

[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES]

THE KINETICS OF GAS EXPLOSIONS: THE THERMAL DECOMPOSITION OF OZONE SENSITIZED BY BROMINE VAPOR¹BY BERNARD LEWIS² AND W. FEITKNECHT³

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The kinetics of the thermal reaction between ozone and bromine below 13° was studied by Lewis and Schumacher.⁴ It was found that bromine reacts with ozone quantitatively, forming a white crystalline oxide of bromine having the composition Br₃O₈ which is slowly deposited on the walls of the vessel. Following the complete disappearance of free bromine, the ozone decomposes into oxygen at a constant rate which is independent of the size and the kind of reaction vessel, ozone concentration (above a certain limit) and inert gases, but which depends on the quantity of oxide formed and on the temperature. Thus it was found that the rate of decomposition of ozone is directly proportional to the original concentration of bromine, namely

$$+ \frac{dp}{dt} = k[\text{Br}_2]$$

and that the temperature coefficient has a value of 3.15 for 10° between 0 and 10°.

These investigators observed that if the temperature is raised to 20° no oxide of bromine is deposited. Instead there is a period of quiescence (lag period) during which no change in pressure occurs, followed by a sudden explosion which is accompanied with the evolution of light. This phenomenon, which involves only the decomposition of ozone into oxygen in the presence of the catalyst bromine, seemed to present a medium by which some light might be thrown on the concept of chain reactions.

The experiments in the transition range between temperatures at which solid oxide is formed and explosions occur are described elsewhere.⁵ They are interpreted on the basis of the formation of an unstable adsorption compound of bromine and ozone at the wall which becomes increasingly more stable with decreasing temperature. The unstable compound, on decomposing, forms an active product which is ejected into the gas phase and starts reaction chains. By lowering the temperature the product of

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⁴ Lewis and Schumacher, (a) *Z. physik. Chem.*, **138A**, 462 (1928); **6B**, 423 (1930); (b) *Z. Elektrochem.*, **35**, 651 (1929); (c) *Z. anorg. Chem.*, **182**, 182 (1929); (d) *Nature*, **125**, 129 (1930).

⁵ Lewis and Feitknecht, *Z. physik. Chem.*, (in press).

this decomposition becomes less active as far as its ability to start reaction chains is concerned. This is shown by the gradually changing character of the reaction from a predominantly gas phase to a wall reaction.

Preliminary Experiments

In some early experiments, on mixing ozone and bromine in certain proportions, we were struck by the remarkably long lag periods which preceded explosions. Their duration was, in some instances, as long as one hour. The time was not easily reproducible.

It was soon discovered that these exceptionally long lag periods were caused by arsenous bromide. Due to the nature of the experimental technique, which involved repeated evaporation and freezing out of bromine on one side of a brass needle valve, arsenic in the latter was attacked and accumulated in the bromine reservoir as a white crystalline arsenous bromide (AsBr_3 , melting point 31°). This compound was carried with the bromine into the reaction vessel and was adsorbed on the walls. Upon replacing the brass needle valve by a specially constructed stainless-steel diaphragm valve, the arsenic compound was eliminated completely and the lag periods were shortened to the order of one minute.

The length of the lag period is influenced by such factors as the ozone and bromine concentrations, the temperature and the activity of the vessel. As far as the lag period was concerned it made considerable difference whether ozone or bromine was admitted to the reaction vessel first. The lag times were shortened from minutes for the order bromine + ozone to several seconds for the order ozone + bromine.

The pressure of ozone just necessary to develop an explosion will be used as a measure of the explosion limit.⁶ It was found to be influenced principally by temperature and the presence of inert gases. Moreover, the slow decomposition (in the event that the ozone pressure was below the explosion limit) was similarly affected.

These experiments led us to the belief that the wall of the vessel is of considerable importance for the development of explosions in this reaction, namely, that it is the seat of the initiation of chain reactions. Other investigators working with quite different systems have recently arrived at the same conclusion.^{7,8}

⁶ The term explosion limit in a two-component system at a definite total pressure, say atmospheric, is usually applied to the percentage combustible necessary to develop an explosion. In a one-component system, as in the present case, pressure is used as a measure of the explosion limit.

⁷ See experiments on the inflammation of hydrogen and oxygen by Alyea and Haber, *Naturwiss.*, **18**, 443 (1930); *Z. physik. Chem.*, **10B**, 193 (1930); Farkas, Haber and Harteck, *Naturwiss.*, **18**, 443 (1930); *Z. Elektrochem.*, **36**, 722 (1930).

⁸ Thompson, *Z. physik. Chem.*, **10B**, 273 (1930); Alyea, *THIS JOURNAL*, **53**, 1324 (1931).

Apparatus

The apparatus used in this investigation was described in its essential details in an earlier work.^{4b} Certain additional features will be mentioned. In order to obtain pure and stable ozone, all greased stopcocks had to be eliminated and metal needle valves used in their stead. The needle valves used here are similar to those used previously with a slight modification to prevent the needle from sticking in the seat of the valve. The cone of the needle was made of a specially hard non-corrosive chrome-nickel-vanadium-tungsten steel. A stainless-steel diaphragm valve separated the bromine reservoir from the rest of the apparatus. It is similar in principle to that of Bodenstein and Dux,⁹ but its principal parts consist of only two pieces, thus limiting the number of soldered joints to one. This joint is on the outside of the lapped-over rim of the diaphragm. The chief advantages of the valve are its simplicity of construction and freedom of exposure of corrosive gases to soldered joints.

The manometer system consisted of a Bodenstein quartz spiral manometer as a null instrument, backed by a mercury manometer and bromonaphthalene manometer (1 mm. Hg = 9.15 mm. bromonaphthalene). By means of a graduated scale in the telescope used for observing movements of the quartz spiral manometer pointer, a change of 0.02 mm. of mercury was observable.

Inert gases were stored in liter flasks. Before being used they were passed very slowly through a liquid-air trap (ether-carbon dioxide mixture for carbon dioxide gas) and a fine porous-plate Pyrex glass filter sealed into the Pyrex tubing to remove any possible suspended material. The filter is similar to the Jena porous-plate filter but is not obtainable commercially in Pyrex glass. Since the Jena filter could not be sealed into Pyrex tubing, a simple method¹⁰ of making them of Pyrex glass was developed by one of us (B. L.) and they have been in use in this Laboratory for a year and a half with excellent results.

The reaction vessels used were two Pyrex glass bulbs (hereafter called vessels I and II) and a quartz bulb, each of 250 cc. capacity, and a number of cylindrical Pyrex glass tubes of various diameters. The experiments were conducted in a temperature-controlled water-bath. The reaction vessel was protected from light exposure.

Materials

The purest Kahlbaum bromine was used. It was distilled at a low temperature under high vacuum through anhydrous magnesium perchlorate and a Pyrex glass porous-plate filter directly into the bromine reservoir and sealed under vacuum.

⁹ Bodenstein and Dux, *Z. physik. Chem.*, **85**, 297 (1913).

¹⁰ Recently a similar filter and method was described by W. F. Bruce and H. E. Bent, *THIS JOURNAL*, **53**, 990 (1931). Scrap Pyrex glass is ground to a fine powder. For a moderate-size grained filter, glass which passes a 60 mesh but not an 80 mesh sieve may be used. For finer filters, small particles should be ground to pass an 80 but not a 100 mesh sieve, etc. A layer of glass about 1.5 mm. deep is placed in a cylindrical mold such as described by Bruce and Bent or a mold made of platinum foil bent into shape as was used here. The procedure which was found satisfactory is to place the mold in a furnace at 890°. It is removed after twenty seconds and allowed to cool, after which the disk of glass separates easily from the mold. The disk is then placed on a small nickel or iron plate and once again heated in the furnace for forty seconds. The times will vary depending on the kind and size of mold. The technique is soon acquired after a little experimentation. The disk is smoothed with a file, placed in a tapered glass tube of the proper size and sealed in with a fine flame in the usual manner. Filters from 1 to 2.5 cm. in diameter have been made in this way.

Ozone was made and concentrated by the method of Riesenfeld and Schwab.¹¹ Pure dry electrolytic oxygen was passed through a Pyrex glass filter and a Siemens ozonizer into an evacuated flask containing a liquid-air trap. The oxygen in the mixture of liquid oxygen and ozone was pumped off and the ozone which remained had a purity of 99 to 100%. This was tested by noting the increase in pressure on exploding some of the pure ozone. The ozone was very stable in the temperature range of these experiments. At ordinary temperatures no increase in pressure could be observed over a period of several hours.

The inert gases used, namely, oxygen, nitrogen, helium, argon and carbon dioxide, were the purest obtainable in tanks. The helium and argon contained a little nitrogen and were 97% and 95.5% pure, respectively. Carbon dioxide was condensed in liquid air and the non-condensable gases were pumped off. It was then stored in the gas form.

Experimental Procedure

The principle of the measurements was to admit bromine and ozone separately into the reaction vessel at a definite temperature and to measure the increase in pressure with time caused by the reaction $2O_3 = 3O_2$. During the reaction the pressure of bromine remains unchanged. Before starting an experiment, all the ozone was allowed to evaporate in its reservoir and was then very carefully admitted to the reaction vessel by cracking the needle valve.¹² Unless otherwise stated, the order of entering the reaction vessel was bromine, inert gas (when used), ozone. Occasionally bromine was added last. The ozone was admitted rather rapidly and the time was taken when 10% was already in the vessel. When not in use both the ozone and bromine were maintained in liquid air in their respective reservoirs. Before each experiment the reaction vessel and also the ozone reservoir were pumped out with a diffusion pump to about 10^{-5} mm. For reasons which will become apparent later most experiments were conducted with 5 mm. of bromine.

In order to show the characteristic way in which bromine sensitizes the decomposition of ozone a number of experiments at 35° are plotted in Fig. 1 for different initial ozone pressures for the first three minutes of reaction. The experiments were made in the quartz vessel.

At low pressures of ozone the reaction commences slowly after the lag period. It then accelerates, goes through a maximum, after which it slows down. The form of the curve cannot be represented by a simple relationship. At higher ozone pressures the velocity is correspondingly greater. Above a definite pressure, in this case 32 mm. of ozone, the velocity rises so rapidly that an explosion results. Thirty-two mm. of ozone is therefore the explosion limit for these conditions. The curve for 30 mm. illustrates a mixture on the verge of explosion, the drop in pressure after the sudden rise being due to the dissipation of heat. The curve for 34 mm. represents an explosion. It will be observed that the lag period varies

¹¹ Riesenfeld and Schwab, *Ber.*, 55, 2088 (1922).

¹² Violent explosions take place if the needle valve is opened suddenly and too wide.

inversely as the ozone pressure and the rate of decomposition increases with the initial ozone concentration.

Activity of Vessel

Whilst the lag period, limit of explosion and rate of the slow reaction could vary in a given vessel to a considerable degree, they proved to be related to each other, namely, a short lag period corresponds to a low explosion limit and a high reaction rate.¹³ It will be evident that these factors are really a measure of the activity of the wall of the vessel. The nature of this activity will be discussed later.

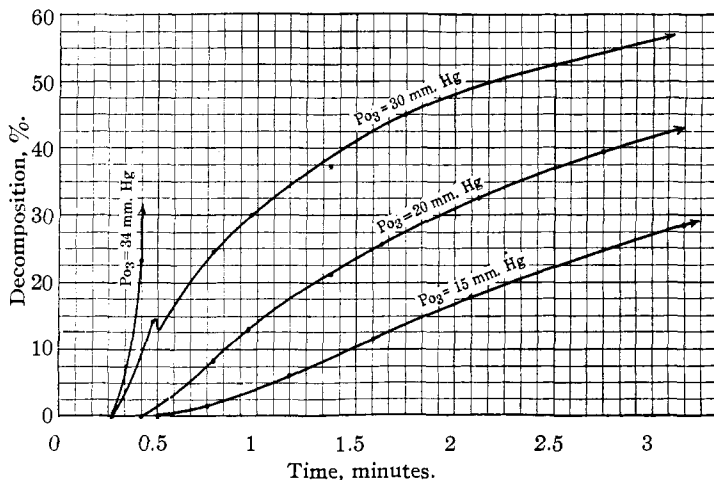


Fig. 1.—Typical curves showing decomposition of ozone: $T, 35^{\circ}$;
Br₂ pressure, 5 mm.

An inactive vessel could be made active by carrying out a reaction near the explosion limit or more effectively by admitting enough ozone to bring about an explosion. Extreme activity was never realized except by a succession of explosions. It therefore made some little difference from which side the explosion limit was approached, it being 1 to 2 mm. lower approached from the explosion or high ozone pressure side than from the slow reaction or low ozone pressure side. In all experiments the explosion limit was determined from the explosion side.

Deactivation of a vessel became more and more pronounced the longer it remained in disuse. For a moderate reversion to inactivity three or four days were required. It also became increasingly more difficult to reactivate. This is illustrated in Table I, in which are given data for different vessels which had remained unused for different periods of time.

¹³ No such relationship was evident between the lag period and explosion limit when different vessels were compared. A vessel showing a long lag period could have quite a low explosion limit and *vice versa* (see Table II).

After each experiment the vessel was pumped out thoroughly and a fresh mixture admitted.

TABLE I

| REACTIVATION OF VESSELS UNUSED FOR DIFFERENT PERIODS OF TIME | | | | | |
|--|-------------|------------|---|-------|---|
| Vessel | Time unused | Temp., °C. | Mixture of gases | Expt. | Remarks |
| Glass bulb | 17 days | 25 | 5 mm. Br ₂ 16 mm. O ₃ (2 mm. above explosion limit) | 1 | No change in 20 minutes |
| | | | | 2 | Lag period 10 minutes; slow reaction |
| | | | | 3 | Lag period 2 minutes; explosion |
| | | | | 4 | Lag period 30 seconds; explosion (vessel very active) |
| Quartz bulb | 1 night | 25 | 5 mm. Br ₂ 23 mm. O ₃ (2 mm. above explosion limit) | 1 | Lag period 1 minute, 15 seconds; slow reaction |
| | | | | 2 | Lag period 32 seconds; explosion |

A decrease in activity was also observed when air or inert gases which were not very carefully purified were admitted to the vessel. A much more marked but similar effect is observed with water vapor. A 0.1 mm. pressure of water vapor is sufficient to inhibit completely an explosion and to reduce the reaction velocity considerably. Even when the vessel was activated each day by the same method, it often showed slight differences in activity which affected not so much the explosion limit as the lag period and particularly the slow reaction at low ozone pressures. Thus for apparently the same conditions many experiments showed the same rate of decomposition whilst others differed considerably. Therefore it was necessary to make frequent tests of the activity of the vessel and to compare only those experiments which had been performed under similar conditions.

The differences in the activities observed may be due mainly to two causes: (1) active products formed during the decomposition or explosion of ozone remain adsorbed on the walls, thereby imparting more active properties to the latter (compare Farkas, Haber and Harteck).⁷ (2) The activity is a property of the wall itself—that is, the surface consists of more or less active spots, according to the views of Taylor.

The experiments indicate, particularly when the activities of different vessels are compared (see Table II), that it is the second factor which is of greater importance while the first exerts, if any, only a small influence. In this connection a highly active vessel which was heated to *ca.* 300° under high vacuum showed only a small decrease in activity. The inactivity of a new vessel or the deactivation of an active vessel by an impurity (such as AsBr₃ or unpurified air) may therefore be due to the adsorption of an impurity on the most active centers. The extreme activity which is observed to follow a number of intensive explosions seems to be due to a temporary change in the nature of the surface.

TABLE II

A COMPARISON OF THE ACTIVITY OF DIFFERENT VESSELS HAVING THE SAME SHAPE AND VOLUME

| Vessel | State of activity | Lag period | Explosion limit |
|----------|-------------------------|------------|-----------------|
| Glass I | New (moderate activity) | 1'30" | 14 |
| Glass I | Very active | 30" | 12.5 |
| Glass II | New (moderate activity) | 1'10" | 16 |
| Quartz | New | 35" | 22 |
| Quartz | Very active | 30" | 19.5 |

The experiments to be described and the data to be given in the following sections will be divided into two main parts: those dealing with the explosion limit and those concerning the slow decomposition below the limit.

Experiments on the Explosion Limit

1. Influence of Bromine on the Explosion Limit at Different Temperatures.—

The main results are given in Fig. 2. The influence of

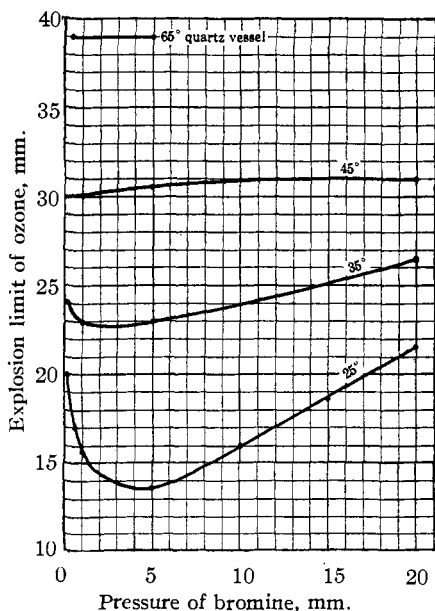


Fig. 2.—Influence of bromine on explosion limit.

bromine on the explosion limit varies with the temperature. Above 35° the limit is uninfluenced by the bromine concentration, even for a 100-fold variation. Below 35° a small influence is observed which becomes more pronounced as the temperature decreases. The limits were determined with an accuracy of ± 0.5 mm. ozone pressure. At about 5 mm. of bromine the explosion limit curve goes through a minimum. For this reason this bromine pressure was used in nearly all subsequent experiments. Below 25° the change in the explosion limits with bromine concentration becomes still more marked, and the deposition of solid oxide becomes increasingly more probable. The phenomena are very different from those at higher

temperatures and rather complex. Experiments in this range form the subject of a paper which is published elsewhere.⁵

2. Influence of Temperature. (a) Effect of Temperature on the Lag Period and the Decomposition Preceding Explosion.—The influence of temperature on the lag period and on the decomposition preceding an

explosion was studied for ozone pressures just above the explosion limits and for a constant bromine pressure of 5 mm. The lag period and the length of time during which decomposition takes place before the explosion sets in decreases with increasing temperature (Fig. 3). Of special interest is the character of the curves. Above 25° the decomposition accelerates rapidly and continuously up to the explosion point, whereas below 25° the transition to the explosion is abrupt and increasingly so as the temperature is lowered.

Confining ourselves to temperatures above 25° the amount of ozone decomposed before explosion sets in depends on the temperature. It is greatest between the temperatures of 35 and 55°.

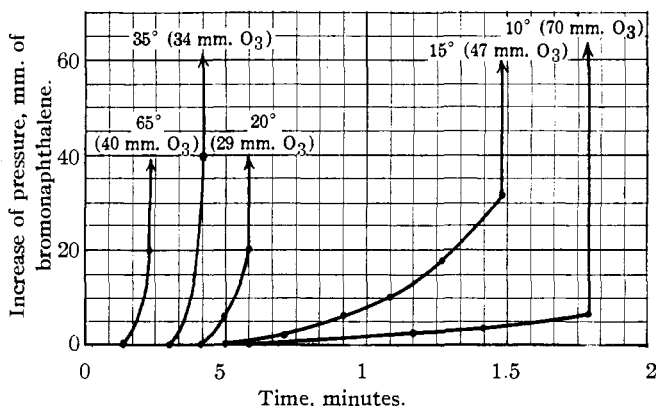


Fig. 3.—Influence of temperature on the reaction preceding explosion.

(b) **Effect of Temperature on Explosion Limit.**—Figure 4 shows that the explosion limit undergoes considerable change with temperature. It goes through a maximum at about 55° and a minimum at about 25°. Usually below 15° no explosions occur except when the vessel is in an exceptionally high state of activity.

A very active vessel may be rendered ineffective for developing an explosion below 15° by carrying out several experiments at an ozone pressure below the explosion limit. Solid oxide of bromine is gradually deposited on the wall, "conditioning" the vessel against explosions. In a vessel conditioned in this way, no explosions occur at 15° far above the normal explosion limit for an active vessel. However, the lag period is still short, indicating that the "conditioning" process does not affect the wall in the same way as the different kinds of deactivation described in a previous section.

3. Effect of Increasing the Surface on the Explosion Limit.—A new glass vessel (No. II) was completely filled with pieces of Pyrex glass tubing

about 1 cm. long, 5 mm. outside and 3.6 mm. inside diameter. The actual change in surface was from 163 sq. cm. to 2067 sq. cm. and in volume from 195 cc. to 134 cc. for the empty and packed vessels, respectively. The increase in the ratio of surface to volume was 19 times. The greatest distance between any two surfaces was approximately 3.6 mm. The explosion limit in the empty vessel was about 16 mm. of ozone at 25°, but in the packed vessel no explosion was possible even up to 100 mm. of ozone. Anticipating our discussion later it is evident that although a large number of chains are started from the walls they are terminated by collisions with the surface before they can develop into an explosion.

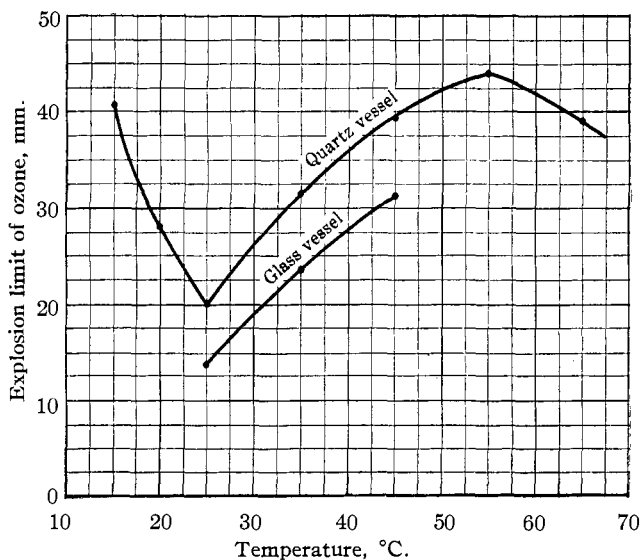


Fig. 4.—Effect of temperature on the explosion limit.

Half the number of glass pieces were now removed, so that half the volume was free. Here the explosion limit was about 29 mm. of ozone, some 13 mm. higher than in the empty vessel. It was found that 100% of the ozone had decomposed during the explosion, indicating that once the latter is started in a free space it travels unhindered through small openings. On several previous occasions the ozone reservoir was blown up due to the propagation of the explosion from the reaction vessel through a slightly opened needle-valve and capillary tubing about 0.1 mm. in diameter.¹⁴ It was estimated that the speed of propagation was of the order of magnitude commonly found for a detonation in gases. From these facts it must be concluded that one is dealing here with detonations rather than

¹⁴ Obviously the explosion will not travel through very small openings such as are encountered in a fine porous glass filter. (See also Riesenfeld and Wassmuth, *Z. physik. Chem.*, **8B**, 314 (1930).)

slow inflammations. This explains the ineffectiveness of the packed half of the vessel in stopping the propagation. It is evident therefore that once the explosion is started the number of chains which terminate at the walls (even when the latter are close together) is insufficient to prevent practically infinite branching of chains.

In view of these results it was considered of importance to study the influence of the size of the vessel on the explosion limit.

4. Influence of Diameter of Vessel on the Explosion Limit.—From the above experiments it appears that under a given set of conditions reaction chains must travel uninterrupted (by walls) for some distance before a sufficient concentration of "reaction carriers"¹⁵ can be developed by chain branching to lead to an explosion. To gain a more distinct idea of this distance the explosion limit was investigated in cylindrical vessels having the same length (12 cm.) but different diameters. Cylindrical instead of spherical vessels were chosen to obtain a greater volume.

Since the explosion limit is affected by the activity, all the vessels were first activated by a number of explosions. Their degrees of activity were similar, judging from the lag period and the rate of decomposition below the explosion limit. Therefore, the explosion limits in these vessels were comparable.

In Fig. 5 the observed explosion limits at 25° are plotted against the diameter of the vessels. The curve so obtained corresponds to a rectangular hyperbola and is represented by the equation

$$(d - a)(p - b) = K$$

where d is the diameter of the vessel in mm. and p the explosion limit; a and b are constants which depend on the activity of the vessel. Deviations from this law are of the order that may be expected from the differences in activity from vessel to vessel. The curve is asymptotic to two lines parallel to the x and y axes whose coordinate values are represented by the constants b and a in the equation. Thus the value of b represents the

¹⁵ By "reaction carrier" is meant one of the intermediate active products generated during the reaction through the medium of which the chains are carried on.

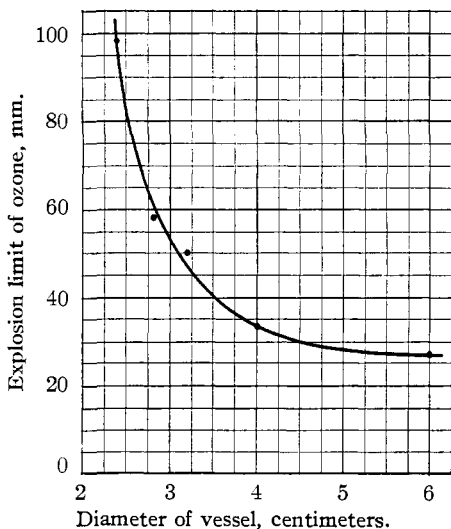


Fig. 5.—Relation between explosion limit at 25° and diameter of vessel.

explosion limit for infinite diameter of vessels of this type which under these conditions is 20 mm. of ozone. The value of a represents the limiting diameter below which no explosion will take place, which under these conditions is found to be 20 mm.

Explosions of ozone alone by direct heating are also prevented in a similar way by proximity of the walls. Thus no explosion occurred in a 4-mm. Pyrex glass tube containing 40 mm. of ozone when it was heated to 400° . (See also Ref. 14.)

Attention is directed to the existence of a similar hyperbolic law between the gas pressure and the condenser voltage when certain explosive mixtures such as $\text{CO} + \text{O}_2$, $\text{H}_2 + \text{O}_2$, $\text{CS}_2 + \text{O}_2$, are ignited by means of a discharge.¹⁶ Although the method of ignition is quite different from that in our experiments the similarity in the results is striking.

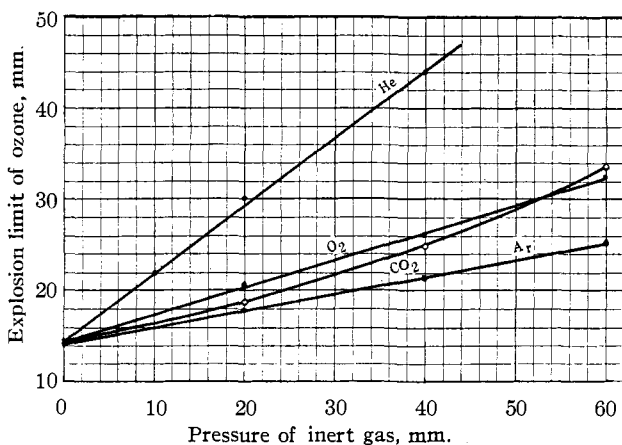


Fig. 6.—Effect of inert gases on the explosion limit at 25° (5 mm. of bromine).

5. Influence of Inert Gases on the Explosion Limit.—The experiments were carried out in the glass vessel I and the quartz vessel at 25° . Preliminary tests showed that the ozone was very stable in the presence of the inert gases alone. The order in which the gases were admitted was: 5 mm. of bromine, varying amounts of inert gases, ozone.

In all cases the inert gas raises the explosion limit. Within the range of these experiments the limit increases directly proportional to the pressure of helium, argon, oxygen and nitrogen. With carbon dioxide the limit increases somewhat faster than by direct proportionality (see Fig. 6). The curve for nitrogen is not shown as it lies very close to and just above that for oxygen. All the curves meet in a common point, 14 mm. of ozone

¹⁶ A. K. Brewer, *Proc. Nat. Acad. Sci.*, **13**, 689 (1927); *THIS JOURNAL*, **52**, 4225 (1930); Finch and Cowen, *Proc. Roy. Soc. (London)*, **A116**, 529 (1927).

at zero pressure inert gas. This is the explosion limit of pure ozone with 5 mm. of bromine at 25° in this glass vessel.

The effectiveness of inert gases in raising the explosion limit increases in the order, argon, carbon dioxide, oxygen, nitrogen, helium.¹⁷ In the quartz vessel the effect is also in the same order but with helium the increase in the limit is now less than corresponds to direct proportionality.

The effectiveness in increasing the explosion limit is in the order of decreasing molecular weight. It is apparent that bromine should have little influence, which is in agreement with experiments described earlier.

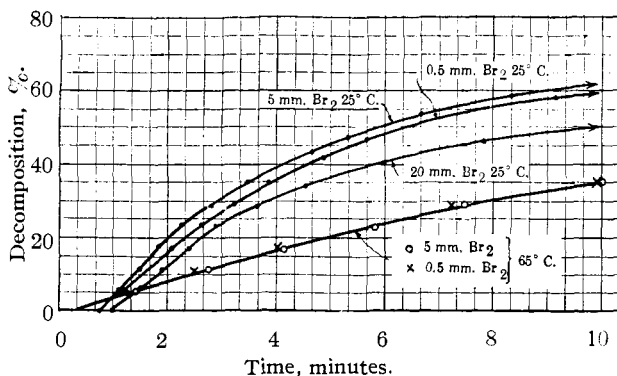


Fig. 7.—Influence of bromine on the rate of decomposition of ozone: pressure of ozone 15 mm.; quartz vessel (explosion limit 20 mm. of ozone).

The Decomposition of Ozone below the Explosion Limit

1. **The Influence of Bromine on the Rate of Decomposition.**—The influence of bromine on the decomposition of ozone below the explosion limit varies with the temperature. At 65° there is no difference in the rate between 0.5 and 5 mm. of bromine (see Fig. 7). At 35° a small effect can be observed. At 25° the reaction is fastest with 5 mm. of bromine, slower with 0.5 mm. of bromine, and still slower with 20 mm. of bromine. The parallelism between these experiments and those on the effect of bromine on the explosion limit is evident (refer to Fig. 2). For a given temperature the fastest rate corresponds to the lowest explosion limit. These facts indicate that the reaction is the same in principle for the slow decomposition as for the reaction leading to explosion.

¹⁷ Experiments on the effect of inert gases on the inflammation limits of mixtures of methane-air, and carbon monoxide-oxygen have been conducted by Coward and Hartwell, *J. Chem. Soc.*, 1522 (1926); F. W. Stevens, *THIS JOURNAL*, 50, 3244 (1928); and Jorissen, Booy and Van Heiningen, *Rec. trav. chim.*, 49, 876 (1930). A different order of effectiveness in raising the limit than in the present experiments was found. This is probably due to the entirely different chemical reactions and experimental conditions.

Below 25° the influence of bromine becomes very marked. The experiments are described fully elsewhere.⁵

2. **The Effect of Temperature on the Rate of Decomposition.**—The rate of decomposition of ozone was studied at different temperatures and at pressures below the explosion limit. One set of experiments is shown in Fig. 8 for 15 mm. of ozone and 5 mm. of bromine. To avoid crowding, only the temperature interval 25–70° is recorded. The results

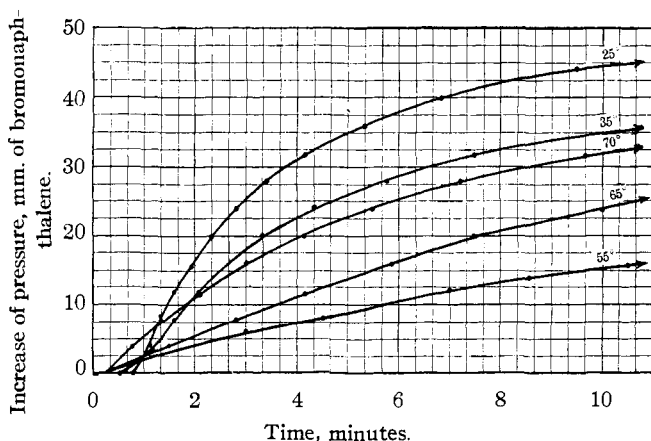


Fig. 8.—Decomposition of ozone at different temperatures: pressure of ozone, 1.5 mm.; bromine, 5 mm.

show that the rate of decomposition decreases as the temperature is raised from 25 to 55° and then increases above this temperature. From 15 to 25° the rate increases once more. Thus there are three distinct regions of temperature coefficients. The temperature coefficients for the first stages of the reaction for different temperature ranges are given in Table III.

TABLE III
TEMPERATURE COEFFICIENTS IN DIFFERENT TEMPERATURE RANGES (15 Mm. O₃;
5 Mm. Br₂, QUARTZ VESSEL)

| Temperature interval, °C. | Temperature coefficient ¹⁸ |
|---------------------------|---------------------------------------|
| 65-55 | 1.7 |
| 55-45 | 0.6 |
| 45-35 | .5 |
| 35-25 | .7 |
| 25-15 | 1.5 |

¹⁸ It has been customary to call temperature coefficients positive if they are greater than one, and negative if they are less than one. The term negative temperature coefficient is, we feel, a misnomer and confusing. We therefore suggest with Prof. A. F. Benton (statement at American Chemical Society Meeting, Indianapolis, March 30-April 3) that it be referred to as a temperature coefficient less than one.

The temperature coefficients are derived by dividing the rates of decomposition for short corresponding time intervals at different temperatures separated by 10° . At higher temperatures these temperature coefficients remain fairly constant during a reaction over a moderately long time.

These results show that the rates follow exactly the explosion limits. For different temperatures the lower the explosion limit the faster the rate of the slow reaction here considered (compare Fig. 4).

It is to be anticipated that the percentage decomposition in a given time will become more nearly the same at all temperatures as the initial pressure of ozone approaches the explosion limit. Table IV shows this clearly.

TABLE IV
COMPARISON OF AMOUNT OF OZONE DECOMPOSED AT DIFFERENT TEMPERATURES NEAR THE EXPLOSION LIMIT. QUARTZ VESSEL USED

| Temp., $^\circ\text{C.}$ | Initial pressure, mm. of ozone | Explosion limit, mm. of ozone | Percentage ozone decomposed in 10 minutes |
|-----------------------------|--------------------------------------|-------------------------------------|---|
| 15 | 40 | 41 | 77 |
| 20 | 27 | 28 | 77 |
| 25 | 20 | 21 | 71 |
| 35 | 30 | 32.5 | 73 |
| 45 | 36.5 | 39 | 70 |
| 55 | 42.4 | 44 | 61 |
| 65 | 38 | 39 | 66 |

The somewhat greater decomposition below 25° is to be ascribed to a gradually changing type of wall reaction with decreasing temperature.⁵

Since no reaction constant can be calculated to which any significance can be attached, another means of comparing the rates at different temperatures and initial pressures is given. This is $\Delta p/\Delta t$ maximum, the change in pressure for an interval of ten seconds at the steepest portion¹⁹ of each curve. For a given initial ozone pressure the steepest portion occurs soon after the reaction has set in (compare Fig. 1). In Fig. 9, therefore, $\Delta p/\Delta t$ maximum is plotted against the initial ozone pressure for different temperatures. Vertical lines represent the explosion limits at the various temperatures. As long as the pressure of ozone is far below the explosion limit, $\Delta p/\Delta t$ changes only slightly. On approaching the explosion limit it increases rapidly up to the explosion point, where it becomes practically infinite. These curves show graphically the suddenness with which the explosion sets in below 20° (see also reference 5).

3. Effect of Increased Surface on the Decomposition.—The decomposition was studied in the vessel packed with glass tubing used in previous experiments. It was mentioned above that no explosions are possible in the fully packed vessel. It is observed (Fig. 10) that regardless

¹⁹ Here there is a minimum retarding effect due to oxygen set free in the decomposition.

of the initial ozone pressure the reaction proceeds to about 90% of completion in a comparatively short period of time, namely, about ten minutes. Furthermore, for a given set of conditions (temperature and ozone and

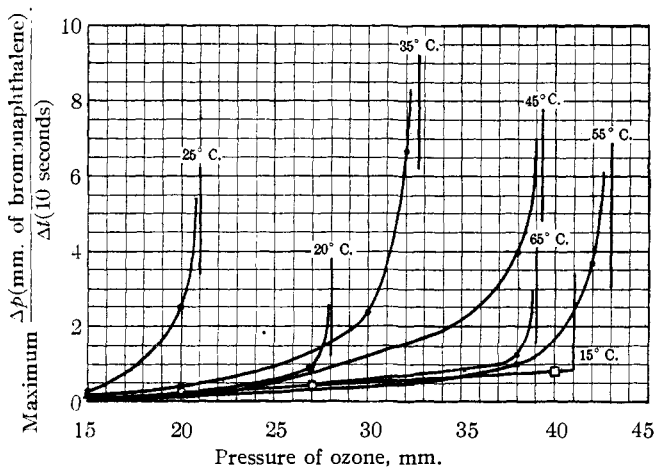


Fig. 9.—Maximum $\Delta p/\Delta t$ for different temperatures.

bromine pressures) the decomposition in a certain time interval is greater in the packed than in the empty vessel (Fig. 11). However, this increase in the rate in the packed vessel in no way compares with the large increase

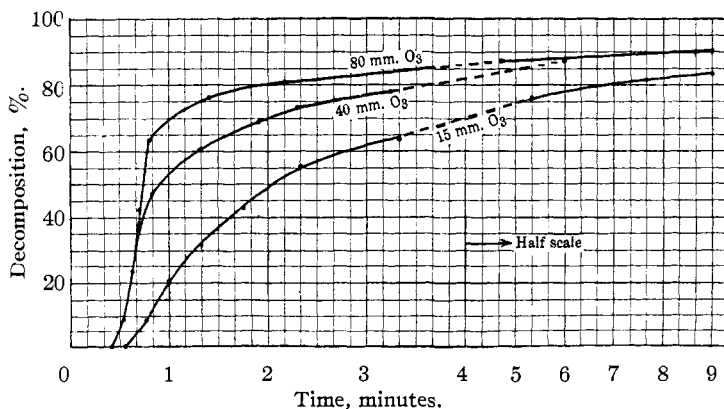


Fig. 10.—Decomposition of ozone in packed vessel at 25° and different ozone pressures.

in the ratio of surface to volume (19:1). This is shown in Fig. 11. The ratio of the reaction rates in the packed and empty vessels at 25°, 15 mm. of ozone, 5 mm. of bromine is calculated to be 1.3 and remains constant over the entire range of the reaction.

The small increase in the rate of decomposition in the packed vessel over

that in the empty vessel indicates that at 25° and above the larger part of the reaction takes place in the gas phase.

4. Temperature Coefficient in the Vessel Filled with Glass Tubing.— In Table V values for the temperature coefficients in the glass-filled vessel for different temperature intervals are given. Comparing these with the temperature coefficients in the empty vessel, it is a striking fact that whereas the value for the interval 15 to 25° in the empty vessel is 1.5 it is only 0.33 in the packed vessel. This means that the decomposition at the lower temperature is much faster in the packed vessel than in the empty vessel. The ratio of the rates in the packed and empty vessels can be calculated to be 5.25 at 15° . This can easily be understood when it is

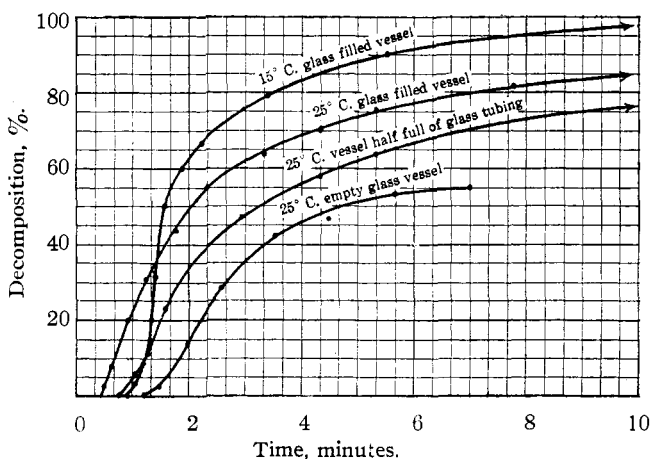


Fig. 11.—Decomposition of ozone: pressure of ozone, 15 mm.; bromine, 5 mm.

remembered that at lower temperatures the decomposition becomes more and more a wall reaction, whilst decomposition in the gas phase becomes smaller.⁵ Owing to the greater rate of formation of the intermediate adsorption compound at 15° than at 25° the amount of ozone decomposed at the wall is greater at the former temperature; but as the number of active carriers shot out into the gas phase diminishes with decreasing temperature, the rate of decomposition at 15° in the empty vessel is smaller than in the packed vessel where the surface has been increased 19-fold. In fact the increase in surface is so great that the decrease of the reaction in the gas phase is more than overbalanced by the increase in the wall reaction. This is one of the first instances²⁰ to be recorded of a heterogeneous reaction possessing a temperature coefficient less than one.

²⁰ Professor H. S. Taylor reported the discovery of another heterogeneous reaction with a temperature coefficient less than one in the catalytic surface conversion of ortho- and para-hydrogen (Meeting American Chemical Society, Indianapolis, March 30-April 3).

TABLE V
TEMPERATURE COEFFICIENTS IN PACKED VESSEL BETWEEN 15 AND 45°

| $\Delta p_{12}/\Delta p_{11}$ ²¹ | Temperature coefficient for initial pressure, 15 mm. of O ₃ |
|---|--|
| $\Delta p_{25}/\Delta p_{15}$ | 0.33 |
| $\Delta p_{35}/\Delta p_{25}$ | .72 |
| $\Delta p_{45}/\Delta p_{35}$ | 1.05 |

As the temperature rises the temperature coefficient also rises until above 45° it is greater than one. This is due to the fact that the intermediate adsorption compound emits active carriers at the higher temperatures and gives rise to chains in the gas phase which multiply rapidly with increasing temperature. On the other hand the wall reaction rate decreases with increasing temperature owing to the decreased adsorption and consequently a smaller number of active carriers is emitted. It is obvious that due to these two factors the temperature coefficient should increase and will eventually reach a temperature at which it is greater than one.

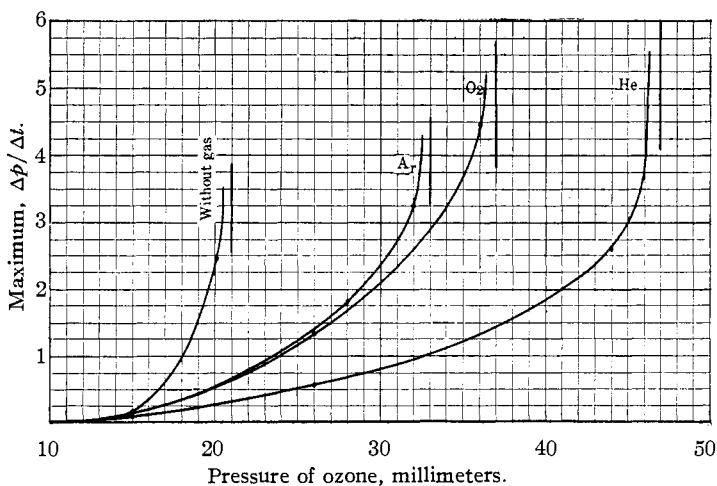


Fig. 12.—Comparison of the effects of inert gases on the maximum rate of decomposition of ozone: pressure of inert gas, 40 mm.; bromine, 5 mm.; temperature, 25°.

5. The Effect of Inert Gases on the Decomposition.—The influence of inert gases on the explosion limit was shown to be greatest for those gases which have small atomic weights and high heat conductivities. To learn more about the mechanism of this influence, the decomposition of ozone below the explosion limit in the presence of like quantities of inert gases was studied. The following results were obtained in the quartz vessel at 25° with 5 mm. of bromine. They are shown graphically in Fig. 12, in

²¹ The rise in pressure for an interval of ten seconds over the steepest portion of the curve was taken for comparing the rate.

which $\Delta p/\Delta t$ for the maximum speed is plotted against ozone pressure for 40 mm. of the inert gases, argon, oxygen and helium. A curve for pure ozone is also shown.

If the pressure of ozone is low, 15 mm.,²² the inert gases exert very little influence on the rate of decomposition. As the ozone pressure is increased the influence of the inert gases becomes marked to a more or less degree depending on the gas. The rate is slowest for helium, faster for oxygen and fastest for argon. Since for like quantities of inert gases the explosion limit is lowest for argon, the rates become even more widely different as the explosion limit for argon is approached. For argon the rate approaches infinity, for oxygen it is slower and for helium very much slower. In the same way on approaching the explosion limit for oxygen the rate is very fast for the latter gas but still very slow for helium. Finally, if the rates of decomposition near the limits of explosion of all the inert gases (for different ozone pressures) are compared they are found to be nearly the same.

Mechanism and Discussion

This rather complex reaction can now be explained satisfactorily from the results of the experiments which have been described. In proposing the following mechanism, no unreasonable assumptions have been made but each step in the process is supported by or deduced from experimental facts.

The whole reaction may be divided into two distinct processes, one which takes place on the walls and the other in the gas phase. In point of view of time the wall reaction precedes the gas phase reaction.

(1) Before any increase in pressure can be observed some process must occur at the wall. The proof for this lies in the numerous observations made of the deactivation of the vessel by impurities such as AsBr_3 and impure air, the long lag periods occasioned by the latter, the gradual step-wise activation of a vessel by previous reactions and explosions, the marked differences in activity in different vessels and the effect of such activity on the slow decomposition and the explosion limit.

(2) This wall process is divided into three distinct phases.

(a) Both ozone and bromine are adsorbed on the walls. As far as the adsorption of ozone is concerned, this is shown very clearly by the marked shortening of the lag period when bromine is admitted to the vessel after the ozone. It will be recalled that here the lag period amounts only to some seconds whereas, when ozone is added after the bromine, the lag period involves minutes. The difference in these times is interpreted as the time taken by the ozone to displace part of the bromine adsorbed on the wall and to become adsorbed itself. Taylor²³ has pointed out that certain adsorp-

²² This pressure is 5 to 6 mm. below the explosion limit of ozone in the absence of inert gases.

²³ H. S. Taylor, *THIS JOURNAL*, 53, 578 (1931).

tion processes may be very slow. In the present case it is not possible to decide whether it is the replacement of bromine by ozone or the slow adsorption of ozone which accounts for this difference in the lag period. It would indeed be very difficult to account for the fact that the temperature coefficient between 25 and 55° is less than one were adsorption of ozone and bromine unnecessary.

(b) An intermediate unstable compound of ozone and bromine is formed at the walls. From general considerations, as both ozone and bromine are necessary for the decomposition or explosion and both constituents are adsorbed, it follows that some type of compound between ozone and bromine must be formed at the walls, apart from all considerations concerning its nature, stability or life-time as an entity. There is no clue to the chemical structure and composition of this oxide. It is not to be confounded with the solid crystalline oxide of bromine Br_2O_3 observed by Lewis and Schumacher,⁴ nor with a volatile oxide of bromine, presumably Br_2O , recently described by Zintl and Reinäcker.²⁴ At 25° and above, the experimental results indicate that this oxide is very unstable. As the temperature is decreased below 25° a continuous increase in stability takes place. Already at a temperature of 15° under favorable conditions the once unstable oxide is observed to go over into the solid crystalline compound.⁵

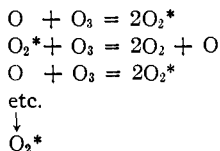
(c) The unstable oxide decomposes immediately and expels or ejects into the gas phase energy-rich groups, most probably oxygen atoms or active oxygen molecules. The more stable adsorption compound at lower temperatures appears to eject groups which are too inactive to initiate further reactions in the gas phase. In support of this are the results showing that at lower temperatures the wall reaction increases and the gas phase reaction decreases and disappears (see also Reference 5).

(3) The active groups, which will be referred to as *reaction carriers*, on colliding with appropriate ozone molecules in the gas phase cause the latter to decompose and at the same time give rise to new active reaction carriers. In this way reaction chains build up and undergo branching or multiplication, the rate of which is dependent on the temperature, the ozone concentration, and the presence of inert gases. They spread out and propagate through the gas phase until they are broken up by collisions with the walls of the vessel. Individual links in the chain are also destroyed by unfavorable collisions with ozone or inert gas molecules. If the concentration of reaction carriers in an element of volume of the gas exceeds a critical value, the chains undergo practically unlimited branching and the reaction goes over into an explosion which leads to the complete decomposition of the ozone in the vessel. If the number of original reaction carriers shot out from the wall is too small (which is affected by tempera-

²⁴ E. Zintl and G. Reinäcker, *Ber.*, **63**, 1098 (1930).

ture, ozone pressure and bromine pressure), the ozone concentration too low, or if a sufficient concentration of an inert gas is present, so that the critical concentration of reaction carriers is not attained, the reaction velocity after reaching a maximum slows down again long before all the ozone has decomposed.

(4) The actual reactions which occur in the chains are unknown. One probable mechanism may be suggested. It is supported to a certain extent by calculations of the velocity of propagation of a detonation wave in ozone. If the chain reaction theory of Lewis,²⁵ and the mechanism suggested by him are considered—namely

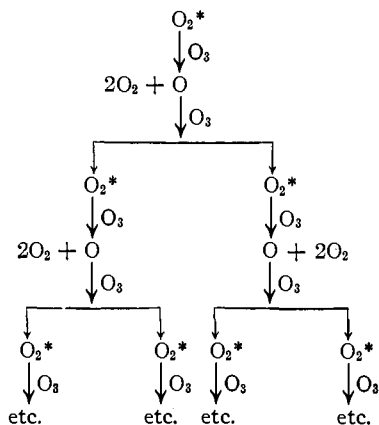


where O_2^* is an active molecule, the reaction carrier turns out to be an excited oxygen molecule with a total energy of 47.2 Kcal. of which 17.7 Kcal. is available as translational energy. (Heat of formation of $\text{O}_3 = 32$ Kcal. and heat of dissociation of $\text{O}_2 = 117$ Kcal.) The velocity of propagation is calculated to be 2150 meters/sec. Using the theory of Chapman and Jouguet,²⁶ which is strictly hydrodynamical and thermodynamical in character and does not consider the individual reactions at all, the velocity is calculated to be 2123 meters/sec. The speed of detonation of ozone has never been determined experimentally, but both theories have been able to account very closely for the velocities of detonations in other gas mixtures for which good experimental values are available. It may therefore be expected that the experimental value for the speed of detonation in pure ozone will be close to the value calculated above. It has been shown that the explosion of ozone in these experiments is in reality a detonation, which furnishes evidence for the probability of the above reaction mechanism.

The way in which branching occurs can be represented in the following scheme. We shall assume that the initial reaction carrier shot off from the wall is an active oxygen molecule. An oxygen atom might do just as well. As mentioned above, any one of the links in the branches may be terminated by unfavorable collisions with other molecules or with the wall. Chains may also terminate by a collision between two oxygen atoms and a third body to form an oxygen molecule. In a spherical vessel this may be a real factor due to the fact that chains start from all points on the wall, spread out spherically in all directions and overlap each other. The overlapping of the chains tends to accumulate reaction carriers and oxygen atoms, the

²⁵ Bernard Lewis, *THIS JOURNAL*, **52**, 3120 (1930).

²⁶ Bernard Lewis and James B. Friauf, *ibid.*, **52**, 3905 (1930), and references contained therein to papers by Chapman, Jouguet and others.



concentrations of which increase on approaching the center of the vessel. Obviously the formation of oxygen molecules from oxygen carriers is a slow process compared with the accumulation of reaction carriers. Referring to the experiments with different sizes of cylindrical vessels, it is obvious that the walls must be far enough apart to prevent the interruption of chains before a sufficient concentration of reaction carriers is built up. It is astonishing how far the carriers have to penetrate into the gas phase before this concentration necessary for explosion is reached.

(5) One may conclude from the results of studies on the photochemical decomposition of ozone that the chains are negligible or very short in the red region of the spectrum,²⁷ while in the ultraviolet²⁸ chains exist but they too are very short. The mechanism given by Schumacher²⁷ involves the formation of active oxygen molecules. These active molecules do not react further and start chains. It is believed that the chains in the present reaction are also propagated through the medium of active oxygen molecules. It is possible that the difference in behavior of the active oxygen molecules in both cases lies in the fact that the energy resides in the molecule in different forms. In this investigation a large amount of the energy is probably in the form of energy of translation which is in a more suitable form to react with ozone. In the photochemical reaction it may be that only a small amount of energy is available as energy of translation and that the efficiency of favorable collisions with ozone is much smaller. The writers realize the difficulties in the way of arriving at precise conclusions in this matter. Although the experiments do not indicate it, it may still be possible that bromine takes part in the chain mechanism in some unknown way. Further experiments are in progress.

(6) From these views, the reason for the influence of bromine on the

²⁷ G. B. Kistiakowsky, *Z. physik. Chem.*, **117**, 337 (1925). (For more complete list of references see H. J. Schumacher, *THIS JOURNAL*, **52**, 2377 (1930).

²⁸ E. Warburg, *Sitzb. preuss. Akad. Wiss.*, 644 (1913).

explosion limit and the slow decomposition below the explosion limit becomes clear. At the lower temperature, say 25° , if too little bromine is present, not enough bromine is adsorbed and too few reaction carriers are emitted from the wall. If too much bromine is present it displaces ozone from the walls and again too few carriers are formed. Somewhere there is an optimum bromine pressure at which a maximum number of carriers is formed. At higher temperatures the bromine has no effect because the surface is covered only partially and does not influence appreciably the ozone adsorbed. The number of carriers formed is therefore constant.

(7) The temperature coefficient of the reaction is divided into three parts. It is greater than one below 25° , less than one between 25 and 55° , and again greater than one above 55° . These may now be explained on the basis of the mechanism given above. There are two main parts of the reaction which are affected by temperature, namely, the wall effect and the gas phase reaction. These gross effects are due to a number of separate causes.

A. Wall effect.

1. Speed of adsorption with temperature.
2. Amount of adsorption with temperature.
3. Speed of formation of unstable intermediate adsorption compound.
4. Speed of decomposition of unstable intermediate adsorption compound.
5. Change of type of intermediate adsorption compound with temperature.

B. Gas phase reaction.

1. Increase in chain length with temperature (speed of chain branching).
2. Diffusivity of the carrier to the wall with temperature.

The temperature coefficients above 25° are explained as follows. (a) The amount of adsorption decreases with increasing temperature. We shall neglect the speed of adsorption, although this probably increases with increasing temperature. (b) Therefore, on the basis of mass effect alone, the speed of formation of the intermediate adsorption compound decreases with increasing temperature. (c) It is assumed that the intermediate compound decomposes fast enough so that the rate of emission of carriers is governed by (a). (d) The length of the chains of branching increases exponentially with the temperature. (e) The diffusivity of the active carriers to the wall increases as some power of the temperature, T^x , where $x = ca. 1.7-2$.

The effect of (a) and (e) is to slow down the rate as the temperature rises by decreasing the number of carriers emitted from the wall and by deactivating them (or others formed in the chains) on the wall. The effect of (d) is to speed up the rate as the temperature rises; (d) increases rather rapidly with temperature, faster than (e). It is possible, however, for the curves of the combined effect of (a) and (e) and that for (d) to possess such a character that they intersect at some temperature in the neighborhood of

55°. Thus between 25 and 55° the effects of (a) and (e) outweigh the effect of (d) and the temperature coefficient is less than one. Above 55° the effect of (d) outweighs the effect of (a) and (e) and the temperature coefficient is greater than one. In other words, when the gas phase reaction (branching of chains) becomes more extensive than the combined wall effects, the temperature coefficient is greater than one and *vice versa*.

Concerning the temperature coefficient of less than one below 25°, it has been shown⁵ that as the temperature decreases below 25° the unstable intermediate compound goes over to a more stable form whose decomposition products are incapable of propagating chains in the gas phase. Therefore, as the temperature decreases the wall reaction becomes more pronounced and the gas phase reaction less. The combination of both effects result in a smaller total reaction occurring at the lower temperature. If the temperature and other conditions are such that solid bromine oxide is formed, the gas phase reaction disappears entirely.⁴ The influence of temperature in the glass-filled vessel has been discussed above.

(8) It remains now to explain the effects of inert gases. At low ozone pressures where the reaction is normally very slow and the branching and spreading of chains is a minimum, the addition of moderate amounts of inert gases (10 to 60 mm.) will have very little effect on the already small branching. However, when the ozone pressure is raised to a point approaching the explosion limit (without inert gas), the branching of chains goes on to a marked degree and the addition of inert gases should produce a greater or smaller effect depending on the gas used. Moreover, whatever the inert gases used, the rate should be the same close to the explosion limit since here the branching becomes practically infinite. These limits are given in Fig. 6.

The manner in which the inert gases effect the branching of the chains may be understood as follows. Three different effects should be considered. These are: (1) the effectiveness of the inert gas in deactivating the reaction carrier. This is (for translational energy) a function of the mass of the inert gas. It is greatest for a mass similar to the carrier itself. (2) The number of collisions the inert gas makes with the carrier. Everything else being equal this is inversely proportional to the square root of the mass of the inert gas. The larger the number of collisions the greater the chance for deactivation. (3) The speed with which the heat energy liberated in the decomposition is transported to the wall—that is, heat conductivity. The heat conductivity of the inert gases used decreases in the order of increasing molecular weight. The greater the heat conductivity, the higher the explosion limit.

It is not possible to calculate quantitatively the exact influence of each inert gas. The combination of these three effects, however, checks well the order of the influence of the inert gases realized in the experiments.

The reason for the relatively small effect of bromine on the explosion follows from these considerations.

(9) It may be worth while to point out what new light this research throws on the general concept of chain reactions. First of all the experiments show that the conditions in the system ozone-bromine-surface are very complicated. The results, therefore, cannot be used for a precise formulation of the chain reaction mechanism, nor for the measurement of the length of the chains.

However, the reaction provides another example of chains starting and ending at the walls, that the chains are initiated by a wall adsorption compound. The results indicate that in this particular case the branching of chains in the gas phase occurs slowly and that it can become practically infinite only after the carriers and chains have penetrated a relatively great distance into the gas phase. Considerable decomposition as a result of branching of reaction chains also takes place under conditions where no explosions occur. The chains may be long or short depending on the conditions of the experiment. It is of interest to point out that as the explosion limit is approached they become gradually longer and longer. This and the fact that inert gases have an identical effect on the decomposition below and above the limit show that the reaction during the slow decomposition is identical with the reaction during explosion and furnishes unequivocal evidence for the chain theory of detonations in gas mixtures.

In contrast to this reaction are a number of other examples like the hydrogen-oxygen and carbon disulfide-oxygen systems.⁸ In these latter reactions the transition from the non-explosive to the explosive stage occurs abruptly. Beyond the explosion limit only a slow reaction occurs (little or no branching of chains) which passes over suddenly at the limit to an explosion (practically infinite branching).

The dependence of the propagation of chains on the way in which the energy is distributed in the initial reaction carriers shot off from the wall or formed in the light reaction and the fact that the explosion involves a single molecule only, would seem to make the ozone explosion very suitable for a study of the fundamentals of gas explosions.

Summary

1. The decomposition of ozone sensitized by bromine vapor has been investigated. The reaction begins only after a lag period, following which an acceleration takes place which culminates in an explosion if the pressure of ozone exceeds a certain critical value. Below this explosion limit the reaction rate goes through a maximum and slows down again.

2. The lag period (ranging from a few seconds to an hour), the explosion limit, and the rate of the slow decomposition depend on the activity of the vessel. The activity is a property of the surface of the wall and can be

influenced by several factors which are discussed. Slow decomposition and particularly explosions render a vessel very active. A vessel so activated retains a considerable part of its activity even if unused for several days.

3. The concentration of bromine between rather wide limits has no influence on the explosion limit nor the slow reaction above 35° . Below this temperature an influence appears which becomes more marked with decreasing temperature. The explosion limit goes through a minimum and the slow reaction a corresponding maximum for 5 mm. of bromine.

4. For a definite bromine concentration the explosion limit goes through a minimum at 25° and a maximum at 55° . Corresponding to this the slow reaction has a temperature coefficient greater than one below 25° , less than one between 25 and 55° and greater than one above 55° .

5. No explosion is possible in a vessel filled with pieces of glass tubing. The results show that below 25° the reaction gradually becomes predominantly a wall reaction while above 25° the reaction takes place mainly in the gas phase. It is shown that the explosion is in reality a detonation.

6. The explosion limit increases with decreasing diameter of cylindrical vessels. A hyperbolic law is found to exist between the explosion limit and the diameter. Under certain experimental conditions no explosions are possible in a vessel smaller than 2 cm. in diameter. It is interesting to observe that reaction chains must travel a considerable distance into the gas phase before an explosion results.

7. The explosion limit is increased proportionally to the pressure of inert gases. The effect increases in the order argon, carbon dioxide, oxygen, nitrogen and helium. The slow reaction is affected similarly.

8. A mechanism based on the experimental facts is proposed. Reaction chains start at the wall due to the emission of an active product of a decomposing wall adsorption compound between bromine and ozone. The chains propagate in the gas phase and may terminate there or on the wall.

9. The photochemical decomposition of ozone is discussed in relation to the present investigation.

10. A method of making porous plate filters of Pyrex glass is described.

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