which was to be extracted out with one of the solvents mentioned above. Since it was necessary to extract with very large amounts of solvent, many times it was imperative that the acid be very insoluble in the solvent in order that the solution remain acid until the end of the extraction process.

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Summary

Distribution ratios of six fatty acids and four inorganic acids were measured between water and several solvents which are not miscible with water. A short discussion of the results is given.

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THE KINETICS OF GAS EXPLOSIONS. III. THE INFLUENCE OF HYDROGEN ON THE THERMAL DECOMPOSITION OF OZONE SENSITIZED BY BROMINE VAPOR, AND THE DETERMINATION OF THE EXPLOSION TEMPERATURE[1]

BY W. FEITKNECHT[2] AND BERNARD LEWIS[3]

In a previous paper[4] it was shown that inert gases exert a small influence on the rate of decomposition of ozone in the presence of bromine as long as the ozone pressure is low. At higher pressures the rate is slowed down and the explosion pressure limit of ozone is increased considerably. The efficiency of inert gases in increasing the explosion limit decreases with increasing molecular weight.

The influence of hydrogen was not included in the previous investigations. It seemed of special interest, as hydrogen increases considerably the photochemical rate of decomposition of ozone with the simultaneous formation of water.[5] Belton, Griffith and McKeown[6] found a similar influence of hydrogen on the thermal decomposition of ozone, whereas Schumacher[7] states that hydrogen has only a slight effect on the thermal

[4] Part I, THIS JOURNAL, **53**, 2910 (1931). Part II, *ibid.*, **54**, 1784 (1932).

[5] Weigert and Böhm, *Z. physik. Chem.*, **90**, 189 (1915); Griffith and Shutt, *J. Chem. Soc.*, **123**, 2752 (1923).

[6] Belton, Griffith and McKeown, *ibid.*, **126**, 3153 (1926).

[7] Schumacher, THIS JOURNAL, **52**, 2388 (1930).

decomposition. It has been found by one of us[8] that ozone is indeed extremely stable in the presence of hydrogen at room temperatures. However, at higher temperatures (80 to 90°), the influence of hydrogen is so great that under certain conditions the ozone may be made to explode violently. The thermal decomposition of ozone sensitized by bromine vapor, at temperatures (<15°) at which the solid oxide of bromine is formed, is unaffected by hydrogen.[9]

The present experiments with ozone–bromine mixtures and hydrogen were carried out in the same way as those with similar mixtures and inert gases described previously.[4] The experimental temperature employed was 25°. The rate of the non-explosive reaction was of the same order as that for corresponding mixtures with other inert gases, and the reaction went to about 70% completion in ten minutes. This strongly indicated that no water was formed, for water in very small amounts (<0.1 mm.) poisons the walls and decreases the rate of decomposition of ozone materially.[4]

A more direct method was employed to detect water formation, if any. A mixture, the original composition of which was 50 mm. ozone, 20 mm. hydrogen and 0.5 mm. bromine, was cooled down to −65° after 87% of the ozone had decomposed. The vessel was evacuated removing all gases except water (if formed) and then warmed up again to 25°. No pressure increase could be detected, although the manometer employed read easily to less than 0.1 mm., indicating that less than 0.5% of the hydrogen could have been transformed to water.

These results do not conflict with the chain mechanism suggested by the authors, for the explanation of the decomposition of ozone sensitized by bromine in which the oxygen atom is an important link, for according to the experiments of Harteck and Kopsch,[10] oxygen atoms do not react readily with hydrogen molecules. The results indicate that the second carrier in the proposed chain, namely, an energy-rich oxygen molecule, also does not react with hydrogen to form water at the temperature of these experiments.

Whenever the ozone concentration was above the explosion limit, the hydrogen was burned to water in the explosion. If the vessel was then evacuated in the usual way, it proved to be very inactive in the next experiment. It was shown previously[4] that the direct introduction of a small amount of water vapor affected the vessel in a similar way. The vessel could be reactivated only after prolonged evacuation accompanied by heating and subjecting the vessel to sparking with a high-tension coil. This was in striking contrast to the unaltered activity

[8] Lewis, forthcoming contribution.

[9] Lewis and Schumacher, *Z. physik. Chem.*, **6B**, 423 (1930).

[10] Harteck and Kopsch, *ibid.*, **12B**, 327 (1931).

of the vessel after a non-explosive reaction, a further proof that in the latter case no water is formed.

The explosion limit of ozone (sensitized by bromine) was found to be greatly increased by hydrogen. It was nearly twice as high as for a similar mixture in which the hydrogen is replaced by helium. Hydrogen, therefore, fits well into the order in which inert gases increase the explosion limit—namely, argon, oxygen, nitrogen, helium and hydrogen.

The final pressure after an explosion was always considerably lower than the pressure calculated on the assumption that all the hydrogen had oxidized to water and all the ozone had decomposed to oxygen. On alternately raising and lowering the temperature of the products, the deviation in pressure from Gay-Lussac's law was such as to indicate that some liquid had condensed on the wall of the vessel at 25°. The experiments could be reproduced very well. The difference between the calculated and observed pressures increased with increasing amounts of bromine and hydrogen but were affected little by changes in the ozone pressure, as can be seen from Table I.

TABLE I

PRESSURE CHANGES IN EXPLOSIONS OF OZONE–BROMINE–HYDROGEN MIXTURES AT 25°

a, expected total pressure after explosion on basis of 100% of water formation; b, total pressure observed after explosion.

Expt.	Vessel	O_3, mm.	H_2, mm.	Br_2, mm.	a	b	a − b
72–11	Glass	40	10	1	66	65.4	0.6
75–3	Quartz	40	10	1	66	65.2	0.8
72–7	Glass	40	10	5	70	67.0	3.0
72–8	Glass	40	10	5	70	67.2	2.8
74–3	Glass	40	10	10	75	70.3	4.7
74–6	Glass	40	10	10	75	70.3	4.7
75–1	Quartz	40	10	10	75	70.1	4.5
75–7	Quartz	40	10	10	75	70.1	4.5
75–9	Quartz	60	5	10	102.5	101.3	1.2
75–7a	Quartz	60	10	10	105	99.8	5.2
75–10	Quartz	60	15	10	107.5	98.2	9.3
75–8	Quartz	60	10	20	115	108.5	6.5
75–11	Quartz	60	15	20	117.5	106.1	11.4

In the first column, the first numbers represent the experimental series, and the numbers after the dash the experiment in the series.

These results can only be due to the formation of hydrogen bromide in the explosion,[11] forming afterward with water a solution with low vapor pressure. To prove this the products of several successive explosions were condensed in a side tube and analyzed. The solution proved to be fairly concentrated in hydrogen bromide.

[11] If any hydrogen bromide were formed in the non-explosive reaction it would have reacted with ozone immediately to give water, oxygen and bromine (see Lewis and Feitknecht, THIS JOURNAL, 53, 3565 (1931); ibid., 54, 1784 (1932)).

The excellent reproducibility and the way in which the amount of hydrogen bromide formed depends upon the initial pressures of bromine, hydrogen and ozone, suggest that the following equilibrium is established in the explosion.

$$2H_2O + 2Br_2 \rightleftharpoons 4HBr + O_2 \tag{1}$$
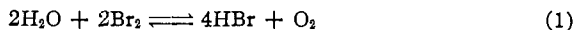
If the amounts of hydrogen bromide and water formed were known, the equilibrium constants calculated from these data could be compared with the equilibrium constants of this reaction at different temperatures derived from independent sources, and an estimate could be obtained of the temperature reached in these low-pressure explosions.

Determination of the Explosion Temperature from the Equilibrium Attained.—Owing to the condensation of hydrogen bromide and water in the lead tube, the use of a simple manometric method of determining the equilibrium was precluded.

TABLE II

ESTIMATED COMPOSITIONS OF MIXTURES IN MM. AFTER EXPLOSION AND EXPERIMENTAL EQUILIBRIUM CONSTANTS OF REACTION (1)

Expt.	H_2O	Br_2	O_2	HBr	$P_{calcd.}$	$P_{obs.}$	$\dfrac{(H_2O + HBr)}{-(P_{calcd.} - P_{obs.})}$	$K_{calcd.}$	$K_{cor.}$
74–3	9	9	55.5	2	75.5	70.3	5.8	5.61×10^3	1×10^3
75–7a	9	9	85.5	2	105.5	99.8	5.3	3.64×10^3	6.6×10^2
75–8	8.5	18.5	85.75	3	115.75	108.5	4.25	2.71×10^3	4.9×10^2
75–10	13.5	8.5	83.25	3	108.25	98.2	6.45	1.49×10^3	2.7×10^2
75–11	13.0	18.0	83.5	4	118.5	106.1	4.6	1.95×10^3	3.5×10^2

The total amount of hydrogen bromide formed in the explosion (Table II, Column 5) could be estimated by a method of trial and error. First a value is assumed and, together with the original pressures of hydrogen, bromine and oxygen (Table I), the total amounts of water, bromine and oxygen are calculated (Columns 2, 3 and 4). Thus the total pressure, $P_{calcd.}$ in Column 6, is known. Column 7 contains the observed pressure. $P_{calcd.} - P_{obs.}$ equals the amount of water and hydrogen bromide condensed out; and since Columns 2 + 5 give the total amount of these products formed, Column 8 represents the pressure of water and hydrogen bromide in the gas phase. Several such values in Column 8 are calculated for different assumed values of hydrogen bromide in Column 5. These vapor pressures are compared with the data of Wrewsky, Sawaritzky and Scharloff[12] on the vapor pressure and composition of the vapor above solutions of hydrogen bromide in water. It turns out that in experiments with 10 millimeters and more of hydrogen and bromine the mixture must correspond approximately to the one having the smallest vapor pressure, or one in which the composition of the liquid and gas phases is identical—in other words, to a mixture with approximately 20 mole per cent. of hydrogen bromide. The final values of hydrogen bromide thus

[12] Wrewsky, Sawaritzky and Scharloff, Z. physik. Chem., **112**, 97 (1924).

estimated are given in Column 5, Table II, and the corresponding vapor pressure of hydrogen bromide plus water at 25° in Column 8. For experiments 75-8 and 75-11 the values in Column 8 are about 1 mm. lower than those which would correspond to the minimum vapor pressure of the hydrogen bromide–water solution. This is partly due to the errors which may accumulate by the addition and subtraction of several somewhat uncertain values and to the solution of a small amount of bromine in these particular experiments with higher bromine concentrations. In general the error in the hydrogen bromide values given is about ±0.5 mm. This is sufficiently accurate for our purpose as it introduces an error of only about ±4.5% in the final explosion temperature.

By substituting the pressures of water, bromine, hydrogen bromide and oxygen in atmospheres in the formula

$$K = \frac{[H_2O]^2\,[Br_2]^2}{[HBr]^4\,[O_2]} \tag{2}$$

the experimental equilibrium constant K can be determined for the different experiments. There is not much variation of the constants in Column 9, Table II. The differences observed are attributable to differences in the temperatures at which the equilibria are frozen out in the different experiments. However, the error in the estimation of hydrogen bromide would introduce about the same differences, so that it is not possible to draw definite conclusions on this point. These K's are calculated for the gas pressure at the temperature 298° K. It will be seen later that the temperature at which the equilibrium is established is approximately 5.5 times higher. The K's should therefore be corrected for the pressures existing at this temperature, and from formula (2) it follows that they should be divided by 5.5. The corrected constants are given in the last column of Table II.

There are two methods by which the equilibrium constant K of formula (2) can be approximately calculated theoretically.

1. By using the Nernst formula:[13]

$$\log K = -\frac{Q}{4.57\,T} + \Sigma v\,1.75\log T + \Sigma vC \tag{3}$$

On introducing the values given by Nernst for the conventional constants C and Σv and the value of Q as the difference between the heats of formation of $2H_2O$ and $4HBr$ (that is, $-115,600 + 48,400 = -67,200$), equation 3 becomes

$$\log K = +\frac{14,700}{T} - 1.75\log T - 0.6 \tag{4}$$

The values for K thus calculated are given in the fifth column of Table III as K_1, for temperatures between 1500 and 2000° A.

[13] Nernst, "Die theoret. u. experimentellen Grundlagen des neuen Wärmesatzes," 1918, p. 112.

TABLE III

CALCULATED EQUILIBRIUM CONSTANTS OF REACTION (1) AT DIFFERENT TEMPERATURES

T.°A.	K_{HBr}	K_{H_2O}	$K_2 = \dfrac{(K_{HBr})^2}{K_{H_2O}}$	K_1
1500	3.66×10^{-5}	5.02×10^{-12}	2.67×10^2	4.36×10^3
1600	6.10×10^{-5}	6.34×10^{-11}	5.87×10^1	9.60×10^2
1700	9.9×10^{-5}	5.7×10^{-10}	1.72×10^1	2.45×10^2
1800	1.51×10^{-4}	4.26×10^{-9}	0.53×10^1	7.41×10^1
1900	2.19×10^{-4}	2.4×10^{-8}	$.20 \times 10^1$	2.51×10^1
2000	3.11×10^{-4}	1.17×10^{-7}	$.83$	0.93×10^1

2. The second method is derived from the fact that

$$K = \frac{[H_2O]^2 [Br_2]^2}{[HBr]^4 [O_2]} = \frac{K^2_{HBr}}{K_{H_2O}} \qquad (5)$$

K can therefore be calculated from the constants of the hydrogen bromide and water equilibria, namely

$$2 \text{ HBr} \rightleftharpoons H_2 + Br_2 \qquad (6)$$
$$2 \text{ H}_2O \rightleftharpoons 2 H_2 + O_2 \qquad (7)$$

Vogel von Falckenstein[14] has shown experimentally that the hydrogen bromide equilibrium follows the formula of Nernst[15] fairly well, namely

$$\log K_{HBr} = -\frac{5223}{T} + 0.553 \log T - 2.72 \qquad (8)$$

The K for the water equilibrium was calculated from the formula given by Lewis and Friauf[16]

$$\log K_a = +\frac{57,295}{4.57T} - 0.848 \log T - 1.474 \times 10^{-4} T + 7.78 \times 10^{-8} T^2$$
$$- 8.72 \times 10^{-12} T^3 + 0.0616 \qquad (9)$$

It should be mentioned that K_a calculated from this formula is $K_a = [H_2O]/[H_2] [O_2]^{1/2}$, while the K_{H_2O} to be used in (5) is

$$K_{H_2O} = \frac{[H_2]^2[O_2]}{[H_2O]^2}$$

Therefore

$$K_{H_2O} = 1/K_a^2 \qquad (10)$$

Columns 2 and 3, Table III, contain these values of K_{HBr} and K_{H_2O} and Column 4 contains K_2, the desired constant by the second method—namely, $K_2 = K^2_{HBr}/K_{H_2O}$.

It is seen that K_1 is roughly one order of magnitude larger than K_2, corresponding to an average temperature difference of 200°. This is roughly of the same order as the uncertainty in temperature arising from the uncertainty in the value of the hydrogen bromide formed.

Comparing K_1 and K_2 with the $K_{corr.}$ of Table II, one observes that the equilibrium constants found correspond to a temperature of about 1600 ± 100°A. This temperature is probably not the maximum explosion

[14] Von Falckenstein, Z. physik. Chem., **68**, 270 (1909); **72**, 113 (1910).

[15] Nernst, Z. Elektrochem., **18**, 687 (1909).

[16] Lewis and Friauf, THIS JOURNAL, **52**, 3905 (1930).

temperature which is possible in the mixtures considered because the experiments were not carried out adiabatically, but is indicative of the temperature at which the equilibria found were frozen out.

Summary

The influence of hydrogen on the thermal decomposition of ozone sensitized by bromine vapor has been investigated. In the non-explosive reaction it is found that hydrogen behaves only as an inert gas retarding the reaction to about the same degree as other inert gases do. No water is formed, indicating that hydrogen does not react readily at room temperature with the oxygen atoms and energy-rich oxygen molecules assumed to play a role in the decomposition of ozone. The explosion pressure limit of ozone is greatly increased by hydrogen, which fits well into the order in which inert gases increase the explosion limit—namely, argon, oxygen, nitrogen, helium and hydrogen. During the explosion the hydrogen is burned to water and the following equilibrium is established

$$2H_2O + 2Br_2 \rightleftharpoons 4HBr + O_2$$

The concentrations of the products are determined and the equilibrium constants calculated. These are compared with the equilibrium constants at different temperatures derived from two independent sources. The temperature at which the equilibria are established is found to be 1600 ± 100° Absolute.

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STERIC HINDRANCE AND COLLISION DIAMETERS[1]

BY HENRY EYRING

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Introduction

A large part of chemistry is interpretable in terms of potential energy diagrams. Stable compounds are configurations of low potential energy which are separated from configurations of still lower energy by energy ridges of approximately 20 kg. cal. or more per mole. If the ridge is much lower than this the rate at which molecules accumulate sufficient energy to pass over the barrier, even at ordinary temperatures, make it impossible to isolate any but the molecular species of lowest energy. Energy barriers are sometimes lowered by two molecules colliding, making a complex from which a new species emerges—a bimolecular reaction. A rearrangement or splitting inside a single molecule is a unimolecular

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[1] Presented except for minor changes September 2, 1931, as part of the symposium on the Kinetics of Chemical Reactions at the Buffalo meeting of the American Chemical Society, by Henry Eyring and J. C. Slater.