A STUDY OF THE PHOTOSENSITIZED DECOMPOSITION OF GASEOUS HYDROGEN AZIDE

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Introduction

The thermal decomposition of aqueous solutions of hydrogen azide with platinum as a catalyst has been studied by E. Oliveri-Mandala[1] who found that it decomposes slowly according to the equation

$$3\ HN_3 \rightarrow 4\ N_2 + NH_3$$

Upon heating hydrogen azide with concentrated sulfuric acid, Schmidt[2] obtained a considerable amount of hydroxylamine together with nitrogen. His investigation of the decomposition products led him to conclude that only the oxidative action of the sulfuric acid, as indicated by the formation of sulfur dioxide, prevents the reaction from being quantitatively representable by the equation

$$HN_3 + H_2O \rightarrow N_2 + NH_2OH$$

He also found traces of ammonia, but nothing else.

Gleu[3] illuminated aqueous solutions of hydrogen azide with ultraviolet light from a quartz mercury lamp and found that the products were mainly hydroxylamine and nitrogen with small amounts of ammonia and traces of hydrazine.

Beckman and Dickinson[4] studied the photochemical decomposition of gaseous hydrogen azide, using monochromatic radiation of wave length 1990 Å. They concluded that the decomposition proceeded by two concurrent reactions, one resulting in the formation of hydrogen and nitrogen, and the other in ammonia and nitrogen. They found[5] that over a pressure range of from 2 mm to 130 mm the quantum yield was substantially constant at 3.0 ± 0.5 molecules of hydrogen azide decomposed per quantum absorbed.

The present paper is concerned with the quantum yield and products of the mercury-photosensitized decomposition of gaseous hydrogen azide. Because the products of decomposition were determined with the use of a somewhat different type of apparatus than was employed in the quantum yield determination, and because the two investigations are in other respects as well quite distinct from each other, they shall, for the sake of clarity, be described separately.

Part I: The Products of Decomposition

Preparation of Hydrogen Azide

Gaseous hydrogen azide was obtained by dropping sulfuric acid (two volumes of concentrated sulfuric acid to one volume of water) on solid sodium azide which had been purified by repeated recrystallizations from aqueous solutions. The hydrogen azide evolved was swept through a long calcium chloride tube into a liquid air trap by a current of hydrogen gas previously dried by passage through another such drying tube. The generating flask was then sealed off and the trap and a 1-liter storage bulb attached to it were evacuated. The liquid air was then removed, allowing the hydrogen azide to volatilize into the storage bulb.

Apparatus and Procedure

A diagram of the apparatus is shown in Figure 1. The hydrogen azide was stored in the flask, E, connected to the vacuum system through two stopcocks, D, which allowed small amounts of hydrogen azide to be admitted to the vacuum system. With mercury cut-offs A and I closed and C and F open the desired quantity of hydrogen azide was admitted into the system with the aid of the doser, D. The hydrogen azide was frozen out by applying liquid air at H and traces of noncondensable gas pumped off. Then, with cut-off F closed, the liquid air was removed from H and the hydrogen azide permitted to vaporize into G where it was illuminated.

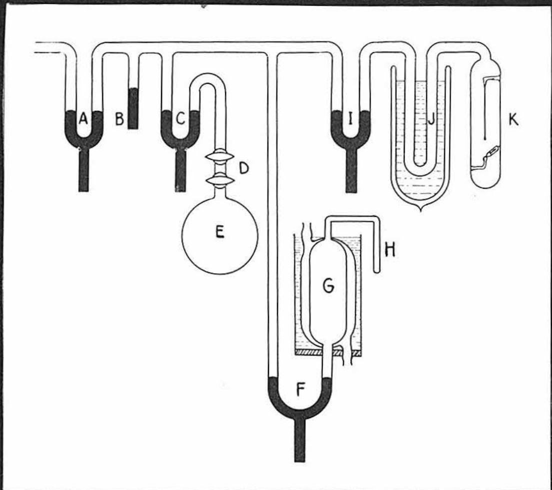

Figure 1. Diagram of Vacuum System (Part I)

The source of radiation was a small, vertical, quartz mercury-vapor lamp around the mercury well of which was fused a quartz jacket through which cooling water was circulated to minimize thermal broadening of the lines of the emitted radiation. To reduce self-inversion of the resonance line an electromagnet in series with the lamp was mounted beside the lamp in such a way that the mercury-vapor arc was deflected against that side of the lamp nearest G.

G consisted of a quartz tube about 8 cm long by 1.5 cm in diameter around which was fused a slightly larger quartz tube provided with outlets for the circulation of constant-temperature water. For almost all of the runs the water was thermostated at 25° C and used only once. In runs at 30° C it was found that a solid substance, formed as an intermediate in the decomposition, distilled from the cell to cooler parts of the apparatus, interrupting the decomposition. Around the water jacket was still another quartz tube in which 25% acetic acid was kept during a run, providing a 5 mm filter on all sides of the cell. Since it is known that hydrogen azide does not appreciably absorb radiation of longer wave length than 2200 Å[5] and since acetic acid removes radiation of wave lengths shorter than 2400 Å, this filter effectively eliminated the possibility of any direct photochemical decomposition of the hydrogen azide.

The progress of the decomposition was followed by observing the rate of increase of pressure in G as indicated by the difference in the mercury levels in the two arms of the cut-off F. The difference in levels was measured with a cathetometer reading to 0.1 mm. A shutter was mounted between G and the lamp so that decomposition could be stopped while pressure readings were being taken.

At the end of a decomposition run or at any time during a run (by sacrificing the remainder of the run), the composition of the non-condensable gases could be determined by applying liquid air at H to freeze out the condensables, closing cut-offs A and C, opening cut-offs F and I, and analyzing the gas by means of a quartz fiber gage, K, and a McLeod gage (not shown)connected at B. This method of analyzing a mixture of two non-condensable gases has been described in some detail in the literature[4,6] and need not be discussed here. Whenever the quartz fiber gage was to be used, liquid air was kept on the U-tube, J, throughout the experiment.

Experimental Results

1. Rate of Change of Total Pressure

The first subject of investigation was the change of total pressure with time under conditions of constant light intensity. The current through the lamp (usually about two amperes) was maintained at as constant a value as possible with the aid of an ammeter and manually controlled rheostat connected in series with the lamp. By operation of the shutter mounted between the lamp and cell G, a charge of hydrogen azide in the cell was irradiated for a short interval of time (usually either 30 or 60 seconds) after which the resulting pressure increase was determined by measuring the difference in mercury levels in cut-off F with a cathetometer. The cell was then illuminated for another short interval and the pressure change noted, this cycle of operations being repeated until the pressure in cell G attained a constant value. Wide variations in the duration of the closed-shutter period during which the pressures were read had no apparent effect upon the characteristics of the decomposition.

A total of fifty-seven decomposition runs were made, most of them with an initial hydrogen azide pressure of about 15 mm. Experiments in which the initial pressures ranged all the way from 6 mm to 20 mm (the limits imposed by the apparatus) changed only the dimensions and not the shapes of the time vs total pressure curves. Figure 2 is typical of such a curve representing one of the decomposition runs. The following data appear to be significant in the interpretation of results:

(a) The average value of the ratio of final total pressure to initial hydrogen azide pressure for fifty seven experiments was 1.651 ± 0.016.

(b) Twelve different analyses of the final non-condensable gases showed only nitrogen within the limits of accuracy of the analyses (about 2%).

(c) Seven different experiments in which the condensables in the final gaseous products were frozen out with liquid air and the drop in pressure measured (allowing for the thermal contraction due to the liquid air) gave the following values for the ratio of condensables to non-condensables: 0.25, 0.18, 0.25, 0.25, 0.24, 0.25, and 0.25.

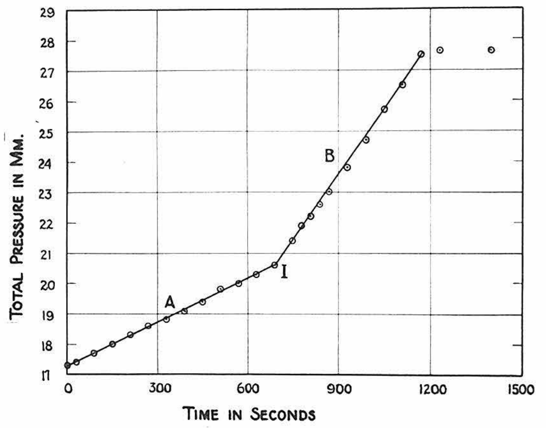

Figure 2. Typical Time vs Pressure Curve

It will be seen that these results are in good agreement with the assumption of an overall decomposition representable stoichiometrically by the equation

$$3\ HN_3 \rightarrow NH_3 + 4\ N_2$$

Corresponding to the experimental facts (a), (b), and (c) noted above, this equation would give:

(a') For the ratio of final total pressure to initial hydrogen azide pressure a value of 1.667.

(b') A final non-condensable gas consisting of 100% nitrogen.

(c') A ratio of condensable to non-condensable constituents in the final gas phase of 0.25.

Although this simple stoichiometric equation is in good agreement with the experimental results noted above for the overall reaction, it is apparent from the shape of the decomposition curve (Fig. 2) that the decomposition is somewhat more complex. No simple relationship was found between the slopes A and B of the curves (cf. Fig. 2). The point I at which the slope changed abruptly was found to be significant, however. The average of forty-six determinations gave a value for the ratio of the pressure at this point to the initial hydrogen azide pressure of 1.175 ± 0.016. An investigation of the composition of the gas at different stages in the decomposition revealed further interesting facts.

2. Change of Composition of Reaction Mixture

Fifteen different analyses of the con-condensable gases produced during ten different runs all indicated the presence of from 2% to 7% hydrogen. No definite relationship between the percent of hydrogen in the non-condensables and the fraction of hydrogen azide dissociated was observed except that after dissociation was complete no hydrogen could be detected. By taking advantage of the fact that the vapor pressure of hydrogen azide is only 0.9 mm at the temperature of an ether-solid carbon dioxide mixture (-80°C) while the vapor pressure of ammonia at that temperature is many times the value which it might attain in the course of an experiment, a rough determination of the way in which the composition of the gas varied during an experiment was possible. Thus with liquid air on the trap, the pressure corresponded to the sum of the partial pressures of hydrogen and nitrogen present, with a carbon dioxide-ether mixture on the trap the pressure corresponded to $H_2 + N_2 + 0.9$ mm of $HN_3 + NH_3$, and of course, with no freezing mixture on the trap the pressure represented the sum of the four gaseous constituents H_2, N_2, NH_3, and HN_3.

Since the presence of cold liquids on the freezing-out trap produced a thermal contraction of the gas in the cell, it was necessary to multiply the observed pressure by an appropriate factor in order to obtain the true value of the pressure at the temperature of the room. These factors were determined by admitting a sample of dry air into the cell and observing the pressure decrease upon applying the cold liquids to the trap in the same manner as was done in an experiment. For liquid air the factor was 1.055 and for a carbon dioxide-ether mixture it was 1.018. The results of this phase of the investigation are shown graphically in Figure 3. As abscissae are plotted the ratios of the pressure at any given time to the initial pressure of hydrogen azide (thus, as mentioned above, 1.18 corresponds to that phase of the decomposition where there is a sudden increase in the rate of building up pressure and 1.67 corresponds to complete decomposition). As ordinates are plotted the compositions of the various separable constituents as percentages of the total gas phase.

A consideration of Figure 3 reveals the following facts:

(1) At the point where ammonia and hydrogen azide exist in equal amounts,namely the inflection point of the time vs pressure curve, almost 100%

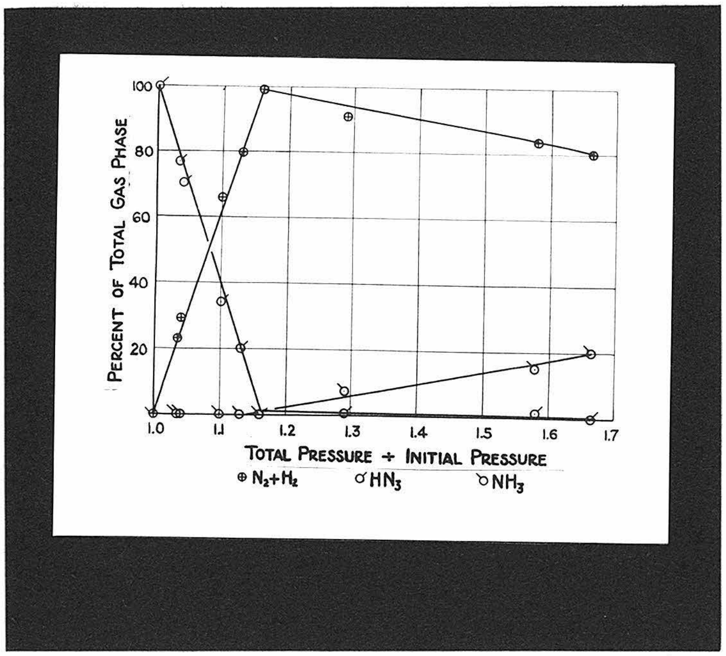

Figure 3. Composition of Gas Phase During Decomposition

of the gas phase is nitrogen.

(2) Hydrogen azide and ammonia do not coexist in the gas phase to a very appreciable extent.

The obvious explanation of these observations is that the ammonia formed from the first decomposition of hydrogen azide combines with some of the excess hydrogen azide to form ammonium azide, the white solid observed by Beckman and Dickinson in the photochemical decomposition. To test this hypothesis a decomposition was carried to the point of inflection, a carbon dioxide-ether mixture applied to the freeze-out trap, H, (Fig. 1) and the non-condensable gas pumped off. The slight amount of white solid which remained in the trap even after removal of the freezing mixture was driven back into the cell by warming H slightly and illumination of the cell was continued, whereupon the pressure proceeded to build up at approximately the rate corresponding to the slope of line B (Fig. 2) of a normal decomposition curve. The same rate of pressure increase was observed upon illumination of some ammonium azide made in the cell by bringing together some unilluminated hydrogen azide with an excess of pure anhydrous ammonia from a flask-reservoir temporarily attached to the apparatus and pumping the excess ammonia off from a carbon dioxide-ether mixture. Moreover, the white solid so formed resembled ammonium azide in the ease with which it sublimed to a cooler part of the cell upon being warmed slightly. The vapor pressure of the white solid was about 0.7 mm at room temperature, which agrees well with the more carefully determined value of 0.66 mm for ammonium azide at 25°C of Frost, Cothran, and Browne[7], published after this work was completed.

Apparently, then, the ammonia formed during the first part of the decomposition immediately combines with excess hydrogen azide to form solid ammonium azide. After the total pressure has built up to approximately 1.18 of its initial value, however, the excess of hydrogen azide has been consumed so that any further ammonia which forms remains as a gas. This accounts for the sudden increase in the rate of change of total pressure at this point which characterized every decomposition run. The remainder of the run, then, consists essentially in the decomposition of ammonium azide to form nitrogen and ammonia. The formation of the small amount of hydrogen and its subsequent disappearance will be discussed in a later section.

3. Thermal Dissociation of Ammonium Azide

It was considered of some interest to know whether or not the molecules now taking energy for decomposition from the excited mercury atoms were ammonium azide molecules or hydrogen azide molecules resulting from a thermal dissociation of ammonium azide in the vapor state to hydrogen azide and ammonia. Curtius and Rissom[8] found ammonium azide to be completely dissociated at 100°C, the only temperature at which their measurements of vapor density were made. In order to obtain some idea of the order of magnitude of the dissociation at room temperature a few semi-quantitative determinations were made as follows: A liter flask with a side arm for freezing out condensables, a dibutylphthalate manometer, and an ammonia flask reservoir with a two-stopcock doser were attached to the vacuum system. After ascertaining that the dibutylphthalate did not dissolve either hydrogen azide or ammonia rapidly enough to interfere with the measurements and that the volume of the system was sufficient to insure complete volatilization of the ammonium azide formed from a single dose each of hydrogen azide and ammonia, a series of determinations were made in two different ways. One way consisted in admitting to the system a dose of hydrogen azide with an excess of ammonia, pumping off the excess ammonia over a carbon dioxide-ether mixture, allowing the ammonium azide sufficient time to come to equilibrium with the gas phase, and then opening the mercury cut-off leading to the dibutylphthalate manometer and measuring the final total pressure, p. The apparatus was so constructed that the additional volume introduced with the manometer was negligible. Knowing the initial pressure of hydrogen azide, p_0, the dissociation, α , is given by the expression: $\alpha = p/p_0 - 1$. The other technique used in determining α differed from this in that the excess of hydrogen azide or ammonia was not removed. Known amounts of these two gases (determinable by calibrating the dosers of the reservoirs against the manometer) were allowed to come to equilibrium and the final total pressure measured on the manometer as before. For this case the value of α is given by the expression: $\alpha = \sqrt{\frac{1}{1+\beta}}$ where $\beta = \frac{p(p_0 + a - p)}{(p - p_0)(p-a)}$ and a represents the initial partial pressure of ammonia.

The two different methods gave results which were entirely concordant within the accuracy of the experiment. Nine runs were made at an average total pressure of 6 mm. The values for α ranged from 0.81 to 0.99 with an average of 0.91. Inasmuch as this phase of the investigation was carried out only semi-quantitatively without the use of various time-consuming experimental refinements, these results might easily correspond to complete dissociation, and were so interpreted. Since this work was done, Frost, Cothran, and Browne[7] have reported an accurate linear relationship between 1/T and log p for the vapor tension of ammonium azide between 15°C and 120°C which, taken together with Curtius' and Rissom's value of 100% dissociation at 100°C, further substantiates the assumption of complete dissociation at room temperature. Thus we may conclude that the second and steeper part of the time-pressure curve consists mainly in hydrogen azide, in equilibrium with ammonia and solid ammonium azide, decomposing to give more ammonia and nitrogen.

4. Effect of Hydrogen

So far three significant features of the experiments have not been explained: (1) the pressure increase during the first part of the run which would not be possible if the only reaction taking place were the one discussed above, namely $4\ HN_3 \rightarrow NH_4N_3(\text{solid}) + 4\ N_2$; (2) the positive indication of hydrogen from the moment decomposition commences and its continued presence throughout most of the run; and (3) the absence of hydrogen in the final products. The first two facts might be explained by assuming that a definite fraction of the hydrogen azide decomposes according to the equation:

$$2\ HN_3 \longrightarrow H_2 + 3\ N_2$$

Beckman and Dickinson[4] found that in the photochemical decomposition 27% of the hydrogen azide decomposed in this way and 73% decomposed concurrently to give ammonia and nitrogen. If 18% be assumed to give hydrogen and nitrogen in this case, both the hydrogen composition and the pressure increase to a value 1.18 times the initial hydrogen azide pressure at the point of inflection are very satisfactorily accounted for. In view of fact (3), above, some reaction involving the consumption of hydrogen must occur. The reduction of hydrogen azide by hydrogen to give ammonia and nitrogen has been reported by Piccard and Thomas[9] and others and might be suspected here. Inasmuch as the reaction $2\ HN_3 + H_2 \longrightarrow NH_4N_3(\text{solid}) + N_2$ involves a decrease in pressure, one might predict that if the partial pressure of hydrogen were increased sufficiently during the first part of a run, a decrease in total pressure might be observed. This prediction was tested experimentally. Figure 4 shows pressure-time curves of 3 experiments in which different amounts of hydrogen were introduced at

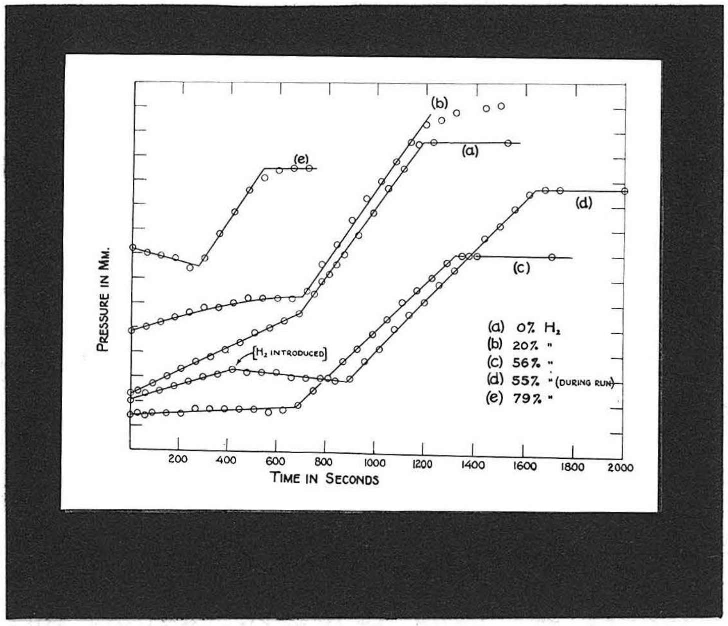

Figure 4. Effect of Hydrogen on Decomposition

the beginning of the decomposition, one in which it was introduced during a run, and a normal decomposition curve for purposes of comparison. Each division on the vertical scale represents a change in pressure of 1.0 mm, but absolute pressures cannot be read from the graph as the curves have been shifted up or down in order to minimize their intersection of one another. The percentages signify the percent which the hydrogen represents of the total volume of hydrogen plus initial hydrogen azide. In experiment (d), where hydrogen was introduced during the run, the partial pressure of the hydrogen added was subtracted from the total pressure in order to make the curve continuous. It is evident from these curves that the rate of pressure increase during the first part of a decomposition run varies inversely with the proportion of hydrogen present, as predicted.

5. Effect of Light Intensity

The variation of rate of decomposition with light intensity was also investigated. The light intensity was varied by placing the mercury arc lamp at different distances from the decomposition cell. Since the lamp could not be regarded as a point source of light, even as a first approximation, the inverse square law relating intensity of illumination with the distance of the body illuminated from the light source could not be applied. It was therefore necessary to calibrate the lamp for this variation. A calibrated Weston Photronic Cell connected to a microammeter was used for this purpose, and found to be very satisfactory. Due to the variation in the rate of decomposition from run to run, it was only possible to compare different rates with corresponding light intensities within the course of a single run. Light intensities ranging from 0.15 normal illumination up to normal were used and the decomposition rates for both parts of the pressure-time curve were found to be accurately linear with intensity of illumination.

6. Miscellaneous Observations

The following runs were made in order to test for side reactions and other effects not accounted for by the mechanism suggested above:

(a) Hydrogen azide at the customary pressure was allowed to stand in the cell for several hours without illumination. No pressure increase was observed, indicating that thermal decomposition is negligible.

(b) Ammonia at a pressure seven times the value of the maximum partial pressure which it reaches in the course of a normal experiment was illuminated in the cell for several hours during which time the pressure increased only two percent. This sensitized ammonia decomposition was studied by Dickinson and Mitchell[10] who found that the hydrogen produced soon almost completely inhibited further decomposition.

(c) A mixture of hydrogen and ammonia in approximately equal amounts was illuminated for two hours with no observable pressure change.

(d) A mixture of hydrogen and nitrogen in equal amounts was illuminated for two hours. The pressure dropped two percent in the first minute and then remained constant. A similar experiment in which twice as much nitrogen was used resulted in twice as great a drop in pressure in the first two minutes after which the pressure remained constant. This initial drop is probably due to the combination of oxygen, present as an impurity in the tank nitrogen used, with some of the hydrogen to form water vapor.

(e) Hydrogen at a pressure of 40 mm was illuminated in the cell for one and one-half hours with no observable pressure change.

(f) A mixture of nitrogen and hydrogen azide in the ratio of 1:2 was illuminated. The pressure-time curve for the decomposition differed in no way from those characteristic of runs with hydrogen azide alone.

Summary of Part I

The experimental results indicate that the reactions of the gaseous hydrogen azide molecules during the early part of the decomposition may be represented by the stoichiometric equations

(1) $2\ HN_3 \rightarrow H_2 + 3\ N_2$

(2a) $3\ HN_3 \rightarrow NH_3 + 4\ N_2$

and (2b) $HN_3 + NH_3 \rightarrow NH_4N_3\text{(solid)}$

Approximately 18% of the hydrogen azide molecules react according to equation (1) and 82% according to equations (2).

After 80% of the hydrogen azide has been decomposed in this manner, reaction (2b) no longer takes place, since at this point the partial pressure of the remaining gaseous hydrogen azide becomes insufficient to form solid ammonium azide with the ammonia formed in reaction (2a). A sudden increase in the rate of change of total pressure occurs at this point as a consequence. The 20% of hydrogen azide which is as yet undecomposed is substantially all in the form of solid ammonium azide. This ammonium azide gradually vaporizes during the remainder of the run, dissociating completely into ammonia and hydrogen azide. As the decomposition proceeds, the partial pressure of ammonia increases rapidly and the partial pressure of hydrogen azide becomes correspondingly small. A third reaction now becomes increasingly important as the decomposition nears completion, namely

(3) $H_2 + HN_3 \rightarrow NH_3 + N_2$

As a result of this reaction the hydrogen disappears from the reaction mixture, and the end products of the reaction are given simply by the equation

(4) $3\ HN_3 \rightarrow NH_3 + 4\ N_2$

Part II. The Quantum Yield

Apparatus

The apparatus used is shown in Figure 5. F is the reservoir flask containing anhydrous hydrogen azide attached to the vacuum system. The latter consisted essentially of a fused quartz reaction cell, I, in which the hydrogen azide was irradiated, and a McLeod gage (attached at C) for reading the total pressure of non-condensable gases produced by the decomposition.

Monochromatic radiation of wave length 2537 Å was obtained by the use of the same quartz mercury-vapor lamp used in the other part of the investigation and a Bausch and Lomb monochromator with quartz lenses and prisms. The beam of monochromatic light emerging from the monochromator passed through two converging cylindrical quartz lenses, through a quartz plate set at an angle of 45° with the axis of the cell I, through the plane fused quartz windows of the cell and onto the receiving vane of a sensitive vacuum thermopile T_T (transmission thermopile). The quartz plate set at an angle of 45° served to reflect a fraction of the incident radiation at right angles onto the recieving vane of a similar thermopile, T_R (reflection thermopile). The two faces of the plate were ground at

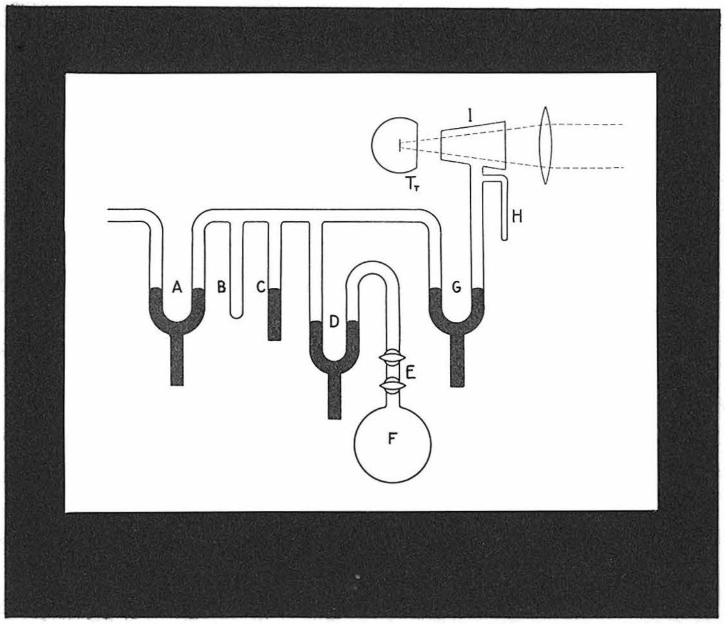

Figure 5. Diagram of Vacuum System (Part II).

such an angle with each other that the reflections from both faces coincided on the thermopile vane, minimizing the area of the light spot. 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. The vanes of the thermopiles were large enough to cover completely the converged beams. The thermoelectric system of each thermopile consisted of six junctions of bismuth and bismuth-tin alloy (95% Bi, 5% Sn) in series, three junctions attached to each vane. The front surfaces of the vanes, which were of aluminum foil, were coated with lamp-black. The thermopiles were mounted in glass containers with plane fused quartz windows attached with wax. The thermopile vessels were continuously evacuated during the runs. Liquid-air traps prevented the access of mercury vapor into the thermopile vessels. The thermopiles were of the compensated type to avoid difficulties occasioned by shifting zero positions.

The continuous recording device consisted of a flat carriage which carried a 25 x 31 cm sheet of photographic 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 focussed 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. In order to avoid the error caused by shrinkage on expansion of the paper during development, drying, etc., the coordinate system was printed upon the paper immediately after removal from the recorder by making a contact print through a coordinate screen made by ruling fine coordinate lines through an opaque silver coating on a glass plate.

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 λ 2537 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 D_R and D_T for thermopiles T_R and T_T respectively, with the cell empty of mercury vapor. To calibrate thermopile T_T two different 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 furnished with the standard lamp. The transmission of the thermopile window for this radiation was known from 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 were made with two standard lamps. A slight trend was observed when the values of the thermopile sensitivity were plotted against the galvanometer deflection, due probably to lack of linearity of the galvanometer scale. To avoid error from this source, the value of the sensitivity corresponding to the observed deflection in each case was used in calculating the quantum yields.

The transmissions for λ 2537 Å of the rear window of the cell and the window of thermopile T_T were obtained by measuring the transmission of a similar piece of quartz plate with the aid of the continuous recording device. A series of such determinations in which the quartz plate was alternately moved into and out of the path of the beam entering thermopile T_T consistently gave a value for this transmission of 0.867.

The ratio of the galvanometer deflections for the two thermopiles with no mercury vapor in the cell was determined by opening the glass tubing connecting the cell to the vacuum system and pushing up into the opening of the cell itself a small diameter glass tube connected to a water aspirator. As soon as aspiration was commenced, the ratio of D_T/D_R jumped to a value of 4.36, where it remained without further change.

With these data and the values of the deflections of the galvanometers for a run with mercury vapor and hydrogen azide in the cell, the energy absorbed in decomposition of the hydrogen azide was calculated as follows, where t_{2537} represents the transmission factor of quartz to λ 2537 Å, A the sensitivity of the transmission thermopile in ergs per second for unit deflection, D_T and D_R the mean deflections during a run of the galvanometer light beams associated with the transmission and reflection thermopiles respectively, E_o the energy entering the cell, E_R the energy passing through the cell and reaching the rear window, and S the duration of the run in seconds:

When no mercury vapor is present in the cell, E_o, for a deflection of D_T divisions, $\dfrac{AD_T}{t^2_{2537}}$

(the division by t^2_{2537} arising from the fact that two quartz plates intervene between the inside surface of the front window of the cell and the surface of the thermopile vane). For this case, however, $D_T = 4.36 \cdot D_R$ so that $E_o = \dfrac{4.36\ AD_R}{t^2_{2537}}$

This expression is independent of whether or not there is mercury vapor present in the cell.

But $E_R = \frac{D_T A}{t^2_{2537}}$

So that $E_0 - E_R$ (energy absorbed in reaction)

$$= \frac{4.36\ AD_R - AD_T}{t^2_{2537}} = \frac{AS(4.36D_R - D_T)}{(.867)^2}$$

Since one quantum of λ 2537 Å is equivalent to 7.75×10^{-12} ergs $\left(hc/\lambda = \frac{6.55 \times 10^{-27} \times 2.998 \times 10^{10}}{2.537 \times 10^{-5}}\right)$ the number of quanta absorbed during a run is given by the expression $\frac{AS(4.36\ D_R - D_T)}{(.867)^2 \times 7.75 \times 10^{-12}}$

The determination of the number of molecules of hydrogen azide decomposed during a run required the following data: (1) the effective volume of that part of the vacuum system into which the non-condensable products of decomposition were allowed to expand at the end of the run for the purpose of measuring (2) the pressure of the non-condensables, and (3) the temperature. In addition it was necessary to know the numerical relationship between the quantity of hydrogen azide decomposed and the quantity of non-condensables produced.

The effective volume of the system was determined experimentally by air expansion from a flask of known volume temporarily attached to the system, and found to be 113.0 cc.

During this determination liquid air was applied to trap H in order to duplicate the actual conditions during a pressure measurement. The pressure of non-condensables was measured on a McLeod gage.

The ratio between the number of mols of hydrogen azide decomposed and the number of mols of non-condensable gas produced was determined experimentally in the first part of this investigation. Since only a small fraction of hydrogen azide was decomposed in the quantum-yield runs, the ratio which was found for the initial stage of the decomposition was used, namely one mol of hydrogen azide decomposed produces 1.18 mols of non-condensable gas.

If we let p represent the pressure of non-condensables resulting from a run and T the absolute temperature, we have the relation: the number of hydrogen azide molecules decomposed $= \frac{p \times 113 \times N}{760 \times 1.18\ RT}$ where N is Avogadro's number and R has the value of 82.1 cc-atm per degree.

Procedure

The procedure was as follows in a typical quantum-yield determination. With the system evacuated, cut-off A closed, cut-offs D and G open, and the mercury in the

McLeod gage as high as possible, the desired amount of hydrogen azide was admitted thru the doser, E. Cut-off D was then closed and liquid air applied to H to freeze out the hydrogen azide. The system was then evacuated in order to remove any traces of non-condensable gas which might be present. Cut-off A was then closed and the liquid air transferred to trap B. After the hydrogen azide had distilled from H to B, the system was again evacuated. This process was repeated again, bringing the hydrogen azide back to trap H. After evacuating,cut-off G was closed, the liquid air removed from H and the hydrogen azide allowed to vaporize and come to room temperature. The pressure of the hydrogen azide in the cell was then determined by reading the difference in the mercury levels in the two arms of cut-off G with a cathetometer. A sheet of photographic paper was put into the recorder, the galvanometer switches closed, and the recording mechanism started. During all of this preliminary preparation, the mercury vapor lamp had been warming up with the monochromator shutter closed. After running for a minute with the shutter closed in order to get a zero reading, the shutter was opened and the hydrogen azide irradiated for thirteen minutes, leaving a minute at the end of the fifteen minutes allowed by the recording mechanism for another zero reading with the shutter closed. Liquid air was then applied to trap H, cut-offs A and D closed, cut-off G opened (after allowing fifteen minutes for the condensables to be frozen out), and connection made with the McLeod gage where the pressure of non-condensable gases was measured. The coordinate system was printed upon the photographic paper and the paper was developed.

A blank run was made which was an exact duplicate of an ordinary run except that the shutter of the monochromater was left closed throughout. The pressure of the hydrogen azide used was about 10 mm; the pressure of non-condensables developed was found to be 1.0×10^{-4} mm, for which allowance was made in calculating the amounts of hydrogen azide decomposed (cf. column 5, Table I).

In order to make sure that the difference in size and shape between cell I, Fig. 5, and cell G, Fig. 1, did not change the characteristics of the decomposition sufficiently to invalidate the use of the factor 1.18 relating the volume of non-condensables produced to the volume of hydrogen azide consumed in the calculation of the quantum yields, the quartz fiber gage was temporarily connected to the apparatus and the non-condensables from a typical quantum yield run at an hydrogen azide pressure of about 10 mm analyzed. Three determinations gave for the hydrogen content 7.5%, 7.7%, and 7.5% , agreeing very well with the values obtained with cell G and the value of 7.6%, corresponding to the factor 1.18.

Experimental Results

The experimental results are summarized in Tables I and II in which the runs are arranged in order of decreasing hydrogen azide pressure. In Table I are given the data from which may be calculated the number of molecules of hydrogen azide decomposed during each run. In the second column is given the initial pressure of hydrogen azide in the cell. The temperature of the system is given in the third column and the total pressure of the non-condensables in the fourth followed by the pressures corrected for the 1.0×10^{-4} mm of non-condensable gas developed in the unilluminated run. In the last column is given the number of molecules of hydrogen azide decomposed, calculated with the equation given above.

Table I

Data for Calculating the Amount of Hydrogen Azide Decomposed

1	2	3	4	5	6
Run	Pressure HN_3	Temp. °K	Pressure non-cond. mm x 10^3	Pressure corrected mm x 10^3	Molecules HN_3 decomp. x 10^{-16}
2	20	296	10.80	10.70	3.36
3	20	296	12.34	12.24	3.85
12	16.1	295	16.24	16.14	5.09
1	16.0	294	6.97	6.87	2.17
13	10.6	295	16.00	15.90	5.01
4	10.0	296	11.40	11.30	3.55
14	7.4	295	12.38	12.28	3.87
10	6.4	294	13.94	13.84	4.38
15	4.1	295	11.41	11.31	3.57
5	4.0	295	7.32	7.22	2.28
11	4.0	295	12.00	11.90	3.75
6	3.3	296	7.45	7.35	2.31
7	1.4	296	6.56	6.46	2.03
8	0.8	293	6.47	6.37	2.02
9	0.3	294	1.48	1.38	0.436

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 Sensitiv. of T_T ergs/sec. per div.	6 Quanta absorbed x 10^{-15}	7 Quantum Yield molecules decomp. per quantum absor.
2	728	17.8	19.3	1.320	9.62	3.50
3	729	19.6	22.4	1.310	10.35	3.72
12	727	26.3	28.6	1.295	13.90	3.66
1	780	11.1	13.3	1.335	6.28	3.46
13	727	26.7	33.9	1.285	13.25	3.78
4	738	20.6	29.9	1.295	9.83	3.61
14	727	23.8	35.5	1.285	10.95	3.53
10	731	28.7	40.6	1.275	13.50	3.25
15	730	24.6	40.0	1.275	10.75	3.32
5	731	16.2	29.6	1.295	6.65	3.43
11	663	27.6	42.3	1.275	11.33	3.31
6	726	17.1	30.9	1.290	7.03	3.29
7	727	17.6	33.3	1.285	6.98	2.91
8	728	26.6	49.3	1.260	10.50	1.93
9	731	27.6	50.2	1.260	11.10	0.39

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 (T_T) and reflected (T_R) beams, obtained from the continuous photographic record. In column 5 are given the values of the sensitivity of T_T corresponding to the various deflections as interpolated from the calibration runs with the standard lamps. In column 6 are given the total number of quanta of radiation of wave length 2537 Å which were absorbed in the decomposition cell as calculated by the formula given above, and in the last column are the corresponding quantum yields.

The relation of quantum yield to hydrogen azide pressure is shown graphically in Figure 6. Below 2 mm the quantum yield falls off rapidly with decreasing pressure but at higher pressures approaches the limiting value of 3.6 molecules of hydrogen azide decomposed per quantum of radiation absorbed.

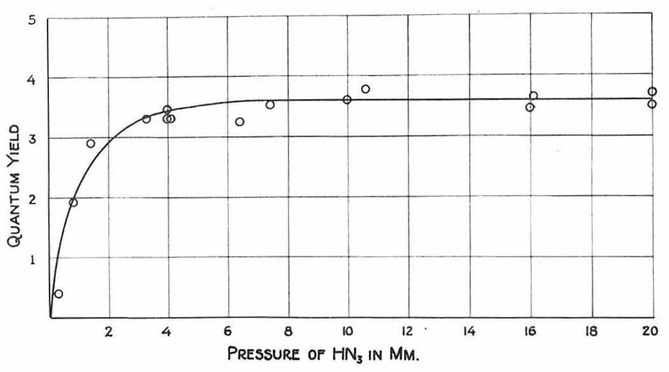

Figure 6. Relation of Quantum Yield to Pressure of Hydrogen Azide

Discussion

The quantum yield determinations apply to the initial stage of the decomposition during which, as was shown in Part I, the reaction follows the stoichiometric relations

$$2\ HN_3 \rightarrow H_2 + 3N_2 \qquad (1)$$

and

$$4\ HN_3 \rightarrow NH_4N_3(\text{solid}) + 4\ N_2 \qquad (2)$$

with 18% of the molecules reacting according to equation (1) and 82% according to equation (2). If one quantum of radiation is required for either reaction (1) or reaction (2), a calculated quantum yield of 3.4 molecules of hydrogen azide decomposed per quantum absorbed is obtained, which is in good agreement with the experimental value 3.6 obtained at the higher pressures. The rapid decrease in quantum yield at pressures below 2 mm is to be expected, since at these pressures the mean time between collisions becomes comparable with the mean life of mercury atoms in the 2 $^3P_1$ state and increasing amounts of the absorbed energy are lost through radiation.

It is to be noted that not all of the 3.4 molecules decomposed per quantum are actually decomposed in the sense of breaking down into ammonia, hydrogen, and nitrogen, some being merely temporarily removed from the gas phase by association with ammonia to form solid ammonium azide. Since the same experimentally determined stoichiometric relations were used in the calculation of both the theoretical 3.4 and the experimental 3.6, this observation applies equally to both. The corresponding quantum yields in terms of hydrogen azide molecules decomposing completely into ammonia, hydrogen, and nitrogen are 2.70 and 2.86 respectively.

It is of interest to note that the observed quantum yield for the mercury photosensitized decomposition of hydrogen azide is also in agreement with the observed quantum yield for the photochemical decomposition by radiation of wave length 1990 Å obtained by Beckman and Dickinson[5] within the limits of experimental error of the latter measurements. The average quantum yield for the photochemical decomposition was found to be 2.97 ± 0.45 molecules of hydrogen azide decomposed per quantum absorbed, when calculated to the formation of ammonia. When calculated to the formation of ammonium azide, as was done in the present work, the quantum yield becomes 3.7 ± 0.5, which is to be compared with the experimental value of 3.6 for the photosensitized decomposition.

One is led to the conclusion that the mechanism of the mercury photosensitized decomposition is probably identical with that of the photochemical decomposition. One may write, therefore, as a possible mechanism[5]

$$h\nu + Hg = Hg^{*} \qquad (1)$$

$$Hg^{*} + HN_3 = Hg + N_2 + HN \qquad (2)$$

$$HN + HN_3 = H_2 + 2\,N_2 \qquad (3)$$

$$HN + HN_3 = N_2 + N_2H_2 \qquad (4)$$

$$N_2H_2 + HN_3 = N_2 + NH_3 \qquad (5)$$

$$NH_3 + HN_3 = NH_4N_3(\text{solid}) \qquad (6)$$

with 18% of the hydrogen azide molecules reacting according to equations (2) and (3) and 82% according to equations (2), (4), (5), and (6).

Summary

The mercury photosensitized decomposition of gaseous hydrogen azide by monochromatic radiation of wave length 2537 Å has been investigated over the pressure range 0.3 mm to 20 mm. The final products of the decomposition were found to be ammonia and nitrogen with ammonium azide and hydrogen as intermediate products during the earlier stages of the decomposition. The quantum yield was found to approach the constant value 3.6 molecules of hydrogen azide decomposed per quantum absorbed. It is shown that the photosensitized decomposition closely parallels the photochemical decomposition described by previous investigators.

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References

1. E. Oliveri-Mandala, Gazz. Chim. Ital., 46, II, 137-59 (1916).
2. K.F. Schmidt. Ber., 57B, 704 - 6 (1924).
3. Karl Gleu, Ber., 61B, 702 - 7 (1928).
4. Beckman and Dickinson, Jour. Am. Chem. Soc., 50, 1870 - 5 (1928).
5. Beckman and Dickinson, ibid, 52, 124 - 32 (1930).
6. Beckman, J. Opt. Soc., 16, 276 (1928).
7. Frost, Cothran, and Browne, Jour. Am. Chem. Soc., 55, 3516 (1933).
8. Curtius and Rissom. J. Prakt. Chem. 58, 273 (1898).
9. Piccard and Thomas, Helv. Chim. Acta, 6, 1039 (1923).
10. Dickinson and Mitchell, Proc. Nat. Acad. Sci. 12, 692 (1926).