

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

Photochemical Investigations. I. The Effect of Ammonia Pressure on the Quantum Yield for the Decomposition of Ammonia¹

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The decomposition of gaseous ammonia brought about by the absorption of ultraviolet light of wave lengths 1960–2200 Å. has been the subject of a number of investigations. Warburg² first measured the quantum yield in about 1911, finding a value of 0.25, that is, the absorption of four quanta led to the decomposition of only one molecule of ammonia. Some years later Kuhn³ repeated the measurements and found a somewhat higher yield of 0.45. In a more recent study⁴ an average yield of 0.25 was obtained, in agreement with Warburg's result. The latter worked with mixtures of ammonia, nitrogen and hydrogen, the total pressure being always 800–900 mm., and found no dependence of the quantum yield on ammonia partial pressures. Kuhn used pressures of pure ammonia ranging from 5 to 900 mm. and also found the yield independent of pressure. Kistiakowsky and the present author employed pure ammonia at pressures of 1–815 mm. There was a slight indication of a maximum quantum yield at about 100 mm. ammonia pressure but the measurements were not accurate enough to conclude definitely that there existed a dependence of quantum yield on pressure.

The present work was begun with a number of objectives in view. If the quantum yield measurements were performed rather accurately, the ammonia photolysis could be used as a convenient actinometer for the study of other gaseous reactions occurring at the same wave lengths. The best gaseous standard in this region at present is hydrogen bromide, which, however, has the distinct disadvantage of attacking the mercury of the pressure measuring system and fouling the apparatus. At the same time sufficiently accurate measurements should determine definitely whether or not there is a change of yield with ammonia pressure, which is of importance in connection with the mechanism of the reaction. While the work was in progress there appeared a

paper by Ogg, Leighton and Bergstrom⁵ reporting a quantum yield of 0.14 at ammonia pressures of 1.2 to 8.5 atmospheres. This result would indicate that either the quantum yield of 0.25 found in two earlier investigations was too high or that the yield decreases on going to high pressures of ammonia.

Experimental Details

Light Source.—Light of wave length 2026–2138 Å. was obtained from a condensed spark discharge between rotating zinc electrodes, the gap being a modification of that used previously.⁴ Each zinc disk was mounted on a smaller hollow copper disk fastened to a hollow brass shaft through which air was blown. Instead of rotating the electrodes once in forty-five minutes, they were motor driven, by chain drive to prevent slipping, so as to make 30–60 revolutions per minute. The electrodes, in parallel with 10 small Dubilier condensers having a total capacity of 0.040 mfd., were connected to a 10 KVA, 15,000 v. transformer.

Monochromatic light was obtained from the spark by means of an f:1.9 monochromator with crystalline quartz optical parts.⁶ This instrument gave exceedingly good separation of the four zinc lines at 2026, 2062, 2100 and 2138 Å. With collimator and exit slits of 1.00 and 0.75 mm., respectively, one of these lines could be obtained to the practical exclusion of the others. The desired line was obtained by adjusting the monochromator so that only it could be observed in a Beck fluorescent ultraviolet spectroscope.

Apparatus and Materials.—The photolysis was carried out in an all-sealed cylindrical fused quartz cell (50 mm. long × 25 mm. diameter) with plane parallel windows. A quartz lens served to make the diverging beam from the monochromator nearly parallel through the cell. The emerging light was focused by a second lens so as to give an image of the monochromator slit on a Coblenz type linear thermopile obtained from the Eppley Laboratory. A Leeds and Northrop high sensitivity galvanometer with the scale at nearly 4 meters was used in measuring the light energy. The thermopile was checked each day against a secondary standard carbon lamp which had been calibrated against lamp C-67 of the Bureau of Standards.⁷ The transmissions of the cell windows and of the ther-

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

(6) The author wishes to acknowledge his indebtedness to Mr. Gustave Fassin, of the Institute of Applied Optics of the University of Rochester and of the Bausch and Lomb Optical Company, who kindly designed and supervised the construction of the monochromator.

(7) The author is indebted to Professor Brian O'Brien of the Institute of Applied Optics of the University for the loan of his standard lamp and of the Beck fluorescent spectroscope.

(1) Presented at the Cleveland Meeting of the American Chemical Society, September, 1934.

(2) Warburg, *Sitzb. preuss. Akad.*, 746 (1911); 216 (1912).

(3) Kuhn, *Compt. rend.*, **177**, 956 (1923); *J. chim. phys.*, **23**, 521 (1926).

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

mopile quartz window were measured for λ 2100 Å. and suitable corrections applied.

The experimental procedure was similar to that used previously, the amount of decomposition being determined by freezing out the ammonia with liquid air and measuring the pressure of nitrogen and hydrogen on a McLeod gage. The apparatus was essentially the same, with minor modifications, as that described in the earlier work,⁴ except that a trap was placed between the McLeod gage and the stopcock separating the reaction system from the pumps, etc., so that in the final distillation of ammonia into the reaction cell the gas did not pass through the stopcock. In a number of preliminary experiments designed to test the composition of the gaseous products of the photolysis a Pirani gage was inserted in the reaction system. This consisted of 50 cm. of 0.05-mm. diameter platinum wire rigidly suspended in a 12 mm. Pyrex tube which was immersed in an ice-bath. The gage was made one arm of a Wheatstone bridge and the current adjusted so that the wire was maintained at a temperature of 54°. A plot of potential drop across the gage, measured on a Leeds and Northrop Type K potentiometer, against the total gas pressure for known nitrogen and hydrogen mixtures was compared with a similar graph for the photolysis products. Known 1:3 nitrogen-hydrogen mixtures were obtained *in situ* by the decomposition of ammonia on a hot platinum wire, thus avoiding any separation of the gases due to the higher diffusion rate of hydrogen.^{4,8}

Ammonia and hydrogen bromide were prepared and purified as previously.

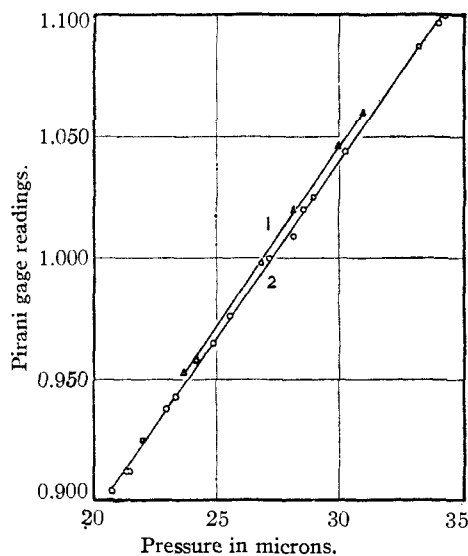


Fig. 1.—Pirani gage readings: curve 1, 77–78% hydrogen; curve 2, O, thermal decomposition of ammonia giving 75% hydrogen; □, photochemical decomposition of ammonia.

Results

Reaction Products.—Preliminary experiments indicated that in the static system used the products of ammonia photolysis are definitely nitrogen

and hydrogen in the ratio of 1:3. By means of the Pirani gage a mixture of nitrogen and hydrogen containing 77–78% of the latter could be readily distinguished from one containing 75% hydrogen. A portion of the sets of curves obtained is shown in Fig. 1. It will be observed that the points corresponding to photochemical decomposition fall on curve 2 corresponding to 75% hydrogen obtained from the thermal decomposition of ammonia on a hot platinum wire and distinctly do not fit curve 1 for 77–78% hydrogen. The latter gas mixtures were obtained by adding known small amounts of purified hydrogen to known amounts of the 75% mixture obtained as for curve 2.

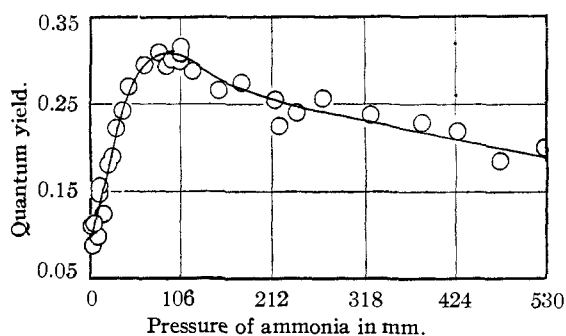


Fig. 2.—Quantum yield for the photodecomposition of ammonia as a function of pressure at λ 2100 Å.

Quantum Yields.—The quantum efficiency for the ammonia decomposition was obtained with the single line λ 2100 Å. at various ammonia pressures ranging from 0.75–840 mm. The results are given in Table I and are shown graphically up to 530 mm. in Fig. 2. It will be noted that as the ammonia pressure is increased the quantum yield increases until a maximum yield of about 0.30 is obtained at 65–120 mm. pressure and then the yield gradually falls off to about 0.18 at 840 mm.

These yields were calculated in the usual way. The number of molecules of ammonia disappearing was obtained from the pressure of nitrogen and hydrogen and the volume of the system. The energy absorbed by the ammonia was determined by the thermopile, proper corrections being applied for the experimentally determined energy losses at the windows of the cell and thermopile and at the lens. It was felt that a determination of the quantum yield for the decomposition of hydrogen bromide, which is generally accepted as being 2.0, by light of the same wave length as used here for ammonia would serve as a test of the experimental accuracy. The experiments with hy-

TABLE I
PHOTODECOMPOSITION OF AMMONIA
2100 Å. Volume, 182 cc. Room temp. 21-31°

Expt.	P_{NH_3} , mm.	Exposure, sec.	Quanta absorbed $\times 10^{-16}$	$P_{N_2+H_2}$, microns	Quantum yield
53	0.75	3600	2.89	1.085	0.111
64	2	2040	3.14	0.909	.087
52	4	3660	8.26	3.18	.114
51	7	1860	7.19	2.78	.114
63	9	2100	7.47	2.47	.099
33	10	1500	4.71	2.47	.156
34	10	1800	5.64	2.81	.148
61	15	1380	8.17	3.40	.124
50	20	1500	8.58	5.23	.180
60	25	1200	6.94	4.45	.190
49	30	1320	7.47	5.64	.223
59	38	1260	8.42	6.88	.243
24	45	1200	6.21	5.68	.271
48	64	1320	10.12	10.10	.294
46	80	1440	10.49	11.96	.309
58	88	1080	8.00	7.90	.294
47	95	1440	12.13	12.35	.301
18	105	1260	6.24	6.46	.308
45	105	1440	9.97	10.04	.299
20	106	1500	5.75	6.15	.316
44	120	1440	10.93	10.67	.288
55	150	1200	7.82	7.01	.266
43	177	1380	11.48	10.67	.275
11	215	1500	5.87	4.87	.245
15	215	1200	5.30	4.56	.256
38	220	1500	10.57	8.08	.226
54	241	1560	9.15	7.44	.241
83	250	1200	6.34	5.27	.246
42	271	1500	12.90	11.19	.257
10	325	1380	6.33	5.07	.238
41	385	1380	11.61	9.01	.229
57	427	1800	11.54	8.49	.219
40	475	1320	9.24	5.81	.185
56	528	1560	10.84	7.30	.200
85	755	1200	6.07	3.60	.176
84	840	1080	6.03	3.77	.183

drogen bromide were performed exactly as with ammonia. The data obtained are given in Table II. A slight thermal reaction of hydrogen bromide with the mercury of the McLeod gage to liberate hydrogen (column 4 of the table) had to be taken into account. This correction increased

TABLE II
PHOTODECOMPOSITION OF HYDROGEN BROMIDE
2100 Å. Room temp. 21-28°

Expt.	P_{HBr} , mm.	P_{H_2} , total, microns	P_{H_2} , thermal, microns	Quantum yield
67	11	10.61	0.21	1.99
66	26	13.88	0.78	1.92
71	36	19.49	1.23	2.22
72	48	14.01	1.58	1.90
68	84	17.36	4.95	2.02
65	182	27.03	14.95	2.02
				Av. 2.01

with increase in hydrogen bromide pressure but was almost negligible at the lower pressures. Regardless of the magnitude of the thermal correction the yield obtained was 2.0. These results would seem to indicate that the experimental procedure was highly satisfactory.

A few experiments with ammonia were performed at wave lengths other than 2100 Å. These are compared in Table III with the corresponding experiments at 2100 Å. The yields are practically the same, indicating no effect of wave length. Similar results were obtained in the previous investigation⁴ at wave lengths 1962, 2090 and 2144 Å. and by Ogg, Leighton and Bergstrom⁵ at $\lambda\lambda$ 2099, 2144 and 2194 Å.

TABLE III
PHOTODECOMPOSITION OF AMMONIA. EFFECT OF WAVE LENGTH ON QUANTUM YIELD

Expt.	Wave length, Å.	P_{NH_3} , mm.	Quantum yield
35, 36	2062	10	0.14
33, 34	2100	10	.15
27, 29	2100, 2138	10	.16
30	2062, 2100	10	.16
18, 20, 45	2100	105-106	.31
19	2100, 2138	108	.32
11, 15, 38	2100	215-220	.24
39	2062	220	.22

Discussion

The average quantum yield for all the experiments performed would be about 0.25 in agreement with previous investigations, but the present measurements are sufficiently accurate so that the dependence of the yield on ammonia pressure is clearly indicated. Warburg's experiments giving a yield of 0.25 were made at total pressures of 800-900 mm. with the ammonia content varying from *ca.* 45 mm. up to pure ammonia. The average yield in the present experiments over the same range of ammonia pressures is also about 0.25. The results reported here also appear to fall in line with those of Ogg, Leighton and Bergstrom, since the yield of 0.18 at approximately one atmosphere is about the same as theirs of 0.14 at higher pressures.

At ammonia pressures greater than *ca.* 65 mm. the reaction probably occurs entirely in the gas phase, *i. e.*, is homogeneous. At lower pressures some of the thermal reactions occurring after the splitting of the ammonia molecule into the fragments NH_2 and H by the absorption of light may possibly occur at the walls. This point is

being tested by the use of various shaped reaction vessels. These experiments should have some bearing on the mechanism, since the present mechanisms for the ammonia photodecomposition assume the reaction to be homogeneous and independent of pressure.

The results with the single line 2100 Å. throw some doubt on one widely quoted result of Kuhn's measurements. His yield of 0.45 was obtained using all four zinc lines at 2026, 2062, 2100 and 2138 Å. On using pure, monochromatic light of λ 2062 Å. Kuhn found a yield of only 0.10. The photolysis was carried out in a vessel which had its quartz windows held onto the walls by a cement and the reaction was followed by measuring the increase in the total pressure by means of a differential manometer. Ammonia was taken up by the cement so that Kuhn had to apply a correction for the decrease in pressure due to this absorption of ammonia. In the experiments with the single line 2062 Å. no increase in pressure was obtained but on applying the correction for the absorption of ammonia by the cement a yield of 0.10 resulted. In a footnote Kuhn called attention to the fact that this result should be checked in an all-sealed quartz vessel. In the present work a few experiments with the single line 2062 Å., Table III, gave the same yields at corresponding ammonia pressures as similar experiments with the single line 2100 Å. These same yields were also

obtained when two lines were used. Furthermore, these yields, instead of being much smaller, are all about the same as those obtained in previous investigations with all four zinc lines. These results would seem to indicate that the yield is the same whether the light absorbed contains a single line, two lines or all four zinc lines and that Kuhn's low result was in error due to the correction he had to apply. Further experiments will shortly settle this question.

In conclusion, the data reported here show a distinct effect of ammonia pressure on the quantum yield for the photodecomposition of ammonia. The reaction might still be used as an actinometer provided that the yield, especially at higher pressures where absorption is complete, is independent of the size and shape of the reaction cell.

Summary

The quantum yield for the decomposition of ammonia by light of λ 2100 Å. is found to be dependent upon the ammonia pressure, the yield rising from *ca.* 0.10 at 1–10 mm. to *ca.* 0.30 at 65–120 mm. and then falling to 0.18 at one atmosphere of ammonia. The yield appears to be independent of the "purity" of the light, contrary to earlier work; the amount of decomposition is the same whether one, or two or more of the four zinc lines of $\lambda\lambda$ 2026, 2062, 2100 and 2138 Å. is used.

ROCHESTER, N. Y.

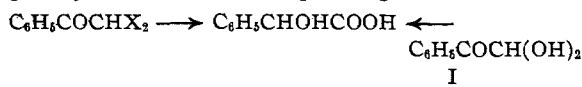
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The Reaction of Alpha-Dihaloacetophenones with Alkali

BY C. HAROLD FISHER AND CHEVES T. WALLING

In most of the cases¹ thus far studied, α -dihaloacetophenones have been found to react readily at room temperature with dilute alkali to give good yields of the corresponding mandelic acids.



Indeed, in several instances substituted mandelic acids may be prepared most expeditiously by this method.

Although no extensive study has been made, it seems that this interesting transformation has

(1) Engler and Wöhrle, *Ber.*, **20**, 2201 (1887); Engler and Zielke, *ibid.*, **22**, 204 (1889); Schweitzer, *ibid.*, **24**, 547, 997 (1891); Houben and Fischer, *ibid.*, **64B**, 2636 (1931); Collet, *Bull. soc. chim.*, [3] **21**, 70 (1899).

been regarded as a benzylic acid rearrangement of the glyoxal, or its hydrate (I), which had been produced previously by a metathetical reaction between alkali and the dihalo ketone. According to this view of the reaction a dihaloacetophenone with substituents in the ortho positions should react in the same way with alkali to give the glyoxal hydrate, which then would undergo the benzylic acid rearrangement² in the normal manner. Evidence to the contrary was obtained in a preliminary examination³ which shows that α , α -dibromo-4-chloroacetophenone dissolves in dilute potas-

(2) It has been shown that steric hindrance does not prevent this rearrangement of phenylglyoxal [Gray and Fuson, *THIS JOURNAL*, **56**, 739 (1934)].

(3) Fisher, *ibid.*, **55**, 5005 (1933)