

NEW LIGHT ON THE NATURE OF THE PHOTODECOMPOSITION OF AMMONIA

Thesis by  
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In Partial Fulfillment of the Requirements  
for the Degree of Doctor of Philosophy

California Institute of Technology  
Pasadena, California

1936

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## INTRODUCTION

Although the photodecomposition of ammonia was one of the first photochemical reactions to be carefully studied, and the initial investigation of Warburg<sup>1</sup> has been followed by many others, the nature of the reaction has remained in doubt. The results of the various investigations are summarized in Table 1.

It will be seen that several investigators obtained as products only hydrogen and nitrogen in 3 : 1 molal ratio, and a quantum yield of about .25 mols of ammonia decomposed per quantum absorbed. Others obtained higher hydrogen to nitrogen ratios, and still others found hydrazine in varying amounts. In this work, evidence is presented which makes possible a reconciliation of some of the apparently conflicting data, and which sheds new light on the nature of the decomposition.

The present investigation includes a study of the reaction products and determination of the quantum yields, for both the direct photochemical decomposition of ammonia, and for the mercury sensitized decomposition. The limits of the amount of decomposition have also been greatly extended; in some cases the partial pressure of the non-condensable products was only .0001 mm. of mercury.

TABLE 1

SUMMARY OF PREVIOUS INVESTIGATIONS  
(PHOTOCHEMICAL UNLESS OTHERWISE NOTED)

Date	Investigator	Press. NH <sub>3</sub> , mm.	% H <sub>2</sub> in non-cond. products, H <sub>2</sub> + N <sub>2</sub>	N <sub>2</sub> H <sub>4</sub> yield	Quantum yield	Minimum amt. prod. (in % H <sub>2</sub> determ.) mm. x 10 <sup>3</sup>
1911	Warburg <sup>1</sup>	45 - 900			0.25	
1926	Kuhn <sup>2</sup>	5 - 800			0.2 - 0.5	100
1926	Dickinson & Mitchell <sup>3</sup>	0 - 1	70(sensi- tized) 87(direct)	small amt.		5
1927	Bates and Taylor <sup>4</sup>		89(sensi- tized) 96(direct)	small amt.		40
1931	Koenig and Brings <sup>5</sup>	250		small amt.		
1931	Gedye and Rideal <sup>6</sup>	44		0 - 57% of NH <sub>3</sub> decomp.		
1931	Wiig and Kistia- kowsky <sup>7</sup>	0 - 760	~ 75		0.24	15
1933	Ogg, Leigh- ton and Bergstrom <sup>8</sup>	1 - 9 atm.	~ 75		0.14	
1935	Wiig <sup>9</sup>	0 - 900	75		0.10 - 0.33	20

## MATERIALS AND APPARATUS

The ammonia was taken from commercial cylinders. The gas was completely soluble in water, and was found to be free of hydrazine and hydroxylamine and practically anhydrous. It was drawn under vacuum into a storage bulb containing some pellets of C. P. potassium hydroxide, and was purified of fixed gases by repeatedly freezing it out in a trap cooled by liquid air and pumping off the non-condensibles. Several samples of ammonia from different sources were used during the course of the investigation with completely concordant results.

The apparatus employed has been, for the most part, previously described<sup>10</sup>. A vacuum system of Pyrex glass was used to contain the gases and to measure quantitatively the gaseous products of the decomposition. This system included fore- and mercury vapor diffusion pumps, MacLeod gage, quartz fibre gage, a reaction cell of quartz (attached to the rest of the system by means of a quartz-Pyrex graded seal), a storage bulb for the ammonia, and several stopcocks and mercury cut-offs. These cut-offs were so placed that the gases being studied could be confined by them away from grease in an all glass (and quartz) system consisting of the reaction cell and the two measuring gages. These instruments could also be separated from one another by mercury cut-offs.

The direct decomposition of ammonia was studied with the aid of a high-voltage condensed spark between aluminum electrodes. They consisted of .25 in. aluminum rods, the ends of which were turned down to a diameter of .17 in. to aid in concentrating the spark. The electrodes were provided with circulating water coolers made of copper tubing. The separation of the electrodes was 2 - 6 mm., and the spark

was blown out by a blast of air. Energy for the spark was supplied by a 10 kw. transformer which operated at 220 - 13,000 volts. A .1 mf. condenser was placed in parallel with the spark.

A water-cooled mercury arc lamp was used as the source of the resonance radiation at  $2537 \text{ \AA}$ . It operated on a direct current of about 4 amperes, and was mounted on the iron core of an inductance coil through which the operating current was made to flow. By this means the lamp was prevented from going out, and at the same time the discharge was concentrated by being deflected toward the front wall of the lamp. A filter was used with the lamp to remove radiation below  $2400 \text{ \AA}$ . It was a glass container with quartz windows, filled with 25% acetic acid.

Vacuum thermopiles and sensitive galvanometers were used to measure radiation in the experiments on quantum yield. The thermopiles had quartz windows attached with sealing wax, and were kept evacuated by a fore-pump and a diffusion pump operating on Apiezon oil. A quartz prism monochromator was used to isolate the line desired. The light leaving the rear slit of the monochromator was refocused on the vane of one of the thermopiles by means of two cylindrical quartz lenses. The quartz cell was inserted in the light path between the cylindrical lenses and this (transmission) thermopile,  $T_t$ , which therefore received the light transmitted by the cell. In order to find the variation in intensity of the light source, the front window of the cell was attached at an angle of about  $45^\circ$ , and the light it reflected was caught at one side by the vane of the second (reflection) thermopile,  $T_r$ . A continuous recording device was used to obtain the variation of light intensity with time. The carriage was driven by a Telechron clock, and supported a sheet of photographic paper on which the galvanometer deflections were printed.

## EXPERIMENTAL METHOD

Since the products measured were very small in amount, it was essential to keep the system thoroughly outgassed. This was achieved by keeping the pumps running almost continuously during the progress of the investigation. It was then found that the all-glass portion of the system, when separated from greased stopcocks by the mercury cut-offs, would retain almost indefinitely a vacuum too small to be measured on the MacLeod gage ( $<10^{-6}$  mm.).

In experiments to determine the composition of the gaseous products obtained from the irradiation of ammonia, a sample of ammonia was purified by freezing it out repeatedly in a series of traps cooled by liquid air, and each time pumping off the non-condensable gases. The final purification was affected in a portion of the all-glass system. The MacLeod and quartz fibre gages were cut off during this operation. The ammonia was then illuminated by either the mercury lamp or the condensed spark. It was then frozen out again in a trap and the pressure and composition of the non-condensable products measured by the combined use of the MacLeod and quartz fibre gages. These products were assumed to contain only hydrogen and nitrogen; and it has been shown<sup>11</sup> that this method of analysis gives accurate results with such mixtures. The quartz fibre gage was frequently calibrated.

Quantum yields were measured by an absolute method. First the quartz plate intended for the front window of the cell was mounted in the approximate position it was later to occupy in the completed cell, and with the monochromator in position, the ratio of the deflections of the two galvanometers determined for the wave length desired. Then the quartz plate intended for the rear window of the cell was put in

the position it was to occupy, and the operation repeated. The quotient of the two ratios thus obtained gave the transmission of the rear window to light of this wave length. The transmission of the window of the thermopile  $T_t$  had been found in like manner.

Next the monochromator and cell windows were removed, and the sensitivity of the transmission thermopile was found at four different light intensities by means of standardized carbon lamps furnished by the Bureau of Standards. The completed plane-sided cell was then mounted in position in front of the thermopile, and the calibration repeated. The quotient of the deflections in the two cases gave the transmission of the cell to the light of the standard lamps, and the values thus obtained could be used in further calibrations made at intervals after the cell had been attached to the vacuum line.

In each experiment on quantum yield, the ratio of monochromatized light transmitted to that reflected was first determined with an empty cell. The purified ammonia was then admitted, and a continuous photographic record taken during the run of the light intensities transmitted and reflected. After the run was over, the ammonia was frozen out again and the pressure and compositions of the products determined as before. Calibrations of the quartz fibre gage were alternated with quantum yield runs, using hydrogen admitted to the system through a palladium tube heated by a gentle gas flame. Blanks were also run, in some of which the shutter of the monochromator remained closed throughout the experiment. In others, the shutter was opened as usual, but the ammonia was kept frozen out. When the thermopiles were in use the room was darkened, and in addition they were further protected from stray light by completely covering them with a black box, in which only the necessary apertures were cut.

A few other experiments of a special nature are described later.

## EXPERIMENTAL RESULTS

Products of the Photochemical Decomposition: The rate of decomposition was higher, the greater the pressure of ammonia, up to about 20 mm. Upon analysis with the quartz fibre gage, the non-condensable products were all found to contain more than 75% hydrogen; this was particularly true when only very small amounts of ammonia were decomposed. Figure 1 illustrates the variation in composition with the amount of gaseous products, starting from the smallest amounts on which accurate data could be obtained (about .001 mm.). It will be noticed that the composition ranges from that of almost pure hydrogen, when very little decomposition is allowed to take place, to somewhat over 75% hydrogen, when larger amounts of ammonia are decomposed.

This result is different from those obtained by previous investigators. Most of them worked, however (see Table 1), with much larger quantities of products. Nor could it be due to some easily reduced impurity in the ammonia, as was shown in the following experiment. 13 mm. of ammonia were put into the cell, purified of fixed gases, and illuminated for 20 min. When the ammonia that was left was frozen out, the pressure of the non-condensable gases was .8 mm., a pressure much larger than those obtained in the other experiments. As expected, these gases were found to contain practically 75 % hydrogen (73.8%). They were then pumped off and the ammonia allowed to distill back into the cell. When illuminated again for a few seconds and then frozen out, the pressure of the non-condensable gases was .0012 mm., and they were once more found to contain more than 75 % hydrogen (81.3%). This type of experiment was repeated several times with similar results.



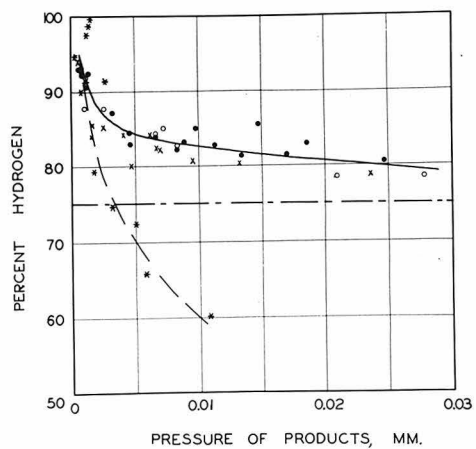


FIGURE 1

COMPOSITION OF THE NON-CONDENSIBLE GASES

- direct photochemical decomposition, 4 mm.  $\text{NH}_3$
- direct photochemical decomposition, 20 mm.  $\text{NH}_3$
- \* mercury sensitized decomposition, 4 mm.  $\text{NH}_3$ , fresh cell
- x mercury sensitized decomposition, 20 mm.  $\text{NH}_3$

Taken together, the results suggest that the decomposition proceeds to hydrogen and hydrazine in the limit:

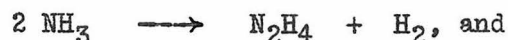


since hydrazine has been found in the photodecomposition products of ammonia<sup>5,6</sup>; and that the hydrazine is destroyed on continued illumination. Therefore it was attempted at first to detect the hydrazine chemically. This was done by exposing a sample of ammonia to the radiation for lengths of time varying as before, then attempting to freeze it, with any hydrazine formed, into a sealing-off trap cooled by liquid air, detaching the trap, breaking it under water, and testing it various ways, microscopic and othersise, for hydrazine. Even with conditions under which hydrazine should have been found, if present, as predicted from the amount of hydrogen produced and the known limits of sensitivity of the tests employed, no hydrazine could be chemically detected.

It seemed possible, however, that the hydrazine remained completely adsorbed on the walls of the reaction cell. Since Dixon<sup>12</sup> has shown that gaseous hydrazine is decomposed by hydrogen atoms, the next attempt to prove the presence of hydrazine was by decomposing it. Ammonia was first irradiated for a short time as before with the aluminum spark. The ammonia was then frozen out in a trap remote from the cell, and mercury vapor allowed to diffuse into the cell. The hydrogen and nitrogen formed in the decomposition of the ammonia likewise remained in the cell, which was then illuminated by a water-cooled mercury arc lamp, and the pressure and composition of the gases measured at intervals. It was expected that hydrogen atoms would be formed by collision of excited mercury atoms with the molecular hydrogen in the cell, as shown by Cario and Franck<sup>13</sup>, and would decompose the hydrazine on the walls, thus changing the pressures of hydrogen and nitrogen. Careful control

experiments were made for comparison, in which exactly the same procedure in every detail was followed, except that the ammonia was first merely put into the cell, allowed to remain for a comparable length of time, and then withdrawn without being irradiated. Instead a comparable amount of hydrogen was admitted to the cell through the palladium tube for irradiation. To reduce cleanup of hydrogen, in some experiments the cell had been first saturated with hydrogen atoms by introducing about 15 mm. of hydrogen, in the presence of mercury vapor, and illuminating it with the water-cooled mercury arc lamp overnight.

It was indeed found, in eight separate experiments, that, in the cases when ammonia had been decomposed in the cell and then withdrawn, hydrogen disappeared rapidly in the first few minutes of illumination by the mercury arc, and more slowly thereafter; at the same time some nitrogen appeared. Figure 2 shows the course of a typical experiment. Similar results were noticed when hydrogen and mercury vapor were illuminated in the cell after a series of quantum yield decompositions had been made in it. Table 2 contains the summarized results of all these experiments. Assuming hydrazine formation, the stoichiometric equations:



were used to calculate the hydrazine formed from the percentage of hydrogen in the fixed gases. Thus, if:

$p$  = pressure of non-condensable gas found ( $\text{H}_2$  and  $\text{N}_2$ ), and

$f$  = fraction of hydrogen in this gas, then

pressure of  $\text{H}_2$  =  $p f$ ,                      pressure of  $\text{N}_2$  =  $p (1 - f)$ ,

equivalent amount  $\text{N}_2\text{H}_4$  =  $p f - 3 p (1 - f) = \underline{4 p (f - 3/4)}$ ,

equivalent  $\text{NH}_3$  decomposed =  $8 p (f - 3/4) + 2 p (1 - f)$

=  $\underline{6 p (f - 2/3)}$ .

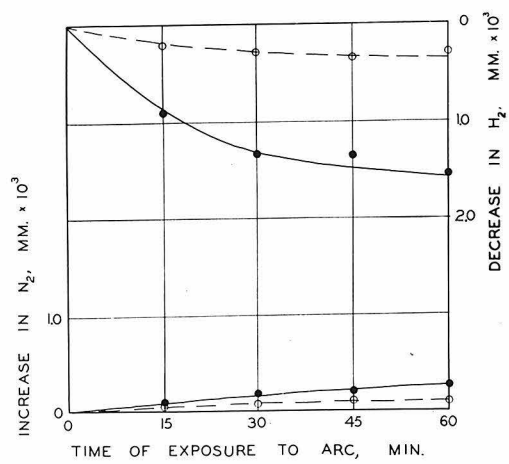


FIGURE 2

CLEANUP OF HYDROGEN AND APPEARANCE OF NITROGEN  
ON ILLUMINATING THE PRODUCTS FOLLOWING DECOMPOSITION OF AMMONIA

- experiment
- control

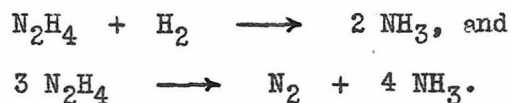
TABLE 2

Cleanup of H<sub>2</sub> on cell walls after decomposition of NH<sub>3</sub>

Test	Press. non-cond. products, mm. x 10 <sup>3</sup> <u>p</u>	% H <sub>2</sub> in non-cond. products 100 <u>f</u>	Eq. amt. N <sub>2</sub> H <sub>4</sub> expected, mm. x 10 <sup>3</sup> <u>4p(f-.75)</u>	Decrease in H <sub>2</sub> , mm. x 10 <sup>3</sup> <u>h</u>	Increase in N <sub>2</sub> , mm. x 10 <sup>3</sup> <u>n</u>	N <sub>2</sub> H <sub>4</sub> found, mm. x 10 <sup>3</sup> <u>h + 3n</u>	% N <sub>2</sub> H <sub>4</sub> recov- ered
1	8.21	82.5	2.463		.43	1.29	
2	11.3	83.35	3.775		.26	.78	
3	7.19	85.3	2.96		.10	.30	
4	8.3	83.5	2.82		.29	.87	
5	16.85	81.45	4.34	1.29	.42	1.71	39.5
6	8.7	83.55	2.98	.55	.00	.55	18.5
7	24.4	80.75	5.6	1.3	.16	1.78	32
8	27.7	78.65	4.06	1.78	.00	1.78	44

That is, if  $\underline{f} = 1$  (pure  $H_2$ ), the equivalent pressure of hydrazine formed =  $\underline{p}$ , and the amount of ammonia decomposed =  $2 \underline{p}$ ; if  $\underline{f} = .75$ , then the amount of hydrazine formed = 0 and the ammonia decomposed =  $\underline{p}/2$ .

To calculate the amount of hydrazine found by decomposition with hydrogen atoms, the equations to be used are:



According to them, if

$h$  = amount of hydrogen disappearing, and

$n$  = amount of nitrogen appearing,

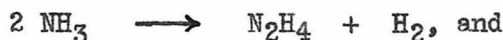
$h + 3n$  = amount of hydrazine destroyed.

It will be noticed that, from Table 2, only about 30 - 40 % of the hydrazine is accounted for in this way; the remainder may possibly resist the attack of the hydrogen atoms for a longer time, or it may escape them by diffusing for some distance over the walls. In any event, however, the experiments are altogether convincing that some substance other than ammonia, hydrogen, or nitrogen is produced in the photochemical decomposition of ammonia; that it escapes being drawn off with the ammonia when the latter is frozen out; that it is decomposed by hydrogen atoms with the disappearance of hydrogen and the appearance of nitrogen; and that it represents a considerable fraction of the ammonia decomposed. It remains only to prove that it is indeed hydrazine.

This proof was obtained by attaching a tube containing a little water, slightly acidified and pumped free of air, to the line leading to the cell. This tube had a finely drawn out tip which could be broken magnetically at any desired time, thus allowing air-free water to enter the cell. The cell was pumped out, ammonia put in, purified as before, and irradiated. The ammonia was frozen out at a distance and the non-condensable products measured. The cell was sealed off, the tip of the tube containing the water was broken, the cell rinsed out, opened,

and the washings tested for hydrazine by adding them to ammoniacal silver nitrate and warming. In all cases silver was reduced. Similar tests made with known amounts of hydrazine revealed that the amounts of hydrazine indicated in the tests were about those to be expected from the amount of gaseous products and their composition; quantitative accuracy was, however, impossible with the small amounts used ( $\sim 10^{-7} - 10^{-8}$  mols  $N_2H_4$ ). Control experiments made under the same conditions, but without irradiation of the ammonia, gave no hydrazine.

Quantum Yield of the Photochemical Decomposition: In the experiments on quantum yield, the non-condensable gases resulting from the decomposition were very small in amount and were found by the quartz fibre gage to contain, on the average, 95% hydrogen. There now seemed sufficient justification to assume that hydrazine was formed to the extent corresponding to the excess of hydrogen found over three times the nitrogen found, according to the stoichiometric relations,



These equations require of the average hydrogen content of 95% that 16 molecules of ammonia decompose to give hydrogen and hydrazine for every molecule that, by any process whatever, gives hydrogen and nitrogen (including decomposition of hydrazine).

The results of the quantum yield experiments on the direct decomposition of ammonia by the 1990 Å. aluminum line are given in Table 3. The volume of the system was found from the known volume of the MacLeod gage bulb by expansion; this was done with liquid air on the traps, just as in the experiments. From this volume,  $V$  cc., the pressure of non-condensable gases in it,  $p$  mm., and the fraction of hydrogen,  $f$ , the use of the formula derived on page 9 permits the calculation of the

TABLE 3

QUANTUM YIELDS OF THE DIRECT DECOMPOSITION OF  $\text{NH}_3$  ( $\lambda = 1990 \text{ \AA}$ .)

Volume of system,  $V$  cc.:  $\begin{cases} 170.9 \text{ cc. in the first four runs} \\ 172.3 \text{ ccc in the remaining runs} \end{cases}$

Fractional transmission:  $\begin{cases} \alpha_1 = .653 \text{ for window of thermopile} \\ \alpha_2 = .70 \text{ for rear window of cell} \end{cases}$

Run	Press. $\text{NH}_3$ , mm.	Press. prod. $\times 10^4$ mm.	% $\text{H}_2$ in prod. 100f	Mol. $\text{NH}_3$ decomp. $\times 10^{-14}$	Time of run, min. $\bar{t}$	Galvanometer defl., divisions $\frac{D_r}{D_t}$	Sensitivity, ergs/sec/div. $\frac{S_r}{S_t}$	Trans. ratio, $\frac{r}{r}$	Quant. abs. $\times 10^{-14}$	Quant. yield
6	5.0	3.5	95.2	33.8	53	4.0	1.35	3.35	47.0	.72
10	12.7	3.6	91.5	29.9	29.75	3.7	1.35	2.96	41.0	.73
5	30.3	6.1	96.5	60.9	46	3.7	1.35	3.14	76.4	.80
9	111.2	3.86	92.9	34.2	24	4.6	1.34	3.25	51.8	.66
(Fresh cell used in these first four runs)										
18	2.2	4.2	94.5	39.45	29.5	4.66	1.38	3.67	46.55	.85
17	5.9	5.65	96.8	57.5	28	4.43	1.38	3.64	61.25	.94
13	6.0	6.37	96.8	64.75	29	5.05	1.38	3.48	68.37	.95
11	13.8	4.63	92.67	40.95	18	4.73	1.38	3.72	51.95	.79
15	14.3	8.2	95.5	80.15	29	5.05	1.38	3.60	85.78	.94
12	29.3	6.4	94.45	60.2	23	4.83	1.38	3.65	69.55	.87
16	30.0	5.0	95.6	49.03	18.5	4.65	1.38	3.69	54.55	.90
14	60.7	4.46	94.1	41.4	19.5	4.27	1.38	3.88	55.77	.74
19	128.2	8.7	90.5	70.2	29.5	4.65	1.38	3.50	81.9	.86
									av. =	.70
									av. =	.87

(Cell saturated with hydrogen atoms for use in these runs)



molecules of ammonia decomposed; it is

$$\left( \frac{p V}{760 \times 24,400 \text{ cc}} \right) \times 6.06 \times 10^{23} \times 6 (\underline{f} - .667).$$

The quanta of radiation absorbed are calculated from the formula,

$$\frac{(D_r S_r r - D_t S_t) t}{\alpha_1 \alpha_2 hc/\lambda}, \text{ where}$$

- $D_r$  = average deflection of the galvanometer of the reflection thermopile,  
 $D_t$  = average deflection of the gasvanometer of the transmission thermopile,  
 $r$  = ratio  $D_t/D_r$  with an empty cell,  
 $S_r$  = sensitivity of the transmission thermopile at a deflection of  $D_r r$ ,  
 $S_t$  = sensitivity of the transmission thermopile at a deflection of  $D_t$ ,  
 $t$  = time of run,  
 $\alpha_1$  = transmission of window of thermopile  $T_t$  to the radiation used,  
 $\alpha_2$  = transmission of rear window of cell to the radiation used,  
 $h$  = Planck's constant,  
 $c/\lambda$  = frequency of the radiation used,

the whole in the consistent units given in Table 3. The first term in the parentheses is the radiant energy which the transmission thermopile would have received in unit time if the cell had been empty, while the last term in the parentheses is the radiant energy it actually received in unit time. The difference, corrected for the loss at the windows, is the energy absorbed in the cell.

Division of the number of molecules of ammonia decomposed by the quanta of radiation absorbed gives the quantum yield. The yields obtained are plotted against ammonia pressure in Figure 3. The quantum yield is seen to be independent of ammonia pressure, and is also independent of the amount of decomposition over moderate two- or three-fold range, although less product was obtained in any case than corresponded to decomposition of .01% of the ammonia. The absolute value averaged

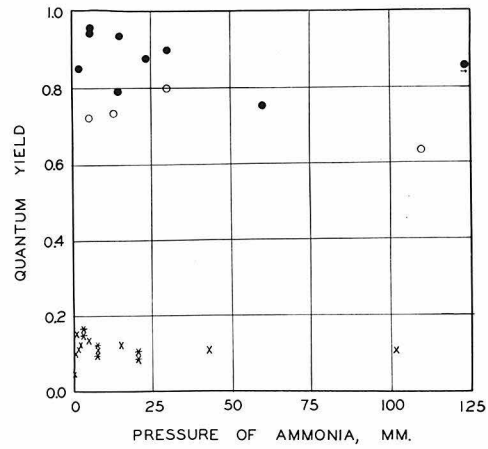


FIGURE 3

QUANTUM YIELD OF THE PHOTODECOMPOSITION OF AMMONIA

- direct decomposition, fresh cell
- direct decomposition, cell saturated with H atoms
- \* sensitized decomposition
- x sensitized decomposition, 95% H<sub>2</sub> assumed

.7 molecules of ammonia decomposed per quantum absorbed, when a cell was used whose walls had been outgassed but not otherwise prepared; see Figure 3. When, however, the cell was first saturated with atomic hydrogen, the quantum yield approached as a limit the significant value of 1.0. This is also shown in Figure 3. Blanks indicated that the amount of dark decomposition was negligible; and when the radiation was allowed to pass through the cell, but the ammonia was kept frozen out, the pressure of non-condensable products which developed was also negligible.

Mercury Sensitized Decomposition: In the sensitized decomposition of ammonia the percentage of hydrogen in the non-condensable products also tended to rise considerably above the theoretical 75%, particularly when only small amounts of ammonia were destroyed. This is likewise shown in Figure 1. It will be noticed that the same curve fits either type of decomposition, except when the ammonia pressure is low, the pressure of products fairly large, and, in addition, a fresh (unsaturated) cell is used. In this event, as shown in Figure 1, hydrogen is cleaned up on the walls to such an extent that its fraction in the gases drops considerably below .75 on continued illumination. When hydrogen alone is similarly illuminated in the cell, its pressure slowly falls off because of cleanup. Otherwise the sensitized and the direct decompositions appear to follow similar courses.

The quantum yield of the sensitized decomposition was, however, much smaller than that of the direct decomposition. It had an average value of .12 molecules of ammonia decomposed per quantum of 2537 Å. radiation absorbed, assuming, as before, the formation of hydrazine. This value was again independent of the amount of decomposition, provided this remained very small, and it was also independent of ammonia pressure, as shown in Figure 3, except below 1 mm., where it fell rapidly to zero. Again 95% hydrogen was obtained, on the average, in the experiments on quantum yield, although in some cases this was not measured. The path of the beam of 2537 Å. light through the cell was visible in the blue-green when ammonia was admitted to the cell. Blanks again indicated that no non-condensable products were obtained when the shutter of the monochromator was kept closed. Complete data on the quantum yields of the sensitized decomposition is to be found in Table 4.

TABLE 4

QUANTUM YIELDS OF THE SENSITIZED DECOMPOSITION OF  $\text{NH}_3$  ( $\lambda = 2537 \text{ \AA.}$ )

Volume of system,  $\underline{V}$  cc.:  $\left\{ \begin{array}{l} 1170.0 \text{ cc. in the first seven runs} \\ 120.7 \text{ cc. in the remaining runs} \end{array} \right.$

Fractional transmission of thermopile and rear cell windows = .847

Run	Press. $\text{NH}_3$ , mm.	Press. prod., $\text{mm.} \times 10^4$ $P$	% $\text{H}_2$ in prod. 100f	Mol. $\text{NH}_3$ decomp., $\times 10^{-14}$	Time of run, min. $t$	Galvanometer defl., divisions	Sensitivity, ergs/sec/div. $\frac{S_r}{S_t}$	Trans. ratio, $r$	Quant. abs. $\times 10^{-14}$	Quant. yield
19	1.4	.84		7.55	23.65	11.2	1.23	1.27	3.67	48.2
31a	3.1	7.45	94.7	68.7	150	14.2	1.16	1.24	4.31	445
31b	3.1	10.6	96.7	105.3	212	14.2	1.16	1.24	4.31	628
30a	8.5	4.56	84.7	34.55	100	13.8	1.17	1.28	4.30	359
30b	8.5	7.5	93.0	64.2	145	13.8	1.17	1.28	4.30	520
27a	20.6	3.88	90.0	30.0	100	12.2	1.225	1.275	3.80	360
27b	20.6	9.57	95.0	90.3	240	12.2	1.225	1.275	3.80	865
26	.25	.32		2.14	26	11.17	1.23	1.26	3.75	44.45
25	.60	.51		3.4	21	11.05	1.23	1.26	3.75	34.85
24	1.3	.64		4.28	21	11.12	1.23	1.26	3.77	38.5
23	2.1	.78		5.24	21	11.17	1.23	1.26	3.77	41.7
18	4.9	1.01		6.45	21	11.28	1.23	1.26	3.67	48.6
28	8.3	1.15		7.55	21	13.4	1.22	1.26	3.82	66.4
29	18.3	.88		5.78	39	5.65	1.27	1.31	3.88	54.3
17	14.3	.87		5.58	16	11.27	1.24	1.295	3.50	43.73
16	38.5	1.35		8.7	21	11.52	1.235	1.33	3.50	80.0
22	103.3	1.78		11.77	26	11.0	1.235	1.38	3.74	109.5

av. = .12

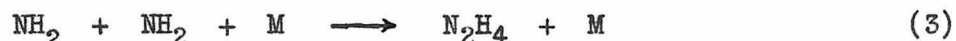
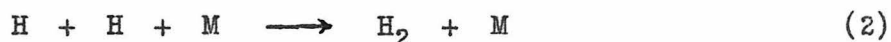
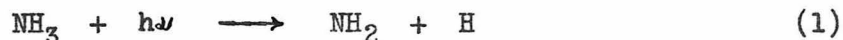
## DISCUSSION

The primary process in the photochemical decomposition of ammonia is almost certainly a dissociation, since the absorption spectrum in the ultraviolet is of the predissociation type<sup>14,15</sup>. The initial process may be considered a rupture of one of the hydrogen-nitrogen bonds:



The most direct experimental evidence for this primary process is the work of Gieb and Harteck<sup>16</sup>, who showed that the photochemical decomposition products of ammonia could affect the conversion of para- to ortho-hydrogen, and therefore presumably contained hydrogen atoms.

In the lower limit of small amounts of decomposition, the products are practically pure hydrogen and hydrazine. The simplest mechanism which accounts for their formation is the following:



By M is meant any body which can absorb energy in a three-body collision, such as the wall or an ammonia molecule. This simple mechanism accounts satisfactorily for all the other experimental facts as well; namely, the quantum yield is substantially unity, and it is independent of ammonia pressure and of the amount of decomposition, provided this last is small. This mechanism requires, moreover, no invention of intermediate compounds of transitory existence.

At the same time, nearly all other possible reactions are eliminated by one or another of these same experimental facts. For example, the reactions



which are considered possible on energetical grounds by Bates and Taylor<sup>4</sup>, are ruled out by the considerations that the quantum yield is independent of ammonia pressure and of the amount of decomposition, respectively. Likewise the reaction



leading to the re-formation of ammonia, is practically ruled out by the fact that the quantum yield is unity, almost within the limit of error. The same consideration also eliminates the possibility of decomposition of ammonia by hydrogen atoms, a conclusion supported by direct experimental evidence<sup>17,18</sup>.

The reaction, with the exception of the primary process, probably proceeds heterogeneously on the walls of the reaction vessel. Hydrogen atoms are known to be strongly adsorbed on glass<sup>19</sup>, and probably also on quartz; and if the amine ( $\text{NH}_2$ ) radicals were able to diffuse to some distance from the decomposition cell, hydrazine should be found in a trap cooled in liquid air and sealed off at a distance from the cell. No hydrazine was detected under such circumstances, however. It is also significant that the small quantities of hydrazine formed in the reaction remain completely adsorbed and do not escape from the cell.

Recombination of hydrogen atoms with amine radicals to give ammonia back is negligible. One possible explanation of this fact is suggested by the further observation of Bonhoeffer<sup>19</sup> that hydrogen atoms are preferentially adsorbed on certain regions of glass walls. It is then necessary to assume further only that the amine radicals are also preferentially adsorbed, and on regions different from those frequented by the hydrogen atoms, to make it appear reasonable that the probability of collisions of hydrogen atoms with the amines on the walls of the cell will be small compared with the probability of collisions of hydrogen atoms with one another and of the amine radicals with one another.

It is reasonable to expect that a little of the hydrazine will be decomposed by the hydrogen atoms, even when its amount is very small. The decomposition of hydrazine in this way will yield some ammonia and some nitrogen<sup>12</sup>, thus slightly reducing the quantum yield below the value of unity and the hydrogen content of the fixed gases below 100%. It seems that the amount of hydrazine obtained must be small compared with the amount required to form a mono-molecular layer on the walls of the reaction cell (~.01 mm.) if most of it is to stay undecomposed. When the reaction is carried too far, the hydrazine decomposes, giving nitrogen and ammonia and reducing the fraction of hydrogen regularly towards .75 as shown in Figure 1. The lower quantum yields obtained by previous investigators seem due to this fact.

For the sensitized decomposition of ammonia, the additional primary process is needed,



Ammonia alone does not absorb this radiation<sup>20</sup>. All the evidence indicates that the sensitized reaction proceeds in much the same manner as the direct decomposition. The same products, hydrogen and hydrazine, are obtained in the limit; the quantum yield, while low, seems independent of ammonia pressure and amount of decomposition, provided this last is, again, small; and the hydrogen percentages in the gaseous products fall off from 100 to 75 % in the same way with increasing amounts of products. The only differences are, first, that the quantum yield is low, which may be due in whole or in part to the fluorescence of the excited ammonia; and, second, that with small pressures of ammonia, a fresh cell, and fairly large amounts of products, the hydrogen will compete successfully with the ammonia to receive the activation energy of the excited mercury, and the comparatively large numbers of hydrogen atoms produced in this way will clean up on the quartz walls, thus reducing the fraction of hydrogen even below .75. Consequently, it seems reasonable to write





## SUMMARY

1. The products of the photochemical decomposition of ammonia have been investigated with the aid of a quartz fibre gage. The pressures of non-condensable products varied from several millimeters of mercury down to the smallest which could be analysed (about .0003 mm.); these were very much smaller than those heretofore investigated.

2. When the pressure of permanent gas produced was not allowed to exceed about .001 mm., it contained over 95% hydrogen. When more ammonia was decomposed, the percentage of hydrogen in general fell off towards 75% as a limit, the remainder being assumed to be nitrogen.

3. The only other product of the decomposition was hydrazine. Its amount corresponded roughly to the amount of excess hydrogen produced, and it could be detected chemically only in the quartz cell in which the ammonia had been originally decomposed. It was also detected by decomposing it in situ with hydrogen atoms.

4. The quantum yield of the direct decomposition was measured by an absolute method. Its value at 1990 Å. was about .7 molecules of ammonia decomposed per quantum absorbed, when a fresh cell was used; but the yield approached as a limit the significant value of 1.0 when the walls of the cell were first saturated with the products of the decomposition and with hydrogen atoms. This yield was independent of the pressure of the ammonia and of the products of the reaction, provided these last were kept below about .001 mm.

5. The collected experimental facts are most easily explained by the simple mechanism involving first the decomposition of the ammonia into a hydrogen atom and an amine radical, followed by the combination in three-body collisions of the hydrogen atoms to form molecular hydrogen and of the amine radicals to form hydrazine.

6. In the decomposition of ammonia sensitized to 2537 Å. by mercury vapor, the reaction follows a course similar to that of the direct decomposition. The products in the limit are again hydrazine and hydrogen, and the fraction of hydrogen in the non-condensable products again falls off in the same way towards .75 with increasing amounts of decomposition. The quantum yield is much lower, however; about .12.

7. This low quantum yield indicates that the quantum of 2537 Å. light is barely sufficient to decompose an ammonia molecule, and permits an estimate to be made of the hydrogen-nitrogen bond energy in ammonia. The value obtained is 105,000 cal.  $\pm$  5,000 cal.

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The following propositions are submitted by Henry J. Welge for his final oral examination:

1. In the initial stages of the photochemical decomposition of ammonia, when effected in quartz vessels, the first stable products obtained are hydrogen and hydrazine.

2. The quantum yield of the direct photochemical decomposition of ammonia is unity, within the limit of experimental error, when only very small amounts of the ammonia are decomposed.

3. In experiments on the rate of solution of carbon dioxide in gently stirred aqueous alkalies, a derivation based on the assumptions that the rate of diffusion of carbon dioxide at any point in the solution is proportional to its concentration gradient at that point, that the dissolved carbon dioxide is consumed by the chemical reaction,



and other reasonable simplifying assumptions, leads to the conclusion that the rate of absorption in the steady state should be, to a first approximation, proportional to the square root of the concentration of hydroxide ion.

4. Iso-butylene and silver ion form in aqueous solution a complex having the formula  $\text{C}_4\text{H}_8 \cdot \text{Ag}^+$ .

5. The results of Baxter and Dickinson (J. A. C. S. 50, 774 (1928)) on the photochemical decomposition of nitrogen dioxide may be equally well explained on the assumption that absorption of light of suitable wave length results in a dissociation,



rather than an activation of the nitrogen dioxide, followed by decomposition on collision.

6. By the use of the Boltzmann velocity distribution law, instead of the assumption of an average molecular velocity, as done by Haber and Kerschbaum (Z. Elektrochemie, 20, 296 (1914)), it may be shown that the dependence of the behaviour of a damped quartz fibre gage on the molecular weight of the damping gas will change if the velocity of the fibre ever becomes comparable with the average speed of the molecules of the gas.