CHEMISTRY OF DISSOCIATED WATER VAPOR AND RELATED SYSTEMS

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CONTENTS

I. INTRODUCTION

Although investigations of the chemistry of dissociated water vapor and related systems were initiated 40 years ago, the major advances have been made within the last 15 years. In consequence an ever-increasing number of publications on this subject have appeared during the last decade; of these a large number have been published in Russian journals. The various investigators have had differing objectives and have used a variety of experimental techniques; their studies have exhibited a plethora of disagreement, contradictory results, and general scientific frustration. In view of this situation and the rapidly growing literature on the subject, a comprehensive unified review appears to be warranted.

A. GENERAL NATURE OF THE PHENOMENON

When dissociated water vapor or dissociated hydrogen peroxide vapor is allowed to condense on a surface cooled below about 120°K, an unidentified combination of hydrogen and oxygen which is unstable above about 160°K is obtained. A similar solid is produced when the products of the reaction of atomic hydrogen with oxygen or with ozone are condensed at these low temperatures. When warmed near 160°K, such solid products invariably transform from glassy to crystalline deposits, simultaneously evolving oxygen, and at room temperature water and hydrogen peroxide remain.

B. SCOPE AND LIMITATIONS OF THE REVIEW

Extensive reviews on reactions of oxygen atoms (109) and on mechanisms and rate constants of elementary gas phase reactions involving hydroxyl and oxygen atoms (14) have appeared recently. Brief references to significant studies on OH and O_2H radicals and superoxides of hydrogen can be found in articles and books surveying the general field of trapped free radicals (20, 59, 153) and cryochemistry (143, 144). Recently Volman (225) has reviewed photochemical gas phase reactions in hydrogen–oxygen systems. The field of combustion reactions involving hydrogen and oxygen has been dealt with by Lewis and von Elbe (128) and Minkoff and Tipper (154). Similarly the radiation chemistry of water vapor and of related hydrogen–oxygen systems has recently been reviewed (129, 215). The present review, therefore, is concerned chiefly with general investigations emphasizing yields of final products and the influence of various experimental parameters thereon (section II), with direct investigations of the gas phase reactions (section III), with the nature of the condensed solid products (section IV), and with postulated reaction mechanisms (section V), all in low-pressure discharged hydrogen–oxygen systems. Investigations of high-pressure discharged systems are also included (section VI).

This review covers the literature through the May 1965, *Chemical Abstracts* and *Current Chemical Papers.* The limitations of this review are that it concerns chiefly material published since 1950, and that it does not include work done using dissociation techniques other than the electrical discharge. An excellent summary and interpretation of experimental results prior to 1950 is given in a paper by Rodebush, Keizer, McKee, and Quagliano (192). Oldenberg (174) and Schumb, Satterfield, and Wentworth (198) have also summarized the principal earlier experimental results.

C. DEFINITION OF TERMS

The term "peroxy-radical condensate" has been suggested and used by Russian workers (209) to denote the products formed by low-temperature (90°K) condensation of discharged water or hydrogen peroxide vapors, and also by the low-temperature reaction of atomic hydrogen with oxygen or with ozone, instead of the more widely used but less definite term "vitreous substance" (95). However, throughout this review, the more general term "condensed product" will be used.

The term "evolved oxygen" will be used to represent the total oxygen evolved on warming the condensed product.

The term "traversed volume" will be used to denote the reaction volume due to cylindrical glass tubing of uniform diameter interposed between the discharge exit and coolant level.

II. GENERAL INVESTIGATIONS AT LOW PRESSURES

A. DISSOCIATED WATER AND HYDROGEN PEROXIDE VAPORS

The reactions of the products of glow discharges in vapors of water and hydrogen peroxide have been studied extensively (198). The earlier work using flow systems established that in water vapor at pressures of 0.1 to 0.2 mm, with a rapid vapor throughput, and with the products condensed quickly in a liquid air cooled trap, hydrogen peroxide is obtained in fairly high concentration (30, 62, 66, 170–175, 190–192). If the trap is cooled with solid carbon dioxide instead of with liquid air, no hydrogen peroxide is obtained and in some cases very little water (152). When the liquid air trap is separated from the discharge tube to allow an increased time for reaction, the yield of hydrogen peroxide decreases, eventually becoming insignificant. If the liquid air trap is placed adjacent to the discharge exit, practically all of the oxygen entering in the form of water is recovered in the trap as water or hydrogen peroxide.

Subsequently it was observed that when discharged water vapor was condensed at about 90°K, a glassy solid deposited which gave off oxygen at temperatures above 160°K, to yield hydrogen peroxide and water (103). According to Jones and Winkler (103), the oxygen evolution proceeded to completion at about 195°K, and the amount of oxygen evolved with warming was proportional to the total amount of product and independent of warming procedure. Water was found at all temperatures between 77 and 160°K, whereas hydrogen peroxide was formed only from products formed below 120°K. The yields of water, hydrogen peroxide, and evolved oxygen increased with decreasing trap temperature. When the volume of reaction chambers inserted between the discharge tube and the trap was increased, the yield of hydrogen peroxide decreased continuously, while the yield of water at first decreased and then increased to a limiting value (103). Packing a given reaction chamber with glass wool drastically reduced the yield of hydrogen peroxide, but had little effect on the yield of water, and packing the trap itself had only a slight effect on product yields (103). As the rate of flow of water was increased, the yield of peroxide tended toward a limiting value which depended upon the power input (83). In a very fast flow system, the peroxide yield was, however, not affected by the distance between discharge and trap (83).

Introduction of small amounts of oxygen in the stream of water vapor, either before or immediately after the discharge, did not affect the amount of peroxide or water formed although an excess of hydrogen atoms was present in the dissociated vapor (83). Coating the walls of the liquid air trap with fused boric acid verified that the yields of hydrogen peroxide and water were not affected by the nature of the cold surface. On the other hand, it was found that the surface in the discharge tube itself played an important role. It was concluded that ionic species are so short-lived that any mechanism invoked to explain the formation of water and hydrogen peroxide at liquid air temperatures would involve mainly OH radicals and H atoms (199).

The products of an electrical discharge through hydrogen peroxide vapor were hydrogen peroxide, water, oxygen, and hydrogen in amounts which depended upon the arrangement and temperature of the trap, reaction time, and surface-to-volume ratio of the reaction vessel (2, 21). Water, hydrogen, and oxygen resulted from the gas phase reactions of the discharged hydrogen peroxide, with hydrogen peroxide being produced only in a trap cooled below 150°K. Products trapped below 120°K evolved oxygen on warming above 160°K. The yields of hydrogen peroxide and evolved oxygen increased as the trap temperature was changed from 90 to 77°K. When the traversed volume was increased, the yields decreased (2). Water was the only product when molecular hydrogen peroxide was caused to react with hydrogen atoms, dissociated hydrogen peroxide vapor, or dissociated water vapor in the presence or absence of H_2 (21).

A relationship (88) has been observed between the yields of final products (H_2O, H_2O_2, and evolved O_2) and a generalized kinetic parameter up/v, where u is the electrical power consumed, v is the flow rate of H_2O_2 or H_2O vapor, and p is the pressure at the entrance to the discharge tube. The shapes of the kinetic curves indicated that water was an intermediate product in the decomposition of H_2O_2 in the discharge tube and that the compositions of discharged H_2O and H_2O_2 vapors differed in oxygen content only. In these studies it was found that the condensed product from the discharged H_2O_2 vapor was twice as rich in H_2O_2 and also in the compound (assumed to be H_2O_4) which evolved oxygen on warming, as was the product obtained from H_2O. The molar ratio of evolved oxygen to H_2O_2 remaining in the trap was approximately 0.3 as opposed to 0.2 for water vapor (103).

When discharged water vapor was trapped at 4.2°K, less evolved oxygen was obtained than at higher temperatures (193). Conversions of 17 to 18% of water to hydrogen peroxide were obtained and only 2 to 4% conversion to oxygen, all of which was of the "evolved" type, when the inlet system to the trap was clean and coated with phosphoric acid. On the other hand, with the inlet system contaminated (presumably with Fe_2O_3), conversion to peroxide was reduced to 0.4% of the water introduced, 31.4% being converted to molecular hydrogen and oxygen. Over half of this oxygen was later evolved on warming. The low yield of peroxide in these experiments and the increase in yield obtained by various successive treatments (193) of the inlet tube suggested that hydroxyl radicals are rapidly consumed, presumably by a heterogeneous reaction, before impinging on the cold surface.

The formation of hydrogen or deuterium peroxide as a primary reaction product when discharged water, hydrogen peroxide, or deuterium oxide vapor is trapped at 77°K was subsequently confirmed (135). When discharged water vapor was allowed to impinge on frozen H_2O_2 at 195°K, no reaction occurred, while dissociated water vapor brought in contact with liquid ozone at 77°K gave the same amount of evolved oxygen on warming as was obtained when the discharged water vapor was trapped in the absence of ozone (135).

Recently, kinetic curves have been obtained for the yield of hydrogen peroxide and the changes in its concentration, and also for the yield of water, as a function of the residence time of water vapor in the discharge zone (165). The yield of hydrogen peroxide showed a distinct maximum, while the yield of water was given by a complex relationship consisting of an exponentially falling curve and a curve having a maximum. When the pressure of water vapor was increased from 0.3 to 1.5 mm, the yield of peroxide dropped but the yield of water was unaffected (191, 165).

Experiments carried out recently (102) at very low flow rates (0.92 mmole of water/hr), low pressures (120 μ), and low current density (200 ma) showed that the yield of hydrogen peroxide was negligible when discharged water vapor was trapped at about 5 mm from the discharge exit, *i.e.*, at a small traversed volume of 1.5 ml, and that the yield increased with increasing traversed volume to a maximum value at a traversed volume of about 300 ml, *i.e.*, approximately 100 cm away from the discharge exit; thereafter, the yield decreased rapidly when the traversed volume was increased and became negligible above about 500 ml. The yield of molecular oxygen, *i.e.*, of oxygen which passed through the trap, was negligible at low traversed volumes and remained so until the traversed volume reached the value of 300 ml corresponding to the hydrogen peroxide maximum; the oxygen yield then increased rapidly and leveled off at the higher traversed volumes. As the traversed volume was increased, the yield of water decreased from a value not much less than the total input at the lowest traversed volume (1.5 ml) used, and leveled off at the higher traversed volumes (200–300 ml) at a value equal to about one-third of the total input. The yield of hydrogen was significant at the lowest traversed volume; as the traversed volume was increased, the yield increased rapidly at first, then almost leveled off in the 200–300-ml region only to swing up again at the traversed volume of maximum hydrogen peroxide yield, and finally leveled off at the higher traversed volumes.

At very low traversed volumes ($\sim$1 ml), the yield of evolved oxygen was very large compared to the yield of peroxide, which was negligible, and increased almost linearly to a maximum value at about 10 ml. Thereafter the yield of evolved oxygen fell exponentially to a minimum value at a traversed volume of about 100 ml. Beyond this the yield of evolved oxygen increased and followed the peroxide yield throughout, with a maximum at about 300 ml (102).

Although the yield of peroxide near the discharge exit was negligible at a flow rate of 0.92 mmole of water/hr, it increased with flow rate rather rapidly and leveled off at higher flow rates (10–15 mmole/hr). This suggested that at very low flow rates peroxide precursors are not present in the gases flowing from the discharge but are formed in the traversed volume (102).

The recombination of the high-voltage discharge products of water vapor on surfaces coated with KCl, K_2CO_3, Al_2O_3, KOH, and silica gel has been studied (61, 62, 214, 220). The recombination reactions were accompanied by a temperature increase and a blue-green luminescence on the coated surface. The principal products at room temperature were hydrogen and oxygen. When the products were trapped at 90°K, H_2O_2, H_2O, H_2, and O_2 were obtained.

Discharges through water vapor have been used to achieve an efficient synthesis of concentrated hydrogen peroxide (32, 60, 157, 163, 219, 227). In one of these methods (219) the reaction gas was allowed to remain in the discharge tube for a relatively long time, and the discharge tube was cooled with liquid air. The concentration of H_2O_2 obtained was about 95%. In another method (60), the dissociated water vapor was passed through a magnetic flux of 14,400 gauss/cm^2 for a length of 35 mm to deflect the H atoms away from the OH radicals and thence through a conduit directly to evacuation. The OH radical stream was condensed in a liquid air trap, to yield a pure concentrated product. Recently, labeled heavy-O peroxide ($H_2{}^{18}O_2$) enriched in the heavy-O isotope has been synthesized from vapor of heavy oxygen water ($H_2{}^{18}O$) in a glow discharge (32, 227).

B. ATOMIC HYDROGEN–MOLECULAR OXYGEN SYSTEMS

1. *Atomic Hydrogen–Gaseous Oxygen*

The early experiments on the reaction of atomic hydrogen with molecular oxygen at pressures of 0.1–0.5 mm and wall temperatures of 30°K yielded essentially 100% H_2O_2, but the yield decreased at higher wall temperatures and became negligible at about 200°K (27, 68). When warmed to about 160°K, the condensed products vigorously evolved oxygen. The rate of formation of hydrogen peroxide was proportional to the oxygen concentration over a considerable range, for constant surface conditions (16, 17). The results were not affected by passing oxygen as well as hydrogen through the discharge (16). At a trap temperature of 77°K, all the inlet oxygen appeared as water and H_2O_2, in about equimolar proportions. At higher trap temperatures, water increased and hydrogen peroxide decreased until at 194°K no hydrogen peroxide was trapped (152). Increasing the distance between the point of mixing and the condensing trap reduced the hydrogen peroxide to a trace while the amount of water formed was only slightly affected. These results are similar to those obtained with a glow discharge through water vapor (*cf.* section IIA).

The character of the surface in the zone of reaction was found to have a marked effect on the amount and nature of the condensible products, as would be expected at low pressures (16). The amounts of condensible products in a liquid air trap placed downstream from the reaction zone decreased with increasing wall temperature in the reaction zone. At surface temperatures between 273 and 523°K, a KCl surface practically eliminated hydrogen peroxide, a "Pyrex" surface gave an intermediate amount which decreased with increasing wall temperature, and a surface treated with phosphoric acid gave the maximum yield of hydrogen peroxide, substantially unaffected by temperature and about ten times that obtained with KCl. Badin (16) suggested that these surface effects are associated in some way with the amount of water present on the surface, a chloride surface being "dry" and phosphoric acid being "wet." The decrease of condensible products with increasing wall temperature must be due to reforming of hydrogen and oxygen from OH or O_2H.

Experiments in which the flow rate of atomic hydrogen was varied while the flow of oxygen (2×10^{-6} mole sec^{-1}) was kept constant proved that all the oxygen could be completely recovered only when the atomic hydrogen flow was greater than 5×10^{-6} g-atom sec^{-1} (146). At higher H/O_2 inputs the yield of water increased slightly at the expense of the evolved oxygen, while the peroxide yield remained constant. When the H/O_2 ratio was too low to ensure complete recovery of oxygen, the yields of peroxide and water decreased, the latter more sharply than the former; the evolved oxygen yield remained about the same. The strong dependence of water yield upon the atomic hydrogen supply is in contrast to the behavior of the other products. Experiments in which oxygen recovery was incomplete showed appreciably more hydrogen in the products than was available as atomic hydrogen.

When the products of the H–O_2 reaction were trapped at 4.2°K, solids of empirical composition close to H_3O_4 were obtained (193). On warming, these solids behaved similarly to those formed at higher temperatures, evolving oxygen and leaving concentrated H_2O_2 at room temperature. The evolved oxygen was accounted for by postulating loosely bound oxygen in the solid in an amount corresponding to $3H_2O_2 \cdot O_2$. The mole per cent of water in the water–peroxide mixtures obtained was between 3.5 and 30 in a series of nine runs, averaging 20%, but in all cases too low to account for oxygen evolution *via* the reaction

$$[H_2O \rightarrow O] \longrightarrow H_2O + {}^1/_2O_2$$

as proposed earlier (68, 69), and in most experiments too low to be derived from the superoxides H_2O_3 and H_2O_4.

Avramenko and Kolesnikova (9–11) have shown that at a pressure of 7 mm, the quantity of H_2O_2 collected in a trap cooled to 77°K at a distance of 40 cm from the point of mixing was clearly dependent upon the condition of the surface of the reaction vessel. Table I shows the results obtained using two experimental arrangements which differed only in that the surface of the reaction vessel of one was conditioned by the products from a discharge in hydrogen and washed with phosphoric acid, while the surface of the other was conditioned by the products from a discharge in water vapor. With the surface conditioned by atomic hydrogen a large amount of H_2O_2 was obtained; with the surface conditioned by the products from a water vapor discharge, only small amounts of H_2O_2 were obtained.

TABLE I

YIELDS OF HYDROGEN PEROXIDE AT DIFFERENT TRAVERSED VOLUMES FOR DIFFERENT SURFACES (10, 11)[a]

Condition of surface	Distance of trap at 77°K from point of mixing, cm	Peroxide yield, molecules/sec
Treated with products from discharged H_2 and washed with H_3PO_4	150	0.04×10^{16}
	150	0.08×10^{16}
	40	7.50×10^{16}
Treated with products from discharged H_2O	150	0.12×10^{16}
	40	0.11×10^{16}

[a] $p_{H_2} = 6$ mm; $p_{O_2} = 0.2$ mm; reaction at $\sim$470° K.

From the results of experiments in which ethylene was added to the H–O_2 system at different distances from the point of mixing (10, 11), it was deduced that the water is formed by a chain reaction rather than by simple radical reactions. The addition of ethylene at a distance of 12 cm, although presumably breaking the chain, did not prevent the formation of considerable water, from which it was concluded that water is formed in the reaction vessel and not in the trap. Removal of the cold surface of the trap to a distance of 150 cm from the atomic hydrogen inlet led to a sharp decrease in the amount of hydrogen peroxide (Table I), thus indicating that most of the peroxide is formed on the cold walls of the trap (11).

2. *Atomic Hydrogen–Solid Oxygen*

When hydrogen atoms produced thermally on a tungsten ribbon were treated with a film of solid oxygen at 20°K, water and hydrogen peroxide were obtained as the products at room temperature (116). The extent of the hydrogen consumption indicated diffusion of hydrogen atoms into the solid.

C. ATOMIC HYDROGEN–OZONE SYSTEMS

1. *Atomic Hydrogen–Gaseous Ozone*

This reaction was first studied by McKinley and Garvin (146) at room temperature in a low-pressure (0.1 mm) flow system using a substantial excess of hydrogen atoms and an ozone–oxygen mixture. As the ozone content of the mixture was increased, the yield of water relative to peroxide and evolved oxygen increased appreciably until for 96% ozone an essentially equimolar mixture of peroxide and water was collected in a cold trap at 77°K. The yields of water, hydrogen peroxide, and evolved oxygen under various operating conditions are compatible with the view that product formation occurs primarily by radical recombination reactions in the cold trap. It was suggested that hydroxyl is the immediate precursor of all the water formed (and of a small amount of peroxide) while perhydroxyl radicals form hydrogen peroxide in the cold trap, and either hydroxyl or molecular oxygen in the pre-trap phase (146).

At low flow rates of ozone, the reaction was complete, and 37% of the total oxygen was found as H_2O, 36% as H_2O_2, and 27% as H_2O_4 (207). When the ozone flow rate was increased, the conversion was reduced to 20–30% and the yield of final products, especially that of H_2O_2 and evolved O_2, decreased. The evolved O_2/H_2O_2 ratio increased with the rate of admission of O_3. When oxygen was used instead of ozone, the yield of H_2O_2 was about the same, whereas the yield of H_2O was reduced to about two-thirds and the evolved oxygen to one-half.

2. *Atomic Hydrogen–Liquid Ozone*

The reaction of atomic hydrogen with liquid ozone was first studied in 1951 by Nekrasov (161), the results being published in 1956 (117). When 100% liquid ozone which had been condensed at 77°K on the walls of a glass reactor was bombarded with hydrogen atoms, the dark blue film of liquid ozone was transformed into a transparent glassy substance, slightly tinted bluish by incompletely reacted ozone. When warmed, the glassy substance started to decompose violently at about 160°K and then melted, whereupon the speed of decomposition increased abruptly. In the decomposition, oxygen separated out and there remained a 33% aqueous solution of H_2O_2 corresponding to an approximately 50% solution of H_2O_4. The molar ratio of oxygen evolved to hydrogen peroxide found was constant and approximately unity (117, 121). No such constancy was found for the proportions of evolved oxygen and water (121). With increasing reaction time the accumulation of products at 77°K continued up to a certain limit and thereafter practically ceased even though H bombardment was continued indefinitely. This limiting yield was dependent on the geometry of the film of liquid ozone (121). Increasing the concentration of atomic hydrogen increased the rate at which the limiting yield of condensed product was attained, but did not change its magnitude. The ratio of evolved oxygen to hydrogen peroxide remaining was independent of the concentration of H atoms as well as the duration of H bombardment. Although the absence of H_2O_2 in the condensed product was not proved at this time (121), it was assumed that H_2O_2 was formed only by the decomposition of H_2O_4 produced by the dimerization of O_2H radicals. That formation of H_2O_4 and H_2O_2 with the participation of H atoms occurs only in the presence of an O–O bond was verified by studying the reaction of atomic hydrogen with N_2O and N_2O_4 (121). In neither case was the formation of H_2O_2 observed. The absence of hydrogen peroxide as a primary reaction product at 77°K in H–O_3 system has recently been confirmed by infrared spectroscopy (231), for products which on warming yielded equimolar amounts of O_2 and H_2O_2.

The influence of the geometry of the reaction vessel on the hydrogen atom–liquid ozone reaction has been studied in detail (135–137, 231). In a U-tube reactor the ratio of oxygen evolved to residual peroxide was always approximately unity, but departed from this value when the reactor geometry was changed. The mechanism of formation of the product which gives a 1:1 ratio is therefore closely related to geometrical and flow parameters. In a cold finger reactor only trace quantities of product were formed.

Oxygen was lost from the liquid layer in the early stages of the reaction and hydrogen atoms degraded very rapidly in the liquid nitrogen cooled zone. When the liquid nitrogen level in the U-tube was raised several inches above the film of ozone, no reaction occurred (231). Decreasing the hydrogen atom concentration increased the ratio of evolved oxygen to hydrogen peroxide to unity even in an inlet tube reactor. Decreasing the area of exposed film of liquid ozone markedly increased the production of H_2O_2 and decreased the amount of evolved oxygen. One mole of water was formed for each mole of consumed ozone (231). A 1:1 ratio of evolved oxygen to residual peroxide was also obtained when deuterium atoms were employed instead of H atoms (135). From these results it was concluded that under certain conditions hydrogen or deuterium atoms react with liquid ozone to give a product which, based upon the stoichiometry of decomposition, can be described as a hydrogen superoxide (117, 121, 231).

Liquid ozone and molecular hydrogen do not react at 77°K (121).

3. *Atomic Hydrogen–Solid Ozone*

The reaction of atomic hydrogen with films of solid ozone has been studied at 70°K (76). Infrared absorption analysis of such reacted films proved to be identical with those of solid mixtures of H_2O–H_2O_2 plus unreacted ozone. Although no chemical analysis of the products was made, molar concentrations of H_2O_2 in the films of about one-third were calculated from the intensities of faint peaks at 2163 and 1110 cm^{-1} (76).

The apparent absence of superoxides when solid rather than liquid ozone is used was explained (166) on the basis of differences in rates of diffusion. With liquid ozone, O_2H radicals diffuse easily into the interior of the film, thus avoiding reaction with hydrogen atoms, and recombine there to form H_2O_4 (121), whereas with solid ozone, O_2H radicals are no longer able to diffuse readily into the interior of the layer and react rapidly on the surface with hydrogen atoms to form hydrogen peroxide.

D. OTHER SYSTEMS

1. *Atomic Oxygen–Molecular Hydrogen*

Little or no reaction has been observed when atomic oxygen produced in a discharge is mixed with molecular hydrogen, even if the mixture is passed into a liquid air trap (191). When reaction does occur, only water is formed (177). Presumably the recombination of oxygen atoms is much more rapid than their reaction with hydrogen. The collision probability for the recombination has been calculated to be 10^{-8} at room temperature (191).

2. *Atomic Oxygen–Water or Peroxide Vapor*

When the products of the reaction of water vapor with atomic oxygen were condensed in a trap at 77°K, no peroxide was found, the only product being a small amount of ozone (135). However, when concentrated (68 wt %) hydrogen peroxide vapor was allowed to react with oxygen atoms, analysis of the products condensed at 77°K indicated decomposition of about 81% of the peroxide and the formation of a small amount of the superoxide H_2O_4 (135).

Contradictory results have been reported for the reaction of oxygen atoms with frozen water at low temperatures. Rodebush and Wahl (190) reported that the reaction does not occur at liquid oxygen temperatures. On the other hand, Avramenko and Kolesnikova (9–11) have concluded that on an H_3PO_4-coated surface cooled by liquid nitrogen, the reaction

$$O + H_2O + \text{cold surface} \longrightarrow H_2O_2 + \text{cold surface}$$

takes place. Recent experiments (135), however, support the earlier conclusion that water films do not react with oxygen atoms at 77°K. Negative results have also been reported for peroxide films at 77°K (135).

3. *Atomic Hydrogen–Water or Peroxide Vapor*

Water vapor is reported not to react with H atoms either in the gas phase or on a cold surface (163).

The gas phase reaction between hydrogen atoms and hydrogen peroxide has been reported to form water only, the yield being a linear function of the peroxide input at all flow rates (21, 68, 69, 164). Material balances (164) showed almost complete conversion of hydrogen peroxide into water.

Alternately freezing peroxide vapor at 77°K and bombarding the film with H atoms caused (164) no reaction between solid peroxide and H atoms.

4. *Ozone–Hydrogen Peroxide*

Mutual decomposition of ozone and hydrogen peroxide occurs in aqueous solutions at 273°K (1) and in the gas phase over the temperature range 293–400°K (224). Almost complete consumption of H_2O_2 occurs when the two reactants are brought together in the gas phase, but passing ozone over solid H_2O_2 at Dry Ice temperature has no appreciable effect (224).

In recent experiments (48) in which 100% ozone was bubbled through cold concentrated (60–87%) H_2O_2, the latter was decomposed, the decomposition increasing with temperature. When ozone was condensed at 77°K upon previously powdered solid peroxide, there was no evidence of reaction even after 76 hr.

5. *Oxygen–Hydrogen Peroxide*

When pre-mixed hydrogen peroxide and oxygen were condensed together at 4.2°K and subsequently warmed, the condensed solids evolved oxygen at about 160°K (193). The evolution of oxygen was similar to the thermal behavior of condensed products from discharged H_2O vapor and from the reaction of atomic hydrogen with oxygen or ozone. The molar ratio of evolved O_2 to H_2O_2 in these experiments varied from 0.18 to 0.25 compared to values ranging from 0.29 to 0.37 for the products obtained from atomic hydrogen and molecular oxygen. Similar experiments at higher temperatures, and specifically at 77°K, under a variety of flow conditions did not yield appreciable amounts of evolved oxygen.

III. DIRECT INVESTIGATIONS OF THE GAS PHASE REACTIONS

A. SPECTROSCOPIC METHODS

1. *Ultraviolet Absorption*

Broida and Kone (29) have used ultraviolet absorption to determine the rate of disappearance of OH in the gases issuing from a glow discharge in water vapor. Their work may be compared with that done earlier by Oldenberg, Frost, and Rieke (62, 173, 175). An ultraviolet absorption method developed for determining absolute OH concentrations showed that OH produced in the water vapor discharge could be carried by fast flow into a reaction vessel in measurable concentrations (5, 14). The possibility that the absorption observed is due to OH *formed* in the reaction vessel cannot, however, be excluded (111).

2. *Microwave Absorption*

The microwave spectrum of OH has been detected by Zeeman modulation in an rf discharge in water vapor (49, 194). Transitions between members of the Λ-type doublets were observed along with a nuclear hyperfine structure and Zeeman effect. The intensity of the microwave lines showed that the abundance of OH was strongly dependent upon pressure and discharge current and that OH radicals could be obtained from the discharge in concentrations approaching 10%, with a lifetime of approximately ${}^1/_3$ sec (195). Similar experiments in the presence of steady magnetic fields were subsequently reported (181).

3. *Paramagnetic Absorption*

The concentrations of several species produced by an rf discharge in water vapor–molecular oxygen mixtures of H_2O pressures from 50 to 200 μ and O_2 pressures from 0 to 300 μ have been determined by epr spectrometry (96). Paramagnetic resonance spectra were observed for atomic oxygen, atomic hydrogen, molecular oxygen, and for the high- and low-field $J = {}^3/_2$ and low-field $J = {}^5/_2$ transitions of OH in the $^2\Pi_{3/2}$ state. At water vapor pressures below 100 μ, OH absorption was absent, while above 130 μ, O absorption was absent. The calculated OH concentrations were always less than 1%; adding oxygen to the system increased the OH concentrations by as much as five times, but did not affect the pressure limits.

4. *Emission Spectroscopy*

The emission spectrum of OH in the $H–O_3$ system has been observed in the visible and infrared regions (39, 147). Kaufman (110) using a grating monochromator determined the concentration of OH in its specific rotation–vibration states by observing its emission in a fast-flow $H–O_3$ system diluted with He. The reaction $H + O_3 \rightarrow OH + O_2$ was found to be very rapid in the mixing zone and accompanied by emission of light in the weak (8, 2) band near 5900 A. For the same system, Peyron (178) observed, in addition to the well-known spectrum (63, 64) of OH $[(^2\Pi);\ \nu = 9]$, an intense ultraviolet emission arising from the $^2\Sigma \pm {}^2\Pi$ transition in OH, arising probably *via* a three-body collision involving two H atoms and an hydroxyl radical or by collisions between two OH $(^2\Pi)$ radicals.

Cashion and Polanyi (31), studying chemiluminescence from the system $H–O_2$, found an infrared emission which could plausibly arise from O_2H. Subsequent experiments (33, 63, 65) with different apparatus failed to confirm these observations. Recently Dixon and Mason (46) have studied the luminescence from the H–O_2 system and observed prominent violet-degraded heads at 6853, 7149, 7562, and 8103 A in contrast to the red-degraded bands earlier observed (147). By analogy with the coarse rotational structure of the violet-degraded HNO bands (35, 43) due to opening of the HNO angle on electronic excitation, the observed spectrum was tentatively assigned to the O_2H radical. It should be noted that McKinley (145) and Mironov (155, 156) were unable to detect O_2H spectroscopically in flames where its existence has long been assumed although Tagirov (218) subsequently reported an infrared emission which he attributed to O_2H.

B. MASS SPECTROMETRIC METHODS

Lossing (132) and Schiff (197) have briefly summarized earlier work on the detection and determination of the thermochemical energies of OH and O_2H radicals in the gas phase in discharged water and peroxide vapors and related oxygen–hydrogen systems. Direct experimental evidence for the existence of O_2H radicals in the gas phase was obtained by Foner and Hudson (52) in a mass spectrometric study of the H–O_2 system. When oxygen mixed with an inert carrier gas (M) was introduced at a distance of 2 cm from the mass spectrometer leak into a stream of hydrogen atoms, a small increase in the ion current at mass 33 was observed. This increase was attributed to the formation of O_2H by the reaction

$$H + O_2 + M \longrightarrow O_2H + M \qquad \text{(Eq 1)}$$

No increase was found in the ion current at mass 34, indicating little or no H_2O_2 formation. Ion currents were detected for OH^+ and H_2O^+, the formation of which was ascribed to the secondary reaction

$$O_2H + H_2 \longrightarrow OH + H_2O \qquad \text{(Eq 2)}$$

Subsequent experiments made without a carrier gas showed the presence of OH radicals only (54, 56), formed presumably by the wall reaction

$$H + O_2H \longrightarrow 2OH \qquad \text{(Eq 3)}$$

rather than by reaction 2. Robertson (187, 188) found that in the absence of a carrier gas and at total pressures in the range 0.1 to 0.5 mm, the concentration of O_2 being about 20 mole %, 2 to 8% of the oxygen was converted to H_2O_2 and 3 to 4% to O_2H radicals. The mass spectrometric analysis was performed within 10^{-2} sec after the oxygen was mixed with the H atoms. Although the presence of H_2O_2 and O_2 radicals made the analysis somewhat uncertain, water vapor and hydroxyl radicals were not present in appreciable quantities at the time the gas was sampled. This is surprising because both the hydrogen that passed through the discharge and the oxygen contained about 2 mole % of water. An observed increase in the O_2H^+ ion intensity with time and pressure suggested that O_2H radicals require third-body stabilization and that the lifetime of the unstabilized radical is about 10^{-12} sec. Hydrogen peroxide formation was ascribed to the secondary reaction

$$H + O_2H \longrightarrow H_2O_2 \qquad \text{(Eq 4)}$$

Both O_2H and OH radicals, as well as H_2O_2, were detected in mass spectrometric study of the products of the thermal reaction of hydrogen with oxygen in the presence of helium as carrier gas (97).

When H_2O_2 vapor was treated with the products of discharges through water and hydrogen peroxide vapors, O_2H radicals were detected (53) in very low concentrations, presumably being formed by the reaction

$$OH + H_2O_2 \longrightarrow O_2H + H_2O \qquad \text{(Eq 5)}$$

The O_2H concentration was high enough to permit the determination of the ionization potential, a value of 11.5 ± 0.1 ev being obtained (53). The strengths of the hydrogen to oxygen bonds in O_2H and H_2O_2 calculated from this value were 47.2 ± 2 and 89.5 kcal/mole, respectively.

Recently Foner and Hudson (58) have studied in extensive detail the production, identification, and determination of thermochemical energies of O_2H radicals in the gas phase. O_2H radicals were found to be produced by the reactions of H with O_2, of H with H_2O_2, of O with H_2O_2, of OH with H_2O_2, by photolysis of H_2O_2, and by low-power electrical discharge through H_2O_2. The last system provided the most intense and convenient source of O_2H radicals. Ion–molecule reactions constitute a potentially serious source of interference in studies of O_2H with conventional mass spectrometers (58). The use of a chopped molecular beam sampling system permitted low ion source pressures (10^{-6} to 10^{-7} mm) and minimized ion–molecule reactions as well as interference from decomposition products (51). The measured values of the ionization and appearance potentials of O_2H were 11.53 ± 0.02 and 15.36 ± 0.05 ev, respectively. The derived energies for the hydrogen to oxygen bond strengths in H_2O_2 and O_2H at 298°K were 89.6 ± 2 and 47.1 ± 2 kcal/mole, respectively.

Reported values for the ionization and appearance potentials of O_2H are summarized in Table II. The discrepancy between the values for the appearance potential (Table II) obtained by Robertson (186) and by Foner and Hudson (57) was ascribed by the latter to interference from decomposition products mentioned above which was eliminated in their work (57). Similar interference from decomposition products had been encountered by others (114, 130).

TABLE II

IONIZATION AND APPEARANCE POTENTIALS OF O_2H FROM DIFFERENT SOURCES

Source of O_2H	$I(O_2H)$, ev	$A(O_2H^+)$, ev	Ref
H_2O_2 + discharged H_2O or H_2O_2 vapor	11.50 ± 0.10	15.41 ± 0.10	53
Discharged H_2O_2 vapor	11.53 ± 0.02	15.36 ± 0.05	58
H_2O_2 vapor		15.36 ± 0.05	57
		16.10 ± 0.40	186
$H + O_2$ reaction	12.2		187, 188

Muschlitz and Bailey (160) have studied the mass spectra of water vapor and mixtures of water and hydrogen peroxide vapors. With water vapor H^-, O^-, and OH^- were the principal ions detected, but O_2^- and O_2H^- ions appeared upon addition of small amounts of hydrogen peroxide vapor. The obvious deduction was that OH^- ion was formed by secondary collisions between H^- and H_2O.

The ionization and appearance potentials of OH from various sources are given in Table III. The hydrogen to oxygen strengths in H_2O and OH calculated from Foner and Hudson's value of 13.18 ± 0.1 ev for $I(OH)$ are 116 ± 5 and 103 ± 5 kcal/mole, respectively (55).

TABLE III

IONIZATION AND APPEARANCE POTENTIALS OF OH FROM DIFFERENT SOURCES

Source of OH	$I(OH)$, ev	$A(OH^+)$, ev	Ref
H_2O vapor		17.50	45
		13.20 ± 0.30	40, 47, 114
H_2O_2 vapor		15.35 ± 0.10	57
		15.60 ± 0.08	130
		16.00 ± 0.30	186
$H_2 + O_2$ reaction		13.25 ± 0.30	40, 47, 114
Thermally dissociated H_2O vapor	13.60		222
Discharged H_2O or H_2O_2 vapor	13.18 ± 0.1	18.19 ± 0.10	55

The gases issuing from the water vapor discharge have also been studied using coaxial ionic and molecular beams instead of perpendicular beams, the simultaneous presence of O and OH in the flow being reported (127). The oxygen atom concentration in samples withdrawn from the flow into the mass spectrometer was twice the hydroxyl concentration, contradicting Kaufman's view (109) that oxygen atoms and hydroxyl radicals cannot be removed from the discharge zone simultaneously because of the fast reaction

$$OH + O \longrightarrow H + O_2$$

the activation energy of which is low, and the preexponential factor high.

Using a mass spectrometer capable of detecting atomic oxygen and atomic hydrogen and using a stirred-reactor technique, Wong and Potter (232) have recently measured the rate of reaction of H with mixtures of atomic and molecular oxygen at temperatures ranging from 350 to 600°K. The atomic oxygen was quantitatively monitored by the mass spectrometer at a mass-to-charge ratio of 8. The reaction was found to proceed by a chain mechanism, four to six atoms of oxygen being consumed for each hydrogen molecule. In the absence of molecular oxygen, the expected ratio is 2 (from the consecutive reactions $H_2 + O \rightarrow OH + H$; $OH + O \rightarrow O_2 + H$); consequently, molecular oxygen must be involved in the chain reaction. Mass spectrometric analysis of the products gave the following qualitative results: O_3, not observed ($<1\%$); H_2O, major product; H_2O_2, not observed ($<1\%$); OH, not observed ($<1\%$); O_2H, not observed ($<1\%$); H, a trace at room temperature, much more at higher temperatures.

C. MISCELLANEOUS METHODS

Measurements of the temperature rise of a probe coated with KCl on which OH radicals were presumed to recombine (214, 220), and determination of the amount of H_2O_2 condensed in a liquid air trap from gases containing OH with the presumption that the H_2O_2 is formed from OH (190) were among the earlier methods used for estimating the concentration of OH radicals in discharged water vapor and related systems. Reexamination of these methods proved that they are sensitive not to OH but to some other unidentified species (195).

Investigations involving the use of catalytic probes, Wrede–Harteck gauges, air after-glow and NO_2 titration, and electron spin resonance for the measurement of atom concentrations in discharged water and peroxide vapors and related systems have been reviewed elsewhere (109). Avramenko (6) observed a characteristic greenish yellow glow when NO was introduced into the gas flowing from the discharge zone in water vapor and concluded that this discharge may be a source of oxygen atoms as well as of OH. The presence of oxygen atoms was also indicated by a glow appearing upon addition of acetylene (14), as was also deduced from observed oxidation reactions (7). Neutral $AgNO_3$ solutions and Fe^{2+} in sulfuric acid medium have been used for estimating the concentration of H and OH produced by the water vapor discharge (44, 50, 151, 217). Electron spin resonance and calorimetric methods (126, 204) have recently been used to measure the concentration of hydrogen atoms and their rate of recombination.

D. RATE CONSTANTS AND THERMOCHEMICAL DATA

Considerable information has recently been obtained from discharge flow experiments at temperatures near 300°K about the rates of elementary reactions involving hydrogen and oxygen. Little significance can be given to early work based exclusively on product analysis (91). In recent studies (37, 38, 112) the concentrations of the labile species have been followed throughout the reaction and the over-all stoichiometry established. The concentrations of H and O in the reacting gases were determined by measuring the intensities of the chemiluminescent HNO and NO_2 (air after-glow) emissions, respectively (37, 38), whereas the concentrations of OH radicals in flow systems were followed by electronic absorption spectroscopy (112).

Rate constants determined for reactions involving OH radicals in the gas phase in low-pressure discharge flow systems are given in Table IV.

TABLE IV

RATES OF REACTIONS INVOLVING OH RADICALS IN THE GAS PHASE AT LOW PRESSURES (1~10 mm)

Reaction	Method	Rate constant at ~300°K, l. mole^{-1} sec^{-1}	Ref
$OH + OH \rightarrow H_2O + O$	Electronic absorption	$(1.5 \pm 0.4) \times 10^9$	112
	Electron spin resonance	$\leq 10^8$	230
$OH + H_2 \rightarrow H_2O + H$	Ultraviolet absorption	$\sim 10^4$	15
	Electron spin resonance	$(5.7 \pm 0.7) \times 10^6$	230
	Electronic absorption	$(4.3 \pm 1.0) \times 10^6$	112
$OH + O \rightarrow O_2 + H$	Chemiluminescent and air after-glow emissions	$(3 \pm 1) \times 10^{10}$	37
	Electronic absorption	$(1.1 \pm 0.4) \times 10^{10}$	112
	Emission	1.2×10^{10}	110
$OH + H \rightarrow H_2 + O$	Electronic absorption	3.6×10^5	112

Rate constants for the termolecular reaction $H + O_2 + M \rightarrow O_2H + M$ are given in Table V.

TABLE V

THIRD-ORDER RATE CONSTANTS FOR THE $H + O_2 + M \rightarrow O_2H + M$ REACTION AT LOW PRESSURES

Third body (M)	Rate constant at ~300°K, cm^6 molecule^{-2} sec^{-1}	Ref
H_2	1×10^{-33}	13
He	$(2.1 \pm 0.2) \times 10^{-32}$	38
Ar	$(2.2 \pm 0.2) \times 10^{-32}$	38
H_2O	$(5.2 \pm 2.1) \times 10^{-31}$	38

Avramenko and Kolesnikova (13) assumed that O_2H radicals formed in the primary process are exclusively removed by the reaction

$$O_2H + O_2H \longrightarrow H_2O_2 + O_2$$

and calculated the rate constant for the reaction

$$H + O_2 + H_2 \longrightarrow O_2H + H_2$$

from the measured rate of formation of H_2O_2. Subsequent work (38) showed, however, that O_2H radicals are predominantly removed by the reactions

$$\begin{tikzcd} & H_2 + O_2 \\ H + O_2H \arrow[ur] \arrow[r] \arrow[dr] & OH + OH \\ & H_2O + O \end{tikzcd}$$

the rate constants of which are presumably 3 × 10^8 l. mole^{-1} sec^{-1}, so that the value of the rate constant obtained by Avramenko and Kolesnikova (13) must be considered inaccurate.

Reaction rate data for $O + H_2$ and $H + O_2$ systems producing OH radicals and H or O atoms are given in Table VI.

Thermochemical data appearing in the recent literature for reactions involving H and O atoms and OH and O_2H radicals in the gas phase are collected in Table VII.

The discharge-flow methods by which most of these kinetic and thermochemical data have been obtained unfortunately suffer from a number of disadvantages; the possible presence of electronically or vibrationally excited species, the contribution of surface reactions, and complications resulting from viscous flow are usually disregarded.

IV. NATURE OF THE CONDENSED PRODUCTS

A. EXPERIMENTAL STUDIES

1. *Decomposition Kinetics*

In most of the experimental work on the kinetics of oxygen evolution from the condensed product, neither rate constants nor activation energies were evaluated. Jones and Winkler (103) observed that above 153°K the rate of evolution first increased with temperature, and then remained practically constant until decomposition was complete. The ultimate amount of oxygen at 195°K was the same as that evolved from comparable amounts of the product warmed to room temperature. Although this observation is in agreement with the work of some others (2, 95), the results of Ghormley (70) showed that a major proportion of the oxygen is evolved only at temperatures above 213°K.

Detailed investigations (161, 171, 209) of the decomposition kinetics at constant temperatures indicated that the condensed product began to decompose in the solid phase at about 160°K, but the process reached its greatest intensity after the system melted (70). The decomposition in the liquid phase has been shown to be homogeneous and first order (171). Assuming that the decomposition in the solid phase also followed a first-order law, activation energies were determined from the rate of change of pressure

TABLE VI

RATE CONSTANTS, PRE-EXPONENTIAL FACTORS, AND ACTIVATION ENERGIES FOR THE REACTIONS $O + H_2 \rightarrow OH + H$ and $H + O_2 \rightarrow OH + O$ at ~300°K

Reaction	Rate constant, l. mole^{-1} sec^{-1}	Pre-exponential factor, l. mole^{-1} sec^{-1}	Activation energy, kcal mole^{-1}	Ref
$O + H_2 \rightarrow OH + H$	2.7×10^3	1.2×10^{10}	9.2	36
	1.9×10^3	1.2×10^{10}	9.4 ± 0.7	37
			6 ± 1	91
	$(3 \pm 1) \times 10^4$			109
	6.7×10^3	2.5×10^9	7.7 ± 1	112
	$(2 \pm 1) \times 10^4$	$(3 \pm 1.5) \times 10^{10}$	8.3 ± 1.5	232
$H + O_2 \rightarrow OH + O$	0.18			38
	0.16	2.3×10^{11}	17.8 ± 1	112
	0.16	1.2×10^{12}	16.8 ± 1	112

TABLE VII

ENTHALPIES AND FREE ENERGIES FOR REACTIONS INVOLVING OH AND O_2H RADICALS IN THE GAS PHASE

Reaction	Kcal mole^{-1} at 300°K		Ref
	ΔH	ΔF	
Reactions of OH radicals			
$OH + OH \rightarrow H_2 + O_2$	-17.8 ± 0.7		89
$OH + OH \rightarrow H_2O + O$	-16.9	-15.62	112
$OH + O_2H \rightarrow H_2O + O_2$	-70.6 ± 4		89
$OH + O \rightarrow O_2 + H$	-16.79	-14.99	112
$OH + O_2 \rightarrow O_2H + O$	55.2 ± 4.5		89
$OH + H \rightarrow H_2 + O$	-1.87	-1.38	112
$OH + H_2 \rightarrow H_2O + H$	-14.6 ± 0.5		89
	-15.03	-14.24	112
$OH + H_2O_2 \rightarrow O_2H + H_2O$	-29.3 ± 4.5		89
Reactions of O_2H radicals			
$O_2H + O_2H \rightarrow H_2O_2 + O_2$	-42.3 ± 6		89
$O_2H + H \rightarrow H_2 + O_2$	-57.0 ± 4		89
$O_2H + H \rightarrow 2OH$	-39.2 ± 4		89
$O_2H + O \rightarrow OH + O_2$	-55.2 ± 4		89
$O_2H + H_2 \rightarrow H_2O_2 + H$	14.7 ± 4		89
$O_2H + H_2O \rightarrow OH + H_2O_2$	30.0		122
Reactions of atomic hydrogen			
$H + O_2 \rightarrow OH + O$	16.0 ± 0.5		89
$H + O_3 \rightarrow OH + O_2$	-77.7 ± 0.5		89
$H + H_2O \rightarrow OH + H_2$	10.6 ± 4		89
$H + H_2O_2 \rightarrow O_2H + H_2$	-14.7 ± 4		89
$H + H_2O_2 \rightarrow OH + H_2O$	-68.5 ± 0.5		89
Reactions of atomic oxygen			
$O + H_2 \rightarrow OH + H$	1.81 ± 0.5		89
$O + H_2O \rightarrow 2OH$	16.4 ± 0.7		89
$O + H_2O_2 \rightarrow OH + O_2H$	-2.9 ± 4		89

TABLE VIII

ACTIVATION ENERGIES FROM KINETIC DATA FOR THE DECOMPOSITION REACTIONS OF THE CONDENSED PRODUCT

Activation energy, kcal mole^{-1}		Ref
Before fusion (178–203°K)	After fusion (213–243°K)	
1.5	17	171
1.4	8	161
1.3 ± 0.1	8.5 ± 0.5	209

on slow uniform heating. The relationship between log k and $1/T$ was described by two straight lines intersecting at the melting point of the system (203°K), indicating that the decomposition is a complex process consisting of at least two stages, one occurring in the solid phase and the other in the liquid phase, and that a definite activation energy can be assigned to each stage. Activation energies calculated on this basis are given in Table VIII. The two-stage oxygen evolution was explained by postulating H_2O_4 which decomposes by different mechanisms in the two phases (161, 171, 209).

2. Oxidation–Reduction Analyses

To determine whether the condensed product contains a species stable only at low temperatures, a large excess of ceric sulfate solution was added directly before the product was removed from the liquid nitrogen bath (86, 146). The mixture was allowed to warm to room temperature and then analyzed for excess ceric ion. More ceric ion was reduced by the mixture under these conditions than when the oxidant was added to condensed product after it had been warmed to room temperature. The increase in apparent moles of peroxide found in the *cold* runs was equal to the moles of oxygen evolved in the *warm* runs. In experiments in which the relative yields of the products varied somewhat, there was qualitative indication that the evolved oxygen and water yields increased and decreased together (146).

Gladney and Garvin in similar experiments used ceric sulfate for oxidation analyses and either acidified potassium iodide or basic sodium arsenite for reduction analyses (86). They also found differences between the apparent peroxide titers of frozen and melted samples, amounting to 3 to 8% for reduction analyses and 1 to 7% for oxidation analyses, indicating the presence of some chemical species stable only at low temperatures. The reproducibility of the titer values was poor; the upper limits gave a reduction/oxidation ratio for the presumed species of about 1:1, consistent with the isomeric peroxide postulated originally by Geib and Harteck (68, 69), while average values gave 2:1, consistent with the quasi-molecular H_2O_3 (71).

TABLE IX

INFRARED ABSORPTION SPECTRA (FREQUENCIES IN CM^{-1}) OF H_2O, H_2O_2, AND PRODUCTS FROM THEIR DISCHARGES CONDENSED AT 77°K (236)

Condensed product		Starting material		Known spectra		
Discharged H_2O_2 vapor	Discharged H_2O vapor	H_2O_2	H_2O	H_2O_2	H_2O	Ref
..	..	550	..	..	520	168
..	..	558	..	..	..	
..	..	568	..	..	..	
..	..	590	..	..	..	
..	..	610	..	656	..	80, 149
..	..	630	..	660	..	72
..	680	660	..	680	..	80
..	..	690	..	690	..	34, 80, 149
..	..	700	..	..	..	
755	730	748	..	..	..	
788	..	775	..	..	..	
..	806	..	805	800	..	80
..	..	810	815	809	812	80, 149, 168
..	850	..	840	878	830	72, 168
850	880	..	850	880	850	80, 90, 149, 183
900	890	..	..	..	..	
920	927	..	..	..	..	
962	936	..	..	..	..	
..	..	..	1045	..	..	
1128	1115	..	..	1110	..	76
1150	..	..	..	..	..	
1215	..	..	1215	..	1220	168
1265	..	1265	..	..	..	
1280	..	..	..	..	..	
..	1300	..	..	1300	..	72, 183
1325	..	1322	..	1332	..	80, 149
..	..	1342	..	1370	..	80
..	1375	1379	..	1378	..	72, 183, 198
..	..	1385	..	1385	..	80, 149
..	..	1412		1410	..	80, 149
..	..	1435	..	1430	..	72
1460	..	1450	..	..	..	
1490	..	1485	..	..	..	
1510	..	..	..	..	..	
1570	..	1570	..	..	..	
1590	..	1590	..	..	..	
1615	..	..	..	..	1620	168
..	..	..	..	..	1644	123
1650	1648	1657	1647	..	1650	80
..	..	..	..	2163	..	76
..	..	..	..	..	2222	123
..	..	..	..	..	2230	168
..	..	..	..	..	2240	80
2325	..	..	..	..	..	
2362	2362	..	..	..	..	
2370	..	..	..	..	..	
2445	..	..	..	..	..	
2470	..	..	..	..	..	
2515	..	2590	..	..	..	
2720	..	..	2700	..	..	
2726	..	..	..	2733	..	72
..	..	2840	..	2810	..	80
..	..	2850	3050	2840	..	80
..	Wide band at 3070–3400 with max at 3250	..	3070	..	3020	168
..		..	3090	..	..	
..		..	..	..	3156	123
..		..	..	..	3176	168
3182		3182	3195	3182	..	80
..		3200	3210	3218	3220	72, 168
3236		..	..	..	3240	168
..		..	3250	3270	3250	80

TABLE IX (*Continued*)

Condensed product		Starting material		Known spectra		
Discharged H_2O_2 vapor	Discharged H_2O vapor	H_2O_2	H_2O	H_2O_2	H_2O	Ref
..		..	3292	3292	3256	80, 123, 149
3337		3325	3320	..	..	
..		3350	..	..	3380	168
..		..	3400	..	3400	168
..		3430	..	..	..	
3544		3570	..	..	..	
3740		..	..	..	..	

3. *Ultraviolet Absorption*

Results of earlier examinations, by ultraviolet absorption methods, of frozen matrices containing OH and O_2H have been summarized by Broida (28). The absorption, at the visible-ultraviolet threshold, of the condensed product obtained from dissociated water or peroxide consisted of a few broad bands at 4020, 3900, 3740, and possibly also 3610 A, which disappeared gradually on warming to about 138°K (74). Robinson and McCarty (189) detected an absorption band at 3110 A in the products from discharges through H_2O_2–Ar and H_2O–Ar mixtures condensed at 4°K. This was identified as the $0 \leftarrow 0$ band of the OH $A^2\Sigma \leftarrow X^2\Pi_{3/2}$ system, shifted by 395 cm^{-1} to the red. Two fainter bands were also observed, 70 cm^{-1} apart, which may be due to Q(1) and R(1) transitions.

4. *Infrared Absorption*

Preliminary studies (73, 81) of the infrared absorption of the condensed product from the water vapor discharge showed besides the well-known bands of ice and solid hydrogen peroxide, a few others, and particularly a strong, sharp band at 1305 cm^{-1}, which was at first attributed to the isomeric peroxide $H_2O \rightarrow O$. Further investigation indicated that this isomer should have the O–O vibration at approximately 880 cm^{-1}, in the same region as the normal H_2O_2 molecule, and that it was not possible to establish the presence of this isomer of H_2O_2 on the basis of the available spectroscopic evidence. Subsequently it was shown that the odd absorption bands and especially that at 1305 cm^{-1} were due, in fact, to traces of nitrogen oxides and oxyacids originating from atmospheric contamination (77, 79).

The infrared absorption, from 2 to 25 μ, of the condensed products from dissociated water vapor or from the H–O_2 system was shown to be identical with that of 1:1 mixtures of water and hydrogen peroxide condensed from the vapor (18). This argues against the presence in the condensed product of appreciable amounts of higher peroxides such as H_2O_4. Detection of O_2H in these studies would rest entirely on the O–O stretching mode because of considerable interference from the very strong and diffuse (even at low temperatures) absorption bands of water and hydrogen peroxide (78).

The infrared spectra of thin films of solid ozone which had been bombarded with hydrogen atoms at 70°K (76) were found to be identical with those of solid mixtures of H_2O and H_2O_2 (80) except for three strong bands at 2110, 1050, and 705 cm^{-1} due to unreacted ozone. From the intensity of the weak peaks at 2163 and 1110 cm^{-1}, the mole fraction of H_2O_2 in the reacted film was calculated to be about one-third (76). If the hypothetical superoxide H_2O_4 were present in any appreciable amount, it should have been detected easily from the typical vibrations of the O_4 "skeleton" (76). Comparison with the sulfur analog H_2S_4 which has Raman bands at 862, 483, 450, 229, and 185 cm^{-1}, suggested that O–O stretching and bending modes would occur in the frequency region studied. It was subsequently pointed out that the failure of Giguere and Chin (76) to detect absorption bands which could be ascribed to H_2O_4 was primarily due to the use of *solid* ozone in the synthesis of the condensed product (166, 235).

No evidence for O_2H was found in the products condensed at 4°K from dissociated water and peroxide vapors and from the H–O_2 system (92). In the infrared spectra of H_2O and D_2O molecules trapped in Ar matrices at 4°K, lines at 3574 and 2635 cm^{-1} were assigned to the OH and OD stretching frequencies, respectively (169). Similarly in frozen (4°K), discharged 50% H_2– (or D_2–) Ar mixtures containing NO, lines at 3596 cm^{-1} (or 2680) were assigned to the OH or OD radical. Evidence for a vibration–rotation structure was, however, absent (169).

A comparative infrared study of the products condensed at 77°K from the H–O_3(liq) system and discharged H_2O, H_2O_2, and D_2O did not reveal any bands related to the presence of hydrogen superoxides (136), although the absence of H_2O_2 at 77°K in the condensed product from H–O_3(liq) system was confirmed (231).

Very recently the infrared absorption spectra of the condensed products from discharged H_2O and H_2O_2 vapors have been shown to differ from those of the starting materials (236). The spectra obtained by Yagodovskaya and Nekrasov (236) are compared to the known spectra of H_2O and H_2O_2 in the solid phase in Table IX. In addition to bands which can be assigned to water and hydrogen peroxide in the solid phase, a group of new bands are shown by the condensed product. The frequencies 900, 920, 927, 936, 962, 1115, 1128, 1150, 1280, 1510, and 2632 cm^{-1} constitute a large group of intense bands which cannot be due to accidental impurities. The appearance of these new bands may be due either to structural changes in water or hydrogen peroxide in the condensed phase—formation of new hydrogen bonds, intermolecular interactions or association (80, 95)—or else to the formation of hydrogen superoxides. From a comparison of the spectra of the condensed products with the spectra of H_2S_4, D_2O_2, and the normal paraffins, the absorption bands 900, 920, 927, 936, 962, 1115, 1128, 1150, and 2362 cm^{-1} were considered to be associated with the presence of H_2O_4 in the condensed product (236).

It may be noted that infrared absorption attributed to O_2H has recently been observed in the product obtained by photolyzing mixtures of HI and O_2 in an Ar matrix at 4°K (150).

5. *Paramagnetic Resonance Absorption*

Paramagnetic resonance absorption has been observed in the products condensed at 77°K from discharged water vapor and related systems. Livingston, Ghormley, and Zeldes (131) observed that at 23,000 Mc, the condensed product from discharged water vapor showed a main peak at $g = 2.0085$ with a shoulder at about 2.027. The shoulder was much less pronounced in observations made at 9000 Mc. The absorption was at first considered to be two unresolved lines, perhaps due to two different free radicals. An absorption line of the same appearance was obtained when D_2O and concentrated H_2O_2 were used instead of water and also when hydrogen or NH_3 passed through a discharge was blended with oxygen and condensed at 77°K. The paramagnetic absorption, as well as the pale yellow color of the products, disappeared on warming to about 140°K, appreciably below the temperature at which oxygen evolution begins. There was no evidence for the presence of atomic hydrogen in any of the samples examined (131).

Sands (196) has observed similarly shaped absorption lines in glass and has shown that such lines can arise from a species having an anisotropic g value which is averaged over random orientations. Livingston, Ghormley, and Zeldes (131) suggested that the absorption line observed in their condensed products might be due to OH or O_2H radicals; in these cases, there could be residual unquenched orbital angular momentum giving rise to anisotropy. As the condensed product from D_2O appeared to be no different from that from H_2O, the hyperfine interactions with the hydrogen were apparently small enough to be masked by the over-all envelope of the anisotropic line.

In subsequent studies sharp separation of the secondary maximum was obtained by using 15,000 Mc/sec (87). The line observed was asymmetric and had a g factor close to 2 and a width of 20–30 gauss. As the frequency was increased, the width of the line increased and its asymmetry became more marked, indicating that the width of the line was due both to anisotropic broadening ($g_{\|} \neq g_{\perp}$) and to a spin–lattice interaction. The line cannot be due to atomic hydrogen which would show a doublet with a 500-gauss separation. Neither can it be due to the O^+H radical as the latter is in a $^3\Sigma_1$ state and would give two narrow lines.

The spectra of discharge products from H_2O and H_2O_2 condensed at 4°K in a hydrogen matrix also consisted in each case of a broad asymmetrical line, the high-field lobe having a double-humped structure (99–101). Since these spectra were obtained in systems considered favorable to O_2H production (53, 56), and since the possibility that the absorption is due to OH is weakened by negative results for trapped NO (which has a similar electronic structure), it was deduced that the observed absorption was due to O_2H (101).

Paramagnetic absorption has also been observed in the products condensed at 77°K from the interaction of atomic hydrogen with oxygen (12, 13) or liquid 100% ozone (166, 210). The spectra were identical with those from discharged H_2O and H_2O_2 vapors. Avramenko and Kolesnikova (12, 13) obtained an epr signal from products condensed at 77°K by placing the trap 4 cm from the point of mixing of H and O_2. In this case the g factor was close to that of diphenylpicrylhydrazyl, and the total width of the signal was 23–26 gauss. Defrosting the condensate led to disappearance of the signal. In tests where a signal was detected, H_2O_2 was found after the tube was opened; in tests with blanks, where no signal was obtained, H_2O_2 was not found. The signals were resolved graphically into two symmetrical components, the areas of which were added to determine the radical concentration. With the condensed product from the H-O_3(liq) system, the g factor of the absorption line was 2.009 and the width about 75 gauss (210).

The paramagnetic absorption of the condensed product has been compared with that of solutions (5 to 98 wt %) of hydrogen peroxide exposed to ultraviolet radiation and frozen to 77°K (104–108, 124, 131, 213, 233, 234). The spectra were identical at all frequencies employed (850–12,000 Mc/sec). Since OH radical is known to be present in irradiated H_2O_2 solutions (98), it was concluded that it must be present in the condensed products. However, secondary reactions are possible in these systems. Subsequent experiments (107) have shown that irradiated 3% H_2O_2 in H_2O, in which case secondary reactions are unlikely, gave only one line which became a doublet after the sample was left for 30 min at 130°K. The single line was assigned to OH, obtained in the primary event during the irradiation of H_2O_2, and it was suggested that OH may be transformed into O_2H on heating or at a high H_2O_2 concentration giving a doublet line (107).

In related studies of γ-irradiated ice, paramagnetic resonance spectra were earlier interpreted to indicate two radical species, H and OH, which, on annealing, disappeared at 100 and 145°K, respectively (140). Subsequent studies (205) showed that the epr spectrum of ice subjected to γ-irradiation at 77°K consisted essentially of a doublet centered at $g = 2.008$ and split by 40 gauss, whereas the corresponding spectrum of irradiated D_2O consisted of a triplet with approximately 6 gauss between adjacent lines. The doublet decayed rapidly above 100°K leaving a residual broad line which was thermally stable up to approximately 145°K. The main spectrum was attributed to OH and the residual line assigned to O_2H. However, species trapped at 77°K from a stream of H_2O molecules subjected to 100-ev electron bombardment did not include OH; in this case two absorption spectra were observed, one of which was attributed to the solvated electron $(H_2O)_n^-$, and the other to O_2H (139).

The ratios, for different systems, of the number of unpaired electrons to the number of molecules of hydrogen peroxide eventually found are given in Table X.

TABLE X

RATIO OF THE NUMBER OF UNPAIRED ELECTRONS TO THE NUMBER OF MOLECULES OF H_2O_2 REMAINING AFTER DECOMPOSITION

Source of condensed product (77°K)	Ratio	Ref
Discharged H_2O vapor	0.0065	131
	~0.0060	87
	0–0.0070	210
Discharged H_2O_2 vapor	0.0110	131
$H + O_2$ reaction	0.0080	131
$H + O_3$(liq) reaction	0.007–0.009	210

On this basis the condensed products contained roughly 0.3% by weight of radical if O_2H is assumed (131, 210) or 0.15% for OH (131). These results suggest that most of the radicals react during condensation and further that the number of radicals present is not sufficient to produce the oxygen subsequently evolved. Thus reactions such as $OH + O_2H \rightarrow H_2O + O_2$ and $O_2H + O_2H \rightarrow H_2O_2 + O_2$ cannot account for more than a minor proportion of the oxygen evolved.

In one investigation (210) it was observed that in the water vapor system the condensed product formed two rings in the trap, one immediately above the level of the liquid nitrogen and the other immediately below. The lower ring showed the characteristic paramagnetic absorption reported earlier (131) whereas the upper ring showed no absorption, although both rings evolved oxygen on warming and yielded hydrogen peroxide in the same concentration. It is clear that in this case the calculation of the radical/peroxide ratio should be based on the peroxide content of the lower ring only and that the over-all ratio would not be significant. This may account for the wide variation in the values reported for the water vapor system (Table X). In the $H–O_2$ and $H–O_3$(liq) systems the product is not separated into rings and this difficulty does not arise.

The accumulated evidence from paramagnetic resonance absorption studies thus indicates that the condensed product contains O_2H up to a maximum concentration of 0.3 wt %, this maximum concentration differing little with the method of preparation.

The epr spectrum of the condensed product is similar to those of "Teflon" and polyethylene which have been exposed to γ-rays at 77°K, to those of certain biological materials containing C–O–O radicals which have been frozen in air (142, 158, 184, 223), and also to that of the potassium peroxide radical K–O–O (23). Thus it resembles spectra which are apparently characteristic of peroxy radicals, which supports the hypothesis that the radical present in the condensed product is O_2H.

6. *Magnetic Susceptibility*

The magnetic susceptibilities of the condensed products from discharged water vapor and from the reaction of atomic hydrogen with liquid 100% ozone have been measured (166, 208) using Mauer's experimental scheme (141) with some improvements for compensation for weight increases (167), the specimen being kept automatically at the same point in the magnetic field. Before the start of decomposition, that is, below 160°K, the condensed products behaved as feebly diamagnetic systems with a susceptibility of $-(0.1–0.2) \times 10^{-6}$ emu. When the temperature was raised above 160°K, the system became increasingly paramagnetic as oxygen was evolved. These results suggest that the molecular oxygen evolved on decomposition of the condensed product is not originally present as such (75, 76, 95). Assuming that the diamagnetism of the undecomposed product was due to H_2O_4, a magnetic susceptibility of 0 to -0.4×10^{-6} emu was estimated for the superoxide, indicating that the valencies in this compound are saturated and that it possesses the chain structure H–O–O–O–O–H (208).

7. *X-Ray and Electron Diffraction*

X-Ray diffraction patterns of the condensed products from discharged water and peroxide vapors and from the reaction of hydrogen atoms with liquid ozone were studied over the temperature range from 77°K to complete melting (221). An intense halo was observed at about 3.43 A, whereas ice and H_2O_2–ice at 77°K gave only weak halos at 3.65 and 3.21 A, respectively. An amorphous phase was found in the condensed products from all three systems; in addition crystalline ice and crystalline H_2O_2 were identified in the deposit from discharged H_2O and discharged H_2O_2 vapors. Only crystalline ice was present at 77°K in the material prepared from liquid ozone, H_2O_2 appearing above 160°K.

Subsequent experiments (138) have confirmed the intense halo at 3.4 A (in addition to low-intensity ice lines) for the product from the hydrogen atom–liquid ozone reaction at 77°K. No change in the pattern was detected when the product was warmed to 90°K for 10 min and then recooled to 77°K, but, when it was warmed to 195°K and then recooled, the X-ray pattern of hydrogen peroxide appeared.

In contrast to these observations a mixture of H_2O and H_2O_2 condensed at 77°K exhibited no discrete lines, although an ill-defined halo appeared at about 3.4 A. When this mixture was warmed to 90°K, for 10 min and then recooled to 77°K, both ice and hydrogen peroxide were indicated, in agreement with earlier unpublished results of Bolz, Mauer, and Peiser (26), who examined the X-ray pattern of hydrogen peroxide condensed from its vapor at 77 and 4°K and found that the condensate was amorphous and did not exhibit the sharp lines characteristic of crystalline materials. Crystallization occurred spontaneously at 90°K, the change in structure being accompanied by evolution of heat.

The X-ray diffraction data thus consistently indicate that the condensed product as formed at 77°K from the hydrogen atom–liquid ozone reaction is not crystalline and does not contain H_2O_2, the latter being produced only upon warming (138, 221). These results indeed support the claim for the presence of a superoxide of hydrogen, which on warming decomposes to H_2O_2, as earlier proposed (121).

In all of these X-ray diffraction studies the condensed product was withdrawn from the vacuum apparatus and measurements were made at atmospheric pressure.

The electron diffraction patterns of the condensed product from the water vapor discharge at 83°K determined *in situ* showed that it has an amorphous structure quite distinct from the structure of amorphous solutions of hydrogen peroxide and of amorphous ice (133), indicating that at 83°K the condensed product contains, in addition to water and hydrogen peroxide, some component responsible for the observed difference in diffraction patterns. The occurrence of a ring corresponding to an interatomic distance of 3.48 A located between the rings for amorphous ice and amorphous hydrogen peroxide solutions indicated that the atoms are packed more closely in the condensed product than in amorphous ice and less closely than in amorphous solutions of hydrogen peroxide. The higher peroxide, probably H_2O_4, on entering the condensed product apparently loosens the atomic packing as compared with that in hydrogen peroxide solutions, but, on the other hand, makes this packing more compact than in the case of amorphous ice, presumably because of the formation of a large number of hydrogen bonds. Phase transitions in the condensed product were not observed up to 153°K; at this temperature all components crystallized (133).

Observed X-ray and neutron diffraction patterns of oxygen consisted of three lines corresponding to 3.15, 1.44, and 1.03 A (85, 93, 94). The electron diffraction patterns obtained with the condensed product contained no such lines (133). This was advanced as evidence for the absence of occluded or adsorbed oxygen in the condensed product.

8. *Warming Curves and Calorimetry*

a. Warming Curves

Hogg and Spice (22, 95) determined warming curves, both simple and differential, for the condensed products from the water vapor discharge and the $H–O_2$ system. The approximate value for the heat evolution accompanying the phase transition at 160°K obtained from these curves was 1–2 kcal/mole of hydrogen peroxide finally present, for both systems; because the precision of the method was inherently low, Hogg and Spice considered this value to be a lower limit and that the true value could not be more than twice as great. In experiments in which the product was recooled to 77°K after the phase transition had occurred (but before melting) and then rewarmed, no further heat evolution was observed. Comparison with warming curves for glasses formed at 77°K from concentrated hydrogen peroxide solutions led Hogg and Spice (95) to conclude that the heat-evolution process is devitrification of an ice–peroxide glass. On the other hand, Ghormley (70) found that warming curves for condensed products do in fact differ from those exhibited by peroxide glasses. According to Ghormley the condensed product partially crystallized between 160 and 200°K, and the resulting crystalline phase began to melt above 200°K. When warmed to 213°K, the liquid bubbled violently, evolving oxygen, and the temperature suddenly rose to as high as 400°K. The resulting H_2O_2 solution when cooled rapidly to 77°K formed a glass which began to crystallize at about 160°K with an abrupt rise in temperature to 215°K, a eutectic temperature of the $H_2O_2–H_2O$ system.

The heat evolved was estimated by Ghormley (70) from his warming curves using 0.757 cal/g for the heat capacity of 60% H_2O_2 (a value previously determined (84) for the range 273 to 300°K), and applying a 28%

correction for the heat capacity of the dewar and thermocouple. The observed temperature increase from 215 to 336°K on this basis indicated a heat evolution of 118 cal/g. Using Jones and Winkler's value (103) of 1:5.8 for the ratio of evolved O_2 to final H_2O_2 the heat evolved was 44 kcal/mole of evolved oxygen. Within the wide limits of possible error, this value corresponds to the heat of decomposition of H_2O_2 (48 kcal/mole of evolved oxygen), but it also corresponds to the heats of decomposition of H_2O_3 and H_2O_4 providing the reactions

$$H_2O_3 \longrightarrow OH + O_2H$$

and

$$H_2O_4 \longrightarrow 2O_2H$$

are assumed to be only slightly endothermic. On the other hand, the heat of decomposition of $H_2O \rightarrow O$ to form O_2 would be only slightly less than the heat of dissociation of O_2 (116 kcal/mole) if the heat absorbed in the reaction

$$[H_2O \rightarrow O] \longrightarrow H_2O + O$$

is small.

Warming curves obtained (206) by a thermographic technique using a rapid differential thermal analysis (182) revealed that as the product was warmed there were in fact three successive heat effects (Table XI), the first and third being exothermic and accompanied by the evolution of oxygen, the second being endothermic without oxygen evolution.

TABLE XI

THERMOGRAPHIC HEATS OF DECOMPOSITION OF CONDENSED PRODUCT (206)

Temp, °K	ΔH
163–198	−72 kcal/mole of O_2
203–213	+62 kcal/g of H_2O_2
218	−35 ± 1 kcal/mole of O_2

b. Calorimetry

Continuous heating of the condensed product in a calorimeter under adiabatic conditions also showed three successive heat effects (185).

(a) An exothermic effect ($\Delta H = -79$ kcal/mole of O_2) starting at 158°K and accompanied by evolution of one-third of the total oxygen, attributed in part to the reaction

$$2O_2H \longrightarrow H_2O_2(s) + O_2 \qquad \text{(Eq 6)}$$

and in part to crystallization of the product.

(b) An endothermic effect ($\Delta H = 100$ cal/g of H_2O_2) beginning at 203°K, without oxygen evolution, attributed to a change in the state of aggregation.

(c) An exothermic effect ($\Delta H = -68$ kcal/mole of O_2) beginning at 218°K, accompanied by the evolution of two-thirds of the total oxygen, attributed to the decomposition of H_2O_4 in the liquid phase

$$H_2O_4(liq) \longrightarrow H_2O_2(liq) + O_2 \qquad \text{(Eq 7)}$$

Subsequent visual and thermometric observations revealed that the method used to calculate ΔH for the third stage was incorrect, and the value was recalculated to be 39 ± 4 kcal/mole of O_2 (211). Furthermore, since the concentration of O_2H in the condensed product has been shown to be not more than 0.3 wt % (87, 131), the disproportionation of O_2H (Eq 6) could account for no more than 4% of the total oxygen evolved, thus discounting the earlier explanation (185) of the first exothermic effect in which 30% of the total oxygen is evolved. Accordingly it was suggested that the first heat effect is the sum of the heats of reactions 6 and 7 and the heat of crystallization of the amorphous portion of the condensed product.

Reported calorimetric heats of decomposition of the condensed products prepared by different methods are given in Table XII.

TABLE XII

HEAT OF DECOMPOSITION OF THE CONDENSED PRODUCT CALCULATED FROM CALORIMETRIC DATA

Source of condensed product	Temp of decomposition, °K	Heat of decomposition, kcal/mole of O_2	Ref
Discharged H_2O vapor		−17.8 ± 2.2 (77°K)	41
	158	−79	185
	218	−68	185
	218	−39 ± 4	211
$H + O_3$(liq) reaction		−26.8 ± 2.6 (77°K)	41
	210	−44	135–137

The values of −17.8 ± 2.2 and −26.8 ± 2.6 (Table XII, ref 41) at 77°K were obtained using samples of known assay in an ice calorimeter (82) modified to suit the experimental conditions. In this work the contribution of O_2H reactions to the heat of decomposition was neglected on the basis of the reported low concentration of these radicals (87, 131). The difference between the values for the condensed product from discharged water vapor and from the $H + O_3$(liq) reaction (41) is greater than the estimated experimental error and was attributed either to a difference between the matrices or to traces of ozone or oxides of nitrogen in the hydrogen atom–ozone product.

Taking the heats of formation of O_2H in the gas phase and H_2O_2 in the liquid phase to be 4.5 and −45.3 kcal/mole, respectively (67), the heat of reaction for

$$2O_2H \longrightarrow H_2O_2(liq) + O_2 \qquad \text{(Eq 8)}$$

was calculated to be −54.3 kcal/mole of O_2 (211). Adding −2.5 kcal/mole for the heat of solidification of H_2O_2 gives −56.8 kcal for the heat of reaction of Eq 6. Using this value and the experimentally determined value of −39 kcal/mole of O_2 for reaction 7, the contribution of crystallization to the first exothermic effect was calculated to be 33.1 cal/g of the condensed product and 2.6 kcal/mole of H_2O_2.

It was shown (211) that a value of -39 ± 4 kcal/mole of O_2 for reaction 7 does not contradict existing thermochemical data and can with some confidence be used in further calculations. Thus the heat of formation of H_2O_4(liq) was calculated to be -6 kcal/mole and the heat of combination of O_2H to form H_2O_4(liq) to be -15 kcal/mole of H_2O_4. Using the cycle

$$\begin{tikzcd}
2O_2H \arrow[r, "\Delta H_x"] \arrow[d, "\Delta H_1 = -15"'] & H_2O_2(s) + O_2 \arrow[d, "\Delta H_3 = 2.5"] \\
H_2O_4(liq) \arrow[r, "\Delta H_2 = -39"'] & H_2O_2(liq) + O_2
\end{tikzcd}$$

the heat of reaction 6 was found to be -56.5 kcal/mole of O_2, in good agreement with the value of -56.8 kcal/mole of O_2 given above and calculated from other data (211).

Calculated heats of formation of superoxides are summarized in Table XIII. In obtaining these values it was assumed that there is no interaction of the matrix with H_2O_4 or H_2O_2 upon decomposition, that the combination of O_2H forms H_2O_4 only, and that O_2H has the same thermal properties as H_2O_2.

TABLE XIII

HEAT OF FORMATION OF H_2O_4 FROM DIMERIZATION OF O_2H RADICALS AT 77°K

State	ΔH_f, kcal/mole	Ref
Liquid	-27.9	41
	-15.0	211
Solid	-4.0	41
	-2 ± 10	135

B. EXISTENCE OF SUPEROXIDES OF HYDROGEN IN THE CONDENSED PRODUCT

1. Experimental Evidence

All the evidence for the existence of superoxides of hydrogen is deductive rather than direct, dating back even to the Mendeleev era (19, 121, 148, 162). Moreover their existence has been claimed primarily to explain the thermal behavior of the condensed products discussed in this review; alternate hypotheses such as adsorption or occlusion of oxygen (2, 95, 229), existence of the so-called "abnormal" hydrogen peroxide (68) or an equivalent collision complex stable only at low temperatures (21, 103), and interaction of trapped free radicals (146) cannot adequately explain a number of observed features, such as the sharp onset of decomposition at 160°K which is independent of the rate and method of heating (70, 95, 103), the further decomposition at 213°K with an activation energy of 8 kcal/mole (161, 209), the constancy of the ratio of evolved oxygen to hydrogen peroxide remaining after decomposition (Table XIV) regardless of the rate of introduction of reactants into the electrical discharge, and the very low concentration of trapped radicals in the condensed product (87, 131, 210). It may be mentioned that the existence of hydrogen superoxides at room temperature has also been postulated (4, 113, 125, 180, 216) but subsequent experiments have disproved these claims effectively (134, 145, 155, 156).

TABLE XIV

RATIO OF EVOLVED OXYGEN TO H_2O_2 FOUND, FOR DIFFERENT SYSTEMS

System	Ratio	Ref
Discharged H_2O	0.200	88
	0.185	103
	0.179	170
	0.180	221
Discharged H_2O_2	0.163	21
	0.300	88
	0.300	221
H + O_2(g)	0.073	172
H + O_3(liq)	~1	221
	1.00	121, 231

It was Ohara (171, 172) who first suggested that O_2H radicals present in the product combine to form the compound H_2O_4 which at higher temperatures decomposes into oxygen and hydrogen peroxide.

The argument for the existence in the condensed product of the higher homologs of H_2O_2, such as H_2O_3 and H_2O_4, is based on the following positive experimental evidence.

(a) At 77°K the condensed product contains unpaired electrons up to a concentration of 0.3 mole % probably in the free radical O_2H (87, 131).

(b) The unpaired electrons disappear at 138°K and partial crystallization begins at about 158°K (70, 221).

(c) Warming curves (70), visual observations (70, 206), and calorimetric measurements (206, 209) show that between 203 and 213°K the product melts completely. Above 213°K oxygen evolution occurs with the liberation of about 39 kcal/mole of oxygen (70, 206, 211); H_2O and H_2O_2 remain.

(d) The lowest eutectic temperature for the H_2O–H_2O_2 system being 217°K, melting of crystals in the product at 203°K indicates an appreciable concentration of some additional molecular species (70).

(e) Magnetic measurements (208) have shown that the condensed product is feebly diamagnetic; if the condensed product contained occluded or adsorbed oxygen, it would be paramagnetic.

Realizing that 0.3 mole % of O_2H cannot account for the total amount of evolved oxygen observed and that release of trapped molecular oxygen cannot account for the observed heat effects, Ghormley (71) suggested that H_2O_3 is the species responsible for oxygen evolution, being formed on a surface below 160°K by the mechanism

$$H + O_2 \longrightarrow O_2H$$

$$O_2H + OH \longrightarrow H_2O_3$$

and argued that H_2O_3 was actually prepared many years ago by Bonhoeffer and Boehm (27). In support of his view Ghormley also cites recent experimental evidence for the existence of H_2O_3 in solution (42).

The observations that in the H–O_3 system, the ratio of evolved oxygen to hydrogen peroxide remaining is approximately unity and that H_2O_2 as such is not present at 77°K suggest the presence of H_2O_4 (121, 231). Calculated average concentrations of H_2O_4 produced in different systems are given in Table XV.

TABLE XV

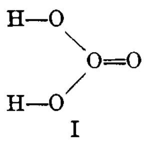
CALCULATED AVERAGE CONCENTRATIONS OF H_2O_4 AT 77°K, FOR DIFFERENT SYSTEMS (221)

System	Concentration of H_2O_2 at $\sim$300°K, mole %	Ratio of evolved O_2 to H_2O_2	Calculated H_2O_4 concentrations, mole %
Discharged H_2O vapor	30	0.18	5
Discharged H_2O_2 vapor	44	0.30	13
H + O_3(liq)	33	1	20

An observation that perhaps augments the case for the existence of H_2O_3 in these systems is the identification of O_3F_2 as a major product obtained from a glow discharge through an O_2–F_2 mixture, the discharge tube being immersed in liquid oxygen (3, 115). It is also interesting to note that F_2O_4, the analog of H_2O_4, was suggested as a possible product in the same system.

2. Bond Energies and Structure of Superoxides

Long ago Mendeleev (148) proposed for H_2O_4 the structure



I

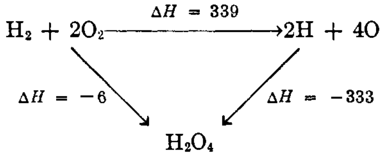
thus representing it as a hypothetical "ozonous acid" analogous to sulfurous and selenous acids. This structure, which presupposes the existence of quadrivalent oxygen, would require an extremely complicated mechanism for the formation of H_2O_4 from O_2H radicals; this reaction would have a considerable energy of activation, a prediction not in agreement with the thermochemical data (70, 206, 211).

The structure $H_2O_2 \cdot O_2$ (II) proposed by Smith (212) is likewise not acceptable since its decomposition into H_2O_2 and O_2 cannot account for the heat evolution observed experimentally (70, 206, 211).

The structure

H–O–O–O–O–H
III

suggested by Bakh (19) does correlate with the thermochemical data. Recently the bond energies in structure III have been calculated (211). Taking the dissociation energies of H_2 and O_2 to be 103 and 118 kcal/mole, respectively (176, 228), and the heat of formation of the compound H_2O_4 to be −6 kcal/mole (211), the sum of the bond energies in structure III was calculated to be 333 kcal/mole using the scheme



Assuming that the energies of the H–O bonds and of the O–O bonds adjacent to them in structure III are the same as those of the corresponding bonds in H_2O_2, the energy of the central O–O bond was calculated. Pauling's (176) values for the bond energies in H_2O_2 (H–O = 110 kcal, O–O = 35 kcal) give a value of 43 kcal, whereas Walsh's (228) values (H–O = 96 kcal, O–O = 65 kcal) give 11 kcal, for the energy of the central O–O bond in structure III. These values are to be compared with the heat of reaction for

$$2O_2H \longrightarrow H_2O_4(\text{liq})$$

which has been reported to be −15 kcal (211).

Benson (24) has examined the theoretical aspects of the stability of H_2O_3 and H_2O_4. Using the law of additivity of bond enthalpies (25), which is obeyed to within a few kilocalories even when species of vastly different electronegativities are bonded to the same atom, values for the H–O and O–O bonds were obtained and used to calculate ΔH_f° (H_2O_3) = −11 kcal and ΔH_f° (H_2O_4) = +10.5 kcal. The values obtained using only thermal data for H_2O and H_2O_2 are ΔH_f° (H_2O_3) = −7 kcal and ΔH_f° (H_2O_4) = +18.1 kcal. According to Benson (24) H_2O_4 is unstable with respect to decomposition into two O_2H radicals by some 6.5 to 14 kcal, either value being such as to render the existence of H_2O_4 extremely doubtful since the split into free radicals would require no nuclear shifts and would thus be expected to occur without activation energy. On the other hand, Benson (24) calculates that H_2O_3 is stable with respect to a split into OH and O_2H by some 17 to 21 kcal and suggests that although it might decompose readily at temperatures above 273°K, its existence at much lower temperatures is feasible.

With respect to the possibility of H_2O_3 formation in the H–O_3(liq) system at 77°K *via* the intermediate O_3H, Benson (24) is of the opinion that the reaction of atomic hydrogen with ozone is so exothermic that the initial products would be OH and O_2, rather than O_3H. Alternate methods whereby H_2O_3 would result from the formation of comparable amounts of OH and O_2H are not kinetically favorable because of the competing processes

$$OH + H_2O_2 \longrightarrow H_2O + O_2H$$

and

$$OH + O_2H \longrightarrow H_2O + O_2$$

and secondary attack of the radicals on any H_2O_3 formed. Thus Benson (24) concludes from thermodynamic and kinetic considerations that H_2O_3 cannot be made by any methods thus far suggested.

V. REACTION MECHANISMS

Results of qualitative and quantitative studies of the low-pressure systems discussed in this review have been interpreted in terms of a variety of proposed mechanisms, none of which adequately accounts for all the observed features. In general, in each of these flow systems the over-all process comprises four successive stages: a discharge tube stage, in which initial dissociation is followed by reactions involving the species thus formed; a pre-trap stage occurring in the zone between the discharge exit and the cold trap in the H_2O and H_2O_2 systems, or between the point of mixing of reactants and the cold trap in the H–O_2 and H–$O_3(g)$ systems; a cold trap stage in which condensible species formed in preceding stages are collected and in which active species may interact at much lower temperatures; a final stage in which the product collected in the cold trap is warmed to room temperature. It is clear, therefore, that any comprehensive mechanism must describe all four stages and that the reactions occurring in any one stage can be elucidated only if the composition of the gases entering that stage is known.

A. DISCHARGE TUBE STAGE

For kineticists interest in the discharge itself lies, not in the complex processes occurring therein, but rather in its function as a source of atoms and free radicals, so that what is of concern is the nature and composition of the gases issuing from the discharge.

There is no doubt that the chief primary process occurring in the water vapor discharge is the dissociation of water molecules under electron impact into H and OH (173, 198). In the earlier investigations it was presumed that the active species issuing from the discharge consisted essentially of H and OH only, the concentration of atomic oxygen being considered negligible (103, 192, 198). However, in 1949 Oldenberg (174) argued that oxygen atoms are also to be expected; in fact, Avramenko (5, 6) at about that time reported NO after-glow experiments which indicated their presence, as was subsequently deduced from mass spectrometric data (127) and oxidation studies (7, 14). Undoubtedly the relative proportions of OH and O in the effluent gases depend upon the type of discharge used and upon experimental conditions (102). In this connection Kaufman (109) points out that it is difficult to reconcile Avramenko's claim (5, 6) that *both* OH and O are major products with the apparent great speed of the reaction

$$O + OH \longrightarrow O_2 + H$$

It has generally been accepted that H_2O_2 is not present in discharged water vapor since it is not found in a Dry Ice cooled trap following the discharge tube (30, 66, 103); Frost and Oldenberg (62) found no ultraviolet absorption due to H_2O_2 in a water vapor discharge, using a *static* system. As for other possible molecular species (H_2O, H_2, O_2) no direct evidence for their existence as such in the gases emerging from the water vapor discharge has been reported, although it is reasonable to expect their presence under favorable conditions.

According to ultraviolet absorption evidence (62) a weak discharge through flowing H_2O_2 vapor causes dissociation into OH, little if any H or O being produced, and the results of one study (21) of reactions in discharged H_2O_2 were interpreted on this basis. However, in a subsequent investigation of the H_2O_2 discharge (88) it was concluded that H_2O is an important intermediate product, and to account for this as well as for Frost and Oldenberg's observation (62) that OH formed in this discharge disappears much more rapidly than it does in an H_2O discharge, it was postulated that the OH produced by the initial scission of H_2O_2 is rapidly consumed by the reaction

$$OH + H_2O_2 \longrightarrow O_2H + H_2O$$

the H_2O thus formed then being dissociated by the discharge, initially into H and OH; dissociation by electron impact of OH into O and H was also considered to be significant. This interpretation of the processes in the H_2O_2 discharge implies that O_2H would be an important constituent in discharged H_2O_2 vapor; in fact, Foner and Hudson (58) have confirmed this by mass spectrometric methods.

B. PRE-TRAP STAGE

In the H–O_2 and H–O_3 gas systems this stage includes the initial reactions between H and O_2 or O_3 and the subsequent reactions involving the various species thus formed.

For the H–O_2 system two initial reactions have been considered

$$O_2 + H + M \longrightarrow O_2H + M \qquad \text{(Eq 9)}$$

$$O_2 + H \longrightarrow OH + O \qquad \text{(Eq 10)}$$

McKinley and Garvin (146) argued that only reaction 9 is important, disregarding reaction 10 on the basis of earlier NO after-glow experiments (191) which apparently indicated the absence of oxygen atoms in this system. On the other hand, Avramenko and Kolesnikova (10, 11) obtained indirect chemical evidence for atomic oxygen when the reaction vessel had been washed with phosphoric acid, and considered that under these conditions the primary step is reaction 10 occurring *on the surface*. Foner and Hudson (54, 58) found OH but not O_2H in mass spectrometric studies of this system at low pressures (~1 mm); nevertheless, they suggested that the primary reaction is probably the formation by reaction 9 of O_2H which then reacts rapidly with H at the wall to form OH. Charters and Polanyi (33) arrived at the same conclusion from their chemiluminescence studies which confirmed the presence of OH and absence of O_2H.

For the initial reaction between H and O_3 in the gas phase only the reaction

$$H + O_3 \longrightarrow O_2 + OH \qquad \text{(Eq 11)}$$

has been suggested (146, 207); convincing evidence for the existence of OH in this system has been reported (39, 63–65, 110, 147).

No *direct* investigations have been made of the reactions occurring in the pre-trap stage in the discharged H_2O or H_2O_2 systems or of the reactions occurring subsequent to the primary reactions in the $H–O_2$ or $H–O_3$(g) systems. The various reaction schemes which have been proposed for this stage have generally been based on assumptions regarding the composition of the gases entering the stage and the nature of the condensed product, and on a knowledge of the final products when the reactions are allowed to go to completion at room temperature. In view of the present uncertainty regarding both the composition of the gases at the beginning of the pre-trap stage and the composition *in situ* of the condensed product, it is clear that those mechanisms heretofore proposed should be considered tentative. Furthermore, some earlier discussions (*e.g.*, 190, 191) were made before the significance of certain aspects (*e.g.*, influence of trapping temperature, oxygen evolution) was realized.

Oldenberg (174) discussed the pre-trap stage in the discharged H_2O system in some detail. In a first attempt to correlate the $H–O_2$ system with the discharged H_2O system, Jones and Winkler (103) presumed the establishment in the pre-trap stage of an equilibrium between two isomeric forms of a quasi-stable complex formed either by the dimerization of OH or by reaction between H and O_2H

$$[H–O–O–H]^* \rightleftharpoons [H_2O \rightarrow O]^*$$

the linear isomer having been suggested earlier by Badin (16). This mechanism subsequently was adapted to include the discharged H_2O_2 system (21). However, the scheme required the existence in the condensed product of the isomeric peroxide $H_2O \rightarrow O$, a compound not otherwise known and one whose existence in the product has not been established (see section IV).

McKinley and Garvin (146), to account for the results of their investigations of the $H–O_2$ and $H–O_3$(g) systems, proposed a set of pre-trap reactions in which the first step was the formation of OH from H and the O_2H presumed to be produced by initial reaction 9; their scheme differed essentially from that of Jones and Winkler (103) in that equivalent metathetical reactions replaced the summation of the formation and decomposition of the quasi-stable complexes. It also describes the discharged H_2O system if it be assumed that molecular oxygen is formed in the discharge.

A quite different mechanism for the pre-trap stage in the $H–O_2$ system has been put forward by Avramenko and Kolesnikova (10, 11). As described above, they considered that reaction 10 occurring on the wall is the initial reaction, so that OH and O rather than O_2H are the important active species in this stage. From their observation that the H_2O yield was much greater than the H-atom input they concluded that water formation in the pre-trap stage proceeds by a chain mechanism.

$$H + O_2 + \text{wall} \longrightarrow OH + O + \text{wall}$$

$$OH + H_2 \longrightarrow H_2O + H$$

$$\begin{tikzcd} & H_2O \\ O + H_2 \arrow[ur] \arrow[dr] & \\ & OH + H \end{tikzcd}$$

C. COLD TRAP STAGE

The presence of H_2O_2 as such in the solid condensed at 77°K from the discharged H_2O and H_2O_2 systems and from the $H–O_2$ system has been well established (133, 138, 221, 236). The often-observed fact that in these systems no H_2O_2 is found in a Dry Ice cooled trap (or indeed at temperatures above about 150°K) indicates that H_2O_2 is not present in the gases entering the trap. It follows therefore that the peroxide found at 77°K has been formed in the trap itself. In view of the low temperature of peroxide formation it is apparent that the peroxide-forming reaction(s) must have little or no activation energy and most plausibly involve the combination of active species.

Possible low-temperature peroxide-forming reactions which have been proposed are

$$OH + OH \longrightarrow H_2O_2 \qquad \text{(Eq 12)}$$

$$H + O_2H \longrightarrow H_2O_2 \qquad \text{(Eq 13)}$$

$$H_2O + O \longrightarrow H_2O_2 \qquad \text{(Eq 14)}$$

There is general agreement that if these reactions occur then they do so heterogeneously on the cold surface.

Reaction 12 was originally invoked to account for peroxide formation in the discharged H_2O system (191, 192) and reaction 13 for the H–O_2 system (66). Since the demonstration of the close similarity of these systems (103), it has been generally presumed that reaction 12 and reaction 13 can both be operative in either system, as well as in discharged H_2O_2 (88) and the H–O_3(g) system (146). Reaction 13 has variously been considered to occur in one step as written, *i.e.*, presuming that O_2H enters the trap as such (146) or in two steps with the O_2H being formed on the cold surface from H and O_2 (66, 118). Reaction 14 has been advanced only by Avramenko and Kolesnikova (9–11). They claim that their experiments, in which H and O_2 were mixed in a reaction vessel (rinsed with H_3PO_4) before entering the cold trap, show that O_2 does not take part in peroxide formation (thus ruling out reaction 13); they exclude reaction 12 on the basis of an apparently faulty interpretation of the results of Foner and Hudson (54). It should be noted that attempts to carry out reaction 14 directly have failed (135, 190).

It has also been suggested (16, 21, 103) that peroxide formation in the trap is the result of stabilization by the cold surface of an unstable intermediate complex formed in the pre-trap stage either from two OH radicals or from H and O_2H (152).

The possible formation in the cold trap of H_2O_3 in the discharged H_2O system has been attributed (71) to the wall reaction

$$OH + O_2H \longrightarrow H_2O_3$$

and of H_2O_4 in both the discharged H_2O and discharged H_2O_2 systems (88) to the reaction

$$O_2H + O_2H \longrightarrow H_2O_4$$

Evidence for the formation of these superoxides in these systems has been reviewed in section IV.

To account for water formation *in the cold trap* the reaction

$$H + OH \xrightarrow[\text{wall}]{\text{cold}} H_2O \qquad \text{(Eq 15)}$$

has invariably been the one proposed for these low-pressure systems.

The H–O_3(liq) system merits separate consideration. There is no pre-trap stage in this case since it is in the cold trap that the reactants are brought together. Furthermore, this system is apparently unique in that, at least under some conditions, the ratio of evolved oxygen to hydrogen peroxide remaining is approximately unity (117, 121, 231). Kobozev, Skorokhodov, Nekrasov, and Makarova (121) have tentatively suggested a reaction scheme in which the initial steps are

$$H + O_3(\text{liq}) \longrightarrow O_2H + O$$
$$H + O_3(\text{liq}) \longrightarrow OH + O_2 \qquad \text{(Eq 16)}$$

The O_2H thus formed was presumed to dimerize within the film of liquid O_3 to form H_2O_4 (which on warming decomposed into H_2O_2 and O_2), the O and OH escaping from the film to enter into gas phase chain reactions with H_2 in the cold trap.

$$OH + H_2 \longrightarrow H_2O + H \qquad \text{(Eq 17)}$$
$$O + H_2 \longrightarrow OH + H$$

It was assumed that most of the molecular oxygen formed by initial step (Eq 16) escaped unreacted from the trap. Formation of H_2O_2 was attributed entirely to decomposition of H_2O_4, thus excluding reactions 12 and 13 whose participation would yield an evolved O_2 peroxide ratio of less than the unity observed. Wojtowicz, Martinez, and Zaslowsky (231) found that the evolved O_2/peroxide ratio was unity only if the geometry of the O_3 film and the H-atom concentration were appropriate, being less than unity otherwise, and significantly that the infrared absorption bands of H_2O_2 were present in products which gave a ratio less than unity and absent in those which gave a ratio of unity. They considered that reaction 16 is the only primary step, the OH formed being converted to water by either reaction 15 or reaction 17. The O_2 was presumed to react with H to form O_2H, which then dimerizes to H_2O_4 or reacts further with H to yield H_2O_2; those conditions which result in an evolved O_2/peroxide ratio of unity are presumably those under which the O_2H forms H_2O_4 only.

D. WARMING STAGE

Schemes which have been invoked to account for the thermal behavior of the condensed product, *i.e.*, for the processes of the final stage, have been reviewed in section IV.

VI. High-Pressure Discharged Systems of Hydrogen and Oxygen

A. INTRODUCTION

Because the recombination reaction of oxygen atoms is much more rapid than their reaction with hydrogen and because the bond in the oxygen molecule is stronger than that in hydrogen, it is to be expected that passage of an electric discharge through a mixture of excess hydrogen and oxygen would give about the same results as passage through hydrogen alone followed by mixing with molecular oxygen. Hydrogen peroxide is produced by electrical discharge through hydrogen–oxygen mixtures at low pressures (~1 mm) only when the effluent gases are cooled well below 190°K. Interest in the industrial potentialities of the reaction has therefore been directed to discharges at about atmospheric pressure, in which case hydrogen peroxide is apparently produced by homogeneous reactions and can be removed by cooling to room temperatures.

Here the use of nonexplosive mixtures is desirable; since excess oxygen gives low yields of hydrogen peroxide, presumably because the latter reacts rapidly with the ozone simultaneously formed, mixtures containing less than 8 to 10 mole % of O_2 are generally used. Both the early history of the process dating to Berthelot in 1880, and the more recent studies have been well summarized by Schumb, Satterfield, and Wentworth (198).

B. FACTORS INFLUENCING HYDROGEN PEROXIDE YIELD

The effect of the temperature in the reaction vessel on the yield and concentration of H_2O_2 obtained by synthesis in the silent electric discharge has been studied recently (120). In the temperature range 238 to 281°K, 80% H_2O_2 was obtained in constant yield, but with further increase in temperature to 335°K both the yield and the concentration decreased sharply. These experiments were carried out at an initial pressure of 500 mm with a mixture containing 96.5% hydrogen and at a rate of flow of 3.7 to 3.8 l./hr. The trapping temperature varied between 198 and 203°K.

When the rate of flow through the reactor was increased, the yield of hydrogen peroxide passed through a maximum, whereas the total consumption of oxygen in the reaction and the water yield decreased (120). The activation energy for the formation of H_2O_2 in the discharge was calculated to be 1.2 kcal/mole, a low value which agrees with that for the photochemical formation of H_2O_2 (225), indicating common features in the two processes.

Vol'nov and Molodkina (226) have also obtained 70–80 wt % solutions of H_2O_2 by a similar method. They found that the concentration of H_2O_2 was highest when (a) the well-dried gas mixture contained 3.5 to 3.7 vol % of O_2, (b) the molybdenum glass or Pyrex reactor was treated with hot concentrated HNO_3 and with H_3PO_4 solution, (c) the time during which the gas mixture remained in the discharge zone was about 3 min when the current density at the electrodes was $(2.0–2.5) \times 10^{-7}$ amp mm^{-2}, and (d) the temperature of the medium surrounding the reactor was 255°K.

When the specific energy of the discharge was reduced from 5.22 to 0.2 w-hr/l. of gas passed through, the fraction of consumed oxygen converted to H_2O_2, designated as the "useful oxygen consumption," increased from 0.42 to 0.8 (179, 200, 203). It was demonstrated that specific energy is the significant parameter for comparing results of experiments carried out in different reactors (179). When the oxygen content of the initial gas mixture was reduced from 60–80 to 3–3.5%, an increase in consumption of oxygen to form H_2O_2 was observed.

Argon in low concentrations acted as an energy-carrier catalyst, while nitrogen at all concentrations greatly reduced the useful oxygen consumption (119). An increase in the consumption of oxygen to form H_2O_2 was observed in experiments in which water vapor was used as an additive, with both electrodes heated to ~345°K (p_{H_2O} 100 mm). The consumption of oxygen to form H_2O_2 and the useful oxygen consumption in the presence of these catalysts were somewhat lower with a glass–aluminum reactor than with an all-glass one; the use of nickel- or tin-plated electrodes caused a large reduction in both values (179, 203).

With a glass–aluminum reactor, increasing the pressure from 1 to 3 absolute atm caused a decrease in oxygen consumed and in water yield, while the peroxide yield passed through a maximum value at 2 absolute atm (200).

Morinaga (159), studying the same system at higher frequencies (500–2000 cps), observed a linear relationship, independent of frequency, between the rate of formation of hydrogen peroxide and of water, and the pulse current. The composition of the hydrogen peroxide–water solution was constant so long as the gap length in the Siemens tube remained unchanged. The peroxide concentration decreased with increasing residence time of the gas mixture, whereas the rate of conversion (%) to peroxide exhibited a saturation effect at residence times of the order of 15–20 sec. The results obtained with several types of packing in the gas space are given in Table XVI. The low values obtained with soda glass and the ceramic packings were attributed (159) to the increased rate of destruction of O_2H and H_2O_2 on these surfaces.

TABLE XVI
THE EFFECT OF DIFFERENT PACKINGS ON PEROXIDE FORMATION (159)

Composition of the packing	Dielectric constant	Peroxide concentration, %	Over-all conversion, %
Blank	1	46.0	2.4
Soda glass	6	4.5	3.7
$2MgO–TiO_2$	20	1.2	3.3
TiO_2	100	1.7	3.6
$BaTiO_3$	1200	2.5	3.5
$95BaTiO_3–5SnO_2$	5500 ~ 6000	0.7	3.2
B_2O_3		45.5	3.1
H_3BO_3		42.1	2.5

C. KINETICS AND MECHANISM

A kinetic analysis of the experimental data (120, 179, 203) obtained for the $H_2–O_2$ reaction in the silent discharge has been reported (201). The treatment was based on the rate of consumption of oxygen (hydrogen being present in large excess) using specific energy as the time parameter, and showed that for all-glass reactors the process could be adequately described by the consecutive irreversible first-order reactions

$$H_2 + O_2 \longrightarrow H_2O_2$$

and

$$H_2O_2 \longrightarrow H_2O + O$$

Subsequently it was shown (202) that in glass-metal reactors the process closely follows the kinetics of the parallel, consecutive, first-order irreversible mechanism represented by

$$\begin{tikzcd} O_2 \arrow[r] \arrow[dr] & H_2O_2 \arrow[d] \\ & H_2O \end{tikzcd}$$

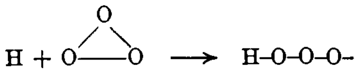
Morinaga (159), drawing an analogy between ozone formation by discharge and the H_2–O_2 reaction, suggested that the elementary processes governing the rate would be those in which electrons participate, and proposed the following mechanism.

$$H_2 + e = 2H + e \qquad (A)$$
$$O_2 + e = 2O + e \qquad (B)$$
$$H + O_2 = OH + O \qquad (C)$$
$$O + H_2 = OH + H \qquad (D)$$
$$OH + H_2 = H_2O + H \qquad (E)$$
$$OH + OH = H_2O_2 \qquad (F)$$
$$H_2O_2 + H = H_2O + OH \qquad (G)$$

If reactions C and D are fast, an equilibrium concentration of OH would be established which concentration would govern the over-all reaction rate.

In an alternate mechanism (119) a major role was ascribed to the dissociation of hydrogen molecules, and to the electron lining on the ozonizer wall which considerably increases the adsorption potential of oxygen and thus takes the place of the cold wall otherwise necessary for the formation of hydrogen peroxide. The possibility of reaction between H atoms and ozone both in the gas phase and on the electron base was also suggested (119). On this basis the following mechanism was proposed.

$$\begin{aligned} H_2 + e &\longrightarrow H + H^{\cdot} \\ H + O_2{}^-{}_{ads}\,S &\longrightarrow H\text{–}O\text{–}O^-{}_{ads}\,S \\ H + H\text{–}O\text{–}O^-{}_{ads}\,S &\longrightarrow H_2O_2 + e_{ads}\,S \end{aligned}$$



$$H + O_3 \longrightarrow H\text{–}O\text{–}O\text{–}O\text{–}$$

$$\begin{aligned} H + O_3{}^-{}_{ads}\,S &\longrightarrow H\text{–}O\text{–}O\text{–}O^-{}_{ads}\,S \\ H\text{–}O\text{–}O\text{–}O\text{–} &\longrightarrow H\text{–}O\text{–}O\text{–} + O \\ H\text{–}O\text{–}O\text{–}O\text{–} + H_2 &\longrightarrow H_2O_2 + OH \\ H\text{–}O\text{–}O\text{–}O\text{–} + H &\longrightarrow H_2O_2 + O \\ 2OH &\longrightarrow H_2 + O_2 \end{aligned}$$

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