The binding forces calculated by Bates and Andrews from thermal data and by the writer from refractions are found inadequate to account for the differences between the displacements of the different nuclei and groups in the molecules.

The atomic polarization is not generally an additive quantity, but tends to be greater, the greater the number of atomic nuclei or groups in the molecule, the greater the number of electric doublets and the more unsymmetrical the arrangement of these doublets in the molecule.

In the calculation of the electric moment of a molecule, the atomic polarization may be disregarded without risk of introducing appreciable error only when the moment is high and the molecule is small and contains but one or two electric doublets.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF PRINCETON UNIVERSITY]

THE PHOTOSENSITIZED AND PHOTOCHEMICAL DECOMPOSITION OF HYDRAZINE

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Perhaps the most important fact now necessary for a complete understanding of the manner in which reactions are brought about by light energy is a knowledge of the action produced directly upon its absorption by the molecule. Taylor[1] has proposed, as a generalization of the facts now known, to state a Second Law of Photochemistry as follows: "The absorption of light is a quantum process involving one quantum per absorbing molecule (or atom). The photochemical yield is determined by the thermal reactions of the system produced by the light absorption." The resultants of this sequence of secondary thermal reactions are determined by ordinary physicochemical methods. The nature of the quantum process presents a more difficult problem. It has been possible in many cases from a complete kinetic study of the reaction to set up a mechanism, based on a postulated primary process, which yields satisfactory agreement with experimental observations. The postulated primary process is then assumed to be that actually occurring. For conclusive evidence as to the primary light action we must turn to that on the optical side furnished directly by molecular spectra. Thus far it has been possible to correlate satisfactorily the nature of the absorption spectrum with a definite primary action only in cases involving diatomic molecules. Those more complex give spectra showing complicated band systems which resist analysis. As a result of

[1] Taylor, "First Report of the Committee on Photochemistry of the Division of Chemistry of the National Research Council."

these two lines of approach the nature of the primary processes and the sequence of secondary reactions appear to be definitely established for several photochemical reactions. These are mainly those involving the halogens and hydrogen halides.

The photochemical decomposition of ammonia has been the subject of more or less exhaustive study.[2] No mechanism has as yet been derived for this reaction which is in complete agreement with experimental facts, nor has the primary process been established beyond question. The simple reaction of an activated ammonia molecule on collision with a normal one to yield nitrogen and hydrogen

$$NH_3' + NH_3 \longrightarrow N_2 + 3H_2$$

does not satisfactorily account for the low quantum yield at high pressures, nor the observation[3] that a rapid decomposition takes place at a pressure of 0.001 mm. of mercury. Photochemical decomposition should cease and fluorescence enter at this low pressure. The ultraviolet absorption bands of ammonia, also, do not show the fine structure ordinarily expected for cases where light absorption leads only to the activation of the molecule. Bates and Taylor[4] pointed out that a primary process of the type

$$NH_3' \longrightarrow N + H + H_2$$

proposed by Kuhn[5] is impossible if the recent values of the heats of dissociation of nitrogen and hydrogen molecules be accepted, and that his postulated secondary reactions are not consistent with several experimental facts.

From considerations involved in the facts that ammonia is decomposed by excited mercury atoms with an energy content of 112,000 calories and that the gaseous reaction products contain hydrogen in appreciable excess of the stoichiometric proportion $N_2{:}3H_2$, the above authors suggested that all molecules might undergo decomposition on light absorption, hydrazine formation being an intermediate stage. The proposed mechanism is

$$NH_3 + h\nu \longrightarrow NH_3' \qquad (1)$$

followed by either

$$NH_3' + NH_3 \longrightarrow N_2H_4 + H_2 \qquad (2)$$

or

$$NH_3' \longrightarrow NH_2 + H \qquad (3)$$
$$NH_2 + NH_3 \longrightarrow N_2H_4 + H \qquad (4)$$
$$NH_2 + H_2 \longrightarrow NH_3 + H \qquad (5)$$

This would then be followed by secondary photochemical hydrazine decomposition, presumably into nitrogen and hydrogen. Such a mechanism,

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[2] For summary of data see Kistiakowsky, "Photochemical Processes," The Chemical Catalog Company, Inc., New York, **1928**, pp. 251–254.

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

[4] Bates and Taylor, THIS JOURNAL, **49**, 2438 (1927).

[5] Kuhn, *Compt. rend.*, **177**, 956 (1923); **178**, 708 (1924); *J. chim. phys.*, **23**, 521 (1926).

although more satisfactory than those previously advanced, does not account for several observations of earlier investigators.[2]

Under the above assumptions hydrazine decomposition would determine materially the characteristics of the ammonia decomposition. It was hoped that an investigation of the photochemical decomposition of hydrazine might lead to a removal of some of the difficulties in the case of ammonia. Hydrazine, while more complex than ammonia, offers a case of a solely nitrogen-hydrogen compound. Its behavior might then lead to a better understanding of the action of radiation upon the nitrogen to hydrogen linkage and perhaps increase our knowledge of such reactions in general.

Hydrazine has been found to be decomposed by ultraviolet light and by excited mercury more readily than ammonia. The results obtained do not support its formation as an intermediate stage in the ammonia decomposition. They do, however, favor a mechanism of the general type as that suggested by Bates and Taylor.

Experimental Method

Apparatus.—Preliminary experiments were made with the flow apparatus and mercury arc described by Bates and Taylor.[4] The usual static system was employed throughout the remainder of the decomposition studies. This consisted of a quartz reaction chamber of about 150-cc. capacity joined by a quartz to pyrex seal and capillary tubing to a constant volume mercury manometer, oil pump and to a hydrazine reservoir through a three-way stopcock. The latter provided means for the admission of various other gases to the reaction chamber. A liquid-air trap in the vacuum line prevented contamination of the pump.

Temperature control was obtained by immersing the reaction vessel in a copper tank through which water was continuously flowing. The water was heated to any desired temperature by previous passage through electric heaters. In the sensitized experiments a large battery jar was substituted for the tank. In any case the temperature could be controlled to about one degree by proper variation of the temperature and rate of flow of the entering water. A stream of air gave efficient stirring.

The total radiation from a vertical Cooper-Hewitt mercury arc of the ordinary type provided the source of illumination. Light reached the reaction vessel through a quartz window in the copper tank. In the purely photochemical experiments the arc was run on 110 volts and 3.5 amperes, cooled only by an air blast. Its distance from the wall of the reaction vessel was about 2.0 cm. In the photosensitized experiments the arc was water cooled, being placed in the tank with the reaction vessel. It was run on 110 volts and 5.0 amperes, and its distance from the reaction vessel was varied from 0.5 cm. to 6 cm. For the sensitized study, which was made after the completion of the photochemical experiments, mercury vapor was supplied by about 0.5 cc. of mercury forced into the reaction vessel from the manometer.

In order to determine the relation of the reaction rate to the incident light intensity a metal frame containing a slit the width of the arc and half its length was soldered to the copper tank. The distance from slit to the quartz window was about 4 cm. Copper gauze screens of suitable dimensions and blackened by oxidation to cut down stray light served to vary the amount of light reaching the reaction vessel. These could be fixed rigidly in the metal frame between the slit and quartz window. Relative light intensities were measured with a Moll thermopile. A shutter controlled from the position of the galvanometer scale governed the admission of light to the vessel and to the thermopile. For these experiments the arc was placed in a water-bath separate from the reaction vessel and run at a constant temperature of 30° on 110 volts and 5.5 amperes. It was started by breaking down the space charge with a high tension coil so that its position was unchanged throughout the series.

The experiments on the thermal decomposition were carried out in the same system described above, the reaction vessel being surrounded by an electric furnace.

Preparation of Materials.—Hydrazine hydrate, $N_2H_4 \cdot H_2O$, was first prepared from Kahlbaum's C. P. hydrazine sulfate, $N_2H_4 \cdot H_2SO_4$.[6] A concentrated solution of the latter was mixed with the calculated amount of highly concentrated potassium hydroxide solution, an equal volume of alcohol added and the precipitated potassium sulfate removed. The mixture was then distilled up to 118° under ordinary pressure, decanted from a further precipitate of potassium sulfate and fractionated at 121–122 mm. pressure. An all-glass distillation apparatus was employed. The portions distilling between 73 and 74°, consisting of 85 to 97.5% of hydrazine hydrate, served for the preparation of anhydrous hydrazine.

The preparation of anhydrous hydrazine was carried out according to the method of Hale and Shetterly[7] with the modifications suggested by Welsh.[8] The all-glass apparatus described by the former authors was employed. The method consists, briefly, in dehydrating the hydrazine hydrate by refluxing for several hours with a large excess of barium monoxide and then distilling the hydrazine in an atmosphere of hydrogen at a pressure below 300 mm. of mercury. This method avoids action of the hydrazine on glass and has been shown to give a product containing 99.7% of hydrazine. A glass tube with a stopcock attached was sealed directly to the distillation apparatus and evacuated. The liquid hydrazine (b. p. 113.5°) was run into this from time to time during the distillation. It was then sealed off and fused to a second such reservoir attached to the reaction bulb. Contact with air was thus avoided. The hydrazine could then be freed from dissolved gases before use by isothermal distillation from the first container into the second. Dissolved ammonia was removed by evacuation at room temperature. The liquid hydrazine was preserved *in vacuo* during the entire research. A sample of its vapor burned over copper oxide gave a pressure of nitrogen closely approximating the theoretical to be expected from a 100% sample of hydrazine. This result, together with the amount of pressure increase upon total decomposition and analysis of the decomposition products, renders the presence of an appreciable amount of the hydrate in the hydrazine vapor employed improbable.

Electrolytic hydrogen and nitrogen from cylinders were used. Hydrogen was purified over hot platinized asbestos and phosphorus pentoxide, and nitrogen over hot copper turnings and phosphorus pentoxide. The ammonia gas employed was a carefully prepared sample stored in a cylinder over sodium.

Procedure.—Before each experiment the hydrazine container was carefully evacuated in case slight decomposition might have occurred by diffusion of the vapor up to the greased stopcock surface. The reaction system was flushed several times with the vapor. The reaction vessel was filled by allowing hydrazine to vaporize into it under its own vapor pressure at room temperature. The initial pressures thus obtained could be varied from about three to ten millimeters. The arc was then started and the reaction followed by noting the increase of pressure at suitable time intervals. An electric contact between a sealed-in tungsten wire and the mercury of the manometer

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[6] Gmelin-Kraut, "Handbuch der Anorganischen Chemie," **1925**, Vol. 1, p. 193.

[7] Hale and Shetterly, THIS JOURNAL, **33**, 1074 (1911).

[8] Welsh, *ibid.*, **37**, 499 (1915).

allowed a delicate adjustment to constant volume. The manometer scale was so arranged that readings could be made to about 0.3 of a millimeter with a fair degree of accuracy. Numerous checks were made on all experiments.

Analysis of Reaction Products.—This could be carried out in the reaction system by means of a small side tube, attached as closely as possible to the quartz bulb and sealed to an electrically heated copper oxide tube through a stopcock. The method of analysis was briefly as follows. Hydrazine remaining after an experiment was first removed by surrounding the side tube with a carbon dioxide–ether freezing mixture, and ammonia determined by replacing this with liquid air. The gases non-condensable in liquid air (H_2 and N_2) were admitted to the copper oxide and the hydrogen burned, the water formed being simultaneously frozen out. The decreases in pressure thus obtained give the amounts of the various gases present; nitrogen was determined by difference. It was necessary to remove any residual hydrazine before admitting the gases to the copper oxide since it was found to reduce this latter in the cold, giving nitrogen and water.

The above method for separating ammonia from hydrazine vapor was shown to give accurate results by analyses of known mixtures of the two. It cannot be employed when the pressure of ammonia gas exceeds approximately 30 mm., the vapor pressure of liquid ammonia at the temperature of a carbon dioxide–ether mixture (−79°).

As carried out, this method of analysis offers the disadvantage that five to six hours are required for its completion. This is due to the slow diffusion of the gases to the freezing zone and the copper oxide. If many analyses are to be made it is desirable to arrange a means of circulating the gases through the system.

Photochemical Decomposition

Course of the Reaction and Products.—Upon illumination with the total radiation from the mercury arc, gaseous hydrazine undergoes decomposition. As will be later discussed, hydrazine vapor shows a marked light absorption in the ultraviolet below about 2400 Å. It is evident, therefore, that it is the portion of the mercury radiation below this wave length which is effective.

As the decomposition progresses the pressure in the system increases to a value three times that of the initial hydrazine,[9] after which no further change occurs. This tripling of the pressure indicates that the final reaction products are nitrogen and hydrogen only, hydrazine decomposition being complete. Analysis of the gaseous products at the end of the reaction confirms this. One experiment gave 64% of hydrogen and 36% of nitrogen, a second, 65% of hydrogen and 35% of nitrogen. The theoretical is 66.7% of hydrogen and 33.3% of nitrogen.

Hydrazine, however, does not decompose directly into the elementary constituents, but into ammonia, nitrogen and hydrogen according to the stoichiometric equation

$$2N_2H_4 \longrightarrow 2NH_3 + N_2 + H_2 \qquad (1)$$

The ammonia subsequently decomposes photochemically into nitrogen and hydrogen

$$2NH_3 \longrightarrow N_2 + 3H_2 \qquad (2)$$

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[9] In several experiments slight overrunning of this three-fold value was obtained. This is undoubtedly to be attributed to traces of hydrazine condensed or adsorbed on the walls of the quartz vessel.

at a slower rate. These facts were ascertained by analysis of the gaseous products at various stages of the reaction. Ammonia was found present up to the end of the reaction. The ratio of ammonia to nitrogen and hydrogen decreased as the reaction proceeded. Table I gives the results of analyses made after varying amounts of decomposition. The initial pressures of hydrazine were constant to about 0.5 of a millimeter.

TABLE I

VARIATION OF COMPOSITION OF PRODUCTS WITH EXTENT OF DECOMPOSITION

Expt.	Press. of total prod., mm.	Press. of NH_3, mm.	Comp. of total products NH_3, %	H_2, %	N_2, %	Comp. non-condensed gases H_2, %	N_2, %
37	6.1	2.2	38	32	30	52	48
35	12.2	3.8	32	34	34	50	50(?)
38	13.4	4.2	31	39	30	56	44
36	16.2	5.1	31	38	31	55	45
39	24.1	1.8	8	55	37	60	40
28	26.5	<0.5	0	65	35	65	35
Theoretical for no decomp. of NH_3			50	25	25	50	50

As the table shows, the actual quantity of ammonia found in the products first increases and then decreases upon continued illumination. All ammonia finally disappears as the pressure attains a three-fold value.

On account of the fact that the rates of hydrazine and of ammonia decomposition are of the same relative order of magnitude, the two reactions could not be isolated in the photochemical experiments. The use of monochromatic light would not affect this since the two substances absorb in practically identical spectral regions. The maximum amount of ammonia obtained in any experiment corresponded to 77% of that to be expected from decomposition according to Equation 1. It will be seen later that a sharp separation was made in the sensitized experiments.

It is of interest to note that gaseous hydrogen azide (HN_3) is photochemically decomposed[10] by ultraviolet radiation from an aluminum spark. In this case, also, the products of the reaction are hydrogen, nitrogen and ammonia (ammonium azide). It is probable that the formation of ammonium azide, noticed on longer illumination, is the result of a secondary reaction between the ammonia produced and hydrogen azide

$$NH_3 + HN_3 \longrightarrow NH_4N_3$$

Rate of the Decomposition.—The photochemical decomposition of hydrazine is more rapid than that of ammonia. In Table II are given the data for a typical experiment. The rates in the last column are the average increases of pressure per minute taken over the intervals of time between manometer readings. It will be noticed that a definite change in rate occurs at a pressure approximately double that of the initial. The apparent constancy over successive periods is due to the method of averaging

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

and to the fact that pressure could not be read to less than several tenths of millimeter.

Table II

Data for a Typical Experiment

Initial $P_{N_2H_4}$ = 8.3 mm. Barometer 760.1 mm. Arc at 110 v. and 3.5 amps.

Time, min.	Press., mm.	Temp., °C.	Rate, ave. Δp/min.	Time, min.	Press., min.	Temp., °C.	Rate, ave. Δp/min.
0	8.3	24.1	0.2	77	20.3	25.0	.08
3	8.8	24.2	.2	98	21.9	25.0	
10	10.1	24.7	.2	125	22.3	25.6	.03
17	11.5	25.4	.2	150	23.6	25.2	
33	15.1	24.0	.2	190	24.2	25.1	.01
42	16.9	24.8	.2	230	24.5	24.3	
50	18.5	25.6	.07	295	24.6	24.1	
65	19.5	23.6	.07				

In Fig. 1 time of illumination is plotted against pressure increase for several representative experiments. Under the experimental conditions, doubling of the pressure generally occurred in thirty to forty minutes, tripling, in four to five hours. The initial hydrazine pressures varied from six to ten millimeters. The half-time values determined from the curves of Fig. 1 indicate the reaction to be unimolecular in character. The

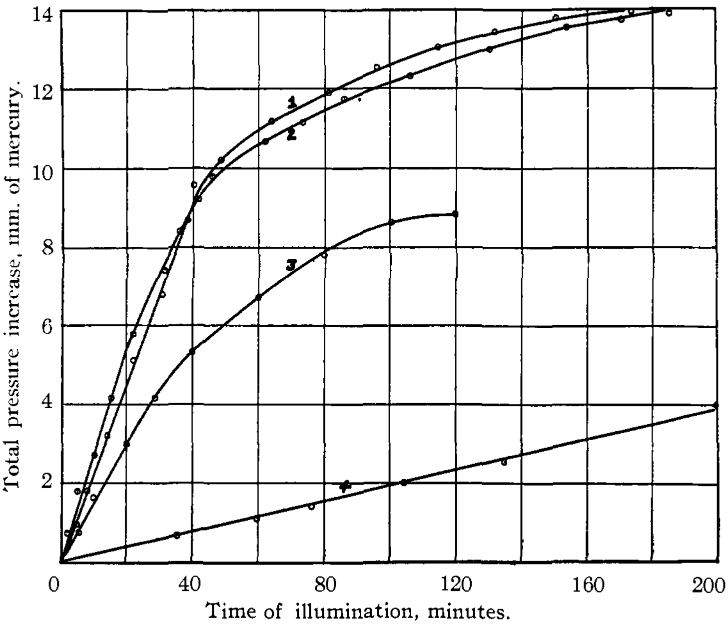

Fig. 1.—Rates of the photochemical decomposition. Curves 1, 2 and 3, hydrazine at initial pressures of 9.8 mm., 8.6 mm. and 4.3 mm., respectively. Curve 4, ammonia at an initial pressure of 14 mm.

apparent unimolecularity is without meaning, since the pressures obtained are the resultants of those given by two reactions. A unimolecular reaction order is also to be expected if the light absorption is not nearly complete. The amount of light absorbed then becomes directly proportional to the concentration of reactant. The first portions of the rate curves are predominantly hydrazine decomposition, the last portions predominantly ammonia. It was impossible with the present experimental arrangement to vary the initial hydrazine pressure sufficiently to determine its effect, but the rate is approximately directly proportional to it (see Figs. 1 and 2).

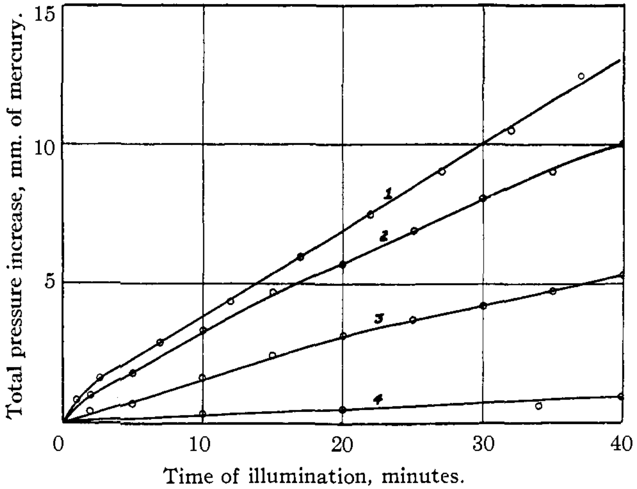

Fig. 2.—Rates of the photochemical decomposition for the first half of the total reaction. Curves 1, 2 and 3, hydrazine at initial pressures of 12.6 mm., 9.9 mm. and 4.3 mm., respectively. These curves represent practically entirely hydrazine decomposition. Curve 4, ammonia at initial pressure of 14 mm.

Temperature.—The rate of decomposition is independent of the temperature over the range studied, 15 to 45°. Experiments were made under practically identical conditions of illumination and hydrazine concentration, the only controllable variable being temperature. The increase in rate of ammonia decomposition in this temperature range is negligible.

Comparison of Hydrazine and Ammonia.—The rate of photochemical ammonia decomposition was investigated in the same system. The conditions of illumination and temperature were identical with those used in the hydrazine experiments. In Fig. 2 the rate curves for hydrazine, up to a doubling of the pressure, are plotted for experiments with conditions comparable to those where ammonia was studied. The ammonia curve is shown on Figs. 1 and 2. The curves given in Fig. 2 represent practically entirely hydrazine decomposition over the initial two-thirds, since ammonia decomposition is slow. Both hydrazine and ammonia curves may be taken as straight lines without appreciable error. A comparison of the slopes, where the pressures are comparable, shows that the hydrazine reaction proceeds at ten times the rate of the ammonia reaction. This result is probably correct within 10%.

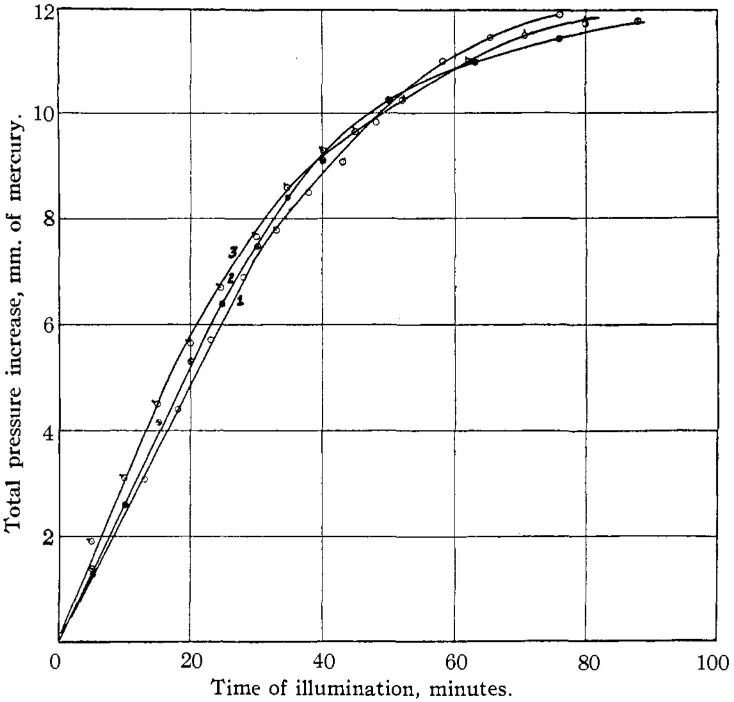

Fig. 3.— Effect of added gases on the rate of photochemical decomposition. Curve 1, hydrazine alone, initial pressure 8.9 mm. Curve 2, hydrazine with hydrogen present; pressure of hydrazine 8.6 mm., pressure of hydrogen, 8.0 mm. Curve 3, hydrazine with ammonia present; pressure of hydrazine 9.1 mm., pressure of ammonia 18.6 mm.

Effect of Added Gases.—Addition of nitrogen, hydrogen or ammonia to the hydrazine does not affect its rate of decomposition. Experiments were made in which these gases were added to hydrazine in concentrations up to twice its concentration. Fig. 3 contains rate curves for experiments with hydrazine alone and with ammonia and hydrogen present initially. The curves coincide within experimental error. Small variations from one experiment to another occurred with hydrazine alone. These may be attributed to small variations in the intensity of the arc and in initial hydrazine pressure. Ammonia decomposition is of course occurring simultaneously with that of hydrazine where ammonia is present, but the increase in rate due to this is negligible as compared with that of the latter.

Thermal Decomposition of Hydrazine

During the course of the photochemical experiments it was thought of interest to investigate the thermal decomposition of gaseous hydrazine since this could be accomplished readily in the same experimental system. It was found that in a quartz bulb hydrazine begins to decompose thermally at about 250°. The reaction products in this case were mainly ammonia and nitrogen in amount indicating decomposition according to the stoichiometric equation

$$3N_2H_4 \longrightarrow 4NH_3 + N_2 \qquad (3)$$

and not

$$2N_2H_4 \longrightarrow 2NH_3 + N_2 + H_2$$

as was found in the photochemical experiments. The compositions of the reaction products in two experiments were: (1) 71% of ammonia, 24% of nitrogen, 5% of hydrogen; and (2) 68% of ammonia, 26% of nitrogen and 6% of hydrogen; the theoretical on the basis of Equation 3 should be 80% of ammonia, 20% of nitrogen and no hydrogen. Consequently, a small amount of reaction takes place in such a manner as to yield hydrogen. Experiment showed no decomposition of ammonia in the quartz bulb in several hours at 500°. It may be noted that the pressure increase observed on total decomposition of a sample of hydrazine was approximately 5 to 3, which is that to be expected from Equation 3.

Since these results indicated a termolecular reaction order, Mr. Askey has carried out a kinetic investigation of the reaction in this Laboratory. His results[11] show that the thermal hydrazine decomposition is heterogeneous, taking place on the quartz surface, and is unimolecular in character. He has also found that on the surface of a heated platinum or tungsten wire the reaction occurs according to the same equation as photochemically.

Photosensitized Decomposition

When sensitized to light of 2537 Å. by mercury vapor, photochemical decomposition of hydrazine occurs. No decomposition takes place on standing in contact with mercury. The results of the sensitized studies are the most important obtained, since in this case the radiation is practically monochromatic, absorption undoubtedly complete and the concentration of the absorbing material unchanged as reaction proceeds. They enable us to formulate a mechanism for the reaction.

Reaction Products.—The decomposition of hydrazine by excited mercury atoms yields ammonia, nitrogen and hydrogen as products and takes place according to the stoichiometric equation

$$2N_2H_4 \longrightarrow 2NH_3 + N_2 + H_2$$

as does the purely photochemical reaction.

Several experiments were made with the flow system previously men-

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[11] Unpublished.

tioned.[4] Hydrazine vapor was passed through the arc, condensable products were removed with liquid air and the permanent gases analyzed. In one experiment these gave 47% of hydrogen and 53% of nitrogen; in a second, 48% of hydrogen and 52% of nitrogen. The theoretical for the above equation is 50% of hydrogen and 50% of nitrogen. The slight deficiency in hydrogen is undoubtedly to be ascribed to clean-up of atomic hydrogen on the walls.

When photosensitized by mercury vapor the rate of hydrazine decomposition so greatly exceeds that of ammonia that a nearly complete separation of the two reactions is possible. A very rapid increase in pressure ends when a doubling of the initial has been reached. This corresponds to complete hydrazine decomposition according to the above equation. Table III gives the results of analyses of the products made at this point.

TABLE III

COMPOSITION OF PRODUCTS FROM THE SENSITIZED REACTION

Expt.	Total products NH_3, %	 H_2, %	 N_2, %	Non-condensable gases H_2, %	 N_2, %
44	45	25	30	45	55
45	49	25	26	50	50
Calcd. for no NH_3 decomp.	50	25	25	50	50
Sensitized NH_3 decomposition				72	28

In another experiment where hydrogen was present initially 48% of ammonia was obtained. The quantity of ammonia found corresponds to 90 to 95% of the theoretical. The excess of nitrogen may be attributed to clean-up of hydrogen. Any error is magnified since nitrogen was obtained by difference. Dickinson and Mitchell[12] found 70% of hydrogen in the products of the sensitized decomposition of ammonia in a static system. Our value, 72%, checks this closely.

Rate of the Decomposition.—The decomposition of hydrazine is the most rapid reaction thus far obtained in this Laboratory with excited mercury. In Fig. 4 is plotted increase of pressure with time of illumination for several typical experiments. The temperature used was 30°. Increase of pressure proceeds rapidly to a point corresponding to a doubling of the initial and to complete hydrazine decomposition. As can be seen from the figure a very sharp break in the curves is evident at this point. Beyond, the pressure increases very slowly toward a three-fold value as decomposition of the ammonia formed proceeds. Ten millimeters of gaseous hydrazine are decomposed in less than three minutes with the arc at 5-mm. distance, in four minutes at 20 mm. and in twelve minutes at a distance of 60 mm. In later experiments the reaction rate was followed more readily by cutting down the light intensity with a blackened copper gauze screen.

Comparison of Hydrazine and Ammonia.—A curve for the rate of

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[12] Dickinson and Mitchell, *Proc. Nat. Acad. Sci.*, 12, 692 (1926).

ammonia decomposition under identical conditions of mercury vapor concentration and illumination with resonance radiation is given on the same figure. The large difference in the rates for hydrazine and ammonia is evident. The curves for hydrazine and for ammonia are linear within experimental error. Comparison of their slopes, $\Delta p/\Delta t$, shows that hydrazine is decomposed at a rate forty times that of ammonia.

The illumination in the purely photochemical and in the sensitized experiments was only roughly the same, as no effort was made to keep it identical. Several experiments with mercury sensitization were made with the arc at a distance of 2 cm., approximately that in the photochemical. The increased intensity of the 2537 Å. line due to water cooling of the arc would be without appreciable influence on the photochemical reaction since hydrazine does not absorb in this spectral region. We may obtain, therefore, a rough estimate of the ratio of the rate of sensitized to photochemical decomposition by comparison of the slope of the curve for these experiments with that of the photochemical. This gives a value for the rate of the sensitized reaction 110 to 120 times the photochemical rate. This value is probably somewhat high since the arc was burning on a slightly

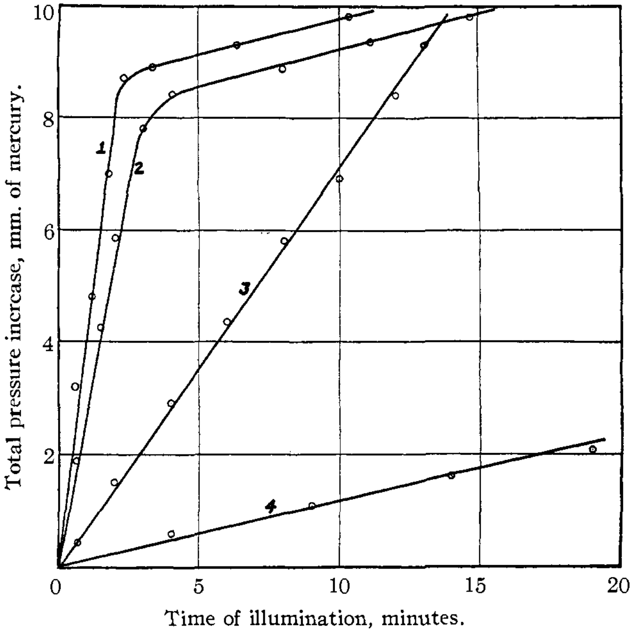

Fig. 4.—Rates of the photosensitized decomposition. Curves 1, 2 and 3, hydrazine; initial pressures 9.4 mm., 9.2 mm. and 10 mm., respectively; arc at distance of 0.5 cm., 2 cm. and 6 cm., respectively. Curve 4, ammonia, initial pressure 16 mm.; arc at distance of 0.5 cm.

higher wattage. From the preceding value we may also calculate that the ratio of sensitized to photochemical ammonia decomposition rate in these experiments is approximately 30 to 1.

Chain Mechanism and Quantum Efficiency.—In order to determine the quantum efficiency in the sensitized hydrazine decomposition, the mercury sensitized combination of hydrogen and oxygen was measured in

TABLE IV

COMPARISON OF RATES OF $H_2 + O_2$ REACTION AND N_2H_4 DECOMPOSITION

A. First Light Intensity

$2H_2 + O_2$			N_2H_4		
Time, min.	Press., mm.	Δp mm. per min.	Time, min.	Press., mm.	Δp mm. per min.
Expt. 58. Satd. gases			Expt. 42		
0	329.4	2.8	0	9.4	4.0
10	301.6	2.6	2.2	18.1	
20	275.4	3.2	Expt. 45		
30	243.8	3.1	0	9.3	4.0
50	180.0	3.2	0.5	11.3	4.5
60	148.1	3.2	1.3	14.9	3.6
70	115.8		1.8	16.7	
Av. Δp/min. = 3.0. Mm.			Av. Δp/min. = 4.0. Mm.		
H_2O[a] formed per min. = 2.0			N_2H_4 decomp. per min. = 4.0		
B. Second Light Intensity					
Expt. 62. Dry Gases			Expt. 61		
0	314.2	0.10	0	9.8	0.40
10	313.2	.11	3	11.0	.50
30	310.9	.14	6	12.5	.47
50	308.1	.11	13	15.8	.40
70	305.9	.13	18	17.8	
90	303.3		Av. Δp/min. = 0.45. Mm.		
Av. Δp/min. = 0.12. Mm.			N_2H_4 decomp. per min. = 0.45		
H_2O[b] formed per min. = 0.24					
Expt. 63. Saturated gases					
0	293.3	0.32			
10	290.1	.35			
20	286.6	.40			
30	282.6	.38			
40	278.8	.40			
50	274.8	.40			
60	270.8				
Av. Δp/min. = 0.37. Mm.					
H_2O formed per min. = 0.25					

[a] With liquid water initially present in the reaction vessel the pressure decrease is the sum of that due to the volume change in the reaction and that due to condensation of water vapor formed; the rate of water formation is, therefore, $^2/_3$ of the total pressure decrease.

[b] Where dry gases were used the rate of water formation is given by twice the pressure decrease. The pressure increase gives directly the rate of N_2H_4 decomposition.

the same system. Mercury vapor concentration and illumination with resonance radiation were identical. Experiments were made with two light intensities. The ratio of hydrogen to oxygen was 2 to 1. It has been shown[13] that the rate of this reaction is independent of total pressure. The results obtained in these experiments are recorded in Table IV.

From the preceding table it is evident that the sensitized decomposition of hydrazine has a rate at least twice that of the combination of hydrogen and oxygen. The latter reaction proceeds through hydrogen peroxide formation,[14] it being possible to obtain practically quantitative yields of this substance by use of a flowing system. In a static system the hydrogen peroxide subsequently undergoes decomposition, the final product being water vapor. Using a flowing method Marshall[14] was able to show that sensitized hydrogen peroxide formation is a chain reaction with chains of at least 4.6 to 6.6 molecules. Since hydrogen peroxide decomposition is represented by the equation

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

the rate of water formation in the present experiments represents the rate of hydrogen peroxide formation. It is apparent, therefore, that hydrazine decomposition is a chain reaction involving chains at least twice as long as those in the former.

Quantum Efficiency.—With the entire arc cooled with water, the condition in our experiment, a value of 3.3 members was found by Marshall for the chain length and of 6.6 molecules for the quantum efficiency. On the basis of the number of molecules disappearing as indicated by pressure change, a calculation of the quantum efficiency in hydrazine decomposition, from the data of Marshall and that of Table IV, gives a value of *13 molecules per absorbed quantum*. This figure may be regarded as a minimum value. Since collisions of excited mercury atoms with hydrogen molecules are known to be practically inelastic, the higher quantum efficiency for hydrazine cannot be due to difference in collision efficiency. It might very well be that collisions with hydrazine are much less efficient than with hydrogen, which would lead to longer reaction chains in the case of the former.

The rate of hydrazine decomposition was found to be forty times that for ammonia with excited mercury. A value of 13 molecules per quantum would, therefore, correspond to a quantum efficiency of 0.3 molecules for the sensitized ammonia decomposition. While not much confidence may be placed in this figure, it should be noted that Warburg[15] found the quantum yields for the photochemical decomposition to be 0.25 mol./$h\nu$ for light of wave length 2025–2140Å.

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[13] Taylor and Marshall, *J. Phys. Chem.*, **29**, 1140 (1925).

[14] Marshall, *ibid.*, **30**, 1078 (1926); Bates and Taylor, THIS JOURNAL, **49**, 2446 (1927).

[15] Warburg, *Sitzb. preuss. Akad. Wiss.*, 746 (1911); 216 (1902).

Effect of Added Gases on the Rate.—A number of experiments were made in which nitrogen, hydrogen or ammonia was added initially to the hydrazine and the decomposition rate determined. The results are best illustrated by the curves of Fig. 5 and Fig. 6. The hydrazine pressures were from 9 to 11 mm. and the other gases were added in amounts up to 200 mm. In the experiments shown in Fig. 6 the rates were considerably reduced by increasing the distance of the arc and partially screening it with a copper gauze.

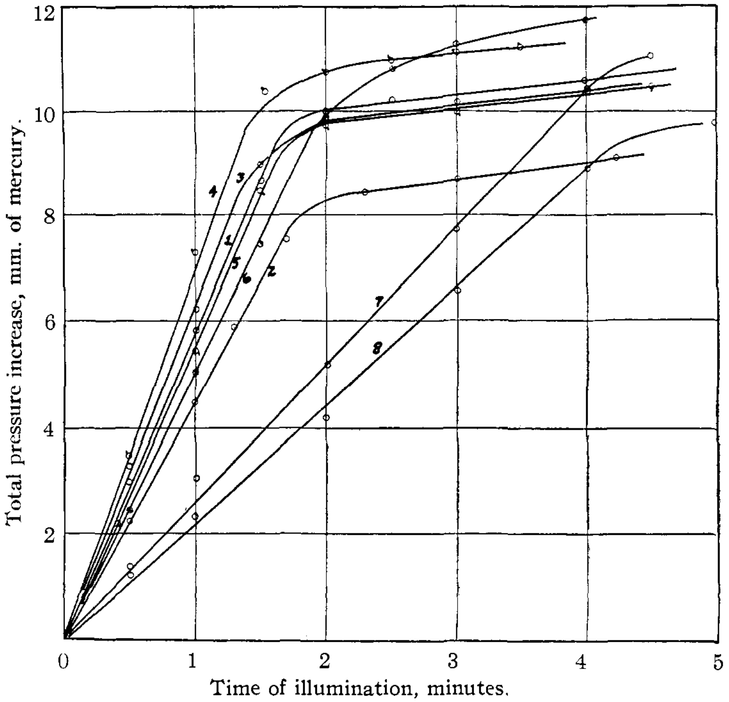

Fig. 5.—Effect of added gases on the rate of the photosensitized decomposition. Curves 1 and 2, hydrazine alone, pressures, 10.5 and 8.5 mm., respectively. Curve 3, hydrazine in presence of nitrogen, pressures, 10.0 and 200 mm., respectively. Curves 4 and 5, hydrazine with hydrogen present; pressure of hydrazine, 10.6 and 9.8 mm., respectively, pressures of hydrogen, 200 mm. and 25 mm., respectively. Curve 6, hydrazine with ammonia present; pressures, 10.8 and 175 mm., respectively. Curves 7 and 8, hydrazine with ammonia and hydrogen present; pressures of hydrazine approximately 10 mm., pressures of ammonia and hydrogen approximately 100 mm. each. Arc at a distance of 0.5 cm. for all these experiments.

Neither the presence of nitrogen, ammonia nor hydrogen exerts appreciable influence upon the rate of the sensitized decomposition. Slight variations in the slopes of the curves occur at random. They are undoubtedly to be attributed to experimental error in reading the time and pressure over small intervals and to slight variations in the arc intensity.

The failure of nitrogen or ammonia pressure to affect the rate is not surprising since their efficiency in quenching excited mercury is known to be very low.[16,17] The failure of hydrogen to affect the rate is, however, interesting. This result is in direct contrast to the sensitized ammonia decomposition which has been shown by Mitchell and Dickinson[17] to be strongly inhibited by small pressures of hydrogen. Practically every collision of excited mercury with hydrogen molecules results in its deactivation.[16] Hydrogen would, therefore, be expected to retard sensitized hydrazine decomposition. Indeed, with hydrogen pressures twenty times that of hydrazine, the retardation would be expected to be directly proportional to hydrogen pressure. The absence of any effect appears to be explicable only on the basis that the energy of those excited mercury atoms colliding with hydrogen molecules is still available for the decomposition of hydrazine.

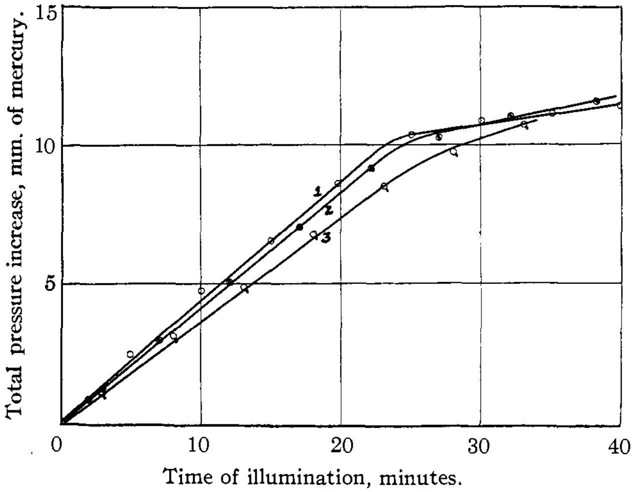

Fig. 6.—Effect of added gases on the rate of the photosensitized decomposition. Curve 1, hydrazine alone; pressure, 10.0 mm. Curve 2, hydrazine with hydrogen present; pressures, 10.0 mm. and 200 mm., respectively. Curve 3, hydrazine with ammonia and hydrogen present; pressures, 9.8 mm., 100 mm. and 100 mm., respectively. Arc at a distance of 6 cm. and screened in these experiments.

We may justifiably assume[18] that a collision of the second kind between

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[16] Stuart, *Z. Physik*, **32**, 262 (1925).

[17] Mitchell and Dickinson, THIS JOURNAL, **49**, 1478 (1927).

[18] See Taylor, *ibid.*, **48**, 2840 (1926), for a partial summary of evidence.

a mercury atom in the 2^3P_1 state and a hydrogen molecule results in the dissociation of the latter

$$Hg' + H_2 \longrightarrow Hg + 2H$$

Hydrogen atoms must, therefore, react with hydrazine. It is our intention to test this conclusion by introducing hydrogen atoms into hydrazine.

Curves 7 and 8 in Fig. 5 for experiments in which mixtures of 100 mm. each of hydrogen and ammonia were admixed with hydrazine show a retardation of the rate, an effect produced by neither gas alone. It cannot, apparently, be attributed to experimental error. We are unable to offer a satisfactory explanation for it.

Effect of Light Intensity.—The reaction rates were considerably reduced by decreasing the light intensity materially and the latter varied by means of the previously described copper gauze screens. Care was taken to prevent variations in the intensity of the 2537 Å. line caused by variations in the running temperature and wattage of the arc. The results are summarized in Table V. Hydrazine pressures were constant to a few per cent. The galvanometer deflections given represent the average of two separate sets of determinations, the average of ten distinct deflections being taken to determine the true deflection for each different intensity. The experiment with no screen intervening was repeated between each of the others as a check. The rates given are the averages for twenty-minute periods taken during the experiment almost to the point of pressure doubling.

TABLE V

EFFECT OF INCIDENT LIGHT INTENSITY ON THE REACTION RATE

	Rates		
	I No Screen	II Screen No. 1	III Screen Nos. 1 and 2
Average Δp per 20 min.	2.40	0.91	0.33
Average Δp per 20 min.	2.00	.90	.35
Average Δp per 20 min.	2.20		
Average	2.20 (k_1)	.905 (k_2)	.34 (k_3)
	Relative Light Intensities		
Average galv. deflection	73.39 (l_1)	30.06 (l_2)	12.34 (l_3)
Ratios of reaction rates	$k_1/k_2 = 2.43$		$k_2/k_3 = 2.65$
Ratios of intensities	$l_1/l_2 = 2.44$		$l_2/l_3 = 2.44$

The results show that the velocity of hydrazine decomposition sensitized with mercury vapor is directly proportional to the incident light intensity.

The Absorption Spectrum of Gaseous Hydrazine

The results of studies of molecular spectra have led to the elucidation of the primary photochemical process in several systems involving diatomic molecules. Franck[19] has pointed out that according to the quantum theory

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[19] Franck, *Trans. Faraday Soc.*, **21**, 536 (1925).

of light absorption the immediate result is the formation of an excited molecule, but that the excited molecule may then undergo spontaneous dissociation without the agency of collisions. This is the type of process occurring in the halogens, hydrogen halides and alkali halides. More complex molecules exhibit such complicated band spectra that detailed analysis has been impossible. It now appears quite certain that an entirely continuous molecular absorption spectrum corresponds to a primary dissociation of the molecules. One consisting of bands possessing a fine structure corresponds to a primary excitation of the molecule, which can then undergo dissociation only on collision, provided, of course, that the absorbed energy is comparable with that required for dissociation.

It was first pointed out by Henri[20] that certain molecules give a type of absorption spectrum consisting of diffuse or continuous bands. These bands are not resolvable into distinct lines even with very high dispersion and low pressures. According to Henri, such molecules as NH_3, H_2S, COS and CH_3NH_2 give this type of spectrum. His interpretation of this phenomenon is that the molecule upon light absorption goes into an electronically excited state, no longer quantized as to rotation, in which the molecule is strongly deformed in contrast to ordinary absorption processes. To such a state he gives the name "Predissociation." Bonhoeffer and Farkas[21] have discussed the ammonia spectrum in relation to predissociation, and have presented theoretical and experimental evidence for the assumption that the primary process is a separation of the ammonia molecule into parts, most probably NH_2 and H. They explain the diffuse bands upon the basis of such a process. Kronig[22] has apparently found justification for this idea from a theoretical viewpoint. From considerations based on wave mechanics he calculates that such a process is possible and also calculates the probability that it will occur. In the conclusion to their paper Bonhoeffer and Farkas state that according to the above idea the following cases of molecular decomposition processes must be distinguished. "First, the 'direct' or 'true photolytic processes' in which the molecule decomposes without the agency of outside collisions; secondly, the 'indirect,' in which the molecule is primarily excited and is then decomposed by collision with another molecule. The direct processes can be of various kinds. Either the molecule is primarily dissociated (I_2 in the continuum, HI), or the primarily excited molecule decomposes spontaneously without radiation (NH_3, predissociation spectrum)."

To obtain optical evidence for the primary process following light absorption by the hydrazine molecule we have investigated its absorption spectrum.

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[20] V. Henri, "Structure des Molécules," Librairie Scientifique J. Hermann, Paris, 1925.

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

[22] Kronig, *Z. Physik*, **50**, 347 (1928).

Experimental

The continuous ultraviolet spectrum from a hydrogen discharge tube served as a light source for the absorption study. The discharge tube was the water-cooled type first described by Bay and Steiner.[23] It was constructed before their later modifications were published. The tube was run on approximately 10,000 volts and a current of 0.35 to 0.4 ampere. Hydrogen pressures of 8–10 mm. were employed. A side reservoir was attached in such a manner that the addition of hydrogen was simplified. As operated the tube provided a very intense source of continuous ultraviolet light extending to a region somewhat below 2000 Å. One to two minutes were sufficient for an intense exposure with a very narrow slit and the spectrograph at a distance of half a meter. Exposures of five minutes were required at a meter distance. When desired the tube could be operated continuously for several hours. Its spectrum contained several emission lines on the continuous background in the visible and near ultraviolet. No attempt was made to identify or remove them as they were beyond the region in which hydrazine absorbs.

A Type E-2 Hilger quartz spectrograph giving an average dispersion of 6 Å. per millimeter between λ = 2492 Å. and λ = 2293 Å. and 5 Å. per millimeter from λ = 2276 Å. to λ = 2199 Å. was employed. The spectrum of the copper arc served for reference. The vapor from a sample of the hydrazine used in the photochemical experiments was employed, the absorption tube being refilled before each exposure. Absorption tubes 20 and 80 cm. in length and pressures from several tenths up to ten mm. were used.

Results

The spectrograms obtained show that gaseous hydrazine absorbs measurably in the ultraviolet below about 2490 Å. Absorption becomes appreciable below 2440 Å. The spectrum consists of a series of faint diffuse bands which appear to become wider and more diffuse toward shorter wave lengths. Apparently continuous absorption then sets in and becomes stronger toward the ultraviolet. With an absorbing thickness of 80 cm. and a pressure of 0.5 mm. the band absorption commences at about 2490 Å., continuous absorption beginning at about 2370 Å. It was not possible to produce absorption of longer wave lengths by increasing the pressure to 10 mm. With the absorbing thickness reduced to 20 cm. and at about 1 mm. pressure, faint indications of the bands are visible down to 2260 Å. Below, a region of apparently continuous absorption extends. Lowering of the pressure to a few tenths of a millimeter did not extend the beginning of the continuum further toward shorter wave lengths. On account of their faintness the bands are scarcely visible on a reproduction of the spectrograms.

There appear to be six or seven separate diffuse bands between 2490 and 2260 Å., separated by equal intervals of about 3 or 4 Å. Those from 2490 to 2370 Å. are more sharply defined. The bands range in width from 8 Å. to approximately 25 Å. toward the ultraviolet. The limits, however, cannot be indicated with precision. They appear to be absolutely continuous and resemble closely those obtained by Henri[20] with methylamine in the

[23] Bay and Steiner, *Z. Physik*, **45**, 337 (1927); *Z. Elektrochem.*, **34**, 660 (1928).

region from 2362 to 2288 Å. and the bands of ammonia, which occur from 2260 to 1600 Å.,[24] although separated by considerably smaller intervals than in these cases. Conclusive evidence as to whether the bands of the hydrazine absorption spectrum may be resolved into fine lines will have to be obtained with an instrument giving higher dispersion. This was not available during the performance of these experiments. It appears for the present, however, that in hydrazine we have also a case of "predissociation."

Discussion

Hydrazine Decomposition.—While the results of the purely photochemical study may be regarded as only qualitative, those obtained in the sensitized decomposition provide quantitative information from which a reaction mechanism may be obtained. The experimental observations for which a theory of the reaction mechanism must account are, briefly: (1) the nature of the products, (2) speed of reaction and chain mechanism and (3) the absence of retardation by hydrogen, which is most easily understandable on the basis that atomic hydrogen reacts with hydrazine.

For the primary process following reception of energy by the hydrazine molecule on a collision of the second kind with excited mercury or by absorption of a light quantum, we need consider only two possibilities. The formation of an activated hydrazine molecule may take place, reaction then occurring only on collision with a normal molecule. Alternatively, the primarily excited molecule may split directly into parts which then undergo reaction with normal molecules.

The mechanism based on the first possibility would be

$$N_2H_4 + Hg' \longrightarrow N_2H_4' + Hg$$
$$N_2H_4' + N_2H_4 \longrightarrow 2NH_3 + N_2 + H_2$$

This leads to a value of two molecules as the maximum possible quantum efficiency. It does not agree with the observed minimum quantum efficiency of 13 molecules or the chain mechanism, nor will it account satisfactorily for the failure of hydrogen to retard the rate.

Formulation of a mechanism based on the second possibility leads to more satisfactory results. Four possible ways in which the primarily excited molecule may split must be considered. These are

$$N_2H_4 + Hg' \longrightarrow N_2H_4' + Hg$$
$$\text{(a)}\quad N_2H_4' \longrightarrow N_2H_3 + H$$
$$\text{(b)}\quad N_2H_4' \longrightarrow 2NH_2$$
$$\text{(c)}\quad N_2H_4' \longrightarrow N_2H_2 + H_2$$
$$\text{(d)}\quad N_2H_4' \longrightarrow NH_3 + NH$$

On the basis of the most recently accepted value of 9.5 volts,[25] or 219,000 calories, for the heat of dissociation of the nitrogen molecule, breakage of

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[24] Leifson, *Astrophys. J.*, **63**, 73 (1926).

[25] Mulliken, *Phys. Review*, **32**, 761 (1928).

a N–H bond requires 90,000 calories of energy. The energy available from an excited mercury atom is 112,000 calories, so that (a) is possible from the standpoint of energetics. The heat of formation of anhydrous hydrazine has not been measured, nor are data for the energy of an N–N bond in such a case available. It is, therefore, impossible to calculate with certainty whether the quantum of absorbed energy is sufficient for the other three processes. Some idea as to the energy required may be obtained in the following manner. The reaction $N_2 + 2H_2 + aq \longrightarrow N_2H_4$ (dissolved) is endothermic by 9500 calories.[26] In solution hydrazine exists as the hydrate. There is justification for the belief that the heats of solution and of hydration are positive, which leads to the conclusion that the formation of anhydrous hydrazine from the elements is endothermic by an amount greater than, say, 10,000 calories. If we take this value for the heat of formation of hydrazine, 90,000 calories as the heat of formation of an N–H bond and values of 101,000 calories for the heat of dissociation of hydrogen and 219,000 calories for that of nitrogen, we may calculate that Process (b) requires 49,000 calories and (d) 49,000 calories. On the assumption that the energy required is that for breaking two N–H bonds independently, minus the heat of combination of two hydrogen atoms, we obtain for Process (c) a value of 80,000 calories. All four types would then be possible with the quantum of 112,000 calories. It is uncertain as to how much confidence may be placed in the results of such calculations.

The sequence of secondary reactions which must follow in case (c)

$$N_2H_2 + N_2H_4 \longrightarrow 2NH_3 + N_2$$

and in case (d)

$$NH + N_2H_4 \longrightarrow NH_3 + N_2 + H_2$$

while accounting for the products, eliminate these as possible mechanisms. They will not account for the observed chain mechanism or for non-retardation by hydrogen. It has been found[27] that hydrazine is formed when ammonia is passed through a cooled high tension arc. The authors state that the most probable explanation lies in a decomposition of the ammonia into NH and H_2 by electron impact, and formation of hydrazine by the reaction

$$NH + NH_3 \longrightarrow N_2H_4$$

In this case ammonia should retard the rate if the mechanism were according to (d). This is contrary to experimental fact.

Assumption of either (a) or (b) as the primary process leads to a mechanism better in accord with our experimental observations. Thus

$$N_2H_4 + Hg' \longrightarrow N_2H_4' + Hg \longrightarrow N_2H_3 + H + Hg \qquad (1)$$
$$N_2H_3 + N_2H_4 \longrightarrow 2NH_3 + N_2 + H \qquad (2)$$
$$H + N_2H_4 \longrightarrow N_2H_3 + H_2 \qquad (3)$$

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[26] Berthelot and Matignon, *Compt. rend.*, **113**, 672 (1891).

[27] G. Bredig and A. Koenig, *Naturwissenschaften*, **24**, 493 (1928).

Reactions such as

$$\left.\begin{array}{r} \mathrm{H} + \mathrm{H} \longrightarrow \mathrm{H_2} \\ \mathrm{N_2H_3} + \mathrm{H} \longrightarrow \mathrm{N_2H_4} \end{array}\right\} \text{wall reaction} \qquad \begin{array}{r}(4)\\(5)\end{array}$$

woud lead to breaking of the reaction chains. With (b) the mechanism would be

$$\begin{array}{rr} \mathrm{N_2H_4} + \mathrm{Hg}' \longrightarrow \mathrm{N_2H_4}' + \mathrm{Hg} \longrightarrow 2\mathrm{NH_2} + \mathrm{Hg} & (1) \\ \mathrm{NH_2} + \mathrm{N_2H_4} \longrightarrow \mathrm{NH_3} + \mathrm{N_2} + \mathrm{H_2} + \mathrm{H} & (2) \\ \mathrm{H} + \mathrm{N_2H_4} \longrightarrow \mathrm{NH_2} + \mathrm{NH_3} & (3) \end{array}$$

The reactions

$$\left.\begin{array}{r} \mathrm{H} + \mathrm{H} \longrightarrow \mathrm{H_2} \\ \mathrm{NH_2} + \mathrm{NH_2} \longrightarrow \mathrm{N_2H_4} \end{array}\right\} \text{wall reaction} \qquad \begin{array}{r}(4)\\(5)\end{array}$$

break the reaction chains. The reaction, $\mathrm{NH_2} + \mathrm{H_2} \longrightarrow \mathrm{NH_3} + \mathrm{H}$, which may be suggested, is endothermic by about 11,000 cal. and probably does not play a material role at room temperatures. Either of the above mechanisms satisfactorily accounts for the observed facts.

Either of the above mechanisms, on the assumption that reactions such as (4) and (5) limit the reaction chains, requires a proportionality of the reaction rate to incident light intensity involving the square root of the latter.[28] In the present instance the rate is directly proportional to the incident intensity. This is reconciled with the postulated mechanisms if we assume that Reactions 4 and 5 take place on the walls of the containing vessel, the rate of disappearance then being unimolecular with respect to the concentrations. It is probable that such reactions never take place except on the walls of the containing vessel. Similar disagreement exists for other photochemical reactions and is thus explained.

The evidence at present available offers no basis upon which to decide which of the preceding mechanisms is the more probable. It may be of interest to record the thermal values for the various secondary reactions given, calculated from the previously assumed thermal date.

$$\begin{array}{r} \mathrm{H} + \mathrm{N_2H_4} \longrightarrow \mathrm{N_2H_3} + \mathrm{H} + 11{,}000\text{ cal.} \\ \mathrm{H} + \mathrm{N_2H_4} \longrightarrow \mathrm{NH_2} + \mathrm{NH_3} + 40{,}000\text{ cal.} \\ \mathrm{N_2H_3} + \mathrm{N_2H_4} \longrightarrow 2\mathrm{NH_3} + \mathrm{N_2} + \mathrm{H} + 28{,}000\text{ cal.} \\ \mathrm{NH_2} + \mathrm{N_2H_4} \longrightarrow \mathrm{NH_3} + \mathrm{N_2} + \mathrm{H_2} + \mathrm{H} - 1000\text{ cal.} \end{array}$$

While the mechanisms formulated are based on the results of the investigation of the sensitized decomposition, there is no reason to believe that the purely photochemical decomposition proceeds by another mechanism.

The spectral evidence offered by the hydrazine absorption spectrum is not entirely conclusive. It is, however, in accord with our suggested mechanism if we accept the Bonhoeffer and Farkas conclusion[21] concerning the process giving rise to a spectrum consisting of continuous bands. Indeed, we may state that if it can be conclusively shown that the hydra-

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[28] Kistiakowsky, "Photochemical Processes," The Chemical Catalog Company, Inc., New York, **1928**, p. 96.

zine bands do not possess a fine structure our results provide strong evidence in support of this idea concerning the Henri "predissociation spectra." A study of the photochemical decomposition of methylamine, which has been definitely shown by Henri to possess a spectrum of this type, should prove of interest in this connection. Such a study is to be undertaken.

This investigation was carried out during the tenure, by one of us (J.C.E.), of a du Pont Fellowship at Princeton University. We take this opportunity of expressing to the E. I. du Pont de Nemours Company of Wilmington, Delaware, our sincere appreciation of this assistance.

Summary

Gaseous hydrazine is decomposed photochemically by the ultraviolet radiation from a quartz mercury arc. A more rapid decomposition is brought about by optically excited mercury atoms. The products of the reaction in both cases are ammonia, nitrogen and hydrogen in amounts indicating a reaction according to the stoichiometric equation $2N_2H_4 \longrightarrow 2NH_3 + N_2 + H_2$. Decomposition of the ammonia formed follows this reaction.

The products from the thermal decomposition in a quartz bulb indicate reaction mainly according to the equation $3N_2H_4 \longrightarrow 4NH_3 + N_2$. The reaction is heterogeneous and unimolecular in character.

The rate of the purely photochemical decomposition is uninfluenced by temperature or by the presence of large concentrations of ammonia or hydrogen. The photochemical decomposition of ammonia proceeds at a rate one-tenth that of hydrazine under the same conditions.

The sensitized hydrazine decomposition is a very rapid reaction. Its rate is forty times that of ammonia under identical conditions. Hydrazine decomposition is a chain reaction. A minimum quantum efficiency of 13 molecules per absorbed quantum has been found for it. The rate of the sensitized reaction is unaffected by the presence of nitrogen, ammonia or hydrogen in large concentrations. The lack of retardation by hydrogen is explained on the basis that hydrogen atoms react with hydrazine. The rate of the sensitized decomposition is directly proportional to the incident light intensity.

The absorption spectrum of gaseous hydrazine has been investigated. Hydrazine vapor absorbs appreciably in the ultraviolet below 2440 Å. The spectrum consists of a series of faint, apparently continuous bands, followed by a region of continuous absorption. The limits of the regions of absorption depend upon the density of the absorbing layer. With the dispersion employed it cannot be stated conclusively that the absorption bands do not possess a fine structure. It appears for the present that hydrazine presents a case of "predissociation."

The results obtained are satisfactorily explained by a reaction mechanism based upon a dissociation of the primarily excited molecule as a primary process and not one involving an activated molecule. Agreement is obtained if the dissociation is either into N_2H_3 and H or $2NH_2$. Thermal calculations for the various primary and secondary processes discussed are given. The nature of the absorption spectrum is in accord with such a mechanism if the idea of Bonhoeffer and Farkas be accepted.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE SOLUBILITY OF CALCIUM CARBONATE (CALCITE) IN CERTAIN AQUEOUS SOLUTIONS AT 25°[1]

BY G. L. FREAR[2] AND JOHN JOHNSTON

RECEIVED MARCH 20, 1929 PUBLISHED JULY 5, 1929

The solubility of calcium carbonate in aqueous solutions, as influenced by the partial pressure of carbon dioxide in the system and by the presence of other salts, is of interest because of its significance in relation to the problem of scale formation in steam boilers and pipes, to the study of bone calcification and of blood equilibria in physiological systems, and to a better understanding of the process of deposition of carbonates under geological conditions. The work to be presented comprises precise determinations of the solubility of calcite at 25° in the presence of carbon dioxide at pressures varying from 0.0003 to 1.0 atmosphere, in water and in a series of solutions of sodium chloride and of calcium sulfate, including solutions saturated also with respect to gypsum ($CaSO_4 \cdot 2H_2O$).

The papers on the solubility of calcium carbonate in water, prior to 1915, have been reviewed in an earlier paper;[3] since that time a number of other contributions have been published.[4] A plot of all of the data,

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[1] From the dissertation presented by G. L. Frear to the Graduate School of Yale University, June, 1926, in candidacy for the degree of Doctor of Philosophy.

[2] Loomis Fellow, 1925–1926; Sterling Fellow, 1926–1927.

[3] Johnston, THIS JOURNAL, **37**, 2001 (1915).

[4] (a) Cavazzi, *Gazz. chim. ital.*, II **46**, 122 (1916); solubility of $CaCO_3$ in water at 0–15° and 1 atm. of CO_2; (b) Bäckström, *Z. physik. Chem.*, **97**, 179 (1921), solubility of calcite and aragonite at 9, 25 and 35° and approximately 1 atm. of CO_2; see also Bäckström, THIS JOURNAL, **47**, 2432, 2443 (1925); (c) Mitchell, *J. Chem. Soc.*, **123**, 1887 (1923), solubility of calcite, and of calcite with nesquehonite ($MgCO_3 \cdot 3H_2O$), at 25° and 4–24 atm. of CO_2; (d) Haehnel, *J. prakt. Chem.*, **107**, 165 (1924), solubility of $CaCO_3$ in water at 18° and 10–56 atm. of CO_2, and up to 50° at 56 atm.; (e) Hastings, Murray and Sendroy, *J. Biol. Chem.*, **71**, 723 (1927), solubility of $CaCO_3$ at 38° in some solutions of NaCl and in serum; (f) with respect to the three crystal forms of $CaCO_3$, see Johnston, Merwin and Williamson, *Am. J. Sci.*, **41**, 473 (1916); Gibson, Wyckoff and Merwin, *Am. J. Sci.*, **10**, 325 (1925); (g) W. D. Kline, "Dissertation," Yale University, 1923.