

of light. The plates were photometered with the aid of microphotometer lent by Professor G. R. Harrison. The accuracy of the final measurements was within a few per cent. No absorption was observed from 6000 to 2150 Å.

Note.—The last filling of the double steel tube with carbon dioxide was in December, 1928. It was left in January, 1929, with liquid carbon dioxide in the shorter arm. In January, 1931, the amount of liquid was still the same as when it was left two years earlier.

Conclusions

Liquid carbon dioxide (1.5 cm. layer) at -51° has been found to be transparent to the visible and quartz ultraviolet. A 16.35-cm. layer of liquid carbon dioxide at room temperature was also found to be transparent except perhaps for a slight continuous absorption below 2500 Å.

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THE KINETICS OF GAS EXPLOSIONS. II. THE THERMAL REACTION BETWEEN OZONE AND HYDROGEN BROMIDE¹

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It was suggested⁴ that the oxygen atom and an active oxygen molecule are the carriers in the reaction chains involved in the thermal decomposition and explosion of ozone sensitized by bromine vapor.^{4,5} In an attempt to detect the presence of free oxygen atoms during this reaction, hydrogen bromide⁶ was added to the mixture, since it is known to react easily with the former.⁷ It was found, however, that ozone reacts with pure hydrogen bromide so rapidly that the chains in the ozone-bromine reaction are dwarfed in comparison with the fast and long chains in this new ozone-hydrogen bromide reaction.

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⁴ Part I. Lewis and Feitknecht, *THIS JOURNAL*, **53**, 2910 (1931).

⁵ Lewis and Feitknecht, *Z. physik. Chem. Bodenstein-Festband*, 113 (1931). See also Lewis and Schumacher, *ibid.*, **138A**, 462 (1928); **6B**, 423 (1930); *Z. anorg. Chem.*, **182**, 182 (1929); *Z. Electrochem.*, **35**, 651 (1929).

⁶ Lewis and Feitknecht, *THIS JOURNAL*, **53**, 3565 (1931). The effect of hydrogen will be described elsewhere.

⁷ Harteck and Kopsch, *Z. physik. Chem.*, **12B**, 327 (1931).

Preliminary experiments indicated that when ozone is added to hydrogen bromide at a pressure of 10 mm. for each gas, an explosion occurs immediately, the hydrogen bromide is oxidized to water vapor and bromine, and any excess ozone is also destroyed. The same action occurs even at temperatures of -77 and -104° at slightly increased pressure. Below the limiting pressure the two gases react at these low temperatures at a fast but measurable rate.

A detailed and comprehensive kinetic study of this reaction disclosed its initial heterogeneity, despite its enormous velocity. The facts leading to the conclusion that the reaction chains start at the walls and then propagate into the gas phase are similar to those given in Part I⁴ of this investigation. In this paper we shall therefore omit detailed experiments but shall point out certain differences and similarities with the ozone-bromine reaction.

Apparatus and Materials.—The apparatus used was the same as described earlier.^{4,8} A Pyrex glass cylindrical reaction vessel 3.5 cm. in diameter and 12 cm. long was used for most experiments. The low-temperature baths used were carbon dioxide-ether (-77°) and boiling ethylene (-104°). Pure hydrogen bromide was prepared from resorcinol and bromine⁹ and was purified by low-temperature distillation. It was kept in the solid state when not in use. Greaseless, non-corrosive needle valves were used in the apparatus to by-pass gases. Pure ozone was prepared as before.^{4,5}

Experimental Procedure.—The reaction could be followed by measuring the decrease in pressure, since the products, water and bromine, have negligible vapor pressures at the low temperatures used. Separate experiments indicated that any reaction between water and hydrogen bromide to form a solid hydrate was negligible.

Usually hydrogen bromide was admitted to the reaction vessel first. At first the pressure increased, and if the initial pressure was above the explosion limit an explosion occurred after a lag of about two seconds. Just below the explosion limit the reaction was complete in ten to twenty seconds after the initial rise in pressure. At considerably lower pressures lag periods varying from three to forty seconds were observed.

For the same pressure and composition the rate of reaction was faster when ozone was admitted first. This probably means that the initial surface adsorption layer, with ozone already adsorbed, favors the initiation of a larger number of chains.

The Non-explosive Reaction.—With an excess of ozone the decrease in pressure in the non-explosive reaction corresponds to the amount of hydrogen bromide used, whereas with excess hydrogen bromide it is approxi-

⁸ Lewis and Schumacher, *Z. Elektrochem.*, **35**, 651 (1929).

⁹ Ephraim and Schärer, *Ber.*, **61**, 2164 (1928).

mately twice as great as the ozone used. This and other data suggest that the reaction follows approximately¹⁰ the formula.



The non-explosive reaction and the lag period preceding it are largely influenced by the activity of the wall. A large increase in activity is obtained when the reaction products of a preceding reaction are left frozen out on the wall.¹¹ The activity increases as the thickness of the layer increases. It reaches a maximum value only after several explosions (compare Fig. 1), but decreases again when this is followed by several non-explosive reactions. The increased activity is due to the increased surface of the frozen reaction products, rather than to a specific chemical effect. An explosion gives rise to more finely divided products.

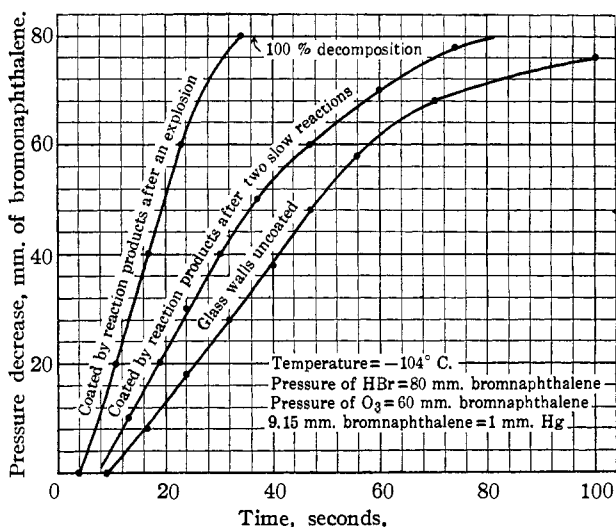


Fig. 1.—Influence of nature of surface on rate of reaction between hydrogen bromide and ozone.

Reaction rates for similar mixtures in a vessel having different activities are shown in Fig. 1. It can be shown that the straight-line portion is due to the lag in freezing out the reaction products and does not represent a zero order reaction. This is evident from Fig. 2, in which the rate is

¹⁰ There are indications that when less ozone than half the hydrogen bromide pressure is used, somewhat more than two molecules of hydrogen bromide may be oxidized by one molecule of ozone but the results obtained so far are not quite conclusive. On the other hand, with excess ozone at higher pressures and especially at the higher temperature (-77°) it is possible that a small amount of ozone is decomposed in addition to that used to oxidize hydrogen bromide in accordance with the above equation.

¹¹ It is impossible to determine whether any or how much of the products are in the form of bromide hydrate.

much smaller for the lower pressures and the curves bend over earlier. If the reaction rates are compared, they are given very well by the relation

$$-\frac{\Delta p}{\Delta t} = k [\text{HBr}]_{\text{init.}} [\text{O}_3]_{\text{init.}} \quad (2)$$

where $[\]_{\text{init.}}$ represents the initial pressures. The k for several experiments is given in the last column of Table I.

TABLE I

THE INITIAL RATE OF THE REACTION BETWEEN HYDROGEN BROMIDE AND OZONE AT DIFFERENT CONCENTRATIONS

Temperature, -104° .		Vessel uncoated. Pressure in mm. of bromonaphthalene	
Pressure of HBr, mm.	Pressure of O ₃ , mm.	$-\frac{\Delta p_{\text{mm.}}}{\Delta t_{\text{sec.}}}$	$k = \frac{\Delta p_{\text{mm.}}}{\Delta t_{\text{sec.}} [\text{HBr}]_{\text{init.}} [\text{O}_3]_{\text{init.}}}$
80	84	1.43	0.021
80	58	1.25	.026
80	38	0.806	.026
60	48	.805	.028
38	44	.52	.031

The small but gradual change in the constants is due to a number of factors which can be shown to decrease the constants at the higher pressures.

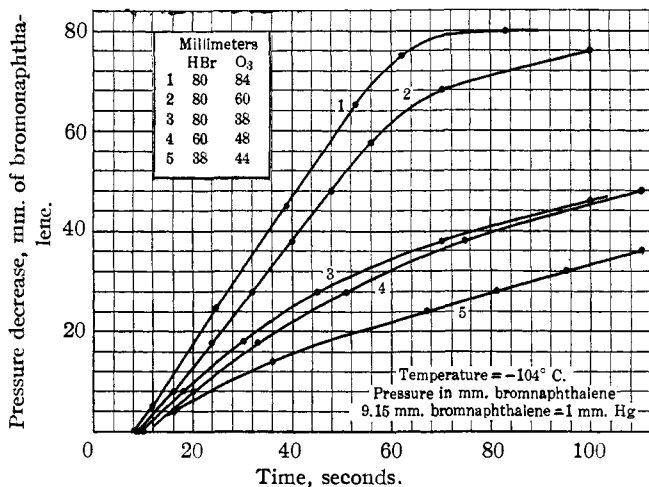


Fig. 2.—Rate of reaction between hydrogen bromide and ozone at different pressures in an uncoated vessel.

Relation (2) is valid in a vessel coated with the reaction products in which the rate of reaction is more than three times as fast as in the uncoated vessel.

From the average of experiments at -77° , k is found to be 0.125, whereas at -104° the average k is 0.026, both in an uncoated vessel. The temperature coefficient is therefore 1.79, which corresponds to a heat of activation of 3800 cal. in this temperature range.

The Effect of Surface and the Influence of Inert Gases on the Non-explosive Reaction.—In a vessel filled with small tubing the reaction was so rapid as to be complete in a few seconds at -104° . In vessels of different sizes with bare or coated walls, the surface, and therefore the activity, was not exactly reproducible. Therefore, no simple relationship could be found between the size of the vessel and the reaction rate. These experiments served, however, to provide additional evidence for the important role played by the surface in starting the reaction.

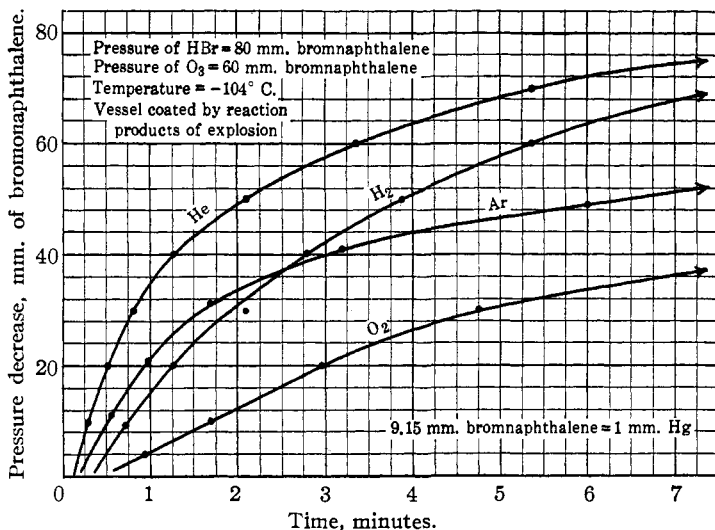


Fig. 3.—Influence of 300 millimeters of inert gas on rate of reaction between hydrogen bromide and ozone.

The rate of reaction decreases markedly with increasing amounts of inert gases. Table II gives the initial rate of pressure decrease for different pressures of four inert gases. The inhibiting influence increases in the order He, A, H₂,¹² O₂. To obtain a more complete picture of the inert gas effects, the curves in Fig. 3 are plotted. It is evident that the curve for argon intersects the curve for hydrogen and that for the latter gas the reaction is completed much earlier. It must be assumed that the inert gases influence only that part of the reaction taking place in the gas phase. It appears that the retarding influence of the inert gases is due to a combined effect of heat capacity and diffusibility. While the monatomic gases can remove less energy from the chain carriers than hydrogen and oxygen, the smaller rate of diffusion in argon begins to impede the reaction, especially at higher pressures, for the reacting gases close to the walls are

¹² Extended experiments with hydrogen indicate that it neither takes part in the reaction nor is acted upon by the reaction products, but that it behaves simply as an inert gas. See reference 6.

quickly used up and fresh gases find it more difficult to diffuse through argon than through hydrogen.

TABLE II
INFLUENCE OF INERT GASES ON THE REACTION BETWEEN HYDROGEN BROMIDE AND OZONE

Temperature, -104° . Vessel coated with reaction products from explosion. Pressure of HBr, 80 mm. of bromonaphthalene. Pressure of O_3 , 60 mm. of bromonaphthalene.

Inert gas	$-\frac{\Delta p_{mm.}}{\Delta t_{sec.}}$ = the initial rate for the following inert gas pressures			
	0	in mm. of bromonaphthalene		
		100	200	300
He	3.2	..	1.16	0.75
A	3.2	1.75	1.00	.58
H ₂	3.2	1.47	0.68	.30
O ₂	3.2	1.52	.50	.12

This marked influence of inert gases is in striking contrast to their slight effect on the ozone-bromine reaction, provided the explosion limit is not approached.⁴

The Explosion Limit.—The explosion limit studied here is what is usually known as the lower explosion limit. If an upper limit exists it cannot be measured conveniently. The transition from non-explosive to explosive reaction is a gradual one. As the pressure is raised, the reaction rate increases, until at the limit the reaction goes over into a general slow inflammation. In contrast with this a sharp detonation occurs if the pressure is raised still more—that is, about 1 mm. It is characterized by a loud click and instantaneous propagation of the explosion through the fine capillaries in the line.

The explosion limit depends on the pressures of both hydrogen bromide and ozone, but the influence of different factors on the explosion limit of equimolecular mixtures only were studied. The results obtained are similar to those found in the ozone-bromine reaction and are listed briefly.

1. The limit depends on the activity of the walls.

TABLE III

Conditions	Temp., $^{\circ}C.$	Explosion limit, mm. of bromonaphthalene total pressure equimolecular mixture
Inactive vessel	-104	400
After several explosions	-104	340
Vessel coated with reaction products from previous explosion	-104	220
Active vessel (uncoated)	-104	340
Active vessel (uncoated)	-77	340
Active vessel (uncoated)	0	160

2. No explosions could be obtained in a vessel filled with small glass tubing.

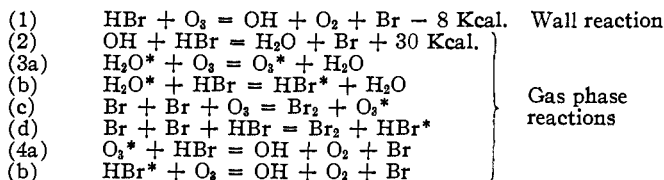
3. A hyperbolic relation was found between the explosion limit and the diameter of cylindrical vessels. Conclusions similar to those in the ozone-

bromine reaction may be drawn: namely, that it is necessary to build up a definite critical concentration of reaction carriers before an explosion results. The results show that the concentration of reaction carriers necessary to bring about an explosion is built up considerably faster in the ozone-hydrogen bromide reaction than in the ozone-bromine reaction.

Effect of Inert Gases on Explosion Limit.—Inert gases increase the explosion limit in the order A, O₂, He, H₂, which is the same order as in the ozone-bromine reaction.

Discussion

The experiments indicate clearly that the initial step in the reaction occurs at the walls between ozone and hydrogen bromide. Some active product, which we believe to be the OH radical, is ejected into the gas phase, where a series of reaction chains develops. The following mechanism is proposed to account for the experimental facts.



where the * indicates an energy-rich molecule.

From the temperature coefficient of the non-explosive reaction a heat of activation of 4000 cal. is found. This probably applies to the wall reaction 1. The calculation of the heat of reaction 1 gives -8000 cal. It is quite reasonable to assume that this value is reduced for the wall reaction to the 4000 cal. found by experiment. Activated O₃* or HBr* formed in 3a and b, c and d, may easily react in the gas phase as in 4a and b. The removal of bromine atoms by the reaction



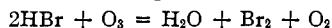
is improbable, since this reaction takes place with difficulty. A schematic diagram similar to that given in the ozone-bromine reaction¹³ shows clearly how branching as well as straight chains may occur.

There are certain striking differences and similarities between the ozone-bromine and the ozone-hydrogen bromide reactions. The slight influence of inert gases in the non-explosive region on the former reaction and their large influence in the latter reaction, together with the fact that explosions are possible in the hydrogen bromide reaction in vessels of smaller diameter than with the ozone-bromine reaction, indicates that in the ozone-bromine reaction the number of reactions in a chain are relatively fewer and take place with difficulty (see also Ref. 4), whereas in the ozone-hydrogen bromide reaction the chains are long and occur with ease.

¹³ Ref. 4, p. 2930.

The order of inert gases in increasing the explosion limit is exactly the same in the two reactions. On the other hand, the order of inert gases in their effect on the non-explosive reactions is different. For the explosion limits, the effectiveness of inert gases lies in their ability to transport to the wall the heat liberated in the fast reaction—that is, their heat conductivities. The higher the heat conductivity, the higher the explosion limit. However, in the non-explosive reaction the effectiveness of inert gases in decreasing the rate probably lies principally in their ability to deactivate carriers and terminate chains. There is no way of predicting the order, since it depends not only on the heat capacity of the inert gas but also on some specificity involving the transfer of energy from the particular carrier in each reaction to the inert gas molecule.

It is interesting that the non-explosive reaction follows the equation



without further decomposition of ozone when it is present in excess. This is probably due to the fact that the energy taken up by ozone in 3a is insufficient to allow it to react with an ordinary ozone molecule (energy of activation *ca.* 29,000 cal.) but is sufficient for reaction 4a, which has a smaller energy of activation. The occurrence of a detonation at higher pressures and temperatures is probably due to the propagation of ozone chains.

The Effect of Hydrogen Chloride on the Ozone–Bromine Reaction and its Reaction with Ozone.—Since hydrogen chloride reacts readily with oxygen atoms,⁷ this gas was used in an attempt to detect the presence of oxygen atoms in the decomposition of ozone sensitized by bromine. It was found that a very small amount, 0.5 mm., was sufficient to slow down the ozone decomposition very markedly and effectively to prevent an explosion at relatively high ozone pressures. The action of hydrogen chloride is obviously the same as that of water vapor—namely, it covers the walls and prevents the starting of reaction chains therefrom.

Larger amounts of hydrogen chloride undergo a very slow reaction with ozone at 0 and 25° which takes hours to complete itself in contrast to the few seconds necessary for the ozone–hydrogen bromide reaction. Chlorine is one of the products and probably also oxides of chlorine, which very likely react with the water to form acids. The reaction appears to be a wall reaction, but no chains are initiated in the gas phase due to unfavorable energy conditions. An extended study of this reaction was not thought profitable for our immediate purpose.

Summary

The kinetics of the non-explosive and explosive reactions between ozone and hydrogen bromide have been studied from 0 to -104° . *Inflammation and detonation have been observed down to -104° .* The de-

pendence of the rate of reaction and the explosion limit on size of vessel, activity of the wall, inert gases and temperature, have been investigated. The reaction affords another example in which *chains are initiated at the wall and are propagated thence into the gas phase*. In the proposed mechanism the OH radical is believed to be the carrier in these reaction chains.

The effect of hydrogen chloride on the bromine sensitized ozone decomposition and its reaction with ozone have been studied. Very small amounts of hydrogen chloride prevent explosions in the former, while its reaction with ozone seems to be confined to a wall reaction.

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

THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE BY THE IODINE-IODIDE COUPLE AT 25°

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Introduction

The reaction system comprising hydrogen peroxide, iodine and iodide ion in neutral and dilute acid solutions has provided the material for a series of investigations extending over some three-fourths of a century, and culminating in the intensive work of Abel.¹ With the last of his papers on the subject, it seemed that these investigations could be regarded as complete, and that this reaction system, while apparently similar to the bromine-bromide system investigated by Bray and Livingston,² was in reality much more complex. In establishing a mechanism for this complex system, Abel deduced for the specific rate of the hydrolysis of iodine (into hypiodous and hydriodic acids) a value which has proved irreconcilable with related experimental results.³ The iodine-iodide reaction system is therefore being re-investigated over a wide range of experimental conditions: that part of the investigation dealing with the pure catalytic decomposition of hydrogen peroxide by the iodine-iodide couple is presented here.

Rate Measurements at the Steady State.—Within a short time after hydrogen peroxide is added to a neutral solution of iodide ion, a *steady state* is reached, in which the main reaction is the catalytic decomposition of hydrogen peroxide



¹ (a) Abel, *Z. physik. Chem.*, **136**, 16 (1928); (b) *ibid.*, **96**, 1 (1920). For a comprehensive historical summary of earlier work by Abel and others, the reader is referred to Ref. 1b.

² Bray and Livingston, *THIS JOURNAL*, **45**, 1251 (1923).

³ (a) Liebhafsky, *Z. physik. Chem.*, **155**, 289 (1931); (b) *THIS JOURNAL*, **53**, 2074 (1931).