

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

## The Photodecomposition of Gaseous Ammonia

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Despite the studies by various investigators of the decomposition of gaseous ammonia in ultraviolet light the mechanism of this apparently simple photochemical reaction remains yet to be unequivocally established. In the course of the authors' studies on the photochemistry of liquid ammonia<sup>1</sup> it was found possible to investigate also the decomposition of the gas without profound changes of apparatus or technique. This investigation included analysis of the products of photodecomposition and measurement of the quantum efficiency at various wave lengths and ammonia pressures up to the vapor tension of the liquid. In addition, a brief study was made of hydrazine vapor and of mixtures of hydrazine and ammonia. It is believed that the results aid in elucidating the mechanism of the photolysis of ammonia.

### Experimental Details

**Apparatus.**—The rotating spark light source, quartz monochromator and thermopile-galvanometer system were those previously described.<sup>1</sup> The reaction system was similar to that previously used, the details being indicated in Fig. 1. "a" is the cylindrical reaction vessel of fused silica, joined by a graded seal to the Pyrex glass of the remainder. "b" is the magnetically operated micro McLeod gage, "c" a bulb for holding small quantities of liquid ammonia and "d" for containing a bit of copper oxide (used in the gas analysis).

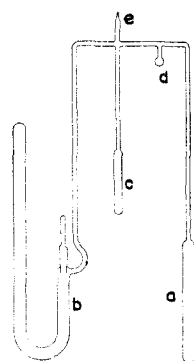


Fig. 1.—Reaction system.

During exposures to monochromatic light at room temperature the silica cell was immersed in the plane-sided water-filled cell previously described. For higher temperatures this was replaced by an electrically heated brass block suitably drilled to contain the vessel and to admit the light beam.

**Materials.**—The ammonia was a synthetic product of high purity, stored over sodium in a steel cylinder fastened to the gas line by a copper-glass seal.

Pure anhydrous hydrazine was prepared by the ammonolysis of hydrazine sulfate with liquid ammonia.<sup>2</sup> The reactants were contained in a small two-legged Faraday tube, and the hydrazine was extracted from the insoluble ammonium sulfate by repeated washing with liquid am-

monia. After evaporation of the latter the leg containing the ammonium sulfate was sealed off, leaving liquid hydrazine stored under dry ammonia gas. The stopcock was sealed to the female part of an interchangeable ground joint, allowing vacuum-tight connection through the male part sealed to the gas line.

Anhydrous hydrogen bromide was prepared by dropping c. p. concentrated hydrobromic acid onto phosphorus pentoxide, passing the gas through red phosphorus and phosphorus pentoxide, and condensing it in a liquid air-cooled trap, the inlet tube being finally sealed off. The trap was provided with a stopcock attached to the female part of a ground joint fitting that on the gas line.

**Preparation of Samples.**—For obtaining ammonia samples the apparatus in Fig. 1 was sealed to the gas line at "e" and evacuated with the diffusion pumps while being baked out. Dry ammonia was then admitted and 0.1–0.2 cm.<sup>3</sup> of liquid was condensed in "c." After freezing the ammonia in liquid air the apparatus was again evacuated and sealed off at "e." The ammonia pressure was then conveniently regulated by surrounding "c" with a bath of constant temperature, the corresponding vapor pressure of liquid ammonia being obtained from the data of Cragoe, Meyers and Taylor.<sup>3</sup> Baths used were ice and partially frozen carbon tetrachloride and bromobenzene. For the maximum ammonia pressure the liquid was kept at 20°. When no excess liquid was desired, ammonia was admitted to a pressure measured by the mercury levels in the safety bubbler. It was frozen with liquid air and the apparatus was sealed off. The final pressure obtained was corrected for ammonia condensed from the dead space in the vacuum line.

Hydrazine and hydrazine-ammonia mixtures were obtained similarly, the hydrazine storage tube being attached by the ground joint. Ammonia was removed from the hydrazine by freezing with solid carbon dioxide and evacuating, and finally by repeated flushing of the apparatus with hydrazine vapor. The hydrazine pressure was read on a small mercury manometer. After the desired amount was obtained the proper quantity of ammonia was admitted, and both gases were then frozen out with liquid air, evacuation and sealing off following.

Hydrogen bromide was obtained similarly, inert gases being first removed by evacuation while the hydrogen bromide was frozen with liquid air.

**Analysis of Products of Photodecomposition.**—The hydrogen-nitrogen mixture from the decomposition of ammonia was analyzed in two ways. The first analyses were carried out *in situ* by freezing the undecomposed ammonia in "c" (Fig. 1), and heating the copper oxide in "d." The water so produced froze out with the ammonia and the residual gas was assumed to be pure nitrogen. Pressure readings were made with the gage. In subsequent experiments the decomposition products were re-

(1) Ogg, Leighton and Bergstrom, *THIS JOURNAL*, **55**, 1754 (1933).

(2) Browne and Welsh, *ibid.*, **33**, 1728 (1911).

(3) Cragoe, Meyers and Taylor, *ibid.*, **42**, 206 (1920)

moved and analyzed<sup>4</sup> by the micro method developed in this Laboratory.<sup>5</sup>

For hydrazine-ammonia mixtures the first method only was used, and reaction of the hydrazine vapor with the copper oxide was prevented by fusing the latter into the glass and covering it with a bead of mercury. After freezing out the hydrazine and ammonia the mercury was volatilized and the analysis was carried out as above.

**Determination of Quantum Efficiencies.**—For studies on ammonia at room temperature the reaction apparatus, filled as above, was put in place in the monochromator box with the silica cell in the water jacket and the proper temperature bath surrounding "c." Exposure to monochromatic light from the spark was then made as previously described.<sup>1</sup> In all cases light reaching the ammonia was totally absorbed. Suitable correction was made for light reflected at the interfaces and absorbed by water and silica. After exposure the ammonia was frozen out in "c" with liquid air and the pressure of nitrogen and hydrogen was measured. The liquid air-cooled space was assumed to be at 90°K., the small gradient section at 190°K. and the remainder at 293°K. After completion of the experiments the respective volumes were determined. Several successive runs were made on each ammonia sample, the respective pressure increases being determined. This procedure is justified by the fact that hydrogen and nitrogen have been shown to exert no influence on the reaction at room temperature.

For work at higher temperatures the water cell was replaced by the heated brass block, the temperature being measured with a thermocouple. Comparison was then made of the amounts of decomposition produced by equal exposures at room temperature and at some higher temperature, respectively. Since the intensity of the spark source remained quite constant and light reaching the ammonia was totally absorbed (the small reflection and absorption losses should be practically independent of temperature), the rates of reaction stand in the ratio of the respective quantum efficiencies. From the separately determined value at room temperature the values at other temperatures were thus calculated.

Measurements at room temperature with hydrazine-ammonia mixtures were made as with pure ammonia. With pure hydrazine vapor total light absorption did not result. The rather broad transmitted beam was integrated with the thermopile and the absorbed light energy and absorption coefficient of the hydrazine thus found.

Measurements of hydrogen bromide decomposition were carried out exactly as for ammonia.

### Experimental Results

**Products of Photolysis.**—The analyses of gas from the photodecomposition of pure ammonia yielded the following average compositions:

	H <sub>2</sub> , %	N <sub>2</sub> , %
Copper oxide method	71.4	28.6
Separate micro method	74.5	25.5

The results may be taken to indicate a hydrogen-nitrogen ratio of close to 3:1.

(4) We are indebted to Mr. S. S. Todd for these measurements.

(5) Blacet and Leighton, *Ind. Eng. Chem., Anal. Ed.*, **3**, 286 (1931); Blacet, MacDonald and Leighton, *ibid.*, **5**, 272 (1933).

Analysis of gas from the illumination of a mixture of ammonia (at 4 atmospheres) with hydrazine vapor (at 9 mm.), gave, by the copper oxide method, 46.4% H<sub>2</sub> and 53.6% N<sub>2</sub>. In view of the apparent tendency of the analyses by copper oxide to run low in hydrogen, these figures indicate a hydrogen-nitrogen ratio close to unity.

**Quantum Efficiencies.**—Measurements were made of the quantum efficiency for the photodecomposition at room temperature of pure ammonia at pressures from 1.2 to 8.5 atmospheres. Light of wave lengths 2194 and 2144 Å. (Cd spark) and 2099 Å. (Zn spark) was used. From the above analytical results, each molecule of ammonia decomposed was assumed to yield two of permanent gas. The results are given in Table I.

TABLE I

Run	λ, Å.	P <sub>NH<sub>3</sub></sub> , atm.	Exposure, sec.	Quanta absorbed × 10 <sup>-17</sup>	P <sub>N<sub>2</sub> + H<sub>2</sub></sub> , mm.	Quantum efficiency φ
1	2144	4.2	600	1.740	0.161	0.143
2		4.2	900	2.558	.213	.129
3		4.2	600	1.685	.139	.128
					Av.	.132
4		1.9	600	1.671	.166	.153
5		1.9	900	2.570	.244	.146
6		1.9	600	1.692	.142	.130
					Av.	.144
7		1.2	900	2.266	.198	.135
8		1.2	900	2.072	.199	.148
					Av.	.142
9		1.2	900	2.196	.209	.149
10		1.2	870	2.519	.191	.119
					Av.	.133
11		1.9	900	2.539	.225	.139
12		1.9	900	2.475	.238	.151
					Av.	.145
13		4.2	900	2.539	.281	.174
14		4.2	900	2.614	.197	.118
					Av.	.146
15		8.5	900	2.710	.277	.161
16		8.5	900	2.561	.259	.159
17		8.5	900	2.475	.209	.132
18		8.5	900	2.402	.247	.162
					Av.	.153
19	2194	8.5	900	2.917	.259	.140
20		8.5	900	2.786	.241	.136
21		8.5	900	2.669	.244	.144
22		8.5	900	2.562	.219	.134
					Av.	.140
23	2099	8.5	2400	2.202	.170	.121
24		8.5	900	0.803	.063	.123
25		8.5	1500	1.375	.112	.128
26		8.5	1500	1.317	.105	.125
					Av.	.124

Runs 1-8 are for a single ammonia sample in the order of decreasing pressure, while 9-18 are on another sample in the order of increasing pressure. The satisfactory agreement of the two series indicates that adsorption of the products by solid ammonia does not introduce a serious error.

The results indicate the quantum efficiency to be essentially independent of ammonia pressure and of wave length of light. The weighted mean of the measurements gives  $\Phi = 0.14$ , with an average deviation of some 5%.

Only one series of runs was made on ammonia decomposition at higher temperatures. The sample (with no excess liquid) had a pressure of 120 cm. at room temperature. The results are given in Table II.

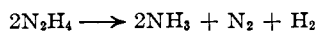
TABLE II

PHOTODECOMPOSITION OF AMMONIA AT VARIOUS TEMPERATURES,  $\lambda = 2144 \text{ \AA}$ .

Temp., °C.	Exposure, sec.	$P_{N_2+H_2}$ , mm.	$\Phi$
20	900	0.311	0.14
250	900	.745	.34
400	900	1.174	.54

These results are admittedly meager, but they do indicate a rather rapid increase of quantum efficiency with temperature.

A few runs were made at room temperature on hydrazine-ammonia mixtures and on hydrazine vapor. The results are given in Table III. From the rapid reaction of hydrazine-ammonia mixtures and the fact that the hydrogen-nitrogen ratio in the products was nearly unity (*vide supra*), it appeared that the over-all effect of illumination was to decompose only the hydrazine, in the fashion given by Elgin and Taylor<sup>6</sup>



Hence the values of  $\Phi$  in Table III represent the number of hydrazine molecules decomposed per light quantum, and are calculated on the assumption that each resultant molecule of permanent gas corresponds to one molecule of hydrazine consumed. The fraction of light absorbed by ammonia in the mixtures is  $\alpha_{NH_3}/(\alpha_{NH_3} + \alpha_{N_2H_4})$ , where the  $\alpha$ 's are the respective absorption coefficients.  $\alpha$  at  $\lambda 2144 \text{ \AA}$ . for ammonia at 3000 mm. pressure was calculated from the data of

(6) Elgin and Taylor, *THIS JOURNAL*, **51**, 2059 (1929). The additional mode of decomposition  $N_2H_4 \longrightarrow N_2 + 2H_2$  found by Wenner and Beckman [*ibid.*, **54**, 2787 (1932)], was shown by these authors to decrease in importance with increasing pressure, and should be negligible at the high pressures obtaining in the present experiments.

Landsberg and Predwoditelev<sup>7</sup> to be 18.78. For hydrazine  $\alpha$  was measured directly and found to be 1.05 at  $\lambda 2144 \text{ \AA}$ . for a pressure of 9 mm.

TABLE III

PHOTOLYSIS OF HYDRAZINE-AMMONIA MIXTURES ( $20^\circ$ ,  $\lambda = 2144 \text{ \AA}$ .)

$P_{NH_3}$ , mm.	$P_{N_2H_4}$ , mm.	Ex- posure, sec.	Fraction of light abs. by $NH_3$	Quanta absorbed $\times 10^{-17}$	$P_{N_2+H_2}$ , mm.	$\Phi$
3000	8	900	0.95	2.995	1.126	1.28
3000	8	900	.95	3.024	0.847	0.95
3000	4	900	.98	3.052	1.107	1.23
3000	4	510	.98	1.141	0.514	1.00
0	9	600	0	1.314	.463	1.19
0	9	600	0	1.377	.567	1.40
						Av. 1.28

These results show that in the hydrazine-ammonia mixtures, where practically all of the light is absorbed by the ammonia, exposure results in a decomposition of the hydrazine nearly as rapid as for the pure vapor.

Two runs were made at  $20^\circ$  on the photodecomposition of hydrogen bromide, to give an actinometric check of the accuracy of the procedure. A slow thermal reaction with the mercury of the gage was corrected for by making blank runs and subtracting the observed pressure increase from that obtained during illumination.

TABLE IV

PHOTODECOMPOSITION OF HYDROGEN BROMIDE ( $20^\circ$ ,  $\lambda = 2144 \text{ \AA}$ .)

$P_{HBr}$ , cm.	Exposure, sec.	Quanta absorbed $\times 10^{-17}$	$P_{H_2}$ , mm.	$\Phi$
220	600	2.016	0.555	1.86
220	600	1.966	.533	1.84

The accepted value for the quantum efficiency of hydrogen bromide decomposition is 2.0. The above results differ from this by little more than the experimental error. They indicate that the other quantum efficiencies obtained in this work may be slightly low, but the correction is considered too small to be significant.

### Discussion

The experimental results of this study are in partial agreement with observations of other investigators. The products of photolysis of ammonia in a static system were found to be hydrogen and nitrogen in the approximate ratio 3:1, in agreement with the results of Wiig and Kistiakowsky<sup>8</sup> and of Gedye and Rideal.<sup>9</sup> The latter

(7) Landsberg and Predwoditelev, *Z. Physik*, **31**, 544 (1925).

(8) Wiig and Kistiakowsky, *THIS JOURNAL*, **54**, 1806 (1932).

(9) Gedye and Rideal, *J. Chem. Soc.*, 1160 (1932).

authors, as well as König and Brings<sup>10</sup> found evidence of appreciable hydrazine formation by the illumination of rapidly streaming ammonia. It would appear that hydrazine is destroyed by remaining in the illuminated zone—a conclusion directly affirmed by the above observation that small amounts of hydrazine artificially introduced into ammonia are rapidly decomposed as a result of absorption of light by the ammonia.

The mean value of the quantum efficiency of ammonia decomposition at 20° was found to be 0.14, essentially independent of ammonia pressure and wave length of light. Warburg<sup>11</sup> found 0.23, Kuhn<sup>12</sup> 0.45, and Wiig and Kistiakowsky<sup>8</sup> 0.25. The cause of the disagreement is difficult to assign. The experimental procedure was somewhat similar to that of Wiig and Kistiakowsky, and in both investigations the results were checked against the hydrogen bromide actinometer. The pressure range in this study was 1.2 to 8.5 atmospheres, whereas the highest pressure used by the other investigators was about one atmosphere. Despite the fact that no trend with pressure was noticed, it is possible that this is the cause of the discrepancy, and that the quantum efficiency does decrease slightly at high pressures. In any event, it appears that the value of 0.45 found by Kuhn is too large, and that  $\Phi$  is at least as small as 0.25, if not smaller.

As to effect of temperature on the photolysis of ammonia, Kuhn found a nine-fold increase of  $\Phi$  between 20 and 500°, whereas Wiig and Kistiakowsky report a mere doubling. The present results are intermediate, showing a four-fold increase of  $\Phi$  between 20 and 400° (Kuhn observed a six-fold increase). The disparity is marked, but a definite increase of  $\Phi$  with temperature is indicated.

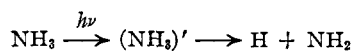
The results with hydrazine-ammonia mixtures agree with the observation of Elgin and Taylor<sup>5</sup> that ammonia does not retard the photodecomposition of hydrazine, although it absorbs in the same spectral range. The value of 1.28 for the decomposition of pure hydrazine at 9 mm. agrees with that of 1.34 found by Wenner and Beckman,<sup>6</sup> although different wave lengths were used.

As for the reaction mechanism, there would appear to be no doubt that the primary process is

(10) König and Brings, *Z. physik. Chem.*, Bodenstein Festband, 595 (1931).

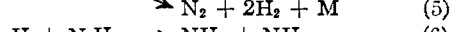
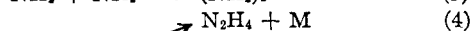
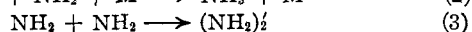
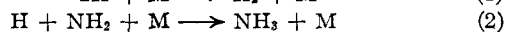
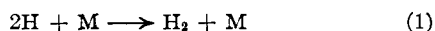
(11) Warburg, *Sitz. preuss. Akad.*, 746 (1911); 216 (1912); 872 (1914).

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



Evidence that predissociation is the primary process is summarized by Bonhoeffer and Farkas.<sup>13</sup> Proof that the products are H and NH<sub>2</sub> rather than H<sub>2</sub> and NH was obtained by Geib and Har-teck,<sup>14</sup> who detected hydrogen atoms in illuminated ammonia by their effect in converting para hydrogen to the equilibrium mixture with ortho. Additional evidence for hydrogen atoms is the photosensitization of oxygen-hydrogen mixtures by ammonia<sup>15</sup> and the photoreaction of ammonia and ethylene.<sup>16</sup> Finally, the work of the authors on the photolysis of liquid ammonia solutions of alkali metals is regarded as evidence for the production of NH<sub>2</sub> radicals.

Following upon the primary process, probably every secondary reaction that can be written occurs to an extent determined by the relative activation energies, pressure, vessel size, etc. However, in the mechanism discussed below, only those reactions are considered which appear, on the basis of experimental evidence, to be of importance in determining the general characteristics of the ammonia decomposition. As will be shown, this mechanism serves to correlate experimental results from several different sources. The reactions we wish to consider are<sup>17</sup>



(1) is known to be a trimolecular process. The authors' studies on the photochemistry of liquid ammonia furnish evidence that (2) is also trimolecular but may be faster than (1) because the larger number of degrees of freedom in NH<sub>3</sub> should permit of a longer-lived collision complex and hence a larger effective collision diameter for M. For the same reasons, the intermediate formation of hydrazine by the association of amide radicals

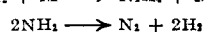
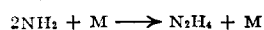
(13) Bonhoeffer and Farkas, *Z. physik. Chem.*, 134, 337 (1928).

(14) Geib and Har-teck, *ibid.*, Bodenstein Festband, 849 (1931).

(15) Farkas, Haber and Har-teck, *Naturwissenschaften*, 12, 267 (1930); *Z. Electrochem.*, 36, 711 (1930).

(16) Taylor and Emeleus, *This Journal*, 53, 562 (1931).

(17) An alternative set of reactions is



This, however, would lead to a value of  $\Phi$  dependent upon ammonia pressure, in disagreement with experimental results.

should be rapid compared to (1) and (2), and may even be bimolecular, as by (3) and (4) in analogy to well-known association reactions of polyatomic molecules. On collision of the complex with a third body, the two processes (4) and (5) may be expected. Presumably the probability of (5) relative to (4) would increase with the kinetic energy of the third body, and hence reaction (5) should be favored by rise in temperature.

The rather large yield



obtained by Gedye and Rideal at low temperatures in streaming ammonia indicates that (5) and (7) are not important at those temperatures; the falling off in hydrazine yield with rising temperature which they observed is then accounted for by the increasing rates of these reactions.

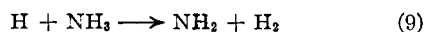
Reactions (6) and (7) account for the destruction of hydrazine, which is not found as a final product in a static system. Direct evidence of this process was obtained from the above studies on hydrazine-ammonia mixtures and it was shown that direct photodecomposition could not be responsible for the disappearance of the hydrazine (because of its relatively small absorption coefficient). The work of Dixon<sup>18</sup> indicates that hydrogen atoms react very rapidly with hydrazine. (6) appears to be the most probable process, and, being an exothermic atomic metathesis, might be expected to require a very small activation energy.

Reaction (7) probably occurs in steps, and at least six possible mechanisms may be written, between which it is impossible to choose at present. Whatever the mechanism of (7), it is probable that it requires an appreciable activation energy. (6) and (7) are consistent with Dixon's observation that in the reaction of hydrogen atoms with hydrazine approximately one mole of ammonia is produced per mole of hydrazine consumed.

Considering the mechanism as a whole, brief consideration shows the quantum efficiency to be small and essentially independent of the concentration of ammonia or other gases. At very low pressures the trimolecular processes (1) and (2) are slow, but the association of amide radicals remains homogeneous and rapid. (4), which followed by (6) determines the rate of regeneration of ammonia, and (5), which largely deter-

mines the rate of formation of hydrogen and nitrogen, are equally affected by pressure. At higher pressures (1) and (2) become important, but since they are opposed reactions their pressure dependence does not sensibly affect  $\Phi$ . With increasing temperatures the increasing rate of (5) and (7) as compared with (4) or (2) accounts for the increase of quantum yield, but sets an upper limit of unity.

The additional reaction

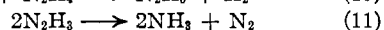
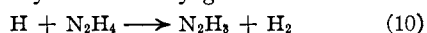


for which Dixon<sup>18</sup> gives a fairly large activation energy, would allow  $\Phi$  a maximum value of 2 at high temperatures. The reverse of this reaction explains the retardation exerted by hydrogen at high temperatures.<sup>12</sup>

The observation of Geib and Harteck<sup>14</sup> on the conversion of para to ortho hydrogen photosensitized by ammonia indicated that hydrogen atoms were consumed by some process much more rapid than trimolecular recombination. This is due to the additional reactions (2) and especially (6).

Melville<sup>19</sup> found that hydrogen atoms (from excited mercury and hydrogen) strongly retarded the photodecomposition of ammonia, a fact readily explained by reactions (2) and (6).

The mechanism proposed here differs appreciably from that of Wiig and Kistiakowsky.<sup>8</sup> These authors give (1) and (2) but favor a simple trimolecular process for the combination of amide radicals. As they point out, this leads to the difficulty that at low pressures these would all be largely wall reactions. To account for the destruction of hydrazine they give



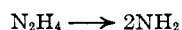
If this mechanism is adopted, in ammonia-hydrazine mixtures the absorption of light by the ammonia (giving H and NH<sub>2</sub>) should result in a quantum yield, for hydrazine decomposition, of unity or less, and a hydrogen-nitrogen ratio of 2:1 in the products. Actually a quantum yield of greater than unity was found, and the hydrogen-nitrogen ratio was close to 1:1. Since these results are entirely compatible with the authors' mechanism, it is felt that the set of secondary reactions proposed here more nearly describes the main course of the reaction than that given by Wiig and Kistiakowsky.

The results of Wenner and Beckman<sup>6</sup> on the photodecomposition of hydrazine may be ex-

(18) Dixon, *THIS JOURNAL*, **54**, 4262 (1932).

(19) Melville, *Trans. Faraday Soc.*, **139**, 885 (1932).

plained by the above mechanism. The primary process



appears most likely on spectroscopic grounds.<sup>20</sup> The secondary reactions considered are (3), (4), (5) and (7). (5), whose rate is independent of  $\text{N}_2\text{H}_4$  concentration, would give  $\Phi = 1$ , and a hydrogen-nitrogen ratio of 2:1. (7), the rate of which depends on  $\text{N}_2\text{H}_4$  concentration, gives  $\Phi = 2$ , and a 1:1 ratio. Hence, neglecting (4), a value of between 1 and 2 increasing with hydrazine pressure, and a percentage of hydrogen between 66 and 50, decreasing with pressure, are to be expected. This is the result obtained by Wenner and Beckman. The fact that the observed values of  $\Phi$  are smaller than those calculated from the percentage of hydrogen is explained by reaction (4).

The results of Wenner and Beckman indicate that at low pressures (5) is considerably more rapid than (4). On the other hand, the evidence from studies of ammonia decomposition indicates that at higher pressures (4) greatly preponderates over (5), at least at room temperature. This suggests that at low pressures (4) and (5) may be wall reactions, with a relative probability considerably different from that of the homogeneous reactions.

If this be true, the independence of quantum yield and pressure in ammonia decomposition might be expected to obtain only at pressures sufficiently great for homogeneous processes to preponderate. It should be emphasized that by the above mechanism the constancy of  $\Phi$  over a wide range of pressure is simply the result of a balance

(20) Imanishi, *Nature*, **127**, 782 (1931).

ing of various effects, and is not due to inherent pressure independence of the rate governing process.

Elgin and Taylor<sup>6</sup> observed that the photosensitized decomposition of hydrazine was not retarded by addition of considerable hydrogen, although the latter is known to be very efficient in deactivating excited mercury atoms, yielding hydrogen atoms. This is explained by (6) followed by (7).

### Summary

A study has been made of the decomposition by short ultraviolet light of gaseous ammonia at fairly high pressures, up to the vapor tension of the liquid at room temperature. A stoichiometric decomposition into nitrogen and hydrogen was observed. The quantum efficiency at 20° was found to be 0.14, practically independent of ammonia pressure and wave length of light, and was observed to increase with temperature.

Study was made of the photolysis of ammonia containing amounts of hydrazine vapor insufficient to absorb an appreciable fraction of light. Analysis of the products and measurement of the quantum efficiency showed the reaction to be essentially a decomposition of the hydrazine photosensitized by ammonia.

The quantum efficiency for the decomposition of hydrazine itself was also measured.

A mechanism has been proposed for the photodecomposition of ammonia and hydrazine which explains the results of this and of previous investigations and is supported by considerable evidence from independent sources.

STANFORD UNIV., CAL. RECEIVED SEPTEMBER 11, 1933