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THE PRODUCTS OF THE PHOTOCHEMICAL DECOMPOSITION OF HYDROGEN AZIDE

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Introduction

Since the first preparation of hydrogen azide by Curtius[1] in 1890, this substance and its salts have been the subject of many investigations. The anhydrous material[2] is a moderately volatile (b. p. 37°), colorless liquid. Although the anhydrous liquid is violently explosive, the vapor may be handled at somewhat reduced pressure without difficulty. Since the gas is colorless, visible radiation may be anticipated to be without photochemical effect. However, we have found the gas to be decomposed by ultraviolet radiation of a sufficiently short wave length; the present paper is concerned chiefly with an examination of the products of this decomposition.

We are indebted to Dr. Don M. Yost for his interest in this work. Financial assistance has been received from a grant made to Professor A. A. Noyes by the Carnegie Institution of Washington.

Preparation of Hydrogen Azide

Sodium azide, NaN_3, was purified by acidifying and distilling an aqueous solution of the salt. The aqueous distillate was just neutralized with carbonate free sodium hydroxide and evaporated to dryness.

Gaseous HN_3 was obtained[3] by dropping sulfuric acid (2 vols. concd. H_2SO_4, 1 vol. H_2O) on solid NaN_3. The HN_3 evolved was swept by a current of air (previously passed through a liquid air trap) through a long calcium chloride tube into a trap immersed in liquid air. 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 HN_3 to volatilize into the storage bulb; the HN_3 pressure was about 13 cm. of mercury.

Apparatus and Procedure

A diagram of the apparatus is shown in Fig. 1. The HN_3 was stored in the flask, A. With the aid of two stopcocks, B, small amounts of HN_3 were admitted to the vacuum system; the mercury cut-offs C and D were kept closed when this occurred. The HN_3 was frozen out by applying liquid air at E, and traces of non-condensable gas pumped off. Then with the cut-offs and the McLeod gage closed, the liquid air was removed from E and the gas illuminated in the quartz tube, F, which was joined to the glass apparatus through a graded seal.

The source of radiation was a condensed, high frequency spark between aluminum electrodes, located about 30 cm. from the tube, F. The electrical energy was supplied through a step-up transformer, the primary current being 50–100 amperes[4] at 220 volts.

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[1] Curtius, *Ber.*, **23**; 3023 (1890).

[2] Curtius and Radenhausen, *J. prakt. Chem.*, **43**, 207 (1891).

[3] Dennis and Isham, THIS JOURNAL, **29**, 216 (1907).

[4] Such an intense source was not essential to the present experiments but was used because it was at hand for other purposes.

50 cycles per second. The secondary voltage was 13,000 volts. A 0.1 mf. condenser was shunted across the spark. The spark was blown out by a blast of air.

At the close of the illumination, liquid air was applied at E or G. The cut-off D was opened and readings were made with the McLeod gage and quartz fiber gage,[5] H. This gage was of the bifilar type[6] and was arranged with the magnetic starting device already described by one of us.[7] Liquid air was maintained at the U-tube, J, throughout the experiment. In some cases the condensable constituents were frozen out in one of the bulbs, G, which was then sealed off for analysis.

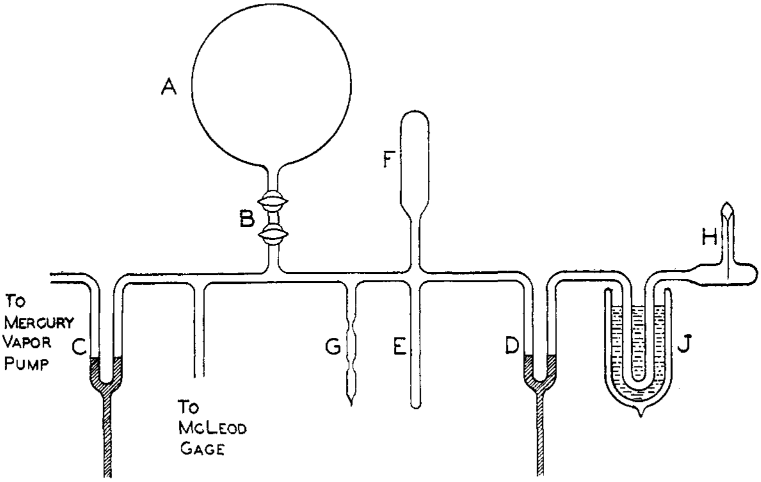

Fig. 1.

Qualitative Observations

It was found that brief illumination of gaseous HN_3 produced a gas non-condensable in liquid air. Somewhat longer illuminations, especially at higher HN_3 pressures (about 5 cm.), produced a white solid on the inside wall of the reaction bulb nearest the spark.

These effects were absent when the radiation was filtered through 5 mm. of 66% acetic acid in a quartz container. The acetic acid removed[8] radiation of wave lengths shorter than 2400 Å. Photographs of the absorption of gaseous HN_3 made with a quartz spectrograph showed that appreciable absorption set in at about 2200 Å. and increased toward shorter wave lengths. Accordingly, short wave length radiation was clearly necessary for the photochemical effects; the important radiation was probably the strong lines at 1854, 1862, 1935 and 1990 Å.

The white solid was volatile, subliming to a cooler portion of the tube when the tube was slightly warmed with a flame; when the tube was

[5] Haber and Kerschbaum, *Z. Elektrochem.*, **20**, 296 (1914).

[6] Coolidge, This Journal, **45**, 1637 (1923).

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

[8] Henri, "Études de Photochimie," Paris, Gauthier-Villars, **1919**, p. 90.

evacuated the solid quickly disappeared. In one experiment, after some of the solid had been formed, the quartz tube, F, was cut off from the apparatus and a little of the solid removed for examination. The polarizing microscope showed the solid to be composed of small optically anisotropic crystals. The remaining solid quickly dissolved in a small amount of water added to the tube. The solution gave with Nessler's reagent the heavy, yellowish-brown precipitate characteristic of ammonia. Another portion of the solution was added to ammoniacal silver nitrate; there was no trace of a mirror or a coloration on heating, showing the absence of hydrazine or other strong reducing agent.

These properties and tests showed that the white solid was ammonium azide, NH_4N_3. Analyses of the non-condensable gas were made with the aid of the quartz fiber gage.

Quantitative Observations

It is well known that at sufficiently low pressures the quartz fiber gage can be used to measure the value of $\Sigma(p\sqrt{M})$, the sum of the products of the partial pressures of the separate components of the gas into the square roots of their molecular weights. Indeed, if τ is the time required for the amplitude of the vibrations to decrease by some definite fraction of its value,[5]

$$\frac{1}{\tau} = a\,\Sigma(p\sqrt{M}) + b \tag{1}$$

where a and b are apparatus constants.

Since, in the present case, the non-condensable gas can contain only nitrogen and hydrogen, we may write

$$\Sigma(p\sqrt{M}) = x(\Sigma p)\,\sqrt{M_{H_2}} + (1 - x)\,(\Sigma p)\,\sqrt{M_{N_2}} \tag{2}$$

where x is the mole fraction of hydrogen and M_{H_2} and M_{N_2} are the molecular weights of hydrogen and nitrogen, respectively. Solution of this equation for x gives[9]

$$x = \frac{\sqrt{M_{N_2}} - \dfrac{\Sigma(p\sqrt{M})}{\Sigma p}}{\sqrt{M_{N_2}} - \sqrt{M_{H_2}}}$$

Measurement of $\Sigma(p\sqrt{M})$ with the fiber gage, and of Σp with the McLeod gage then permits the calculation of x.

The gage was calibrated with air, nitrogen and hydrogen. The calibration plot of $1/\tau$ *vs.* $\Sigma(p\sqrt{M})$ was a straight line at pressures below 2×10^{-2} mm. When the products had higher pressures, a portion was confined (for example in the McLeod gage) and was expanded after the remainder had been pumped off. The gage was tested as an analytical instrument by making measurements of the mole fraction of hydrogen in

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[9] Dickinson and Mitchell, *Proc. Nat. Acad.*, **12**, 694 (1926).

hydrogen–nitrogen mixtures made up to a known composition. The results of these tests are given in Table I.

TABLE I

ANALYSIS OF KNOWN MIXTURES OF HYDROGEN AND NITROGEN

Σp, mm.	$\Sigma(p\sqrt{M})$	x_{H_2}, by analysis	x_{H_2}, by synthesis	Δ
0.935×10^{-2}	4.60×10^{-2}	0.098	0.093	+0.005
.987	4.69	.139	.142	− .003
.625	2.82	.219	.218	+ .001
1.371	3.30	.746	.760	− .014

Analyses of the non-condensable gas resulting from illumination of HN_3 showed 10 to 15 mole per cent. of H_2. There are several possible ways in which H_2 and N_2 as well as NH_4N_3 might result: (1) decomposition of HN_3 into NH_4N_3 and N_2, and subsequent decomposition of NH_4N_3 (or NH_3) into N_2 and H_2; (2) decomposition of HN_3, giving simultaneously NH_4N_3, N_2 and H_2; (3) decomposition of HN_3 into N_2 and H_2 and subsequent formation of NH_3 (as, for example, by $H_2 + HN_3$ (activated) $= NH_3 + N_2$). Experiments in which sufficiently little decomposition is allowed to take place should in case (1) lead to $x_{H_2} \cong 0$, in case (3) to $x_{H_2} \cong 0.25$ and to intermediate values in case (2).

A series of exposures was made in which the time of illumination and the pressure of HN_3 were chosen to give amounts of products covering a wide range. The results are given in Table II.

TABLE II

DEPENDENCE OF COMPOSITION OF PRODUCTS ON EXTENT OF DECOMPOSITION

p_{HN_3}, mm.	Time, sec.	$p_{H_2+N_2}$, mm.	x_{H_2}
1.5	25	3.21×10^{-2}	0.091
12	7	5.37	.098
12	10	6.42	.091
29	56	32.1	.112
16	90	54.6	.147
7.5	240	62.0	.136
18	90	64.9	.153

Although the amount of non-condensable products was varied 20-fold, there appears to be no tendency for x_{H_2} to approach either 0 or 0.25 at zero decomposition. It is concluded, therefore, that the formation of N_2 and H_2 and of NH_4N_3 occurs simultaneously (case (2)). Since the mole fraction of H_2 is increased somewhat by prolongation of exposure, it appears that subsequent decomposition of NH_4N_3 or NH_3 occurs. NH_3 is known[10] to be photochemically decomposed by radiations of the wave lengths 2025–2139 Å.

Since, in the decomposition products, the total number of gram atoms of nitrogen must be three times the total number of gram atoms of hy-

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[10] Warburg, *Sitzb. preuss. Akad. Wiss.*, **1912**, p. 216.

drogen, the amount of ammonia in the products can be predicted from the amounts of nitrogen and hydrogen if no other products are formed. The number of moles of ammonia expected to be finally present can be easily shown to be given by

$$N_{NH_3} = \frac{pv}{4\,RT}(1 - 4x_{H_2})$$

where p, v and T are the total pressure, volume and temperature of the nitrogen–hydrogen mixture. A determination of the amount of ammonia formed was made at the end of each of three illuminations. For this purpose the liquid air was applied, not at E but at the end of the chain of bulbs, G, the last of which was then sealed off. This bulb was dipped in liquid air and its tip then broken under ammonia free water, the water rushing in and filling the bulb. By then breaking the tip at the other end of the bulb, the contents were transferred to a 2cc. colorimeter tube containing 1 cc. of Nessler's reagent. The same amount of Nessler's reagent was added to each of two other colorimeter tubes and these were made up with measured amounts of 0.000474 *M* NH_4Cl solution to colors which approximated and bracketed the color of the unknown. The results are given in Table III.

TABLE III

COMPARISON OF AMOUNTS OF NH_3 EXPECTED AND FOUND

$p_{H_2} + p_{N_2}$ (mm. Hg)	v, cc.	x_{H_2}	NH_4Cl soln., cc.	N_{NH_3} calcd. micromoles	N_{NH_3} found, micromoles
0.0617	476.5	0.1122	0.511	0.219	0.242
.1054	478	.1532	.666	.317	.315
.1214	480	.1365	.740	.358	.351

The number of moles of NH_3 calculated from the composition of the non-condensable gas and the number found by colorimetric analysis agree well within the error of the latter determination; hence it appears unlikely that any products other than H_2, N_2 and NH_3 are formed in considerable amount. The mole fraction of hydrogen, 0.09, in the non-condensable gas initially produced (Table II) corresponds stoichiometrically to 73% decomposition of the HN_3 into NH_3 and N_2 and 27% into H_2 and N_2.

The Molecular Weight of Hydrogen Azide

In the literature, the conclusion that hydrogen azide vapor consists of unassociated HN_3 molecules appears to be based upon a single vapor density determination by the Victor Meyer method at the boiling point of chloroform.[3] In extension of this result, we have made several molecular weight determinations by means of the quartz fiber[11] and McLeod gages.

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[11] A new fiber gage was used in these measurements. It differed from the first only in having a *single* flat fiber 4 cm. long and was found entirely satisfactory. A single fiber with elliptical cross section has been used by Coehn and Jung, *Z. physik. Chem.*, **110**, 709 (1924).

The hydrogen azide was admitted in the usual manner. It was then pumped down to a pressure of about 0.02 mm. The trap, J, was packed in ice and readings of the two gages were made. From the value $\Sigma(p\sqrt{M})$ obtained from the fiber gage was subtracted 0.0030 mm. corresponding to the $p\sqrt{M}$ of the mercury vapor present. The remainder, divided by the pressure, as read on the McLeod gage, gave $\sqrt{M}$. The results are given in Table IV.

TABLE IV

MOLECULAR WEIGHT OF GASEOUS HN_3

p (mm. × 10^2) (McLeod)	$\Sigma(p\sqrt{M}) \times 10^2$ (Quartz fiber)	M	Dev. from av.
2.26	15.46	44.9	1.3
2.00	12.90	39.7	3.9
1.47	9.96	43.3	0.3
1.24	8.75	46.5	2.9
		Av. 43.6	2.1

Summary

Gaseous hydrogen azide has been found to be decomposed by ultraviolet radiation from an aluminum spark, giving hydrogen, nitrogen and ammonia (ammonium azide). These products are formed by concurrent reactions; on brief illumination 27% of the decomposition gives H_2 and N_2 and 73% gives NH_3 and N_2.

By means of the quartz fiber and McLeod gages, the molecular weight of hydrogen azide has been determined as 43.6 ± 2.1.

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THE SPECIFIC HEATS AT LOW TEMPERATURES OF MANGANOUS OXIDE, MANGANOUS–MANGANIC OXIDE AND MANGANESE DIOXIDE[1]

BY RUSSELL W. MILLAR[2]

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The present article is one of a series from this Laboratory dealing with the thermodynamic properties of the oxides of metals which are important in metallurgical processes. Preceding articles have dealt with zinc oxide,[3] but it is now proposed to extend the investigations to many other oxides, as well as to several sulfides.

The specific heats of the oxides of manganese so far determined have been confined, with the exception of those of Russell[4] at low temperatures,

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[2] Associate Chemist, Pacific Experiment Station, Bureau of Mines.

[3] (a) Maier, THIS JOURNAL, **48**, 356 (1926); (b) Maier and Ralston, *ibid.*, **48**, 364 (1926); (c) Maier, Parks and Anderson, *ibid.*, **48**, 2564 (1926).

[4] Russell, *Physik. Z.*, **13**, 59 (1912).