

1. The decomposition can be made to take place as a homogeneous reaction in Pyrex and in certain other glasses.
2. The homogeneous decomposition can be carried out so as to be very closely of the second order with respect to ozone.
3. The specific reaction rate for different samples which decompose in accordance with the second order may vary markedly.
4. If there is a true second-order rate for pure ozonized oxygen, it has at 100° and 1 atm. total pressure a specific rate as low as $1.5 - 1.7 \times 10^2$ cc./moles sec.).
5. For ozonized oxygen which decomposes in accordance with the second order, the specific rate is closely inversely proportional to the total pressure.

PASADENA, CALIFORNIA

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THE THERMAL DECOMPOSITION OF OZONE. II. THE EFFECT OF OXYGEN AND ACCIDENTAL CATALYSTS ON THE RATE

BY OLIVER R. WULF¹ AND RICHARD C. TOLMAN

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1. Introduction

As shown in the preceding article of this series,² all investigators agree that the rate of decomposition of ozonized oxygen is markedly decreased by increase in total pressure, and for ozone that decomposes as a second-order reaction, the specific rate is very closely inversely proportional to the total pressure. Two possible explanations of this fact present themselves. (a) The decomposition of ozone is inhibited by oxygen, the specific second-order rate being inversely proportional to the concentration of oxygen. This hypothesis was believed by Jahn to be true, and was the fact used by him in support of his mechanism of ozone decomposition. In the present article, however, we shall especially avoid any assertions as to mechanisms. (b) The decomposition of ozone is inhibited by some unknown negative catalyst present in ozonized oxygen (perhaps formed at the time of ozonization), and the specific second-order rate is inversely proportional to the concentration of this negative catalyst, so that with changes in pressure the specific rate is inversely proportional to total pressure. This entirely logical but somewhat artificial hypothesis has not previously been considered. Its consideration at the present time is forced by the experiments of Chapman and Jones,³ who actually added

¹ National Research Fellow in Chemistry.

² Wulf and Tolman, *THIS JOURNAL*, **49**, 1183 (1927).

³ Chapman and Jones, *J. Chem. Soc.*, **97**, 2463 (1910).

oxygen to ozone mixtures and found almost no inhibiting effect. Nevertheless, as a result of our own work to be described in this article, we shall find that hypothesis (a) must be regarded as the correct one.

As a preliminary to the discussion of the experimental material to be presented, a critique of the previous work of Jahn, and of Chapman and Jones in this connection is essential.

2. Critique of Jahn's Experiments on Changing the Total Pressure

As exhibited by Table XI of the previous article, Jahn⁴ showed very definitely that ozone which decomposes in accordance with the second order has a specific rate which is inversely proportional to the total pressure. This fact was also substantiated by our calculations on the work of Chapman and Jones and our own experiments on the effect of total pressure.

This result, however, cannot be immediately interpreted as due to an inhibiting effect of oxygen, since any negative catalyst present in the ozone would also have its concentration increased by increasing the total pressure and hence could lead to similar results. In other words, experiments solely on change in total pressure cannot distinguish between the two hypotheses (a and b) stated above, and we must go to experiments in which there is an actual change in the amount of oxygen associated with a given amount of ozone, in order to obtain such a distinction.

3. Critique of Jahn's Experiments on Dilution with Air

The first experiments in which an actual change was made in the ratio of oxygen to ozone were performed by Jahn, using the dynamic method at 127° and diluting his ozonized oxygen with air. If we make the tentative assumption that the nitrogen in the air is inert toward the decomposition, we then have a basis for determining whether the oxygen in the added air did have an inhibiting effect on the decomposition. Jahn's values (changed to our units) for the specific rate of decomposition in his various mixtures of ozonized oxygen with air are given in Col. 4 of Table I, from which one erratic value has been eliminated.

Col. 5 gives the product of the experimental specific rate by the partial pressure of the oxygen. This should be a constant in accordance with hypothesis (a), which makes the specific rate inversely proportional to the concentration of the oxygen. Col. 6 gives the results of our calculations of the product of the experimental specific rate by the partial pressure (approximate) to which the original oxygen-ozone mixture was reduced by the dilution. This should be a constant in accordance with hypothesis (b), which makes the specific rate inversely proportional to the concentration of negative catalyst, which is itself proportional to the concentration of the original ozonized oxygen mixture. The greater

⁴ Jahn, *Z. anorg. Chem.*, **48**, 260 (1906).

TABLE I
 JAHN'S EXPERIMENTS ON THE EFFECT OF DILUTING WITH AIR

| Expt. no. | Barometer, mm. | P_{O_2} , mm. | $k_2 \times 10^{-2}$, cc./ (moles sec.) | $k_2 \times 10^{-2}$ $\times p_{O_2}$ | $k_2 \times 10^{-2}$ $\times p$ |
|-----------|-------------------|--------------------|---|--|------------------------------------|
| 31b | 746 | 212 | 7.27 | 2.03 | 0.746 |
| 40 | 770 | 358 | 5.33 | 2.51 | 1.79 |
| 27 | 757 | 372 | 4.88 | 2.39 | 1.77 |
| 28 | 752 | 383 | 4.43 | 2.23 | 1.70 |
| 29 | 750 | 434 | 4.05 | 2.31 | 1.89 |
| 31a | 746 | 437 | 4.30 | 2.47 | 2.04 |
| 30 | 750 | 653 | 2.62 | 2.25 | 2.16 |

Av. 2.31

constancy in Col. 5 gives preliminary evidence in favor of hypothesis (a), but can perhaps hardly be accepted as conclusive, especially in view of the apparently contradictory results of Chapman and Jones which we must next consider.

4. Critique of the Experiments of Chapman and Jones on the Addition of Oxygen to Ozone

After Jahn's work, a set of experiments was made by Chapman and Jones³ for the express purpose of testing the effect of oxygen on ozone decomposition, by comparing the rates of decomposition in two bulbs, one containing ozonized oxygen at 0.5 atm. and the other a sample of the same ozone at 0.5 atm. to which oxygen had been added up to a total pressure of 1 atm. Their results were presented graphically, the decomposition curves for the samples to which oxygen had been added lying only slightly below the others. From this, Chapman and Jones concluded, in contradiction to Jahn, that oxygen did not have an inhibiting effect on the decomposition of ozone.

To obtain a better grasp of their results we have calculated the second-order constants for their runs by the method described in Ref. 10 of the previous article, and obtained the results shown in Table II.⁵

TABLE II
 EXPERIMENTS OF CHAPMAN AND JONES ON THE EFFECT OF THE ADDITION OF OXYGEN

| Fig. 3 Expt. no. | $k_2 \times 10^{-2}$, cc./ (moles sec.) Mixture at 0.5 atm. | $k_2 \times 10^{-2}$ cc./ (moles sec.) O_2 added to a total press. of 1 atm. |
|---------------------|--|---|
| I | 51.6 | 47.1 |
| II | 5.01 | 4.49 |
| III | 4.75 | 4.23 |
| IV | 4.81 | 4.04 |

⁵ In accordance with the considerations of Section 6a of the previous article, we have corrected the scale of pressure measurements on their figure by a factor, 2. The conclusions as to the effect of oxygen on rate of decomposition of ozone, however, are not thereby altered, since all the curves are on the same figure.

It will be noted that the specific second-order rate k_2 is in every case only slightly reduced by the addition of oxygen, and by no means cut in half, as would be demanded by hypothesis (a), which makes the rate inversely proportional to the concentration of oxygen.

Hence it will be seen that the previous literature of the subject rather favored hypothesis (b), that ozonized oxygen contains some unknown negative catalyst which inhibits the rate of ozone decomposition. This hypothesis would then explain at the same time the decrease in specific rate when the total pressure is increased, since this leads to an increase in the concentration of the negative catalyst, and the lack of effect when the concentration of the ozone mixture is left unaltered and extra oxygen forced into the bulb.

We must now describe our own experiments which finally lead to the conclusion that hypothesis (a) is really the correct one, and that the results of Chapman and Jones are probably due to impurities in the oxygen which they added to their bulbs.

5. Experiments on the Addition of Oxygen to Bulbs Containing Ozone Mixture

Our first experiments on the effect of oxygen on rate of decomposition were made with the four-bulb apparatus described in Section 6b of the previous article. All four bulbs were filled with the same ozonized oxygen at a pressure somewhat less than 0.5 atm. and two of them were then sealed off. Extra oxygen from an auxiliary bulb was then admitted to the other two through a stopcock *lubricated with concd. sulfuric acid*, and they were also sealed off. Keeping one of each set of bulbs as a control, the other two were immersed for equal lengths of time in a water-bath at 100°. After removing these two bulbs and "freezing" in tap water, the contents of all four bulbs were analyzed for ozone by iodimetric methods and the specific rates calculated, assuming second order.

The results of three such experiments are given in Table III. In one of the experiments Linde tank oxygen was used, and in the other two electrolytic oxygen from sodium hydroxide solution. The ozone was in every case formed by the silent discharge, using the same source of oxygen as that for the addition.

TABLE III
EXPERIMENTS ON THE EFFECT OF THE ADDITION OF OXYGEN, USING MODIFIED STATIC METHOD

| Source of oxygen | Reaction time, min. | Total pressure p , mm., original gas | Total pressure p' , mm., oxygen added | $k_2 \times 10^{-2}$, cc./ (moles sec.), original gas | $k_2' \times 10^{-2}$, cc./ (moles sec.), oxygen added |
|------------------|---------------------|--|---|--|---|
| Linde tank | 37 | 296 | 501 | 4.05 | 4.45 |
| Electrolytic | 45 | 289 | 523 | 2.23 ^a | 1.74 |
| Electrolytic | 45 | 289 | 524 | 2.59 | 2.06 |

^a Correcting by the inverse pressure effect to 1 atm., we should here obtain the very low value. $k_2 = 0.85 \times 10^{-2}$ cc./ (moles sec.).

The relatively small change in specific rate with added oxygen would at first sight seem to confirm the negative effect observed by Chapman and Jones. On further analysis of the data, however, we are struck by the fact that the Linde tank oxygen, which was presumably the less pure of the two, actually accelerated the rate, while the presumably somewhat purer electrolytic oxygen somewhat decreased the rate. This led us to suspect that the added oxygen contained positive catalysts for ozone decomposition, and that the true inhibiting effect of oxygen in these experiments as well as in the experiments of Chapman and Jones might be masked by the accelerating effect of the suspected catalyst.

6. Set-up of Dynamic Apparatus for the Study of Accidental Catalysts in Ozonized Oxygen

It seemed desirable to initiate special experiments for the study of different kinds of ozonized oxygen and the catalysts which they might contain. Indeed, it may not be out of place to emphasize here that researches on ozone usually lack any demonstration of the character of the ozone used, in particular of the absence of disturbing impurities. A half dozen experiments upon ozone prepared in as many different ways may indeed be of greater value than six times the number made upon one kind of ozone, a fact usually not sufficiently appreciated.

For these special experiments it was decided to go to somewhat higher temperatures and employ the dynamic method. This method is not as well adapted for accurately determining the order of reaction of a single sample of gas. It was, however, far better for our present purposes, since it gave almost immediate information as to the rate of decomposition of a given sample of gas, since it could be conveniently switched from one kind of gas to another, and

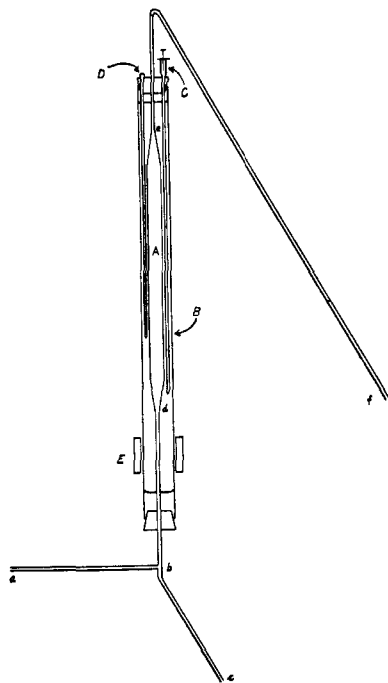


Fig. 1.

since it greatly cut down the time of accumulating data. Its use for many gas reactions can be recommended at the present moment when data are so urgently needed in this field of chemistry.

The reaction chamber for our apparatus was made of a tube of Pyrex, as shown at *A* in Fig. 1. It was approximately 34 cm. long overall from

d to *e*, and 25 cm. long in the portion of constant bore of 1.4 cm. The connecting tubing was 0.3 cm. in bore.

The reaction chamber was contained in a larger Pyrex tube *B*, 54 cm. long and having an inside diameter of 3.4 cm. A heating coil *E* was wound near the lower end of this tube, over a single layer of asbestos paper and covered with heavy asbestos insulation. The tube was provided with a mercury regulator *C* and a thermometer *D*, and was filled nearly full of paraffin.

The volume of the reaction chamber was 43.9 cc. from a point midway between *d* and the lower surface of liquid paraffin, to the upper surface of the paraffin. The temperature varied somewhat in different parts of the bath owing to strong convection currents, but the temperature distribution did not change from run to run, since the thermoregulator held the temperature at a given point within about $\pm 0.5^\circ$. The average value of the temperature was investigated by inserting the thermometer at different places, and was about 147.7° . Absolute values for the volume and temperature were not of prime importance for our immediate purposes, since we were interested primarily in relative rates for different kinds of ozone rather than in absolute rates.

7. Remarks on the Time of Passage through the Reaction Chamber in Dynamic Experiments

To determine the time of reaction in dynamic experiments it is always customary to assume that the time of passage of each molecule through the chamber is the quotient of the volume of the chamber by the volume rate of gas flow. This quotient gives an average value for the time taken by the molecules to get through the apparatus; however, except in the case of unimolecular reactions, it is evident that the calculations will not be correct unless the above assumption is justified. Indeed, it seems probable that the assumption has sometimes been made when not actually justified, as possibly, in the case of Clement's⁶ experiments, provided the shape of his tubes was really such as shown in his figure.

For our work the walls of the reaction tube were made of a shape approximating that of stream-line flow, to avoid turbulence and stagnant spaces. The rate of flow used, moreover, was always kept as low as less than twice the volume of the tube per minute. It is evident, however, even without turbulence and stagnant spaces, that the rate of flow will vary inwards from the walls, since for the lamina flow of a continuous fluid through a tube, the velocity is zero at the walls and increases inward as a parabolic function of the distance. Under this distribution of velocities we should at first sight expect molecules at different distances from the center to take different times in passing through the tube.

⁶ Clement, *Ann. Physik*, **14**, 341 (1904).

The effect which we believe in our apparatus overweighs the difference in the velocity of the various cylindrical layers of flowing gas is the diffusion of the molecules from one layer to another. To investigate this we may use Einstein's⁷ relation connecting the average displacement of a molecule $\bar{\Delta x}$ with coefficient of diffusion D and time t ,

$$\bar{\Delta x} = \sqrt{(4D/\pi)t} \quad (1)$$

Substituting the value of the self-diffusion coefficient of oxygen at room temperature, 0.2 sq. cm./sec., we thus find that the average time required for a molecule to acquire a displacement of 1 cm. in any direction is about four seconds, which is small compared with the average time of 38 seconds required for the molecules to pass through the whole length of the tube in our experiments with the highest rates of flow. It is evident, therefore, that transverse diffusion will be sufficient to remove the difficulty arising from the different velocities in different parts of the tube.

A further difficulty arises, however, from the effect of diffusion parallel to the direction of motion, which will make some of the molecules pass more rapidly and some more slowly through the tube. It has seemed safe to neglect this effect for our present purposes, especially as we are mainly interested in relative rather than absolute rates.

8. Sources of Oxygen and Ozone

For the work to be described, three sources of oxygen were used: tank oxygen made by the Linde process, oxygen generated electrolytically from sodium hydroxide solution, and oxygen generated electrolytically from sulfuric acid solution and passed through a heated tube to decompose the small amount of ozone present. These three kinds of oxygen will be referred to as "Linde," "caustic," and "acid" oxygen. Two kinds of ozone were also used in the work, one prepared by passing the "caustic" oxygen through the silent discharge in a Siemen's ozonizer and the other by electrolysis of sulfuric acid with a high current density. These will be called "caustic" and "acid" ozone.

New forms of electrolytic generators of large current capacity for "caustic" and "acid" oxygen and for "acid" ozone were developed for this work and will be described in another place.

Before introduction into the reaction chamber, the "caustic" and "acid" oxygen and ozone were dried by passage over concd. sulfuric acid, bubbling being purposely avoided.

9. Experimental Technique of Rate Determination with the Dynamic Set-up

Before making analyses of the gas entering and leaving the reaction chamber, the system was always swept out with the gas to be used for a

⁷ Einstein, *Ann. Physik*, **17**, 558 (1905).

time which was long compared with that necessary to change completely the gas in the apparatus.

When the desired steady conditions had been reached, analyses were made first of the final and then of the initial concentration of the ozone entering and leaving the reaction chamber, by taking timed samples from the exit tubes at *f* and *c* in Fig. 1. The exit not in use was closed by a drop of distilled water.

The analyses were made by absorption of the samples in 2% neutral potassium iodide solution. After subsequent acidification the liberated iodine was titrated against standard thiosulfate.

The absorption in the potassium iodide solution was carried out in a somewhat unusual way, by allowing the gas to flow quietly into a long test-tube, containing a sufficient quantity of potassium iodide solution at the bottom, the gas exit being held about 2 cm. above the liquid surface. The sample was thus collected by upward displacement of air in a tube of considerably larger volume than itself. The tube was then covered and absorption allowed to continue for some time (half an hour or more).

This technique was adopted in order not to disturb the conditions of gas flow, which would have been seriously affected by insertion of the exit tubes under the liquid, since bubbles would not start until the electrolytic generators, which were open on the hydrogen side, had built up sufficient pressure.

Two factors which might have made the above method impracticable were turbulence and an undue increase in the concentration of hydroxyl ion at the surface of the potassium iodide. The slow rates of flow employed and the small quantities of ozone collected minimize, however, the possible difficulties that these factors might cause. In addition, the behavior of the fog bank produced by the outflowing gas showed that turbulence was absent and a direct comparison with the bubbling method using a tank as the source of oxygen showed that the analyses by this method were satisfactory.

From the values of the initial and final concentrations, C_1 and C_0 , thus obtained, and the time of reaction t calculated from the volume of the reaction chamber, and the rate of flow of the gas given by the current used in the electrolytic generators, the value of the second-order constant k_2 could then be calculated in accordance with the equation⁸

$$k_2 = \frac{1}{t} \left(\frac{1}{C_1} - \frac{1}{C_0} \right) \quad (2)$$

⁸ The calculations of k_2 were actually performed in the following manner. The number of moles of oxygen generated per second is evidently $I/4F$, where I is the current and F is the value of Faraday's equivalent. A portion of this oxygen, however, is in the form of ozone when passing through the reaction chamber, so that we may write

10. Determinations of the Order of Decomposition by the Dynamic Method

As just stated, the specific reaction rates were calculated on the assumption that the decompositions proceeded in accordance with the second order, and hence it was desirable to test this at the higher temperature and with the new method now being employed.

The only way of doing this with our apparatus was to use different times of decomposition for successive samples of ozone, and see if the specific rates calculated as second order agreed. This has the disadvantage that we thus compare the values of k_2 calculated for different times of decomposition of different samples of ozone, rather than for different times of decomposition of the same sample of ozone, and we know that different samples of ozone may decompose with quite different rates. Nevertheless, as we shall later see, our "acid" ozone was always found to have nearly the same stability, and the factors influencing the stability of our "caustic" ozone were found to be fairly closely correlated with the ozonizability of the "caustic" oxygen as shown by the value of C_0 . Hence, such a test of order should be reasonably satisfactory for the "acid" ozone and for the "caustic" ozone, provided the C_0 values did not vary greatly. for the rate of flow in moles per second past any boundary in the reaction chamber,

$$\text{Rate} = (I_1/4F)(1 - 1/3\alpha) \quad (1)$$

where I_1 is the current at the time the issuing sample was taken for analysis, and α is the fraction of the total oxygen in the form of ozone. Neglecting changes as the mixture passes through the reaction chamber, we may then write for the time of passage

$$t = \frac{V_{\text{chamber}}}{\frac{I_1}{4F}(1 - 1/3\alpha) \frac{RT}{p}} \quad (2)$$

where p is the reading of the barometer.

To calculate the concentration of the gas from its titer, we have for the number of moles of ozone $N/2000 \times \text{titer}$, where N is the normality of the thiosulfate, and for the volume of gas that contained this ozone $[(I/4F)(1 - 1/3\alpha)t_a]RT/p$, where t_a is the time of collecting the absorption sample, giving us for the concentration,

$$C = \frac{N/2000 \times \text{titer}}{\frac{I}{4F}(1 - 1/3\alpha) t_a \frac{RT}{p}} \quad (3)$$

Substituting in the expression for the second-order specific rate and collecting numerical factors we then obtain

$$k_2 = \frac{I_1(1 - 1/3\alpha)^2 (RT)^2 t_a \times 2000}{(4F)^2 p^2 V_{\text{chamber}} N} \left(\frac{I_1}{\text{titer}_1} - \frac{I_0}{\text{titer}_0} \right) \quad (4)$$

For all the runs made, α was taken as having the same constant value, 0.015 in all equations, the temperature was taken as 420.7°, the pressure was taken as 740 mm. = 0.974 atm., and the volume of the reaction chamber as 43.9 cc.

As a sample calculation, the numerical factors for the first value of k_2 given in Table IV, when substituted in Equation 4, give

$$\begin{aligned} k_2 &= \frac{5.00(1 - 0.005)^2(82.07 \times 420.7)^2 \times 60 \times 2000}{(4 \times 96500)^2(0.974)^2 \times 43.9 \times 0.009763} \left(\frac{5.00}{2.06} - \frac{5.00}{6.59} \right) \\ &= 1.95 \times 10^4 \text{ cc./}(\text{moles sec.}) \end{aligned}$$

The tests of order actually carried out on the two kinds of ozone have already been reported under the discussions of order given in the first article of the series, as shown in Tables IV and V. They demonstrate satisfactorily that the ozones used actually did decompose in accordance with the second order.

11. The Ozonizability of "Caustic" Oxygen

Our first investigations with the new apparatus were made upon "caustic" oxygen and "caustic" ozone. One of the first phenomena that we encountered was a difference in the ozonizability of different samples of "caustic" oxygen, even though the rate of flow and voltage in the ozonizer were kept constant.

In general, the ozonizability of the oxygen, as measured by the concentration of the ozone formed, was greater when the generator was first started for a series of measurements than later on. In case the generator had been recently replenished with distilled water, the concentration would fall in about two and one-half hours to a fairly constant value of the order of one-half to one-third that at the start. In case the generator had been used for a considerable time, the fall in concentration would be less and reach a constant value in a shorter time. By special experiments it was shown that this fall in concentration was not due solely to the change in the temperature of the bath surrounding the ozonizer itself.

In addition, with continued use, it was found that as the electrolyte in the generator was depleted of water, the initial ozonizability of the oxygen decreased. On replenishing the electrolyte with distilled water at a later date (actually a small addition of the order of 5% of the total), the ozonizability of the oxygen was found to undergo a marked increase. This phenomenon was noticed at least four times.

12. The Stability of "Caustic" Ozone

Not only did we find different ozonizability for the different samples of "caustic" oxygen, but the resulting "caustic" ozone had different degrees of stability, and in general there was a tendency for the more ozonizable oxygen to give more stable ozone. This is shown in Table IV, where all the results obtained with "caustic" ozone are arranged in the chronological order of the experiments, Col. 1 giving the voltage on the primary of the ozonizer transformer. Since the time of passage through the ozonizer was always slow enough so that the rate of flow itself had little effect on the concentration of ozone formed, the values of C_0 given in Table IV for any given voltage on the transformer may be taken as a rough measure of the ozonizability of the oxygen. Examining now the results in the table obtained with a constant transformer voltage of 50 v., it will be noticed that high values of C_0 , indicating high ozonizability, tend to be correlated with low values of k_2 , indicating high stability.

Included in the table are also some results obtained at voltages other than 50. Here it is particularly interesting to note that with very low voltages, the concentration C_0 may drop to extremely low values, and the corresponding k_2 be extremely high. Hence, high values of C_0 and low values of k_2 tend to be correlated also when the changes in C_0 are brought about by changes in the action of the ozonizer.

This general correlation between C_0 and k_2 is also shown graphically in Fig. 2, where the values of k_2 given in Table IV, omitting eight values that

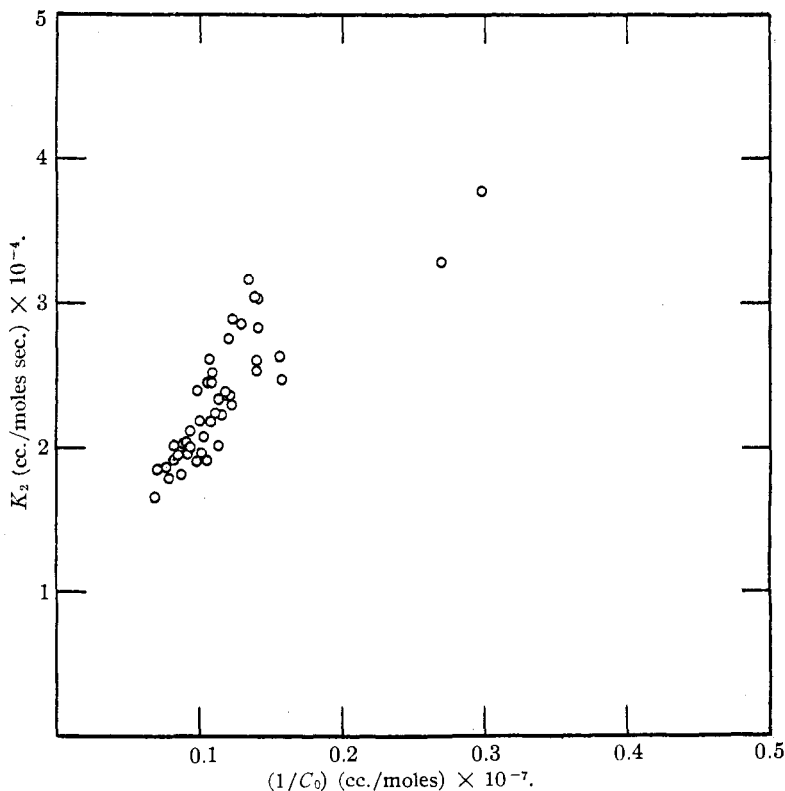


Fig. 2.

fall outside the figure, are plotted against the reciprocal of C_0 . (A tendency toward a similar correlation between high stability and high C_0 was also found in our earlier static experiments at 100° as will be noted from Table II in the first article of this series.)

The above results seem to indicate that our "caustic" oxygen may contain in varying amounts some impurity (caustic spray, hydrogen?) which acts adversely on the formation of ozone during the passage of the oxygen through a Siemen's ozonizer, and also accelerates the decomposition

of ozone. It also appears from the results obtained at high and low voltages that the concentration of this impurity is reduced by the action of the ozonizer. This point of view as to the presence of a positive catalyst for ozone decomposition in "caustic" oxygen will find further confirmation when we describe our experiments on the mixing of "caustic" oxygen with "acid" ozone.

TABLE IV
"CAUSTIC" OZONE

| V , volts | t , sec. | $C_0 \times 10^7$, moles/cc. | $C \times 10^7$, moles/cc. | $k_2 \times 10^{-4}$, cc./($\text{moles} \times \text{sec.}$) | V , volts | t , sec. | $C_0 \times 10^7$, moles/cc. | $C \times 10^7$, moles/cc. | $k_2 \times 10^{-4}$, cc./($\text{moles} \times \text{sec.}$) |
|----------------|---------------|----------------------------------|--------------------------------|---|----------------|---------------|----------------------------------|--------------------------------|---|
| 50 | 96.1 | 11.74 | 3.67 | 1.95 | 50 | 64.1 | 9.24 | 3.77 | 2.45 |
| | 96.1 | 10.61 | 3.37 | 2.11 | | 64.1 | 9.44 | 3.66 | 2.61 |
| | 96.1 | 8.99 | 3.06 | 2.24 | | 64.1 | 9.48 | 3.81 | 2.45 |
| 50 | 38.1 | 10.14 | 5.27 | 2.39 | 40 | 48.0 | 11.18 | 5.36 | 2.03 |
| | 37.8 | 9.21 | 4.90 | 2.52 | | 48.0 | 10.91 | 5.38 | 1.96 |
| | 47.3 | 8.15 | 3.85 | 2.89 | 22 | 48.0 | 3.71 | 2.34 | 3.28 |
| | 47.1 | 7.74 | 3.79 | 2.86 | | 47.1 | 3.36 | 2.10 | 3.77 |
| | 64.1 | 7.45 | 2.97 | 3.16 | 16 | 46.9 | 1.06 | 0.59 | 15.98 |
| | 64.5 | 7.22 | 2.99 | 3.04 | | 46.9 | 0.99 | .30 | 50.68 |
| | 96.1 | 7.09 | 2.31 | 3.03 | 40 | 46.9 | 7.25 | 3.53 | 3.11 |
| | 96.1 | 7.11 | 2.42 | 2.83 | | | | | |
| 50 | 96.1 | 14.43 | 4.36 | 1.66 | 20 | 47.6 | 1.15 | 0.88 | 5.64 |
| | 96.1 | 13.12 | 3.92 | 1.86 | | 47.6 | 1.15 | .88 | 5.64 |
| | 96.1 | 11.61 | 3.70 | 1.91 | | 47.3 | 1.14 | .87 | 5.80 |
| | 96.1 | 10.60 | 3.49 | 2.00 | 16 | 47.6 | 0.90 | .66 | 8.42 |
| | 96.1 | 9.30 | 3.15 | 2.18 | | 47.3 | .83 | .56 | 12.29 |
| | 96.1 | 8.48 | 2.88 | 2.38 | | 47.1 | .99 | .65 | 11.34 |
| 50 | 96.1 | 12.15 | 3.63 | 2.01 | 70 | 47.3 | 9.87 | 5.15 | 1.96 |
| | 96.1 | 12.26 | 3.76 | 1.92 | | 47.1 | 9.53 | 5.13 | 1.91 |
| | 96.1 | 10.74 | 3.49 | 2.01 | | 46.6 | 8.88 | 4.84 | 2.01 |
| | 96.1 | 9.69 | 3.31 | 2.07 | | | | | |
| | 96.1 | 8.88 | 2.98 | 2.33 | 50 | 38.4 | 11.46 | 6.37 | 1.81 |
| | 95.1 | 8.26 | 2.89 | 2.36 | | 38.4 | 10.23 | 5.85 | 1.90 |
| | | | | | | 48.0 | 8.73 | 4.51 | 2.23 |
| 50 | 192.2 | 14.22 | 2.35 | 1.85 | | 48.0 | 8.21 | 4.31 | 2.29 |
| | 192.2 | 12.65 | 2.37 | 1.79 | | 64.1 | 7.14 | 3.31 | 2.53 |
| | | | | | | 64.1 | 7.15 | 3.26 | 2.60 |
| 50 | 64.1 | 11.01 | 4.51 | 2.04 | | 90.6 | 6.31 | 2.62 | 2.47 |
| | 64.1 | 10.02 | 4.18 | 2.18 | | 90.6 | 6.41 | 2.53 | 2.63 |
| | 64.1 | 8.51 | 3.72 | 2.36 | | | | | |
| | 63.6 | 8.31 | 3.38 | 2.75 | | | | | |

13. The Stability of "Acid" Ozone

Having found these considerable variations in the specific rate of decomposition of "caustic" ozone, we next turned to a study of the rate of decomposition of "acid" ozone, as shown in Table V and Fig. 3. It will be

immediately noted that this is a superior ozone; not only does it have on the average a lower specific rate of decomposition than the "caustic" ozone, but one which varies much less with initial concentration, although there is still a slight correlation between high concentration and high stability.

TABLE V
"ACID" OZONE

| t , sec. | $C_0 \times 10^7$, moles/cc. | $C \times 10^7$, moles/cc. | $k_2 \times 10^{-4}$, cc./moles sec.) | t , sec. | $C_0 \times 10^7$, moles/cc. | $C \times 10^7$, moles/cc. | $k_2 \times 10^{-4}$, cc./moles sec.) |
|---------------|----------------------------------|--------------------------------|--|---------------|----------------------------------|--------------------------------|--|
| 48.0 | 5.37 | 3.54 | 2.00 | 96.1 | 5.82 | 2.97 | 1.72 |
| 48.0 | 5.32 | 3.54 | 1.96 | 96.1 | 5.89 | 3.05 | 1.65 |
| 64.1 | 5.13 | 3.10 | 1.99 | 48.0 | 7.01 | 4.46 | 1.69 |
| 64.1 | 5.17 | 2.95 | 2.27 | 48.0 | 6.90 | 4.32 | 1.81 |
| 48.0 | 6.89 | 4.57 | 1.53 | 96.1 | 3.93 | 2.40 | 1.69 |
| 64.1 | 6.03 | 3.61 | 1.74 | 96.1 | 3.89 | 2.30 | 1.85 |
| 64.1 | 5.97 | 3.70 | 1.60 | | | | |
| | | | | 96.1 | 4.36 | 2.37 | 2.00 |
| 48.0 | 3.68 | 2.73 | 1.96 | 96.1 | 4.27 | 2.43 | 1.85 |
| 48.0 | 3.46 | 2.53 | 2.22 | | | | |
| 64.1 | 3.18 | 2.23 | 2.09 | 96.1 | 6.94 | 3.49 | 1.50 |
| 64.1 | 3.02 | 2.17 | 2.01 | 96.1 | 6.90 | 1.17 | 7.38 |
| 48.0 | 7.60 | 4.78 | 1.62 | 38.4 | 8.20 | 5.47 | 1.58 |
| 48.0 | 7.16 | 4.65 | 1.57 | 38.4 | 7.86 | 5.17 | 1.73 |
| 64.1 | 6.33 | 3.83 | 1.61 | 48.0 | 7.77 | 4.70 | 1.75 |
| 64.1 | 6.27 | 3.75 | 1.68 | 48.0 | 7.52 | 4.65 | 1.71 |
| 96.1 | 5.35 | 2.89 | 1.66 | 64.1 | 7.21 | 4.12 | 1.63 |
| 96.1 | 5.45 | 2.89 | 1.69 | 64.1 | 7.33 | 4.37 | 1.45 |
| | | | | 96.1 | 6.10 | 3.07 | 1.68 |
| 48.0 | 7.83 | 4.76 | 1.71 | 96.1 | 6.23 | 2.91 | 1.91 |
| 48.0 | 7.47 | 4.76 | 1.58 | | | | |
| 96.1 | 5.57 | 3.01 | 1.59 | 48.0 | 6.64 | 4.02 | 2.04 |
| 96.1 | 5.45 | 2.95 | 1.62 | 48.0 | 6.29 | 3.76 | 2.22 |
| 48.0 | 6.88 | 4.46 | 1.64 | | | | |
| 48.0 | 6.74 | 4.46 | 1.58 | 96.1 | 5.37 | 2.78 | 1.80 |
| | | | | 96.1 | 5.39 | 2.87 | 1.69 |
| 48.5 | 3.90 | 2.91 | 1.79 | | | | |
| 48.5 | 3.73 | 2.76 | 1.94 | 96.1 | 5.54 | 2.83 | 1.80 |
| | | | | 96.1 | 5.54 | 2.94 | 1.67 |
| 48.0 | 3.17 | 2.41 | 2.09 | 48.0 | 7.07 | 4.49 | 1.69 |
| 48.0 | 3.01 | 2.33 | 2.02 | 48.0 | 6.89 | 4.47 | 1.63 |
| 96.1 | 2.72 | 1.76 | 2.08 | | | | |
| 96.1 | 2.64 | 1.79 | 1.88 | 96.1 | 6.08 | 3.09 | 1.66 |
| | | | | 96.1 | 5.72 | 3.00 | 1.65 |
| 48.0 | 8.59 | 5.19 | 1.59 | 96.1 | 5.75 | 2.93 | 1.74 |
| 48.0 | 8.37 | 5.04 | 1.64 | 48.0 | 7.03 | 4.56 | 1.60 |
| 96.1 | 6.30 | 3.15 | 1.66 | 48.0 | 6.64 | 4.33 | 1.68 |
| 96.1 | 6.21 | 3.16 | 1.62 | | | | |
| 48.0 | 4.28 | 3.18 | 1.67 | | | | |
| 48.0 | 3.98 | 2.79 | 2.22 | | | | |

These results have led us to consider the "acid" ozone as the best that we have prepared, and to use it for our further researches.

14. The "True" Specific Rate of Ozone Decomposition

Figs. 2 and 3 provide some basis for a decision as to the probable value for the "true" second-order specific rate of decomposition of pure ozone, since the higher the concentration of ozone formed the less it appears to be affected by accidental catalysts, and the less of course the actual rate of

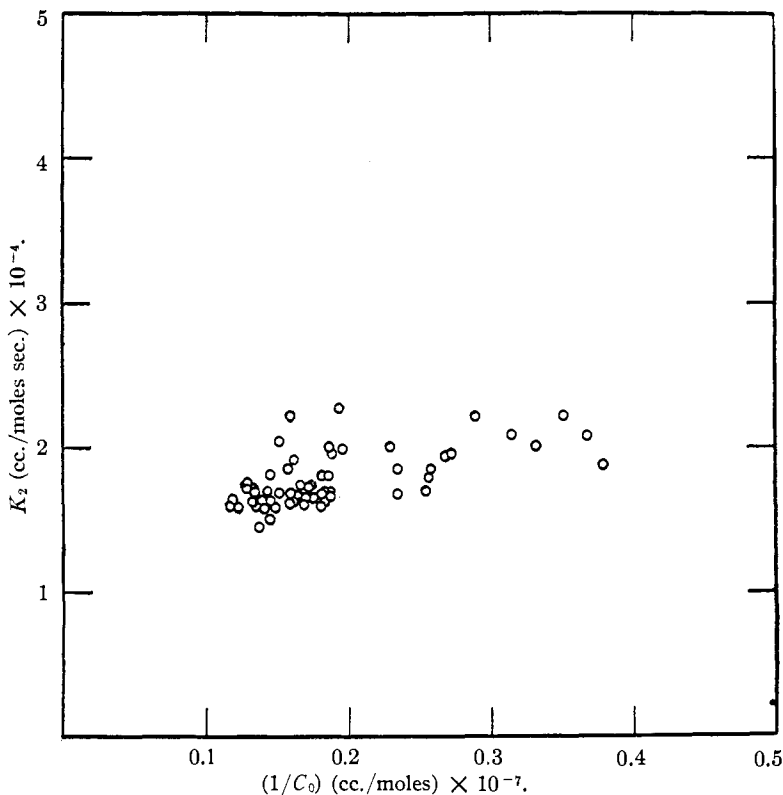


Fig. 3.

decomposition is affected by any simultaneous first-order reaction. For this reason in both the figures we have roughly extrapolated back to zero values of $1/C_0$ or infinite values of C_0 . This gives a limiting value for the second-order specific rate of ozone decomposition at one atmosphere and 147.7° of about 1.3×10^{-4} cc./moles sec.).

The conclusion thus obtained is, however, of course not certain, since even our best ozone may have contained a considerable but fairly constant amount of catalyst.

15. Experiments on the Injection of Oxygen into the Ozone Stream

Having obtained in "acid" ozone a reproducible source of gas, we were now ready to investigate the catalysts which might be carried by different kinds of oxygen, by injecting the oxygen into the stream of ozone before its entry into the reaction chamber and determining the effect on the rate of ozone decomposition.

Such experiments should also assist in deciding between the two hypotheses (a and b), which gave possible explanations of the increase in specific rate which accompanies a decrease in the total pressure of an oxygen-ozone mixture. In accordance with hypothesis (a), this increase in rate is due to the decreased concentration of oxygen, and in accordance with hypothesis (b) the increase in rate is due to the decreased concentration of some negative catalyst present in ozonized oxygen. Hence, in our injection experiments, where a two-fold dilution was made at *constant total pressure*, we should expect no effect from the injection of *pure* oxygen on the basis of hypothesis (a), since the concentration of oxygen was not appreciably changed, while on the basis of hypothesis (b), we should expect a two-fold increase in rate to accompany the resulting two-fold dilution of the assumed negative catalyst.

Our actual injection experiments had to be made with oxygen whose purity could only be determined by interpreting the results of the experiments themselves. Nevertheless, since the added oxygen would be most likely to contain positive catalyst, we could conclude that hypothesis (b) would require *at least* a two-fold increase in rate.

To carry out the injection experiments, two small cylindrical mixing bulbs were introduced into the train just before the reaction chamber, and connections made so that the "acid" ozone and diluting gas entered the first cylindrical bulb at opposite sides of the upper end.

The specific rates k_2 obtained with the undiluted ozone and with the addition of the different diluents are given in Table VI, in the order in which the experiments were actually carried out. The check measurements on the undiluted ozone were interspersed with the measurements on the diluted ozone, the dotted lines showing the groups of check measurements that went with the groups of dilution measurements.

Our first experiments, diluting with "caustic" oxygen, showed a considerable increase in the specific rate k_2 , but much less than the two-fold increase required by hypothesis (b). It seems natural to conclude that the actual increase was due to the same positive catalyst, whose presence in caustic oxygen had already been suspected on the basis described above.

Our next experiments were made by diluting with "caustic" ozone. Since the ozonizer might be expected to act similarly to a Cottrell precipitator and thus remove suspended impurities, and since the monatomic oxygen

TABLE VI
VALUES OF $k_2 \times 10^{-4}$ cc./ (MOLES SEC.)

| "Acid" ozone, undil. | Dil. with "caustic" oxygen | Dil. with "caustic" ozone | "Acid" ozone, undil. | Dil. with Linde oxygen | Dil. with "acid" oxygen |
|----------------------|----------------------------|---------------------------|----------------------|------------------------|-------------------------|
| 1.72 | 2.38 | | 2.04 | 3.44 | |
| 1.65 | 2.21 | | 2.22 | 3.44 | |
| 1.69 | | | | | |
| 1.81 | | | Av. 2.13 | 3.44 | |
| ----- | | | | | |
| 1.69 | 2.62 | 2.07 | 1.80 | | 1.96 |
| 1.85 | 2.28 | 1.98 | 1.69 | | 1.74 |
| | | 1.94 | | | |
| | | 1.91 | | | |
| ----- | | | | | |
| 2.00 | 2.16 | 1.72 | 1.80 | | |
| 1.85 | 2.33 | 1.54 | 1.67 | | 1.61 |
| | | | 1.69 | | 1.51 |
| | | | 1.63 | | |
| ----- | | | | | |
| 1.50 | 1.99 | 1.68 | 1.66 | | |
| (7.38) | 2.25 | 1.95 | 1.65 | | 1.41 |
| | | | 1.74 | | 1.73 |
| Av. 1.75 | 2.28 | 1.85 | 1.60 | | 1.66 |
| | | | 1.68 | | |
| | | | Av. 1.69 | | 1.66 |

produced in the discharge might oxidize harmful impurities, we were not surprised to find that this diluent produced a considerably smaller increase in the specific rate k_2 than the "caustic" oxygen.

The logical possibility now presented itself, that "caustic" oxygen and "caustic" ozone themselves contained enough negative catalyst to prevent the two-fold increase in specific rate demanded by hypothesis (b). For this reason we next went to Linde tank oxygen, which would not be expected to contain negative catalyst if this is produced by electrical treatment, and would almost certainly contain positive catalyst. Hence, on the basis of hypothesis (b), it should give at least a two-fold increase in rate. As a matter of fact it gave only a 60% increase as shown in the table.

Finally we diluted with "acid" oxygen which should presumably be the best oxygen we had available. We then found practically no effect on the rate of decomposition.

The foregoing results are thus in disagreement with the hypothesis that oxygen-ozone mixture contains any unknown negative catalyst for ozone decomposition, and we must conclude that Jahn's original hypothesis that the second-order decomposition of ozone is inhibited by oxygen is correct. The experiments also show that oxygen is very liable to contain positive catalysts for ozone decomposition, and that the result of Chapman

and Jones, who found almost no inhibiting effect on ozone decomposition when they increased the concentration of oxygen by direct addition, is almost certainly to be accounted for by the presence of positive catalyst in their oxygen.

Summary

The foregoing article has led to the following conclusions.

1. The decrease in the specific second-order decomposition rate which accompanies increase in the total pressure of oxygen-ozone mixtures is due to the inhibiting effect of oxygen on the decomposition.

2. The result of Chapman and Jones, who found almost no inhibiting effect from the direct addition of oxygen to ozone mixtures, is to be explained on the basis of positive catalyst accidentally present in the oxygen which they added.

3. By electrolysis under suitable conditions from sulfuric acid, oxygen and ozone can be prepared which contain either no catalyst for ozone decomposition or at least a nearly constant amount.

4. Linde tank oxygen and oxygen freshly prepared by electrolysis from caustic solution may contain considerable amounts of catalyst for ozone decomposition. The amount of catalyst in oxygen from sodium hydroxide solutions is greatly reduced by passage through the silent discharge in a Siemen's ozonizer.

5. Different samples of oxygen show different degrees of ozonizability in the Siemen's ozonizer, and there is a tendency for high ozonizability to be correlated with low specific second-order decomposition rate.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE PHARMACEUTICAL LABORATORY OF THE UNIVERSITY OF
UTRECHT]

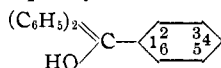
THE USE OF METHOXYTRIPHENYL CARBINOLS AS ONE-COLOR INDICATORS¹

By I. M. KOLTHOFF

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The one-color indicators in use at the present time are colored in alkaline and colorless in acid solution. This work is a study of the constants and properties of a series of indicators which are colorless in alkaline and colored in acid solution. Triphenyl carbinol



is colored in sulfuric acid but the salt is hydrolyzed when diluted with

¹ The writer is indebted to Mr. H. Lund and Professor M. Gomberg, University of Michigan, for the preparations used in connection with this work. See H. Lund, *This Journal*, **49**, 1346 (1927).