In spite of the similarity in chemical properties of gold and silver, the kinetics of the hydrogen-oxygen combination over the two metals show little in common. It appears that no simple mechanism for the reaction in contact with gold is adequate to account for the observed results.

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STUDIES IN PHOTOSENSITIZATION. I

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The field of photosensitization by mercury vapor has been extended during the past year to processes which do not involve hydrogen. Dickinson and Sherrill[1] showed that ozone was formed from the collision of excited mercury atoms and oxygen. Since the energy of the quantum corresponding to the 2536.7 Å. line is insufficient to decompose an oxygen molecule, they assumed that the reaction occurred through the collision of an excited and normal oxygen molecule.

Olson and Meyers,[2] investigating in more detail the reaction between hydrogen and ethylene reported by Marshall and Taylor, have shown that the reaction does not go smoothly to form ethane. Ethylene itself is polymerized, there being at the beginning of the reaction an increase in pressure which falls off again as the polymerization proceeds. They also found that the rate of the hydrogen-ethylene reaction was proportional to the square root of the hydrogen concentration.

Senftleben[3] has found that the excited mercury atoms will decompose water vapor. Measuring the change in heat conductivity of water vapor when mixed with varying amounts of hydrogen and oxygen, he found that the change which occurred when water vapor and mercury were illuminated indicated that hydrogen was the sole product in the vapor phase. He, therefore, postulated the formation of hydrogen peroxide which condensed out.

The work here presented has as its object an attempt to broaden the field still further by the development of improvements in light sources for use in photosensitized processes and for general photochemical purposes, and by a study of a number of photosensitized and photochemical reactions. Those investigated are the hydrogenation and polymerization of ethylene and acetylene, the reaction of hydrogen and oxygen to form hydrogen peroxide and the decomposition of water, ammonia, ethylene, ethyl and methyl alcohols, acetone, formic acid, hexane, benzene and

[1] Dickinson and Sherrill, *Proc. Nat. Acad. Sci.*, **12**, 175 (1926).

[2] Olson and Meyers, THIS JOURNAL, **48**, 389 (1926).

[3] Senftleben, *Z. Physik*, **37**, 529, 539 (1926).

ethylamine. A preliminary report on part of this work has already been published.[4]

Apparatus and Methods

The experimental arrangement used at the beginning of this work will be designated as the static system and was modeled directly after that of Taylor and Marshall. It consists of a quartz reaction chamber of about 100cc. capacity joined by capillary tubing to a mercury manometer, gas buret system and oil pump. An electric contact between a sealed-in platinum wire and the mercury in the manometer was used to keep the reaction system at constant volume and the course of the reaction was determined by a change in pressure. A change of 0.5 mm. could be detected. In the photosensitized studies the quartz vessel was immersed in a tank through which water was constantly running, with a vertical Cooper-Hewitt arc of the ordinary type at a distance of about 5 mm. from the vessel. Mercury vapor was furnished by about 1 cc. of mercury placed in the quartz tube. When the purely photochemical reactions were under observation the arc was placed outside the tank and allowed to run hot, the light reaching the reaction system through a quartz window in the side of the tank.

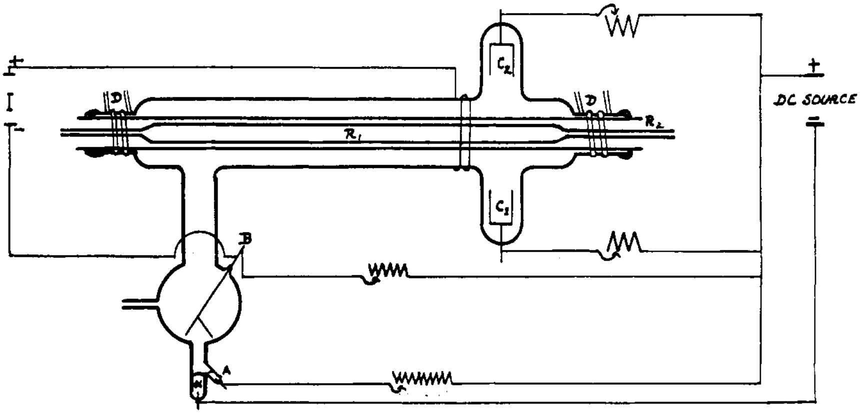

Fig. 1.

The inefficiency of this method was soon quite evident. It had many disadvantages. The arcs, which were run at 10 amperes and 18 volts, deteriorated rapidly. The mercury-vapor pressure in the reaction system could not be controlled independently of that in the arc, which had to be kept low to prevent reversal. Finally, only a very small fraction of the resonance light emitted by the arc could be used in the reaction.

These difficulties were overcome by the development of a cooled mercury arc, based on one used by Langmuir[5] to study the characteristics of arcs at different vapor pressures. The arc proper is made entirely of G702P Pyrex glass with tungsten leads (Fig. 1). Through the center are two concentric quartz tubes R_1 and R_2. R_1 is the reaction vessel while R_2 is a water jacket to prevent R_1 from becoming overheated by the action of the arc. The outside glass system is sealed to the quartz by means of rubber composition tape and an outside layer of Gooch crucible tubing, wired and shellacked. This permits operation at 100°. It is advisable, however, to have these seals protected by the two coils of lead pipe D, through which cold water may be kept

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[4] Taylor and Bates, *Proc. Nat. Acad. Sci.*, **12**, 714 (1926).

[5] Langmuir, *Gen. Elec. Rev.*, **27**, 538 (1924).

running. N is the negative electrode and A, B, C_1 and C_2 are all positive. N and A are tungsten leads covered with just sufficient mercury to cause the two surfaces to come together on jarring the system. An arc is formed which immediately jumps to B, which is a nickel cone welded to tungsten. This serves the purpose of an electrode and at the same time deflects the mercury vapor from N against the walls of the bulb, which is kept in a water-bath. This regulates the vapor pressure in the arc to that of mercury at the temperature of the bath. The arc can be brought up to electrodes C_1 and C_2 by breaking down the space charge with the induction coil, the secondary of which is shown at I. C_1 and C_2 are two nickel cylindrical electrodes.

The wiring connections are shown in the drawing. The potential necessary depends to a large extent upon the geometry of the arc. In the one in use for this work R_2 is 45 cm. long and 2.5 cm. in diameter; R_1 is 37 cm. long and 1.5 cm. in diameter, the surrounding glass arc being 40 cm. long and 5 cm. in diameter. The side tubes containing C_1 and C_2 are 3.5 cm. in diameter and 5 cm. long. The side tube with the bulb and mercury reservoir is 30 cm. long and 3.5 cm. in diameter, while the diameter of the bulb is 6 cm. This has a drop of 35 volts from C_1 and C_2 to N when running at 18 amperes. The slide wire resistances are of such size and capacity (depending on the voltage of the power source) that the current from A to N is 0.5 ampere, B to N, 5 amperes, and from C_1 and C_2 to N up to 10 each. C_1 and C_2 must have separate resistances or the current would flow entirely to one of them, giving an unevenly distributed discharge. After the arc has been started, electrode B may be disconnected, but A should remain in the circuit to insure a steady arc.

Due to leaks around the seals it was not found feasible to run the arc without a mercury pump in continual operation. If the arc is run with air present in too large quantities, not only do the electrodes become oxidized, causing the arc to emit a pink glow, but the mercury tends to wet the glass between A and N, making it impossible to start. When the arc is first set up or after a long period of disuse the nickel electrodes must be degassed by the passage of a higher current than is ordinarily used.

The temperature of the water in R_2 should if possible be kept above that of the bulb to prevent distillation of mercury from N, which would cut down the light reaching the reaction.

In practice this system has always been used as a means of studying reactions by a flowing method. The gases, before entering R_1, are saturated with mercury at any desired temperature (usually about 50°) by passing them through a glass spiral, in every turn of which is a globule of mercury. In this way the gas passes over 15–20 separate surfaces and is insured of complete saturation. It was by this means that we were able to show that the idea of Rideal and Hirst that the reactions were some sort of catalytic phenomenon in which the mercury surface played a part was erroneous. For the first time the reactions were conducted in the absence of liquid mercury, and yet we obtained rates which were enormously greater than theirs. More concerning the general characteristics and optimum running conditions of the arc will be set forth in that part of this paper which deals with the hydrogen-oxygen reaction.

In the course of these studies it became desirable to do some work involving absorption spectra, for which a fairly intense source of continuous low wave length (2500–1900 Å.) ultraviolet light was necessary. A search of the literature revealed that the best means of producing such light must lie either in a high-frequency discharge under water[6] or a hydrogen discharge tube.[7] As ordinarily employed these are not very

[6] Henri, "Études de Photochemie," Gauthier-Villars et Cie., Paris, **1919**, p. 8.

[7] Tingey and Gerke, THIS JOURNAL, **48**, 1838 (1926).

intense and exposures of at least an hour are necessary for spectrographic work.

Attempts to put more energy into an under-water discharge failed, due to the disruptive force of such discharges, which not only make a suitable container difficult to devise, but also cause the spark to emit iron lines as well as the continuous spectrum.

The hydrogen discharge tube yielded better results. This was made of 702EJ Pyrex glass joined at the two points S to 702P to allow the tungsten electrodes to be sealed into the system. These were of 40-mill wire, bent in the form of a spiral with two turns. They are placed 50 cm. apart and in such a position as to allow the light from the discharge to pass through the center of one and out by the quartz window P, sealed on with de Khotinsky cement. The two bulbs were 8 cm. in diameter and the joining tube 5 cm. A 5 kilowatt 110-volt transformer, delivering 25,000 volts on the secondary, was used to excite the discharge. It was run with 60 volts and 140–120 amperes on the primary. The hydrogen pressure was about 17 mm. The tube had to be continuously cooled with a blast of air and could not be run for more than one minute at a time, since it became hot enough to soften and collapse. This, however, was quite sufficient for an exposure, as the accompanying spectrographs (Fig. 5) show.

The lines are mostly those of mercury and a band unidentified. No effort was made to remove them as they are outside the range desired for study and in that region where the more easily obtained tungsten filament serves the purpose.

The Polymerization and Hydrogenation of Ethylene and Acetylene

The work on ethylene was done in the fall of 1925 prior to the publication of Olson and Meyers. It is in entire accord with their observations at low pressures and in some cases makes possible an interpretation of the mechanism involved.

Tank hydrogen purified by passing over hot platinized asbestos and phosphorus pentoxide was used. Tank ethylene, which showed a purity of 99.5% on analysis, was used directly after drying with phosphorus pentoxide. Acetylene was prepared by dropping water on calcium carbide covered with alcohol and was purified by a chain of wash bottles containing concentrated sulfuric acid and solutions of cupric and ferric chloride, mercuric chloride and sodium hydroxide and finally dried over soda lime and by passing through a trap surrounded with carbon dioxide-ether mush. The static system was employed.

The data of a typical run are shown in Table I. The arc was burning at 17 volts and 10 amperes. The alternate jumps of rate at the end of the reaction are due to the inability to read pressure changes to less than 0.5 mm.

TABLE I

60.1 cc. of H_2, 30.3 cc. of C_2H_4. Bar. 754 mm.

Time, min.	Press., mm.	Temp., °C.	Rate, cm./pr., last interval
0	660	15.1	...
25	650	..	2.4
35	644	15.4	3.6
45	637	..	4.2
55	630	..	4.2
125	588	14.8	3.6
135	582	..	3.6
150	573	..	3.6
181	553	14.9	3.9
200	540	..	4.1
209	534	..	4.0
230	520	..	4.0
245	511	..	3.6
255	505	..	3.6
277	491	..	3.7
295	481	..	3.3
310	472	..	3.6
320	465	14.8	3.8
330	460	..	3.4
340	454	..	3.6
350	448	..	3.6
360	442	..	3.6
365	439	..	3.6
370	436	..	3.6
375	433.5	..	3.0
380	431.5	15.4	2.4
385	430.5	..	1.2
390	429.5	..	1.2
395	428.5	15.4	1.2
400	427.5	15.3	1.2
405	427	..	0.6
410	426	..	1.2
415	425.5	..	0.6
420	424.5	..	1.2
425	424	..	0.06
430	424	..	0
435	423.5	15.3	0.06
440	423.5	..	0

The lower initial velocity, rising to a fairly constant value, which was obtained by Olson and Meyers, is evident. That the reaction is not solely

$$C_2H_4 + H_2 \longrightarrow C_2H_6$$

is also quite clear, since the reaction should have stopped when the original partial pressure (439 mm.) of hydrogen was reached. This is shown still better by Table II, in which is given a summary of the results indicating an overrunning of the theoretical stopping point for several different ratios of hydrogen to ethylene.

Table II

Summary Showing "Overrunning" of Theoretical Stopping Point

No.	Init. press., mm. H_2	C_2H_4	Final press., mm.	Overrunning
1	621	71	622	7
2	439	221	423.5	15.5
3	285	296	261	24
4	44	664	645[a]	19

[a] Still going when stopped.

The course of these four reactions is shown in Fig. 2 with $-\Delta P$ plotted against time. The horizontal dotted lines indicate theoretical stopping points.

We found that this overrunning was due to polymerization of the ethylene, not by the ultraviolet light, as was claimed by Berthelot and Gaudechon,[8] but solely by the agency of the excited mercury atoms. (This fact has also been shown by Olson and Meyers to be true at low pressures.) Two hundred and fifty-three mm. of ethylene showed no change in pressure when illuminated in the presence of mercury by the hot arc for ten hours, nor upon the addition of 410 mm. of hydrogen and illumination for twelve hours more. Two hundred and forty-three mm. of ethylene, however, decreased to 19 mm. after nineteen hours' illumination with the cooled arc, with an initial increase in pressure of 2 mm. (Fig. 3).

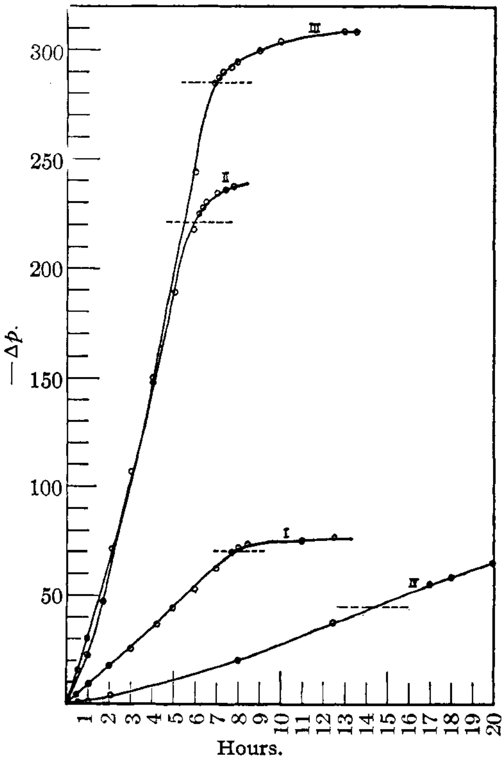

Fig. 2.

One possible explanation of an increase in pressure in a system containing ethylene alone is the formation of acetylene and hydrogen. Using the new type arc and a flowing method, acetylene was shown to be present by streaming the products directly from the arc to a solution of ammoniacal cuprous chloride. A red precipitate of copper acetylide was obtained,

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[8] Berthelot and Gaudechon, *Compt. rend.*, **150**, 1169 (1910).

Ethylene which had not been subjected to the action of excited mercury gave no test. It will be shown later that hydrogen can also be identified as one of the products.

Returning to the use of the static system, the polymerization of acetylene was investigated. Unlike ethylene, acetylene is polymerized to the yellow solid cuprene both in ultraviolet light and also by excited mercury atoms. The rate of reaction is greater with the cooled arc and the layer of cuprene is heaviest in that part of the reaction system adjacent to the arc, while with the hot arc a more even distribution of the solid is obtained. The layer formed prevents a prolonged run, since it soon cuts down the light intensity and slows down the reaction.

The effect of illuminating a hydrogen-acetylene-mercury mixture with the cooled arc was of much interest. Cuprene was deposited on all portions of the reaction vessel except that adjacent to the arc, which became coated with a colorless oil. The cuprene which condenses in this region is immediately acted upon by the hydrogen atoms. This is a very pretty proof of the fact, known from the work of R. W. Wood[9] on the absorption of the 2536.7 Å. line by mercury vapor, that all the activation of mercury atoms occurs in a very thin layer just inside the quartz wall upon which the light falls. In a typical run, 465 mm. of hydrogen and 219 mm. of acetylene were illuminated for thirty hours, giving a final pressure of 412 mm. An analysis of the resulting gases showed from a 32.8cc. sample, 31.4 cc. of hydrogen and 1.4 cc. of unsaturated hydrocarbons. There were no saturated hydrocarbons in the gas phase.

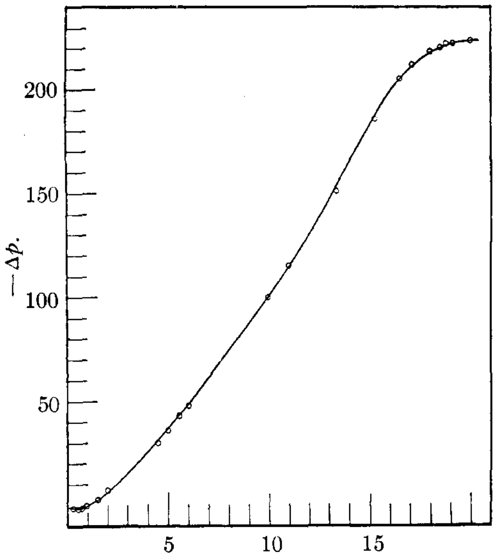

Fig. 3.

Discussion

The polymerization of ethylene, it can be shown, is the result of an extremely complex series of reactions. The collision of an ethylene molecule and an excited mercury atom very evidently results in the reaction

$$C_2H_4 + Hg' \longrightarrow C_2H_2 + H_2 + Hg$$

The reactions

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[9] Wood, "Researches in Physical Optics," Columbia University Press, **1913**.

$$C_2H_4 + Hg' \longrightarrow C_2H_2 + 2H + Hg \qquad (1)$$
$$C_2H_4 + Hg' \longrightarrow C_2H_3 + H + Hg$$

are very definitely barred. The first requires 138 kilogram calories. Both, moreover, are not possible because the chances of two hydrogen atoms combining are negligible compared to the probability of formation of a free ethyl group by a collision between a hydrogen atom and the large excess of ethylene molecules present, and experiment shows hydrogen and an increase in pressure, neither of which would be possible under those circumstances.

The subsequent reactions which may occur are many, but most of these would be of a second order compared with a particular few. The acetylene may be polymerized in the two ways

$$C_2H_2 + Hg' \longrightarrow C_2H_2' + Hg$$
$$C_2H_2' + (n - 1)\ C_2H_2 \longrightarrow (C_2H_2)_n \text{ (cuprene)} \qquad (2)$$
$$C_2H_2 + h\nu \longrightarrow C_2H_2''$$
$$C_2H_2'' + (n - 1)\ C_2H_2 \longrightarrow (C_2H_2)_n \qquad (3)$$

There is also the possibility of the acetylene activated by (2) or (3) reacting in some way with the ethylene. The hydrogen may be dissociated

$$H_2 + Hg' \longrightarrow 2H + Hg \qquad (4)$$

with the consequent reactions

$$H + C_2H_4 \longrightarrow C_2H_5 \qquad (5)$$
$$H + (C_2H_2)_n \longrightarrow (C_2H_2)_nH \text{ etc.} \qquad (6)$$

Unpublished work by Mr. W. H. Jones, mentioned by Taylor,[10] has shown that free ethyl groups, liberated in ethylene, produce reactions which ultimately result in the formation of high-boiling hydrocarbons

$$C_2H_5 + C_2H_4 \longrightarrow C_4H_9$$
$$C_4H_9 + C_2H_4 \longrightarrow C_6H_{13}, \text{ etc.} \qquad (7)$$

Ethyl groups formed in (5) would react in this manner. Our results on the hydrogenation of acetylene show, by the absence of saturated hydrocarbons in the gas phase, that ethane is not formed by the action of acetylene and hydrogen.

These reactions fit in for the most part with the experimental data found on the polymerization. It is to be remarked that not only the primary reaction (1) originates in the narrow zone where mercury atoms in the 2^3P_1 state are present, but also the secondary reactions, with the exception of (3). Olson and Meyers observed that when their arc was allowed to heat up during the initial rise or at any time during the polymerization, no change in pressure occurred. This shows that (3) either does not occur or is of a much lower order of magnitude in the presence of ethylene in large excess. So that, while (1) will be occurring all the time, the subsequent reactions will depend upon the concentrations of hydrogen and acetylene in the zone containing the excited mercury. The initial rise will be regulated by the tendency of these molecules to

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[10] Taylor, *Proc. Am. Phil. Soc.*, **65**, 96 (1926).

diffuse away. By a comparison of the initial rise obtained by Olsen and Meyers with ours, we find them to be proportionately greater at low pressures. For example at 0.85 mm. the rise is 0.145, or $^{1}/_{6}$ of the total pressure; at 0.62 mm. it is 0.125, or $^{1}/_{5}$, and at 250 mm. it is 2 mm. or $^{1}/_{130}$ of the original total pressure. This is in accord with the influence of diffusion of acetylene and hydrogen on the initial rise, since the rate of diffusion would vary inversely as the pressure.

The overrunning of the theoretical stopping point in the hydrogenation is also explained by this mechanism. As the concentration of ethylene is increased, the probability of reactions (1) and (7) taking place is increased and so the overrunning is greater.

Hydrogen Peroxide from Hydrogen and Oxygen

Marshall has already reported the formation of hydrogen peroxide as an intermediate step in the photosensitized reaction of hydrogen and oxygen to water, as was predicted from the original chain mechanism postulated for this reaction by Taylor and Marshall. With the development of the new type of arc, giving sufficient energy to employ the flowing method which is necessary for the study of formation of hydrogen peroxide, we have investigated the conditions which favor its production.

Tank hydrogen and oxygen were passed through a tube containing phosphorus pentoxide, saturated with mercury as has been described and then passed through the arc. Hydrogen peroxide was frozen out in a trap surrounded with carbon dioxide snow and ether and titrated against 0.1 *N* potassium permanganate. The rate of flow of the two gases was determined by two water flow meters, calibrated over the desired range.

Preliminary experiments showed that the hydrogen peroxide was due entirely to the mercury present, and was not formed if the gases were sent through the arc without being saturated with mercury vapor. Ozone, however, was present in both cases, as was determined by bubbling the products through a potassium iodide solution, and by the odor. This showed that ozone was not the agent which produced the peroxide.

In Table III is given a summary of the results which show that it is possible to obtain hydrogen peroxide as the sole product by having a fairly rapid rate of flow and an excess of hydrogen.

Table III

Formation of Hydrogen Peroxide

Rate of flow, liters per hour		Time of run, min.	Mg. total product	$KMnO_4$	Mg. H_2O_2	H_2O/Hg
H_2	O_2					
100	50	10	..	4.1	7.2	82
60	29	10	6	3.5	6	113
101	28	16	7	4.3	7.3	157
19	11	22	6	0.85	1.5	37
14	51	20	5	.38	0.5	8

The arc was run at 13 amperes with the surrounding bath at 17°. The temperature of the saturator was 25°. The total products were found by weighing and the hydrogen peroxide was calculated from the titration. In the final column are the ratios of mercury atoms entering the system to hydrogen peroxide molecules formed. It can be seen from this that the efficiency of the mercury decreases with increasing oxygen concentration and either too high or, especially, too low rates of flow.

By increasing the temperature of the saturation by mercury a much higher yield of hydrogen peroxide was obtained. In these runs, however, it was found impossible to make any satisfactory measurements of the ratios of total products to hydrogen peroxide.

TABLE IV

FORMATION OF HYDROGEN PEROXIDE AT INCREASED TEMPERATURE OF SATURATION BY MERCURY

No.	Rate of flow, liters per hour H_2	O_2	Temp. of bath, °C.	Cc. of 1 *N* $KMnO_4$	Mg, H_2O_2	H_2O_2/Hg
1	99	49	17	34.7	59	95
2	93	48	17	51.5	82.4	115
3	120	55	17	42.4	67.8	76.8
4	118	54	17	43.5	69.6	78.9
5	49	26	17	37.5	60.0	206
6	48	26	17	35.2	56.4	199
7	102	10	17	67.5	113.7	258
8	100	10	17	38.7	61.9	145
9	100	50	1	29.6	47.3	73.9
10	100	50	1	25.7	41.2	70.7
11	97	50	17	58.4	93.5	164
12	94	49	18	44.0	70.4	127
13	97	49	30	38.6	61.8	109
14	96	49	40	23.5	37.6	67
15	93	49	45	18.6	29.8	54

The arc was operated at 35 volts, 18 amperes, with the mercury saturation at 50°. Each run lasted 10 minutes. In Run 15, with the bath at 45°, the arc became constricted.

In all of these experiments the mercury appeared at the end of the reaction tube, just beyond the illuminated area, in the form of the oxide. Practically no oxide was deposited in the reaction vessel proper. The large number of hydrogen peroxide molecules formed per mercury atom entering shows that each atom is activated many times in passing through the illuminated zone. In Run 7, where the ratio of hydrogen peroxide to mercury is 258, each mercury atom must absorb and transfer at least 43 quanta, according to Marshall's measurements, which shows 6 molecules formed for every quantum absorbed. The atoms can be shown to have been in the illuminated zone two seconds in this run, which gives a time interval of 0.04 second between activations. This is enormously larger than the value usually assigned to the life of an excited mercury atom in the 2^3P_1 state (10^{-2} sec.). These facts, however, show that the formation of the mercuric oxide is a secondary effect, probably due to the decomposition of the peroxide on the mercury. The non-reproducibility of the results may be accounted for by this, and by photochemical decomposition of the peroxide.

The last seven runs illustrate the efficiency of the arc at various vapor pressures of mercury and very clearly indicate the range of 10–20° as the best operating temperature.

Photosensitized Decompositions

The dissociation of ethylene into hydrogen and acetylene very naturally led to an examination of the possibilities of other such processes brought about by excited mercury atoms. Water, ammonia, ethylene, methyl and ethyl alcohols, hexane, benzene, acetone, formic acid and ethylamine were all decomposed and those products of decomposition which passed through a liquid-air trap analyzed. No substance studied was unaffected by the excited mercury.

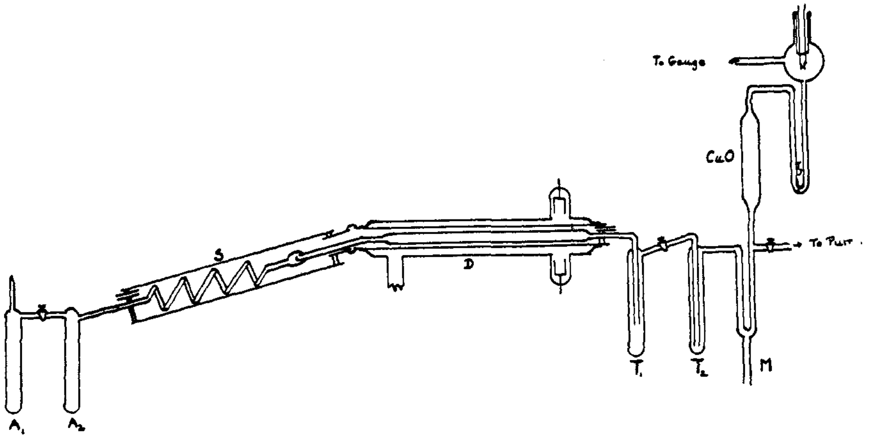

Fig. 4.

The experimental arrangement is shown in Fig. 4. The substance under examination is placed in A_1 and vacuum distilled to A_2. A_1 is cut out by the stopcock and with liquid air around A_2 and the arc running the whole system is pumped down until the McLeod gage reads about 10^{-5} mm. The pump is then shut off and traps T_1 and T_2 are cooled in liquid air. The substance is then distilled over with the arc not running, as a blank, and the pressure read. This is necessary as some of the materials studied dissolve appreciable quantities of gas at liquid air temperatures. By distilling and pumping out, however, it is possible to obtain only very small pressure increases upon subsequent distillations. The largest of these is of the order of 10^{-3} mm., which is negligible in comparison with those obtained by the decompositions. The arc is then started and the substance again distilled. The distilling gas is saturated with mercury in the spirals and after passing through the arc all condensable material taken out at T_1 and T_2, the remaining gases being collected in the bulb of the gage. A run lasted, usually, for about 10 minutes. The pressure is recorded at frequent intervals, at first on the McLeod gage, and then on a side tube reading higher pressures. The gases which pass through the liquid air are nitrogen, oxygen, hydrogen, carbon monoxide and methane. These can be analyzed by means of the platinum filament and copper oxide tube. The mercury cut off at M is raised and the trap T_3 immersed in liquid air. The glowing filament will cause a decrease in pressure if there is oxygen present, but in the presence of methane and no oxygen there is a slight increase, due to the decomposition of the hydrocarbon. This increase was thus a useful indication of the absence of air. When there is such an increase, or when a decrease occurred to a constant pressure, the filament is turned off and the copper oxide heated. Carbon monoxide, hydrogen and methane are thus removed and the residual gas (in the case of ammonia and ethylamine) assumed to be nitrogen. The relative amounts of carbon dioxide and water in the products of combustion can be found by replacing the liquid air around T_3 by carbon dioxide snow and again reading the pressure.

When a comparison is desired between the photosensitized and photochemical reactions the mercury saturator is removed and the whole system cut down and cleaned with nitric acid to remove mercury. The pumping is then carried out for four or five hours through a liquid-air trap which prevents any diffusion of mercury vapor back to the reaction system.

The following typical data from two runs illustrate the method.

Ammonia—saturated with mercury at 50°

	Pressure in mm. of Hg
5 minute blank run with arc off	2×10^{-4}
arc running	
1 minute	0.55
3 minutes	2.3
5 minutes	3.9
8 minutes	6.1
10 minutes	7.8
arc off	
Filament burning ten minutes	7.8
Copper oxide tube heated two hours	0.87

Formic Acid (Hg at 50°)

	Pressure in mm. of Hg
10 minutes blank	3×10^{-4}
arc running	
1 minute	3.5
3 minutes	10.8
6 minutes	24.4
arc off	
Filament	24.4
CuO	0.7
Changing liquid air to CO_2 snow	17.8

A summary of the results is presented in Table V. The pressures recorded are those resulting from a ten-minute run.

Water Vapor.—The appearance of oxygen in our products of decompo-

TABLE V

COMPARISON OF PHOTOCHEMICAL AND PHOTOSENSITIZED RATES

Subs.	Residual gas without Hg vapor, mm.	Gas anal., %	Residual gas with Hg vapor, mm.	Gas anal., %	Ratio of photosensitized to photochemical rate
H_2O	None	....	1.2	H_2, 73; O_2, 27	...
NH_3	0.04	H_2, 96; N_2, 4	7.8	H_2, 89; N_2, 11	200:1
C_2H_4	None	....	24.1	H_2, 88; CH_4, etc., 12	...
CH_3OH	0.03	....	18.0	H_2, 58; CH_4 + CO, 42	600:1
C_2H_5OH	.7	....	38.0	H_2, 46; CO + CH_4, 54	50:1
C_6H_{14}	.016	....	17.0	H_2, 96; CH_4, 4	1000:1
C_6H_6	.01	....	0.3	H_2, 60; CH_4, 40	30:1
$(CH_3)_2CO$	4.7	CO + CH_4, 100	9.6	CO + CH_4, 100	2:1
HCOOH[a]	0.06	....	24.4	CO, 76; H_2, 24	400:1
$C_2H_5NH_2$	.34	N_2, 4; H_2, 96	20.4	H_2, 96; CH_4, 3.7; N_2, 0.3	60:1

[a] Six minutes' operation.

sition is probably due to the flowing method used. Senftleben, who found only hydrogen in his reaction vessel after decomposition, was employing a static system, and ozone formed either by low wave length light or excited mercury is known to attack mercury to give the oxide. This does not preclude the possibility of the formation of hydrogen peroxide as an intermediate step. Senftleben has pointed out that the only initial process of decomposition possible with the energy obtained from a quantum of 2536.7 Å. is the dissociation of a water molecule into a hydrogen atom and an hydroxyl group.

$$H_2O \longrightarrow H + OH$$

The secondary reactions

$$H + H \longrightarrow H_2$$
$$H + OH \longrightarrow HOH$$
$$OH + OH \longrightarrow H_2O_2$$

are all equally probable and not all water molecules originally dissociating would result in the formation of hydrogen and hydrogen peroxide. This fits in with our results in that the efficiency of the mercury in dissociating water is low compared with the other processes, with the exception of benzene. A test of the products contained in the trap showed no hydrogen peroxide, but any condensing there would be immediately decomposed by the mercury present.

The fact that there is an excess of hydrogen (73%) over stoichiometric proportions (67%) can be explained as being due to the same processes which caused Senftleben to obtain no oxygen at all.

Ammonia.—The results on the photochemical and photosensitized decompositions of ammonia are the most important observed in these studies. As can be seen from the table the ratio of the photosensitized to photochemical rates is 200:1, showing that decomposition of ammonia is brought about by energy equivalent to a quantum of wave length 2536.7 Å.

Furthermore, in both types of reaction there is present in the product an excess of hydrogen over stoichiometric proportions (75%). This points to the formation of an intermediate compound such as hydrazine which is removed by the liquid air. The condensate in one of our runs of long duration was tested with a solution of silver nitrate after the ammonia had evaporated off. A black precipitate insoluble in an excess of ammonia was obtained. The reason for the presence of more hydrogen (96%) in the photochemical reaction products than in the photosensitized process (89%) is probably explained by Dickinson and Mitchell[11] who published a note on ammonia decomposition simultaneously with our original report. Using a static system, they obtained these same differences to a greater extent (87 and 70%) and explained them by the clean-up effect shown by hydrogen which has been dissociated by the action of excited mercury. This clean-up would naturally be greater in a static system than in one in which gases were continuously flowing.[12]

These new facts make possible a better conception of the mechanism of the photochemical decomposition of ammonia than has been given heretofore. Warburg[13] measured the quantum yield and found it to be 4 quanta per molecule for light of wave length 2025–2140 Å. Kuhn[14] has made, more recently, a very comprehensive study of the reaction, measuring quantum yields for various temperatures, pressures and wave lengths. Using the same interval of the spectrum as did Warburg, he obtained a yield of 2–2.5 $h\nu$/mol. for 20°. If he increased the temperature, the efficiency of the light rose also, till at 500° the yield was 0.3 $h\nu$/mol. The velocity increased proportionally with the quantum yield, being 9 times as great at 500° as at 20°. This temperature coefficient, which amounts to about 50% for every 100° does not obey the ordinary Arrhenius equation but remains constant with $(K_T + 10)/K_T = 1.05$ over the whole range studied. The reaction is independent of the pressure between 5 mm. and 900 mm. Using only the line at 2063 Å. he found that the quantum yield decreased to 10 $h\nu$/mol. He showed, further, that the reaction rate became smaller as the decomposition proceeded, due apparently to the hydrogen formed, which has a very strong retarding effect on the reaction. Nitrogen was without effect. From these facts he derived a mechanism which not only does not account for the intermediate

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[11] Dickinson and Mitchell, *Proc. Nat. Acad. Sci.*, **12**, 692 (1926).

[12] The presence of larger percentages of hydrogen in our reaction products than in those of Dickinson and Mitchell is probably due to our use of a flowing method. In a static system the intermediate products would remain in the illuminated zone and would be further decomposed to nitrogen and hydrogen, while in a flowing system they are immediately removed from the illuminated area and condensed in the traps.

[13] Warburg, *Sitzb. preuss. Akad. Wiss.*, **1911**, 746; **1912**, 216.

[14] Kuhn, *Compt. rend.*, **177**, 956 (1923); **178**, 708 (1924); *J. chim. phys.*, **23**, 521 (1926).

product found by us, but which is also impossible according to the latest available values for the heats of dissociation of hydrogen and nitrogen.

Kuhn assumed that following the absorption of a quantum by a molecule

$$NH_3 + h\nu \longrightarrow NH_3'$$

the activated molecule might return to the normal state by reëmission or react according to one of the following equations

$$NH_3' \longrightarrow N + H + H_2$$
$$NH_3' + NH_2 \longrightarrow N_2 + 3H_2$$

However, the first of these is endothermic to the extent of 63,000 cal., if we accept the values of 260,000 cal. and 100,000 cal. for the heats of dissociation of nitrogen and hydrogen. He further suggests that the reason for the high quantum yields at elevated temperatures is the formation of hydrogen and nitrogen by this reaction

$$H + NH_3 \longrightarrow N + 2H_2$$
$$N + NH_3 \longrightarrow N_2 + H_2 + H$$

This is in direct contradiction to his explanation of the slowing up of the reaction in the presence of hydrogen, which he says is caused by the activated ammonia molecules dissociating hydrogen molecules by collisions of the second kind

$$NH_3' + H_2 \longrightarrow NH_3 + 2H$$

The fact that the quantum of 112,000 cal. will decompose ammonia shows that there is necessary no additional activation other than the absorbed quantum which is equivalent to 128,000 cal. The molecules reacting have the same energy as the average energy of all the molecules. This is further demonstrated by the fact that the temperature coefficient remains constant. The explanation of the low quantum yield by assuming reëmission of the light by some of the molecules before reaction can take place does not agree with the independence of the reaction of any pressure change. If such were the case, a lowering of the mean free path 180 times, which corresponds to a pressure change from 5 to 900 mm., should affect the reaction. The proportionality of the rise in quantum yield and the increased velocity also indicate that every absorbing molecule reacts.

From these considerations we have been led to suggest a mechanism which, while not entirely satisfactory, is in better accord with all the data available. After the absorption

$$NH_3 + h\nu \longrightarrow NH_3' \qquad (1)$$

every activated molecule undergoes an initial reaction. This may occur in either of two ways

$$NH_3' + NH_3 \longrightarrow N_2H_4 + H_2 \qquad (2)$$
$$NH_3' \longrightarrow NH_2 + H \qquad (3)$$

If (3) were the process occurring, the amino group would then react either with an ammonia molecule or a hydrogen molecule, if any were present.

$$NH_2 + NH_3 \longrightarrow N_2H_4 + H \qquad (4)$$
$$NH_2 + H_2 \longrightarrow NH_3 + H \qquad (5)$$

While exact thermal data are of course unavailable on Reactions (4) and (5), it is quite probable that they will go.[15]

It is to be observed that these reactions would result in little or no pressure change and so would not be measured in the quantum yields. The decomposition of hydrazine would determine the measured reaction. This might occur photochemically, thermally or both. The sudden drop in yield to 10 $h\nu$/mol. when a narrower band of spectrum is used points to the inability of hydrazine to absorb these wave lengths. The deficiency of the yield at low temperatures would be due to the reversal of Reaction (4). The increased yield and velocity with rising temperature might be due to a faster decomposition of the hydrazine preventing this reversal, or to a more rapid recombination of hydrogen atoms, which would be effective in the same way. In connection with the latter, it is of interest that the value of the temperature coefficient corresponds to the increase in collision frequency. A more detailed treatment of this phase of the reaction is not feasible, however, with the evidence on hand.

It may be pointed out that Reaction (5) and the reversal of (4) would account for both the slowing up of the reaction with time and the large retarding effect of admixed hydrogen.

There are several difficulties with this mechanism. It does not account for the fact observed by Warburg that hydrogen does not affect the reaction at low temperatures, nor is the maximum quantum yield of two in accord with Kuhn's value of three for high temperatures. However, there is no alternative explanation which fits the sum total of the data as well as this one, which is certainly a step in the right direction.

An attempt was made to show the presence of hydrazine after illumination of ammonia by the hydrogen discharge tube already described. It was hoped that absorption bands would appear which would differ from those of ammonia. We were, however, unable to detect any change in the absorption spectrum of ammonia after illumination for fifteen minutes.

In the course of this work it was observed that instead of a single band at 2260 Å., as reported by Leifson,[16] there were two distinct bands. Measurements showed them to extend from 2266–2262 Å. and from 2262–2259 Å. (Fig. 5). The next band toward lower wave lengths, which marks the beginning of the series of bands described by Leifson as extending down to 1500 Å., begins at 2254 Å. It was not possible to distinguish the exact limits of the interval separating the two bands and so the center was recorded. A densitometer curve of one of the plates is given in Fig. 6.

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[15] See Taylor, *Proc. Roy. Soc. (London)*, **113A,** 85 (1926).

[16] Leifson, *Astrophys. J.*, **63,** 73 (1926).

Ethylene.—The resulting products from the decomposition of ethylene (H_2, 88%; C_2H_2, etc., 12%) bear out in general the conclusions already advanced concerning the decomposition of this substance. The appearance of hydrocarbons in the gas phase after cooling in liquid air, however, seems to indicate that there are reactions occurring other than a pure dehydrogenation. There is a possible explanation of this in that any ethane formed, and also ethylene, would exert a constant, small vapor pressure at liquid-air temperatures and be burned by the copper oxide. In support of this is the fact that we were never able to burn these products to less than 0.3 mm. pressure, even with liquid air surrounding the trap.

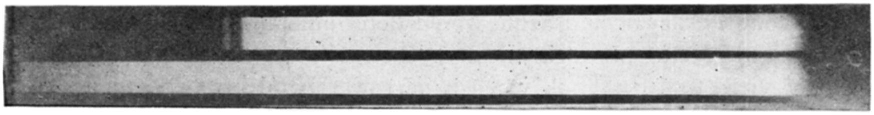

Fig. 5.

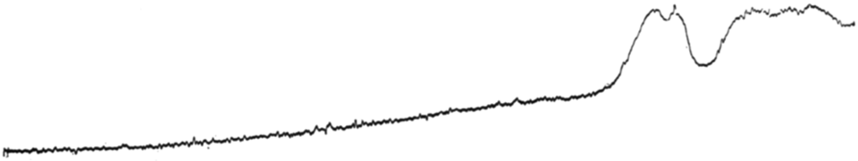

Fig. 6.

Ethyl and Methyl Alcohols.—The decomposition of the alcohols takes place through the intermediate formation of the aldehydes. Tests for acetaldehyde and formaldehyde were given by the products condensed in the liquid-air traps. While ethyl alcohol was apparently more easily decomposed, the ratio of the photosensitized to photochemical decomposition was greater in the case of methyl alcohol.

Hexane.—Hexane showed the largest divergence between the photosensitized and photochemical rates. Here again the process seems to be one of dehydrogenation, with only a small amount of hydrocarbon appearing in the gas phase.

Benzene.—While the pressure of the gaseous products is here the lowest obtained (0.3 mm.), it does not necessarily hold that this is due to the inefficiency of the excited mercury atoms in decomposing this substance. A heavy, tarry residue is deposited on the reaction vessel and a strong odor of diphenyl is present. If the reaction brought about by the mercury is one of dehydrogenation, as it is in most of the cases, it is evident that a hydrogen atom must be split off, since each carbon has but one hydrogen attached.

$$Hg' + C_6H_6 \longrightarrow Hg + C_6H_5 + H$$

The probability of two hydrogen atoms recombining before reacting with a benzene molecule is extremely small, which would account for the small amount of gas formed. The appearance of such large proportions of hydrocarbons (40%) can be accounted for only upon the assumption that, in addition to dehydrogenation, a mercury atom, by transferring the energy, can also bring about a complete rupture of the benzene ring.

Formic Acid.—The decomposition of formic acid can take place in two ways

$$HCOOH \longrightarrow H_2O + CO \qquad (1)$$
$$HCOOH \longrightarrow H_2 + CO_2 \qquad (2)$$

Ramsperger and Porter[17] have shown that on illumination with a hot arc 64% of the decomposition occurs according to (1). Our results show, with the excited mercury, 76%. This is of much interest since it proves that the same quantum of energy transferred by a mercury atom can decompose a molecule in two ways. This cannot be due to the photochemical reaction, since the latter is only 0.25% of the total reaction, and we get 24% going according to (2). There are two means whereby the mercury atom may accomplish this "two type" decomposition. It may involve a steric effect of the collision of the mercury atoms and the molecule, or it may be that the energy, once transferred, is distributed in different ways among the vibrational degrees of freedom and thus brings about two kinds of reactions. Some evidence as to which is the case is being sought in this Laboratory at the present time by illumination of formic acid with monochromatic light. If both types of reaction still occur, it is purely a matter of the distribution.

Acetone.—This substance is so photosensitive itself that only a twofold increase in velocity was observed. In the photosensitized reaction, however, the product condensing in the liquid-air trap had a yellow color which was absent in the purely photochemical reaction.

Ethylamine.—This is another example of the type of reaction exhibited by ammonia. An intermediate compound is formed, giving a large excess of hydrogen in both types of decomposition.

Summary

1. A new type of cooled mercury arc for use in mercury sensitized and general photochemical reactions has been described.

2. By increasing the energy input into a high-pressure hydrogen discharge a continuous ultraviolet spectrum to 1900 Å. can be obtained and recorded with short exposure.

3. Ethylene condenses under the influence of excited mercury atoms with an initial rise in pressure. This does not occur by the action of light alone. The initial rise is due to the formation of acetylene and hydrogen and is regulated by the diffusion of these products from the zone of the excited mercury atoms.

4. Acetylene is polymerized by both excited mercury atoms and by ultraviolet light. Acetylene cannot be hydrogenated by hydrogen activated by excited mercury.

5. Hydrogen peroxide, formed in the mercury photosensitized reaction between hydrogen and oxygen, can be obtained as the sole product under certain conditions.

6. Water, ammonia, ethylene, ethyl and methyl alcohols, benzene, hexane, formic acid, acetone and ethylamine are decomposed by excited mercury atoms.

7. The decomposition products of ammonia show an excess of hydrogen over stoichiometric proportions. A mechanism is advanced for the photochemical decomposition of ammonia based on this and other data. The absorption spectrum of ammonia has been studied.

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[17] Ramsperger and Porter, THIS JOURNAL, **48**, 1267 (1926).

8. Excited mercury atoms can decompose a formic acid molecule in two ways.

PRINCETON, NEW JERSEY

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

THE MAGNETIC SUSCEPTIBILITIES OF THE POSITIVE IONS OF VANADIUM

BY SIMON FREED

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The view of Lewis[1] that the magnetic moments associated with the electrons in atoms or molecules usually neutralize each other in pairs has been confirmed by magnetochemical observations and by the analyses of spectra.[2,3,4] No atom or molecule containing an odd number of electrons is known to be diamagnetic.[5] However, there are numerous examples of paramagnetic atoms and molecules which contain an even number of electrons. Aside from the oxygen molecule, all such cases are to be found toward the centers of the long periods of the Periodic Table. The ions of vanadium investigated here occur in the first of these periods.

Hund's[6] remarkable success in arriving at the magnetic moments of the ions of the rare earths in solution, from spectroscopic information alone, has raised the hope that the electronic configurations of all ions in solution might be determined and that an insight into their behavior might be obtained from spectroscopic data and the quantum theory.

A word should be said upon the relation of spectra to magnetic moments. In the evaluation of spectral lines it has been found possible to assign definite quantities of angular momentum to the electron (or electrons) in each orbit. The angular momentum of an electron is intimately related to its magnetic moment. More recently, the electron itself is pictured as spinning and the ratio in Bohr units of its magnetic moment to its mechanical moment is two. In general, the ratio between the magnetic moment and the resultant mechanical moment is some simple rational fraction, a value deduced in each case from observations on the anomalous Zeeman effect.

Hund[6] supposed that the regularities found in the spectra of other ions existed in the spectra of the rare earths. This assumption led him to

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[1] Lewis, THIS JOURNAL, **38**, 762 (1916); "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., New York City, **1923**.

[2] Lewis, *Chem. Reviews*, **1**, 231 (1925).

[3] Kemble, "Molecular Spectra in Gases," p. 304, *Bul. Nat. Res. Council*, **1926**, No. 57.

[4] Sommerfeld, "Three Lectures in Atomic Physics," Methuen and Co., London **1926**, Lecture III.

[5] Taylor and Lewis, *Proc. Nat. Acad. Sci.*, **11**, 456 (1925).

[6] Hund, *Z. Physik*, **33**, 855 (1926).