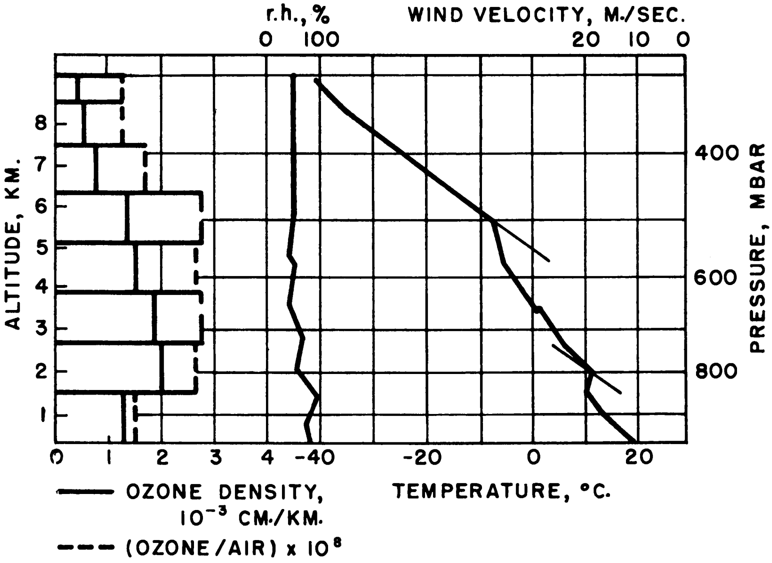

Figure 4. Tropospheric ozone distribution measured by an aircraft

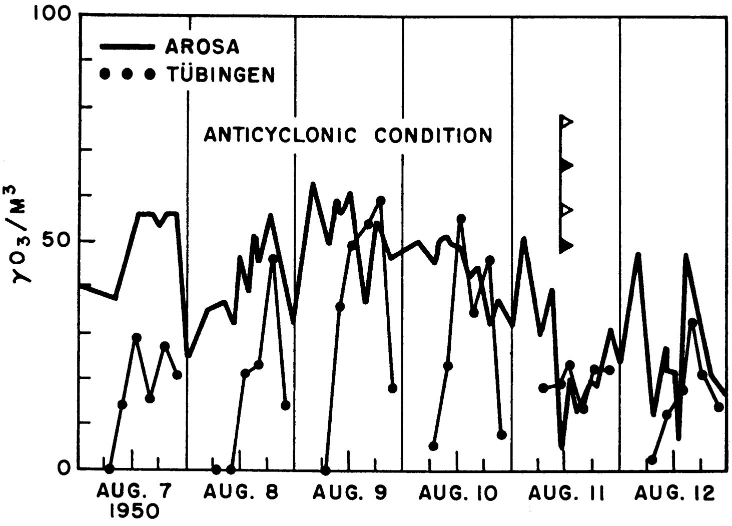

Figure 5. Ozone density

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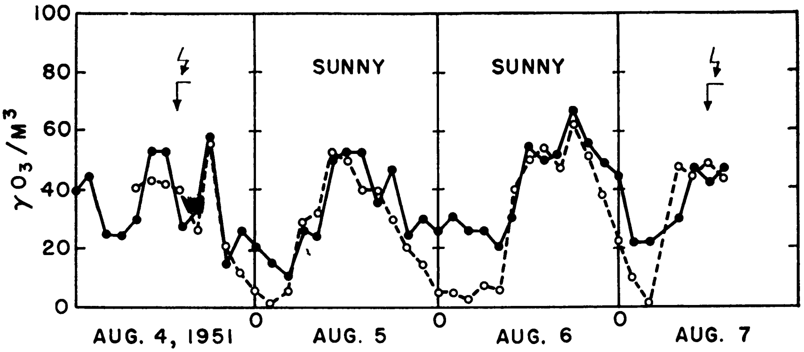

Figure 6. Comparison of independent ozone measurements

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Products of Ozonization of Some Olefins

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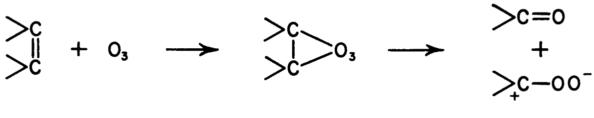
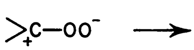
The products of the ozonization of 2-butene in acetic acid and of 2,3-dimethyl-2-butene in isopropyl alcohol are compared with known substances. The monomeric ozonides of methyl trimethylacrylate and of trimethylacrolein are described. Some unsymmetrically disubstituted ethylenes give epoxides instead of ozonides, when ozonized in inert solvents.

Through the work of many investigators it has been shown in the last few years that the reaction of olefins with ozone takes place in the following way:



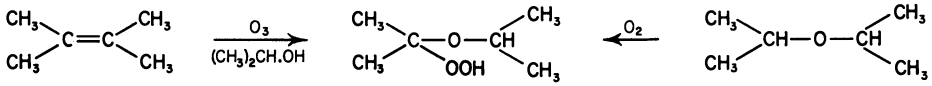


1. Polymerization
2. Addition of H-X
3. Addition of aldehydes and, under special conditions, also of ketones
4. Rearrangement to esters, lactones, or anhydrides

The first intermediate, which never has been isolated and therefore must be very unstable, is called the *Primärozonid* or initial ozonide (*1*). Nothing can be said with certainty at this moment about its special structure.

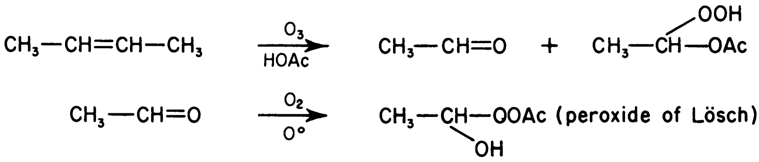
The most important intermediate seems to be the zwitterion which arises from the spontaneous cleavage of the initial ozonide. From the zwitterion all reaction products which have been found from different starting materials under different conditions can be explained.

Instead of ozonizing tetramethylethylene in the presence of methanol, the methanol as solvent has been replaced by isopropyl alcohol:



The hydroperoxy ether, formed as reaction product, was identical with the first autoxidation product of diisopropyl ether.

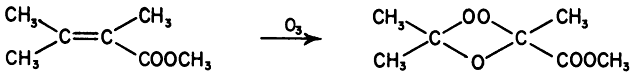
A further example for the ozonization of an olefin in the presence of a solvent containing active hydrogen is the ozonolysis of 2-butene in acetic acid as solvent. The hydroperoxy ester was isolated as a pure and rather stable liquid. It is different from a crystalline autoxidation product of acetaldehyde (the "peroxide of Lösch") which has the same empirical formula. Therefore, this peroxide cannot have the constitution of a hydroperoxy ester.

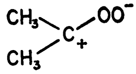


One important fact which is consistent with the theory that olefins are built by an addition process is the impossibility of getting monomeric ozonides from aliphatic olefins with four substituents at the double bond. In this case the one cleavage product of the olefin is a ketone which, because of its relatively inert C=O double bond, cannot add to the zwitterion in an intermolecular process.

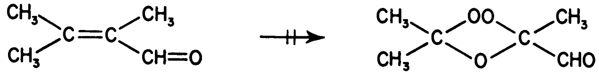
If this inertness of the keto group is the reason that no aliphatic ketozonide could be obtained, then in such cases, where especially highly reactive ketones would be produced, ketozonides should be obtained.

Von Bornhaupt (*5*) therefore investigated the ozonization of methyl trimethyl acrylate in pentane as the solvent and found among the reaction products in 45% yield the monomeric ozonide (boiling point$_{0.5}$ 29–30°, melting point −3°):

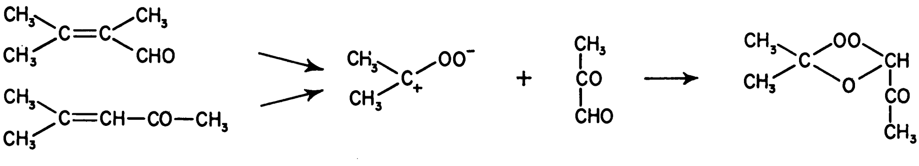


The constitution of the ozonide was proved by analysis and by reduction to acetone and methyl pyruvate. The formation of this new ozonide can be explained by the addition of methyl pyruvate to the zwitterion  . Indeed, it is known that the keto group of pyruvic acid is much more reactive than that in simple ketones.

In another part of his work von Bornhaupt (*5*) synthesized the corresponding aldehyde, the trimethylacrolein. Also in this case the formation of a ketozonide seemed possible, because the keto group in methyl glyoxal is very reactive:

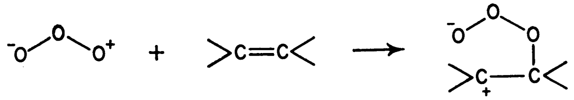


However, the ozonide obtained (boiling point 37–9°) was shown by its infrared spectrum to be identical with the ozonide of mesityl oxide. Therefore, the methyl glyoxal (which in both cases should be the one intermediate) adds to the zwitterion not as a ketone but as an aldehyde:

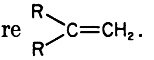
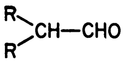
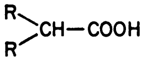


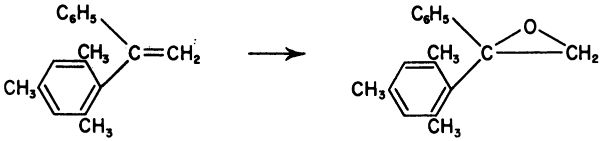
If the formation of an ozonide had involved an intramolecular rearrangement instead of the recombination of two cleavage products, two different ozonides would have been produced.

These experiments give some further evidence about the formation of the ozonides from the initial ozonides. Concerning the formation of the initial ozonides from the olefins and ozone, the latter seems to be an electrophilic reagent. Meinwald (*4*) proposed that it reacts in the following manner with the polarized olefin:

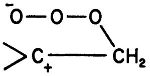


Usually this first addition product instantaneously gives the initial ozonide by a nucleophilic attack of the second or third oxygen atom on the carbonium ion.

There are some cases in which the double bond of the unsaturated compound was not cleaved during the ozonation. This is especially true for some unsymmetrical olefins of the structure  $R_2C{=}CH_2$. In these cases aldehydes or carboxylic acids of the types  $R_2CH{-}CHO$ and  $R_2CH{-}COOH$ were found. Products which were more closely related to the original olefins in their structure were the epoxides, found by Bartlett (*2*) in the case of highly branched aliphatic olefins of this type, and enols, found many years ago by Fuson (*3*) with corresponding aromatic olefins. One of the examples of Fuson —namely, the ozonization of 1-phenyl-1-mesitylethylene—was reinvestigated. The epoxide (melting point 101–2°) was actually the initial product, just as in the case of Bartlett:



This compound, under the influence of acids, easily rearranges to the enol of Fuson. To avoid this rearrangement during the ozonization, some drops of triethylamine were always added. Exactly the same reaction takes place with the unsymmetrical dimesitylethylene (epoxide, melting point 102°).

In these cases the first intermediate,  $>\underset{+}{C}(O{-}O{-}O^{-}){-}CH_2$ owing to steric hindrance, cannot be transformed to an initial ozonide but instead loses one molecule of oxygen with the formation of an epoxide.

Di-*p*-anisylethylene reacts with ozone to give dianisyl ketone; under very mild conditions dianisylethylene gives an ozonide, which is very unstable at room temperature, either exploding or decomposing to give the ketone. Therefore the formation of epoxides during ozonizations seems to be limited to olefins with strong hindrance at one of the carbon atoms. Diphenylethylene reacts normally under formation of a liquid ozonide. Also mono-*p*-anisylethylene (*p*-methoxystyrene) gives only the ozonide (melting point 70–1°). It therefore seems that an unsymmetrical olefin with two strong electron-donating groups prefers the formation of an epoxide instead of an ozonide, though this fact at the moment cannot be explained satisfactorily.

In the case of the *trans*-di-*tert*-butylethylene there was formed a crystalline compound which rearranges even at —50° to the ozonide in an exothermic reaction. The nature of this compound is now being investigated.

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(5) von Bornhaupt, B., unpublished manuscript.

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Some Abnormal Ozonization Reactions

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Ozonization reactions heretofore known to yield abnormal products and therefore classed as abnormal have been found to proceed normally when carried out at low temperatures in hydroxylic solvents such as methanol. The method described will be of considerable value in the elucidation of structures of organic compounds. A mechanism has been proposed to account for the formation of normal products in the ozonization of organic compounds containing allylic groups.

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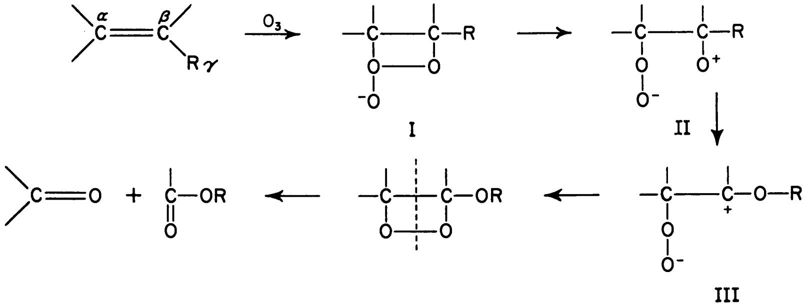
A recent publication from this laboratory (*5*) presented evidence in favor of a mechanism of ozonization of unsaturated substances differing somewhat from that previously proposed by Criegee and Werner (*1*). Inasmuch as the results of abnormal ozonization reactions (*3, 8, 10, 11*) were used in partial support of Criegee's mechanism, it was thought advisable to reinvestigate some of these ozonizations from the recent point of view.

In accordance with Criegee's mechanism as applied to abnormal ozonizations (*4*), an unsaturated substance which contains electron-donating groups attached to a carbon atom adjacent to a double bond will produce zwitterions which will rearrange in such a manner as to produce abnormal products. This can be illustrated by the following sequence of reactions, in which R contains an electron-donating atom attached to a carbon adjacent to the double bond:



The process of ozonization is thus seen as a competition between the migration aptitude of the α- and the γ-carbon atom to determine if the ozonization proceeds normally or abnormally.

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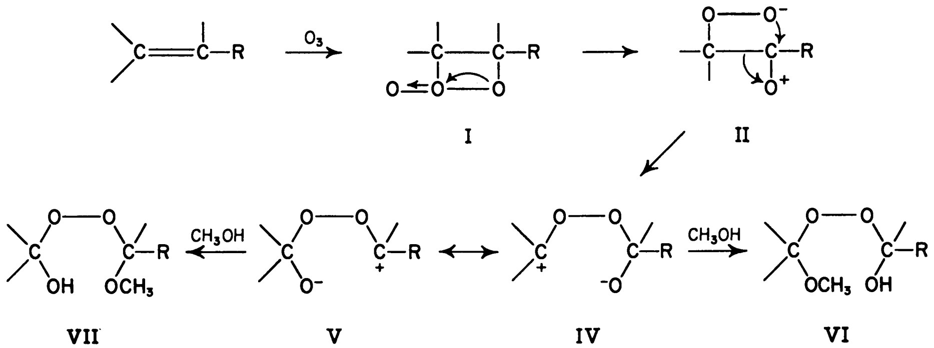
Previous experiments in this laboratory showed that the course of ozonization in hydroxylic solvents may not proceed through zwitterion III. Additional support to this view is now supplied by the present investigation, which failed to give even traces of abnormal products from ozonizations that are known to yield abnormal products in nonhydroxylic solvents. Therefore, the course of ozonization in the presence of hydroxylic solvents should be represented as follows:



It can thus be seen that zwitterions IV and V would be stabilized by the interaction of the alcohol with them, and the ozonide would have no opportunity to form and decompose abnormally. Whether zwitterions IV and V are formed in equal amounts depends upon the groups which are attached to the double bond and the carbon atom to which the ozone molecule initially adds. The final products, VI and VII, may be considered as hemiperacetals or hemiperketals and could be isolated only under special conditions. However, they can be easily decomposed with either sulfurous acid or sodium bisulfite and the ketones or aldehydes formed determined quantitatively as their 2,4-dinitrophenylhydrazones.

Several representative compounds from which abnormal products had been previously isolated in ozonizations carried out by other investigators were selected to test the above theory. Ozonizations were carried out in pure methanolic solutions at about —20° C. and in each case the yield of peroxide, based on the ozone consumed, was determined quantitatively. Overozonization was avoided, inasmuch as excess ozone is known to cause side reactions or decomposition of the peroxides (*5*). The peroxides thus formed were reduced with aqueous sodium bisulfite and the carbonyl compounds isolated as their 2,4-dinitrophenylhydrazones, which were separated quantitatively by chromatography through a mixture (2 to 1) of silica gel and Celite. In no case were any of the abnormal products found. The results are summarized in Table I.

Table I. Products from Ozonizations Reported as Abnormal

Olefin	Abnormal Product Reported	Yield, %	Normal Products Obtained (Present Work)	Yield, %	Peroxide Yield, %
Cinnamyl alcohol	Formic acid (*11*)	60[a]	Glycolic aldehyde Benzaldehyde	77 84	96.2
α-Methylallyl ethyl ether	Acetic acid (*11*)	35[a]	α-Ethoxypropional Formaldehyde	96 34	96.0
Crotonaldehyde	Formic acid (*11*)	10[a]	Acetaldehyde Glyoxal	97.6 93.6	97.1
Coumarone (benzofuran)	Catechol (*10*)	10	Salicylaldehyde	97	96.5
Geraniol	Formaldehyde (*3*)	23	Glycolic aldehyde Levulinic aldehyde Acetone	62.3 90.5 40.8	95.0

[a] Per cent of total acids after oxidation with silver oxide.

The results indicate conclusively that ozonizations heretofore assumed to be abnormal are really normal if carried out in methanol, which reacts with the intermediate products, thereby preventing rearrangements of the ozonides and the production of abnormal products. Moreover, even when cinnamyl alcohol was ozonized in methyl chloride at −70° C., no abnormal products were isolated, as shown recently in this laboratory by P. P. Otto.

The products shown in Table I, column 4, were obtained and identified by the following procedure. In each case an aliquot equal to that used for active oxygen determinations (usually 0.5 to 1.0 cc.) was added at 0° C. to a five- to tenfold excess of sodium bisulfite in 10 cc. of water. The solution was then allowed to warm to room temperature and, if no volatile compounds were expected, it was warmed slightly. Then a twofold excess of 2,4-dinitrophenylhydrazine reagent was added and the mixture was heated on the water bath for 0.5 hour. After cooling and adding water if necessary, the precipitate formed was separated, washed with water, and dried in the desiccator under reduced pressure.

Products Obtained

From Cinnamyl Alcohol. The dried phenylhydrazone mixture was extracted several times with hot chloroform and the chloroform-soluble portion chromatographed on a silica gel-Celite (2 to 1) column. The band which was eluted with 5% ethyl ether in petroleum ether proved to be the 2,4-dinitrophenylhydrazone of benzaldehyde; yield, 83.7%; melting point, 235–7° C.

The insoluble portion from the chloroform extraction was recrystallized from pyridine; yield, 77%; melting point, 314–16° C. Literature melting point of 2,4-dinitrophenylhydrazone of glyoxal, 311–12° C. (*2*).

All attempts to isolate formaldehyde or its derivatives from the original mixture gave negative results.

When the ozonization of cinnamyl alcohol was carried out in methyl chloride at −70° C., followed by removal of the solvent at −10° and immediate reduction of the residue with sodium bisulfite and conversion of the aldehydes to their corresponding 2,4-dinitrophenyl-hydrazones, benzaldehyde and glycolic aldehyde were obtained in yields of 98 and 70%, respectively. No formaldehyde was detected.

α-Methylallyl Ethyl Ether. The mixture of the 2,4-dinitrophenylhydrazones obtained in this case was extracted with hot chloroform and the extracts were chromatographed as before. The column was then eluted with a solution of 5% ethyl ether in petroleum ether. The first eluate contained the 2,4-dinitrophenylhydrazone of α-ethoxypropional; yield 96%; melting point, 126° C. Literature value, 127° C. (*6*).

The top of the moving band in the column was the 2,4-dinitrophenylhydrazone of formaldehyde. This was cut from the column and eluted with ether; yield, 34%; melting point, 164–5° C. Literature value, 166° C.

The chloroform-insoluble portion proved to be the osazone of methyl glyoxal formed by the acid cleavage of α-ethoxypropional. This had a melting point of 285° C. Literature melting point, 287° C. (*7*). No abnormal products were isolated.

From Crotonaldehyde. The mixture of the 2,4-dinitrophenylhydrazones was extracted with hot chloroform and the soluble portion chromatographed as before. The first band was eluted with a solution of 5% ethyl ether in petroleum ether and the eluate proved to be the 2,4-dinitrophenylhydrazone of acetaldehyde; yield, 97.6%; melting point, 148° C.

The second band was eluted with 25% ethyl ether in petroleum ether and proved to be the 2,4-dinitrophenylhydrazone of unreacted crotonaldehyde; melting point, 185–7° C.

The chloroform-insoluble portion was the osazone of glyoxal; yield, 96.3%; melting point, 311° C.

From Coumarone. The 2,4-dinitrophenylhydrazone obtained in this case was dissolved in chloroform and chromatographed as before. It was eluted with 10% ethyl ether in petroleum ether and proved to be the 2,4-dinitrophenylhydrazone of

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salicylaldehyde; yield, 97%; melting point, 249–50° C. Literature melting point, 252° C. (*2*).

From Geraniol. The geraniol used was purified in accordance with the method of Knights and Waight (*3*) and ozonized in pure methanol in the usual manner. The mixture of 2,4-dinitrophenylhydrazones obtained after reduction with sodium bisulfite was extracted with hot ethanol and the solvent removed. The residue was recrystallized from aqueous ethanol; yield of acetone 2,4-dinitrophenylhydrazone, 40.8%; melting point, 123–4° C.

The ethanol-insoluble mixture of phenylhydrazones was extracted several times with hot chloroform and the solvent removed. The reddish residue was then recrystallized from pyridine; yield of levulinic aldehyde, 2,4-dinitrophenylhydrazone, 90.5%; melting point, 232° C. Literature melting point, 235–6° C. (*9*).

The chloroform-insoluble portion was recrystallized from pyridine; yield of glyoxal osazone, 62.3%; melting point, 313° C. All attempts to isolate formaldehyde, the abnormal product of ozonization, proved unsuccessful.

Acknowledgment

The results reported here for geraniol were carried out in this laboratory by Rachel Keto. The authors are also indebted to Lucidol Division of Wallace and Tiernan, Inc., for financial support of this investigation.

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Structural Relationships in Addition of Ozone to Double Bonds

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Ozone is the best reagent for the location of double bonds in organic molecules, because of its ease and velocity of addition and general freedom from rearrangements and secondary reactions. Some recently prepared compounds, however, show a very reduced rate of addition of ozone in solution. In general, aromatic double bonds add ozone at about 10% the rate of isolated double bonds. Anethole can be converted readily to anisaldehyde without appreciable attack on the aromatic ring system. β-Pinene is an unusual case. Its double bond should add ozone readily, yet it is almost impossible to get any of the expected product by ordinary ozonolysis. Hydrogens alpha to the double bond peroxidize almost as fast as the double bond ozonizes. The large excess of oxygen in the stream soon removes the β-pinene from the reaction mixture. Highly branched olefins such as 3,4,5,5-tetramethyl-2-hexene and 3,5,5-trimethyl-2-heptene ozonize readily with 6% ozone in oxygen to give the expected products on hydrolysis; 3,3,6-trimethyl-4-*tert*-butyl-4-heptene, 3,3,5-trimethyl-4-isobutyl-4-hexene, and 2,2,5-trimethyl-3-*tert*-butyl-3-hexene add ozone from a 6% stream at about one tenth the rate of ordinary olefinic double bonds. The internal location of the double bonds in these molecules and the small probability of the molecules being so coiled as to be capable of attack by ozone account for the observations.

Ozone has been used to determine the location of double bonds since 1855 (*5*), although the method did not receive widespread acceptance until after the extensive work of Harries (*4*) and Briner (*1*). Present knowledge of the structure of unsaturated hydrocarbon polymers and rearrangements leading to olefin systems is entirely dependent on the elegant degradation possible through the use of ozone. This method will continue to be of wide application, although some new olefins will be described which show greatly reduced reactivity toward ozone. The present work compares the reactivity of ozone with a variety of types of double bonds.

In OZONE CHEMISTRY AND TECHNOLOGY;
Advances in Chemistry; American Chemical Society: Washington, DC, 1959.

When a stream of ozonized oxygen or air, usually under 6% ozone, is passed through a solution of an olefin, such as 2,4,4-trimethyl-2-pentene, absorption occurs as fast as the ozone is introduced and no ozone escapes through the solution until all the olefin has been converted to ozonide. If an aromatic hydrocarbon such as benzene is ozonized rather than an aliphatic olefin, absorption of ozone is not complete and several times the theoretical amount of ozone must be used to effect complete ozonization. When a molecule has both an aromatic system and an aliphatic double bond, the aliphatic bond may react selectively, with little or no reaction with the aromatic system. Anethole will absorb a mole of ozone and produce, on hydrolysis of the ozonide, a very good yield of anise aldehyde. Complete saturation of the molecule requires almost 10 moles of ozone, however.

Tetraphenylethylene, which does not add bromine, is reported to give a good yield of benzophenone on ozonalysis (*3*).

Ozonolysis in the Terpene Field

There are some interesting examples of selective ozonolysis in the terpene field. Limonene is ozonized at the 8,9- double bond in preference to the 1- double bond. This is indicated by the fact that the amount of formaldehyde found is almost equal to the amount of ozone introduced, up to 1 mole. In like manner, terpinolene yields acetone in an amount nearly equal to the ozone passed, up to 1 mole. β-Pinene should add ozone readily and form formaldehyde and nopinone on ozonolysis. Practically none of these products can be obtained by ordinary ozonolysis techniques. The hydrogens alpha to the double bond, with probable additional activation from the general strain of the system, are so active to peroxidation by oxygen that little ozonide is formed, because of the large excess of oxygen present.

There appears to be little selectivity with respect to ordinary olefins. If commercial diisobutylene, a mixture of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene, is partially ozonized, the same ratio of products is obtained as on complete ozonization.

Unusual Rearrangements

The author has been interested in alcohols and olefins in the C_{10} and C_{15} range with considerable branching, in the search for unusual types of rearrangements. Some complex molecules which show normal reactivity toward ozone are: 5-methyl-5-decene (*2*), 3,5,5-trimethyl-2-heptene (*6*), 3,4,5,5-tetramethyl-2-hexene (*6*), and 4-isopropyl-5, 5-dimethyl-3-heptene. Olefins that ozonize about one tenth as fast as normal are 3,3,6-trimethyl-4-*tert*-butyl-4-heptene, 3,3,5-trimethyl-4-isobutyl-4-hexene, and 2,2,5-trimethyl-3-*tert*-butyl-3-hexene. Complete details of the preparation of these compounds will be published elsewhere. For example, 3,3,6-trimethyl-4-*tert*-butyl-4-heptene was prepared in almost quantitative yield by dehydrating 3,3,6-trimethyl-4-*tert*-butyl-4-heptanol with 1-naphthalenesulfonic acid. Higher temperatures gave cleavage. The olefin gave no test for double bond readily with bromine and infrared spectra were negative for double bond absorption at 6 to 6.2 microns, yet the theoretical amount of water was obtained on dehydration. The final products of ozonolysis confirmed the structure by yielding *tert*-amyl *tert*-butyl ketone and isobutyraldehyde. The same products were obtained in smaller yield when the olefin was partially ozonized, indicating no selective ozonization of components of a mixture.

Studies in this field continue with olefins obtained from the following alcohols: 3,3-dimethyl-4-*tert*-butyl-4-octanol, 2,2-dimethyl-3-*tert*-butyl-3-heptanol, 3,3-dimethyl-4-isobutyl-4-ocanol, 3,3,6-trimethyl-4-*n*-propyl-4-hexanol, and 3,3,6-trimethyl-4-isopropyl-4-hexanol.

Present limited observations indicate that, in the C_{10} to C_{15} range, ozonization will be abnormal in rate if there are three groups with branching attached to the double bond.

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Initial Attack of Ozone on an Unsaturated System

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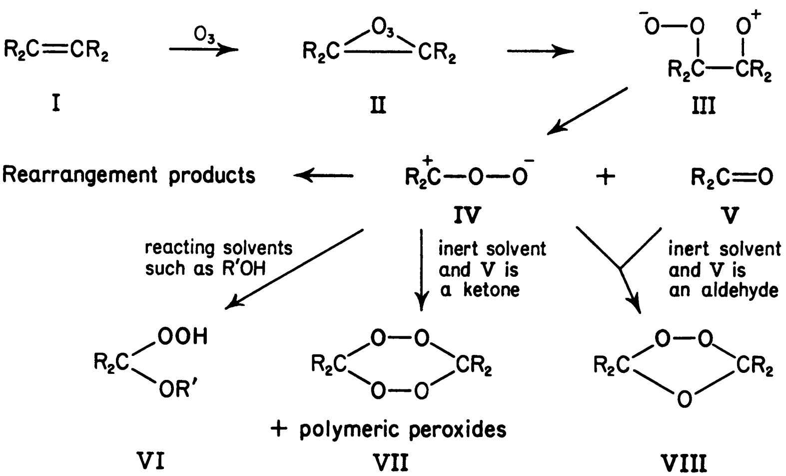
A general theory of attack, which is supported by work from the University of Texas, is deduced from the ideas of many people. A two-step attack is proposed. The first step is electrophilic and is made by a terminal oxygen atom. The central atom, which is nucleophilic, completes the attack. The position of attack on anthracene and the specificity of attack which occurs with unsymmetrical olefins support this theory.

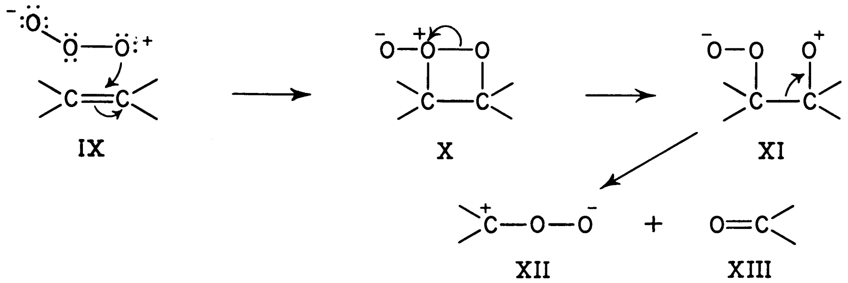
The Criegee mechanism (*13–15, 17*) for ozonolysis has been of tremendous importance in giving a better understanding of the course of the ozonolysis reaction—in particular, the nature and fate of the active oxygen-containing ozonolysis products. It leaves in doubt, however, the nature of the initial attack of ozone on an unsaturated system and of the intermediates leading to the formation of the primary cleavage products, the zwitterion (IV) and the aldehyde or ketone (V).



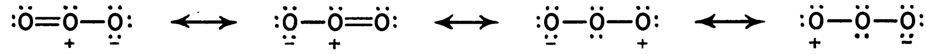
The initial ozone attack could occur in two general ways. The first is a one-step simultaneous attack of both reactive centers of the ozone molecule on both reactive centers of the unsaturated molecule. This mechanism is championed by the Australians, Brown (*9, 11*) and Badger (*1–4*). The other possibility is a two-step attack of the reactive centers of the ozone molecule on the unsaturated system.

After a decision between these two broad, general mechanisms is reached, additional questions must be answered. If the first mechanism is in effect, does the attack involve the terminal oxygen atoms or adjacent oxygen atoms? If the second mechanism is in effect, does the first step involve an electrophilic, nucleophilic, or radical attack? Does the first step involve a terminal or a central atom? If it involves a terminal atom, is the attack completed in the second step by the middle or the other terminal atom? Further, one must explain why the double bond is so easily cleaved and why no intermediate from the initial ozone attack has ever been isolated.

This paper attempts to mold the ideas of many people into a general theory and reports work from the University of Texas which adds support to the theory.



Agreement seems finally to have been reached that the ozone molecule has an obtuse apex angle and, therefore, should be considered a hybrid of the following structures (*20, 26*). The work of Wibaut and coworkers (*6, 19, 21, 24, 25, 27, 28*) has



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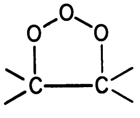
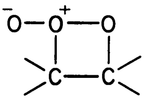
XIV XV

furnished strong evidence for the two-step attack, the first step being electrophilic. It has been generally assumed that the central, positively charged atom makes the electrophilic attack. Meinwald (*22*), however, has pointed out that in structures XIV and XV, which are the only ones considered to make any appreciable contribution to the ozone hybrid, the central oxygen atom has its full quota of eight electrons and cannot be electrophilic. Only in structures XV is there an electrophilic center and it is the terminal oxygen atom.

In the proposed theory a terminal oxygen atom makes the initial, electrophilic attack. After this, either the central or other terminal atom could complete the attack, because both are nucleophilic. Completion by the other terminal atom would lead to the formation of intermediate XVI, whereas XVII would be produced if the central atom completed the attack.



XVI



XVII

Structure XVI is favored by some people because of the greater stability it should have. On the other hand this seems to the present author to be the best argument against it, as it has never been isolated.

Structure XVII should be very unstable. The partial positive charges should

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cause the oxygen-oxygen bond to break completely—e.g., X—to produce XI which likewise would be highly unstable. The positive charge on the oxygen atom of XI would weaken the carbon-carbon bond of XI, causing breakdown to the proved intermediates of the Criegee (*13–15, 17*) mechanism (XII and XIII).

Work carried out at the University of Texas supports this picture. Two approaches to the solution of the problem are being made. The first deals with the position of attack on various aromatic systems. According to the molecular orbital theory, the one-step simultaneous attack of a "double-bond" reagent upon an aromatic system will occur first at the bond with the lowest "bond localization energy" (the one with the greatest double bond character), whereas the two-step attack will occur initially at the position with the lowest "atom localization energy" (most reactive carbon atom in the molecule) (*7–11, 18*). With some aromatic substances, such as anthracene, these positions are different. With anthracene the bond with the lowest bond localization energy is the 1,2 bond (*7–11, 18*). Osmium tetroxide, a known double bond reagent, attacks here (*12*). The positions with the lowest atom localization energies are the 9,10 positions. Here electrophilic substitution and oxidation occur.

What will ozone do? Waters (*23*) has ozonized anthracene in acetic anhydride and obtained anthraquinone. He did not state his yield, however, nor show how much ozone was absorbed. It is not certain whether ozone, or oxygen catalyzed by ozone, produced the anthraquinone.

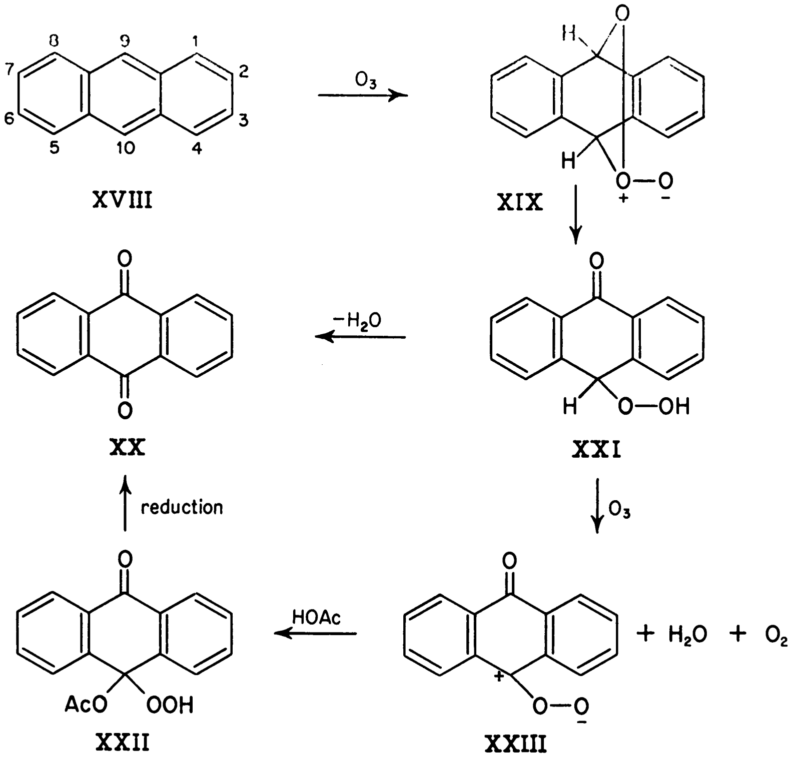
The ozonolysis of anthracene is being studied in detail at the University of Texas. In acetic acid the ozone is absorbed nicely and the anthracene slowly goes into solution as it reacts. It requires the reaction of approximately 3 moles of ozone per mole of anthracene to complete the reaction. At the end some anthraquinone has precipitated in the reaction vessel. This amounts to a 28% yield. The filtrate is peroxidic. Upon reduction with sodium iodide, a 41% yield of anthraquinone results, making a total yield of 69%. It is certain that the anthraquinone formation is due to the ozone reaction, because (1) an active oxygen-containing compound is produced which is reduced to anthraquinone, (2) oxygen alone under the same conditions gives no reaction, and (3) oxygen plus a trace of ozone produces anthraquinone in amounts roughly proportional to the amount of ozone passed through the system, but not at all proportional to the amount of oxygen passed through the system. This is excellent evidence for the two-step attack.

In regard to the exact mechanism of the anthraquinone formation, which is 69% of the reaction, it does not seem likely that the entire 3 moles of ozone is required. Perhaps the other 31% of the reaction occurs by the one-step mechanism at the 1,2 bond of anthracene. If this occurred, the reaction should continue until both outer rings are destroyed. This would require a considerable proportion of the 3 moles of ozone absorbed during the reaction. Two facts must be taken into account in any mechanism suggestion. Some anthraquinone is produced by spontaneous decomposition of an active oxygen-containing product and the remainder is produced by reduction of an active oxygen-containing product.

The following mechanism meets these requirements. Ozone attacks at the 9,10 positions to give an intermediate such as XIX, which rearranges to XXI, or the corresponding perhydroquinone. Spontaneous loss of water, facilitated by the glacial acetic acid solvent, would produce anthraquinone (XX) directly. Oxidation of XXI (or the corresponding perhydroquinone) would lead to zwitterion (XXIII) which would stabilize itself by reaction with the solvent to give XXII. Reduction of XXII would produce anthraquinone (XX).

The other approach being made at the University of Texas has to do with the specificity of ozone attack which occurs with unsymmetrical olefins. This is analogous to the specificity observed in the additions of unsymmetrical reagents such as hydrogen chloride to unsymmetrical olefins.

This may first be illustrated with an example already reported (*5, 13*), the ozonolysis of isobutene (XXIV) in inert solvents. The major product is an ozonide



(XXXI). This would have to be produced by interaction of intermediates XXX, and not XXXII, as Criegee (*13–15, 17*) found that zwitterions do not add to the carbonyl group of ordinary ketones. This preferential production of intermediates can be explained on the basis of the terminal oxygen atom, electrophilic attack, plus inductive effects in isobutene, leading to the formation of XXVII. On the other hand, a central oxygen electrophilic attack, besides being unlikely, would result in the preferential formation of XXVIII, which would break down to give the wrong intermediates (XXXII) for ozonide (XXXI) formation. The attack shown in XXVI is unlikely, although it could be argued that, if it broke down, it would give intermediates XXX preferentially, on the basis that the zwitterion of XXX, being a tertiary carbonium ion, would be more stable than the one in XXXII. To the present author the addition of ozone according to Markownikoff's rule to give an unstable adduct (XXVII), which can break down in only one way, is a sounder explanation of the specificity of ozone attack. This places the ozone attack on a double bond in the same category as that of other reagents which show a specificity in their reactions with unsymmetrical olefins.

The conclusions reached in the preceding example are based on indirect evidence, which is that certain intermediates (XXX) are necessary to produce the ozonide (XXXI). It would be better to get absolute evidence by actually "trapping" and identifying the zwitterion preferentially formed. This has been done at the University of Texas by the ozonolysis of 1,2-dibenzoylpropene (XXXIII) in methanol.

The products were phenylglyoxal (XXXVII) in 61% yield and the methoxyhydroperoxide (XXXV) (melting point 60–1°) in 74% yield. It was felt that the actual yields were much better. The materials were difficult to isolate. The methoxyhydroperoxide (XXXV) had to originate from zwitterion XXXVI which was "trapped" through its reaction with methanol. This specificity of reaction can be explained, as in the other case, by the terminal oxygen attack of ozone and inductive effects in 1,2-

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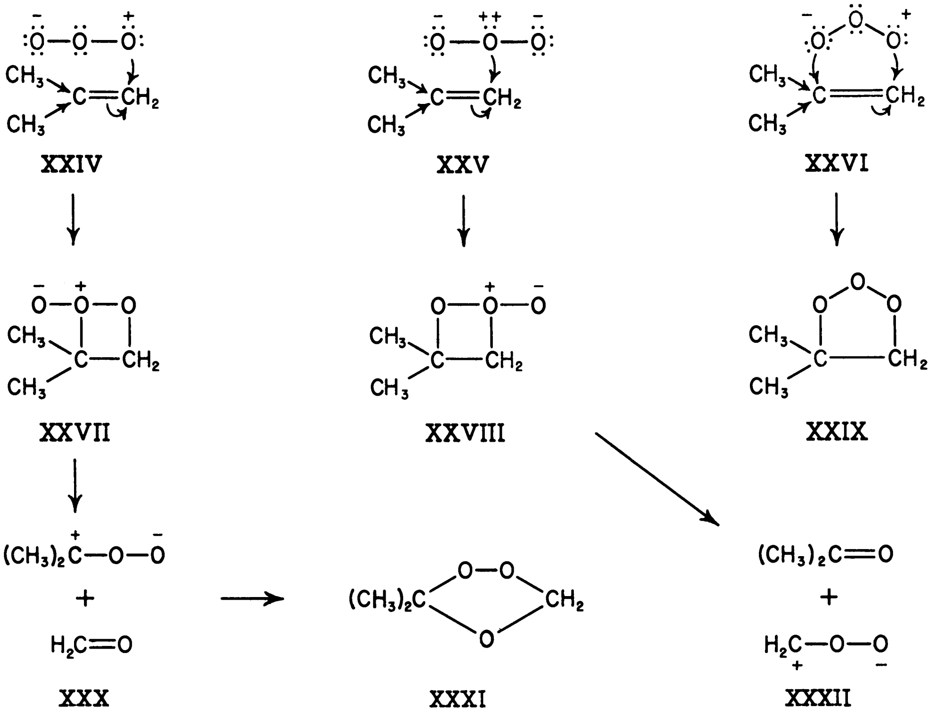
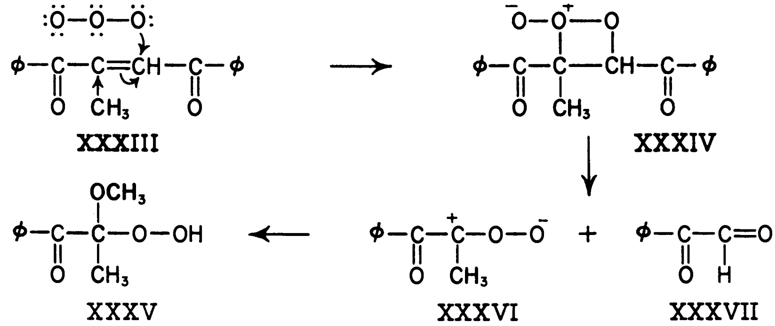


dibenzoylpropene (XXXIII). Evidence for the structure assigned to XXXV was its reduction to 1-phenyl-1,2-propanedione which was isolated as the pure semicarbazone (melting point 211–12°) in 76% yield. In addition, the elemental analyses and molecular weight determinations checked for the structure assigned. The material gave a positive lead tetraacetate test (*16*) for a hydroperoxide. The infrared spectrum showed a strong carbonyl band at 5.9 microns and a hydroxyl band at 2.9 microns.



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Improved Synthesis of Aromatic Aldehydes from Ozonolysis of Olefins

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Improved yields of aromatic aldehydes have been obtained from the ozonolysis of aromatic substituted olefins by employing a rapid steam distillation of the freshly ozonized olefins. This observation supports a mechanism for ozonolysis which involves a primary ozonide trioxolane structure.

The reaction of ozone with olefins usually results in cleavage of the double bond and the formation of aldehydes, ketones, and/or carboxylic acids, depending upon the reaction conditions and the structures involved. For aldehydes, the intermediate ozonides are ordinarily treated with a mild reducing agent—for example, hydrogen or zinc—or subjected to neutral hydrolysis. Yields in excess of 70% are exceptional for the reduction methods, while hydrolysis gives considerably lower yields.

This work describes a simple method which not only eliminates the reduction or hydrolysis step but gives aldehyde yields that are usually 86 to 90% or better. The method in its present state of development seems to be limited, however, to the production of aromatic aldehydes.

The method consists merely of a rapid steam distillation of a freshly ozonized olefin. Table I lists a number of olefins to which the method has been applied, with the products and the yields that have been obtained.

Table I. Compounds Ozonized and Steam Distilled

Compounds	Aldehyde Products	Yield, %
Stilbene	Benzaldehyde	93[a]
3,5-Dimethoxystilbene	Benzaldehyde	87
	3,5-Dimethoxybenzaldehyde	89
3,5-Dihydroxystilbene	Benzaldehyde	86
	3,5-Dihydroxybenzaldehyde	50[b]
3,5-Diacetoxystilbene	Benzaldehyde	88
	3,5-Diacetoxybenzaldehyde	94
Styrene	Benzaldehyde	87
Anethole	Anisaldehyde	92
Isosafrole	Piperonal	87
Estragole	*p*-Methoxyphenylacetaldehyde	37
1-Dodecene	...	Trace

[a] Based on 2 moles of benzaldehyde from 1 mole of stilbene.
[b] Isolated as thiosemicarbazone from steam distillation pot residue.

In all instances the products were isolated and identified except for the 1-dodecene experiment, where only trace amounts of water-insoluble aldehyde functionality were

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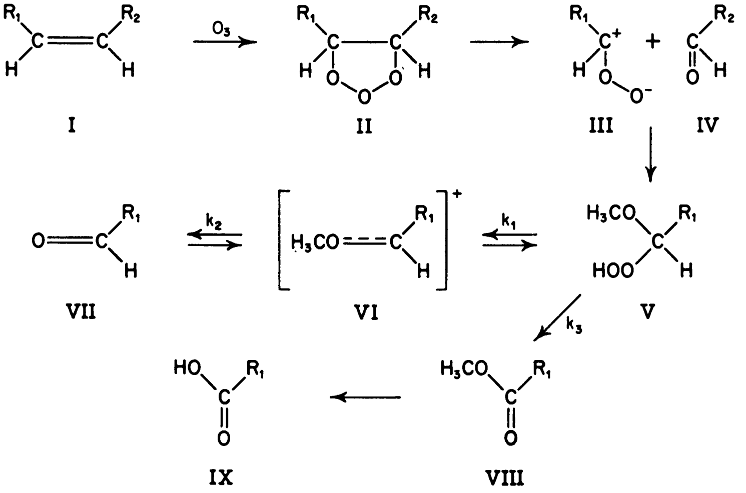
detected. Characterization of the steam distillate and pot residues from the ozonolysis of 1-dodecene indicated the presence of water-insoluble carboxylic acids (15 mole %), water-insoluble active oxygen compounds (28 mole %), and esters. Characterization of products from estragole indicated the presence of esters and water-insoluble active oxygen compounds (10 mole %).

The high yields of aromatic aldehydes that are produced by this method can be explained by, and indeed support, Criegee's (*3*) proposed mechanism for ozonolysis if the equilibria involved and relative rates of side reactions are considered. In terms of a primary ozonide trioxolane structure, II, which recently has been argued by Meinwald (*7*), Criegee (*4*), and Maggiolo (*6*) as the most probable initial intermediate in the ozonolysis of double bonds, cleavage results in the formation of aldehyde and the zwitterion, III, which, in the presence of a polar solvent (methanol), forms the hydroperoxide, V. Hydrolysis of V by steam renders the aldehyde, VII. Rapid removal of aldehydes by steam distillation drives the equilibrium from V to VII and prevents the loss of cleavage material to the irreversible heterolytic rearrangement of V to VIII.



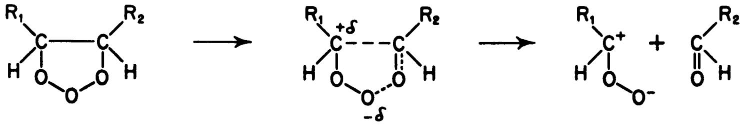
To satisfy the yields of aromatic aldehydes obtained (Table I), rates k_1 and k_2 must be considerably greater than the heterolysis rate, k_3. This seems reasonable because equilibration of V and VII when aldehyde is removed should occur readily in the aromatic series where R_1 can offer substantial resonance stabilization to the transition state, VI, by enhancing the cationic character of the carbonyl carbon. In Briner's early work (*1*, *2*) on the hydrolysis of stilbene and isoeugenol ozonides, advantage was not taken of these equilibria and rate differences. As a consequence almost half of the final cleavage products after extensive hydrolytic treatment without aldehyde removal were carboxylic acids, IX.

Failure of aliphatic aldehydes to be produced in high yields by application of this steam distillation method to estragole and 1-dodecene may be attributed to the increased stability of the intermediate hydroperoxides toward hydrolysis. In other words, the conversion rates of the corresponding intermediates, V to VI to VII, are so slow that the hydroperoxides are either steam distilled and/or undergo the relatively more rapid oxidative rearrangement to VIII and subsequent conversion to IX.

Supporting these arguments by analogy is the recent work of Kreevoy and Taft (*5*), in which aromatic acetals were found to hydrolyze some 40 to 800 times faster than aliphatic acetals.

The low aldehyde yield from the hydroxy-substituted portion of 3,5-dihydroxystilbene (Table I) can be attributed to the inability of the hydroxyaldehyde to steam distill and consequent loss to heterolytic rearrangements, part to carboxylic acids and part to resinification. The latter may have been caused to a considerable degree by a Dakin-type rearrangement.

Clearly in the case of the stilbenes, if the above proposal mechanisms are correct, half of the aldehydes produced must have resulted from the hydrolysis of hydroperoxide intermediates. With the unsymmetrical olefins, styrene, anethole, isosafrole, estragole, and 1-dodecene, this may not be the case. If cleavage of the primary ozonide is unimolecular, then the inductive and resonance contributions of substituents R_1 and R_2 in X should determine the direction of cleavage. Thus, if R_1 is more capable than R_2 of stabilizing the development of a positive charge on the adjacent carbon atom, the preferred cleavage will be as written. In view of these considerations, it is not possible to decide whether all or part of the aldehydes obtained from the unsymmetrical olefins resulted from hydrolysis of an intermediate hydroperoxide or directly from cleavage. The fact that large portions of the products from estragole and 1-dodecene were not aldehydes, however, still indicates that their respective intermediate hydroperoxides did not prefer hydrolysis, and remained as such, underwent rearrangement, or were lost to other by-product formations.



X

The realization that high yields can be obtained under the driving conditions of the steam distillations described in this paper suggests that other and equally simple methods for aldehyde removal may achieve the same high yields. Research in this direction could prove rewarding, particularly where the aldehyde products are not steam distillable or where the ozonolysis intermediates may require special conditions for their conversion to aldehydes. Even more intriguing for future research, however, is the verification or disproof of the mechanisms proposed here.

Experimental

The following ozonization and steam distillation cleavage is typical of the procedures employed.

Seventy-two grams (0.30 mole) of 3,5-dimethoxystilbene were dissolved in a solution consisting of 600 cc. of methylene chloride and 400 cc. of methanol, then cooled to dry ice–acetone temperatures. While the reaction solution was being stirred, a 5.6% ozone in oxygen stream was bubbled through until approximately 14 grams (0.30 mole) of ozone had been absorbed. Immediately following the addition of the ozone, the cold reaction solution was subjected to a rapid steam distillation. Four cuts of steam distillate were made, each amounting to approximately 1.8 liters. During distillation of the fourth cut a crystalline solid, which later proved to be 3,5-dimethoxybenzaldehyde, formed in the condenser and the aqueous distillate. Each of these cuts was extracted with ether, and the ether extracts were then dried with anhydrous sodium sulfate. Evaporation of the respective ether extracts yielded the following products:

		Analysis by Ultraviolet Absorption, %	
Cut No.	Weight, Grams	Benzaldehyde	3,5-Dimethoxybenzaldehyde
1	30.3	74	24
2	31.8	14	84
3	7.6	10	85
4	8.1	12	87

These cuts were combined and then distilled through a short column to give 27.3 grams of benzaldehyde, boiling point, 49–53° C. (2 mm.) and 44.5 grams of 3,5-

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dimethoxybenzaldehyde, boiling point 121–5° C. (2 mm.). Based on the original 72 grams of 3,5-dimethoxystilbene this represents an 87% yield of benzaldehyde and an 89% yield of 3,5-dimethoxybenzaldehyde. On standing, the 3,5-dimethoxybenzaldehyde cut solidified, melting point, 44–6° C. Recrystallization from hexane raised the melting point to 46–7° C. (literature melting point, 45–6° C.). A mixture melting point with a highly purified, authentic sample of 3,5-dimethoxybenzaldehyde exhibited no depression.

In some instances 100 to 200 cc. of water were added to the freshly ozonized reaction mixture before steam distillation. This in no way affected the yields, provided that steam distillation immediately followed the addition of the water. When experiments with ozonized 3,5-dimethoxystilbene were allowed to stand with or without water overnight before steam distilling, however, the yields of aldehyde were reduced to 51 to 59%.

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(4) Criegee, R., *Ann.* **585,** 1 (1953).
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Ozonolysis of Pyrroles, Furans, and γ-Pyrones in Connection with Reactivity of Bonds in Ring System

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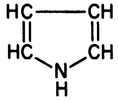
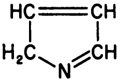
Scission products were studied from the ozonolysis of some pyrrole homologs, dimethylfurans, and methyl homologs of γ-pyrone. The results show that the pyrroles react not only according to the imino structure, but also according to a limiting structure by which the α- and β-carbon atoms are linked by a single bond. The dimethylfurans react according to this same limiting structure, as well as according to the classical structure. The study of methyl homologs of γ-pyrone shows that the pyrone ring reacts according to classical as well as polar structures.

Pyrrole and its homologs show an aromatic character in some respects, but are in general less saturated in their behavior than benzene and its derivatives. To pyrrole itself the imine structure (I) is assigned. There are indications that certain pyrrole derivatives can react according to a pyrrolenine structure (II or III).


I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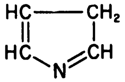
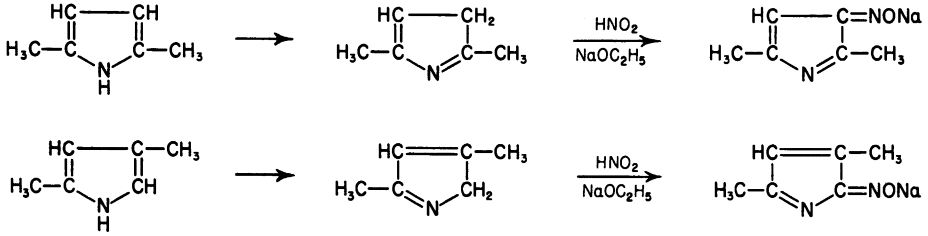

III

Angeli, Angelico, and Calvello (*1*), when making amyl nitrite and sodium ethylate react with 2,5-dimethyl- or 2,4-dimethylpyrrole, obtained the sodium salts of the isonitroso compounds. To these they attributed the following structures:



Therefore, the Italian investigators assumed that these dimethylpyrroles react according to a pyrrolenine structure. However, this assumption does not correspond to the results of recent physical measurements. Bonino (*2*) studied Raman spectra of pyrrole and some of its homologs, but did not find any indication of the presence of tautomeric forms. Analogous results were obtained by Lord and Miller (*9*) who made a thorough investigation based on Raman and infrared spectra of pyrrole and of some pyrroles containing deuterium atoms. Therefore, it was of interest to apply the ozonolysis method to pyrrole and its homologs.

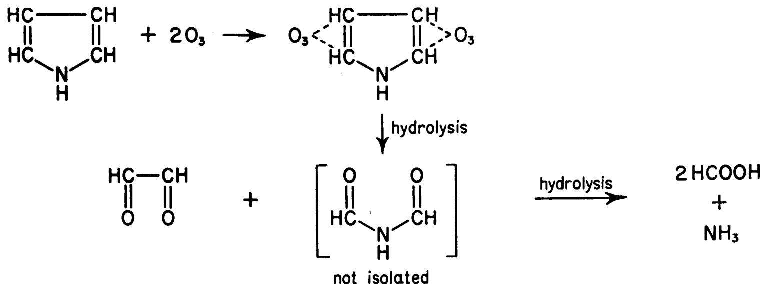
Studies in collaboration with Gulјé (*4, 13*) showed that ozonization of pyrrole and its homologs proceeds satisfactorily if the reaction takes place at —60° C., with chloroform as the solvent. Despite the low reaction temperature, more or less resin is sometimes formed, but with all the compounds under investigation the characteristic scission products could be separated.

The measurements indicated that each molecule of a pyrrole homolog takes up about 1.6 to 1.7 moles of ozone. After hydrolytic scission of the reaction product, 80 to 87% of the nitrogen bound in the pyrrole molecule is recovered in the form of ammonia (methylamine). If the quantity of ammonia is assumed to be a measure of the quantity of pyrrole which has reacted with ozone, the conclusion can be drawn that 1 molecule of pyrrole homolog has reacted with 2 molecules of ozone.

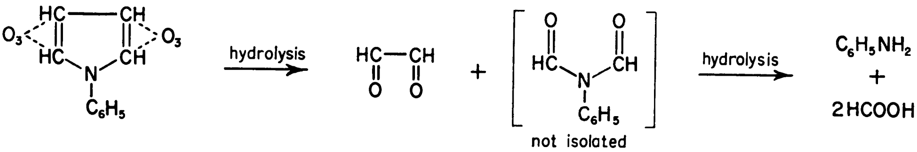
The other scission products formed by hydrolytic decomposition of the ozonides are dicarbonyl compounds, acetic acid, and/or formic acid. In some cases very slight quantities of nitric acid are found. The dicarbonyl compounds have been identified in the form of the dioximes. The quantitative analysis of the mixture of dioximes is carried out according to a method described by Haayman and Wibaut (*5*).

In another series of experiments the mixture of ozonides was treated with hydriodic acid, whereby dicarbonyl compounds are formed. By reacting the dicarbonyl compounds with *p*-nitrophenylhydrazine, the corresponding *p*-nitrophenylosazones are obtained. These are isolated from pyridine by recrystallization and identified by mixed melting point. The quantitative analysis of the mixture of nitrophenylosazones is carried out by a chromatographic method.

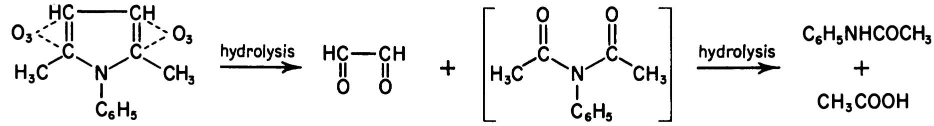
Ozonolysis of pyrrole itself gave glyoxal in a yield of 15% (isolated in the form of *p*-nitrophenylosazone). Formic acid and ammonia were also found. These products may have been formed according to the classical formula of pyrrole:



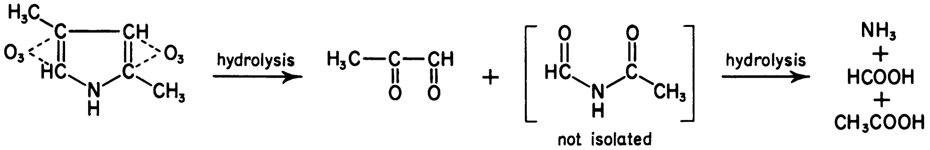
Ozonolysis of *N*-phenylpyrrole gave, besides glyoxal in a 38% yield (isolated in the form of the *p*-nitrophenylosazone), aniline in a 58% yield (isolated in the form of tribromoaniline). This result agrees well with the classical structure:



As the ozonization is carried out at −60° C., the phenyl group is hardly attacked. 1-Phenyl-2,5-dimethylpyrrole also reacts according to the classical structure; in this case the acetanilide has been isolated as a tribrominated derivative:



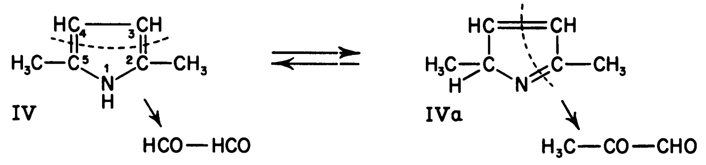
In the ozonolysis of 2,4-dimethylpyrrole, methylglyoxal is formed in 41% yield (isolated in the form of the *p*-nitrophenylosazone), as well as formic acid, acetic acid, ammonia (79%), and a small quantity of nitric acid (0.8%), isolated in the form of the nitron nitrate. This result is in good agreement with the imine structure:



The following experiments show that other structures also have to be considered.

In the ozonolysis of 2,5-dimethylpyrrole (IV), methylglyoxal and glyoxal are formed in addition to ammonia (83%), formic acid, and acetic acid. The yield of the dioximes is about 24% and of *p*-nitrophenylosazones, 29 to 33%. For the molecular ratio, methylglyoxal to glyoxal, values of about 5 to 7 are found by analysis of the mixture of oximes; a value of 7 has been found by analysis of the mixture of *p*-nitrophenylosazones. The dioximes and the *p*-nitrophenylosazones of both dicarbonyl compounds have been isolated in a pure form and were identified by mixed melting points with authentic samples.

The experimental data do not warrant calculation of an accurate value for the molecular ratio, methylglyoxal-glyoxal. However, it is certain that the mixture of dicarbonyl compounds consists mainly of methylglyoxal. This compound must be formed from a structure in which the second and third carbon atoms are linked by a single bond. In this connection one might consider the α-pyrrolenine structure (IVa) formed from the imine structure by the shifting of a proton.



It is impossible to imagine, however, how from this structure the nitrogen could be split off as ammonia. Investigations into the ozonolysis of pyridine homologs showed that the C=N bond does not react with ozone, but rather undergoes hydrolytic splitting in the latter stage of the reaction—i.e., during decomposition of the ozonide. Oxidative splitting of the C=C bond in the pyrrolenine structure, together with hydrolytic splitting of the C=N bond, would result in the formation of α-aminopropanal (or α-aminopropionic acid), but not of ammonia.

Reaction of ozone with 2-methylpyrrole gives rise to a strong resinification, even at a temperature as low as −60° C. However, the scission products, glyoxal and methylglyoxal, have been isolated (7 and 2%, respectively).

The ozonolysis of 2,3-dimethylpyrrole yielded methylglyoxal (4.6%), dimethylglyoxal (11.5%), and a small quantity of glyoxal. The mixture of scission products contained ammonia (86%) and a very slight quantity of nitric acid.

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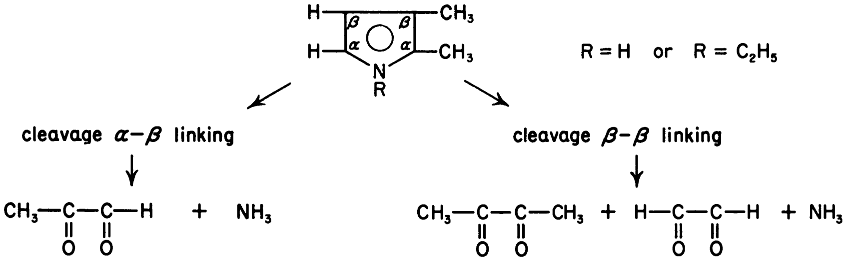
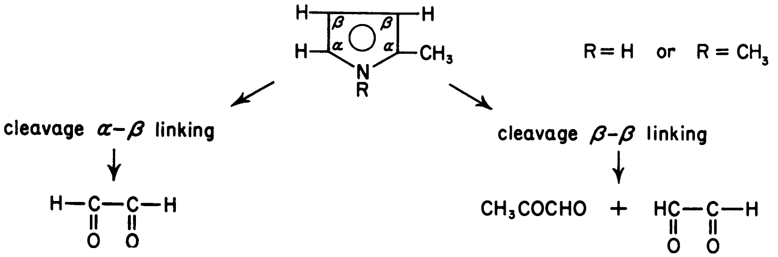
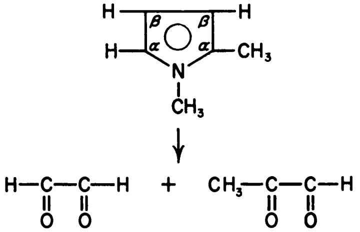


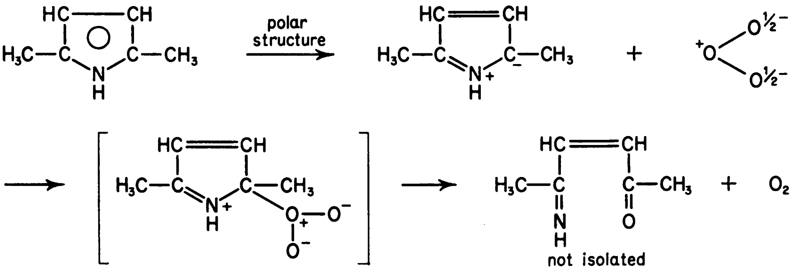


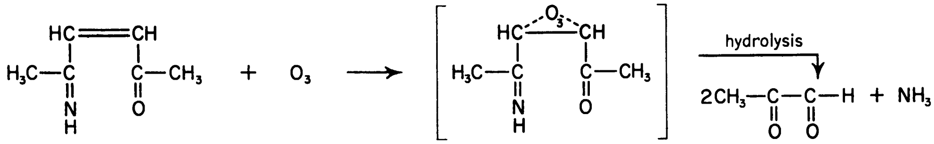
As in the ozonolysis of 2,3-dimethylpyrrole, 86% of the nitrogen was recovered in the form of ammonia; a reaction according to a pyrrolenine structure cannot be considered.

The 1-ethyl-2,3-dimethylpyrrole whose nitrogen atom carries an ethyl group cannot be converted into a pyrrolenine form. Ozonolysis of this pyrrole derivative, however, not only yielded methylglyoxal (2.9%) but also dimethylglyoxal (8.6%). The ozonolysis of 1,2-dimethylpyrrole yielded glyoxal (5.1%) and methylglyoxal (8.3%). Here again, conversion of the pyrrole derivative in a pyrrolenine form is impossible.



In all these cases the methylglyoxal or the dimethylglyoxal has been formed from a structure in which the α- and β-carbon atoms are linked by a single carbon bond. It is assumed that the pyrroles can react with ozone according to polar valence structures. According to the reaction scheme outlined below, which contains various unproved assumptions, the polar form of the pyrrole homolog will react with molecules of ozone, while on decomposition of the reaction product, the nitrogen will be split off as ammonia (or as a primary amine).





From 1 molecule of the polar form of 2,5-dimethylpyrrole, 2 molecules of methylglyoxal can be formed. This is in agreement with the experimental fact that the ozonolysis of 2,5-dimethylpyrrole yields a considerable quantity of methylglyoxal.

Ozonolysis of Furans

This work was carried out in collaboration with Jibben (*8, 11, 12*).

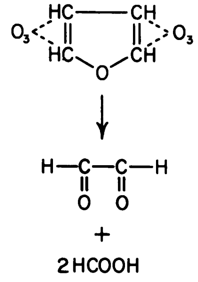
Furan and its methyl homologs react rapidly with ozone, even at a low temperature (−60° C.). On an average, 1 mole of the furans investigated consumed 1.6 moles of ozone.

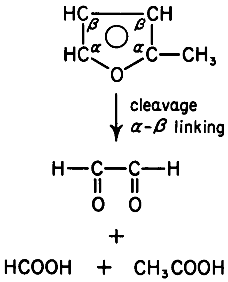
The ozonides (which are explosive) were decomposed by reduction with hydriodic acid; the dicarbonyl compounds formed were determined as *p*-nitrophenylosazones.

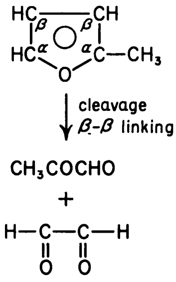
The ozonolysis of furan itself yields glyoxal (about 46% by weight) and formic acid. Interesting results, however, have been obtained in the ozonolysis of methyl furans.

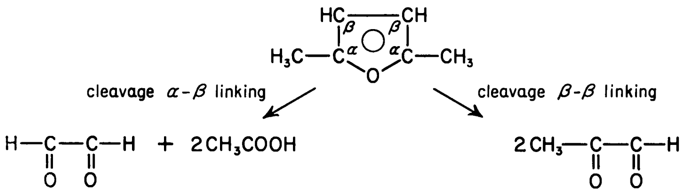
2-Methylfuran is rapidly attacked by ozone at −60° C. Glyoxal and methylglyoxal in a molecular ratio of 5 to 2 and a total yield of 35% were obtained as scission products of the highly explosive ozonide.

Among the scission products formed in the ozonolysis of 2,5-dimethylfuran were found glyoxal and methylglyoxal in a molecular ratio of 1 to 1.4 and a total yield of 48%. Formic acid and acetic acid were also formed. This means that in the cleaving of the furan ring a linking between an α- and a β-carbon atom may remain intact.



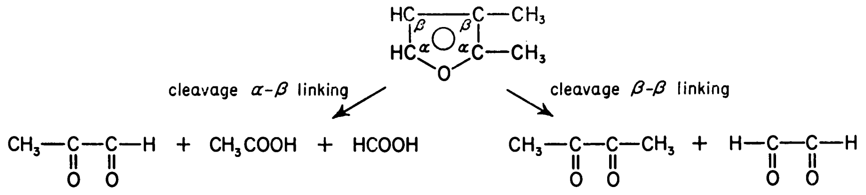




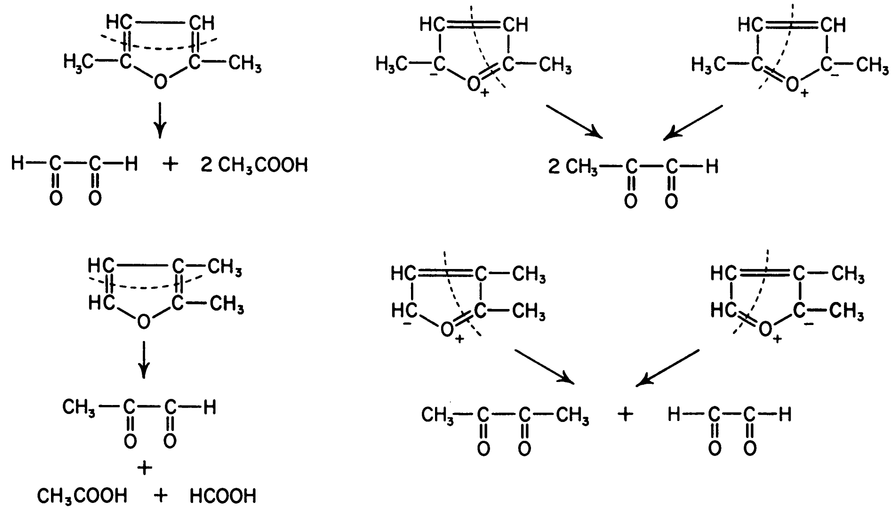


Analogous results have been obtained in the ozonolysis of 2,3,5-trimethylfuran, which yields methylglyoxal and dimethylglyoxal. The ozonolysis of 2,3-dimethylfuran yields three dicarbonyl compounds—glyoxal, methylglyoxal, and dimethylglyoxal.

These experimental results may be explained by the supposition that the furan nucleus can react according to polar structures. This hypothesis would also be in



accordance with the experimental finding that 1 mole of furan consumes less than 2 molecules of ozone, as a polar form contains only one C=C bond.

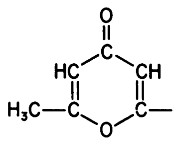


The experiments show that the way these furan homologs react with ozone may be different from what might be expected from the classical structure, and that mesomeric forms play a part.

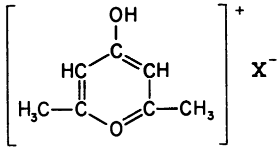
Ozonolysis of γ-Pyrones

The problem of the structure of the γ-pyrone nucleus arose when it was discovered that the conventional formulas established on the basis of degradation and synthesis were unable to account for all the properties of γ-pyrones. 2,6-Dimethyl-γ-pyrone, for instance, does not form a phenylhydrazone; its double bonds are not reduced by zinc and glacial acetic acid.

About 50 years ago Collie and Tickle (*3*) discovered that 2,6-dimethyl-γ-pyrone (V) forms well-crystallized salts with acids. The structure of these salts is now expressed by structural formula VI.



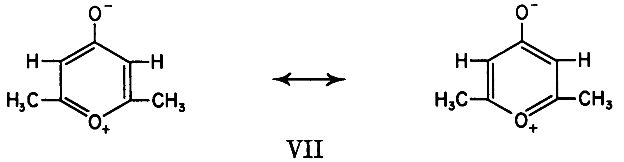
V



VI

2,6-Dimethylpyrone itself has a dipole moment of 4.6 D, which value is independent of the temperature (*7, 10*). If structure V should be assigned to 2,6-dimethyl-γ-pyrone, the dipole moment calculated according to vector addition would be 2.2 D;

from the experimental value of 4.6 D units it follows that dimethyl-γ-pyrone is a mesomeric form and that polar structures have to be taken into account—for instance, the limiting structures, VII.

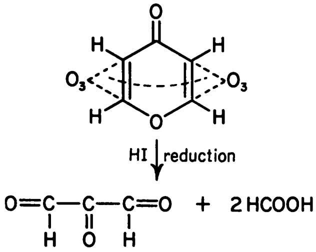


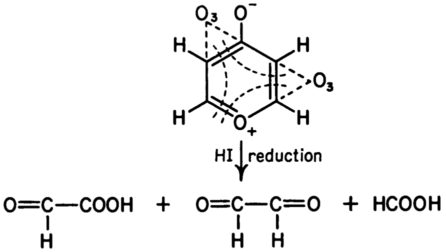
VII

Herzberg and Wibaut (*6, 14*) have studied the ozonization and the ozonolysis of γ-pyrone and its methyl homologs. Although exact measurements of the reaction velocities were not possible, it was found that the γ-pyrones react with ozone at a faster rate than benzene or toluene. On the other hand, the velocity of the ozonization of γ-pyrones is much smaller than would be expected for a compound containing two isolated double bonds.

At a temperature of —20° C. and in chloroform solution, the γ-pyrones take up 2 molecules of ozone. This means that only the C=C bonds react with ozone, which was also found when ozone reacted with other heterocyclic rings, such as pyridine, pyrrole, and furan. The ozonides were decomposed by reduction with hydriodic acid, whereby carbonyl compounds are formed, as well as acetic acid and in some cases formic acid. By reacting the carbonyl compounds with *p*-nitrophenylhydrazine, the corresponding nitrophenylhydrazones or *p*-nitrophenylosazones are formed. The separation of the mixture of hydrazones and osazones is carried out by a chromatographic method. The quantitative determination of the separated nitrophenylosazones (or hydrazones) is carried out by means of spectrographic measurements.

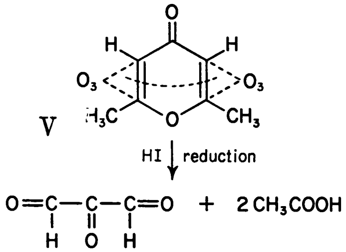
The ozonolysis of γ-pyrone yields mesoxal dialdehyde (0.03 mole), glyoxylic acid (0.12 mole), glyoxal (0.12 mole), and formic acid (3.1 moles).

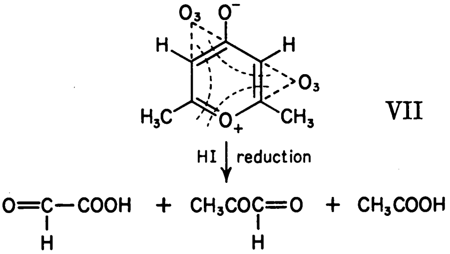




The formation of mesoxal dialdehyde is characteristic of the classical structure; the formation of glyoxylic acid can be most readily explained from a polar structure. Formic acid can be formed from the two structures. The total yield of fission products corresponds to about 73% of the original γ-pyrone.

In the ozonolysis of 2,6-dimethyl-γ-pyrone the following scission products are to be expected:

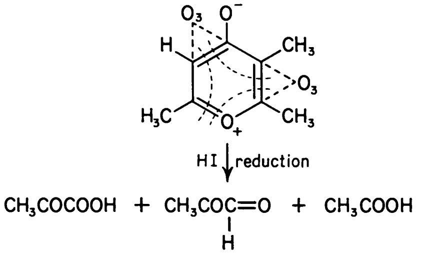


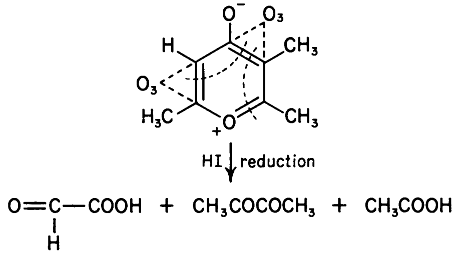


The following have been isolated and determined quantitatively in the form of the *p*-nitrophenylosazones: mesoxal dialdehyde (0.03 mole), glyoxylic acid (0.2 mole), and methylglyoxal (0.16 mole). These figures represent minimum values. Acetic acid (1.5 moles) and formic acid (1.1 moles) have also been found. The total yield of scission products corresponds to about 73% of the original 2,6-dimethyl-γ-pyrone. Mesoxal dialdehyde can be formed from structure V; methylglyoxal is characteristic of structure VII, and acetic acid can be formed from the two structures. The formation of glyoxylic acid can be most readily explained from structure VII. However, the formation from structure V via an abnormal ozonide rearrangement must not be precluded. Also, the formic acid may be formed via an abnormal ozonide rearrangement from structure V. It follows from these experiments that 2,6-dimethyl-γ-pyrone reacts with ozone according to different limiting structures.

In the ozonolysis of the hydrochloride of 2,6-dimethyl-γ-pyrone, a greater amount of methylglyoxal—i.e., 0.22 mole—is found than in the ozonolysis of dimethylpyrone itself.

In the ozonolysis of 3-methyl-γ-pyrone and of tetramethyl-γ-pyrone, scission products are formed which are characteristic for polar structures. In the ozonolysis of 2,3,6-dimethyl-γ-pyrone particularly interesting results were obtained. The following characteristic scission products have been isolated: pyruvic acid (0.11 mole), dimethylglyoxal (0.07 mole), methylglyoxal (0.08 mole), glyoxylic acid (0.11 mole), and acetic acid (1.85 moles). This means that the trimethyl-γ-pyrone reacts according to mesomeric polar structures.

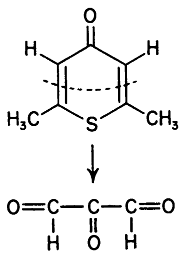


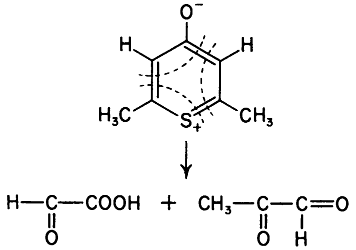


Besides these scission products formic acid (0.6 mole) is found. This may be formed via an abnormal ozonide rearrangement from the nonpolar structure. The total yield of fission products is about 65% of the original trimethylpyrone.

Ozonization of Thio-γ-pyrones (*6*). Thio-γ-pyrone and 2,6-dimethylthio-γ-pyrone react with ozone at a slower rate than the corresponding γ-pyrones. The thio-γ-pyrones take up 3 molecules of ozone. Not only do the C=C bonds react with ozone, but oxidation of the sulfur atom also occurs. When the reaction product of the ozonization is treated with dilute alkali and hydrogen peroxide, the solution contains alkali sulfate in an amount corresponding to the sulfur content of the thiopyrone.

The ozonolysis of 2,6-dimethylthio-γ-pyrone yields mesoxal dialdehyde (0.12 mole), glyoxylic acid (0.04 mole), methylglyoxal (0.02 mole), acetic acid (0.53 mole), and formic acid (0.82 mole). These scission products have been formed from mesomeric structures:





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Ozonolysis of 4,22-Stigmastadien-3-one

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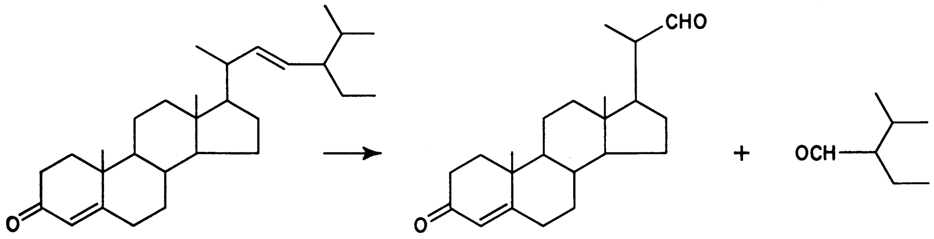
The ozonolysis reaction was used to prepare the steroidal aldehyde, 3-ketobisnor-4-cholen-22-al from 4,22-stigmastadien-3-one. Methylene chloride was used as the solvent. When aldehydes are prepared by ozonolysis, exactly the right amount of ozone must be added. An infrared method makes it possible to follow quantitatively the rate of disappearance of double bonds and locate the end point exactly.

The ozonolysis reaction has been used widely as an analytical tool for determination of the structure of olefins. An excess of ozone is usually added and the structure is deduced from whatever products can be isolated. In this structure work there is a rather broad choice of solvents.

Ozonolysis has become more useful of late as a synthetic method. The authors wished to use the ozonolysis reaction for the preparation of the steroidal aldehyde, 3-ketobisnor-4-cholen-22-al (II), from 4,22-stigmastadien-3-one (I).



I II III

Here the objective was to cleave the side-chain double bond selectively and, at the same time, to keep the nuclear double bond intact. This is a reasonable objective, as the side-chain double bond has a much higher electron density than the nuclear double bond which is conjugated with the electron-withdrawing carbonyl group and, hence, the isolated bond should react much more rapidly with the electrophilic ozone.

In using the ozonolysis reaction as a preparative method for aldehydes, certain limiting considerations are immediately encountered. There is a more limited choice of solvents, and an excess of ozone should be avoided. Ethyl acetate has frequently been used as a solvent for ozonolysis reactions. It readily dissolves a variety of compounds, but in the preparation of aldehydes it is not a generally satisfactory solvent, as large amounts of acids are formed [possibly because of the presence of some ethanol

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(*1*)]. Formic and acetic acids have proved particularly good for the preparation of some aldehydes, but the solubility of stigmastadienone in these solvents is low. Certain halogenated hydrocarbon solvents, which dissolved more stigmastadienone, have been investigated. When ozone was passed into chloroform (stabilized with ethanol) at −60° C., some of the ozone reacted, presumably with the ethanol, to form acidic materials. When the experiment was repeated on methylene chloride at −78°, a saturated solution of ozone in methylene chloride was formed, deep blue in color, from which nearly all of the ozone could be recovered by sparging with nitrogen. This solvent was therefore chosen for the ozonolysis of stigmastadienone.

When aldehydes are prepared by ozonolysis, exactly the correct amount of ozone must be added, because excess ozone converts aldehydes to acids and peracids. In addition, alcohols, ethers, double bonds, or other functional groups present in the molecule may be attacked. This brings up the problem of determining when to stop the ozonolysis reaction. The theoretical amount of ozone may be added, but several cases are recorded in which more than one molar equivalent of ozone is required to cleave one double bond. One may stop when ozone appears in the effluent gas from the reactor. However, preliminary experiments have shown that at this low temperature ozone begins to overflow very soon after the reaction has started. A more useful method has been to stop the ozonolysis when the reaction mixture no longer shows unsaturation. This may be detected qualitatively by the use of bromine in carbon tetrachloride, tetranitromethane, etc. An infrared method makes it possible to follow quantitatively the rate of disappearance of trans double bonds and to locate the end point more exactly. The method was applied to the ozonolysis of stigmastadienone with good results.

The ozonolysis was performed in methylene chloride, and aliquots of the reaction mixture were removed at timed intervals and assayed by the infrared method for the amounts of each double bond remaining. Portions of some of the spectra which were obtained are shown in Figure 1. The absorption of the side-chain double bond appears at 10.26 microns, of the nuclear double bond at 6.2 microns, and of the aldehydes (*2*) formed by the ozonolysis of the side-chain double bond at 5.86 microns. By using the base-line technique of Heigl, Bell, and White (*4*), it was possible to calculate the amount of side-chain double bond present in each sample. The amounts of nuclear double bond and of aldehyde present were also calculated. These results are recorded graphically in Figure 2.

These data now indicate exactly when to stop the ozonolysis reaction so as to have maximum selectivity: at the point in the x axis where the two double-bond disappearance curves are the farthest apart—i.e., 1.1 ± 0.5 molar equivalents of ozone. The yield of aldehyde should be 70 to 85% and should correspond to the separation of the two curves on the y axis.

The aldehyde formation curve gave evidence that the cleavage of one mole of side-chain double bond yielded one mole of aldehyde, the other end of the double bond being converted to something else. This was in agreement with the results observed by Criegee (*1*).

The ozonolysis was therefore repeated under a variety of conditions and new curves were constructed for each. The results were best at low temperature (−78° C. was better than −53° C.), at a high olefin concentration (as high as the solubility limitations would permit), in nonpolar solvents, and with a small amount of pyridine present in the solvent. The dramatic effect of the inclusion of approximately 1% pyridine is shown in Figure 3. The selectivity was greatly improved, the nuclear double bond remaining intact until the side-chain double bond had almost completely reacted. The aldehyde formation curve indicates that approximately two molecules of aldehyde were formed from the cleavage of each double bond. These curves represent optimal conditions and were selected from runs at various pyridine concentrations.

Figure 3 indicates that maximum selectivity in the pyridine–methylene chloride system should be obtained by using 1.6 to 1.7 molar equivalents of ozone. The experi-

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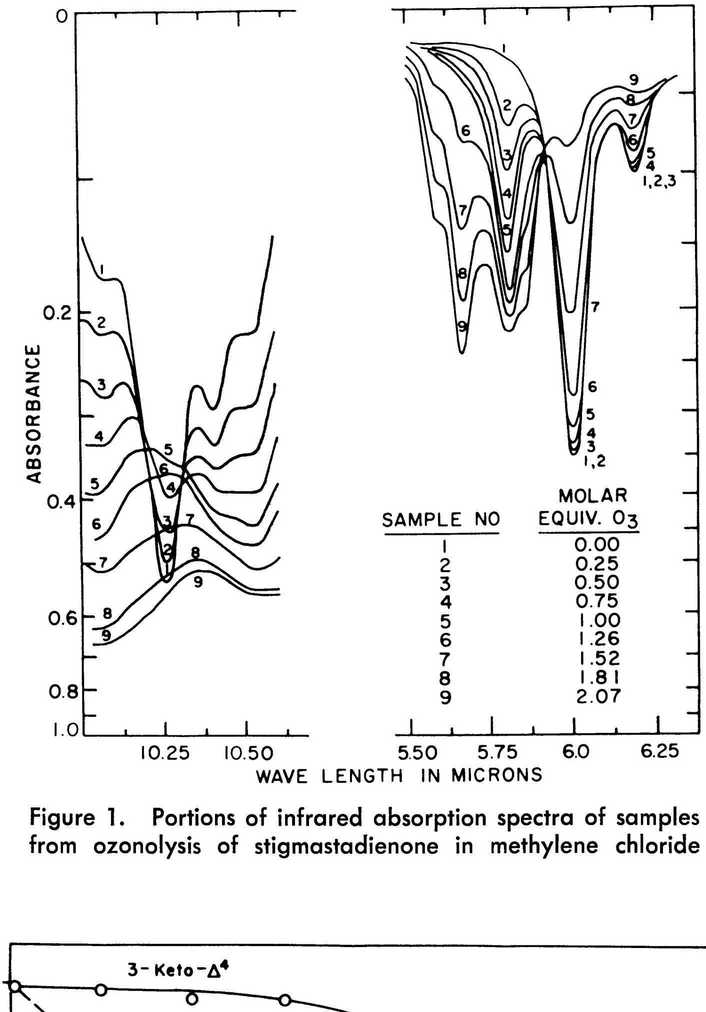

SAMPLE NO	MOLAR EQUIV. O_3
1	0.00
2	0.25
3	0.50
4	0.75
5	1.00
6	1.26
7	1.52
8	1.81
9	2.07

Figure 1. Portions of infrared absorption spectra of samples from ozonolysis of stigmastadienone in methylene chloride

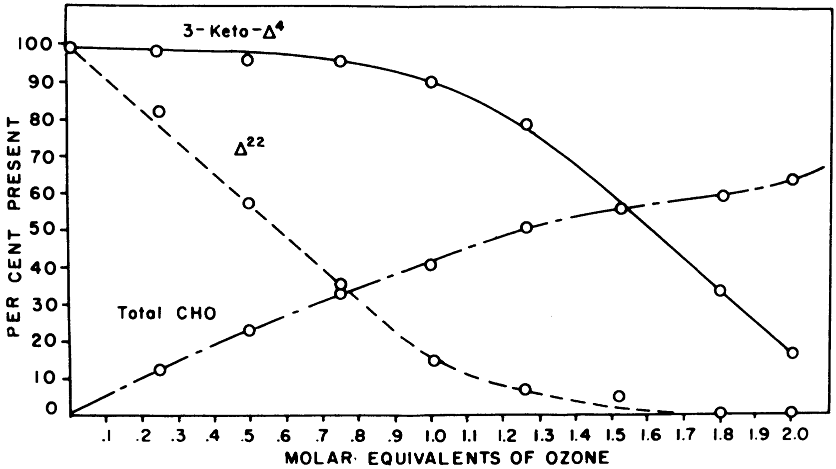

Figure 2. Ozonolysis of stigmastadienone in methylene chloride

Rate of reaction at Δ^{22} and Δ^4 and rate of appearance of aldehyde products

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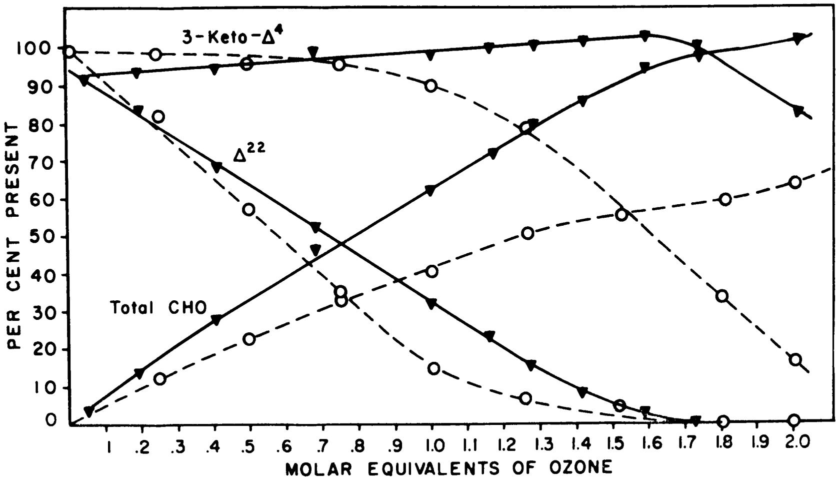


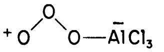
Figure 3. Ozonolysis of stigmastadienone in methylene chloride

ments were repeated using this amount of ozone, the mixture was subjected to zinc decomposition, and the steroidal aldehyde was isolated by crystallization. The yields were in good agreement with the prediction (Table I).

Table I. Yields of Bisnoraldehyde from Ozonolysis of Stigmastadienone

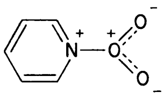
Solvent	Molar Equiv. Ozone	Yield Predicted	Found
$MeCl_2$	1.07	70–85	82
$MeCl_2$ + 0.94% pyridine	1.66	95	94

It was of interest to consider the role of the pyridine in this ozonolysis reaction. Sixma, Boer, and Wibaut (*6*) have shown that the electrophilic reactivity of ozone can be catalyzed by acids of the Lewis type. This may be due to the formation of a salt like intermediate IV, which would be expected to show enhanced electrophilic reactivity.

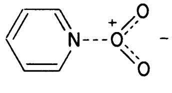

$^{+}O{-}O{-}O{-}\bar{Al}Cl_3$

IV

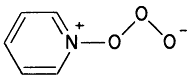
ity. Nucleophilic agents, such as pyridine and pyridine oxide, on the other hand, would be expected to form compounds, or at least complexes (in these nonpolar solvents) such as V, VI, and VII.


V

or


VI

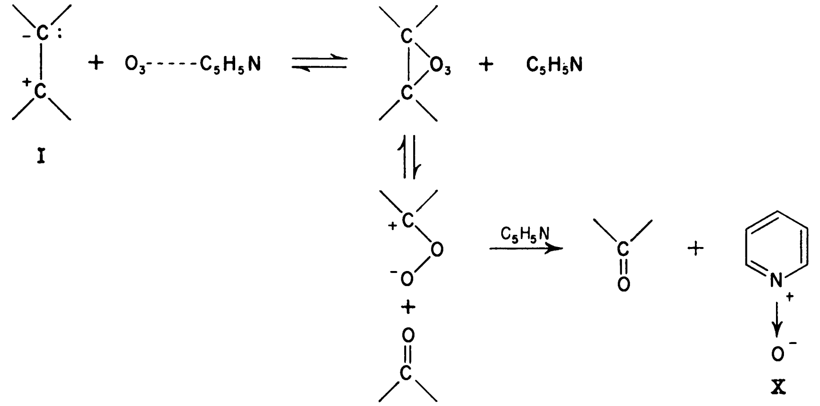
or


VII

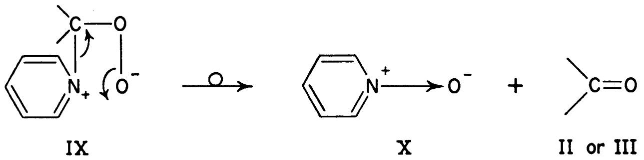
These, in turn, would be expected to show diminished electrophilic reactivity and possibly, in some cases, nucleophilic reactivity (*5*). This may explain the loss of aldehyde which was observed when a large amount of pyridine was present during the ozonolysis reaction.

Whether it is a pyridine-ozone complex which is reacting with the double bonds in a more selective manner or whether the selectivity arises because of the diminishing of the instantaneous ozone concentration by formation of the pyridine or pyridine oxide complex is not certain.

The appearance of the second molecule of aldehyde is attributed to a mode of stabilization of the zwitterion (*1*) intermediate by reaction with the pyridine to form pyridine oxide and a second molecule of aldehyde:



This may occur by addition of the pyridine to the zwitterion (VIII) (which it probably solvates), followed by rearrangement:



Pyridine oxide was shown to bind large quantities of ozone, from which all of the pyridine oxide could be recovered by addition of methanol. This apparently accounts for the additional ozone required for the ozonolysis when pyridine is present. Unfortunately, pyridine oxide could not be demonstrated in the reaction mixture. It was shown, however, in a separate experiment that pyridine oxide reacted readily with bisnoraldehyde at room temperature. The isolation was not attempted at —78°C.

The ozonolysis mixtures still required reductive treatment to obtain high yields of aldehyde. The reduction was apparently necessary to destroy the pyridine oxide-ozone intermediates which were postulated above. It was possible, however, to eliminate the reduction step if the more reactive formaldehyde was added to destroy the reactive intermediates. The results obtained by treatment of several aliquots of an ozonolysis reaction mixture are shown in Table II.

Table II. Decomposition Methods as Applied to Ozonolysis Reaction Mixtures

Treatment	Yield	$[\alpha]_D$ of Product[a]
Formaldehyde	91.8	+81.4
Zinc reduction	93.0	+84.3
No reduction	77.2	+80.1
Dimethylsulfoxide	82.2	+80.5
Trioxymethylene	75.9	+80.8

[a] $[\alpha]_D$ of pure 3-ketobisnor-4-22-al is +85° ($CHCl_3$).

Formaldehyde was distinctly better than the other methods of treatment, but not comparable to zinc reduction. The following reducing agents were also tried: aqueous sodium bisulfite, aqueous ferrous sulfate, sulfur dioxide, aqueous sodium thiosulfate, catalytic hydrogenation [pyridine oxide is difficult to hydrogenate (*3*)], calcium hydride and acetic acid, and stannous chloride and acetic acid. Only stannous chloride–acetic acid was effective. It gave material of very good quality, but the yield was slightly less (84 to 85%) than by the usual zinc decomposition method.

Acknowledgment

The authors are indebted to A. E. Fonken and M. Grostic for the measurement and both qualitative and quantitative interpretation of infrared spectra, to William A. Struck and his associates for analytical data, and to Melvin Newman and Donald Cram for valuable suggestions during the course of the work.

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Oxidative Degradation of Polymers in Presence of Ozone

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The action of ozone-oxygen mixtures (2% ozone) on polyethylene in the temperature range from 25° to 109° C. and on polystyrene in the range from 55° to 154° C. has been studied. The products and the rates of the reaction were followed by the changes in the infrared spectra of the polymers during ozonization. The main products appear to be aldehydes and ketones in the case of polyethylene, while an ozonide or peroxidic complex, stable at intermediate temperatures, forms during polystyrene ozonization. The activation energy is of the order of 9 kcal. for polyethylene; for polystyrene it is considerably less. Rates of ozonization and oxidation of deuterated polystyrenes indicate that tertiary carbons are the seat of oxidation reaction.

The action of ozone as a vigorous oxidizing agent of elastomers and other polymers is well known (*1*). This report presents the results of a study in which the action of ozone on such polymers as polyethylene and polystyrene was examined. Infrared spectra were used as a tool for product analysis and rate measurements. Polyethylene showed a much higher tendency to ozone oxidation than polystyrene. The temperature range studied varied from 25° to 109° C., and the oxidation was measured in terms of minutes. In the case of polystyrene the temperature range from 55° to 154° C. produced equivalent results but only when the ozonization was measured in terms of hours. Styrene polymers with deuterium atoms substituting hydrogens on the chains were synthesized, and their ozonization rates were studied in an attempt to elucidate the mechanism of ozone attack on the polymer.

Experimental

Apparatus. A Welsbach ozonator, Model T-25, produced an oxidizing mixture of ozone (2%) and oxygen (98%). The rate of flow was kept constant at 0.025 cubic foot per minute. The polymer films, effective thickness 0.002 to 0.006 inch, were used free or directly on the rock salt plates on which they were cast. The reaction vessel containing the films was kept in a constant temperature bath. The ozone mixture was preheated to approximately the temperature of the bath by passing through a spiral tube immersed in the same bath prior to entering the reaction vessel.

Polyethylene. The polyethylene was Alathon No. 1, with a molecular weight between 18,000 and 19,000 (Du Pont). It was dissolved in hot carbon tetrachloride, and

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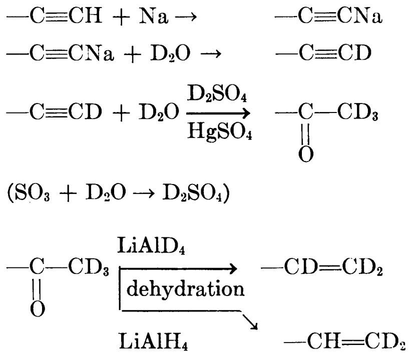
the films were cast either on rock salt plates which were used directly or on the surface of mercury. The films were dried overnight in a vacuum oven at 50° C.

Polystyrenes. α-Deuteriostyrene was prepared by reduction of acetophenone with lithium aluminum deuteride and dehydration of the ensuing alcohol. β-Deuteriostyrene was prepared by the hydrolysis with deuterium oxide of the Grignard of β-bromostyrene (*4*). β, β-Dideuteriostyrene and α, β, β-trideuteriostyrene were synthesized by the following scheme:



$$—C\equiv CH + Na \rightarrow \quad —C\equiv CNa$$

$$—C\equiv CNa + D_2O \rightarrow \quad —C\equiv CD$$

$$—C\equiv CD + D_2O \xrightarrow[HgSO_4]{D_2SO_4} —\underset{\underset{O}{\|}}{C}—CD_3$$

$$(SO_3 + D_2O \rightarrow D_2SO_4)$$

$$—\underset{\underset{O}{\|}}{C}—CD_3 \xrightarrow[\text{dehydration}]{LiAlD_4} —CD{=}CD_2$$

$$—\underset{\underset{O}{\|}}{C}—CD_3 \xrightarrow[LiAlH_4]{\text{dehydration}} —CH{=}CD_2$$

The following method was used to prepare α, β-dideuteriostyrene

$$(PBr_3 + 3D_2O \rightarrow 3DBr + D_3PO_3)$$

$$—C\equiv CD + DBr \xrightarrow[\text{peroxide} + O_2]{\text{Dibenzoyl}} —CD{=}CDBr$$

The Grignard of β-bromodeuteriostyrene was then prepared and yielded α, β-dideuteriostyrene upon hydrolysis.

The monomers as well as undeuterated styrene were polymerized in sealed glass tubes, in the absence of catalysts, in a constant temperature bath at 80° C. The mean molecular weight of the obtained polymers was in the range of 1,000,000 except for the β-deuterio- and the α, β-dideuteriopolystyrenes. In this case the molecular weight was much lower even after a polymerization time of several weeks. The reason for this inhibition lies perhaps in the presence of impurities in the samples from the Grignard or the bromide. The polymers were reprecipitated from methanol and dried overnight in a vacuum oven at 60° C.

The structure of the polymers was verified by infrared spectra and by spectrographic means (*3*). This method, using water samples collected upon combustion of each polymer in a pure oxygen atmosphere, involves essentially the excitation of hydrogen and deuterium atoms by a microwave exciter. The alpha lines in the Balmer region are resolved and measured by spectrograph, and their intensities are compared with those of standard samples so that the per cent content of deuterium may be determined.

Results and Discussion

Polyethylene. The action of ozone on polyethylene was studied in the temperature range from 25° to 109° C. The reaction was followed qualitatively and quantitatively by infrared spectra. The products appeared to be of the same nature as those of O_2 oxidations of polyethylene (*2*)—i.e., the formation of aldehydic and ketonic groups as indicated by the appearance of a strong absorption band in the region of 5.9 microns, and the existence of hydroxyl groups as shown by the 2.9-micron band. Polyethylene is readily oxidized in the presence of ozone, as even short period ozonizations carried out at temperatures as low as 25° C. yielded considerable concentrations of carbonyl and hydroxyl groups. Pure O_2 oxidations did not yield comparable results until the reaction temperature was raised approximately

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100° higher, thus manifesting the vigorous accelerating effect of ozone as an oxidizing agent.

Kinetically the reaction was followed by the rate of increase of the carbonyl band at 5.9 microns. This was accomplished by applying the Beer's and Lambert's law relationship.

$$\mathrm{Log}\ (I/I_0) = -edC$$

It was assumed that I/I_0, the per cent transmittance, may be used in the kinetic equations instead of C, the concentration of carbonyl, because the film thickness, d, and the extinction coefficient, e, remain constant. Plots of log (I/I_0) *vs.* time of ozonization showed that the reaction had a very high initial rate of oxidation which gradually decreased with time (Figure 1). It was indicated that the reaction takes place mainly on the surface of the polymer, while in the later states when most of the active sites on the surface have been destroyed, diffusion of oxidizing gas into the polymer becomes the rate-controlling process. This chemisorption theory was verified further by calculating the activation energy of the process, which was 9.2 kcal. (Figure 2).

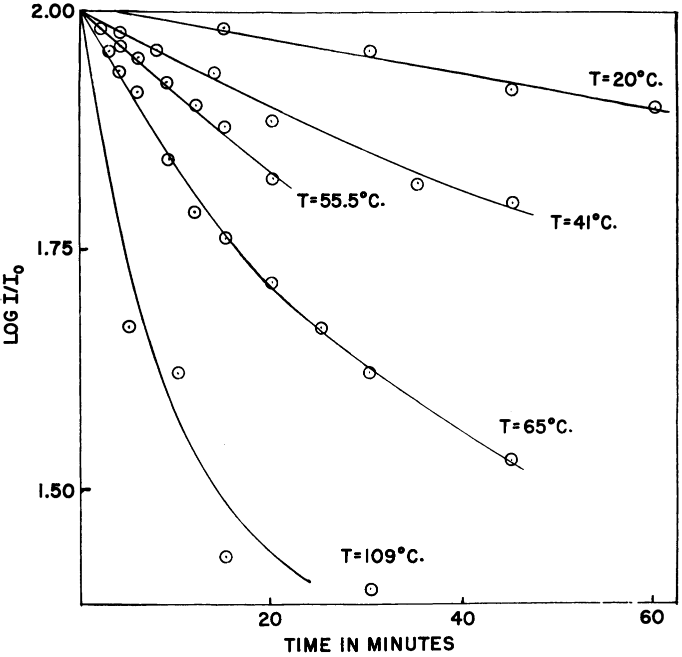
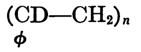


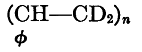
Figure 1. Ozonization of polyethylene

Rate of increase of $>$C=O band (5.85 microns)

Ozonization of Polystyrenes. The action of ozone on the polymers

A. $(\mathrm{CH}\text{—}\mathrm{CH_2})_n$

B.

$(\underset{\phi}{\mathrm{CD}}\text{—}\mathrm{CH_2})_n$

C.

$(\underset{\phi}{\mathrm{CH}}\text{—}\mathrm{CD_2})_n$

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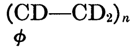
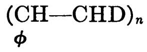
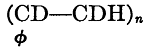

$(\underset{\phi}{\mathrm{CD}}\text{—}\mathrm{CD_2})_n$

E.

$(\underset{\phi}{\mathrm{CH}}\text{—}\mathrm{CHD})_n$

F.

$(\underset{\phi}{\mathrm{CD}}\text{—}\mathrm{CDH})_n$

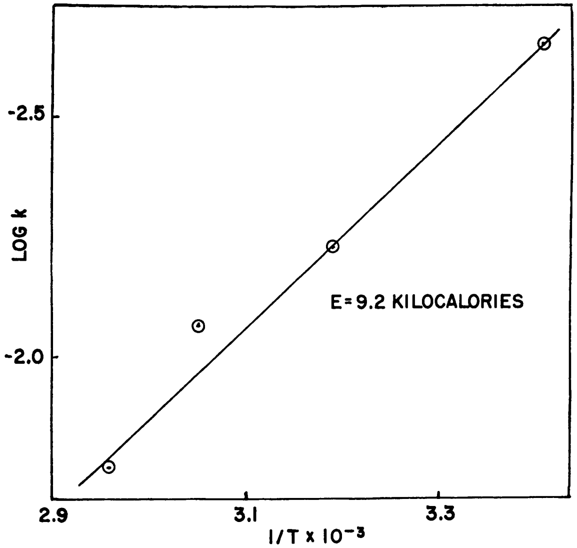


Figure 2. Activation energy of ozonization of polyethylene

was studied in the temperature range from 65° to 154° C. The changes in the spectra of ozonized polystyrenes were identical for all polymers studied, deuterated and undeuterated. This seems to indicate that the reaction proceeds through the same mechanism in all compounds.

It was seen from the infrared spectra that polystyrene is not as susceptible to ozonization as some other polymers—i.e., polyethylene is ozonized readily even at room temperature. The following conclusions can be drawn from a study of the temperature range from 65° to 155° C. The first change in the spectra of polystyrenes during ozonization is the appearance of a weak band at approximately 5.7 microns. Its main characteristic is that it appears immediately at the start of the reaction, its rate of increase continuously decreasing and quickly diminishing to a point where no further increase of absorption is observed at 5.7 microns. At temperatures below approximately 140° C. (the melting point of polystyrenes) the intensity of this band remains constant, regardless of temperature, over long periods of ozonization. At temperatures above 140° C. (approximately), it again remains constant but for short periods, depending on the reactivity of the polymer—i.e., long period for $(\underset{\text{ø}}{\mathrm{C}}\mathrm{D}\text{—}\mathrm{CH}_2)$ while $(\underset{\text{ø}}{\mathrm{C}}\mathrm{H}\text{—}\mathrm{CDH})$ is very reactive, and after this steady-state period a rapid oxidation takes place as evidenced by the rapid increase of the 5.9-micron carbonyl band. These observations indicate that the 5.7-micron band is due mainly to an intermediate forming on the surface layers between the polymer substrate and the ozone. Its structure probably involves a complex of peroxidic or ozonide structure. This intermediate is stable to further oxidation or other reactions at low temperatures, while at higher temperatures it decomposes rather readily under the influence of oxygen, ozone, and high temperature to yield carbonyl compounds and other secondary products.

The results of the study on the rates of ozonization of deuterated polystyrenes, as measured by the rate of increase of the 5.7-micron absorption band in the infrared spectra, are outlined in Figures 3 to 7.

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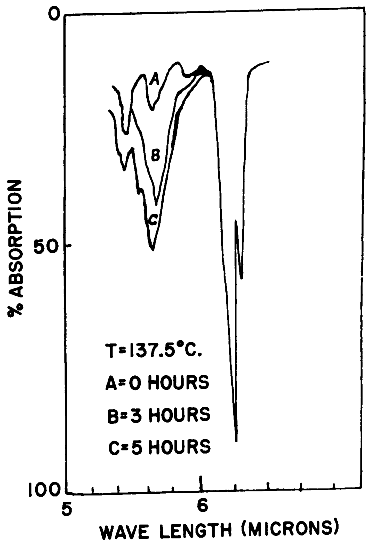

Figure 3. Spectra of oxidized $(\underset{\phi}{CD}-CH_2)_n$ in 2% ozone

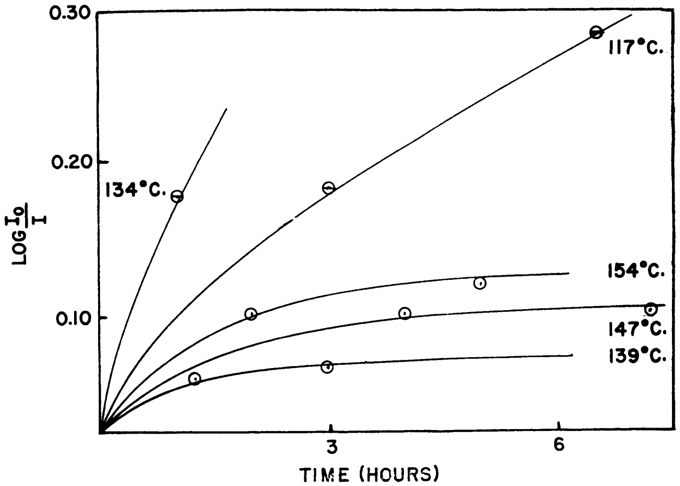

Figure 4. Rate of increase of 5.7-micron band in ozonization of polystyrene

⊙ $(\underset{\phi}{CD}-CD_2)_n$

⊖ $(\underset{\phi}{CH}CHD)_n$

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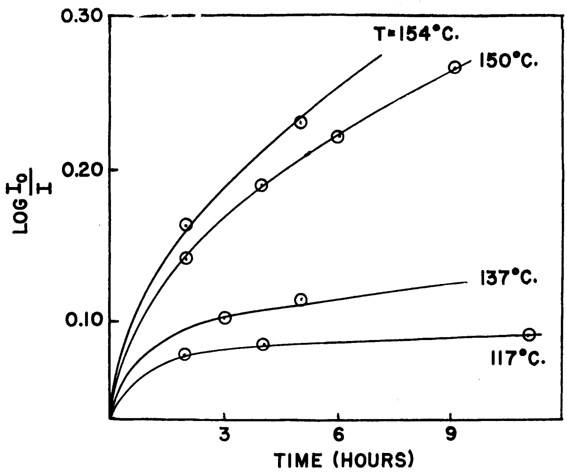

Figure 5. Rate of increase of 5.7-micron band in ozonization of $(\underset{\phi}{\mathrm{CH}}\text{–}\mathrm{CD_2})_n$

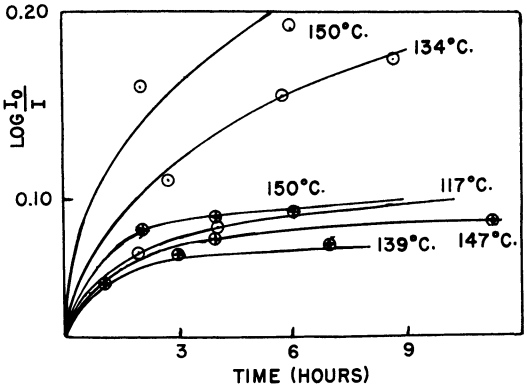

Figure 6. Rate of increase of 5.7-micron band in ozonization of polystyrenes

In ozonizations where the temperature of the reaction was above 140–5° C. (perhaps the melting point of the polymer) further oxidation was indicated by the appearance of various carbonyl bands in the range of the spectrum from 5.7 to 5.95 microns. This complicates the kinetics of the reaction and changes the order of the rates, as was observed in the rate curves.

The formation of the 5.7-micron complex appears to possess a very low activation energy, on the order of approximately 5 kcal. This probably indicates a surface reaction which is limited by the rate of diffusion of the oxidizing gases into the interior of the polymer film.

These observations apply for all the polymers studied, deuterated and undeuterated. On comparing the rates of the six different compounds, however, it is observed that they vary from polymer to polymer, depending on the reactivity of

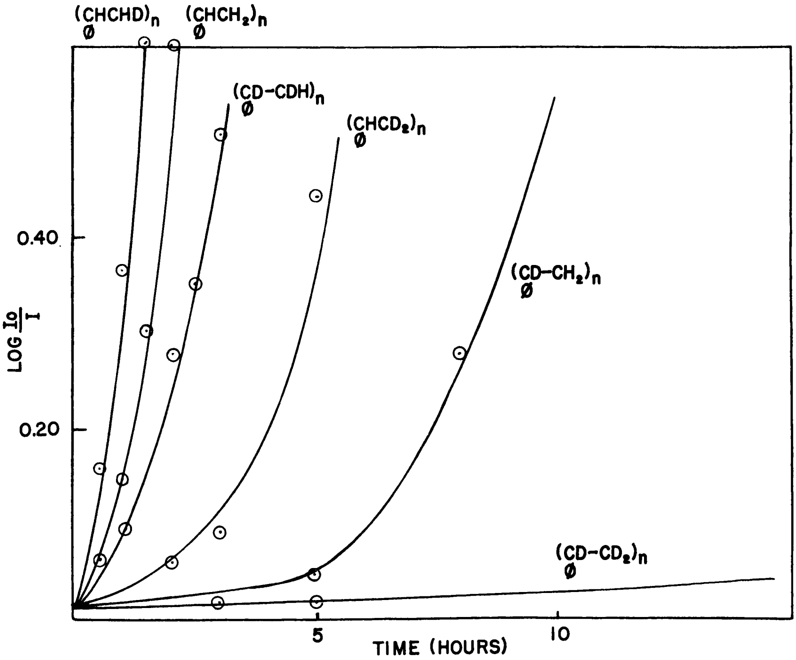

Figure 7. Rates of oxidation of deuterated polystyrenes

I. 230° C.
⊕ $(\underset{\phi}{\mathrm{CD}}-\mathrm{CH_2})_n$
⊙ $(\underset{\phi}{\mathrm{CD}}-\mathrm{CDH})_n$

the compound as defined by the substitution of deuterium atoms for hydrogen at specific points in the polymer chain. This reactivity appears to be of the same order as was observed in the O_2 oxidation rates (*3*)—i.e., the trisubstituted deuteriopolystyrene possesses the highest resistance to oxidation or ozonization, while the β-deuterio and undeuterated polystyrenes show the highest tendency to be oxidized. The order of reactivity of the six polymers toward ozonization decreased in the following order:

A. $(\underset{\phi}{\mathrm{CH}}-\mathrm{CHD})_n$ B. $(\underset{\phi}{\mathrm{CH}}-\mathrm{CH_2})_n$ C. $(\underset{\phi}{\mathrm{CH}}-\mathrm{CD_2})_n$

D. $(\underset{\phi}{\mathrm{CD}}-\mathrm{CDH})_n$ E. $(\underset{\phi}{\mathrm{CD}}-\mathrm{CH_2})_n$ F. $(\underset{\phi}{\mathrm{CD}}-\mathrm{CD_2})_n$

This indicates that the tertiary carbon, alpha to the benzene ring, is directly involved in the formation of the complex intermediate and is perhaps the seat of ozone attack.

Figure 7 shows for comparison purposes the relative rates of oxidation of deuterated polystyrenes in an oxygen atmosphere. The rates of ozonization of the polymers varied in the same order.

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Influence of Molecular Structure and Substituents on Antiozonant Properties of Aryl Diamine Compounds

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The influence of molecular structures and substituents on the antiozonant properties of a series of related aromatic diamine compounds was studied. The relative effectiveness of the compounds was determined by viscometric techniques and by comparison of the rate of degradation of protected vulcanizates. Results indicate that unsymmetrical *p*-phenylenediamine derivatives are less effective than analogous symmetrical compounds as antiozonants. The protective capacity of the antiozonants decreases as the size or number of the *N*-hydrogen substituents, or the distance between the amine groups, increases. The comparative stability of the free radicals of aryl diamines, in terms of the theory of resonance, is utilized to explain the relative inhibiting properties of the chemicals examined.

Degradation of elastomers during weathering is now generally accepted as due largely to the powerful oxidizing properties of atmospheric ozone. During the fabrication of rubber and synthetic rubber items, manufacturers have attempted to improve the resistance of their products to ozone deterioration by utilizing chemical additives, known as antiozonants. Although the addition of such chemicals as aromatic amines has extended considerably the service life of rubber vulcanizates, they are still subject to comparatively early surface cracking. For this reason, a fundamental study was made of the various chemical additives used currently to determine whether molecular structure and substituent groups influence their antiozonant properties.

A simple, rapid, and reliable viscometric technique for evaluating the protective capacity of commercially available materials as inhibitors of ozone-induced polymer chain scission has been described (*1*). This work included the results of an evaluation of several chemicals such as *N,N'*-di-*sec*-butyl-*p*-phenylenediamine, nickel dibutyl dithiocarbamate, 1-(*m*-aminophenyl)-2,5-dimethylpyrrole, and 2,6-di-*tert*-butyl-4-methylphenol as antiozonants; *N,N'*-di-*sec*-butyl-*p*-phenylenediamine exhibited superior inhibiting characteristics. However, because of the potential toxic effects and relatively high vapor pressure of this chemical, its use is considered impractical.

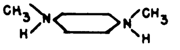
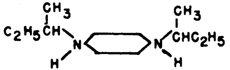
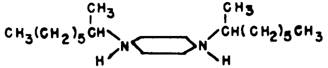
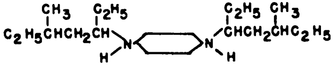
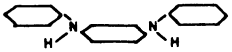
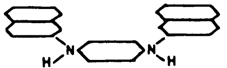
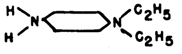
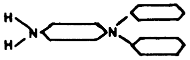
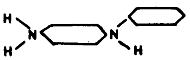
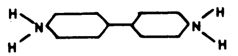
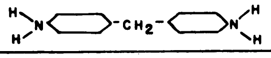
A method was reported (*2*) for modifying the molecular structure of *N,N'*-di-*sec*-butyl-*p*-phenylenediamine to make it more suitable for use as a retarder of the effects of ozone on elastomers. Several workers (*7, 11, 12*) developed additional *p*-phenylenediamine derivatives for this purpose. A number of the chemicals—e.g., *N,N'*-diphenyl-*p*-phenylenediamine, *N,N'*-di-2-naphthyl-*p*-phenylenediamine, and isomers of *N,N'*-dioctyl-*p*-phenylenediamine—are now available commercially for use by rubber compounders.

This paper presents the results of an investigation of some of the above materials and other structurally related aryl diamine chemicals. Data are also presented on the comparative inhibiting properties of three representative protectant chemicals used as additives in typical SBR vulcanizates.

Experimental

Test Compounds. The aromatic diamine chemicals were obtained from various commercial sources and used without further modification. A list of these materials is presented in Table I.

Table I. Aryl Diamine Additives

P-PHENYLENEDIAMINE	
N,N'-DIMETHYL-P-PHENYLENEDIAMINE	
N,N'-DIETHYL-P-PHENYLENEDIAMINE	
N,N'-DI-SEC-BUTYL-P-PHENYLENEDIAMINE	
N,N'-DI-SEC-N-OCTYL-P-PHENYLENEDIAMINE	
N,N'-DI-3(5-METHYL HEPTYL)-P-PHENYLENEDIAMINE	
N,N'-DIPHENYL-P-PHENYLENEDIAMINE	
N,N'-DI-2-NAPHTHYL-P-PHENYLENEDIAMINE	
N,N-DIMETHYL-P-PHENYLENEDIAMINE	
N,N-DIETHYL-P-PHENYLENEDIAMINE	
N,N-DIPHENYL-P-PHENYLENEDIAMINE	
N-PHENYL-P-PHENYLENEDIAMINE	
BENZIDINE	
P,P'-METHYLENEDIANILINE	

Elastomers. The elastomer used in this study was a butadiene-styrene (SBR) rubber.

Viscometry Techniques. *o*-Dichlorobenzene solutions, containing 0.5 gram of purified elastomer per 100 ml. of solution, unprotected and protected by the addition of 8 parts of antiozonant per 100 parts of rubber, were prepared by techniques described previously (*1*).

All polymer solutions were ozonized (*1*) by passing a stream of ozonized oxygen, supplying approximately 1×10^{-3} mole of ozone per hour, flowing at a rate of 0.05 cubic meter per hour through 600 ml. of elastomer solution, at room temperature. Aliquot portions of the ozonized solution were removed at preselected time intervals for measurement with a Cannon-Fenske-Ostwald viscometer, having a calibration constant of 0.01698 centistoke per second at 25° C.

Ozonization of Vulcanizates. Control or unprotected test specimens, containing the ingredients listed in Table II, were prepared on a laboratory rubber mill (*5*). Compounds protected by *N*,*N'*-diphenyl-*p*-phenylenediamine, *N*,*N'*-di-2-naphthyl-*p*-phenylenediamine, and *N*,*N*-dimethyl-*p*-phenylenediamine were made by incorporating 8 parts of antiozonant per 100 parts of rubber in the control compound, prior to curing.

Table II. Unprotected Vulcanizate Formulation

Ingredients	Parts (by Weight)
SBR polymer	400
NBS standard channel black	160
NBS standard zinc oxide	20
NBS standard sulfur	8
NBS standard benzothiazolyl disulfide	7
NBS standard stearic acid	6

All milled specimens were cured for 25 minutes in standard 6 × 6 × 0.075 inch ASTM molds, using a pressure of 4000 pounds per square inch and a platen temperature of approximately 150° C.

Experimental 1 × 6 inch test specimens of the unprotected and protected vulcanizates were elongated 20% and ozonized for 15 minutes at room temperature, using a stream of ozonized oxygen flowing at 0.10 cubic meter per hour and furnishing approximately 1×10^{-3} mole of ozone per hour. The test strips were examined visually during ozonization to determine the time required to obtain initial surface cracking.

After ozonization, the relative protective capacity of the antiozonants was evaluated by comparing surface replicas (*1*) and crack depth measurements (*6*) of the ozonized vulcanizates.

Results

Influence of Molecular Structure. The changes in per cent of initial viscosity index with ozonization time for SBR solutions protected by symmetrical and unsymmetrical aryl diamine compounds are shown in Figures 1 and 2. Figure 3 compares

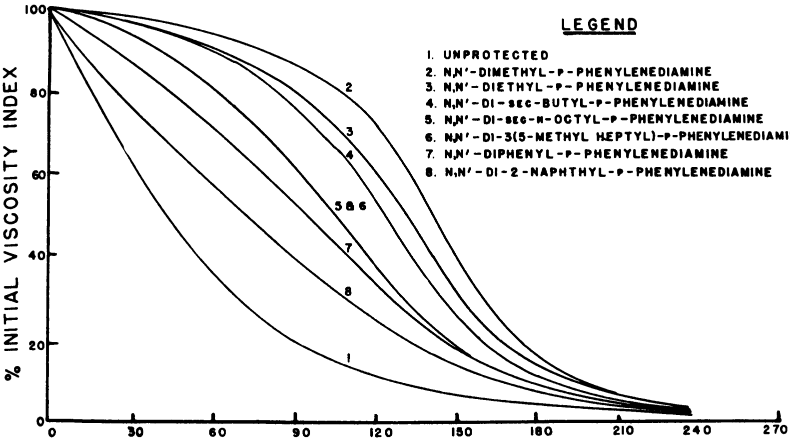


Figure 1. Influence of amine-group substituents of symmetrical aryl diamines

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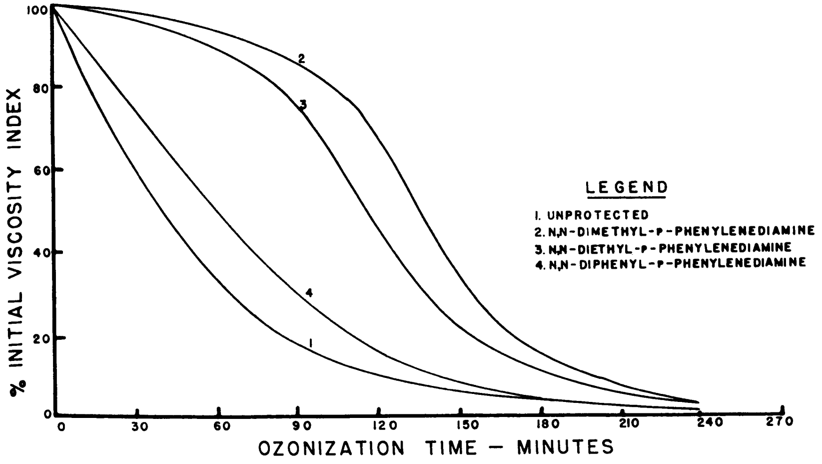

Figure 2. Influence of amine-group substituents of unsymmetrical aryl diamines

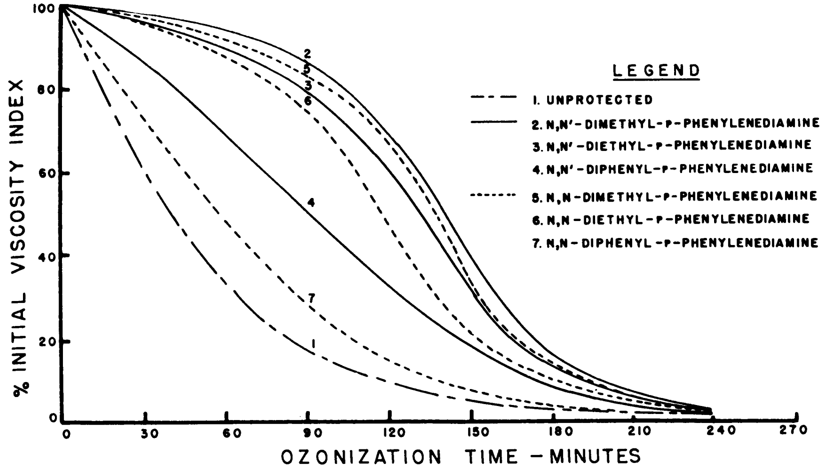

Figure 3. Comparison of symmetrical and unsymmetrical aryl diamines

the relative effectiveness of symmetrical and unsymmetrical methyl, ethyl, and phenyl amine-group substituted *p*-phenylenediamine compounds. The relative efficiency of three of the aryl diamine compounds as inhibitors of ozone degradation of SBR vulcanizates is shown in Table III and Figures 4 and 5.

The following observations were made: In general, symmetrical *p*-phenylenediamine compounds provide greater protection against elastomer attack by ozone than unsymmetrical derivatives with equivalent amine-group substituents. The protective capacity of the symmetrical and unsymmetrical *N*-substituted *p*-phenylenediamine derivatives studied progressively decreases with a corresponding increase in size of amine-group substituent; the protective effect of unsymmetrical compounds generally decreasing more rapidly than that of symmetrical derivatives with amine-group substituents of identical chain-length. In terms of their relative effectiveness as inhibitors of ozone-induced polymer chain scission, the branched and straight-chain alkyl-sub-

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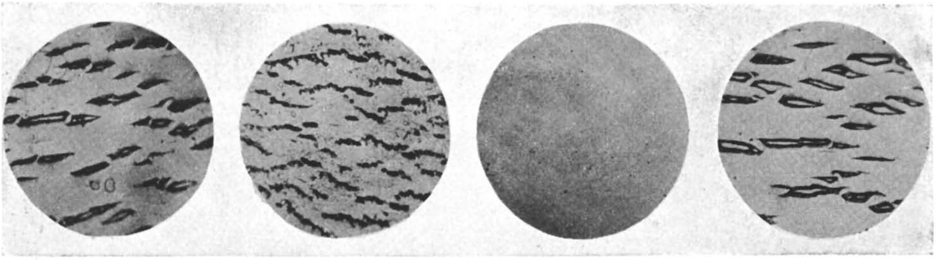
Table III. Initial Cracking of Vulcanizates

Specimen	Exposure Time, Minutes
Control	5
N,*N*′-Di-2-naphthyl-*p*-phenylenediamine	7
N,*N*′-Diphenyl-*p*-phenylenediamine	10
N,*N*-Dimethyl-*p*-phenylenediamine	19



N,N′-di-2-naphthyl-p-phenylenediamine **N,N′-diphenyl-p-phenylenediamine** ***N,N′-dimethyl-p-phenylenediamine*** **Unprotected**

Figure 4. Effect of antiozonants (8 p.h.r.) on surface cracking of SBR vulcanizates (40X)

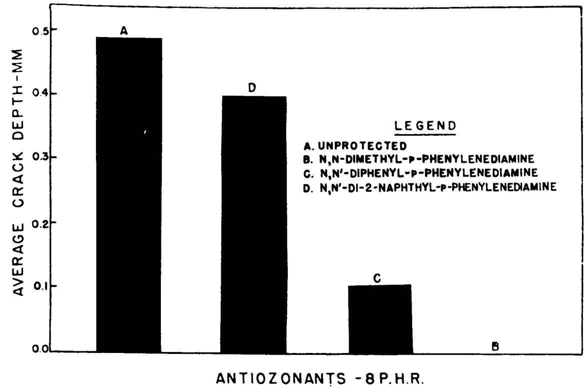


Figure 5. Effect of antiozonants on crack depth of SBR vulcanizates

stituted *p*-phenylenediamine chemicals exhibit definite superiority over similar aryl-substituted compounds. The protective effects shown by the additives in the SBR vulcanizates parallel the antiozonant properties indicated by viscometric measurements.

Influence of Amine-Group Substituents. Figure 6 shows the influence of the number of amine-group substituents on the protective capacity of aromatic diamine chemicals. An increase in the number of *N*-phenyl–group sustituents produces a corresponding decrease in the antiozonant properties of the diamine.

Influence of Ring Substituents. The influence of para ring substituents on the antiozonant characteristics of aromatic diamine chemicals is shown in Figure 7. Data indicate that the protective capacity of the additives decreases as the distance between the amine groups of the aromatic diamines increases.

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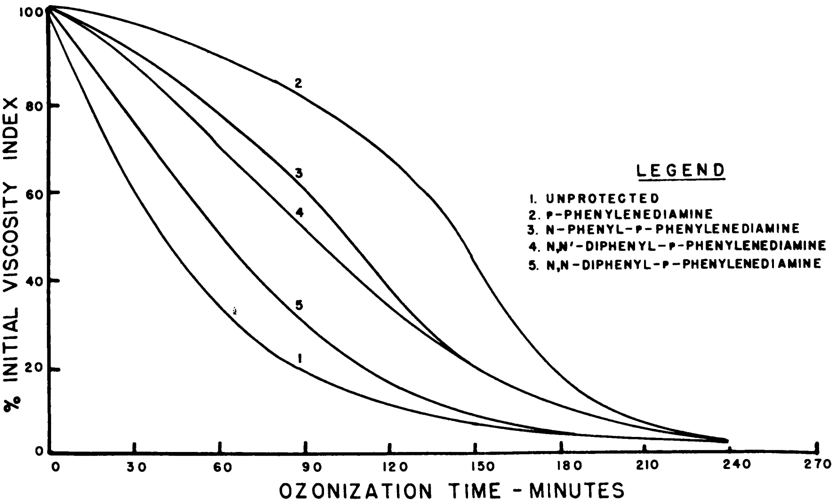


Figure 6. Influence of number of amine-group substituents

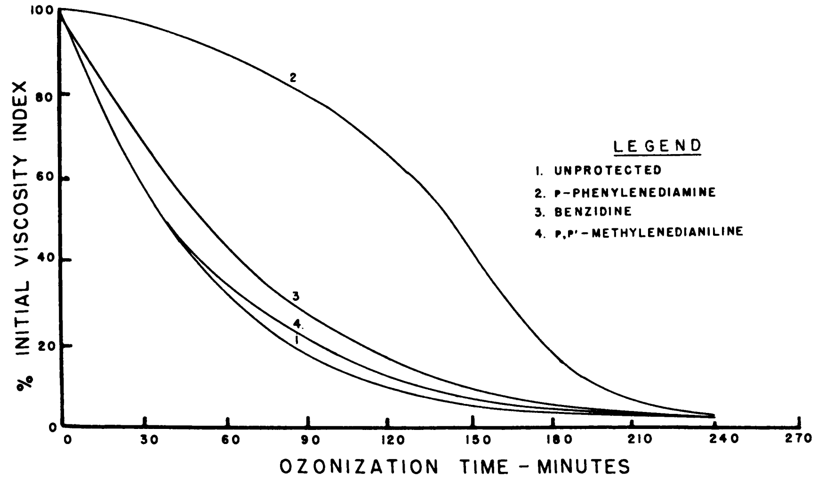


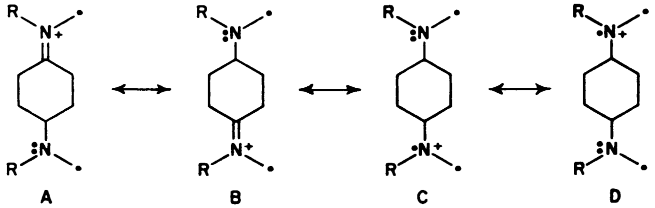
Figure 7. Influence of ring substituents

Discussion

It is generally recognized that the unsaturated bonds or weak linkages of the polymer chains are attacked during the ozonization of elastomeric materials. Because previous work (*1*, *8*) has shown that the protection afforded SBR by *p*-phenylenediamine derivatives involves a progressive deterioration of the antiozonant, it is assumed that the driving force of the antiozonant inhibiting mechanism is due to the greater rate of reaction of ozone with aromatic diamine chemicals than with SBR. No systematic investigation has been reported, however, to explain the varying degrees of protection exhibited by antiozonant chemicals.

Examination of postulated reactions (*8*) of *p*-phenylenediamine derivatives with ozone reveals that the antiozonant depletion is characterized by the intermediate formation of intensely colored products, or Wurster's salts (*3*), which are considered to be free radicals (*4*). Further ozonization of the antiozonant produced nitro and quinone compounds (*8*).

The free radicals may be resonance hybrids of structures such as



where R represents a hydrogen atom or an alkyl or aryl group substituent. Structures such as A and B resemble quinones having an odd electron at a carbon atom. The benzenoid configurations represented by structures C and D have an odd electron at a nitrogen atom and may be designated as semiquinones. The resonance structures of similar aryl diamine chemicals such as benzidine correspond substantially with that found in the *p*-phenylenediamine series.

Because it is generally accepted that resonance influences the chemical properties of substances in which it occurs, consideration of the comparative stability of the free radicals, in terms of theory of resonance (*9, 10*), provides substantiation of the compounds' relative efficiencies as antiozonants.

1. The free radicals described are most reactive when the hydrogen atoms of the amine groups lie on the same side of the benzene ring, and their activity is lowered if the molecule is forced out of a planar configuration by amine-group substituents. It is evident from this that the rate of reaction of the free radicals with ozone decreases as the resonance is inhibited by the substitution of alkyl or aryl groups for the *N*-hydrogens.
2. The formation of a valence bond lowers the energy of resonance. In addition, a molecule with a large number of bonds should have a lower activity than an analogous structure with a smaller number of bonds. Therefore, the rate of ozone attack of the free radical becomes progressively slower as the size of the amine-group substituent is increased.
3. Dialkyl or diaryl group substituents hold the molecule more rigidly out of the plane of the benzene ring than corresponding monosubstituted amine groups. The free radicals produced from unsymmetrical *p*-phenylenediamine derivatives should react more slowly with ozone than those formed from analogous symmetrical compounds.
4. A particularly strong interaction exists between the two amine groups that are para to each other. Substituent groups that separate the reacting centers of the molecule inhibit the resonance of the free radical.

Therefore, free radicals formed on ozonization of chemicals such as benzidine and *p,p'*-methylenedianiline would react more slowly with ozone than corresponding structures produced from *p*-phenylenediamine.

It can be concluded from the data presented in the figures that the relative effectiveness of the related aryl diamine chemicals studied corresponds with the comparative stability of their free radicals, in accordance with the theory of resonance.

Acknowledgment

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Accelerating Action of Ozone in the Autoxidation Processes

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Numerous experimental facts have demonstrated the entrainment action of ozone upon oxygen molecules, the latter participating in the autoxidation in which they would have remained inactive if ozone were not present. This entrainment accelerates the reaction rate. The number of molecules entrained by one molecule of consumed ozone increases greatly as the ozone becomes more diluted with oxygen. It appears that all these facts are characteristic properties of ozone. The acceleration of the autoxidation by ozone, described in this paper, was applied especially in the ozonization of certain olefins, to prepare their ozonides.

By the term "quantitative ozonization" is implied not only the yields of the products formed but also the amounts of ozone consumed. Prior to the studies described in this paper quantitative ozonization had not been systematically studied.

In a systematic study program on the ozonization of various classes of organic compounds, the reaction of ozone with aldehydes had a prominent place. The behavior of an energetic oxidant like ozone with respect to compounds such as aldehydes, which are oxidized very easily, was observed. It has long been known that aldehydes oxidize spontaneously in the presence of oxygen, as do numerous other compounds. This phenomenon has, therefore, been called autoxidation, and this word is used here, in spite of the fact that it is no longer to be considered quite correct.

The first measurements were made in collaboration with Demolis and Paillard (*13*). A solution of benzaldehyde in carbon tetrachloride was subjected to oxygen containing a known amount of ozone. The course of the reaction was followed quantitatively with an apparatus not described here. (Detailed descriptions of equipment and processes are given in the original papers.) The results of typical determinations are described in the following paragraphs.

In the flask containing potassium iodide solution for the determination of unreacted ozone a great deal of liberated iodine was found. Thus a considerable proportion of ozone passed through the solution of aldehyde, the latter appearing to be only slightly sensitive to the oxidizing action of ozone. The analysis of the aldehyde solution showed clearly, however, that it had been heavily oxidized to benzoic acid and perbenzoic acid, and much more oxygen had been taken up in this oxidation than corresponded to the amount of ozone consumed.

It was, therefore, concluded that the ozone had caused considerably more oxygen to participate in the oxidation than would be expected in the absence of ozone. [In all these experiments ozonized oxygen or ozonized air was bubbled through the solutions. Recently it was observed that if a Warburg-type apparatus (*18*) is used, the same results are obtained by simply agitating liquids in the appropriate atmospheres.] The ozone functioned not only as an oxidizing agent, but also as an oxidation catalyst.

The word "catalyst" was used frequently in the author's first papers. Although it conveys the idea very well, it is not correct, as at least part of the ozone is actually consumed in the reaction. Therefore, in the present paper ozone is referred to as an autoxidation-accelerator.

Generality of the Phenomenon

First observations led to speculations on the possibility that we might be dealing with a reaction affecting not only aldehydes but autoxidation in general. To establish this, the author undertook, with Nicolet and Paillard (*16*) and later with Biedermann (*7*), several series of studies on autoxidation, including the classical cases of sulfurous acid and the alkali sulfites and bisulfites. In all these cases the addition of ozone to oxygen or to air led to an oxygen uptake in excess of that found in the absence of ozone, with the formation of sulfuric acid, alkali sulfates, or bisulfates, respectively. The autoxidation of stannous chloride, which is quite a different compound, was studied in collaboration with Bever (*6*), and the same phenomenon was found. At the time of the author's first publications, in collaboration with others, three German organic chemists, Fischer, Dull, and Volz (*25*), also recognized this autoxidation accelerator effect in the case of aldehydes undergoing reaction with ozonized oxygen, but it is not apparent that these workers visualized the general scope of their discovery.

The accelerating action of ozone was also observed in a homogeneous gaseous system—i.e., in the slow oxidation of saturated hydrocarbons, such as propane, butane, hexane, heptane, and several octane isomers (*9*).

Thus, a complete new range of investigations was undertaken, including studies of the reactivities of the various compounds undergoing autoxidation, the influence of temperature, the influence of the various solvents used (the phenomenon is investigated chiefly in solutions), and the action of light. Light accelerates autoxidation and the bubble tubes must be kept in the dark to isolate the role of ozone in these investigations. Further, such so-called antioxidants as hydroquinone, which slow down and even stop the autoxidation completely, act in a similar way if they are added to an autoxidizable system exposed to oxygen and ozone (*21*). Thus, ozone definitely acts upon the autoxidation by mobilizing an additional number of oxygen molecules.

Effect of Ozone in Autoxidations. To appreciate this effect what is called the oxidation yield has been determined (abbreviated RO, from the French equivalent of oxidation yield, "rendement d'oxydation"). This value relates the amount of supplementary oxygen bound when one passes from the oxidation with oxygen (or air) alone to the oxidation with oxygen (or air) containing a known percentage of ozone, all other conditions remaining identical. The amount of reacted oxygen can be found by analysis of the oxidation products after the experiments.

Considering, for example, the autoxidation of benzaldehyde, the formation of one molecule of benzoic or of perbenzoic acid involves combination with one or two atoms of oxygen, respectively. In the autoxidation of an alkali sulfite, each molecule of sulfate formed utilizes one bound atom of oxygen. Thus, from the analyses, the oxidation yield, RO, is obtained and is reported as the ratio (multiplied by 100 in order to make the comparison easier) of the amount of reacted oxygen in excess to the amount of ozone consumed.

When the oxidation yield exceeds 100, it follows that the oxygen molecules have undergone reaction by virtue of the presence of ozone. However, in the case of aldehydes it is possible to go one step further and state that the oxygen has already under-

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gone reaction if the oxidation yield is greater than 33%; for this 33% is due to the direct oxidizing action of ozone itself—that is, the action of its active oxygen as determined by the classical ozone assay (the liberation of iodine from a potassium iodide solution).

To emphasize the significance of the role of ozone, use is made of two more values which are defined below based upon oxidation yield, RO. One is the utilization coefficient of ozone called α, which indicates the number of bound oxygen atoms in excess for each molecule of ozone consumed; it is a function of RO:

$$\alpha = \frac{3\ \mathrm{RO}}{100}$$

If $\mathrm{RO} = 100$, α is equal to 3. If $\alpha > 3$, oxygen molecules have certainly taken part in the oxidation. The other, N, is the number of oxygen molecules used in the oxidation per molecule of ozone consumed. It is related to RO and to α by the equation

$$N = \frac{3 \times \mathrm{RO}}{2 \times 100} = \frac{\alpha}{2}$$

N, of course, has actual meaning only if $\mathrm{RO} > 100$ and N and α are actually average values of numerous individual determinations.

Table I presents numerical values for the autoxidation of aldehydes and sodium bisulfite in a current of ozonized oxygen.

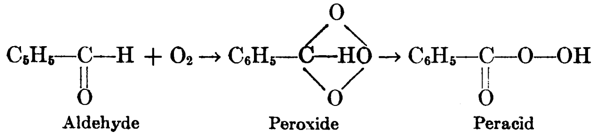
Table I. Autoxidation of Several Aldehydes and Sodium Bisulfite

Molecule undergoing autoxidation	C_6H_5CHO	$CH_3(CH_2)CHO$	$CH_3OC_6H_4CHO$	$NaHSO_3$
Solvent	Hexane	Carbon tetrachloride	Carbon tetrachloride	Water
Temperature, ° C.	0	0	0	0
Ozone concentration, vol. %	0.9	1.5	2.4	0.09
RO	370	580	240	450
α	11	17.6	7.2	13.5
N	5.5	8.7	3.6	6.7

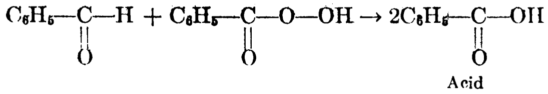
These values show clearly the pronounced accelerating action of ozone upon the autoxidation rate; this action becomes still more pronounced, if the ozone concentration in oxygen or in air is diminished.

Chemical and Physicochemical Mechanism of the Autoxidation

Probable Autoxidation Mechanism under Ordinary Conditions. For some time it was believed that this reaction proceeded in the following manner: Oxygen adds to the aldehyde, forming a very unstable peroxide. This peroxide isomerizes to a peracid (in the present case perbenzoic acid), which is stable enough for assay. The steps are represented as follows:



This sequence of transformations constitutes the actual autoxidation. In the subsequent step the peracid reacts with the aldehyde, which remains in substantial excess during a large part of the reaction, to produce the acid—i.e., benzoic acid.



$$C_6H_5-\underset{\substack{\|\\O}}{C}-H + C_6H_5-\underset{\substack{\|\\O}}{C}-O-OH \rightarrow 2C_6H_5-\underset{\substack{\|\\O}}{C}-OH$$

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Physical chemical evidence suggests that the transformation of aldehyde to the peracid proceeds by a chain reaction in which certain short-lived radicals are intermediates.

The next step, in which the acid is formed, is the same as that envisaged in the chemical concept of this change. As this reaction is important for understanding autoxidation, the author studied its kinetics in cooperation with Lardon (*15*). At ordinary temperatures the reaction is so slow that the perbenzoic acid persists for a short time; thus, it must be taken into account when establishing the equation for the bound oxygen, mentioned above.

Application of Infrared Absorption Spectroscopy

Recently, infrared spectroscopy has been applied to the study of the autoxidation process. The method used by the author and coworkers has also been applied for several years to study the ozonization of unsaturated organic compounds; it does not appear to have been utilized elsewhere.

In particular the autoxidation of benzaldehyde was investigated. Its choice as the initial subject for study was unfortunate, as the use of an impure sample of perbenzoic acid for determination of its absorption spectrum, not previously recorded, led to erroneous conclusions. These were later rectified after taking new measurements on a pure crystalline sample of the peracid (*12*). For the present study the two main bands at 1728 to 1730 and at 1270 cm.$^{-1}$ are to be borne in mind. These bands made possible a demonstration of the acceleration of the autoxidation due to ozone and the influence of such acceleration in ozonide formation. Three spectral series (Figures 1, 2, and 3), obtained in collaboration with E. Dallwigk, are discussed below.

In Figure 1 comparative spectra are shown for the autoxidation of benzaldehyde in the presence of either pure oxygen or oxygen with ozone in the indicated concentrations.

A 1-hour reaction changes the spectrum of the aldehyde (spectrum I) by making the two bands of perbenzoic acid appear (spectrum II) one at 1730 cm.$^{-1}$ as a shoulder on the 1707-cm.$^{-1}$ band of the aldehyde and the other, distinct, at 1270 cm.$^{-1}$. After 2 hours the 1730-cm.$^{-1}$ band is nicely developed and the band at 1270 cm.$^{-1}$ is more pronounced (spectrum III). After 3 hours both bands (spectrum IV) have developed still further.

Spectrum V shows the highly accelerating action of ozone upon the autoxidation. Actually, although the ozone concentration was low, $C_{O_3} = 0.76\%$ and the oxidation lasted for only 10 minutes, the two peracid bands are stronger than in spectrum IV, which involved a 3-hour reaction with ozone-free oxygen.

In order to show the dilution effect better, still another spectrum (spectrum VI) is included in the figure, which was also obtained with a reaction of only 10 minutes, but involved much higher ozone concentration, $C_{O_3} = 3.36\%$. In comparing spectra V and VI, it is noted that, in spite of the higher ozone concentration, the bands under consideration are in both cases almost equally well developed.

Table II.

C_{O_3}, %	RO	α	N
3.36	250	7.5	3.7
0.76	840	25	12.5

This effect is also illustrated by the numerical values of Table II, which have been calculated for RO, α, and N according to the formulas given above.

In the special case under discussion the amount of bound oxygen due to the ozone accelerator effect was determined not by chemical analysis but from spectroscopic data, by calculating the perbenzoic acid concentration, C, from the well-known formula:

$$\log I_0/I = \epsilon Cl$$

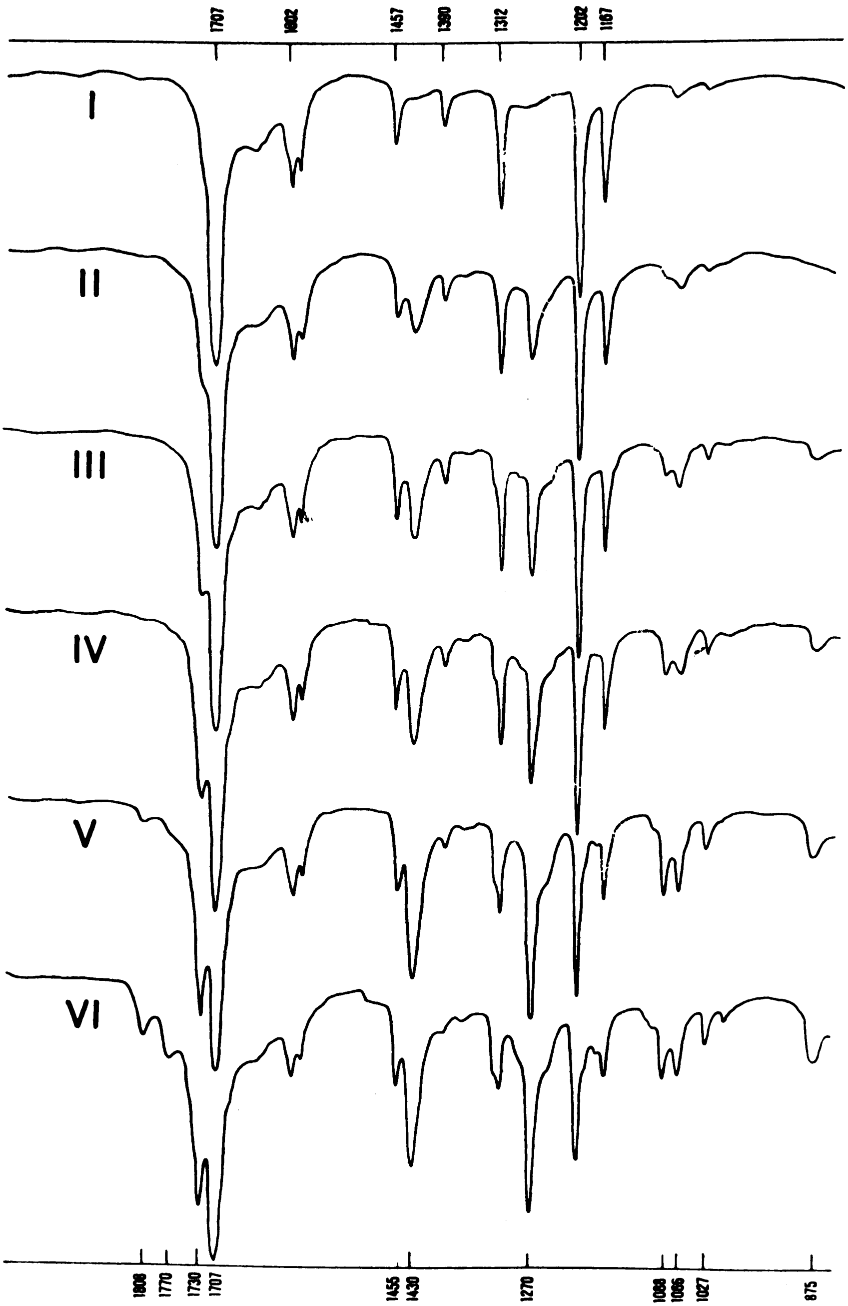

Figure 1. Spectra of 0.20M solution of benzaldehyde in carbon tetrachloride

Spectra
- I. Unexposed solution
- II. Solution after 1-hour exposure to oxygen at 8 liters/hour
- III. Solution after 2-hour exposure to oxygen at 8 liters/hour
- IV. Solution after 3-hour exposure to oxygen at 8 liters/hour
- V. Solution after 10-minute exposure to oxygen containing 0.76% ozone
- VI. Solution after 10-minute exposure to oxygen containing 3.36% ozone

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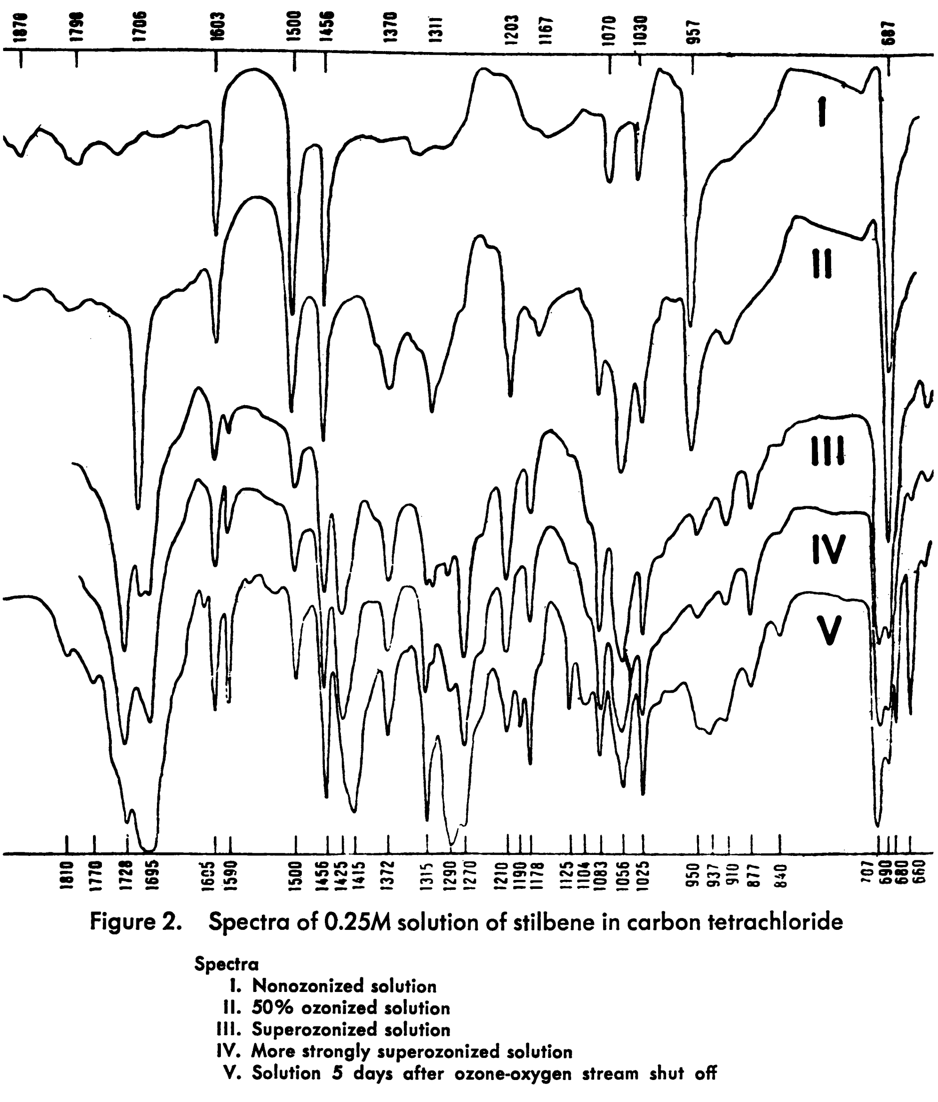

Figure 2. Spectra of 0.25M solution of stilbene in carbon tetrachloride

Spectra
I. Nonozonized solution
II. 50% ozonized solution
III. Superozonized solution
IV. More strongly superozonized solution
V. Solution 5 days after ozone-oxygen stream shut off

where I_0/I is measured at 1270 cm.$^{-1}$, l is the thickness of the absorbing liquid layer, and ϵ is the molecular extinction coefficient for the 1270-cm.$^{-1}$ band. The value of ϵ was previously reported to be 520 (*12*). This simplified calculation was made possible because consideration of the benzoic acid was omitted; under the conditions existing the effect of benzoic acid would hardly be noticeable on the spectrum. For a dilution roughly fivefold, the number of oxygen molecules participating in the oxidation is almost quadrupled (Table II).

Thus it was established by the infrared study of aldehyde autoxidation that the first product obtained is the peracid. It does not follow, however, that other intermediates are not formed—for example, radicals in a chain reaction—but their instability is such that they cannot be detected by infrared spectrography.

In Figure 2 the accelerated autoxidation due to ozone is shown in the spectroscopic examination of the ozonization of an olefin, *trans*-stilbene, in carbon tetrachloride. The first determinations were made in these laboratories in 1952 in collaboration with Susz

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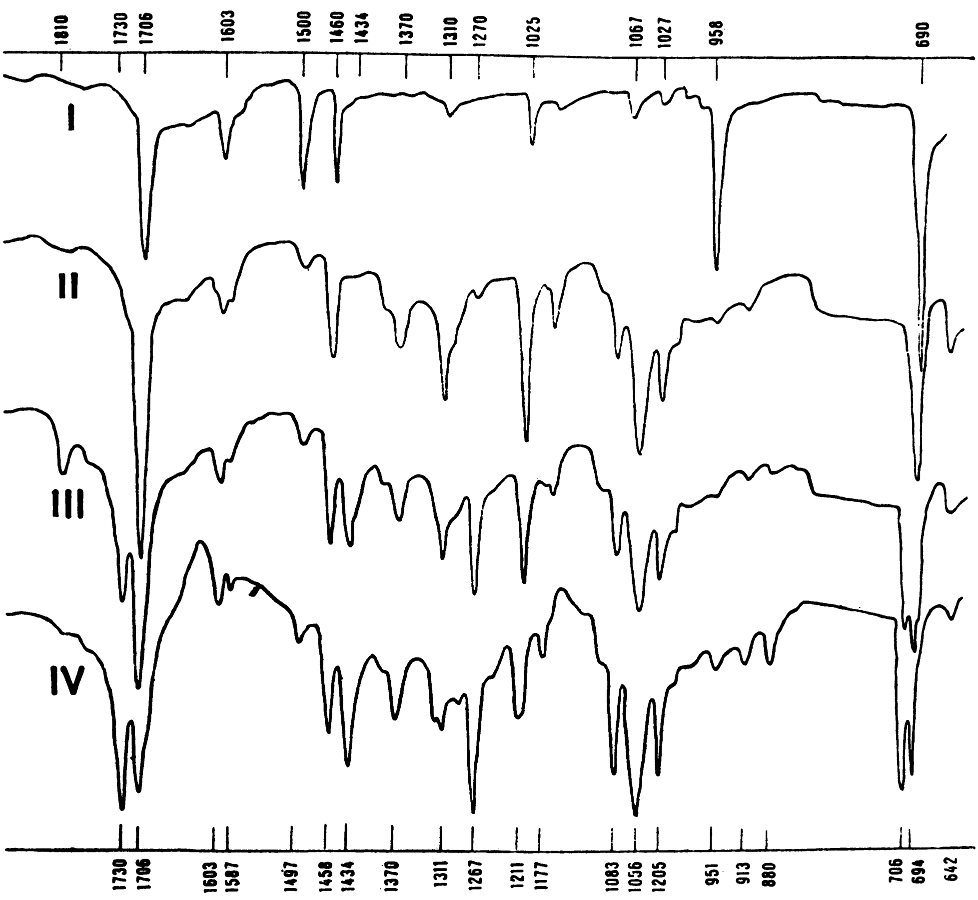

Figure 3. Spectra of various concentrations of *trans*-stilbene and benzaldehyde in carbon tetrachloride

Spectra
- I. Nonozonized 0.25*M* *trans*-stilbene and 0.025*M* benzaldehyde solution
- II. About 90% ozonized 0.25*M* *trans*-stilbene and 0.025*M* benzaldehyde solution
- III. Superozonized 0.25*M* *trans*-stilbene and 0.025*M* benzaldehyde solution
- IV. More strongly superozonized 0.125*M* *trans*-stilbene and 0.05*M* benzaldehyde solution

and Dallwigk in the course of research on infrared absorption spectra of ozonides (*20, 28*).

Spectrum I shows the stilbene solution; 50% ozonization (spectrum II) produces a strong band at 1706 cm.$^{-1}$. In the spectra determined in 1952, the band obtained at 10% ozonization developed regularly up to 70% ozonization. At this point in the investigations, the perfect agreement of this frequency with the vibrational bands of the CO group of the benzaldehyde was most striking. But it seemed impossible to attribute this band to the aldehyde, in view of its instability in a solution through which oxygen plus ozone are constantly bubbled.

Criegee and others (*23*) published new results, which led to the resumption of these investigations. He pointed out that the infrared spectra of really pure ozonides contained no bands in the range of spectral frequencies of CO group vibrations. This was verified in these laboratories with a sample of pure *trans*-stilbene ozonide obtained from Criegee.

Thus it was concluded that the aldehyde could indeed be protected from the action of ozone by the high affinity of the double bond for ozone. Indeed (*4, 19*), thermochemical measurements have shown that the heats of ozonization are of the order of 80 to 120 kcal.

In order to solve this problem, it was only necessary to effect ozonization of a stilbene solution to which some benzaldehyde had been added. The results of these investigations were definitely positive, as shown in the spectra of Figure 3. Full details have been published (*10, 11, 24*). The following points should be emphasized, which emerge from a consideration of the spectra shown in Figure 2: first, on pursuing the ozonization the development (spectra III and IV) of the two bands due to perbenzoic acid, already referred to; and secondly the appearance and very marked development (spectra II, III, IV, and V) of a band at 1056 cm.$^{-1}$—i.e., in the region of the ozonide bands according to Criegee and others (*23*).

In Figure 3 it is seen that, if a *trans*-stilbene solution containing benzaldehyde (spectrum I) is ozonized, the CO band due to the aldehyde at 1706 cm.$^{-1}$ does not disappear but becomes much stronger (spectrum II). Therefore, a material with a CO band must have been produced which shows the same frequency as that of the aldehyde. Thus a protective action of the double bond against the autoxidation accelerated by ozone is plainly manifest. In the latest measurements it has been found that the stilbene double bond protects benzaldehyde against autoxidation due to oxygen alone; thus substances with a double bond may act also as antioxidants.

Furthermore, the protective action of the stilbene double bond becomes less and even ceases as soon as if the double bond were saturated by increasing ozonization. At this moment the two bands of perbenzoic acid appear and develop (spectra II and IV), indicating that autoxidation has set in. This proves that the CO band at 1706 cm.$^{-1}$ must be ascribed to benzaldehyde, because perbenzoic acid, under these experimental conditions, can be derived only from the autoxidation of this aldehyde.

Very similar phenomena have been studied and observed with other olefins, such as anethol and isoeugenol (*10, 11, 24*). In these cases the CO bands which appear almost at the beginning of the ozonization likewise develop in a definite way, denoting the definite formation of anisaldehyde and vanillin, respectively.

It seemed desirable to point out the connection between these two phenomena—namely, autoxidation and production of ozonides, which at first glance seem to have nothing whatsoever to do with each other. This connection is of practical interest, because it is useful to know that aldehydes, such as anisaldehyde or vanillin, are already present to a considerable extent in the "prefabricated" state—that is, before the reductive hydrolysis to which the ozonization products are finally submitted with a view to scission of the ozonides formed.

Effect of Ozone Dilution

The dilution effect seems to be fairly characteristic of the ozone action upon autoxidation. The logical method of investigation would be to use oxygen-ozone mixtures in all proportions, including mixtures having exceedingly low concentrations of oxygen.

As it is not possible to use pure ozone as a gas, mixtures of oxygen and ozone were used with an inert gas, nitrogen, in collaboration with Biedermann (*7*). The principal results are given in Table III.

Table III. Effect of Ozone Dilution

Mixture composition, %				
Ozone	0.9	0.8	1.0	1.0
Oxygen	99	49–50	5	1.2
Nitrogen	...	49–50	95	98–99
Acid formed, mg.				
Benzoic acid	**361**	**196**	**131**	**107**
Perbenzoic acid	**79**	**71**	**33**	**Traces**
α	**9**	**5.5**	**2**	**1.7**
N	**4.5**	**2.7**	**1**	**0.8**

Thus the ozone utilization balance shows that, by operating with ozone containing less oxygen, the amount of perbenzoic acid decreases and tends to reach zero and that, parallel to this phenomenon, the values for α and N drop so as to reach asymptotically 1 and 0, respectively.

Thus, ozone in the absence of oxygen forms any acid only by reacting with aldehyde; it reacts by means of its active oxygen only, the limiting value for α being 1. But if the oxygen concentration is very low, the number of molecules mobilized for autoxidation can also only be low.

In continuing to pursue investigation of the ozone dilution effect, the author tried to ascertain the limiting dilution for which the increased autoxidation could be observed. Table IV is a series of results which (*21*) refer to the investigation of a solution of propionaldehyde in carbon tetrachloride; the reproducibility of the values determined for RO, α, and N was considered satisfactory.

Table IV. Propionaldehyde in Carbon Tetrachloride

C_{O_3}, %	RO	α	N
4.2	220	6.6	3.3
2.0	380	11.4	5.7
1.2	580	17.4	8.7
0.43	1050	31.6	15.8
0.16	1410	42.4	21.7
0.01	1630	48.8	24.4

The increase in the number of molecules mobilized for autoxidation proceeds regularly with ozone dilution until a dilution of one volume ozone in 10,000 volumes of oxygen—i.e., $C_{O_3} = 0.01\%$—is reached. If the ozone is diluted still further, especially beyond 1 volume of ozone per 100,000 volumes of oxygen—$C_{O_3} = 0.001\%$—several difficulties are encountered which could not be overcome completely. First of all, the accurate assay of the unused ozone became difficult. It was assumed, as a first approximation for simplification, that at such small dilutions the ozone is used up completely; therefore, the values for N are lower than they should be. [This work with very high dilutions was done in collaboration with Papazian (*17*).]

In Table V the values for N in two series of measurements with benzaldehyde in carbon tetrachloride are shown; the first series deals with dilute ozone in oxygen, the second with dilute ozone in air.

Table V. Benzaldehyde in Carbon Tetrachloride

C_{O_3} in oxygen, %	0.01	0.001	0.0001	0.00001
N	180	980	3700	7000
C_{O_3} in air, %	0.01	0.001	0.0001	0.00001
N	70	500	1900	3600

These results show (even if only approximately) a regular progression of the dilution effect. Furthermore, the values of N obtained in the series of experiments on ozone diluted with air are lower than those corresponding to ozone diluted with oxygen. Thus, as was expected, the increase of oxygen concentration is the important factor in the dilution effects.

Attempts were made to increase the ozone dilution further by using air-ozone mixtures of concentrations lower than $C_{O_3} = 0.00001\%$. But difficulties were encountered because of atmospheric ozone; at the altitude of Geneva (350 to 400 meters) there is about 0.000001% of ozone in the air. Thus, to prepare such mixtures of air and ozone, ordinary air was first deozonized by passing it through tubes heated to temperatures above 800° C. Furthermore an aldehyde reagent was used, butyraldehyde dissolved in iso-octane, which is much more sensitive to autoxidation than benzaldehyde in carbon tetrachloride.

In Table VI the results of a series of such experiments are shown; these experi-

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ments were of an orienting nature only, in view of the many errors that can intervene at such extreme dilutions.

Table VI.

C_{O_3}, %	0.00001	0.000001	0.0000001
N	18,000	74,000	200,000

The order of increase in the number of oxygen molecules participating in the autoxidation shows clearly that the dilution effect can still be noticed under the extreme conditions at which the work was done.

The reagent, butyraldehyde in iso-octane, has proved to be extremely sensitive to the action of ozone. It was, therefore, used in studies with Perrottet (*18*) for ozone measurements in the atmosphere at various altitudes. Although this method is only approximate, the numerical values with increasing altitude are of the same order of magnitude as those obtained by photometric measurements of light absorption by ozone, a rather exact method. At the Gornergrat, for a 3200-meter height an ozone concentration of 0.0000038% was measured and the photometric group working at the Jungfraujoch at a 3450-meter height reported an ozone concentration of 0.0000031% (*22*).

This dilution effect is not only found with aldehydes. In experiments done with Biedermann (*8*) this regularity is confirmed in the oxidation of sodium bisulfite down to 1 volume of ozone in 10,000 volumes of oxygen, $C_{O_3} = 0.01\%$.

Interpretations

In this paper special stress is laid on the experimental data, which characterize the ability of ozone to entrain itself in the autoxidation molecules of oxygen which would have remained inactive if no ozone were present. The following interpretation is brief because the hypotheses developed in the author's laboratory are not yet fully satisfactory.

In order to explain the autoxidation processes, one generally has recourse to the chain-reaction mechanism, depending on the existence of highly unstable intermediates often of a hypothetical nature only. Examples of such unstable compounds are found in the papers by Bodenstein on the autoxidation of acetaldehyde (*2*) and by Haber and Franck on the oxidation of sodium bisulfite (*26*). This mode of explanation was not pursued in the present work, as it would have necessitated the addition of new hypotheses to explain the incorporation of the ozone molecule into the proposed chain reactions. But one may consider, in a simplified manner, that ozone starts the chain by means of its active oxygen. It has been stated (*27*) that peroxides, especially benzoyl peroxide, act as autoxidation catalysts.

Since the autoxidation mechanism is so complex because of all the intervening factors, the author has limited himself to considering the energy basis of the problem (*3*), which is much simpler. On replacing oxygen by ozone in the oxidation one obtains for the activation energy of the autoxidation reaction a supplementary energy—namely, the oxidation energy liberated when ozone transforms into oxygen, 34 kcal. per gram-mole of ozone. Expressed differently, the reaction chains induced by ozone would then be of an energy type.

This energy interpretation is corroborated by the acceleration, already referred to, of the autoxidation by light. For, as shown by Bäckström (*1*), it is the absorption of this radiant energy which initiates the reaction chains. According to this author, however, the absorption of light by the autoxidizable molecule transforms it into an unstable body, a radical.

The more completely the ozone molecule is surrounded by oxygen molecules—i.e., the higher the concentration of oxygen molecules with respect to ozone molecules—the better the supplementary energy is utilized. This qualitative interpretation of the reaction probably represents the limit of our present understanding. There is no doubt that other factors enter into play here, especially surface actions which the author was led to consider (*5*) by observing that the autoxidation takes place between gas and liquid; this, at least in part, at the separating surface of these two phases.

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Role of Formazan Reaction in Proving Structure of Ozone-Oxidized Carbohydrates

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The formazan reaction is useful for investigating the structure of ozone-oxidized carbohydrates. Ozonizing sugar alcohols in an aqueous solution, aldoses arise during the oxidation process which have been identified by the formazan reaction. Polysaccharides also can be oxidized with ozone and then converted into their formazans. Polysaccharides not containing a free primary alcoholic group do not yield formazan. This finding seems to indicate that the formazan group takes the place of the primary alcoholic group. The new formazans have been successfully transformed to metallic complexes, tetrazolium, and thionic acid phenylhydrazide derivatives. The reaction can also be used to establish the structure of the sugar portion of ozone-oxidized glycosides.

When Harries (*2*) at the beginning of the present century carried out his fundamental experiments with a view to ozonizing organic compounds, he also studied the effect of ozone on certain sugar alcohols. His initial studies showed that the primary alcoholic hydroxyls of sugar derivatives can be oxidized to form aldehyde groups by utilizing ozone.

Various experiments made in this institute in recent years (*5, 10–13*) showed that the formazan reaction lent itself readily to studies of the structure of oxidized sugar derivatives whenever free aldehyde groups were present. Obviously, it was a useful reaction for investigations into the structure of ozone-oxidized carbohydrates, among them the sugar alcohols that had been studied by Harries.

The present work showed, in perfect agreement with Harries, that on ozonizing sugar alcohols in an aqueous solution, they begin to oxidize and aldoses arise in the course of the oxidation process. For instance, D-mannose was prepared from ozone-oxidized D-mannitol; with the aid of the formazan reaction, D-mannose was then identified as D-manno-*N,N'*-diphenyl formazan (*8*).

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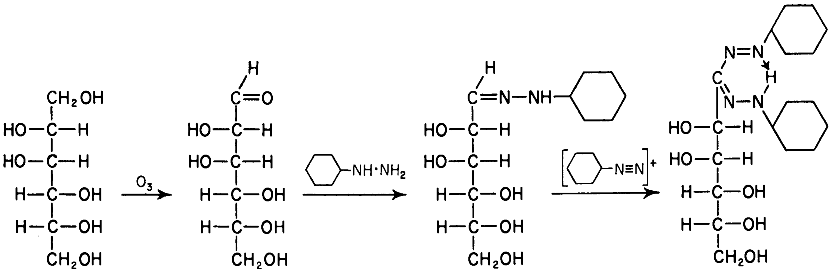


To an aqueous solution of mannitol, ozonized for 7 to 14 hours, phenylhydrazine was added. When the solution was kept in the refrigerator overnight, mannose phenylhydrazone separated. On coupling it in pyridine solution with an ice cold solution of diazotized aniline, D-manno-*N*,*N*′-diphenyl formazan, crystallizing in brownish red needles, was obtained.

To establish optimum conditions for the conversion of mannitol to mannose by 1% ozone, aqueous solutions were ozonized in gas washing bottles provided with shrunken glass filters for 7 and 14 hours, in concentrations of 0.8, 1.6, 3.2, and 4.8 10^{-1} mole per liter. Under these conditions, the lowest concentration and the longer time of ozonization were found to be favorable for the formation of mannose (Figure 1).

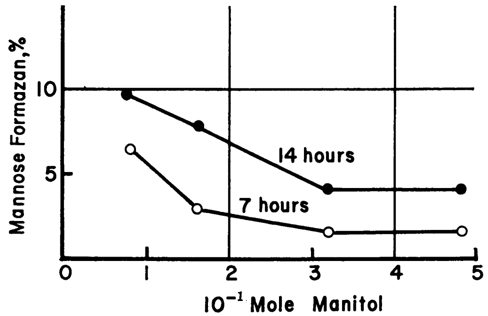
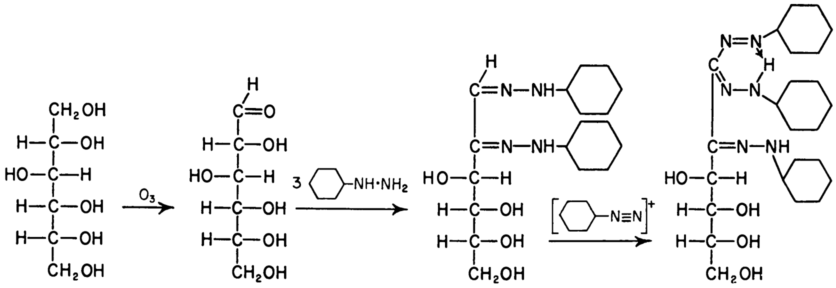


Figure 1. Optimum conditions for ozone oxidation of mannitol

Other sugar alcohols, such as D-sorbitol and D-dulcitol, give an aldose phenylhydrazone which is hard to isolate and convert to the formazan. Therefore, the aldose (D-glucose from D-sorbitol) was transformed into glucosazone, which was identified with the aid of the formazan reaction as D-glucosazone formazan (*4*).

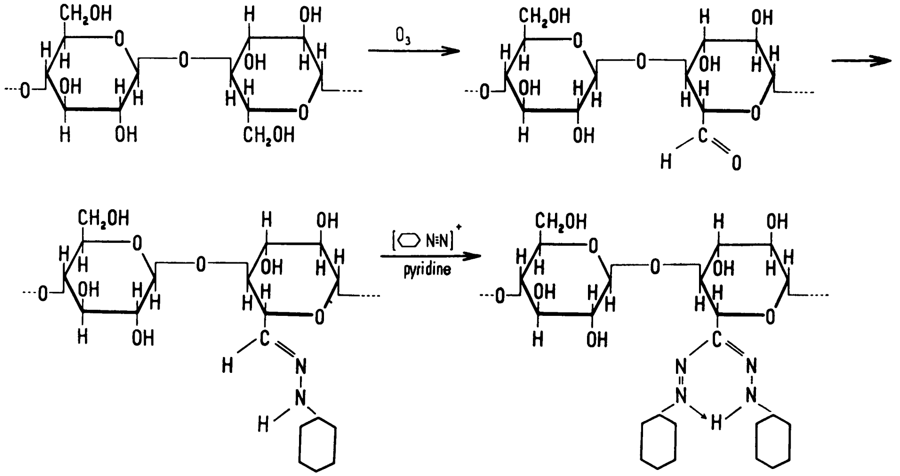


Sucrose likewise yields glucosazone identifiable as glucosazone formazan. This indicates that in sucrose it is the hydroxyl group on the first carbon atom of D-fructose which oxidizes to an aldehyde group. As has been observed by several authors (*1, 7, 14*), in the course of the formation of osazone the disaccharide bond (*2, 5*) breaks up and glucosazone forms from both components of the disaccharide upon the addition of phenylhydrazine.

From ozone-oxidized sugar alcohols no formazan derivatives have yet been isolated in which the primary alcoholic hydroxyls, presumably present at both ends of the molecule, have oxidized to aldehydes. However, bisformazans, conspicuous for their capacity to crystallize and their insolubility in water, have been successfully prepared by other means (*13*).

Polysaccharides, such as cellulose and starch, can be oxidized with ozone and then converted to their formazans. A cellulose wad or a sample of starch powder, finely divided or suspended in water, was placed in a gas-washing bottle with a shrunken glass filter and ozonized at room temperature for 8 to 18 hours, carefully washed, and reacted in acetic acid with phenylhydrazine. This resulted in vividly yellow phenylhydrazones of the oxidized polysaccharides. By the reaction with an ice-cold solution of diazotized aniline in pyridine and ethyl alcohol, the bright red formazans of the ozone-oxidized polysaccharides were obtained.

Polysaccharides not containing a free primary alcoholic group—e.g., xylan—have failed to yield formazan upon oxidation with ozone. This finding and the observations made in the present work in connection with ozone-oxidized sugar alcohols seem to support the suggestion that the formazan group takes the place of the primary alcoholic group.



It has long been known that oxidation of simple formazans gives tetrazolium compounds which, even under biological conditions, are easily reduced once more to red formazans. For instance, triphenyltetrazolium chloride, prepared by oxidizing triphenyl formazan, is an approved biological indicator.

Like the sugar formazans (*9*), the formazans prepared from ozone-oxidized polysaccharides readily oxidize with *N*-bromosuccinimide to the corresponding colorless tetrazolium compounds.

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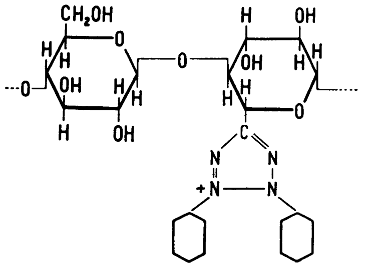
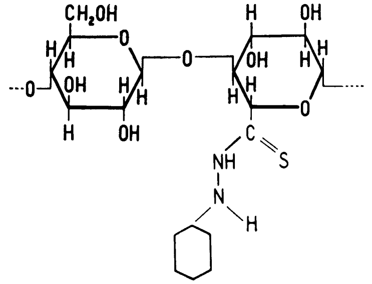
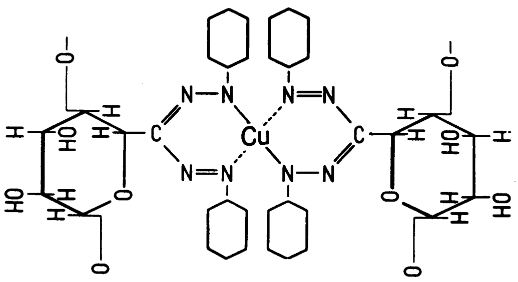


As in the formazans of the simple sugars (*15*), those of the ozone-oxidized polysaccharides undergo reductive disintegration by the action of hydrogen sulfide. Thus, the formazan of ozone-oxidized starch gives the corresponding thionic acid phenylhydrazide.



Again, similar to the simple formazans (*6*), those of the ozone-oxidized polysaccharides readily form complex salts with heavy metals. The probable structure of a copper complex obtained from the formazan of ozone-oxidized cellulose is:



Particularly fine colors are displayed by the metal complexes of formazans derived from viscose rayon. The copper, cobalt, and uranium cellulose complexes represent a new type of the so-called chemically colored threads.

Under the electron microscope the uranium complexes of the formazans of ozonized polysaccharides display a distinct shading effect, the polysaccharides showing a deep black color. On this basis it is to be hoped that a new electron microscopic method will soon be elaborated (*6*).

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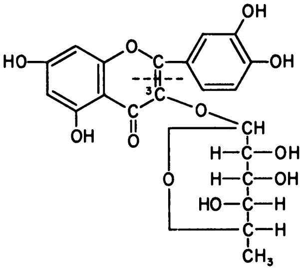
The formazan reaction can also be used to establish the structure of the sugar portion of ozone-oxidized glycosides. Some earlier investigations in this laboratory with glycosides containing aromatic or cyclic aglycones show that the latter is attacked during ozonization, while a considerable part of the sugar portion remains unchanged and can be isolated, even if it is disaccharide (*3*). For instance, from α-phenylmannoside treated with ozone it was possible to isolate D-manno-*N*,*N*′-diphenyl formazan, and from ozonized quercitrin, L-rhamno-*N*,*N*′-diphenyl formazan.



In these cases the oxidation of the sugar portion is obviously preceded by the disintegration of the aglycon.

Experiments to disclose the theoretical and practical value of ozone-oxidized carbohydrates and the nitrogenous derivatives prepared from them are being continued.

Acknowledgment

The author wishes to express his thanks to Adam Major for his assistance in the experimental part of this work and to Ilona Batta for making the microanalyses.

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Ozone Oxidation of Sulfides and Sulfoxides

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The stepwise oxidation of organic sulfides to sulfoxides and sulfones with ozone is reported. In the case of carboxymethylmercaptosuccinic acid, it is the only successful oxidation to the sulfoxide known. The yields in most cases are essentially quantitative with respect to both the sulfur compound and ozone.

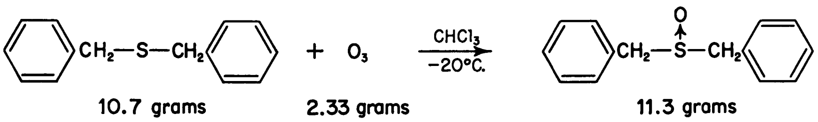
The formation of dialkyl and alkylaryl sulfones, and in some cases their intermediate sulfoxides, by the oxidation of sulfides with ozone has been described in the literature (*2*, *5*). However, no mention was made as to the amounts of ozone required for these oxidations. In an excellent paper (*1*) on the use of ozone as a titrimetric agent for olefinic double bonds, Boer and Kooyman state that, under the conditions studied, dialkyl sulfides consume ¼ to ⅓ mole of ozone per mole of sulfide and dibenzothiophene consumes 1 mole. None of these ozonated products was analyzed as to its sulfoxide or sulfone content.

The present investigation shows that ozone reacts with dialkyl and diaryl sulfides according to the equation:

$$R_2S \xrightarrow{O_3} O_2 + R_2SO \xrightarrow{O_3} O_2 + R_2SO_2$$

When run in nonpolar solvents, the reaction is stoichiometric in the formation of both aliphatic and aromatic sulfoxides and aliphatic sulfones.

The reaction was carried out on numerous aromatic and aliphatic sulfides and sulfoxides. Among the compounds made in essentially quantitative yields were dibenzyl sulfoxide, dibenzyl sulfone, dimethyl sulfone, diphenyl sulfoxide, thionyldiglycolic acid, and carboxymethylthionylsuccinic acid (Table I).



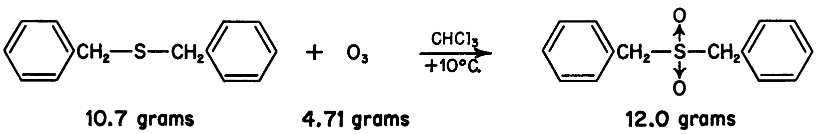


Table I. Yields from Ozonization Experiments

Sulfide	Sulfoxide, %	Sulfone, %
Dibenzyl	98	98
Dimethyl (sulfoxide)		90
Diphenyl	95	Colored product showing attack other than on sulfur atom
Dibenzothiophene		Same as diphenyl sulfide
Thiodiglycolic acid	98	No oxidation beyond sulfoxide
Carboxymethylmercaptosuccinic acid	98	

Some difficulty was encountered in the formation of aromatic sulfones. When the ozonation was carried out in chloroform in a reactor using a glass frit for the dispersion of ozone, a solid precipitated which clogged the frit as the second equivalent of ozone was added.

In acetic acid there was no precipitate, but the product from the addition of two equivalents of ozone was colored and contained both the sulfoxide and the sulfone. In a reactor in which the ozone was dispersed by a high-speed stirrer, the precipitate formed in chloroform did not interfere with the addition of ozone, but the results were the same as they were in acetic acid. Attempts to oxidize diphenyl sulfide and dibenzothiophene cleanly to the sulfones using several solvents and ozone or hydrogen peroxide as the oxidizing agents gave the same results. More work on this phase is clearly indicated.

Carboxymethylmercaptosuccinic acid and thiodiglycolic acid were oxidized cleanly to their respective sulfoxides, but thiodiglycolic acid could not be oxidized to its sulfone at room temperature in chloroform, acetic acid, acetonitrile, or water containing molybdate ion. This is no doubt due to the slow rate of oxidation of the sulfoxide to the sulfone, which can readily be explained on the basis of electronic theory. This is apparently the first successful preparation of carboxymethylthionylsuccinic acid by any method (*3*).

The well-controlled attack of ozone on the sulfur molecule can best be explained by the assumption that a terminal oxygen of the ozone molecule executes an electrophilic attack on the sulfur, forming a new bond with the sulfur. [Compare with Meinwald's work (*4*) for the analogy in the attack of ozone on the double bond.] Thereupon, the second and third atoms of the ozone are liberated as molecular oxygen. This theory explains the fact that only one oxygen from each ozone molecule is added to the sulfur. If one assumes an attack of the apex oxygen of the ozone molecule, it is difficult to understand why only one of the oxygen atoms stays associated with the sulfur.

Although the configuration of ozone which has a positive charge on one terminal oxygen and a negative charge on the other, as opposed to a positive charge on the apex oxygen and a negative charge on a terminal oxygen, contributes little to the structure of the molecule (*6*), an analogy can be drawn with other ionic addition reactions. The ionic configuration of the bromine molecule contributes little to its structure, yet it adds to an olefin first as a bromine cation.

In the course of these studies the most convenient apparatus in which to run these reactions was found to be a flask with a stirrer which has a gas inlet through it. This gives as good a dispersion of the gas in the liquid as does a fritted glass diffuser, and greatly simplifies the manipulations accompanying the reaction. It has the additional advantage that an insoluble product, if formed, does not interfere with the continuation of the reaction.

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Preparation of Tertiary Amine Oxides by Ozonization

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It is reported in the early literature that unsymmetrical amine oxides or those of high molecular weight cannot be prepared by the action of ozone on the amine. This study shows that an unsymmetrical amine oxide, such as *N*-ethylpiperidine oxide, and a symmetrical high molecular weight amine oxide, such as tri-*n*-hexylamine oxide, can be prepared by ozonization in methanol solution.

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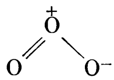
Although the formation of tertiary amine oxides using such active oxygen reagents as hydrogen peroxide and peracids (*2*) is well known, the reaction with ozone has received little attention. Strecker and Baltes (*4*) established this reaction by ozonating trimethylamine and identifying the product as trimethylamine oxide. In ozonating substitution products of ammonia, they observed that oxidation by addition of oxygen occurs only when the substituents on the nitrogen are similar and have a low molecular weight. They stated that ozone behaved like the other oxidants by forming tertiary amine oxides, but differed by forming only a symmetrically substituted amine oxide of low molecular weight. Repeated attempts to isolate the amine oxide from the (ozonization) of dimethylaniline were unsuccessful.

The authors extend the knowledge of the action of ozone on tertiary amines and show that both an unsymmetrically substituted amine oxide and a high molecular weight amine oxide can be prepared by ozonization. *N*-Ethylpiperidine, an unsymmetrical tertiary amine, was chosen to test the statement of Strecker and Baltes. Although its amine oxide had been prepared through hydrogen peroxide oxidation by Werner and Wolffenstein (*6*), the authors ozonated the amine in methanol solution at dry ice temperature. It was not isolated but was converted to the picrate, which crystallized out of the methanol solution. After purification, the amine oxide picrate was identified by elemental carbon, hydrogen, and nitrogen determinations. Perchloric acid titration, according to the procedure of Clark and Wang (*1*), gave the milliequivalent weight of the *N*-ethylpiperidine oxide picrate.

The first three tertiary amines in the aliphatic series were studied by Strecker and Baltes. The authors studied tri-*n*-butylamine, tri-*n*-hexylamine, and tri-*n*-heptylamine. Each amine was ozonated at dry ice temperature and treated with picric acid. The tri-*n*-butylamine oxide picrate readily deposited as crystals on standing. Although the latter two amine oxides formed oily products at first, on long standing in the refrigerator they gave crystals of the amine oxide picrates. The purified amine oxide picrates were analyzed by direct titration with perchloric acid.

The structure of ozone (*5*) may be represented as a resonance hybrid of four structures: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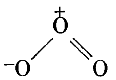
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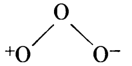
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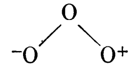
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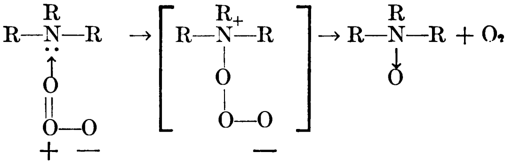
Structures I and II are reported as the main contributing forms. Meinwald (*3*) used these to explain the addition of ozone to certain olefins. A similar mechanism can be postulated to explain the reaction of ozone on tertiary amines:



The reaction may be explained as an electrophilic attack of the terminal oxygen of ozone on the nucleophilic nitrogen to form a transitory intermediate which yields the amine oxide.

The reaction of ozone with these tertiary amines is very rapid, but the addition of ozone is not stoichiometric: About 1.2 to 1.7 moles of ozone per mole of the tertiary amine were used. The yields of the amine oxides, isolated as the picrates, were about 50% of theory.

Experimental

Ozonization. The ozone was generated from oxygen using the Welsbach T-23 ozonator. The oxygen flow through the ozonator was 0.10 cubic foot per minute. The ozone concentration was about 40 mg. per liter.

The amine solution was placed in a cylindrical glass tube, 2 cm. in diameter and 30 cm. in length, equipped with a fritted-glass disk at the bottom for dispersing the gas and a standard 24/40 joint at the top. This reactor was placed in a Dewar cylinder and was cooled with a dry ice–alcohol mixture. By frequent careful addition of small dry ice particles, the desired temperature was maintained within 5° C.

After passage through the amine solution, any unreacted ozone was absorbed in 2% potassium iodide solution contained in a gas washing bottle. The volume of the ozonated oxygen, passed through the solution and stripped of ozone by the amine solution or potassium iodide solution, was measured with a wet-test meter. The reaction of ozone with tertiary amines was so rapid that at an ozone flow of 56 mg. per minute no excess ozone appeared in the potassium iodide trap during the reaction. The addition of ozone was stopped when the potassium iodide showed the yellow color due to iodine.

Several attempts were made to isolate the amine oxide as a hydrochloride salt. Usually the salt did not crystallize, but a hygroscopic oil resulted on evaporation of the solvent. Isolation was simplified by using picric acid, for the picrates crystallized on standing.

The experimental technique consisted of ozonization at dry ice temperature in a solvent such as methanol, in which both the picric acid and amine oxide were soluble, and addition of the cold solution of amine oxide to the alcoholic solution of picric acid. On standing in the refrigerator, crystals of the picrate separated from the solution. These crystals were filtered, dried under a vacuum, and weighed. Then they were purified from methanol and analyzed.

Analysis. The amine oxide picrates were determined according to the procedure of Clark and Wang. A sample of 0.2 to 0.4 meq. of the picrate was dissolved in 10 ml. of glacial acetic acid. About 3 drops of methyl violet indicator were used. The color change from deep to light blue was used as the end point. The solutions were titrated with standard 0.1*N* perchloric acid in glacial acetic acid with a microburet.

Results

This procedure was tested using both amine picrates and amine oxide picrates. The milliequivalent weights of the picrates determined were within 1% of the theoretical value.

The results of preparing amine oxides are summarized in Table I.

Table I. Preparation of Amine Oxides

			Oxide Picrate, Meq. Wt.	
Compound Ozonated	Yield %	M. P., ° C.	Calculated	Found
N-Ethylpiperidine[a]	57.5	147–9[b]	358	356, 360
Tri-*n*-butylamine	57.1	110–1	430	429, 434
Tri-*n*-hexylamine	23.2[c]	34–6	515	512, 511
Tri-*n*-heptylamine	48.2	44–6	557	558, 554

[a] $C_7H_{15}NO \cdot C_6H_2(NO_2)_3OH$, analyzed by Clark Microanalytical Laboratory.

	C	H	N
Calcd.	43.56	5.06	15.64
Found	43.76	4.98	15.58, 15.71

[b] Werner and Wolffenstein reported 142–4° C. as the melting point of the amine oxide picrate.

[c] First crop of crystals.

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Synthesis of Polyamide by Ozonolysis of Oleic Acid

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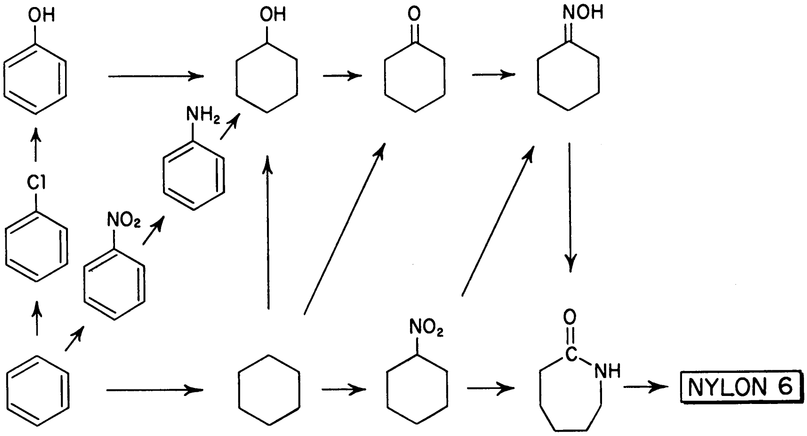
From studies on the ozonolysis of oleic acid, the author found a new synthesis of ω-aminononanoic acid, from which a polyamide, polynonanoamide, is prepared. This polyamide (Nylon 9) has characteristic properties which are as good as Nylon 6—6 and Nylon 6 as a material for synthetic fibers.

Since 1935, when Carothers discovered the fiber-forming properties of polyamides, many chemists in the world have studied the synthesis of the raw materials for various polyamides, aliphatic diamines, aliphatic dibasic acids, caprolactam, and the ω-amino fatty acids. The known synthetic routes to polyamides from ω-amino fatty acids are as follows:

1. Polycaproamide via caprolactam, which is derived from phenol or benzene (Nylon 6).
2. Polycaproamide via butynediol, which is derived from acetylene (Nylon 6).
3. Polyheptanoamide via tetrahydrofurfuryl alcohol, which is derived from furfural (Nylon 7).
4. Polyundecanoamide via undecylenic acid, which is derived from ricinoleic acid (Nylon 11).

①



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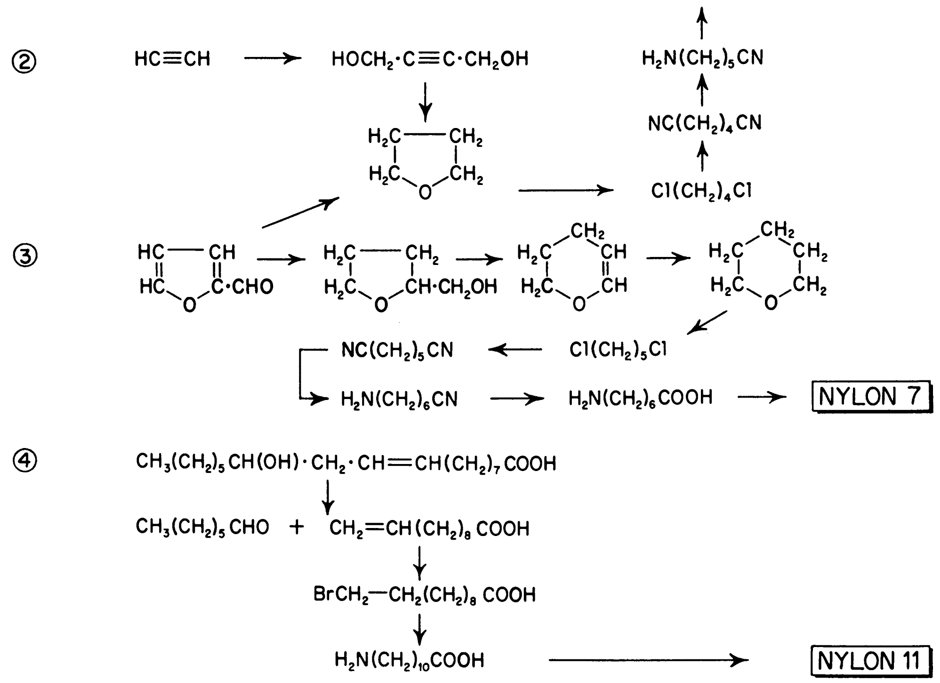
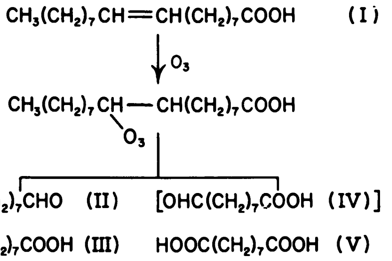
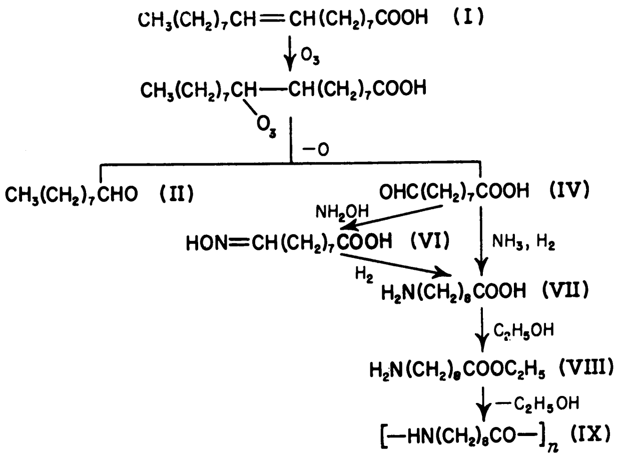


Since 1951, the ozonolysis of oleic acid (I) from sperm oil has been studied in this laboratory; good yields of nonyl aldehyde (II), nonanoic acid (III), and azelaic acid (V) have been obtained.



These studies showed that azelaic half aldehyde (IV), an intermediate product, is usually obtained in some quantity by decomposition of oleic acid ozonide. Reductive decomposition of the ozonide was then tried to preserve both aldehyde groups. Sodium sulfite as the reducing agent gave the first successful result. Azelaic half aldoxime (VI) could then be easily obtained from azelaic half aldehyde (IV) and hydroxylamine. Finally, ω-aminononanoic acid (VII) was obtained by neutral reduction of azelaic half aldoxime (VI).

The ω-aminononanoic acid, like other ω-amino fatty acids, is dehydrated and polymerized easily by heating. Ethyl ω-aminononanoate (VIII) was prepared and distilled in vacuo for the purification of ω-aminononanoic acid (VII). Ethyl ω-aminononanoate (VIII) purified gives the polymer, polynonanoamide (IX, or Nylon 9), by heating at reduced pressure followed by the splitting off of alcohol.



Later experiments showed that ω-aminononanoic acid (VII) can be prepared catalytically from azelaic half aldehyde (IV) without difficulty by action of ammonia and hydrogen. This simplified the process.

This process led to a new synthetic route to polynonanoamide (IX), Nylon 9; the polyamide was named Azelon.

The polyamide obtained in these experiments was identified as polynonanoamide; Coffman and his coworkers had prepared this compound in 1948 via the polyanhydride of sebacic acid. The first fiber-forming polyamide was obtained by Carothers from an amino acid—viz., ω-aminononanoic acid—a discovery in 1935 which led to intensified research on the polyamides and culminated in the development of Nylon 6–6.

The polyamide, Nylon 9, is extruded in cold water by pressure of an inert gas; it is a white, opaque material which is cut into chips for subsequent spinning or molding operations.

As Table I shows, the material melts at 195–7° C. and has a lighter specific gravity (1.05 compared with 1.14) than Nylon 6 and 6–6. As it is soluble in such solvents as *m*-cresol and strong acids like analogous polyamides, the resistance of the material to chemical reagents, generally speaking, is much higher than that of Nylon 6. The material can be readily melt spun and oriented by drawing.

Table I. Nylon 9 Polyamide

Melting point, °C.	195–7
Specific gravity	1.0497
Ash, %	0.16
Ether extract, %	0.22
Amino terminal group, meq./g.	0.014
[η]	1.03
Resistance to Chemical Reagents	
Acetic acid 100%, 70° C.	Soluble
Formic acid 97%, 40–45° C.	Soluble
Hydrochloric acid 30%, boiling	Partly soluble
Sulfuric acid 80%, room temp.	Soluble
m-Cresol, room temp.	Soluble
Phenol, 90%, room temp.	Soluble
Sat. sol. $ZnCl_2$-methanol, room temp.	Soluble

When Nylon 9 has acquired a high degree of orientation by drawing 4.5 to 5 times, it shows a tenacity of 5.0 to 5.5 grams per denier and an elongation of 20 to 25% (Table II).

The incidence of the amide linkage in the polyamide chain is considerably lower than in Nylon 6 and 6–6, and this increased hydrocarbonlike character of the material is shown in a lower moisture-absorbing capacity as well as a little lower dyeing affinity.

Table II. Test for Nylon 9 Filament

Denier, D	59.6
No. of monofilament, *n*	10
Tenacity	
Dry, grams/denier	5.07
Wet, %	4.45
Variety of strength, %	5.6
Elongation	
Dry, %	25.8
Wet, %	30.1
Twist number, *t/m*	5.0
Water absorption, %	1.4
Shrinkage in boiling, water, %	11.2
Young's modulus, kg./sq. mm.	373
Average stiffness, grams/denier	22.5
Average toughness, denier/cm.	0.90
Recovery at 10% elong., %	
Moment	77.0
Full	93.6
Recovery at 5% elong., %	
Moment	92.3
Full	97.0

One of the most characteristic properties of the polyamide is an unusual stability, which is unchanged even after several hours in the molten state. In other words, there is no equilibrium between the monomer, the ring compound, and the polymer as in Nylon 6. As the same is true in the case of Nylon 11, this is probably due to the facility of ring compound formation according to the size of a ring which a monomer may be able to make. Accordingly, it is assumed that this phenomenon is caused by the so-called Prelog's "medium-sized ring effect," in which the yield of C_9- to C_{11}-membered rings is minimum in every synthesis of the macrocyclic ring from C_5 to C_{20} aliphatic compounds.

Nylon 9, which is extremely stable to heat, does not show even a slight change in the wide range of about 100° C. over its melting point. With this polyamide, unlike other polyamides, the molten polymer is driven directly to the spinneret after polycondensation. There is no monomer in the polymer to be washed out. These facts have simplified the process.

The nonyl aldehyde coproduct of the azelaic half aldehyde is a useful intermediate; after being transformed into the corresponding alcohol, acid, or amine, it is a raw material for plastics. Several years ago, I. Sakurada, Kyoto University, the inventor of Vinylon, found that when nonyl aldehyde is used instead of formalin for acetalization of poly(vinyl alcohol), the properties of Vinylon yarns are considerably improved, especially in elastic recovery.

The oleic acid starting material is available in large quantities throughout the world from a wide variety of animal fats and vegetable oils. The polyunsaturated acids, linoleic and linolenic acids, could be used also, as their first double bond is at the 9-position.

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Vertical Atmospheric Ozone Distributions

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The observations reported make it possible to identify air masses of different origin in the stratosphere and to prove very slight vertical movements of the atmosphere by means of the ozone variation. Thereby a useful factor has been obtained for investigation of general atmospheric circulation and perhaps also for weather forecasting. During the International Geophysical Year the institute at Weissenau is carrying out observations of the vertical ozone distribution in polar, mean, and equatorial latitudes with the recently developed ozone radio sonde to gain a wider range of information on interdiurnal, meridional, and seasonal fluctuations of the vertical ozone distribution.

In recent years knowledge of the variations of the vertical ozone distribution at least for mean latitudes has been considerably widened, especially by using balloon-borne ultraviolet spectrographs, and the importance of these variations for the analysis of mass transfer processes in the atmosphere (*14*, *17*) can already be seen. Below an altitude of 35 km., ozone is a quasiconservative element of the air, because the time in which the photochemical equilibrium is re-established amounts at 30 km. of altitude to 10 days, at 25 km. to 100 days, and at 20 km. to 1 year. Up to the present time, the average height of the balloon ascents was about 33 km., but in May 1956 at Weissenau an altitude of 44 to 45 km. was reached for the first time. With the spectrograph employed, the spectrum at this altitude extends down to 2700 A. It is somewhat astonishing that no radiation could be observed in the ozone-oxygen window at 2150 A. Figure 1 shows the ascent curve obtained by optical and barometric observation. Thus, altitudes can now be reached at which the vertical ozone distribution still shows considerable variations, as has already been determined by rocket ascents and during eclipses of the moon (*13*). A continuous study of these variations appears of importance because a possible direct influence by variable ultraviolet radiation of the sun at this altitude on the ozone layer and thereby on the lower atmosphere would be readily apparent.

Instruments

Balloon-Borne Ultraviolet Spectrographs. By using the spectrograph, from the spectral intensity distribution $I\ (\lambda, h)$ in the ultraviolet region of the solar spectrum, the ozone amount, $x(h)$, at a height h above the instrument was determined. As the ozone concentration $\epsilon(h)\ \frac{\text{cm.O}_3}{\text{km.}}$ is determined by differentiation of the integral curve $x(h)$, $x(h)$ must be determined within 1 to 2%.

In OZONE CHEMISTRY AND TECHNOLOGY;
Advances in Chemistry; American Chemical Society: Washington, DC, 1959.

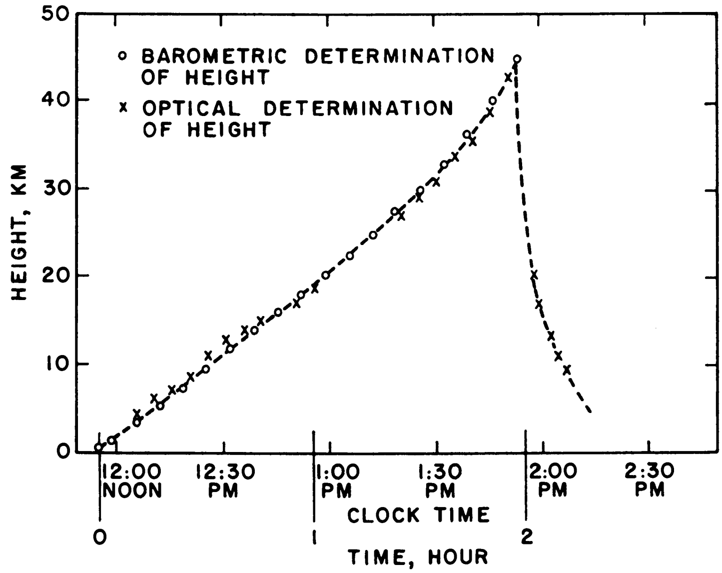

Figure 1. Time-altitude curve for the balloon ascent on May 30, 1956 (7-kg. Darex balloon, 3-kg. spectrograph)

Because of the overlapping Fraunhofer lines in the ultraviolet solar spectrum, the exact distribution of the spectral intensity I (λ, h) is also a function of the optical qualities of the spectrograph itself. The shape of a spectral line is strongly influenced by the width of the slit and the spectral dispersion of the instrument, the degree of uniformity of the light illuminating the slit, and the characteristics and processing of the photographic plate and its position relative to the focal plane. I (λ, h) will therefore differ somewhat for spectrographs of various constructions.

In order to obtain a homogeneous observation material, the spectrographs should be of a standard type which remains optically constant during flight (temperature, etc.). The author has developed a very stable and also very light spectrograph (*6*, *14*). The optics, barograph, and thermograph are mounted in a closed metal case. The apparatus proved to be so stable that even after rough landings it needed no readjustment.

The photometric evaluation of the spectra has to be carried out very carefully. The transmittance of the three-stage filter employed in front of the slit was calibrated by means of a physical method (Fraunhofer diffraction) (*11*, *12*). A special procedure was used for checking the path of the three intensity curves of the spectrum (*6*). As a result of all these precautions, an accuracy to 1.5% for a single measurement of $x(h)$ was obtained. The errors in $\epsilon(h)$ then amount to ± 1, 0.5, and 0.3×10^{-3} cm. of ozone per km. for altitudes of 5, 25, and 30 km., respectively.

Ozone Radio Sonde. Considering the strong fluctuations of the vertical ozone distribution an ozone radio sonde was developed which works simply and supplies the calibration required for homogeneous observation material (*3*, *4*). The radio sonde incorporates the use of filters for the ultraviolet region as in previous constructions (*1*, *19*), and of a selenium photoelement. The light currents are amplified by a three-stage amplifier and their intensities are transmitted to the receiving ground station by an ammeter and a rotating Morse cylinder. This optical method seemed to be the most suitable for an ozone sonde which will be used at various stations where no specialists are available.

If the optical ozone sonde is to work well, the sunlight must be divided in a suitable way into two separated spectral regions: one region influenced by ozone (ultraviolet light) and one not influenced by ozone (blue light). To obtain sufficient measuring precision with a simple instrument, the ozone reading must result from the quotient, ultra-

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violet light/blue light. This means that the two spectral regions must not overlap each other contrary to the previously developed ozone sondes. Some filters now available are acceptable for the ultraviolet light range below 3250 A., which is affected by ozone. They are of sufficient constancy and transmittance (color and interference filters). As regards the spectral transmittance curve, there is an optimum in the region of 3100 A. of the degree of ozone absorption and sunlight intensity. Figure 2 shows various filters for ultraviolet light. The former color filter GG 19 made by Schott is very good. Unfortunately, for the first sondes only filter GG 19+ was available, with a transmittance maximum at a wave length somewhat too long for the desired purposes. Recently an interference edge filter has been developed (Schott, Mainz) showing a very high transmittance maximum and a very abrupt descent at longer wave lengths (Figure 2, No. 4). In the future this filter will be used. The blue light is isolated by combination of filters UG 11 and WG 1 with a transmittance maximum at 3700 A.

The selenium photoelement with a quartz layer is constant and low priced. In the spectral region used for the measurements, its sensitivity varies only very little as compared to photocells with metal layers, where selectivity enters considerably into the measurements. Above the photoelement there is a quartz sphere, the inside of which is covered with a magnesium oxide layer, to render the illumination of the cell independent of the sun's angle of incidence.

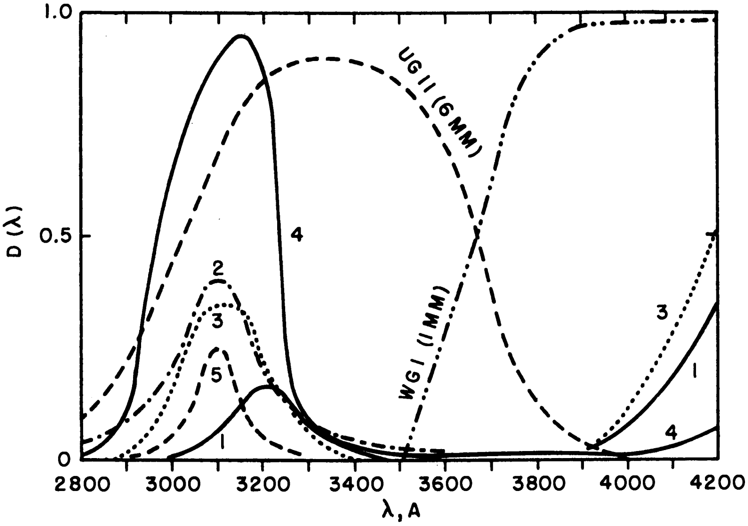

Figure 2. Some optic filters in the ultraviolet region

1. Schott filter GG 19+
2. Interference filter with a 200-A. half width
3. Schott filter GG 19
4. Interference edge filter
5. Interference filter with a 100-A. half width

The light falling on the photoelement is extinguished by a rotating dial at a frequency of 50 sec^{-1}. The photocurrents are amplified 1000 times by the three-stage RC amplifier. For checking the amplifier, a direct voltage impulse (600 $sec.^{-1}$) is amplified at the same time. The impulse generator consists of a Reinartz circuit (0.2 watt) with a frequency of 152 megahertzes. Figure 3 shows the block diagram of the sonde. The filters are mounted on a disk which rotates step by step and closes the electric circuits required for the various measurements. The sequence of the automatic measurements of the sonde is:

1. Intensity of ultraviolet light influenced by ozone
2. Intensity of blue light not influenced by ozone
3. Pressure

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch033

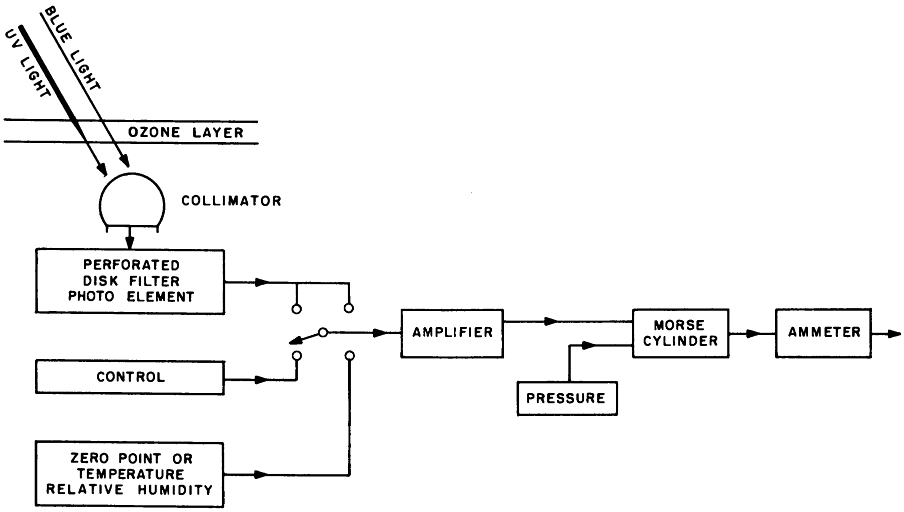

Figure 3. Block diagram of ozone radio sonde

4. Control voltage for checking the amplifier
5. Temperature (may be measured by a Wollaston wire not influenced by radiation)

As one such cycle lasts 20 seconds, an ozone measurement takes place every 200 meters. The sonde weighs 4 kg. and reaches an altitude of 28 to 30 km. with a 2-kg. neoprene balloon.

In order to check the calibration of the ozone sonde, several ascents were made with both the sonde and ultraviolet spectrograph. Figure 4 gives the single measurements of ultraviolet light, etc., for one ascent. In Figure 5 the results obtained by means of the sonde and the spectrograph are compared and found to agree sufficiently. These measurements were made with the inferior ultraviolet filter GG 19+ (Figure

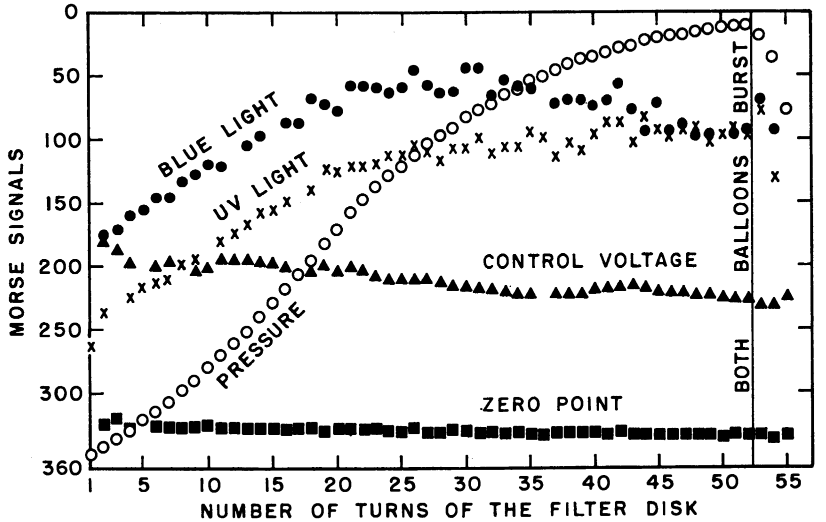

Figure 4. Sonde measurements during one ascent

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch033

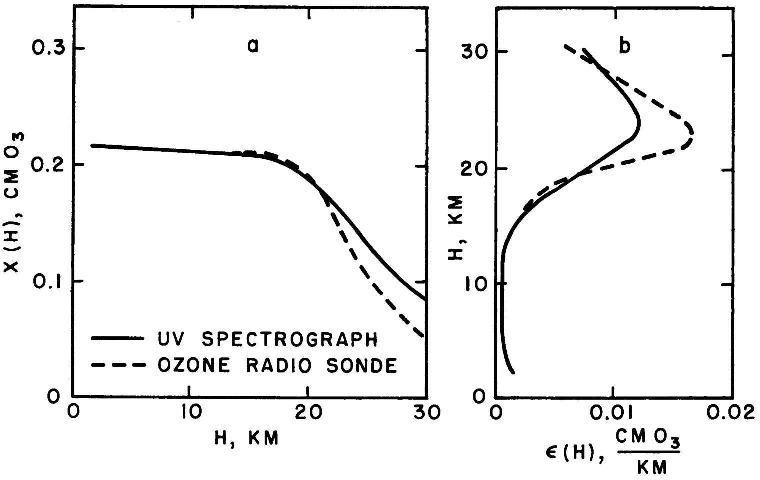

Figure 5. Ozone distribution

2) and the error amounts to 20% of $\epsilon(h)$ for an altitude of 25 km. The interference edge filter (Figure 2, No. 4) reduces this error to about 3%; thus the sonde work as well as the ultraviolet spectrograph, as recent sounding ascents have shown.

Variations of Observed Vertical Ozone Distributions

Seasonal Variations. Figure 6 surveys the integral curves $x(h)$ for various seasons as obtained at Weissenau (48° N) (*9*). The ozone amount between 0 and 20 km. shows particularly strong variations in spring, because of the strong meridional ozone gradient at this altitude. In polar zones there is much ozone below 20 km. in

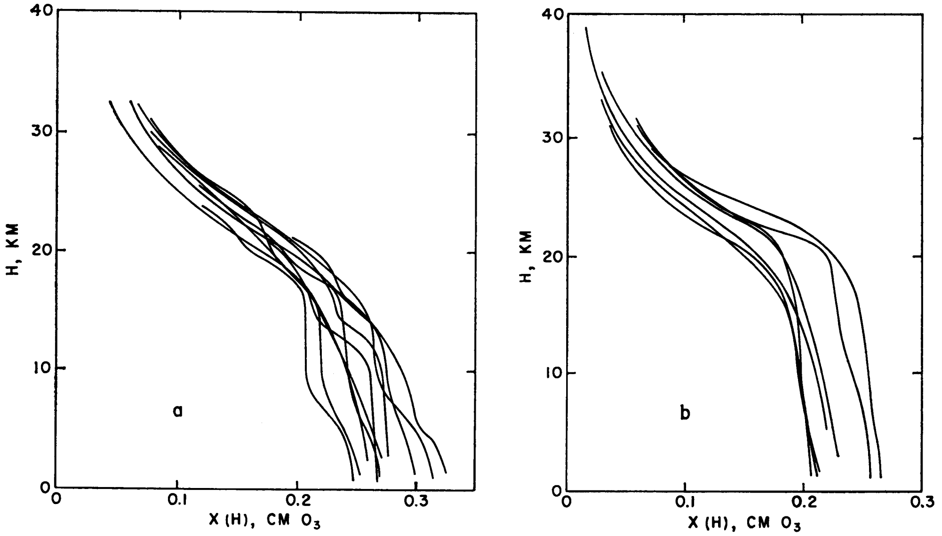

Figure 6. Integral curves *x*(*h*) observed by balloon ascents at Weissenau

a. **Summer and spring**
b. **Autumn and winter**

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch033

spring and summer, while at lower altitudes only very little ozone is found. Meanwhile recent direct measurements with the radioozonsonde made by the author in northern Norway and equatorial Africa confirmed this picture of the meridional variations of ozone gained previously by indirect methods ["Umkehr" effect and moon eclipses (*13*)]. Whether or not the air is rich in ozone depends on whether the air comes from lower or higher latitudes. In autumn these meridional gradients are much weaker.

The balloon ascents permitted, for the first time, determination of the seasonal fluctuations of the ozone content at various heights which produce the seasonal changes of the total ozone amount, with its known maximum in spring in mean and higher latitudes. Figure 7 shows that the annual ozone course differs for the different

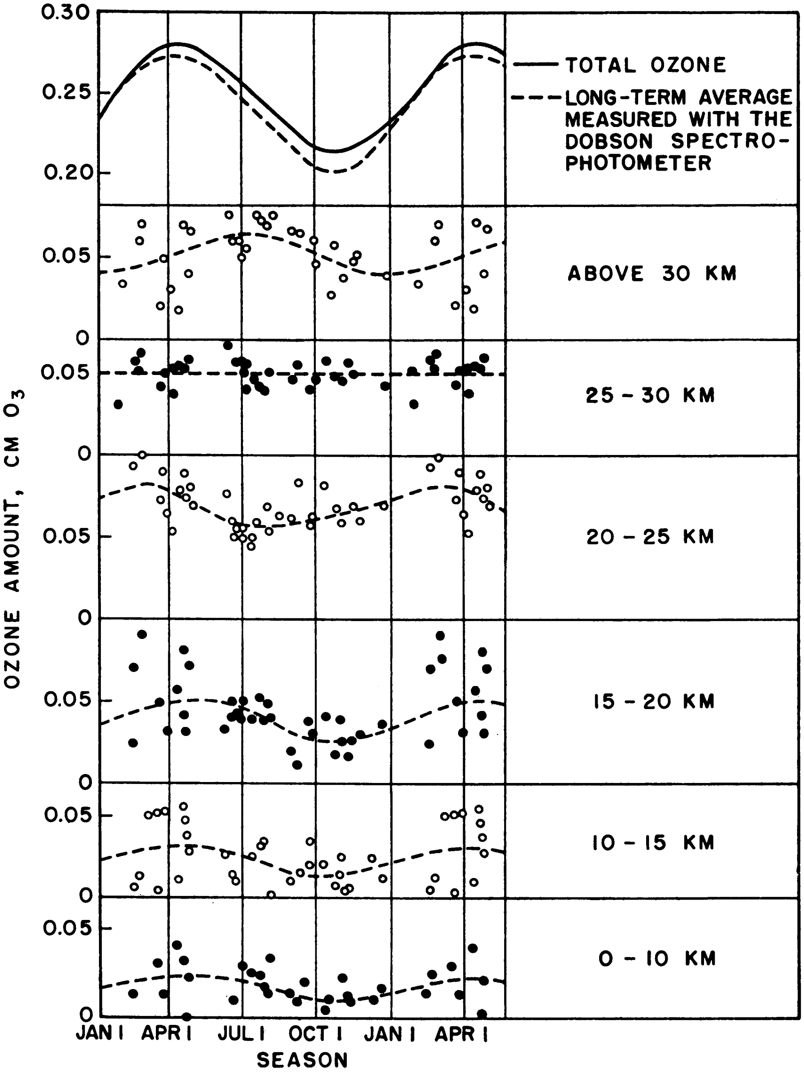

Figure 7. Annual variation of ozone amount at different altitudes at Weissenau

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch033

heights. The summer maximum above 30 km. is caused photochemically (lower mean zenith distance of the sun) and is consistent with the photochemical theory. The spring maximum below 20 km. is mainly caused by ozone-rich air brought down from polar latitudes.

The summer minimum at an altitude between 20 and 25 km. is probably caused by a higher reaching turbulence which brings more ozone down than can be produced photochemically. It is striking that between 25 and 30 km. there is no seasonal variation. Obviously photochemical and atmospheric factors have no great influence in this region or they compensate each other.

Apart from these factors there seems to exist another influence on the annual fluctuations of the ozone; this factor can be seen in Figure 8, which gives the mixing ratio of ozone and air. The curves for January are 1 to 2 km. lower than those for October. Lowering of the stratosphere with a speed of 0.1 mm. per second causes by convergence the new rise of the ozone in November, according to the equation

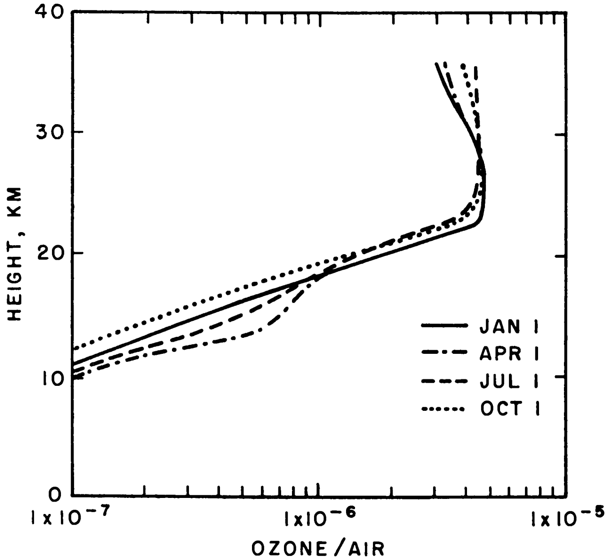

Figure 8. Ozone-air ratio for different seasons

$$\frac{d[O_3]}{dt} = -V_h\left(\frac{d[O_3]}{dh} - \frac{d\rho}{\rho dH}[O_3]\right) \quad (1)$$

where $[O_3]$ is the number of ozone molecules per cubic centimeter, V_h is the vertical speed in the atmosphere, and ρ is the air density.

The last effect shows the importance of the ozone variation in the analysis of world wide circulations in the atmosphere.

Variations of Single Ozone Distributions. According to the dispersion of the points in Figure 7, single ozone distributions show strong variations. The most striking fact is that there are distribution curves with several peaks (Figure 9). While the photochemically caused primary maximum at 23 km. always exists, there is a secondary nonpermanent maximum at 15 km. and a tertiary one at 6 km. Sometimes the maxima are sharply separated from each other; sometimes they are smooth and merge into each other. In rare cases, the first maximum at 23 km. seems to split up into two maxima with a distance in altitude of about 2 km. A more perfected observational method will probably show still more details. However, the three maxima mentioned

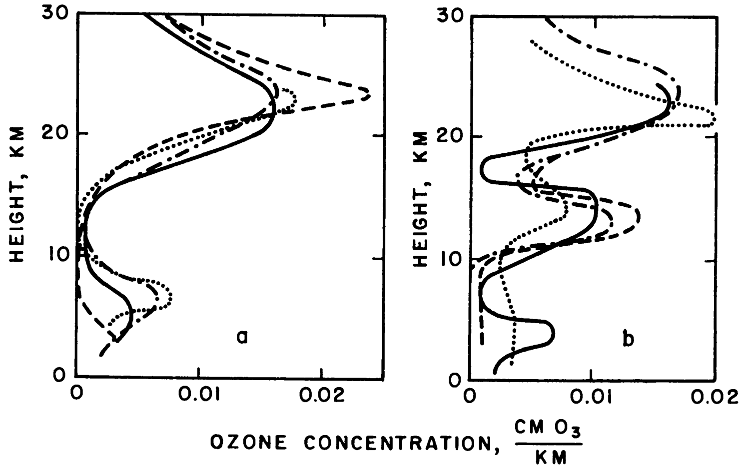

Figure 9. Ozone distribution with several peaks in spring and summer

a. **Air from subtropical latitudes**
b. **Air from polar latitudes**

are often very distinct and are always at the same altitudes, so that we can consider them as one of the main characteristics of the ozone fluctuations. The tertiary maximum lies between the earth and the tropopause and the secondary between the tropopause and the well-known zone of the minimum of the mean wind speed at 20 km., in which the change from west to east winds occurs in summer also.

The tertiary and secondary maxima are probably caused by horizontal transfers of air of different ozone contents (*6*). The secondary maximum at a height of 16 km. can very clearly be attributed to advection. The secondary maximum in spring and summer will always occur when the air in these altitudes originates from polar regions. On the other hand, this maximum does not appear when the air comes from subtropical regions. In autumn, however, the secondary maximum was not observed or was very weak, even when the air came from polar regions (*5, 9*). This corresponds to the above-mentioned very slight meridional gradient of the ozone content at this season. In Figure 9,*a*, it is striking that very little ozone is found in the region between 8 and 16 km. Probably this ozone-poor air streams from the tropical latitudes to higher ones through the gap between the tropical and mean latitude tropopause.

In all cases where there was a secondary ozone maximum an abrupt change of the wind was observed at the same height.

However, not all variations of the horizontal ozone distribution can be attributed to advection of air masses of different ozone content. It is striking that the primary maximum changes its form sometimes: at one time it is sharper, at another smoother. This effect cannot be caused by changes of the photochemical conditions or advection. Figure 10 gives ozone distributions with sharp and smooth maxima measured during one month in autumn in which the advective influence is small. It can be seen that the form of the curves for the ratio of ozone to air is the same, especially for the two ascents to higher altitudes, but that they lie at different heights. These differences must be cause by vertical air motions. It is striking that the curves cross each other at an altitude of 20 km., which means that at this altitude the vertical movements change their signs. The speed of this vertical movement can be estimated, from the intervals between the ascents and from the establishment of the photochemical equilibrium, to be at least 1 to 10 cm. per second.

For the regions of the tertiary and secondary ozone maxima, some ascents showed very short deviation or regionally restricted variations. Very often the same distributions were determined for ascent and descent of the balloon, but in some cases there are clear differences. Figure 11 gives an instructive example. Because of the position on the chart of the individual observations and the estimated error magnitude, the differences between ascent and descent must be considered as real. As shown in Figure 12, the tertiary and secondary maxima have been displaced to contrary directions between ascent and descent. A study of Figure 12 indicates that this variation must also be caused by vertical movements. At an altitude of 9 to 10 km. these movements obviously change their signs. At an altitude of 5 km. there is an upward speed of 10 cm. per second and at 15 km. one of 10 cm. per second, while at altitudes of 9 and 24 km. the vertical movements disappear. On the basis of these observed variations in the vertical ozone distribution it is possible to prove directly the so-called "zero layer" in which the vertical movements often change their signs. According to Figure 10, a second "zero layer" seems to exist in an altitude of 20 km. From recent ozone soundings, a correlation can be found between the circulation in the troposphere and stratosphere. So in the statistical mean the ground air pressure is low if the first ozone maximum is smooth and it is high if the latter is sharp (7). Ozone thus assists research on the dynamic relations between the troposphere and the lower stratosphere.

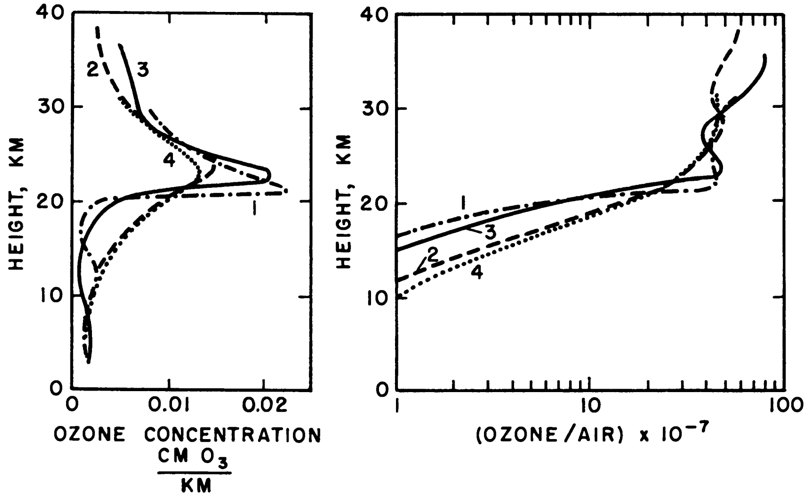

Figure 10. Sharp and smooth primary ozone maxima during ascents at Weissenau in autumn of 1953

1. September 8
2. September 28
3. October 23
4. October 28

Upward and downward movements alter the number of ozone molecules in the volume unit according to Equation 1. It is seen at once that there is no alteration if O_3/ρ is constant—that is, if the ozone shows the same decrease with height as the density of the atmosphere. This is nearly the case in the region between 25 and 35 km. Below 25 km., the ratio O_3/ρ is mean proportional to ρ^{-1} to ρ^{-3}. In this region the ozone amount is increased by a downward current, and vice versa.

If the vertical ozone distribution is lowered between 10 and 20 km. by 1 km., this means—e.g., for autumn—an increase in the total thickness of the layer of 0.013 cm. of ozone, approximately 6%. Table I shows the ratio at different seasons. The last

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch033

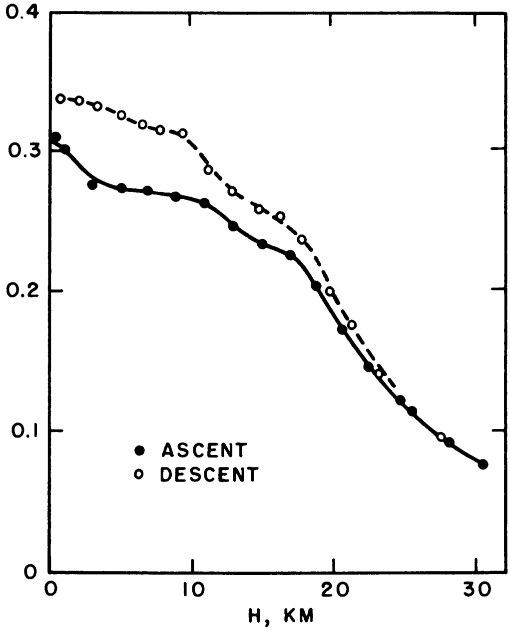

Figure 11. Integral curve $x(h)$ during ascent and descent of balloon at Weissenau on August 1, 1955

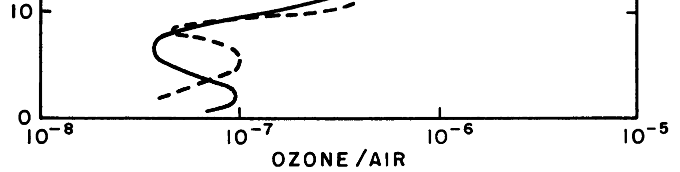

Figure 12. Vertical distribution of ozone-air ratio for measurement in Figure 11

column shows the observed mean interdiurnal fluctuations of the total ozone amount for comparison (*2*). In spring the fluctuations will be due 50% to advection and 50% to vertical movements. In autumn, however, vertical movements will be of most importance. The diurnal mean ozone variations given in Table I indicate a mean amplitude of upward and downward movements of about 1 km. between altitudes of 10 and 20 km.

Table I. Seasonal Variation in Vertical Ozone Distribution in Stratosphere

	Vertical Displacement of Ozone Distribution, Cm. O_3				
	Raised by 1 Km.		Lowered by 1 Km.		
Season	Between 10 and 15 km.	Between 10 and 20 km.	Between 10 and 15 km.	Between 10 and 20 km.	Obsd. fluctuations
Jan. 1	−0.004	−0.014	+0.007	+0.019	±0.014
April 1	−0.008	−0.016	+0.011	+0.021	±0.012
July 1	−0.007	−0.015	+0.009	+0.019	±0.005
Oct. 1	−0.002	−0.009	+0.003	+0.013	±0.007

A further factor influencing the vertical ozone distribution is the vertical turbulence. This is, however, not the cause of fast fluctuations. If, for instance, a considerable change should be caused by turbulence at an altitude of 30 km. against the tendency to re-establish the photochemical equilibrium, the exchange factor must temporarily show a value of 0.1 to 1 gram per cm.-second, which would be 10 to 100 times larger than the mean value at this altitude.

Ozone Balance

The vertical turbulence, on the other hand, has a considerable influence on the mean ozone distribution below 20 km. According to the photochemical theory, there should be no ozone below 10 to 15 km., because at 5 km. only about one ozonizing light quantum per cc.-second is absorbed (*8*). As cosmic radiation and electric discharges produce far too little ozone (*6*), tropospheric ozone of the amount of 1 to 4×10^{-3} cm. of ozone per km. must be brought down from the photochemical layer by vertical mixing processes (*16*), whereby it is continually destroyed on the ground and in lower air layers. This turbulent ozone stream is given by

$$O_3 = \frac{N_A}{\rho_0}\left[A(h)\,\frac{d\,\frac{[O_3]}{[M]}}{dh}\right] \qquad (2)$$

where

$[M]$ is the numbe of air molecules per cc.
$A(h)$ is the so-called "exchange factor"
N_A is Avogadro's number
ρ_0 is the density of air (STP)

From the observed mean tropospheric ozone distribution it follows that (*5, 6*)

$$O_3 = 1.10^{11}\,\frac{O_3 \text{ molecules}}{\text{sq. cm.-second}}$$

The same value for ozone destruction resulted from ozone fluctuations near the ground (*6, 18*). On the basis of the deviations in vertical ozone distribution from the photochemically calculated distribution there also results a value of 1.10^{11} cm. of ozone per sq. cm.-second for the chemical regeneration (*6*). Therefore, the ozone balance seems to be maintained.

All over the world 10^9 metric tons of ozone per year are destroyed and photochemically regenerated. Without the photochemical regeneration, the ozone amount would decrease to one tenth of its present value within 3 years. Atmospheric oxygen will thus go through the ozonized state in 10^6 years. This fact shows the importance

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which the ozone may have had in the creation of the terrestrial atmosphere in its present state.

Conclusions

The results of limited ozone measurements by balloon ascents allow a far more detailed analysis of the factors influencing ozone distribution than the measurements of the total ozone amount made over many years at various locations by the Dobson instrument.

Some fundamental relations between ozone distribution and air movements have been obtained by means of balloon ascents. The exact analysis of the fluctuations of total ozone amount, in conjunction with wind and temperature observations, permits something more definite to be said about ozone fluctuations at greater altitudes and the air movements connected with them. The course of the total ozone amount from February 27 to March 19 is an example of this (*15*). The strong influx of warm air on February 19 to 28, 1956, into layers below 10 km. caused a rapid decrease in the ozone amount; accordingly, the warm air was of a subtropical character with little ozone. The increase on March 8 up to an amount of 0.335 cm. of ozone on March 12 coincided with a condition of mostly northern winds at all altitudes for several days. The increase was caused by the influx of air rich in ozone—that is, of polar air—below 20 km. (secondary and tertiary maxima). When on March 12 the wind changed in the 100-mb region from NNE to WSW, the ozone amount began to decrease; this means that the secondary maximum was reduced by the influence of subtropical air. This had been happening for 3 days before the tropospheric influx of warm air on March 15, by which the tropospheric ozone was also reduced. This example shows how changes of the ozone and thereby of the weather conditions make their way from higher to lower altitudes. A further striking fact is an abnormally quick increase on the morning of March 1, which can hardly be accounted for by advection only. Probably a strong local lowering of the atmosphere below 20 km. was also influential.

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Vertical Ozone Distributions from Absorption and Radiation by Ozone

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The fundamental innovation of the VODARO technique (vertical ozone distributions from absorption and radiation by ozone) is application of infrared observations to determination of the vertical distribution of ozone. As with most new developments, the initial discovery must be followed by a period of modifications and testing before anything like perfection and wide usage can be expected. This is a summary of one year's data applied to computations of temperature changes in the stratosphere.

The first widely distributed publication which announced the use of infrared methods in determining ozone distributions (*3–5*) appeared in 1956, culminating a year-long study of data that had been collected at the Atmospheric Research Observatory since its establishment in 1953. Shortly after the appearance of this announcement, the present authors were informed that Goody of the University of London was working independently on a similar scheme (*6*).

There were several substantial differences between the methods developed in London and in Flagstaff, but the important feature of both was that infrared observations—in particular, measurements of emission by the ozone in the 9.6-micron band—were utilized. These methods attracted so much interest that the International Ozone Committee of the World Meteorological Organization appointed a panel on infrared methods, whose function was the recommendation of standardized procedures for more general use of the VODARO technique, in particular for the International Geophysical Year, combining the developments arising from the work done in Flagstaff and in London. This panel met in London early in 1957. Those participating were R. M. Goody (convener) and W. T. Roach, University of London; M. V. Migeotte, E. Vigroux, and H. A. Gebbie, University of Liége; H. K. Paetzold, Max Planck Institute, Weissenau; C. D. Walshaw, Oxford University; L. D. Kaplan, Princeton University; and E. S. Epstein, representing A. Adel.

VODARO measurements, in addition to those being carried out in this country and in England, are under way at Arosa, Switzerland, under the direction of Migeotte; and Paetzold is planning installation of equipment at Weissenau, Germany, where he will be able to make direct comparisons among the results of VODARO, umkehr measurements, and direct balloon observations of the vertical ozone observations. These comparisons are, of course, essential, and the importance of Paetzold's efforts along this line cannot be minimized.

Nature of the VODARO Method

Several parameters are observed: total amount of ozone (Dobson spectrophotometer), absorption in the 9.6-micron band, and emission from the ozone at several different zenith distances. The value of each of these observations may be expressed as the sum of contributions from the different layers of the ozone. Total amount of ozone is, of course, merely the sum of the amounts in each layer; the infrared absorption, however, is pressure-dependent and a pressure-dependence term must be introduced. The sums are somewhat more complicated for the emission, but still are easily calculated. The problem is to find a distribution of ozone which will give rise to the observed parameters. The technique for doing this is but a numerical exercise; several methods have been used (*2*).

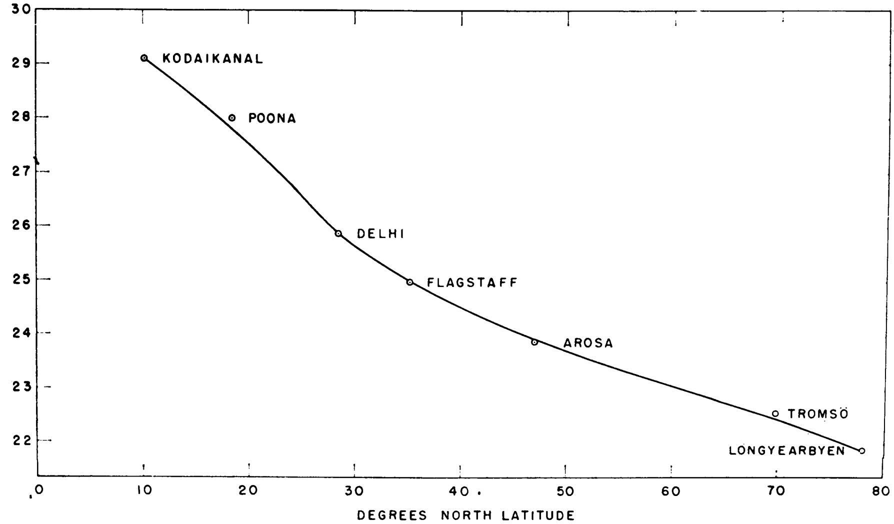

Figure 1. Height of center of gravity of ozone as a function of latitude

All points other than that for Flagstaff are results of umkehr observations.

The results presented here were achieved prior to the London meeting and therefore represent a slightly less advanced technique. Nevertheless, all evidence points to the conclusion that the required refinements in methods of computation will largely cancel out one another, and that the ozone distributions presented here are valid. Part of the evidence comes from comparisons of results reported here with distributions computed by others using different methods in other parts of the world. For example, if the mean height of the center of gravity of ozone is plotted against latitude, the point representing the Flagstaff results falls almost precisely on a curve drawn through the results of umkehr determinations made elsewhere (Figure 1). Also, the manner in which the amounts of ozone at various heights vary with the seasons shows that the Flagstaff results are in substantial agreement with those achieved on the basis of balloon assents by Paetzold (*7*), working in Germany (*4*).

In Flagstaff, sets of data sufficient for determining ozone distributions have been observed on a routine basis since August 1954. The present results are based on

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Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch034

observations made during 1955, on 197 different days (*1*). For each day the vertical distribution of ozone was computed, representing conditions as they existed at approximately local noon. Each set of observations requires approximately one hour's observing time. A picture of the over-all behavior of the ozone during the year may be gleaned from Figure 2. Isopleths of ozone density for mean monthly conditions have been drawn and are labeled in units of thousandths of centimeters of ozone reduced to standard temperature and pressure, per kilometer of air. The immediately obvious features are the shift with season of the height of the maximum concentration of ozone, from about 18 km. late in the winter, to about 28 km. in late summer, and the sharp decrease in densities between spring and summer at low levels.

One effect of the presence of ozone in the atmosphere is the existence of an additional mechanism for the exchange of energy among the earth's surface, the various portions of the atmosphere, and space. This mechanism is the radiative transfer of thermal energy in the 9.6-micron band of ozone. Given the distributions of ozone and of temperature in the atmosphere, it is possible to compute the divergence of the flux of radiation, and from this the rate of loss, or gain, of energy, or of temperature, for any point in the atmosphere. In the past, computations of this nature were, of necessity, based on mean distributions of ozone, leading to results of somewhat vague significance. The most recent computations of this nature are those of Plass (*8*), who employed three model ozone distributions. His results, and those presented here, are similar, and the methods by which the computations were performed differ in only minor details. The important difference is that the results presented here refer to a specific place at specific times (*2*).

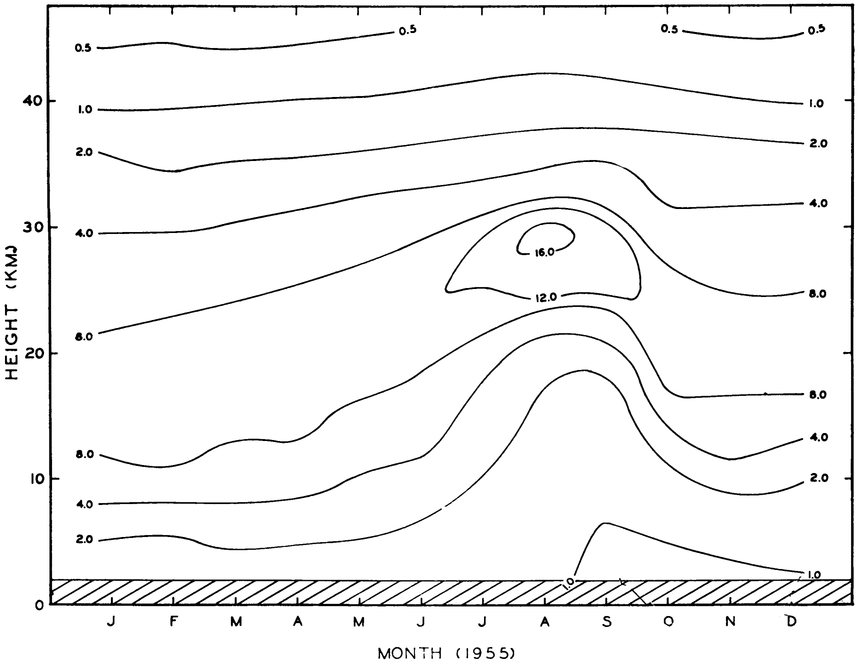

Figure 2. Isopleths of ozone density for 1955

Isopleths are drawn to fit monthly mean values and labeled in units of 10^{-3} cm. of ozone NTP per km. of air.

Results at Flagstaff

For each month of 1955, the mean ozone distribution as determined by application of the VODARO technique, along with the mean temperature conditions for those months, was utilized to compute the rates of temperature change due to radiation in the 9.6-micron ozone band. The results are shown in Figure 3, where the isopleths are labeled in units of degrees absolute per day. For the most part, the pattern remains fairly constant throughout the year. Below 5 or 6 km. there is generally very slight radiational cooling; above 27 to 30 km. there is considerably more intense cooling, with rates exceeding 3° abs. per day during the summer near 45 km. Plass's results indicate that the rate of cooling continues to increase with greater elevation.

Between these two zones of cooling is a zone of heating, and in this zone the most pronounced seasonal variations occur. The height of the region of maximum heating varies from about 18 km. in the early spring to almost 25 km. in the late summer. Similarly, the maximum rate of heating varies from as little as about 0.13° per day in the winter to more than 1° per day in the summer. A seasonal variation can be discerned in the height of the isopleth of zero temperature change between the zones of warming and stratospheric cooling.

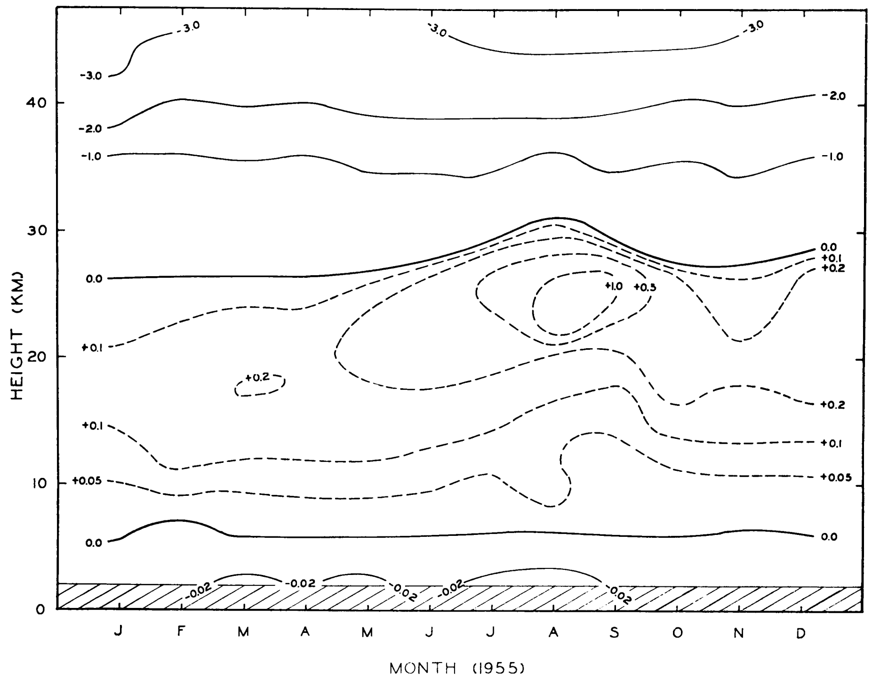

Figure 3. Lines of equal rate of change of temperature due to radiation in 9.6-micron ozone band

Isopleths are drawn to fit monthly mean values and labeled in units of K/day

The relatively intense heating which takes place near 25 km. in the summer is an unanticipated feature of these results. But with hindsight it is easily understood. First consider the distribution of ozone observed during the summer (Figure 2). There was very little ozone at low levels, and a very sharp maximum concentration of ozone just below 30 km. Thus, the thermal emissions from the earth, at a time when the surface of the earth is warmest, could pass almost unabsorbed through the lowest 20

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km. or so of the atmosphere, but only to be absorbed strongly by the bulk of the ozone between 25 and 30 km., where the lesser density of the air means that a given increment of energy has a greater effect in terms of temperature.

In any case, the thermal effects of ozone in the stratosphere, even at heights as low as 20 km., cannot be neglected. The ozone is by all reasonable standards only a very minor constituent of the atmosphere, but we may be still only on the verge of discovering the full importance of its role in the physics of the atmosphere. To this end continued observations and new methods of attack are of greater importance than ever.

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Atmospheric Ozone and Its Relation to Meteorological Conditions

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Atmospheric ozone in Tokyo has been determined at the Meteorological Research Institute by Stair's method. The principal apparatus consisted of a cadmium phototube and a glass filter. The instrumental calibration for determining the total amount of ozone was made through simultaneous observations with Dobson's spectrophotometer. Using the observed data of the day-to-day variations in atmospheric ozone concentration, the relation of the ozone to the meteorological conditions at higher levels and to the location of jet streams was determined. The range of ozone concentration in Tokyo coincides closely with that observed in Washington, D. C., and other cities in the temperate zone.

The determination of atmospheric ozone in Tokyo has been carried on at the Meteorological Research Institute (35° 42′N, 139° 39′E) by using Stair's method (*5*). The principal apparatus consists of a cadmium phototube which is sensitive to the spectral ultraviolet of wave length shorter than 3250 A. and a glass filter which is transparent to radiant energy of wave lengths longer than 3000 A. (Figure 1). The sensitivity of the phototube has been checked several times with an incandescent electric lamp (in a quartz glass envelope) of known color temperature and three glass filters having different spectral transmittances. The spectral distribution of the transmittance of each filter has been examined repeatedly with a Beckman monochrometer. There was no appreciable change in the sensitivity of the phototube during the period of observation.

The total transmittance of the filter to the incident solar radiation changes according to the amount of ozone and the optical depth of the air mass. The instrumental calibration for determining the total amount of ozone was made through simultaneous observations with Dobson's spectrophotometer. The results of these calibrations are shown in Figure 2, in which the amount of ozone is expressed in 10^{-3} cm.

The total amount of ozone measured during the period from June 1953 to September 1955 is given in Figure 3. As shown in Figure 3, there is a maximum amount of ozone in the spring and a minimum amount in the fall. The range of ozone concentration in Tokyo obtained by Stair's method coincides closely with that observed in Washington, D. C., and other places in the temperate zone.

Recently, Normand (*3*) and the present authors (*2*) studied the relation between

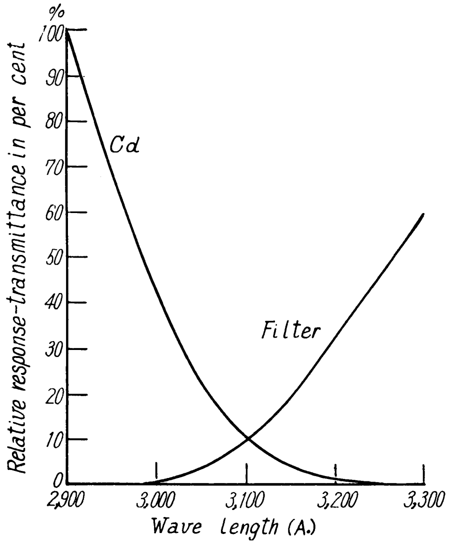

Figure 1. Sensitivity of experimental apparatus

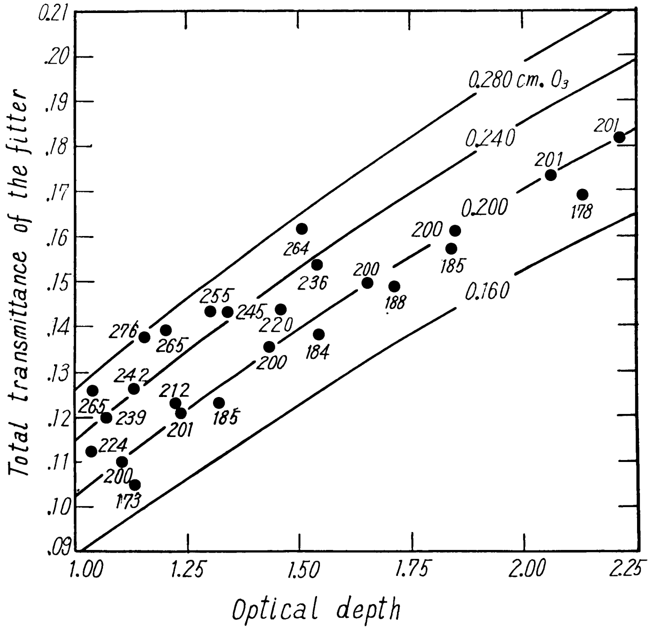

Figure 2. Total amount of ozone as determined by instrumental calibration

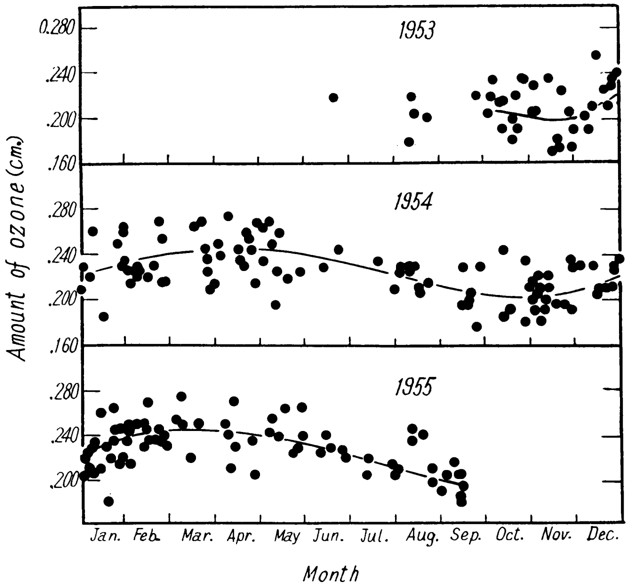

Figure 3. Total amount of ozone measured during period from June 1953 to September 1955

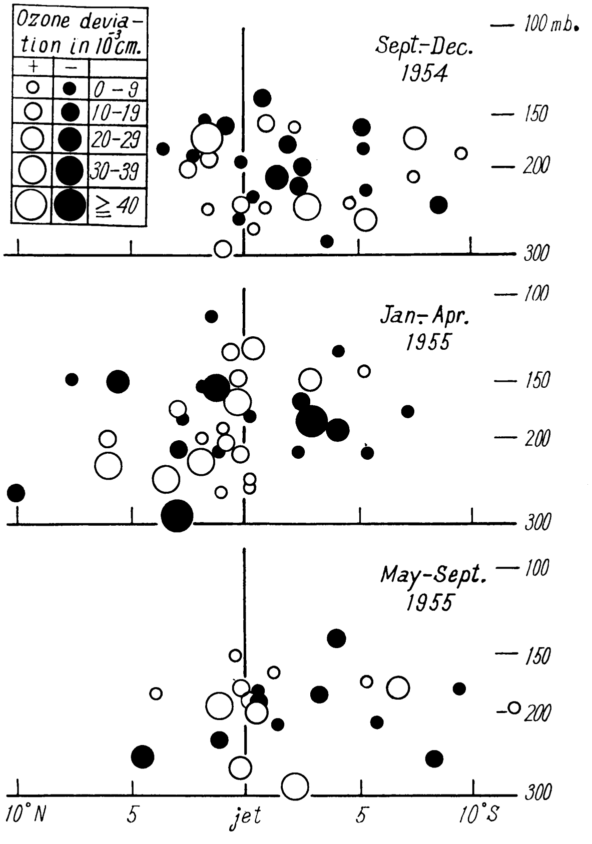

Figure 4. Relation between ozone and location of jet streams

the day-to-day variation in ozone concentration and the meteorological conditions at higher levels. The ozone concentration increases when a trough in the upper layer passes over an observation point; it decreases by the passage of a ridge. Langlo (*1*) pointed out that a sudden change in ozone concentration often occurs between the latitudes 25° and 45°. Because the polar and tropical air masses are in contact in this zone, it is expected that the ozone concentration will be larger on the northern side of the polar front and smaller on its southern side. Ramanathan (*4*) suggested that the sudden change in concentration in this area might be related to the atmospheric jet stream.

Using the observed data of the day-to-day variations in the atmospheric ozone in Tokyo, the relation between the ozone and the location of jet streams was determined. The results showed that there is no correlation between the sense of variation in ozone concentration and the position of jet stream in relation to the observed point. However, great deviations in ozone concentrations occurred chiefly in the region below the axis of a jet stream (Figure 4).

Figure 5 shows the topographic relation between the ozone concentration which was observed on the ground and the air pressure at 300 millibars. Generally speaking, the maximum amount of ozone is observed near and south of the middle part of troughs; this may be attributed to the decline of the vertical movement in that region.

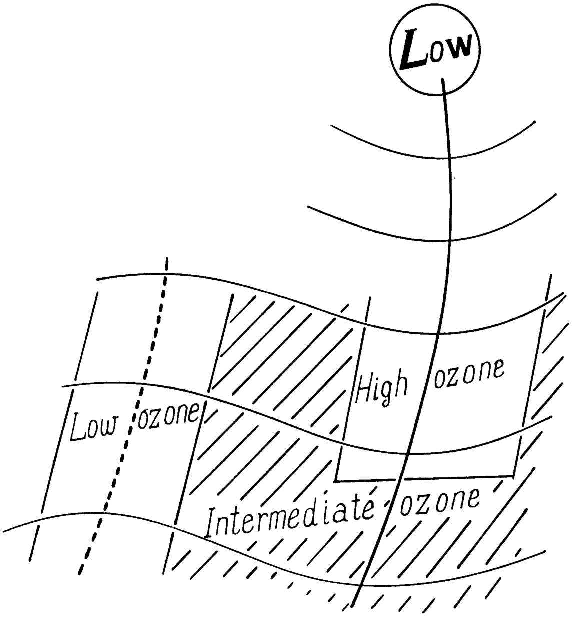

Figure 5. Topographic relation between ozone on ground and air pressure at 300 millibars

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Ozone in Los Angeles Atmosphere

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Shortly after World War II the presence of more than the usual amount of oxidant which arises principally from ozone in natural air was suspected of existing in the Los Angeles atmosphere. The cracking of stressed rubber was an early symptom. Chemical measurements with phenolphthalin and potassium iodide reagents confirmed oxidant concentrations up to 100 p.p.h.m., especially on days associated with other manifestations of smog—namely, eye irritation, crop damage, and reduced visibility. Ultraviolet absorption data in 1952 confirmed the suspicion that ozone was a primary component of the total oxidant. Laboratory studies demonstrated that trace amounts of organics and nitrogen dioxide produced ozone photochemically in chemical systems closely simulating atmospheric conditions. Theoretical studies have indicated that certain primary photochemical processes in polluted atmospheres can give rise to observed oxidant values.

Man's interest in atmospheric ozone began more than 100 years ago when C. F. Schönbein, who was responsible for its discovery, claimed its presence in the normal earth's atmosphere (*34*). Schönbein's ozonometer consisted of paper soaked in potassium iodide and starch; for years data thus obtained were subject to the criticism that the chemical reaction used was not specific to ozone.

However, it was not until some 80 years later that another oxidant, nitrogen dioxide, was identified in the atmosphere (*10, 31*). Furthermore, these findings cast doubt on the previously obtained ozone data. Paneth undertook to clarify the situation (*24*), since some chemists were inclined to deny altogether the presence of ozone in the atmosphere. He set out to make the old chemical method (*17, 40*) more reliable and reported ozone and nitrogen dioxide values varying from 0 to 3 p.p.h.m. (*24, 25*) by volume.

The first undisputed determinations of ozone in the earth's atmosphere were made by spectroscopists studying the radiation from the sun and the stars (*7, 9*). It was soon recognized that most of the ozone thus measured was concentrated in the higher atmosphere (*39*). Starting in 1931, several investigators using the characteristic strong absorption of ozone in the ultraviolet (2200 to 3000 A.) with artificial light sources over long optical paths made direct measurements of the ozone content near the earth (*2–4, 6, 11, 12, 38*). By 1941 the chemical and spectroscopic methods agreed to values of 0 to 3 p.p.h.m. as the normal but variable concentration of ozone in the lower atmos-

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phere. At times, and in some areas, there occurred concentrations of nitrogen dioxide from 0 to 2 p.p.h.m.

The identification and measurement of ozone in the Los Angeles smog have had a history not unlike those of the early days of ozone in normal atmospheres. The early clue to the presence of more than ordinary levels of ozone or oxidant was given by the excessive cracking of stressed rubber in the Los Angeles Basin as compared to other locations. Haagen-Smit followed this lead and, using the rubber cracking (*1*) and phenolphthalin reagent (*22*) methods, made estimates of ozone and oxidant during smog attacks (*13*). His data indicated oxidant concentrations in the range of 0 to 100 p.p.h.m. Littman, using a modification of the classical potassium iodide technique (*19*), reported oxidant values of 0 to 60 p.p.h.m. He also used the method of Paneth (*24*) to determine the ozone in a smog sample and recently reported his results (*21*).

Regener and his coworkers, in collaboration with Littman, obtained evidence of ozone in smog by its absorption in the ultraviolet (2600 to 3200 A.) using photographic spectrometry (*27*). Renzetti, using photoelectric spectrometry in the ultraviolet based on the same principle as Regener's instrument (*26*), reported values for ozone up to 35 p.p.h.m. (*29*).

These investigations gave qualitative evidence of the presence of ozone in smoggy atmosphere in Los Angeles. The concentrations certainly have exceeded those of normal clean air, and may at times have reached 100 p.p.h.m.

However, the quantitative picture is still far from clear. The different responses of the various techniques suggested the need for an intensive intercomparative study of the analytical methods, as well as extensive simultaneous determinations of oxidant in the atmosphere with as many of these methods as possible.

Methods of Analysis

The problem of identifying and measuring ozone in the complex gaseous-aerosol mixture which is smog is formidable. There are such gases present as nitric oxide, nitrogen dioxide, sulfur dioxide, hydrocarbon vapors from methane up to probably xylene, plus such partial oxidation products as aldehydes, ketones, and acids. The search for a method of high specificity has been an intensive one.

The very clue which first stimulated the search for ozone—namely, cracking of stressed rubber—was developed by Haagen-Smit into a useful method (*1*). Specially treated rubber is cut into rectangular strips 50 × 8 × 1.5 mm., which are bent into a loop, then placed in a tube 13 mm. in diameter. A flow rate of approximately 1 liter per minute of the air sample is maintained past the strip. A calibration curve, using known amounts of ozone in air versus time to initial cracking, must be developed for each piece of stock rubber. This technique is currently in use in Los Angeles in monitoring ozone in smog for the purpose of calling "alerts" when the ozone concentration exceeds 50 p.p.h.m. Values up to 100 p.p.h.m. have been reported by this method when the rubber has been calibrated with a stream of ozone in air, standardized with a 2% potassium iodide (in distilled water) midget impinger bubbler system. An accuracy of ±10% is claimed for this method. Figure 1 shows a photograph of this apparatus.

Haagen-Smit introduced a method (*22*) for measuring oxidant in the atmosphere after his laboratory investigations suggested that the presence of oxidants other than ozone should be found in smog. This method is based on the oxidation of phenolphthalin ($C_{20}H_{16}O_4$) to phenolphthalein ($C_{20}H_{14}O_4$) and subsequent colorimetric determination of the oxidant in the air sample. For concentration ranges of interest, sampling of 1 liter per minute for 10 minutes gives adequate color development. The calibration curve is derived by obtaining absorbance versus known concentrations of aqueous hydrogen peroxide. The semiautomatic instrument using this method is shown in Figure 2. Values up to 110 p.p.h.m. of oxidant are reported as hydrogen peroxide. However, when this system is standardized with an ozone-in-air stream, which in turn is monitored with 2% potassium iodide, the response to atmospheric oxidant is cut down to 0.33 to 0.50 of the peroxide determination.

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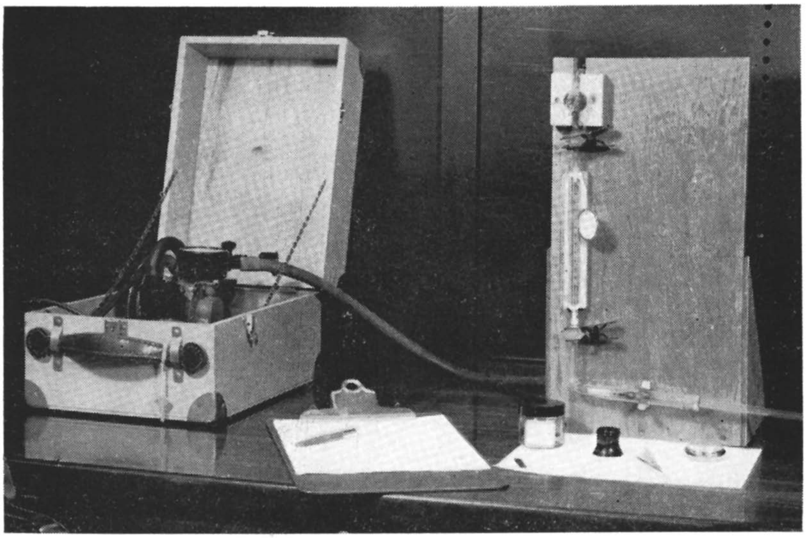

Figure 1. Ozone rubber cracking apparatus

Littman (*19*) developed a continuous automatic oxidant recorder based on the use of 20% potassium iodide in neutral (pH = 7) buffered solution, as shown in Figure 3. The calibration is based on the assumption that the iodine is released in stoichiometric proportion to the amount of ozone according to the equation

$$O_3 + 2KI + H_2O \rightleftharpoons O_2 + I_2 + 2KOH \quad (1)$$

Littman has obtained values of 0 to 60 p.p.h.m. of oxidant as ozone, assuming the above stoichiometry, in Los Angeles smog.

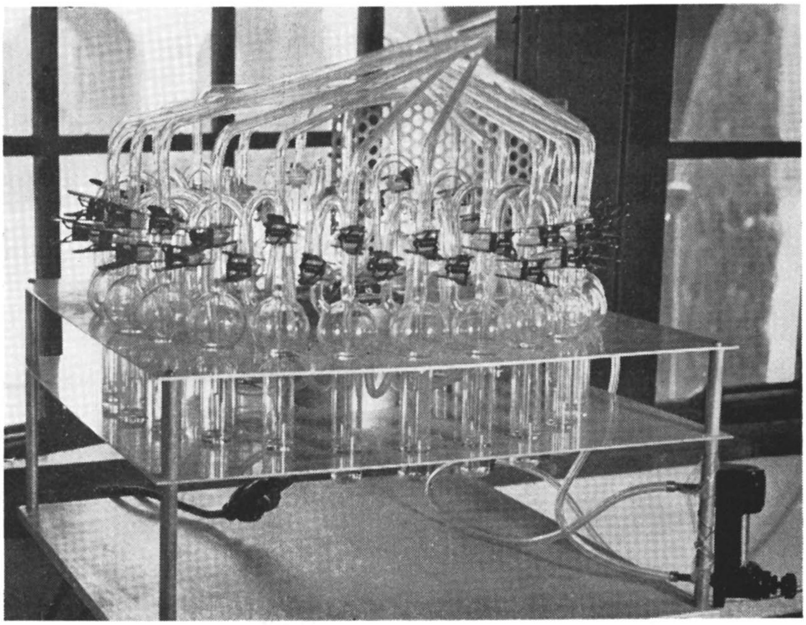

Figure 2. Phenolphthalin oxidant apparatus

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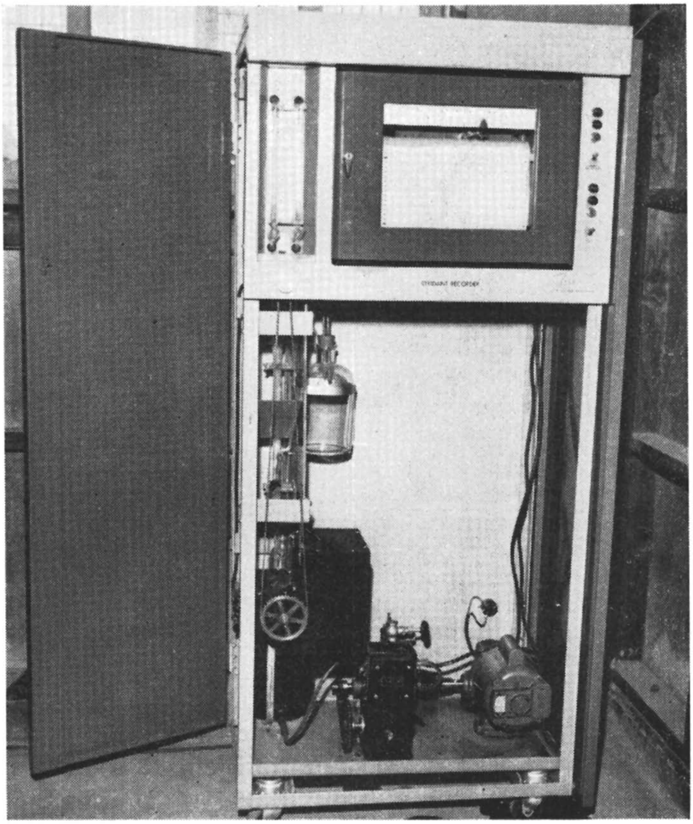

Figure 3. Potassium iodide oxidant recorder

Renzetti (*29*) developed an automatic continuous ozone recorder based on the previous work of Regener and of Stair (*35*) (Figures 4 and 5). This method used the absorption data of Vigroux (*41*) for the wave lengths 265, 280, and 313 mμ in the computation of ozone concentrations according to the formula

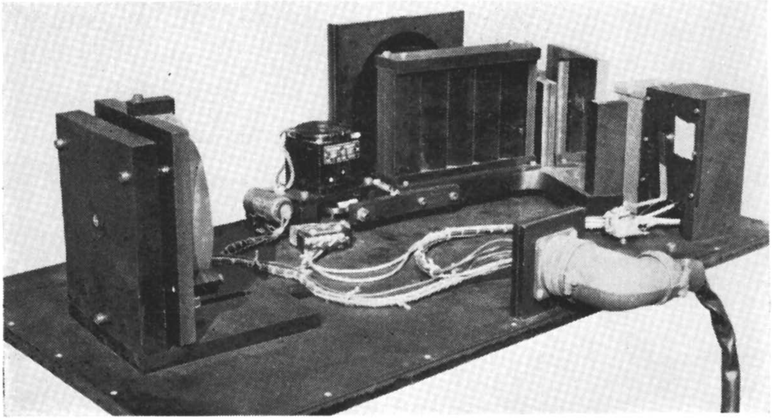

Figure 4. Optical system of spectrometer

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Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch036

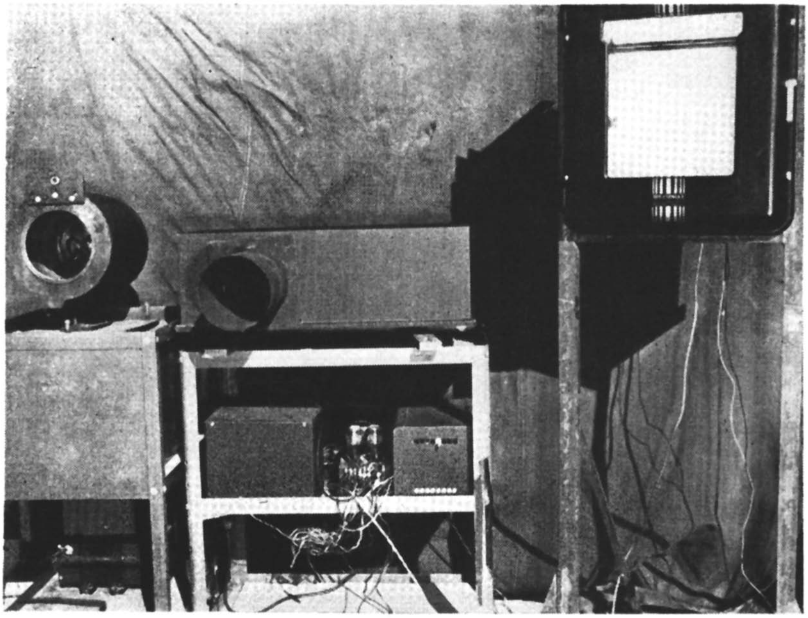

Figure 5. Ozone ultraviolet spectrometer

$$C_t - C_O = \frac{\log\left[\frac{I^0{}_{\lambda_{265}}}{I^0{}_{\lambda_{313}}} \cdot \frac{I_{\lambda_{313}}}{I_{\lambda_{265}}}\right]}{s(\alpha_{\lambda_1} - \alpha_{\lambda_2})} \qquad (2)$$

where C_O = concentration of ozone in atmosphere at night, which was always approximately zero (say 2 p.p.h.m.).

s = optical path

α_{λ_1} = 0.123 km.$^{-1}$ p.p.h.m.$^{-1}$ where λ_1 = 265 mμ

α_{λ_2} = 0.00087 km.$^{-1}$ p.p.h.m.$^{-1}$ where λ_2 = 313 mμ

$\frac{I^0{}_{\lambda_1}}{I^0{}_{\lambda_2}}$ = ratio of received radiation intensities at reference condition (C_O = 2 p.p.h.m.)

$\frac{I_{\lambda_2}}{I_{\lambda_1}}$ = ratio of received radiation intensities at time t

c = concentration of ozone at time t

A similar procedure was used for other pairs of ratios involving I_{λ_1} and I_{λ_3} where $\lambda_3 = 280$ mμ.

Recently the Franklin Institute has set up a long-path infrared spectrometer (up to 500 meters) in Los Angeles to determine, among other studies, the ozone concentrations in smog by its absorption at the 9.6-micron band.

Atmospheric Oxidant and Ozone Data

Haagen-Smit (*13*) established the pattern of the diurnal variation of oxidants and ozone early in the smog history with both the rubber cracking and phenolphthalin measurements. The characteristic sharp rise in the morning, a peak in the middle of the day, a slower decay in the afternoon, and almost zero oxidant at night (average of 2 p.p.h.m.) were the essential features. The phenolphthalin oxidant values as hydrogen peroxide were generally higher than the corresponding ozone by rubber cracking. The phenolphthalin data since August 1953 for Pasadena have been pub-

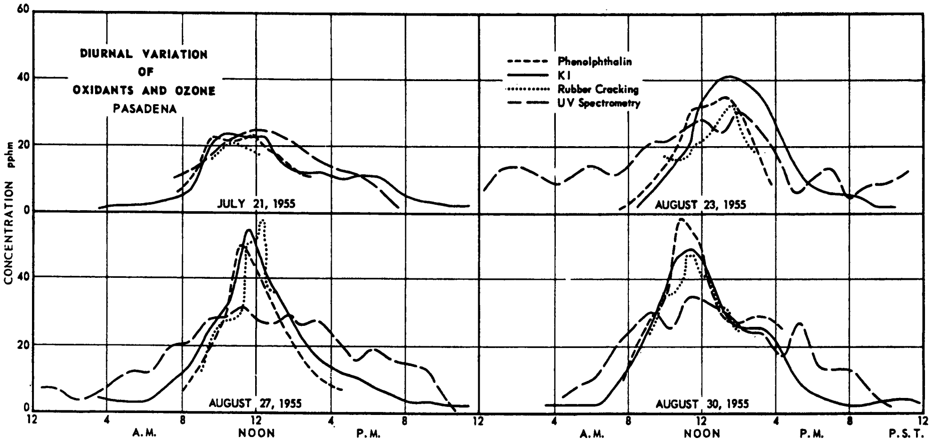

Figure 6. Diurnal variation of oxidants and ozone at Pasadena

lished in the progress reports of the Air Pollution Foundation, the last of which (*8*) shows results through August 1955. As indicated previously, phenolphthalin oxidant as hydrogen peroxide reached a peak of 110 p.p.h.m. in 1955.

Littman obtained data at Pasadena on atmospheric oxidant with the continuous automatic potassium iodide recorder. He reports (*21*) some data that show essentially identical response to atmospheric oxidant with the rubber cracking method and the 20% neutral buffered potassium iodide recorder. Although his report does not so state, it is assumed that his rubber stock was calibrated with an ozone-in-air stream monitored by 2% potassium iodide as outlined by Haagen-Smit. Littman reports further that, in collaboration with Regener, agreement on the average to within 10% was obtained in atmospheric oxidant measurements with his potassium iodide recorder and long-path ultraviolet absorption spectrometry. Finally, he used the method of Paneth (*25*) and identified ozone by its ultraviolet absorption spectrum up to 45% of the original atmosperic oxidant (*21*).

Renzetti (*30*) has recently reported the results of an extensive comparative study of oxidants and ozone in Pasadena obtained during the smog season of 1955. Four techniques were applied simultaneously: phenolphthalin, rubber cracking, 20% potassium iodide, and ultraviolet absorption. Figure 6 presents data of four typical smog days, whereas Figure 7 presents averages over extended periods.

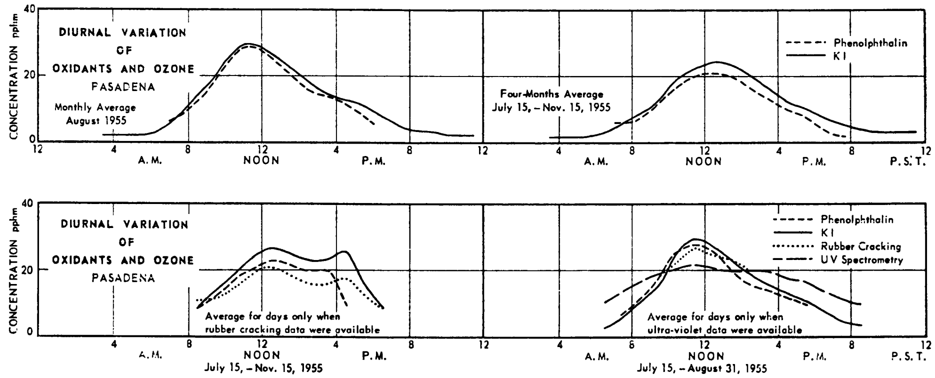

Figure 7. Diurnal variation of oxidants and ozone at Pasadena over extended periods

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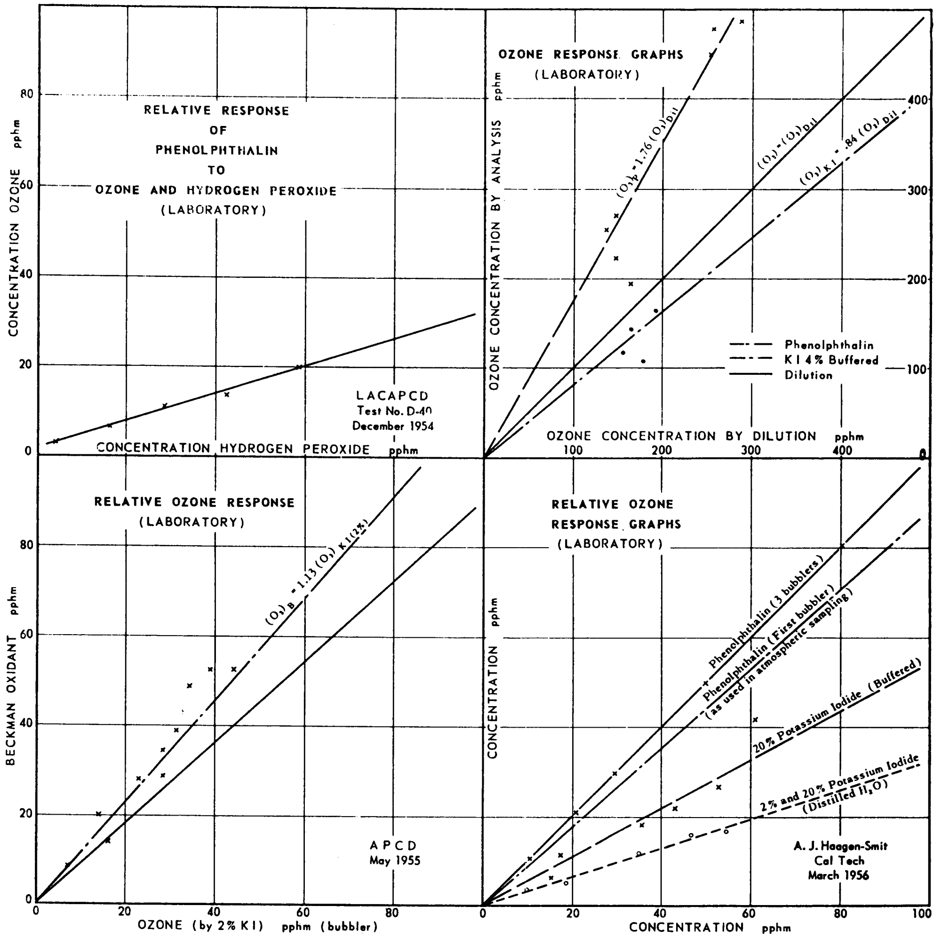

Figure 8. Relative response of various reagents to ozone

For this experiment the three chemical systems were standardized to a 2% potassium iodide–monitored, ozone-in-air stream. Figure 8 presents the calibration curves used to calculate the atmospheric data. In the case of phenolphthalin, a somewhat arbitrary ratio of 2 was used for the relation, $\frac{\text{oxidant as } H_2O_2}{\text{oxidant as } O_3}$. Unpublished data obtained recently by both R. A. Austin Chemical Laboratory, Pasadena, and the Armour Research Foundation, Chicago, would indicate at least 2.2 for this ratio. The absorption coefficients used in the ultraviolet determinations are 10 to 20% low according to a recent report (*16*).

Recently, the Air Pollution Foundation sponsored additional laboratory studies stimulated by the arrival of an Ehmert ozone instrument (*5*). The Chaney Chemical Laboratories of Glendale, Calif., ran a comparative response study using the 2% potassium iodide midget impinger system used in the above standardizations; a 1% potassium iodide–1% potassium hydroxide midget impinger system suggested by the ASTM Committee D-22 Methods for Atmospheric Sampling and Analysis; and the Ehmert instrument. These results indicate that the ASTM method gives 10% higher and the Ehmert, 10% lower, values than the 2% potassium iodide colorimetric determination.

In summary, it can be said of atmospheric oxidant that, on the average, 75 ± 25% can be identified as ozone. When properly standardized, the techniques discussed yield essentially the same response to the smog oxidant. However, the rather large differences among the laboratory response curves to ozone indicate the urgent need to clarify the chemistry of these systems. In particular, there is real need to have available an absolute ozone calibration method in the range of 0 to 100 p.p.h.m.

Mechanism of Ozone Formation

In this section is discussed the experimental evidence that suggests the mechanisms that can produce the levels of ozone concentration observed in smog. Accordingly, the work carried out by Haagen-Smit, Littman, Scott, Miller, and their coworkers from 1950 to the present is reviewed.

Laboratory Experiments of Haagen-Smit. This work was carried out at California Institute of Technology, and was sponsored in part by the Los Angeles County Air Pollution Control District.

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In duplicating the ozone formation observed in polluted air, it was essential to adhere to a rather narrow concentration range of hydrocarbon and nitrogen dioxide (*14, 15*). This was confirmed by a set of experiments in which the hydrocarbon, 3-methylheptane, and nitrogen dioxide concentrations were systematically varied. Artificial light from a bank of Westinghouse 40-watt, blue fluorescent light bulbs was used for the irradiation to eliminate the variable intensity of sunlight. The bulbs were arranged in the form of a U, four bulbs to a side and spaced so that when a 5-liter flask was placed in the center, the bulbs were approximately 0.5 inch from the sides and bottom of the flask. An oxygen atmosphere adjusted to 30% humidity and an irradiation time of 10 hours were selected as standards in the experimental procedure. The ozone formed was measured by the cracking observed on bent rubber strips (*1*) suspended in 5-liter flasks during irradiation.

It was found advantageous to use as ozone measure the sum of the depth of all cracks as measured under the microscope (100×) using an ocular micrometer. The measurement of crack depth was made on freshly cut surfaces exposed by making longitudinal cuts through the test strip 1 mm. from the edges.

The calibrations against known ozone concentrations were made in flasks of the same size as those used in the irradiation experiments. In the concentration range used, the total crack depth was proportional to the ozone concentration, 1.0 mm. corresponding to 3 p.p.m. of ozone.

When 2-butene in concentrations of 3 p.p.m. and nitrogen dioxide in concentrations varying from 0 to 20 p.p.m. are irradiated, cracks begin to appear at a concentration approximating 0.2 to 0.4 p.p.m. of nitrogen dioxide. The cracking increases with increased nitrogen dioxide concentration until at about 2 to 3 p.p.m. a maximum is reached. After passing this maximum, the rubber cracking diminishes and at about 20 p.p.m. of nitrogen dioxide, only a few cracks appear during the 10-hour irradiation. The results of these experiments at concentrations of 0.5, 1.0, 2.0, and 3.0 p.p.m. of 2-butene and varying concentrations of nitrogen dioxide (Figure 9) are similar to those obtained with 3-methylheptane.

The general shape of the curves obtained in these experiments can be attributed to at least two simultaneous reactions: the formation of ozone, and the removal of ozone by both nitrogen dioxide and the oxidation products of the hydrocarbon. That nitrogen dioxide does react with ozone is well known, and especially at higher concentrations this removal of ozone plays an important role. In experiments at the upper limits of nitrogen dioxide concentrations, when no cracking appears after 10 hours, longer irradiation did produce cracking. It is most likely that during this induction period, the nitrogen dioxide concentration decreased until it came within the range of ozone formation. This shift in the composition of the mixture is also brought about by the reaction of nitrogen dioxide with the hydrocarbon and its oxidation products. When ozone formation stops, nitrogen dioxide is practically absent.

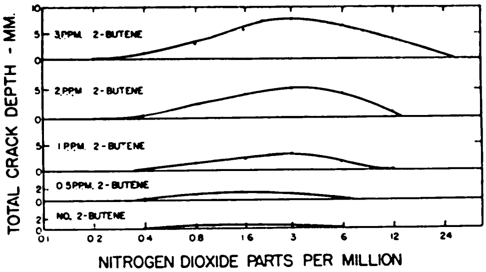

Figure 9. Rubber cracking with 2-butene and nitrogen dioxide with artificial light in oxygen

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch036

The rubber strip suspended in the flask during irradiation continually removes the ozone formed, and is in competition with products that will react with ozone. Although the reaction with the rubber strip takes from 20 to 30 minutes to remove the ozone nearly quantitatively from a 5-liter flask, the rate at which the rubber reacts with the ozone is sufficiently greater than the degradation reaction to show considerable ozone formation. The average rate of ozone formation during the first 10 hours of irradiation of 3-methylheptane (3 p.p.m.) and nitrogen dioxide (1 p.p.m.) is about 0.8 p.p.m. per hour. After 100 hours slight cracking is still observed, and the total crack depth corresponds to 20 p.p.m. of ozone, which clearly indicates a chain reaction of considerable extent.

The high values obtained in these experiments are possible only because the rubber strip continuously removes the ozone formed. If, however, the ozone is not removed, it will react with the hydrocarbon and its oxidation products and the nitrogen oxides. Consequently, the ozone, measured after a certain length of irradiation time in the absence of rubber, will represent the excess of ozone caused by different rates of these reactions. The reaction by which ozone is formed is only slightly faster than those which destroy it. When attempts were made to isolate any ozone, only the slight excess resulting from the difference in the rate of these reactions was isolated. In the analysis of air samples it is this excess of ozone which is measured.

In duplicating these phenomena in the laboratory, hydrocarbons and their oxidation products were irradiated in the presence of nitrogen dioxide. The ozone concentration, measured by two methods, was determined after exposure for different lengths of time. One method was by rubber cracking, in which the rubber was introduced after and not during the irradiation as previously described. In the other method, advantage was taken of the difference in vapor pressures of ozone and nitrogen dioxide. By passing the irradiated mixture through several traps held at −183° C., only ozone passes through, while nitrogen dioxide with its higher boiling point (24° C.) is trapped. The ozone passing through the traps was determined by both the phenolphthalin and the potassium iodide methods.

In irradiation experiments using 3 p.p.m. of 3-methylheptane and 1 p.p.m. of nitrogen dioxide, it was found that a level of 0.9 p.p.m. of ozone was reached after 4 to 5 hours, which then remained nearly constant for 20 hours. When duplicate flasks were kept in the dark for 1 hour before measuring the ozone content, the ozone concentration was reduced to one half the value obtained directly after irradiation. In order to keep the ozone concentration at 1 p.p.m. for 20 hours, approximately 14 p.p.m. of ozone must have been formed during that time. The experiments in which the rubber strips were suspended in the flasks during irradiation indicated the formation of 12 p.p.m. of ozone during the period between 5 and 25 hours. These experiments, although of a qualitative nature, support the conclusion reached earlier: that a considerably greater amount of ozone is produced than could be expected on the basis of a stoichiometric reaction of 3 p.p.m. of hydrocarbon and 1 p.p.m. of nitrogen dioxide.

Similar observations have been made using 2-butene in the photochemical oxidation with nitrogen dioxide. At concentrations of 3 p.p.m. of 2-butene and 2 p.p.m. of nitrogen dioxide, a level of 0.5 p.p.m. of ozone is reached after only 15 minutes, as compared to several hours required in the case of 3-methylheptane. The maximum ozone level obtained with 2-butene is lower than that found with 3-methylheptane. This is attributed to side reactions which may occur between butene and ozone, forming ozonides, and thereby removing butene from the reaction mixture. These reactions are greatly reduced in experiments where rubber strips are suspended in the flask during irradiation, for then the ozone is continuously removed and prevented from reacting with the olefin. Under these conditions butene forms more ozone at a faster rate than does 3-methylheptane. This method is probably a better measure of the nuisance value of the ozone-forming reactions because it indicates the total ozone-forming capacity of a particular compound. The ozone formed may react with many acceptors present in polluted air, which function as the rubber pieces in the laboratory experiments.

Relative Ozone-Forming Potential of Organic Compounds. The phenomenon of ozone formations being limited to definite relative proportions of hydrocarbon and nitrogen dioxide, observed with 3-methylheptane and 2-butene, is apparently equally true for other hydrocarbons and their oxidation products. At a concentration of 3 p.p.m. and varying concentrations of nitrogen dioxide, the hydrocarbons, *n*-butane, *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, 1-*n*-hexene, and diisobutylene, gave curves similar to the one obtained with 3-methylheptane, with optimum ozone formation at from 1 to 3 p.p.m. of nitrogen dioxide. Ozone formation during photochemical oxidation is not limited to hydrocarbons; it is also shown by their oxidation products—acids, aldehydes, ketones, and alcohols.

A comparison of a number of organic compounds tested for a 10-hour irradiation is shown in Figure 10 and Table I.

As the length of the carbon chain in the straight chain paraffins increases from four to nine atoms, the ozone-forming capacity becomes greater. Methane, ethane, and propane were found to be inactive. The highly branched hydrocarbon, 2,2,3-trimethylbutane (triptane), does not cause measurable rubber cracking during the 10-hour irradiation period, which parallels its well-known resistance to oxidation. Introduction of a double bond increases ozone formation, which is more pronounced when the bond is in the 2 position. Cis and trans configuration does not affect the activity, as shown by *cis*- and *trans*-2-butene and -2-pentene. The optimum ozone formation is shown with olefins of four to six carbon atoms. The introduction of a second double bond, as in butadiene, doubles the activity when compared to that of the corresponding 1-butene.

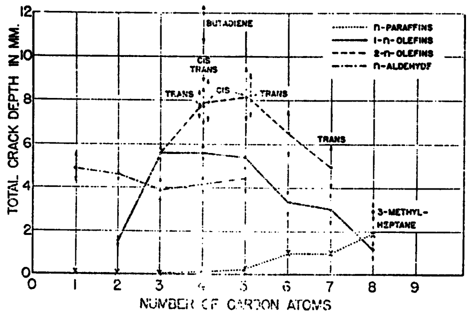

Figure 10. Photochemical rubber cracking with 3 p.p.m. of organic compound and 2 p.p.m. of nitrogen dioxide after 10 hours' exposure

Table I. Photochemical Ozone Formation with Organic Compounds (3 P.P.M.) and Nitrogen Dioxide (2 P.P.M.) in Oxygen

(Irradiation, 10 hours; humidity, 30%; *t*, 30°–33° C.)

	Saturated Hydrocarbons		Unsaturated Hydrocarbons		Alcohols		Aldehydes and Ketones		Miscellaneous Compounds	
No. of Carbon Atoms		Total crack depth, mm.		Total crack depth, mm.		Total crack depth, mm.		Total crack depth, mm.		Total crack depth, mm.
1	Methane	0			Methanol	5	Formaldehyde	4	Formic acid	0
2	Ethane	0	Ethylene	2	Ethanol	5	Acetaldehyde	4	Acetic acid	0
			Acetylene	0.5					Ethyl bromide	0.1
									Ethyl nitrate	0.5
									Nitroethane	2
									Ethyl mercaptan	5
3	Propane	0	1-Propene	5	1-Propanol	6	Propionaldehyde	4		
					2-Propanol	6	Acetone	0	Propionic acid	4
4	*n*-Butane	0.1	1-*n*-Butene	5	1-Butanol	6	*n*-Butyraldehyde	4		
			cis-2-*n*-Butene	8	2-Methyl-2-propanol	0	Biacetyl	7	Butyric acid	6
			trans-2-*n*-Butene	8					Butyl nitrite (without NO_2)	12
			Butadiene	12						
			Isobutene	5						
5	*n*-Pentane	0.2	1-*n*-Pentene	5	Amyl alcohol	6			Pyridine	2
			cis-2-*n*-Pentene	8						
			trans-2-*n*-Pentene	8						
6	*n*-Hexane	1	1-*n*-Hexene	4	Cyclohexanol	4				
			2-*n*-Hexene	7						
			Benzene	0						
7	*n*-Heptane	1	Methylbenzene	0.6	Phenyl ethyl alcohol	1				
	3-Ethylpentane	1								
	2,2,3-Trimethylbutane	0								
8	*n*-Octane	2	1,2-Dimethylbenzene	6						
	3-Methylheptane	3	1,3-Dimethylbenzene	7						
9	*n*-Nonane	3	1,3,5-Trimethylbenzene	7						

In OZONE CHEMISTRY AND TECHNOLOGY;
Advances in Chemistry; American Chemical Society: Washington, DC, 1959.

Pronounced activity was established for the alcohols and aldehydes with one to five carbon atoms. *tert*-Butyl alcohol did not form ozone during the 10-hour irradiation period. The effect of substituting the hydrogen by different functional groups has been studied for ethane. The ozone-forming capacity of the resulting compounds is indicated by the total crack depth in millimeters obtained after 10 hours of irradiation.

Functional Group	Total Crack Depth, Mm.	Functional Group	Total Crack Depth, Mm.
—ONO	10	—COOH	0.5
—SH	5	—C_3H_7	0.2
—CHO	4	—C_2H_5	0.1
—NH_2	4	—Br	0.1
—NO_2	2	—CH_3	0
—ONO_2	0.5	—H	0

Previously it has been reported that biacetyl, bibutyryl, pyruvic acid, and butyl nitrite produce ozone upon irradiation without the addition of nitrogen dioxide. In the absence of nitrogen dioxide, ozone formation can be established by irradiation of biacetyl at a concentration of 40 p.p.m.; in its presence the rate of formation is still pronounced in the 1-p.p.m. range, and equals that of 2-butene. Butyl nitrite without the addition of nitrogen dioxide is even more active than 2-butene. After 94 hours the total crack depth of the rubber pieces corresponds to the production of 80 p.p.m. of ozone, demonstrating again a chain mechanism in its formation.

In photochemical experiments conducted in sunlight and in concentrations of 3-methylheptane and nitrogen oxides approximating those known to occur during smog periods, ozone formation is proportional to the product of the hydrocarbon and nitrogen oxide concentrations. Similar conclusions can be drawn from the experiments with 2-butene (Figure 9).

Haagen-Smit's findings can be summarized as follows:

Ozone is formed from the photochemical oxidation of organic vapors in the presence of nitrogen dioxide.

In order for the ozone concentration to attain appreciable values, the range of concentrations for the reactants are very limited, as shown in Figures 11 and 12.

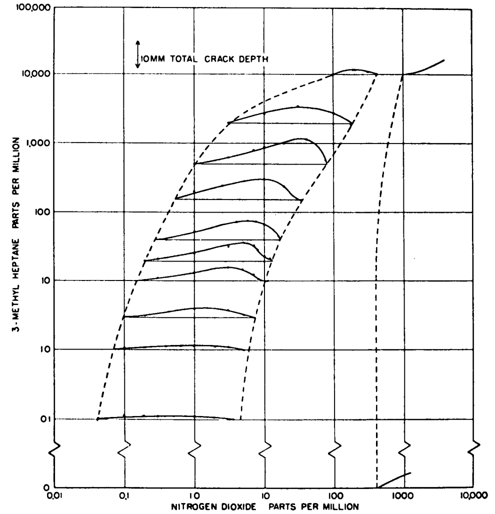

Figure 11. Logarithmic plot of area of ozone formation

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch036

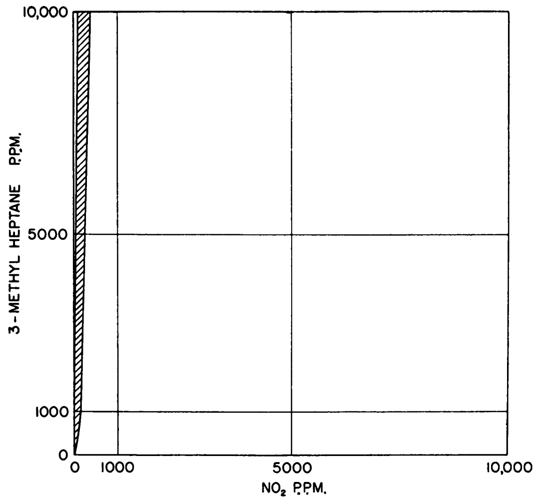

Figure 12. Linear plot of area of ozone formation

As a result of a survey of organic vapors, it was established that the classes of compounds shown in Table I were most important to ozone formation in smog.

The experimental evidence suggests that the total ozone formed in the photochemical reaction is related to the concentrations of the reactants by the relation

$$[O_3]_{\text{total}} = K[NO_2][RH] \tag{3}$$

Laboratory Investigations of Stanford Research Institute. This work was sponsored by the Smoke and Fumes Committee of the American Petroleum Institute. The philosophy of experimentation of these investigators was to use the actual smoggy air as a substrate for laboratory experiments (*20, 32*).

The daily fluctuations of oxidant concentration were followed for several years by means of an automatic oxidant recorder at the Stanford Research Institute's Pasadena Laboratory (*19*). Typical oxidant curves showed a characteristic pattern: low concentrations at night increasing to a maximum around noon, and disappearing again at sunset. Maximum concentrations varied greatly, with values as high as 60 p.p.h.m. occurring during smoggy weather. Concentrations at night seldom exceeded 5 p.p.h.m. The variations from day to day were greater than those from month to month. Nevertheless, an annual cycle did exist, with high concentrations occurring more frequently from May through October than during the rest of the year.

However, if air was irradiated with artificial sunlight before entering the recorder, a totally different pattern resulted. The air was passed through a 50-liter flask, irradiated with four H400 E-1 mercury vapor lights. The average residence time of the air was about 20 minutes. Since the mercury arcs gave off no radiation below about 3000 A., they were not capable of forming ozone directly by dissociation of oxygen. A typical oxidant pattern resulting from this arrangement is shown in Figure 13. The characteristic division between daytime and nighttime has disappeared and oxidant concentrations of the same order of magnitude as those existing in daytime resulted from irradiation of night air.

Continued monitoring of outside air showed that the oxidant formed by irradiation of night air followed a daily and an annual cycle. The daily cycle frequently showed two maxima, one around 7:00 P.M., the other about 8:00 A.M. High concentrations of oxidant could be formed regularly by irradiation of night air during fall and winter,

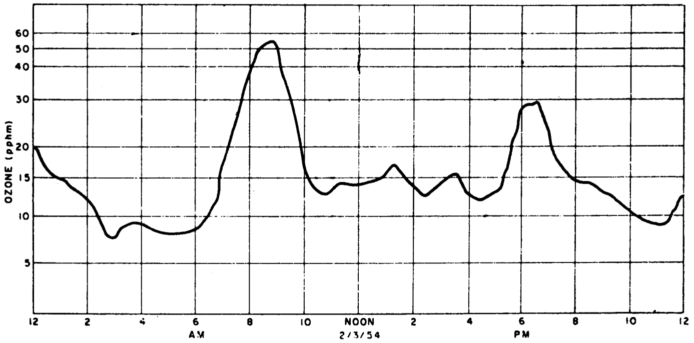

Figure 13. Diurnal variation of ozone formed by constant irradiation of outside air

from September through March. During the summer months little, if any, oxidant was formed at night, despite the fact that high concentrations occurred in the daytime during that period.

Isolation of Oxidant Precursors. The observation that oxidant could be formed experimentally by the action of light on polluted urban air led to an investigation of those impurities in air which, upon irradiation, formed oxidant. The term, "oxidant precursors," was coined to describe these materials, and a series of experiments was started to determine their physical and chemical properties.

That light was responsible for the formation was demonstrated by using two oxidant recorders, one which indicated the oxidant concentration in untreated air and the other, in irradiated air (Figure 14).

Attempts were made to determine the region of active light by use of optical cutoff filters. The results, summarized as follows, indicate that primary light acceptor(s) absorb in a rather broad region, beginning near the short wave end of the visible spectrum and extending to below 3600 A.

Filter	Cut Off below	Level of Ozone Formation
Light envelop and flask walls	2800 A.	Maximum
Window glass, 1/8 inch	3100 A.	No reduction
Solex glass	3400 A.	Definite, small reduction
X-ray lead glass	3700 A.	50% reduction
Corning glass filter No. 373	4000 A.	Substantially complete reduction

Attempts were then made to determine some of the chemical properties of the precursors by subjecting the air (prior to irradiation) to the action of various scrubbers in an effort to remove the precursors. These experiments indicated that passage through a bed of activated carbon or through a combustion furnace at 760° C. removed or destroyed the precursors. On the other hand, when the incoming air was scrubbed

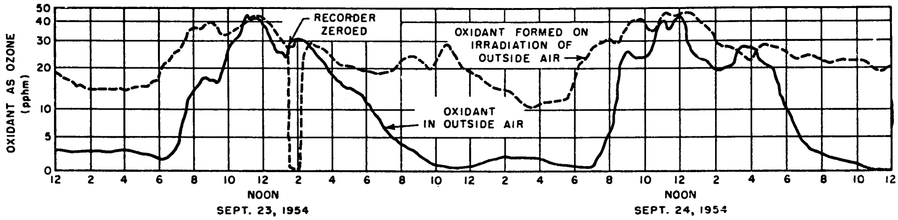

Figure 14. Diurnal variation of oxidants from natural and artificial irradiation of Pasadena air

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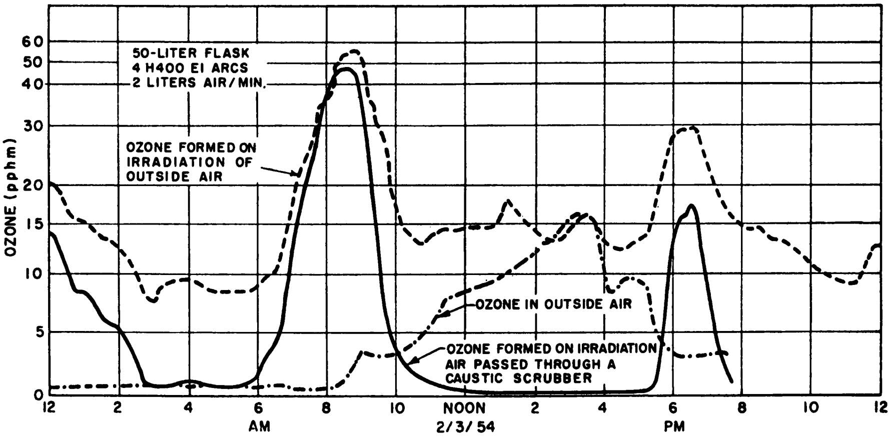

Figure 15. Diurnal variation of ozone from natural and artificial irradiation of Pasadena air

countercurrently through packed columns 4 feet long with 5% sodium hydroxide, the bulk of the oxidant precursors remained (Figure 15), although the concentration of acid gases such as carbon dioxide, sulfur dioxide, and nitrogen dioxide was greatly reduced by this procedure. Similarly, a 5% solution of semicarbazide buffered to pH 4 with phosphoric acid had no effect (Figure 16), although this agent effectively removes carbonyl compounds such as aldehydes and ketones. A particle filter capable of removing particulate material down to 0.2 micron in diameter also had no effect.

Freezeout traps were used next in an attempt to separate or trap the precursors.

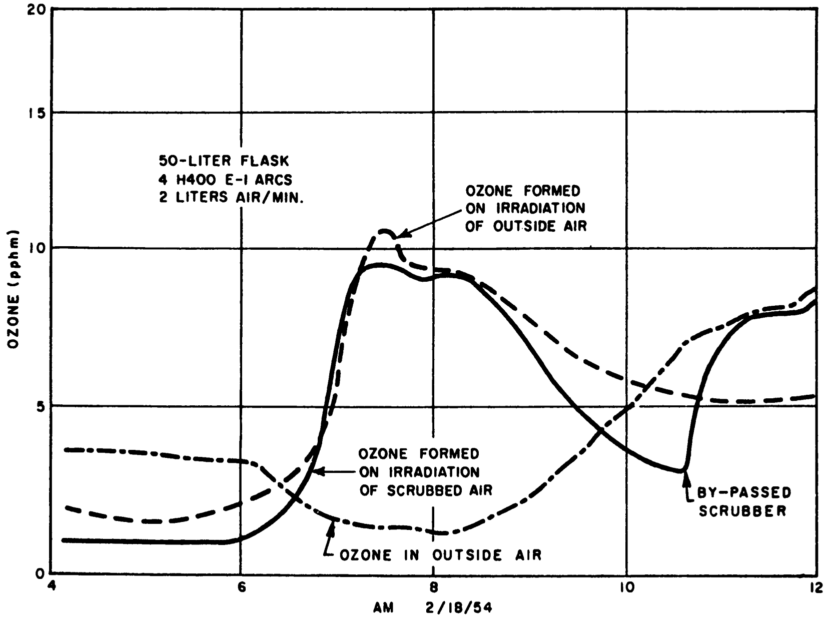

Figure 16. Ozone formation in irradiated scrubbed Pasadena air

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A trap packed with stainless steel helices and cooled in dry ice–acetone produced no significant reduction in the amount of oxidant formed upon irradiation of air passed through the trap. When a liquid oxygen–cooled trap was used in series with the dry ice trap, essentially complete retention of the oxidant precursors resulted (Figure 17). Upon removal of the coolant bath, the bulk of the precursors was released (Figure 17). Thus, this technique for the collection and concentration of the substances which yield oxidant on irradiation promised to make their analysis feasible and gave hope for their eventual identification.

Numerous freezeout collections were made and analyzed. The air was drawn through a semicarbazide column and a caustic scrubbing column. The stream was then split; one half passed through an irradiated flask and then into a series of traps, and the other half passed through a dark flask on its way to the traps. By examining the contents of the traps, it was hoped to obtain a differential analysis which would be easier to interpret, because irradiation should introduce a change which could be picked out from the general background common to the dark and irradiated samples.

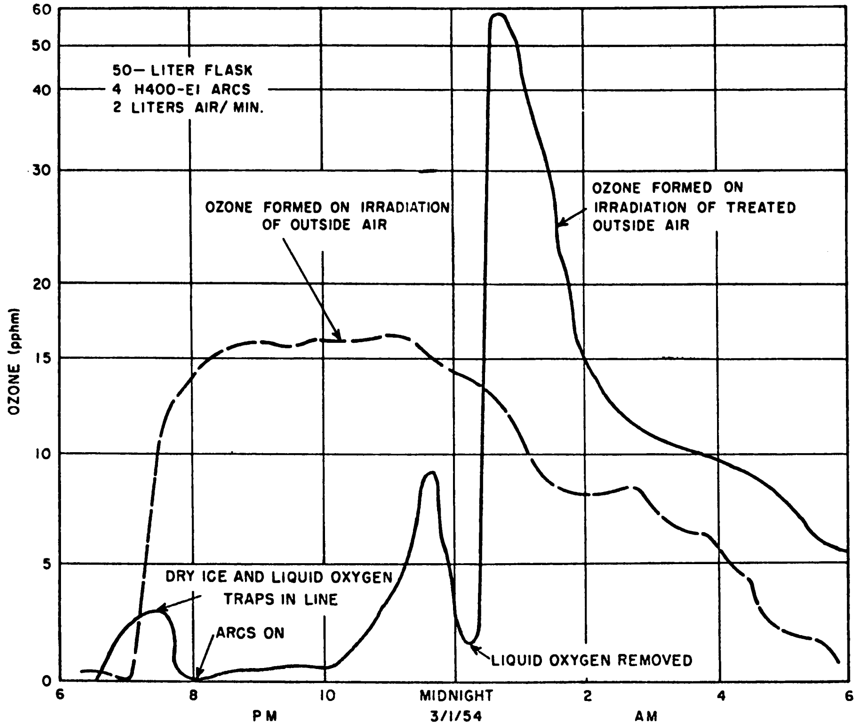

Figure 17. Ozone formation in irradiated treated Pasadena air

Various trap designs were tried, and it was concluded that traps packed with stainless steel helices gave the best recovery of precursors.

The samples were analyzed using infrared, ultraviolet, and mass spectrometric methods. After being collected in liquid oxygen–cooled traps, the samples were kept in liquid nitrogen. After connections were made to the mass spectrometer, the noncondensable fraction was pumped off and the remaining sample was introduced into the inlet system by gradually warming the trap to room temperature. Samples for infrared and ultraviolet analyses were handled similarly, but the transfer was accomplished by freezing the sample over into the optical cell which was equipped with a cold finger.

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch036

The results of these analyses indicated that the bulk of the material retained in the liquid oxygen traps consisted of carbon dioxide and water. The balance of the sample was made up of organics. The general distribution of the mass peaks resembled a gasoline mass spectrum with the high molecular end attenuated. Comparison of spectra of irradiated and nonirradiated samples showed a consistent decrease of olefin and diolefin mass peaks on irradiation (particularly m/e 39, 43, and 67), but in general, large differences in composition of the samples made meaningful comparison difficult.

The infrared analyses showed absorption bands in the region of 3.4, 6.9, and 7.3 microns caused by carbon-hydrogen bonds; bands of 5.8 and 8.3 microns indicative of acetone; carbon dioxide bands of 4.3, 13.9, and 15 microns; and a doublet at 6.3 microns, caused possibly by organic nitrates. Several minor unidentified bands were also present. The ultraviolet spectra showed no significant absorption bands.

Chemical analyses were performed on several samples to detect nitrogen oxides not found by spectral analyses. A modified Griess reagent was used, and the contents of several freezeout traps were examined by venting them through an irradiated flask into a scrubber containing the reagent. Alternatively, ozone was added to the flask and permitted to react with its contents, as Griess reagent responds to nitrogen dioxide but not to nitric oxide. Relatively large amounts of nitrogen dioxide were found in these cases (more than could be accounted for by the nitrogen dioxide present at the time of collection). Thus, nitrogen dioxide was apparently formed during the collection and/or irradiation of the air sample. This pointed a way toward a possible mechanism of oxidant formation.

The formation of ozone from mixtures of nitrogen dioxide and hydrocarbons has been described by other investigators (*13*). In this laboratory a series of experiments was run using oxidant recorders and irradiated flasks. A mixture of carbon-filtered air and 40 p.p.h.m. of nitrogen dioxide was run into the recorder until an equilibrium level was established. A small quantity of hydrocarbon was then added to the flask from a syringe and permitted to flush into the recorder. The resulting oxidant curves indicate that relatively large amounts of an oxidant can be formed by irradiating synthetic mixtures of a variety of hydrocarbons and nitrogen dioxide.

Photolysis of Nitrogen Oxide in Outside Air. Since hydrocarbons exist in outside air, it seemed important to determine whether they were capable of producing similar results. When nitrogen dioxide was added to a stream of carbon-filtered night air at a time when no precursors were present and the air was passed through an irradiated flask into an oxidant recorder, a level of oxidant was established because the recorder is somewhat sensitive to nitrogen dioxide. When the carbon filter was removed so that the mixture consisted of untreated outside air and nitrogen dioxide, the recorder rapidly climbed to a higher level, indicating that an additional amount of oxidant had been formed. Thus, substances normally present in outside air reacted during photolysis of nitrogen dioxide to produce oxidant above that due to nitrogen dioxide itself.

As it had been previously demonstrated (by means of caustic scrubbers) that even a substantial reduction of the nitrogen dioxide present in outside air did not have a gross effect on its oxidant-forming ability, these experiments appeared to be largely of academic interest. A possible connecting link was nitric oxide, but its known rate of oxidation to nitrogen dioxide is slow and its presence in outside air had not been established.

This line of research received further impetus when a nitrogen dioxide and nitric oxide recorder was developed by the institute. This instrument was based on the absorption of nitrogen dioxide in a modified Griess reagent and subsequent colorimetric determination of its amount. In its simplest form the instrument responded only to nitrite in solution (which may originate from nitrogen dioxide or organic and inorganic nitrites), but a modification determined nitric oxide as well. This was achieved by filtering the incoming air through activated charcoal, which passes nitric oxide but retains nitrogen dioxide and nitrites, followed by a gas-phase oxidation of nitric oxide to nitrogen dioxide using ozone. The resulting nitrogen dioxide was then determined colorimetrically.

Monitoring of the atmosphere at Pasadena indicated that nitric oxide is normally present in quantities well in excess of those of nitrogen dioxide. Its concentrations ranged from 2 to 30 p.p.h.m.

The oxidation rate of nitric oxide (by oxygen) in these concentrations is slow. But under the conditions of these experiments, using irradiated 50-liter flasks and mixtures containing 1 to 10 p.p.m. of hydrocarbons and 0.1 to 1.0 p.p.m. of nitric oxide, a rapid oxidation to nitrogen dioxide appeared to take place, accompanied by the formation of some ozone.

The low boiling point of nitric oxide (−156° C.) made its retention in freezout traps cooled with liquid oxygen unlikely, at least on the basis of its partial pressure. Nevertheless, experiments set up to check this point showed that nitric oxide was quantitatively retained. On revaporization, at least part of the nitric oxide appeared in the form of nitrogen dioxide. Others, too, have observed this phenomenon.

The effect of irradiation on the oxidant and nitrogen dioxide concentrations of night air apparently produced a significant increase of nitrogen dioxide concentration, but not enough to account for all of the oxidant formed. Thus, experimental observations relating to formation of oxidant in the Los Angeles atmosphere can be explained by the basic assumption that ozone is formed by the photolysis of nitrogen dioxide, aided by a rapid conversion of nitric oxide to nitrogen dioxide in the presence of certain hydrocarbons.

Richards' and Littman's results can be summarized as follows:

The important wave length range of radiation was 3000 to 4000 A. for the photochemical production of ozone in smog.

The photochemical hypotheses was furthered by the demonstration that irradiated night air formed oxidant.

It was confirmed that ozone is formed from the photolysis of nitrogen dioxide and organic vapor.

It was suggested that nitric oxide was an important precursor to ozone formation.

Experimental Studies of Armour Research Foundation. This research was sponsored by the Air Pollution Foundation.

Miller and coworkers used a 2-liter Vycor photolysis flask wrapped in aluminum foil except for an opening to admit the collimated radiation from a Hanovia Type A mercury arc that was filtered with a borosilicate glass filter to cut out radiations at wave lengths below 3000 A. (*23*). The use of the reflective lining on the flask to form a multiple reflection system was necessary to achieve sufficient light intensity with this system. A relatively uniform radiation flux was thereby obtained. The radiation intensity, as determined with a photoelectric probe, was approximately the same as that of noon sunlight in the ultraviolet region but considerably less in the visible region.

At the conclusion of photolysis, the reaction mixture was passed through liquid oxygen–cooled traps packed with glass beads and then through a train of three bubblers containing alkaline phenolphthalin reagent. Oxidant values were obtained by spectrophotometric measurement of the partially oxidized reagent mixture. Controlled experiments revealed that nitrogen dioxide was efficiently trapped in the freezeout traps and did not contribute to oxidation of the reagent. Presumably, oxidants less volatile than nitrogen dioxide (peroxides, etc.) would also be trapped. The physical evidence, therefore, points strongly to ozone as the principal oxidant product of the photochemical reaction.

Typical results of irradiation of nitrogen dioxide and 3-methylheptane in oxygen are given below. No ozone was obtained when either the nitrogen dioxide or the hydrocarbon was omitted. Recovery of nitrogen dioxide from the freezeout traps was checked by analysis with a modified Griess reagent. A tendency toward high recovery by this method has not been completely resolved, but the results consistently show low recovery (or none) in photolyses in which an appreciable quantity of ozone was found.

Time, Hours	Concentration, P.P.M.			
	3-Methylheptane	NO_2, initial	Ozone	NO_2, recovered
3	13.2	1.36	0.89	0.08
1	14.7	1.47	0.33	1.44
1	8.9	0.76	0.38	1.07
3	20.4	0.93	0.86	0.24
17	10.0	0.48	0.53	0.18
3	3.5	0.65	0.97	0.05
3	0.97	0.50	0.59	0.20
5	0.00	1.11	0.0	1.47
3	3.9	0.72	0.2[a]	0.51
3	2.3	0.72	0.44	—
3	1.35	0.48	0.39	0.51
3	0.04	0.50	0.0	0.76
3	3.3	0.00	0.00	0.00

[a] Corning-7380 glass filter, 2 mm. thick, cut out 3130-A. radiation but passed 60% of 3660 A.

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Miller's findings can be summarized as confirming the following:

Ozone is formed from the photolysis of nitrogen dioxide and organic vapor for reactant concentrations below 1 p.p.m.

The photolysis of nitrogen dioxide alone produces ozone of the order of 0.1 p.p.m.; when organic vapor concentrations above 0.2 p.p.m. are added, there is an enhancement of ozone production.

Nitrogen dioxide is consumed in the reaction, probably as a result of the reaction of nitric oxide and the organic vapor, indicating that nitrogen dioxide is more than the radiation absorber.

Infrared Studies of Franklin Institute. In this work, sponsored by the American Institute, the decision to study the smog reactions with infrared spectrometry was based on having an analytical method as unequivocal as possible in identifying particular compounds in the presence of an unknown mixture. Infrared absorption can provide necessary selectivity, but ordinary equipment does not have nearly enough sensitivity to detect substances at low concentrations of smog. Accordingly, first experiments were done with concentrations of reactants many times higher than are found in polluted air.

In these experiments either nitrogen dioxide or ozone was mixed with an organic compound at concentrations of about 1 p.p.t. in air or oxygen and allowed to react with or without artificial sunlight; the products were analyzed by means of standard infrared techniques. Alkyl nitrate, alkyl nitrite, aldehyde, and peroxyacid were typical products of the nitrogen dioxide–organic compound reaction.

Ozone, which has played a central role in studies of the Los Angeles smog, was not detected as a product in this first study. Ozone was found to react slowly with saturated hydrocarbons but rapidly with olefins. Peroxyacids were identified among the products when ozone was reacted with aldehydes.

During these first studies it became obvious that it would be desirable to study these reactions at concentrations nearer to those encountered in polluted air. This required design and construction of a special reaction vessel and infrared absorption cell. This cell utilized a multiple reflection system of the White type. By adjustment of the two mirrors at the right-hand end of the cell shown in Figure 18, it is possible to obtain any integral multiple of four passes through the cell. Inasmuch as the mirrors at the right end are 3 meters from the smaller mirror at the left end, 144 passes through the cell gives a total path length of 432 meters. Since infrared paths of approximately 500 meters could be obtained, it was possible to detect reaction products at concentrations of a few tenths of 1 p.p.m.

In the first experimental program carried out with this cell (*36*), ozone as a product was found in concentrations of 1 to 2 p.p.m. and less when nitrogen dioxide and

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch036

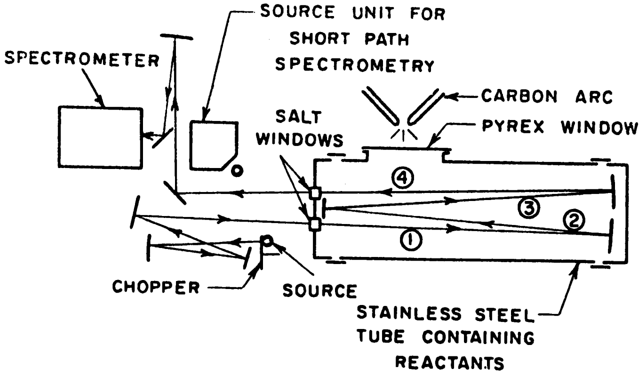

Figure 18. Schematic diagram of long-path cell

various organic compounds were reacted. In these experiments reactants at a few parts per million in oxygen or air were irradiated with an AH-6 arc enclosed in borosilicate glass as shown in Figure 18. The variation of ozone concentration with time of irradiation was found to depend, in a complex way, on the structure of the organic compound and on the concentration of both reactants (Figure 19). The transitory formation of ozone by the photolysis of nitrogen dioxide in oxygen was demonstrated; it was shown that, if the fast back reaction between ozone and nitric oxide is suppressed by the addition of nitrogen pentoxide to react with the nitric oxide, the ozone will quickly accumulate in the system (Figure 20) (*36*).

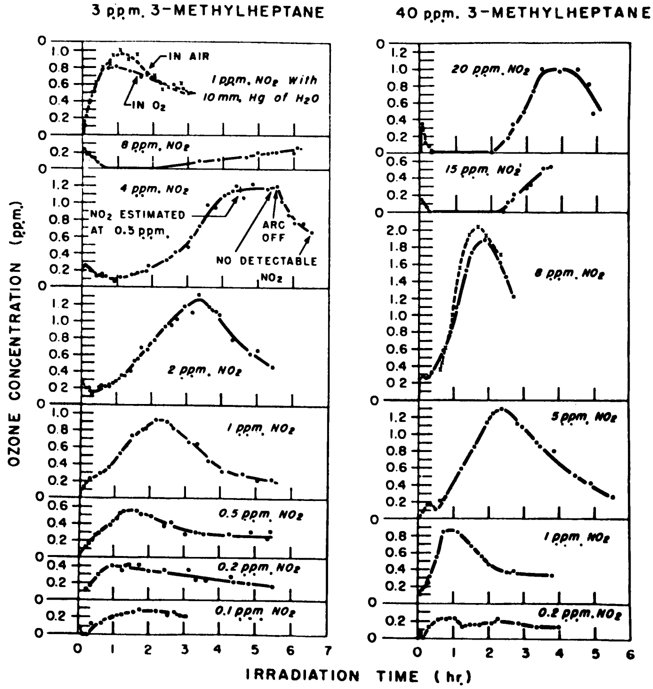

Figure 19. Formation of ozone by irradiation of 3-methylheptane and nitrogen dioxide

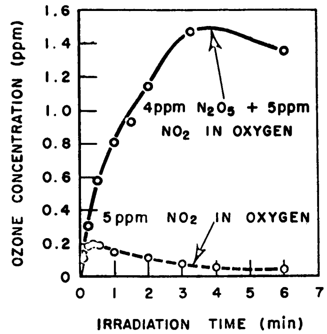

Figure 20. Effect of nitrogen pentoxide on photolysis of nitrogen dioxide in oxygen

Other products observed in this first study with the long-path cell were aldehyde, alkyl nitrate, formic acid, carbon monoxide, carbon dioxide, and water. Several prominent absorptions which apparently all belong to one compound could not be identified. This interesting product, referred to as compound X, has been subjected to considerable study in an attempt to determine its structure and physical properties. Aside from ozone, it is probably the most important product of these reactions (*37*).

Compound X. Obtaining samples of compound X for study presented some difficulty. When organic compounds and nitrogen dioxide are photolyzed at high concentrations (on the order of millimeters of mercury), alkyl nitrate is the chief nitrogen-containing product and compound X is not formed. The only successful technique of preparation of compound X is actual photolysis of mixtures of organic compounds and nitrogen dioxide at low pressures in the presence of oxygen. Diacetyl was found to give the best results—i.e., it gave the least amount of side products.

With 100 p.p.m. each of diacetyl and nitrogen dioxide in 1 atm. of oxygen, about 2 hours of AH-6 arc irradiation were necessary for most of the reactants to be converted to products. At these low pressures of reactants a large volume of gas was required in order to give enough compound X for a liquid sample to be collected. Therefore, the reaction was conducted in the 500-meter, long-path absorption cell. At the end of the reaction, products were slowly pulled through a trap cooled by a dry ice–isopropyl alcohol mixture. This trap passed some of the products, such as acetaldehyde, carbon dioxide, and carbon monoxide, but trapped compound X, or at least part of it. It also trapped water vapor and some unreacted diacetyl. However, an infrared spectrum, a mass spectrum, and a nuclear magnetic resonance spectrum of the compound were obtained and it was possible to perform quantitative tests of its chemical properties.

The infrared spectrum of the compound X from diacetyl is shown in Figure 21. It shows the following features:

The CH absorption is weak compared to other strong bands in the spectrum, indicating a methyl compound.

There is a strong single carbonyl band at 5.75 microns similar in shape and wave length to the carbonyl bands of aldehydes, ketones, peroxyacids, and esters, and different from the double carbonyl bands of acids, acid anhydrides, and diacyl peroxides. There is a neighboring, weaker band at 5.4 microns which might be considered a part of a double carbonyl band, but this seems doubtful because the two branches of a double carbonyl band are usually of approximately equal intensity and are usually closer together. The indications are that compound X from diacetyl is an acetyl compound—a logical product.

The bands at 5.4, 7.7, and 12.6 microns indicate the presence of nitrogen in the molecule for the following reasons:

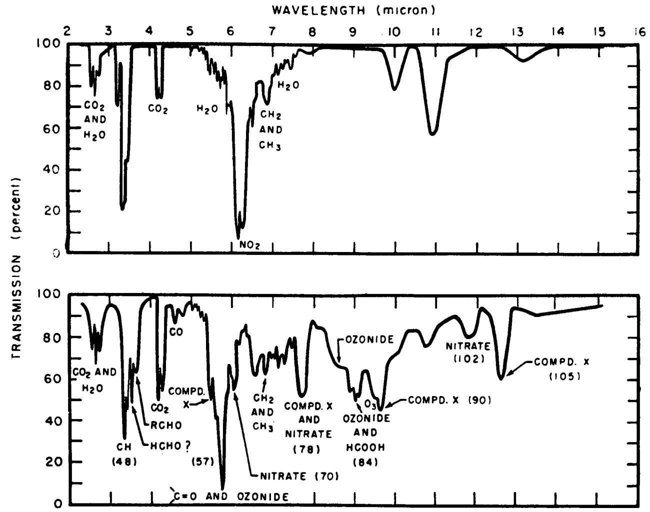

Figure 21. Products of reaction of 10 p.p.m. of 1-pentene and 5 p.p.m. of nitrogen dioxide in 1 atm. of dry oxygen

Path length, 240 meters
***A.* Before irradiation**
***B.* Irradiated by AH-6 mercury arc**

a. bands near 5.4 microns arise from the nitric oxide stretching vibration in nitric oxide, nitrosyl chloride, and nitrogen tetroxide; few other compounds have bands here.

b. Alkyl nitrates, nitroso compounds, and nitrogen tetroxide absorb near 7.7 microns.

c. Alkyl nitrites have a strong band near 12.6 microns which is supposed to originate in the nitric oxide group.

There is a particularly strong band in the spectrum which had not previously been assigned to compound X. This is the band at 8.6 microns. Identification of this band was important because it was the only major unidentified band in the spectra of the reaction products from organic compounds and nitrogen dioxide, other than the bands which were obviously due to compound X. This band, unlike the bands at 5.4, 5.74, 7.7, and 12.6 microns, appears in the spectrum of the sample of compound X prepared from diacetyl but not in a sample prepared from dibutyryl. Thus, compound X is probably really a homologous series of compounds, of which only the lowest member possesses a band at 8.6 microns. The products of the reaction of nitrogen dioxide with 2-pentene or with methyl ethyl ketone also showed this band. The sample prepared from dibutyryl also has a moderate strength band at 9.6 microns which had been observed in the spectra of reaction products.

The decomposition products of compound X were examined for clues to its structure. In one experiment a sample was allowed to decompose for over a week at room temperature in oxygen. The infrared spectrum of the products showed carbon dioxide and a small amount of organic nitrate. It is clear from this that the original molecule contained nitrogen. The surprising weakness of the product spectrum led to the suggestion that adsorption on the cell walls was occurring rather than decomposition. But the marked increase in carbon dioxide concentration argues against this. There was no nitrous oxide, nitric oxide, nitrogen dioxide, nitrogen pentoxide, nitrous acid, nitric acid, nitrite, or nitro compound evident.

In another experiment compound X was decomposed by heating in nitrogen at 185° C. for 2 hours. The spectrum of the products of this reaction showed small

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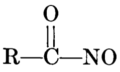
amounts of carbon dioxide, carbon monoxide, formaldehyde, methanol, probably nitromethane, and methyl nitrite. There was no nitrous oxide, nitric oxide, nitrogen dioxide, nitrogen pentoxide, nitrous acid, nitric acid, or nitrate evident. Unfortunately, it has not been possible to draw many conclusions from these products, although they do indicate again that nitrogen is present in the molecule. On one occasion a 2-drop sample of compound X exploded with extreme violence, again showing this compound's instability.

Compound X dissolves in water, probably hydrolyzing, to form a strongly acid solution which can act as either an oxidizing agent or a reducing agent—i.e., it liberates iodine from potassium iodide solution, and it decolorizes potassium permanganate. The solution gives the brown ring test for nitrite and nitrate. When a few drops of compound X were mixed with a few drops of water and the mixture was evaporated back into the long-path cell, the spectrum showed that nitric acid had been formed.

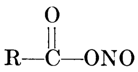
An important property of compound X is its rapid production of ozone when photolyzed in oxygen. The only other compounds found to produce ozone readily on photolysis are the nitrites. In its ozone-producing properties, compound X behaves like a nitrite.

Taken all together, evidence indicates that compound X is a compound of one of these types:



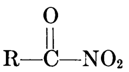
$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NO$

(I)



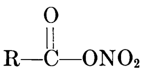
$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}ONO$

(II)



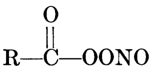
$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NO_2$

(III)



$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}ONO_2$

(IV)

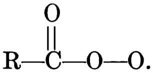


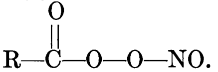
$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OONO$

(V)

Formula V, which could be called peroxyacyl nitrite, appears to be the most likely. Such a compound seems likely to have all the observed physical and chemical properties of compound X, and a mechanism for its formation can easily be written as follows:

Acyl radicals are prduced in photolysis of diacetyl, when hydrogen is abstracted from aldehyde, or when an oxygen atom or an ozone molecule reacts with olefin.

The acyl radicals add oxygen to give the peroxyacyl radical,  $R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}O$. This reaction seems probable because, at the concentrations at which compound X is formed, the acyl radical collides with oxygen several thousand times more frequently than with any of the other possible reactants. The likelihood of the reaction is also indicated by the fact that the low temperature oxidation of aldehyde in pure oxygen produces peroxyacids.

The peroxyacyl radical adds nitric oxide to produce  $R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}O{-}NO$. This is consistent with the fact that nitric oxide is itself a free radical with an unpaired electron and is commonly used as an inhibitor of free radical reactions.

Whatever the exact formula of compound X, it obviously contains nitrogen, and it is likely that it is formed in the reaction between a free radical and nitric oxide. It appears to be the key to the understanding of many of the observed facts, as pointed out below.

Mechanism of Ozone Formation

The identification of compound X as an acyl nitrogen compound fits in with observed facts of ozone formation in nitrogen dioxide–organic compound photochemical reactions. A summary of the mechanism follows.

First, photolysis in the absence of organic material is considered, based on data presented in a previous paper (*36*). Nitrogen dioxide is photolyzed by the ultraviolet radiation present in sunlight:

$$NO_2 \rightarrow NO + O$$

The oxygen atom so produced reacts with an oxygen molecule:

$$O + O_2 \rightarrow O_3$$

In the absence of an organic material this ozone reacts quickly with the nitric oxide produced by the photodissociation,

$$NO + O_3 \rightarrow NO_2 + O_2$$

preventing accumulation of a significant amount of ozone. These three reactions predict that equal steady-state concentrations of ozone and nitric oxide will be formed when nitrogen dioxide in oxygen is irradiated with ultraviolet radiation (assuming the steady-state concentration of atomic oxygen is insignificant). Actually, the ozone formed under these circumstances is observed to disappear under continued irradiation, and nitric oxide appears to accumulate in the system. This is ascribed to the occurrence of a slower side reaction which either produces nitric oxide or consumes ozone. A good possibility is

$$O + NO_2 \rightarrow NO + O_2$$

If some other reactant was introduced into the system to remove nitric oxide in competition with the ozone–nitric oxide reaction, it was predicted that the ozone would accumulate. Nitrogen pentoxide was found to produce the predicted effect; photolysis of the nitrogen dioxide–nitrogen pentoxide–oxygen system yielded substantial quantities of ozone.

When nitrogen dioxide is photolyzed in the presence of an organic substance (in oxygen), free radicals arising during the oxidation of the organic material are believed to play a part similar to the nitrogen pentoxide—that is, they react with the nitric oxide to form compound X, allowing ozone to accumulate in the system. This mechanism readily accounts for the parallelism between the rate of compound X formation, the rate of ozone formation, and the rate of nitrogen dioxide disappearance which was reported previously (*36*). The mechanism also explains the fact that photolysis of nitrogen dioxide–organic compound–air mixtures sometimes produces ozone concentrations in excess of the initial nitrogen dioxide concentration. The reason for this is that compound X is photolyzed in air to produce ozone (discussed below). In this reaction nitrogen dioxide is probably first formed and is then quickly photolyzed, leading to ozone and probably to regeneration of compound X.

The chain oxidation of the organic material presumably is initiated by the attack of an oxygen atom on an organic molecule. There are a number of ways each oxygen atom used in this initial attack may lead to the formation of many free radicals capable of reacting with nitric oxide. These are chain branching during oxidation; photolysis of intermediates formed during oxidation, such as aldehydes; and photolysis of compound X itself. For this reason only a fraction of the oxygen atoms produced by the photolysis of nitrogen dioxide are consumed in initiation reactions, while the majority react with molecular oxygen to form ozone.

The observation made by Haagen-Smit and Fox and confirmed by long-path cell studies—that there is an upper limit concentration of nitrogen dioxide above which ozone is not produced within a limited irradiation time—is readily explained. With a high initial concentration of nitrogen dioxide, photolysis produces nitric oxide more rapidly than it can be consumed by free radicals produced from the organic material. With continued irradiation, the rate of formation of nitric oxide is slowed down because nitrogen dioxide is depleted. The free radicals then slowly consume nitric oxide to form compound X, eventually reducing the nitric oxide concentration sufficiently to allow ozone to accumulate. This delay in formation of ozone was observed in studies with the long-path cell. It was also observed that the limiting concentration of nitrogen dioxide is reduced by increasing the initial hydrocarbon concentration. This is explained by the fact that, with greater hydrocarbon concentration, capacity to consume nitric oxide by the free radical mechanism is increased.

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Photolysis of Compound X, Butyl Nitrite, and Diacetyl. A relatively pure sample of compound X was prepared from diacetyl and nitrogen dioxide by means of the photolysis and cold trap collection technique described previously. This sample was then vaporized back into the long-path cell, mixed with 1 atm. of oxygen, and photolyzed with the AH-6 arc. The exact partial pressure of compound X could not be measured because of the presence of an unknown percentage of water vapor. However, if the compound X infrared bands are comparable in strength to those of nitrites and nitrates, its partial pressure was in the part per million range. Ozone was quickly formed in the photolysis. This is shown in Figure 22.

When photolyzed in oxygen, *n*-butyl nitrite was found to produce ozone readily. The rate of ozone production and the amount of ozone produced were comparable to the rate and amount observed in the photolysis of compound X.

Pure diacetyl, dibutyryl, and pyruvic acid have all been reported to produce ozone on photolysis in oxygen. First attempts to verify this result with use of the long-path infrared technique were frustrated by appearance in the spectrum of a band of methanol which masked the absorption resulting from ozone. This difficulty was overcome by the use of the following technique:

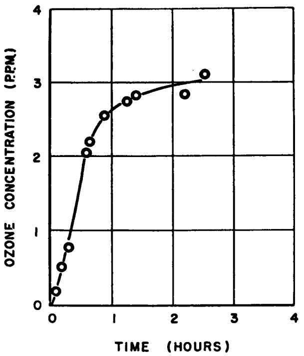

Figure 22. Ozone formation from compound X

The diacetyl was photolyzed, and the spectrum was recorded in the ozone-methanol region (9 to 10 microns). The ozone was removed by the addition of a relatively large amount of nitrogen dioxide, and the spectrum was again recorded. The second spectrum was then subtracted from the first.

The resulting difference spectrum was a good ozone spectrum. Three different concentrations of diacetyl were used, each in 1 atm. of dry oxygen. They were photolyzed 20 minutes with the AH-6 arc, and then the spectra were recorded.

The amount of water vapor present was found to have no important effect on the amount of ozone produced. The dry atmospheres in which the diacetyl was photolyzed undoubtedly contained traces of water vapor.

An attempt was made to detect ozone as a product of the photolysis of 20 p.p.m. of pyruvic acid in 1 atm. of oxygen. None was detected, though a few tenths of 1 p.p.m. of ozone would have produced an identifiable absorption band.

The amount of ozone formed in the photolysis of diacetyl is small compared to amounts formed by photolysis from compound X or *n*-butyl nitrite. It is also small compared to amounts formed in reactions involving organic compounds and nitrogen dioxide. The ozone formation from diacetyl must be the result of reactions involving free radicals and oxygen. Perhaps the photolysis of the nitrogen-containing compound X or *n*-butyl nitrite also produces ozone through a free radical mechanism, and the

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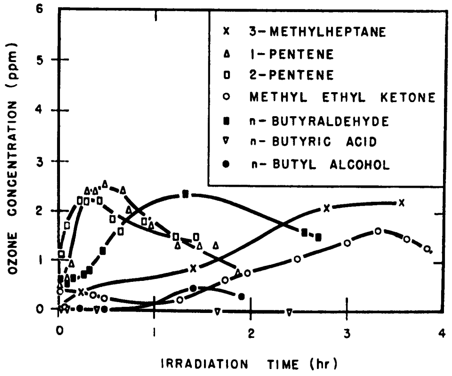

Figure 23. Ozone formation with various organics and nitrogen dioxide

greater amount of ozone is formed because of the greater reactivity of the radicals. However, it is believed that these compounds first yield nitrogen dioxide, which then is photolyzed to yield ozone.

These results can be summarized as follows:

Ozone, as observed by its infrared absorption band, is formed in the photolysis of nitrogen dioxide and organic vapors (Figure 23).

A new acyl nitrogen compound is formed simultaneously with the ozone in these same experiments. Moreover, this compound, tentatively identified as peroxyacyl nitrite, also forms ozone upon irradiation.

It was established that nitrogen dioxide is consumed in these reactions (Figure 24).

It was established that the photolysis of nitrogen dioxide alone in oxygen produces a steady-state concentration of ozone (Figure 24).

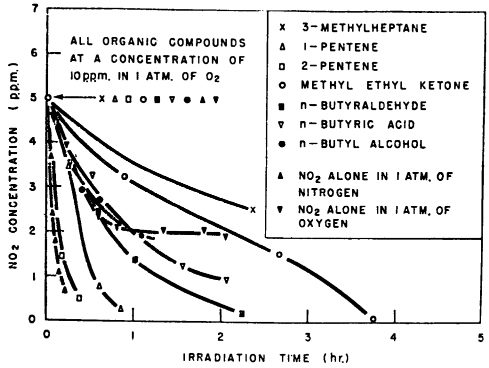

Figure 24. Disappearance of nitrogen dioxide upon irradiation

Primary Photochemical Processes

This section is devoted to the results of some theoretical studies on solar radiation, absorption rates, and primary photochemical processes in smog, undertaken by Leighton (*18*). In work sponsored by the Air Pollution Foundation, Leighton made a critical analysis of the chemical effects that sunlight and sky radiation may have on smog formation in urban atmospheres. The radiant energy available for photochemical processes was estimated by taking into consideration factors such as atmospheric transmissions, path lengths in contaminated layers, scattering by particulate matter, and surface reflections. From published absorption spectra, estimates were made of the maximum rates of absorption which could occur under realistic atmospheric conditions by all of the known and probable molecular species present in polluted air. Since only absorbed radiation can be effective in photochemical processes, these estimations served to eliminate some postulated reactions and to focus attention on others which, fortunately, are relatively few in number.

Solar Radiation. Of all the factors which collectively determine the amount and spectral distribution of the radiation entering a surface layer of the atmosphere, the best established appear to be the spectral irradiance outside the atmosphere and the attenuation by molecular scattering. The absorption coefficients of ozone are well established, but no easy method exists for determining the amount of ozone in a vertical profile of the atmosphere at a given time. The measurement of the particulate content of the atmosphere and its correlation with atmospheric transmission is a field in which much remains to be accomplished. Surprisingly few data exist on the spectral distribution of sky radiation and its variation with solar elevation and atmospheric conditions. The effect of clouds is of secondary importance, as intense smog generally occurs under a clear sky.

Within the layer uncertainties exist as to what absorbing species are present, what amount of each is present, how the concentration varies with height, and how the rate of absorption is affected by particulate diffusion.

Some of these factors are so variable and so difficult to determine that one may expect at best only approximate estimates of absorption rates. For this purpose the following equation was developed:

$$k_a = \Sigma \alpha_{\gamma\lambda}{}^{-1} J_\lambda \tag{4}$$

where k_a = fraction of absorbing substance receiving photons per unit time

α_λ = decadic absorption coefficient of substance under study

γ^{-1} = conversion factor

J_λ = function of the transmission coefficients involving scattering, absorption by standard components of the atmosphere, and the solar zenith angle

Table II. Values of J_λ

(Given in photons cm.$^{-2}$ second^{-1} 100 A.$^{-1}$)

			z		
λ, A.	0°	20°	40°	60°	80°
2900	1.2×10^{11}	6×10^{10}	5×10^{9}	4×10^{6}	———
3000	1.53×10^{14}	1.23×10^{14}	5.5×10^{13}	6.0×10^{12}	1.5×10^{8}
3100	1.32×10^{15}	1.21×10^{15}	8.6×10^{14}	3.4×10^{14}	8.2×10^{12}
3200	2.59×10^{15}	2.39×10^{15}	2.0×10^{15}	1.2×10^{15}	0.18×10^{15}
3300	4.18×10^{15}	4.00×10^{15}	3.39×10^{15}	2.21×10^{15}	0.58×10^{15}
3400	4.31×10^{15}	4.14×10^{15}	3.70×10^{15}	2.43×10^{15}	0.71×10^{15}
3500	4.75×10^{15}	4.56×10^{15}	3.97×10^{15}	2.74×10^{15}	0.83×10^{15}
3600	4.84×10^{15}	4.67×10^{15}	4.09×10^{15}	2.89×10^{15}	0.88×10^{15}
3700	5.71×10^{15}	5.53×10^{15}	4.87×10^{15}	3.48×10^{15}	1.12×10^{15}
3800	5.43×10^{15}	5.26×10^{15}	4.67×10^{15}	3.38×10^{15}	1.07×10^{15}
3900	5.07×10^{15}	4.93×10^{15}	4.40×10^{15}	3.24×10^{15}	1.01×10^{15}
4000	7.15×10^{15}	6.95×10^{15}	6.25×10^{15}	4.67×10^{15}	1.46×10^{15}
4100	9.24×10^{15}	8.99×10^{15}	8.12×10^{15}	6.12×10^{15}	1.93×10^{15}
4200	9.34×10^{15}	9.10×10^{15}	8.25×10^{15}	6.29×10^{15}	2.01×10^{15}
4400	10.4×10^{15}	10.1×10^{15}	9.25×10^{15}	7.22×10^{15}	2.42×10^{15}
4600	11.5×10^{15}	11.3×10^{15}	10.4×10^{15}	8.26×10^{15}	2.93×10^{15}
4800	12.0×10^{15}	11.8×10^{15}	10.9×10^{15}	8.84×10^{15}	3.29×10^{15}
5000	11.4×10^{15}	11.2×10^{15}	10.5×10^{15}	8.54×10^{15}	3.27×10^{15}
5250	11.9×10^{15}	11.7×10^{15}	11.0×10^{15}	9.11×10^{15}	3.68×10^{15}
5500	12.2×10^{15}	12.0×10^{15}	11.3×10^{15}	9.42×10^{15}	3.88×10^{15}
5750	12.2×10^{15}	12.0×10^{15}	11.3×10^{15}	9.48×10^{15}	3.98×10^{15}
6000	12.2×10^{15}	12.0×10^{15}	11.3×10^{15}	9.57×10^{15}	4.13×10^{15}
6250	12.2×10^{15}	12.0×10^{15}	11.4×10^{15}	9.82×10^{15}	4.60×10^{15}
6500	12.1×10^{15}	11.9×10^{15}	11.4×10^{15}	9.96×10^{15}	5.14×10^{15}
6750	11.9×10^{15}	11.7×10^{15}	11.3×10^{15}	10.0×10^{15}	5.59×10^{15}
7000	11.7×10^{15}	11.6×10^{15}	11.2×10^{15}	10.0×10^{15}	5.63×10^{15}
7500	11.1×10^{15}	11.0×10^{15}	10.6×10^{15}	9.57×10^{15}	5.67×10^{15}
8000	10.5×10^{15}	10.4×10^{15}	10.1×10^{15}	9.18×10^{15}	5.71×10^{15}

Table II gives values of J_λ for an intermediate set of conditions; details are in Leighton's report (*18*). This equation uses the weak absorption approximation; it neglects surface reflection, and it takes no account of the effects of diffusion within the absorbing layer. The weak absorption approximation will make the calculated rates too high, and neglecting the surface reflection will make them too low; as a result these two errors partially cancel each other. Any accounting of internal diffusion on absorption rates will depend on the directional distribution of the diffused radiation and on whether the rate near the surface on the average rate throughout the layer is the more important. Until more is known of these factors, the effects of diffusion within the layer must be regarded as indeterminate.

Absorption Rates and Primary Photochemical Processes. Leighton developed absorption rates for a large number of smog components from the above equation. In each case, k_a is expressed in seconds^{-1} and k_aC in p.p.h.m. hour^{-1} for concentration (C) of 10 p.p.h.m. for each absorber, except in the case of oxygen ($C_{O_2} \cong 21\%$).

Absorption rates and estimated upper limits for the rates of primary photochemical processes in urban air are summarized in Figure 25 and Table III. At other concen-

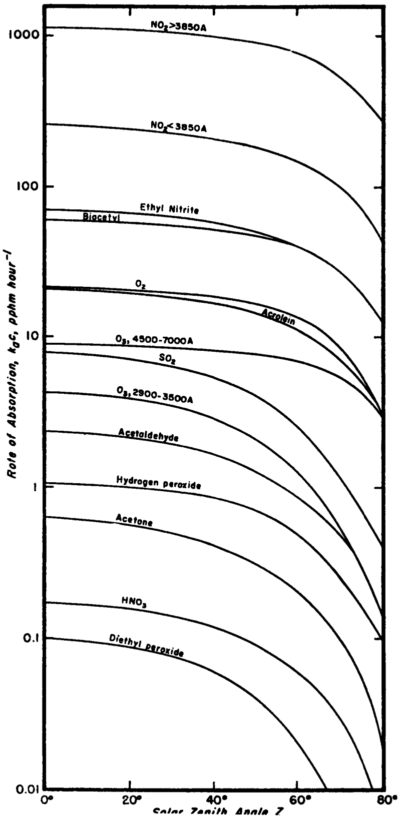

Figure 25. Comparison of absorption rates

Summary of absorption rates in p.p.h.m. hour^{-1} as function of solar zenith angle, under radiation conditions of Table II. Rates are for absorber concentrations of 10 p.p.h.m. except for oxygen, which is at 0.2 atm.

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Table III. Summary of Primary Photochemical Processes in Urban Air

Absorber	Primary Photochemical Process	Estd. Upper Limit for Primary Photochemical Rate in Urban Air, P.P.H.M. Hour^{-1}[a]	
		$z = 20°$	$z = 60°$
NO_2, < 3850 A.	$NO_2' \rightarrow NO + O$	250	105
Organic nitrites	$RCH_2ONO' \nearrow RCHO + HNO$? $RCH_2ONO' \searrow RCH_2\dot{O} + NO$	70	40
Diketones (glyoxal, biacetyl)	$(RCO)_2' \nearrow R_2CO + CO$ $(RCO)_2' \searrow 2\,R\dot{C}O$	60	40
	$(RCO)_2' + x \rightarrow ?$	—	—
Particulate metal oxides (10 γ)	$O_2 + e \rightarrow O_2^-$ org. $+ (MO)^+ + MO$	30[b]	20[b]
O_2 (0.2 atm.)	$O_2' + B \rightarrow ?$	~10[b]	~10[b]
O_3, 4500 to 7000 A.	$O_3' \rightarrow O_2 + O$	9	7
	$O_3' + B \rightarrow ?$	$\sim 10^{-3}$	$\sim 10^{-3}$
O_3, 2900 to 3500 A.	$C_3' \rightarrow O_2 + O$	4.5	1.5
Olefinic aldehydes (acrolein, crotonaldehyde)	$RCH = CHCHO' + O_2 \rightarrow ?$	2	1
Aliphatic aldehydes	$RCHO' \rightarrow \dot{R} + \dot{C}HO$	0.5 to 1.8	0.2 to 0.7
NO_2, A3850 A.	$NO_2' + B \rightarrow ?$	1[b]	1[b]
H_2O_2	$H_2O_2' \rightarrow 2\dot{O}H$	1	0.5
Aliphatic ketones	$RRCO' \rightarrow \dot{R} + R\dot{C}O$	0.4	0.15
Nitric acid	$HNO_3' \rightarrow \dot{O}H + NO_2?$	0.15	0.06
Organic peroxides	$ROOR' \rightarrow R\dot{O} + \dot{O}R$	0.1	0.02
SO_2	$SO_2' + SO_2 \rightarrow SO_3 + SO$	$\sim 10^{-4}$[b]	$\sim 10^{-4}$[b]

[a] Absorber concentration (except metallic oxides and O_2) = 10 p.p.h.m. Oxygen = 0.2 atm.
[b] Highly uncertain, even as upper limits.

trations the rates will be proportional to the concentration. The primary processes considered are only those resulting from absorption by the absorber indicated.

Because of variations in both radiation conditions and absorber concentrations, the actual absorption rates in an urban atmosphere will be highly variable. For example, Figure 26 shows the effect of concentration changes on the absorption rate

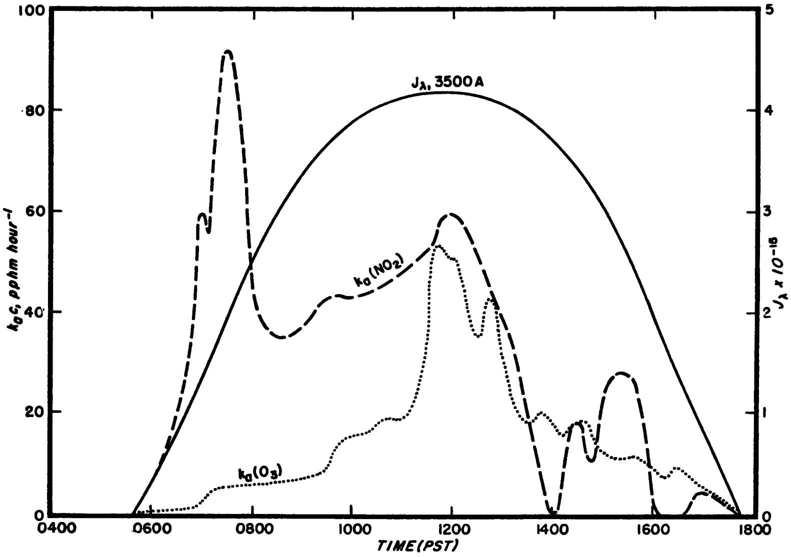

Figure 26. Effect of observed variations in concentration on absorption rates

of nitrogen dioxide below 3850 A., and the upper limit of the absorption rate of ozone (assuming the oxidant is all ozone) resulting from the observed concentrations of nitrogen dioxide and oxidant at Pasadena, Calif., on Sept. 13, 1955 (*8*). If the concentrations were constant, the absorption rate curves in Figure 26 would be symmetrical with the curve for J_λ. The effects of short term changes in radiation conditions may be of the same magnitude as those of concentration changes, but until more information is available on monochromatic irradiance, particularly diffuse irradiance, it is not possible to take similar account of them in urban air.

The observed rates of increase in oxidant concentration on the mornings of smoggy days in the Los Angeles Basin are for the most part between 1 and 15 p.p.h.m. hour^{-1}, although occasional very sharp increases may run up to 100 p.p.h.m. hour^{-1} or more. These sudden sharp increases in oxidant concentration may be due to photochemical reactions, or they may be due to meteorological changes—e.g., wind trajectory. For instance, the curve of oxidant concentration in Figure 27 shows an average rate of increase from sunrise until 11:00 A.M. of 2.8 p.p.h.m. hour^{-1}, while between 11:00 and 11:45 A.M. the rate of increase is 36 p.p.h.m. hour^{-1}.

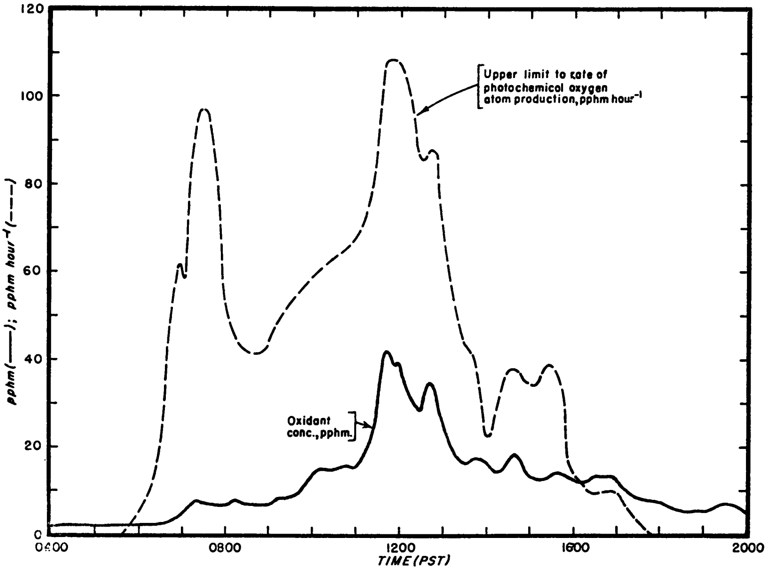

Figure 27. Comparison of rate of oxygen atom production with oxidant concentration on single day

On the composite average curve in Figure 28, the rate of increase in oxidant concentration from 7:00 to 11:00 A.M. ($z = 80°$ to $z = 44°$) averages about 2 p.p.h.m. hour^{-1}. The average rate of increase in oxidant concentration at 10 stations in the Los Angeles Basin (*28*) for the period of August through November 1954 was 1.8 p.p.h.m. hour^{-1} at $z = 60°$, while the rate of increase on the day of greatest oxidant value at each station during this period averaged 7.6 p.p.h.m. hour^{-1} at $z = 60°$. Additional work along these lines is developed by Rogers (*33*).

Referring to Table III, it is seen that at concentrations of the order of 10 p.p.h.m. the only absorbers capable of initiating primary photochemical processes at rates exceeding the observed average rates of increase in oxidant concentration are nitrogen dioxide, organic nitrites, diketones, and possibly particulate metallic oxides (at 10 γ) and oxygen. No satisfactory evidence exists on the concentration of organic nitrites and diketones, and it is not yet known whether absorption by particulate metallic

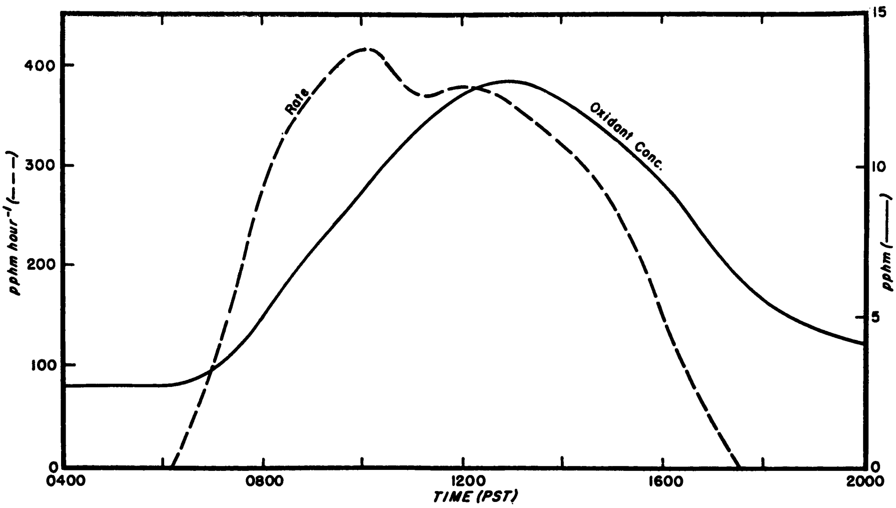

Figure 28. Comparison of averaged rates of oxygen atom production and oxidant concentration

oxides or by oxygen will lead to any reaction in urban atmospheres. Absorption by ozone will be important only if it leads to dissociation, and will in this case simply supplement the rate of production of oxygen atoms by photodissociation of nitrogen dioxide. Absorption by the aldehydes may contribute to smog formation, particularly in view of the fact that they have been observed at concentrations up to 30 p.p.h.m. in the atmosphere, but secondary chain reactions would be required for aldehyde absorption alone to lead to oxidant formation at the observed rates, and there is no evidence that such chain reactions occur in the atmosphere. There is no evidence that hydrogen peroxide exists in concentrations sufficient to be an important contributor. Reactions initiated by absorption by nitric acid, organic peroxides, and sulfur dioxide are probably too slow to contribute significantly to smog formation.

It seems to be important to obtain information on the following points:

The concentrations of organic nitrites and diketones in urban atmospheres.

Possible reactions following absorption by metallic oxides.

Possible reactions following absorption by oxygen.

Possible reactions following absorption by nitrogen dioxide in the visible region.

Reactions following absorption by aldehydes and ketones, including diketones, in urban air.

The importance in urban atmospheres of absorbers such as nitrous acid and organic compounds other than those considered here.

Pending this information and consideration of secondary reactions, the foregoing analysis supports the conclusion already reached by other investigators that, although other primary processes undoubtedly contribute, the photodissociation of nitrogen dioxide into nitric oxide and oxygen atoms is of major importance in smog formation.

The oxygen atoms resulting from absorption by nitrogen dioxide will be supplemented by those from the photodissociation of ozone, and as these are the only primary processes known to produce oxygen atoms in urban air, the sum of the absorption rates of nitrogen dioxide and ozone sets an upper limit to the rate of oxygen atom production. In Figure 27 this sum is compared with the observed oxidant concentration on a single day, while in Figure 28 the same comparison is made on the basis of a composite average of observations at a number of stations over a period of one month. The peak in rate of oxygen atom production, at 7:30 A.M. in Figure 27 and at 10:00

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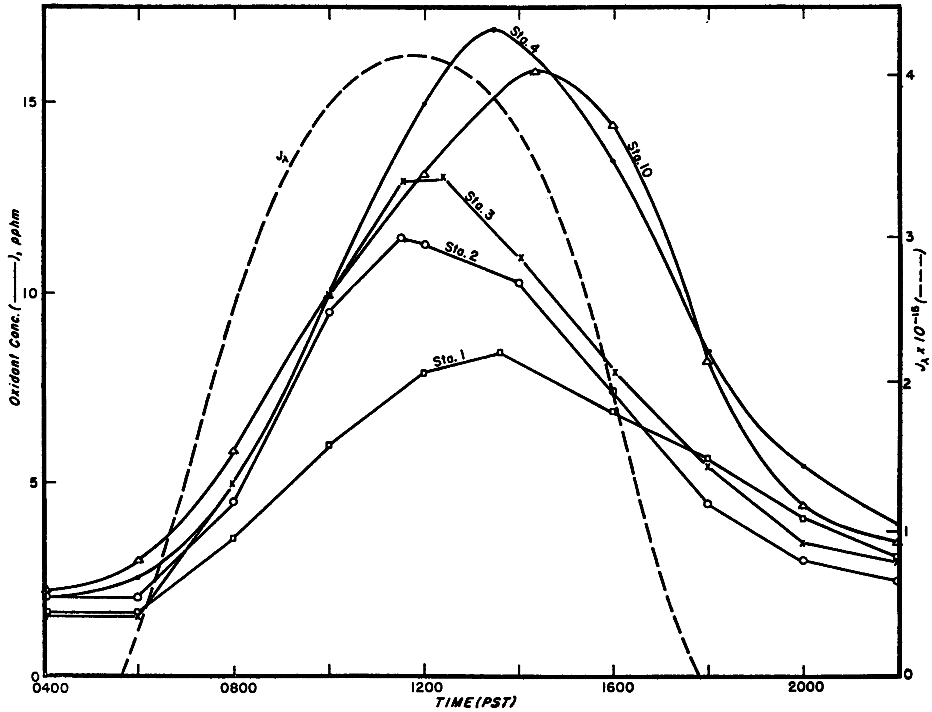

Figure 29. Comparison of solar irradiance with diurnal variations in oxidant concentration

A.M. in Figure 28, is due to the morning peak in nitrogen dioxide concentration. However, the time displacement of the averaged oxidant concentration curve relative to the rate curve in Figure 28 is not entirely due to changes in nitrogen dioxide concentration. This is shown in Figure 29, where curves of the average oxidant concentration versus time over a 4-month period at each of five stations in the Los Angeles Basin (*28*) are compared with a representative curve of J_λ. Since J_λ includes all of the factors influencing absorption rate which are directly dependent on solar zenith angle, plots of absorption rate at constant absorber concentrations will be symmetrical with this curve.

The shape of the averaged oxidant concentration curves and their time displacement relative to the absorption rate curves (Figures 28 and 29) indicate that the oxidant is produced by a photochemical process and continuously removed by a dark process. This dark process may be either chemical or physical, or both. If this is the case, the observed rate of change in oxidant concentration is equal to the difference between the rates of production and removal, and during the morning hours the actual rate of oxidant production may be substantially greater than the observed average rate of increase in concentration. If true, this will impose a further limitation on the number of primary photochemical processes which may be of significance.

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The author has borrowed freely from the writings of many investigators in order to put this review together, and he is indebted to them for their results. In addition to their published results these workers have given freely of their time for helpful conversations.

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Ozone Absorption Coefficients in the Visible and Ultraviolet Regions

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A comparison is made of the ozone absorption coefficients in the visible and ultraviolet regions measured by the authors with those reported by Vigroux. The experimental methods are described, especially with regard to the nature of the absorbing gas, the method of measurement of absorption intensity, and the experimental arrangement. In general, the two sets of results agree reasonably well in the regions of the Hartley, Huggins, and Chappuis bands. In the Hartley band region the agreement is much better between the authors' results and Vigroux's than between those of Ny and Choong and either. The agreement between the authors' results and those of Vigroux in establishing a reliable and consistent set of ozone absorption coefficients is discussed.

When the authors' results on absorption coefficients of ozone in the visible and ultraviolet regions were published (*1*), a similar set of results appeared in the literature published by Vigroux (*3*). Prior to this, the results of Ny and Choong (*2*) had been accepted as the best available data. The authors' results have been adequately compared with these.

A uniform and consistent set of ozone absorption coefficients is highly desirable, because these data are important in atmospheric problems and quantitative ozone technology. A comparison of the authors' results with those of Vigroux should establish a more reliable set of ozone absorption coefficients.

Experimental Methods

The schematic arrangement of the apparatus used by the authors for preparing and purifying ozone (*4*) is shown in Figure 1. The gas pressure in the ozonizer was kept below 12 cm. of mercury to prevent oxygen from condensing in the liquid nitrogen trap along with the ozone. The ozone was purified by repeated fractional distillation in the sample trap, shown on the right side of Figure 1. Thus, in all measurements almost pure ozone was used.

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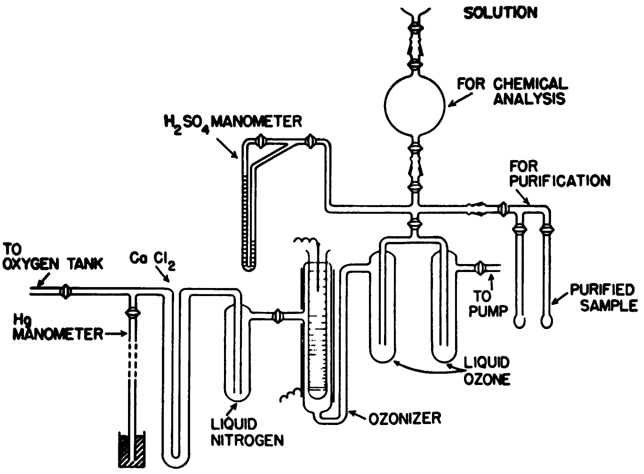

Figure 1. Schematic diagram of experimental arrangement for preparation and purification of ozone

Vigroux used a mixture of ozone and oxygen, ozonized oxygen, which was prepared in a similar way as the authors'. Because no further purification was made, the gas in these measurements usually consisted of a mixture of ozone and oxygen.

The quartz absorption cell the authors used was 10 cm. long. Because this cell was in direct communication with the purification system, the purified ozone was vaporized directly into it from the sample trap. Pressure measurements were made with a sulfuric acid manometer, by a calibrated expansion method, or with a mercury manometer, depending on the pressure desired. For each preparation of purified condensed ozone, an analysis was made of the purity by conventional chemical methods. For the several preparations analyzed, the purity ranged from 90 to 95% with an average of 92%.

In Vigroux's measurements, the ozone concentration in the ozonized oxygen was determined by chemical methods, from which the reduced pressure was calculated for the path lengths used. These measurements were carried out for the spectral region from 3100 to 3400 A. to establish a quantitative relationship between reduced pressure and concentration. In subsequent absorption coefficient measurements in other spectral regions, the corresponding reduced pressure of ozone was determined by this relationship. One arm of a cross-shaped absorption tube was always used to obtain the absorption spectrum in this region—hence the reduced pressure for that path length—and the other arm was used for other spectral regions of interest. The reduced pressure corresponding to the path length for the latter was calculated from the ratio of the actual lengths of the two arms.

For absorption measurements, the authors used a Cary recording spectrophotometer in which the absorbances were displayed directly on a recorder chart as the different spectral regions were scanned. In this instrument, the absorption cell is located between the exit slit and photomultiplier tube detector, thus minimizing any photochemical effect during the measurement. Corrections were applied to the recorded absorbances for any ozone decomposition during the time of measurement.

Vigroux used photographic methods to obtain the absorption spectrum with the medium Hilger spectrograph. The absorption intensity was obtained by conventional methods of photographic photometry. In photographing the spectrum, the absorption cell was placed between the light source and slit of the spectrograph, the absorbing gas being essentially exposed to the full beam of the light source.

The two experimental methods have been described in detail (*1*, *3*, *4*).

Comparison of Results

It is convenient to discuss three regions of the absorption spectrum, separately: the Hartley band from 2000 to 3000 A., the Huggins band from 3000 to 3500 A., and the Chappuis band from 4000 to 7500 A. The results of the ozone absorption coefficients measurements are displayed in Figures 2, 3, and 4, respectively. The absorption coefficients measured by the authors are tabulated in Table I.

Table I. Absorption Coefficients of Ozone

In Hartley Band Region						In Chappuis Band Region		In Huggins Band Region			
Wave length, A.	*k*, cm.$^{-1}$, base 10	Wave length, A	*k*, cm.$^{-1}$, base 10	Wave length, A.	*k*, cm.$^{-1}$, base 10	Wave length, A.	*k*, cm.$^{-1}$, base 10	Wave length, A.	*k*, cm.$^{-1}$, base 10	Wave length, A.	*k*, cm.$^{-1}$, base 10
						4342	0.0007	3002	4.59	3249	0.210
						4443	0.0014	13	3.71	53	0.171
2002	3.74	82	86.2	62	108	4543	0.0016	23	3.23	55	0.177
12	3.70	92	90.1	69	102	4629	0.0037	34	2.83	69	0.096
22	3.63	2400	93.7	75	103	4644	0.0037	44	2.50	72	0.117
32	3.71	02	95.3	82	96.7	4685	0.0033	54	2.18	76	0.107
42	3.83	12	98.9	2692	95.4	4746	0.0044	63	1.98	80	0.152
52	4.02	22	103	95	94.6	4838	0.0089	75	1.66	95	0.061
62	4.36	32	107	2702	89.1	4883	0.0077	86	1.53	3300	0.058
72	4.85	38	111	12	84.3	4951	0.0093	96	1.24	04	0.088
82	5.22	44	112	18	84.4	5055	0.017	3107	1.13	08	0.077
92	5.82	52	116	22	79.9	70	0.018	11	1.09	12	0.102
2102	6.39	58	118	32	75.4	5123	0.016	17	0.98	27	0.035
12	7.18	63	118	42	68.6	60	0.018	28	0.85	33	0.047
22	8.09	72	122	46	69.3	5265	0.024	30	0.80	39	0.070
32	9.20	78	124	52	66.6	5344	0.031	34	0.84	54	0.023
42	10.3	82	123	62	60.6	5371	0.031	38	0.76	58	0.022
52	11.7	90	127	72	56.8	5397	0.031	46	0.62	65	0.033
62	13.1	92	127	82	52.4	5476	0.035	48	0.64	67	0.032
72	14.6	2500	130	92	48.4	5528	0.038	51	0.60	72	0.045
82	16.5	08	127	2802	43.6	5581	0.040	55	0.64	86	0.017
92	18.3	19	133	12	39.7	5685	0.049	59	0.59	92	0.016
2202	21.0	27	130	22	36.4	5763	0.052	67	0.47	96	0.021
12	23.0	39	134	30	35.2	89	0.051	70	0.49	98	0.019
22	25.4	43	130	42	30.4	5841	0.048	72	0.47	3401	0.025
32	28.4	53	135	52	27.5	5893	0.047	76	0.50	18	0.0092
42	30.9	62	132	62	24.3	5945	0.048	79	0.45	21	0.011
52	34.3	66	127	72	22.2	5997	0.054	90	0.33	25	0.0092
62	37.6	71	131	82	19.3	6038	0.055	94	0.38	30	0.013
72	40.9	75	130	92	17.4	6101	0.052	98	0.36	35	0.012
82	44.8	79	128	2902	15.5	6205	0.045	3200	0.38	39	0.016
92	48.9	87	133	12	13.5	6309	0.039	01	0.37	53	0.0079
2302	52.8	97	126	22	12.3	6413	0.033	05	0.30	57	0.0094
12	56.6	2604	128	32	10.7	6517	0.027	11	0.234	62	0.0080
22	60.6	17	121	42	9.44	6622	0.023	15	0.223	68	0.0054
32	64.8	24	123	52	8.33	6726	0.018	21	0.290	72	0.0071
42	69.2	35	114	62	7.25	6832	0.014	24	0.253	83	0.0032
52	73.6	43	118	72	6.32	6937	0.011	27	0.277	88	0.0030
62	78.2	50	112	82	5.52	7042	0.0088	39	0.146	95	0.0047
72	83.2	54	111	92	4.78	7146	0.0072			3507	0.0032
						7250	0.0057	41	0.160	14	0.0047
						7353	0.0046	45	0.154	24	0.0030
						7456	0.0046				
						7560	0.0038				

Hartley Band. For the region from 2000 to 3000 A., a plot of Ny and Choong's results has been included in Figure 2. In general, there is fairly good agreement between the results of Vigroux and the authors, especially in the region of the wings of the band. The results of Ny and Choong are consistently higher, ranging from a few to 20% higher than the authors' and almost consistently about 20% higher than Vigroux's. Because Ny and Choong's results are consistently too high, they are less acceptable.

The discrepancies between the results of Vigroux and the authors lie mostly in the region of the absorption maximum. Vigroux's values are about 10% lower than the authors' in this region and the discrepancy appears to originate at the points of inflection of the broad continuum at about 2350 and 2700 A. Disregarding the discrete bands in this region, the underlying continuum may be examined. For example, if the latter is traced starting from the long wave length wing of the continuum, an abrupt displacement is noted at about 2700 A. There is no evidence of a similar displacement

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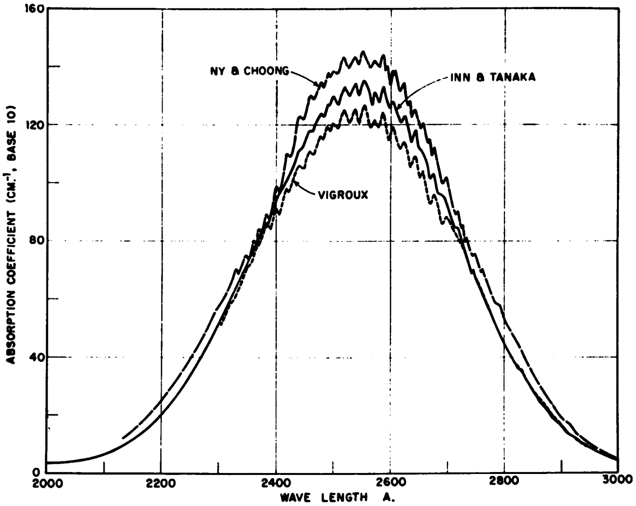

Figure 2. Absorption coefficients of ozone in region of Hartley band, 2000 to 3000 A.

in the shape of the continuum in either the authors' or Ny and Choong's results. Such displacement is rather unusual in absorption continua, although it is observed where two or more continua are superposed. The displacement may be explained on the basis of rapidly changing spectral sensitivity of the photographic emulsion, because most emulsions, unless specially sensitized, exhibit such a characteristic at about this wave length. If the shape of the continuum on Vigroux's curve were drawn in, there would be remarkably good agreement throughout the spectral region between it and the authors' curve, certainly within experimental error.

For the discrete bands in this region, the absorption intensities are somewhat greater in Vigroux's results than in the authors'. This is undoubtedly due to the better dispersion and resolution of his spectrograph. However, the differences are small and do not cause a serious discrepancy.

The results of the authors seem more acceptable and are the best values in this region for the absorption coefficient of ozone.

Huggins Band. Figure 3 shows the absorption coefficients in the region from 3000 to 3500 A. Again, there is good agreement between the results of the authors and Vigroux, especially for the continuum underlying the discrete bands. This is remarkable because the absorption coefficient changes about 200-fold within a spectral region of 500 A. despite the distinct differences in the experimental methods.

There are significant differences in the intensities of the discrete bands lying above the continuum. Because this results from spectral resolution and dispersion, Vigroux's results are more acceptable and represent the best values in this region. Furthermore, Vigroux's measurements (*3*) on the change in absorption coefficient with temperature in this region are of great importance in establishing a reliable set of absorption coefficients applicable to spectroscopic measurements of atmospheric ozone.

Chappuis Band. Figure 4 shows the absorption coefficients of ozone in the region from 4000 to 7500 A. Again there is general agreement between the authors' results and Vigroux's. The very low absorption coefficients in this region made measurements especially difficult. Although the relative differences between the authors' results and Vigroux's seem large for certain regions in the absorption band, the absolute differences are small.

There is good agreement between the results for the long wave length wing of the

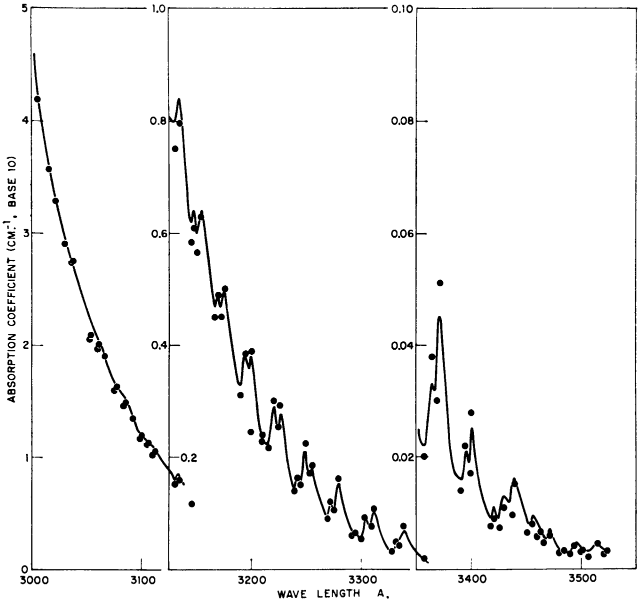

Figure 3. Absorption coefficients of ozone in region of the Huggins band, 3000 to 3500 A.

— Authors' results
● Vigroux's results

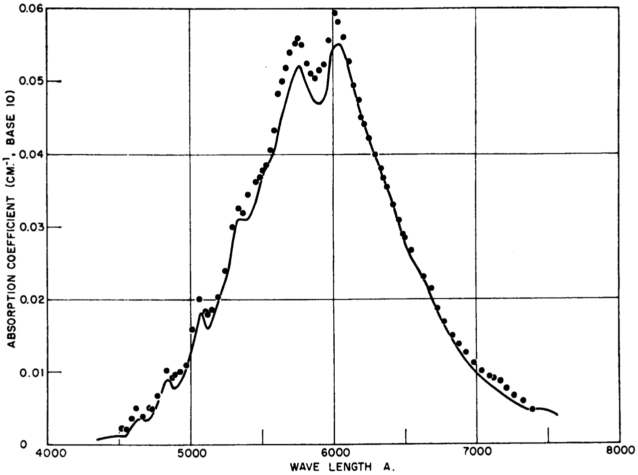

Figure 4. Absorption coefficients of ozone in region of Chappuis band, 4000 to 7500 A.

— Authors' results
● Vigroux's results

band, except at the extreme long wave length end, which is not too important. There is a more significant difference at the maximum and the short wave length wing, especially for the overlying diffuse but discrete bands. Because of the broadness of the diffuse bands, resolution and dispersion may not appreciably be responsible for the difference. The difference probably results from the inherent difficulties in measuring absorption for such a weakly absorbing band. As the results agree within 10% throughout most of the region, it is sufficient to accept an average of the two results unless an absorption coefficient with a better accuracy is required.

Conclusion

The satisfying agreement between the authors' results and Vigroux's for the absorption coefficients of ozone in the regions from 2000 to 3500 A. and from 4000 to 7500 A. considerably strengthens the establishment of a consistent set of data. This agreement was obtained despite the distinct differences in the experimental methods and thereby supports the validity and accuracy of the reported data. On the basis of these consistent results, the application of reliable supporting absorption coefficient data to any ozone measurement will place greater confidence on the derived quantitative results.

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Measurement of Ozone in Terms of Its Optical Absorption

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The unique absorption spectrum of ozone provides an ideal physical basis for measuring its concentration in the atmosphere even in the presence of significant quantities of other atmospheric pollutants, whether of gaseous or particulate character. Various types of optical equipment have been considered, both for measurement of the total amount of ozone and for determination of its vertical distribution and horizontal concentration. Natural sunlight furnishes a suitable and convenient light source for measuring the total amount and vertical distribution of ozone. Special sources having high radiant intensity within the spectral region of 2500 to 3600 A., where ozone has a high optical absorption, are desired for use in measuring the horizontal concentration of ozone. The light source, whether the sun or some special source such as a mercury arc lamp, may be employed with a simple filter radiometer or with a more or less elaborate prism or grating spectroradiometer as desired. In most of the recent work at the National Bureau of Standards a double, quartz prism spectroradiometer has been used at Washington, D. C., Climax, Colo., Los Angeles, Calif., and Sunspot, N. M., in ozone studies.

Since about 1845 (*44*) there has been an interest in ozone and in its measurement and its effect, either directly or indirectly, upon life and other activities. Often there has been a difference of opinion regarding its quantity and effects upon life processes. In fact, there has on occasion been a doubt as to its existence. At times it has been cloaked with unique health-giving properties which are inconsistent with present information.

Although a large number of measurements have been made, usually by some chemical method, many of them are today considered worthless because, in many cases, the chemical processes involved are now known to have been affected by other atmospheric components. It is only during the past two or three decades that accurate data on ozone have been obtained through the use of improved methods of measurement.

Because ozone is highly unstable and usually exists in but small quantities near

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the earth's surface relative to its greater presence at higher altitudes, some method of production at these higher levels must be postulated. The action of short wave solar radiation is generally held as the principal source of energy for the production of ozone. The effects of cosmic rays, lightning, particle radiation from the sun, or operation of purely chemical reactions within the atmosphere are thought to be negligible relative to short-wave ultraviolet in the production of ozone in the upper atmosphere.

The photochemical reaction which produces ozone from the atmosphere requires radiation of wave lengths shorter than about 2400 A. These radiations are sufficiently energetic to break the chemical bond of the oxygen molecule and produce free oxygen atoms. The oxygen atoms can react with the oxygen in the atmosphere to produce ozone.

The principal molecular components of the atmosphere are oxygen, nitrogen, carbon dioxide, argon, and water vapor. These may vary somewhat with altitude, but, except for water vapor, they extend to high levels in roughly the same relative proportions as found near the earth's surface. They and the other minor normal components of a clean atmosphere are optically highly transparent throughout the visible and ultraviolet spectrum down to near 2000 A. When radiant energy of wave lengths below 2400 A. is absorbed, dissociation processes may be operative. The production of ozone is the most noteworthy of these processes, as the oxygen is broken up and diffuses among the other components of the earth's upper atmosphere.

Although completely dissociated at the higher levels, at somewhat lower levels not all the oxygen is dissociated and by some more or less unknown process recombination occurs, resulting in a mixture of O_3, O_2, and O_1. Whether three atoms of O_1 combine to form O_3 or an O_1 combines with an O_2 is not known. Penndorf (*35*) and Blacet (*2*) have suggested that a three-body collision involving a foreign body may play a part in this recombination. Just what is the process or just how it operates is not clear. The ozone's being highly opaque to the short wave length ultraviolet effectively shields the gas at still lower levels from such radiation, so that decomposition occurs (*4*). The end result is therefore an equilibrium condition in the upper atmosphere between the production and decomposition of ozone by sunlight of the different wave lengths, which is exemplified by the building up of a maximum density of ozone at an intermediate level. This distribution of ozone has been found by different investigators at various times and places to lie usually between about 10 and 20 miles high (*17, 24, 42, 50, 60*).

Methods of Ozone Evaluation

Five principal methods of ozone evaluation have been employed by different investigators at different times and places. These may be roughly classified with some variations as follows:

Chemical measurement of ozone in terms of the release of iodine in a buffered potassium iodide solution. Recent improvements in this method permit the continuous recording of ozone concentration in terms of colorimetry or potentiometer readings (*13, 27*).

Color measurement of ozone in terms of oxidation of phenolphthalin ($C_{20}H_{16}O_4$) to phenolphthalein ($C_{20}H_{14}O_4$). In this method hydrogen peroxide is used to develop a standard curve (*29, 34*).

Physical measurement of ozone in terms of the rate of cracking of bent or stretched rubber (*3*).

Measurement of ozone in terms of the response of certain plants, especially for damage to upper leaf surfaces (*19, 54*).

Optical measurement of ozone in terms of its ultraviolet, luminous, or infrared absorption.

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The first four methods for the measurement of ozone are not discussed here, except for noting that each of them is more or less qualitative in comparison with the optical method. This is especially the case under conditions wherein the atmosphere contains a number of other pollutants such as exist in the Los Angeles area. Under conditions of polluted atmosphere, disagreement often results among scientific workers (*28*) as to what constitutes a certain identification and true measure of ozone. Haagen-Smit (*18*) early concluded from results of chemical and photochemical experiments that the major portion of the oxidant component of the Los Angeles smog consisted of various organic peroxides rather than ozone. Ozone plant damage is often complicated by the presence of other atmospheric oxidants (*19*). Furthermore, ozone plant damage occurs only in the presence of large amounts of ozone. Crabtree and Biggs (*5*) found that certain free radicals may produce rubber cracking of a type which cannot be distinguished from that resulting from exposure to high concentrations of ozone. Hence, only some optical method remains as a possible reasonable means for the accurate evaluation of ozone concentrations in the atmosphere, especially when the ozone is associated with other pollutants or oxidants.

Ozone in gaseous form in which it is normally encountered exhibits selective absorption in several regions of the spectrum. Within the Hartley band, centered at 2500 to 2600 A. in the short wave ultraviolet, the absorption is most intense. Next comes the Huggins band which is centered at slightly longer wave lengths and extends to about 3400 A. Data on the absorbance of ozone in this spectral region as given by Tsi-Ze and Shin-Piaw (*57, 58*) are reproduced in Figure 1 (*49*). These or similar data have been employed by the various investigators whose works are reported in this paper in their determination of the amount of ozone in the atmosphere. [Recent data, however, indicate appreciably lower ozone absorption coefficients throughout most of the ultraviolet spectrum (*21*).]

Two ozone bands situated near 9.5 microns in the infrared (*1*) show considerable absorption, near 50% for a single atmosphere, but are markedly temperature and pressure sensitive. This property is useful in certain work as will be noted below. Finally, ozone exhibits some absorption in the visible spectrum, in particular within the yellow-orange region, resulting in giving the gas a light blue color when viewed in bulk. This absorption is weak but may be used to supplement or check experimental work which employs the ultraviolet bands.

The absorption of ozone in the visible spectrum is especially useful and has been used in analyzing some of the Smithsonian data, which are extensive but do not extend to include an appreciable amount of the ultraviolet region. Wulf (*61*) and others (*14, 25*) have made considerable use of these data, deducing ozone concentrations which are in fairly good agreement with those obtained through the use of ultraviolet measurements.

The high optical opacity of ozone within the Hartley and Huggins bands, with the absorption centered at 2500 to 2600 A. and extending to about 3400 A., has furnished a unique possibility for its measurement in terms of its relative or absolute spectral absorption. Several optical methods, each based upon this characteristic of ozone, have been set up at the National Bureau of Standards (*46, 48–51*). These dealt with the measurement of the total amount, vertical distribution, and local concentration of ozone by three general methods. The first, employed in the measurement of total ozone, was based upon the relative absorption of the ultraviolet solar radiant energy by the terrestrial atmosphere as the air mass changed during the day. The second method was employed in the evaluation of the vertical distribution of the ozone and was based upon similar solar radiation changes as the instruments were carried aloft by balloons. The third method had to do with the measurement of ozone concentration in the lower atmosphere (at the earth's surface) and was based upon the relative spectral optical absorption of a horizontal beam from an artificial ultraviolet source.

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch038

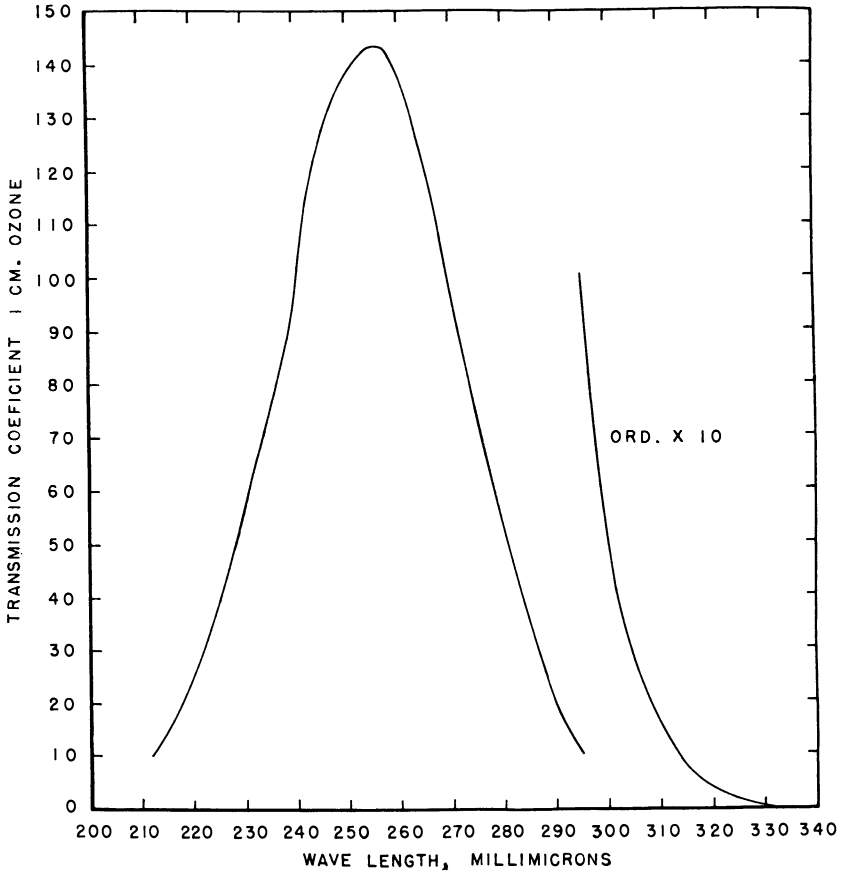

Figure 1. Absorbance of ozone

Total Ozone

The measurement of the total amount of ozone has received greatest attention and may probably best be made by means of a double, quartz prism spectroradiometer or spectrophotometer. The detector may be a thermopile (*36*), photoelectric cell (*48, 49, 52*), or the photographic plate (*11, 17, 20, 22, 32, 42*). The thermopile has the advantage of measuring radiant energy of the different wave lengths directly in absolute units when once calibrated. However, its low sensitivity rules against its use in rapid work in the ultraviolet spectrum where energy values are low. Advantages such as high sensitivity, direct recording, and freedom from the development of plates and their variation in sensitivity generally rule in favor of photoelectric detection.

Data on total ozone obtained by the National Bureau of Standards at Climax, Colo., and at Sunspot, N. M. (*48, 49, 52*) with a double, quartz prism spectroradiometer employing a photoelectric detector are illustrated in Figures 2, 3, and 4. Small differences in atmospheric scattering between the three sets of data result from differences in altitude of the two stations and from clearness of the atmosphere at the times the measurements were in progress. Close agreement between the ozone values is significant. The equipment employed in these investigations was designed primarily for the purpose of evaluating the spectral distribution of the radiant energy from the sun. Spectral energy data obtained at Sunspot, N. M., during June

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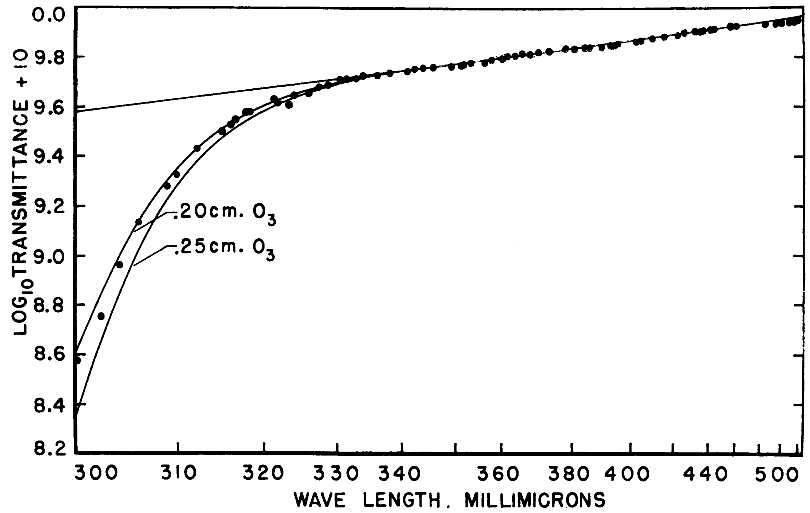

Figure 2. Atmospheric transmittance at Climax, Colo. (altitude, 11,190 feet), and determination of total ozone above observing station

Mean of data for 4 clear days in September 1951

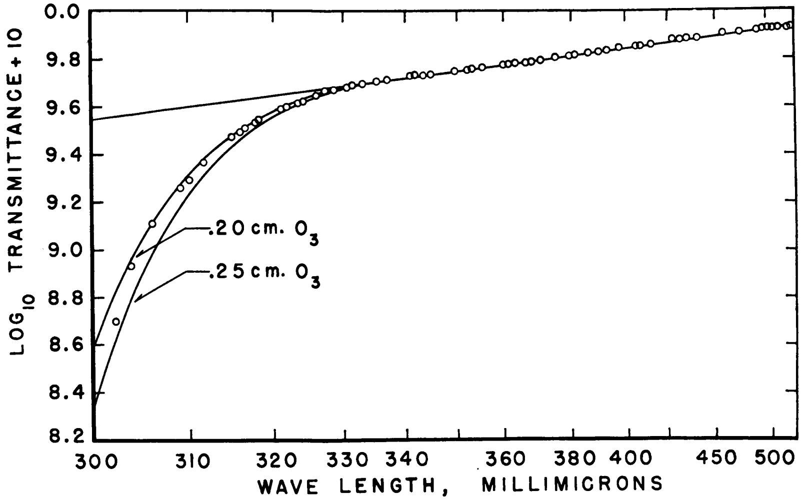

Figure 3. Atmospheric transmittance at Sacramento Peak (Sunspot), N. M. (altitude, 9200 feet), and determination of total ozone above observing station

Mean of data for 4 clear days in July 1953

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch038

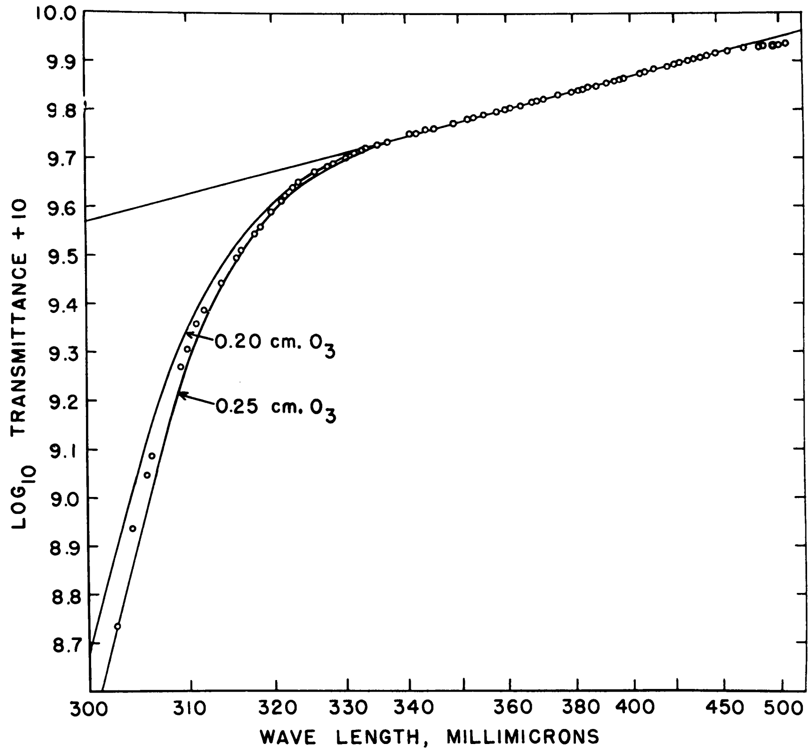

Figure 4. Atmospheric transmittance at Sacramento Peak (Sunspot), N. M., and determination of total ozone above observing station

Mean of data for 4 clear days in June 1955

1955 are given in Figure 5. A photoelectric detector was employed and, by use of a synchronous electric motor, wave length drive, and a strip recorder, the observed data were automatically plotted on a paper chart. The instrument was either pointed directly at the sun (*52*) or else a direct beam of light from the sun was reflected onto the entrance slit by means of a heliostat (*48, 53*). This arrangement permitted the integration of the radiation from the entire solar disk while it eliminated almost completely the scattered radiation from the sky.

About 1930, Dobson (*7*) set up a double, quartz prism instrument, the Dobson ozone meter, for use in measuring ozone only by isolating two wave lengths in the ultraviolet solar spectrum; from their relative intensities the absorption caused by ozone could be determined and, hence, its amount. Any two wave lengths may be employed such that one of them lies well within the ozone absorption band while the other is just outside, or almost outside, the band. This instrument is likewise photoelectric so that ozone measurements may be made rapidly. However, since the ultraviolet solar spectrum is modified greatly by thousands of Fraunhofer lines or bands and since their apparent structure is greatly affected by instrumental slit width, errors may be introduced through slit width changes or wave length shifts resulting from temperature changes within the instrument. In this respect the scanning of the complete spectrum and the use of many wave lengths in ozone evaluation is to be preferred.

An early method developed at the National Bureau of Standards (*45, 46, 51*) and recently employed by Miyake and Kawamura (*30*) for the measurement of the total

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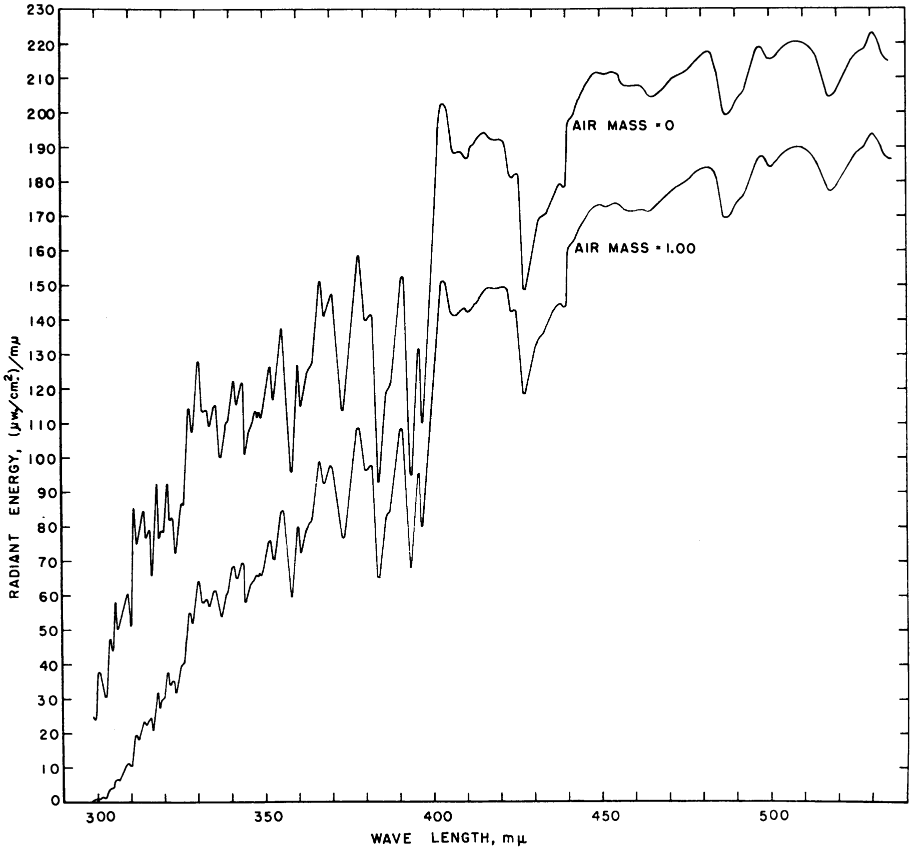

Figure 5. Spectral distribution of radiant energy from the sun at Sunspot, N. M.

Mean for 4 clear days in June 1955

amount of ozone, incorporated a single phototube having a sensitivity confined to the spectral region of wave lengths shorter than about 3600 A. The phototube was used in conjunction with a simple amplifier and groups of two to four glass filters having effective total transmittances for sunlight of about 20 to 75%. This permits the breaking up of the short wave solar spectrum in such a way that ozone changes are readily evaluated in terms of changes in the observed filter transmittances.

This method requires a knowledge of the relative spectral intensity of the ultraviolet solar radiant energy outside the terrestrial atmosphere within the spectral range of 3000 to about 3400 A., in addition to transmittance data on the filters and relative spectral response data for the phototube. Furthermore, it is assumed that the solar radiant energy (outside the atmosphere) remains constant during the course of the ozone measurements. As an alternative, the instrument may be calibrated by comparison with another type of ozone meter—for example, a double, quartz prism spectroradiometer or a Dobson ozone meter. This photoelectric instrument has the advantage of being simple, light in weight, low in cost, and rapid in operation. It thus lends itself to use in field work in the accumulation of extensive data over wide areas or time intervals.

Data obtained at Sunspot, N. M., during the summer of 1949 (*45*) with the simple photoelectric-filter instrument are given in Figures 6 and 7. Small changes in

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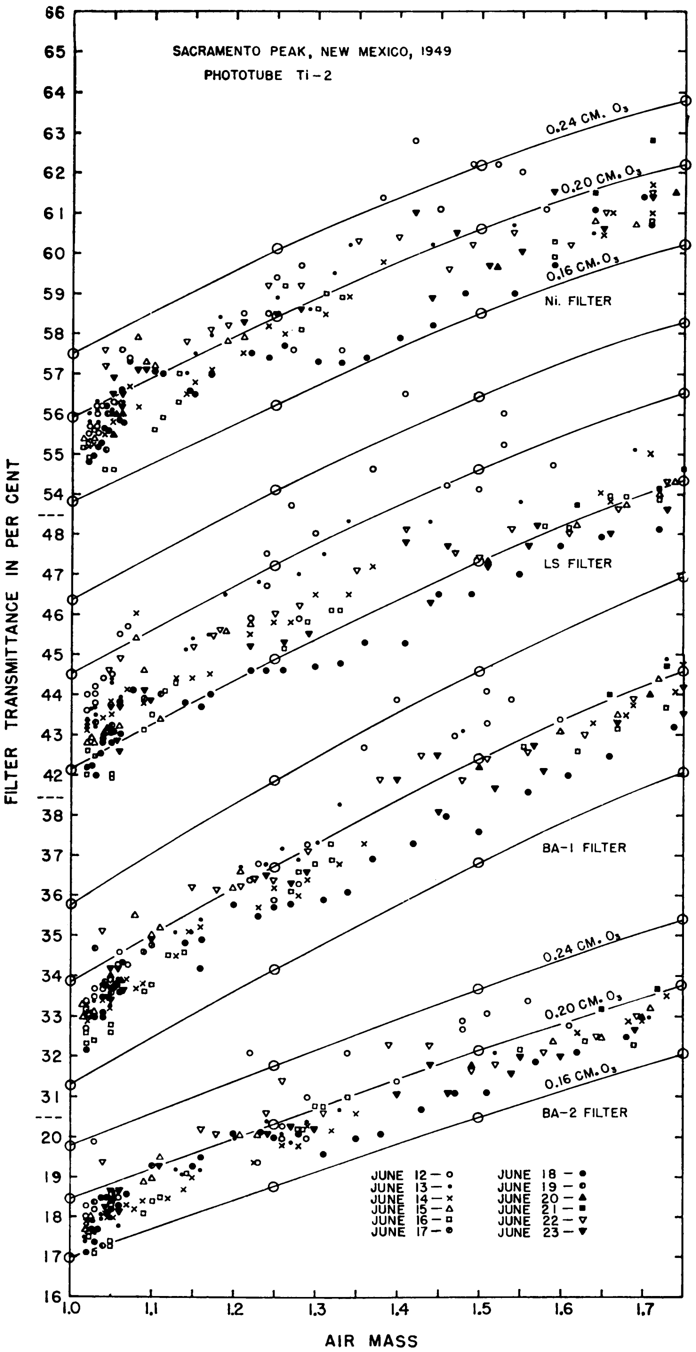

Figure 6. Amount of ozone in stratosphere over Sacramento Peak, N. M.

Data for several days in June 1949, based on observations with phototube (titanium No. 2) and filter ozone meter

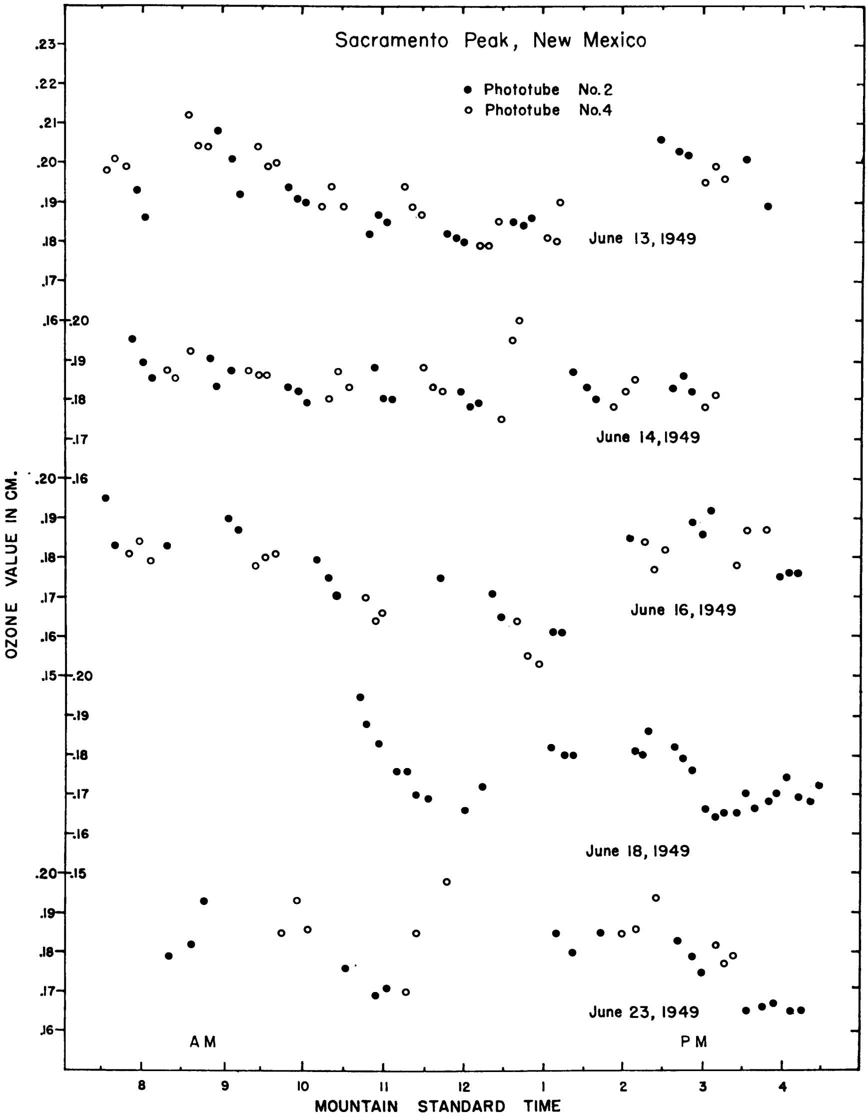

Figure 7. Amount of total ozone above Sacramento Peak, N. M., as function of time of day

Values obtained with two phototubes for selected clear days in June 1949

the total amount of ozone are apparent from an examination of these charts. Some result from uncorrected errors because of scattering by dust or clouds; other changes are real. The larger changes from day to day are important and illustrate the usefulness of an instrument of this type in continually monitoring the amount of atmospheric ozone.

The mean values for day-to-day measurements made at Washington, D. C., over a period of 9 years (*47*) are given in Figure 8. Each plotted point represents the mean value for a single day. Greatest weight was given to measurements made near the noon hour, when the sunlight was observed through the least atmosphere. Similar

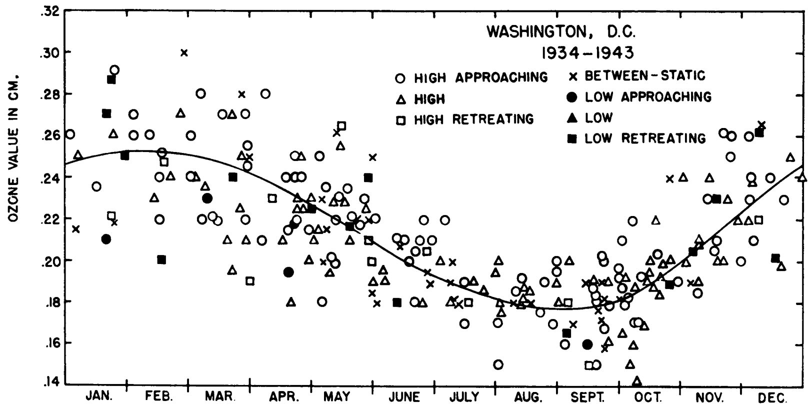

Figure 8. Seasonal variation of ozone at Washington, D. C. (altitude, 300 feet), using phototube and filter ozone meters

data taken by Fritz (*15*) at Washington, D. C., using a Dobson ozone meter, over a period of 25 months are in close agreement. His work substantiated high ozone values in the spring with much lower values during the late summer and fall.

Ozone data obtained at high latitudes by Tønsberg and Olsen (*56*) at Tromso, Norway, follow a slightly different seasonal variation but are likewise high in the early spring months and low in late summer and fall. Measurements made at 12 European stations and recently summarized by Normand (*31*) are in general agreement with those illustrated in Figure 8. The data taken by Miyake and Kawamura (*30*) in Japan with a phototube and filters are also similar to those obtained by Stair (*47*) and by Fritz (*15*) at Washington and by Lejay (*26*) in France. This is to be expected, as the latitudes of the three stations differ but little.

Vertical Distribution of Ozone

It was pointed out earlier that the natural equilibrium condition for the production and dissociation of ozone resulted in an ozone maximum at some intermediate level in the upper atmosphere. From measurements at different times and by different observers (*6, 12, 16, 32, 33, 37, 39, 41, 42, 50*) this maximum has been found to vary in height, thickness, and in general structure, with short and long period fluctuations possibly associated with weather conditions and seasonal variations. On occasion double maxima may appear (*41*). Little is yet known, however, about specific relationships between the ozone changes and meteorological conditions except in the instance of seasonal variations (*6, 8, 10, 15, 26, 30, 47*) and certain large air mass movements (*9, 56, 59*). There is a great need for continuous observations of both the total and the vertical distribution of ozone in order to establish possible relationships between ozone distribution and concentration and solar variation, atmospheric circulation, and weather.

The vertical distribution of ozone may be measured by optical means with instruments situated permanently at the earth's surface, although better by their transport through the ozone layer. Some of the early measurements by Goetz *et al.* (*16, 17*) were by the former method—known as the Umkehr effect. This method permits the determination of the ozone distribution in terms of the change in the relative scattering of the ultraviolet solar radiation (at two selected wave lengths) of the zenith sky as a function of the zenith angle of the sun. This method continues to be employed, although it does not permit as high accuracy as the transport methods.

Early work at the National Bureau of Standards (*50*) and at a number of other laboratories (*16, 37, 42*) in the study of the vertical distribution of ozone made use of balloons, usually unmanned, for carrying radiometric or photographic equipment through a part or most of the ozone layer. The NBS instrument consisted of a phototube and filter-type ultraviolet meter (*46, 50, 51*) which was combined with an audiofrequency generator and radio transmitter. The radiofrequency wave was modulated by the phototube response to sunlight as the instrument was carried upward through the atmosphere. The magnitude of the response was proportional to the solar intensity through the several filters. The amount of ozone above the instrument and hence, its vertical distribution, was obtained by calculation from the observed changes in the apparent filter transmittances. The mean of data obtained in 18 balloon flights at the National Bureau of Standards employing this method (*47, 50*) is given in Figure 9 along with other data by other early observers (*32*). The Regeners (*37, 39, 42*) employed spectrographs in similar unmanned balloon flights and evaluated the ozone vertical distribution in terms of spectral change of the ultraviolet solar radiation at specific wave lengths. Recent data obtained by V. H. Regener (*38*) in unmanned balloon flights over New Mexico in 1950 are illustrated in Figure 10.

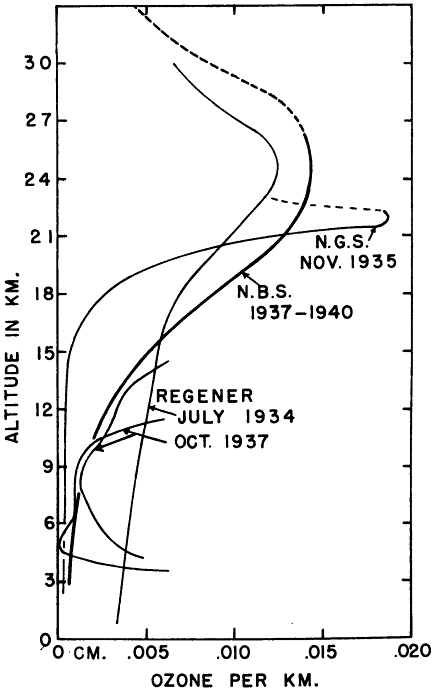

Figure 9. Vertical distribution of ozone in stratosphere

NBS curve is mean of June and July measurements obtained in 18 unmanned balloon flights using phototube and filter ozone meters. NGS measurements obtained with spectrograph in manned balloon. Regener measurements obtained with spectrograph in unmanned balloons

In the Regener flights (*38, 41*) the entrant spectrograph tube was directed downward onto a white magnesium oxide surface which was directly illuminated by the

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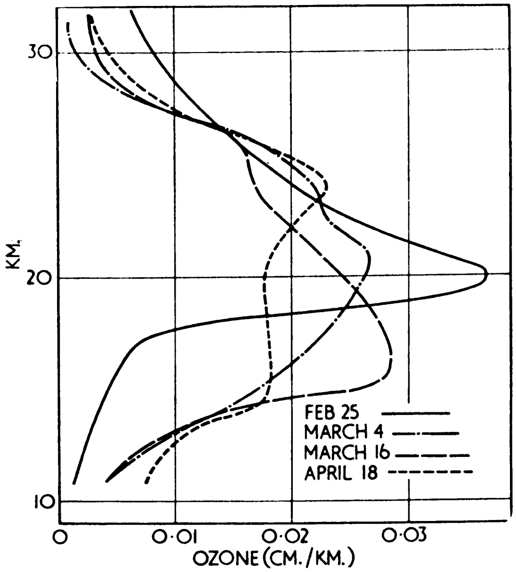

Figure 10. Vertical distribution of ozone (indicating double maxima) over New Mexico in 1950 using spectrographs in unmanned balloons

sun. The exposure time was 8 minutes, during which three exposures were obtained through a three-step filter consisting of different absorbances of evaporated platinum on a quartz plate. Thus, definite transmittance ratios between the three sets of spectra were employed in the evaluation of the vertical distribution of the ozone. The illustrated data (Figure 10) show the possibility of double ozone maxima on three of the four flights. However, although irregularities exist in some of the NBS and NRL curves, in no case has any definite evidence of a double maximum appeared in their data. It may be in this case that erratic observations have not been properly taken into account (*23*); however, Paetzold (*33*) has reported definite double or triple ozone maxima on numerous occasions.

The work of the National Geographic Society group (*32*) differed primarily in that a manned balloon was employed so that more elaborate equipment could be used and more careful control of the photographic processes and calibrations could be established. The results of this flight differ from that of all the unmanned flights in indicating a very sharp ozone maximum at a somewhat lower altitude. Results from flight to flight may differ because of differences in instrumentation and technique or because of actual change in atmospheric conditions. Hence, there exists a great need for routine experiments with stable equipment.

The development of a unique method (*12*), originally described by Strong (*55*) in 1941, whereby it is possible to determine the mean height of the ozone layer through measurements of the pressure-sensitive infrared absorption of the ozone molecule and comparison with determinations of the total amount of ozone based upon ultraviolet spectroscopic measurements has given added impetus to routine ozone vertical distribution determinations. This method permits the evaluation of the approximate vertical distribution of the ozone solely from the use of surface observations. Preliminary results (*12*) indicate that there is no simple relation between the vertical distribution of ozone and the total amount present in the atmosphere at any given time. When routine measurements are established over a network of stations by this (or any other satisfactory) method, it may be possible to establish some definite relationship between ozone distribution and movement and other factors such as weather conditions, atmospheric circulation, and solar variations.

The use of rockets offers a unique opportunity for the penetration of the entire ozone layer in contrast to the partial penetration afforded by balloons. Except for the meager data obtained by the Umkehr effect (*17, 56*) and from calculations based on the pressure-sensitive infrared absorption of ozone (*12, 55*), no absolute data on the vertical distribution of ozone have been obtainable (before the use of rockets) to altitudes above about 32 km. Little credence could be given to data obtained by either the Umkehr effect or to the infrared method for altitudes above about 40 to 50 km., as both methods are indirect and require appreciable optical absorption to permit practical application.

Rocket experiments by personnel of the Naval Research Laboratory (*22–24*) have extended ozone observations to altitudes up to 70 km. In this work V-2 or Aerobee rockets were employed and a grating spectrograph was carried in the head of the vehicle. Side windows provided with a bead of lithium fluoride served to illuminate the spectrographs as the rockets rotated in flight. On the first flight exposure times of 3.6, 0.66, and 0.12 seconds were employed. On later flights a single exposure time of about 1 second was employed. Calibration of the resulting spectra permitted the evaluation of the relative spectral energy distribution of the sunlight and hence, of the amount of ozone in the light path above the instrument in a manner similar to that employed in some of the balloon flights.

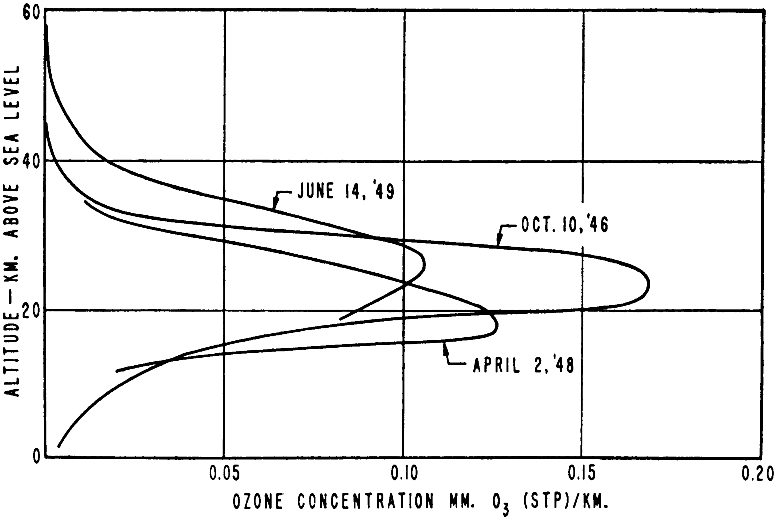

Figure 11. Vertical distribution of ozone over New Mexico obtained with spectrographs carried through ozone layer by rockets

Data on three successful flights by Naval Research Laboratory personnel are reproduced in Figure 11 (*24*). While data obtained by a rocket spectrograph in this manner cannot be considered highly accurate, the large variations in the vertical distribution of ozone at high altitudes are indicative of a certain amount of air movement at these levels. It appears that air motion upsets the ozone equilibrium conditions by the equivalent of altitude changes at times of as much as 5 or 6 km. Furthermore, it has been established by these experiments that ozone extends up to and sometimes above 70 km. The maximum relative concentration of ozone has been

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found to vary between about 25 and 30 km. This may be considered as the ozone equilibrium level.

This maximum relative concentration must not be confused, however, with the maximum of total ozone which usually exists at a much lower level—that is, between about 20 and 25 km.

Surface Ozone

The concentration of ozone in the surface atmosphere has been found to vary widely both in time and location. Its presence ordinarily has little or no significance except in certain localities, as, for example, where rubber goods may be stored or employed or when associated with intense smog conditions as exist in the Los Angeles basin. Its presence results from a number of causes, mostly not yet well understood. Some is produced by discharges from high tension wires and other electrical machinery, some by lightning, and some diffuses or is carried downward by air currents. Most of the high concentrations are found in connection with combustion of hydrocarbons and are apparently produced through chemical and photochemical processes not yet fully established (*28*).

As noted previously, ozone is unique in having a high optical opacity within the Hartley band centered around 2500 to 2600 A. This furnishes an ideal basis for the physical measurement of the surface concentration of the ozone in terms of its relative spectral absorption at these wave lengths in relation to that at longer wave lengths. Stair *et al.* (*49*) devised a filter radiometer for this purpose, wherein the amount of ozone in parts per hundred million was determined as a function of the ratios of filter transmittances of the radiant energy from a mercury arc lamp situated at a distance of 1450 feet from the detecting device. The detecting system consisted of a photomultiplier tube and associated equipment. In this arrangement the light beam is modulated so that alternating current equipment may be employed throughout. Some results obtained with this equipment on an evening at Washington, D. C., when a small amount of ozone was intermittently present, are illustrated in Figure 12 (*49*). Although the particular equipment setup was adapted only to night operation, by the use of ultraviolet filters and of mercury arcs rich in the emission lines of 2804 and 3655 A., day operation should be feasible.

Regener (*40*) employed a special spectrograph in the measurement of ozone in the presence of smog at Los Angeles, using an intense hydrogen arc as the light source. The light path was 1000 feet. Three wave lengths within the spectral range of 2665 to 2807 A. were employed in the ozone evaluation. By using an eccentric rotating disk as a shutter, a gradually varying exposure along the slit length was obtained. From the resulting spectra a number of ozone determinations were made from each photograph. Results in agreement to within 10% of those obtained with the potassium iodide method were reported. In Regener's work it was assumed that the principal selective absorption within this part of the ultraviolet spectrum was due to ozone. Such an assumption appears reasonable in the light of present information on the relative spectral transmittances of known substances in the atmosphere.

Recently the Air Pollution Foundation (*43*) set up a spectroradiometric ozone meter (designed by R. S. Estey) which incorporates many of the features and principles employed in the instruments developed by the National Bureau of Standards (*49*) and by Regener (*40*). This meter employs a high intensity mercury arc (type CH3) together with a Corning 9863 filter which confines the radiant energy principally to the ultraviolet spectrum. A simple spectroradiometer employs four 30° quartz prisms with a 1P-28 photomultiplier as a detector. The design of the electronics and strip recorder follow closely to that of the NBS instrument except that a frequency of 120 instead of 510 cycles per second is employed (the natural modulation of the lamp as operated on 60 cycles per second alternating current). In this instrument

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Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch038

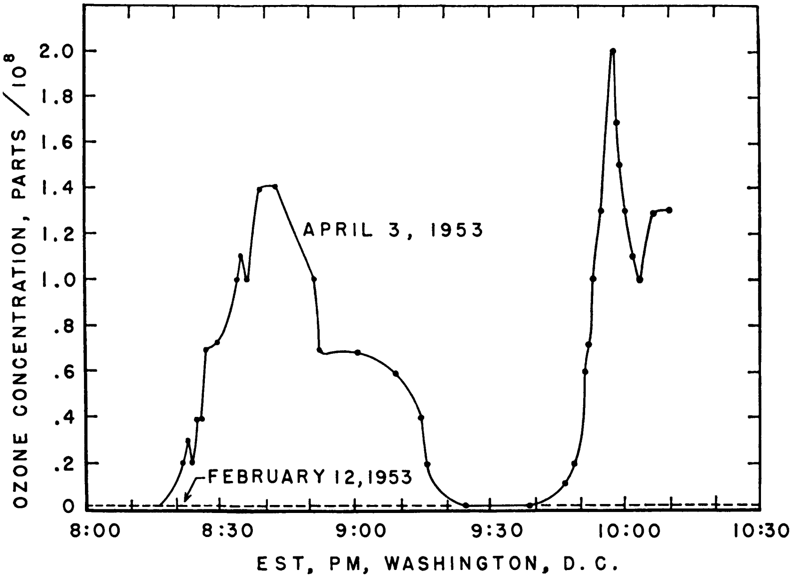

Figure 12. Variation in surface ozone on two evenings at Washington, D. C.

Measurements made with mercury arc source and photomultiplier and filter ozone meter through 1450-foot distance (*49*)

the air path length is 300 feet and the ozone content is calculated in terms of relative absorption at 2650, 2804, and 3132 A. The spectrum may be swept as desired, but in the original instrument two sweeps, 1 minute apart, were made each 15 minutes. The NBS instrument similarly swept through the different filter combinations once each minute.

A compact photoelectric instrument (*28*) recently developed by H. Kruger Associates of San Gabriel, Calif., takes advantage of the high opacity of ozone at 2537 A. through the use of a beam of radiant energy of that wave length. A light path of only 10 inches is employed. This instrument is essentially a double-beam ultraviolet filter photometer and has an extremely high sensitivity, full-scale sensitivity being something less than 100 p.p.h.m. of ozone. The electronic sensitivity of this instrument is probably too high for practical purposes. Improved operation could possibly be had through increasing the path length, thereby permitting the use of less sensitive electronic circuits as well as decreasing the effect of the small amount of ozone produced near the lamp source.

Optical methods of ozone determination may be combined with the chemical types in one way or another. For example, Littman and Marynowski (*28*) improved and modified a method earlier employed by Paneth and Edgar (*34*) using a silica gel to absorb the ozone gas from the atmosphere. Afterward the ozone was flushed into an optical cell, where its concentration was measured in terms of its ultraviolet absorption as compared with that resulting from known concentrations of synthetic ozone-oxygen mixtures.

In conclusion, it now appears that the spectroradiometric methods of ozone evaluation have, contrary to an earlier appraisal (*34*), become both practical and preferred for use in routine ozone measurements.

As this is a summary paper covering some of the work of many investigators, it has not been possible to give all the details in any case. In some cases important work may have escaped notice. However, the list of references at the end of the paper should provide the reader with an opportunity to pursue further along any particular line of investigation.

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The Mechanism of Ozone Formation in Electrical Discharges

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Many investigations have provided data on the dependence of the rate of ozone formation on the gross characteristics of the discharge, the current carried, and the energy absorbed, yet the nature of the reaction is imperfectly understood. Some of the simpler aspects of ozone formation are considered in relation to other phenomena, in order to outline the nature of the problems that arise in attempting to trace the identity and extent of the reactions concerned.

Two principal requirements must be satisfied in order to interpret experimental data on the synthesis of ozone in gaseous discharges in terms of a detailed reaction mechanism: data on the absolute rate of reaction as a function of the parameters that describe that state of a partially ionized gas which is called a discharge; and an adequate quantitative theory predicting the absolute rate of any one of the many reactions by which the synthesis of ozone may occur.

A knowledge of the reaction mechanism is important to both science and technology: It would build yet another bridge between chemistry and physics, in particular between photochemistry and the physics of discharges and of the upper atmosphere; and it would illuminate the chemical engineering problem of generating ozone on an industrial scale more economically than hitherto.

The task of identifying which of the possible reactions contribute to the observed synthesis, and of deducing their relative contributions to the observed rate of synthesis, is analogous to the task of interpreting the data for the photochemical synthesis of ozone. It is, however, much more complex.

The first step in most photochemical reactions involves a transition of high probability (an optically allowed transition) from the ground state to an electronically excited state of a reactant species; the excited state either initiates the observed chemical change or spontaneously dissociates into fragments which initiate those chemical changes.

Any allowed transition effected by photons can also be effected by electron impact, the cross section for the latter process passing through a maximum for an electron energy usually three to five times the vertical excitation energy. All optically disallowed transitions, however, can also be effected by electron impact; and the maximum cross section for the process often occurs for an electron energy only slightly in excess of the vertical excitation energy.

In most forms of gaseous discharge the electrons present have a distribution in energy, and consequently, in general, and certainly in molecular oxygen, the primary generation of molecules in electronically excited states includes those states corresponding not merely to allowed transitions but also those associated with disallowed transitions, for which latter the cross sections for excitation by photon absorption are too small to be associated with a readily detectable rate of reaction.

Another major consideration is associated with the complexity of the problem of identifying the reaction mechanism in discharges in relation to those for the same reactant system but initiated by the absorption of photons. The techniques for measuring the number of photons absorbed by a given mass of reactant gas are well established. On the other hand, those for deriving in a gaseous discharge the corresponding number of electron impacts leading to a particular product—for example, a particular electronically excited state—are much less well developed. The techniques for measuring the concentration of electrons, and their energy distribution function, are still somewhat controversial (*43*); for molecular gases data for the absolute magnitude of the cross sections for electronic excitation by electrons remain almost nonexistent, except for some allowed transitions that result in ionization of the molecule (*55*).

Diverse approaches have been made in attempting to describe the kinetics of discharge reaction. Some earlier investigators examined the stationary state of a system in respect of the species recognizable chemically, and understandably appear to have been influenced by the classical analysis of a system in thermodynamic equilibrium while failing to recognize that the final state in a continuously maintained discharge is a stationary state.

Warburg (*76*) was perhaps the first to recognize that useful information could be gained by studying the limiting behavior of a reactant system reached when the concentration of the resultants is indefinitely decreased. Apparently independently, and using a different kind of technique, Kirkby working in Townsend's laboratory (*38*) recognized the same advantage. And others, notably Brewer (*8*) and Finch (*27*), pursued the problem in the same way by employing a technique that maintained a negligibly small concentration of resultants. Warburg, however, linked the data for the rate of reaction in ozone with those for the stationary state (*81*); and nearly half a century elapsed before a return was made, by Devins (*18*), to the analysis of the stationary state. Yet although Devins's approach seeks to link the data for ozonizer discharges in oxygen with those of the photochemists, he does not discuss his analysis of the stationary state in a discharge in relation to the earlier one of Warburg (*81*); nor does he compare the rate of ozone synthesis, either per unit charge transported by, or per unit energy used to maintain the discharge, with the data of other investigators, and relate his analysis with that of Deegan and Emeléus (*17*). And until this task of critically reviewing all relevant data is accepted, no coherent and convincing picture of the mechanism of ozone synthesis in discharges is likely to emerge.

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Experimental Data on Kinetics of Ozone Synthesis in Gaseous Discharges

The kinetics of discharge reaction resemble those of photochemistry in that the rate coefficient is referred to a physical characteristic of the environment other than pressure and temperature. In photochemistry the relevant parameters have long been seen to be the density of the photon flux traversing the reactants, and the extent of its absorption. In dealing with discharge reactions somewhat analogous parameters have been used in defining a convenient reaction rate coefficient. The intensity of the electron flux through the gas, which is fairly simply related to the density of the current carried by the gas, has attracted many and the corresponding rate coefficient is often described as the "current efficiency." Others have preferred the energy supplied per unit time to maintain the discharge, which, if not measured calorimetrically, also requires a knowledge of the electric field maintaining the flow of charged particles.

Thus two varieties of rate coefficient have been extensively used. One is the number of reactant molecules chemically changed (or alternatively the number of product molecules formed) per unit (electronic) charge transported, β, which is formally, but not physically, analogous to the electrochemical equivalent in electrolysis. This concept was refined by Kirkby into the "activity" of a discharge, $P = d\beta/dz$, the

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differential of the current efficiency with respect to the distance, z, between the electrodes (or the number of molecules chemically changed per cm. of unit charge transport). Kirkby had adduced experimental evidence that the activity may vary with position in a given discharge (*39*). The second coefficient, η, often called the "energy efficiency," is the number of reactant molecules chemically changed per unit energy supplied to maintain the discharge, and is of direct relevance to the economics of any discharge reaction such as the conversion of oxygen into ozone.

Alternatively these rate coefficients may be expressed in terms of the number of molecules of final product, which is the procedure usually adopted in describing the synthesis of ozone; in this case the values derived from experiment when adjusted for the stoichiometric factor set lower limits to the coefficients referred to reactant molecules.

The relation between the two empirical rate coefficients for discharge reaction, β and η, can be traced in terms of the gas pressure, p, the electrode spacing, z, and the corresponding potential difference between the electrodes maintaining the discharge.

Kirkby (*38*) was the first to show that β may be a function of pz, and it is apparent (*39*) that the variation of z at constant pressure and current is much more likely to lead to data amenable to interpretation than studies of the dependence of β on p at constant electrode spacing. Later (*40*) he showed that $P/p = (1/p)d\beta/dz$ is a reaction rate coefficient of a form suitable for comparison with theory.

The field, X, at any point, z, in the direction of current flow, is given by $X = dV/dz$, where V is the potential at the plane, z, relative to an electrode, conveniently the cathode. Townsend had shown that P/p for the generation of ions by electron impact is in many cases a function of X/p (*72*, *73*), and Kirkby demonstrated that this also holds for the synthesis of water from electrolytic gas (*40*).

The second empirical rate coefficient, the energy efficiency, η, is the quotient of the reduced activity, P/p, and the field-to-pressure ratio, X/p, both quantities relating to some given plane perpendicular to the direction of current flow; or $\eta = (P/p)/(X/p) = P/X$. If any region of a discharge is uniform, P/p, η, and X/p are characteristics of the whole region.

The following considerations provide a guide to what may be expected for the upper limit to the value of η for ozone generation in discharges attributable to electron-reactant collisions without making reference to the detailed theory outlined below. If, in accordance with the photochemical data, the primary step of the reaction mechanism is the dissociation of the oxygen molecule, and if this step absorbs E e.v., it follows that the energy absorbed per ozone molecule that could be formed is 0.5 E e.v. The hypothetical limiting case is that all the electron energy is absorbed in this way, and it follows that the upper limit to η is $1/(0.5\ E)$ ozone molecules per electron volt supplied to maintain the discharge. Spectroscopic data show that E must exceed the dissociation energy of the ground state, 5.11 e.v., and probably lies close to the vertical excitation energy of the $^3\Sigma_u^-$ state, about 8 e.v. Consequently η cannot exceed 40×10^{-2} ozone molecule per electron volt, and a probable upper limit is 25×10^{-2}. But because other electron impact processes that do not contribute to ozone formation can occur simultaneously, the maximum attainable value of η must be less than the upper limiting value.

An indication of the fraction of the energy supplied to a low-pressure positive column discharge which can be absorbed in effecting any group of electron-reactant collisions giving a "single" product is afforded by the data for the radiation emitted. For the radiation transmitted by glass and emitted from hydrogen or nitrogen, Ångström found this fraction to be about 0.05 (*1*), not much smaller than is attained in modern illumination practice (*74*); for a wide range of conditions, at constant pressure, the intensity of radiation per unit volume varies linearly with the current, an example of P/p for radiation being constant when X/p is constant. For the processes that lead to the emission of 2537 A. radiation from mercury, Barnes and Thayer have reported that up to 0.6 of the input energy may be accounted for in that way (*4*).

In OZONE CHEMISTRY AND TECHNOLOGY;
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A plausible estimate for maximum attainable value of η for ozone formation in the positive column in oxygen is thus 20×10^{-2} molecule per e.v.; however, a higher value may hold for other forms of the discharge, including that realized in ozonizers.

In principle these more elaborate definitions of the empirical rate coefficients might be expected to simplify any review of the existing data for the synthesis of ozone from oxygen. But in many investigations one or more of the relevant discharge parameters has been either not measured or not recorded. And although the ozonizer discharge has long been commercially attractive, it has not been studied much in relation to what appear to be the relevant parameters, nor has its relation to the well-characterized cold cathode glow discharge been the subject of much investigation. Yet it is these two forms of discharge for which the most extensive and reliable experimental data on ozone synthesis are available.

The information hitherto available relating these two forms of discharge is meager. That the cold cathode glow discharge can be realized in molecular gases at pressures above about 5 mm. of mercury and up to atmospheric pressure has long been known (*24*); but the current densities are very many orders of magnitude larger than in ozonizer discharges at comparable pressures. On the other hand, if the current density is reduced to the order of magnitude characteristic of ozonizer discharges at atmospheric pressure, the nature of the discharge in oxygen and in other gases may be profoundly changed (*13*). Nevertheless there are indications that an ozonizer discharge may be regarded to a first approximation as a periodically reversed glow discharge of relatively very low current density (*49,51*), at least for low pressures.

Lunt and Meek (*49*) and later Lunt and Swindell (*51*) studied ozonizer discharges in nitrogen, $p =$ ca. 1 mm. Hg and $z =$ ca. 1 cm.; the spectra of the luminous zones closely resembled those of a glow discharge in nitrogen for the same pressure and for a current density of about 0.5 ma. cm.$^{-2}$, about four orders of magnitude greater than in the ozonizer discharge.

Devins (*18*) assumed that the ozonizer discharges in oxygen studied by him may be regarded as similar to the more or less ideal plasma of the uniform positive column of a glow discharge because, in other experiments, Manley (*52*) found that, at atmospheric pressure, X/p is nearly independent of the alternating potential applied to the electrodes.

Some investigations have been made on the radiation from ozonizer and other discharges in which ozone is generated from oxygen. Most of these are qualitative, in the sense that the nature of the radiation was not identified spectroscopically and no determinations were made of the intensity of radiation per unit current density, or per unit energy consumed in maintaining the discharge (*63, 71, 77*). Other investigations on ozonizer discharges in nitrogen indicate that there are no serious problems in studying the nature and intensity of the radiation (*35, 56*).

The complicated nature of the wave form of the current flowing through an ozonizer when a (nearly) sinusoidal alternating potential is applied across the electrodes appears to have been recognized first by Decombe (*16*) and by Erlich and Russ (*20*) long before Warburg (*79*) made oscillographic studies. Rummel (*64*) describes studies of the wave form of the total current carried by an ozonizer, but does not appear to have discussed the fraction of that current which is carried by the partly ionized gas. The partly conducting gas is equivalent electrically to an impedance, Z, that does not conform with Ohm's law and which shunts the capacitance, C_2, associated with the discharge space. That combination of Z and C_2 is in series with the capacitances C_1 and C_3 associated with the inner and outer walls, respectively. The problem of measurement in ozonizer discharges is thus to determine, from measurements of the applied potential and total current, or otherwise, the current carried by Z_a and the potential across it.

It is evident that the theory of power and current measurement for alternating potentials applied to a load consisting of any combination of pure capacitance, inductance, and (ohmic) resistance cannot be applied to an ozonizer in which discharges occur. The failure of many investigators to recognize this has caused much confusion, and has introduced many errors difficult to estimate in their derivations of the current carried by Z_a from measurements of the root mean square values of potentials and currents.

A related problem arises in the characterization of the discharge currents occurring in gas pockets in the insulation of high voltage alternating current power transmission cables, but the emphasis in those investigations is no longer on the kinetics of chemical change, in this case the degeneration of the dielectric. Considerable attention has been paid to the electrical characterization of the discharge, although the significance of these investigations for ozonizer discharges has not been studied. There is, however, an extensive literature with many cross references (*2*, *3*, *53*, *61*, *62*, *70*).

Warburg gave a theory of ozonizer discharges in 1903 which appears never to have been reconsidered or refuted (*78*); his analysis led to the identification of the maximum potential across the electrodes, the frequency of reversal, and the total flow of charge transported by the ionized gas, as the relevant parameters. For alternating current operation this means that the relevant quantities to measure are the peak voltage and the mean current; such measurements were first carried out by Gray in 1904 working in Warburg's laboratory (*30*). Gray used periodically reversed steady potentials (direct current) and measured the flow of charge per cycle ballistically. Much later, Warburg (*79*) appears to have largely abandoned his 1903 theory, and, although providing experimental evidence from oscillograms that the current in an ozonizer may be far from sinusoidal in form, used the rules for sinusoidal currents to compute the mean current from the r.m.s. value of the current. While the ratio of the mean value to the r.m.s. value of the current carried by an ozonizer may remain nearly constant over a wide range of electrode voltage (*45*), the absolute value of the mean current cannot be inferred with certainty from r.m.s. values. But even when the refinement of measuring the mean current as a function of the peak voltage is adopted, there remains the problem which no one other than Warburg in 1903 seems to have been interested to solve; the determination of the fraction of the total measured mean current associated with the transport of charge by the ionized gas, as distinct from the fraction associated with dielectric displacement.

Another group of complications that has attracted little attention relates to the diverse devices used to obtain rate coefficients relating to oxygen (or air) uncontaminated by ozone. Warburg adopted the method of progressively increasing the velocity of the gas through the discharge to derive the limiting value of β, which he also treated analytically, taking into account the progressive increase in the concentration of ozone as the gas moves through the discharge. An ingenious but empirical treatment of the values for η was given later by Becker (*6*).

But what does not appear to have been studied is the change in the nature of the discharge as the velocity of the gas through it is varied, and the additional effects associated with the progressive increase in the concentration of ozone in the direction of flow.

The choice of another group of investigators has been to use stationary gas, and to remove the ozone formed by refrigerating the walls of the discharge tube. Inevitably there is then a concentration gradient, and the analysis of that variation in concentration has not been attempted, although Emeléus and Beck (*21*, *50*) have developed the formal theory of such diffusion. It may be that when liquid air or nitrogen is used as the refrigerant the characteristics of the discharge are changed from those at room temperature. As Broida and his colleagues have shown recently (*5*, *11*, *12*, *37*), if liquid helium is used as the refrigerant, a new chemistry of frozen free radicals appears. In oxygen discharges, in place of liquid ozone or a solution of oxygen in ozone, there is deposited on the walls of the discharge tube a glassy solid which evaporates to a violet solid (*5*, *11*, *12*).

Thus both experimental methods give data for the rate coefficients of ozone syn-

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thesis that relate to averages over imperfectly determined ranges of conditions. And no one has yet attempted to show how far these two methods applied to the same form of discharge lead to consistent data.

In view of all these uncertainties it is the more interesting to enquire what measure of consistency can be traced by reviewing the more significant investigations in oxygen. For only when that is known is it possible to consider what phenomena must be explicable by any theory of the mechanism of ozone synthesis in discharges. Ideally, many data relating to ozone synthesis by discharges in mixtures of oxygen with other gases, especially nitrogen, water vapor, carbon monoxide, carbon dioxide, argon, helium, and neon (*15*) should also be taken into account.

Ozonizer Investigations in Oxygen. Gray in 1904 appears to have been the first to investigate β for ozone formation in ozonizer discharges; using periodically reversed steady potentials and oxygen at atmospheric pressure, Gray found $\beta = 540$ for a wide range of values of the charge transported (*30*). Later (*31*) he found that β increased from 280 to 450, corresponding to a progressive increase in the electrode potential. A restatement of Gray's later data in terms of β, P/p, X_m, and η, is given in Table I. The values of X_m, the mean field across the gas space, are based on the values found by Gray, using Warburg's 1903 theory, for the extinction voltage of the discharge; these values of X_m may be less than the true values, and consequently lead to values of η which may be correspondingly too high. The data show that X_m/p increases only slightly as the potential applied to the electrodes is increased, but P/p and η increase by a factor of about 1.5. These data are probably the earliest establishing the approximate magnitude of P/p and η for ozone synthesis in ozonizer discharges from purely electrical measurements.

In Table I and the subsequent text β, P, and η refer to the number of ozone molecules formed, and not to the number of reactant molecules changed, by the discharge; p is in millimeters of mercury; z is the width of the gas space in ozonizers, or the relevant part of the interelectrode distance, in centimeters; V is the electrode potential, in volts; X_m and X are in volts cm.$^{-1}$; and X_m/p and X/p are in volts cm.$^{-1}$ mm. Hg^{-1}.

Table I. Restatement of the Data of Gray (*31*)

V	X_m/p	β	P/p	$\eta \times 10^2$ [a]
7,960	35.4	280	5.8	16.4
8,590	35.6	306	6.3	17.7
9,220	36.6	318	6.6	18.1
9,010	36.8	352	7.3	20.0
10,400	37.7	368	7.6	20.2
11,000	38.0	394	8.1	21.3
11,700	39.3	416	8.6	21.9
12,200	39.3	450	9.3	23.7

[a] Conversion to practical units is given very closely by: 180 grams per kw.-hr. = 10×10^{-2} molecule per e.v.

Investigations at about the same time by Pohl (*60*) led to P/p values of about 1.6; but he measured the r.m.s. value of the ozonizer current, which may be considerably in excess of the mean value, and this may explain why his values of P/p are much less than those found by Gray.

Warburg, Pohl, and Lind (*42*) were impressed by the analogy between β and the electrochemical equivalent in electrolysis, but only Kirkby at this time (*39*) seems to have perceived that the numerical values of β for discharge reaction may be expected to be much the larger because, as he clearly demonstrated for the synthesis of water from electrolytic gas, β increases as the electrode separation is increased, current and gas pressure being kept constant. About 20 years later Warburg (*82*), apparently unaware of Kirkby's pioneer work, investigated the dependence of β for the synthesis of ozone on the width of the discharge space z, and on the pressure, in concentric all-glass ozonizers using low frequency alternating potentials to excite the discharge. His measurements were based on a modification of his 1903 theory by St. Sachs (*65*), and, although not free from uncertainties, attempted to derive values of the mean discharge current and the corresponding mean field across the gas space X_m from measurements of r.m.s. values. A restatement of his data in terms of P/p, X_m/p, and η, considered as functions of pz and j_m, the mean current density, is given in Table II. The values of P/p for atmospheric pressure in Table II are about half those found by Gray (Table I); the apparent discrepancy is probably attributable to erroneously large values of the mean current, which were derived from measurements of the r.m.s. values. Nevertheless, the use of the parameter pz appears to coordinate the data relating to widely different conditions in terms of P/p. Warburg's choice of r.m.s. values for measurement of voltage probably also largely accounts for the differences between the values of η derived from his data and those of Gray as given in Table I; nevertheless for atmospheric pressure the two sets of values of η are of about the same magnitude.

Table II. Restatement of the Data of Warburg and Rump (*82*)

Frequency of electrode potential: 50 cycles per second
j_m = mean current density. μa. per sq. cm.
pz = mm. Hg × cm.
X_m = apparent mean field strength, volts cm.$^{-1}$

p	pz	j_m	P/p	X_m/p	$\eta \times 10^2$
52	5.2	7.6	3.6	74	4.9
101	10.1	7.4	3.8	51	7.4
152	15.2	7.1	4.0	42	9.5
198	19.8	6.9	4.0	39	10.1
760	76	3.5	3.6	29	12.3
		5.0	4.0	29	13.7
		7.2	4.2	29	14.2
760	1′4	2.7	3.8	32	12.2
		3.8	3.8	32	12.2
		5.1	4.2	32	13.5
		7.9	4.2	32	13.1
		24[a]	3.1	—	—
		53[a]	3.1	—	—
760	117	3.8	3.2	—	—
		6.6	3.2	—	—
		7.2	3.3	—	—
760	226	4.7	3.8	17	22
		8.0	3.7	17	21

[a] Frequency of electrode potential: 500 cycles per second.

Ozonizer Power Measurement. Warburg and Leithäuser (*80*) sought to measure the power consumed in the discharge by using the electrometer wattmeter method. Although in principle this method may be used when the current (and voltage) wave form is far from sinusoidal, these investigators did not recognize that large errors are likely to occur when, as in their procedure, the voltage applied to the electrometer needle is only a small fraction (ca. 0.01) of the potential across the electrodes and is derived from a resistance shunting the ozonizer. Consequently their values for η (for high streaming velocities) ranging up to about 9×10^{-2} are suspect; they are somewhat smaller than the values that can be derived from Gray's data (Table I) and those of Warburg and Rump (Table II) for atmospheric pressure.

Stark (*68*) appears to have been the first to prefer calorimetry to avoid the pitfalls of measuring the power consumed in the discharge by electrical methods. His data for low concentrations of ozone correspond to $\eta = 7.85 \times 10^{-2}$, irrespective of the frequency of the potential applied to the ozonizer electrodes in the range 50 to 10^4 cycles per second.

A calorimetric method was also used by Susz (*69*), but was so tedious that he abandoned it for the three ammeter method without, however, citing data to compare the results of the two methods. The data he cites for ozone synthesis appear to relate to power measured by the latter method, which gives erroneous values for any load of variable impedance such as an ozonizer discharge; for the most part they relate to room temperature and atmospheric pressure, and correspond to values of η lying in the range of 4×10^{-2} to 10×10^{-2}, but one observation for an ozonizer refrigerated to $-180°$ and for $p = 200$ gave $\eta = 13.8 \times 10^{-2}$. Later calorimetric determinations of the ozonizer power by the Geneva school of Briner (*9*) have given yields corresponding to values of η of about 16×10^{-2}; the true values are probably higher, because no allowance appears to have been made for losses by leakage and in the glass dielectric.

These calorimetric determinations leading to values of η provide no useful data about the discharge unless they are combined with measurements of the peak electrode voltage and the mean current; consequently the data for η cannot be related to those for β and P/p provided by Gray, Warburg, and Devins. The technique is tedious and it is more convenient to use either the electrostatic wattmeter method in which the needle is operated at the line voltage, or direct evaluation of $\int VI\,dt$ by the oscillographic method. The errors in this variant of the electrometer method when used on ozonizer discharges excited by alternating potentials of frequencies from 50 to 400 cycles per second is not more than ±2%, and the errors in the oscillographic method may be comparable (*44*).

The recent investigations of Devins (*18*) on ozonizer discharges in oxygen are particularly interesting because an attempt is made to link the data with those for the kinetics of the photosynthesis of ozone. The mean current meter used to measure the ozonizer current was shunted by a large capacitance, so that uncertain errors are present in the measurements; and no allowance was made for the displacement current. Data which are given in diagrams that are difficult to scale accurately are cited to show that the reaction rate is proportional to the current at a given pressure, but a careful scrutiny suggests that the phenomena are more complicated; a restatement of the data in terms of β, P/p, and η is given in Table III after allowing for the facts that Devins's Figure 6 relates to 301 mm. of mercury and that the scale for dp_{oz}/dt should be doubled (*19*). Devins's view, however, is that all his experimental data for the initial rate of reaction are consistent with his Figure 4, corresponding to which $P/p = 4.55$ (*19*), the derivation being given below.

Table III. Restatement of the Data of Devins's Figures 1, 2, and 6 (*18*)

p, Mm.	dp_{oz}/dt, Mm. Sec.$^{-1}$	I, Ma.	j	β	P	P/p	$\eta \times 10^2$	Fig. No.
69	0.368	0.3	3.0	51.5	257	3.73	18.7	1
100	0.56	0.3	3.0	78.5	392	3.92	19.6	1
200	1.08	0.30	3.0	151	755	3.78	18.9	1
300	0.45	0.06	0.6	158	1580	5.27	26.4	6
300	0.952	0.14	1.4	143	1430	4.77	23.8	6
300	2.04	0.30	3.0	143	1430	4.77	23.8	6
300	0.40	0.06	0.6	280	1400	4.67	23.4	2
300	0.80	0.14	1.4	240	1200	4.00	20.0	2
300	1.69	0.30	3.0	237	1185	3.98	19.9	2
300	1.87	0.30	3.0	262	1310	4.28	21.4	1
500	2.54	0.30	3.0	356	1780	3.56	17.8	1
					Av.	4.14	20.7	

dp_{oz}/dt = initial rate derived by scaling graphs.
I = current, ma.
j_m = mean current density, μa. cm.$^{-2}$.
X_m/p assumed to be 20 volt cm.$^{-1}$ mm. Hg.$^{-1}$.

Because Devins cites no measurements of the electrode potential or frequency, to derive values of η from his data it is necessary to estimate the value of X_m in the discharge space for which $z = 0.2$ cm.

Recent data for the electric strength of oxygen appear to be lacking. At low pressures it is only slightly greater than that of air (*14*, *23*) and for air (uniform field) in the range of present interest, $pz = 20$ to 200 mm. Hg × cm., it is given approximately by $X_b/p = 50 + 10^3/pz$ (*66*); and it is probable that values of X_b/p computed in this way are an upper limit to the values X_m/p in Devins's experiments, because the voltage necessary to start a discharge is often considerably greater than to sustain it. From determinations for oxygen of the ratio of the ozonizer power to the

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mean current in ozonizers comparable in size to that of Devins, X_m/p is about 20 volt cm.$^{-1}$ mm. Hg^{-1} (*46*), and this value has therefore been used in Table III in conjunction with Devins's data to derive values of $\eta = (P/p)/(X_m/p)$.

Devins's Figure 4 corresponds to the relation

$$dp_{oz}/dt = 0.65 \times 10^{-2}\, p$$

where p_{oz} is the partial pressure of ozone and p is the initial oxygen pressure. From the volume of the discharge space, 8.07 cm.^{3}, and the temperature 298° K, it follows that, when $I = 0.31$ ma.

$$\beta = 1.40 \times 10^2\, (dp_{oz}/dt)$$

since $z = 0.2$ cm., it follows that, irrespective of the current,

$$P/p = 5\, \beta/p = 4.55$$

For $X_m/p = 20$, the corresponding constant value for η is about 23×10^{-2}; alternatively, if the data for the electric strength are used, η rises from about 3.8×10^{-2} to about 4.1×10^{-2} as the total pressure is increased from 70 to 500 mm. of Hg. For the same ozonizer it was found later that, at atmospheric pressure, the initial rate of ozone formation corresponds to a value $\eta = 14.7 \times 10^{-2}$ (*19*); this would correspond to a value of $X_m/p = 31$, somewhat higher than has been assumed.

Devins's interpretation of his initial reaction rates (dp_{oz}/dt) is that they relate to a negligibly small, or zero, concentration of ozone. His value $P/p = 4.55$ is, however, considerably lower than any found by Gray (Table I), although the corresponding value $\eta = 23 \times 10^{-2}$ is close to the highest values found by Gray. The apparent discrepancy in the values for P/p obviously cannot be attributable to the fact that Devins measured only part of the total current. Until all such discrepancies in the data for ozonizer discharges are resolved, it seems doubtful whether any detailed interpretation can be attempted.

Glow Discharge Investigations in Oxygen. It is next of interest to consider data for ozone synthesis in direct current glow discharges at low pressures, refrigeration of the discharge tube to −180° C. being used to ensure that the partial pressure of ozone was relatively low.

The data of Henry (*34*) are the simplest to analyze: they relate to initial rates of ozone synthesis at $p = 2.4$ mm. Hg and mainly to positive column reaction because the rate of synthesis in the negative zones (cathode surface to Faraday dark space–positive column boundary) was relatively negligible. The cross section of the tube was about 0.8 cm.^{2}, and hence the current density was about 1.25 I ma. cm.$^{-2}$. Judged by the rough sketch given, the positive column was about 10 cm. long.

Henry's data are restated in Table IV in terms of β, P/p, X/p, and η. The values of P and X reflect the uncertainties in the length of the positive column, but the values of η are unaffected. The value for V_{PC}, the voltage along the positive column, has been taken to be the total voltage diminished by the cathode fall, assumed to be 400 volts. The value of p was taken to be that recorded, but P/p and X/p should involve values of the reduced pressure, that equivalent to the gas density; thus if the average gas temperature were not much greater than that of the refrigerating liquid air, the true values of P/p and X/p would be smaller than those listed in Table IV by a factor of about 3. The power supplied per unit length of the positive column $W_a = XI$ mw. per cm., increases progressively and rapidly. This strongly suggests that if for $I = 0.1$ ma. the equivalent pressure should be taken to be about three times the actual pressure, for $I = 4.0$ ma. when W_a is about 13 times larger, the equivalent pressure may be much closer to the actual pressure because of the much greater heating of the gas. A plausible estimate is that X/p falls from about 17 to about 10 as W_a increases from 120 to 1600 mw. per cm. Such a trend in X/p would not be inconsistent with other data (*25*) in respect of the tube radius and the estimated values of the reduced pressure.

Table IV. Restatement of the Data of Henry (*34*)

Reaction assumed to occur only in positive column of estimated length $z = 10$ cm.
I = total current, ma.
pz = 24 mm. Hg × cm.
V_{PC} = voltage across positive column assuming cathode fall to be 400 volts
W_a = power supplied to positive column = XI mw. per cm.

I	β	P	P/p	V_{PC}	X	W_a	X/p	$\eta \times 10^2$
0.1	144	14.4	6.0[a]	1200	120	120	50[a]	12.0
0.25[b]	70	7.0	2.9	1100	110	280	46	6.4
0.50	82	8.2	3.4	800	80	400	33	10.3
0.75	73	7.3	3.0	700	70	530	29	10.4
1.0	69	6.9	2.9[c]	600	60	600	25[c]	11.5
2.0	63	6.3	2.6	500	50	1000	21	12.6
3.0	44	4.4	1.8	450	45	1350	19	10.0
4.0	40	4.0	1.7[d]	400	40	1600	17[d]	10.0

[a] Estimated corrected values after allowing for temperature not much above −180°: $pz = 74$, P/p = ca. 2.0, X/p = ca. 17.

[b] Values of β, hence of P/p and η, are anomalously small, probably because of adventitious error.

[c] Estimated corrected values after allowing for gas temperature of about −160° C.: $pz = 55$, $P/p = 1.25$, $X/p = 11$.

[d] Estimated corrected values after allowing for gas temperature of about −120° C.: $pz = 40$, $P/p = 1.0$ $X/p = 10$.

If some such adjustment were admitted, it is plausible to infer that the corresponding trend in P/p is from about 2.0 to 1.0; that would be roughly consistent with the relatively small decrease observed in η from about 12×10^{-2} to 10×10^{-2}. Such trends in P/p and in η would be expected if the mean electron energy were to fall correspondingly with X/p, as it is known to do at much lower current densities (*33*).

The data would also then be apparently consistent in terms of X/p with the somewhat higher values of P/p and η in Table III and with the estimated value $X_m/p = 20$, for which in other ozonizer discharges values of η about 11.5×10^{-2} were found for high streaming velocities at room temperature and atmospheric pressure (*47*).

The slightly earlier investigation of Brewer and Westhaver (*8*) relates to a glow discharge between metal electrodes in a tube 3.5 cm. in diameter and immersed in liquid air for a distance of 13.5 cm. from the anode; from the cross section of the tube, the mean current density is about 0.1 I ma. per sq. cm. No synthesis was observed except in the positive column, and as in Henry's experiments, there are no data for the effect of varying the electrode spacing at constant pressure. The data from Brewer and Westhaver's Table I and others derived from their Figures 1 and 2 are restated in terms of P/p, X/p, and η in Table V.

Table V. Restatement of the Data of Brewer and Westhaver (8)

z = 13.5 cm., extension of refrigerated positive column.
W_a = power input to the positive column = 10^{-3} XI watt cm.$^{-1}$

I,Ma.	P	pz	β	P	P/p	V_{pc}	X	X/p	$\eta \times 10^2$	W_a	Ref. (*8*)
20	0.5	6.75	6.0	4.45	8.9	215	15.9	31.8	2.8	0.32	Tab. 1
2	1.0	13.5	62.9	4.66	4.66	750	55.5	55.5	8.4	0.11	Fig. 2
15	1.0	13.5	33.8	2.50	2.50	400	29.7	29.7	8.4	0.45	Fig. 2
20	1.0	13.5	20.2	1.50	1.50	315	23.4	23.4	6.4	0.47	Tab. 1
55	3.5	47.3	23.6	1.76	0.50	540	40	11.4	6.4	0.20	Fig. 2
20	3.5	47.3	20.3	1.50	0.43	—	—	—	—	—	Fig. 1
50	3.5	47.3	4.9	0.36	0.10	230	16	4.57	2.1	0.80	Fig. 2
20	5.0	67.5	19.9	1.48	0.30	350	25.9	5.18	5.7	0.52	Tab. 1
20	9.0	122.	18.3	1.37	0.15	420	31.1	3.46	4.4	0.62	Tab. 1
10	12.0	162	18.2	1.35	0.11	570	42.0	3.5	3.2	0.42	Fig. 2
20	12.0	162	16.9	1.25	0.10	430	31.8	2.5	3.9	0.64	Fig. 1
40	12.0	162	6.2	0.46	0.04	310	23.0	1.9	2.0	0.92	Fig. 2
20	13	175	16.4	1.22	0.09	440	32.6	2.52	3.7	0.65	Tab. 1

As in Henry's experiments, there is considerable uncertainty about the mean temperature of the gas. The range of power input per centimeter of positive column overlaps that in Henry's experiments, but although it is distributed over a larger cross-

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sectional area, the cooling area per unit volume is smaller. Hence it is plausible to assume that the lowest and highest values of W_a in Table V are associated with average gas temperatures not greatly different from the lowest and highest, respectively, estimated for Henry's experiments (see footnotes to Table IV). While the values of η remain unchanged, these rough estimates would change the highest value of X/p to about 18.5, and the associated value of P/p to about 1.55; and they would change the corresponding data associated with the highest values of W_a to $P/p = 0.06$ for $X/p = 2.7$ ($I = 50$) and to $P/p = 0.025$ for $X/p = 1.2$ ($I = 40$).

Although no great reliance can be placed on these adjusted values, some adjustment in the sense made is inevitably required. The principal conclusions that emerge from these adjusted values are the following.

First, the value $\eta = 8.4 \times 10^{-2}$ for $X/p = 18.5$ lies close to the values derived from other investigations; and as this value relates to a gas in which ozone (vapor pressure about 0.11 mm. Hg at −180° C.) forms about one tenth of the total concentration, it may be regarded as not inconsistent with the higher values already cited, which relate to very much lower fractional concentrations of ozone. Secondly, η has the relatively high value of about 2×10^{-2} when X/p lies in the range 1 to 2.

Quite apart from these adjusted values, the data show clearly that, at constant pressure in the range 1 to 2 mm. of mercury, both P/p and η fall more or less rapidly as the current or current density is increased; only for $p = 1$ mm. and $I = 2$ to 15 ma. is η constant (*8,* Figure 2), and in no case was the reaction rate proportional to the current, but increased more slowly. This seems to be an indication of some destructive mechanism, the total rate of which increases with the current. The corresponding increase of the mean gas temperature does not appear to account for the whole effect, for at $p = 1$ mm., P/p and η diminish markedly as I is increased from 15 to 20 ma., although W_a is practically unchanged.

There seems to be little direct experimental evidence on the rate coefficient for the decomposition of ozone in a discharge, β_d. In the Warburg-Leithäuser theory of 1909 (*81*), the rate coefficient, β_d, for ozone decomposition was assumed to be independent of the current (at constant pressure), as is (approximately) β for ozone synthesis. However, Möeller (*58,* p. 112) when describing the Warburg-Leithäuser theory makes the following undocumented statement: The ozone yield, βI, for zero ozone concentration increases more rapidly than the current, and the same holds in a more marked degree for the corresponding yield of oxygen from ozone, $\beta_d I$.

Brewer and Westhaver suggest that β_d may be considerably larger than β in the same apparatus. On the other hand Henry describes the decomposition as not occurring in the gas, and only on the refrigerated tube surfaces when the pressure is close to the steady-state pressure. He found that the rate decomposition of ozone on the wall of a discharge tube is very sensitive to the state of the surface; his observations are consistent with those of other investigators working with un-ionized gas (*57*).

Concerning the stationary state in a discharge, there is also little unambiguous evidence about the conditions in the discharge relative to those attained when the ozone concentration is negligible. Warburg and Leithäuser claimed to have shown that the ozone concentration in the stationary state of an ozonizer discharge decreases slowly as the current is increased; this appears to be at variance with the data represented in Devins's Figure 2. Warburg seems to have thought that his demonstration that the characteristics of a point-to-plane discharge in oxygen depends on the ozone concentration (*75*) implies that the same holds for ozonizer discharges; evidence for the latter was provided by the investigations of St. Sachs (*65*).

For −73° C., the data of Beill (*7*) at atmospheric pressure correspond to a value of 780 for the ratio $p_{O_2}{}^2/p_{O_3}$ used by Devins in his analysis of the kinetics, while for 20° C. the value is about 8300; these values are two and three orders of magnitude larger than those cited by Devins in his Table I for the pressure range 70 to 400 mm. Hg. The early data of Briner and Durand (*10*) show that at −180° C., the ratio must have been of the order unity in an ozonizer discharge, and the same holds for a glow discharge at −180° C., as is shown by the data of Henry and of Brewer and Westhaver.

Formal Theory of Discharge Reaction and Mechanisms of Ozone Synthesis

The state of affairs in approaching the identification of the mechanism of ozone synthesis in discharges is perhaps tidier than the experimental results reviewed above, but more frustrating, because so many data are lacking about the detailed state of a partly ionized gas in a discharge, the kinds of species present, and the kinds of collisions they can make. Furthermore, one main group of experimental data relates to the relatively well characterized conditions in the positive column of a low pressure cold cathode glow discharge; but the other relates to ozonizer discharges in a much higher range of pressure, a discharge form which, although known for a century, has attracted few physical investigations.

The formal theory of excitation and chemical reaction in the cold cathode glow discharge was given by Emeléus and Lunt (*22*) in 1936 in a form convenient for discussing the phenomena in the negative zones and the more or less ideal plasma of a uniform positive column, the discharge being envisaged as that attainable in a cylindrical tube between plane electrodes; there are, however, contemporary statements relating to excitation (*59*). For uniform positive column conditions Lunt (*48*) has given a revised and amplified account.

Ideally, the analysis of Emeléus and Lunt enables computation of the reaction rate coefficients, P/p, $\beta = \int_{z_1}^{z_2} p\,(P/p)dz$ where z_1 and z_2 correspond to any two planes perpendicular to the direction of charge transport, and $\eta = P/X = (P/p)/(X/p) = \beta/V$ where $V = \int_{z_1}^{z_2} X dz$, X being the field maintaining the measured charge transport.

For the conditions in a uniform positive column, which appears to be the important zone for ozone synthesis, S, the rate coefficient of any specified kind of electron-reactant collision occurring at the rate

$$S\, n_e\, n_r \text{ collisions per cc. per second}$$

where n_e and n_r denote the concentrations of electrons and reactants, respectively, is given by

$$S = k \int_{V_e}^{\infty} V^{0.5}\, Q(V) f(V) dV \tag{1}$$

In this relation $Q(V)$ is the cross section for the reaction as effected by electrons of energy V and is zero for $V < V_e$, the critical energy; $f(V)$ is the electron energy distribution function, and k is a numerical factor equal to 1.87×10^8 when V is expressed in electron volts and when $Q(V)$ is in units of πa_0^2.

If W is the electron drift velocity in the direction of the electric field, the current density or amount of (unit) charge transport per square centimeter per second is $n_e W$. Since P is defined as the reaction rate coefficient per unit charge transport, it follows that

$$P = \frac{\phi\, S\, n_e\, n_r}{n_e\, W} = \phi\, S\, n_r / W \tag{2}$$

where ϕ is a factor analogous to the photochemical quantum yield and takes into account the special circumstances determining the yield that may arise in discharges (*22*). Since $n_r = 3.54 \times 10^{16}\, p_r$, where p_r is the partial pressure of the reactant concerned in millimeters of mercury, it follows that

$$P/p = 3.54 \times 10^{16}\, \phi\, (S/W) \tag{3}$$

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Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch039

If more than one kind of electron-reactant reaction is involved simultaneously, as is probably the case for the oxygen-ozone reaction, P must be replaced by the sum of all the P's concerned, and in deriving these latter from theory, correspondingly, S must be replaced by the sum of the S's concerned.

When the current density is so low that the gas consists almost exclusively of molecules unchanged by the discharge, so that p, the total pressure, is sensibly the same as p_r, the partial pressure of the reactant, a special case arises when W, and $\bar{V}$, the mean electron energy, are functions of X/p as in the experimental conditions adopted by the Townsend school for their measurements (*73*). For then S is a function of X/p only, and is computable when $f(V)$ and $Q(V)$ are also known. Relation 3 then becomes

$$P/p = 3.54 \times 10^{16} \phi f_1 (X/p) \tag{4}$$

and correspondingly

$$\eta = P/X = 3.54 \times 10^{16} \phi f_2 (X/p) \tag{5}$$

and in this case when ϕ is also independent of the current density for any given value of X/p, it follows that

$$P/p = a \tag{6}$$

The circumstances are different when the species engendering the observed reaction can be simultaneously generated by an additional two-stage electron impact process that involves as the intermediate stage the generation of a metastable species. For the simplest conditions theory then leads to a relation of the form, for X/p constant:

$$P/p = a + b j \tag{7}$$

where a and b are constant factors and j is the current density. What appears to be the first identified case of this kind relates to the excitation of the 7 ^3P state in a discharge through mercury vapor (*26, 55,* p. 71), 6 $^3P_{0,1,2}$ being the metastable intermediate state.

When contrariwise, the experimental data for constant X/p can be represented by a relation of the form

$$P/p = a - c j - d j^2 - \cdots \tag{8}$$

there is a strong indication that one or more unsuspected deactivating processes are operative for the immediate product of a two-stage process, or for the final product. An example of each kind is afforded by the experimental data for the intensity of emission per unit current density of the Vegard-Kaplan and second positive bands, respectively, from a uniform positive column discharge through molecular nitrogen (*35*).

There are some limitations to the computation of P/p and η from Relations 3, 4, and 5.

In principle, $f(V)$ for oxygen can be determined as Smit has done for helium (*67*), but the necessary auxiliary data are lacking, and no approximate solution appears to have been attempted. In the absence of experimental data for positive column discharges, it is necessary to assume a form for $f(V)$, the Maxwellian form being usually regarded as a good approximation. $\bar{V}$ and W are known functions of X/p (*33*), but their validity for the much higher current densities associated with the data of Tables IV and V is uncertain. For the form and amplitude of $Q(V)$ for each electron impact reaction likely to contribute to the observed synthesis of ozone, it is necessary to rely mainly on the indications from theory. But the maximum value of ϕ, the number of ozone molecules formed per oxygen molecule excited by electron impact, may be taken as 2 in accordance with the photochemical data.

Despite these limitations and uncertainties, some success has attended this quantitative theoretical approach to the interpretation of experimental data in uniform field conditions when the phenomena appear to be concerned with a single immediate

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch039

product of electron-reactant collisions, although in no case have the experimental data been extensive enough to provide a stringent test of the theory. In all cases the Maxwellian form has been assumed to be a valid approximation to $f(V)$, for which there is some justification for uniform positive column discharges in molecular gases. In addition to the results reviewed (*22*), this approach gives reasonably good agreement with more recent experimental data (*28, 29, 32*) for the Townsend coefficient of ionization, and for the formation of negative ions (*47*).

To make such comparisons in terms of P/p or η, it is preferable to select experimental data relating to conditions for which p_r/p does not differ significantly from unity, for $\bar{V}$ and W are known as functions of X/p only for the reactant gas. Usually it is not difficult to choose such experimental conditions, and they are often those in which ϕ may be expected to attain its maximum value. Ideally this restriction on p_r/p is unimportant, but the fact that no data are available for $\bar{V}$ and W for either ozone or ozone-oxygen mixtures is a deterrent to the more complicated task of making such comparisons for the stationary state, and it is consequently doubtful whether Devins's use of Relation 1 in that connection (*18*) can lead to useful conclusions.

In oxygen the vertical transition that can account for the low-pressure photochemical synthesis of ozone is ${}^3\Sigma_g{}^- \rightarrow {}^3\Sigma_u{}^-$, and at high pressures it appears that the transition of low probability ${}^3\Sigma_g{}^- \rightarrow {}^3\Sigma_u{}^+$ also plays a part. As these transitions can also be effected by electron impact, they are the first choice in formulating a mechanism likely to account for the synthesis occurring in discharges. The first is an allowed transition involving an energy absorption of about 8 e.v., so that the excited molecule immediately dissociates into ${}^1D$ and ${}^3P$ atoms; when effected by electron impact, the maximum value of $Q(V)$ is estimated to be about 1 $\pi a_0{}^2$ and to occur for $V = 40 \pm 5$ e.v. (*41, 54*). The vertical excitation energy for the disallowed transition to the ${}^3\Sigma_u{}^+$ state is about 6 e.v., so that dissociation follows at once, in this case into two ${}^3P$ atoms. The maximum value of $Q(V)$ is estimated to be about 0.2 $\pi a_0{}^2$ and to occur for $V =$ ca. 9 e.v. (*28, 29, 32*). For $\phi = 2$ it follows that the upper limit to the value of η for ozone generated in each of these ways is about 25×10^{-2} and 33×10^{-2} molecule per e.v., respectively.

Thus in a uniform positive column discharge, the simultaneous occurrence of these two excitation processes by electron impact to an extent that would leave a considerable margin for energy absorption in other processes provides a mechanism that could account for the highest observed values given in Tables IV and V. But the crucial question is whether this mechanism can account for the trend of P/p and η with X/p and with the current density j, and can also account for the absolute magnitudes observed.

The data in Tables IV and V show that P/p and η increase rapidly as X/p is increased, but these increases are also associated with a progressive decrease in j. The mechanism envisaged involves two simultaneous processes, for each of which P/p may be expected to conform with Relation 6 and thus to be independent of j. Consequently an increase of $\bar{V}$ with X/p, for which there is ample independent evidence for other discharges, provides a qualitative explanation of the trend of the observed values of P/p and η with X/p. But as there are no data relating to a range of j when X/p is constant, no conclusion can be drawn as to whether the experimental data conform with Relation 6, or with Relations 7 or 8 which are characteristic of a mechanism different from that envisaged.

While there is no important uncertainty about the value for η, values for P/p and X/p may be smaller than those tabulated by a factor between 1 and 3, depending on the actual temperature of the gas in the discharge (Tables IV and V). Unless that temperature, and hence the reduced values of X/p, are determined or estimated, the experimental values for P/p and η cannot be compared with the values calculated from theory for the mechanism envisaged. If the provisional rough estimates of the gas temperature given in the discussion of Tables IV and V are to be accepted, it can be said that the agreement between the calculated and the experimental values is within

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an order of magnitude. But this diffuse agreement could scarcely be held to establish the validity of the reaction mechanism postulated.

The earlier analysis by Deegan and Emeléus (*17*) is based on somewhat different considerations: it starts by equating R_{av}, an average volume rate of ozone generation, with $\phi\ n_e\ n_r\ \Sigma(S)$ (cf. Relations 1 and 2) where the summation extends to a number of electron impact reactions likely to generate oxygen atoms, including vertical transitions to the $^3\Sigma_u{}^+$ and $^3\Sigma_u{}^-$ states, and then seeks the range of $\overline{V}$ that is consistent with plausible extreme values for $n_e\ n_r$ with $\phi = 2$. They selected Brewer and Westhaver's data for $I = 20$ ma. (Table V) to compute $R_{av} = 1.7 \times 10^{16}$ molecules per cc. per second for the (nominal) pressure range 2.8 to 14, or $p_{av} = 8.4$, ignoring the fact that both R and X/p change greatly; and it was assumed that the gas temperature was −180° C. This procedure is equivalent to considering the rate, R, for the reduced pressure $p = 25.2$ or $n_r = 8.7 \times 10^{17}$, and to a reduced value $P/p = 0.052$, practically the same value as that given in Table V for $p = 9$ when the gas temperature is taken to be −180° C. The free variables thus become in effect only n_e and $\overline{V}$. For the computation of $\Sigma(S)$ it was assumed that $Q(V)$ in Relation 1 had the constant value $0.8\ \pi a_0{}^2$ for $6.0 < V < 6.2$ e.v. and for $V > 7$ e.v. By assuming that n_e lies between 10^9 and 10^{11} cm.$^{-3}$, it was found that V must lie in the range 0.75 to 1.4 e.v.

This conclusion, although valuable, provides no more than an agreement in order of magnitude between the observed and calculated rates, when it is appreciated that this apparently narrow range of $\overline{V}$ corresponds to an increase in $\Sigma(S)$ by a factor about 250. If the mean gas temperature is assumed to be somewhat higher, so that $n_r = 5 \times 10^{17}$ cm.$^{-3}$, and $\overline{V}$ is assumed to be 1.0 e.v., n_e is found to be 7.5×10^9, corresponding to which $W = 1.7 \times 10^6$ cm. per second. These values give a much closer agreement with the data for low current densities (*33*): the values for $\overline{V}$ and W correspond very closely to $X/p = 1.5$, while the corresponding reduced value from experiment is about 2. And again because of the lack of data at constant X/p, it cannot be said that the experimental data are characteristic of the mechanism postulated.

Emeléus and Deegan suggested that a closer agreement between the experimental and calculated values might be reached if, in addition, it were supposed that stepwise excitation resulting in dissociation occurred via the highly metastable $^1\Delta_g$ and $^1\Sigma_g{}^+$ states. In this case, unless deactivation takes place to a large extent, P/p would be expected to vary with j according to Relation 7; and if these additional reactions were to play a predominant role, it might account for the fact that the observed values of η are so large when the reduced value of X/p is 1.5 or less.

However, other factors may need to be taken into consideration in formulating a plausible reaction mechanism. As the current density is increased in actual experimental conditions, there is usually a corresponding progressive increase in the temperature of the gas, so that there is a corresponding decrease in p_r/p, the fractional concentration of the reactant species, which has been implicitly assumed to be oxygen molecules in the zero vibrational level, $^3\Sigma_g{}^-$, $v = 0$. While the effect of temperature may be small in increasing the fractional concentration of the higher vibrational levels, all of which are highly metastable, direct excitation by electron impact might be responsible for a much larger effect. These considerations illustrate the need for caution in selecting experimental conditions, and in using the theoretical Relations 1 to 8 when it is assumed that p_r/p is very close to unity; and they are important in any analysis of the stationary state in discharges when p_r/p is less than unity for both ozone and unchanged oxygen molecules, and may not be negligible for other species present.

The possibility that a significant fraction of the reactant gas may be converted into vibrationally excited molecules in the ground electronic state is associated with a further complication of the reaction mechanism which requires to be explored. For any value of v in excess of some critical value, which appears to about 2, vertical transitions from the $^3\Sigma_g{}^-$ state generate molecules in the $^3\Sigma_u{}^-$ state that do not dissociate

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but spontaneously radiate, emitting bands of the Schumann-Runge system; and there can be no corresponding generation of ozone. Nondissociating molecules in the $^3\Sigma_u{}^+$ state may be generated in a similar way, but because these are metastable some may be dissociated by electron impact. The occurrence of such processes which involve as the initial step the generation of vibrationally excited reactant molecules in the ground electronic state may be regarded, in terms of the mechanisms previously postulated, as equivalent to ϕ having a value less than 2, and possibly also to negative values of $d\phi/dj$ in which case P/p would vary according to Relation 8.

Until the nature of ozonizer discharges is more clearly determined, it is doubtful whether the statistical theory of electron-reactant collisions for positive column conditions remains applicable although Devins (*18*) has recently assumed that it does. The early data of Gray (Table I) and the possibly less certain data of Warburg and Rump (Table II) yield values of P/p that are not very sensitive to the current density for ozonizer discharges; this holds also for the recent data of Devins (Table III). This is in marked contrast with the data of Henry (Table IV) and of Brewer and Westhaver (Table V). There is also a large difference between the highest attained values for η: despite uncertainties in the values for ozonizer discharges, they appear to be about twice those for the uniform positive column.

Thus these two forms of the discharge appear to differ considerably in their potency to effect the synthesis of ozone; possibly also the reaction mechanisms involved are different.

The kind of reaction mechanism that may occur in uniform positive column discharges can be perceived in broad outline, but many auxiliary data are lacking to present a quantitative expression in forms convenient and precise for comparison with experiment; and the experimental data for ozone synthesis in discharges are inadequate to describe correspondingly precisely the electrical state of the gas in which synthesis has been observed.

These gaps in knowledge hinder the identification of the reaction mechanism in discharges; and until they can be filled it is doubtful whether the present data for the synthesis by discharges can be linked coherently with those for the photosynthesis and for other reactions in un-ionized gases.

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Effect of Gaseous Diluents on Energy Yield of Ozone Generation from Oxygen

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The effect of various diluent gases on the energy yield of ozone generation from oxygen in commercial ozonators is discussed. The greatest loss in energy yield is noted for the presence of less than 1% of hydrogen, water, or Freon 12 (dichlorodifluoromethane). Up to 50% of carbon dioxide or argon reduces the energy yield to about 85% of that expected with pure oxygen. Carbon monoxide or nitrogen, in amounts of less than 10%, apparently increases the energy yield of ozone generation. In greater amounts, it gradually but steadily reduces the energy yield.

The object of this investigation was to study ozone generation in commercial ozonators. Primary concern has been placed on ozonators using oxygen feed. The effect of certain foreign substances in the oxygen has been studied with respect to the energy yield of ozone generation.

These studies are considered important because ozone is a competitive chemical. It must be produced at the lowest possible cost. Some contaminants in oxygen were known to decrease energy yield; others were questionable or even unknown.

Commercial ozonators may use either air or oxygen as a feed gas. As long as the components of these gases are within known limits, ozonator performance can be predicted with reasonable certainty. Recently, however, the size of some ozone plants has increased to a point where it is economically feasible to recycle the oxygen back to the ozonators. This means that the ozone-oxygen mixture is passed into a reaction of some kind. The ozone is used up in the process, but the oxygen is recovered from the reaction and returned to the ozonator. Intrinsically, this oxygen which is returned to the ozonator may be contaminated; and the contaminants may be materials not normally found in commercial oxygen.

In this investigation, various diluent gases were added to the oxygen to see their effect on the energy yield of ozone generation and on the total production of ozone.

The results in some cases indicate that only trace amounts of the impurity can be tolerated. In other cases, small amounts even increase the energy yield of ozone generation.

Published references were studied carefully (*1–7*). Unfortunately, these earlier investigations were seldom conducted in such a way that valid comparisons could be made to present-day commercial ozonator operation. Several variables are considered important in ozonator performance.

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F is the gas flow rate in pounds per hour of dry gas.

W is the electric power in watts.

a is the energy input per unit mass of gas treated, a ratio of W/F, expressed as watt-hours per pound.

c is the ozone concentration expressed as weight fraction.

B is the energy yield of ozone generation expressed as pounds of ozone per kilowatt-hour of power.

The measure of ozonator performance selected was the energy yield of ozone generation, B. It is a parameter of the product. The energy input level of ozonator operation, a, is also considered a most important independent variable. With these two points in mind, it is more significant to point out the inconsistencies encountered in the references of other investigators.

The gas flow rate, F, if measured, was not always kept constant. The measurement of electric power, W, was often neglected. Obviously, the energy input, a, can be calculated only in those cases in which electric power was measured. Notwithstanding these omissions, the range of operating conditions was not always comparable to present-day ozonators. Commercial ozonators are operated in the range of 50 to 100 watt-hours per pound of gas treated. However, it was not uncommon to find in these previous investigations, ozonators operated between 300 and 400 watt-hours per pound of gas. Concentration, c, was the one parameter of ozonator performance which served as a common denominator.

Few of the earliest experimenters were concerned with the operation of ozonators at optimum energy yields. This could explain the experimental results often reported. The demand of industry for ozone at a price which could be competitive made it necessary to restudy the effects of certain gaseous contaminants in oxygen with respect to the energy yield of ozone generation. With these things in mind, experiments were planned and conducted with a full scale unit ozonator designed and furnished by The Welsbach Corp.

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Equipment

A schematic diagram of the ozonator and associated equipment is shown in Figure 1.

Aviator's breathing grade oxygen, used because of its low moisture content, was delivered to the ozonator through a pressure regulator, an iron case meter, and an orifice manometer. Suitable connections were provided for measuring the frost point, pressure, and temperature.

In a similar manner the diluent gas was delivered to a T-connection upstream of the ozonator. The gas flow rate was measured by an orifice manometer, with suitable connections for pressure and temperature measurement. All flowmeters had been previously calibrated according to accepted standard procedures.

A sampling point was provided for analysis of the mixed gases. This served as a check on the ratio of gases as determined by the flow rate measurements.

The ozonator was constructed of stainless steel. Tempered glass windows were bolted on each end of the assembled ozonator, using steel rings. Cooling water was supplied and withdrawn at connectors located on top of the ozonators. The dimensions were:

Jacket length	42.75 inches
Length of corona space	41.00 inches
Inside diameter S.S. tube	3.122 inches
Volume of ozonator and associated connections	0.685 cu. ft.

A standard Welsbach ozonator dielectric comprising a 3-inch borosilicate glass tube with a wrinkled open end was used. An internal conductive coating of metallic aluminum served as an inner electrode. Electrical contact was established bv means

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch040

of an aluminum wire spring bent to bear on the inside of the tube and fastened to the high voltage connector.

Pressure was controlled by the regulator, and the total throughput of gases was controlled by a throttle valve at the outlet. A sample trap was provided for determination of ozone concentration by the neutral potassium iodide method.

The electric power supply and metering system are shown schematically in Figure 2. Power was supplied to the ozonator from a high voltage transformer which was supplied by a Sola constant voltage transformer and a variable ratio transformer. A voltmeter, ammeter, and wattmeter were connected in the primary of the main transformer. An electrostatic voltmeter was used to measure the secondary potential.

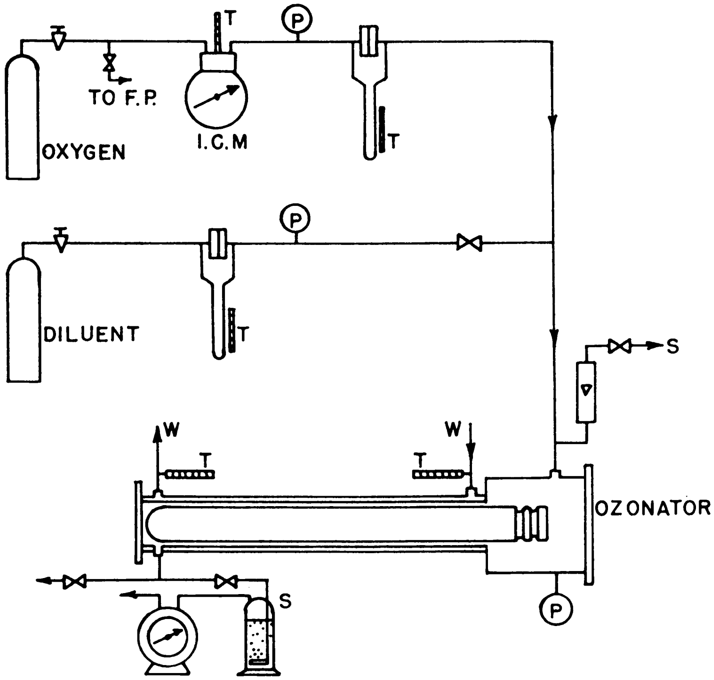

Figure 1. Schematic diagram of apparatus

P. Pressure
T. Temperature
W. Water
S. Sample
F.P. Frost point

In a typical experiment the ozonator was operated at some energy input level which would be expected in normal installations. At least 30 minutes were allowed to establish steady-state conditions. The readings of flow rate meters, associated pressures, and temperatures as well as electrical meters were recorded. The samples of the inlet ozonator gases were analyzed for composition; samples of ozonator output gases were analyzed for ozone concentration.

The results have been calculated in terms of energy yield of ozone generation expressed as pounds of ozone per kilowatt-hour of electric power, and plotted against the weight per cent of diluent gas in the oxygen as supplied to the ozonator.

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch040

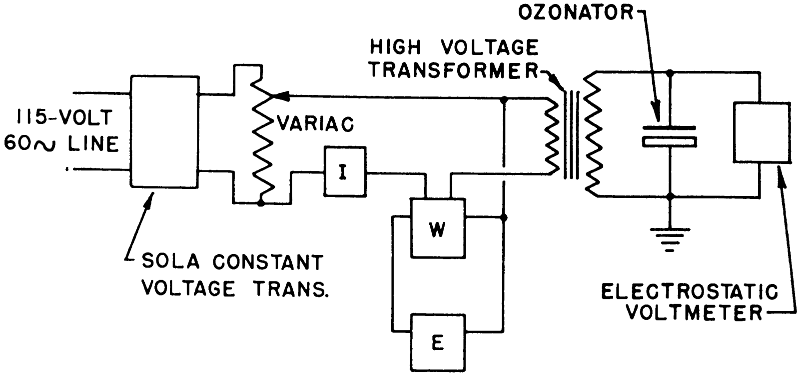

Figure 2. Schematic diagram of electrical apparatus and meters

I. Ammeter
E. Voltmeter
W. Wattmeter

Effect of Hydrogen

The results of mixing hydrogen with oxygen are shown graphically in Figure 3. It is apparent that even amounts of hydrogen as low as a few hundredths of 1% will adversely affect the energy yield of ozone generation. One explanation is that the hydrogen readily combines with oxygen to form water. The presence of water in the oxygen could account for such a reduction in energy yield. Another explanation is that the hydrogen per se is responsible for the change as reported. An attempt was made to differentiate between these two possible explanations.

In this experiment, where hydrogen was admixed with the oxygen, the amount of water produced in the ozonator was determined by the frost point method. The difference between inlet and outlet moisture content was taken as the amount produced by the reaction. Only about 4% of the hydrogen added was converted to water. The reduction in energy yield of ozone generation was greater than would be produced by this amount of water added as such.

It is concluded that hydrogen itself is in part responsible for the reduction in

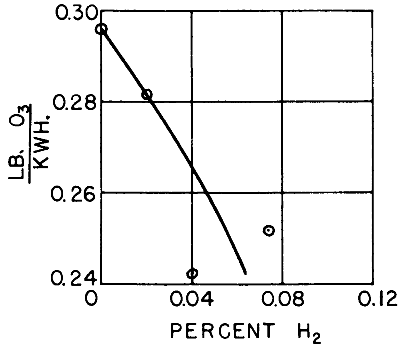

Figure 3. Effect of hydrogen

F. 1.47 lb./hr.
W. 99 watts
a. 68 watt-hr./lb.

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch040

energy yield. Some of the hydrogen—in this case at least 4%—is converted to water in the presence of oxygen in the discharge. The presence of this water will admittedly reduce the energy yield, but fails to account for all of the loss as shown.

Effect of Moisture

The results shown in Figure 4 are taken from the weighted average of several experiments. For this reason, the energy inputs are given as a range, instead of specific values. These results show that the presence of moisture is to be avoided, if high energy yields of ozone are desired. From such a study as this, it was possible to calculate the water produced in the reaction of hydrogen and oxygen in the discharge. The results here are purposely shown in terms of two independent variables: frost point, and weight of water in oxygen. It is true that −60° C. frost point is not equal to 0 p.p.m. of water. However, the frost point of the gas was the variable that was measured experimentally. The weight of water, as shown here, is a calculated value, and is correct except for the range very close to 0 p.p.m. The means of presentation in Figure 4 do not allow a more accurate comparison of the two variables.

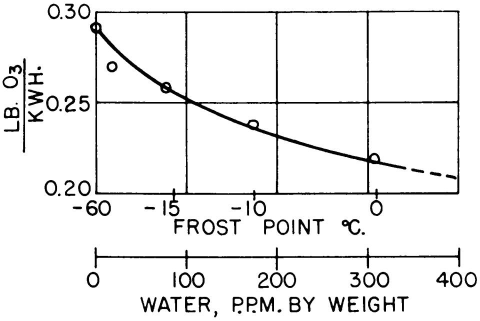

Figure 4. Effect of moisture in oxygen

F. 0.8 to 1.8 lb./hr.
W. 105 to 109 watts
a. 59 to 128 watt-hr./lb.

It is concluded that for optimum ozonator operation, the oxygen feed should be dried to a frost point of at least −60° C., and that introduction of water to the oxygen should be avoided in all cases.

Effect of Freon

In Figure 5 are shown the results of adding Freon 12, dichlorodifluoromethane, to oxygen. This particular study was undertaken because installation of commercial ozonators, leak testing of all joints, flanges, etc., are often performed by adding some Freon 12 to the system. The presence of trace amounts of Freon in a propane flame renders it a vivid green. The question was: How important is the complete removal of Freon after a leak testing operation? It appears that as little as trace amounts will cause serious reduction in the energy yield of an ozonator.

Effect of Argon

In Figure 6 are shown the results of adding argon to oxygen. Little change is noted in the energy yield for increments of argon up to about 10%. For larger

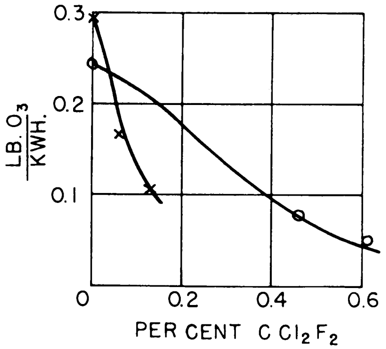

Figure 5. Effect of Freon 12

F. 1.14 lb./hr.
W. 98 watts
a. 86 watt-hr./lb.

amounts, a gradual reduction in the energy yield is noted. At 50% argon, the observed yield is 88% of that obtained with pure oxygen. One purpose in the study of argon was to use it as an inert diluent to reduce the possibility of flame and explosion in ozonization reactions. From this study it is possible to predict the expected loss in ozone production as a result of the use of argon in such an application. Another purpose of this study was to find the effect of amounts of argon that would be expected normally in commercial oxygen. As this amount is less than 1%, it is concluded that no adverse effect should be expected.

Effect of Carbon Dioxide

In Figure 7 are shown the results of adding carbon dioxide to oxygen before ozonizing. Here again, as in the case of argon, it is possible to reduce the hazard of flame and explosion in ozonization reactions by using carbon dioxide as an inert diluent. In the primary purpose of this investigation, however, the amounts of carbon dioxide expected were the result of oxidation of organic constituents in the oxygen—no more than several hundred parts per million. It is apparent that little loss in energy yield is expected for carbon dioxide up to 10%. Using 50% carbon dioxide will reduce the energy yield to about 85% of that expected with pure oxygen. In the previous

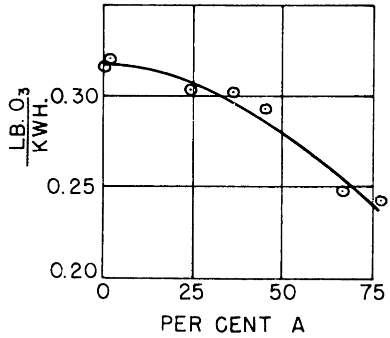

Figure 6. Effect of argon

F. 1.23 lb./hr.
W. 81 watts
a. 66 watt-hr./lb.

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch040

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example it was shown that 50% argon would give an energy yield of 88% of that expected with pure oxygen. The possibility of reactions within the discharge are understandable with carbon dioxide, but not with argon. Just what it is that produces the same decrease in energy with two different diluents is not explained by these results. Future experiments will be necessary to answer these questions.

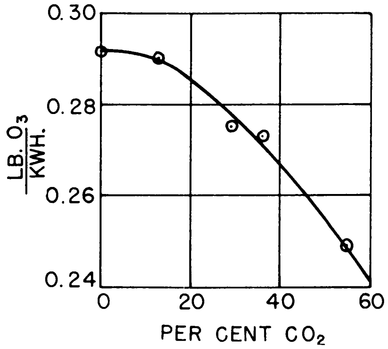

Figure 7. Effect of carbon dioxide

F. 1.52 lb./hr.
W. 100 watts
a. 66 watt-hr./lb.

Effect of Nitrogen

In Figure 8 are shown the results of mixing nitrogen with oxygen. The most surprising thing is that energy yield is increased when nitrogen is employed in the range from 1 up to about 10%. When above 10% nitrogen is present in oxygen, the energy yield shows a gradual but steady decrease. One important conclusion is that commercial oxygen for ozonators need not be 99.5% pure. The 96 to 97% purity would not only give a higher energy yield of ozone but also be more economical to produce.

The shape of the curve as drawn might leave reasonable doubt as to the expected maximum. Other experiments were conducted for increments of nitrogen less than 6% and the results are shown in Figure 9. It is concluded that the addition of even small

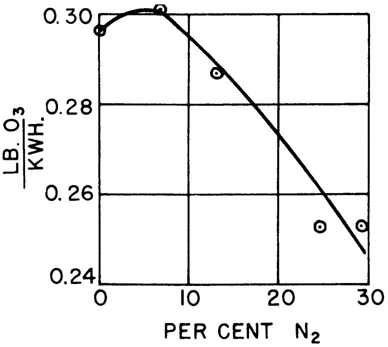

Figure 8. Effect of nitrogen

F. 2.10 lb./hr.
W. 98 watts
a. 47 watt-hr./lb.

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch040

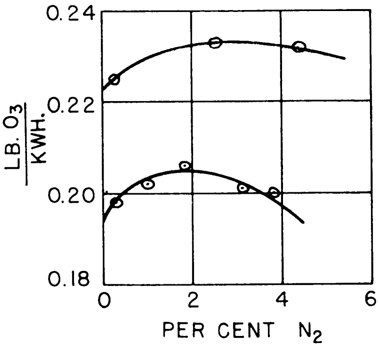

Figure 9. Effect of nitrogen

F. 0.7 to 1.2 lb./hr.
W. 85 to 105 watts
a. 87 to 93 watt-hr./lb.

amounts of nitrogen, of the order of 1 to 2%, is sufficient to produce these unexpected results. The control of nitrogen to within optimum values is important in commercial ozonator operation.

Effect of Carbon Monoxide

In Figure 10 are shown the results of mixing carbon monoxide with oxygen. This is another diluent which gives a surprising and unexpected increase in the energy yield. Somewhat less carbon monoxide than nitrogen is necessary to produce this increase. The presence of carbon monoxide can be expected in the products of the recycled oxygen system. If the organic contaminants are burned, carbon dioxide and water are expected; but it is not unreasonable to expect some incomplete oxidation products, including carbon monoxide. It is conceivable that the control of an optimum carbon monoxide content will be a factor that some ozone plants cannot afford to ignore.

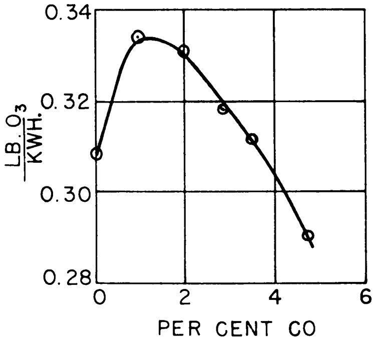

Figure 10. Effect of carbon monoxide

F. 1.52 lb./hr.
W. 90 watts
a. 59 watt-hr./lb.

Conclusions

Of the seven diluents studied, the greatest loss in energy yield resulted from the presence of less than 1% of hydrogen, water, or Freon 12.

A gradual decrease in energy yield resulted from addition of either carbon dioxide or argon to oxygen; amounts up to 50% reduced the energy yield to only 85% of that expected with pure oxygen.

Finally, the presence of either carbon monoxide or nitrogen in amounts up to 10% apparently increased the energy yield of ozone generation in oxygen. In amounts greater than 10%, a gradual decrease in energy yield resulted.

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Inhibiting Action of Hydrocarbons on Ozone Formation by Silent Electrical Discharge

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The reaction mechanism of ozone formation was studied to clarify the inhibiting action of hydrocarbons. The rate of ozone formation varies linearly with the hydrocarbon concentration, regardless of the type of hydrocarbon.

Ozone formation by silent electrical discharge is inhibited perfectly by admixing hydrocarbons in air (*1*). This was the main reason for the success of the slow oxidation of hydrocarbons by silent electrical discharge. It also caused the great difficulty in preparing ozone by the same process.

An investigation was made to clarify the mechanism of the inhibiting action.

Reaction Mechanism

Ozone formation probably consists of the following elementary reactions (*8*).

$$O_2 + e^* \xrightarrow{k_1} O + O^* + e \qquad (8.3\text{ ev.}) \qquad (1)$$

$$O + O_2 + M \xrightarrow{k_2} O_3 + M \qquad (24.1\text{ kcal.}) \qquad (2)$$

$$O + O + M \xrightarrow{k_3} O_2 + M \qquad (116.4\text{ kcal.}) \qquad (3)$$

$$O_3 + e^* \rightarrow O + O_2 + e \qquad (4)$$

Reaction 4 can be neglected, as its rate is too slow to compare with the others.

The slow oxidation of hydrocarbons proceeds by the following chain reaction, the so-called peroxide process, as described previously (*1–7*):

$$O_2 + e^* \xrightarrow{k_1} O + O^* + e \qquad (1)$$

$$RH + O + M \xrightarrow{k_4} R\cdot + OH + M \qquad (5)$$

$$RH + OH + M \rightarrow R\cdot + H_2O + M \qquad (6)$$

$$R\cdot + O_2 \rightarrow RO_2\cdot \qquad (7)$$

$$RO_2\cdot + RH \rightarrow RO_2H + R\cdot \qquad (8)$$

In the oxygen-hydrocarbon mixture, Reactions 2, 3, and 5 are mutually competitive,

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so ozone formation may be inhibited when the rate of Reaction 5 is greater than that of Reaction 2.

Inoue (*2–7*) found that the rate-determining step of the hydrocarbon oxidation is Reaction 1 and that all reactions take place in a stationary state.

Then

$$\begin{aligned}\frac{d[O]}{dt} &= 2k_1[O_2][e] - k_2[O][O_2][M] - k_3[O]^2[M] - k_4[RH][O][M] \\ &= 0\end{aligned} \tag{9}$$

Therefore, [O] is constant.

Then the rate of ozone formation is

$$\frac{d[O_3]}{dt} = k_2[O][O_2][M] \tag{10}$$

From Equations 9 and 10

$$\frac{d[O_3]}{dt} = 2k_1[O_2][e] - k_3[O]^2[M] - k_4[RH][O][M] \tag{11}$$

When the oxygen concentration is constant, both the first and second terms in Equation 11 become constant. The rate of ozone formation, accordingly, can be expressed by the first-order function of the hydrocarbon concentration.

When

$$\frac{d[O_3]}{dt} = 0$$

$$k_4[RH][O][M] = 2k_1[O_2][e] - k_3[O]^2[M] \tag{12}$$

Then the critical concentration of hydrocarbon for the perfect inhibition of ozone formation is

$$[RH]_{\text{critical}} = \frac{2k_1[O_2][e] - k_3[O]^2[M]}{k_4[O][M]} \tag{13}$$

Therefore, $[RH]_{\text{critical}}$ becomes constant when both $[O_2]$ and the discharge current are definite.

Experimental Work

To identify Equation 11 experimentally, the rates of ozone formation from air were observed by changing the concentration of admixed hydrocarbons. The experiment was performed by using the apparatus shown in Figure 1.

Under experimental conditions in Table I, the maximum ozone concentration reached about 1.0 volume %, so that the variation of oxygen concentration could be neglected. The amounts of hydrocarbons admixed were measured by weighing the change of the weight of evaporation in the feeder in Figure 1. The quantitative analy-

Table I. Experimental Conditions

Discharge tube	
Effective length	12.0 cm.
Space gap	3.0 mm.
Outer diameter of inner tube	3.80 cm.
Effective volume	42.5 cc.
Discharge voltage	15.0 kv.
Discharge current	1.45 ma.
Reaction temp.	20.0° C.
Total pressure	760.0 mm. of Hg
Flow rate	11.0 l.air/hour
Space velocity	4.15 min.$^{-1}$

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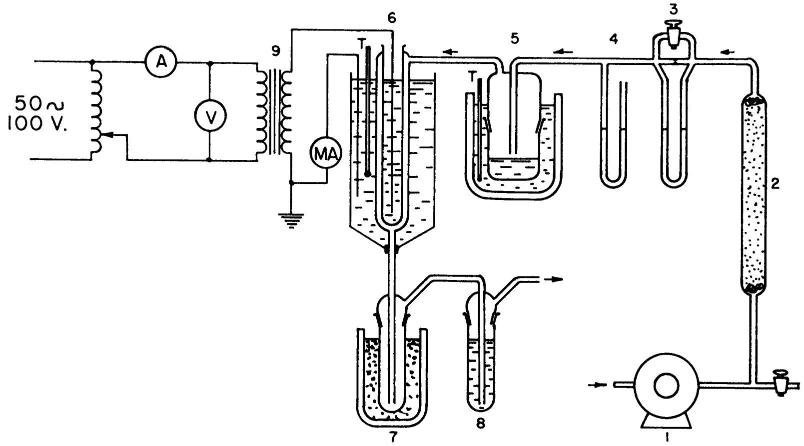

Figure 1. Apparatus

1. Blower
2. Silica gel tube
3. Flowmeter
4. Manometer
5. Hydrocarbon evaporator
6. Discharge tube
7. Cooled trap
8. Potassium iodide solution
9. Transformer

sis of ozone was carried out by the iodine method. The total error of the experiment was within ±3%. The results are shown in Table II.

Table II. Experimental Results

Hydrocarbon	G./Hour	Concn. of Hydrocarbon, Vol. %	Mm. Hg	Rate of O_3 Formation, Mole/Hour × 10^3
Cyclohexane				
	0.000	0.000	0.00	5.89
	0.092	0.223	1.69	4.61
	0.227	0.549	4.18	2.67
	0.290	0.702	5.34	1.98
	0.550	1.331	10.12	0.12
	0.850	2.051	15.64	0.09
n-Hexane				
	0.164	0.388	2.96	3.58
	0.250	0.589	4.50	2.38
	0.304	0.740	5.49	1.82
	0.335	0.792	6.03	1.50
	0.509	1.201	9.23	0.13
n-Heptane				
	0.056	0.114	0.87	5.22
	0.120	0.245	1.86	4.53
	0.160	0.326	2.48	4.04
	0.264	0.538	4.10	3.05
	0.311	0.633	4.82	1.99
	0.749	1.502	11.50	0.08

In Figure 2, the amounts of ozone formed during a 10-minute period are plotted against the concentrations of *n*-hexane, cyclohexane, and *n*-heptane. The rate of ozone formation changes linearly with the hydrocarbon concentration (Equation 11). And $[RH]_{critical}$ was about 1.1 volume % (8.5 mm. of mercury) for air.

No marked difference in inhibiting action was observed on changing the type of hydrocarbon.

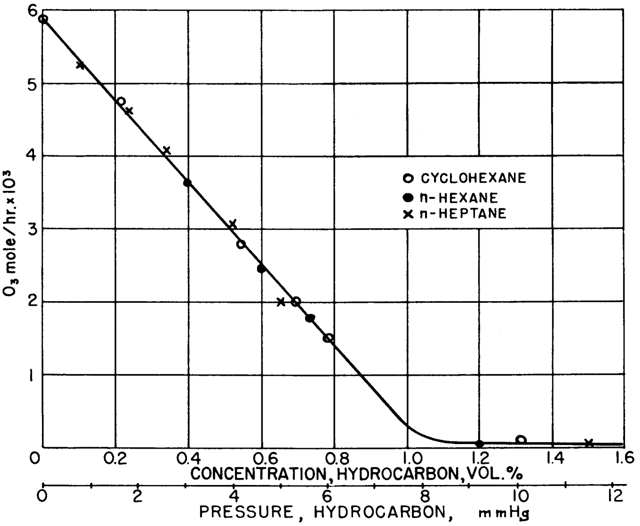

Figure 2. Effect of hydrocarbon concentration on ozone formation

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Origin of Secondary Electrons in Ozonizer Discharge

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The potential width of the photosensitive non-self-maintained region and the onset potentials of the self-maintained region of discharge in chlorine, bromine, iodine, oxygen, nitrogen, and water vapor enclosed in ozonizer tubes were measured. The data were elucidated by a mechanism suggested for the origin of secondary electrons for ozonizer discharge, indicating that gas particles adsorbed on the electrode surface ionize under positive ionic (or photon) bombardment and contribute to the secondary emission.

Depending upon the origin of the electrons, the electric discharge in gases may be divided into two classes: non-self-maintained and self-maintained discharge.

In the first, the primary electrons responsible for the production of electron avalanches are generated by some external agencies like radioactive or light rays. The discharge exists as long as these rays are in operation. This may be illustrated by the phenomenon involved in the Geiger region of the counters. The potential applied to the wire and cylinder of the counters is only sufficient to energize electrons to cause ionization by collision; this will happen only when an electron is introduced into the system by external agencies.

In the self-maintained discharge, the gas-intensified photoelectric or ionization current develops a mechanism by which new electrons can be generated in sufficient number by secondary processes in a sensitive portion of the discharge, to replace externally imposed ionization. That is, in the case of a self-maintained discharge, the agencies developed in the discharge space—e.g., photons, positive ions, etc.—produce electrons which in turn cause avalanches and their generators; a cyclic operation takes place. This will happen when the externally applied voltage is larger than a minimum value which is often referred to as the threshold potential, V_m, of the self-maintained discharge. The varied secondary processes responsible for the maintenance of the discharge are as follows:

A. In the gas phase
  1. Ionization and excitation by electron impact
  2. Ionization by positive ion impact
  3. Photoelectric action in the gas
  4. Action of metastables in the gas

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B. At the cathode
  1. Electron bombardment
  2. Positive ionic bombardment
  3. Photoelectric effects
  4. Impact of metastable atoms
  5. Field currents

Secondary Emission in Discharges with Metallic Electrodes

Considerable experimental evidence is available to show that in discharges in Geissler tubes and other systems involving metallic electrodes, the secondary emission from the cathode by bombardment by positive ions (Process B1) and photons (B3) are significant. These secondary electrons originate from the free electrons forming the Fermi gas in a metal. It is known that the highest level occupied by an electron in a metal at absolute zero is referred to as the Fermi level, μ electron volts above from the lowest. The emission of secondary electrons from the metallic cathode is relatively very simple and refers to the same process as is involved in the photoelectric emission. When the energy, E, imparted to a metallic electron by an incident photon is greater than $\mu + \phi$ (where ϕ is the work function of the surface), it is liberated into the free space, possessing the energy difference $E - (\mu + \phi)$ e.v.

The processes involved in the bombardment of a solid surface by positive ions are, however, very complicated and give rise to varied phenomena; the most important and significant one for the point under consideration is the liberation of secondary electrons. Even in this process, the essential requisite is that sufficient energy be supplied to the metal electron to enable it to leave the metal. There appear to be two ways in which a positive ion can supply energy to an electron in the metal. In the first, the energy comes from the kinetic energy of translation of the ion relative to the metal; in the second, it is made available by changes in the electronic structure of the ion (*1*). As emphasized by Massey and Burhop (*1*), a large part of the electron emission appears to be due to the first process.

Secondary Emission in Ozonizer Discharges with Glass Electrodes

There exist no free or Fermi electrons in glass, which is considered to be a semiconductor with a very low specific conductivity (10^{-5} to 10^{-3} ohm^{-1} cm.$^{-1}$). The question then arises: Where do the secondary electrons originate in ozonizer tubes when the discharge enters the self-maintained region?

It has been suggested (*6*) that in discharges with glass electrodes, the gas layers adsorbed on the glass surface form the source of the secondary electrons. This is arrived at from a very interesting finding that the discharge in mercury vapor, enclosed in an ozonizer from which the adsorbed water vapor layers were removed, could be struck and maintained only at very large fields of the order of 10^4 volts per cm., while the self-maintained discharge could be initiated at 900 volts per cm. in the same vessel when it contained the preadsorbed water vapor layers. Thus the existence of the adsorbed gas layers on the surface of an electrode facilitates the liberation of secondary electrons at comparatively much lower applied fields. It is therefore suggested (*6*) that on receipt of sufficient energy by photonic or positive ionic bombardment, the adsorbed particles ionize and contribute to the liberation of secondary electrons.

Deductions from Hypothesis for Origin of Secondary Emission in Ozonizer Discharges

It is apparent that the threshold potential, V_m, of the self-maintained region of the ozonizer discharge is primarily dependent upon the nature, especially the ionization potential, V_i, of the adsorbed gas medium. A deduction from this is that for a

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given geometry of the ozonizer tubes, the threshold potential, V_m, should be less in bromine ($V_i = 11.8$ e.v.), iodine ($V_i = 10.4$ e.v.), etc., than in water vapor ($V_i = 13.0$ e.v.). Or, for a given pressure of bromine or iodine enclosed in a known ozonizer, V_m should be less when the adsorbed layers contained only bromine or iodine than when the electrode walls contain water vapor as adsorbed layers.

Over a definite voltage region below the threshold potential, V_m, the discharge is non-self-maintained and exists whenever any external ionizing radiation is incident. The limit of this non-self-maintained region is V_n and that of the self-maintained region is V_m. The potential width of the non-self-maintained region is thus given by $V_m - V_n$. V_n corresponds roughly to the beginning of the proportional region of the counter, at which the field across one mean free path is sufficient to cause ionization by collision of the gas particles, is a function of the ionization potential of the gas medium, and is relatively unaffected by the changes of the electrode surface. Further, as envisaged in the above hypothesis, the field at V_m is sufficient to impart energy corresponding to the ionization potential of the adsorbed medium. If V_i is designated as the ionization potential of the gaseous medium and V_{si} as that of the adsorbed phase, the following simple form of a quantitative expression can be written:

$$V_m - V_n = f_1\ (V_{si} + \phi) - f_2\ (V_i)$$

where f_1 and f_2 represent the functional abbreviation. Further, if it is assumed that f_1 and f_2 are similar, we get

$$V_m - V_n = f\ (V_{si} - V_i + \phi)$$

This expression is only approximate and possibly a crude form relating the ionization potential of the gas phase and that of the adsorbed medium with the potential width of the non-self-maintained region which can be observed experimentally. If allowance is made for the possible incorrectness of the assumption that f_1 and f_2 are similar functions, it would appear from the above expression that the non-self-maintained region should be appreciable in systems in which $V_{si} - V_i$ is marked.

Experimental Verification of Deductions

The threshold potentials V_m, of the self-maintained region, and the potential width ($V_m - V_n$) of the non-self-maintained region were investigated in bromine, methanol, iodine, oxygen, and nitrogen introduced in nondegassed vessels which contained adsorbed water vapor layers and in degassed vessels in which the adsorbed layers were removed prior to introduction of the gas or vapor under investigation. The experimental details of this investigation will be given elsewhere. Unlike its behavior in Geisler tubes and Geiger-Müller counters, the non-self-maintained region in ozonizer discharge in iodine, bromine, etc., is extremely photosensitive, in the sense that even visible light produces pulses or initiates the discharge which exists only as long as the radiation is in operation.

Table I gives a typical series of results on the variation of V_m of pressure of bromine introduced into degassed and nondegassed ozonizers. In accord with the deduction from the above hypothesis on the origin of the secondary electrons in ozonizer discharges, V_m was larger in nondegassed vessels in which the electrode surface con-

Table I. Variation of Threshold Potential with Pressure of Bromine Vapor in Degassed and Nondegassed Ozonizers

Pressure,	V_m, in kv.	
Mm. Hg	Degassed	Nondegassed
0.0028	0.546	0.92
0.23	1.15	1.22
1.07	1.775	...
4.59	3.58	4.09

tained chiefly a water vapor ($V_{si} = 13.6$ e.v.) layer than in degassed vessels in which the adsorbed layers contained bromine ($V_{si} = 11.8$ e.v.). The difference in the ionization potential of an atom adsorbed on the surface and of the same atom existing in the free state is not known.

Table II gives the data on the potential width of the photosensitive non-self-maintained region ($V_m - V_n$) in a number of media investigated. The external source of light employed was a 200-watt bulb. It is apparent from the data in almost all gases or vapors that $V_m - V_n$ is related to the difference in the ionization potentials of the particles existing in the homogeneous and the adsorbed phase, which can be followed from the above hypothesis. The data clearly point out the significance of the adsorbed vapor in controlling the potential width $V_m - V_n$.

Table II. Potential Width of Photosensitive Non-Self-Maintained Region ($V_m - V_n$) in Various Media

Homogeneous Medium	Pressure of Vapor, Mm. Hg	Ionization Potential: Of adsorbed medium, V_{si}, e.v.	Ionization Potential: Of gas phase employed V_i, e.v.	$V_{si} - V_i + \phi$[a], E.V.	$V_m - V_n$, Volts (R.M.S.)	References
Iodine vapor	0.45	13.0[b]	10.4	$2.6+\phi$	1500	[c] *(9,10)*
	0.45	10.4[d]	10.4	ϕ	10	[c] *(10)*
Bromine	0.0028	13.0[b]	11.8	$1.2+\phi$	374	[c]
	0.23	13.0[b]	11.8	$1.2+\phi$	476	[c]
	0.0026	11.8[d]	11.8	ϕ	5	[c]
Methanol	17.8	13.0[b]	10.8	$2.2+\phi$	100	[c]
	20.5	13.0[b]	10.8	$2.2+\phi$	82	[c]
	21.4	10.8[d]	10.8	ϕ	120	[c]
Chlorine	20.0	13.0[b]	12.9	$0.1+\phi$	Undetectable	[c] *(8)*
Nitrogen	26.0	13.0[b]	14.5	$-1.5+\phi$	Undetectable	[c] *(4,7)*
Oxygen	10.0	13.0[b]	13.6	$-0.6+\phi$	Undetectable	[c]
	330	13.0[b]	13.6	$-0.6+\phi$	400 ?	*(2,3)*
Water	13.5	13.0[b]	13.0	ϕ	Undetectable	[c] *(5)*

[a] Work function of surface under discharge not known.

[b] In nondegassed vessels—i.e., adsorbed vapor layers ($V_i = 13.0$ e.v.) present on electrode surface.

[c] Present investigations.

[d] In degassed vessels—adsorbed phase on electrode surface was same as in homogeneous gas phase—$V_{si} = V_i$.

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Effect of External Light on Ozonizer Discharge

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Current, passing through an ozonizer containing an electronegative gas and excited by alternating current fields, is decreased in magnitude by external light. This photoreduction (Joshi effect, $-\Delta i$) was markedly susceptible to changes in the nature of electrode surface by deposition of films and/or by aging. Adsorbed layers, held on the electrode surface by van der Waals forces, were responsible for $-\Delta i$. Under light, adsorbed molecules dissociate to give electronegative atoms and/or radicals; these inhibit by processes of electron capture the secondary emission, which results in the loss of electron avalanche production and, therefore, in the reduction in current.

During investigation of the kinetics of the familiar reaction between hydrogen and chlorine excited by electrical fields in ozonizer tubes, Joshi (*11, 22*) of Banaras observed in 1938 that the current, i, flowing through the system decreased markedly on exposure of the discharge tube to external light. This photoreduction of i, referred to as the Joshi effect, $-\Delta i$, is contrary to theoretical considerations of photo- and thermoelectric effects and of electric discharge in gases and has been observed in almost all electronegative gases and vapors (*21*). It has been established that $-\Delta i$ is distinct from the well known photoelectric effect: while the latter increases linearly with millionfold increase of light intensity, I, the effect $-\Delta i$ attains saturation at large I.

Unlike the Budde effect which is observed in unexcited halogens, $-\Delta i$ is noticed under all frequency ranges from extreme red (7070 A.) to x-rays. It has been shown (*21*, *22*) that $-\Delta i$ is not analogous to the Penning effect which involves a rise in the sparking potential (followed by a decrease in the discharge current) of a mixture of gases—particularly helium and neon—due to photodestruction of their metastables. The new phenomenon $-\Delta i$ has evoked much interest in view of the work done by Thomson, Townsend, Loeb, and others, which reveals that external radiation is an indispensable factor for the inception of a discharge (*32*).

Experimental Technique

The experimental technique employed in the investigation of $-\Delta i$ is very simple and involves measurement of ozonizer current in an electronegative gas or vapor, in the dark and light (*4*, *23*). Ozonizer tubes made of soft soda, hard and borosilicate glasses, and fused silica were employed. These were evacuated by suitable vacuum pumps and filled with purified gases like oxygen, chlorine, bromine, iodine, and water vapor, at a desired pressure. They were excited by high alternating potentials of 50, 100, and 500 cycles per second obtained by suitable step-up transformers (see Figure 1).

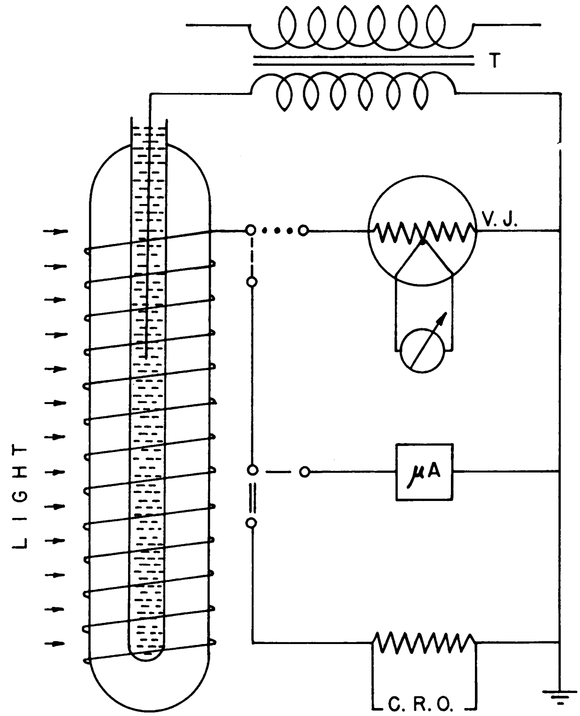

Figure 1. Experimental setup for investigation of effect of external light on ozonizer discharge

V. J. = Cambridge vacuo-junction

The alternating current flowing through the system was measured by a microammeter or a sensitive galvanometer coupled with a suitable rectifier. The current was also investigated by a cathode ray oscillograph. The current measurements were made when the excited system was in the dark and when exposed to light of a known wave length obtained from the combination of mercury arc lamp and a suitable filter or to the continuous radiation from a 200-watt bulb (visible) or hydrogen discharge tube (ultraviolet) (*36*). The observed values of the current in the dark and under light were referred to, respectively, as i_{dark} and i_{light}. The difference between these values gave the absolute value of $-\Delta i$; the relative value which appeared suitable for comparative purposes was given by $100(-\Delta i)/i_{dark}$.

Dependence of Phenomenon on Electrode Surface

Soon after the discovery of the phenomenon, the significance of the nature of the electrode surface as distinct from the homogeneous gas phase, in controlling the magnitude of $-\Delta i$, was recognized. Experimental findings of the influence on $-\Delta i$ of surface films, presorbed gases, aging under discharge, etc., contributed much to understanding the origin of the phenomenon.

Influence of Surface Films. That the electrode surface of the discharge tubes does not remain inactive but plays a significant role in the production of $-\Delta i$ has been inferred from the pronounced influence on the magnitude of $-\Delta i$ of the change in the nature of the excited surface, brought about by deposition of certain films on the electrode surface. Cheryan (*2*) studied the variation in the magnitude of $-\Delta i$ by coating the ozonizer walls with about 50 substances.

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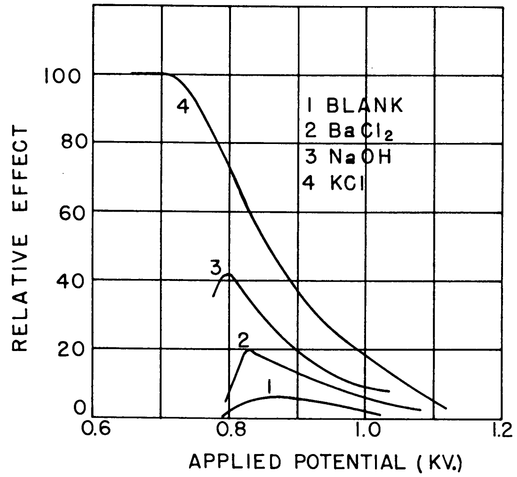

Figure 2. Influence of surface films on phenomenon —Δ*i* in air

Figure 2 gives a typical series of results on —Δ*i* in air with different wall materials (*37*). At a pressure of 140 mm. of mercury and at 0.9 kv., the effect —%Δ*i* was 3 in blank (glass) vessels while it was 17 with sodium hydroxide, 38 with barium chloride, and 43 with potassium chloride coating on the annular walls of the discharge tube. Essentially similar augmentative influence of potassium chloride on —Δ*i* was also noticed in water vapor (*25*). This catalytic action of potassium chloride on —Δ*i* was utilized to demonstrate the surface sensitivity of —Δ*i*. It was observed that the magnitude of —Δ*i* in water vapor increased linearly with the length of the ozonizer irradiated with either blank or potassium chloride-coated surface. The slope of the line appeared to give an exact measure of the influence on —Δ*i* of the nature of the surface; and was two times greater with potassium chloride than with a blank surface (see Figure 3). The marked variation in the value of the slope due to a change in

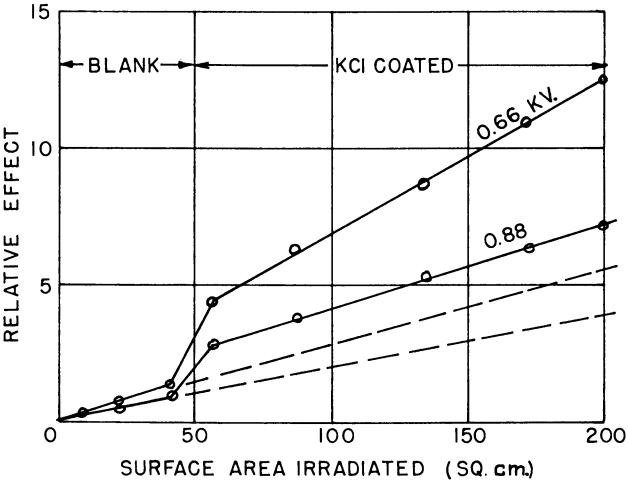

Figure 3. Influence of potassium chloride on variation of phenomenon —Δ*i* in the electrode surface

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the nature of the surface revealed the significance of the latter in determining the magnitude of $-\Delta i$.

Influence of Presorbed Gases. The influence on $-\Delta i$ of the preadsorbed gases on the electrode surface was investigated by Rao (*27*). Pure, dried chlorine was introduced into a vessel under a pressure of 300 mm. of mercury and was subjected to discharge intermittently for about 14 hours. Later, the gas was completely pumped out; the discharge tube was not degassed deliberately. It was filled with dried air at a fixed pressure. The system in this condition showed a pronounced $-\Delta i$ corresponding to 88% photodiminution of the current. When dried air was introduced at the same pressure into a fresh vessel and tested, no effect could be noticed. These results emphasized the marked significance as a determinant of $-\Delta i$, of traces of impurities, especially the adsorbed gases or/and the changes produced on the electrode surface by the applied fields.

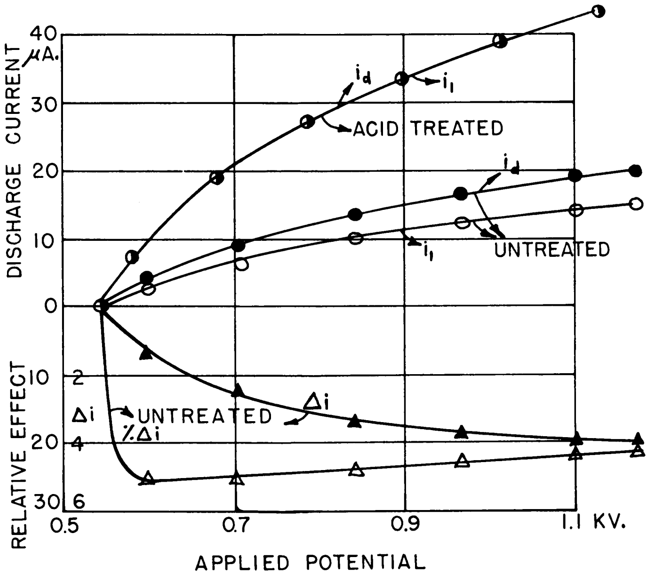

Figure 4. Influence of removal of surface alkali on phenomenon $-\Delta i$ in water vapor

Influence of Acid Treatment. The presence of free alkali on the surface of glass and its influence on adsorption and allied phenomena are well known. McBain (*17*) pointed out the significance of acid treatment of glass vessels to remove the alkali in quantitative treatment of the phenomenon mentioned. The removal of surface alkali caused a marked change in the production of $-\Delta i$ (*20*). This last effect was studied in Siemens-type vessels, some of which were prewashed with chromic acid and boiling distilled water and dried under vacuum for 24 hours; others were used as they were prepared from fresh glass.

Figure 4 gives a typical series of results on $-\Delta i$ in water vapor enclosed in acid-washed and untreated ozonizers. In untreated discharge tubes, appreciable effect corresponding to 25% current suppression under light was observed; under the same conditions of pressure and exciting potential, no $-\Delta i$ could be noticed in acid-treated vessels. The nature and the volume of the gas were the same in the two series of experiments. The only difference was that the surface of one vessel was freed from surface alkali by treating the discharge tube with acid solution, while the other was not. The marked influence on the production of $-\Delta i$ of surface alkali offered further evidence for the dependence of the phenomenon on the electrode material rather than on the homogeneous gas phase.

Influence of Aging. The data in Figure 5 show the effect on $-\Delta i$ of aging—viz., continued exposure to discharge at a fixed potential. The system was excited at a constant applied field and the magnitude of $-\Delta i$ was noticed at increasing intervals of time. The effect $-\Delta i$ increased progressively with time *t*, tending to attain a maximum value at large values of *t*. In general, the rate of increase of $-\Delta i$ obeyed a relationship

$$-\%\Delta i = kt^{1/m} \qquad (1)$$

where *k* and *m* are constants, as indicated by the linear graphs obtained when log $(-\%\Delta i)$ was plotted against log *t* (see curve 2, Figure 5) (*20, 33*). Equation 1 is similar to Bangham and Burt's equation for the rate of sorption of a number of gases

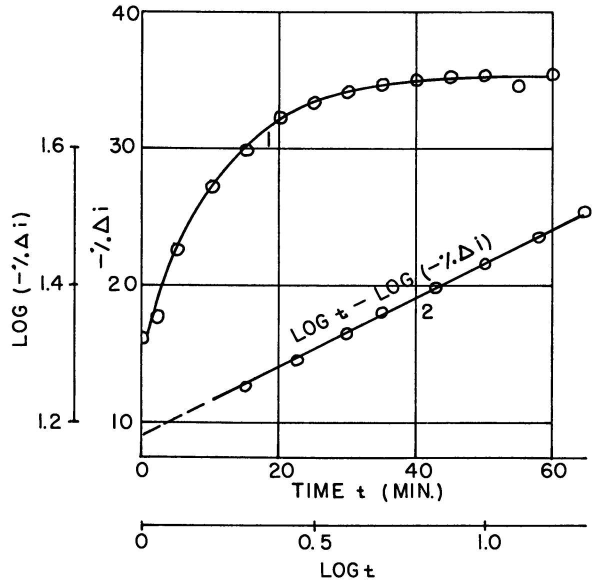

Figure 5. Influence of aging on phenomenon $-\Delta i$

on glass (*1*). Further, the rate of increase of $-\Delta i$ during aging appeared to obey a first-order law (*26*).

This time development of $-\Delta i$ with aging appeared to be permanent, in the sense that when the discharge was discontinued and tested after a rest period of 10 hours, the same magnitude of $-\Delta i$ was noticed. This irreversible augmentation of $-\Delta i$ with time of exposiure to discharge in elementary gases like chlorine and iodine is incomprehensible on the basis of the possible reactions in the homogeneous gas phase. Dissociation of chlorine and iodine into atoms and their later conversion into negative ions by capture of electrons seem to be the probable changes to be expected under discharge; these are, however, sensibly reversible: When the exciting mechanism ceases to operate, the charged particles are lost by a number of processes like recombination and diffusion. The observed influence of aging on the magnitude of $-\Delta i$ gave a clear indication that the processes occurring under discharge, presumably changes chemical in nature, at or/and on the electrode surface, were of fundamental importance in governing the mechanism for the occurrence of $-\Delta i$.

Influence of Longitudinal and Transverse Irradiation. Employing ozonizers of slightly different design from the familiar Siemens type (Figure 6), Deo (*3*) and Rao

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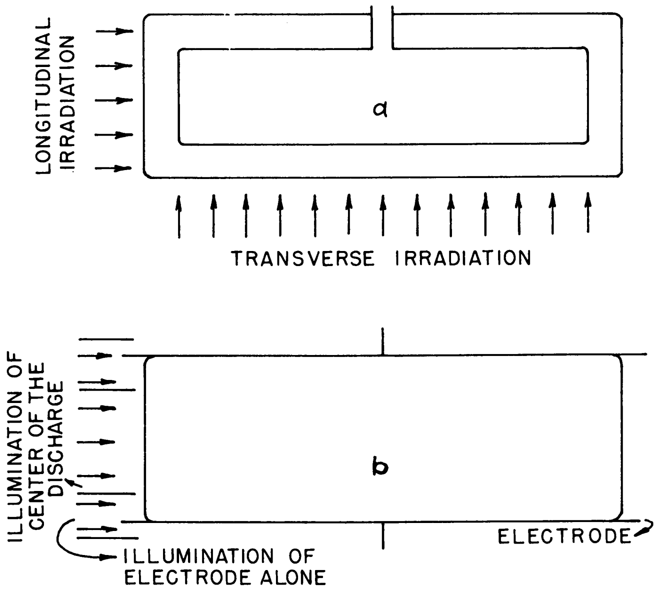

Figure 6. Schematic representation of irradiation of ozonizer wall and homogeneous gas phase

(*27*) investigated the variation of $-\Delta i$ in chlorine and iodine vapor, respectively, with the system irradiated longitudinally, on the end-on position—and transversely—in the broad side-on position (see Figure 6,*a*). Other conditions being equal the relative effect $-\%\Delta i$ in iodine vapor was found to be 20 in the former mode of irradiation and about three times this value—i.e., 60%—in the latter. Similar results were obtained in chlorine. In both types of irradiation the entire gas bulk was exposed to light, but in the former case, only a part of the surface was exposed to light (due to multiple reflection); and in the transverse illumination, a comparatively large quantity of the electrode surface was exposed to light. The observed disparity in the magnitude of $-\Delta i$ indicated the significance of the electrode surface as a determinant of $-\Delta i$. Harries and von Engel (*6*) employed essentially the same method of scanning; cylindrical tubes filled with chlorine were used (Figure 6,*b*). When the position near the electrodes was illuminated, the pulses constituting the current, *i*, were inhibited; when the center of the discharge tube was irradiated, no diminution in the pulse height was recorded.

Joshi's Hypothesis

In agreement with the above data emphasizing the significance of the electrode surface in controlling the magnitude of $-\Delta i$, Joshi (*10*) suggested for the first time that an adsorptionlike layer characterized by a low work function formed on the electrode surface was responsible for $-\Delta i$. He further postulated that light releases electrons from the above boundary layer; these photoelectrons are captured by excited particles, atoms, or/and radicals with large electron affinity, to form slow-moving negative ions which reduce *i* as a space charge effect.

Adsorption and the Phenomenon. The concept of an adsorptionlike layer visualized by Joshi as being responsible for $-\Delta i$ appeared helpful in elucidating a large number of observed facts including those indicated above, especially the influence on $-\Delta i$ of aging. Because the latter two stages visualized in the hypothesis are instantaneous and reversible, the change in the magnitude of $-\Delta i$ during aging, according to the above hypothesis, was determined almost entirely by the extent to which the adsorption-like layer was formed.

The observations that an equation similar to that postulated by Bangham and Burt, applicable to adsorption processes, is followed by an increase of $-\Delta i$ during aging; and that a first-order equation is obeyed, indicated that the adsorbed layer visualized by Joshi was perhaps akin to chemisorption, distinct from van der Waals adsorption. When a gas is introduced into a nude vessel, a known quantity, depending upon the pressure and temperature of the gas, is taken up instantaneously by the solid in the form of molecular layers due to nonspecific van der Waals forces; this is followed by slow uptake of gas by the Langmuir sites after acquisition of the necessary activation energy. This last is obtained by bombardment by molecules arriving from the gas phase with excitation energy acquired by kinetic collisions; this is controlled by a probability factor which is very small under normal conditions, accounting for the slow rate of sorption, and is apparently appreciable under conditions of electrical discharge, as evidenced by the observation that under discharge the rate of sorption of hydrogen and other gases on glass is relatively very fast (*9*, *35*, *38*).

Predischarge Adsorption as a Determinant of the Phenomenon. The finding that Equation 1 was applicable to the development of $-\Delta i$ during aging apparently supported the hypothesis that an adsorptionlike layer formed on the electrode wall during aging was fundamental to $-\Delta i$. According to Joshi's theory, the lines log $(-\Delta i)$ *vs.* log t should pass through the origin; the graphs representing the data in water, chlorine, iodine, and oxygen in untreated discharge tubes gave a Y-axis intercept. It follows simply from the hypothesis that the Y-axis intercept might be due to the predischarge chemisorption. This suggests that the magnitude of $-\Delta i$ observed in a gas introduced into a nude or degassed vessel from which the preadsorbed gases have been removed, should increase with increase in the predischarge interval.

Experimental Data on Influence of the Predischarge Interval on $-\Delta i$

The above deduction was examined in two media—water and iodine vapor. Siemens' ozonizers made of soft soda glass were employed. These were degassed following the method of Razouk and Salem (*28*), and were filled at a desired pressure with water or iodine vapor.

Table I gives a typical series of results on the dependence of $-\Delta i$ in water vapor on the predischarge interval; and Table II refers to the potential variation of $-\Delta i$ in iodine vapor observed immediately after the introduction of the vapor into the degassed vessel and after aging at 0.45 kv. for 1 hour.

Table I. Influence of Predischarge Interval on the Phenomenon $-\Delta i$ in Water Vapor

p_{H_2O} = 31.8 mm. Hg (30° C.); applied potential = 0.66 kv.

Predischarge Interval, Minutes	i_{dark}, μa.	i_{light}, μa.	$-\%\Delta i$
0.5	98.0	85.5	12.8
30	87.0	76.0	12.6
120	65.0	56.0	13.8
300	41.0	36.0	12.2

Appreciable $-\Delta i$ was recorded both in water and iodine vapor enclosed in a degassed vessel. Further, the data in Table I show that the magnitude of $-\Delta i$, contrary to the deduction from Joshi's hypothesis, was unaffected by increase in the predischarge interval, indicating that the magnitude of $-\Delta i$ was not really controlled by the amount of predischarge adsorption and that the increase in $-\Delta i$ during aging was also apparently not due to the increase in chemisorption.

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Table II. Potential Variation of the Joshi Effect in Iodine Vapor in a Degassed Vessel

Pressure of iodine vapor, mm. Hg.	0.47
Temperature of system, ° C.	31
Detector	Vacuo-junction
Source of irradiation	200-watt bulb
Ozonizer	2

Kv.	i_{dark}	i_{light}	$-\Delta i$	$-\%\Delta i$
		Before aging		
0.22	26	0.5	25.5	94
0.28	39	1.5	37.5	96
0.33	32	3.6	28.4	89
0.39	27.1	6.9	20.2	75
0.44	24.6	10.5	14.1	57
0.50	20.3	16.9	3.4	17
0.55	22.4	21.9	0.5	2.2
0.61	24.9	24.8	0.1	0.4
0.66	27.3	27.3	...	...
0.72	29.5	29.5	...	...
0.77	32.5	32.5	...	...
		After aging		
0.22	23	...	23	100
0.28	32.5	...	32.5	100
0.33	29.8	0.2	29.6	99.3
0.39	26.9	1.3	25.6	95.1
0.44	23.8	4.5	19.3	81.1
0.50	21.0	7.3	13.7	65.2
0.55	18.5	10.8	7.7	41.6
0.61	17.0	14.1	2.9	17.0
0.66	16.5	15.0	1.5	9.9
0.71	18.2	17.9	0.3	1.6
0.77	21.0	21.0	...	...

General Mechanism of the Phenomenon

On the basis of the above findings and on oscillographic data presented elsewhere (*19*, *31*), it has been suggested (*13*, *19*, *22*, *31*) that the instantaneous adsorption or van der Waals adsorption on the Langmuir layer on the electrodes is the chief seat of $-\Delta i$. In the dark, under applied fields, ionic bombardment causes excitation, leading to dissociation of surface-adsorbed molecules. Irradiation enhances the dissociation of surface molecules leading to the production of electronegative atoms and radicals which capture the secondary electrons to form negative ions.

It can be shown that the instantaneous current in a discharge is primarily controlled by the number of avalanches created by the so-called secondary electrons released from the cathode by any possible process—e.g., the positive ionic bombardment. In discharges with ozonizer tubes, the circumstances are slightly complicated by the fact that the glass electrode surface usually holds gases and vapors adsorbed in the form of molecular layers on firmly held atoms and molecules on Langmuir sites. The van der Waals adsorption involves evaporation and condensation processes. In the dark, an equilibrium exists with the release of a certain number of electrons, negative ions formed by the capture of a few secondary electrons with atoms and/or radicals obtained by dissociation during positive ionic bombardment of surface adsorbed molecules, and also undissociated particles. In these, the electrons only produce avalanches and contribute to the current. This mechanism implies that external light enhances the dissociation of adsorbed molecules to produce an increased number of atoms and/or radicals; these, on account of their large electron affinity, capture the secondary electrons to form negative ions. This amounts to a reduction under light of the secondary emission and therefore the discharge current. The augmentative influence on $-\Delta i$ of the continued exposure to discharge may be attributed, on the above hypothesis, to the production of compounds like sodium iodide, sodium hydroxide, etc. This is not unlikely. Rodebush and Klingelhoeffer (*29*) observed a white deposit on glass walls of an electrodeless discharge tube containing chlorine. Kellner (*12*) found a yellow substance formed on glass walls when bromine was subjected to ozonizer discharge. Ludeking (*16*) estimated the amount of $NaI/NaIO_3$ formed when iodine was exposed to spark discharge. These results follow from the electrolytic nature of

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conduction of electricity through glass. This is in accord with the finding that the influence on $-\Delta i$ of aging is appreciable in soft soda glass and not noticed in borosilicate glass and fused silica vessels (*30*). It is apparent, therefore, that the time development of $-\Delta i$ during aging under discharge is primarily due to the production on the electrode surface of compounds like sodium chloride, sodium bromide, and sodium hydroxide.

The influence of the surface films seems to be twofold in favoring $-\Delta i$. First, these substances enhance the amount of van der Waals adsorption. Faraday (*5*) and later Imhori (*8*) and Harris and Schumacher (*7*) showed that large adsorption of water vapor on a glass surface could be traced to the presence of free alkali. Lennard-Jones and Dent (*15*) have analyzed the various forces available at the surface of a polar substance like potassium chloride; of these, van der Waals type appeared significant. The favorable influence on $-\Delta i$ of these surface films like potassium chloride and sodium chloride produced during aging or by deposition on the electrode walls is presumably connected with the polar nature of these substances. The effect $-\Delta i$ in water vapor is in the order: $KCl >$ blank $> Al_2O_3$ (*14*); potassium chloride is highly polar; glass is known to be semipolar; and aluminum oxide is nonpolar. Based on the data on a number of chemical reactions, Norrish (*18*) attributed the observed catalytic activity of polar substances to the electrostatic forces that exist on the surface of a polar substance; "they make the reactant molecules vulnerable for attack or dissociation" thereof into atoms and/or radicals which combine with other constituents to give the resultants.

No data are available on the energy requirements for the dissociation of a molecule adsorbed on the surface of a solid substance, as distinct from one existing in the homogeneous gas phase. Nevertheless, if we assume that the photodissociation of water occurs as in homogeneous phase, then water dissociates at $\lambda = 2250$ A.; however, it has been observed that $-\Delta i$ in water vapor is appreciable over the range 6600 to 2537 A. and is linearly variant with the frequency of the radiation (*24*). The dissociation of surface-adsorbed water at longer wave lengths to give $-\Delta i$ is apparently due to the existence on the electrode surface of polar substances which, as indicated above, make the molecules vulnerable to dissociation. The marked variation of $-\Delta i$ with the removal of surface alkali by acid treatment and with the production of the effect during aging under discharge or deposition of films like potassium chloride, sodium chloride, etc., follow simply from the above mechanism.

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Chemical Reaction in Silent Discharge

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The high frequency oscillatory current during the silent electrical discharge in an ozonizer affects the chemical reaction in some way. A parallel relation exists between the high frequency current and the yield of hydrogen peroxide from hydrogen and oxygen, but not between the low frequency base current and the yield.

The silent electrical discharge in an ozonizer is always accompanied by some sort of high frequency electrical oscillations. The phenomenon has been pointed out by various authors (*1–3, 6, 7*). There is an oscillation with a frequency of several hundred kilocycles which can easily be detected by an ordinary wave meter or with an oscilloscope. According to the above authors, the oscillation has been explained as displacement current, which is produced in the ozonizer circuit in accordance with the time constant of the circuit itself. This high frequency current, though its amplitude is considerable, supposedly does not have any appreciable effect on chemical reactions which may occur in the discharge. The reaction is controlled rather by the energy consumed when low frequency current of 50 or 60 cycles is used for the initiation of the electrical discharge. The most direct measure of the process of chemical reaction is furnished by the energy consumption in an ozonizer; this energy is simply that measured by a low frequency wattmeter or similar equipment.

Nevertheless, the series of investigations undertaken in this institute shows that the high frequency oscillatory current affects in some way the chemical reactions in the silent discharge. The high frequency current of several hundred kilocycles plays a more important role than the low frequency base current.

With a wave meter it is possible to detect generally two sorts of high frequency oscillation—one of several hundred kilocycles, mentioned above, and another of several kilocycles, which corresponds to the numbers of pulses of discharges taking place on the surface of the ozonizer electrode during a period of one cycle of low frequency base current. The latter oscillation has nothing to do with the chemical reaction (*4*).

Results and Conclusions

A hydrogen-rich gas mixture of hydrogen and oxygen will produce hydrogen peroxide under silent electrical discharge in an ozonizer (*4*). In this case if the yield of hydrogen peroxide is plotted against the volume per cent of oxygen in the gas mixture, a curve is obtained with a minimum yield at 3.5% of oxygen. On the other hand, if the values of high frequency oscillatory current and of low frequency base

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current, are plotted against the volume per cent of oxygen, then at 3.5% of oxygen there is a minimum in the high frequency curve and a maximum in the low frequency curve, respectively. Thus, a parallel relation is obtained between the yield of hydrogen peroxide and the high frequency current, but not between the yield and low frequency current.

In an oscillogram of current of a silent discharge in an ozonizer, there is a hairlike pulse current image on the wave form of 50-cycle base current which we may call "hair" (*5*). In an experiment of ozone formation in an ozonizer, the mean square length, $\sqrt{\Sigma a^2}$, where a is the length of each hair in the oscillogram, corresponds to the mean high frequency current which accompanies the pulse in an ozonizer. By means of an appropriate wave filter circuit it was possible to separate the current whose frequency was more than 200 kc. This high frequency current was measured with a help of thermocouple-type ammeter. The experimental results (Figure 1) show that the high frequency current is related linearly to $\sqrt{\Sigma a^2}$. The total quantity of electricity transferred from one electrode to the other during one period of 50-cycle alternating current is expressed by the total length of the hairs in the oscillogram.

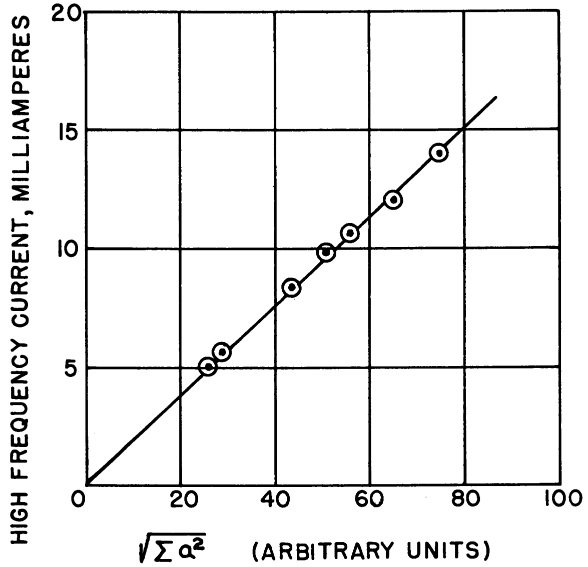

Figure 1. Relation of high frequency current to $\sqrt{\Sigma a^2}$

If the yield of ozone is plotted against the total length of the hairs, a linear curve is obtained (Figure 2). These experimental results show good agreement with the previously developed theory.

Though the mechanism of the influence of high frequency current on chemical reactions is not yet fully elucidated, it is possible to perceive some sort of effect of the highly oscillating current accompanying the silent discharge on the discharge reaction. Further research is in progress in this laboratory.

Part of this experiment was carried out in the chemical laboratory of Tokyo Metropolitan University, Setagaya, Tokyo, Japan.

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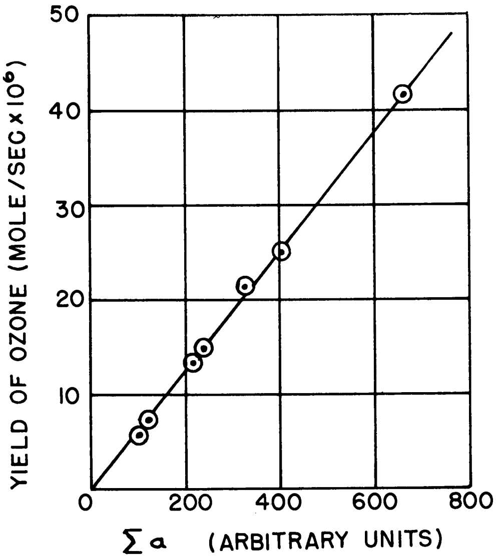

Figure 2. Relation of hair length to ozone yield

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Electrical Characteristics of the Ozonizer

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Extensive studies (*1, 4*) have been made on the chemical reaction involved in silent electric discharge. Also, studies have been undertaken to explain the characteristics of silent electric discharge purely on the basis of electrotechniques (*2, 3, 5, 6*). The authors have studied the electrical characteristics of an ozonizer to find relations between the gaseous reaction occurring in the silent discharge and the electrical conditions governing it.

The chemical reaction and the electrical characteristics of silent electric discharge have been correlated by studies on an ozonizer. Usually, the space in silent discharge is terminated by dielectrics which act as the stabilizing resistance with a little loss and prevent concentration of the discharge. An alternating current must be used.

Experimental Equipment and Conditions

The silent discharge tube is a cylindrical tube of hard glass. The construction and dimensions are given in Figure 1. The air gap and thickness of the glass tube are

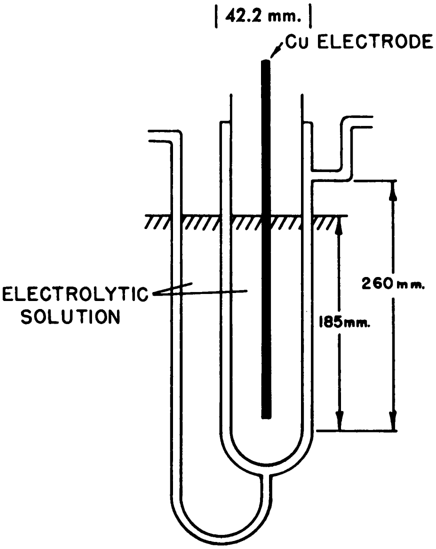

Figure 1. Silent discharge tube

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1.6 and 1.4 mm., respectively. Both inside and outside this double glass tube there is an electrolytic solution (copper sulfate solution) which is used as the electrodes.

The experiments were carried out at atmospheric pressure. The air went through the discharge tube at the rate of 0 to 5.5 liters per minute, and a 10,000-volt alternating current was applied across the electrodes. As the discharge was sometimes unstable and locally concentrated immediately after application of the voltage, measurements were begun after the discharge spread uniformly throughout the air gap of the discharge tube.

The measuring circuit is shown in Figure 2. A condenser, C_P, is inserted to remove influences resulting from the impedance of the electric power source. R is a shunt resistance used to measure the current wave form. The voltage wave form was measured by a cathode-ray potential divider.

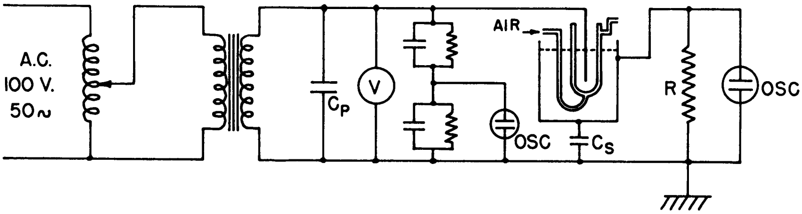

Figure 2. Measuring circuit

To observe the whole wave form, an ordinary cathode-ray oscilloscope, operated with the saw-tooth time base, was used. A single sweep cathode-ray oscilloscope, which could start sweeping at any desired phase of the applied voltage, was used to measure the details of a desired part of the current wave form.

Character of the Discharge

The discharge appears to occur as though innumerable fine threads were stretched in the discharge space of the tube. The current wave form was observed with the ordinary cathode-ray oscilloscope. The fundamental wave leads the voltage wave by about 90° as shown in Figure 3, and high frequency pulsating currents superpose on the fundamental one near the knob (at maximum of current wave form as shown in Figure 3, A). Thus, the discharge consists of innumerable local ones. To observe these high frequency local discharges in detail, the single sweep cathode-ray oscilloscope is used. Figure 4 shows an example of the oscillograms obtained: An individual pulsating current is an impulsive wave that recedes exponentially, and the tail length of the wave depends on the resistance, R, inserted in the circuit to measure the current. Increase in the value of R results in an increase in tail length.

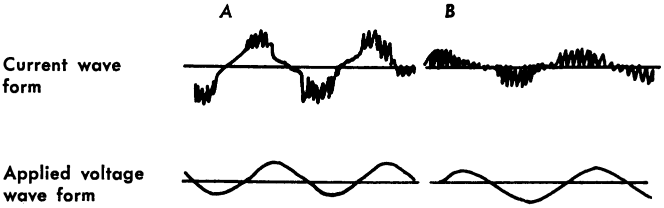

Figure 3. Fundamental and voltage wave of discharge

A. $R = 172$ KΩ *B*. $R = 50$ KΩ

Inserting an inductance coil instead of the resistance, the authors measured the terminal voltage of the coil and obtained repeating high frequency damped oscillations as shown in Figure 5.

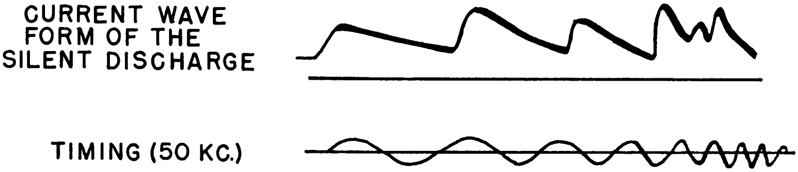

Figure 4. Oscillogram by single sweep oscilloscope

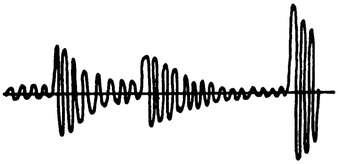

Figure 5. Terminal voltage of the inductance coil instead of the resistance

Measurements of the frequency of the oscillation indicated that the decrease in inductance resulted in the increase in frequency. As these phenomena are similar to the discharge of a condenser charge through the resistance or the inductance, the capacity of the condenser was evaluated from the values of the resistance, the tail length, and the inductance to be about 200 $\mu\mu$f., irrespective of the values of the resistance and the inductance.

Figure 6 shows the oscillogram which was photographed by the rapid time sweep to study the details of the wave front of the wave form shown in Figure 4. Several steps are observed at the wave front; these indicate that the discharges of very steep front waves occur successively at such short time intervals as about 0.2 to 0.3 μsecond. This wave has an appearance of a single pulsation when observed using the slow time sweep. From Figure 6, it seems that one discharge initiates successive discharges in the neighboring space. Hence, one pulsation does not correspond to a single discharge, but to a series of discharges.

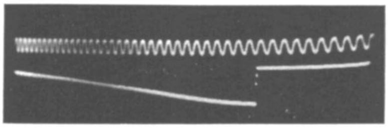

Figure 6. Current wave form of discharge; timing, 500 kc.

From these considerations on the local discharges, the equivalent circuit for a single discharge is proposed in Figure 7, where C_a and C_g correspond to the capacities of the air gap and glass of the discharge tube per unit area, C_s is the stray capacity of the vessel to the earth, and C_o is the capacity of portions where the air gap becomes so wide that the discharge does not occur. Assuming that the total discharge area of the tube is S, the capacity, C, between the electrodes of the discharge tube is

$$C = C_a C_g S/(C_a + C_g) + C_o \qquad (1)$$

Table I shows values of these capacities measured with the capacity meter. Assuming in this equivalent circuit that the discharge occurs when the applied voltage

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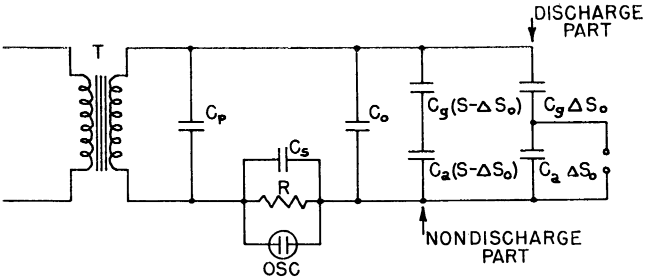

Figure 7. Proposed equivalent circuit for a single discharge

T. Transformer

Table I. Capacities Measured between Electrodes of Discharge Tube

	Measured Capacity, μμf.
C_a	0.77
C_g	3.1
C_o	15.0
C	115.0
C_s	90.0
C_p	1000.0
C_i	30000.0

across the air gap in the discharge space reaches the breakdown voltage, V_s, that the discharge ceases when the voltage recedes to V_d, and that the change in applied voltage during the time of a single discharge is negligibly small because the time interval of the single discharge is very small in comparison with the impressed alternating current period, then the equivalent circuit for a single discharge is as shown in Figure 8. The resistance of the discharge path and that of the electrolytic solution are omitted; they are negligibly small because the front of the impulsive wave is very steep.

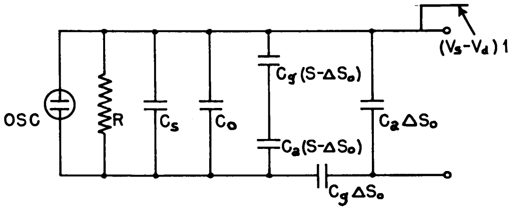

Figure 8. Revised equivalent circuit for a single discharge

The authors evaluated the current at the instant the discharge occurred in the circuit. If ΔS_0 is the area of a discharge space, then

$$\Delta S_o C_a C_g/(C_a + C_g)$$

is negligibly small in comparison with C, as $\Delta\ S_0$ is very small. The current, I_d, is expressed by the following equation:

$$I_d \doteqdot \frac{C_g \Delta S_o}{(C_s + C)R}(V_s - V_d)e^{-\frac{1}{(C_s+C)Rt}} \tag{2}$$

where t is the time duration of the impulse.

As shown in Table I, C and C_s are 115 and 90 $\mu\mu$f., respectively; hence, $C_s + C = 205$ $\mu\mu$f. This value agrees with the measured value, 200 $\mu\mu$f., within experimental error.

The wave forms produced when the inductance coil is inserted are explained by this equivalent circuit. The current form of the discharge tube is explained by considerations on the local discharges. As shown in Figure 3, *A*, no pulsation of current is observed in a certain region of the half cycle after the maximum value. It is considered that the discharge does not occur in this region. In a detailed examination into a part of the discharges, it is assumed that the discharge in the air gap occurs when the voltage across the air gap reaches the sparking potential V_s at the time denoted by point 1 in Figure 9 and that the discharge ceases in a very short time.

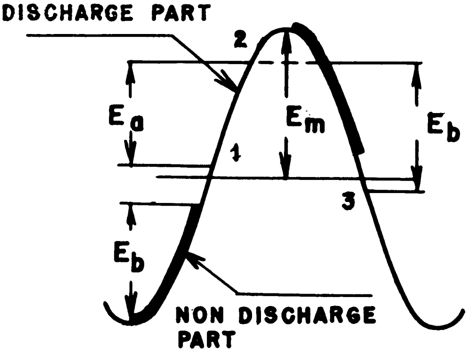

Figure 9. Details of discharge to determine rate of occurrence

Then the applied voltage increases by $E_a = (1 + C_a/C_g)(V_s - V_d)$ and reaches point 2 in Figure 9. The voltage across the air gap becomes V_s again, and the discharge occurs. Thus, when the applied voltage is high enough, the discharges occur one after another every time the voltage increases by E_a. If the voltage across the air gap does not rise high enough for discharge even at the peak value of the applied voltage, the next discharge occurs when the voltage decreases after passing its maximum value. During the following half cycle, the voltage becomes lower than the last discharge voltage, given by point 2, by $E_b = (1 + C_a/C_g)(V_s + V_d)$. A similar discharge takes place in the following half cycle. Hence, the first discharge after the maximum of the voltage wave occurs when the voltage decreases by E_b from the maximum value, and no discharge occurs in regions denoted by fat lines in Figure 9. This explains why the observed wave form has no pulsation in these regions. Therefore, E_b does not depend upon the applied voltage under certain operating conditions of the discharge tube. Experimental results also show that E_b does not change with the applied voltage. In the tube test, $E_b = 12$ kv. Consequently, $V_s + V_d = 9.6$ kv. is obtained.

The rate of occurrence of the discharge was considered, to obtain the current in the discharge period. From considerations similar to those above, the discharge takes place in the area ΔS during a change ΔE in the applied voltage when the applied voltage is higher than the preceding discharge by E_b or lower by E_a; hence $\Delta S/\Delta E$ is constant at portions shown as 1, 2, and 3 in Figure 10. Although $\Delta S/\Delta E$ cannot be considered constant at every part of the applied voltage, it is accepted that $\Delta S/\Delta E$ is almost constant throughout the whole discharge region. Actually the discharge occurs intermittently, and the area of the discharge space increases

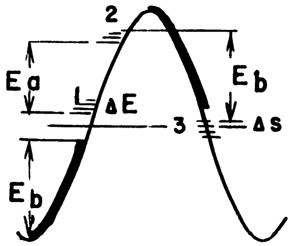

Figure 10. Details of discharge to determine current

stepwise as shown by the solid line in Figure 11. But the above assumption means that the area of discharge, S, increases linearly with E as shown by the broken line, and that dS/dE is constant. This was verified by electrical power diagrams obtained with the cathode-ray wattmeter.

Assuming that $\Delta S/\Delta E$ is almost constant in the whole discharge region, the average terminal voltage of the condenser is proportional to the applied voltage; in fact, the terminal voltage of the condenser increases stepwise. The power diagram should have a parallelogramic feature, because the slope of the diagram differs, depending on whether discharge is taking place or not. The power diagram obtained experimentally is on the whole a parallelogram with fine fluctuations in the discharge region (Figure 12).

The value of dS/dE was considered. If the applied voltage changes by E_a, the whole discharge space must reach the sparking potential once. Accordingly, the discharge also occurs once. Hence, $dS/dE = S/E_a$ is obtained, where S is the total discharge area.

By these relations, the authors evaluated the average discharge current, I_{dm}, when the voltage $E_m\sin_w t$ is applied. When $(C_s + C)R << 1$, the effect of the

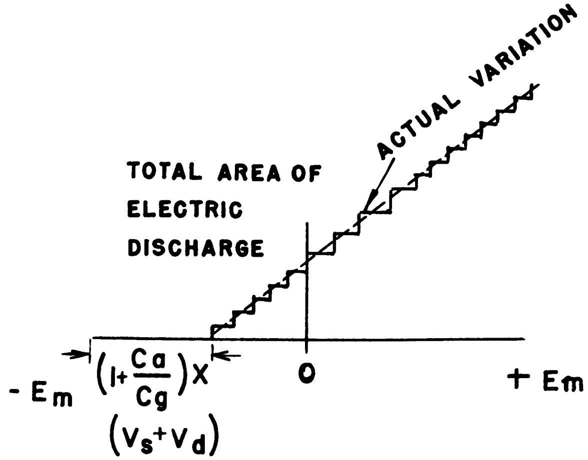

Figure 11. Area of discharge space

——— Actual
– – – Assumed

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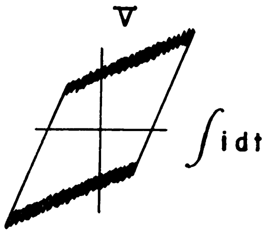

Figure 12. Experimental power diagram

preceding half wave is negligible, and from Equations 2 to 4, Equation 5 is obtained.

$$dE/dt = \omega E_m \cos \omega t \tag{3}$$

$$dS/dE = S/E_a = S/(1 + C_a/C_g)(V_s - V_d) \tag{4}$$

$$I_{dm} = \int_{t_o}^{t} \frac{C_g}{(C_s + C)R} \times \frac{S\omega E_m}{1 + C_a/C_g} \cos \omega\tau \times e^{-\frac{1}{(C_s+C)R}(t-\tau)}\, d\tau \tag{5}$$

where $\omega t_o = \sin^{-1} (E_b - E_m)/E_m$

This equation means that the wave tail of each discharge current is superposed on each other and the average current, I_{dm}, goes through the discharge tube.

Evaluating Equation 5, the authors obtained

$$I_{dm} = \frac{C_g S}{C_a + C_g} \times \frac{\omega C_g E_m}{\sqrt{1 + \omega^2 (C_s + C)^2 R^2}} \cos [\omega t - \tan^{-1} \omega (C_s + C) R]$$

$$- e^{-\frac{1}{(C_s+C)R}(t-t_0)} \cos [\omega t_o - \tan^{-1} \omega \times (C_s + C) R] \tag{6}$$

When $(C_s + C)R << 1$, the e term is negligible except where t is close to t_o, and Equation 6 becomes

$$I_{dm} \doteqdot \frac{C_g S}{C_a + C_g} \omega C_g E_m \cos \omega t \tag{7}$$

The current through the discharge tube is the sum of the average discharge current and the charging current, I_c, of the capacity between the discharge tube and the lead wire, where

$$I_c = \frac{\omega C E_m}{\sqrt{1 + \omega^2 (C_s + C)^2 R^2}} \cos [\omega t - \tan^{-1} \omega\, (C_s + C) R] \tag{8}$$

$$\doteqdot \omega C E_m \cos \omega t \tag{9}$$

Therefore, the total current, I, is represented by

$$I_c \doteqdot \omega C E_m \cos \omega t \quad \text{in nondischarge region} \tag{10}$$

$$I = I_c + I_{dm} \doteqdot \omega (C_g S + C_o) E_m \cos \omega t \quad \text{in discharge region} \tag{11}$$

If the average value of the discharge current consists of the wave tail length of each discharge current superposed on each other, the form of the knob appearing at the discharge part of the current wave form in Figure 3 is caused by superposition of the wave tails of impulse waves. Because the wave tail length of each impulse wave changes, depending on the value of inserted resistance, the form of the knob also changes according to the value of the inserted resistance. In fact, when the current wave form is observed while the value of the inserted resistance is varied, there is a change in the form of the peak as seen by comparing Figure 3, *A*, with Figure 3, *B*. The mean value, I_m, of the current through the discharge tube is obtained as follows:

$$E = E_m/\sqrt{2} = \text{effective value of voltage} \quad (12)$$

$$I_m = \frac{2}{\pi}\,\omega C E_m = 4\sqrt{2}\,fCE \quad (13)$$

where f = frequency of electric source, and $2E_m < E_b$.

$$I_m = \frac{\omega}{\pi}\left[\int_{-\frac{\pi}{2\omega}}^{t_0} \omega C E_m \cos \omega t\, dt + \int_{t_0}^{\frac{\pi}{2\omega}} \omega (C_g S + C_o) E_m \cos \omega t\, dt\right] \quad (14)$$

$$= \frac{2}{\pi}\,\omega (C_g S + C_o) E_m + \frac{\omega}{\pi}(C - C_g S - C_o) E_b \quad (15)$$

$$= 4\sqrt{2} f (C_g S + C_o) E - 2fC_g S (V_s + V_d) \quad (16)$$

where $2E_m \geq E_b$.

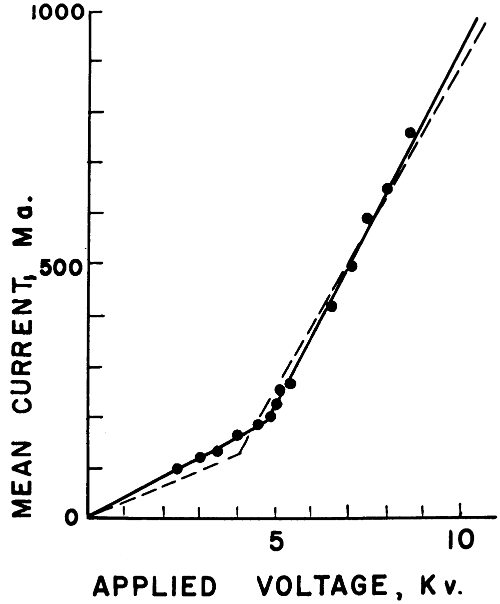

Figure 13. Effect of applied voltage on mean current

——— Experimental
– – – Calculated

Figure 13 shows the relation of the mean current *vs.* the applied voltage, both the one obtained experimentally and the one calculated by the above equation. There is good agreement between the two.

For the power, P, dissipated in the discharge tube, evaluation of the power for the discharge current only is sufficient. Hence,

$$P = 0 \quad (17)$$

where $2E_m < E_b$

$$P = \frac{\omega}{\pi}\int_{t_0}^{\frac{\pi}{2\omega}} \frac{\omega C_g^2 S E_m^2}{C_a + C_g} \sin \omega t \times \cos \omega t\, dt$$

$$= fC_g S (V_s + V_a)[2\sqrt{2}\,E - (1 + C_a/C_g)(V_s + V_d)] \quad (18)$$

where $2E_m \geq E_b$

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The power is measured by the cathode-ray wattmeter method. Let the deflecting sensibility of each pair of deflection plates be D_1 and D_2, respectively; C_i is the capacity of the current calculating condenser, which is inserted in place of the resistance, R, to measure the current. Then the area of the diagram, A, is given by

$$A = \int_{t=0}^{t=\frac{1}{f}} D_1 E d\left(\frac{D_2}{C_i}\int_0^t I\cdot dt\right) = \frac{D_1D_2}{C_i}\int_{t=0}^{t=\frac{1}{f}} EI\,dt \qquad (19)$$

$$= \frac{D_1D_2}{C_i f} P \qquad (20)$$

and the electric power is given by

$$P = C_i f A / D_1 D_2 \qquad (21)$$

Figure 14 shows the electric power, both the experimental and calculated values. The electric power increases in proportion to the increase in applied voltage after the discharge begins, and there is good agreement between the experimental and calculated values.

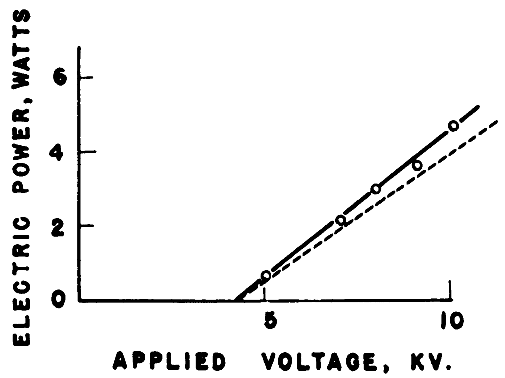

Figure 14. Effect of applied voltage on electric power

——— Experimental
– – – Calculated

Conclusion

The current wave form in the silent discharge is explained, and the voltage-current characteristics obtained show good agreement with experimental results.

From these facts, the very high frequency pulsation is the basic problem of the silent discharge. The authors suppose that the chemical reaction is affected by the average value of the current.

To clarify further the relations between the silent discharge and chemical reactions, the discharge starting voltage, V_s, in the silent discharge and the extinguishing voltage, V_d, should be measured. The wave form and density of the current along the discharge path also should be examined.

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Toxicity of Ozone

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Repeated exposures to 2.4 p.p.m. by volume of ozone induced some hemorrhage and edema in lungs of rats. Adaptation to ozone was noted after 32 hours of accumulated exposure. Twenty per cent of 102 mice died after continuous exposure to 2.4 p.p.m. by volume of ozone for 24 hours. Chronic exposure to ozone decreased the weight gain of young rats, and concentrations greater than 1.2 p.p.m. by volume and longer than 7 hours per day significantly affected their growth. The 0.1. p.p.m. values as the maximum allowable concentration of ozone for an 8-hour work day appears reasonable. Ozone did not reach or react with the blood of chronically exposed animals. There was no change in hematocrit or hemoglobin values.

With the increasing use of ozone in industry, the presence of an ozone layer above 50,000 feet, and the occurrence of ozone in smog conditions as in the Los Angeles area, the chronic toxicity of this gas has become an important problem.

Conflicting reports (*5, 7*) have appeared as to the actual toxicity of ozone. These discrepancies are probably due to the use of crude ozonizers with high current densities, moist air, the use of unreliable methods of analysis, and organic materials readily attacked by ozone.

In an attempt to clarify these discrepancies, Mittler and coworkers have conducted an experimental program (*8*). They found that the LD_{50} of ozone for a 3-hour exposure was 12.6 p.p.m. by volume for mice, 13.1 p.p.m. for rats, and 24.7 p.p.m. for guinea pigs. As a continuation of this program, experiments were conducted to determine the physiological effects of ozone and the chronic toxicity of this gas.

The ozone chamber used for these experiments is 4 feet wide, 7 feet high, and 6 feet long (Figure 1). It was designed to hold a 50-cage animal rack and can be easily adapted for use with larger animals. The chamber is lined with aluminum sheet to prevent undue decomposition of ozone and has three windows on each side and a standard aluminum glass door for observational purposes.

Ozone is made by drawing room air in through a Cuneo Micro Kleen filter to a Lear-Romee oil pump which compresses the air to 10 p.s.i. The air is then passed through a Lectrodryer (Pittsburgh Lectrodryer Corp., Pittsburgh, Pa.) to be dried. This clean dry air enters the Welsbach Ozonator T-23 (Welsbach Corp., Philadelphia, Pa.), where the ozone is generated at a concentration near 6000 p.p.m. The concentrated ozone is mixed with incoming room air at the duct shown in the lower

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Figure 1. Ozone chamber for chronic toxicity studies

left-hand corner of Figure 1. An exhaust fan pulls the air into, through, and out of the chamber, with a complete change about once every minute. The ozone concentration is sampled at six positions in the chamber by means of the aluminum tubes seen at the right-hand side of Figure 1.

The concentration of 2.4 p.p.m. of ozone was first selected for the study, because the acute studies had shown that definite lung damage occurs at concentrations greater than 2.4 p.p.m. On the other hand, no damage was apparent at concentrations less than 2.4 p.p.m. in a single exposure for periods up to 24 hours.

Effects of Chronic Exposure to Ozone on Lungs of Rats

Two 100-animal groups of 2- to 3-month-old albino Wistar rats were used in the chronic toxicity tests. Group A was exposed to 2.4 p.p.m. of ozone for 4 hours per day for 5 days a week, while group B was exposed to 2.4 p.p.m. for 16 hours per day for 4 days a week. A 10-animal sample from each group was sacrificed after accumulated exposures of 32, 48, 64, 80, 96, 112, 144, 160, and 176 hours. The lungs were examined visually for typical ozone-induced hemorrhages. Edema was assessed by the Joffe (*6*) modification of the Rahn method, based on the ratio of the weight of the lungs as removed from the animal before and after drying (Table I).

Exposure to 2.4 p.p.m. for 16 hours per day 4 days per week induced lung damage. The animals which received this exposure showed severe lung damage at the end of 32 hours. However, after the third exposure they began to recover slightly, apparently adapting themselves to ozone. When the animals had received

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Table I. Chronic Toxicity of Ozone for Albino Rats[a]

Total Exposure Time, Hours	No. of Animals Examined	Lungs: Wet/dry weight ratio	Lungs: Gross Appearance[b]: Hemorrhagic	Lungs: Gross Appearance[b]: Edematous	Day of Autopsy
16-Hour Exposures to 2.4 P.P.M. by Volume of Ozone, 4 Days per Week					
0	25	4.53[c]	...	...	...
32	10	4.69	1 Sl 1 M 8 S	10 Sl	Wed.
48	10	4.65	1 N 5 Sl 4 M	10 Sl	Thurs.
64	10	4.73	3 N 7 Sl 3 M	10 Sl	Fri.
80	10	4.84	3 N 7 Sl	7 Sl 3 M	Tues.
96	10	4.69	2 N 7 Sl 1 M	10 Sl	Wed.
112	10	4.65	1 N 7 Sl 1 M	10 Sl	Thurs.
128	10	4.81	1 N 8 Sl 1 M	8 Sl 2 M	Fri.
144	10	4.70	1 N 9 Sl	7 Sl 2 M 1 S	Tues.
160	7	4.72	7 Sl	1 N 5 Sl 1 M	Wed.
176	6	4.58	2 N 4 Sl	6 Sl	Thurs.
4-Hour Exposures to 2.4 P.P.M. by Volume of Ozone, 5 Days per Week[d]					
0	25	4.53	...	...	...
32	10	4.76	10 N	10 N	Mon.
48	10	4.78	9 N 1 Sl	10 N	Fri.
64	10	4.75	9 N 1 Sl	8 N 2 Sl	Thurs.
80	10	4.68	9 N 1 Sl	7 N 3 Sl	Wed.
96	10	4.74	10 N	6 N 3 Sl 1 S	Tues.
112	10	4.63	9 N 1 Sl	9 N 1 Sl	Mon.
128	10	4.62	9 N 1 Sl	8 N 2 Sl	Fri.
144	10	4.64	10 N	9 N 1 Sl	Thurs.
160	7	4.59	7 N	6 N 1 Sl	

[a] Some deaths occurred during exposure: 1 after 64 hours, 3 during 80- to 96-hour exposure, 1 after 128 hours, 1 during 128- to 144-hour exposure.

[b] N Normal, Sl slight, M moderate, S severe.

[c] Standard deviation for controls 0.104.

[d] Some deaths occurred during experiment: 1 after 64 hours, 1 after 92 hours, 1 after 108 hours, and 1 after 132 hours.

a total of 64 hours of exposure, they had reached a plateau of the extent of lung damage which was maintained until the end of the experiment. It is possible that the 3-day nonexposure period plus the acclimatization to repeated ozone exposure prevented further increase in lung damage. These results agree with those of

Stokinger, Wagner, and Wright (*10*), who reported that a 4- to 6-week tolerance to ozone was developed from a single 6-hour exposure to 1 p.p.m. of ozone.

In the experiment with repeated 4-hour exposures at 2.4 p.p.m. damage to the respiratory system was not visible until after 64 hours of cumulative exposure. Even after the cumulative exposure to ozone of 144 hours in the 4-hour interval experiment, there was less damage than at the 48- or 64-hour period in the 16-hour exposure series. The animals which survived in the 4-hour exposure experiment appeared to become resistant and showed only slight damage to the respiratory tract. One of the conclusions reached was that the wet-dry ratio of the lungs is not significant as a method for assessing lung damage in animals exposed to low concentrations of ozone. During the exposure to 2.4 p.p.m. the gross appearance gave more information than the edema method of Joffe.

Effects of Continuous Exposure to Ozone on Survival of Mice

The data on continuous exposure of 102 mice to 2.4 p.p.m. of ozone for 241 hours indicate that at this level the exposure was fatal to 20% of the total number of exposed animals (Table I). At the end of 96 hours, 8.8% of the animals exposed were dead. These data do not appear to agree with the report of Stokinger and associates (*10*) that the LD_{50} for mice is 4.8 p.p.m. of ozone for 4 hours. Recently, Diggle and Gage (*3*) reported that the LD_{50} for ozone for mice at a 4-hour exposure is 10 to 12 p.p.m. by volume.

Table II. Survival of 102 Mice during Continuous Exposure to 2.4 P.P.M. by Volume of Ozone

Exposure, Hr.	No. of Survivals	Dead, %
98	93	8.8
124	92	9.8
146	91	10.8
170	90	11.8
241	87	14.7
241[a]	81	20.6[a]

[a] Total dead 7 days after exposure.

The data agree somewhat with the results reported by Mittler and associates (*8*), in which the LD_{50} was found to be 12.6 p.p.m. for a 3-hour exposure. These differences may be attributed to the analytical methods used in determination of the ozone. Stokinger and his colleagues used a modification (*2*) of the Smith-Diamond method (*9*); Diggle and Gage used the neutral potassium iodide method of Gluckauf and associates (*4*). The aluminum chloride modification of the potassium iodide method of Thorp (*11*) was utilized throughout this study. If it can be assumed that the ozone produced by each investigation is uncontaminated and if the LD_{50} is then used as a yardstick, one can conclude that the Smith-Diamond method in which the spectrophotometric determination is made of the iodine released after acidification yields an ozone analysis 2½ times lower than the neutral or acid-buffered potassium iodide-sodium thiosulfate method.

Effect of Repeated Daily Exposure to Low Concentration of Ozone on Weight Gain of Young Rats

Young male albino Wistar strain rats (averaging about 50 grams) were exposed to ozone 5 days a week for various lengths of time per day for 4 weeks. The animals were weighed at weekly intervals and at the end of the 4-week period the total gain in weight of the animals was determined. Table III summarizes the results of the experimental data and the statistical treatment. To characterize fully the data, an empirical equation was derived to relate the difference in weight gain to

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Table III. Summary of Statistical Analysis of Weight Gain of Rats Exposed to Ozone

Expt.	Group	5 Days/Week, 4-Week Treatment		No. of Animals	Mean Weight Gain, G.	Residual Variance	Residual Standard Deviation	Standard Error of Mean	95% Confidence Limits	$y_c - y_e$[a]	t
		P.P.M.	Hr./day								
I	1	1.2	7	46	178.00	245.26	15.66	2.31	±4.66	13.00	3.91[b]
	2	0.6	16	45	176.73	368.74	19.19	2.88	±5.81	14.27	3.68[b]
	3	Control	A	48	191.00	282.72	16.80	2.43	±4.86		
II	4	1.2	3	43	181.40	271.57	16.47	2.51	±5.70	2.66	0.96
	5	2.4	3	51	151.39	425.76	20.62	2.89	±5.78	32.67	7.90[b]
	6	Control	B	49	184.06	372.35	19.29	2.75	±5.50		
III	7	1.2	16	47	150.87	436.39	20.89	3.05	±6.10	42.11	11.08[b]
	8	Control	C	43	192.98	230.66	15.17	2.31	±4.66		
IV	9	1.8	7	20	196.55	146.89	12.12	2.56	±5.35	20.80	6.46[b]
	10	1.8	3	20	207.85	75.61	8.70	1.93	±4.03	9.50	3.60[b]
	11	1.2	11.5	20	198.00	168.32	12.97	2.90	±6.06	19.35	5.77[b]
	12	Control	D	20	217.35	70.76	8.41	1.88	±3.92		
V	13	0.6	10	29	184.00	279.96	16.70	3.12	±6.39	13.60	2.74[b]
	14	Control	E	21	197.60	387.19	19.70	4.30	±8.96		

[a] Mean gain of controls minus mean gain of exposed in grams.
[b] Significance at 99% level.

the ozone concentration and the number of hours of exposure per day. The equation utilized the fact that when either the time of ozone exposure or the ozone concentration is zero, the weight difference is also zero

$$Y = x_1x_2\,(b_0 + b_1x_1 + b_2x_2) \tag{1}$$

where Y is the difference in weight gain between the control group and treated group, x_1 is the ozone concentration, x_2 is the time of exposure, and b_0, b_1, and b_2 are constants. The method of least squares was used to estimate the value of the constants from the experimental results of the first 12 groups

$$Y = x_1x_2\,(-1.126488 + 0.6887692\,x_1 + 0.06514642\,x_2) \tag{2}$$

From Equation 2 a series of values of Y for various combinations of ozone concentrations and exposures ranging from 1 to 20 hours and 0 to 3 p.p.m. was determined with the digital computer. Figure 2 is a graph of the difference in weight gain plotted against exposure time for a series of constant ozone concentrations and Figure 3 shows the weight gain difference plotted against ozone concentration for a series of constant exposures.

From the experimental and calculated results the tolerance limits of exposure of rats to ozone might be determined, as shown by the following two examples.

1. If a difference in weight gain of control and treated rats of 10 grams is taken as the point where injury occurs, with reference to Figure 2, the following combinations for a 5 days per week exposure for 4 weeks are obtained: 2.4 p.p.m. for 1.5 hours, 1.8 p.p.m. for 3 hours, 1.2 p.p.m. for 7 hours, and 0.6 p.p.m. for 16 hours.
2. If a 15-gram difference is used as the point where injury occurs, the following combinations are obtained: 2.4 p.p.m. for 2 hours, 1.8 p.p.m. for 4 hours, 1.2 p.p.m. for 9 hours, and 1 p.p.m. for 19 hours.

Below these limits it might be assumed that a young growing rat could remain in ozone atmosphere without deleterious effects.

These experimental results concur with maximum allowable concentration value of ozone of 0.1 p.p.m. for an 8-hour day, adopted by the American Conference of Governmental Industrial Hygienists in 1955 (*1*). However, it is very difficult to determine ozone reliably below 1 p.p.m. As the odor of ozone can be readily detected below 0.1 p.p.m. (*12*), the rule utilized in these laboratories is to maintain ventilation so that the odor of ozone cannot be perceived.

To determine whether the amounts of food consumed by ozonized and control animals were different, two groups of young rats were used. One group was placed in the ozone chamber and given an exposure of 2.4 p.p.m. for 3 hours daily for 4 weeks. The other group was merely placed in the chamber and exposed to air for

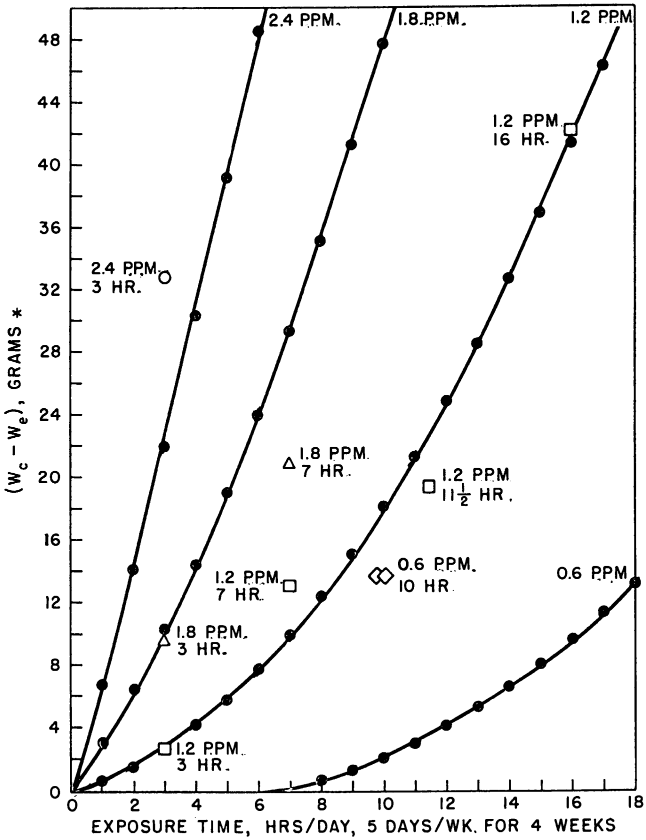

Figure 2. Effect of exposure time, *E*, upon weight gain with constant ozone concentration

● Calculated values

◇, △, ○, □ Experimental data

* Weight gain of control rats minus weight gain of exposed rats

the same period of time. The food consumption and weight gain were tabulated for both groups; an analysis of variance of the data from the two groups is presented in Table IV.

Table IV. Relationship between Food Intake and Adjusted Weight Gain

Group	No. of Rats	Mean Food Intake, G.	Dev. from Exptl. Mean Intake, G.	Mean Weight Gain, G.		Variance Ratio, *F*
					Adjusted[a]	
Exposed[b]	17	468.1	−29.0	132.8	139.90	37.71
Control	18	524.4	27.3	161.6	154.51	

Experimental mean food intake = 497.1 grams
Regression coefficient = 0.2451 gram per gram of food

[a] $y = y - bx$, where y = adjusted mean gain, b = regression coefficient, and x = mean food intake.

[b] 2.4 p.p.m. or 3 hr. per day for 5 days per week. for 4 weeks.

When the mean gain in weight of both groups is adjusted to a common food intake, a highly significant *F* value of 37.7 is obtained, which indicates that the quantity of food consumed does not explain the difference in weight gain of the two

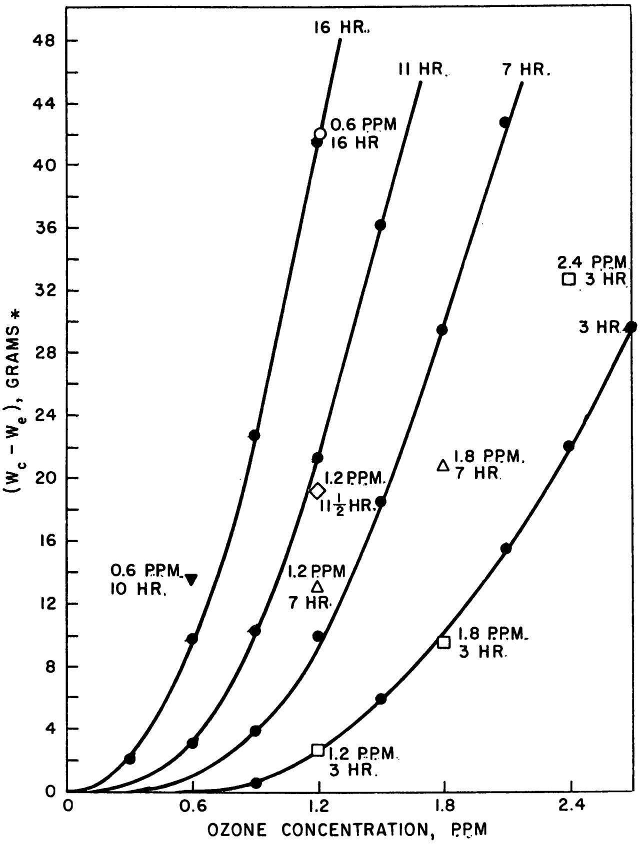

Figure 3. Effect of ozone concentration upon the weight gain of young rats with exposure time constant

● Calculated values

▲, □, ◇, ○ Experimental data

* Weight gain of control rats minus the weight gain of exposed rats

groups. It appears that animals exposed to ozone did not utilize the food eaten as efficiently as the controls.

Effect of Ozone on Blood

The problem of whether ozone itself reaches and reacts with the blood was studied. Earlier in vitro studies had shown that ozone does not oxidize the ferrous ion of oxyhemoglobin to the ferric ion to produce methomoglobin when 39.6 p.p.m. is bubbled at a rate of 150 ml. per minute directly into whole blood. Ozonized plasma, on the other hand, showed a definite increase in absorbance at 250, 280, and 350 mμ (Table V). Consequently, blood plasma from 27 young rats exposed to 2.4 p.p.m. of ozone for 3 hours per day, 5 days per week for 8 weeks, and two animals exposed to an acute dose of 40 p.p.m. of ozone for 3 hours and 20 minutes was examined spectrophotometrically. The absorbances obtained did not differ significantly from those obtained for plasma for 30 control animals.

The hemoglobin content and hematocrit values were determined on the blood

Table V. Effect of Ozonization on Absorbance of Rat Blood Plasma

	Wave Length, Mμ		
Plasma[a]	250	280	350
Ozonized[b]	0.57	0.71	0.155
Control	0.29	0.53	0.031

[a] 1:100 0.066 *M* phosphate buffer.
[b] 30.10 p.p.m. O_3 for 15 min. at 250 ml./min.

from 31 young rats exposed to 2.4 p.p.m. of ozone for 3 hours per day, 5 days per week for 8 weeks. The average hemoglobin content for 27 control rats was 14.6 and 14.9 grams per 100 ml. for the exposed rats. The average hematocrit was 46.8% for the controls and 47.8% for the exposed rats. Both sets of values fall within the normal ranges for rats. Therefore, it is concluded that ozone does not reach the blood of animals that have been chronically exposed to ozone. It appears that the ozone reacts with the inner surface of the respiratory tract and decomposition occurs before it can enter the blood stream.

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Toxicity of Ozone in High Altitude Flight

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Ozone is found at high altitudes in such concentration that, pressurized in a cabin to ground level or near ground level pressure, it could exhibit harmful effects on man and material. Protecting factors, such as heating in the compressor, decomposition in contact with various substances, and use of oxygen masks, lessen such harmful effects considerably. But the existence of such a hazard has to be known. Studies on the toxic effect of ozone on man indicate that such effect is restricted to the respiratory tract. Man seems to be more sensitive than the usual laboratory animals. In sensitive persons, concentrations as low as 2 p.p.m. may cause severe irritation within less than 1 hour.

The presence of ozone in the atmosphere, known since ozone was first detected and named by Schoenbein in 1840, has been investigated with ever-increasing interest. The development of special spectrophotometers, carried aloft by balloons and in recent years by rockets, has made it possible to study not only its total amount but also its vertical distribution in the atmosphere. Classical studies are those of Goetz, Meetham, and Dobson (*8*). In the past ten years measurements were carried out by Regener (*15*), Johnson, Purcell, and Tousey (*10*), and Paetzold (*13*), among others. As these are all basically measurements of ultraviolet absorption of layers of a certain thickness, the ozone concentration is usually expressed as thickness of a layer of air—for example, centimeters of ozone per kilometer of air. Usually these values are referred to as under conditions of standard pressure and temperature. To convert these units into units that are more meaningful to the toxicologist, such as parts per million by volume, they have to be multiplied by the proper density ratio, considering temperature and pressure at specific altitudes. Such values for various geographical latitudes are available in the form of tables (*9*).

When the values for ozone from the above-mentioned studies are averaged, the ozone concentration is smaller than 1 p.p.m. below 33,000 feet, reaches a peak of 6 p.p.m. at 80,000 feet, and falls below 1 p.p.m. again above 114,000 feet. Both the location of the peak and the concentration are subject to considerable fluctuation, so that much greater peak concentration may occur at various altitudes depending on latitude, season, and weather conditions.

Commercial airplanes begin to pressurize their cabins at altitudes below 10,000 feet. Above this altitude cabins have to be pressurized, if the passengers do not use additional oxygen supply. Without oxygen, a pressure of about 10 p.s.i., corresponding

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to 10,000 feet of altitude, has to be maintained in the cabin regardless of flying altitude, to maintain tolerable respiratory conditions.

Because the compressor not only pressurizes but also ventilates the cabin, there is a limit on altitude for the pressurized cabin. Above 80,000 feet a compressor becomes ineffective; it is not able to maintain pressure and ventilation at the low density of the atmosphere. Above this altitude lies the realm of the sealed cabin (*17*).

We do not know how much ozone may actually be present in a pressurized cabin of future aircraft, as other factors, such as heating of the air passing the compressor or contact with various substances, may destroy part of the ozone and use of oxygen masks would prevent inhaling of ambient air entirely; still, the possibility of inhaling ozone exists. The use of ozone as a rocket oxidizer (*14*) may add to such a possibility.

The second factor that must be known is the toxicity of ozone to man at ground level conditions. From such values the toxicity of ozone at other than ground level conditions can easily be derived.

Although the toxicity of ozone to animals has been studied relatively often, studies on humans are few. Extended reviews of such toxicity studies have been compiled by Thorp (*19*) and Stokinger (*16*). Thorp (*20*) also suggested that the presence of nitrogen oxides, which may be generated in certain ozonizers, may aggravate the toxicity of ozone.

While studies on the influence of other gases on the toxicity of ozone are most interesting, the toxicity of pure ozone must be known first. Nitrogen oxides do not seem to exist in the atmosphere with ozone, but rather are present at considerably higher altitudes in the so-called *D* layer (*3*).

As there is much confusion in the literature on the actual toxicity of ozone, experiments on animals were conducted at Armour Research Foundation under contract with School of Aviation Medicine, US Air Force. The results of these studies on acute and chronic exposure to ozone are reported here and by Mittler and coworkers (*12*).

The results indicate great differences in the LD_{50} rate for various laboratory animals. On the basis of these results it was decided that only studies on man could produce reliable information on the toxicity of ozone to man. Such studies were conducted by the School of Aviation Medicine, utilizing the existing facilities of Armour Research Foundation.

Procedure and Methods

A group of five subjects was selected, ranging in age from 19 to 54 years. Chest x-ray pictures and ECG recordings were taken before and after the 2-week period of experiments. Before and after the exposure to ozone, the following recordings were carried out:

Circulation. Blood pressure, pulse rate (pulse rate recorded also during exposure at 15-minute intervals).

Blood. Red blood cell count, hematocrit, hemoglobin in grams per 100 ml. of blood, white cell count, differential count, total serum protein.

Respiration. Respiration rate (recorded also during exposure at 15-minute intervals). Respiration functional test: tidal volume, vital capacity, maximal breathing capacity, residual capacity, and diffusion coefficient for oxygen (DO_2) expressed in cubic centimeters of oxygen per minute per pressure of oxygen at 1 mm. of mercury.

Tests of Taste and Smell.

Subjective Symptoms.

Usual clinical laboratory methods were used for circulation and blood. With a normal spirometer for the determination of the residual capacity, the method of Fenn, Otis, and Rahn (*6*) was used for respiration. Nitrogen concentration was determined with the Lilly-Anderson nitrogen meter, which was calibrated with correction for discharge current, pressure, and carbon dioxide (*1*).

The pulmonary diffusion coefficient was determined by the carbon monoxide method of Krogh (*5, 11*). Deviating from the original method, a much smaller concentration of carbon monoxide was used, 0.004% instead of 1.0%. This made it possible, after further dilution, to determine the carbon monoxide concentration by means of indicator tubes (Mine Safety Appliances Co.), the color of which was compared with calibrated standards (*4, 21*).

Taste was tested by offering the subject aqueous solutions of sucrose (2 to 16% in steps of 2.0%) and sodium chloride (1 to 4% in steps of 0.5%), in an irregular pattern of concentrations, in which the subject had to say if the taste was the same, stronger, or weaker than that of the sample offered before.

For testing the sense of smell a threshold method was adopted. Three solutions were prepared—A, B, and M. All three solutions had 70% aqueous ethyl alcohol as carrier. A was a blank; B contained 0.02% of amyl acetate (pleasant odor); and M contained the same amount of lauryl mercaptan (unpleasant odor). The subject had to distinguish between the faint smell of alcohol and the additional smell of the pleasant or unpleasant substances. The concentrations were chosen so that under normal conditions all subjects made not more than two errors in 15 presentations.

The subjective symptoms were arbitrarily classified somewhat along the classification of Thorp (*19*) as symptomatic, irritant, and severe irritant. Symptoms are named symptomatic when the subject experiences the first sensations, such as irritation of the throat and tickling in the nose. When the symptoms become permanent and unpleasant, they are named irritant, as well as when occasional coughing is observed. The symptoms are labeled severe irritant when coughing is produced by deep inspiration, pressure or pain in the chest appears, breathing becomes laborious and more frequent, and a constant sharp pain in the throat is felt.

For exposure to ozone, a special chamber, 4 feet wide, 7 feet high, and 6 feet long, constructed by Armour Research Foundation, was used. Usually one, but sometimes two, subjects were placed simultaneously in this chamber. An exhaust fan provided a complete air change in the chamber about once every minute, thus avoiding any accumulation of carbon dioxide and water vapor. Control with a thermometer and an Assmann psychrometer showed that average room temperature and humidity were never exceeded.

The highest ozone concentration applied was 6 p.p.m. for 1 hour, and the longest exposure time was 2.5 hours at 1.2 p.p.m.

To determine individual sensitivity, all subjects were first exposed to about 1.2 p.p.m. for a maximum of 2.5 hours. Subjects who exhibited irritant symptoms were not admitted to higher concentrations but were exposed repeatedly to about the same concentration.

Unless stated otherwise, concentrations of ozone are presented in parts per million by volume.

Results

The findings on a small group of five people do not have the conclusive significance of a statistical evaluation of a large group. However, as each subject served as its own control and all subjects were exposed repeatedly, the results indicate the general tendencies of the physiological effects of ozone on man. Beginning with the subjective symptoms, the results are presented in Figure 1. The symptoms are indicated as follows: An empty figure means symptomatic; a figure filled half black means irritant; and a totally black figure indicates severe irritant. These figures are placed in a diagram plotting ozone concentration against exposure time in a double logarithmic calibration.

The subdivision of the diagram in regions of various degrees of toxicity is that used by Thorp (*19*).

In general, the data correspond to Thorp's diagram. However, the measuring

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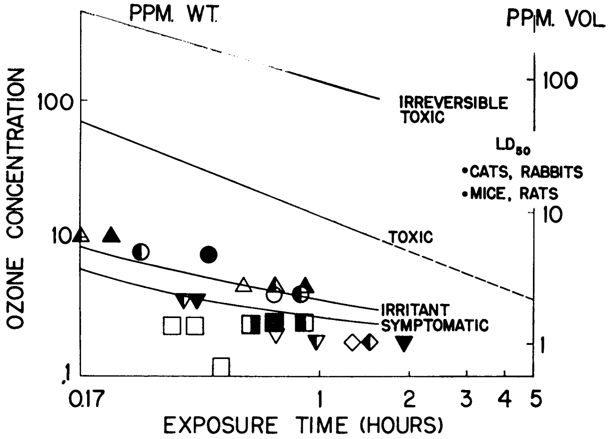

Figure 1. Sensitivity of five subjects to ozone of various concentrations at various exposure times

Subject.	△	▽	◇	□	○
Age, years	54	40	40	21	19

Black fillings indicate degrees of toxic reaction

points are scattered over a wide area, indicating great individual differences in sensitivity to ozone. Many values are located below the symptomatic line in the nonsymptomatic region, even some irritant and severe irritant values. As this holds true for three out of five individuals, it may be concluded that the sensitivity of humans is somewhat higher than that of the common laboratory animals.

A relationship between age and sensitivity cannot be observed. It is not surprising that severe irritation follows irritation in a shorter interval at higher concentrations than at lower ones.

No effect of ozone on the circulation or blood could be detected which differed from the normal fluctuation of such values. Therefore, no data are presented.

The effect of ozone on the respiratory system is illustrated in Figure 2, plotted as

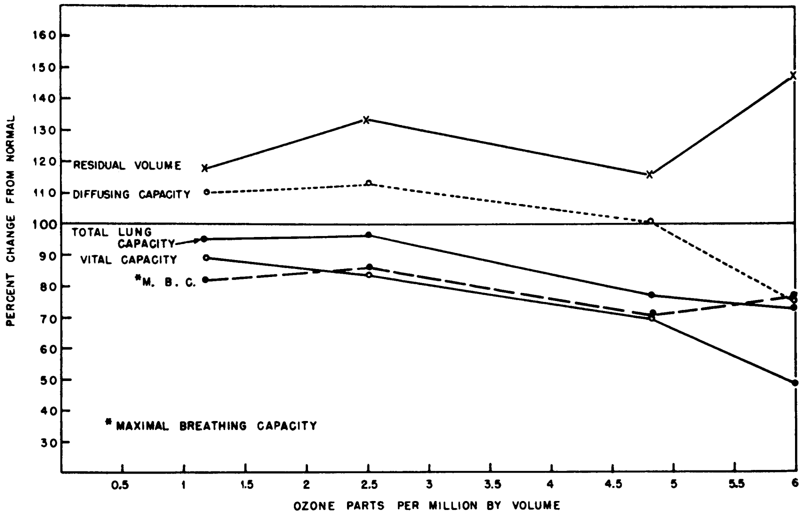

Figure 2. Results of lung function tests expressed as per cent deviation from normal in relationship to concentration of ozone

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch047

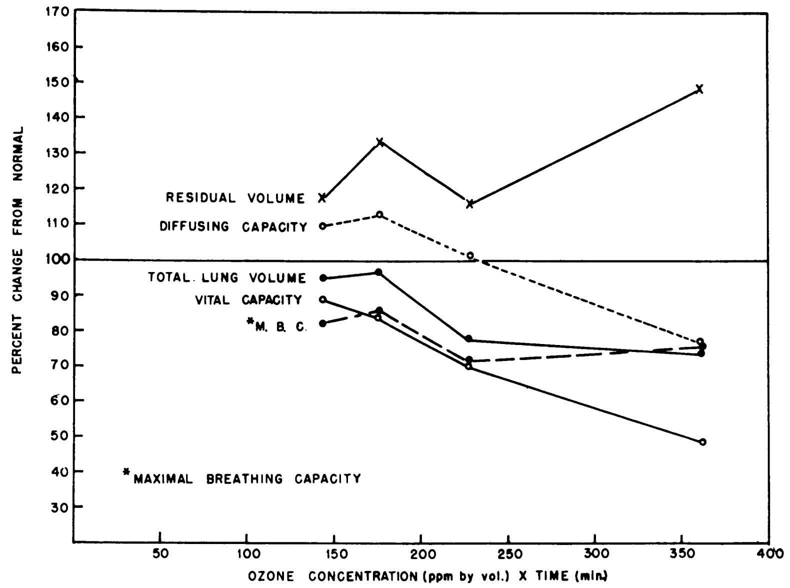

Figure 3. Results of lung function tests expressed as per cent deviation from normal in relationship from product concentration × time

deviation from normal in per cent against concentration. Two measurements—residual volume and diffusing capacity—range above normal at about 1 p.p.m., while total lung volume, maximal breathing capacity, and vital capacity are below normal and decrease further with increasing concentration. In Figure 3, similarly plotted, but with the abscissa in units of concentration times time instead of concentration, this tendency seems even more pronounced. Both figures indicate that the diffusing capacity eventually becomes subnormal. In relation to concentration, a sharp bend toward subnormal values occurs between 4.5 and 5 p.p.m.

Figure 4 shows how the amount of air normally inhaled and exhaled, the so-called

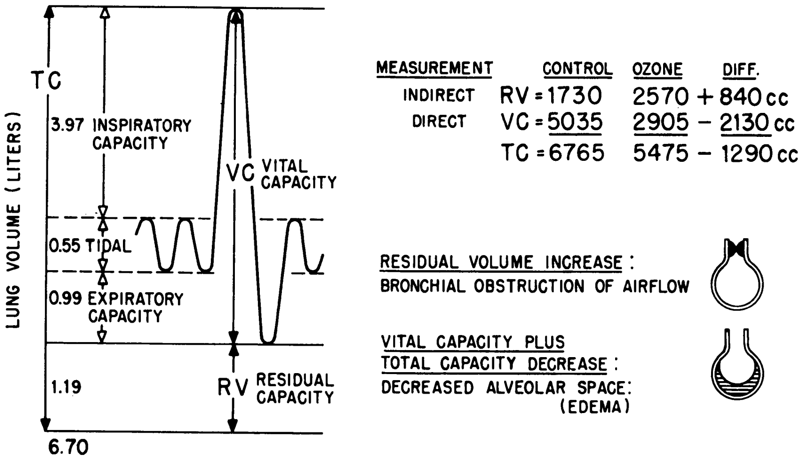

Figure 4. Characteristic effects of ozone on some respiratory quantities

tidal volume, can be enlarged by adding the inspiratory and the somewhat smaller expiratory capacity. This happens normally in various degrees according to muscular exercise. The largest volume which can be reached is the vital capacity. But the lung cannot be emptied completely; even at the deepest expiration a certain volume remains, the residual capacity.

Figure 4 contains data from a subject exposed 1 hour to 6 p.p.m. of ozone, which may be regarded as a typical example of the effects of ozone above 5 p.p.m. First, the vital capacity is diminished from 5030 cc. down to 2905 cc. or to 57.7% of its original value. At the same time, the residual capacity is increased from 1730 to 2570 cc. The smaller vital capacity can easily be felt; subjectively one is unable to expire very deeply. It should be assumed that the increase of residual capacity is nothing more than the decrease of vital capacity. But in summing up both to the total capacity, they do not compensate each other; the total capacity is smaller after ozone exposure. There is one possible explanation: The decrease of the vital capacity is caused by edematous fluid, the increase of the residual capacity by a bronchial obstruction which will not permit a complete opening of entries into the alveoli. Histological studies on animals after ozone exposure show that the alveoli may be filled with edematous fluid, but a real obstruction has not been observed.

So the decrease of the vital capacity seems to be real. Figures 2 and 3 show how the vital capacity decreases more and more with increasing concentration and almost linearly with the concentration-time product.

The soft tissues of the respiratory tract seem to be the only tissues attacked by ozone. An effect on the conjunctiva of the eyes was neither felt subjectively nor observed by inspection to any remarkable degree in these studies, but it has been described by others.

In the tests of taste, no clear effect could be found on ability to distinguish between concentrations of sodium chloride and sucrose. However, the sense of smell was affected. Table I shows the results obtained from a subject first exposed to 2.41 p.p.m. (4 p.p.m. by weight) for 1 hour, 30 minutes, and on another day, to 4.16 p.p.m. (6.9 p.p.m. by weight) for 22 minutes. A minus sign indicates inability to recognize the smell properly; in parenthesis the smell is indicated with which the sample was confused. After exposure to ozone, the number of errors is higher than in the controls, and a certain piling of errors, especially at the higher concentration, can be observed. While the errors made in the controls consist of a confusion of a blank A with a previously offered pleasant or unpleasant smell, the errors after exposure especially to the higher concentration consist of misjudging a smell, which indicates a true injury to the sense of smell.

Table I. Effect of Ozone Concentration on Smell

	Ozone Concn., 4 P.P.M. Wt. Expos. Time, 1 Hr. 30 Min.			Ozone Concn., 6.9 P.P.M. Wt. Expos. Time, 22 Min.			
	Substance	Control	O_3	Substance	Control		O_3
1.	A	+	+	B	+		+
2.	B	+	+	A	+		+
3.	A	+	+	M	+		− (A)
4.	M	+	− (B)	M	+		+
5.	B	+	+	B	+		− (A)
6.	A	− (B)	+	B	+		+ (?)
7.	M	+	− (A)	A	+		− (B)
8.	B	+	+	A	+		+
9.	A	+	+	M	+		− (A)
10.	M	+	+	M	+		− (B)
11.	A	+	− (M)	A	− (M)		− (M)
12.	A	− (M)	+	A	+		+
13.	M	+	− (M)	B	+		+
14.	A	+	− (M)	B	+	+	+
15.	B	+	+	M	+		− (B)
	Errors	2	5		1		7

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Discussion and Conclusions

The impact of ozone on man as an animal is directed on the soft tissues of the respiratory tract. Beginning at the throat, longer exposure time and higher concentrations tend to carry the injury to the tissues deeper toward the alveoli. Edema, observed on animals histologically, seems to begin in men at concentrations above 4 to 5 p.p.m. at exposure times in the range of an hour, as recorded by lung function tests. At this, or still higher concentrations and exposure times, the permeability of the alveolar wall may be injured according to a decreasing diffusing coefficient for oxygen. However, the difficulties of such measurements do not permit a definite statement at the present time. A definite impairment of the sense of smell was found. No effects on blood pressure, pulse rate, and blood itself could be observed.

Subjective symptoms, such as burning in the throat, feeling of oppression of the chest, and difficulty in breathing, are subject to a large individual variety. Burning of the eyes was not observed.

It can be concluded that ozone acts only very superficially on wet soft tissues. It is not able to penetrate deeply. This is confirmed by studies of Bohr and Mear (*2*), who transfused blood of rabbits, poisoned by ozone, into normal rabbits without any harmful effect. These authors also ventilated only one lung of an animal (turtle or rabbit) with air containing ozone without harmful effects on the normal lung.

In two experiments on inhaling air with 4.8 p.p.m. of ozone, the exhaled air contained practically no ozone, as determined by the starch-iodine method of Thorp (*18*). This suggests that ozone decomposes completely in the respiratory tissues.

Usually the effect of ozone is described as that of a "very strong oxidizing agent." Though this is not deniable, a more detailed explanation of its action is very desirable. While the third atom of ozone, split off first, may have the properties of nascent oxygen, it seems likely that ozone produces certain radicals which exhibit "chain reactions." In this respect, ozone may have some factors in common with pure oxygen at high pressure (*7*).

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Factors Modifying Toxicity of Ozone

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Ozone in single, acute exposure is a highly poisonous substance to laboratory animals. No experimental evidence was found that this toxicity is modified to a significant degree by the presence of nitrogen oxides that may accompany ozone production. Seven factors have been experimentally found that may modify the toxicity of ozone. Four of these—youth, physical exertion, alcohol, and respiratory infection—tend to augment the injurious response or act to the detriment of the host; intermittent exposure, premedication, and pre-exposure either reduce or eliminate the injurious effects of ozone. Consideration has been given these factors in the evaluation of possible hazards to populations from ozone-containing smogs.

Ozone has been established without question to be a component of Los Angeles smog (*6, 14*). As an agent of distress and potential disease, ozone has been well documented (*15*). Whether ozone of itself is capable of becoming a health hazard in urban atmospheres is less certain, however. New information derived from animal experimentation on ozone atmospheres and nitrogen oxide–ozone atmospheres under varying condition is presented here in the hope that it will permit a more exact evaluation of the potential hazards to urban and working populations exposed to ozone. This becomes especially important in the light of the recent report of Kleinfeld (*8*) on ozone injury of the lungs among welders using the new inert gas–shielded arc process. These represent the first instances of human injury from ozone ever reported.

Lethal Doses

Ample evidence has been presented (*15*) to show that ozone in acute exposures is a highly toxic and lethal substance. The LD_{50} values for three rodent species are given in Table I. The LD_{50} value is the dose of a substance that will on the average kill 50% of a significant number of animals exposed under specified conditions. Several experimentally simple and statistically sound methods of obtaining LD_{50} values are available; the one used in this work is that of Weil (*19*). The susceptibility or natural tolerance varies considerably with the species, the hamster being the least susceptible of the species tested. Although insufficient numbers of other species have been exposed to ozone to determine accurate LD_{50} values, the dog would appear to resemble the hamster in natural tolerance to ozone on the basis of the evidence at hand; the rabbit has a tolerance between that of the rat and the hamster.

Table I. Lethal Ozone Doses for Small Animals

(Duration of exposure, 4 hours)

Animal Species	Av. Body Wt., G.	Ozone LD_{50},[a] P.p.m. by Vol.	Range,[a] P.p.m. by Vol.
Mouse, albino, male	22	3.8	3.6–4.1
Rat, albino, male	250	4.8	3.6–6.4
Hamster (*Cricetus auratus*), male	75	10.5	9.1–12.1

[a] Determined by method of Weil (*19*).

Comparison of the LD_{50} values for ozone with those for the industrially well known and highly toxic gas, phosphine, shows a value for phosphine (*10*) of 60 p.p.m. for the rat under similar conditions of exposure, indicating ozone to be approximately 12 times more toxic in single acute doses. The high toxicity of ozone is all the more remarkable when it is noted that but one quarter of the inhaled ozone reaches the lungs (*7*), where it produces pulmonary edema, hemorrhage, and eventual death. Taking this into account, the absolute amount of ozone killing the rat is but 0.025 ml. of pure ozone gas at standard temperature and pressure, or 50 γ; a similar value for the mouse is 4 γ of ozone. This assumes a respiratory minute volume (volume of air inspired during 1 minute by an animal while at rest) of 100 ml. for the rat and 10 ml. for the mouse. The order of 1000 γ of phosphine is required to kill the rat, assuming that 50% of the inhaled gas reaches the lungs. These figures provide striking evidence of the highly lethal character of ozone.

In all experiments reported here ozone was determined by the alkaline–potassium iodide method of Smith and Diamond (*13*) as modified by Byers, Saltzman, and Hyslop (*2*). The total oxides of nitrogen were determined by the phenoldisulfonic acid method; nitrogen dioxide by the specific method of Saltzman (*11*). The accuracy of the ozone method is still under experimental scrutiny. It is possible that some factorial upward revision of the ozone values reported here may have to be made at a future date. A correction factor of approximately 2 appears probable at this date. The method, however, was the best available at the time these experiments were performed.

Toxicity of Ozone Prepared from Air and Oxygen

Because of the possibility that ozone prepared by electric discharge (Vita air ozonizer, Vita Aire Process Co., Milwaukee, Wis.) from laboratory, oil-compressed air might have toxic qualities different from that prepared from oxygen, a series of toxicity tests in mice was made at varying concentrations of ozone and periods of exposure utilizing the four possible combinations of air, oxygen, and air cleaned by scrubbing with chromic acid and sodium hydroxide (Table II). No conspicuous difference in toxicity to mice occurred from any of the different means of preparation of ozone when tested at concentrations between 4 and 10 p.p.m.; if any tendency was evident, the ozone prepared from oxygen and scrubbed diluting air was slightly less toxic than that from air and diluted with unwashed air.

Effect of Concentration and Time. A study was made in mice to determine whether ozone obeyed the toxicologic rule that the product of the concentration and time of exposure produced a constant, toxicologic response, $CT = K$, over a concentration range of from 1 to 50 p.p.m. If a positive correlation is found, such information permits interpolation and extrapolation of the variables of exposure without the labor of experimental determination. A plot of the values in Table II from 2.5 to 50 p.p.m. of ozone shows reasonably good linearity, with the exception of the single response to 4 p.p.m. of ozone prepared from air. When the entire experience of the other three tests at this level was used, however, close agreement to linearity was found. No fatal

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Table II. Mortality of Mice Following Exposure to Ozone at Varying Concentrations and Times and Prepared by Different Means

Ozone Concn., P.p.m.	Exposure Concn. × Time, *CT* Value P.p.m.-Hr.	Ozone from Air Diluted with		Ozone from Oxygen Diluted with	
		Unwashed air	Washed air or oxygen	Unwashed air	Washed air
1	15	0/10[a]			
1	1200[b]	0/25			
2.5	6	0/5			
	10	3/10			
	37	4/5			
4	16	6/10	2/10	5/10	2/20
6	24	12/20		8/10	
8	48	10/10			
10	20	5/10	6/10	5/10	4/10
	72	10/10			
24	72	10/10			
50	25			10/20	

[a] Numerator: Number of animals that died. Denominator: Number of animals exposed.
[b] Discontinuous exposure for 6 hours daily, 5 days per week.

response to quiescent exposure to ozone at 1 p.p.m. was observed, no matter what the duration (cf. Table VII).

Negative Role of Nitrogen Oxides in Ozone Toxicity. There is an erroneous impression, unfortunately widespread, gained from the misinterpretation of certain studies (*16, 17*) that "the contamination of ozone with oxides of nitrogen has been partly responsible for the observed toxicity and that ozone is not nearly so toxic as it has been thought to be" (*1*). There are at least two reasons for this misimpression.

1. The reported animal toxicity data were insufficient to permit the conclusion that nitrogen oxides associated with ozone production contributed to the over-all toxicity.
2. The reported experiments dealt with abnormally high concentrations of nitrogen oxides (approximately 50% of the ozone concentration).

In all ordinary methods of ozone production by electric discharge the amounts of nitrogen oxides are relatively insignificant (*12*). The evidence surrounding this question (*15*) weighed heavily against the conclusion that nitrogen oxides contributed significantly to the toxicity of ozone, but left the matter open to further experimentation. The question was finally resolved in further experiments in which mice were subjected to various mixtures of ozone and oxides of nitrogen, and the resultant toxicity was compared with that from ozone alone (Table III). Although a uniformly increasing degree of mortality in mice is observed with an increasing concentration of ozone alone, no such increase was demonstrated in mice exposed to increasing concentrations of nitrogen oxides mixed with ozone. Not until the total concentration of irritant gases far exceeded the LD_{50} for ozone alone (4 p.p.m.) were comparable lethal effects produced by the mixture (10 p.p.m. of nitrogen oxides and 4 p.p.m. of ozone). Other similar experiments have been performed on several occasions with similar results. Thus, contrary to past assertions, no evidence was found for ascribing the toxic effects of ozone to nitrogen oxides.

Indeed no basis for such a view is known, if one considers the toxicity of the individual nitrogen oxides in relation to that of ozone. The experimental evidence is the following:

1. Pure ozone, prepared from pure tank oxygen and mixed with air purified by careful scrubbing, is of itself highly toxic.
2. The lower nitrogen oxides, N_2O and NO, are not significantly toxic (*18*) nor would they be likely contaminants in ozone-generating sources.
3. NO_2 has an LD_{50} value for rats of 65 to 75 p.p.m. for a 4-hour exposure (*4*), a toxicity of a lower order of magnitude than ozone.
4. Nitrogen pentoxide, the reaction product of NO and NO_2 in the presence of ozone, is far less toxic than ozone, as shown by the low toxicity given in Table III

Table III. Mortality of Mice Following Single Exposures to Ozone and Ozone–Nitrogen Oxide Mixtures

(4-hour exposures. Numerator, number of animals dead. Denominator number of animals exposed)

Total Nitrogen Oxides Concn., P.p.m. by Vol.	Ozone Concentration, P.P.M. by Volume					
	<0.5	1	2.5	4	6	8
<0.2	...	0/10	3/10	6/10	7/10	20/20[a]
1–2	...	...	...	5/10	...	...
4–5	...	...	...	2/10	...	10/10
10	...	...	...	8/10	...	...
17[b]	0/10					
35[c]	0/10					
500[d]	2/6 (rats)					

[a] Mortality of other species at this ozone concentration. Rat, 6/6; rabbit, 2/3; dog, 0/1.
[b] Containing 4 p.p.m. NO_2.
[c] Containing 5.5 p.p.m. NO_2.
[d] Nitric acid vapor containing 65 p.p.m. NO_2, 6-hr. exposure.

following exposures of animals to mixtures of NO_2 and ozone. Moreover, preliminary toxicity measurements of relatively pure solid N_2O_5 made by the action of ozone on phosphorus pentoxide–dehydrated, fuming nitric acid showed no deaths upon exposures to at least 42 p.p.m. of N_2O_5. This N_2O_5 preparation contained at the time of the exposure tests a maximum of 30 p.p.m. of NO_2 (presumably due to the spontaneous decomposition in the animal-exposure atmosphere), according to the new and sensitive method of Saltzman (*11*). In the opinion of the present writer, the claims Diggle and Gage (*3*) make for the high toxicity of N_2O_5 are not supported by their reported data.

5. Nitric acid vapor requires concentrations around 500 p.p.m. to produce lethal effects in small animals, as shown in Table III.

The entire question of nitrogen oxide impurities associated with the generation of ozone by electric discharge in air has been discussed by Saltzman, Byers, and Hyslop (*12*). Maximal amounts of nitrogen oxide impurities were 8.5% of the ozone generated, but less than 5% was the rule under normal operating conditions of a typical commercial ozone generator whose output was studied in detail. Barring the possibility of the presence of some unknown factor of extremely high toxicity such as free radical NO_3 that might form in greater quantities than found in these experiments under special or unusual conditions, there appear to be no reasonable grounds for the claims that nitrogen oxides contribute significantly to the toxicity of ozone electrically generated in present-day devices.

Irritation and Odor Levels. It is characteristic of the physiologic action of ozone to cause discomforting reactions in man other than the severely acute responses mentioned above for animals. It is common among individuals to experience headache and dryness of the throat, respiratory passages, and eyes upon continued exposure to concentrations above 0.1 p.p.m. For this reason as well as others mentioned below, the threshold limit for ozone was recently revised downward from 1 to 0.1 p.p.m. by the Threshold Limits Committee of the American Conference of Governmental Industrial Hygienists. Concentrations below 0.1 p.p.m. are discomforting to some individuals because of the disagreeable odor of ozone. Considerable variation in odor threshold, as well as in susceptibility to headache and eye and throat irritation, is common among individuals, but most can detect the odor of ozone at a few hundredths of 1 p.p.m., a level well below the threshold limit for general comfort.

Effects of Age. The age of the animal has been repeatedly found to have an important effect on the acute toxic response to ozone exposures. Results of representative experiments in mice (Table IV) show that 4 p.p.m. of ozone for 4 hours was at least an LD_{50} for young, 19-gram, white mice, whereas the same exposure in old mice produced almost no mortality in groups of equal numbers of animals. A similar effect has been reported for the respiratory irritant sulfur dioxide (*5*); 1- to 2-month-old guinea pigs died after 8-hour exposure to 18 mg. per cu. meter, but 50 mg. per cu. meter were required to kill 1- to 1.5-year-old animals.

Table IV. Effect of Age on Susceptibility to Ozone Toxicity

(Male mice, 4-hr. exposures)[a]

	Mortality[b]	
	Young mice, 19-g.	Old mice, 35-g.
Expt. I	6/8	0/8
Expt. II	5/10	1/10

[a] Nitrogen oxide concentration averaged 0.1 p.p.m. Ozone concentration, 4 p.p.m. by vol.

[b] Numerator: no. of animals dead. Denominator: No. of animals exposed.

Respiratory Infection. It is a common finding that exposures to ozone bring out or activate latent, subclinical respiratory infections in animals, resulting in a full-blown respiratory disease that often ends fatally. The concentrations of ozone responsible for this exacerbation were around 1 p.p.m., concentrations incapable in themselves of producing fatal respiratory injury. This characteristic associated with ozone has been observed in the rodent species on autopsy following ozone exposure.

Intermittent Exposures. In an effort to discover means of reducing the unfavorable responses to ozone, the effect of intermittent exposure to ozone was investigated. Adult male white mice were subjected to inhalation of ozone at 4 p.p.m. for 30 minutes, alternated with 20-minute exposures to air. The total time of exposure to ozone was 4 hours, an exposure capable of killing at least 50% of the animals if administered without interruption for 4 hours. The results of a representative experiment (Table V) show that interrupted exposure to ozone reduces the fatal effects of ozone in mice and indicate a means of reducing the effects of this hazardous substance.

Table V. Effect on Animal Toxicity of Interrupted Ozone Exposures

Male mice, 20-g.

Ozone Concn., P.p.m. by Vol.	Mortality[a]	
4	2/10	30 min. ozone, 20-min. air. Total 4-hr. exposure to ozone
4	6/10	Continuous 4-hr. exposure to ozone

[a] Numerator: No. of animals dead. Denominator: No. of animals exposed.

Prophylaxis of Ozone Toxicity. Pursuing the study of the means of reducing or preventing the toxic effects of ozone, various reducing agents were tested on the hypothesis that they might combat a potent oxidizing agent, ozone. Table VI shows that when vitamin C is administered prior to, but not after, exposures to lethal concentrations of ozone, it is effective to a measurable degree in reducing mortality of exposed mice. The vitamin C was administered intraperitoneally in saline in amounts of 10 mg. per mouse. Mercaptoethylamine, a reagent of claimed efficacy in radiation injury and in high-pressure oxygen toxicity, increased the mortality from ozone exposure. On the other hand, fortifying the vitamin C with other vitamins and reducing agents such as pantothenate, cysteine glycuronate, glycine, and glutamate resulted in almost complete protection against fatal ozone exposures. The occasional animals that did not survive the treatment died uncharacteristically several days following the ozone exposure, indicating death was due to causes other than ozone injury, presumably infection, that could be prevented by administration of suitable antibiotics; small animals, succumbing to the effects of ozone exposure, regularly die within 24 hours after the start of exposure. The prophylactic effect of vitamin C has been independently confirmed by another investigator in these laboratories.

The capacity of the reducing mixture to prevent the effects of nitrogen dioxide was less than that for ozone, indicating a different mode of action of nitrogen dioxide on the lung.

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Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch048

Table VI. Effect on Mice of Reducing Agents on Ozone and Nitrogen Dioxide

Agent	Reducing Agent: Before ozone exposure	Reducing Agent: After ozone exposure	Saline Control	*CT* Value P.p.m.-Hr.
	Ozone			
Vitamin C				
Expt. I	5/10	8/10	8/10	50
Expt. II	1/10		4/10	30
β-Thiolamine[a]				
Expt. I	10/10		2/10	24
Expt. II	10/10		5/10	26
Reducing mixt.[b]	3/10[c]		9/10	42
	Nitrogen Dioxide			
Reducing mixt.	3/10		7/10	540
	5/10		10/10	600

[a] β-Mercaptoethylamine, courtesy Squibb Institute, New Brunswick, N. J.

[b] Courtesy J. B. Roerig & Co., Chicago, Ill., consisting of vitamin C, cysteine, potassium glycuronate, calcium pantothenate, glycine, and sodium glutamate.

[c] Deaths of these animals were believed not due to ozone but to respiratory infection, as they occurred atypically several days after usual time and are presumably preventable by antibiotic treatment.

Interesting as the foregoing findings are, they scarcely compare in significance with the following two aspects of ozone toxicity: effects of physical stress, and the marked tolerance acquired in animals following shortly after brief exposures to noninjurious levels of ozone.

Enhancement of Toxicity from Physical Activity. When rodents were subjected to the physical activity imposed on them by being in a motor-driven rotating cage, while at the same time being exposed to otherwise noninjurious concentrations of ozone, the animals died of the combined effects, with a typical ozone toxicity response of pulmonary edema and hemorrhage. Atmospheres containing 1 p.p.m. of ozone caused death of animals being exercised in a rotating cage at 7 r.p.m. for 15 minutes each hour for 6 hours' total exposure (Table VII). (The ozone used in experiments performed at 1 p.p.m. of ozone was generated in a U. S. air ozonizer, Scottdale Ozone Co., Scottdale, Pa.) No amount of repeated daily 6-hour exposure to this concentration of ozone up to 200 days without exercise produced any mortality or any observable change in the exposed rats (data line 1). On the other hand, subjecting the animals to exercise while inhaling ozone gave an LD_{50} within 6 hours for exposed adult rats of different ages (data lines 2 and 3). Exercise alone in rotating cage was without effect, as shown in the last data line in Table VII. Mice responded similarly.

Table VII. Increase of Ozone Toxicity from Superimposed Exercise

(Ozone concentration 1 p.p.m. by volume. Exercise. 15 min./hr., 7 r.p.m.)

No. of Animals	Av. Body Wt., G.	Treatment: Ozone	Treatment: Concurrent exercise	Mortality[a]
25	230–380	200 days, 6 hr. daily	No	None (0/25)
10	144	6 hr.	Yes	6/10
10	264	6 hr.	Yes	5/10
10	250	No	Yes	None (0/10)

[a] Numerator: No. animals dead. Denominator: No. animals tested.

Tolerance

Perhaps the most striking and unusual feature of ozone toxicity is the marked tolerance to multilethal doses of ozone that develops in rodents after brief exposures to ozone. Increased tolerance to ozone was first observed in rats that had been previously exposed for many days to 1 p.p.m. of ozone and then challenged in the rotating cage while being exposed to ozone as described above; the anticipated number of deaths did not occur. These results are shown in Table VIII, data lines 1 and 2. The longer the animals were given previous exposure to 1 p.p.m. only, the longer the survival on repeated challenging exposures to ozone with exercise.

Table VIII. Development of Tolerance to Ozone as Shown by Pre-exposure to Ozone Followed by Exercise during Ozone Exposure

(All ozone concentrations 1 p.p.m. by volume. Exercise: 15 min. per hr. 7 r.p.m. Exposure: 6 hr. daily, unless otherwise indicated)

No. of Animals	Av. Body Wt., G.	Pre-exposure, to Ozone (without Exercise) Hr.	Mortality[a] on Subsequent Days of Exposure to Ozone with Exercise					
			Days					
			1	2	3	4	5	6
9	236	90	0/9	0/9	0/9	3/9	0/6	3/6
10	304	150	0/10	0/10	0/10	0/10	0/10	1/10
10	258	18	0/10	0/10	0/10			
3	240	—	2/3	0/1	0/1			
10	248	6	0/10	0/10	1/10			
3	245	—	2/3	0/1	0/1			
10	251	3	0/10	2/10				
2	245	—	1/2	0/1				
10	212	1	1/10	1/9	1/8			
3	210	—	1/3	0/2	0/2			

[a] Numerator: No. of animals dead. Denominator: No. of animals tested.

In an effort to determine the minimal time of ozone exposure required for the rats to develop significant tolerance, successively shorter periods of ozone pre-exposure were tested, from 18 hours to 1 hour. Tolerance to ozone is successively decreased in degree when pre-exposure is thus shortened, although some tolerance is demonstrated with as little as 1-hour pre-exposure to 1 p.p.m. of ozone (data lines 9 and 10). Tests for tolerance were made 24 hours after the start of the initial exposure, thus demonstrating the very rapid development of ozone tolerance. Because the 6-hour exposure to 1 p.p.m. of ozone developed a reproducible tolerance of significant degree, 6 hours was taken as a convenient pre-exposure time for subsequent studies to determine the duration of tolerance to ozone from a single exposure.

Duration of Tolerance to Ozone. Tolerance to ozone lasting for 4 to 6 weeks was developed in rats from a single 6-hour exposure to 1 p.p.m. of ozone. For this demonstration a large group of adult male albino rats was given a single, 6-hour exposure to 1 p.p.m. of ozone. From this group, smaller groups of 10 rats each were subsequently tested for tolerance, as described above, after 1 day and 1, 2, 3, 4, and 6 weeks.

All the rats given a single, 6-hour exposure to ozone showed tolerance to otherwise lethal exposures whether challenged on the day following the 6-hour exposure, or 1 week, 2, 3, or 4 weeks later. Rats challenged on the 6th week, however, died (7 of 10 exposed), showing that ozone tolerance may extend from 4 to 6 weeks. Controls not previously exposed to ozone, when placed in the same activity cage with ozone-exposed animals, died either during ozone exposure in the activity cage—i.e., within 6 hours—or shortly thereafter. Rats exposed 6 hours to 1 p.p.m. of ozone and then subjected the next day to exercise only in the activity cage with no ozone showed no mortality and no untoward effects ascribable to either the exercise or the previous day's exposure to ozone.

To make further assurance that the tolerance observed in the activity cage experiments was real and not the result of some unsuspected or adventitious finding associated with the conditions of the experiment, rats with a previous exposure to ozone were later challenged by exposure to ozone alone at multilethal doses (7 to 11 p.p.m. of ozone). No previously exposed rat succumbed to a 4-hour exposure, whereas all rats with no previous exposure to ozone died. On autopsy, the tolerant rats showed no pulmonary edema and hemorrhage, whereas this was the cause of death in the nontolerant rats. The characteristic spasmodic breathing of animals exposed to lethal concentrations of ozone was still present in the tolerant animals.

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In preliminary experiments no "spread" of tolerance to ozone appeared to occur among rats that had previously been exposed to either nitrogen pentoxide or hydrogen peroxide and then challenged in the usual way to ozone combined with exercise. Further work will have to be done, however, to confirm these preliminary observations.

No tolerance in rats was acquired from single intraperitoneal exposures to ozone, pointing to a reaction characteristic of lung tissue in the development of ozone tolerance.

Effect of Alcohol on Tolerance. A most interesting effect of alcoholic ingestion on the development of tolerance to ozone was demonstrated in the following way. Rats given water containing 10% ethyl alcohol by volume as the sole liquid intake for 6 weeks were exposed to 1 p.p.m. of ozone for 6 hours by the usual procedure for the development of tolerance. When subsequently tested for tolerance 2 weeks later by quiescent exposure to 8 p.p.m. of ozone, all five of five rats tested succumbed, showing no tolerance to ozone at this time. A similar group of five controls with no prior exposure to ozone died as expected. This interesting finding is being explored further.

Discussion

From evidence introduced here (Table I) and elsewhere (*8, 15*) ozone can no longer be seriously denied to be one of the more highly poisonous gases. The rapidly lethal effects in small animals from exposure to a few parts per million by volume of pure ozone, the aggravation of the ozone effects in exercised animals, and the pulmonary involvement in shielded arc welders to relatively low concentrations of ozone, all attest to its highly injurious character. Oxides of nitrogen have been shown to be associated contaminants, both in certain types of smogs and in ozone industrially produced from air by means of electric discharge, and thus must enter into any consideration of the toxicity of ozone that is found in either of these instances. A critical review of the toxicities of nitrogen oxides with regard for the amounts that may accompany the production of ozone, however, reveals no convincing evidence that the oxides of nitrogen contribute significantly to the toxic effects of ozone (Table II). The most interesting and important findings reported here are the many ways in which the highly injurious effects of ozone may be increased, reduced, or even abolished. The increased susceptibility to the lethal effects of ozone of the very young of several species of animals, compared with the aged of the species, is readily demonstrable, and is appreciable (Table IV). The increased response to pulmonary irritation found in early age is not unique for ozone, but is well documented for the upper respiratory irritant, sulfur dioxide (*5*).

The enhancement of ozone injury in animals by activity during exposure to ozone has been the most striking demonstration of all. The lethal outcome of otherwise noninjurious concentrations of ozone results undoubtedly from a multiplicity of factors in addition to that of the more obvious reactions associated with activity such as increased respiration and circulation rates. Hormonal releases, for example, in the form of catechol amines, epinephrine, and norepinephrine, as well as in certain adrenocorticosteroids (compounds B and F) have been reported in tumbled rats (*9*), a condition not completely unrelated to that in cage-activated rats, especially during the terminal phases on the exposure. How much of a role these hormones play in these experiments, however, still remains to be determined.

Methods of reducing or abolishing the fatal effects of ozone were also numerous. Pulmonary changes associated with aging increased the capacity of the host to resist otherwise fatal doses of ozone. Whether this is due to increased thickening of the alveolar septa with age, reduced metabolic rate, or other factors is under study in these laboratories. Interrupted exposure to ozone acts to the advantage of the host and, although not particularly striking in the manner demonstrated in these experiments, the interrupted exposure technique could be utilized to decisive advantage in protecting individuals against injurious ozone exposures. During interruptions presumably tolerance to ozone would be developing.

It is interesting that the grave effects of pulmonary edema and hemorrhage from acute exposure of ozone may be prevented in animals by so simple a procedure as a combination of vitamins and reducing agents prior to ozone exposure (Table VI). The clues furnished by such substances on the mechanism of action of ozone, and related oxidative pulmonary irritants such as nitrogen dioxide, are considerable; from such information a definitive hypothesis of action of these pulmonary irritants may be formulated and tested.

The finding of marked tolerance in animals to ozone, developing rapidly and enduring long, may have considerable bearing on responses of populations to ozone-containing smogs. Several factors indicate this. No human symptoms referable to ozone action have been noted in Los Angeles–type smog, despite reports of significant ozone levels. Ozone tolerance of measurable degree was noted in animals exposed for but 1 hour to 1 p.p.m. Ozone is a rather ideal substance for epitomizing the toxicologic concept, $CT = K$—i.e., equal mortalities resulted in animals exposed to 4 p.p.m. of ozone for 6 hours ($CT = 24$ p.p.m.-hours) or to 50 p.p.m. for 0.5 hour ($CT = 25$ p.p.m.-hours).

Thus it would not seem to represent too great an extrapolation of the data to assume that if tolerance develops at 1 p.p.m. for 1 hour, some tolerance could conceivably develop at 0.1 p.p.m. for 10 hours. Further, if the response of the human lung to ozone may be assumed to be similar to that of the animals tested in these studies, one might reasonably conclude that no severe effects on human populations would result from ozone exposures occurring in Los Angeles–type smog, owing to the often repeated exposures to very low-grade ozone concentrations, of the order of a few tenths part per million.

Acknowledgment

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Bactericidal Activity of Ozone and Chlorine against *Escherichia coli* at 1° C.

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The bactericidal effects of ozone solutions were tested against *E. coli* suspensions at 1° C., and the lethal dose was determined as that quantity of ozone necessary to produce a detectable residual in solution. Under the conditions of the experiments this was 0.4 to 0.5 mg. per liter. A comparison of the bactericidal activity of chlorine under similar conditions emphasized the different mode of action of the two agents.

Quantitative studies on the bactericidal activity of ozone are difficult because of the instability of ozone solutions. The decomposition of ozone in solution is described as occurring in a stepwise fashion, producing hydroperoxyl and hydroxyl radical (*1*), both of which exhibit considerable biological activity. The decomposition process is temperature-dependent and is catalyzed by hydroxyl ion concentration (*1, 6*).

The usual process of bubbling ozone through a bacterial suspension and then measuring the oxidizing residual iodometrically fails to give an accurate interpretation of the ozone present. Adler and Hill (*1*) have pointed out, for example, that potassium iodide solutions measure total oxidizable capacity rather than ozone itself.

Preliminary to biological investigations, a study was needed on the chemistry and kinetics of ozone solutions and an evaluation of the analytical techniques of ozone mensuration under conditions appropriate to this problem. The detailed results of these studies have been presented (*4*). Ozone solutions at 1° C. and pH 2(0.01*N* sulfuric acid) are relatively stable, demonstrating little decomposition over a period of 8 hours. The analytical method of choice for ozone determination in such solution was the ferrous ion method of analysis, in which the ferrous ion, as $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, is oxidized to the ferric state and then the excess is back-titrated with potassium permanganate.

It was decided that by dosing bacterial suspensions by dilution from such stable solutions of ozone (at 1° C. and pH 2), a more definitive interpretation of ozone activity could be made.

To obtain additional information about ozone activity at the concentrations of greatest biological interest, oxidation-reduction (OR) potentials of buffered bacterial suspensions were determined after addition of various amounts of ozone.

Methods

Bacteria were grown in nutrient broth (Difco) at 37° for 18 hours. Test suspensions were diluted to approximately 5×10^4 cells per ml. in 0.1*M* phosphate buffer

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Advances in Chemistry; American Chemical Society: Washington, DC, 1959.

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(pH 6.8), chilled to 1° (30 to 45 minutes), and challenged with the ozone or chlorine (Zonite) from stock solutions. After the desired contact interval, the reaction was stopped by addition of excess sodium thiosulfate, the solutions were returned to room temperature, and plate counts were made by standard procedures (*2*). The ozone was generated in a laboratory ozonator (Welsbach Co., Model T-23) using oxygen (commercial sources) as the gas supply. The ozone-oxygen mixture was bubbled through a 0.01*N* sulfuric acid (pH 2) solution in a gas scrubber. The ozonator oxygen gas tank and water cooler for the ozonator were located in a large walk-in refrigerator, where all the low temperature work was performed. Glass-distilled and deionized water (specific conductance at 25° $= 0.94 \times 10^{-6}$ reciprocal ohm) was used in all experimental work.

The ferrous-ferric ion analytical technique was used to determine the ozone concentration of the stock solution. Enough ferrous ammonium sulfate was added to an aliquot of ozone to bring 100 ml. of the solution to about 0.005*N* and the nonoxidized ferrous ions were then back-titrated with 0.1*N* potassium permanganate. The chlorine concentration was determined iodometrically (*2*).

Oxidation-reduction potential measurements were made with a platinum-calomel electrode system connected to a Beckman Model H-2 pH meter. The buffered bacterial suspensions were similar to those in the dose-contact time experiments. To these suspensions, successive equal aliquots of an ozone solution were added at 1°, and the oxidation-reduction potential was measured in millivolts.

Results

Table I summarizes the information obtained on the bactericidal properties of ozone. The bactericidal dose of ozone for *E. coli* under these experimental conditions (1% survivors) is between 0.4 and 0.5 mg. per liter. The dose of ozone necessary to effect this kill is critical. At the lethal dose, a contact time greater than 1 minute is not necessary. At ozone concentrations near or immediately less than the lethal dose, the bactericidal action is irregular, probably an expression of the instability of ozone solutions.

Table I. Bactericidal Properties of Ozone

Date	Initial O_3 Concn., Mg./L.	% Surviving after Various Contact Times					
		1 min.	2 min.	4 min.	8 min.	16 min.	32 min.
6/30	1.00	<1	<1	<1	<1	...	...
7/6	0.75	<1	<1	<1	<1	<1	<1
7/12	0.63	<1	<1	<1	<1	<1	<1
7/14	0.53	<1	<1	<1	<1	<1	<1
7/18	0.42	75	<1	71	<1	73	46
8/2	0.31	96	97	74	70	92	...
8/9	0.21	33	82	99	99	79	69

Table II presents the results of the chlorination studies. Chlorine (as Cl_2) at a concentration of 0.25 to 0.30 mg. per liter is effective at 1° C. and pH 6.8 in reducing the bacteria count to 1% of the control in 1 to 10 minutes.

Table II. Results of Chlorination Studies

Initial Cl Concn., Mg./L.	% Surviving						
	1 min.	2 min.	4 min.	8 min.	16 min.	32 min.	64 min.
1.10	<1	<1	<1	<1	<1	<1	<1
0.52	<1	<1	<1	<1	<1	<1	<1
0.35	1.5	<1	<1	<1	<1	<1	<1
0.27	2.0	1.5	1.6	1.2	1.0	<1	<1
0.25	24	19	12	13	8	7	5
0.17	70	53	39	24	15	4	<1
0.10	87	66	64	46	46	45	40

Figure 1 emphasizes the difference in the bactericidal activity of ozone and chlorine.

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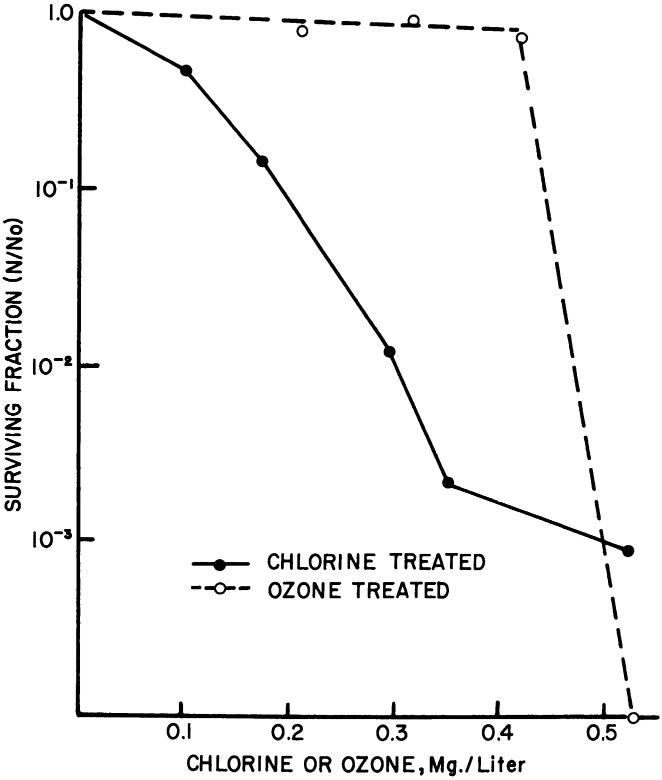

Figure 1. Bactericidal activity of ozone and chlorine

When the surviving fraction of bacterial cells are plotted against concentration, with a common contact interval, the chlorination studies present a typical logistic-type curve; ozone produces an immediate kill at the critical concentration.

To obtain additional information about ozone activity at the concentrations of greatest biological interest, oxidation-reduction potentials of buffered bacterial suspensions were determined after addition of various amounts of ozone. It was reasoned that the oxidation-reduction potential at or close to the lethal concentration would exhibit a demonstrable change indicative of the corresponding activity. Figure 2 presents the results of the experiment; there is a sharp break in the redox potential at an ozone concentration comparable to the level found to represent the lethal dose in the dosage-contact time experiments. A differential plot of the same data emphasizes this information (Figure 3).

Discussion

The lethal dose of ozone for *E. coli* (0.4 to 0.5 mg. per liter) under these experimental conditions is higher than the values obtained by other workers (*3*, *5*), who determined the ozone residual as total oxidizable constituents remaining after bubbling the ozone through a test solution. This slightly higher ozone value may be the result of temperature dependency or of use of the dose required rather than residual accumulated. Each test solution can be assumed to have a certain ozone demand.

A comparison of the bactericidal activity of ozone and chlorine emphasizes the different modes of action of the two agents. The surviving fraction of chlorine-treated bacteria decreases in geometric progression as a function of time or concentra-

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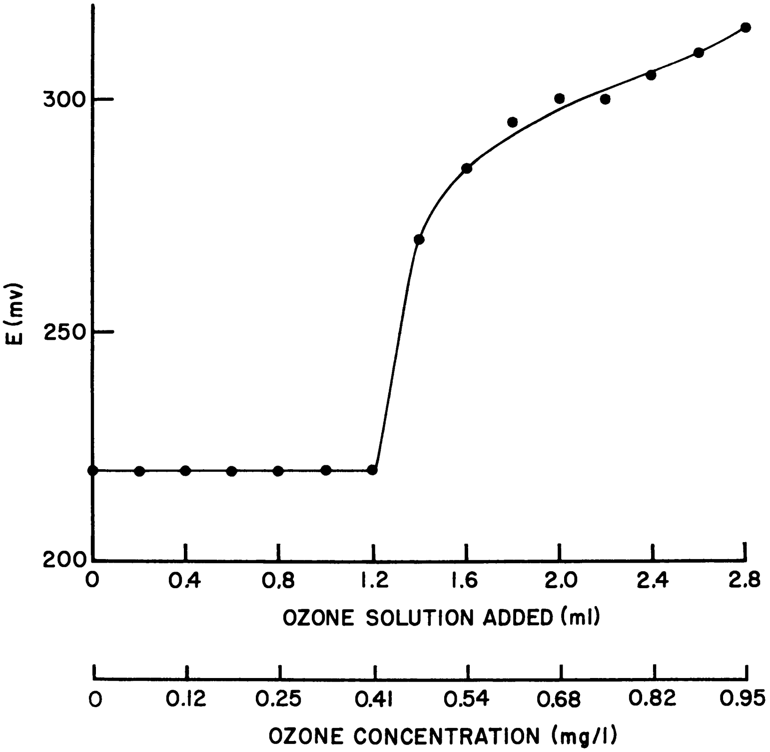

Figure 2. Effect of added ozone on oxidation-reduction potential

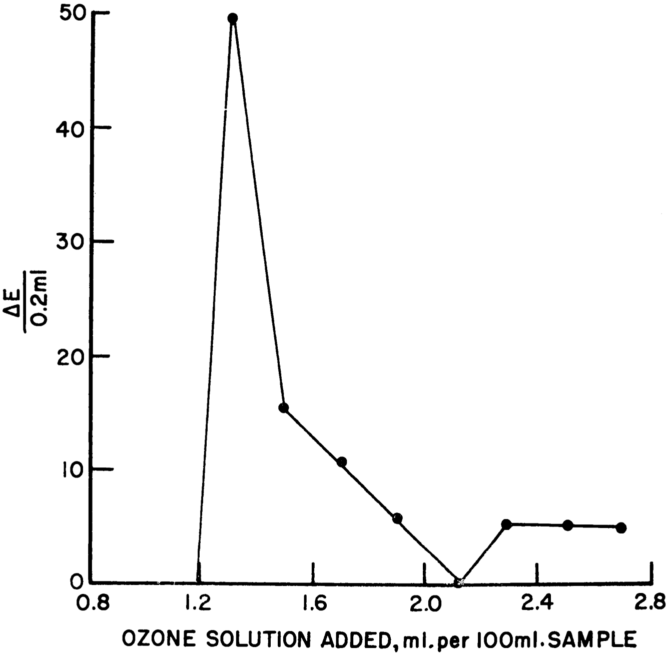

Figure 3. Effect of added ozone

tion (Figure 1). Ozone on the other hand demonstrates an all-or-none type of effect within the contact of 1 minute; there is no effect until a certain critical concentration is achieved and then there are no detectable survivors. This critical concentration is that quantity of ozone necessary to produce a detectable residual in solution.

This information supports the theory of Bringmann (*3*), that ozone acts as a general protoplasmic oxidant.

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Sterilization of Empty Containers for Food Industry

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A novel method for sterilizing glass containers with ozonized air has been developed. When used to replace a sulfur dioxide sterilization process, it resulted in substantial operating economies. Operation of a fully automatic soft drink plant is described.

A process for rapid sterilization of the interior of empty containers, with ozonated air under pressure, was tested for the first time in 1952–53. The results were satisfactory, and a large Swiss factory preparing soft drinks with a mineral water base has since adopted the new process for sterilizing bottles prior to filling. This is the plant of the Société des eaux minérales d'Eptingen at Sissach, near Bâle, the most modern soft drink factory in Switzerland.

Prior to 1954 the plant was equipped with a modern installation for sterilizing bottles with sulfur dioxide. The drawbacks of this process, and particularly the high operating costs, inspired the company management to look for some other means of sterilization.

The present ozone sterilization installation at Sissach, the only one of its kind, was preceded by a pilot plant test. For over half a year the results of ozone and sulfur dioxide sterilizations were compared. For rapidity of sterilization and the vigor of its bactericidal action, ozone was in every way equal to sulfur dioxide, even with ozone dosages only one hundredth as great. The operating cost with ozone proved to be only about one twentieth the cost with sulfur dioxide. Figure 1 is a schematic outline of the plant-scale process, whose application has been completely satisfactory from the start some 2½ years ago.

Sterilization Apparatus

Figure 1 is a schematic diagram of the plant-scale process. The ozonated air for the sterilization process is produced as follows: Completely oil-free air is supplied by a compressor specially equipped for the project. The compressor operates intermittently and automatically, furnishing air as required. Air pressure is maintained at 71 p.s.i. (5 kg. per sq. cm.) in a supply tank which smooths out sudden changes in pressure. On leaving this tank the purified air is cooled by water coils to a temperature of 15° to 18° C.

To dry the air for generating ozone, a system of dehydration by cooling was chosen, as pure air compressed to 71 p.s.i. was available. It sufficed, at this pressure, to reduce the temperature of the compressed air to −35° C. in order to reduce the humidity to

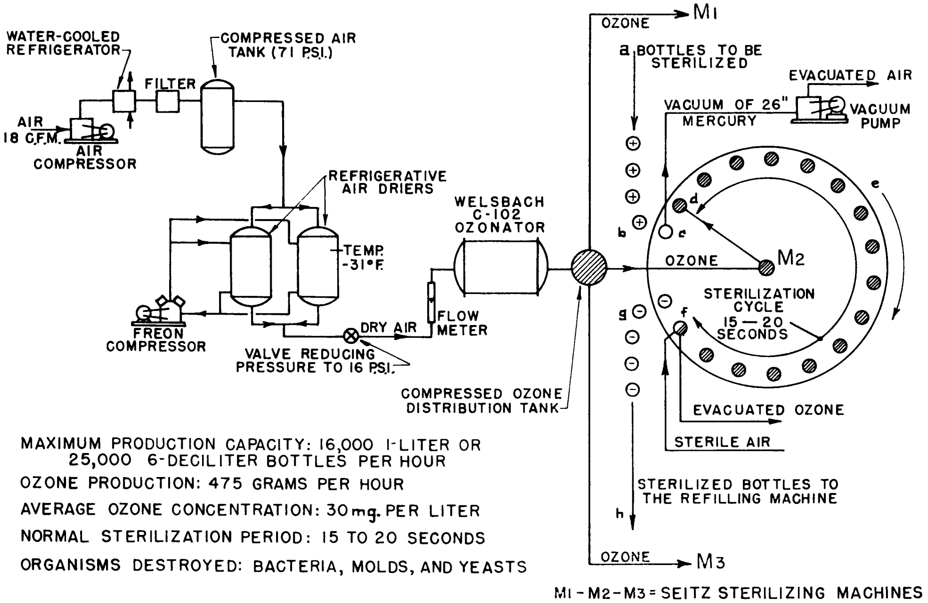

Figure 1. Schematic diagram of installation for automatic sterilization of empty bottles with ozone

about 30 mg. per cubic meter of free air, corresponding to a dew point temperature of −50° C.

The air-drying installation comprises two identical drying towers. Each tower is sufficient to ensure drying of the air for 1 day by means of a refrigeration machine. The tower used for drying the air the previous day is defrosted by the humid air before the air passes through the tower on stream, in which the temperature is further reduced to less than −35° C.

The pressure of the dry air leaving the cooling tower is then reduced by a valve to 16 p.s.i., so that ozone is finally available at the sterilizing machine at a pressure of at least 14 p.s.i. The air is ozonized at the desired pressure and concentration by a Welsbach C-102 industrial ozonator.

The sterilization process itself is based on the following principle:

The bottles to be sterilized, having been freshly washed, rinsed, and drained for about 30 seconds, are brought continuously on the chain conveyor, *ab*, to the Seitz sterilizing machine, converted to the use of ozone. The factory has three sterilizing machines, designated in Figure 1 as M_1, M_2, and M_3. Two of these machines were previously used for sterilization with sulfur dioxide. They have been converted by the manufacturer. The third is new; it was specially constructed for use with ozone in accordance with experiments made during the tests.

As soon as it arrives (*c*) in the rotating sterilizing machine, the bottle is automatically connected to a pump which induces a vacuum in the bottle of about 26 inches of mercury. The air is evacuated in about 1 second. During the next second the vacuum pump is automatically disconnected (at *d*) to allow the ozonated air under pressure of 14 p.s.i. to enter the bottle. The ozonated air is fed through a pneumatic storage and distribution tank which supplies one or several machines. The bottle, refilled with ozonated air under pressure, follows the rotation of the machine along path *def*, designated as the sterilization cycle. At *f* the compressed ozone is freed from the bottle and escapes through a vent. Sterile air at atmospheric pressure replaces the ozone. The sterile bottle leaves the sterilizing machine at *g* on a chain conveyor which brings it to the filling machine. On its way from *g* to *h* a protective screen of ultraviolet rays protects the mouth of the bottle from reinfection.

The replacement of the ozonated air with sterile air at the exit of the sterilizing machine is desirable to avoid the presence of ozone in the atmosphere of the plant.

The normal concentration of ozone is about 30 mg. per liter of compressed gas. This concentration is sufficient to ensure sterilization at the end of the cycle, which lasts 15 to 20 seconds, according to the speed of the machine.

The production capacity of this installation is 16,000 1-liter bottles or 25,000 6-dl. bottles per hour. At this rate of output the ozone consumption is 475 grams.

The speed of sterilization is an economically important factor. The same production rhythm must be maintained with the sterilizing machines when ozone is used as when sulfur dioxide is used. Any undue prolongation of the sterilization cycle would require the construction of larger machines for the same output.

Discussion

For the success of rapid sterilization with ozone, the bottles should contain no water in the bottom. The inside wall of the bottle is covered with only a thin film of water, which is sufficient to ensure instantaneous humidification of the dry ozonated air the moment it enters the bottle. Because sterilization with ozonated water would be slower, it is necessary to have the bottom of the bottle dry. The formation of a thin mist in the bottle indicates an adequate humidification of the ozonated air.

Evacuation of the air before introduction of the ozone under pressure allows a high concentration of ozone to be reached quickly in the bottle. The result is an appreciable reduction in the sterilization cycle. Figure 2 illustrates the difference between sterilizing without first evacuating the air, and sterilization according to the method at present used. Curve *B* illustrates the process employed at Sissach. It indicates the variations of ozone concentration in the bottle during the sterilization cycle, expressed in per cent of the maximum concentration recorded at the end of the operation. At the end of the second second of time, the bottle contains a concentration equal to 80% of the concentration recorded at the end of the operation.

When preliminary evacuation does not take place, the concentration of ozone in

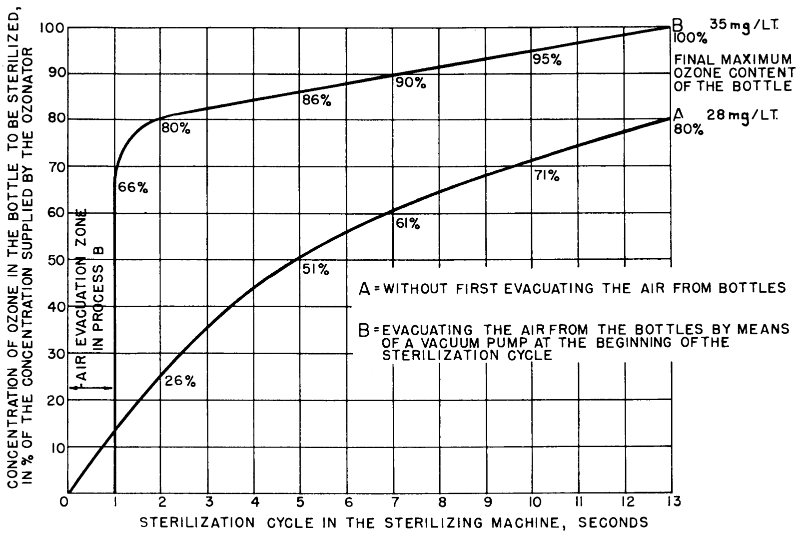

Figure 2. Effect of evacuating air from bottle before introduction of ozone

Relative ozone content of bottles during operation under pressure of 14.7 p.s.i.

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the bottle increases much more slowly, and at the end attains a maximum of only 80% of the concentration obtained by the preliminary evacuation process (curve *A*). Thus, if the air is not pumped out of the bottle, a considerable extension of the sterilization cycle is necessary.

During experiments which preceded the adoption of the new ozone process, the results of sterilization with sulfur dioxide were compared with the results of ozone sterilization (with preliminary evacuation). Table I is based on data from a report by the laboratory of the Institute of Hygiene and Bacteriology of the University of Berne. The table presents the results of sterilization obtained with flasks strongly infected with yeasts, molds, spore-forming bacteria, and other common bacteria. Most of the control flasks contained a considerable number of bacteria, estimated at several thousand per flask. Of the 15 flasks treated with sulfur dioxide, only six came out of the machine sterile. In the two batches of 30 flasks treated with ozone, only one flask still contained three live bacteria.

Table I. Comparative Results of Sterilization in Two Automatic Sterilizing Machines[a]

	Processes		
	Sulfur dioxide (10-second cycle)	Ozone (13-second cycle)[b]	
	Maximum Amount of Sterilizing Agent in Flask, Mg. per Liter		
Control Flasks	3000 to 3500	35	
+++	+	−	−
+++	+	−	+
+++	++	−	−
+++	+	−	−
+++	−	−	−
+++	−	−	−
++	−	−	−
+++	−	−	−
+++	+	−	−
++	+	−	−
+++	−	−	−
++	−	−	−
+++	++	−	−
+++	+	−	−
+++	++	−	−

[a] +++ = strongly infected (more than 1000 organisms per flask). ++ = moderately infected (100 to 1000 organisms per flask). + = slightly infected (1 to 100 organisms per flask). − = sterile.

[b] Double series.

The superiority of ozone over sulfur dioxide is undeniable, even considering the different lengths of the sterilization cycles (10 seconds for sulfur dioxide and 13 seconds for ozone). The ozone dosage used was only one hundredth of that of sulfur dioxide.

Although excellent results are obtained by ozone sterilization in 13 to 15 seconds, it is recommended that the sterilization cycle be maintained if possible at no less than 18 seconds.

Figures 3 and 4 show various parts of the Sissach sterilization installation. Figure 3, *A*, shows the air compressor installation, and adjacent to it, the two vaccum pumps for emptying the bottles. At the right is the tank holding clean air compressed to 71 p.s.i. Figure 3, *B*, shows the installation for drying air by refrigeration. Figure 4, *A*, shows the Welsbach C-102 ozone generator with the indicating and automatic control panel for the entire ozone generating installation. On the left is the compressed ozone distribution tank from which the ozone is piped to the three sterilizing machines. Figure 4, *B*, is of the Seitz sterilizing machine.

This first plant for direct sterilization of empty bottles with ozonated air opens the way to new industrial applications in the food field. A study is currently in progress

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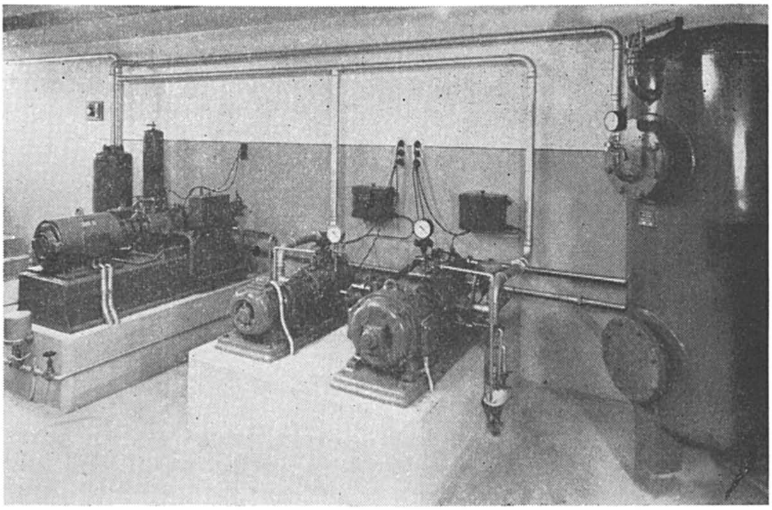
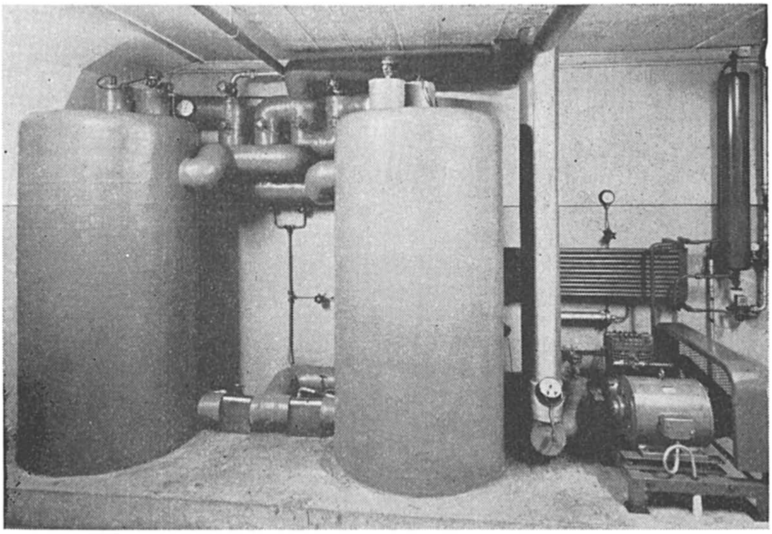


A



B

Figure 3. Ozone sterilization installation at Sissach, Switzerland

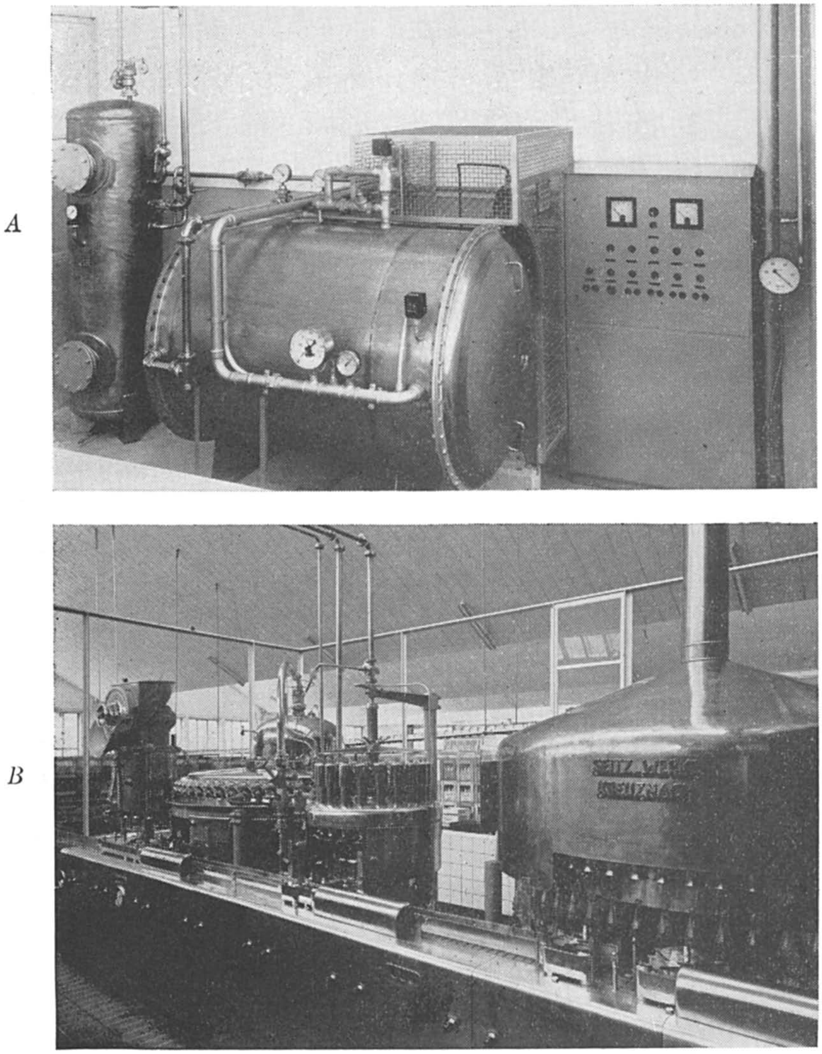


Figure 4. Ozone sterilization installation at Sissach

to adapt the process to the milk industry for sterilizing bottles which will be filled with absolutely sterile milk prepared by a new process. A large Swiss milk company has been operating a pilot plant for more than a year.

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Disinfection and Sterilization of Sewage by Ozone

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All microorganisms and toxin in raw sewage can be completely killed or inactivated in 30 minutes by treatment with ozone. The period of treatment is related to the efficiency of contact between ozone and the agent. Removal of suspended solids from sewage by filtration does not significantly decrease the time required to sterilize or the quantity of ozone used. Between 100 and 200 p.p.m. of ozone produced sterility under the experimental conditions used.

A research program was conducted by the Armour Research Foundation for the Chemical Corps, Fort Detrick, Frederick, Md., to study and evaluate methods for sterilizing sewage containing pathogenic microorganisms.

In any research institution where infectious microorganisms are being studied and may be discharged into the sewage, it is important, from a public health view, to ensure the inactivation of these infectious forms before sewage is discharged to normal disposal channels. At present heat is the method of sterilization most commonly used in such situations. Other possible methods of sewage sterilization were analyzed. Of the methods available, treatment with gaseous ozone was selected for further study.

The treatment of sewage effluents was studied by bubbling ozone through untreated or autoclaved sewage samples to which had been added tracer microorganisms, infectious bacterial spores, influenza virus, or the toxin produced by *Clostridium botulinum*.

Review of Literature

The initial literature survey disclosed that of the methods of sterilization, other than heat, chemical sterilization with ozone appeared to be more promising. Several reports indicate that ozone is being successfully used for water disinfection in France, where 136 municipal water plants serving approximately 8,000,000 people are in use. Ozonization is accomplished by injecting an air stream containing 2.5 to 5 grams of ozone per cubic meter of air into water. The process of ozonization occurs in self-contact columns and the retention time is 3 to 5 minutes. Prior to ozonization, the water is usually pretreated by sedimentation, coagulation, and filtration through sand. All the pathogenic and saprophytic organisms usually found in water are destroyed by

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this combined treatment. Ozone is also used in the United States in water treatment plants at Philadelphia, Pa., and Whiting, Ind. Philadelphia uses a residual of 0.13 to 0.2 p.p.m. for disinfection (*7*).

Dickerman *et al.* (*4*) reported that 1.5 p.p.m. of ozone will reduce a count of 70,000 spore-forming organisms per ml. of water to 0 within 5 minutes. They indicate that raw stream water with low organic content would require an ozone residual of 2 p.p.m. applied for at least 5 minutes to give a complete kill. When organic contents are high, larger concentrations and longer contact time are needed.

Ozone has been suggested as an agent for treating sewage wastes, and has been used in limited experimental runs as coagulating agent and to reduce the biological oxygen demand (B.O.D.) in sewage (*5, 6*). There is also indication that ozone added to the effluent after coagulation and filtration will reduce the bacterial count. Two patents have been granted for treatment apparatus which uses ozone and ferrous sulfate for flocculation and coagulation of sewage (*2, 3*).

Although ozone destroys bacteria and has been used in water disinfection, no data are available as to its effectiveness as a sterilizing agent for raw sewage containing pathogenic microorganisms. Therefore, studies were initiated to obtain experimental data on the bacteriological effectiveness of ozone sterilization.

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Experimental Techniques

The first experiments were purely feasibility studies, and, therefore, variations were used in the techniques.

For ozone production, a Welsbach laboratory ozonator, Model T-23, was used. The quantity of ozone in the gas stream, which contained from 1.0 to 5% ozone, was regulated by varying the voltage, by changing the input gas from dry air to dry oxygen, or by varying the flow rate of the gas through the ozonator.

The following organisms were selected as representative of groups for test purposes:

Bacillus anthracis
Toxin of *Clostridium botulinum*
Influenza virus
Bacillus subtilis var. *niger*

Bacillus subtilis var. *niger* was used as the simulant for pathogenic microorganisms. Prior to inoculation into the sewage, the *B. subtilis* var. *niger* cultures were heat-shocked at 80° C. for 10 minutes to eliminate all vegetative forms. Known concentrations of the culture were added to autoclaved Fort Detrick sewage, or distilled water, and then treated with ozone. It was possible to use pathogenic organisms at Fort Detrick in place of simulants as inocula for the raw sewage.

Various types of apparatus were used to bring ozone and liquid in contact. In the initial experiments, the inoculated sewage was circulated by a small pump. Leaks in the system and operational difficulties caused a change to batch treatment of the sewage in gas wash bottles. The sizes of the gas bubbles were reduced by attaching fritted-glass disks, cylinders, and tubes to the delivery tube in the gas wash bottle. In the final experiments, the gas bottles were replaced by glass columns 2 inches in diameter and 2, 4, or 8 feet high. The delivery tube at the bottom of the column was a fritted-glass cylinder. The 4-foot contact columns were utilized at Fort Detrick and all pathogenic work, including all equipment which could have been contaminated, was done in biological safety cabinets. Figure 1 illustrates the equipment necessary for ozonating sewage in the glass columns.

The quantity of ozone in the gas stream, before and after passing through the sewage, was determined by the iodometric method.

Bacterial counts on the inoculated sewage and the treated sewage were determined by appropriate dilution and plating on tryptose phosphate dextrose agar. The plates were counted after 24 to 48 hours' incubation at 37° C. In addition, in several experi-

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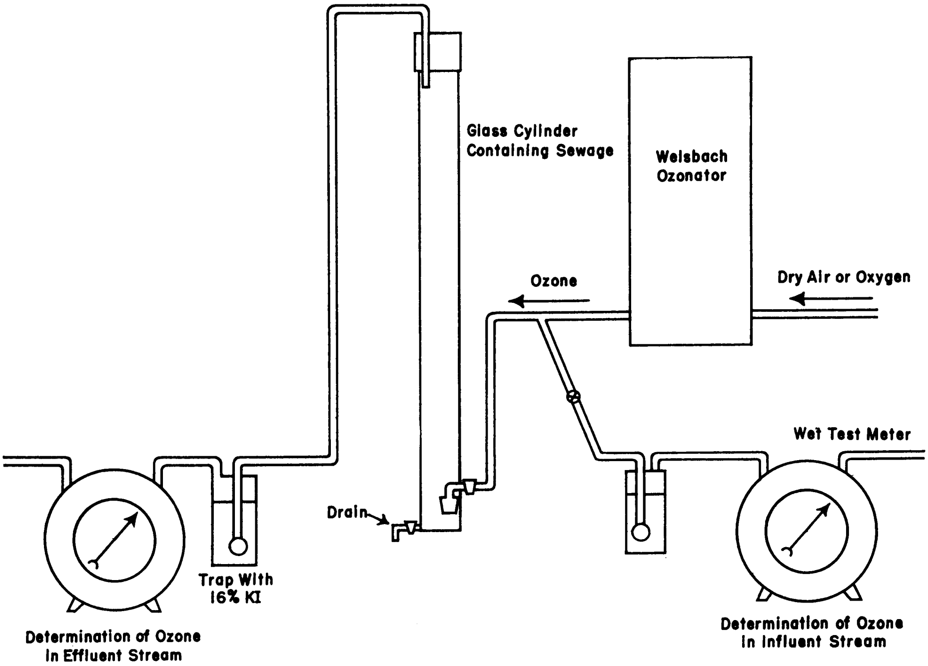

Figure 1. Equipment for ozonating sewage in glass columns

ments the most probable number (M.P.N.) per 100 ml. was determined (*1*). The sterility of raw sewage inoculated with *B. anthracis* spores was checked by inoculating mice as well as by culture. The inactivation of the botulinum toxin was tested in mice; the inactivation of the influenza virus was determined with embryonated eggs.

Results

Table I shows survival of *B. subtilis* var. *niger* spores in sewage with increasing time of treatment. Results of experiments were included in the average, regardless of variations in flow rate or concentration of ozone in the stream. This table indicates a marked reduction of organisms. This would be considered adequate for disinfection of sewage, but does not satisfy the rigid 100% sterilization requirement for Fort Detrick.

Table I. Average Survival of *B. Subtilis* Var. *Niger* Spores in Sewage after Ozone Treatment[a]

Period of Treatment, Min.	No. of Samples	Survival, Log %
1	2	−0.10
2	1	−0.66
5	3	−1.17
15	6	−1.57
30	9	−1.88

[a] Approximately 250 ml. of sewage treated in 10-inch gas wash bottles. Initial count was 1 to 2 × 10^8 spores/ml.

The experimental data were examined to determine whether any correlation exists between variations in the experimental procedures and the efficiency of the ozone sterilization system. It can be concluded that there was no definite correlation among the flow rate of the gas stream, per cent concentration of ozone in the gas stream, and per cent survival of spores. The flow rate variations ranged between 0.005 and 0.16 cu. foot per minute, and the concentration of ozone in the gas stream was in the range of 1.5 to 5%. On the other hand, the height of the column of liquid being treated had a marked effect on the survival of *B. subtilis* var. *niger* spores. No definite statement on this difference can be made. The data obtained with 2-, 4-, and 8-foot columns are summarized in Table II.

Table II. Effect of Column Height on Survival of *B. Subtilis* Var. *Niger* Spores after Ozone Treatment[a]

Height of Column, Ft.	Treatment, Min.	No. of Samples, Sterile/Total	Log Av. % Survival
2	15	0/2	−2.00
2	30	4/10	−3.63
4	15	0/4	−3.13
4	30	14/15	−5.00
8	20	5/5	Sterile
8	30	5/5	Sterile

[a] Experiments conducted at ARF with autoclaved Fort Detrick sewage inoculated with 1 to 2 × 10^8 *B. subtilis* var. *niger* spores/ml.

Increasing height gives decreasing log average per cent survival. Although the total number of samples ozonized in the 8-foot column is smaller than the number in the 2- or 4-foot column, the fact that all samples in the 8-foot column are sterile after 20 as well as after 30 minutes' treatment indicates that the 8-foot column is superior to the 2- or 4-foot column.

To determine the effect of suspended solids, samples of sewage were treated with ozone under identical conditions, except that a portion of each sample was filtered prior to inoculation and ozonization (Table III).

Table III. Bacteriological Results of Ozone Treatment on Filtered and Unfiltered Sewage[a]

O_3 Treatment, Min.	Log % Survival of *B. subtilis* var. *niger* Spores[b]	
	Filtered	Unfiltered
20	−1.15	−0.16
30	−1.69	−1.00
45	−1.85	−1.80

[a] Average of 3 lots of sewage in 3 separate experiments. In each experiment the same lot of sewage was used to obtain filtered and unfiltered values.

[b] Initial count was 10^8 *B. subtilis* var. *niger* spores/ml.

The log of average per cent survival indicates fewer survivors with filtered than with unfiltered sewage within the first 30 minutes of treatment, but after 45 minutes the difference is insignificant.

Tables I, II, and III show the trend or pattern of the various parameters rather than portray any definite representative experiment.

Tables IV through VII show the results of biological work performed at Fort Detrick.

Table IV. Results of Experiments with *B. Subtilis* Var. *Niger* Spores Inoculum

Type of Liquid	Initial Count, Org./Ml.	*B. subtilis* var. *niger* Spores Surviving/100-Ml. Exposure to O_3, Min.			
		30	60	90	120
Buffered distilled water	22.1 × 10^7	> 240	7.6	0	—
	6.6 × 10^7	0	10[a]	240[a]	0
Raw sewage count, 7.3 × 10^7	8 × 10^7	> 240	>240	<2.2[b]	0

[a] Suspected contamination due to contaminated syringe.

[b] Sample contaminated.

Table V. Results of Experiments on Raw Sewage with *B. Anthracis* Spores Inoculum

Initial Count, 10^7 Org./Ml.	*B. anthracis* Spores Surviving/100 Ml. Exposure to O_3, Min.				
	30	60	90	120	150
2.5	>240	>240	>240[a]	0	—
2.3	>240	>240	0	0	0
3.7	>240	0	0[b]	0	0

[a] Contaminated.

[b] Sample contaminated with *B. anthracis* spores.

Table VI. Results of Experiments on Raw Sewage with Botulinum Toxin Inoculum[a]

(Initial count.[b] 6×10^5 to 1×10^6 mouse minimum lethal doses/ml.)

Dilution of Treated Liquid	No. Dead/No. Inoculated[c] Exposure to O_3, Min.				
	0	30	60	90	120
None	...	0/8	0/8	0/8	0/8
1×10^{-1}	...	0/4	0/4	0/4	0/4
1×10^{-2}	4/4	0/4	0/4	0/4	0/4
1×10^{-3}	...	0/4	0/4	...	...
1×10^{-4}	4/4	0/4	...	...	0/8
1×10^{-5}	3/4	0/4	0/4	0/4	0/8
2×10^{-5}	3/4	...	...	...	...
2.5×10^{-5}	...	0/8	0/8	0/8	0/8
4×10^{-5}	0/4	...	...	...	...
5×10^{-5}	...	0/8	0/8	0/8	0/8
1×10^{-6}	...	0/8	0/8	0/8	0/8
2×10^{-6}	...	0/8	0/8	0/8	0/8
4×10^{-6}	...	0/6	0/6	0/6	0/6

[a] Summary of results of three experiments.

[b] Number of minimum lethal doses for mice present in 1 ml.

[c] Mice inoculated with 0.5 ml. of each dilution of untreated or treated sewage.

Table VII. Results of Experiment on Raw Sewage with Influenza Virus Inoculum

(Initial count. $1 \times 10^{3.22}$ EID/ml.)

Dilution of Treated Liquid	No. Positives/No. Inoculated Exposure to O_3, Min.				
	0	30	60	90	120
None		0/10	0/10	0/10	0/10
1×10^{-1}	4/5	0/10	0/10	0/10	0/10
1×10^{-2}	4/7	0/10	0/10	0/10	0/10
1×10^{-3}	2/9	0/10	0/10	0/10	0/10
1×10^{-4}	0/8	0/10	0/10	0/10	0/10
1×10^{-5}	0/9	0/10	0/10	0/10	0/10
1×10^{-6}	0/9	0/10	0/10	0/10	0/10

A summary of the data for ozone used to obtain sterility is presented in Table VIII. To ascertain that complete sterilization was attained, on several occasions ozonized samples were held at room temperature for 5 days and then cultured. Subcultures were also prepared from samples and incubated for 5 days. No growth was found after this holding period, or on subculture, as determined by the most probable number method. The term "ozone used" is defined as the calculated value of the difference between the milligrams of ozone entering and leaving the reaction column. The ozone used in milligrams is then applied to the amount of the sample being sterilized and is reported as parts per million by weight. The ozone used probably includes ozone dissolved, ozone reacted, and ozone decomposed in the sewage. The duration of treatment, type of samples, organism used, column height, and ozone used are also given so that their relationship may be observed. A smaller number of samples are listed in Table VIII because data on ozone used were obtained in only a part of the experiments.

Here one can observe a marked difference between the ozone used to sterilize

Table VIII. Ozone Used to Obtain Sterility in Sewage or Water

No. of Samples	Type of Samples	Organism Used	Period of Treatment, Min.	Column Height, Ft.	Average O_3 Utilized, P.P.M.	Range of O_3 Utilized, P.P.M.
			ARF Experiments			
2	Water	*B. subtilis*[a]	45–60	2	98	59–113
12	Sewage	*B. subtilis*[a]	30	4	92	59–113
			Fort Detrick Experiments			
2	Water	*B. subtilis*[a]	30–90	4	395	347–728
1	Raw sewage	*B. subtilis*[a]	90	4	425	. . .
3	Raw sewage	*Anthrax*[b]	90	4	672	669–675
3	Raw sewage	*Toxin*[c]	30	4	250	210–290

[a] Initial count of *B. subtilis* var. *niger* spores in experiments at ARF was 1 to 2 × 10^8/ml., at Fort Detrick 0.66 to 2.2 × 10^8.

[b] Initial count of *B. anthracis* spores was 0.23 to 0.37 × 10^8/ml.

[c] Initial concentration of botulinum toxin was 1 × 10^6 mouse minimum lethal dose/ml.

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distilled water at Armour Research Foundation and at Fort Detrick. A larger quantity of ozone was used to sterilize raw than autoclaved sewage, as expected. However, the magnitude of the difference can be explained through the operational difficulties: possible leaks in the line leading to the contact column and in the column itself, possible decomposition of ozone in the line used to carry ozone to the columns (length of line 1 foot at the foundation, 10 to 15 feet at Fort Detrick), and finally, possible inaccuracy in titration procedure due to difficulty in working through the gloves in the biological safety cabinets. Thus, for practical purposes, it is assumed that the data obtained on ozone used at the foundation are more reliable.

Under the conditions of these experiments, all the microorganisms inoculated into raw sewage could be completely sterilized or inactivated, as demonstrated by both cultural methods and animal inoculations. *B. anthracis* and *B. subtilis* var. *niger* spores were completely killed by 90 minutes of ozonization and probably could be killed within 60 minutes. Botulinum toxin, Type A, and influenza virus, strain PR 8, were completely inactivated by 30 minutes of ozonization. The results of ozone treatment of *B. subtilis* var. *niger* spores and *B. anthracis* spores in raw sewage confirm the suitability of *B. subtilis* var. *niger* spores as a simulant for pathogenic microorganisms in respect to resistance to ozone treatment.

Conclusions

Ozone is a satisfactory means for disinfection and sterilization of sewage. From the log per cent survival, it is apparent that even after 5 minutes there is better than 99.9% kill. All of the microorganisms and the toxin are completely killed or inactivated within a contact period of 30 minutes in raw sewage, with a few exceptions, by treatment with ozone. The period of treatment appears to be related to the efficiency of contact between ozone and the agent.

Removal of suspended solids from sewage by filtration does not significantly decrease the time required to sterilize or the quantity of ozone used.

The quantity of ozone used to produce sterility under the experimental conditions at Armour Research Foundation lies between 100 and 200 p.p.m.

The ozone utilized was inefficient during the experiments, as approximately 90% of the applied ozone was recovered. It is felt that a much higher ozone utilization can be achieved through the use of suitable equipment. However, inasmuch as the objective of this phase of the investigation was to evaluate the bacteriological effectiveness of the system, no attempt was made to improve the ozone consumption beyond that necessary for success of the experiments.

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Mechanism of Gas Phase Decomposition of Ozone. Thermal and Photochemical Reactions

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Most of the known data on the thermal decomposition of ozone can be explained quantitatively in terms of the simple atomic mechanism

$$M + O_3 \underset{2}{\overset{1}{\rightleftharpoons}} O_2 + O + M$$

$$O + O_3 \xrightarrow{3} 2O_2$$

in which Reactions 1 and 2 are at their low pressure limit. There is no evidence for a direct bimolecular reaction or an energy chain mechanism. Surface reactions do not appear to be important in this system. The relative efficiencies of various gases as M in Reactions 1 and 2 are: $O_3 = 1.00$, $O_2 = 0.44$, $N_2 = 0.41$, $CO_2 = 1.06$, and $He = 0.34$. Quantitatively reproducible results are difficult to achieve. The energy chain mechanism proposed previously to account for the high quantum yields in the far-ultraviolet photolysis is inconsistent with both the photochemical results obtained with red light and the postulated thermal mechanism.

The rate of the gas phase decomposition of ozone has been studied by many investigators under a wide range of conditions, yet no completely satisfactory mechanism has ever been proposed for either the thermal or photochemical decompositions.

Thermal Decomposition

The early workers (*19*) investigated the pyrolysis of dilute ozone and attempted to explain their results in terms of the simple Jahn mechanism

$$O_3 \underset{2}{\overset{1}{\rightleftharpoons}} O_2 + O \qquad \text{Rapid equilibrium} \qquad (1,2)$$

$$O + O_3 \rightarrow 2O_2 \qquad \text{Rate determining} \qquad (3)$$

in which it is assumed that the oxygen atoms are at their equilibrium concentration with respect to Reactions 1 and 2. The reproducibility of these dilute ozone experi-

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ments was very poor, and no conclusive evidence was ever presented that the rate is exactly inversely proportional to the oxygen concentration, as required by this mechanism. Garvin, however, reinvestigated the thermal decomposition of dilute ozone, employing a flow technique (*6*). He found the rate to be nearly inversely proportional to the oxygen concentration and independent of the concentration of added nitrogen.

Several investigations have been carried out using concentrated ozone obtained by the fractional distillation of dilute ozone (*8, 12–14, 17*). Most of the results were represented empirically in terms of simultaneous first- and second-order reactions.

The most satisfactory study, with respect to both the experimental methods employed and the wide range of conditions covered, appears to be that of Glissmann and Schumacher (*8*). They studied the reaction between 70° and 110° C. in vessels varying in size from 0.5 to 12 liters in the presence of added oxygen, nitrogen, helium, and carbon dioxide. The following mechanism involving simultaneous bimolecular and atomic reactions as well as an energy chain was proposed:

$$O_3 + O_3 \rightarrow 3O_2 + 69\ \text{kcal.} \qquad \text{Bimolecular} \qquad (4)$$

$$\left.\begin{array}{r} O_2 + O_3 \rightarrow O_2 + O_2 + O \\ M + O + O_2 \rightarrow M + O_3 \\ O + O_3 \rightarrow 2O_2^* + 93\ \text{kcal.} \end{array}\right\} \qquad \begin{array}{l} \text{Atomic} \qquad (5) \\ \qquad\qquad (2) \end{array}$$

$$\left.\begin{array}{r} O + O_3 \rightarrow 2O_2^* + 93\ \text{kcal.} \\ O_2^* + O_3 \rightarrow O_2 + O_2 + O \end{array}\right\} \qquad \begin{array}{l} \text{Energy chain} \qquad (3) \\ \qquad\qquad (6) \end{array}$$

$$O_2^* + M \rightarrow O_2 + M \qquad (7)$$

There is, however, an error in this scheme, because it may be shown (*4*) that Reaction 5 must have the same form of pressure dependence as Reaction 2. This error does not show up markedly in their experiments on ozone-oxygen mixtures, because, according to their mechanism, the atomic reaction is important only under conditions where the ozone concentration is small. This mechanism does not account for the marked acceleration which is observed when inert gases, especially carbon dioxide, are added. Schumacher (*15*) pointed out that this must be due to the effect of the inert gases on the rate of Reaction 5, but he was at a loss to explain why the acceleration is the greatest under conditions where Reaction 4 should predominate. Another difficulty with this mechanism is, as discussed by Geib (*7*), that the value assigned (*15*) to the rate constant of Reaction 4 yields a steric factor of close to 100, which is high for this type of bimolecular reaction.

Sutphen (*18*) measured the rate of the thermal decomposition between 25° and 115° C. over a wide range of total pressures from 29 mm. of mercury to 6 atm. He concluded that all the steps of the complex mechanism proposed by Glissmann and Schumacher are required to account for his results. This includes the reactions which were proposed to be initiated by activated oxygen molecules formed in the reaction. Sutphen also concludes that Reaction 2 does not reach its low pressure limit over this range of pressures.

A reinvestigation of the thermal decomposition was undertaken in an effort to discover the exact mechanism of this interesting reaction (*2*). The experimental procedure presented here is similar to that of Glissmann and Schumacher (*8*).

Experimental. Two sources of oxygen were employed: tank oxygen passed over hot copper oxide and oxygen formed by the pyrolysis of potassium permanganate. Both sources gave equivalent results after the latter had been dried to remove the large quantity of water that was present.

The oxygen was condensed at the temperature of liquid nitrogen, slowly distilled through a glass-wool trap cooled in liquid oxygen, and slowly distilled through a borosilicate glass ozonizer. The ozone-oxygen mixture was condensed at the temperature of liquid nitrogen and opened to the pumps until nearly all of the oxygen was removed. The ozone was twice trap-to-trap vacuum-distilled, the final portion of the second distillation being discarded. After the reaction vessel reached reaction temperature, the ozone was allowed to evaporate into it. Oxygen was then added. At the latter

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two points the danger of explosion is high. The dead space was flushed with oxygen and the pressure readings were begun. The initial ozone pressures ranged from 90 to 230 mm. of mercury, and the decomposition was usually followed to a final ozone pressure of about 10 mm. of mercury.

The pressure was measured using a borosilicate glass Bourdon gage which was sensitive to 0.1 mm. of mercury as a null instrument to a mercury manometer. The final pressure was measured after the reaction vessel had been heated above 200° C. for 8 hours or longer. The maximum dead space of 14 cc. was efficiently flushed with oxygen at the start of each experiment and was duly corrected for in the calculation (*2*) of the ozone concentrations. The hollow-bore vacuum stopcocks used in the system were lubricated with Halocarbon (high temperature grade) stopcock lubricant. The usual precautions were taken to minimize the amount of mercury vapor in the system.

Quantitative Data. RESULTS. Four initial experiments were carried out at temperatures close to 100° C. in two different reaction vessels. Two of the experiments, one with about 500 mm. of mercury of oxygen added initially, were carried out in a 537-cc. borosilicate glass sphere and the other two in an irregularly shaped, 461-cc. borosilicate glass vessel with about 45% greater surface.

The results of these four experiments are tabulated in Table I. The results of six similar experiments of Glissmann and Schumacher at nearly the same temperature are tabulated in Table II. In one of their experiments 610 mm. of nitrogen was added. The results are in qualitative agreement but they cannot be compared exactly, except in terms of a specific mechanism, because the total pressures were not the same.

Table I. Comparison of Results of Experiments with Proposed Mechanism

Experiment	1	2	3	4
Vessel	I	I	II	II
Temperature, ° C.	99.3	99.4	99.9	100.0
Pressure after total decomposition[a]	620.2	301.3	207.2	208.1
$k_s \times 10^3$ at 95 mm. of ozone[b]	... (124)	131 (115)	110 (99)	104 (101)
$k_s \times 10^3$ at 70 mm. of ozone[b]	159 (135)	144 (135)	126 (120)	126 (122)
$k_s \times 10^3$ at 55 mm. of ozone[b]	165 (143)	153 (150)	148 (139)	152 (141)
$k_s \times 10^3$ at 40 mm. of ozone[b]	172 (153)	183 (180)	172 (170)	178 (173)
$k_s \times 10^3$ at 20 mm. of ozone[b]	190 (169)	231 (243)	258 (255)	280 (258)

[a] Mm. of mercury.

[b] Values listed are second-order rate constants in liter per mole-second. Values in parentheses are predicted by mechanism and rate constants developed here.

Table II. Comparison of Results of Glissmann and Schumacher (8) with Proposed Mechanism

Experiment	46	45	43	40	39	66[d]
Vessel	II[c]	II	II	II	II	II
Temperature, ° C.	99.8	99.8	99.8	99.8	99.8	99.8
Pressure after total decomposition[a]	767.8	408.8	254.6	120.6	50.7	125.9 (oxygen)
$k_s \times 10^3$ at 95 mm. of ozone[b]	... (122)	131 (131)	113 (110)	... ...	... ...	... ...
$k_s \times 10^3$ at 70 mm. of ozone	127 (131)	145 (149)	126 (131)	... (87)	... ...	... (354)
$k_s \times 10^3$ at 55 mm. of ozone	136 (135)	160 (165)	144 (151)	101 (101)	... ...	415 (406)
$k_s \times 10^3$ at 40 mm. of ozone	144 (142)	178 (188)	166 (181)	132 (126)	... ...	475 (478)
$k_s \times 10^3$ at 20 mm. of ozone	153 (152)	... (229)	... (257)	197 (203)	119 (114)	605 (641)

[a] Mm. of mercury.

[b] Values listed are second-order rate constants in liter per mole-second. Values in parentheses are predicted by mechanism and rate constants developed here.

[c] One-liter spherical vessel.

[d] 610 mm. of nitrogen present.

Experiments 3 and 4 (Table I) represent nearly identical conditions and, therefore, indicate the order of reproducibility of present results.

The same general trends occur in both sets of experiments. The second-order rate constants increase markedly during a given run, the magnitude of this effect decreasing with increasing oxygen pressure. These second-order rate constants were obtained by taking tangents at various points on an inverse O_3 concentration *vs.* time plot. All of the data of Glissmann and Schumacher were plotted in this manner in order to obtain the best rate constants. At a given ozone pressure, the addition of oxygen accelerates the rate at high ozone pressures and inhibits it at lower pressures.

DISCUSSION. The simple atomic mechanism (Reactions 1 to 3) appears to be compatible with the qualitative features of the thermal decomposition of ozone. An attempt was made, therefore, to test quantitatively.

Although the rate law derived from this mechanism is completely integrable, it was simpler to test the data in terms of the differential rate expression. This expression, assuming Reactions 1 and 2 to be at the low pressure limit, may be put in the following form:

$$(M)/k_s(O_3) = (k_2/2k_1k_3)(M)(O_2)/(O_3) + 1/2k_1 \qquad (8)$$

where

$$(M) = (O_3) + a_{O_2}(O_2) + a_{N_2}(N_2) + a_{CO_2}(CO_2) + a_{He}(He) \qquad (9)$$

and

$$k_s = -[d(O_3)/dt]/(O_3)^2. \qquad (10)$$

To test this proposed mechanism, $(M)/k_s(O_3)$ was plotted against $(M)(O_2)/(O_3)$. The best fit was obtained using

$$(M) = (O_3) + 0.44(O_2) + 0.41(N_2) + 1.06(CO_2) + 0.34(He) \qquad (11)$$

All 47 experiments of Glissmann and Schumacher (*8*) were plotted in this manner except experiments 31, 37, and 94, which had numerical or typographical errors in the tabulated data. Their results yielded straight lines (*2, 5*) for all experiments, including those with added inert gases with an average error of less than 5%, except at very high ozone concentrations at the higher temperatures studied. This is excellent agreement, considering that k_s may vary by a factor of more than 6 at a given temperature depending upon the conditions (see Tables I and II). Table I shows that all four experiments fit this same mechanism with an average error of less than 10%.

The values of k_1 and k_1k_3/k_2 obtained from the intercepts and slopes of these graphs yielded excellent Arrhenius plots. Because results around 99.8° C. without added inert gases agree well with the results of Glissmann and Schumacher under the same conditions in terms of the proposed mechanism, it appears that the large body of data presented by them is reliable. The values of the rate constants, activation energies, and *a*'s presented in this paper were obtained by reinterpretation of the results of Glissmann and Schumacher. From these are obtained the values (for M equal to O_3):

$$k_1 = 4.61 \pm 0.25 \times 10^{12} \exp(-24{,}000/RT) \qquad \text{Liter/mole-second}$$

$$k_1k_3/k_2 = 2.28 \pm 0.16 \times 10^{15} \exp(-30{,}600/RT) \qquad \text{Second}^{-1}$$

The values obtained by Garvin (*6*) for the quantity k_1k_3/k_2 at much higher temperatures are nearly identical with those obtained from the above expression. From known thermal data (*11*)

$$K_{eq} = k_1/k_2 = 7.7 \times 10^4 \exp(-24{,}600/RT) \qquad \text{Moles/liter}$$

$$k_2 = 6.00 \times 10^7 \exp(+600/RT) \qquad \text{Liter}^2\text{/mole}^2\text{-second}$$

$$k_3 = 2.96 \times 10^{10} \exp(-6000/RT) \qquad \text{Liter/mole-second}$$

The rates observed by Glissmann and Schumacher are appreciably higher than those predicted by the above mechanism when the absolute rate of the reaction is greater than about 1×10^{-6} mole per liter-second. Three possible explanations of these abnormally high rates have been considered: first, secondary activation of ozone by the activated oxygen molecules formed in Reaction 3; secondly, a direct bimolecular reaction; and, finally, the possible existence of temperature gradients in the system.

The importance of secondary activation (energy chains) would depend on the ratio of the ozone concentration to the rate of deactivation of the activated oxygen molecules. Because this rate of deactivation should be nearly temperature independent, the effect of energy chains should be equally important at 70° and 90° C. for the same ozone and oxygen concentrations. However, the observed rates were normal at 70° C. and high at 90° C. at similar concentrations. If a direct bimolecular reaction is to compete with Reaction 1, it must have an activation energy of less than 24 kcal. because the frequency factor of k_1 is higher than would be expected for an ordinary bimolecular reaction. On the other hand, unless this possible direct bimolecular reaction to form oxygen has an activation energy appreciably greater than Reaction 1, it should compete equally as well at 70° C. as at 90° C. Again this is contrary to the observed results.

The possible existence of temperature gradients in reacting systems has been treated theoretically (*3*), and it is predicted that their magnitude should be proportional to the absolute rate of the reaction—i.e., to the rate of heat evolution in this case. Harteck and Dondes (*9*) have observed a temperature rise of a few degrees in the center of a vessel of rapidly decomposing ozone, and it would seem likely that temperature gradients also should exist under some of the conditions studied by Glissmann and Schumacher. A similar effect has been observed by Allen and Rice (*1*) in the decomposition of azomethane near the explosion limit. Because the magnitude of this rate increase over the predicted rate is apparently dependent only on the absolute rate of the reaction (although these increases are in general not large compared with the average experimental error, making them difficult to treat quantitatively), it would seem that these abnormalities in the data can be best explained in terms of the existence of small temperature gradients. The observed rates are about 25% high, corresponding to an average temperature increase of 2.3° C., when the rate is 6.8×10^{-6} mole per liter-second.

The value of a_{O_2} (Equation 9) is known only within ±20%. When sufficient oxygen is present to contribute appreciably to M, the reverse reaction, Reaction 2, is fast enough that the effect of M on the over-all rate is limited. For this reason a_{O_2} cannot be determined more accurately with the data available. The values obtained for k_1 and, therefore, k_2 are nearly independent of the value chosen for a_{O_2}. The value for k_3 varies by ±10% when a_{O_2} is varied by ±20%. If accurate data were available in the very low ozone region where the Jahn mechanism prevails, k_3 could be obtained independently of a_{O_2}. The values of a found for the inert gases are accurate to about ±10%, because they may be measured under conditions where Reaction 1 is nearly rate-determining. The uncertainty in the activation energies of k_1 and k_2 is 0.5 kcal., and of k_3 it is approximately 0.7 kcal.

No trend is observed in the data which can be attributed to surface effects even though the surface-to-volume ratio was varied by a factor of nearly 6. (The vessels used by Glissmann and Schumacher had the following volume-to-surface ratios in cm.: I = 0.85, II = 2.1, and IV = 4.74.) This indicates that surface reactions, if present at all, must contribute to less than 10% of the rate. Harteck and Dondes (*9*) found that increasing the surface by a factor of 100 increased the rate by a factor of only 4 to 6. This also seems to indicate that surface effects are small in an unpacked vessel.

This atomic mechanism requires, of course, that the O atom concentration be less than that which would be present if equilibrium prevailed with respect to Reactions 1 and 2. The ratio of this steady-state O atom concentration to that calculated from the equilibrium of Reactions 1 and 2 depends on the relative rates of Reactions 2 and 3 and, therefore, on the ratio $(M)(O_2)/(O_3)$. The predicted values for the ratio of O atom concentrations are given in Table III as a function of $(M)(O_2)/(O_3)$ and of

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Table III. $(O)_{ss}/(O)_{eq}$ as a Function of Temperature and $(M)(O_2)/(O_3)$

$(M)(O_2)/(O_3)$, Mm. Hg	° C.						
	200	130	110	90	70	25	0
1,000	7.5[a]	23.4	33.0	45.4	60.0	88.0	95.6
2,000	13.9	37.9	49.6	62.4	74.9	93.5	97.9
3,000	19.5	47.8	59.6	71.3	81.7	95.6	95.5
6,000	32.6	64.6	74.6	83.2	90.0	97.7	99.3
9,000	42.1	73.1	81.4	88.1	93.0	98.5	99.5
12,000	49.2	78.5	85.4	90.8	94.6	98.9	99.6
15,000	54.8	82.0	88.0	92.5	95.8	99.1	99.7
18,000	59.2	84.5	89.7	93.7	96.5	99.3	99.8
21,000	62.9	86.5	91.0	94.6	96.9	99.4	99.8
24,000	65.9	87.9	92.0	95.2	97.3	99.4	99.8
27,000	68.5	89.0	93.0	95.7	97.5	99.5	99.8
30,000	70.7	90.0	93.5	96.1	97.8	99.6	99.9
60,000	82.8	94.9	96.8	98.1	98.9	99.8	...
120,000	90.5	97.3	98.4	99.0	99.4	99.9	...
240,000	95.0	98.6	99.2	99.5	99.8	...	...
480,000	97.5	99.2	99.5	99.7	99.9	...	...

[a] Values listed are $(O)_{ss}/(O)_{eq} \times 100$.

temperature. This table shows that under the typical dilute ozone conditions of 3% ozone in an atmosphere of oxygen $[(M)(O_2)/(O_3) = 11{,}100$ mm. of mercury] the oxygen atom concentration will be only about 77% of its equilibrium value at 130° C. and about 87% at 100° C. Therefore, even under these dilute conditions, the rate should not be exactly second-order nor should it be exactly inversely proportional to the oxygen concentration. Under the conditions used by Garvin (*6*) the rate should be about one half of that predicted by the Jahn mechanism.

Detailed calculations have been made on the results of all previous workers to compare these results with the proposed mechanism and rate constants (*2*). The reproducibility was very poor in most of these earlier investigations but in nearly every case the lowest rates observed approached closely to those predicted by this simple atomic mechanism, even in vessels of very large surface-to-volume ratios. These calculations seem to indicate that a trace catalyst was present in most of the studies and when this was eliminated, the simple atomic mechanism prevailed. Apparently Glissmann and Schumacher were the only early investigators who were able to eliminate this trace catalyst completely. No reliable evidence was ever presented to indicate that the surface played an important role even in those cases where catalysis was occurring—e.g., packing the vessel with glass wool (*9*) could easily introduce a trace catalyst which was actually homogeneous in its action.

The results of Sutphen (*18*) support the complex mechanism proposed by Glissmann and Schumacher and indicate that the unimolecular decomposition of ozone is not at its low pressure limit. Results of all 67 of these experiments have been compared with the integrated form of Equation 8; typical data are tabulated in Table IV, where t_{obsd} is compared with t_{calcd} from this integrated equation. Except for the experiments in which 6 atm. of oxygen were present, Sutphen's results fit the proposed mechanism with an average error of 10 to 15% with only a few exceptions. Experiments 228, 233, and 234, in which energy chains are proposed to be important, fit the simple atomic mechanism well. (The percentage decomposition was so great in Experiment 228 that any error in the final ozone pressure would be greatly magnified in t_{calcd}.) Experiments 262 and 275, which were cited as evidence against the simple atomic mechanism, are actually in agreement with it. The rates observed in the presence of 6 atm. of oxygen were much faster than the predicted rates. However, this cannot be due to a homogeneous bimolecular reaction as proposed by Sutphen, because the authors have observed a low temperature rate slower by a factor of 5 than the rate predicted by Sutphen's bimolecular rate constant. The most obvious explanation of these high rates is the introduction of a trace catalyst with the oxygen or the formation of such a catalyst during the discharge which took place in the reaction vessel. The first of these might also explain the high rates in experiments 205 and 215. The fast rates at very high oxygen pressures appeared to be exactly second-order.

Table IV. Comparison of Sutphen's (*18*) Results with Proposed Mechanism

Expt.	Temp., ° C.	$P^{\circ}_{O_3}$, Mm. Hg	$P^{f}_{O_3}$, Mm. Hg	$P^{\circ}_{O_2}$, Mm. Hg	P_{CO_2}, Atm.	t_{obsd}, Sec.	t_{calcd}, Sec.	$\frac{t_{calcd}}{t_{obsd}}$
178	99.5	62.4	42.1	191.8	...	900	956	1.06
183	99.5	63.1	28.4	194.1	6.16	900	882	0.98
186	115.5	62.0	11.3	190.7	1.00	900	890	0.99
189	115.5	63.0	9.9	192.6	6.13	900	780	0.87
210	99.5	15.11	6.75	209.0	...	3000	3423	1.14
202	115.5	31.12	7.48	228.7	...	960	918	0.96
206	99.5	62.37	32.59	387.9	6.00	900	1154	1.29
213	115.5	28.13	8.51	390.4	6.00	1200	1184	0.99
205A	99.5	20.47	15.22	572.1	...	1560	2071	1.33
269	99.5	10.09	5.06	19.07	...	9000	9807	1.09
232	99.5	28.49	20.43	...	...	2400	2948	1.23
275	99.5	88.26	46.94	...	...	1860	1942	1.04
273	99.5	86.07	43.88	755.4	...	1800	2006	1.12
258	115.5	9.20	6.16	18.68	...	1500	1530	1.02
226	115.5	29.00	22.47	...	...	600	693	1.16
262	115.5	87.86	47.86	...	...	600	486	0.81
276	115.5	85.79	34.19	743.1	...	720	630	0.87
233	99.5	28.60	16.12	...	0.262	600	632	1.05
234	99.5	28.76	7.22	...	3.88	600	557	0.93
228	115.5	29.20	3.02	...	4.05	600	377	0.63
215	85.5	62.81	44.02	199.3	...	900	1450	1.61
212	115.5	15.12	7.74	4612	...	4800	10180	2.12
197	115.5	63.61	24.24	4483	...	1800	4054	2.25
198	99.5	62.53	48.28	4079	...	1080	3730	3.46
208	99.5	14.69	10.00	4322	...	7200	26437	3.66
216	85.5	61.08	47.81	4680	...	2700	20495	7.58
287	70.0	89.08	53.33	4564	...	0.15[a]	2.33[a]	15.7
289	70.0	61.36	39.25	4564	...	0.18[a]	2.31[a]	15.5
280	25.0	88.45	76.71	4540	...	1.73[a]	456[a]	264
290	25.0	124.9	108.4	4598	...	2.48[a]	324[a]	262

[a] × 10^5.

Reproducibility. Results. To test the reproducibility of results, a series of 17 experiments was carried out on ozone-oxygen mixtures at temperatures between 80° and 100° C. These all gave rates 0 to 15% above the predicted values. Although the experimental procedure was continually improved, these deviations (which amounted to less than 10% between most of the runs) could neither be eliminated nor explained. During any given experiment the ratio of the actual rate to the predicted rate remained approximately constant. No difference was observed between the two sources of oxygen which were used. High initial rates were observed in those cases where temperature gradients would have been predicted from interpretation of the results of Glissmann and Schumacher. Initial stirring of the ozone-oxygen mixtures had no effect on the rate or the order of reproducibility.

Four experiments were carried out in which 8 to 20 mm. of water vapor was present in the ozone-oxygen mixtures at 90° and 100° C. These gave rates from 12 to 19% above the predicted rates, and there was little correlation between the amount of water present and the magnitude of the rate increase. These rates are considered to be significantly faster than those obtained with the pure ozone-oxygen mixtures. An attempt was made to introduce 0.7 mm. of hydrogen peroxide vapor into a vessel containing approximately 175 mm. of ozone at 90° C. This resulted in an immediate explosion. Hydrogen peroxide (0.2 mm.) was successfully introduced in a similar experiment in which only about 100 mm. of ozone was present. This gave an average rate only 11% faster than the rate predicted in the absence of the peroxide.

The system was then completely rebuilt and all stopcocks were replaced with packless metal valves in an effort to eliminate any source of catalysis which might be caused by the stopcock lubricant. However, there was no evidence that Halocarbon grease is not entirely inert to ozone. Ozone (194 mm.) and oxygen (284 mm.) were sealed off in the opaque reaction vessel which was thermostated at 29.8° C. After 2 weeks, 111 mm. of ozone remained in the vessel; this was heated to 70° C. so that data at two different temperatures could be obtained from the same sample. At 29.8° C. a rapid loss of ozone was observed during the first 5 to 10 hours, and then the rate became almost exactly second-order in ozone over the entire 2-week period. The second-order rate constant was 5.81×10^{-5} liter per mole-second which may be compared with the value of 28.9×10^{-5} which would be predicted by Sutphen's (*18*) proposed bimolecular rate constant and the value of 1.7×10^{-5} which would be predicted by the proposed atomic mechanism. The rate at 70° C. with this same sample was nearly 50% faster than the predicted rate suggesting that some impurity had been included. A control run was made at 90° C. on a similarly prepared sample, and this gave rates 70 to 300 times the rate predicted by our atomic mechanism. It was concluded that metal oxides had been introduced into the reaction vessel. Therefore, this system was abandoned.

A series of experiments was initiated in which the ozone was formed in the reaction vessel by a method similar to that developed by Sutphen (*18*). Purified tank oxygen (400 mm.) was sealed off in the reaction vessel and this was partially condensed by cooling the lower portion of the vessel in liquid nitrogen. A Tesla coil discharge was passed through the vessel above the surface of the liquid and nearly all of the oxygen was converted to ozone in this manner. After the ozone had evaporated at room temperature, the vessel was heated to 70° C. and the rate was followed as usual. The initial run gave rates from 2 to 4 times faster than the predicted rates, and a second run with the same sample of oxygen gave rates which were even faster by another factor of 1.5 to 2. Because it appeared that a catalyst was being formed in the discharge, this procedure was also abandoned.

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DISCUSSION. The cause of the 10% deviations among the various experiments under similar conditions was not discovered, but a possible explanation might be the inclusion of a trace catalyst in varying amounts. The results of most of the other workers were not so reproducible, although only in a very few cases were experiments rerun under nearly identical conditions. Only the results of Glissmann and Schumacher appear to be free of any such uncertainty in the reproducibility (when compared in terms of proposed mechanism), but even in their thorough investigation control experiments were not carried out. Reproducibility results were close enough to those predicted by the proposed atomic mechanism over a wide enough range of conditions to lend considerable support to the claim that these are the only significant reactions which occur in this system.

The results obtained with added water vapor set an upper limit on the effect of water, but it would be difficult to prove that the observed increase in the rate was not due entirely to an impurity introduced with the water vapor. The results with added hydrogen peroxide were somewhat inconclusive, because it decomposes rapidly on the surface of a borosilicate glass vessel at 90° C. During the few minutes which elapsed between the introduction of the peroxide and the taking of the first pressure reading, most of the peroxide may have decomposed. Thus the lack of any large effect of hydrogen peroxide (other than the explosion which it apparently caused) does not prove that it may not have been an important trace catalyst in some of the earlier work or even in the present investigation.

The rates obtained at 29.8° C. were slower by a factor of 5 than the rates which would be expected from Sutphen's (*18*) bimolecular mechanism, even though there was some type of catalysis taking place as shown by the anomalous results obtained at 70° C. with the same sample. Therefore, the low temperature rates obtained by Sutphen cannot be explained by a homogeneous bimolecular reaction. These data set an upper limit on the rate of a possible direct bimolecular reaction, but do not rule out the simple atomic mechanism as the only mechanism even at low temperatures, because some catalysis was obviously occurring. This dual temperature technique would appear to be an interesting method of studying the role of accidental catalysis in this system. The results of this low temperature run point out the high stability of ozone to thermal decomposition at room temperature. Even in this system where impurities are suspected, extrapolation of the observed results would indicate that a sample containing 5% ozone in an atmosphere of oxygen could be stored at room temperature for nearly 2 months before the ozone concentration would fall below 4%. In a system where only the homogeneous atomic mechanism is occurring (if this can be attained), this storage time could be over 6 months.

The two experiments in which the ozone was formed in the reaction vessel point out some of the problems involved in such a technique. The oxygen source and experimental techniques were identical to most of the previous experiments, in which the highest rate ever obtained was only 1.25 times the predicted rate. Therefore, some catalyst must have been formed in the discharge. Most of Sutphen's results are in accord with the proposed mechanism, even though he used this technique in all his experiments. However, in his system the ozone preparation took less than 10 minutes, while in the experiments reported here it required 2 to 3 hours.

Photochemical Decomposition

The photochemical decomposition of ozone has long been cited as an example of one of the few systems in which it is necessary to propose an energy chain mechanism. This came about from the observation that at very short wave lengths quantum yields as high as 6 were observed (*10*), whereas the primary photochemical process

$$O_3 + h\mu \longrightarrow O_2 + O$$

followed by Reactions 2 and 3 would give a maximum quantum yield of 2. Therefore, Reaction 6 is usually included to account for these high quantum yields.

This previously proposed photochemical mechanism is not consistent with the present interpretation of the thermal decomposition, because there is no evidence that Reaction 6 occurs even at very high ozone concentrations. The results obtained with visible light (*16*) also tend to rule out any such energy chain, because they may be explained very well in terms of a simple mechanism involving Reactions 12, 2, and 3 even under conditions where the high quantum yields were observed with ultraviolet light. The value of k_3/k_2 obtained (*2*) from this simple mechanism was 0.0104 mole per liter and may be compared with the value of 0.0053 calculated at 17° C. from the proposed rate constants. This difference should not be considered too seriously until further data are available, because this original work was rather crude and there was some uncertainty in the earlier work as to whether the quantum yield was based on ozone or oxygen. At any rate, the observed quantum yields are definitely a function of wave length, and this would not be the case if an energy chain involving Reactions 3 and 6 were involved.

To arrive at a photochemical mechanism which is consistent with all of the observed photochemical as well as thermal results, the various possible energy levels or excited states of the primary photochemical products should be considered in detail. Such a mechanism has been proposed (*5*), which can account for the high quantum yields observed in the far ultraviolet. However, this is somewhat speculative, because the experimental difficulties encountered in the photochemical studies appear to be even more insurmountable than those encountered in the thermal decomposition. More quantitative data are needed on the photochemical system before its mechanism can be definitely established.

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Implications of Data on the Gas Phase Decomposition of Ozone

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The kinetic data on the decomposition of ozone via oxygen atoms are considered in terms of their implications for the possible existence of direct bimolecular reactions of ozone molecules and energy chains carried by excited oxygen. A direct bimolecular reaction of ozone to form oxygen if it exists at all, must have an activation energy of between 17 and 21 kcal., but not higher. Energy chains carried by excited oxygen are unlikely on several theoretical considerations, in accord with the limits estimated for the rate of such reactions from the data. The anomalies in the rate constants for the reactions $O_3 + M \rightleftharpoons O_2 + O + M$ are understandable in terms of the theory of unimolecular reactions. In the case of ozone it is essentially a unimolecular reaction at its low pressure limit. Finally, the processes occurring in an electric discharge through oxygen are considered. Oxygen atoms are a very rapid catalyst for the synthesis of ozone and the limiting yields are probably fixed by the local temperatures and the processes causing direct dissociation of ozone rather than oxygen atom attack.

The decomposition of ozone, perhaps one of the simplest possible systems from a chemical viewpoint, has been an extremely complex and difficult study kinetically. The reaction is enormously sensitive to homogeneous catalysis by traces of halogens, light, oxides of nitrogen, hydrocarbons, peroxides, and mercury vapor, and to heterogeneous catalysis by metals and metal oxides. Because ozone is produced by passing electric discharges through oxygen, the problem of eliminating these trace catalysts is one of obtaining oxygen free from traces of nitrogen, oxides of nitrogen, and hydrogen-containing compounds such as water, because under the influence of the discharge all will produce one or another of the above-mentioned catalysts. The kinetic study is further complicated by the fact that the reaction is strongly exothermic (34.5 kcal. per mole of ozone), so that temperature gradients of measurable magnitude are quickly established in a flask containing decomposing ozone gas. This self-heating in fact imposes severe limits on the range of experimental condi-

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tions in which the decomposition may be studied, because the limits of the thermal explosion are reached at partial pressures well below 1 atm.

Mechanism of Pyrolysis

Despite these complexities, or eccentricities, it appears that the homogeneous, thermal, gas phase decomposition of ozone can be described by a very simple mechanism, which is a modification of the one first proposed by Jahn (*8*):

$$\mathrm{M} + \mathrm{O_3} \underset{2}{\overset{1}{\rightleftharpoons}} \mathrm{O_2} + \mathrm{O} + \mathrm{M} \; -24.6 \text{ kcal.} \tag{1, 2}$$

$$\mathrm{O} + \mathrm{O_3} \xrightarrow{3} 2\mathrm{O_2} + 93 \text{ kcal.} \tag{3}$$

where M represents a suitably weighted sum of all the substances (including ozone) present in the gas phase. It has recently been shown (*1, 4*) that all of the work on dilute ozone (*5, 12*), most of it not very quantitative, and the more precise and very extensive work on concentrated ozone by Glissmann and Schumacher (*6*) can be fitted to the above mechanism with the results (*1, 4*):

$$\begin{aligned} k_1(\mathrm{M} = \mathrm{O_3}) &= 4.61 \times 10^{12} \exp\,(-24{,}000/RT) \text{ liter/mole-sec.} \\ k_2(\mathrm{M} = \mathrm{O_3}) &= 6.00 \times 10^{7} \exp\,(+600/RT) \text{ liter}^2\text{/mole}^2\text{-sec.} \\ k_3 &= 2.96 \times 10^{10} \exp\,(-6{,}000/RT) \text{ liter/mole-sec.} \end{aligned} \tag{4}$$

The effects of various "foreign" gases are represented by:

$$\mathrm{M} = \mathrm{O_3} + 0.44\,\mathrm{O_2} + 0.41\,\mathrm{N_2} + 1.06\,\mathrm{CO_2} + 0.34\,\mathrm{He} \tag{5}$$

where the coefficients represent the efficiency of the respective gas (relative to ozone) in both activation and deactivation of ozone.

If a stationary state for oxygen atoms is assumed, the above mechanism gives:

$$(\mathrm{O})_{ss} = \frac{k_1(\mathrm{O_3})(\mathrm{M})}{k_2(\mathrm{O_2})(\mathrm{M}) + k_3(\mathrm{O_3})} \tag{6}$$

and for the rate of decomposition of ozone:

$$\begin{aligned} \frac{-d(\mathrm{O_3})}{dt} &= 2k_3(\mathrm{O})_{ss}(\mathrm{O_3}) \\ &= \frac{2k_1k_3(\mathrm{O_3})^2}{k_2(\mathrm{O_2})\left[1 + \dfrac{k_3(\mathrm{O_3})}{k_2(\mathrm{O_2})(\mathrm{M})}\right]} \end{aligned} \tag{7}$$

which differs from the original Jahn (*8*) result by the bracketed term in the denominator of Equation 7. In two extreme cases which are never quite realized in laboratory practice, the rate expression reduces to:

A. Concentrated O_3

$$[k_3(\mathrm{O_3}) \gg k_2(\mathrm{O_2})(\mathrm{M})] \; \frac{-d(\mathrm{O_3})}{dt} \rightarrow 2k_1(\mathrm{O_3})(\mathrm{M}) \tag{8}$$

$$\xrightarrow[\text{(if M}=\mathrm{O_3})]{} 2k_1(\mathrm{O_3})^2 \tag{9}$$

B. Dilute O_3

$$[k_3(\mathrm{O_3}) \ll k_2(\mathrm{O_2})(\mathrm{M})] \; \frac{-d(\mathrm{O_3})}{dt} \rightarrow \frac{2k_1k_3}{k_2}\,\frac{(\mathrm{O_3})^2}{(\mathrm{O_2})} \tag{10}$$

From the above data, $k_3/k_2 = 493 \exp\,(-6600/RT)$ mole/liter, which has the value 0.187 atm. at 30° C. and 2.04 atm. at 100° C. Case A is thus 90% realized at 30° C. only in mixtures containing less than 15 mm. of oxygen and more than 90 mm. of ozone. At 100° C., Case A is 90% achieved in mixtures with less than 100 mm. of oxygen if $O_3 > 100$ mm. Case B is easily achieved at 30° C., but only with difficulty at 100° C.—i.e., at 1 atm. of oxygen only if $O_3 < 0.02$ atm.

These cases illustrate some of the observed paradoxes of the ozone decomposition. Pure ozone decomposes at a second-order rate with an apparent activation energy which changes as the reaction proceeds, from 24 kcal. (k_1) to about 30 kcal. (k_1k_3/k_2). Adding oxygen to pure ozone accelerates its rate of decomposition, while adding oxygen to dilute ozone inhibits its rate of decomposition. (Compare Equation 8 with $M = O_3 + 0.44O_2$ against Equation 10. Addition of foreign gases to pure ozone—e.g., N_2, CO_2—accelerates the rate, while their addition to dilute ozone has no effect.) This results in the well known behavior, observed during single runs with concentrated ozone, that the apparent second-order rate constant continues to increase over the course of the reaction.

Glissmann and Schumacher (*6*) interpreted their data in terms of a mixed mechanism including a direct bimolecular reaction $2O_3 \xrightarrow{B} 3O_2$. In the reinterpretation of these data, Benson and Axworthy (*4*) decided that there was no evidence for such a reaction. [A reappraisal of the more recent work of Ogg and Sutphen (*9*) similarly shows that their data do not require the introduction of such a direct bimolecular reaction.] For such a reaction to contribute, let us say 10% to the scheme proposed, k_B would have to be about 0.2 k_1 (Equation 9) over the pressure and temperature range studied. The frequency factor of Reaction B would be expected to be about 10^{-1} to 10^{-3} times the frequency of collisions which would be about 2×10^{11} liter/mole-sec. If $k_B = 0.2\ k_1$ is set at 100° C., E_B must be between 18 and 21.5 kcal. per mole, depending on the steric factor used. The observed rate of decomposition of concentrated ozone (*1*) at low temperatures, where such a reaction has the best chance of being observed, verifies these frequency factors and activation energies as upper and lower limits, respectively, for such a proposed bimolecular path.

It is very difficult as well as tedious to obtain reproducible rate constants under these conditions, because the slowness of the decomposition is such that even slight amounts of catalysis can throw the results off by a considerable amount.

Energy Chains and Thermal Gradients

Because Reaction 3 is exothermic by 93 kcal., and requires 6 kcal. per mole activation energy, the product oxygen molecules share between them 99 kcal. of excess energy. If this is present as translational energy, each oxygen product molecule will have 49.5 kcal. of excess translational energy which is not expected to be effective in exciting ozone molecules to dissociation. Because of the requirements for momentum conservation, only 3/5 of this energy is actually available for conversion to internal excitation in a collision with a normal ozone, which would be about 20 kcal. This is sufficient for dissociation of ozone. But excess translational energy is always very quickly degraded, so that translationally excited oxygen molecules will not be expected to be efficient as energy chain carriers.

The available energy is not sufficient to excite any but the low-lying, metastable, singlet, electronic states of oxygen (*7*). On grounds of spin conservation not more than one such state should be expected, so that the remaining energy of from 61 to 76 kcal. would be present as vibration plus rotation of the two oxygen product molecules. Of the two electronic states, the lower ($^1\Delta g$) has insufficient energy (22.5 kcal.) to dissociate ozone. The upper state ($^1\Sigma g$) has enough energy (37.6 kcal.), but the collisional transfer to ozone violates spin conservation and would be expected to be very inefficient.

Very little is known about the transfer of vibrational energy from one molecule to another, but for dissimilar species such as oxygen and ozone it would be expected to be very inefficiently transferred in such large amounts as would be required for an energy chain. It seems much more reasonable to expect vibrationally excited oxygen molecules to lose their energy preferentially in collision with other oxygen molecules

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and in steps of 1 or 2 quanta at a time. Thus the *a priori* evidence would oppose the existence of energy chains in this system.

The kinetic evidence against energy chains has been examined by Benson and Axworthy (*1, 4*). If we look at the mechanism for energy chains, the original scheme becomes:

$$\begin{aligned}
&O_3 + M \underset{2}{\overset{1}{\rightleftharpoons}} O_2 + O + M \\
&O + O_3 \xrightarrow{3} 2O_2^* \\
&O_2^* + O_3 \xrightarrow{4} O_2 + O_2 + O \quad \text{(chain)} \qquad (11) \\
&O_2^* + M' \xrightarrow{5} O_2 + M \text{ (deactivation)}
\end{aligned}$$

where M′ is written to point out the different possible efficiencies of various gases in this reaction as opposed to Reactions 1 and 2. Applying the stationary state treatment to both O and O_2^* leads to:

$$-\frac{d(O_3)}{dt} = \frac{2k_1k_3(M)(O_3)^2}{2k_2(O_2)\left[1 + \frac{k_3(O_3)}{k_2(M)(O_2)}\left\}1 - \frac{2}{\left[1 + \frac{k\,(M')}{k_4\,(O_3)}\right]}\right\{\right]} \qquad (12)$$

which differs from the previous expression, Equation 7, by the term in brackets, involving the ratio $k_5(M')/k_4(O_3)$. The maximum expected value of this ratio would be $\leqslant 1$ in pure ozone—i.e., $M' = O_3$—which would imply equal chances of excitation or deactivation on collision of O_2^* with ozone. Because a value of 1 would imply explosion of pure ozone, it is certain that the true value is considerably less than 1.

This has the net effect of increasing the stationary state of oxygen atoms above the thermodynamically expected limit and thus enhancing the rate. However (*1, 4*), such enhancement would be expected to depend solely on the ratio of $(O_3)/(M)$ and to be independent of temperature. Benson and Axworthy have shown that there is no evidence to support such an effect and that the enhancements observed are explicable on grounds of the temperature gradients produced by the decomposition. In terms of available data, the precision is sufficient to conclude that $k_5/k_4 \geqslant 15$, which would support the previously stated speculations on energy transfer.

Unimolecular Features

The rate constants found for the individual steps 1 and 2 show a number of anomalies. In the first place, the activation energy for Reaction 1 is less than the energy change for the process, which leads to the corollary anomaly that the activation energy of 2 is negative. Lastly, the frequency factor of 1 is greater than collision frequencies by a factor of about 20. Reaction 3, aside from its great exothermicity, has a normal frequency factor for such a reaction and presents no strange features. The steric factor is about 0.1, which is just about what one would calculate from transition state theories.

These anomalies appear understandable, however, when the decomposition of ozone is looked upon from the point of view of a unimolecular reaction at its low pressure limit. With three internal vibrations and a maximum of two active rotations, the mean lifetime of the average ozone molecule undergoing decomposition is expected to be very short (*2*) compared to collision times, even at 1-atm. pressure. In consequence, the stationary state concentrations of critically energized O_3^* molecules, which contribute to the over-all decomposition, are far below the concentrations calculated at equilibrium and the slow step in the reaction becomes the rate of activation of ozone.

If we designate by $(O_3)_i^*$ the stationary state concentration of ozone mole-

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cules having internal energy $E \geqslant E^* = \Delta E_1°$, in excess of that required for decomposition, the detailed mechanism can be written as:

$$\begin{gathered} \mathrm{M} + \mathrm{O}_3 \underset{b_i}{\overset{a_i}{\rightleftharpoons}} (\mathrm{O}_3)_i{}^* + \mathrm{M} \\ (\mathrm{O}_3)_i{}^* \underset{d_i}{\overset{c_j}{\rightleftharpoons}} \mathrm{O}_2 + \mathrm{O} \\ \mathrm{O} + \mathrm{O}_3 \xrightarrow{3} 2\mathrm{O}_2 \end{gathered} \tag{13}$$

If we now apply stationary state methods to $(O_3)_i{}^*$ and O we find:

$$(\mathrm{O})_{ss} = \frac{\Sigma c_i(\mathrm{O}_3)_i{}^*}{d(\mathrm{O}_2) + k_3(\mathrm{O}_3)} \tag{14}$$

where $d = \Sigma d_i$ and:

$$(\mathrm{O}_i)_{ss}{}^* = \frac{a_i(\mathrm{O}_3)(\mathrm{M})}{b_i(\mathrm{M}) + c_i} + \frac{c_i d_i(\mathrm{O}_2)(\mathrm{O})_{ss}}{b_i(\mathrm{M}) + c_i} \tag{15}$$

where, on substitution and rearrangement:

$$\Sigma c_i(\mathrm{O}_i)^* = \frac{(\mathrm{M})(\mathrm{O}_3)\Sigma\left(\dfrac{a_i c_i}{b_i\mathrm{M} + c_i}\right)[d(\mathrm{O}_2) + k_3(\mathrm{O}_3)]}{(\mathrm{M})(\mathrm{O}_2)\Sigma\left(\dfrac{b_i d_i}{b_i\mathrm{M} + c_i}\right) + k_3(\mathrm{O}_3)} \tag{16}$$

[It is assumed here that oxygen atoms are at thermal equilibrium. This is valid, because they are involved only in second-order or higher reactions (*3*). The sums in these expressions are over-all internal energy states whose total energies are in excess of $\Delta E_1°$.]

This gives finally, for the rate of decomposition of ozone:

$$\frac{-d(\mathrm{O}_3)}{dt} = \frac{2k_3(\mathrm{M})(\mathrm{O}_3)^2\left[\Sigma\left(\dfrac{a_i c_i}{b_i\mathrm{M} + c_i}\right)\right]}{d(\mathrm{M})(\mathrm{O}_2)\left[\Sigma\left(\dfrac{b_i d_i/d}{b_i(\mathrm{M}) + c_i}\right)\right] + k_3(\mathrm{O}_2)} \tag{17}$$

At high pressures where $b_i\mathrm{M} > c_i$ for all energy states of $(O_3)_i{}^*$ contributing significantly to the reaction, this reduces to:

$$\frac{-d(\mathrm{O}_3)}{dt} \xrightarrow[\mathrm{M}\to\infty]{} \frac{2k_3(\mathrm{O}_3)^2\Sigma\left(\dfrac{a_i c_i}{b_i}\right)}{d(\mathrm{O}_2) + k_3(\mathrm{O}_3)} \tag{18}$$

The densities needed for such a condition to be fulfilled are satisfied virtually only in solution, not in the gas phase.

At low pressures, on the other hand, where the bulk of $(O_3)_i{}^*$ which are important decompose much faster than they collide (the condition actually met with in the gas phase reaction):

$$\frac{-d(\mathrm{O}_3)}{dt} \xrightarrow[\mathrm{M}\to 0]{} \frac{2k_3(\mathrm{M})(\mathrm{O}_3)^2(\Sigma a_i)}{(\mathrm{M})(\mathrm{O}_2)\left(\Sigma\dfrac{b_i d_i}{c_i}\right) + k_3(\mathrm{O}_3)} \tag{19}$$

If this is compared with the previous expression (Equation 7) we can make the following identifications:

$$\begin{aligned} k_1 &= \Sigma a_i = \Sigma K_i b_i \\ k_2 &= \Sigma\frac{b_i d_i}{c_i} \end{aligned} \tag{20}$$

where $K_i = a_i/b_i =$ the equilibrium constant for the concentration of $(O_3)_i{}^*$. If now it is assumed that b_i may be replaced by $\lambda Z = \lambda \times 2 \times 10^{11}$ liter/mole-sec. where Z

is the collision frequency of $O_3{}^*$ and O_2 (assumed to be 2×10^{11}) and λ is the probability of deactivation of $O_3{}^*$ on collision, K_i can be estimated as follows.

The experimental activation energy gives us the difference between the average energy of the states that contribute to reaction, $(O_3)_i{}^*$, and normal ozone. At 100° C. this gives 25.3 kcal. of internal energy for the average $(O_3)_i{}^*$ that is responsible for reaction. The vibration frequencies of Wilson and Badger (*11*) are used here (705, 1043, and 1110 cm.^{-1}); 1.3 kcal. of the above energy are in rotation.

If we now compute the number of ways of distributing this energy among the internal modes of ozone, we find approximately 65 vibrational states, assuming that small discrepancies may be taken up in rotation and by anharmonicities. From a statistical point of view we can approximate $K_i = g_i e^{-E_i^*/RT}$ where $g_i \sim 65$ and $E_i^* = E_{\text{act.}} = 24$ kcal.

If the moments of inertia have changed this should be included in g_i, as should any significant changes in frequency and contributions from anharmonicity.

This finally yields for A_1, the pre-exponential factor of k_1, the value $1.3\ \lambda \times 10^{13}$ liter/mole-sec., which on comparison with the experimental value of k_1 (for $M = O_2$), gives $\lambda_{O_2} \approx 1/6$, which seems of reasonable order of magnitude.

Benson and Axworthy (*4*) have shown by a similar calculation that $\lambda_{O_2} \leqslant 1/50$, and from efficiencies of triple collisions that $\lambda_{O_2} \leqslant 1/140$. The true value is probably somewhere near 1/50, which is also consistent with our deduction on the efficiency of energy chains.

The high pre-exponential factor of Reaction 1 is thus due to a very large entropy of activation for $O_3{}^*$. Such large factors are generally not met with in bimolecular reactions. They do occur in this special type of bimolecular reaction, however, which involves energy transfer. Rice (*10*) has discussed similar effects in the closely related reactions $M + X_2 \rightarrow M + 2X$, which have even higher frequency factors.

Competitive Reactions Involving Oxygen Atoms

The Ozonizer. The data obtained permit us to answer some questions concerning competitive reactions of oxygen atoms and in particular the reactions going on in an ozonizer, which are responsible for ozone production.

There are three principal paths for the production of ozone from oxygen in an ozonizer. These involve synthesis from atoms, from metathetical reactions of metastable molecules, and finally from dissociative recombinations of ions. Illustrative examples of each might be:

$$\begin{aligned} &O + O_2 + M \xrightarrow{2} O_3 + M \\ &O_2{}^*({}^3\Sigma_u{}^+) + O_2 \xrightarrow{7} O + O_3 \\ &O_2{}^- + O_2{}^+ \xrightarrow{8} O_3 + O + \text{energy} \end{aligned} \tag{21}$$

Competing with these processes for the destruction of both oxygen atoms and ozone is:

$$\begin{aligned} &O + O_3 \xrightarrow{3} 2O_2 \\ &O + O + M \xrightarrow{9} O_2 + M \end{aligned} \tag{22}$$

From the point of view of ozone production, it can be shown from the data that Reaction 3 will not compete seriously with the synthetic Reaction 2 under conditions usual in ozonizers. Thus $R_2/R_3 = k_2(O_2)(M)/k_3 = 5.3\ (M)(O_2)/(O_3)$ at 30° C. and $0.2(M)(O_2)/(O_3)$ at 100° C. When $M = 1$ atm., this gives for the limiting stationary concentrations of (O_3) when $R_2 = R_3$; $(O_3)/(O_2) = 5.3$ at 30° C. and 0.2 at 100° C. Both values are in excess of ozone yields actually achieved in ozonizers. If we assume that Reaction 9 proceeds at every termolecular collision, we can show that it will be faster than Reaction 2 as long as the ratio $O/O_2 \leqslant 1/100$.

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It thus appears that a possible and fast mechanism for the production of ozone is by way of oxygen atoms which act as catalysts for the conversion of $O_2 \rightarrow O_3$. Because oxygen atoms are essentially slow in destruction of ozone, the limiting stationary process must be the destruction of ozone via the same type of process which is responsible for oxygen destruction—e.g., electron bombardment—or else the increase in temperature of the discharge which would finally provoke the thermal decomposition of ozone and make Reaction 3 a limiting process.

This can be rather serious, because the chief mode of removal of oxygen atoms if their concentration is 1% of oxygen or greater, is by the exothermic Reaction 9, producing 119 kcal. per mole of oxygen. Because the half life under these conditions ($O_2 = 1$ atm.) will be of the order of 1 to 5 microseconds, rather high instantaneous temperatures can be produced, heat diffusion being relatively slow compared to these times.

An alternative mode of reaction, which is not so fast and which could lead in principle at least to the establishment of high ozone concentrations, might be via the generation of large concentrations of metastable $O_2(^3\Sigma_u{}^+)$. Their long lifetime with respect to radiative processes and collision processes could lead to delayed production of ozone (Reaction 7) outside of the discharge zone and hence to inherently greater yields. Unfortunately, nothing appears to be known concerning their reaction.

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Kinetic Considerations of Efficiency of Ozone Production in Gas Discharges

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Various schemes for the production of ozone from oxygen in an electric discharge are considered. There are a number of low energy paths available through O^{-1} ions and at least one excited state of O_2. Despite the availability of these paths, the efficiency of the discharge is very low, partly because of the slow thermal dissipation of energy in the discharge itself. The remainder results from the relatively high gas temperature occurring in the discharge, which causes thermal decomposition of the ozone.

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The synthesis of a metastable material from its elements presents conflicting aspects of kinetic, thermodynamic, and practical interest. Ozone production from oxygen is typical of many such syntheses, but it is extreme. The enthalpy change is very large, $\Delta H°$ (1 atm.) $= +34$ kcal. per mole, at the same time that the entropy change is both fairly large and unfavorable, $\Delta S°$ (1 atm.) $= -16.7$ cal. per mole° C. (*6*). Thus, there is no reasonable set of temperatures and pressures at which the equilibrium constant would be sufficiently large to make the use of catalysts feasible, if such existed. The reversible oxidation of oxygen in an electrochemical cell might be the most efficient method of production, and its expenditure of energy might be closest to the theoretical, $\Delta F° = +39$ kcal. per mole. However, electrochemical methods have not succeeded in competing with gas discharge methods.

The reaction,

$$68 \text{ kcal.} + 3O_2 \rightarrow 2O_3 \qquad (1)$$

should take place efficiently in the gas phase, but the requirements are rather severe. Because of the unfavorable free energy charge, the energy input of 68 kcal. cannot be made available thermally. It must be provided in the form of excited states or atoms of O, which react to form O_3 predominantly. Thus, the system must be converted to one whose free energy is higher than O_3, so that the conversion to O_3 will be spontaneous. If O_2 molecules could be excited to a metastable state, O_2*, possessing about 34 kcal. per mole, then the reaction

$$2O_2^* + O_2 \rightarrow 2O_3 \qquad (2)$$

could occur as a thermoneutral termolecular (or two consecutive bimolecular) process at a reasonable rate. The method of excitation must not destroy O_3, and the competing second-order process of collisional de-excitation of O_2* must be slow compared to Reaction 2. There is a metastable state of O_2, $(^1\Sigma_g{}^+)$, which is 37.5 kcal. per mole

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above the ground state of O_2. This should fulfill the requirements, but there is no evidence that it can participate in such a reaction. Theoretically, Reaction 2 is not favored, as it involves a change in spin multiplicity. It is also in conflict with data on the decomposition of ozone. If Reaction 2 were at all measurable, its reverse reaction should be extremely fast. Benson and Axworthy (*1, 2*) have shown, however, that the reverse of Reaction 2 must have an activation energy in excess of 20 kcal. if its pre-exponential factor is 2×10^9 liters/mole-sec. Thus, k_2 will be too small for Reaction 2 ever to be fast in the range from 0° to 100° C. Higher temperatures cannot be considered, because of the increasing rate of decomposition of O_3 with temperature by an O atom mechansim. Any such low energy path would be incompatible with the existence of O_3 at room temperature. In calculating the efficiency of such a process, the mode of excitation must be considered. The production of photons is very inefficient energetically, and the absorption intensities would be extremely small for the production of such metastable states.

The first known metastable state, compatible with the data on O_3 decomposition, which could lead to O_3 formation is ${}^3\Sigma_u{}^+$ at 103 kcal. above the ground state. This state could produce O_3 by:

$$O_2({}^3\Sigma_u{}^+) + O_2 \rightarrow O_3 + O + 10 \text{ kcal.} \tag{3}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{4}$$

which should be reasonably fast at room temperature (*1, 2*). Such a scheme could produce O_3 at a cost of 51.5 kcal. per mole, neglecting the inefficiency of producing the ${}^3\Sigma_u{}^+$ and the losses by deactivation. There is very little information on the chemical reactions of this state. The photochemical synthesis (*7*) of O_3 at 2537 A., $P \sim 1300$ atm. and $\Phi(O_3) \sim 1.14$, can be explained by it. The state produced is the ${}^3\Sigma_u{}^+$ by a forbidden absorption.

In the gas discharge method, ozone is produced from O atoms, which were produced by dissociating O_2 by inelastic collisions of electrons. The over-all reaction is:

$$\left.\begin{aligned} \tfrac{1}{2}O_2 + e^{-1} &\rightarrow e^{-1} + O - 59 \text{ kcal.} \\ M + O + O_2 &\xrightarrow{\text{Eq. 4}} O_3 + M \end{aligned}\right\} \tag{5}$$

Neglecting the energy of producing excitation electrons, the cost is 59 kcal. per mole. Current figures (*8*) of about 410 kcal. per mole have been given for large scale commercial ozonizers. The threshold energy for these electrons is 118 kcal. per mole (5.09 e.v.). Lower energy processes involving the abundant negative ions, O^{-1} and $O_2{}^{-1}$, should be possible in a gas discharge in O_2.

A probable initiation process requiring only 3.6-e.v. threshold electrons is dissociative attachment,

$$e^{-1} + O_2 \rightarrow O + O^{-1} - 83 \text{ kcal.} \tag{6}$$

using the recent values for the electron affinities of O^{-1} and $O_2{}^{-1}$ of 1.5 e.v. (*3*) and 1 e.v. (*5*), respectively. If this is followed by Reaction 4 plus

$$O^{-1} + O_2 \rightarrow O_3 + e^{-1} - 10 \text{ kcal.} \tag{7}$$

which should be relatively fast even at 25° C., the total cost for O_3 will be only 41.5 kcal. per mole. An exothermic process, competing with Reaction 7 at 1 atm., with very low activation energy is

$$O^{-1} + O_2 + O_2 \rightarrow O_3 + O_2{}^{-1} + 13 \text{ kcal.} \tag{8}$$

This may be faster than Reaction 7, but it is essentially wasteful. The temperature must be sufficiently high so that the equilibrium

$$e^{-1} + O_2 \rightleftharpoons O_2{}^{-1} \tag{9}$$

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lies largely to the left; otherwise the electron is lost. This is probably the case at 25° C. and the low electron densities prevalent in gas discharges. Reaction 9 and its reverse are likely to be very slow at room temperature because they will be collision controlled—i.e., $M + O_2 + e^{-1} \rightarrow O_2^{-1} + M$.

The following termolecular process is the only one in the discharge which does not use O atoms to make O_3:

$$e^{-1} + O_2 + O_2 \rightarrow O_3 + O^{-1} - 60 \text{ kcal.} \qquad (10)$$

It would require a threshold electron energy near 2.6 e.v. If this reaction is followed by Reaction 7 or 8, it would cost only 30 kcal. per mole, or less than the previous minimum theoretical estimate. This can occur only because the cost of producing the 2.6-e.v. electrons, which is not small, is neglected. This process would not be probable unless there were an excited state of O_2^{-1} about 4.1 e.v. above the ground state, which does not appear likely (*5*).

In all these ionic processes, O^{-1} and e^{-1} are O_3 destroyers. The equilibria for the following reactions lie far to the right:

$$O^{-1} + O_3 \xrightarrow{11} O_2 + O_2^{-1} + 82 \text{ kcal.} \qquad (11)$$

$$e^{-1} + O_3 \xrightarrow{12} O_2 + O^{-1} + 10 \text{ kcal.} \qquad (12)$$

These reactions probably require no activation energy and so are very fast.

Although these relatively rapid, kinetic processes produce O_3 at a cost of from 30 to 59 kcal. per mole, most industrial and laboratory processes have efficiencies some 10-fold lower (*8*). All the postulated mechanisms involve electrons of fairly high energies. There is a considerable energy cost in maintaining such a high temperature electron gas in a discharge. Even for a photochemical synthesis, the energy cost is high for producing photons of the required wave length. Also, chemical processes in the discharge dissipate energy thermally. For every mole of O_3 produced by Reaction 4, 24.5 kcal. of heat will be liberated. Similarly, O_3 is attacked by O, by O^{-1}, and by e^{-1}. The reaction of $O + O_3 \rightarrow 2O_2$ liberates 93 kcal. of heat, O^{-1} (Reaction 11) liberates 82 kcal., and e^{-1} (Reaction 12) liberates 10 kcal. In addition, excitation and ionization of O_2 are considered energy-wasting processes.

Because all heat dissipated in the gas must eventually be conducted to the walls, the maintenance of a low temperature in the discharge requires a narrow gap (walls close together), low currents, and low space velocities (low specific rates of O_3 production). These requirements are opposite to the conditions which would be suggested by the known sensitivity of ozone to wall catalysis and the enhanced rate of destruction of such carriers as O, O^{-1}, and e^{-1} at walls. All of these contribute to low efficiency O_3 production. To the extent that heat is not successfully dissipated, the mean temperature rises and the thermal decomposition of O_3 becomes increasingly important.

A simplified scheme represents most of the important processes in producing and destroying O_3 in a typical gas discharge:

$$\left.\begin{aligned} e^{-1} + O_2 &\xrightarrow{j} 2\,O + e^{-1} \\ O + O_2 + M &\xrightarrow{\text{Eq. 4}} O_3 + M \\ O + O_3 &\xrightarrow{\text{Eq. 13}} 2\,O_2 \\ e^{-1} + O_3 &\xrightarrow{\text{Eq. 14}} O_2 + O + e^{-1} \end{aligned}\right\} \qquad (15)$$

Processes involving O_2^{-1} and O^{-1} are minor in comparison, and their features are essentially the same. Probably half or more of the O_3 produced comes from Reaction 4.

The reactions $O + \text{wall} \rightarrow \frac{1}{2}\ O_2$ and $O + O + M \rightarrow O_2 + M$ may be ignored, because they will not be important until $O/O_2 > 0.01$, an unlikely ratio at 1 atm. of O_2. The reverse of Reaction 4 may be included, in principle, in Process 14. As O atoms have a half life at 1 atm. of O_2 of about 10^{-5} second (*1, 2*) by Reaction 4, stationary states are quickly established in the discharge even at very high flow velocities. If the usual stationary state conditions are applied to O and O_3, the maximum possible concentration of O_3 is given by its stationary state:

$$\left(\frac{O_3}{O_2}\right)^2 \frac{k_{14}}{k_j} + \left(\frac{O_3}{O_2}\right) - \frac{k_4(M)}{k_{13}} = 0 \tag{16}$$

Two limits are possible for the ratio O_3/O_2, depending on whether $4k_{14}/k_j$ is very large or small:

$$\left(\frac{O_3}{O_2}\right)_{\max} \begin{cases} \xrightarrow{4k_{14} \gg k_j} \left[\dfrac{k_j k_4(M)}{k_{14}\, k_{13}}\right]^{1/2} \\ \xrightarrow[4k_{14} \ll k_j]{} \dfrac{k_4}{k_{13}}(M) \end{cases} \tag{17}$$

With the usual high voltage arc, the electron temperature is of the order of 20 to 50 e.v. For the bulk of the electrons, k_j should not be too different from k_{14}, although perhaps larger by a factor of about 3 to 10. The ratio will be independent of gas temperature. The ratio $k_4(M)/k_{13}$ can be readily calculated from the data of Benson and Axworthy (*1, 2*) and, at $M = 1$ atm. of O_2, has the values 2.3(27° C.), 0.20(100° C.), 0.063(150° C.), 0.024(200° C.), and 0.006(300° C.). Even if $k_{14}/k_j = 100$, maximum yields of O_3 of the order of 15% at 27° C. and 4.5% at 100° C. should be obtained. However, the yields are strongly dependent on the gas temperature.

The temperature equation in an ozonizer is

$$\frac{K}{dC_p} \nabla^2 T + \frac{1}{dC_p} \dot{Q} = \frac{\partial T}{\partial t} \tag{18}$$

where K = thermal conductivity, d = density, C_p = specific heat at constant pressure, T = temperature, t = time, and $\dot{Q}$ = specific rate of heat production in the gas. If this is idealized as a thin layer of gas flowing between infinite plates of separation $2x_0$ cm., the problem simplifies to a one-dimensional flow. The stationary state temperature distribution is, assuming $K = \infty$ at the walls and T_w = wall temperature,

$$T - T_w = \frac{\dot{Q}(|x| - x_0)^2}{2K} \tag{19}$$

where x is measured from a plane half way between the walls.

The solution of the time-dependent problem for an initial uniform temperature distribution is known (*4*). Constant density is assumed, but the correction is not important except for large gradients. The mean time required to establish this distribution is given by

$$t_{1/2} \sim \frac{2x_0^2 d}{K} C_p \tag{20}$$

For O_2 at 1 atm., 25° C., and $2x_0 = 0.3$ cm., $t_{1/2} \sim 0.25$ second. For much shorter reaction times, conduction is ineffective and the reaction can be considered adiabatic. As temperatures may be extremely high, this provides a sharp limit on the rate of production. One solution might be pulse operation in which O atoms are produced in less than 10 μsec. and then react to form O_3. Unfortunately, the heat liberated in this process would produce catastrophic temperatures, because it would be produced in the next 10 μsec.

The average temperatures, $\dot{T}$, are obtained by integrating Equation 19 between the walls.

$$\dot{T} - T_w = \frac{\dot{Q}x_0^2}{6K} = \frac{T_M - T_w}{3} \tag{21}$$

where T_M is the maximum stationary temperature which occurs at the center of the vessel (Equation 19). If 5% production of O_3 from pure O_2 is assumed in a residence time of 1 second at an average energy dissipation of 350 kcal. per mole of O_3, then $T_M - T_w = 150°$ C., and $\dot{T} - T_w = 50°$ C. Although the conditions are close to those of usual operations, the temperatures are rather high and provide a sharp limit on the maximum possible O_3 concentrations. Longer residence times should reduce these temperatures. In practice, there would be a more wasteful dissipation of heat in maintaining the discharge over large periods.

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Kinetics of Photolysis of Low Concentrations of Nitrogen Dioxide in Air

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Rate constants obtained at high concentrations are valid for estimating the rates of reaction at low partial pressures of atmospheric contaminants. Kinetic studies may be carried out at trace concentrations. Results are given for determining the rate of reaction of nitrogen dioxide with ozone.

Photochemical studies using trace reactant concentrations have been reported with increasing frequency in recent years, largely because of a rapidly developing interest in the chemistry of polluted atmospheres. These studies have been illuminating, but the exacting procedures of chemical kinetics necessary to obtain rate constants (*1*) were not followed.

Photochemical reactions that occur in polluted atmospheres have been studied. Because nitrogen dioxide should be important in these reactions, investigation was directed to reactions of this compound; its photolysis at trace concentrations was carried out in highly purified air. The purpose was to determine whether the pertinent rate constants measured in the usual pressure ranges were valid at the very low partial pressures of atmospheric contaminants and to determine the feasibility of carrying out kinetic studies at trace concentrations. Detailed kinetic studies at concentrations below 5 p.p.m. in purified air show that rate constants have been valid in this range.

Instruments and Apparatus

Instrumentation for the research was developed prior to formulation of the problem. This fortunate situation arose because the instruments were developed for monitoring the lower atmosphere for ozone, nitric oxide, and nitrogen dioxide; these compounds are usually present in polluted atmospheres at concentrations below 1 p.p.m. by volume. On hand were an automatic recording nitrogen dioxide analyzer (*11*), a neutral potassium iodide oxidant recorder (*8*), and an ozone photometer (Model 53 ultraviolet, Harold Kruger Instruments, San Gabriel, Calif.). Each of these instruments has a sensitivity of 1 to 2 p.p.h.m. parts of carrier gas at atmospheric pressure. Without their prior development, the photochemical study would have been impossible.

The flow sheet for the apparatus is shown in Figure 1. A carrier gas, usually air, is blown through the apparatus with a small diaphragm pump. From the pump, the air passes through a purification train, a mixing manifold, a reaction vessel, and an analysis manifold. In the purification train, the air passes through a glass wool plug, a Lectrodryer (Pittsburgh Lectrodryer Co., 500 32nd St., Pittsburgh, Pa.), a Drierite tower, an Ascarite tower, and a second Drierite tower. It then passes through a Millipore filter, a platinum catalyst furnace, and two traps cooled by liquid oxygen,

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the second of which is packed with activated charcoal. The air then passes through a mixing manifold consisting of three Venturi-type mixers. At the throat of each mixer is a side tube for introducing the gases to be studied. (A Drierite column is shown in Figure 1, but this was replaced by the Lectrodryer.)

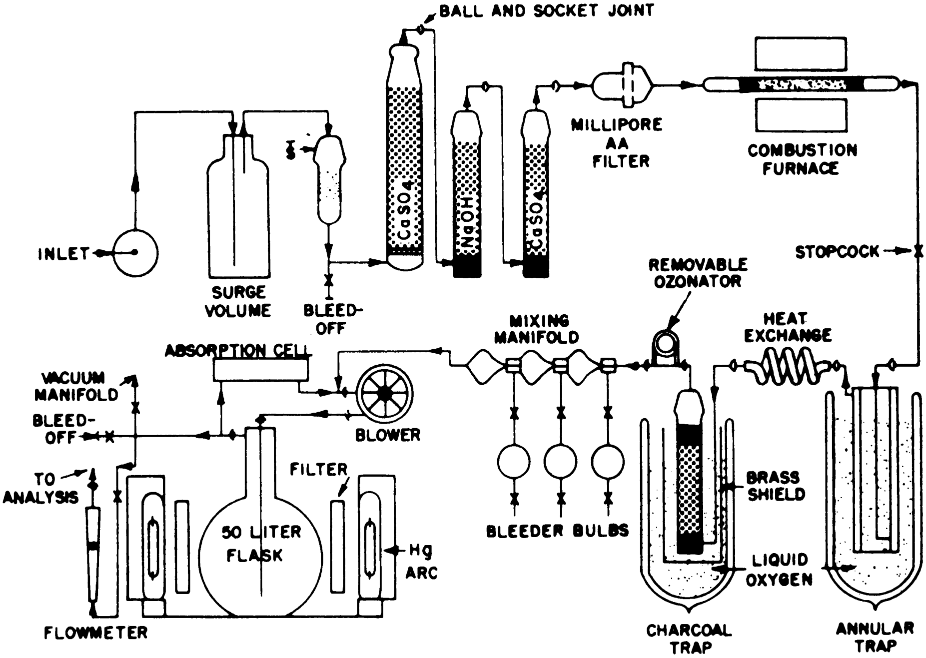

Figure 1. Schematic flow sheet of air-purification train, mixing manifold, and reaction vessel

Nitrogen dioxide, for example, is added by means of a bleeder bulb to the throat of one of the mixers. The air containing nitrogen dioxide enters the 50-liter reaction flask through the throat of an all-glass blower. The blower circulates air in the flask and through a bypass to a Kruger ozone photometer. The air then passes to the analytical section. This section consists of a continuous nitrogen dioxide analyzer, a neutral potassium iodide oxidant recorder, and, when necessary, a second Kruger photometer.

Experimental

The light intensity, studied in the reaction flask using uranyl oxalate as an actinometer, was determined with considerable accuracy. Relative light intensities are shown in Figure 2 in approximately the correct positions in the flask cross sections. The light intensity in the center of the flask is set equal to 1.00.

The absorption coefficient of nitrogen dioxide was measured for several mercury lines by Holmes and Daniels (*5*). The resolved spectra of the nitrogen dioxide-nitrogen tetroxide system were separated by Hall and Blacet (*4*). The value they found for the absorption coefficient at 3660 A. was in essential agreement with that obtained by Holmes and Daniels. The absorption cross section of 5.8×10^{-19} sq. cm. for nitrogen dioxide at 3660 A. was calculated from the data of Holmes and Daniels.

The photolysis of nitrogen dioxide has been studied by Norrish (*9*), Baxter and Dickinson (*2*), Holmes and Daniels (*5*), and Hall (*3*). A recent study was made by Norrish and Thrush (*10*).

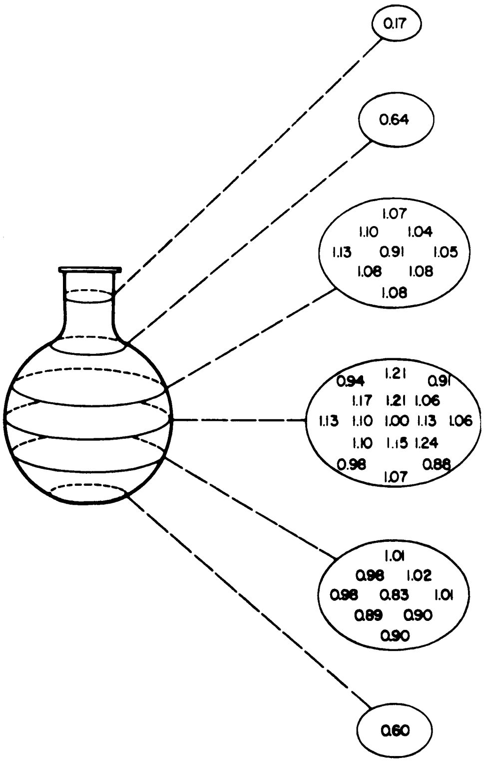

Figure 2. Relative light intensities in 50-liter flask

Starting near 3660 A. and going to shorter wave lengths (3130 A.), the photolysis proceeds by

$$h\nu + NO_2 \rightarrow NO + O \qquad (1)$$

with a quantum yield near unity. Following Reaction 1,

$$O + O_2 + M \rightarrow O_3 + M \qquad (2)$$

$$O_3 + NO \rightarrow O_2 + NO_2 \qquad (3)$$

where $M = N_2$ and/or O_2, may be presumed to occur. All quantities are known for calculating the rate of production of oxygen atoms, because Reaction 2 is fast, the rates of producing oxygen and ozone are equal. From the rate of formation of ozone and the steady-state ozone concentration, the rate of Reaction 3 can be calculated.

A plot of the ozone levels obtained in the photolysis of nitrogen dioxide is shown in Figure 3 together with the theoretical curve and least squares fit of the data. From this, k_3 was 3.0×10^7 liter mole^{-1} sec.$^{-1}$, compared with a value of 1×10^7 obtained by extrapolating the data of Johnston and Crosby (*6*) from —42° C. to room temperature. The observed steady-state ozone levels are in agreement with the rise and decay times of the ozone levels upon opening and closing the shutters. Although Reaction 3 is among the fastest measured by direct observation, the decay of ozone upon shuttering the arcs requires several minutes. This demonstrates the effectiveness of studying fast reactions using trace concentrations of reactants.

When concentrations of nitrogen dioxide above 1 p.p.m. are photolyzed in air at

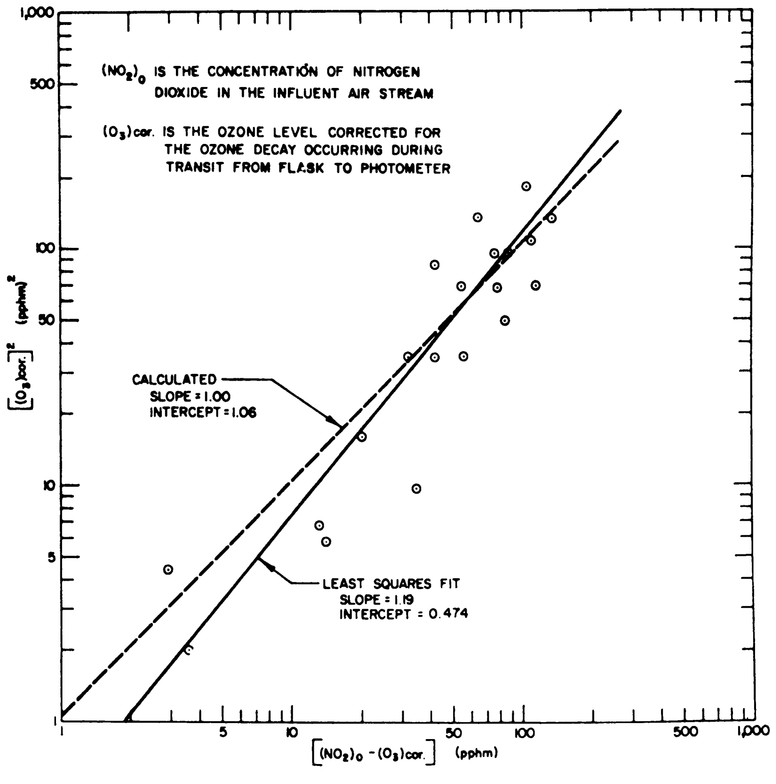

Figure 3. Calculated and observed ozone levels in photolysis of nitrogen dioxide in purified dry air

atmospheric pressure, a transient ozone peak results. This effect has been ascribed to the reaction

$$O + NO_2 \rightarrow O_2 + NO \qquad (4)$$

At least two additional reactions must be taken into account:

$$M + O + NO_2 \rightarrow NO_3 + M \qquad (5)$$

$$NO_3 + NO \rightarrow 2NO_2 \qquad (6)$$

assuming Reaction 6 to be fast and Reaction 5 to be rate-determining. To separate the rate constant for Reaction 4 from that of Reaction 5, nitrogen dioxide was photolyzed at concentrations below 5 p.p.m. in nitrogen at atmospheric pressure and at a nitric oxide–nitrogen dioxide ratio sufficiently low to keep the reaction.

$$M + O + NO \rightarrow NO_2 + M \qquad (7)$$

from competing. Under these conditions, the quantum yield of nitrogen dioxide disappearance had a value of 0.5. From this

$$k_5 \cong 3k_4$$

and the net effect of Reactions 4, 5, and 6 is to lead to the transient ozone peak. As the nitric oxide–nitrogen dioxide ratio increases in the photolysis of nitrogen dioxide in nitrogen, the quantum yield of nitrogen dioxide disappearance approaches zero. The ratio of the rate of Reaction 7 to Reaction 4 plus 5 can be obtained from the relation-

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ship of the quantum yield to this ratio. If low concentrations of oxygen are substituted for nitric oxide and the quantum yield is measured as a function of the oxygen-nitrogen dioxide ratio, the ratio of the rate of Reaction 8 to the rates of Reaction 4 plus 5

$$O + O_2 + M \rightarrow O_3 + M \tag{8}$$

can also be obtained. Because the rate of Reaction 8 is known, the rates of Reactions 4, 5, and 7 can be obtained. With this information, the transient ozone peak may be described qualitatively and a quantitative mechanism provided for its description. Therefore, several systems are available for measuring the rates of oxygen atom reactions. For example, in the photolysis of nitrogen dioxide in nitrogen at high ratios of nitric oxide to nitrogen dioxide, the only significant reactions are 1 and 7:

$$NO_2 + h\nu \rightleftarrows O + NO \tag{1,7}$$

This system is being used in a study of the rates of reaction of atomic oxygen with various materials.

A second rate of a reaction studied at high partial pressures was measured at low concentrations: In the reaction of ozone with nitrogen dioxide,

$$O_3 + NO_2 \rightarrow NO_3 + O_2 \tag{9}$$

$$NO_3 + NO_2 \rightarrow N_2O_5 \tag{10}$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \tag{11}$$

Because the 50-liter flask served as a continuous flow stirred tank reactor, the rate constant, k_9 was easily obtained by two semi-independent methods.

$$\frac{d(NO_2)}{dt} = -2k_9\,(NO_2)_s(O_3)_s = Q/V\,[(NO_2)_s - (NO_2)_o]$$

$$\frac{d(O_3)}{dt} = -k_9\,(NO_2)_s\,(O_3)_s = Q/V\,[(O_3)_s - (O_3)_o]$$

In these equations, $(NO_2)_s$ and $(O_3)_s$ are the steady-state concentrations of nitrogen dioxide and ozone, respectively, while $(NO_2)_O$ and $(O_3)_O$ are their concentrations in the influent stream. Q is the air flow rate through the reactor, and V is the reaction volume. The results of this study are given in Table I.

Table I. Determination of Rate of Reaction of Nitrogen Dioxide with Ozone

			k_9, P.P.H.M.$^{-1}$ Min.$^{-1}$	
Q/V, Min.$^{-1}$	$(NO_2)_o$, P.P.H.M.	$(O_3)_o$, P.P.H.M.	From O_3	From NO_2
0.052	22	52	...	3.0×10^{-4}
0.053	37	60	2.2×10^{-4}	5.2
0.053	95	60	5.7	6.4
0.087	44	36	3.0	3.5
0.052	67	80	8.7	4.5
0.053	53	26	7.5	3.4

The mean value of k_9 is 48×10^{-5} p.p.h.m.$^{-1}$ min.$^{-1}$ as compared with a value of 110×10^{-5} calculated from the data of Johnston and Yost (*7*).

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Three Years of Ozone Sterilization of Water in Paris

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Filtered water at Saint-Maur is treated with enough ozone so that the residual concentration, at the immediate exit of the columns where water and ozonized air came into contact, is 0.10 p.p.m. when the water temperature is below 10° C., 0.05 p.p.m. when it is above 10° C. The treatment is controlled by recording equipment at the plant, which measures the electric potential produced by the dissolved ozone. For average treatment 1.1 p.p.m. are used, although dosage actually fluctuates between 0.6 and 1.5 p.p.m. and is occasionally higher if the river accidentally becomes heavily contaminated. The treated water never shows *E. coli*. The amount of *C. perfringens* is reduced by 50% with respect to that of the filtered water. Organic matter is reduced only slightly. The color is reduced by 5 p.p.m. The basic taste threshold is reduced from 3 to 0. Phenol in doses of 10^{-7} is destroyed by 0.1 p.p.m. of ozone. Preformed chlorophenols can be destroyed up to a dose between 1.0 and 1.6×10^{-7}. Effects upon these taste-producing compounds have been studied within the limits of the normal output of the plant.

The Saint-Maur ozone plant at Paris, the purpose of which is to sterilize filtered Marne river water, was put into operation in February 1953. The design was based upon information derived from the operation of pilot plants dating from the beginning of the century as well as operation of a large plant at Saint-Maur, the construction of which was achieved in the period, 1914 to 1918.

Before World War I, chlorination was not well understood and taste and odor difficulties were often associated with the use of chlorine. On the other hand, ozone left no odor or taste and also improved the appearance of the water. Thus authorities concentrated their attention on ozone.

But because of economic difficulties and the shortage of electricity following World War I, a provisional hypochlorite sterilization process was installed at Saint-Maur which operated until 1953. Meanwhile, interest in ozonation lagged as chlorination became better understood and more widely used. But, with increased industrial activity, pollution of the Marne river became worse, and unpleasant tastes were imparted to the water. So the ozone plant constructed in 1914–18 was operated experimentally from 1925 to 1930. It treated 90,000 cubic meters (24,000,000 gallons) of water daily. On the basis of these experiments, it was decided to construct the present Saint-Maur plant.

Ozone is the choice, according to the French concept, because it not only sterilizes but also eliminates unpleasant odors and tastes. In the water delivered to the consumer, no chemical product remains, such as a chlorine derivative, which is always there after chlorine sterilization. Chlorine compounds are always suspected of damaging health, if ingested even in small amounts over prolonged periods of time by the human organism. This is different from the United States concept, which is that the water should not only be sterilized but protected in the distribution system by the carrying of a residual of chlorine all the way to the consumer's tap.

In Paris, when water is chlorinated as at the Ivry plant, it is always dechlorinated with sodium hyposulfite before being pumped to the consumer. The water-borne disease rate since 1930 has under these circumstances been less than 1.5 infections per 100,000 inhabitants, and today the trend is to less than 1 per 100,000.

Although the new Saint-Maur plant was first put in operation in 1953, its original conception and design date back some 25 years, contracts being awarded in 1933. The work was then interrupted by the war and postwar shortages. Thus, some of the improvements in ozonator design which might have been expected in a plant starting up in 1953 were not incorporated in the Saint-Maur plant.

Marne river water has the following average characteristics:

pH	7.8 to 8.2
Turbidity, p.p.m.	3 to 200 (10 cm. — 1.5 meters, Secchi disk)
Total hardness, p.p.m.	200 to 300 $CaCO_3$
Alkalinity, p.p.m.	200 to 250 $CaCO_3$
Organic matter, p.p.m.	1.5 to 4.0 O_2 (alkaline $KMnO_4$)
Dissolved oxygen	7.0
Temperature, ° C.	0–25
Plankton	Asterionella, Synedra, Cyclotella (spring to autumn)

Industrial pollution from sugar refineries, distilleries, starch manufacturing plants, and a paper plant is only moderate. The taste threshold (Baylis method) varies from 2 to 4 and is occasionally higher.

The water is filtered through rapid and slow filters. During periods of floods, 6 to 8 p.p.m. of ferric chloride are added for flocculation.

There are rapid fluctuations in water treatment volume as well as water quality. Thus sterilization equipment must be flexible.

Design Considerations

Based upon the operation of the 1914–18 plant, it was concluded that every effort must be made to reduce electrical energy consumption. To decrease installation costs, it was decided to use 500-cycle current, thus obtaining more ozone from a given size of apparatus. Half of the ozonators were of compact cylindrical-electrode design which, in their day, were considered the latest technological development. To augment the output further, it was decided to decrease air temperature and moisture content and to recover and recirculate the ozonized air leaving the contact columns. The recovery of ozonized air was necessary to prevent odor nuisance.

The ozone dosage for sterilization was selected as 1.2 p.p.m. For flexibility, it was planned to have 12 separate ozonizing units, each with a capacity of 25,000 cubic meters per day (6,600,000 gallons per day) plus four similar units in reserve.

The criteria for sterilization were that there should be a detectable ozone residual after at least 1 minute above 20° C., 5 minutes at 10° to 20° C., and 10 minutes between 0° and 10° C.

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch056

Construction Details

The first contracts were signed in 1933; but as subsequent studies indicated the difficulty of housing all the equipment in the old plant, it was decided in 1935 to construct a new building. This structure is rectangular in shape, 55 meters (180 feet) by 21 meters (69 feet) by 22 meters (73 feet) high. It houses the contact columns and all equipment and control apparatus.

The 16 contact columns are of square section, 3.75 meters (12 feet) by 8 meters (26 feet) high with an effective contact depth of 6.3 meters (20 feet). Each column is fed by a siphon with an atmospheric lock which when unprimed rapidly interrupts the flow of filtered water and guarantees perfect insulation between conduits for filtered and sterilized waters. The water flow is distributed among the columns by partially closed sluice gates which compensate for the various losses in head in the columns according to their position in the plant.

Serving these contact columns are 16 ozonizers, 16 compressors for ozonized air, and eight groups of frequency changers, 50 to 500 cycles. Each of the latter serves two groups of ozonizers. There are corresponding electrical control stations and three groups of air conditioners (two operating plus one spare) each comprising a group of ammonia compressors, a condenser, and a refrigeration chamber for water removal.

Half of the plant uses plate ozonators of the Otto design and half ozonizers of the tubular Van der Made design. The ozonized emulsion is introduced through eight cylindrical, porous diffusers at the bottom of each column in one half of the plant; in the other, it is introduced through 96 nozzles per column.

The ozonized air is conducted through stoneware pipelines with pitch joints. The circuits are arranged so that the pressure runs are as short as possible and the negative pressure sections are longer. Thus the top of each column is open to atmosphere and the moist air collectors, air conditioners, dry air collectors, and ozonizers are all operated under negative pressure.

The original air conditioners each consisted of four bundles of pipes, containing gaseous or liquid ammonia, and housed in four insulated compartments of an insulated locker. The moist air passed over the first tube bundle (defrost cycle), melting off accumulated ice, then circulated over two refrigerated bundles and finally over the fourth bundle which contained gaseous ammonia. The last bundle warmed the air to about 5° C. while cooling the ammonia. The first three bundles alternated in a frost-defrost cycle.

The compressors for the ozonized air are of a water ring (seal) type constructed

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch056

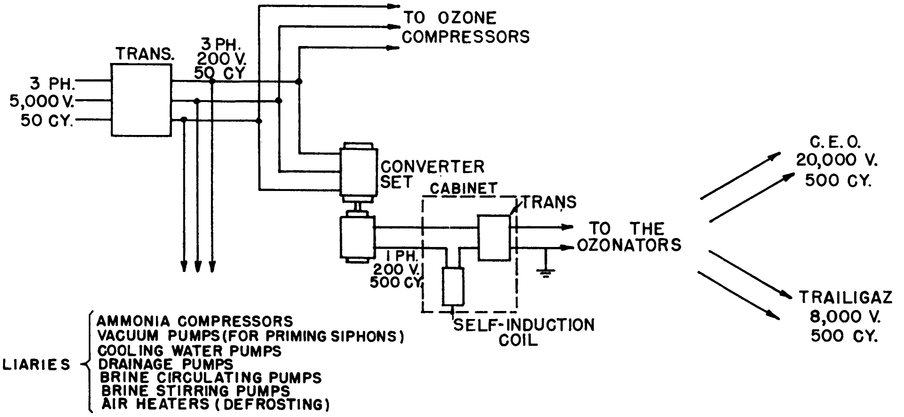

Figure 1. Schematic diagram of electrical installation

of stainless steel. They draw air through the air conditioners and ozonizers and force it through the head of water in the columns. Each unit has a capacity of 700 kg. of air per hour.

Electrical energy is furnished to the plant at 5000 volts, 50 cycles, three phase. Two 1300-kva. transformers step the voltage down to 115 volts. The 50-cycle power is converted to 500 cycles by alternators with a capacity of 36 kw. A single motor drives two alternators, and a self-induction coil is used to regulate the power factor and ensure operational stability. The 500-cycle current is stepped up to 10,000 volts for the tubular ozonizers and 18,000 to 20,000 volts for the plate type.

The tubular ozonizers consist of six housings, each containing 30 electrode-tube assemblies. Each set of six housings is fed by a single alternator and serves a single contact column. Each electrode-tube assembly consists of a glass tube surrounded by water which serves as one electrode (grounded). The second electrode is a stainless steel tube spaced concentrically within the glass tube.

The plate ozonizers consist of four groups each with six pairs of hollow Alpax (an aluminum-silicon alloy) plates through which cooling water circulates. A pair of glass dielectrics is placed between each pair of plates. The maximum power input is 1.5 kw. per cell.

The schematic diagrams (Figures 1 and 2) show the electrical and ozone circuits.

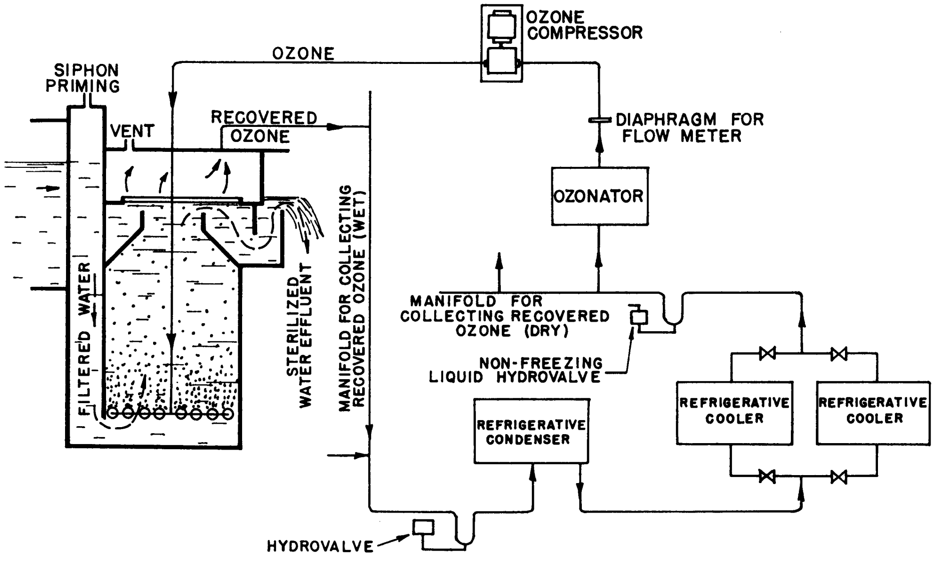

Figure 2. Schematic diagram of ozone circuit

Initial Operation

Although the plant was scheduled for completion in 1938, the first trial runs could not be made until 1941. It was apparent from these that the air-conditioning installation was inadequate—the frost which deposited was much fluffier than had been anticipated and its thermal conductivity was too low. The whole system was delicate to operate and lacked flexibility. Attempts to improve its operation were not satisfactory and it was eventually decided to abandon the single-step, direct expansion ammonia system. Because of war and postwar conditions, nothing more could be undertaken until 1949–50.

The new air-conditioning system is a two-step process. The first, a continuous one, reduces the temperature to about 0° C., removing water by condensation. The second step was designed to reduce the temperature to −6.5° to −7.5° C., but has reached −12° to −13° in actual runs. For the first step, the tube bundles from the earlier installation are used with calcium chloride brine (10° Bé.). The second step is accomplished in three pairs of tubular bundles installed in six tight boxes. Calcium chloride brine (27° Bé.) is circulated in these. The bundles are used discontinuously, being defrosted by a current of warm air. The brine solutions are circulated by pumps and cooled by circulation through insulated tanks in which the ammonia coils are immersed. As in the first installation, there are two operating units and one spare unit. The new system has been found foolproof and flexible.

Operation of Plant

At the beginning there were serious operating difficulties, largely due to the long period of time which elapsed between initial construction and eventual operation of the plant. To make certain that the water delivered to the customers was safe, weak chlorination was continued for several months until the ozone treatment had been firmly established by practical operation, after which chlorination was abandoned.

The ozone persistence criteria for sterilization, described above, proved cumbersome in practice and it was soon found that the desired sterilization could be obtained with smaller dosages of ozone. Briner (*1*), Bringmann (*2*), Buffle (*3*), and Kessel, Allison, Moore, and Kaime (*5*) agree on the speed of the bactericidal and antiviral action of ozone in doses of less than 1 p.p.m. The action is much faster than that of chlorine and its derivatives; it takes only about 1 minute.

The contact time in the Saint-Maur columns is 3 minutes at normal output and 1 minute 45 seconds at the maximum output of 50,000 cubic meters per day per column. The latter value is frequently reached in actual runs. The author has tried to determine a certain minimum ozone dose at the outlet of the column immediately after treatment. At first it was thought that because of its rapid action, traces of ozone in the water at the outlet of the columns would be a sure sign of sterilization, as the water-ozone contact time is always between 1 minute 45 seconds and 3 minutes. Experience proved this to be wrong. First a residual ozone value of 0.05 p.p.m. was adopted and no attention was paid to the persistence method. However, on different occasions 10 *E. coli* per liter of ozonized water prior to auxiliary chlorination were found, so the following criteria were finally adopted which for 2.5 years have guided the production of perfectly sterilized water.

There must be 0.10 p.p.m. of ozone present as residual at the contact column exits, if the temperature of the water is below 10° C., and 0.05 p.p.m. if the water reaches temperatures of more than 10° C.

This criterion has furnished a good margin of security, as indicated by the constantly good results obtained.

Control Tests

Initially the ozone residuals were checked by chemical tests every 2 hours. Eventually a monitoring device was developed which registered the difference in potential between the ozonized and filtered water. The apparatus is simple and foolproof and has been used successfully for 3 years. One such master device checks on the combined flow of ozonized water, and eventually there will be similar monitoring devices on the individual columns. As the ozone demand fluctuates with irregularities in water quality and water volume, the ozone residual also changes and these changes must be compensated for immediately. A typical registration curve, with an indication of the causes of variations in residual, is shown in Figure 3.

It is probable that, at water temperatures above 20° C., a residual of less than 0.05 p.p.m. is safe for perfect disinfection; however, the registration device is not sensitive below 0.05 p.p.m. Thus to be safe, the limit is set at 0.05 p.p.m.

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch056

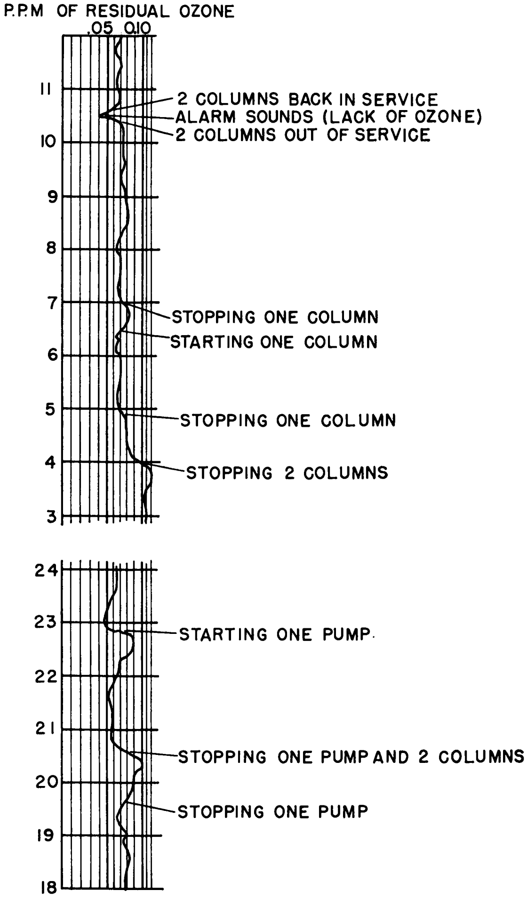

Figure 3. Example of graphs recording residual ozone

Ozone Dosage

Because ozone is only slightly soluble in water and is unstable in nature, readily decomposing into ordinary oxygen, only a portion of that applied is actually utilized in the sterilization process. Part of the ozone is not absorbed by the water and passes off the top of the contact columns. For instance, in routine treatment at Saint-Maur 0.5 gram of ozone per kilogram of air is present at the column outlet in winter and 1 gram per kg. in summer. This is 20 to 40% of the amount applied; thus, in 1 day up to 160 kg. of ozone might be dispersed into the atmosphere around the plant if a closed air circuit were not used.

The actual ozone dosage at Saint-Maur based on 3.5 years' operation, is of the order of 1 p.p.m. The minimum is 0.6 p.p.m. The amount actually used or lost in the water is less, however, as these figures include the excess ozone at the column outlets. Because the ozonizers cannot be operated below certain limits, this causes "excess" dosages, when the ozone demand of the water is less than 0.6 p.p.m., even at maximum column output of 50,000 cubic meters (twice rated flow).

Once or twice a year, for several hours or days, there is an exceptionally heavy ozone demand, presumably caused by the dumping of industrial wastes into the river.

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At such times the ozone capacity of the plant is exceeded by the demand and it is necessary to add chlorine in addition to ozone.

The actual maximum production of the plant at such times is 450 kg. a day, producing an ozone dosage of 1.6 to 2 p.p.m., depending on water flow. The maximum guaranteed is 1.2 p.p.m. for 300,000 cubic meters of water or 360 kg. a day. Eventually it should be possible to produce 550 kg. a day with 12 of 16 columns in operation, as originally contemplated. Figure 4 shows daily ozone dosages for January to September 1956.

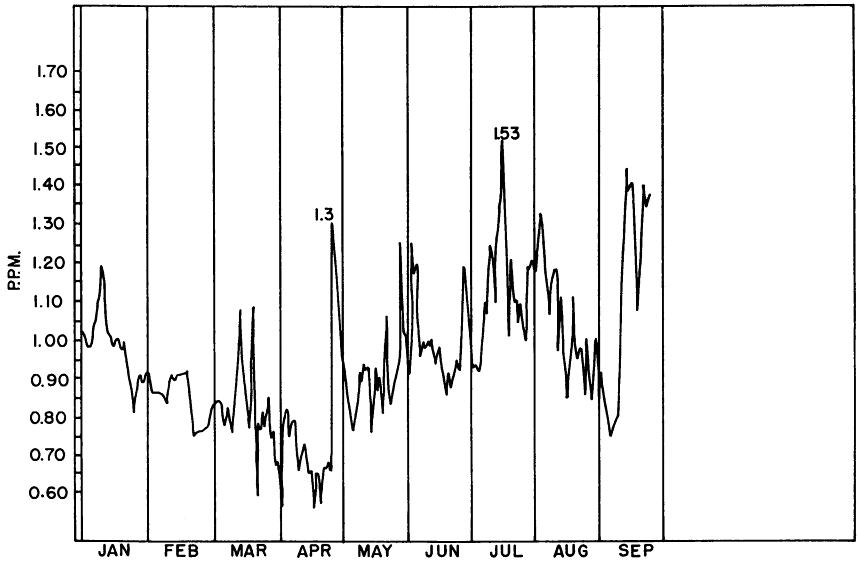

Figure 4. Proportion of ozone in water treatment (1956)

Bactericidal Action

Since the abandonment of complementary hypochlorite treatment, the ozonized water has never shown the presence of *E. coli.* Thus the safety of this method of disinfection seems excellent on the basis of classical criteria. In 1952, with hypochlorite, *clostridium perfringens* was reduced from an average of 40 units to 31 units per liter. In 1955, with ozone, an average of 50 units per liter was reduced to 22.

The coliform count for the untreated water varies from 15,000 to 100,000 units per liter, with an average of 30,000 to 50,000.

Effect on Organic Matter

Compared to chlorine treatment, there is very little, if any, difference in the organic matter (as measured by alkaline permanganate) after ozone. In each case the reduction is less than 10%.

Effect on Tastes

One of the main reasons the Saint-Maur plant was built was to improve water taste. Complaints from water users have practically ceased since 1939. However, it has been determined that the unpleasant tastes prior to 1939 resulted from wastes from a plant which has since been shut down. Actually, greater industrialization has taken place along the Seine rather than the Marne and has created taste problems at

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch056

the Ivry plant, where chlorine dioxide has been used experimentally to cope with unpleasant tastes.

At Ivry, probably for the first time in France, tastes have been studied for 2 years by the dilution method of Baylis. But, because the population of Paris is so sensitive to tastes, and floods the water bureau with telephone calls at even the slightest taste of unneutralized chlorine, the dilution method at 30° C. is run rather than the more usual odor dilution test at 60° C.

At Saint-Maur, taste complaints have disappeared entirely since ozone equpiment was installed, except for times when chlorine was used simultaneously. However, 30° taste dilution tests have recently been run as a matter of record. At 30° C. taste threshold for raw water is 2 to 3; filtered water, 1; ozonized water, 0.

To ascertain the effects of ozone on industrial pollution better, several experiments were made with a single column treating 25,000 cubic meters a day.

Experimental Runs. 1. Addition of phenol, 2×10^{-8}; ozone treatment, 1.6 p.p.m.; contact time, 3 minutes. Threshold of untreated water, 3. (To make the water taste bad, as the phenol alone did not cause any bad taste, chlorine was added to the untreated water, and to the ozonized water, and the excess was neutralized.)

Threshold of the treated water, tasteless.

2. Addition of phenol, 10^{-7}. Threshold of untreated water, 15. Threshold of treated water, 0. Ozone absorbed, 0.2 p.p.m. of residual ozone prior to the addition of phenol and 0.1 p.p.m. during the addition.

The registration equipment immediately showed the passage of contaminated water in the fluctuation of the 0.1 p.p.m. of residual ozone.

3. Addition of waste from a coke-oven plant (phenols and tars and sulfur-containing products having a bad odor), 20 liters per cubic meter of untreated water.

Threshold of untreated water (bitter taste). Threshold of treated water, close to 2 (a muddy taste). Ozone absorbed, roughly 0.1 p.p.m.

4. Addition of phenol, 10^{-7}.

Threshold of untreated water, 15. Threshold of treated water, 0.

5. Addition of synthetic chlorophenol, 10^{-7}.

Threshold of untreated, 40. Threshold of treated water, 0. Ozone absorbed, rather weak.

6. Addition of synthetic chlorophenol, 1.6×10^{-7}.

Threshold of untreated water, 55. Threshold after treatment varies according to conditions from 0 to 4 (taste of chlorophenol); thus the possibility of taste destruction is indicated for the dosages actually used (1.6 p.p.m., or the actual maximum at the plant for treating large amounts of water) for a contact time of 3 minutes (in a column having a normal flow of 25,000 cubic meters per day).

Effect on Color

Because the filtered water has little color, the effect is small. But viewed through sufficient depth, the ozonized water has a bluish tint, compared with the yellowish tint of chlorinated water. The color of the filtered water varies from 4 to 10; ozonized water, 0 to 5; chlorinated, 3 to 8.

Other Effects

When the ozone plant first started up, a large number of fish died suddenly at the Aquarium of the France d'Outremer Museum, which is served with water from Saint-Maur. The cause was eventually traced to gas embolism in the gills of the fish, which came about through the presence of air bubbles in the water. The pumped water is saturated after ozone treatment, and the bubbles were released as the head decreased and as the temperature of the water increased during the long run through the pipelines in the museum.

Water Treatment Volume

Initially (1933), the maximum output of the filter plant and pumping station was only 200,000 cubic meters a day (53,000,000 gallons per day). The present output of the ozone plant is 300,000 cubic meters (79,000,000 gallons per day), which has already been reached and even exceeded for short periods. As head losses are lower than anticipated, it should be possible to double the design output to 600,000 cubic meters a day, if the ozone production could be suitably increased during peak demand periods.

Ozonized Air Circuit

The tar or pitch joints in the stoneware pipelines have been a source of frequent mishaps and leakage, accounting for the bulk of maintenance expenses at Saint-Maur.

Leaks at the water seals of the compressors have also been troublesome. One compressor has been fitted with graphite-stainless steel rings which seem to have solved the difficulty.

Even traces of ozone in the atmosphere cause severe discomfort to the workers, although individual tolerance varies greatly. If more concentrated ozone is inhaled, symptoms similar to those provoked by chlorine occur. Neoprene gas masks are available for protection of the workers.

Refrigeration Equipment

The new two-step process has operated without serious trouble since February 1953. It has usually sufficient capacity to cool the air to —12° or —13° C., and experimental runs at —18° C. have been made.

However, maintenance of the steel tubes of the heat exchangers has been a troublesome problem. The wet ozonized air on the outside of the tubes is very corrosive. Oil-base paints will stand up for only a few months. After a number of comparative trials, a high-polymer base paint has been selected, but it will be some time before this can be fully evaluated.

There has also been corrosion from the calcium chloride brine on the inside of the tubes in spite of pH control. Inhibitors are now being investigated.

Ozonizer Maintenance

The running of the ozonizers is beset with maintenance problems. The tubular stainless steel electrodes corrode and gradually become coated with oxides. They must then be disassembled and cleaned. This corrosion is due rather to nitric acid, which forms with the ozone, than to the ozone itself. The amount of nitric acid decreases as the air becomes drier and cooler. Thus, the amount of nitric acid, expressed as nitrogen, drops from 20 mg. per kg. of air containing 2.2 grams of water to 10 mg. per kg. for air containing 0.8 gram of water. This small amount of nitric acid has only a negligible effect on the water treated.

The hollow Alpax plates of the plate ozonators corrode occasionally from contact with the cooling water. They are protected from scale by treating the cooling water with 2 p.p.m. of hexametaphosphate.

The flat dielectrics stand up better than the original tubes, but their replacement is difficult and time-consuming. During the first months of operation, breakage of the cylindrical dielectrics was frequent. Improvements in the cooling system and tube assembly helped somewhat, but not until borosilicate glass tubes were substituted for the original soft glass was any real improvement achieved. Occasional replacements are still necessary and this is a continuing maintenance expense.

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch056

Electric Energy Consumption

The most important items of expense are salaries for personnel, depreciation, and electric energy for the ozonizers. The next most important item is electrical energy for the air compressors and refrigerative units. As these various energy consumptions are interrelated, they cannot really be considered separately.

Influence of Moisture

The original design provided for a dew point of —6.5° C., or 2.2 grams of moisture per kg. of dry air. However, during experimental runs in 1949 it was apparent that this dew point was dangerously close to the maximum permissible limit. By adopting the two-step cooling scheme described above, it was possible to achieve dew points of —12° to —13° C., without additional refrigeration equipment. At this moisture content, ozonizer output is much more stable. It was possible to make experimental runs at —18° C. dew point. Figure 5 shows the influence of moisture on ozonator production. As yet not enough experimental values are available to establish the optimum moisture content, but it is intended to equip one column with a silica gel drier for further studies.

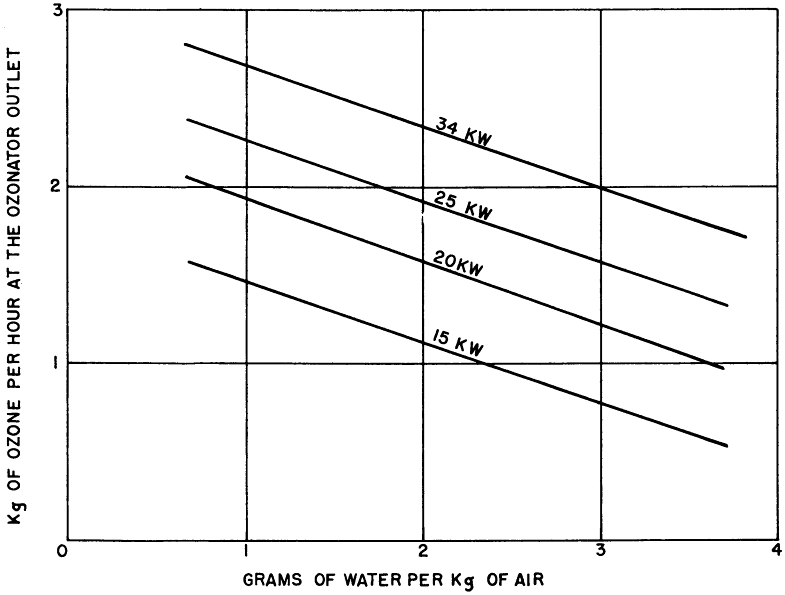

Figure 5. Effect of humidity on ozone production

Value of Air Recovery

The air entering the columns contains at least 2.5 grams of ozone per kg. of dry air; the air leaving contains 0.5 gram in winter and 1 gram in summer. Thus there is vital interest in recovering this ozone.

It is difficult to show a correct balance sheet for this operation. By recycling the air, the need for air filters is eliminated. On the other hand, the recovered air is always saturated with moisture, which would not be the case in most climates for

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atmospheric air. Also, for a given quantity of electrical energy applied, less ozone is generated in the recovered (partially ozonized) air than would be produced in air free of ozone. The over-all yield in the recovery is always low.

Figure 6 shows how ozone produced varies with the amount recovered. The upper curve is based on the operation of a single bank of plate ozonizers with an energy consumption of 35 kw. and normal air flow of 700 kg. per hour. If as much as 1 gram of ozone per kg. of air is recovered, the ozone output is increased from 1600 grams per hour (with fresh air) to 1800 grams per hour. As power input remains the same, this would mean a power saving unit of ozone of 11%. Actually, this 11% saving is a maximum, and under normal conditions 5 to 8% would be more typical. With tubular ozonizers, the values are similar.

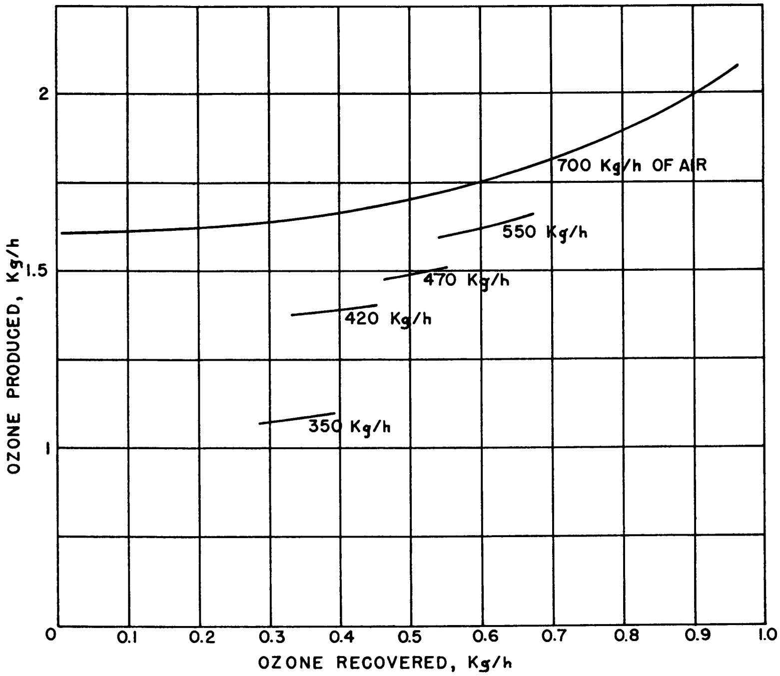

Figure 6. Relation of ozone produced to amount recovered

If the ozonizers are operated at higher concentrations (lower air flows) the saving is reduced. If the water and air were circulated countercurrently, savings would be still smaller or practically nonexistent.

Higher Concentration

At higher concentrations, ozone is more easily dissolved in the water; and of course for a given water flow, less air need be compressed and dried. Unfortunately, as the concentration rises, the ozonizer yield drops.

The compressors at Saint-Maur operate at constant speed with an output of 700 kg. per hour and an energy consumption of about 20 kw. Experiments have been made with a single compressor equipped with a variable-speed drive to vary the air flow. The lower curves in Figure 6 show the reduction in ozone output at decreased air flow, power input remaining constant at 35 kw.

Because of the high ratio of compression energy to ozone generation energy

(20 kw./35 kw. = 0.57 minimum) use of ozonators of a more modern design, capable of efficient production of ozone at 10 grams per kg. of dry air, would result in appreciable operating economies. Over-all energy consumption for the plant would be reduced by about one third.

Reduction in Column Height

Because a reduction in column height would reduce compression energy, assays of the water at ⅓ and ⅔ column heights have been made. Although these tests are not complete or conclusive, there is little indication that column height can be safely reduced.

Stability of Ozonizer Operation

The most difficult problem encountered was the instability of operation of the tubular ozonators. The power absorption of each battery changed continuously and irregularly. Matters were even worse when the soft glass tubes were replaced with borosilicate glass. A similar phenomenon, although milder, was observed with the plate machines.

This condition of instability comes from the fact that the ozonator circuit combines a capacitative ozonizer load with reactive components in the transformer, self-induction coil, and alternator; this results in a resonating circuit. To overcome this difficulty, the self-inductance was increased. With this added impedance and with ozonator voltage increased from 8000 to 10,000 volts, it was possible to achieve stable operation.

However, operation at low power inputs was still unstable. Rather than providing the variable inductance necessary to cope with this condition, it was decided to operate only in the range of 18 to 36 kw., which is stable.

Experiments with thorough drying have shown that the stability is improved at lower power inputs with drier air.

The dielectric properties of the glass vary from shipment to shipment and also change in actual use, thus aggravating the problem of stabilizing the ozonizer operation.

Energy Consumption

It is customary to express electrical energy consumption in terms of grams of ozone produced. In the case of Saint-Maur, this is difficult because of the closed circuit arrangement. It is more meaningful to use the quantity of energy needed to make available to the water 1 gram of ozone—this is the figure of interest to a designer.

The results at Saint-Maur differ greatly with the two types of ozonizers. At maximum power, 35 kw. at the high-voltage input terminals of the ozonizer, the plate machine consumes 19 watt-hours per gram of ozone with air recovery, 22 watt-hours without air recovery; at 20-kw. input, 15 and 20 watt-hours, respectively. In both cases air flow is 700 kg. per hour.

With the tubular ozonators (Figure 7) yields are higher. They produce the same amount of ozone at 25 kw. that the plate types produce at 35 kw. In both cases substantial losses in the frequency changer must be added. It is doubtful that the reduction in the size of equipment resulting from the use of 500 cycles is worth while.

With the ozonizers run at full power, the compressors require 12 watt-hours per gram of ozone and the air conditioners 6 to 8 watt-hours.

On an over-all basis the average, computed from the main wattmeter of the plant and including all losses, is 39 watt-hours per gram of ozone available for water treatment (equivalent to 17.7 kw.-hr. per pound of ozone).

For the year 1955, 89,000,000 cubic meters of water were treated and 3,800,000 kw.-hr. of electrical energy were used, or 43 watt-hours per cubic meter. Thus average ozone dosage was 1.1 p.p.m.

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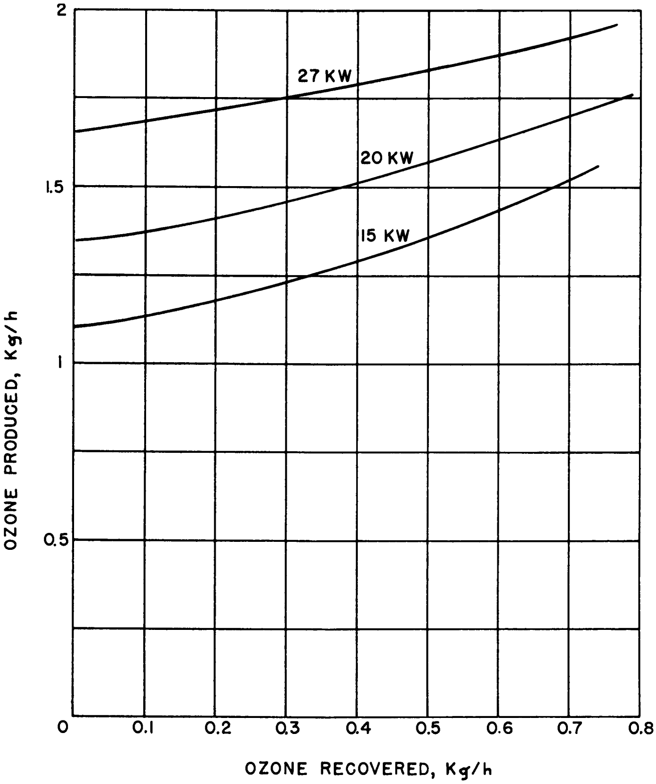

Figure 7. Production of ozone in tubular ozonator

Over-all Costs

For 1955, expenditures (in francs) were as follows:

Electric energy, 5.8 francs per kw.-hour	22,000,000
Salaries and wages	18,000,000
Maintenance	5,000,000
Depreciation (30-year basis)	50–60,000,000

The treatment costs therefore were 1.1 to 1.2 francs per cubic meter.

If the same plant were to be built today, savings in cost could be made. It is perhaps possible to foresee costs reduced to 25 watt-hours per gram of ozone, a value actually reached in Philadelphia in 1949 for a plant of the same size as the Paris plant.

Discussion

In the opinion of United States scientists, the ozonization of city waters may be looked upon as a special kind of a treatment, reserved for highly polluted waters containing a great deal of industrial waste, causing obnoxious tastes and odors which otherwise cannot be handled. But it may also be said that ozonization is the ideal technical treatment, that it is economic, and that it can eliminate chlorination completely. This is sometimes heard in France.

Ozone is effective against certain unpleasant tastes, but there is a limit to this efficiency, as was shown in the experiments. The U. S. literature corroborates this—for instance, reports from Whiting, Ind., show that much larger dosages than at Saint-Maur are not fully effective. It has not been demonstrated that ozone is a panacea for all unpleasant tastes. The author's tests showed it to be more effective against phenols than against coke plant effluent. As far as is known, there is little in the literature to indicate the effect of ozone treatment on earthy, moldy, and musty types of tastes; Hann (*4*) gives some data in terms of odor index, as is the U. S. custom.

Certain French hygienists recommend ozone for all waters, even those with little pollution. Their principal reason is that chlorine might be harmful to the health. This is a feeble argument, lacking scientific proof. Nor is it sufficient to say that ozone is simpler and safer to use than chlorine and not much more expensive. Ozone is not simple to use and the plant must be supervised by experts. Stand-by chlorination equipment must be available in case of power failure.

Only the future can determine whether ozone is the best means of combating offensive odors. One likely competitor is chlorine dioxide, which is being used experimentally at the Ivry plant at Paris. It is as expensive as ozone, but easier to apply. Although this plant has been running experimentally for a year, the author is not yet convinced of its merits and is inclined to give ozone the edge.

Acknowledgment

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Ozone Production and Costs

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The Philadelphia ozonation plant has some unusual design features. Because it was a pioneering project, some changes later proved necessary; satisfactory modifications were found. Equipment to produce completely dust-free and thoroughly dried air proved its value. Guaranteed capacities of ozone generation and efficiencies have been exceeded. With long operation there has been no appreciable change in either. Maintenance has been greatly below that forecast, and constant attendance has proved unnecessary. Operational costs are not inconsistent with costs for other oxidation processes used in water treatment. Overhead costs for this plant are not comparable with those for a plant built at present. Reduction of tastes and odors and removal of manganese have been appreciable, and good bacterial and coliform organism kills have resulted.

Philadelphia's ozonation plant, placed in service in early 1949, is located at the Belmont Water Treatment Plant; treating water pumped from the Schuylkill River. Ozone-generating capacity of the plant is 1250 pounds per day. At the time of installation this was the largest in the world and 16 times larger than any other plant treating water in America. Its ozone-generating units were of a type previously used only in one very small plant. The project was, therefore, something of a pioneering development.

The Schuylkill, over 125 miles long, has in recent years been cleaned, by dredging from its source to the Fairmount Dam, which forms the pool as source of Belmont's water, and pollution has been minimized. In the forties, however, the conditions were very different. The Schuylkill, which has its sources in the coal mining areas, received a great amount of coal culm, also acid mine drainage, then passed through a limestone region where the acid reacted with limestone. It then passed through a highly industrialized area, where both industrial and domestic wastes were received, largely untreated—the former from some 40 different industries, the latter from several communities of considerable size.

For a source of public supply, the Belmont raw water was, in the forties, unusually polluted bacteriologically, and by a variety of organic wastes which caused tastes and odors. Manganese content sometimes exceeded 5 p.p.m. The water contained a great amount of coal culm and some clays; the turbidities ranged, in yearly averages, up to 1200 p.p.m., with readings sometimes reaching 3000 p.p.m.

At the Belmont plant, a 35,000,000-gallon basin provided actual detentions approximating 16 hours at the rate of 36,000,000 gallons per day. Aided by alum ap-

In OZONE CHEMISTRY AND TECHNOLOGY;
Advances in Chemistry; American Chemical Society: Washington, DC, 1959.

plication at times of high turbidities, the settled turbidity was usually between 10 and 30. This water was then treated with chlorine, with alum and lime to flocculate, and with carbon for taste and odor removal. It was passed through baffled mixing basins, 2-hour settling basins, and rapid sand filters, followed by postchlorination.

Manganese passed through the rapid sand filters; therefore, ozonation could not be applied to filtered water without loading the distribution system with mineralized manganese. Point of ozonation was chosen as the presettled water before application of the chemicals.

Pilot plant tests had previously been run with a 2-gallon-per-minute and a 1,000,000-gallon-per-day unit. These indicated the effectiveness of ozonation, and that the maximum application required would be less than 4 p.p.m. This was adopted as the design capacity, and the plant was built to produce the 4 p.p.m. dosage on a flow of 36,000,000 gallons per day, with two generators out of service (*3*).

Description of Plant

Atmospheric air is cleaned by passage through electrostatic filters, compressed to about 10 p.s.i.g. by five 400-cu. foot per minute rotary blowers, cooled by water coils, followed by refrigerated coils, to under 50° F., thereby drying to under 50 grains of moisture per pound of dry air, and passed through one of four crushed aluminum dryers to produce dew points below —60° F., equal to a moisture content of less than 1 grain per pound of dry air.

Ozone is generated by 50 generators manufactured by the Welsbach Corp., each guaranteed to produce 25 pounds of ozone per 24 hours. The generator shells are water-cooled and of all stainless steel; each generator utilizes 85 borosilicate glass tube electrodes, 3 inches in diameter, coated on the inside with graphite for current distribution, protected by Bitumastic enamel. Current is stepped up to 15,000 volts for generation.

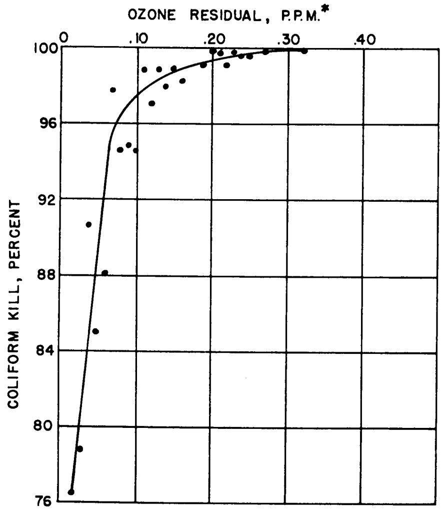

Figure 1. Coliform kill by ozone

Points plotted are averages of monthly average kills at various ozone residuals, 1950 to 1955

*** (*1*)**

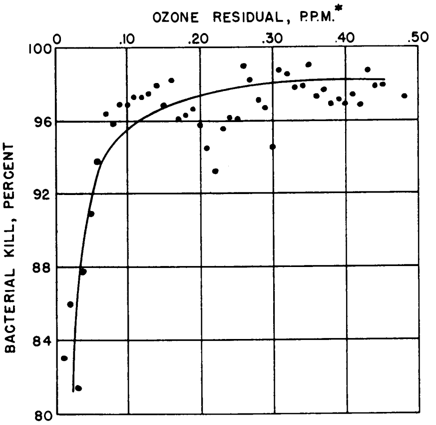

Figure 2. Bacterial kill by ozone

Points plotted are average kill shown by 90% of all individual tests (37° count, 24 hours, on agar) for various ozone residuals, 1950 to 1955 * (*1*)

Ozonized air is conducted underground to three contact chambers, where it is diffused into the water at a depth of 18½ feet. Water enters the top of these 25-foot square chambers on one side, and passes downward and across the chambers. At

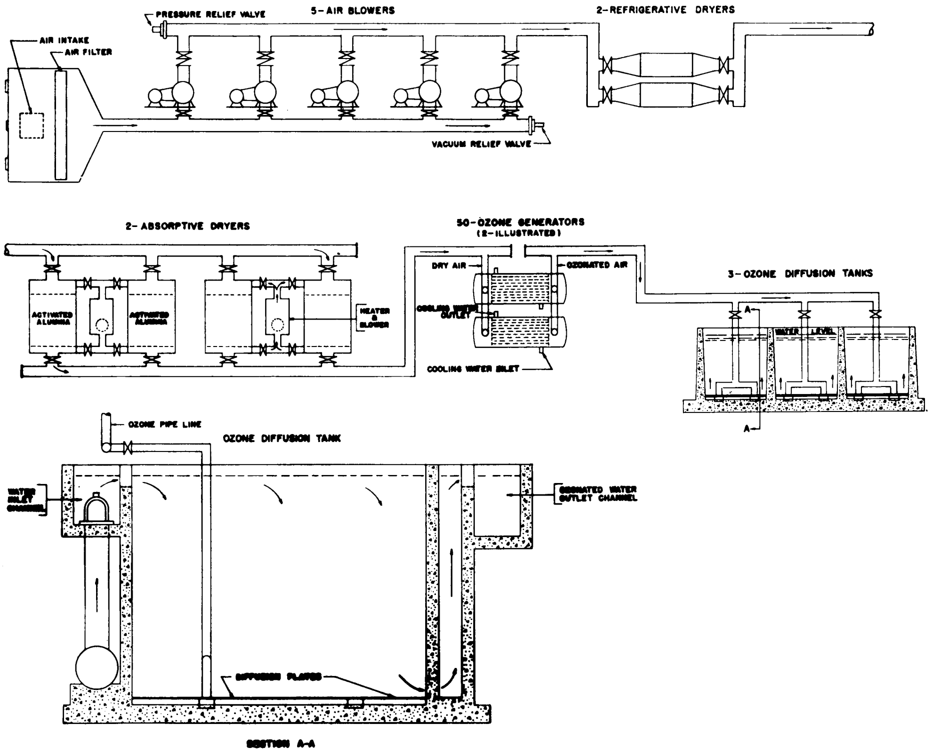

Figure 3. Schematic layout of ozonation plant

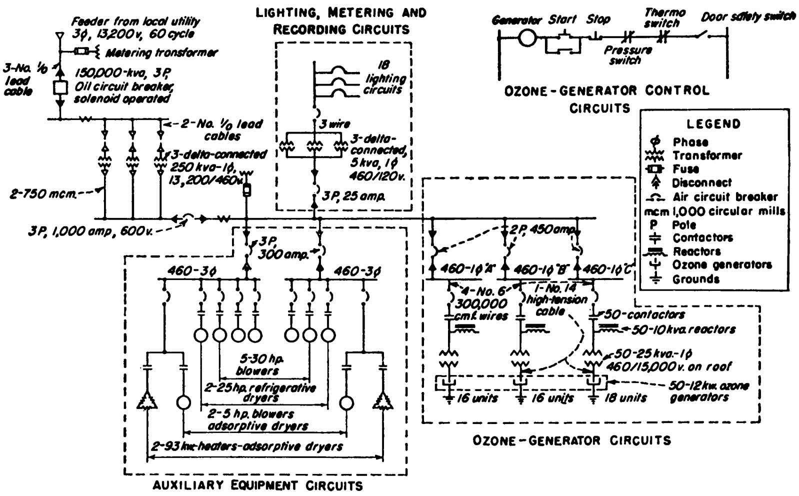

Figure 4. Electrical wiring diagram

maximum flow the theoretical contact is 10 minutes. Diffusion was originally by porous plates, later replaced by porous tubes.

Capital Costs

Cost of construction of this plant (engineering, inspection, and other expenses figured at 20% of the contract costs) totals $1,000,000, divided as follows: equipment, 70%; electric service, main supply transformers, switch gear, etc., 4%; housing structure, 10%; contact or diffuser tanks, 16%.

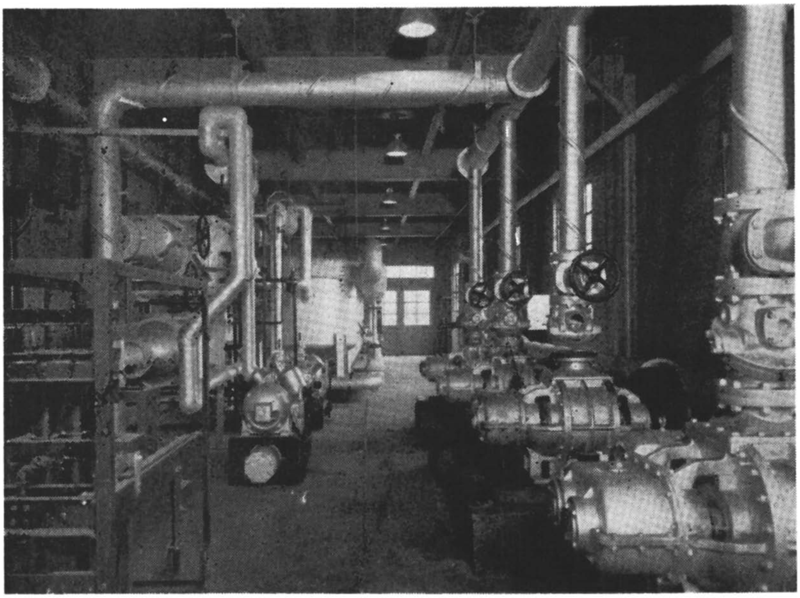

Figure 5. Refrigerative dryers and air blowers

Publication Date: January 1, 1959 | doi: 10.1021/ba-1959-0021.ch057

Figure 6. Refrigerative dryers

Difficulties Encountered

Refrigerative Dryers. In designing the plant, ample air was provided to operate down to 0.5% ozone concentration, if this proved most efficient. This was not the case, and not long after the plant was placed in operation, the river was cleaned to the extent of reducing ozone requirements. With the resultant low air demand, refrigerative coils froze and the compressor units required frequent service. As emergency correction the water supply to the water cooling section was shut off, throwing the

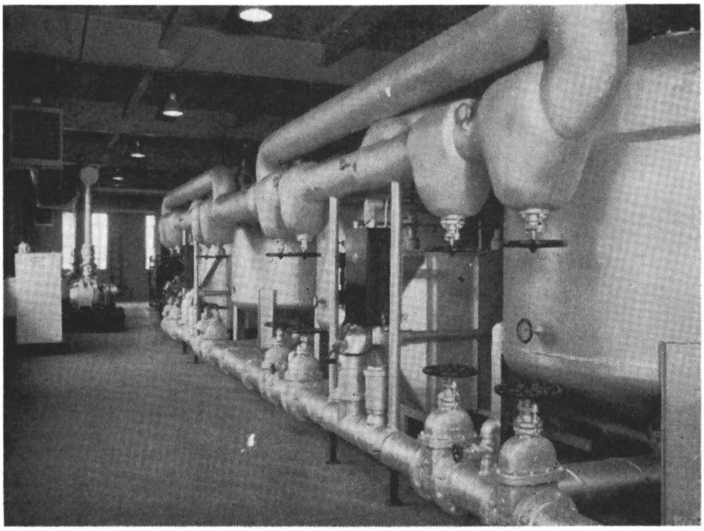

Figure 7. Adsorptive dryers

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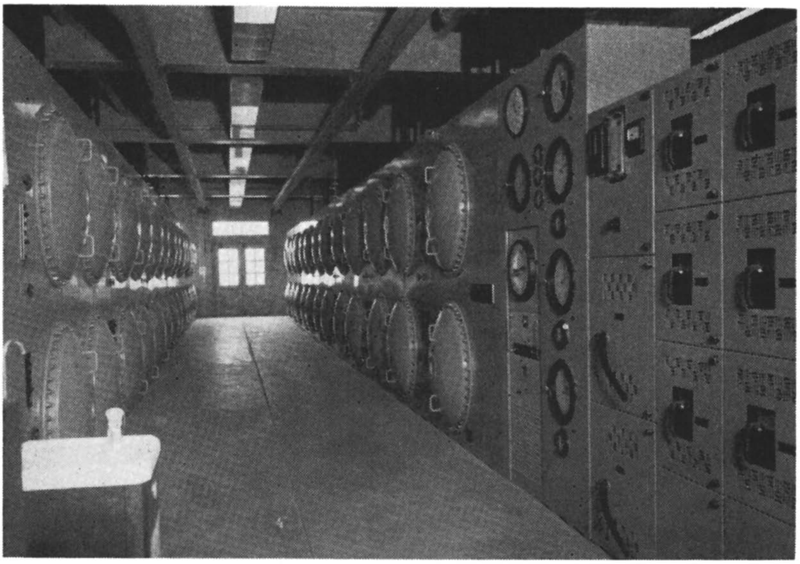

Figure 8. Ozone generating equipment and control panel

whole cooling load to the refrigerative section. Proportioning valves have since been installed to control the refrigeration proportionally to the loading.

Adsorptive Dryers. It quickly developed that the adsorptive dryers were not being properly dried. After drying, instead of —60° F. the dew point might run only to —20° F., and then only for a short time. Reddish brown deposits started to form in the generator tubes.

The adsorptive units are dried by passage of hot air downward through the alumina bed, the moisture picked up then being dropped out in a standard commercial

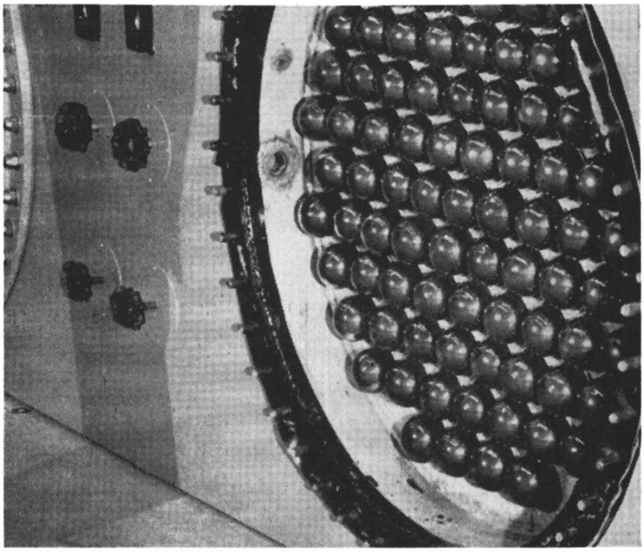

Figure 9. Ozone generator header and tubes

unit, consisting of a chamber containing coils through which cooling water is circulated. The condensed moisture is led off through a trapped opening to drain.

The floor of the chamber was continually flooded. This was corrected completely by relocation and adjustment of the drain trap.

Electrical Leads. In the original installation No. 14 neon sign cable was installed through ½-inch conduit from the transformers to the electrodes of generator units. These cables, fully insulated for 15,000 volts to ground, burned off frequently at the end of insulation nearest the generator electrode. Many different types of insulated cable were tested with the same result. The cause was never satisfactorily determined; however, it was found that bare wire of a larger size gave no such difficulty, and this was installed on all units, passing through a glass tube as insulator through the roof only. Metal guard cages were provided below the roof.

Reactor Hum. Reactors, installed to correct the power factor, produced a variety of tones and pitches which were very disturbing and sometimes very loud. All reactors were returned to the manufacturer, who impregnated them free of charge, almost completely eliminating sound.

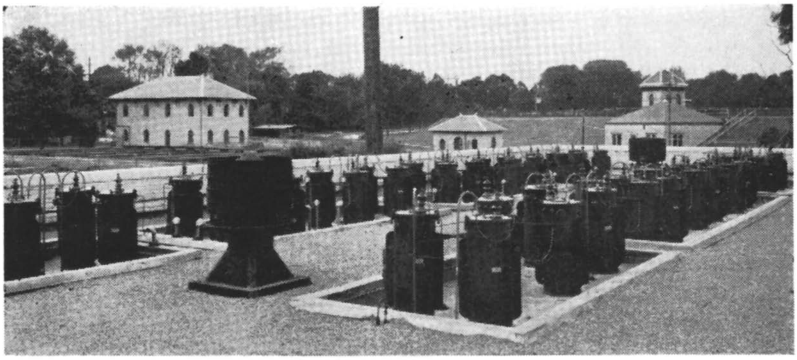

Figure 10. Transformers

Transformers. Three of the 460- to 15,000-volt transformers shorted and burned out in the first year and a half of operation. The manufacturers concluded that the built-in impedance of 2% was not enough. They recommended the addition of 180 ohms' resistance on the high voltage side, to equal total impedance of 4%. This was done and only one transformer has failed in the past 6 years.

Valves. Considerable difficulty was experienced with leaking valves on the ozone lines near the generators. Different types of packings were tested until a satisfactory material and shape solved the difficulty. Teflon valve seats and packings have since been used.

Generators. When placed in service, two units developed leaks at the header tube connections which had not appeared under test. These were welded in place. One tube developed a pinhole leak. This was cut out and replaced by a new tube.

Elevation Control. Elevation was controlled in the diffusion chambers by a 42-inch butterfly valve, electrically operated. The valve design included a raised seat for the butterfly. This valve, at times, opened to a certain point, then fluttered with such force as to break the driving linkage. Eventually the valve was removed from the line, the raised seat machined out, a new butterfly installed, and heavier driving mechanism provided.

Ozone Diffusion. In the original installation, the stainless steel piping fed the ozonated air into a 5-inch-wide distribution channel, formed into the concrete floor of each tank, and covered with nonporous concrete slabs. Ozonated air was distributed

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outward through circular openings in the walls of this channel into a shallow chamber, beneath porous plates. It passed upward through the 1-inch porous plates to diffuse throughout the 18½ feet of water above. The inside of the channel and the entire tank bottom under the plates was coated with Bitumastic to avoid attack by ozone. Joints between the plates were poured with hot Bitumastic. All metal support units were of stainless steel.

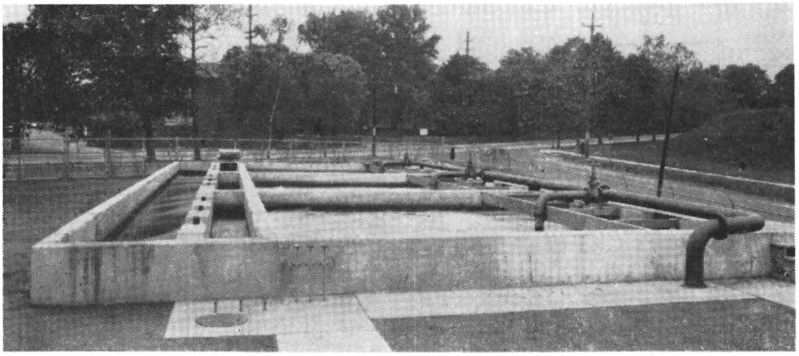

Figure 11. Contact chambers

It proved impossible to keep joints between the plates sealed, apparently because of shrinkage of the Bitumastics. Tests on one day indicated that as much as 20% of the ozone applied to one tank was escaping to the atmosphere. The ozone was decomposing the concrete of the distribution channel in spite of the coatings applied.

Replacements of these bottoms by porous stainless steel diffuser tubes was proposed, but the manufacturers, after some trials, stated they could not furnish the uniformity, between different tubes, which was considered necessary.

Finally porous tubes of fused alumina were installed, 72 per tank, 3-inch diameter, 36-inch length, ⅜-inch thickness, with air permeability of 25 cu. feet per minute per sq. foot, at 2-inch head. All pipes, bolts, etc., were of stainless steel. Tests following installation of these tubes indicated that 90 to 95% of the ozone was being used in the reactions.

Atmospheric Pollution. Because of the difficulty of keeping diffuser plates sealed, and the resultant ozone waste to the atmosphere, grass and shrubbery nearby were destroyed, and, on damp days, or when the wind shifted to carry from the plant toward the neighboring houses just across the street, the neighbors complained, justifiably.

Light-weight covers of protected, corrugated, galvanized steel were placed over the tanks, with suction lines to a blower discharging upward through a stack, to the atmosphere. Along one edge of each cover an opening was left, about 1 inch wide, while the suction was from the opposite side of the tank. The blower delivery was 10,000 cu. feet per minute, while ozonated air volume is less than 1000; therefore, discharge from the diffuser tanks is diluted more than ten times before reaching the atmosphere.

These covers and blower were installed before the diffusion tank bottoms were changed, and proved insufficient at that time, but since the change to porous tubes no difficulties have been experienced.

Operation

The contract for ozonation equipment placed upon the contractor responsibility for operating the ozone-generating plant for 90 days, during which time he was to

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train personnel, employed by the city, in both operation and maintenance of the plant.

The city's group of four shift men operated the plant exclusively for about 4 years, one man being in the building at all times. Since that time these operators, originally filter plant operators, have been assigned to operate the slow sand filters and posttreatment, as well as ozonation. Readings are recorded each 3 hours on all operations. The operators are out of the ozone plant from 1 to 2 hours out of each 3. There appears to be no reason to change this arrangement.

A mechanical engineer was assigned responsibility for operation and maintenance of this plant, as his first responsibility. A major part of his time was devoted to inspections, or mechanical work at other locations, and for the past 3 years he has devoted very little time to this plant.

Data on operation of the plant are given in Table I, for the years 1950 to 1955.

Table I. Belmont Ozonation Plant Operation Data, 1950 to 1955

	1950	1951	1952	1953	1954	1955	Av. 1950–55
O_3 produced, lb./day	541	476	301	398	469	377	427
% capacity	43	38	24	32	37	30	34
Max. monthly av.	687	637	354	707	788	524	...
% capacity	55	51	28	57	63	42	...
Min. monthly av.	344	346	219	234	273	255	...
% capacity	27	24	18	19	22	20	...
Max. day production	902	822	436	800	869	618	...
% capacity	72	66	34	64	69	49	...
Min. day production	120	81	65	77	130	91	...
% capacity	10	6	5	6	10	7	...
Total production	193,085	172,892	34,601	140,696	171,877	123,606	139,459
Days operated	357	363	115	354	363	328	313
Total water treated, mg.	12,264	11,882	2,856	12,097	12,436	11,886	10,570
O_3, lb./mg.	15.7	14.7	12.1	11.6	13.8	10.4	13.2
O_3 applied, p.p.m.	1.89	1.76	1.45	1.39	1.65	1.25	1.58
O_3, lb./gen. unit/ 24 hours	27.1	23.5	25.9	24.6	25.6	24.8	25.3
Total kw.-hr. (all uses)	2,430,813	2,309,043	411,700	1,570,900	1,738,500	1,296,500	1,626,243
Av. cost per kw.-hr, $	0.01021	0.01016	0.0126	?	?	0.0133	?
O_3, kw.-hr./lb.	12.6	13.4	11.9	11.1	10.1	10.5	11.6
Kw.-hr./mg. treated	198	194	144	130	140	109	154
Cooling water, mg./d operated	0.985	0.923	0.633	0.806	0.923	0.837	0.851
Total mg.	342.00	335.51	72.95	285.24	335.28	274.82	274.30
Gal./lb. O_3	1774	1933	2093	2027	1950	2223	1965
Cost at $9.00 /mg.	$3038	$3019	$657	$2567	$3017	$2475	$2469
Air use, million cu. ft.	?	336.900	?	192.926	275.418	223.611	?
C.f.m. per gen. unit, av.	?	31.8	31.2	23.2	28.6	31.1	?

The plant was operated only 85% of the time, treating an average of 10,570,000,000 gallons per year. Rate of generation averaged only 34% of capacity. Cooling water use averaged 851,000 gallons per day, or 1956 gallons for each pound of ozone produced. Electric current use averaged 154 kw.-hr. for each million gallons of water treated.

Maintenance

Maintenance has been by regular mechanics employed on the filter plant, or by mechanics and electricians employed in the pumping station division. Three exceptions have been a continuing contract for servicing of the refrigeration equipment by manufacturers' representatives, the work of the mechanical engineer mentioned under operation, and manufacturers' servicing of the dew point recorder, which has been required on several occasions.

Nearly all of the difficulties encountered were taken care of by the contractor for the equipment, under the contract.

Approximately two dozen leaks have developed in the generator tube connections to headers, which have been welded in place. Only one hole through a tube has been recorded, about 2 inches from one end. It was welded and then ground smooth.

Glass electrode tube failures have been few, even including the leaks, which allow the generator to fill partially with water, and destroy one or more tubes. Under the original contract, the contractor supplied 5% extra electrode tubes. No more than one half of these have been actually required thus far.

At the time of installation, on the basis of information from other ozone plants, it was estimated that the stainless steel tube surfaces would have to be cleaned every 6 months. Only 20 of the 50 units have ever been cleaned. Those uncleaned are not in bad condition. This is the finest evidence of the efficacy of the complete air cleaning and drying.

Efficiencies

Production. Tests on the equipment, when first installed, showed that generation of ozone would exceed the 25 pounds per unit per 24 hours, necessary to meet the specifications, when air flow was such as to produce concentrations in the range of 0.33 to 1.11%. Tests above this range were not made. The best production (28.0 to 28.4 pounds) was shown at around 0.9% and there were evidences of some reduction at higher concentrations. At 0.65% or less, production barely met the specification.

Production throughout the total period of operation has averaged 25.3 pounds per unit per 24 hours.

In the original tests production at 0.67% concentration was 26.3 pounds per unit. In 1954, a 4-day check test, under similar conditions, operating 12 generators, having an average of 11,160 hours of operation, produced 26.1 pounds per unit per day. This was less than 1% change, with generators which had operated, without cleaning, equal to 16 months' continuous service.

Current Use. Average use of electric current for all purposes has been 11.6 kw.-hr. per pound of ozone generated. From the standpoint of practical operations this is the only figure which is of value; therefore, circuits were not metered to break down the use. However, an estimated breakdown indicates the following approximate current uses (kilowatt-hours per pound of ozone):

Air blowers	2.0
Refrigerative and absorptive dryers	1.0
Lights, fans and heaters, recording equipment, miscellaneous	0.25
Blower at diffusion tanks for waste dilution and discharge	0.25
Generator units (remainder)	8.1
Total use	11.6

Costs

Complete operational costs are available only for the years 1950, 1951, and 1955 (Table II). Operational labor and expense are indicated as 21.2%, maintenance 8.9%, electric current 59.3%, heating 2.8%, cooling water 7.8%. Total operational costs averaged $3.03 per million gallons of water treated, and $0.23 per pound of ozone produced. This plant was operated only 98, 99, and 90% of the time in the three years, and at only 43, 38, and 30% of capacity; therefore fixed items of expense greatly affect costs per unit produced or treated.

In each of the three years overhead costs on the plant amounted to about $5.00 per million gallons. However, in 1950, overhead costs per pound of ozone generated were 31 cents, and in 1955 they were 48 cents due to reduction in application from 1.89 to 1.25 p.p.m., with consequent reduced production.

Combined operational and overhead costs have amounted to $8.03 per million gallons. The $3.03 per million gallons operational cost total is not inconsistent with the cost of other methods used for oxidation in water treatment. Overhead such as with

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Table II. Costs of Belmont Ozonation Plant in 1950, 1951, and 1955

	1950	1951	1955	Av.	% of Operation Costs
Operation					
Labor	$ 6,366.93	$ 5,939.05	$ 7,508.54	$ 7,817.08	21.2
Expense	1,626.46	2,010.27			
Maintenance					
Labor	1,800.00[a]	3,154.00	3,346,46	3,292.36	8.9
Expense	301.95	1,274.68			
Elec. current cost	24,741.25	23,447.55	17,307.45	21,832.08	59.3
Heating	1,039.80	1,100.00[a]	893.28	1,011.03	2.8
Cooling water	3,038.00	3,019.00	2,475.00	2,844.00	7.8
Total absolute costs	38,914.39	39,944.55	31,530.73	36,796.55	100.0
Per mg. treated	3.17	3.36	2.56	3.03	
Per lb. O_3 produced	0.20	0.23	0.26	0.23	
Overhead					
Interest on $1 million at 2%	$20,000	$20,000	$20,000		
Depreciation on $1 million at 4%	40,000	40,000	40,000		
Total	60,000	60,000	60,000		
Per mg. treated	4.90	5.05	5.05	5.00	
Per lb. O_3 produced	0.31	0.35	0.48	0.38	
Grand totals					
Per mg. treated	$ 8.07	8.41	7.61	8.03	
Per lb. O_3 produced	0.51	0.58	0.74	0.61	

[a] Estimated.

this plant is not commonly involved with other methods in general use, though such need may be readily conceived where large contact basins are not already available.

This complete plant, operated at 80% of capacity, producing 1000 pounds of ozone per day, depreciated over 25 years, would carry overhead equal to 16 cents per pound produced, and operational costs would be somewhat more than this amount, or a total of about 35 cents per pound. However, modern technology, less than 10 years after design of this plant, already assures new plants in which costs will be, perhaps, no more than half.

Dosage Control

Amount of ozone application is controlled by the number of generators placed in operation. The amount of ozone being generated is determined from the cubic feet per minute passing through the plant and an iodometric titration of 1 cu. foot of the ozonated air passing to the contact tanks.

The amount of dosage specified is ordinarily determined from the residual in the ozonated water leaving the contact tanks. Residuals are determined by the standard *o*-tolidine arsenite test (*1*), as specified for free residual chlorine. Tests are made on the site, immediately on sampling, not after delay due to return to the laboratory. This is very important because of the rapid change in residual.

The method of control could be based on manganese removal, as residual of 0.1 p.p.m. removes 80% and produces bacterial and coliform kill of 95 to 97%. If manganese removal is over 80%, therefore, good kill of organism is assured. One fault of this method is that it fails to show if the dosage is more than needed, as manganese removal does not appreciably increase with higher residuals.

Effects of Ozonation

Tastes and Odors. During the early years of operation, considerable trade wastes were received; more recently this has not been true. Ozonation proved effective on removal of materials causing taste and odor, particularly the phenolics. In the first year of operation it produced a 70% reduction in the cold odors. In 1951 the average reduction was 55%; the odor intensities were measured by the standard threshold method (*2*). With reducing intensity of odors in the river water, the percentages were recorded as 47% in 1952 and 45% in 1953. Since 1953 thresholds of odors in the raw water have been too low to warrant percentage comparisons.

On musty organic odors and tastes of natural origin, as from leaves and weeds, ozonation has not proved entirely effective, though it has definite effects. In 8 months of 1951 and 1952 raw water characteristics were very similar. With ozonation functioning in 1951 only 20% of the plant effluent samples were determined as having musty odors, while in 1952 without ozonation, in spite of other treatments used, musty odors were present in 28% of the samples.

Disinfection. Kill of coliform organisms, and of bacteria which grow at 37° C., on agar is shown in Table III, by yearly averages. These indicate practically identical percentages for the two classes, and kills definitely proportioned to the ozone residuals. The kills were approximately 90.5% for average ozone residual of 0.06 p.p.m., 94.5% for 0.08 p.p.m., and 98% for 0.16 and 0.20 p.p.m.

Table III. Average Yearly Kill of Bacteria (90% of Tests)

		Percentage Kill			
	Ozone Residual, P.P.M.[a]	Coliform organisms		Bacteria[b]	
1950	0.20	97.7	97.7	97.6	98.2
1951	0.16	97.8		98.9	
1952	0.20	97.5		98.0	
1953	0.08	96.5	94.3	95.5	94.6
1954	0.08	92.1		93.8	
1955	0.06	90.5		90.7	90.7
1956 (Jan.-Sept.)	0.033	78.7		78.5	

[a] Determined by standard *o*-tolidine-arsenite method for free residual chlorine (*1*).
[b] Determined by counts on agar, at 37° C. for 24 hours.

In Figure 1 is shown the percentage kill of coliform organisms against various residuals. Each point plotted represents the average of all monthly kills when the ozone residual averaged as indicated. Kills are 95% with less than 0.1 p.p.m. residual and 99% with 0.2 p.p.m. and over.

Figure 2 shows the kill of 37° bacteria at the various ozone residuals. The points plotted were determined by averaging the kill shown by 90% of all bacteria tests, correlated with the various residuals, throughout the 6 years 1950 to 1955. Kills of better than 95% are indicated for residuals of 0.1 p.p.m. and upward.

Manganese Removal. In 1950, 1951, and 4 months of 1952, with 0.32, 0.46, and 0.30 p.p.m. of manganese in the water before ozonation, and with ozone residuals of 0.20, 0.16, and 0.20 p.p.m., the removal of manganese was, respectively, 78.2, 82.5, and 80.0%. The removal without ozonation in 8 months of 1952 was 42.8%. These figures represent the result of ozonation or no ozonation, lime and alum application, mixing, settling, and passage through rapid sand filters.

Based on monthly averages, it appears that in this period, removals with 0.10 p.p.m. of ozone residual were just as great as with residuals up to 0.25 p.p.m.

Since 1952, application of chlorine before filtration, to reduce the postdosage required to produce free residual in distribution, has made removal figures noncomparable.

Air bubbles, attaching to oxidized manganese particles, have caused flotation on flumes and settling basins, requiring installation of water sprays to stop surface accumulations.

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Development of European Ozonation Techniques

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The historical development of European ozonators and ozone production are reviewed. The Otto, van der Made, and Siemens processes for generating ozone are described. Recent improvements and innovations are indicated. Two distinct operations are considered: conditioning of the air to be submitted to the electric discharge, and contact between the ozone and the water.

During the first 20 years of this century—that is, from the birth of the first industrial ozonators—considerable interest was focused on ozone utilization. Numerous and diversified applications appeared. Nearly all of them led to failure and disappointment, which is not surprising, considering that industrial ozone production appeared too early in a world which at that time was underdeveloped technologically. In Europe ozone was, and still is, used merely for the sterilization of drinking water.

Considered from this aspect, ozonization comprises three distinct operations: (1) ozone production in itself, (2) conditioning of the air to be submitted to the electric discharge, and (3) contact between ozone and water.

Ozone Generators

All industrial ozone generators are based upon the principle of the electric discharge through dielectrics which act as stabilizing resistances, counteracting any increase or localization of the density of the high tension discharge. The essential presence of such dielectrics establishes electrical conditions under which the discharge takes place, at the same time introducing an electrical capacity effect and a leading power factor of 0.4 to 0.6.

From the electrical point of view, therefore, the ozonator appears as a condenser which allows a rather significant amount of energy to pass through. Accordingly, the alternating electrical strains applied to the molecular structures of the dielectrics produce heat through a dissipation of energy, and the dielectrics have to be cooled by conduction or convection.

In other respects, the electrodes themselves are subject to heating. This results in Foucault's currents, in an electronic emission on the active surface of the electrodes, and finally in a secondary heating through convection, conduction, and radiation, due to the immediate vicinity of the dielectrics and the discharge itself. Therefore, the electrodes cannot be thermally insulated from the system, and cooling must be provided.

For ozonator electrodes and dielectrics, one of the four arrangements shown in Figure 1 can be adopted, in which the discharge takes place either between two dielec-

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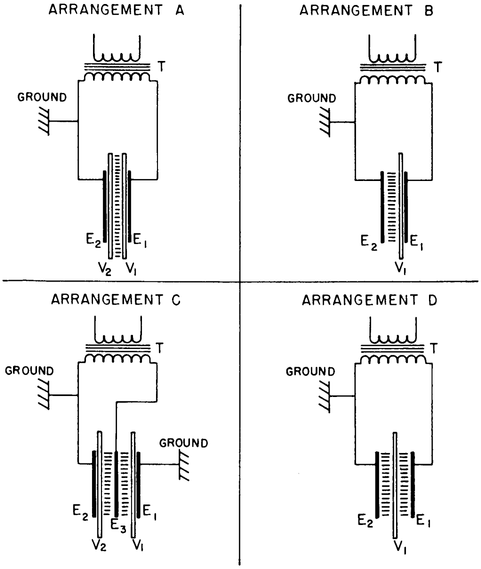

Figure 1. Arrangement for ozonator discharge

E. Electrode
V. Glass dielectric
T. Transformer

trics or between a dielectric and a bare electrode. With any of these arrangements, one of high tension poles can be grounded.

Two dielectrics (arrangement *A* or *C*) are seldom used in actual practice. For equal discharge density, an applied tension higher than that corresponding to a single dielectric assembly is necessary. Therefore, the energy of the discharge with two dielectrics can only be less than that of the single dielectric assembly. The double dielectric (arrangement *A*), the only one applied industrially with success, provided an obvious interest for an era when stainless steels were unknown, because these dielectrics protected the electrodes from corrosion due to high tension discharge in the air.

Of the two assemblies possible with one dielectric, arrangement *D* has been rejected industrially because of the practical impossibility of cooling the dielectric. Arrangement *B* is the basis of the most interesting of the accomplishments in the matter of ozone production.

In Europe from 1907 to 1930, three ozone generating processes were successfully submitted to the test of industrial applications: the Otto, the Van der Made, and Siemens processes. Since 1930, there has been a tendency toward improving the production equipment of these processes with a view to reducing its size and eliminating certain production drawbacks, such as the too frequent breakage of dielectrics.

Otto Ozonators. Before 1930, Otto ozonators, built and put into use in numerous municipal water treatment plants, were of the flat electrode type with two dielectrics, assembled as in arrangement *A*, Figure 1, and supplied with 500-cycle current.

An ozonator comprised a certain number of individually producing units grouped in an insulated enclosure, glazed on the front and rear surfaces. The two outer electrodes were hollow plates at ground potential, cooled by circulating water through them. The high tension plate was water-cooled by the use of two waterfalls which isolated the high tension from ground. Figure 2 shows such an ozonator with five

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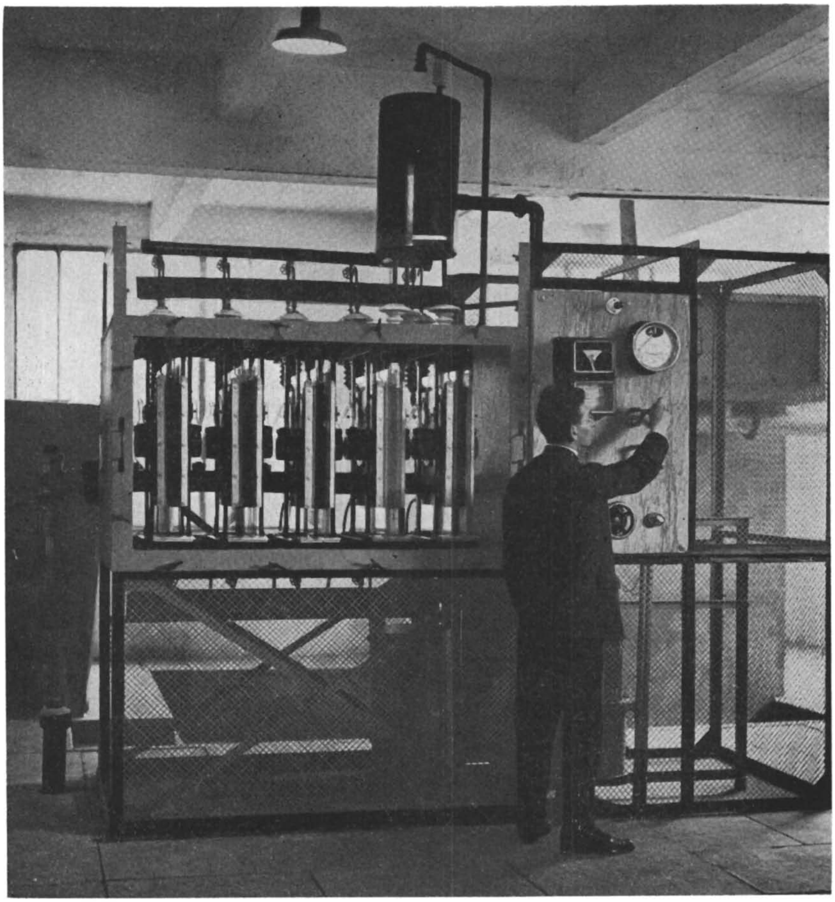

Figure 2. Otto ozonator, flat-electrode type, with five ozonator elements

High tension electrode cooled with water

ozonator elements. One of the waterfall devices can be seen at the top of the photograph.

In 1930 certain structural modifications appeared, which had little effect on production efficiency. In general, they rendered the ozonators less bulky and cheaper to construct. The ozone-producing elements were grouped in the manner of a filter press and were called ozonator blocks. Each block contained one to six elements. The plates, originally of cast iron, were now of Alpax, an alloy of aluminum and silicon. Batteries of four blocks arranged as shown in Figure 3 provided greater production capacity in less space. The cooling arrangements remained substantially the same.

In 1938, to eliminate the handicaps of cooling the high tension electrode with water, transformer oil was used for cooling. It was circulated in a closed circuit, which included a pump and a water-cooled heat exchanger, and was conducted to and from the high tension electrodes by means of long borosilicate glass tubes. Although this arrangement eliminated electrical losses caused by the water falls, the improvement was partially offset by the electrical consumption of the circulating pump. Figure 4 shows an ozonator of this type.

At the end of World War II, the use of 500-cycle current for supplying Otto

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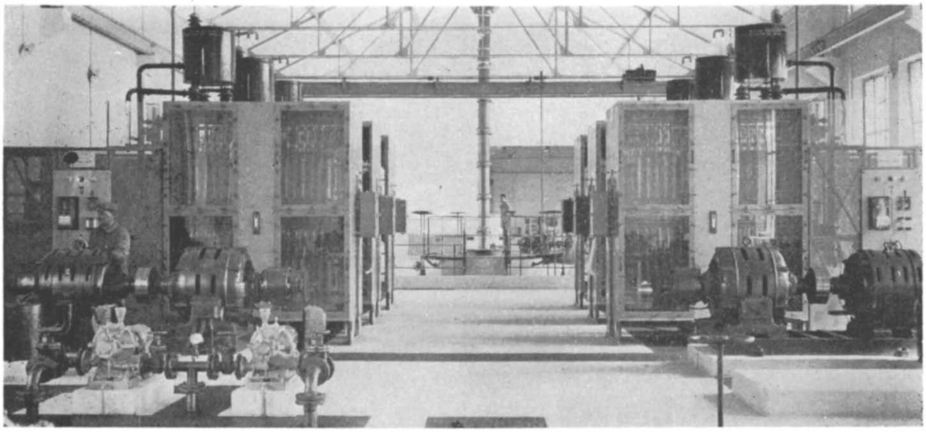

Figure 3. Otto ozonator with ozone-producing elements grouped in batteries of four blocks

High tension electrode cooled with water

ozonators practically disappeared. Thenceforth they were designed to function at the normal distribution frequency of 50 cycles.

About 1948, hollow plates of stamped and welded steel were introduced. While these reduced costs, it was difficult to achieve completely flat and parallel faces and plates which would not become deformed. These problems have not yet been solved satisfactorily, and this innovation cannot be considered successful because of more frequent dielectric breakage.

In 1954, oil cooling was abandoned, largely because of the difficulty of keeping the circuits leak-tight. A block model ozonator was developed wherein the high tension

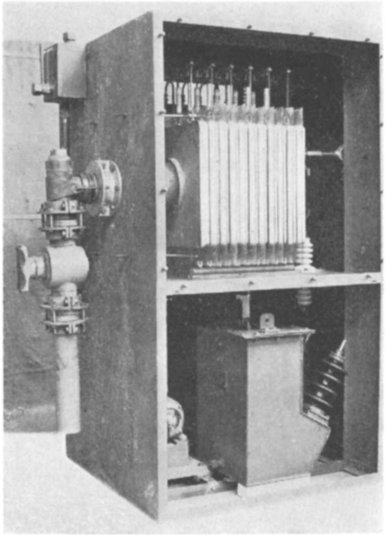

Figure 4. Otto ozonator

High tension electrode cooled with insulating oil electrode was cooled only by radiation and convection of air within the ozonator cage. The low tension electrodes remained water-cooled.

The final development has been the adoption in this latest design of arrangement *B* (Figure 1), whereby there is only one dielectric per discharge. Also, the dielectrics are thinner (2.6 mm. instead of 2.5 to 3.5 mm.), and tolerances are closer. Energy yields of 18 watt-hours per gram of ozone are attained (concentration not specified). Even this design has weaknesses: The high tension plate of Alpax is corroded by the action of the discharge; the low tension steel plates are prone to cooling water corrosion, and their lack of flatness increases dielectric failure.

Van der Made Ozonators. Derived from the original Siemens ozonator, the van der Made differs only in the ingenious method of rigidly centering the high tension electrodes. These tubular ozonators, designed as in arrangement *B*, Figure 1, have undergone only minor modifications since their introduction. A horizontal glass dielectric is surrounded by cooling water, which serves as the grounded electrode. The high tension electrode is spaced concentrically within the glass tube, leaving an annular discharge space.

The more recent models are distinguished from the older models (prior to 1930) by a central electrode of stainless steel instead of aluminum, dielectrics of borosilicate glass instead of ordinary glass, an improved method of fixing the dielectric tubes into the end plates, and a change in the exterior shape of the housings for the units.

Siemens Ozonators. The Siemens ozonator, one of the first ozone generators capable of successful industrial application, has undergone no technical modifications since about 1933. It is supplied by a 10,000-cycle current. Curiously, the generator is very similar to the venerable Berthelot ozonator. The basic generating cell is of semicrystal glass of special composition. It is of tubular design with two concentric glass dielectrics assembled according to arrangement *A*, Figure 1. The outer glass tube is supported vertically in a tank through which water circulates. The water plays at the same time the part of a grounded electrode and a means of cooling. The high tension electrode is likewise of water, which is circulated through the inner glass tube. A number of such cells are arranged in parallel.

The cooling of the high tension electrodes is by a means similar to that of the first Otto ozonators, except that the break in the high tension circuit is accomplished by a rain of droplets into insulating oil instead of a fall through air.

This ozonator, despite the qualities it displayed at the time of its introduction, has not been very successful. Expensive because of the use of the 50- to 10,000-cycle converter set, it seems fragile and difficult to operate.

Ozono Ozonators. These generators, developed by the engineer Niccoli about 1936 for the Ozono Co. of Milan, are derived from the Otto plate block-ozonator. They differ in details as well as the following points: The cooling plates are circular and made of thin steel (0.5 mm.) by stamping two half-shells, united by crimping, and made tight by soldering. The dielectrics are of micanite and are spaced by radial strips. There are special check-plates, ensuring a reasonable tightening of the elements constituting a block, and the method of suspending the plates automatically ensures their centering. The ozonator is in the form of a desk.

A circulation of insulating oil operating by means of a thermosiphon ensures the cooling of the electrodes with oil, which in turn is cooled by water. The ozonators operate on 50-cycle current. The units are well constructed. It is regrettable that they have been supplied with air dried by calcium chloride, which reduced their production efficiency. The specific energy yields for these ozonators have never been made public.

Conditioning of Air before Discharge

In Germany. Prior to 1933, all industrial ozonators were supplied with air dried by calcium chloride. It was the Siemens Co. which first used silica gel. The dryer de-

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signed by this company was a continuous-operation type with two adsorption cells reactivated in closed circuit. The changing over of the air streams at the time of reactivation was ensured by a solenoid valve, itself regulated by a timer with adjustable electrical contacts.

In France. In 1938, the first silica gel dryer applied to the Otto process was put in operation. Since then, this method of drying has normally been used in all Otto ozonation plants, except the Saint-Maur plant, which alone uses cooling.

After 1952, Otto ozonation equipment used two stages of drying to condition the air: The first stage ensures the cooling of the air down to +5° C. by means of a heat exchanger immersed in a brine bath containing also the evaporator of the refrigerator; the second stage ensures the final drying by passing the air through silica gel.

Ozone plants established according to the van der Made processes use calcium chloride as a dehydration agent. Only recently has silica gel drying been adopted.

In Switzerland. The very fine ozone sterilization plant built at Berne includes a novel air-drying installation designed by the Carba Co., Berne.

After passing through a dust filter, the air is compressed to 5 kg. per sq. cm. (71 p.s.i.), cooled in a circulating water heat exchanger, then cooled down to −30° to −40° C. in an exchanger served by a refrigerator before expanding to operating pressure. Under these conditions, the dryness attained is about 30 mg. of water per kg. of dry air (dew point, −60° F.).

This completely automatic installation operates well, but seems much too expensive to run. The specific electrical consumption is 210 watt-hours per cubic meter of air, which brings the consumption for the ozonated air at a concentration of 10 grams per cubic meter, to 21 watt-hours per gram of ozone. This electrical consumption is much higher than that necessary for the production of ozone itself, and five to six times higher than that required for a drying system using activated alumina or silica gel.

In Italy. The air-drying method used in most installations of the Ozono-Niccoli type was absorption by calcium chloride. The use of porous adsorbents did not appear until around 1938.

Bringing Ozone and Water into Contact

After the ozone is produced, it must be made to act upon the water. This problem, which is a matter of bringing large volumes of gases and liquids into adequate and continuous contact, has been approached in a variety of ways. Two methods were introduced about 1930. One was developed by Otto, the other by Van der Made.

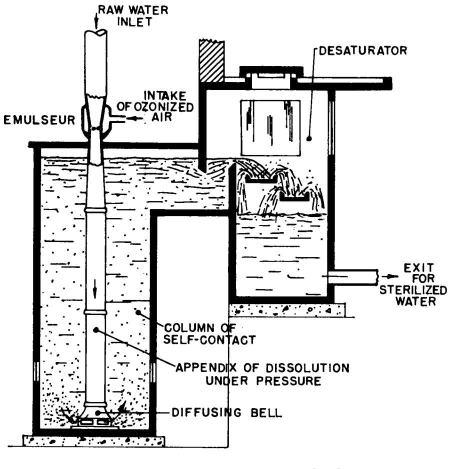

Figure 5. Water pump and deep tower

According to the Otto method (Figure 5), the ozonated air is aspirated by a sort of water pump called an *émulseur.* The resulting emulsion is carried along at increasing pressure through a vertical tube, *l'appendice de dissolution,* to the bottom of a deep tower, the *colonne de self-contact,* where it rises again, freeing myriads of fine bubbles which prolong and improve the contact between water and gas. The dissolving appendix, immersed for its entire length, releases the emulsion at the base of the self-contact column by means of a diffusing bell, which imparts a circular movement to the water entering the column. The column is cylindrical or prismatic, made of reinforced concrete, with a depth of 5 meters (16 feet). The water leaves the column over a weir at the top and passes through a series of cascades called a desaturator, which removes any dissolved ozone.

This desaturation has been incorporated to conform to the "Recommandations du Conseil Supérieur d'Hygiène Publique de France de 1924," which stipulate that after treatment the water must contain no substance foreign to its original composition. However, today there is a tendency toward elimination of final desaturation in order to maintain the ozone in contact with the water as long as possible.

The apparatus utilized in the Van der Made system is a column of suitably protected steel in small installations, reinforced concrete in large ones. The column is divided into sections of horizontal perforated celluloid plates with 0.7-mm. holes. Both the water and air enter at the bottom and pass upward through several of these plates. This method provides good mixing and allows utilization of low concentrations of ozone. Another novel characteristic of this process is the recovery of excess ozone at the top of the column and its recycle through drier, ozonator, and piston-type compressor. By use of a variable speed compressor, the quantity of ozone injected can be varied in accordance with the quality of the water.

Because of a number of problems—e.g., weakness of the perforated plates, too low an ozone concentration, too large a volume of air, and costly maintenance of the compressor and other equipment because of corrosive action of ozone—this method has been modified in later installations. The perforated plates have been eliminated, and the air is diffused through plastic diffusers. Stainless steel rotary, liquid ring compressors are used. In some cases, even the Otto method of *émulseurs* and self-contact columns is employed.

Contact Processes Since 1930

Chlorator Process. This process uses a small contact column and injector, whereby a portion of the water is treated to dissolve a relatively large amount of ozone. This portion is then added to the main water stream. The success of the method requires a high concentration of ozone (10 to 20 grams per cubic meter) and a static pressure of 0.6 to 2.0 kg. per sq. cm. Anywhere from one half to one sixth of the total water may be required in the ozonized stream.

Torricelli Process. This mixing method was developed by Alfred Torricelli of Berne. Its advantages are the ability to dissolve more ozone in the water through higher pressures and improved contact, and to attain virtually complete absorption of the ozone in the water.

The Kerag Process. This system uses a high-speed agitator of stainless steel, which rapidly mixes the ozonized air and water intimately. After mixing, the water-ozone passes into a contact basin.

These three systems have been introduced only recently, and they are compared in a paper by Torricelli (*1*).

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Fifty Years of Ozonation at Nice

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Since 1906 the water of Nice, France, has been sterilized by ozone. Operating data are given for two treating plants. Water sterilized by ozone does not have an unpleasant taste. Mineral substances are not generally modified by the process, and no foreign substances are introduced. A clear water containing ozone in solution which persists from 3 to 10 minutes, according to the temperature of the treated water, is sterile from a practical standpoint.

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In 1904 the city of Nice, authorized by the French Higher Council of Public Hygiene, adopted ozone, and 2 years later the sterilization of water by ozone was put in practice on an industrial scale for the first time in France. Since then, numerous towns have followed the example of Nice.

In 50 years, the population of Nice has increased from 150,000 to 250,000 inhabitants; the number of water works has increased from one to four; the quantity of water sterilized daily by ozone has increased from just over 5,000,000 to almost 20,000,000 gallons. However, the process of sterilization remains the same because it has always produced good results.

Sources of Water

One quarter of the water comes from the Sainte Thécle springs and the remaining from the Vésubie River. The springs of Ste. Thécle emerge from limestone fissures in the midst of cultivated land. The water is frequently polluted, especially during periods of rain and irrigation; it is brought by a stone aqueduct to the Bon-Voyage plant where it is filtered and sterilized.

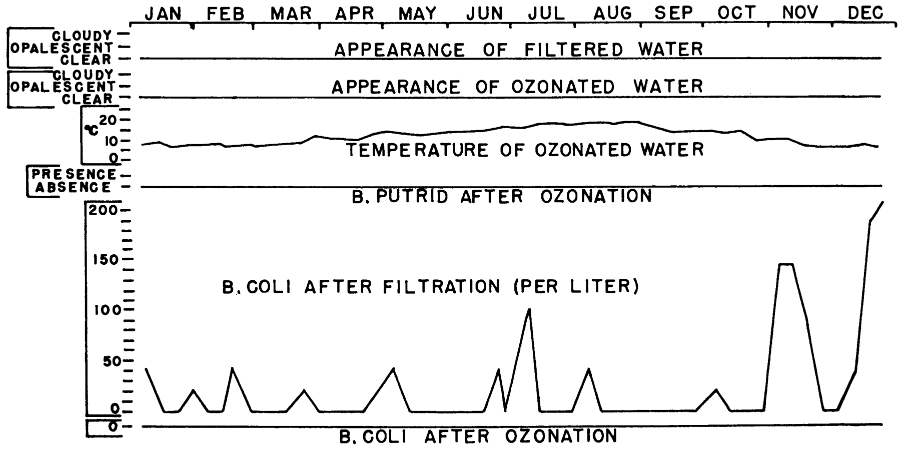
The Vésubie is a torrential river. A water intake has been installed at the elevation of Saint-Jean La Rivière about 20 miles from Nice. The banks of the upper and middle Vésubie are populated with summer resorts, and the water is often turbid. The water is stored in five uncovered masonry reservoirs having a total capacity of over 21,000,000 gallons. It is filtered and sterilized at the Rimiez plant as needed.

On arrival at Nice, the water from Ste. Thécle and La Vésubie is often opalescent, turbid, or even muddy, and always contains pathogenic bacteria and various saprophytic germs. Before delivery for utilization, it is filtered and ozonated.

Properties of Water Sterilized by Ozone

Organoleptic Characteristics. Viewed in depth, the filtered water often looks gray. After ozonation, the water appears blue, like the water from glaciers.

During floods, the water of the Vésubie often tastes and smells earthy, but after



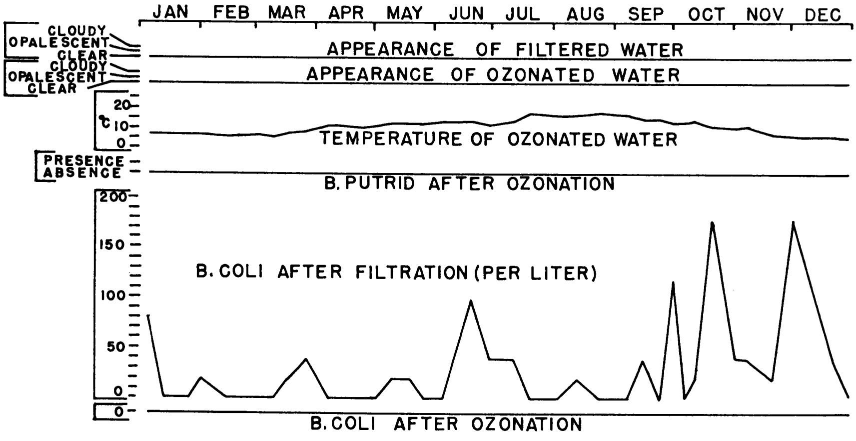
SHUT-DOWNS: CANAL FROM THE VESUBIE-APRIL 26, OCTOBER 18

Figure 1. Operating data for Bon-Voyage plant

ozonation it is odorless and tasteless. Unlike chlorine or chlorine products, ozone never generates unpleasant tastes.

Chemical Composition. Ozone often adds oxygen to the treated water through aeration accompanying the purification process. Because of the chlorophyllian action of sand-filter algae, the water can become supersaturated with oxygen. This phenomenon explains the oxygen reduction sometimes observed after ozonation. Thus ozonation plays the part of a regulator of the oxygen content of the water.

The action of ozone appreciably reduces not only the proportion of free ammonia in the water, but also the proportion of albuminoid ammonia and organic substances. Mineral substances are in general not modified by the ozonation process. However,



SHUT-DOWNS: CANAL FROM THE VESUBIE - APRIL 26, OCTOBER 18
NO. 1 SECONDARY CHANNEL-APRIL 26, MAY 4, OCTOBER 18 & 25
NO. 2 SECONDARY CHANNEL-APRIL 26, MAY 4, OCTOBER 18 & 25

Figure 2. Operating data for Rimiez plant

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calcium carbonate is sometimes lightly precipitated and reduced iron, if present, is oxidized to the insoluble hydroxide.

Ozonation of water introduces no foreign substances. On the contrary, because of the noticeable reduction in organic substances, the ozonated water is less conducive to the development of foreign bacteria.

Bacteriological Examinations. A clear water containing ozone in solution which persists from 3 to 10 minutes, according to the temperature of the treated water, is sterile from a practical standpoint. Sampling and bacteriological examinations are carried out according to the technique and methods of the Montsouris Laboratory. Examinations are made for *E. coli, Enterococcus,* and *Cl. perfringens,* and a count is made on gelatin.

In 1955 1770 samples of Nice ozonated water were examined. None revealed the presence of pathogenic bacteria. Ozonated water is often sterile—that is, devoid of all germs. The usual number of harmless bacteria and sporulating germs varies from 5 to 15 per ml.

Figures 1 and 2 give operating data for the Bon-Voyage and Rimiez plants which use water from the Vésubie River. As can be seen, the treated water from the two ozone plants is excellent from all points of view.

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Drinking Water Purification

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A comparison of conventional means of mixing ozone with water for disinfection with two recently developed methods shows that the newer methods permit more effective utilization of ozone. Operating experiences with pilot plants utilizing these systems are described. With the new methods ozone dosage requirements can be reduced by as much as one half, while maintaining full bactericidal efficiency.

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France, the birthplace of ozone water treatment, is the only country in Europe to remain faithful through half a century to the idea of using ozone to purify drinking water.

The foremost authorities on hygiene in that country, among whom were the late Professors Roux and Calmette of the Pasteur Institute, have never ceased to consider the treatment of water with ozone to be the best disinfecting process known. It does not add to the water any injurious foreign substance. Moreover, ozone never generates unpleasant tastes, as chlorine and its derivatives do; on the contrary, it can destroy most unpleasant tastes and odors. Color due to organic decomposition products in water can also be removed.

Ozone water purification plants constructed in France about the beginning of the century are still in operation. Those who manage them seem aware that ozone is an ideal way to purify drinking water and that there is nothing at present available which can replace it.

Unfortunately, in the treatment of drinking water the real question of the wholesomeness of the water supply in all its aspects has been too often neglected, with emphasis only on the problem of the destruction of pathogenic bacteria. Though doubtless the most important, this is not the only question which should be taken into consideration. The aim of the hygienist should be to assure the community water which is not only safe, but also agreeable to drink. At present, ozone best meets these requirements.

Up to now, ozonation of drinking water has been considered too difficult, especially in comparison with chlorination. The outlay for the relatively expensive installations and the high costs of operation were objectionable. In most cases the plants have seemed unprofitable. It appears, moreover, that all the European ozonation plants still employ water-treatment processes which do not permit proper utilization of all the ozone produced by the ozonators. Perhaps 40% of the ozone is lost because of the difficulty of dissolving the gas in the water with the available means. On the other hand, there is no doubt of the actual efficacy of the ozone water treatment in the French plants in operation.

In OZONE CHEMISTRY AND TECHNOLOGY;
Advances in Chemistry; American Chemical Society: Washington, DC, 1959.

The author has been occupied with the problem of the best utilization of ozone for the purpose of reducing the consumption of the gas to a minimum while endeavoring to obtain maximum bactericidal action. As a result of this research, a new water treatment process fulfilling the desired objective was introduced for the first time at Berne in 1951.

At present in Europe, water is treated with ozone according to the old Otto process or the Van der Made process. As far as is known, other processes have not become established. These two are the original systems proposed by those who introduced ozone into France.

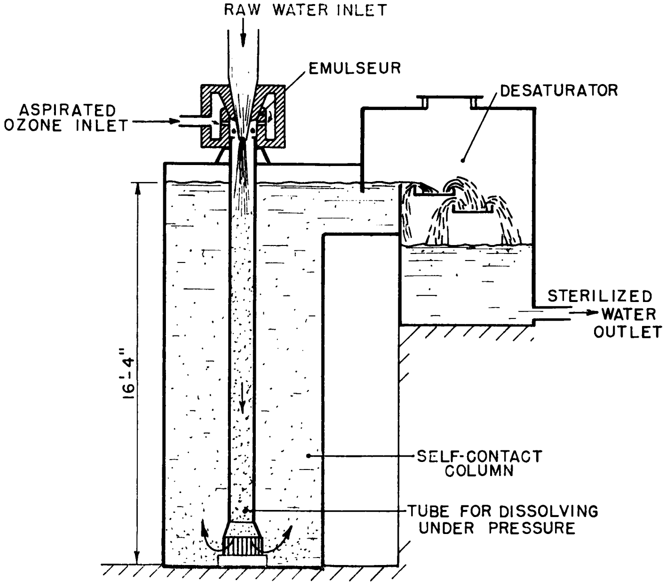

Figure 1. Schematic section of Otto apparatus for ozonating water

Figure 1 is a schematic section of the Otto sterilization apparatus, the most commonly utilized. It is used generally in combination with Otto plate ozonators. The water to be treated comes under pressure to the *émulseur,* a sort of water jet pump. The vacuum produced by the water is sufficient to suck in the ozonated air from the ozonator, and the mixture of the two fluids is carried to the bottom of the self-contact column, which is a tower 5 meters (16 feet 4 inches) in depth. The water falls freely from a weir at the top of the tower, where most of the gas escapes.

The retention time in the tower is 8 to 10 minutes. For each cubic meter of water to be treated, 300 to 600 liters of ozonated air at a concentration of 2 to 3 mg. per liter are required (a dosage of 0.6 to 1.8 p.p.m.). The disinfection is excellent as long as excess ozone is introduced into the émulseur. Loss of ozone which cannot be dissolved in the water is considerable.

This method of water treatment is not economical when electricity must be purchased. It is suitable for mountain districts where the water arrives naturally under pressure at the place where it is to be treated. Then the cost of electricity to operate a pump for the émulseur is avoided, and excess water pressure also can be used to generate the electricity necessary for the ozonation. But such favorable conditions are rare, especially for large centers of population.

Figure 2 is a schematic section of the sterilization apparatus generally utilized with Van der Made ozonators. It is a simple ozonation tower in which the water to be

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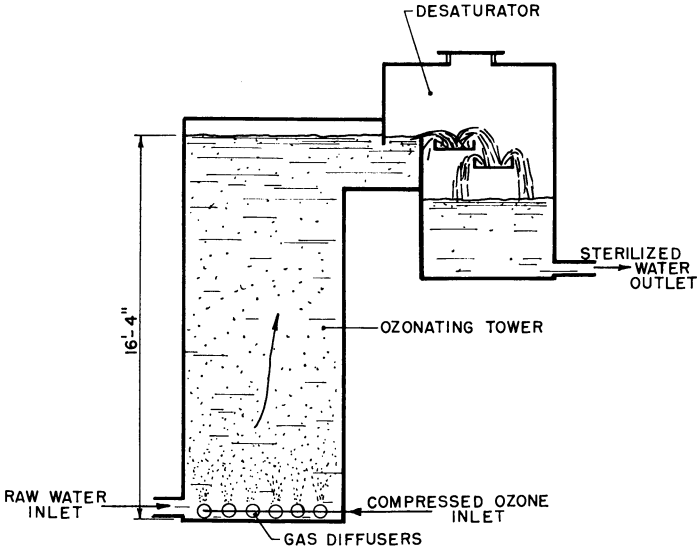

Figure 2. Schematic section of Van der Made apparatus for ozonating water

treated enters at the bottom and leaves at the top. The ozonated air is injected at the bottom through porous diffusers, with the aid of a compressor placed between the ozonator and the ozonation tower. The ozone dosages approximate those of the Otto process and the losses are likewise considerable.

In these two processes the ozonation conditions are such that efforts to dissolve the ozone in the water at a high rate encounter great difficulties. The ozone content of the water reaches its maximum at the bottom of the tower, and the ratio then diminishes as the ozonated air, meanwhile losing its ozone, sweeps the water toward the exit at the top of the tower.

Attempts have been made to improve the Van der Made process by recovering the ozone which escapes from the top of the ozonation tower by passing it through a dryer and recycling it through the ozonator. This scheme has produced results of dubious value and apparently is seldom used, but it is an indication of the importance attached to limiting the ozone losses, which are of important economic consequence.

Since 1947 an effort has been made to stimulate interest in Switzerland in favor of using ozone to treat drinking water. During this period several small installations for ozonating water have appeared in Switzerland. Most of these were soon abandoned because of defects and general inefficiency. Unfortunately, ill-conceived efforts such as these have created indecision and hesitation among those who might have been inclined to adopt ozone.

Processes Demonstrated at Berne

In 1951 the proper treatment of water with ozone was unknown in Switzerland. Officials of the Berne Water Bureau accepted the proposal to construct near the Könizberg reservoir a pilot plant equipped with a Welsbach C-4 ozonator to supply ozone to the two water treatment systems by which the water was to be completely and economically purified.

The two water treatment processes included one used in the United States by Welsbach Corp., Philadelphia, Pa., and a new process of the author's invention, which

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was being tried for the first time. The latter involved the use of Welsbach ozonators, which had been found suitable for this application.

Each of the two ozonation application systems was constructed of concrete and designed to treat 25 cubic meters (6600 gallons) of water per hour. They were served alternately by the single ozone-generating plant which ran continuously day and night for nearly 8 months beginning October 1951, to the complete satisfaction of the Berne Water Bureau as well as ourselves.

The first system, applying the process used by Welsbach Corp. at the Philadelphia plant, is designated the Welsbach system (W). It permits ozonation of water under conditions much superior to the known European processes.

The system is depicted schematically in Figure 3. For an hourly water flow of 25 cubic meters, a reinforced concrete tower of 90-cm. inside diameter is used. The tower is open at the top, and the water to be treated moves slowly from top to bottom, just the opposite of the French systems where the water moves concurrently with the bubbles of ozone. The depth of the water in the ozonation tower is 5 meters. The average contact time of the water and gas in the tower is about 8 minutes. The ozonated gas, in the form of fine bubbles, is injected under pressure through a porous gas diffuser into the bottom of the tower, and the bubbles of ozonated air rise countercurrent to the flow of water.

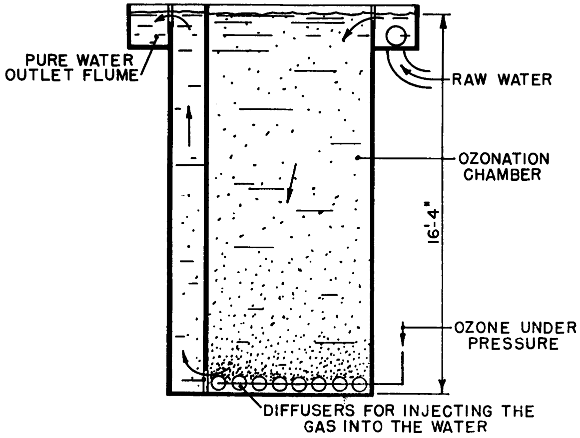

Figure 3. Schematic section of Welsbach apparatus for ozonating water

The ozonated water leaves the tower at the bottom; a channel brings it to the level of the intake so as to maintain a constant level of water in the tower. A certain number of valves for taking water samples are arranged at the principal points of the system, so as to enable one to follow the changes which occur in the water during treatment. These water-sampling points correspond to various accurately determined water-ozone contact times.

The second system for water treatment, shown schematically in Figure 4, depicts the application of the new process, called the Torricelli (T) process.

The installation is characterized by an ozonation chamber hydraulically closed by the pressure of the water to be treated, which flows through it. For these demonstrations, the ozonation chamber was contained in a reinforced concrete cylinder 125 cm. in inside diameter and 230 cm. in inside height. It was compartmented as indicated in Figure 4.

The water enters the ozonation chamber by a vertical descending channel 35 cm. in diameter and leaves by an ascending channel. It moves through the system under its own head, according to the principle of communicating vessels. The loss of pressure

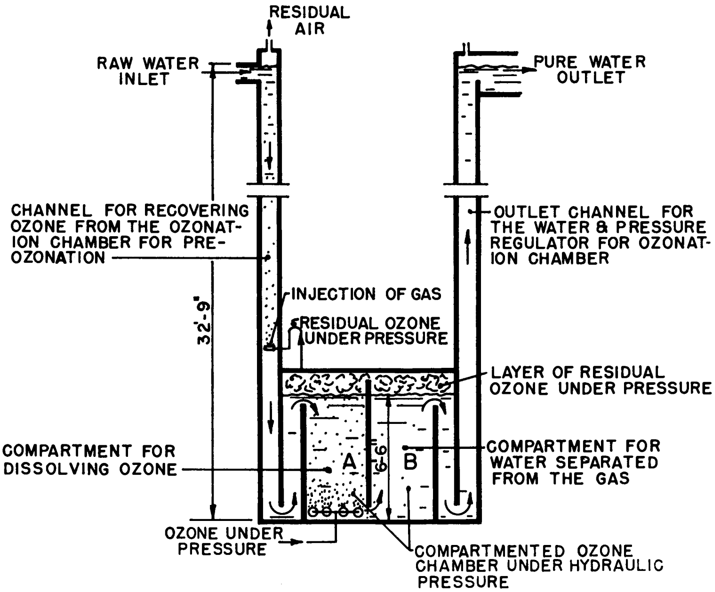

Figure 4. Schematic section of Torricelli apparatus for ozonating water

Ozone chamber with two contiguous compartments at same level

in the system is insignificant. The difference of level between the bottom of the ozonation chamber and the point at which the water leaves the apparatus was, for these tests, 9.5 meters.

The ozonation chamber includes, besides the baffles or partitions necessary to direct the flow of water and to hinder the escape of the gas through the inlet and outlet channels, two main compartments, *A* and *B*. The first serves to dissolve the ozone in the water; ozone enters through injectors or porous gas diffusers placed at the bottom, under a layer of water which need not be more than 2 meters. The water circulates from top to bottom, vertically or obliquely, so that the hydraulic pressure increases up to the point at which the water passes near the injectors or the diffusers. At Berne porous ceramic diffusers were used to introduce the gas into the water.

The water saturated with ozone leaves compartment *A* at the bottom where the ozone is dissolved, and moves slowly through compartment *B*. In compartment *B*, because of the absence of turbulence, the ozone tends to remain in solution at its maximum ratio, and decomposes slowly unless the ozone demand of the water is so high that oxidizable substances still are present.

The undissolved gas, which contains a small amount of ozone, accumulates under pressure at the top of the ozonation chamber. This gas is exhausted through a pipe which leads to the channel where the raw water enters. The residual ozone is thus recovered for the purpose of preozonating the water. In a permanent installation the outflow of the gas under pressure from the ozonation chamber is regulated by a control activated by the level of the water in this chamber. The undissolved gas finally escapes at the top of the water entrance channel, the bubbles of gas moving countercurrent to the flow of water. The velocity of the water in the preozonation channel is not sufficient to carry the bubbles of gas towards the ozonation chamber.

The time for the water to move through the two compartments, *A* and *B*, of the ozonation chamber is normally 5 minutes, or 2.5 minutes per compartment. This is long enough when the water treatment aims mainly at disinfection; it provides a margin of safety sufficient to ensure the complete destruction of the pathogenic bacteria which may be found in the most polluted of the Swiss water supplies.

The average speed at which the water moves through the ozonation chamber is 80 cm. per minute. In the entrance channel leading to the ozonation chamber the rate is five times greater.

Practical considerations require the hydraulic pressure in the ozonation chamber to be held between 7 and 10 meters of water. Under these conditions of average pressure the system can work to best advantage. For the tests a pressure of 9.5 meters was used.

Results of Berne Pilot Plant

The pilot plant installed at the City of Berne's Könizberg reservoir commenced operation in the autumn of 1951. It operated alternately with the two water-treatment systems constructed for the tests. During this period more than 130 tests were carried out with the collaboration of the laboratory personnel of the Berne Water Bureau. Excellent disinfection results were obtained.

The results of disinfection in the Welsbach tower were completely satisfactory. Despite the inevitable losses of ozone from the top of the open tower, which were in any case considerably smaller than in the European processes currently utilized, the efficiency can be considered good when this process is combined with the use of Welsbach ozonators. These deliver the ozonated gas directly at the desired ozone concentration and at the pressure necessary for injection.

The results of disinfection with the Torricelli system were surprising because they easily exceeded the most optimistic expectations. A speedy disinfection was possible with a small ozone dosage. The ozone dissolved in the water at a high rate because of the recovery system adopted to avoid ozone losses.

The results of the great number of bacteriological tests carried out cannot be condensed into understandable tables because the tests differed too much one from another. In most cases they are not readily comparable because the conditions of operation were often intentionally modified. Accordingly, it is necessary to consider each bacteriological test separately on the basis of the conditions which prevailed during the operation.

At the end of the pilot plant trial period a series of four tests was carried out under comparable conditions. By providing a comparison between the two disinfection systems employed, these tests show the characteristics of each.

These final tests, to which great importance was attached, were undertaken in June 1952 under stable conditions of water quality and temperature, natural and artificial degrees of infection, and alternate ozone dosages used for disinfection.

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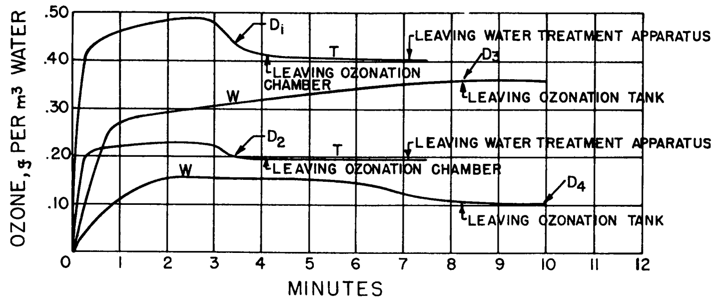

Figure 5. Destruction of *B. coli* in strongly polluted waters by Welsbach and Torricelli processes with Welsbach ozonator

Effective quantities of ozone dissolved in water during disinfection, injecting 0.25 and 0.50 gram of O_3 respectively, per cubic meter of water

D_1—D_4. Limit at which end of destruction of *B. coli* has been verified in strongly infected water (7,000,000 *B. coli* per 100 ml. of water)

Welsbach (W) and Torricelli (T) processes with Welsbach ozonator

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To follow more easily the process of destroying the germs with ozone, a container of water was installed which had been artificially strongly polluted with *B. coli*. By this means it was possible to introduce a known quantity of bacteria into the water. Figures 5 and 6 show the results obtained.

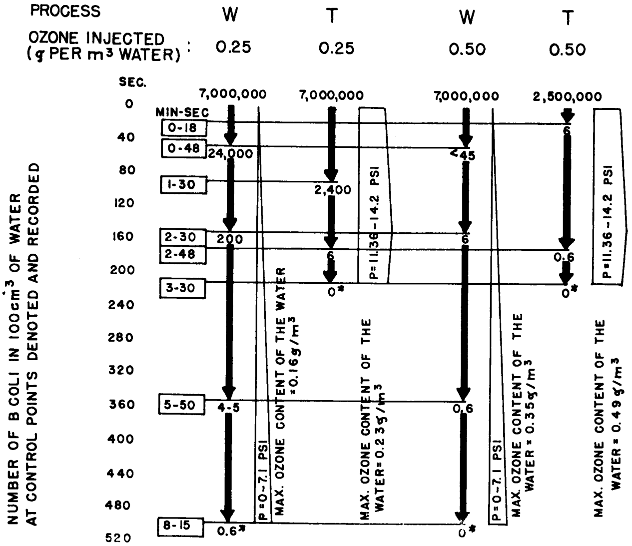

Figure 6. Destruction of *B. coli* in water artificially very strongly polluted

P. Pressure during destruction of bacteria, p.s.i.
* Final test on at least 2 samples of 100 ml. of water
Cubic meter = 264 gallons

For these tests the ozone dosages injected into the water were in one case 0.25, and in the other 0.50 gram per cubic meter of water, for each system. The preceding tests had demonstrated that these doses sufficed to give good disinfection. The concentration of ozone in the ozonated air was 10 grams per standard cubic meter.

By means of sampling valves placed along the course of the water through each installation, it was possible to determine at the same time the ozone content of the water and the rate of destruction of the *B. coli* at short, regular intervals. These comparable tests provided interesting conclusions on the efficiency of the two processes.

Clear, unfiltered well water was used for the four tests. The absence of iron and manganese, as well as a degree of oxidizability not exceeding 5 mg. of permanganate per liter, classified it among waters responding to treatment with small quantities of ozone. The temperature of the water was 11° C. At this temperature, the coefficient of distribution of the ozone between the gaseous and aqueous phases is 0.37.

$$\text{Coefficient of distribution } (D) = \frac{\text{mg. of ozone per liter of water}}{\text{mg. of ozone per liter of gas}}$$

for equivalent pressures and temperatures in the two phases.

By raising the concentration of ozone in the ozonated gas and reducing the volume of gas with respect to that of the water to be treated, the proportion of dissolved ozone can be increased. Welsbach ozonators lend themselves especially well to this operation because they deliver directly under pressure an ozonated gas at the highest practical ozone concentration. Figure 5 gives the bacteriological results for the four tests. The speed of the bactericidal action in the Torricelli process is astonishing despite a great reduction in ozone dosage. It was possible to destroy 70,000 *B. coli* per ml. of water twice as quickly and with half as much ozone in the Torricelli ozonation chamber as in the Welsbach ozonation tower. For complete destruction, 3.5 minutes and 0.25 gram of ozone injected per cubic meter of water were sufficient.

To understand these results it is necessary to refer also to Figure 6, which indicates the variations in ozone content of the water for the same tests from beginning to end of the operation.

Figures 5 and 6, moreover, confirm what the laboratory experiments had already demonstrated: Destruction of *B. coli* can be accomplished in water which contains only 0.15 mg. of ozone per liter. At this ratio 8 to 10 minutes is always sufficient for destruction.

With regard to the amount of ozone injected into the ozonation chamber, the ozone content of the water is high during the first 3 minutes in the Torricelli ozonation chamber. This can be explained by assuming that the ozone demand of the water for oxidation of readily oxidizable substances has been generally satisfied during preozonation—that is, before the water arrives in the ozonation chamber proper. As regards the quantity of ozone injected, the ratio of dissolved ozone is especially high in the treatment of Berne water because this water is relatively free of readily oxidizable substances.

The quantity of ozone necessary for disinfection of a water supply depends on the quality of the water, in particular its content of substances readily oxidized by ozone. As a rule this quantity should be established by preliminary tests, during which it is ensured that for the few minutes necessary to complete destruction, the ozone content of the water goes no lower than 0.2 mg. per liter.

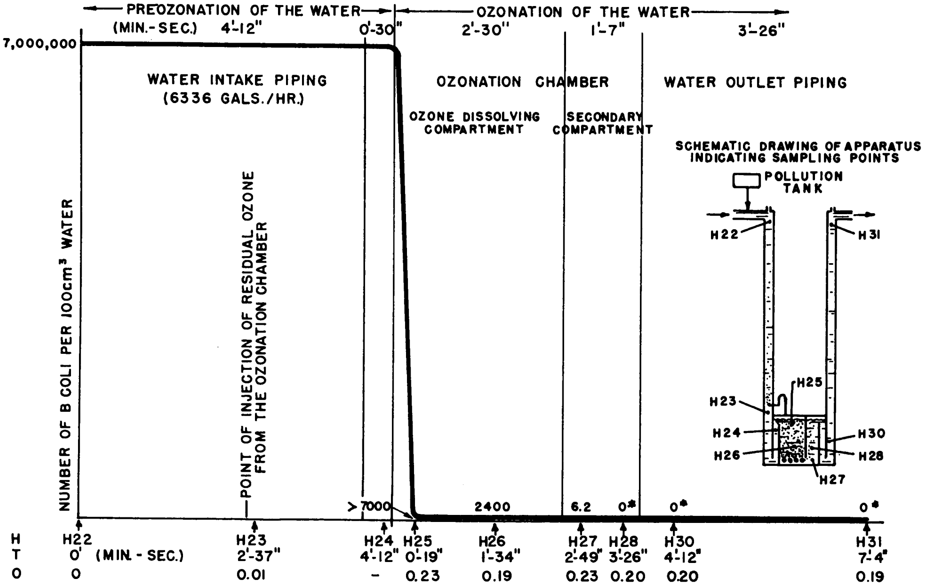

Figure 7. Rate of destruction of *B. coli* in Torricelli apparatus with 0.25 gram of ozone injected per cubic meter of water under head of 10 meters

Könizberg pilot plant at Berne, June 1952

H. Sampling valves
T. Intervals of time
O. Ozone content of water, mg. per liter
* Bacteriological test on at least 2 × 100 ml. of water

The preozonation of the water by means of excess ozone from the ozonation chamber has been introduced chiefly to utilize all the ozone injected into the ozonation chamber water. In eliminating ozone losses, the first concern was to reduce the operating and installation costs appreciably. But it was also desired to see if, by satisfying part of the ozone demand of the water before the actual disinfection operation by means of the recovered ozone, it would be possible to obtain a subsequently more powerful bactericidal action with smaller ozone dosages. The object has been attained.

While the purpose of the preozonation before the water enters the ozonation chamber is not to destroy the bacteria, it was nevertheless interesting to consider the possible bactericidal effect initiated during preozonation. Figure 7 shows that the residual ozone from the ozonation chamber, when the ozone dosage is only 0.25 gram per cubic meter of water, has no bactericidal effect whatever.

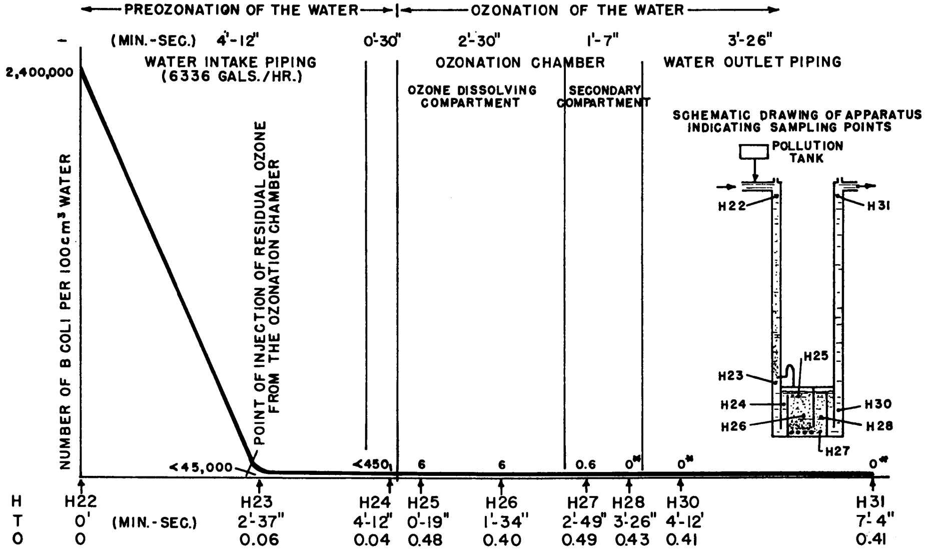

Figure 8. Rate of destruction of *B. coli* in the Torricelli apparatus with 0.50 gram of ozone injected per cubic meter of water under a head of 10 meters

Könizberg pilot plant at Berne, June 1952

H. Sampling values
T. Intervals of time
O. Ozone content of water, mg. per liter
* Bacteriological test on at least 2 × 100 ml. of water

On the other hand, Figure 8 shows a perceptible bactericidal effect in the preozonated water when 0.5 gram of ozone per cubic meter of water has been injected into the ozonation chamber. More than 99.9% of the *B. coli* has been destroyed by the residual ozone before entering the ozonation chamber.

The results demonstrate remarkable progress in the field of ozone treatment of drinking water. They show that smaller dosages and shorter retention times are possible, allowing substantial reduction in costs.

Processes Currently Used in Berne Plant

The extraordinarily favorable results obtained with the pilot plant described above have not prevented the Berne Water Bureau from adopting, after a long wait, water treatment systems of its own design. Despite the recommendation not to modify the new Torricelli process, which had aroused perceptible interest, the bureau combined the process, using the ozonation chamber under hydraulic pressure with some special systems for introducing the ozonated air into the water. Yet, while conserving the principle of the pressure chamber of the process, they did not use the residual ozone from the ozonation chamber.

The full-scale Berne ozonation plant has been operating since the spring of 1955. Constructed to treat a maximum of 1000 cubic meters (264,000 gallons) of water per hour, it is divided into two installations able to function independently. The capacity of each is 500 cubic meters of water per hour.

One of the installations is fed from Welsbach ozonators, the other from Van de Made ozonators. Each installation has a compartmented ozonation chamber closed hydraulically under a pressure of about 7 meters of water. But the system for exhausting residual gas from the chamber under pressure is changed, so that it no longer serves its original purpose.

The two systems for disinfecting water are depicted schematically in Figures 9 and 10. In the first system (I) the ozonated gas is injected at the bottom of the first compartment of the ozonation chamber by means of Chlorator émulseur injectors activated by water under pressure. For this injection of gas, one sixth to one fourth of the total quantity of water to be treated is used. The gas thus introduced into the ozonation chamber immediately mixes at one end of the chamber with the remaining raw water which arrives through a descending vertical channel. The undissolved gas held under pressure at the top of the ozonation chamber is not used to preozonate the water; it is simply evacuated through a pipe which discharges into the ascending channel through which the water leaves the ozonation chamber. The advantages of the Torricelli process are consequently appreciably reduced; the residual ozone from the ozonation chamber cannot contribute to raising the ratio of dissolved ozone in the water of the ozonation chamber, which is one of the objects of preozonation.

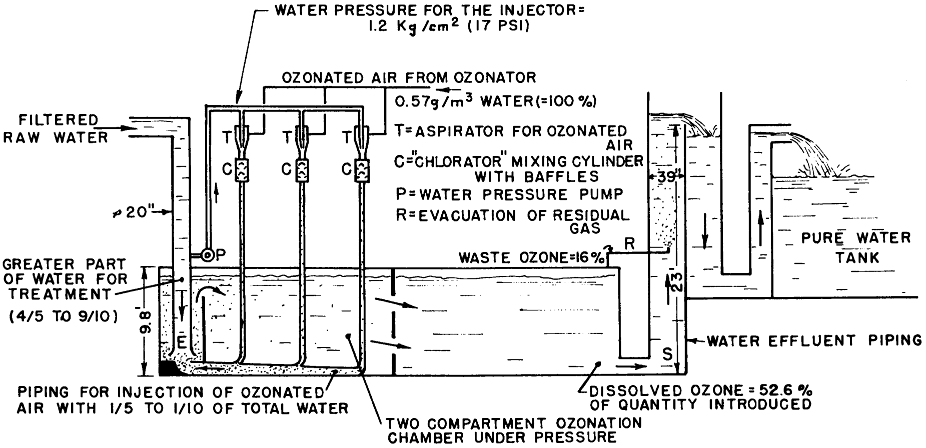

Figure 9. Berne ozonation plant treatment apparatus, Installation I

To disinfect 500 cubic meters of water per hour (132,000 gallons)
Ozone generation by Welsbach ozonators (max. 320 grams of O_3 per hr.)
Water treatment system. Chlorator combined with ozonation chamber under hydraulic pressure (Torricelli process modified by Scheller)
Normal ozone dosage per cubic meter of water, 0.4 gram
Ozone concentration in air. 10 grams per cubic meter
Retention time of water in ozonation chamber, about 10 minutes

In the second system (II) there is a compartmented ozonation chamber closed hydraulically under pressure. But here the ozonated air does not come into contact with

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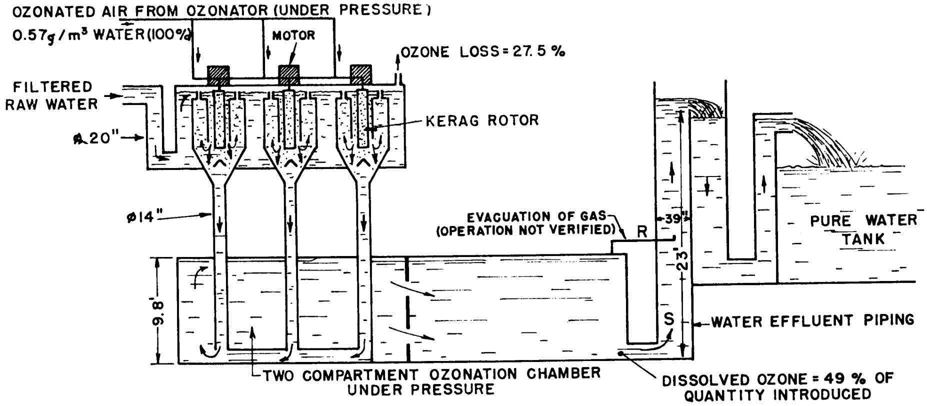

Figure 10. Berne ozonation plant treatment apparatus, Installation II

To disinfect 500 cubic meters of water per hour
Ozone generation by Van der Made (Degremont) ozonators (max. 570 grams of O_3 per hr.)
Water treatment system. Kerag combined with ozonation chamber under hydraulic pressure (Scheller combination)
Normal ozone dosage per cubic meter of water, 0.5 gram
Ozone concentration in air. 10 grams per cubic meter
Retention time of water in ozonation chamber, about 10 minutes

the water in the bottom of the chamber. It is forcibly mixed at the top of the installation with the water to be treated, although this is not yet under pressure. After this intensive mixing with a Kerag mixer, the water descends into the chamber, which is closed hydraulically under pressure, without carrying along the undissolved gas. This body of gas, with the ozone it contains, escapes freely through an aeration chimney. It is a net loss. The ozonation chamber under pressure is useless for dissolving the

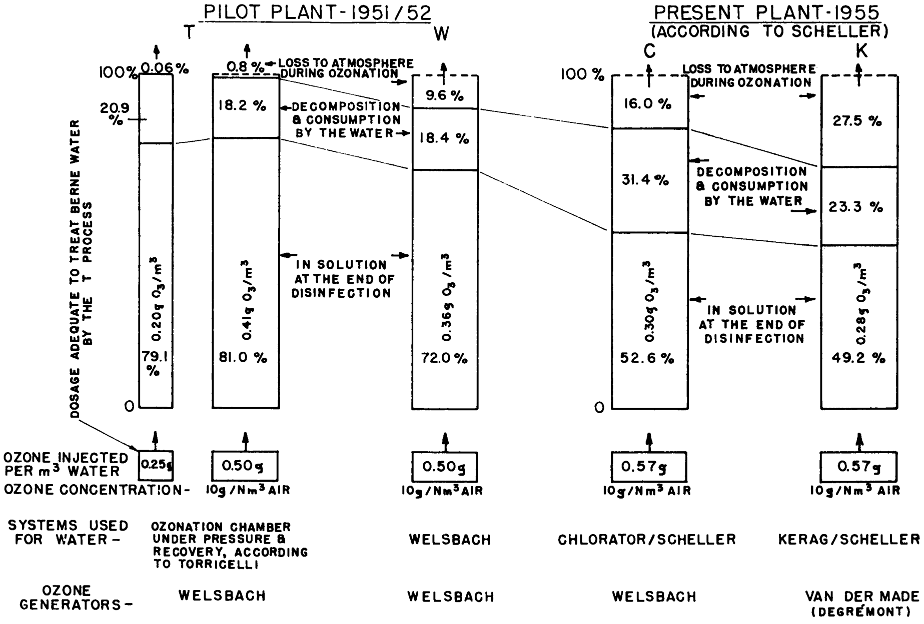

Figure 11. Ozone utilization in processes tested and now in use at Berne

ozone, as the bubbles of gas do not arrive there, contrary to the hopes of its builders. Its function remains limited to retarding the stripping of the ozone from the water while it passes through the chamber.

From information (*1*) published by the director of the Berne Water Bureau, the data in Figure 11 were compiled to show ozone utilization for the different water treatment processes described here. This method of considering the established results allows a comparison of the respective processes. The great differences among these methods in the utilization of ozone give a better understanding of why the ozone dosages differ noticeably from one process to the other, while finally resulting in the same bactericidal effect.

The two processes demonstrated in the Berne pilot plant are, at equal bactericidal efficiency, more reasonable and economical than the processes which have been substituted for them. With the more advantageous Torricelli processes it is possible to realize an appropriate economy, as 0.25 gram of ozone per cubic meter of water can be considered the normal average dosage necessary for complete purification of well water supplying the Könizberg reservoir. The Berne Water Bureau concedes that an average ozone dosage of 0.5 gram per cubic meter of water is necessary with its two processes.

The schedule compiled by Scheller shows that the ratio of utilization of ozone is poor with the Kerag process. A good part of the ozone introduced into the water (27.5% when the dosage is 0.57 gram per cubic meter of water) escapes immediately.

The figures are better for the Chlorator process. However, the passing of the residual ozone from the ozonation chamber into the water effluent channel is tantamount to complete loss of this ozone, which could advantageously be used up without cost. The ozone loss is 16%.

In the Welsbach and Torricelli processes the ozone losses are 9.6 and 0.06%, respectively, for the normal dosages which should be employed in practice.

In addition to lower efficiencies, whose influence on operating costs is appreciable enough, the Kerag and Chlorator processes also have other disadvantages. The systems introduced into the Berne plant for dissolving ozone in the water appear unnecessarily complicated and expensive to operate. To operate the water pumps necessary for the Chlorator system, the electrical consumption is 27 kw.-hours per kg. of ozone injected; to operate the Kerag mixer, 13 kw.-hours per kg. are required. The other two processes eliminate these useless costs completely.

Table I. Electrical Consumption in Kilowatt-Hours to Produce 1 Kg. of Ozone and Inject It into Water

	Present Berne Installation[a]		Pilot Plant Demonstrations at Berne	
	Chlorator with Welsbach ozonators	Kerag with Van der Made ozonators	Welsbach with Welsbach ozonators	Torricelli with Welsbach ozonators
Drying and compressing air (100 cubic meters of air per kg. of ozone)	21	21	14.3	15.4
Ozonator	17	28	18	18
Injection into water	27	13	0	0
Total	65	62	32.3	33.4

[a] From Scheller (*1*).

Table I compares operating costs of the various systems. Next, it being understood that the injected ozone dosages vary according to the process, Table II gives the actual electrical consumption for treating 1000 cubic meters of water.

A comparison of the costs of ozonating water in the Berne plant with what they might have been if the proposed processes had been adopted without modification, leaves one bewildered. The fact that the Berne Water Bureau has not adopted one

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Table II. Electrical Consumption to Disinfect 1000 Cubic Meters of Water at Berne

Systems	Normal Ozone Dosage. Gram per Cubic Meter of Water	Kilowatt-Hours
With Chlorator émulseur	0.4	26
With Kerag mixer	0.4	31
Welsbach	0.4	13
Torricelli	0.25	8.35

of the processes proposed at Könizberg in 1952 is astonishing. A plausible explanation seems to be that they expected to achieve the same result by other means.

Obviously, had they adopted the simpler process recommended by Welsbach, the operating costs would be less than half of the actual costs in installation I, which actually utilizes the more economical Welsbach ozonators. And if they adopted the new process, with Welsbach ozonators, the operating costs would be reduced to less than a third. In other words, the Berne plant cannot be cited as a sensible and economical example of water treatment.

Berne does have a very fine ozonation plant, in which the water can be treated effectively. On the other hand, many interested visitors get the impression that ozone purification of water is very expensive, which is not true.

Situation in Germany

The tests and demonstrations carried out in Switzerland have not yet led to the installation of large water treatment plants in this country. On the other hand, these tests have aroused interest in Germany, where the situation grows more critical day by day in the matter of supplying water to most large cities. The author and his associates were asked to install a small pilot plant at Düsseldorf early in 1955 to treat the water supply, which is pumped from wells along the Rhine.

Parallel tests carried out with ozone and activated carbon quickly demonstrated the undeniable superiority of ozone from all points of view. It was possible to transform this polluted Rhine water into excellent, crystal-clear drinking water by means of relatively small ozone dosages (0.7 to 1.0 gram per cubic meter of water). A series of promising tests has been undertaken with this pilot plant at Ludwigshaven am Rhein, Krefeld, Duisberg, and elsewhere.

The city of Düsseldorf is at present constructing (before finally deciding upon a full-scale ozonation plant) preliminary installation to treat 400 cubic meters of water per hour.

At Sipplingen, on the German shore of the Lake of Constance, where they are making ready to pump 10,000 cubic meters of water per hour for the city of Stuttgart 130 km. to the north, a second small pilot plant has just been installed to purify the water with the new process recommended for Berne. There is nothing to report on these tests yet.

In Europe, with the exception of France and Belgium, where a certain amount of experience has already been acquired in this field, an arduous period of struggle is still in process to publicize the advantages of ozone in the treatment of water supplies. The next few years will be decisive, and it seems possible that ozone has the greatest chances of taking root in Germany.

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