solutions of iodine in these solvents does not result in a discharge of the iodine color. Unlike chlorine and bromine, therefore, iodine does not combine directly with the halogenoid under the specified conditions.

Addition of solid iodine to a concentrated aqueous solution of sodium azido-dithiocarbonate results in the immediate separation of a heavy, black oil.

Iodine reacts at once with silver azido-dithiocarbonate suspended in chloroform with formation of silver iodide. The filtrate is found to contain no iodine, however, unless this reagent has been used in excess. Therefore, no union of iodine with azido-carbondisulfide may be assumed to take place. The reaction of the substances in chloroform appears to follow a course similar to that of the reaction between iodine and sodium azido-dithiocarbonate in aqueous solution, and may be expressed by the equation

$$I_2 + 2AgSCSN_3 = 2AgI + (SCSN_3)_2$$

Summary

Solid azido-carbondisulfide reacts explosively with chlorine and bromine. In certain non-aqueous solvents more controllable reactions take place, with probable formation of the compounds $ClSCSN_3$ and $BrSCSN_3$. Bromine reacts with silver azido-dithiocarbonate in ether to form a tribromo-azido-dithiocarbonate, Br_3SCSN_3, and in chloroform and carbon tetrachloride to form a mixture of the monobromo and tribromo compounds. The extreme instability of these compounds precludes their exact analysis and description.

Iodine forms no compound with azido-carbondisulfide under the conditions investigated.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

HYDROGEN PEROXIDE FORMATION PHOTOSENSITIZED BY MERCURY VAPOR

BY ABRAHAM LINCOLN MARSHALL

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This paper represents an effort to clear up some of the uncertain points in the photochemical combination of hydrogen and oxygen when sensitized to λ 2536.7 Å. from a cold mercury arc by means of mercury vapor. In a previous paper[1] this reaction was studied in a static system and the rates of reaction observed at that time were not at all reproducible. It was found, however, that for individual experiments the rate of reaction was best represented by the equation

$$\frac{d}{dt}(H_2O) = K\left(\frac{p_{H_2}}{p_{H_2} + p_{O_2}}\right)$$

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[1] Marshall, *J. Phys. Chem.*, 30, 34 (1926).

It was found that in practically all the experiments the reaction came to an end at a point corresponding within the experimental error to that calculated on the basis of the reaction $H_2 + {}^1/_2O_2 = H_2O$. Also, with gas mixtures of composition $2H_2 + O_2$, the rate-time curves were linear over the whole range of the reaction, which stopped abruptly when all the gas had combined. On the basis of this and a previous investigation, it was suggested by Taylor[2] and Marshall[1] that the reaction involved hydrogen peroxide as an intermediate product, the postulated mechanism being

$$Hg' + H_2 = 2H + Hg$$
$$H + O_2 = HO_2$$
$$HO_2 + H_2 = H_2O_2 + H$$

with subsequent decomposition of the hydrogen peroxide vapor by a variety of processes of which one was undoubtedly the oxidation of mercury vapor.[3] That this supposition was correct was shown subsequently by Marshall,[4] who was able to remove quite large quantities of hydrogen peroxide from the reaction system by the use of a streaming method.

In the light of this result, it seemed that a further study of this reaction might bring to light some fresh factors of interest. In the original investigation liquid mercury was always present in the system and was relied on to keep the concentration of mercury vapor constant. The deposition of mercury on the walls of the reaction chamber altered the amount of light entering the system and the presence of liquid mercury made it impossible to determine the real temperature coefficient of the reaction. In the present investigation the gas mixtures were circulated by means of a glass mercury reciprocating pump (H) at a rate of about 250 liters per hour. The gas was saturated with mercury vapor at a known pressure in the saturator (A) before entering the reaction vessel (C). The temperature of the reaction system was controlled by means of the water-bath (E). Hydrogen peroxide was removed from the gas stream by means of a very efficient gas scrubbing bottle (G). A large reservoir (F) which was kept at constant temperature was introduced into the system to control the rate of pressure change which was measured on the manometer (K) and also reduce fluctuations in the manometer due to the motion of the mercury column in the pump (H), which was continually changing the volume of the system within certain limits.

Design of Arc

The design of the quartz mercury arc used in such an investigation is very important as it is essential to obtain constant illumination. In previous work the author has used the regular vertical type of Cooper-Hewitt lab.-arc, cooling the cathode end to a point about 1 cm., above the

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[2] Taylor, *Trans. Faraday Soc.*, **21**, 560 (1926).

[3] Elder and Rideal, *ibid.*, **23**, 550 (1927).

[4] Marshall, *J. Phys. Chem.*, **30**, 1078 (1926).

mercury level. This, however, is unsatisfactory as it is almost impossible to keep the mercury pressure in the arc constant. An improved type of arc (B) was used in the present investigation, similar to that described by Taylor.[5] The electrodes were made *entirely* of tungsten and it was found possible to carry currents up to 25 amperes without any blackening of the quartz walls of the arc. The arc was connected directly to a mercury diffusion pump which was always kept in operation while the arc was running. The cathode end of the arc was immersed in water (D) which was flowing rapidly over the arc structure; the temperature was controlled within 1° by means of an electric heater. In this manner it was possible to vary the temperature over the range 13–80°.

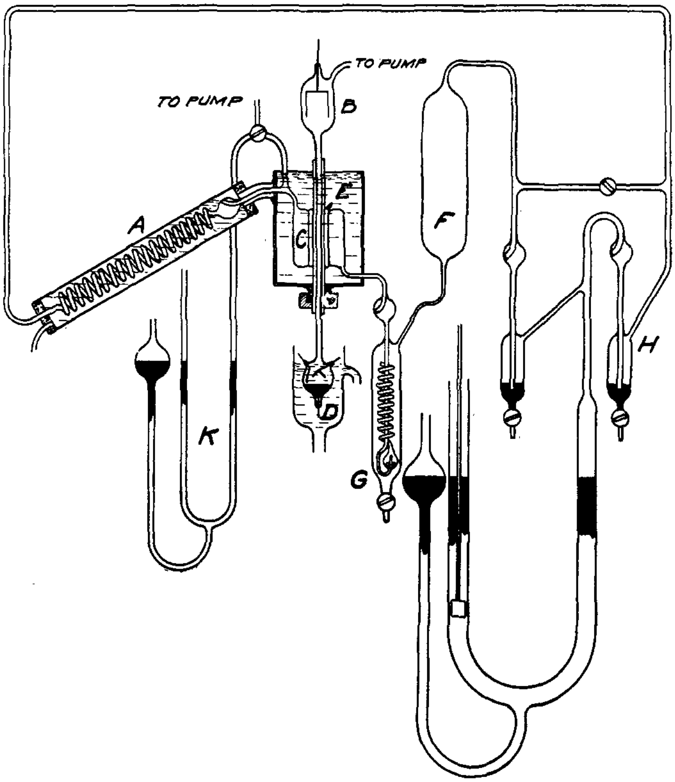

Fig. 1.

Kinetics of Reaction

Table I gives the data for a typical experiment. In subsequent tables the rate will be given for the steady state. It was observed throughout the investigation that during the first five to ten minutes of an experiment

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[5] Taylor, THIS JOURNAL, **48**, 2844 (1926).

the rate was gradually accelerating to a constant value characteristic for the conditions under investigation. It was thought that this might be due to temperature changes in the system caused by heating from the arc and to the fact that the arc has to operate for some time before reaching a steady state.

Table I

Data for Typical Experiment

Temperature of Hg in arc, 30°; temperature of reaction chamber, 67°; gas saturated with Hg vapor at 50°; p_{H_2}, 520 mm.; p_{O_2}, 212 mm.; arc current, 15 amps.

Time	Press., mm.	Δp, mm./min.
0	165	
2	186	10.5
4	215	14.5
5	249	17.0
8	282	16.5
10	318	18.0
13	376	19.4
15	415	19.5
17	454	19.5
19	496	21.0
21	541	22.5
23	593	26.0
Finish	608	

The last column gives the rate of pressure change in mm. per minute.

In this experiment 410 cc. of H_2O_2 gas was formed. Since the total pressure change was 443 mm., the amount of hydrogen peroxide formed would correspond to a volume for the apparatus of 1570 cc. The estimated volume was 1500 cc.; no measurement of this was made, however, as the reservoir was destroyed by an explosion before the experiments were completed. It is certain, however, that the main product of the reaction is hydrogen peroxide.

In Table II are given the data for a series of experiments varying the relative concentrations of the two gases. In the last experiment listed the oxygen concentration was very high and the result is somewhat uncertain since the rate gradually decreased with time; quite large quantities of yellow mercuric oxide were formed in the cell and in the tube leading to the scrubbing bottle, which seriously interfered with rate measurements in the later stages of the experiment. In most of the experiments to be described practically no mercuric oxide deposited in the reaction chamber and only small quantities in the tube leading to the absorber. After each experiment, however, the system was washed out with nitric acid and water to remove any oxide formed.

In all the ensuing experiments the reaction was carried on for a sufficient period to ensure a reliable value for the rate. The fourth column gives a measure of the total amount of reaction, from which the duration of the experiment can be calculated. The fifth column gives the total amount of peroxide formed measured as cc. of gas at 0° and 760 mm. pressure. When the ratio (cc. H_2O_2)/(total pressure change in mm.) falls below 1.10, it indicates that in the later stages of the reaction some of the peroxide initially formed was being decomposed; this always showed in the experiments as a decrease in rate. A value of the ratio of 1.10 corresponds to pure peroxide as the reaction product. The value of the data in these two columns is to indicate the extent to which it is possible to avoid decomposition of the peroxide.

TABLE II

DATA WITH VARYING CONCENTRATIONS OF THE TWO GASES

Gas saturated with mercury vapor at 50°; temperature of reaction chamber, 60°; temperature of mercury in arc, 30°; arc current, 15 amps.

p_{H_2}, mm.	p_{O_2}, mm.	Rate in mm./min.	Total press. change	Cc. of H_2O_2 formed	N_{H_2}	Rate/N_{H_2}
581	237	17–22	443	408	0.79	24.7
740	130	20	236	212	.92	21.7
425	368	12.3	597	326	.58	21.2
146	699	3	106	43	.155	19.9

In Table III the results are given for another series of experiments with an arc current of 1 ampere.

TABLE III

RESULTS WITH ARC CURRENT OF 1 AMPERE

Gas saturated with mercury vapor at 40°; temperature of reaction chamber, 60°; temperature of mercury in arc, 40°; arc current, 1 amp.

p_{H_2}, mm.	p_{O_2}, mm.	Rate in mm./min.	Total press. change	Cc. of H_2O_2 formed	N_{H_2}	Rate/N_{H_2}
581	239	1.52	148	146	0.71	2.14
775	58	2.00			0.93	2.15
781	10	2.1			0.99	2.12
364	475	0.92			0.43	2.14

The constancy of the reaction velocity constants given in the last column of Tables II and III shows that in these experiments the rate of hydrogen peroxide formation is proportional to the mole fraction of hydrogen present.

$$\frac{d}{dt}(H_2O_2) = K\frac{p_{H_2}}{p_{H_2} + p_{O_2}}$$

In the previous investigation[1] using the static system, this same equation was found to hold for the rate of water formation, which seems to indicate that in the previous experiments the rate of decomposition of hydrogen peroxide was of the same order of magnitude as its rate of formation. One of the interesting features of this work is the removal of practically all of the hydrogen peroxide undecomposed.

Variation of Rate with Mercury Concentration

An attempt was next made to study the effect of the various other controllable variables on the rate of the reaction. It was possible to vary the mercury vapor concentration over a twenty-five fold range and the results obtained are listed in Tables IV and V.

TABLE IV

RESULTS WITH VARIABLE MERCURY VAPOR CONCENTRATION

Temperature of reaction chamber, 65°; temperature of mercury in arc, 30°; arc current, 15–15.5 amps.; p_{H_2}, 580 mm.; p_{O_2}, 250 mm.

Temp. of Hg, saturator, °C.	Rate in mm./min.	Total press. change	Cc. of H_2O_2 formed	p_{Hg} in mm.
19	6.3	436	467	0.0013
31	11.8	414	463	
41	16.0	434	449	.006
50	17–22	443	407	
61	18.6	476	417	.03

A later series of experiments with different operating conditions is given in Table V.

TABLE V

LATER RESULTS WITH VARIABLE MERCURY VAPOR CONCENTRATION

Temperature of reaction chamber, 95°; temperature of mercury in arc, 41°; arc current, 3 amps.

Temp. of Hg saturator, °C.	Rate in mm./min.	Total press. change	Cc. of H_2O_2 formed
19	2.93	293	329
31	5.20	391	421
64	5.47	330	250

It was observed that quite large quantities of mercuric oxide were formed in the experiments with high mercury concentrations and the yield of hydrogen peroxide for a given pressure change was much lower, pointing to a considerable amount of decomposition.

Variation of Rate with Mercury Pressure in Arc

A number of experiments were performed varying the temperature of the mercury in the arc and the results are given in Tables VI and VII.

TABLE VI

RESULTS WITH VARIABLE MERCURY ARC TEMPERATURE

Temperature of reaction chamber, 69°; temperature of mercury saturator, 50°; arc current, 3.1 amps.; p_{H_2}, 580 mm.; p_{O_2}, 250 mm.

Temp. of Hg in arc, °C.	17	40	51	87
Rate in mm./min.	2.5	7.5	7.0	2.0

This was all one experiment; the total pressure change was 443 mm. and 417 cc. of H_2O_2 was formed. The next experiment was made without removing any mercuric oxide formed in the previous one.

Temp. of Hg in arc, °C.	40	11	32	40	52
Rate in mm./min.	6.0	2.2	5.6	6.1	5.7

Total pressure change, 502 mm.; cc. of H_2O_2 formed, 293.

It will be observed that in the experiment with the dirty cell the amount of peroxide decomposed was quite large. It may well be that mercuric oxide plays an important role in this decomposition. In Table VII is listed later series of experiments which were performed under better controlled conditions.

Table VII

Later Experiments with Variable Mercury Arc Temperature

Temperature of mercury saturator, 31°; temperature of reaction chamber, 95°; arc current, 3 amps.

Temp. of Hg in arc, °C.	Rate of mm./min.	Total press. change	Cc. of H_2O_2 formed
13	1.40	199	218
29	3.22	221	246
41	5.20	391	420
49	4.66	396	444
61	3.17	403	469
81	1.76	275	326

This indicates that under these conditions the optimum concentration of mercury vapor for securing the largest amount of resonance light is about 0.01 mm.

Variation of Rate with Arc Current

In the next series of experiments the arc current was varied over as wide limits as possible.

Table VIII

Results with Widely Varied Arc Current

Temperature of mercury in arc, 52°; temperature of mercury saturator, 50°; temperature of reaction chamber, 70°; p_{H_2}, 580 mm.; p_{O_2}, 250 mm.

Arc current	25	15	10
Rate	18.2	13.3	12.3

Total pressure change, 464 mm.; cc. of H_2O_2 formed, 327.

The data given in this table were collected in a single experiment and are not so reliable as those in the following table but are included to give a complete record of all the experiments carried out.

Table IX

Results with Widely Varied Arc Current

Temperature of Hg in arc, 42°; temperature of mercury saturator, 31°; temperature of reaction chamber, 95°.

Arc current	Rate	Total press. change	Cc. of H_2O_2 formed
15.5	14.9	337	331
21	20.9	360	371
9.7	11.0	366	395
5	7.75		
3	5.20	391	422

All the data obtained on the variation of rate with arc current are plotted in Fig. 2. It will be observed that in this graph the rate is proportional to the current up to 6 amps. and then commences to diverge from strict proportionality so that at 21 amps. the rate has fallen to two-thirds of that calculated from the 6 amp. rate. It is quite probable that the amount of resonance radiation given by the arc varies in a similar manner with the current, in which case the reaction rate would be proportional to the first power of the light intensity. Measurements are now in progress to check up quantitatively on this part of the problem.

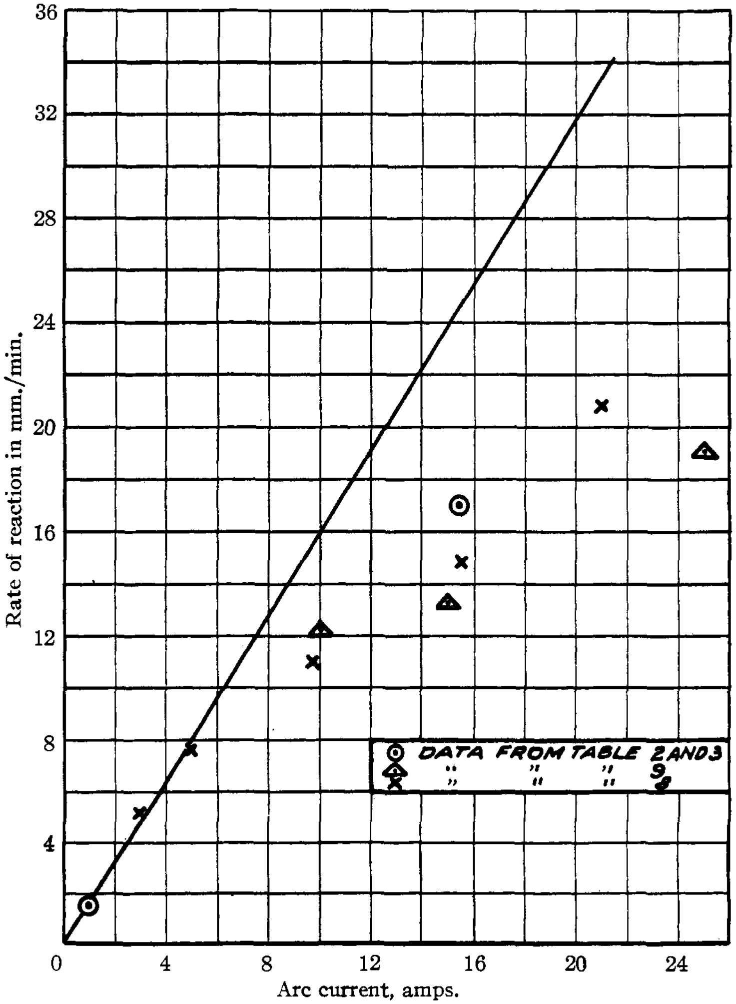

Fig. 2.

True Temperature Coefficient of Reaction

In the first half of this investigation very little difficulty was experienced in obtaining reproducible results, but towards the end it became more difficult and the source of the difficulty was never definitely located. For this reason, the experiments on the temperature coefficient are not as reliable as those given above. They are, however, the average results of a large number of experiments and give the temperature coefficient within a factor of a few per cent. In Table X we have the result of a single experiment while Table XI is the average of a large series.

TABLE X

RESULTS OF ONE EXPERIMENT

Temperature of mercury saturator, 30°; temperature of mercury in arc, 40°; arc current, 3 amps.; p_{H_2}, 598 mm.; p_{O_2}, 241 mm.

Temperature of reaction chamber, °C.	Rate in mm./min.	N_H (average)
96	4.56	0.735
40	3.08	0.783

When these results are calculated for the same mole fraction of hydrogen the temperature coefficient for a 10° rise in temperature comes out as 1.13.

TABLE XI

AVERAGES OF RESULTS

Temperature of mercury saturator, 32°; temperature of mercury in arc, 50°; p_{H_2}, 600 mm.; p_{O_2}, 260 mm.

Temperature of reaction chamber, °C.	Rate in mm./min.		Temperature of reaction chamber, °C.	Rate in mm./min.	
Arc current 15 amps.			*Arc current, 5 amps.*		
100	12.3		100	4.32	
100	10.6		40	3.3	T. C. = 1.044
100	11.8		100	3.80	
50	9.9	T. C. = 1.038	40	3.09	
50	8.8				
100	10.5				
50	9.6				
Averages					
100	11.3				
50	9.4				

From this last series of measurements, it appears that the temperature coefficient is about 1.04. This is the order of magnitude usually found for a true photochemical reaction and if correct seems to indicate that the amount of energy absorbed by the system from the arc is independent of temperature.

Summary

1. The kinetics of the photochemical reaction between hydrogen and oxygen when sensitized by mercury vapor is given by the equation

$$\frac{d}{dt}(H_2O_2) = K\frac{p_{H_2}}{p_{H_2} + p_{O_2}}$$

2. The optimum concentration of mercury vapor for the reaction is about 0.005 mm.; while higher concentrations give a greater rate of re-

action, this is offset by decomposition of the hydrogen peroxide initially formed.

3. The mercury vapor lamp gives the most resonance radiation (λ 2536.7 Å.) with a mercury pressure of about 0.01 mm.
4. The rate of reaction is roughly proportional to the arc current, suggesting that the rate varies as the first power of the light intensity.
5. The temperature coefficient of the reaction is 1.04.
6. The product of reaction is predominantly hydrogen peroxide, the maximum rate of formation observed being two grams per hour.

Schenectady, New York

[Contribution from the Chemical Laboratory of the University of California]

THE SYSTEM $MgSO_4$-H_2O FROM 68 TO 240°[1]

By Homer Louis Robson

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Five hydrates of magnesium sulfate may exist in contact with aqueous solutions of the salt near their boiling points. These are the monoclinic or ordinary hexahydrate, the penta-, tetra-, five-fourths and monohydrates.[2] Of these, the hexahydrate is the stable phase from 48.4[3] to 68° and may be followed up to 100°. The transition point of the hexahydrate to the monohydrate was found by Van't Hoff, Meyerhoffer and Smith[4] to be 68°, and the monohydrate is the stable phase from this temperature up to 240°. They also found the transition of the hexahydrate into the five-fourths hydrate to lie between 68 and 72°[5] and that of the pentahydrate into the tetrahydrate to lie close to 77.5°. The transition

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[1] Part of a thesis submitted to the Faculty of the Graduate Division of the University of California in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Other hydrates of magnesium sulfate are the dodecahydrate prepared by Fritsche (a) (Fritsche, *Pogg. Ann.*, **42**, 577 (1842), see also observations by F. G. Cottrell, mentioned by Van't Hoff, Meyerhoffer and Smith, *Sitzb. preuss. Akad. Wiss.*, **1901**, 1035), the rhombic heptahydrate or epsom salt (b) (for properties see E. S. Larsen, "The Microscopic Identification of the Non-Opaque Minerals," Bulletin 679, U. S. Geol. Survey, **1921**, and Groth, "Chemische Krystallographie," Part 2, **1908**, p. 429), the tetragonal hexahydrate prepared by L. de Boisbaudran (c) (de Boisbaudran, *Ann. chim. phys.*, (4) **18**, 260 (1869)), the monoclinic heptahydrate prepared by Loewel (d) (Loewel, *Ann. chim. phys.*, (3) **43**, 405 (1855); Groth, ref. 2 b, p. 431), and the dihydrate.

[3] Carpenter and Jette, This Journal, **45**, 578 (1923). The rhombic heptahydrate is the stable phase below this temperature.

[4] Van't Hoff, Meyerhoffer and Smith, *Sitzb. preuss. Akad. Wiss.*, **1901**, 1034.

[5] The nearness of this point to that found for the hexahydrate—monohydrate transition caused them to doubt the identity of the five-fourths hydrate (ref. 4, footnote to page 1037).