THE QUANTUM YIELD IN THE PHOTOCHEMICAL DECOMPOSITION OF GASEOUS HYDRAZINE

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Introduction

The photochemical decomposition of gaseous hydrazine by the total radiation from a quartz mercury arc and the photosensitized decomposition by excited mercury atoms have been studied by Elgin and Taylor.[1] The products of the decomposition were identified as ammonia, hydrogen and nitrogen. A minimum quantum yield of thirteen molecules of hydrazine decomposed per quantum absorbed was obtained for the photosensitized decomposition by comparing the rate of decomposition of the hydrazine with the rate of formation of water from hydrogen and oxygen under similar conditions. No determination was made of the quantum yield for the purely photochemical decomposition.

The present investigation is concerned with the determination of the quantum yields in the photochemical decomposition of gaseous hydrazine by monochromatic radiation of wave length 1990 Å.

Experimental Method

Preparation of Anhydrous Hydrazine.—The anhydrous hydrazine was prepared by the dehydration of hydrazine hydrate with fused potassium hydroxide. Hydrazine hydrate, obtained from the Eastman Kodak Company, was refluxed for three hours in an atmosphere of hydrogen with fused potassium hydroxide in an all-Pyrex glass apparatus. The hydrazine was then distilled in a stream of hydrogen at a pressure of 30 to 100 millimeters of mercury. The distillate was refluxed with more potassium hydroxide and again distilled. This process was repeated three times. Analysis of the distillate by the iodate method[2] indicated a purity of 98.9%.

Barium monoxide is recommended by Hale and Shetterly[3] for the dehydration of hydrazine hydrate. It was found in the present work that even the best available barium monoxide was less satisfactory than the fused potassium hydroxide which was used.

The product from the above operations was given a final distillation from potassium hydroxide in a stream of nitrogen. Three fractions were collected and sealed off in tubes containing fused potassium hydroxide. Each tube contained an internal thin-walled tip which could be broken by means of a glass-encased magnetically operated hammer after the tube had been sealed to the vacuum system and the system evacuated. The middle fraction of the anhydrous hydrazine was introduced into the system in this manner without exposure to the atmosphere after the final distillation. The hydrazine was distilled *in vacuo* at room temperature into a series of smaller similar tubes (containing fused potassium hydroxide) which were stored in the dark and attached to the vacuum system as needed.

[1] Elgin and Taylor, THIS JOURNAL, 51, 2059 (1929).

[2] Bray and Cuy, *ibid.*, **46**, 1858 (1924).

[3] Hale and Shetterly, *ibid.*, **33**, 1071 (1911).

Apparatus.—A diagram of the apparatus is shown in Fig. 1. Anhydrous liquid hydrazine (prepared as described above) was stored in contact with fused potassium hydroxide in the reservoir B, which was attached to the vacuum system. The vacuum system consisted essentially of a fused quartz reaction cell L in which the hydrazine was irradiated, a McLeod gage (attached at E) for reading the total pressure of nitrogen and hydrogen produced by the decomposition, a quartz fiber gage H for analyzing the nitrogen–hydrogen mixture, and several mercury cut-offs and freezing-out traps. The system was evacuated by a mercury vapor pump through the cut-off A. The quartz fiber gage H consisted of a single fiber of elliptical cross section and was fitted with an electromagnetic starting device.[4] Some trouble was experienced initially from room vibrations but this difficulty was eliminated by mounting the gage on a very massive support which rested upon several layers of hair felt. The use of the quartz fiber gage as a means for analyzing nitrogen–hydrogen mixtures has been shown to give satisfactory results.[5]
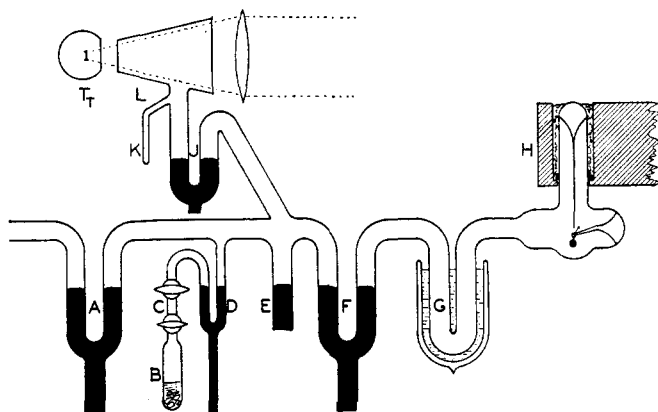

Fig. 1.—Diagram of apparatus.

Monochromatic radiation of wave length 1990 Å. was obtained by the use of a condensed aluminum spark and a Bausch and Lomb ultraviolet monochromator in the manner previously described.[6] The beam of monochromatic light emerging from the monochromator passed through two converging cylindrical quartz lenses, through the plane fused quartz windows of the reaction cell L and onto the receiving vane of a sensitive vacuum thermopile T_t (transmission thermopile). The reaction cell was constructed with the front window at an angle of 45° with the axis of the cell so that a fraction of the incident radiation was reflected at right angles onto the receiving vane of a similar thermopile T_r (reflection thermopile). The thermopiles were connected to two Leeds and Northrup high-sensitivity galvanometers which were set up in conjunction with an automatic recording device so that continuous records were made of the deflections of both galvanometers. From these continuous records the amount of radiant energy absorbed by the reaction mixture could be determined for each run with an accuracy which was independent of fluctuations in the intensity of the radiation or of changes in the absorption of the mixture during the run.

The vanes of the thermopiles were large enough to cover completely the converged beams. The thermoelectric system of each thermopile consisted of six junctions

[4] Beckman, *J. Opt. Soc.*, **16**, 276 (1928).

[5] Beckman and Dickinson, THIS JOURNAL, **50**, 1870 (1928).

[6] Beckman and Dickinson, *ibid.*, **52**, 124 (1930).

of bismuth and bismuth-tin alloy (95% Bi, 5% Sn) in series, three junctions attached to each vane. The thermopiles were mounted in glass containers with plane fused quartz windows attached with wax. The thermopile vessels were continuously evacuated during the runs so that constant sensitivity was secured. Liquid-air traps prevented the access of mercury vapor into the thermopile vessels.

The continuous recording device consisted of a flat carriage which carried a 25 × 31 cm. sheet of photograph paper and was moved vertically at a constant speed by means of a screw which was driven by a synchronous motor. Two beams of light from a strongly illuminated vertical slit were reflected from the two galvanometer mirrors and focused upon the photographic paper by means of two one-diopter spherical lenses placed directly in front of the galvanometer mirrors. A 50-diopter cylindrical lens which extended horizontally across the width of the paper changed the narrow lines of light thus formed into two intense circular spots of light less than half a millimeter in diameter. The apparatus was adjusted so that the zero positions of the two spots of light were near the two edges of the paper with the deflections toward the opposite edges. This arrangement permitted the utilization of the full width of the paper for each beam, as no confusion resulted from the crossing of the two beams. To avoid the error caused by shrinkage on expansion of the paper during development, drying, etc., the coördinate system was printed upon the paper immediately after removal from the recorder by making a contact print through a coördinate screen made by ruling fine transparent coördinate lines through an opaque silver coating on a glass plate.

The thermopiles, galvanometers and leads were carefully shielded, thereby obtaining complete freedom from electrical disturbances caused by the spark. The galvanometer deflections were found to be exactly proportional to the galvanometer current throughout the range used in these experiments. The thermopiles were of the compensated type, to avoid difficulties occasioned by shifting zero positions. It was found that the zero positions were quite constant and the error introduced from this source was negligible.

Calibration.—The determination of the number of quanta absorbed by the reaction mixtures required the following data: (1) the calibration of the transmission thermopile T_t, (2) the transmission factors for λ1990 Å. of the rear window of the reaction cell and the window of the thermopile T_t, and (3) the ratio of the galvanometer deflections for thermopiles T_r and T_t with the cell evacuated. To calibrate thermopile T_t carbon lamps calibrated by the Bureau of Standards were used. A brass plate with a hole of known area was placed in front of the thermopile window in such a way that light from the standard lamp passing through the hole was entirely intercepted by the receiving vane. The intensity of radiation at the hole was known from the calibration of the standard lamp. The transmission of the thermopile window for this radiation had been determined by previous experiments to be 0.914. By dividing the product of the intensity of radiation, the area of the hole and the transmission of the window by the scale deflection, the number of ergs per second required for unit deflection was obtained. A number of determinations at various lamp currents using two standard lamps gave consistent results with the average value 1.230 ergs per second per unit of deflection.

The transmissions for λ1990 Å. of the rear window of the cell and the window of thermopile T_t were obtained before the cell was assembled, with the aid of the continuous recording device. With both thermopiles in place, a piece of thin quartz plate was placed in the position later taken by the front window of the cell and a record of the galvanometer deflections was taken with the spark in operation. The rear window of the cell was then placed in front of thermopile T_t in the position it would ultimately occupy when the cell was in place, and another record of the galvanometer deflections taken. The transmission of the window was then found from a comparison of the two records. Five such determinations gave a mean value of 0.720 for the transmission of the rear

cell window. For convenience, to prevent dismantling thermopile T_t, a duplicate window from the same stock of quartz was substituted for the actual thermopile window in determining the transmission of the latter. The mean value of five determinations of the transmission of the thermopile window was 0.653.

The ratio of the galvanometer deflections for the two thermopiles with the cell evacuated was checked several times during the course of the investigation. For runs 1 to 9 the ratio was 3.15 and for runs 10 to 22 the ratio was 2.86, the different values being due to a change in the apparatus between runs 9 and 10.

Procedure.—The procedure was as follows in a typical quantum yield determination. With the system evacuated, cut-offs A and F closed, cut-offs D and J opened, and with the mercury in the McLeod gage connection E as high as possible, the desired amount of hydrazine was admitted through the doser C. Cut-off D was then closed and a mixture of ether and solid carbon dioxide was applied to the trap K to freeze the hydrazine. The system was then evacuated to remove any traces of non-condensable gas which might be present. Cut-off J was then closed and the freezing mixture removed from the trap K, allowing the hydrazine to vaporize. The freezing mixture was again applied, cut-off J opened and the system again evacuated. This process was repeated a third time. With cut-off J closed and the freezing mixture removed, the pressure of the hydrazine was measured by the difference in mercury levels in the cut-off J. A sheet of photographic paper was put into the recorder and the galvanometer switches were closed. The hydrazine was then irradiated for a definite time, usually fifteen minutes, after which liquid air was applied to the trap K, cut-offs A and D were closed, cut-off F was opened and the connection made with the McLeod gage. (Liquid air was kept on the trap G throughout the run to keep mercury vapor out of the quartz fiber gage H.) Cut-off J was then opened allowing the non-condensable gases to flow into the McLeod and quartz-fiber gages on which readings were taken. The coördinate system was printed upon the photographic paper and the paper was developed.

It was found that when gaseous hydrazine stood in the reaction cell there was a slow development of non-condensable gas even in the dark, presumably due to some slow wall reaction, since the rate of pressure development was greatest when the cell was new or freshly cleaned and decreased after the cell had been in use for some time. To correct for this effect, the system was evacuated after the above readings were taken, cut-off J closed, the liquid air removed from the trap K and the hydrazine allowed to stand in the reaction cell for the same length of time as during the run. Liquid air was then applied at K, cut-off J opened and the pressure of the non-condensable gas read on the McLeod gage, all mercury levels being at the same levels as before. This pressure correction was always small, amounting to only 1 or 2% of the total pressure of non-condensable gas. The pressures were so small that satisfactory quartz

fiber readings for a composition correction could not be made. However, experiments extended over longer time intervals indicated that the non-condensable gas produced in the dark was of nearly the same composition as the non-condensable gas produced photochemically, so no appreciable error was introduced by neglecting entirely any slight changes in composition which might have been produced by the very small amounts of products of the dark reaction.

Experimental Results

The products of the decomposition have been identified by Elgin and Taylor as ammonia, hydrogen and nitrogen. The presence of ammonia was confirmed in the present investigation by the Nessler test. This test was made after irradiation by freezing the undecomposed hydrazine with ether–carbon dioxide mixture. The ammonia was then frozen in a side tube by applying liquid air. This tube was sealed off from the apparatus and the tip broken under ammonia-free water. Upon adding Nessler's reagent to the solution, a distinct reddish brown color developed proving the presence of ammonia. Blank tests without irradiation proved the absence of ammonia in the hydrazine.

The results of the quantum yield determinations are given in Tables I and II in which the runs are arranged for convenience in order of decreasing hydrazine pressure. In Table I are given the data from which may be calculated the number of molecules of hydrazine decomposed during each run. In the second column is given the initial pressure of hydrazine in the cell, which is also the pressure throughout the entire run since in none of the runs was more than 0.1% of the hydrazine decomposed. The temperature of the system is given in the third column and the total pressure of the non-condensable products in the fourth column. From the latter value must be subtracted the correction pressure for the dark reaction, given in the next column, to obtain the true pressure of the hydrogen plus nitrogen produced by the photochemical decomposition. In the sixth column is given the value for X_{H_2}, the mole fraction of hydrogen in the non-condensable gas as determined by the quartz fiber gage. In the last column is given the number of molecules of hydrazine decomposed, calculated from the equation

$$N_{N_2H_4} = \frac{4 \, \bar{N} P_{H_2 + N_2} V}{760 \, RT} \, (^3/_4 - X_{H_2}) \tag{1}$$

where $\bar{N}$ is the Avogadro number and R has the value of 82.1 cc. atm. per degree. V is the effective volume of the system determined experimentally by air expansion with liquid air on traps G and K exactly as in the measurement of the non-condensable gas pressures. For runs 1 to 9 the volume was 137.2 cc. and for runs 10 to 22 the volume was 141.9 cc. The above equation may be obtained from the perfect gas law and the consideration

that the number of gram atoms of hydrogen and nitrogen in the products (NH_3, H_2 and N_2) must equal the number of gram atoms of hydrogen and nitrogen in the decomposed N_2H_4.

In Table II are given the data from which may be calculated the number of quanta of radiation absorbed during each run. The duration of the irradiation in seconds is given in column 2. In columns 3 and 4 are given the mean values D_t and D_r of the galvanometer deflections for the transmitted (thermopile T_t) and the reflected (thermopile T_r) beams, obtained from the continuous photographic record. In column 5 is given the total number of quanta of radiation of wave length 1990 Å. which entered the reaction mixture during the run, computed from the relation

$$Q_E = \frac{1.230 \, \beta \, D_r \, t}{\alpha_1 \alpha_2 \, hc/\lambda} = 2.65 \times 10^{11} \, \beta \, D_r \, t \tag{2}$$

the factor 1.230 being the number of ergs per second of radiation falling on the vane of thermopile T_t for unit deflection. β is the ratio of the galvanometer deflections for thermopile T_r to the deflections for thermopile T_t with the reaction cell evacuated, and t is the time of irradiation. α_1 and α_2 are the transmission factors of the rear cell window and the window of thermopile T_t for radiation λ 1990 Å. and have the values 0.720 and

TABLE I

DATA FOR CALCULATING AMOUNT OF HYDRAZINE DECOMPOSED

1	2	3	4	5	6	7
Run	Press. N_2H_4, mm.	Temp., °A.	Press. non-cond., mm. $\times 10^3$	Press. corr., mm. $\times 10^3$	X_{H_2}	Molecules N_2H_4 decomp. $\times 10^{-15}$
22	14.0	298	3.06	0.05	0.587	9.05
1	13.0	300	4.15	.06	.582	12.22
2	13.0	301	3.83	.05	.582	11.27
17	12.0	298	2.97	.05	.613	7.41
18	12.0	298	3.00	.05	.611	7.57
5	11.0	299	3.99	.05	.598	10.72
10	10.5	302	3.11	.08	.628	6.75
6	10.0	298	3.64	.05	.608	9.13
13	9.8	300	2.99	.07	.616	7.19
3	8.0	300	4.06	.05	.618	9.39
4	8.0	301	3.91	.07	.621	8.78
15	7.0	300	3.22	.06	.629	7.05
16	7.0	298	3.07	.08	.619	7.21
9	6.0	299	3.63	.06	.613	8.73
11	6.0	302	3.04	.08	.644	5.75
19	5.0	298	2.81	.06	.639	5.62
20	5.0	298	2.91	.06	.634	6.10
21	3.5	300	2.68	.05	.634	5.61
8	3.0	300	3.47	.06	.622	7.76
12	3.0	302	2.59	.08	.644	4.85
14	2.0	298	2.33	.08	.629	5.03
7	2.0	299	2.85	.06	.634	5.77

TABLE II

DATA FOR CALCULATING AMOUNT OF RADIATION ABSORBED

1 Run	2 Expt. time, sec.	3 Galv. defl., D_r	4 Galv. defl., D_t	5 Quanta entering $\times 10^{-15}$	6 Quanta leaving $\times 10^{-15}$	7 Quanta absorbed $\times 10^{-15}$	8 Quantum yield, Y
22	780	9.38	0.00	5.55	0.00	5.55	1.63
1	900	9.58	.56	7.22	.13	7.09	1.72
2	900	9.48	.93	7.16	.22	6.94	1.63
17	780	9.31	.00	5.52	.00	5.52	1.34
18	780	9.64	.00	5.72	.00	5.72	1.33
5	870	11.49	.89	8.37	.20	8.17	1.31
10	780	8.54	.39	5.05	.08	4.97	1.35
6	900	9.37	1.12	7.06	.27	6.79	1.34
13	787	9.58	0.74	5.73	.15	5.58	1.29
3	900	11.40	1.68	8.58	.40	8.18	1.14
4	900	9.87	1.13	7.43	.27	7.16	1.23
15	780	11.13	1.55	6.58	.32	6.26	1.12
16	780	10.42	1.46	6.16	.30	5.86	1.23
9	900	11.07	1.67	8.34	.39	7.95	1.10
11	780	10.82	1.74	6.40	.36	6.04	0.96
19	780	10.22	1.90	6.05	.39	5.66	1.00
20	780	9.81	2.24	5.81	.46	5.35	1.14
21	780	9.93	4.55	5.88	.94	4.94	1.13
8	900	10.83	4.26	8.15	1.02	7.13	1.09
12	780	9.17	5.57	5.42	1.15	4.27	1.13
14	780	10.03	9.95	5.93	2.06	3.87	1.30
7	900	10.92	8.99	8.22	2.14	6.08	0.96

0.653, respectively. In column 6 is given the total number of quanta which left the reaction mixture, as computed from the relation

$$Q_L = \frac{1.230 \, D_t \, t}{\alpha_1 \alpha_2 \, hc/\lambda} = 2.65 \times 10^{11} \, D_t \, t \qquad (3)$$

By subtracting the value in column 6 from that in column 5 there is obtained the value given in column 7, namely, the total number of quanta absorbed by the reaction mixture during the run. Finally by dividing the value in column 7, Table I, by the corresponding value in column 7, Table II, the photochemical yield, Y, recorded in column 8, is obtained. This value represents the number of molecules of hydrazine decomposed per quantum absorbed of radiation of wave length 1990 Å.

Before discussing the relation between quantum yield and the pressure of hydrazine, attention should be called to the fact that the calculated values of Y are greatly affected by small errors in the determination of X_{H_2}, as will be seen from Equation 1. Thus, with a value $X_{H_2} = 0.60$, an error of 0.01 in X_{H_2} will cause an error of about 7% in the value of Y. To avoid the use of this equation, attempts were made to measure the ammonia pressures directly, as was done at higher pressures by Elgin and Taylor by freezing the hydrazine with ether–carbon dioxide mixture. It was found, however, that it was impossible to measure ammonia pressure

accurately at very low pressures. Since the values of X_{H_2} are known with considerable accuracy, it was felt that the direct measurement of the ammonia pressure would introduce greater errors than are introduced by the use of Equation 1.

It will be seen from column 8, Table II, that despite random variations, there is a definite increase in the quantum yield with increasing pressure of hydrazine, the values of Y ranging from about unity at the lower pressures to a value of 1.7 at the higher pressures. The quantum yield at pressures higher than 14 mm. could not be studied at room temperature since this pressure is the saturation pressure of hydrazine. At pressures lower than 2 mm. the light absorption was so small that neither the amount of radiation absorbed nor the amount of products formed could be measured satisfactorily.

The values of X, the mole fraction of hydrogen in the non-condensable gas, which are recorded in column 6 of Table I, also show a variation with the hydrazine pressure, a mole fraction $X = 0.58$ being obtained at the higher pressures and a mole fraction $X = 0.64$ at the lower pressures.

Discussion

The results of the present investigation are not in agreement with the conclusions of Elgin and Taylor[1] that the photochemical decomposition of hydrazine proceeds according to the stoichiometric relation
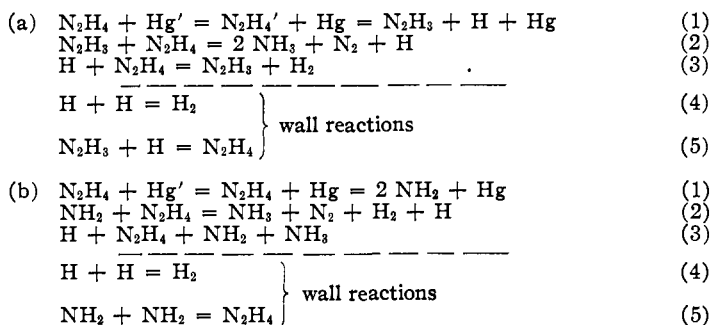
$$2 N_2H_4 = 2 NH_3 + N_2 + H_2$$

with the subsequent decomposition of the ammonia. If this conclusion is correct, then the mole fraction X of hydrogen in the non-condensable gas must be exactly 0.50 at the start of the decomposition before an appreciable amount of ammonia has decomposed. In the present experiments less than 0.1% of the hydrazine was decomposed in any run and it was found that the mole fraction of hydrogen varied from 0.58 at the higher hydrazine pressures to 0.64 at the lower pressures. These values do not agree with the analyses of the non-condensable gas reported by the previous investigators (Ref. 1, Table I) which showed approximately 50 mole per cent. of hydrogen even when more than one-fourth of the hydrazine was decomposed. The authors state that the analysis was accomplished by burning the hydrogen with copper oxide and that from five to six hours were required for the completion of an analysis, due to the slow diffusion of the gases. Under such conditions it is conceivable that the observed percentage of hydrogen may be too low on account of incomplete combustion. Indeed, it may be mentioned that if X is computed from their recorded values of ammonia and non-condensable gas pressures, using the stoichiometric relation

$$X = {}^2/_3 - \frac{p_{NH_3}}{6 \, p_{H_2 + N_2}}$$

a minimum value of $X = 0.57$ is obtained.   Therefore, since the initial value of X is not 0.50, but since, as our experiments show, the value of X is a function of the hydrazine pressure, it appears that the photochemical decomposition of hydrazine does not follow the simple stoichiometric equation given above but must proceed in at least two different ways, one of which yields low values of X and is favored at high pressures while the other yields higher values of X and is favored at low pressures.

Elgin and Taylor[1] have discussed at some length possible mechanisms for the decomposition of hydrazine.   They found that the results of their investigations of the photosensitized decomposition could be explained by either of the following mechanisms
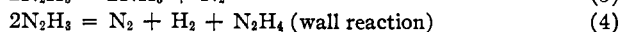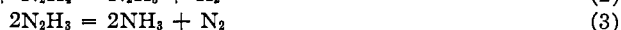
$$
\begin{array}{lll}
\text{(a)} & N_2H_4 + Hg' = N_2H_4' + Hg = N_2H_3 + H + Hg & (1) \\
& N_2H_3 + N_2H_4 = 2\,NH_3 + N_2 + H & (2) \\
& H + N_2H_4 = N_2H_3 + H_2 \qquad . & (3) \\
\hline
& H + H = H_2 \qquad\qquad\Big\} \text{ wall reactions} & (4) \\
& N_2H_3 + H = N_2H_4 & (5)
\end{array}
$$

$$
\begin{array}{lll}
\text{(b)} & N_2H_4 + Hg' = N_2H_4 + Hg = 2\,NH_2 + Hg & (1) \\
& NH_2 + N_2H_4 = NH_3 + N_2 + H_2 + H & (2) \\
& H + N_2H_4 + NH_2 + NH_3 & (3) \\
\hline
& H + H = H_2 \qquad\qquad\Big\} \text{ wall reactions} & (4) \\
& NH_2 + NH_2 = N_2H_4 & (5)
\end{array}
$$

It will be seen that each of these mechanisms will account for a high quantum yield (their observed minimum quantum yield = 13 molecules N_2H_4 decomposed per quantum absorbed) and for the failure of hydrogen to retard the rate of the decomposition.   The failure of hydrogen to retard the rate of decomposition was observed for both the photochemical and photosensitized decompositions but is of particular interest only for the latter case where hydrogen atoms are known to be formed by collisions between excited mercury atoms and hydrogen molecules.   Although the above mechanisms were formulated on the basis of the results of their investigation of the photosensitized decomposition, the authors state "there is no reason to believe that the purely photochemical decomposition proceeds by another mechanism."   It is clear, however, that the new experimental data disclosed in the present article show that the purely photochemical decomposition cannot be explained by either of the above mechanisms for the following reasons.   (1) The low quantum yield for the photochemical decomposition does not indicate a chain mechanism.   (2) The observed mole fraction of hydrogen in the products is greater than given by the above mechanisms.

In the photochemical decomposition of gaseous hydrazine produced by the absorption of radiation of wave length 1990 Å. the primary step undoubtedly involves the splitting of the molecules into substituent parts,

since this radiation lies well within the region of continuous absorption.[1,7] Whether the splitting occurs at a N–H bond or at the N–N bond has not yet been established. Although Imanishi has concluded that the absorption of 5.5 volt radiation (2244 Å.) causes a rupture of the N–N bond, his conclusions are merely conjectures and are without experimental support. If one assumes that the primary dissociation results in the splitting of a hydrogen atom from the hydrazine molecule, a mechanism can be readily set up which will account for the experimental facts.

The steps in the mechanism are as follows

$$N_2H_4 + h\nu = N_2H_3 + H \tag{1}$$
$$H + N_2H_4 = N_2H_3 + H_2 \tag{2}$$
$$2N_2H_3 = 2NH_3 + N_2 \tag{3}$$
$$2N_2H_3 = N_2 + H_2 + N_2H_4 \text{ (wall reaction)} \tag{4}$$

This mechanism assumes that collisions between N_2H_3 and N_2H_4 molecules do not result in chemical reaction. The N_2H_3 molecules can react with themselves in two competing reactions, namely, a homogeneous bimolecular reaction resulting in the formation of ammonia and a wall reaction resulting in the regeneration of hydrazine.

It may be seen that this mechanism is in substantial agreement with the experimental data. The quantum yield lies within the range one to two. The mole fraction of hydrogen in the non-condensable gases lies between the limits one-half and two-thirds. Further, the quantum yield increases and the mole fraction of hydrogen decreases with increasing hydrazine pressure, since increasing pressure favors reaction 3 in comparison with reaction 4.

Upon the basis of the above mechanism a definite relationship should exist between the quantum yield Y and the mole fraction of hydrogen X; namely

$$Y = \frac{4X - 3}{X - 1}$$

A comparison of the observed quantum yields with the quantum yields calculated from this equation using the observed mole-fractions of hydrogen is given in Table III. The fact that the calculated values are slightly higher than the observed values except at the higher pressures suggests the possible occurrence of other wall reactions such as

$$H + N_2H_3 = N_2H_4 \tag{5}$$
$$H + H = H_2 \tag{6}$$

which would have the effect of lowering the quantum yields with decreasing pressure.

On the basis of the above mechanism, it is evident that the value of Y depends upon the manner in which the N_2H_3 molecules divide themselves between the homogeneous and heterogeneous reactions. If α represents

[7] Imanishi, *Nature*, **127**, 782 (1931).

TABLE III

COMPARISON OF OBSERVED AND CALCULATED QUANTUM YIELDS

Press. N_2H_4 mm.	X_{H_2}	$Y_{obs.}$	$Y_{calcd.}$	Press. N_2H_4, mm.	X_{H_2}	$Y_{obs.}$	$Y_{calcd.}$
14.0	0.587	1.63	1.58	7.0	0.629	1.12	1.29
13.0	.582	1.72	1.60	7.0	.619	1.23	1.37
13.0	.582	1.63	1.60	6.0	.613	1.10	1.42
12.0	.613	1.34	1.42	6.0	.644	0.96	1.18
12.0	.611	1.33	1.44	5.0	.639	1.00	1.22
11.0	.598	1.31	1.52	5.0	.634	1.14	1.26
10.5	.628	1.35	1.32	3.5	.634	1.13	1.26
10.0	.608	1.34	1.45	3.0	.622	1.09	1.35
9.8	.616	1.29	1.41	3.0	.644	1.13	1.18
8.0	.618	1.14	1.39	2.0	.629	(1.30)	1.29
8.0	.621	1.23	1.37	2.0	.634	0.96	1.26

the fraction of N_2H_3 molecules which react on the walls according to Equation 4, then $\alpha = 2 - Y$. From the observed values of Y it follows that from 0 to 70% the N_2H_3 molecules react homogeneously to form ammonia and 100 to 30% react upon the wall with the partial regeneration of hydrazine.

Summary

The quantum yields for the photochemical decomposition of gaseous hydrazine by monochromatic radiation of wave length 1990 Å. have been investigated over the pressure range 2 to 14 millimeters of mercury. It was found that the quantum yields range from 1.0 (molecules of N_2H_4 decomposed per quantum of radiation absorbed) at the lower pressure to 1.7 at the higher pressure.

The products of the decomposition were found to be ammonia, nitrogen and hydrogen, in agreement with the results of previous investigators, but the relative proportions of these substances are in disagreement with the earlier data. It was found that the composition of the products is a function of the hydrazine pressure, with more hydrogen formed at the low hydrazine pressures than at the high pressures.

It is shown that the mechanisms which have been previously proposed for the photosensitized decomposition of hydrazine are not applicable to the photochemical decomposition. A possible mechanism for the latter is suggested which is consistent with the experimental data.

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