7 and 19. This mechanism will explain the catalysis below the value of a_{H^+} at which oxidation of iodine by hydrogen peroxide begins.

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THE PHOTOCHEMICAL DECOMPOSITION OF AMMONIA

BY EDWIN O. WIIG[1] AND G. B. KISTIAKOWSKY

The mechanism of the apparently simple photochemical decomposition of ammonia by ultraviolet light is still far from being settled. The reaction has been studied by Warburg and by Kuhn in light of wave length 2025–2140 Å. The former[2] obtained a quantum yield of 0.25, whereas the latter[3] found an average of 0.45 molecule of ammonia decomposed per quantum of light energy absorbed. In the far ultraviolet, 1600–1900 Å., the quantum yield reported by Kassel and Noyes[4] is 0.69 ± 0.24. These quantum yields have been calculated on the assumption that the photochemical decomposition follows the equation

$$2NH_3 = N_2 + 3H_2 \tag{1}$$

However, Bates and Taylor[5] state that the products of decomposition contain 96% hydrogen and 4% nitrogen and express the view that hydrazine is formed, some of which may subsequently decompose. Recently, just as this work was completed, Koenig and Brings[6] reported hydrazine as a product of the photochemical decomposition of ammonia by ultraviolet light. By repeatedly flowing ammonia gas back and forth through a quartz vessel exposed to the radiation from a zinc spark for fifty hours and by continuously freezing out the hydrazine, a very minute quantity of the latter was condensed, sufficient for a qualitative test. Warburg and Kuhn determined the amount of reaction by measuring the increase in pressure, so that their low quantum yields might be accounted for by assuming that the reaction which occurs is largely

$$2NH_3 = N_2H_4 + H_2 \tag{2}$$

instead of equation (1). Kuhn found that on complete decomposition of ammonia the pressure doubled; this, however, does not prove much since hydrazine would also decompose under such treatment.

It is evident then that the composition of the gas resulting from the photolysis of ammonia should be determined under the same conditions

1 National Research Fellow in Chemistry.

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

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

4 L. S. Kassel and W. A. Noyes, Jr., THIS JOURNAL, **49**, 2495 (1927).

5 J. R. Bates and H. S. Taylor, *ibid.*, **49**, 2438 (1927).

6 A. Koenig and T. Brings, *Z. physik. Chem.*, Bodenstein Festband, 595 (1931).

that obtain during quantum yield measurements.   It was the object of the present work to determine the nature of the gas formed when ammonia is exposed to ultraviolet light and to obtain the quantum yields for the reaction at room temperature and at higher temperatures.

Experimental Details

Light Source.—A condensed spark discharge served as the source of ultraviolet light.   The spark gap was an adaptation of one described recently by Forbes and Brackett.[7]   It consisted of two metallic disks 8 cm. in diameter and 5 mm. thick with V shaped edges.   The disks—made of aluminum, zinc or cadmium—were mounted at right angles one above the other (Fig. 1) and were driven through reduction gears and insulated shafts by two Telechron clock motors.   They revolved at the rate of one rotation in forty-five minutes, offering to the spark a steady supply of fresh surface and keeping its location sharply defined.   The electrodes were connected, in parallel with a condenser,
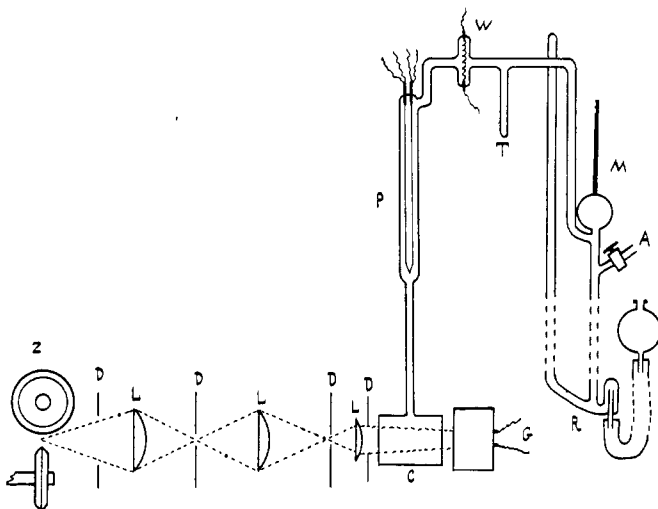

Fig. 1.—Apparatus: Z, spark electrodes; D, diaphragms; L, crystal quartz lenses; C, reaction cell; G, thermopile; P, Pirani gage; W, Pt wire for NH$_3$ decomposition; T, trap; M, McLeod gage; R, mercury manometer and leveling bulb; A, connection to the pump and gas storage bulbs.

to the poles of a 5 KVA, 10,000 v. transformer.   A stream of air was blown across the spark gap.   The arrangement worked very satisfactorily and the only source of complication was the home-made condenser, which heated gradually on continuous operation and caused a slow but steady decrease of light intensity.

The difficulty in obtaining large quartz prisms sufficiently transparent to wave lengths in the neighborhood of 2000 Å. led to the use of focal isolation instead of a monochromator in obtaining monochromatic radiation.   The arrangement, shown schematically in Fig. 1, gave an approximately monochromatic beam, as shown by the fact that, according to thermopile measurements, as much as 95% of the radiation was ab-

[7] Forbes and Brackett, THIS JOURNAL, 53, 3973 (1931).

sorbed by ammonia when zinc electrodes were used. Spectrograms of the light source confirmed this.

Apparatus and Materials.—The rate of ammonia decomposition was followed by measuring the pressure of hydrogen and nitrogen formed on freezing out ammonia. A McLeod gage and a Pirani gage were incorporated in the apparatus. By calibrating the latter with differently proportioned mixtures of nitrogen and hydrogen and by using both gages in each measurement, the possibility was given to determine not only the pressure but also the composition of the gases resulting from ammonia decomposition. The apparatus is shown schematically in Fig. 1. The quartz cell for the photolysis was of cylindrical shape, 50 mm. long and 25 mm. in diameter, with sealed polished windows. The McLeod gage was of usual construction and had a volume of *ca.* 150 cc. The Pirani gage consisted of 35 cm. of a platinum wire 0.076 mm. in diameter, suspended rigidly in the form of four loops in a 12 mm. tubing and silver soldered to platinum leads. The current through the gage was kept constant and the potential drop was measured by means of a Wolf potentiometer. The temperature of the wire was from 100 to 300° above the temperature of the surrounding constant-temperature (25.0°) water-bath. The gage was calibrated—using the McLeod gage of the system as standard—on carefully purified hydrogen admitted from a storage bulb and on a 1:3 nitrogen-hydrogen mixture prepared *in situ* by decomposing ammonia on the glowing platinum wire (Fig. 1). Tungsten wire was also used for this purpose with identical results.

The volume of the system was corrected for the effect of cooling the trap T (Fig. 1) in freezing out ammonia.

In high temperature experiments the quartz cell was wrapped with resistance wire and asbestos insulation. The temperature in these experiments was measured by a calibrated thermocouple in immediate contact with the quartz cell.

The source of ammonia gas was c. p. ammonium hydroxide solution contained in a storage flask connected with which was a tube of potash sticks and powdered sodium hydroxide, followed by a stopcock and suitable traps for condensing ammonia by cooling with liquid air. After freezing out the desired amount of ammonia with liquid air, the condensation bulb was surrounded with a carbon dioxide–acetone freezing mixture or a hydrochloric acid–ice mixture and the ammonia was allowed to distil into a second bulb surrounded by liquid air. A similar distillation from this bulb allowed the ammonia to expand into the reaction system. The first and last portions were discarded in each distillation.

Hydrogen bromide was prepared by dropping a c. p. 82% solution of hydrobromic acid on phosphorus pentoxide and passing the gas over red phosphorus and phosphorus pentoxide into a condensation bulb surrounded by carbon dioxide–acetone mixture and the hydrogen bromide was allowed to distil into a second bulb surrounded with liquid air. This was followed by a similar distillation into a third bulb from which another distillation sent the hydrogen bromide into a storage bulb connected with the pumping and reaction systems. The liquid hydrogen bromide in the last distillation was colorless.

The light energy was measured by means of a Moll "large surface" thermopile connected with a Leeds and Northrup galvanometer. A fixed diaphragm in front of the reaction cell, slightly smaller than the thermopile surface, aided in focusing the light on the pile. The galvanometer, thermopile and connecting wires were carefully shielded against electrical disturbances from the spark discharge. The calibration of the thermopile against a Bureau of Standards calibrated lamp was carried out exactly as recommended by the Bureau.

A typical experiment was carried out as follows. Ammonia was admitted into the reaction system, frozen in the trap T by means of liquid air and pumped until the pressure of any residual gases (on repeated evaporation and condensation of ammonia)

was less than 1×10^{-4} mm.   The mercury leveling bulb was raised to fill the McLeod gage completely and the rubber tubing connecting the leveling bulb to the gage column clamped with a screw pinchcock.   The stopcock shown in Fig. 1 prevented mercury from flowing into the main line of the pumping system.   The liquid air was removed and the ammonia evaporated into the quartz cell and Pirani gage, its pressure being measured on a manometer sealed into the lower part of the McLeod gage column.   After the decomposition, photochemical or thermal, the ammonia was frozen, evaporated and again frozen, the mercury leveling bulb lowered and the gaseous products allowed to expand into the McLeod gage, when the necessary readings on the gages were taken.

Experimental Results

Reaction Products.—The dependence of the quantum yield calculations on the nature of the products formed suggested the advisability of first investigating the composition of the gaseous products.   Ammonia at pressures ranging from 13 to 377 mm. was exposed to the radiation of the zinc and aluminum sparks.   Various lengths of illumination from one minute upward were employed, giving pressures of the products varying from 0.008 to 0.086 mm.   Photochemical decompositions were alternated with thermal decompositions on the glowing wire.   Three Pirani and three McLeod gage readings were taken alternately for each point.   The results are shown in Fig. 2. Similar results were obtained in other series of experiments in which total radiation of the spark discharge was employed.   The results show that the products of thermal and photochemical decompositions are identical.

Fig. 2.—Pirani gage readings on the products of the thermal and photochemical decomposition of ammonia: ☉, pure hydrogen; ○, products of thermal decomposition; ⊕, products of photochemical decomposition.

As it has been repeatedly shown that in the thermal decomposition a 1:3 nitrogen–hydrogen mixture is obtained, the same applies to the photochemical reaction.   The limits of errors are difficult to estimate but the photochemical products contained certainly not more than 80 and not less than 70% hydrogen and in all probability were much nearer to the stoichiometric ratio.
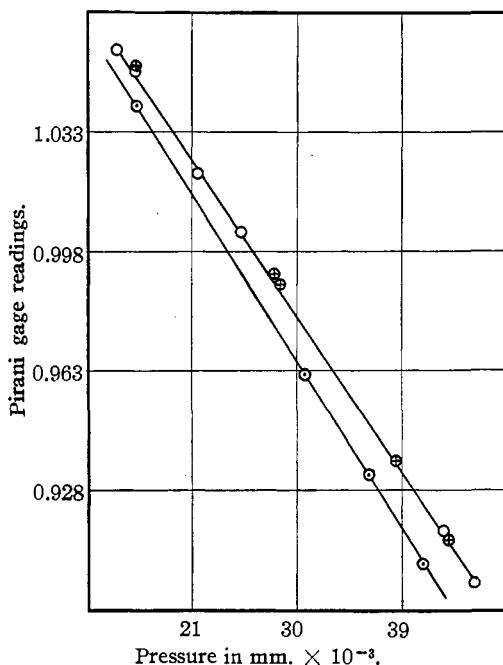
In some earlier series of these experiments the procedure in obtaining a 1:3 nitrogen hydrogen mixture was somewhat different. Ammonia was decomposed on the glowing wire to the extent of 0.2–0.3 mm. and the excess of decomposition products, on condensing ammonia, was pumped out until the desired pressure was obtained. Sometimes also a 1:3 mixture was admitted from a storage flask to a pressure of 0.2–0.3 mm. and later reduced by pumping. In all these experiments rather irregular results were obtained and it appeared that the products of photochemical decomposition contained more than 75% hydrogen. These results were
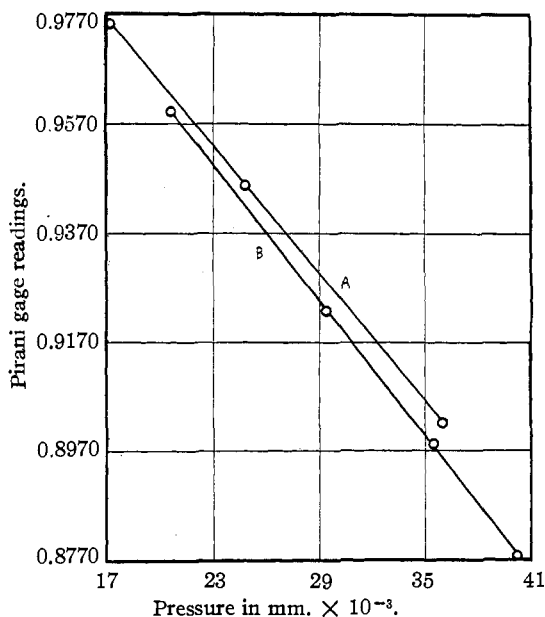

Fig. 3.—Comparison of methods of calibrating Pirani gage on $3H_2:1N_2$ mixtures: A, pressures reduced from 0.2 mm.; B, gas pressures produced by decomposition of NH_3 in situ.

ultimately traced to a partial separation of nitrogen and hydrogen while reducing their pressure by pumping. At the low pressures employed, hydrogen, due to its higher diffusion rate, is more rapidly removed from the system on opening the stopcock leading to the pumps than is nitrogen. As a result, the remaining mixture contains more than the original 25% nitrogen and a difference in composition is found in comparing the products of photochemical decomposition. The difficulty was avoided by decomposing ammonia on the glowing wire only until the desired pressure of nitrogen and hydrogen was obtained. All final results were obtained by this method. A comparison of the two methods is shown in Fig. 3.

Quantum Yields.—Ammonia was exposed for a period of ten to twenty minutes to the light obtained by focal isolation from the zinc, aluminum and cadmium sparks. The light energy was measured by means of the thermopile before and after the photolysis. Energy measurements were made with the quartz cell empty and filled with ammonia at the desired pressure, the difference giving the energy absorbed by the ammonia. Usually the intensity of the light source slowly decreased during an experiment. All experiments in which the energy absorbed by ammonia changed by more than 20% during the photolysis were discarded. The quantum yields rejected for this reason always agreed very well with those experiments in which the light source was more constant.

Occlusion of nitrogen and hydrogen by the solid ammonia would tend to give a low quantum yield. That no such occlusion occurred was shown in the following way. Ammonia at 25 mm. pressure was decomposed until the pressure of the products was 0.175 mm. Sufficient ammonia at high pressure, which had been carefully pumped until free of residual gases, was rapidly let into the reaction system. The total ammonia pressure was now 280 mm. and when this was frozen out the pressure of the nitrogen and hydrogen was again found to be 0.175 mm. A second experiment with the ammonia at pressures of 10 and 675 mm. gave 0.0239 and 0.0230 mm. of nitrogen and hydrogen, a change of less than 4% for a 67.5-fold increase in ammonia.

After the experiments were all completed, the rear window of the quartz reaction cell was cut away and, using the monochromatized light from the zinc spark, measurements were made of the energy falling on the thermopile without and with the rear window. The ratio of energy without to that with the window was 1.29. A similar quartz window on the thermopile was found to transmit 91.5% of the visible light with which the thermopile was calibrated and only 77.5% of the ultraviolet light falling on it. This gives a factor of 1.18 or a total factor of $1.18 \times 1.29 = 1.52$, by which the energy, as measured by the thermopile, is to be multiplied to obtain that reaching the ammonia within the cell.

Some doubts were felt concerning the accuracy of the absolute value of the quantum yields calculated by means of these corrections. They were based on the observation that the various parts of the thermopile surface differed in light sensitivity. With constant light intensity four equal areas gave mean galvanometer deflections of 2.23, 2.07, 2.68 and 3.32 cm., the first value being that obtained for the center section of the surface. The source of ultraviolet light was not homogeneous but appeared most intense at the center. Thus in our photochemical experiments the energy of the ultraviolet light falling on the thermopile was greater than that indicated by calibration against a uniform light source. Since the quantum yield for the decomposition of hydrogen bromide in the region with which

we are dealing is known to be 2.0,[8] it was decided to check our system on this substance.

Pure hydrogen bromide was admitted to the quartz cell and its photochemical decomposition followed exactly as in the case of ammonia. It was observed that hydrogen bromide underwent a slight thermal decomposition at room temperature. This slight reaction was determined before and after each photochemical decomposition and corrected for in calculating the quantum yield. In one experiment, for example, a total of 0.1142 mm. of hydrogen was evolved, while the correction amounted to 0.0026 mm. The average of the quantum yields found for hydrogen bromide, as shown in Table I, is 3.33 instead of the value of 2.0 found by Warburg. This latter value cannot be doubted. Not only is it the result of a very careful direct investigation, but it is also supported by numerous independent observations concerning the reactions of hydrogen and bromine atoms. Thus it must be concluded that the quantum yields for ammonia decomposition obtained by means of thermopile measurements must be further divided by 1.66. These corrected values are given in the following tables, II–V.

TABLE I

QUANTUM YIELDS FOR THE DECOMPOSITION OF HYDROGEN BROMIDE AT ROOM
TEMPERATURE

Zn spark, mean λ = 2090 Å.

P_{HBr}, mm.	Time of illumination, sec.	P_{H_2}, mm.	Mean energy absorbed, ergs/sec.	Quantum yield, mole/quantum
38	983	0.0886	2951	3.77
37	917	.1016	4015	3.40
28	967	.1116	4033	3.53
20	831	.0941	4678	2.99
12	710	.0240	1400	2.98
			Mean	3.33

The quantum yields of the ammonia decomposition obtained at room temperatures (21–30°) are given in Tables II, III and IV. A typical experiment showed the following data and calculations:

Mean λ, 2090 Å.; apparent volume of system, 204 cc.; temp., 26.7°; NH_3, 110 mm.; galvanometer deflection of 1 cm. = 235.3 ergs/sec.; time of exposure, 1071 sec.; pressure ($N_2 + 3H_2$), 0.0692 mm.

At start of experiment { Av. galv. defl. without NH_3 in cell = 13.15 cm.
                          Av. galv. defl. with NH_3 in cell = 1.54 cm.

At end of experiment { Av. galv. defl. without NH_3 in cell = 12.55 cm.
                        Av. galv. defl. with NH_3 in cell = 1.31 cm.

Mean energy absorbed by NH_3 = $\left[\dfrac{(13.15 - 1.54) + (12.55 - 1.31)}{2}\right] \times 235.3 \times$
1.18×1.29 = 4090 ergs/sec.

Total energy absorbed by NH_3 = 466 × 10^{15} quanta

[8] E. Warburg, Sitzb. preuss. Akad., 314 (1916).

Molecules NH_3 decomposed $= 6.06 \times 10^{23} \times \dfrac{204}{22,400} \times \dfrac{0.0692}{2 \times 760} \times \dfrac{273}{299.7} =$
$$229 \times 10^{15}$$

Apparent quantum yield $= \dfrac{229 \times 10^{15}}{466 \times 10^{15}} = 0.49$ molecule/quanta

Corrected quantum yield $= \dfrac{0.49}{1.66} = 0.30$ molecule/quanta

TABLE II

QUANTUM YIELDS IN THE DECOMPOSITION OF AMMONIA AT ROOM TEMPERATURE

Zn spark, mean $\lambda = 2090$ Å.

P_{NH_3}, mm.	Time of illumination, sec.	$P_{H_2 + N_2}$, mm.	Mean energy absorbed, ergs/sec.	Quantum yield, mole/quantum
815	780	0.0322	4506	0.17
630	751	.0371	5426	.17
630	758	.0330	5308	.15
515	1059	.0521	4843	.19
513	1354	.0713	4542	.22
239	779	.0459	4391	.26
228	771	.0384	4373	.22
219	891	.0207	1938	.22
111	879	.0514	4022	.27
111	786	.0534	4710	.27
111	812	.0581	4477	.30
110	1071	.0692	4090	.30
106	841	.0242	2532	.21
70	810	.0228	2428	.22
59	768	.0399	3736	.26
57	866	.0476	3489	.30
12	817	.0273	3087	.21
10	871	.0239	3055	.17
5	885	.0197	2314	.18
				Mean .23

TABLE III

QUANTUM YIELDS IN THE DECOMPOSITION OF AMMONIA AT ROOM TEMPERATURE

Al spark, mean $\lambda = 1962$ Å.

P_{NH_3}, mm.	Time of illumination, sec.	$P_{H_2 + N_2}$, mm.	Mean energy	Quantum yield, mole/quantum
430	814	0.0192	1931	0.24
430	1679	.0148	698	.25
225	1223	.0228	1479	.25
190	1122	.0256	1748	.26
110	1091	.0327	2081	.29
103	1407	.0388	1913	.29
51	1460	.0340	1941	.24
12	1419	.0267	1547	.24
4	1403	.0097	731	.19
4	1996	.0149	673	.22
1	2013	.0120	566	.21
				Mean .24

TABLE IV

QUANTUM YIELDS IN THE DECOMPOSITION OF AMMONIA AT ROOM TEMPERATURE

Cd spark, mean λ = 2144 Å.

P_{NH_3}, mm.	Time of illumination, sec.	$P_{H_2+N_2}$, mm.	Mean energy absorbed, ergs/sec.	Quantum yield, mole/quantum
116	1427	0.0207	910	0.29
112	1131	.0177	1433	.20
109	1370	.0113	587	.26
				Mean .25

Kuhn[9] reported a nine-fold increase in quantum yield of ammonia decomposition on increasing the temperature from 20 to 500°. As Kuhn has not given any details of his measurements it seemed desirable to repeat his work, particularly since photographs of ammonia absorption spectra taken at high temperatures showed several new bands appearing in the region 2100–2500 Å. and those present at room temperature being enhanced. As measurements of light energy absorbed by ammonia at 500° offered considerable difficulties, the energy measurements were carried out at room temperature. The error thus introduced is negligibly small since with our monochromatizing system about 90% of energy is absorbed and, as photographs showed, absorption in this (2100 Å.) region increases with temperature. After determining the energy absorbed ammonia was frozen out, the cell quickly heated to the desired temperature and ammonia vaporized. After completion of illumination ammonia was frozen out again, the cell quickly cooled and a second measurement of absorbed light energy made. Before each experiment the cell was degassed at 500°.

In calculating the quantum yields given in Table V corrections have been made for ammonia decomposed while energy measurements were performed and for a very slight thermal decomposition in the cell at high temperatures.

TABLE V

QUANTUM YIELDS FOR THE DECOMPOSITION OF AMMONIA AT HIGH TEMPERATURES

Zn spark, mean λ = 2090 Å. Time of illumination, 600 sec.

Temp., °C.	P_{NH_3}, mm.	$P_{H_2+N_2}$, mm.	Mean energy absorbed, ergs/sec.	Quantum yield, mole/quantum
300	150	0.0200	1834	0.34
	95	.0328	2543	.40
				Mean .37
500	148	0.0511	3206	0.49
	142	.0397	2403	.50
	89	.0351	2314	.46
				Mean .48

The Reaction Mechanism.—The results here obtained may be summed up as follows. The gaseous products of decomposition are very nearly

[9] W. Kuhn, *Compt. rend.*, 178, 708 (1924).

a 1:3 nitrogen–hydrogen mixture, irrespective of the time of illumination. The quantum yield is 0.25 at room temperature and about double this value at 500°. It does not depend on ammonia pressure over the range 800 to 1 mm., wave length of radiation from 2150 Å. to 1960 Å., intensity of radiation varied seven-fold and amount of decomposition varied seven-fold.

These results are in partial agreement with the data already recorded in the literature. From the description of Koenig and Brings[6] it is apparent that hydrazine is present only in traces even in rapidly flowing ammonia. Our results point in the same direction. Moreover, it is possible to show that low, if any, yield of hydrazine is not due to its secondary photochemical decomposition. Experiments of Elgin and Taylor[10] indicate that the photochemical decomposition of hydrazine has a quantum yield not much greater than unity. The absorption spectrum of hydrazine[11] is continuous and thus absorption certainly follows Beer's law. A rate of photochemical decomposition of hydrazine sufficiently rapid to explain our failure to detect this substance would require light absorption coefficients at least 10^5 higher than those of ammonia in the region 2150–1970 Å. From Elgin's qualitative description such large values seem to be out of the question.

Bates and Taylor assumed hydrazine formation, finding excess hydrogen in decomposition products of ammonia. Their experimental set-up favored, however, an accumulation of hydrogen, due to its rapid diffusion, in the analytical part of the apparatus. An effect of this type was discussed here on previous pages and Professor H. S. Taylor in a personal discussion suggested it as a possible explanation of his and Bates' results.

The results of Dickinson and Mitchell[11] which also indicate an excess of hydrogen in photochemical decomposition of ammonia are somewhat inconclusive as the authors themselves admit.

The value of the quantum yield here obtained agrees excellently with the value given by Warburg. In view of this agreement one may safely conclude that Kuhn's value is erroneous. Possibly the use of a surface thermopile without correcting it for unequal sensitivity caused an error similar to one described on previous pages. The pronounced decrease in the quantum yield, which Kuhn found on improving the monochromacy of radiation, is impossible to explain. It cannot be incorporated in any theory of the reaction which has been set up and we are inclined to attribute it to some unknown experimental error.

Kassel and Noyes[4] found a quantum yield about 0.69 in the spectral region 1600–1900 Å.

As the authors point out, this value may be somewhat too high. From

[10] Elgin and Taylor, THIS JOURNAL, **51**, 2059 (1929).
[11] Dickinson and Mitchell, *Proc. Nat. Acad. Sci.*, **12**, 692 (1926).

kinetic considerations (see later) it seems more likely that with these short wave lengths the same quantum yield obtains as in the region above 1950 Å. However, an increase of quantum yield is not impossible from the point of view of the most likely reaction mechanism and only some future experiments can decide the correctness of Kassel and Noyes' value.

Kuhn[3] reported a nine-fold increase in quantum yield from 20 to 500°, while here only a doubling has been observed. In absence of any experimental details it is impossible to say whether Kuhn measured the quantum yield or only the reaction velocity at high temperatures and whether some light of wave lengths longer than 2100 Å. was present. In the latter case the change of ammonia absorption with temperature may partly account for Kuhn's results. On the other hand, in the present experiments the quartz cell may have been more opaque to radiation while heated to high temperatures. This is quite in accord with the generally observed shift of absorption to longer wave lengths in liquid and solid systems. Furthermore, some of the gas formed in ammonia decomposition may have been adsorbed on the walls of the quartz cell after cooling. Thus the doubling of quantum yield between room temperature and 500° appears rather as the lower limit of the temperature coefficient of the quantum yield.

As has been pointed out by Lind[12] the temperature coefficient observed by Kuhn is almost identical with the value found by Wourtzel[13] for the ammonia decomposition by α-particles.

This agreement undoubtedly supports Kuhn's value as contrasted with ours. For the following considerations the numerical value of the temperature coefficient is, however, not of paramount importance. Its existence shows the presence of some secondary reactions requiring activation energy and favoring the decomposition.

Further facts to be considered in setting up a mechanism of ammonia decomposition are that neither nitrogen nor hydrogen has any effect on reaction rate at room temperature[2,14] but that the latter retards the rate at 500°.[3]

Bonhoeffer and Farkas[15] have shown that ammonia is decomposed photochemically at pressures as low as 10^{-3} mm. This, together with the absence of rotational structure in absorption bands of ammonia and lack of fluorescence, led the authors to suggest that ammonia molecules decompose without intervention of collisions in a predissociation[16] process. The time interval between light absorption and dissociation in such proc-

[12] "Chemical Effects of α-Particles," Chemical Catalog Company, New York, 1928, p. 215.

[13] Wourtzel, Le Radium, 11, 342 (1919).

[14] Coehn and Pringent, Z. Elektrochem., 20, 275 (1914).

[15] Bonhoeffer and Farkas, Z. physik. Chem., 134, 337 (1928).

[16] V. Henri, "Structure des Molecules," Paris, 1925.

esses has been variously estimated as 10^{-10}–10^{-11} sec., thus a time compara-
ble to average time between molecular collisions at atmospheric pressure.
It is, however, necessary to assume that collisions have no effect on dissocia-
tion of excited ammonia molecules since otherwise a change of quantum
yield with pressure would have been observed. Thus the deficiency of
quantum yield must be due to some secondary reactions in which the
dissociation products recombine again to form ammonia molecules. There
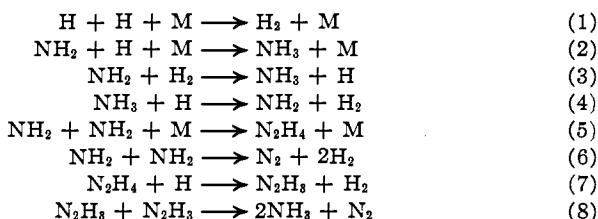are two energetically possible ways in which ammonia could decompose

$$\text{I} \quad NH_3 + h\nu \longrightarrow NH + H_2$$
$$\text{II} \quad NH_3 + h\nu \longrightarrow NH_2 + H$$
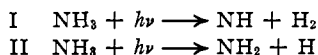
The first scheme leads however to reaction mechanisms which do not agree
with experimental facts. The reaction $2NH \longrightarrow N_2 + H_2$ would give a
quantum yield unity. The reaction $NH + H_2 \longrightarrow NH_3$ would require
retardation by hydrogen. The reaction $NH + NH_3 \longrightarrow N_2H_4$ would re-
sult in a quantitative formation of hydrazine since no mechanism is avail-
able for its decomposition (the reaction $N_2H_4 + NH \longrightarrow NH_3 + N_2 + H_2$
would again give a quantum yield unity).

The second mode of decomposition has numerous observations in
its favor.

Thus Farkas, Haber and Harteck[17] were able to sensitize hydrogen–
oxygen and carbon monoxide–oxygen reactions by decomposing photo-
chemically ammonia added to the gas mixtures. Taylor and Eméleus[18]
sensitized in the same manner polymerization and hydrogenation of ethyl-
ene, while Hill and Vernon[18] reduced tungstic oxide by decomposing am-
monia at low pressures. All these effects are interpreted as indicating
the presence of hydrogen atoms.

The secondary reactions to be considered if ammonia decomposes accord-
ing to the second scheme are

$$H + H + M \longrightarrow H_2 + M \tag{1}$$
$$NH_2 + H + M \longrightarrow NH_3 + M \tag{2}$$
$$NH_2 + H_2 \longrightarrow NH_3 + H \tag{3}$$
$$NH_3 + H \longrightarrow NH_2 + H_2 \tag{4}$$
$$NH_2 + NH_2 + M \longrightarrow N_2H_4 + M \tag{5}$$
$$NH_2 + NH_2 \longrightarrow N_2 + 2H_2 \tag{6}$$
$$N_2H_4 + H \longrightarrow N_2H_3 + H_2 \tag{7}$$
$$N_2H_3 + N_2H_3 \longrightarrow 2NH_3 + N_2 \tag{8}$$

For reactions 2 and 5 the triple collisions are not absolutely necessary
on account of a larger number of internal degrees of freedom available, but
are rather likely.

In considering the reaction mechanism at room temperature, reactions
3 and 4 may be neglected. The first would require a retardation by

[17] Farkas, Haber and Harteck, *Naturwissenschaften*, **12**, 267 (1930).
[18] Taylor and Eméleus, THIS JOURNAL, **53**, 562 (1931).

hydrogen; the second has been shown to occur extremely slowly by Boehm and Bonhoeffer.[19] For the decomposition at high temperatures, on the other hand, these reactions are probably quite important, the one producing the observed retardation by hydrogen, the other the increase of quantum yield.

The simplest scheme of secondary reactions at room temperature involves processes 1, 2, 6. It leads, however, to a quantum yield dependent on total pressure; since reaction 1 requires triple collisions, reaction 6 certainly does not, while 2 is doubtful. In the more general case, when it is assumed that reaction 2 requires triple collisions at low pressures but does not at high, a pronounced minimum of quantum yield would be obtained in the transition pressure region of reaction 2. This is certainly not the case experimentally since if anything a slight maximum was observed at intermediate pressures with zinc spark.

The remaining possibility involves reactions 1, 2, 5, 7, 8. The quantum yield is now determined by the ratio $\kappa_2^2/\kappa_1\kappa_5$ which must be equal to eight if the quantum yield is 0.25. Since it is quite possible that all these reactions require triple collisions, the quantum yield may be independent of pressure. It will be also independent of light intensity and amount of decomposition. Reaction 1 needs no further justification and reaction 2 is also quite likely to occur. Reaction 5 is made plausible by the finding of traces of hydrazine in ammonia decomposition experiments by the flow method.

Reactions 7 and 8,[20] necessary to explain the absence of larger amounts of hydrazine, may appear somewhat artificial. However, independent evidence can be adduced in their favor. Elgin and Taylor[10] found that in the presence of excited mercury the decomposition of hydrazine was about twice as fast as the rate of water formation. Using an incorrect value of Marshall[21] for the quantum yield of the latter reaction, they attempted to derive a chain mechanism for hydrazine decomposition. In the meantime Frankenburger and Klinkhard[22] have shown that water formation has a quantum yield near unity. Thus two molecules of hydrazine must be decomposed by each excited mercury atom. This finds a most simple explanation in the scheme

$$N_2H_4 + Hg^* \longrightarrow N_2H_3 + H + Hg$$
$$N_2H_4 + H \longrightarrow N_2H_3 + H_2$$
$$2N_2H_3 \longrightarrow 2NH_3 + N_2$$
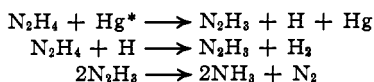
The scheme accounts for the quantum yield, the nature of the reaction products and also for the observation of Elgin and Taylor that in presence

[19] Boehm and Bonhoeffer, Z. physik. Chem., 119, 385 (1926).

[20] Reaction 8 could be replaced by $N_2H_3 + NH_2 \longrightarrow N_2 + H_2 + NH_3$. A decision is impossible at present.

[21] Marshall, J. Phys. Chem., 30, 1078 (1926).

[22] Frankenburger and Klinkhard, Trans. Faraday Soc., 431 (1931).

of excess hydrogen the rate of hydrazine decomposition remains unchanged. In the latter case the primary reaction is $Hg^* + H_2 \longrightarrow Hg + 2H$ followed by the two last reactions of the preceding scheme. The reactivity of hydrogen atoms toward hydrazine and their inertia toward ammonia are quite analogous to their behavior toward methane and higher saturated hydrocarbons.[23]

Results obtained in the extensive work on electric discharges through ammonia and on allied phenomena are somewhat discordant and no binding conclusions can be drawn.

Steiner's[24] conclusion that in the reactions of atomic nitrogen and hydrogen hydrazine is formed by the reaction $2NH_2 + M \longrightarrow N_2H_4 + M$ agrees with the one proposed here. However, Steiner's conclusions should be reviewed in the light of the unquestionable fact that hydrogen atoms decompose hydrazine.

Koenig and Wagner[25] find that by decreasing electric current and increasing ammonia flow through silent discharges, the net reaction $2NH_3 \longrightarrow N_2H_4 + H_2$ can be made to occur almost quantitatively. A decomposition of ammonia by electron impact in the way suggested by the authors: $NH_3 \longrightarrow NH + H_2$, followed by the reaction $NH + NH_3 \longrightarrow N_2H_4$, accounts for these results much better than the decomposition $NH_3 \longrightarrow NH_2 + H$. In the latter case a quantitative yield of hydrazine could hardly be expected judging from the photochemical reaction.

Results which do not agree with the mechanism of ammonia decomposition proposed herein are contained in the work of Gedye and Allibone[26] on ammonia decomposition by high speed electrons. They find that the hydrazine yield increases with decreasing pressure in the range 700 to 50 mm. If NH_2 radicals are formed here, hydrazine formation is a triple collision process, the decomposition a bimolecular reaction and roughly a proportionality of the yield with pressure should be expected. Formation of NH radicals does not make the explanation simple either. The suggestion of the authors that hydrazine formation is a wall reaction would require an extraordinary chemical inertia of whatever radicals and atoms are formed, so that these have time to diffuse to the walls.

One difficulty of the proposed ammonia decomposition mechanism has not been touched upon yet. Accepting the velocity constant of hydrogen atom recombination as determined by Steiner and Wicke[27] or by Senftleben and Riechemeyer[28] it is found that reactions 1, 2, 5 must proceed chiefly in the gas phase near the upper limits of ammonia pressures here

[23] Bonhoeffer and Harteck, *Z. physik. Chem.*, **139**, 64 (1928).

[24] Steiner, *Z. Elektrochem.*, **36**, 807 (1930).

[25] Koenig and Wagner, *Z. physik. Chem.*, **144A**, 213 (1930).

[26] Gedye and Allibone, *Proc. Roy. Soc.* (London), **A130**, 346 (1931).

[27] Steiner and Wicke, *Z. physik. Chem.*, Bodenstein Festband, 817 (1931).

[28] Senftleben and Riechemeyer, *Ann. Physik*, **6**, 105 (1930).

investigated. Near the low limit of this pressure however the atoms and radicals have a 1000:1 chance to diffuse to the walls before reaction. Thus it becomes necessary to assume that the ratio $\kappa_2^2/\kappa_1\kappa_5$ is the same for wall and gas reactions.

While this new assumption is not very satisfactory, it offers at any rate new means of testing the theory by studying ammonia decomposition at low pressures in vessels with walls prepared either to accelerate or retard the hydrogen atom recombination. Such experiments are considered for the near future by one of us.

Concluding, we would like to thank Professor G. S. Forbes for his frequent help and the loan of some of the equipment used in this work.

Summary

1. The gaseous products of the photochemical ammonia decomposition are a 1:3 nitrogen–hydrogen mixture even under conditions excluding a photochemical decomposition of hydrazine.

2. The quantum yield of ammonia decomposition at room temperature is 0.25 independent of pressure, light intensity and time of illumination.

3. At 500° the quantum yield is 0.5 or more.

4. The bearing of these results on other work on ammonia decomposition is discussed and a mechanism of ammonia decomposition is developed.

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THE SORPTION OF GASES BY IRON

BY ARTHUR F. BENTON AND T. A. WHITE[1]

Introduction

As a result of numerous researches in recent years in the field of adsorption of gases by catalytically active solids, three processes, apart from compound formation, have become clearly recognized—physical adsorption, activated adsorption and solution. The characteristics and interrelationships of the two types of *ad*sorption are now reasonably clear.[2]

In the attempt to distinguish adsorption from solution, it has been customary to assume that the former is always rapid, while the latter is ordinarily slow. However, since it has been shown that activated ad-

[1] Du Pont Fellow in Chemistry.

[2] (a) Benton, THIS JOURNAL, 45, 887, 900 (1923); (b) Benton and White, *ibid.*, 52, 2325 (1930); (c) Taylor, *ibid.*, 53, 578 (1931); (d) Taylor and Williamson, *ibid.*, 53, 2168 (1931); (e) Taylor and McKinney, *ibid.*, 53, 3604 (1931); (f) Benton and White. *ibid.*, 54, 1373 (1932).