order to remove any solid radioactive material which might have been carried over, then treating the distillate with excess bromine in carbon tetrachloride, evaporating in a vacuum, and testing the residue with a β-ray electroscope.

With the shutter closed, no change in β-activity could be observed in the tube, and no activity appeared in the trap. Upon opening the shutter and allowing ultraviolet radiation to reach the vapor, still no difference was observed in the tube, but β-activity appeared, with increasing intensity, in the trap. When the tube was heated instead of irradiated at a point some 10 cm. removed from the metal deposit, identical observations as to β-activity were made. The volatile radioactive product formed appeared on subsequent treatment to be inseparable from the unchanged lead tetramethyl frozen with it in the trap.

It may be concluded from this evidence that free methyl groups are produced during the photolysis of lead tetramethyl. Since the β-activity observed is that of radium E, the facts that no decrease in activity was observed in the tube, and that the activity in the trap increased on standing, indicate that radium D was carried over while radium E (a bismuth isotope) was not. Loss in β-activity in the tube due to removal of a portion of the radium D would be slow in appearing. No α-activity tests were made. These experiments could perhaps be carried out in more quantitative fashion by using thorium B rather than radium D, since thorium B and its immediate decomposition products have β-activities and half lives which would make possible direct and immediate observations of the rate of disappearance of the metal in the tube. Applications of the method to the study of free radical production in other photochemical reactions are obvious.

Summary

Continuous absorption in the ultraviolet, producing decomposition into metallic lead and hydrocarbons, has been observed for lead tetramethyl and tetraphenyl. The method of radioactive indicators has been applied to determine quantum yields for lead tetramethyl vapor and for both compounds in solution, and to show the formation of methyl radicals during the photolysis of lead tetramethyl vapor. Short chains, retarded by oxygen, are indicated in the vapor; deactivation or recombination reduces the quantum yield in solutions.

STANFORD UNIVERSITY, CALIF.

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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 521]

The Mercury-Photosensitized Decomposition of Arsine

BY NORWOOD L. SIMMONS AND ARNOLD O. BECKMAN

Introduction

The photochemical and mercury-photosensitized decompositions of ammonia have been studied by many investigators. The photo-decompositions of phosphine have also been studied[1] although reliable quantum yield data are still lacking. The present investigation is concerned with the mercury-photosensitized decomposition of the related compound arsine and the quantum yield for the reaction.

Cheesman and Emeléus[2] have reported that the photochemical decomposition of arsine results in the formation of hydrogen and a brown solid film which deposits on the walls of the reaction vessel and was assumed to be arsenic. Since the continuous absorption of arsine begins at 2390 Å., it is apparent that the sensitized decomposition by mercury atoms activated with 2537 Å. may be investigated without the occurrence of any direct photochemical decomposition.

Experimental Procedure

Arsine was prepared by the action of dilute sulfuric acid on an alloy of arsenic and zinc prepared according to the directions of Cohen.[3] The gaseous arsine was swept by a current of dry nitrogen through drying tubes containing calcium chloride and phosphorus pentoxide into a trap immersed in liquid air. The arsine was purified by repeated distillations *in vacuo* and was stored in a glass bulb at a pressure of about 200 mm. No thermal decomposition during storage was observed. The molecular weight of the gas, as determined by means of the quartz fiber gage attached to the system, agreed closely with the calculated value 77.95 for arsine.

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(1) Melville, *Proc. Roy. Soc.* (London), **A138**, 374 (1932); **A139**, 541 (1933).

(2) Cheesman and Emeléus, *J. Chem. Soc.*, 2847 (1932).

(3) Cohen, *Z. physik. Chem.*, **25**, 483 (1898).

Apparatus and Procedure.—The apparatus was substantially the same as that described by Wenner and Beckman,[4] consisting of a vacuum system including a quartz reaction vessel, quartz fiber gage, McLeod gage and mercury cut-offs suitably placed so that all stopcocks were eliminated from the reaction system. For all experiments other than the quantum yield determinations the reaction cell consisted of a cylindrical quartz vessel with outlet tubes at each end which facilitated the ready removal by volatilization of the arsenic film formed during the decompositions. For the quantum yield determinations the reaction cell was a rectangular vessel fitted with polished plane parallel windows and was attached to the vacuum system through a ground joint so that the cell could be easily detached for the removal of the arsenic film. The ground joint was completely sealed with mercury during the decompositions.

The source of radiation was a water-cooled quartz mercury arc. For the preliminary investigations it was found unnecessary to filter out the short wave length radiation capable of producing direct photochemical decomposition, for experiments showed that the rate of decomposition dropped to less than 0.5% of its initial value when the mercury vapor was removed from the reaction cell by freezing-out with solid carbon dioxide–alcohol mixture, showing that the direct decomposition was negligible in comparison with the sensitized decomposition. For the quantum yield determinations, however, monochromatic radiation of 2537 Å. wave length was obtained by means of a Bausch and Lomb ultraviolet monochromator.

The radiant energy measurements were taken with the aid of two vacuum thermopiles and the continuous recording device previously described. The thermopiles were calibrated by means of Bureau of Standards carbon lamps in the usual manner. All calibrations were frequently checked throughout the investigation.

The usual procedure was to admit arsine into the evacuated reaction cell, measure the pressure, and irradiate the gas for the desired length of time. The condensable constituents of the reaction mixture were then frozen out with liquid air and the pressure of non-condensables was measured. After pumping off the non-condensable gases, the condensables were vaporized and their pressure determined. During all runs mercury vapor was present at the partial pressure corresponding to the prevailing room temperature, which varied from 24 to 27°.

Experimental Results

The Reaction Products.—When arsine, in the presence of mercury vapor, was irradiated with the radiation from the cold mercury arc, a rapid increase in pressure occurred and a brown film was formed on the walls of the quartz reaction cell. After removing the condensable constituents with liquid air, the non-condensable gas was analyzed by means of the quartz fiber gage and found to consist solely of hydrogen, after correcting for the vapor pressure of arsine (approximately 1×10^{-4} mm. at liquid air temperatures). When the solid film was irradiated for long periods of time, no gases or other products were detectable. The film dissolved readily in hot nitric acid and the resulting solution gave characteristic arsenic tests. In one run, after most of the condensable constituents had disappeared, the non-condensables were removed and the remaining condensable material analyzed with the quartz fiber gage. The molecular weight of the material agreed well with that of arsine, showing no gaseous, condensable products formed during the decomposition. At any time during a decomposition, the increase in total pressure was always found to be equal to one-third of the non-condensable gas pressure. (In measuring pressures, an experimentally determined temperature-correction factor was applied when liquid air or solid carbon dioxide surrounded the freezing-out traps.)

It was found that the amount of hydrogen formed was always a little less than the amount which corresponded to the amount of arsine decomposed. The amount of arsine was determined by pumping off the hydrogen and measuring the residual arsine or by subtracting the hydrogen pressure from the total pressure. The two methods checked closely. Table I shows some typical results. In the last column are given the percentage yields of hydrogen as calculated for the reaction $AsH_3 = As + 3/2\ H_2$. The percentage of hydrogen obtained appears to be independent of the arsine pressure, size of reaction vessel, light intensity and the amount of decomposition, with the average value of 95%. These results are similar to those obtained by Melville[1] in the decomposition of phosphine. Whether the loss was due to clean-up on the quartz walls or to adsorption of the arsenic film could not be determined.

TABLE I

YIELD OF HYDROGEN

Initial p_{AsH_3}, mm.	Final p_{AsH_3}, mm.	p_{H_2}, mm.	Yield of H_2, %
0.01475	0.01247	0.00328	95.9
.0359	.00176	.0485	94.7
.0487	.0402	.0119	93.3
.0494	.0023	.0656	92.8
.0880	.0118	.1042	91.2
.1400	.0166	.1752	94.6
.815	.018	1.127	94.3

Recombination of Arsenic and Hydrogen.—When hydrogen and mercury vapor were irradiated in a cell having a film of arsenic on the walls,

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[4] Wenner and Beckman, THIS JOURNAL, 54, 2787 (1932).

with liquid air on the trap, a condensable gas was formed. When the hydrogen was pumped off and the condensable material vaporized and irradiated, it was found to decompose at exactly the same rate as arsine, producing hydrogen in an amount equal to 94.7% of the theoretical yield assuming the substance to be arsine. It appears, therefore, that the excited mercury atoms cause not only the decomposition of arsine into arsenic and hydrogen but produce also the reformation of arsine from these products.

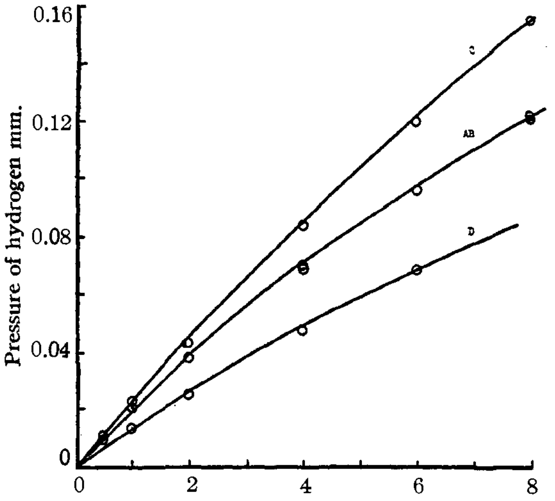

Fig. 1.—Showing dependence of rate of decomposition upon arsine pressure, hydrogen pressure and arsenic film on cell window.

To see what effect the recombination of arsenic and hydrogen would have upon the quantum yield, conditions comparable with those under which the quantum yields were measured were carefully reproduced. With a thin film of arsenic on the window, hydrogen at a pressure of 0.02 mm. was irradiated for twelve minutes with liquid air on the trap. The pressure of arsine formed was found to be less than 0.0001 mm., showing that the recombination is negligible in comparison with the decomposition.

Effect of Arsenic Film.—The thickness of the arsenic film on the walls of the reaction cell had a marked effect upon the rate of decomposition. Even when the film was somewhat transparent to visible light, the rate of decomposition was reduced substantially to zero. That the film of arsenic is very opaque to 2537 Å. was shown by the measurements of the transmitted radiation taken during the quantum yield determinations.

It was of some interest to calculate the minimum thickness of arsenic film which is barely visible to the eye. It was found that the arsenic film formed an image on the front window of the reaction cell corresponding roughly to the cross section of the light beam. Assuming that all of the arsenic formed by the decomposition of the arsine is deposited in this area and that the density of the arsenic is that of the gray form, it was calculated from the experimental data that the thinnest arsenic film visible by either transmitted or reflected light is about 200 atoms thick.

Dependence of Rate upon Pressures of Arsenic and Hydrogen.—Figure 1 shows the effect upon the rate of arsine decomposition of the arsenic film on the window, the pressure of arsine and the pressure of hydrogen. As coördinates are plotted the times of irradiation by the constant-intensity light source and the pressures of hydrogen formed as measured after expansion from the reaction cell into the McLeod gage.

In experiments A and B, arsine (p_{AsH_3} = 4.5 and 13.5 mm., respectively) was irradiated, starting with a clean cell window and allowing the arsenic film to build up during the entire run. Since the two curves coincide, the rate of decomposition is independent of the arsine pressure in this pressure region. The marked inhibitory effect of the arsenic film is shown by comparison of these experiments with experiment C which was performed under similar conditions (p_{AsH_3} = 3.9 mm.) except that the front cell window was heated to volatilize the arsenic film after each reading of the hydrogen pressure and before continuing the irradiation. The slight curvature of curve C indicates that the hydrogen formed during the decomposition exerts a slight inhibitory effect. That the effect is indeed slight is also shown by experiment D, in which the arsenic film left on the window at the end of experiment B was allowed to remain for experiment D. Since the initial slope of curve D is substantially the same as the final slope of curve B, the rate of the decomposition was not appreciably altered by the large amount of hydrogen present at the end of experiment B.

At very low arsine pressures a large excess of hydrogen produces a decrease in the rate of decomposition. Thus, at p_{AsH_3} = 0.07 mm., the addition of 0.40 mm. of hydrogen decreased the rate from 0.00847 to 0.00675 mm. arsine decomposed per minute.

Collisional Diameter of Arsine Molecules.—At very low arsine pressures the rate of decomposition decreases as the result of incomplete deactivation of the excited mercury atoms by collision with arsine molecules. The experimentally determined rates are shown in Fig. 2. By plotting 1/rate against $1/P_{AsH_3}$ a straight line is obtained from which one finds that at $p_{AsH_3} = 0.123$ mm. the rate of decomposition is half the high-pressure rate. Experiments showed that at these low arsine pressures the broadening of the λ 2537 absorption line was inappreciable. If one assumes (a) that none of the fluorescence radiation was reabsorbed, (b) that every collision of an arsine molecule with an excited mercury atom results in deactivation, and (c) that the reaction mechanism remains the same at low as at high pressures, one may calculate the mean collisional diameter, σ_{12}, for the reaction of arsine molecules with excited mercury atoms by equating the mean time between collisions of arsine molecules with an excited mercury atom to the mean life of a mercury atom in the $6\,^3P_1$ state ($\tau = 1.08 \times 10^{-5}$ sec.).[5] The value obtained, $\sigma_{12} = 16.0 \times 10^{-8}$ cm. is very large in comparison with the values for ammonia ($\sigma_{12} = 2.05 \times 10^{-8}$ cm.) and for hydrogen ($\sigma_{12} = 2.93 \times 10^{-8}$) obtained from mercury fluorescence measurements,[6] and indicates that the assumptions which were made are not permissible.

Another calculation of collisional diameters is of interest in connection with the mechanism of the decomposition. From the data given in the preceding section on the decrease in rate of decomposition upon the addition of hydrogen, one may obtain evidence that the products formed by the reaction of hydrogen molecules with excited mercury atoms are capable of decomposing arsine. Since 0.40 mm. of hydrogen added to 0.07 mm. of arsine reduced the rate of decomposition 20%, the relative numbers of collisions of hydrogen and arsine molecules with excited mercury atoms must be in the ratio of 1:4 if one assumes that collisions of hydrogen molecules with mercury atoms do not result ultimately in decomposition of arsine. The relative numbers of collisions are also directly proportional to $p\sigma_{12}^2$ and inversely proportional to the reduced mass of the molecules. Taking $\sigma_{12} = 2.93 \times 10^{-8}$ cm. for hydrogen, one may calculate that for arsine $\sigma_{12} = 75 \times 10^{-8}$ cm. This improbable value indicates that the products resulting from collisions of hydrogen molecules with excited mercury atoms must result in decomposition of arsine.

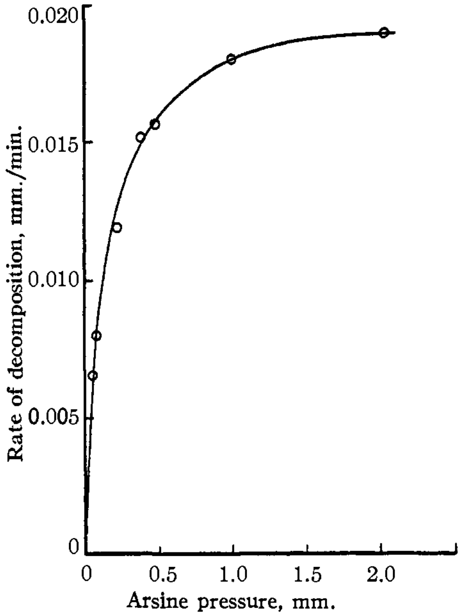

Fig. 2.—Showing decrease in rate of decomposition at low arsine pressures.

Dependence of Rate upon Light Intensity.—The intensity of the radiation was changed by varying the distance between the light source and the reaction cell. The relative intensities were measured by means of a microammeter and a photronic cell placed at the position occupied by the reaction cell. The rate of decomposition was found to vary directly with the intensity of radiation.

Quantum Yield for Arsine Decomposition.—The quantum yield determinations were made at arsine pressures sufficiently high to eliminate fluorescence of the excited mercury atoms. The amount of decomposition was in all cases so small that the hydrogen pressure was insignificant in comparison with the arsine, eliminating deactivation of excited mercury atoms by collision with hydrogen molecules. The recombination of arsenic and hydrogen was shown above to be negligible. The remaining disturbing factor, namely, the arsenic film on the cell window, could not be eliminated, so that to obtain the true quantum yield for the decomposition it was necessary to extrapolate the observed apparent quantum yields obtained with varying amounts of decomposition to the point of zero decomposition.

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[5] Garrett, *Phys. Rev.*, **40**, 779 (1932).

[6] Mitchell and Zemansky, "Resonance Radiation and Excited Atoms," The Macmillan Co., New York, 1934, p. 204.

The experimental data are shown in Table II.

TABLE II

QUANTUM YIELD DATA

p_{AsH_3}, mm.	Time of irradiation, sec.	Molecules AsH_3 decomposed $N \times 10^{-15}$	Quanta absorbed $N \times 10^{-15}$	*Mean no.* As atoms on window $N \times 10^{-15}$	Apparent quantum yield
3.5	1800	5.69	7.19	10.74	0.792
7.5	1080	4.20	4.37	5.24	.962
12.0	1080	5.87	8.96	14.97	.653
20.0	600	3.42	3.37	1.62	1.012
20.0	2400	9.00	10.15	12.87	0.886
20.0	1830	8.42	8.46	5.02	.995
21.0	900	5.61	8.31	9.52	.675
21.0	1080	4.33	11.40	47.34	.381
21.0	1080	6.75	10.18	13.19	.662
21.0	1800	9.05	10.04	4.30	.902
25.0	900	4.57	3.88	6.14	1.176
40.0	1200	5.25	7.10	9.72	0.739
40.0	2700	12.40	18.87	23.01	.655
40.0	2400	7.96	13.61	32.65	.584
54.0	1080	6.29	8.55	10.89	.735
59.0	720	5.81	6.13	2.77	.949
59.0	750	4.98	6.09	6.90	.818
59.0	720	4.10	5.77	11.21	.711
59.0	600	4.17	4.30	1.99	.973
97.0	1080	10.50	12.00	5.00	.877
109.0	1080	7.65	11.73	20.03	.653

The number of arsine molecules decomposed in each run was calculated from the equation $N_{AsH_3} = 2\tilde{N}PV/(3RT \times 0.95)$ where $\tilde{N}$ is Avogadro's number, P is the pressure of hydrogen, and V is the effective volume of the system as determined experimentally by the expansion of a known amount of hydrogen with liquid air on the traps as in the quantum yield runs. The factor 0.95 corrects for the deficient hydrogen yield as noted above.

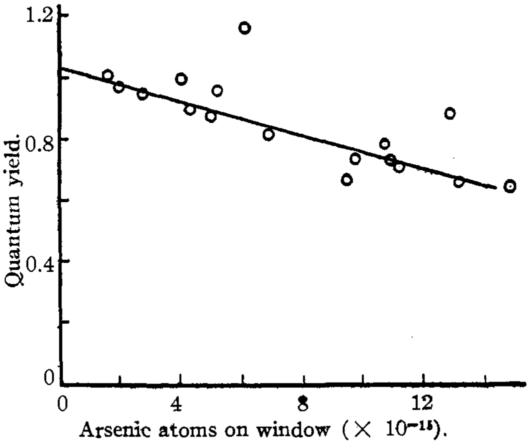

Fig. 3.—Showing dependence at apparent quantum yield upon the arsenic film on the cell window.

The number of quanta absorbed was calculated as the difference between the number of quanta entering and leaving the reaction mixture

$$N_Q = \frac{1.29\,\tau\,(\beta D_R - D_T)}{f^2\,hc/\lambda} = 2.29 \times 10^{11}\,\tau\,(\beta D_R - D_T)$$

where 1.29 is the number of ergs per second of radiation required for unit deflection of the transmission thermopile galvanometer, τ is the time of irradiation, β is the ratio of transmission thermopile galvanometer deflections to the reflection thermopile galvanometer deflections when the cell is empty (*i. e.*, free from both arsine and mercury vapor). D_R and D_T are the galvanometer deflections for the reflection and transmission thermopiles; f is the experimentally determined transmission factor for the cell windows for λ 2537 Å. (f = 0.853).

In Fig. 3 the apparent quantum yields are plotted as ordinates with the mean number of arsenic atoms on the cell window as abscissas. By extrapolation of the apparent quantum yields to the point of zero decomposition, the true quantum yield is found to be 1.03. This value is thought to be accurate within 5%.

Discussion

Cario and Franck[7] have assumed that the collision of an excited mercury atom in the 6 $^3P_1$ state with a hydrogen molecule results in the formation of two hydrogen atoms. If this assumption is correct, the experimental result that the presence of hydrogen does not appreciably alter the rate of arsine decomposition may be explained by a mechanism of the following type:

$$Hg + h\nu = Hg' \quad (1)$$

$$Hg' + AsH_3 = AsH_2 + H + Hg \quad (2a)$$

$$Hg' + H_2 = H + H + Hg \quad (2b)$$

$$H + AsH_3 = AsH_2 + H_2 \quad (3)$$

$$AsH_2 = As + H_2 \quad (4)$$

However, since the quantum yield is two for the above reactions, other reactions must take place which lead either to the reformation of arsine or to products incapable of decomposing arsine.

$$H + AsH_2 = AsH_3 \quad (5)$$

$$H + H = H_2 \quad (6)$$

There appears to be no simple explanation why reactions (5) and (6) should necessarily occur at just the proper rate to reduce the quantum yield to unity, particularly over the wide pressure range of the experiments. One suspects that the unit

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[7] Cario and Franck, *Z. Physik*, 11, 161 (1922).

quantum yield is not fortuitous and that the above mechanism may be incorrect.

The experimental results may be simply explained if one assumes that the collision of a hydrogen molecule with an excited mercury atom results not in the formation of two hydrogen atoms as assumed by Cario and Franck[7] but in the formation of one hydrogen atom and a mercury hydride molecule, as postulated by Compton and Turner.[8]

The evidence in favor of this postulate has been summarized by Mitchell and Zemansky.[9] Upon this basis one may write for the mechanism of the arsine decomposition:

$$h\nu + \text{Hg} = \text{Hg}' \qquad (7)$$

$$\text{Hg}' + \text{AsH}_3 = \text{AsH}_2 + \text{H} + \text{Hg} \qquad (8)$$

$$\text{Hg}' + \text{H}_2 = \text{HgH}' + \text{H} \qquad (9)$$

$$\text{HgH}' + \text{AsH}_3 = \text{AsH}_2 + \text{H}_2 + \text{Hg} \qquad (10)$$

$$\text{AsH}_2 = \text{As} + \text{H}_2 \text{ (wall)} \qquad (11)$$

$$\text{H} + \text{H} = \text{H}_2 \quad \text{(wall)} \qquad (12)$$

This mechanism is in agreement with the experimental results of unit quantum yield and a rate of decomposition which is directly proportional to light intensity and is independent of the pressure and hydrogen and arsine in the pressure region where deactivation by fluorescence does not occur. The very slight inhibitory effect of hydrogen may be due to a slight wall reaction between the mercury hydride molecules and hydrogen atoms.

The reaction between atomic hydrogen and arsine is not included in the above mechanism. From an energy standpoint, hydrogen atoms should be capable of dissociating arsine. Whether or not the reaction actually occurs is a matter which has not been settled experimentally. Bonhoeffer[10] has shown that arsine is formed by the reaction of arsenic with hydrogen atoms produced in a discharge tube. The fact that an arsenic coating was formed on the walls of the apparatus during the reaction might be interpreted as evidence that some of the arsine was subsequently decomposed by the hydrogen atoms. However, from the meager information which was given, the arsenic coating may be explained equally well in other ways, such as direct vaporization of arsenic as a result of the high surface temperature produced by the action of the hydrogen atoms on arsenic, dissociation of unstable intermediates as AsH or AsH_2, or direct photochemical dissociation of arsine by the absorption of radiation from the hydrogen discharge tube. The fact that Bonhoeffer recovered arsine after the arsine molecules had traveled some distance through the apparatus in the presence of hydrogen atoms indicates that the decomposition of arsine molecules by hydrogen atoms is a slow reaction, if it occurs at all. For the above mechanism it is not necessary to assume that hydrogen atoms are incapable of dissociating arsine. It is necessary only to assume that the rate of this reaction is small in comparison with the rate of reaction 12. This assumption appears to be entirely reasonable.

Summary

1. The mercury-photosensitized decomposition of gaseous arsine corresponds to the stoichiometric equation $\text{AsH}_3 = \text{As} + 3/2\ \text{H}_2$. About 5% of the hydrogen disappears during the reaction, presumably by clean-up on the walls of the reaction cell. An arsenic film forms on the cell window during the decomposition.
2. The rate of decomposition is directly proportional to the intensity of the radiation and is independent of the arsine pressure at high pressures. At low pressures the rate is decreased on account of the fluorescence of activated mercury atoms.
3. The decomposition is very slightly inhibited by hydrogen.
4. Recombination of arsenic and hydrogen occurs with the formation of arsine, but the rate is negligibly slow in comparison with the rate of decomposition of arsine.
5. The quantum yield for the decomposition is 1.03 ± 0.05 molecules of arsine decomposed per quantum of λ 2537 Å. radiation absorbed.
6. A mechanism for the decomposition is proposed.

PASADENA, CALIFORNIA RECEIVED DECEMBER 9, 1935

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(8) Compton and Turner, *Phil. Mag.*, **48**, 360 (1924).

(9) Mitchell and Zemansky, "Resonance Radiation and Excited Atoms," The Macmillan Co., New York, 1934, p. 77.

(10) Bonhoeffer, *Z. physik. Chem.*, **113**, 205 (1924).