other molecule, and that only this energy rich HO_2 can react with hydrogen to form hydrogen peroxide, one can explain the experimental results. Experiments in which the effect of varying oxygen concentration on the hydrogen peroxide yield was studied show that the yield is inversely proportional to the oxygen concentration when atomic hydrogen is run into a mixture of hydrogen and oxygen (See Fig. 4). Energy rich HO_2 may be deactivated by collision with oxygen molecules.

The author wishes to take this opportunity to thank Dr. G. I. Lavin for assisting with this work and Professor H. S. Taylor for his advice and criticism.

Summary

1. The products of an electrical discharge through water vapor at pressures below 1 mm. cause the oxidation of carbon monoxide even when they have been drawn several decimeters from the discharge.

2. One of the products of such a discharge recoverable in large quantities is hydrogen peroxide.

3. The effects of added gases and of varying the discharge current on the yields of carbon dioxide and hydrogen peroxide have been determined.

4. The effect of interposing dehydrogenation and dehydration catalyst surfaces in the active gas stream from the water vapor discharge on the carbon dioxide yield has been studied.

5. The yields of hydrogen peroxide and carbon dioxide from mixtures of oxygen, carbon monoxide, and atomic and molecular hydrogen have been determined under various conditions.

6. Mechanisms have been postulated to explain the observed carbon dioxide and hydrogen peroxide yields.

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The Mercury-Sensitized Decomposition of Hydrogen Azide

BY ALBERT E. MYERS AND ARNOLD O. BECKMAN

Introduction

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

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

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

$$HN_3 + H_2O \longrightarrow N_2 + NH_2OH$$

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 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.

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 recrystallization from aqueous solutions. The hydrogen

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[1] E. Oliveri-Mandalà, *Gazz. chim. ital.*, **46**, II, 137–159 (1916).

[2] K. F. Schmidt, *Ber.*, **57**, 704–706 (1924).

[3] Karl Gleu, *ibid.*, **61**, 702–707 (1928).

[4] Beckman and Dickinson, THIS JOURNAL, **50**, 1870–1875 (1928).

[5] Beckman and Dickinson, *ibid.*, **52**, 124–132 (1930).

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 Fig. 1. From the storage flask E the desired quantity of hydrogen azide was transferred to the reaction cell G by applying liquid air at H. After traces of non-condensable gas were pumped off, cut-off F was closed, liquid air removed and the HN_3 irradiated. Constant temperature was maintained by the circulation of thermostated water around G. A filter consisting of 5 mm. of 25% acetic acid also surrounded the reaction cell to remove radiation of wave lengths shorter than 2400 Å. which would produce direct photochemical decomposition. The source of radiation was a water-cooled quartz mercury vapor lamp.

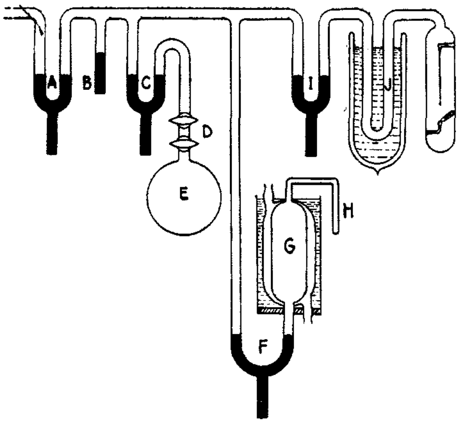

Fig. 1.—Diagram of vacuum system (Part I).

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.

The composition of the non-condensable gases was 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

Rate of Change of Total Pressure.—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 thirty or sixty 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 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 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) The ratio of condensable to non-condensable products was found to be 0.25 ± 0.01.

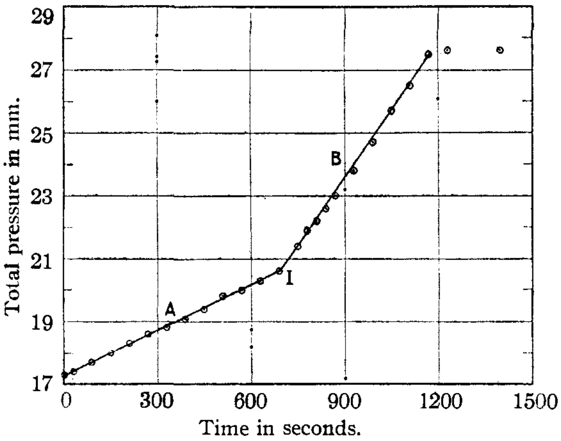

Fig. 2.—Typical time *vs.* pressure curve.

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

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

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(6) Beckman, *J. Opt. Soc.*, **16**, 276 (1928).

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 over-all 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 value for the ratio of the pressure at this point to the initial hydrogen azide pressure was found to be 1.175 ± 0.016.

Change of Composition of Reaction Mixture.—Analyses of the non-condensable gases produced during ten different runs all indicated the presence of from 2 to 7% hydrogen. No definite relationship between the percentage 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°) 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 $H_2 + N_2 + NH_3 + 0.9$ mm. of HN_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 to correct to room temperature. 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 Fig. 3. As abscissas 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.

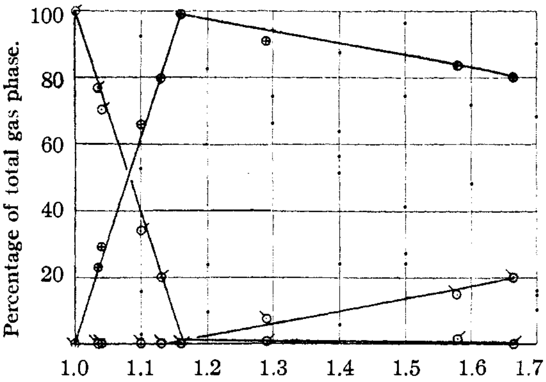

Fig. 3.—Composition of gas phase during decomposition: ⊕, $N_2 + H_2$; ♂, HN_3; ъ, NH_3.

A consideration of Fig. 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% of the gas 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° of Frost, Cothran and Browne,[7] published after this work was completed.

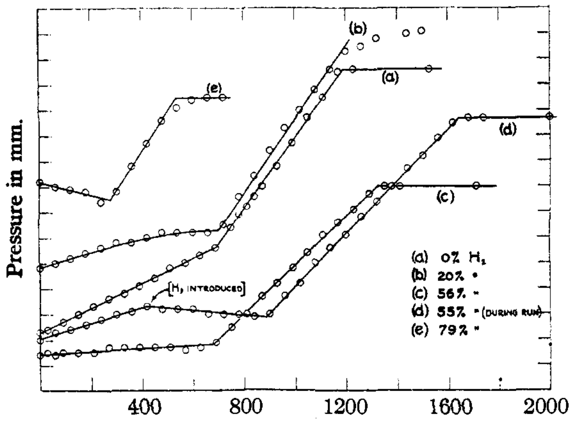

Fig. 4.—Effect of hydrogen on decomposition.

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.

Thermal Dissociation of Ammonium Azide.—That ammonium azide does not enter into the reaction is shown from the work of Frost, Cothran and Browne,[7] who have reported a linear relationship between $1/T$ and $\log p$ for the vapor tension of ammonium azide between 15 and 120° which, taken with Curtius and Risson's[8] determination of 100% dissociation at 100°, indicates complete dissociation of ammonium azide in the gas phase during the present experiments.

Effect of Hydrogen.—Three significant features of the experiments remain to be interpreted: (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, $4HN_3 = NH_4N_3(\text{solid}) + 4N_2$; (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 $2HN_3 = H_2 + 3N_2$.

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. In the present experiments, 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 ammonia and nitrogen has been reported by Piccard and Thomas[9] and others and might be suspected here. Inasmuch as the reaction $2HN_3 + H_2 = NH_4N_3(\text{solid}) + N_2$ involves a decrease in pressure, one might predict that if the partial pressure of hydrogen were increased sufficiently during the first part of the run, a decrease in total pressure might be observed. This prediction was tested experimentally. Figure 4 shows pressure–time curves of three experiments in which different amounts of hydrogen were introduced at the beginning of the decomposition, one in which it was introduced during a run, and a normal decomposition curve for

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[7] Frost, Cothran and Browne, This Journal, 55, 3516 (1933).

[8] Curtius and Rissom, *J. prakt. Chem.*, **58**, 273 (1898).

[9] Piccard and Thomas, *Helv. Chim. Acta*, **6**, 1039 (1923).

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 percentage 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 decreases with increasing percentages of hydrogen, as predicted.

Effect of Light Intensity.—The light intensity was varied by placing the mercury arc lamp at different distances from the decomposition cell. A calibrated Weston photronic cell connected to a microammeter was used to determine relative light intensities. 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.

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

$$2HN_3 = H_2 + 3N_2 \qquad (1)$$
$$3HN_3 = NH_3 + 4N_2, \text{ and} \qquad (2a)$$
$$HN_3 + NH_3 = NH_4N_3 \text{ (solid)} \qquad (2b)$$

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

$$H_2 + HN_3 = NH_3 + N_2 \qquad (3)$$

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

$$3HN_3 = NH_3 + 4N_2 \qquad (4)$$

Part II. The Quantum Yield

Apparatus.—The apparatus used is shown in Fig. 5. F is the reservoir 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.

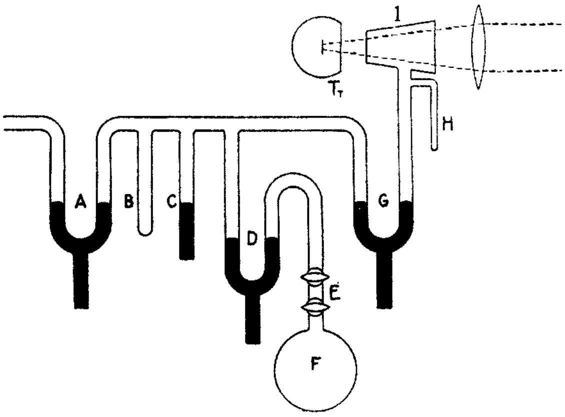

Fig. 5.—Diagram of vacuum system (Part II).

Monochromatic radiation of wave length 2537 Å. was obtained by the use of a Bausch and Lomb monochromator. 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 receiving vane of a similar thermopile, T_r (reflection thermopile). The two faces of the plate were ground at such an angle with each other that the reflections from both faces coincided on the thermopile vane. 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 The apparatus and method of calibration were substantially the same as that described by Wenner and Beckman.[10]

The transmissions of the rear cell window and the window of the thermopile T_t were found to be 0.914 for radiation from the standard lamp and 0.867 for λ 2537 Å.

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.

Method of Calculating Results.—The energy absorbed in decomposition of the hydrogen azide was calculated as follows, where t represents the transmission factor of the quartz windows to λ 2537 Å. A represents the sensitivity of the transmission thermopile in ergs per second for unit deflection, D_t and D_r the mean galvanometer deflections associated with the transmission and reflection thermopiles, respectively, E_1 represents the average energy per second entering the cell, E_2 the average energy per second passing through the cell and reaching the rear window and S the duration of the run in seconds.

The energy absorbed during a run is equal to

$$E_1 - E_2 = \frac{AS(4.36D_r - D_t)}{(0.867)^2}$$

Since one quantum of λ 2537 Å. is equivalent to 7.75×10^{-12} ergs, the number of quanta absorbed is given by the expression

$$N_Q = \frac{AS(4.36D_r - D_t)}{(0.867)^2 \times 7.75 \times 10^{-12}}$$

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 moles of hydrogen azide decomposed and the number of moles 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 mole of hydrogen azide decomposed produces 1.18 moles of non-condensable gas.

If p represents the pressure of non-condensables resulting from a run and T the absolute temperature, the number of hydrogen azide molecules decomposed = $(p \times 113 \times N)/760 \times 1.18\ RT$ 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, the desired amount of hydrogen azide was admitted through 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 to remove any traces of non-condensable gas. Cut-off G was closed, the liquid air removed from H and the hydrogen azide allowed to 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. The recording mechanism was started, and the hydrogen azide irradiated Liquid air was then applied to trap H, cut-offs A and D closed, cut-off G opened (after allowing the condensables to be frozen out), and the pressure of non-condensable gases was measured with the McLeod gage.

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 decomposed, the quartz fiber gage was connected temporarily to the apparatus and the non-condensables from a typical quantum yield at a hydrogen azide pressure of about 10 mm. analyzed. Three determinations gave for the hydrogen content 7.5, 7.7 and 7.5%, agreeing 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

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[10] Wenner and Beckman, THIS JOURNAL, **54**, 2787 (1932).

which the runs are arranged in order of decreasing hydrogen azide pressure.

TABLE I

DATA FOR CALCULATING THE AMOUNT OF HYDROGEN AZIDE DECOMPOSED

1 Run	2 Press., HN_3, mm.	3 Temp., °K.	4 Press., non-cond., mm. × 10^3	5 Molecules HN_3 decomp. × 10^{-16}
2	20	296	10.70	3.36
3	20	296	12.24	3.85
12	16.1	295	16.14	5.09
I	16.0	294	6.87	2.17
13	10.6	295	15.90	5.01
4	10.0	296	11.30	3.55
14	7.4	295	12.28	3.87
10	6.4	294	13.84	4.38
15	4.1	295	11.31	3.57
5	4.0	295	7.22	2.28
11	4.0	295	11.90	3.75
6	3.3	296	7.35	2.31
7	1.4	296	6.46	2.03
8	0.8	293	6.37	2.02
9	0.3	294	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, × 10^{-15}	7 Quant. yield, molecules dec. per quantum absd.
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

The relation of quantum yield to hydrogen azide pressure is shown graphically in Fig. 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.

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

$$2HN_3 = H_2 + 3N_2 \text{ and} \qquad (1)$$

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

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.

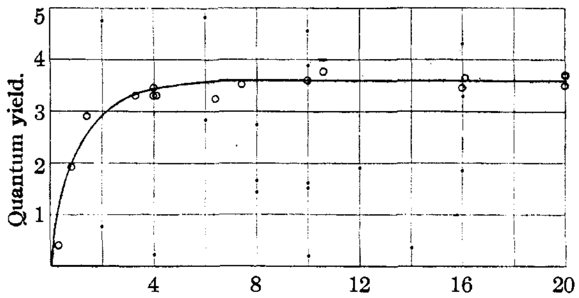

Fig. 6.—Relation of quantum yield to HN_3 pressure.

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,[8] 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]

$$\begin{array}{rcll} h\nu + \mathrm{Hg} & = & \mathrm{Hg}^* & (1) \\ \mathrm{Hg}^* + \mathrm{HN_3} & = & \mathrm{Hg} + \mathrm{N_2} + \mathrm{HN} & (2) \\ \mathrm{HN} + \mathrm{HN_3} & = & \mathrm{H_2} + 2\mathrm{N_2} & (3) \\ \mathrm{HN} + \mathrm{HN_3} & = & \mathrm{N_2} + \mathrm{N_2H_2} & (4) \\ \mathrm{N_2H_2} + \mathrm{HN_3} & = & \mathrm{N_2} + \mathrm{NH_3} & (5) \\ \mathrm{NH_3} + \mathrm{HN_3} & = & \mathrm{NH_4N_3}\ \text{(solid)} & (6) \end{array}$$

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 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 for the initial stage of the decomposition was found to approach the value 2.86 molecules of hydrogen azide decomposed per quantum absorbed when calculated to the formation of ammonia or 3.6 when calculated to the formation of ammonium azide. It is shown that the photosensitized decomposition closely parallels the photochemical decomposition described by previous investigators.

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NOTES

The Iodimetric Determination of Copper[1]

BY JOHN R. CALDWELL

It is desirable to have a general method for reducing absorption by analytical precipitates in cases where the usual expedients are impracticable. It has been found that the presence of certain protective colloids, and of some organic compounds such as nitrobenzene, exerts a profound influence upon the physical nature of analytical precipitates. When used under appropriate conditions, these agents may have a twofold function, they not only bring about rapid flocculation and settling of the precipitate, but also alter the nature of its surface so that the adsorptive capacity and further reactivity are greatly reduced. This property of protective colloids is of general application and has been employed with considerable success in several standard analytical procedures. Among these are included modifications of the Volhard chloride titration[2] and the iodimetric determination of copper. The latter will be discussed in detail.

In the iodimetric determination of copper, blue iodo-starch is carried down by precipitated cuprous iodide and renders the end-point indistinct. At least two attempts have been made to remedy this condition[3,4] but both have certain disadvantages. It was found that a solution of white shellac in alcohol would alter the nature of the surface of the precipitate and reduce adsorption of blue iodo-starch color.

Experimental.—Standard sodium thiosulfate solution was added until most of the iodine was consumed. At this point, 0.5 to 1.0 ml. of 4% alcoholic solution of white shellac was added. This solution was put in slowly from a medicine dropper while swirling the contents of the flask. The precipitate was allowed to settle for twenty to thirty seconds, and the titration completed. Instead of a dark blue solid suspended in a turbid solution, there was a heavy cream-colored precipitate which settled out in a few seconds leaving a clear, blue supernatant liquid that contained practically all of the iodo-starch color.

Results.—Samples of electrolytic copper ranging from 0.05 to 0.31 g. were titrated according to the above procedure. In a series of twelve determinations, the sum of plus and minus errors was +0.0001 g., showing that no systematic error was introduced. Two copper ores were

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(1) Presented before the division of Colloid Chemistry at the 88th meeting of the American Chemical Society, Cleveland, Ohio, September 10–14, 1934.

(2) J. R. Caldwell and H. V. Moyer, *Ind. Eng. Chem., Anal. Ed.*, **7**, 38 (1935).

(3) A. H. Low, "Tech. Methods of Ore Anal.," John Wiley and Sons, 1922, 9th ed., p. 79.

(4) E. H. Smith, *Chemist Analyst* **18**, 6 (1929).