[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ROCHESTER]

Photochemical Investigations. III. The Effect of Cell Size on the Quantum Yield for the Decomposition of Ammonia[1]

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Recently suggested mechanisms[2-4] for the photolysis of ammonia are based on experimental data which apparently show the quantum yield independent of pressure. However, a later investigation[5] demonstrated that there is a change in the quantum efficiency with a change in the total ammonia pressure. This dependence might be due to a change in the character of the homogeneous gas reactions occurring after the primary dissociation brought about by light or to a change from a homogeneous reaction to a heterogeneous reaction taking place on the walls of the reaction cell. As the thermal decomposition of ammonia is known to be heterogeneous and probably involves hydrogen atoms and NH,[6] one might be inclined to be suspicious of the photo-reaction in the absence of evidence of homogeneity or heterogeneity. In view of this, no mechanism accounting for the pressure dependence of the yield was suggested in the previous paper.[5] The experiments reported here were carried out in a reaction cell of somewhat different size from that previously used in an attempt to settle this point.

Experimental Details

The light source, apparatus and materials were the same as used earlier,[5] except for the replacement of the previous cell by another. Both cells were cylindrical with plane parallel windows on the ends and all seams fused. The first cell (Cell 1) was 25 mm. in diameter by 50 mm. long with an area–volume ratio of 200 mm.$^{-1}$ while the new cell (Cell 2) was 40 mm. in diameter and 35 mm. long with an area–volume ratio of 157 mm.$^{-1}$. At the conclusion of the experiments with each cell the rear window was cut off and its transmission measured. Previous to removing the windows, hydrogen bromide was decomposed in the cells, using exactly the same procedure as in ammonia photolysis.

(1) Presented in part at the Schenectady and Troy, N. Y., Intersectional Meeting of the American Chemical Society, October 25–26, 1935.

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

(3) Ogg, Leighton and Bergstrom, *ibid.*, **56**, 318 (1934).

(4) Farkas and Harteck, *Z. physik. Chem.*, **B25**, 257 (1934).

(5) Wiig, THIS JOURNAL, **57**, 1559 (1935).

(6) Frankenburger, *Z. Elektrochem.*, **39**, 97 (1933).

Results

In order to compare the photolyses in the two cells the quantum efficiency for the ammonia decomposition was determined, as in the earlier work, for the single Zn line λ 2100 Å. at ammonia pressures ranging from 4–886 mm. The results are shown in Table I. These yields were calculated on the assumption that the non-condensable gas remaining after freezing out the ammonia with liquid air consisted of 75% hydrogen and 25% nitrogen. The energy measurements upon which these quantum yields depend were checked by measuring the quantum efficiency for the decomposition of hydrogen bromide. Using the experimentally determined correction factors for the energy losses at the cell window, lens and

TABLE I

PHOTOLYSIS OF AMMONIA IN CELL 2

λ 2100 Å. Volume, 215 cc. Room temp. 24–30°

Expt.	p_{NH_3}, mm.	Exposure, sec.	Quanta absorbed $\times 10^{-14}$	$p_{N_2+H_2}$ microns	Quantum yield
B-32	4	1920	276	0.56	0.072
31	9	1740	481	1.53	.114
15	12	1380	355	0.81	.081
30	15	1740	616	2.81	.163
29	18	1560	378	1.97	.185
14	22	1320	556	2.96	.189
28	28	1800	716	4.49	.222
27	35	1800	706	4.45	.224
13	43	1440	741	4.99	.242
26	54	1380	713	4.87	.243
25	65	1745	969	7.01	.259
12	83	1200	628	4.53	.257
24	93	1380	966	7.01	.259
23	100	1260	636	4.16	.232
17	109	1440	777	5.27	.242
22-B	120	900	502	3.72	.263
16	130	1380	652	4.64	.251
22-A	173	1500	827	5.58	.239
11	204	1620	820	5.31	.229
21	211	1380	867	5.68	.231
20	326	1500	1040	6.11	.207
10	390	1320	671	4.16	.218
19	454	1500	1140	6.11	.192
18	520	1200	668	3.12	.165
33	608	1200	710	3.21	.160
36	673	1500	1070	4.75	.158
34	742	1320	807	3.70	.163
37	812	1500	851	3.44	.144
35	886	1560	1080	4.02	.142

thermopile window, the average quantum yield found for the hydrogen bromide photolysis was 2.14. This is in good agreement with the value of 2.01 found by experiment in the previous investigation and with the accepted value of 2.0. The results with hydrogen bromide given in Table II have been corrected to make the average yield 2.00 and the data for ammonia in Table I have been corrected similarly. The correction is small and might have been neglected but it serves to refer the data in Cells 1 and 2 to the same standard. All the experiments performed have been listed in these two tables except runs B1–9 which were performed on old hydrogen bromide that had been stored in contact with phosphorus pentoxide for several months. The yields in these experiments were very erratic. The later experiments of Table II, as in the earlier work, were carried out with freshly prepared hydrogen bromide which, as may be seen, gave easily reproducible results.

TABLE II

PHOTOLYSIS OF HYDROGEN BROMIDE IN CELL 2

λ 2100 Å. Room temp. 26–28°

Expt.	P_{HBr}, mm.	$P_{H_2, total}$, microns	$P_{H_2, thermal}$, microns	Quantum yield
B-40	54	16.13	1.74	1.95
41	54	14.27	1.40	1.99
38	58	10.61	1.28	1.95
39	58	10.04	1.18	2.15
42	64	18.56	1.88	1.97
			Av.	2.00

From Table I it is apparent that the same sort of pressure dependence of the yield obtains as in the earlier cell. For convenience of comparison the data in Table I of the earlier work[5] and

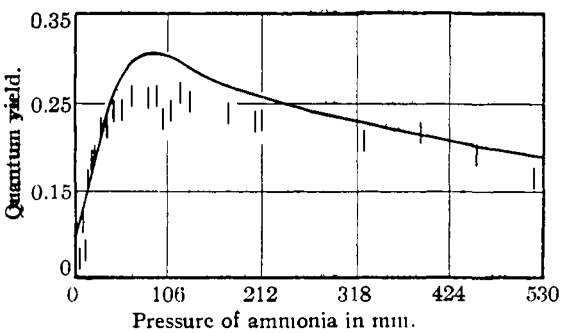

Fig. 1.—Quantum yield for the photo decomposition of ammonia as a function of pressure at λ 2100 Å.: full curve, cell 1; vertical lines, cell 2.

the present data have been plotted as shown in Fig. 1. The full curve is the curve in Fig. 2 of the preceding paper[6] and shows the variation of quantum yield with pressure in experiments performed with Cell 1. The vertical lines, which correspond in length to a quantum yield of 0.025 and whose mid-point is the actually determined value, represent the individual experiments in Cell 2 as given in Table I. Some measurements made with a third cell (Cell 3) of the same diameter as Cell 1 but 100 instead of 50 mm. long gave yields which fit the curve for Cell 1.

After the completion of this work there appeared a paper by Welge and Beckman[7] reporting an investigation of the photodecomposition of ammonia in the region of very minute amounts of decomposition. Their results show that in their apparatus at pressures of products of 0.05 mm. or greater the non-condensable gases consist of 75% hydrogen and 25% nitrogen, but when the amount of decomposition is decreased down to pressures less than 1 micron the gas contains about 95% hydrogen and approaches 100% as a limit. Based on the percentage of hydrogen and that the stoichiometric reactions involved are

$$2NH_3 = N_2 + 3H_2 \text{ and}$$
$$2NH_3 = N_2H_4 + H_2$$

Welge and Beckman find quantum yields approaching unity. They suggest that perhaps the low quantum yields obtained by others[2,3,5] are due in part to a change in composition of the gaseous products.

In the experiments of Wiig and Kistiakowsky the products were shown to be $3H_2 + N_2$ down to 8 μ pressure with the full light of the zinc spark and down to 16 μ with the monochromatic light and conditions used in the quantum yield determinations. The amount of decomposition in every experiment with λ 2090 Å. corresponded to a pressure of products of 19.7 μ or greater. The quantum yields of *ca.* 0.25 obtained are based, therefore, on a known composition of products and are real. In the present studies the products of the exposure of ammonia to the full light of the zinc spark were shown[5] to be 75% hydrogen and 25% nitrogen down to pressures of 22 μ. The pressures of the decomposition products in the data used here vary from about 0.6–12 μ.

Subsequently, the constancy of the composition of the products down to about 2 μ pressure has

(7) Welge and Beckman, THIS JOURNAL, 58, 2462 (1936).

been tested. If the non-condensable product at 1 μ is 100% hydrogen, the calculated quantum yield on the assumption of 75% hydrogen and 25% nitrogen would be[7] about 0.25. The maximum value of the yield (Fig. 1) comes at an ammonia pressure of about 100 mm. and has a value of about 0.30 in Cells 1 and 3 for λ 2100 Å. and *ca.* 12 μ of products. If this efficiency is for products containing $3H_2 + N_2$, then on reducing the time of exposure so as to obtain only 1 μ of products the calculated yield should approach 0.25 as the gas approaches 100% hydrogen. Cell 3, as it is the only one intact, was used for making the test. The cadmium line at λ 2144 Å. was chosen since decompositions up to 30 μ could be obtained readily with the higher intensity available. The results are given in Table III.

TABLE III

PHOTOLYSIS OF AMMONIA IN CELL 3

λ 2144 Å. P_{NH_3} = 105 mm. Vol. = 230 cc. Temp., 21–27°

Expt.	Exposure, sec.	Quanta absorbed, $\times 10^{-14}$	Pressure of products, microns	Quantum yield
C-135	2580	3236	29.96	0.354
136	2220	2320	21.81	.360
142	2100	976	8.44	.332
139	600	725	6.55	.344
143	1500	621	5.60	.349
140	360	454	4.12	.345
141	180	230	1.73	.288
138	180	185	1.30	.266
137	120	137	0.98	.274

These yields at λ 2144 Å. are slightly higher than those reported for λ 2100 Å. The data of Ogg, Leighton and Bergstrom show the same tendency to higher values at λ 2144 as compared with λ 2100 Å. Whether or not this difference is real is of no importance here. The yield, it will be observed from Table III, is about 0.345 for products varying from 30 μ, where the composition has been determined with certainty, down to 4 μ. At pressures of products less than 2 μ the yield falls sharply which, on the basis of Welge and Beckman's results, might indicate a change in composition. All the experiments indicated in Fig. 1 produced more than 4 μ of non-condensable gas except a few runs at low or high pressures where the yields are less than 0.20 (*e. g.*, *ca.* 0.10 in Expts. B-15, 31, 32). If the gas were 100% hydrogen in these few experiments, the yield should still be about 0.25, so that a change in composition cannot account for these low yields.[8] It seems, therefore, that the variation in quantum yield at ammonia pressures ranging from at least 30–700 mm. is real and not due to a change in composition of gaseous products. In the decomposition of ammonia by α-particles, Luyckx[9] likewise finds an increase in the yield per ion pair as the ammonia pressure is decreased to about 100 mm. and points out that earlier data[2,10] show the same tendency, although no such claim was made.

Discussion

The plot in Fig. 1 shows a small but very definite difference in the quantum yields in the two cells at about 60–300 mm. ammonia pressure. In this pressure range the reaction apparently becomes heterogeneous. The experiments of Welge and Beckman[7] also indicate that the reaction must be at least partly a wall reaction, since saturation of the walls with atomic hydrogen previous to photolysis results in a higher yield. By means of the effect of hydrogen atoms on the para- to ortho-hydrogen transformation Farkas and Harteck[4] have shown that the hydrogen atom concentration, [H], in ammonia undergoing photolysis, decreased with decrease in total pressure for total ammonia and hydrogen pressures less than 140 mm. When the surface was increased by filling the reaction cell with lengths of quartz tubing, [H] decreased. While these experiments were performed at 400 and 300°, respectively, and not at room temperatures, they nevertheless indicate the heterogeneous character of the reaction.

The dependence of the quantum yield on ammonia pressure is readily accounted for by making use of the following reactions. The individual reactions have been suggested at various times but not as presented here.

$$NH_3 + h\nu \longrightarrow (NH_3)' \longrightarrow NH_2 + H \quad (1)$$
$$H + H \text{ at wall} \longrightarrow H_2 \quad (2)$$
$$NH_2 + H + M \longrightarrow NH_3 + M \quad (3)$$
$$NH_2 + NH_2 + M \longrightarrow N_2H_4 + M \quad (4)$$
$$NH_2 + NH_2 \longrightarrow N_2 + 2H_2 \quad (5)$$
$$N_2H_4 + H \longrightarrow NH_3 + NH_2 \quad (6)$$

(8) There is a striking difference in the intensities used in the experiments of Welge and Beckman and those in Fig. 1. In the latter the number of quanta absorbed varies from 300 to 1300 $\times 10^{14}$, the smaller number coming at low ammonia pressures, where absorption is weak. The average is about 800 $\times 10^{14}$. For approximately the same exposures, the number of quanta absorbed in the experiments of Welge and Beckman varies from 41–86 $\times 10^{14}$, the average being 60 $\times 10^{14}$. Whether or not this accounts for the difference in the composition of the products obtained in the two investigations is difficult to state.

(9) (a) Luyckx, *Bull. soc. chim. belg.*, **43**, 117 (1934); (b) Luyckx, Revue de Questions scientifiques, Nov., 1935, p. 441.

(10) Kuhn, *J. chim. phys.*, **23**, 521 (1926).

The evidence for reaction (1) is cited by numerous workers.[2-4,7] Farkas and Harteck, as well as Welge and Beckman, have suggested that the union of hydrogen atoms, (2), is a wall reaction. Reactions (3) and (4) followed by (6) account for the decrease in rate observed by Melville.[11] As pointed out by Taylor and Jungers,[12] reaction (3) (and also (4) followed by (6)) provides one reason for the low quantum yield in ammonia photolysis, and also accounts for the NH_2D and NHD_2 which they found in mixtures of ammonia, deuterium and mercury vapor exposed to a quartz mercury arc. The presence of hydrazine, as demanded by reaction (4), has been shown by various investigators.[7] The reaction between hydrazine and hydrogen atoms, (6), has been shown experimentally by Dixon[13] to proceed rapidly. The exact nature of this reaction is open to question,[2,3,9,14] but reaction (6) as given here appears to be probable.[3] The NH_2 formed in (6) disappears in (3), (4) or (5), and the equations may readily be combined to give the observed reaction products, $3H_2 + N_2$.

As the ammonia pressure is decreased from about one atmosphere down to about 100 mm. reactions (2) and (5) would be favored as against (3), (4) and (6) and the quantum yield should increase. At the maximum, as the different yields in the two cells indicate, the reaction becomes heterogeneous and regeneration of ammonia can now begin to occur at the walls. Thus, a rapid fall in yield is to be expected as the wall effect increases, which is in agreement with observation. The above mechanism leads to the rate equation

$$-\mathrm{d}(NH_3) = \frac{I_{\mathrm{abs.}}\sqrt{k_2(k_5 - k_4M)}}{k_3M + k_5\sqrt{\dfrac{k_2}{k_5 - k_4M}}}$$

which should hold for pressures greater than about 100 mm.; below that the reaction is both homogeneous and heterogeneous, the proportions of each depending on the pressure. At high pressures k_2 would involve three-body collisions, at intermediate pressures three-body collisions and wall reaction. The rate, it will be observed, is proportional to the energy absorbed and the quantum yield independent of light intensity, which is in agreement with observation[2,4,15] for the intensities used. As the pressure is increased above 100 mm. the denominator in the above equation increases more rapidly than the numerator and the quantum yield falls. For moderately high pressures (1.2 to 8.5 atmospheres) as in the experiments of Ogg, Leighton and Bergstrom the quantum yield would probably change very little. When the value of M attains very large values as in liquid ammonia or aqueous solutions of ammonia, the rate approaches zero. This is in agreement with the observed facts as both liquid ammonia[16] and aqueous solutions of ammonia[17] undergo no appreciable photodecomposition. The suggested mechanism also explains the lower yield in the larger cell, Cell 2, since diffusion of hydrogen atoms to the walls would be slower.

From the proposed mechanism one would predict that the addition of an inert gas to ammonia at a pressure of about 100 mm. should result in a decreased quantum yield. Likewise, the addition to ammonia at pressures of 10–40 mm. of a foreign gas so as to make the total pressure about 100 mm. should give an increased yield. These effects would account for Warburg's constant quantum yield of 0.23 at total pressures of ammonia, nitrogen and hydrogen of 800–900 mm. The work is being continued with a view to testing these and other points.

Summary

The quantum efficiency for the photolysis of ammonia by λ 2100 Å. is found to depend upon the size of the reaction cell, being slightly, but definitely, smaller in a cell of larger diameter. The reaction appears to become heterogeneous at ammonia pressures less than about 300 mm. and may be partly heterogeneous at higher pressures. A mechanism for the photodecomposition is suggested and discussed.

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(11) Melville, *Trans. Faraday Soc.*, **139**, 885 (1932).
(12) Taylor and Jungers, *J. Chem. Phys.*, **2**, 452 (1934).
(13) Dixon, THIS JOURNAL, **54**, 4262 (1932).
(14) Elgin and Taylor, *ibid.*, **51**, 2059 (1929); Wenner and Beckman, *ibid.*, **54**, 2787 (1932).
(15) Unpublished results in this Laboratory.
(16) Ogg, Leighton and Bergstrom, THIS JOURNAL, **55**, 1754 (1933).
(17) Kuhn, *Compt. rend.*, **178**, 708 (1924).