gen was re-admitted at room temperature. This result suggests that most of the nickel is effectively "massive" nickel in the catalyst as normally prepared.

When the sample is heated at 400° in helium a substantial increase of magnetization takes place. The thermomagnetic curve then becomes near that expected for massive nickel. Such a process could occur through some degree of sintering, by some reduction of nickel oxide, or by a precipitation process involving dissolved aluminum. The mixture is obviously so complex as to require much more work before any definite conclusion may be drawn. There is no indication of a substantial fraction of the nickel being in extremely small particles as found by Weil,[10] but such particles might have been revealed if we had extended our measurements to lower temperatures. It should also be pointed out that Raney nickel prepared in different ways doubtless has quite different particle size distribution curves.

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[CONTRIBUTION FROM THE JAMES FORRESTAL RESEARCH CENTER, PRINCETON UNIVERSITY]

The Reactions of Atomic Hydrogen with Ozone and with Oxygen[1]

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The reactions of oxygen and ozone with atomic hydrogen at room temperature have been studied in a low pressure flow system and the products (trapped at liquid nitrogen temperature) have been determined. 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. Hydroxyl is the immediate precursor of all water formed (and of a small amount of peroxide) while the fate of perhydroxyl is the formation of hydrogen peroxide (in the cold trap) and either hydroxyl or molecular oxygen in the pre-trap phase.

Introduction

The important free radical reactions in the oxidation of hydrogen have been the subject of many studies in which atoms or radicals produced by the action of an electric discharge have been mixed with a variety of stable molecules. These low pressure, short contact time studies include the work of Boehm and Bonhoeffer,[2] Geib and Harteck,[3] Rodebush,[4] and Badin[5] on the molecular oxygen–atomic hydrogen reaction. Related studies of the reactions of dissociated water and peroxide vapors have been made by Rodebush,[4,6] Winkler,[7,8] Giguere[9] and Oldenberg.[10,11]

In all of these systems, the products, when trapped at liquid air or liquid nitrogen temperatures after a contact time of about 0.1 second, form a glass which, upon warming, "melts" at about −115° with considerable frothing and oxygen evolution, then freezes to a crystalline mass, and eventually melts to a concentrated aqueous peroxide solution.[3,7] When the products are trapped at higher temperatures the yields of hydrogen peroxide and evolved oxygen decrease, until, at and above −120°, only water is recovered.[2,4a,7,8] The variation with temperature of the distribution of products between peroxide and water in both the oxygen–atomic hydrogen and dissociated water vapor reactions have been shown by Winkler[7] to be very similar. Such experiments show that peroxide is formed only in the trap (at temperatures less than −115°) and that some water is also formed there.[12,13] In addition, it is generally true that the effect of an increased contact time at room temperature or above is to reduce sharply the yields of peroxide and evolved oxygen, while the water yield tends to increase slowly.[4a,5,7,8]

The results of a study of the low pressure reaction between atomic hydrogen and ozone and a reexamination of the reaction between atomic hydrogen and oxygen are reported here. The two systems are interpreted in terms of a set of reactions that may also be used to explain the behavior of dissociated peroxide and water vapors.

Experimental

Apparatus and Reagents.—A conventional kinetic vacuum system was used. Both it and the preparation and analysis of the reagents are described briefly elsewhere.[14,15] The reaction cell used for these studies was a cylinder, 60 mm. i.d. by 100 mm. long, containing a centrally located capillary nozzle, 0.27 mm. i.d. through which ozone or oxygen

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was bled into the hydrogen atom stream. Products were trapped in a U tube trap, 27 cm. length of 25 mm. tubing, located nine cm. downstream of the nozzle. The volume of the reactor and tubing down to the coolant level on the trap was 160 ml. Except as otherwise noted the trap was cooled with liquid nitrogen during the experiments.

Typical experimental conditions were pressures of 0.1 to 0.3 mm., at room temperature, and flow rates (moles/second) of 10–14 × 10^{-6} for H_2, 2–10 × 10^{-6} for H, and 2–10 × 10^{-6} for oxygen–ozone. Thus contact times at room temperature were 0.03 to 0.08 sec.

Analysis of Products.—Subsequent to analysis for atomic hydrogen and establishment of a steady flow rate, the condensable products were trapped for a convenient time interval, usually one hour, at the end of which gas flows were stopped and the system was brought to atmospheric pressure with helium. The trap was removed, capped as quickly as possible, and re-evacuated without being removed from the coolant. The trap was then warmed to room temperature, weighed and the gas pressure determined. This pressure, corrected for the volume of the manometer system and for the vapor pressure of the aqueous peroxide solution gave the moles of evolved oxygen. At this point the contents of the trap were treated with a measured excess of standardized ceric sulfate in 3 *N* sulfuric acid and the excess ceric ion was determined with potassium iodide and standardized sodium thiosulfate. Finally, the entire trap was dried, re-evacuated and reweighed. The weight of peroxide corresponding to the ceric titration and the weight of evolved gas (as oxygen) were subtracted from the total weight of the trap contents and the difference was calculated as water.

In separate experiments it was shown that the water used to saturate the hydrogen (about three mole per cent.) was completely recovered as a mixture of peroxide and water. Values reported in the tables have been corrected for this "blank."

Several analyses were made of the evolved gas. Combustion over cupric oxide showed no hydrogen. No infrared absorption of ozone was found, the sensitivity of this test being about 0.3% ozone. The gas was very slightly reactive toward neutral KI, an effect we believe to be due to traces of peroxide vapor. Thus we find only oxygen in the evolved gas from the oxygen–atomic hydrogen reaction, in confirmation of Winkler's results for dissociated water vapor.[7]

In experiments in which an extremely high flow rate of water was maintained through the discharge, Giguere[9] has observed the evolution of hydrogen from the products prior to the start of the frothing that accompanies the evolution of oxygen. He has suggested that atomic hydrogen could be adsorbed or occluded in the trapped products.[16] Our runs, at much lower flows, do not show this phenomenon.

Results

The Oxygen-Atomic Hydrogen Reaction.—Experiments in which the flow rate of atomic hydrogen was varied while the flow of oxygen was kept constant are summarized in Table I. Oxygen (at a flow rate of 2 × 10^{-6} mole/sec.) was completely recovered when the atomic hydrogen flow was greater than 5 × 10^{-6} g. atoms/sec. At even higher H/O_2 inputs the yield of water increased slightly (at the expense of the evolved oxygen) while the peroxide remained constant. When the H/O_2 ratio is too low to assure complete recovery of oxygen, the yields of peroxide and water decrease, the latter more sharply than the former. The evolved oxygen yield remains about the same. The strong dependence of water yield upon the atomic hydrogen supply is in contrast to that of the other products. The runs in which oxygen recovery was incomplete show appreciably more hydrogen in the products than was available as atomic hydrogen.

TABLE I

PRODUCT DISTRIBUTION IN THE OXYGEN–ATOMIC HYDROGEN REACTIONS

P = 0.1 mm., room temp.

Input, moles/sec., × 10^6			Contact time, sec.	Product, yields, moles/mole O_2 recovered			% recy. of O_2
H_2	H	O_2		H_2O	H_2O_2	O_2(e)	
14	2.0	2.08	0.06	0.192	0.802	0.103	67
13	2.6	2.09	.06	.301	.759	.093	72
13	4.5	2.00	.06	.320	.768	.073	95
12	5.5	2.04	.05	.360	.753	.069	100
10	9.4	2.74	.06	.378	.726	.086	98
10	9.6	2.72	.07	.402	.739	.060	97
8	10	1.78	.04	.432	.747	.045	101
9	11	1.95	.03	.419	.757	.033	103

The Ozone–Atomic Hydrogen Reaction.—In the studies of this system ozone–oxygen mixtures were substituted for oxygen. All experiments were performed with a substantial excess of hydrogen atoms present, and complete recovery of the nozzle gas was achieved. Flow rates of 10 × 10^{-6} g. atoms/sec. of atomic hydrogen and of 1.4 to 2.0 × 10^{-6} mole/sec. of oxygen–ozone mixture were used. As the ozone content of the mixtures increased the yield of water relative to peroxide and evolved oxygen increased appreciably until for pure ozone an essentially equimolar mixture of peroxide and water was obtained. These results are summarized in Table II.

TABLE II

PRODUCT DISTRIBUTION IN THE OZONE–ATOMIC HYDROGEN REACTION

P = 0.1 mm., room temp., reaction volume 160 cc.

Input (moles/sec., × 10^6)			O_3, %	Prod. yields, moles/mole of oxygen–ozone mixture recovered			% recovery of O_2 + O_3
H_2	H	O_2, O_3		H_2O	H_2O_2	O_2(e)	
10	10	1.78	31	0.640	0.773	0.062	100
9	11	1.71	55	.723	.833	.086	99
10	10	1.44	70	.771	.873	.093	100
9	11	1.66	96	.901	.918	.112	101
10	10	1.73	95	.890	.902	.126	100

Analytical Behavior of the Evolved Oxygen.—Additional evidence concerning the nature of the species causing gas evolution was obtained by modifying the analytical procedure. In several runs a large excess of ceric sulfate solution was added directly to the trap contents before it was removed from the liquid nitrogen bath. The mixture was then allowed to warm to room temperature and was

TABLE III

COMPARATIVE ANALYSES OF THE PRODUCTS OF THE OXYGEN–ATOMIC HYDROGEN REACTIONS IN THE COLD (c) AND AFTER WARMING TO ROOM TEMPERATURE (w)

Atomic hydrogen flow 10 × 10^{-6} mole/sec., H_2 flow 10 × 10^{-6} moles/sec.

Input, moles/sec., × 10^6	Pressure, mm.	Contact time, sec.	Moles of product/Mole O_2 recovered			Recy., %
			H_2O	H_2O_2	O_2(e)	
1.82(w)	0.1	0.06	0.447	0.722	0.055	99
1.89(c)	.1	.06	...	.780	...	..
1.87(w)	.1	.06	0.454	.726	.049	100
				Δ = 0.056	Av. = 0.052	
1.77(c)	0.09	0.04	...	0.805	...	..
1.78(w)	.09	.04	0.432	.757	0.045	101
				Δ = 0.048		

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(16) We are indebted to Professor Giguere for a very enlightening discussion of the nature of the trapped products.

analyzed for excess ceric. Under these conditions more ceric ion was reduced by the mixture than when the oxidant was added to the warmed solution. The results of two sets of experiments (made with different reactors) are shown in Table III.

In both cases the increase in apparent moles of peroxide found in the "cold" runs is equivalent to the moles of evolved oxygen in the "warm" runs. In some of our earlier experiments, in which the relative yields of the products varied somewhat there was also a qualitative indication that the evolved oxygen and water yields increased and decreased together.

Trapping of Hydrogen Peroxide.—The failure of other workers to trap out peroxide at −80° is not due to trapping inefficiency. We have distilled peroxide through our system at flow rates and pressures comparable to the discharge experiments and have recovered the peroxide completely in a trap at −80°. Nor is the appearance of water in the traps due to decomposition of the trapped peroxide by reaction with atomic hydrogen. Solid aqueous peroxide has been bombarded with hydrogen atoms for a period longer than the duration of our other experiments without any noticeable loss in peroxide content. No oxygen evolution was induced.

Discussion

The mechanism presented below for these reactions rests on the assumption that the free radicals formed are sufficiently long lived that a large portion of them reacted in the cold trap to form peroxide and water, and that the effective pre-trap reactions lead to water formation or to the regeneration of radicals. Because of the similar behavior of the several systems mentioned in the introduction, results of studies of all of them are applied in the following interpretation.

The elementary steps in the mechanism are tabulated below

Initial reactions

$$H + O_2 + M \longrightarrow HO_2 + M \qquad (I)$$

$$H + O_3 \longrightarrow OH + O_2 \qquad (II)$$

Pre-trap reactions

$$HO_2 + H \longrightarrow OH + OH \qquad (III)$$

$$HO_2 + H \longrightarrow H_2 + O_2 \qquad (IV)$$

$$OH + H + M \longrightarrow H_2O + M \qquad (V)$$

$$OH + H_2 \longrightarrow H_2O + H \qquad (VI)$$

$$HO_2 + H_2 \longrightarrow H_2O + OH \qquad (VII)$$

Reactions in the cold trap

$$H + OH \longrightarrow H_2O \qquad (VIII)$$

$$H + HO_2 \longrightarrow H_2O_2 \qquad (IX)$$

$$OH + OH \longrightarrow H_2O_2 \qquad (X)$$

Oxygen evolution upon warming

$$OH + HO_2 \longrightarrow H_2O + O_2 \qquad (XI)$$

The Oxygen-Atomic Hydrogen Reaction.—The initial step here is almost certainly (I), for which Lewis and von Elbe have estimated the rate constant at 300°K. to be 8×10^{12} cc.^{2}/mole sec.[17] The alternative

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

is probably unimportant in view of Rodebush's failure to detect oxygen atoms in this system.[4b,18]

The reactions in a liquid nitrogen cooled trap are most likely to be heterogeneous radical and atom recombinations (VIII, IX and X). Metathetical reactions requiring an activation energy are quite improbable at this temperature. If none of these three is effective above −115°, the last two will account for all the peroxide, and the first will account for the increase in water yields upon lowering the trapping temperature from −80 to −195°.[4,7] Giguere's evidence for adsorbed hydrogen in the products trapped from dissociated water vapor[9] makes (VIII) and (IX) likely. The evidence for (X) is tenuous and is discussed in connection with the ozone–atomic hydrogen reaction.

The pre-trap phase must include steps to account for (a) the formation of molecular hydrogen and oxygen, (b) the probable formation of water, (c) the consumption of molecular hydrogen and (d) the absence of hydrogen peroxide in the vapor. In most cases no decision is possible concerning whether or not these reactions are homogeneous.

Molecular hydrogen is formed during the pre-trap phase. Jones' and Winkler's[7] experiments on dissociated water vapor show a mole for mole increase in hydrogen and oxygen yields with increasing contact time. Badin[5] and Rodebush[4b] observed similar losses in the oxygen–atomic hydrogen reaction. Pre-trap water formation is also established by the experiments cited above. These phenomena may be accounted for by the reactions (III, IV and V). The rate of (V) has been determined by Oldenberg and Rieke[11] as 4.9×10^{17} cc.^{2}/mole^2/sec. (with $M = H_2$). This should be rapid enough to account for most of the pre-trap water.

The essential difference between the scheme presented here and that developed by Badin and by Winkler lies in reactions (III) and (IV) which we suggest are metathetical rather than the summation of the formation of a quasi-stable complex and its decomposition. Reaction (IV) becomes apparent at long contact times but may be as rapid as (III). In the presence of excess atomic hydrogen, (IV) merely lowers the apparent rate of (I). Reaction (III) is the major hydroxyl producing reaction and therefore the limiting precursor of water. The two sequences (I, III, V or VIII, I, IX) are consistent with our observations that complete oxygen recovery is obtained only when a 2.5-fold excess of atomic hydrogen is present and that there is a gradual shift in product distribution toward water with additional increase in the H/O_2 input ratio.

Molecular hydrogen consumption is indicated by the runs in Table I in which incomplete recovery of oxygen was found. A more striking demonstration of the importance of H_2 in this general type of system may be found in Batzold and Winkler's[8] study of the reactions of molecular peroxide with atomic hydrogen, dissociated water and dissociated peroxide vapors. When a limited flow of atomic hydrogen and an excess of H_2 were mixed with varying amounts of peroxide the rate of water formation

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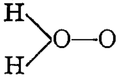
(17) B. Lewis and G. von Elbe, "Combustion, Flames and Explosions in Gases," Academic Press, Inc., New York, N. Y., 1951, p. 59.

(18) We are indebted to the referee for pointing out that this reaction ($E^* \geq 11$ kcal./mole) could compete with (I) at the pressures used. Thus only the negative chemical and spectroscopic tests rule it out.

was a linear function of the peroxide flow rate. When dissociated water vapor and excess molecular hydrogen were mixed into peroxide a similar water production rate occurred, but was not maintained to as high flow rates as in the first case. Dissociated water or peroxide alone mixed into molecular peroxide produced water only up to a maximum rate distinctly lower than obtained in the other two cases. (In addition to indicating a chain reaction involving molecular hydrogen, these experiments show a much lower atomic hydrogen concentration in dissociated water than expected for complete dissociation, and indicate a quantitative similarity between the active gases emerging from peroxide and water discharges). The reactions (VI and VII) which both consume hydrogen and permit the continuation of a chain probably occur. Unfortunately neither the above mentioned experiments nor von Elbe's study of peroxide photolysis in the presence of hydrogen[19] permit a choice between these reactions, since both OH and HO_2 are present in appreciable amounts in these cases.[20]

The appearance of peroxide as a product only in traps colder than −115° and the spectroscopic evidence for its absence in the gas phase[10] are arguments either for reactions (IX) and (X) as the sole peroxide producers or for a quasi-stable [HOOH] complex as proposed by Badin and Winkler.

The postulate of such a complex has served to explain much of the work in this field. Such a complex must be stabilized to normal hydrogen peroxide (and a trace of the postulated abnormal[2] form ) below −115° and it must partially decompose to water or hydrogen and oxygen on surfaces at higher temperatures. With the limited "degrees of freedom" available to such a complex an extremely long life would not be expected at the experimental pressures unless appreciable stabilization could occur by means of molecular or surface collisions. If these are important either peroxide should be detectable in the vapor phase (or in a trap at −80°) or it must be assumed that it is rapidly decomposed by reactions such as

$$H + H_2O_2 \longrightarrow H_2O + OH$$

$$OH + H_2O_2 \longrightarrow H_2O + HO_2$$

The net results of these two reactions, which are found to be quite rapid[8,21] is the production of radicals capable of further pre-trap or trap reactions. Thus it appears necessary to require the presence of hydroxyl and perhydroxyl even in the presence of a complex. In view of this, we think that no simplification in the mechanism is introduced by this concept.

The phenomenon of evolved oxygen cannot be ascribed to adsorbed or occluded oxygen in view of our analytical results; nor do they have the stoichiometry required for the thermal decomposition of hydrogen peroxide. Giguere[22] has identified an O–O infrared absorption in the products from dissociated water vapor that could reasonably be in HO_2. This coupled with the slow nature of the oxygen evolution at about −120° [7] suggests that the evolution is controlled by the migration of radicals through the glassy material and their reaction. One such reaction that is consistent with our analytical results is (XI) where HO_2 is assumed to react with ceric ion as one equivalent of peroxide.

The Ozone–Atomic Hydrogen Reaction.—Spectroscopic evidence has been obtained[14] to show that an initial reaction in this system produces OH by (II). Qualitative studies of the radiation from the newly formed hydroxyl indicate that the reaction is very fast, and that it occurs in a "Polanyi diffusion flame" surrounding the nozzle through which the ozone is admitted to the system. Since, in the presence of excess atomic hydrogen, the oxygen formed in (II) can be expected to react *via* (1), this system differs from the oxygen–atomic hydrogen system only in the vastly greater concentration of hydroxyl radicals. In effect, an ozone–oxygen mixture and pure oxygen (at the same flow rates) produce the same number of HO_2 radicals and the former produces hydroxyls in proportion to the ozone flow rate. The increase in water yield with ozone content is a strong evidence for the importance of hydroxyl as a water precursor. However, if all hydroxyls led to water through reactions discussed above, the peroxide yield would be expected to remain constant for all ozone mole fractions and the water yield would rise to about 1.4 when the nozzle reagent was pure ozone. That this does not happen shows the occurrence of hydroxyl reactions that yield peroxide, either directly or *via* oxygen formation. Such reactions could occur in the pre-trap phase although there is considerable evidence against this view as discussed above. A more attractive possibility is the direct formation of peroxide in the cold trap by reaction (X). It is free from the objections which may be raised against pre-trap reactions, and is consistent with the greater intensity of the evolved oxygen phenomenon (requiring trapped radicals) in the ozone than in the oxygen systems. Although we have not analyzed the evolved gas in the ozone system, the similarity of the product there and in the case of oxygen makes highly probable the assumption that the gas is oxygen.

The Reaction in Dissociated Water and Peroxide Vapors.—These may be correlated with the above scheme by adopting Oldenberg's[23] suggestion that an appreciable amount of hydrogen and oxygen probably is formed in the discharge because any discharge capable of dissociating water should dissociate hydroxyl. On this basis the gas mixture emerging from the discharge in these systems would be very similar to that in the pre-trap phase of the oxygen–atomic hydrogen system.

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[19] G. von Elbe, THIS JOURNAL, **55**, 62 (1933).

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