THE MERCURY-SENSITIZED PHOTOCHEMICAL DECOMPOSITION OF ARSINE

THESIS BY

NORWOOD L. SIMMONS

In Partial Fulfillment of the Requirements

for the Degree of Master of Science

California Institute of Technology, Pasadena, California

1935

THE MERCURY-SENSITIZED PHOTOCHEMICAL DECOMPOSITION OF ARSINE

Considerable work has been done on both the mercury-sensitized and the simple photo-decomposition of ammonia. The behaviour of phosphine in both cases has likewise been studied (1). The quantum yields of the direct decompositions have been determined but no reliable data on the quantum yields in the sensitized reactions have been obtained. In the mercury-sensitized decomposition of both substances, a strong inhibition of the rate by atomic hydrogen was reported. In this investigation the mercury-sensitized decomposition of arsine has been studied, and the quantum yield of the reaction determined.

It has been observed (2) that the photochemical decomposition of arsine resulted in the deposition of a solid brownish-black film on the reaction cell window. This film was not examined, but was assumed to be arsenic. Hydrogen was also formed in the decomposition. Continuous absorption was found to begin at 2390 Å when the arsine was at one atmosphere pressure. Therefore, by eliminating the shorter wave lengths, it is possible to study the mercury-sensitized decomposition with little or no simultaneous direct decomposition.

Preparation of Pure Arsine

Arsine was prepared by the action of dilute sulfuric acid on an alloy of arsenic and zinc. This alloy was prepared according to the directions of Cohen (3). Gaseous arsine was swept by a current of nitrogen (previously passed through concentrated sulfuric acid) through a long calcium chloride tube and through a phosphorus pentoxide tube into a trap immersed in liquid air. The generating flask was then closed off, and the trap and a one-liter storage bulb attached to it were evacuated. The arsine was purified by repeated distillation, the first and last portions in every case being rejected. It was then brought into the storage bulb with liquid air and kept under a pressure of about 200 mm. mercury. The amount of thermal decomposition at room temperature was negligible, a pressure of hydrogen of less than 1×10^{-3} mm. building up in the storage bulb over a period of a few days.

The molecular weight of the arsine at low pressures was determined by means of a quartz-fibre gauge, designed and calibrated as described by Beckman (4). The results of these determinations are given in Table I.

Table I

Molecular Weight of Gaseous AsH_3

p (mm.$\times 10^3$)	$p\sqrt{MW} \times 10^3$	M	Average Deviation
2.87	24.8	74.6	7.3
5.02	47.3	88.7	6.8
5.79	52.6	82.4	0.5
	Average:	81.9	4.9

This agrees with the calculated value for AsH_3 of 77.95.

Apparatus and Procedure

The apparatus used was essentially the same as already described by Wenner and Beckman (5). The salient features are a quartz reaction vessel, a quartz-fibre gauge, a McLeod gauge, and mercury cut-offs so placed that the entire system during a run was bounded by glass and mercury. For all work other than the quantum yield measurements, a cylindrical quartz reaction vessel was used. This vessel was 2 cm. in diameter, 10 cm. long, and equipped with graded-seal outlets at both ends. This was to enable getting rid of the arsenic film by simply opening one end of the cell directly to the pumps and torching the arsenic out and into a liquid air trap. For the quantum yield measurements a cell made up of flat plates of quartz was used which was attached to the rest of the system by a quartz-pyrex ground joint to enable removal of the arsenic when necessary. During all runs this joint was covered by a mercury column. Monochromatic light of wave length 2537 Å was obtained by the use of a water-cooled quartz mercury-vapor lamp with a magnet attached so as to deflect the arc and a monochromator and lens system as already described. A blast of cold air blown through the front slit of the monochromator onto the face of the lamp was found to increase the amount of 2537 Å light several fold. The thermopile system and continuous recording device used has already been described. The transmission thermopile was calibrated against a Bureau of Standards lamp. The ratio of the galvanometer deflections for the two thermopiles was obtained with the cell emptied of all mercury vapor. The ratio was checked several times during the course of the investigation.

The procedure for the ordinary runs consisted of measuring the pressure of arsine either in the entire system with the McLeod gauge or in the reaction cell manometrically with the mercury cut-off, freezing out the arsine in the reaction-cell trap, closing the cut-off between the cell and the remainder of the system, illuminating the gas and mercury vapor, freezing out the remaining condensible gases, expanding the non-condensibles, measuring their pressure on the McLeod gauge, and pumping off, and, finally, expanding the condensible gases and measuring their pressure. During all runs, a concentration of mercury vapor equivalent to its vapor pressure at room temperature prevailed. No attempt was made to control this more accurately, as all the light effective in producing activation is absorbed in the first few millimeters of mercury vapor.

The Reaction Products

When arsine in the presence of mercury vapor was illuminated with the full radiation from the mercury arc, a pressure increase occurred and a brown film deposited on the quartz cell walls. That no direct decomposition was taking place was proven by freezing out all the mercury vapor in a solid carbon dioxide-alcohol trap between the cut-off and the cell and illuminating. The amount of decomposition was less than 0.5% of the amount when mercury vapor was present. After an appreciable increase in pressure had occurred, liquid air was applied and the non-condensible gas formed expanded into the entire system and its molecular weight measured with the quartz-fibre gauge after correcting for the vapor pressure of arsine, which is approximately $1x10^{-4}$ mm. at liquid air temperatures; the value obtained showed the gas to be hydrogen. When the solid film alone was illuminated for long time intervals no gas formed. It dissolved readily in hot, concentrated nitric acid and the solution gave the characteristic arsenic tests. A film of the solid was examined under a polarizing microscope. It was found to be isotropic. It dissolved in boiling water very slowly, but the solution did not give a precipitate with silver nitrate or with hydrogen sulfide, so that it is quite likely the arsenic was in the colloidal state (6). In one run after most of the condensible gas had disappeared, a portion of the remainder was expanded into the whole system, and its molecular weight found to be that of arsine. During a run, at any time, the gain in pressure was always found to be equal to one-third the non-condensible gas pressure. All pressures measured with liquid air on a trap are corrected by the necessary factor as determined separately. A series of runs was made to determine the percentage yield of hydrogen produced, assuming that the arsine decomposes according to the equation:

$$AsH_3 = As + \frac{3}{2} H_2$$

Table II gives some typical results.

Table II

Yield of Hydrogen

Initial pressure of AsH_3 (mm)	Final pressure of AsH_3 (mm)	Pressure of H_2 formed (mm)	Percentage yield of H_2
0.815	0.018	1.127	94.3%
0.0880	0.0118	0.1042	91.2
0.1400	0.0166	0.1752	94.6
0.0487	0.0402	0.0119	93.3
0.01475	0.01247	0.00328	95.9
0.0494	0.0023	0.0656	92.8
0.0359	0.00176	0.0485	94.7

The final pressure of arsine could be measured directly by pumping off the hydrogen for one-half minute. The loss of arsine under these conditions was negligible, as found by experiment. The experimental set-up allowed all the hydrogen to be removed in a very short time of pumping. It could also be obtained by difference between final total pressure and pressure of hydrogen. The two methods checked. The percentage of hydrogen formed seems to be fairly independent of pressures, vessel size (both vessels already described were used in these runs), light intensity, and amount of decomposition. The values are in agreement with those obtained on phosphine by Melville. There was some evidence obtained which indicated that most of the lost hydrogen was adsorbed by the arsenic film. However, this was not conclusive, and there was found to be considerable clean-up of monatomic hydrogen alone in a clean quartz vessel.

Recombination of As and H_2

When H_2 and mercury vapor were illuminated in the cell containing a film of arsenic on the walls, and liquid air on the cell trap, a condensible gas was formed. In order to see if this gas were arsine, it was freed from hydrogen and a portion of it decomposed. It decomposed at practically the same rate as the ordinary arsine and the hydrogen formed was 94.7% of the theoretical amount, which proves that it is arsine. In order to get some idea of the rate of recombination, hydrogen was introduced into the cell, which had an appreciable amounts of arsenic on the walls, and illuminated without liquid air on the trap. The results of two such experiments at pressures of H_2 of 0.04825 mm. and 1.127 mm. gave ratios of H_2 to AsH_3 of 35:1 and 63:1 when the final pressures after 15 or 20 minutes illumination, were measured. That this ratio is greatly dependent on the amount of arsenic on the windows was proven by an experiment in which the conditions of a quantum yield run were reproduced as nearly as possible, except that no arsine was initially present. A pressure of hydrogen of 0.02 mm was put into the cell, which had a small amount of arsenic on the windows (about 10×10^{15} atoms, compare with quantum yield runs), and illuminated for 12 minutes, with liquid air continually on the trap. The pressure of arsine formed was $<$ 0.0001 mm, which gives a ratio of hydrogen to arsine of $>$ 200:1.

Inhibition of the Rate by an Arsenic Film

After several runs had been made without cleaning the cell, it was noticed that the rate was extremely slow. A pressure of 0.4 mm of arsine was illuminated in the cell for 75 minutes and no hydrogen was formed, although the film was not completely opaque to visible light. That the film is exceedingly opaque to 2537 Å light was proven by measurement of the transmitted radiation with the thermopiles. Using the density of grey arsenic, 5.73, and knowing the total number of arsenic atoms on a definite area of the windows, from the amount of decomposition and the surface exposed, the thickness of the arsenic film when it could barely be seen by visible light was found to be 200 atoms. Further data on the decrease of the rate by the arsenic will be given in the quantum yield experiments.

Dependence of the Rate on Pressures of Arsine and Hydrogen

Some difficulty was first encountered in getting reproducible results in the rate experiments, but the lamp current was controlled with a voltage regulator, and it was then found that duplication could be achieved within one or two percent.

The results of a series of runs, in which the pressure of arsine was varied, the amount of H_2 present was varied, and the amount of arsenic on the windows was varied, is presented in Figure I. For all curves, the pressure of H_2 formed is plotted against the time. The pressure of H_2 formed was measured in the entire system, by expanding after each reading, whereas the arsine was always kept in the cell, so that the pressures of H_2 read off the curves are not the pressures of hydrogen prevalent in the reaction cell during the intervals.

An examination of the curves shows that the rate is independent of the pressure of arsine in the region 4.5 - 13.5 mm, that the arsenic film has a much stronger inhibitory effect than the hydrogen, that the effect of hydrogen on the rate is very slight. Curve number five should coincide with curve number three, if the above arguments hold. The explanation for its failure to do so is that not all the activated mercury atoms were being deactivated by molecular collision. Figure number two corroborates this. In this curve, the rate of decomposition in mm/min. is plotted as a function of the arsine pressure. Not until an infinitely large arsine pressure is reached does complete deactivation of excited mercury atoms by arsine molecules occur, but the increase in the rate is negligibly small after a pressure of about 2 - 3 mm is reached. There is a slight spurious effect due to the differing amounts of arsenic on the windows, in the value of the rates in Figure 2, but as the arsenic was removed after each run, and the

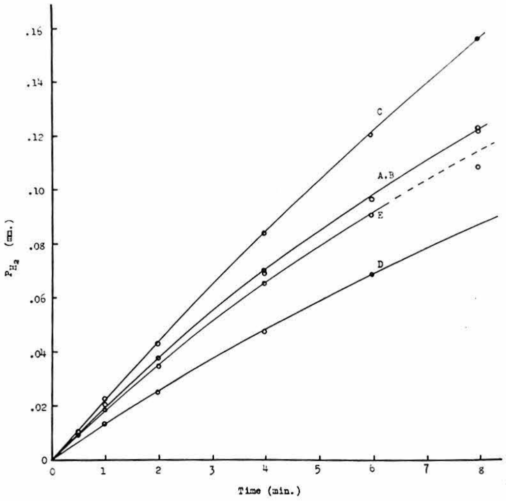


Figure 1. Showing Inhibition of Decomposition by Arsenic film on Cell Window and by Hydrogen.

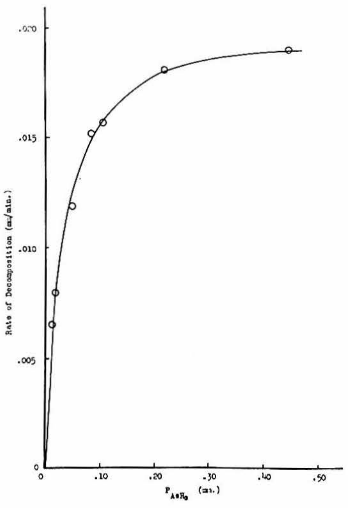
Curve A: Starting with no arsenic on window. P_{AsH_3} = 4.5 mm.

Curve B: Starting with no arsenic on window. P_{AsH_3} = 13.5 mm.

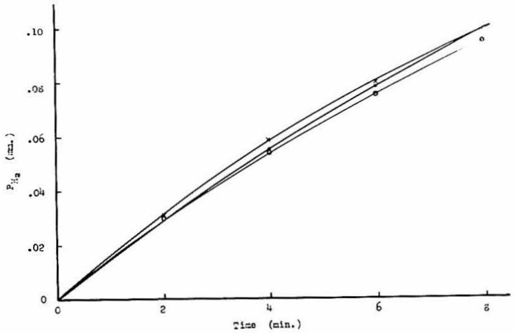
Curve C: Starting with no arsenic on window; arsenic torched off window after each reading. P_{AsH_3} = 3.9 mm.

Curve D: Starting with arsenic from Run B on cell window. P_{AsH_3} = 4.1mm.

Curve E: Starting with no arsenic on window; arsenic torched off window after each reading. P_{AsH_3} = 0.6 mm.



<u>Figure</u> <u>2.</u> Showing dependence of rate upon arsine pressure.



<u>Figure</u> <u>3.</u> Showing dependence of rate upon hydrogen pressure.

P_{AsH_3} = 4.5 mm. in each run. Starting with no arsenic on cell window. Arsenic left on cell window during the run.

Upper curve: H_2 left in cell during run.

Middle curve: H_2 pumped off after each reading.

Lower curve: Starting with 0.1 mm H_2. Hydrogen left in cell during run.

effect of hydrogen is very slight, the rates as given are easily within a few percent of the true initial rates. If 1/R is plotted against $1/P_{AsH_3}$, a reasonably straight line is obtained, and it may be seen that the pressure of AsH_3 at which $R = \frac{1}{2} R_\infty$ is 0.123 mm. That there is theoretical justification for a straight line will be pointed out. If we assume that every collision between excited mercury and arsine results in decomposition of arsine and a deactivation of mercury, as is indicated by the quantum yield of unity, and also that every collision between excited mercury and hydrogen molecules results in deactivation of the mercury, then a comparison of this value, 0.123 mm with Stuart's (7) value of 0.2 mm of hydrogen as the pressure necessary to reduce fluorescence of excited mercury to one-half, should yield information as to the ratio of the collision diameters of arsine and hydrogen.

Figure 3 gives the results of three consecutive experiments, with light conditions and arsine pressure the same, showing the small effect hydrogen has on the rate. Again, the amount of hydrogen formed is plotted against time. The experiments were run in the order of enumeration. Another typical experiment illustrating the effect of hydrogen was the illumination of a small pressure of arsine in the presence of a large amount of hydrogen. This run was bracketed by two runs on arsine alone at the same pressure, and the same light intensity. The results are given in Table III.

Table III

Inhibitory Effect of Hydrogen

P_{H_2} at start	P_{AsH_3} at start	P_{AsH_3} at end	P_{AsH_3} decomposed
0	0.0707	0.0536	0.0171
0.4	0.0714	0.0579	0.0135
0	0.0707	0.0539	0.0168

The time of illumination in each run was two minutes.

An attempt was made to compare the inhibition of the arsine decomposition by hydrogen with that of ammonia in the sensitized decomposition by hydrogen, but as the ammonia could not be handled in the system at low enough pressures, this was given up. However, it was observed that under the same conditions, the rate of the arsine decomposition was about 20 times as fast as that of the ammonia. These rates were measured at high pressures of both gases, so that inappreciable fluorescence of mercury was occurring.

Proportionality of the Rate to Light Intensity

That the rate is a linear function of the light intensity (light absorbed) was proven by varying the distance of the light source from the reaction cell, and measuring the rate of decomposition and the intensity of the incident radiation. The entire radiation of the arc was used in these, as in all previous experiments. The intensities were measured by means of a Weston photronic cell and microammeter, the cell being put in the same position as the reaction vessel before and after each rate run. In order for the effect of the arsenic film to cancel out, the same amount of decomposition was carried out in all runs. The intensity was varied four-fold.

Table IV

The Rate as a Function of the Light Intensity

Experiment No.	Intensity in Microamperes	Rate$\times 10^2$; mm. Hg formed per minute	Rate of formation of $H_2 \times 10^2$ per minute per microampere	Relative Rates (relative to average)
3	9.6	1.26	0.1312	1.034
5	11.5	1.62	0.1413	1.113
2	18.7	2.23	0.1192	0.940
4	34.5	4.15	0.1203	0.948
1	39.5	4.83	0.1223	0.964

Quantum Yield of the Reaction

In order to obtain a quantum yield that is characteristic of the reaction

$$Hg^{*} + AsH_3 = As + \frac{3}{2} H_2 + Hg$$

it is necessary to eliminate all other factors that influence the amount of light absorbed and the amount of decomposition. These include recombination of atomic hydrogen with arsenic on the walls, deactivation of excited mercury atoms by hydrogen, inhibition of the rate by the arsenic film, and fluorescence of excited mercury atoms. All these effects were eliminated quite simply. In all quantum yield runs, only a very little decomposition was allowed to take place. As already pointed out, under the conditions obtaining in these runs, the amount of recombination of arsenic with atomic hydrogen is negligible, even when liquid air is kept on a trap and there is only the hydrogen present. In all runs the ratio of arsine pressure to the mean pressure of H_2 during the run was $>$ 300:1 and usually about 1000:1, so that the ratio of collision between excited mercury and arsine to that between excited mercury and H_2 is exceedingly large. All pressures worked with were high enough so that no appreciable fluorescence of excited mercury occurred. The inhibition of the rate by the arsenic film could not be eliminated during a run, so that a plot of apparent quantum yield against the mean value of arsenic atoms on the window during each run is necessary to give us the true quantum yield at zero arsenic on the window. That the effect of the arsenic was simply a diminution of light transmitted was proved by experiments done on the empty cell with and without arsenic on the windows.

Table V gives the data obtained in the quantum yield runs. In the 5th column is given the number of molecules of arsine decomposed, calculated from the equation

$$N_{AsH_3} = \frac{2 \; N P_{H_2} \; V}{3 \; RT \times 762.9 \times 0.95}$$

where N is the Avogadro number, P_{H_2} is the pressure of hydrogen measured in mm. of mercury at room temperature, V is the effective volume of the system determined experimentally by hydrogen expansion with liquid air on the trap exactly as in the quantum yield measurements. The value 762.9 is the equivalent of 1 atm. in mm. of mercury at 25° C. The above equation may be derived from the perfect gas law and the consideration that every molecule of arsine yields 95% of the theoretical 3/2 molecule of H_2.

Table V

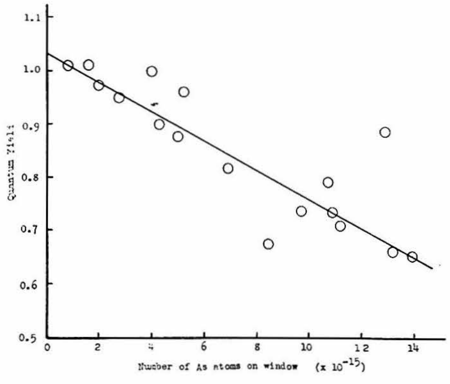
Quantum Yield Data - Photosensitized Arsine Decomposition

Run No.	p_{AsH_3} (mm)	Temp. (°K)	Exposure Time (sec)	Molecules AsH_3 Decomposed ($\times 10^{-15}$)	Galv. Defl. D_T	Galv. Defl. D_R	Quanta Entering ($\times 10^{-15}$)	Quanta leaving ($\times 10^{-15}$)	Quanta Absorbed ($\times 10^{-15}$)	Apparent Quantum Yield	Av. No. As Atoms on wall ($\times 10^{-15}$)
1	59	297	720	5.81	8.6	9.35	7.55	1.42	6.13	.949	2.77
3	59	297.5	750	4.98	7.6	8.8	7.39	1.30	6.09	.818	6.90
4	59	297	720	4.10	6.55	8.5	6.85	1.08	5.77	.711	11.21
6	54	297.5	1080	6.29	6.55	8.4	10.17	1.62	8.55	.735	10.89
8	21	298	900	5.61	15.0	11.3	11.39	3.08	8.31	.675	9.52
9	12	298	1080	5.87	16.1	10.7	12.94	3.98	8.96	.653	14.97
10	21	297	1080	4.33	9.2	11.3	13.67	2.27	11.40	.381	47.34
11	97	298	1080	10.50	5.7	11.1	13.41	1.41	12.00	.877	5.00
12	21	298	1080	6.75	13.7	11.2	13.56	3.38	10.18	.662	13.19
13	109	297	1080	7.65	4.4	10.6	12.82	1.09	11.73	.653	20.03
14	59	298	600	4.17	9.0	9.7	5.53	1.23	4.30	.973	1.985
15	25	298	900	4.57	12.3	7.5	6.41	2.53	3.88	1.176	6.14
16	20	298	600	3.42	15.75	9.7	5.53	2.16	3.37	1.012	1.62
17	7.5	298	1080	4.20	15.7	7.55	7.75	3.88	4.37	.962	5.24
18	40.0	298	1200	5.25	7.8	8.1	9.24	2.14	7.10	.739	9.72
19	21.0	300	1800	9.05	8.4	7.9	13.50	3.46	10.04	.902	4.30
20	20.0	300	2400	9.00	8.5	6.5	14.81	4.66	10.15	.886	12.87
21	40.0	300	2700	12.40	6.0	8.8	22.57	3.70	18.87	.655	23.01
22	40.0	300	2400	7.96	4.3	7.0	15.97	2.36	13.61	.584	32.65
23	20.0	298	1830	8.42	12.2	7.8	13.56	5.10	8.46	1.000	4.02
24	3.5	299	1800	5.69	13.3	7.4	12.66	5.47	7.19	.792	10.74

Quantum Yield Data - Photosensitized Ammonia Decomposition

Run No.	p_{NH_3} (mm)	Temp. (°K)	Exposure Time (sec)	Molecules NH_3 Decomposed ($\times 10^{-15}$)	Galv. Defl. D_T	Galv. Defl. D_R	Quanta Entering ($\times 10^{-15}$)	Quanta Leaving ($\times 10^{-15}$)	Quanta Absorbed ($\times 10^{-15}$)	Quantum Yield
25	143	298.5	7260	1.60	1.3	4.9	33.80	2.16	31.64	0.051
26	101	298.5	7260	1.235	3.6	9.15	61.26	5.81	55.45	0.022
27	76	300	9600	1.35	2.8	6.8	62.00	6.14	55.86	0.024

Note: The volume of the system was 145.9 cc for Run 1 and 113.57 cc for all subsequent runs. The ratio of galvanometer deflections D_T/D_R was 4.90 for Runs 1 to 13 inclusive and 4.16 for all subsequent runs.



<u>Figure 4.</u> Showing extrapolation of apparent quantum yields to obtain true quantum yield for the decomposition.

The number of light quanta apparently entering the cell during a run may be calculated from the equation

$$Q_E = \frac{\beta \times D_R \times 1.29 \times t}{T^2 \quad hc/\lambda}$$

where β is the ratio of the galvanometer deflections for the transmission thermopile to that of the reflection thermopile when the cell is empty (of both arsine and mercury vapor). D_R is the deflection of the reflection thermopile. The factor 1.29 is the number of ergs per second of radiation falling on the vane of the transmission thermopile for unit deflection. This value was obtained by calibration against a standard lamp, and is accurate to within 2%. t is the time of irradiation. T is equal to the transmission factor of the back window of the cell and the window of the thermopile for radiation λ 2537 Å, and T^2 (transmission of both surfaces) has a value of 0.728. The number of light quanta leaving the reaction mixture is given by the expression

$$Q_L = \frac{D_T \times 1.29 \times t}{T^2 \quad hc/\lambda}$$

where D_T is the deflection of the transmission thermopile. By subtracting one expression for Q_L from that for Q_E there is obtained an expression for the total number of quanta absorbed by the reaction mixture during the run:

$$Q_A = \frac{(\beta D_R - D_T) \times 1.29 \times t}{T^2 \quad hc/\lambda}$$

$$= 2.286 \times 10^{11} \times (D_R - D_T) \times t \text{ quanta.}$$

D_T is the amount of light not absorbed by the mercury vapor, or, in other words, light coming through the monochromator other than the center of the λ 2537 Å line. That all effective radiation is absorbed by the mercury vapor has been proven by the interposition of thin layers of mercury vapor in front of the reaction cell, in which case no reaction took place. The reason for D_T being somewhat larger for the lower arsine pressures is thought to be due to pressure broadening of the absorption curve by the higher arsine pressures, so that more light becomes effective. The same thing was observed with ammonia. Of course, D_T changes greatly with changes in the condition of the lamp, all other factors being constant.

It will be seen from Table V and Figure 4 that the quantum yield is independent of pressure from 10 to 100 mm pressure. The extrapolated curve gives a value for the true quantum yield at 24° - 27°C of 1.02. This value is thought to be accurate within 5%. No attempt was made to thermostat the cell in these runs, but it is unlikely that the temperature coefficient is large enough to change the yield much from 24°C to 27°C.

Experiments were made to see if any of the H_2 formed were occluded or adsorbed by the relatively large amounts of arsine on freezing down. No loss in H_2 due to this cause was found. The actual volume of the cell used for quantum-yield runs was 9.25 cc, and the converging light beam was passed through the center of the cell. At the end of a run, the arsine was frozen out, the H_2 expanded into the entire system and its pressure measured with all cut-offs at correct positions. The volume of the system for all but the first run was 113.57 cc. The pressure of H_2 was always corrected for the vapor pressure of arsine, which was taken as 1 x 10^{-4} at liquid air temperatures.

Table VI

Pressure Broadening of the Absorption Curve of Hg Vapor for λ 2537 Å

Pressure AsH_3 in cell (mm)	Ratio D_T/D_R	Relative amounts of radiation transmitted
0.0	1.435	1.000
6.0	1.317	0.918
115.0	0.394	0.274
NH_3 in cell		
0.0	2.09	1.000
8.0	1.56	0.746
86.0	0.381	0.182

In the above runs, mercury vapor was always present. Runs were made continuously, so that lamp conditions were constant. The reason for zero pressure readings of D_T/D_R in arsine and ammonia runs not checking is that the lamp was not the same in the two series of runs. However, fractional decreases of the ratio are comparable. It is seen that the effect is more pronounced with ammonia than with arsine. In the experiments with ammonia a visible blue fluorescence was observed in the front of the reaction cell. This fluorescence has been analyzed by Mitchell (8). This fluorescence persisted at the front wall of the cell even after opening to the vacuum pump for 15 minutes, which is evidence for the strong adsorption of ammonia on quartz.

Discussion

Of the many possible mechanisms for the photosensitized decomposition of arsine, the following are of interest:

1\. $Hg + h\nu = Hg'$

2\. $Hg' + AsH_3 = AsH_2 + H + Hg$

3a. $AsH_2 = As + H_2$

3b. $AsH_2 + AsH_2 = 2As + 2H_2$

4\. $H + H = H_2$

and

1\. $Hg + h\nu = Hg'$

2\. $Hg' + AsH_3 = AsH + H_2 + Hg$

3\. $AsH + AsH = 2As + H_2$

Both mechanisms are in agreement with the experimental results of a quantum yield of unity which is independent of the intensity of radiation and independent of the arsine pressure in the pressure region where deactivation by fluorescence does not occur. The first mechanism may be preferable, for the pressure of hydrogen atoms in the reaction mixture is indicated by the hydrogen clean-up which lowers the H_2 yield to 95% of the theoretical amount. It does not appear likely that a sufficient amount of atomic hydrogen would be formed by the direct reaction of hydrogen molecules with activated mercury atoms to account for the observed clean-up, since the H_2 pressure in the quantum-yield runs was always extremely small in comparison with the arsine pressure.

Summary

1. The mercury-photosensitized decomposition of gaseous arsine has been studied. The reaction corresponds to the stoichiometric equation

$$AsH_3 \quad = \quad As \ + \ \frac{3}{2} H_2$$

About 5% of the hydrogen produced disappears during the reaction, presumably the result of clean-up on the walls of the reaction vessel.

2. The rate of decomposition is directly proportional to the intensity of the radiation and is independent of the arsine pressure in the region 4.5 to 13.0 mm. At lower pressures the rate progressively decreases on account of increasing deactivation of the activated mercury atoms by fluorescence.

3. The decomposition is slightly inhibited by hydrogen and strongly inhibited by the arsenic film which forms on the cell windows as a result of the decomposition.

4. Recombination of arsenic and hydrogen occurs with the formation of arsine but the rate of recombination is negligibly slow in comparison with the rate of decomposition of arsine.

5. The quantum yield for the mercury-photosensitized decomposition of gaseous arsine is 1.02 ± 0.05 molecules of arsine decomposed per quantum of λ 2537 radiation absorbed.

6. Rough determinations of the quantum yield for the mercury-photosensitized decomposition of gaseous ammonia show a yield of 0.02 - 0.05 molecules of ammonia decomposed per quantum of λ2537 radiation absorbed.

Acknowledgement

The author wishes to express his thanks and appreciation to Professor A.O. Beckman, under whose supervision this research was done, for his advice and assistance during the course of the investigation.

References

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

(2) Cheesman and Emeleus, Jour. Chem. Soc., 1932, 2847.

(3) Cohen, Zeit. phys. Chem., 25, 483 (1898).

(4) A.O. Beckman, J. Opt. Soc. Am., 16, 276 (1928).

(5) Wenner and Beckman, J. Am. Chem. Soc., 54, 2787 (1932).

(6) Berichte, 58, B, 99 (1925).

(7) Stuart, Z. Physik, 32, 262 (1925).

(8) Mitchell, J. Am. Chem. Soc., 49. 2699 (1927).