There are insufficient data to draw many conclusions about the reaction at 160°. The strong dependence of the quantum yields on absorbed intensity shows that there must be a chain reaction. There is also a chain reaction at the same temperature at 2700 Å. which shows a similar dependence on absorbed intensity. The ethylene yield increases at 3650 Å. with decreasing intensity whereas it is constant at 2700 Å. This result would mean that ethylene is formed in the chain reaction at 3650 Å. and in a chain stopping reaction at 2700 Å. However, this conclusion cannot be verified at present.

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The Imine Radical[1]

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We have made an over-all weight balance of the decomposition that occurs when hydrazoic acid is passed through a quartz furnace at about 1000° and 0.1 mm. pressure and the products brought in contact with a cold finger placed 1 to 2 cm. beyond the outlet end of the furnace. Under these conditions we find that only 5 to 10% of the hydrazoic acid entering the furnace can be recovered from the cold finger on warming to room temperature. No other gas comes off and the only other product is ammonium azide. Our experiments are in accord with the over-all equation $6HN_3 \rightarrow 7N_2 + H_2 + (NH)_4$. All experiments with the blue material should be done behind a safety glass screen. While we have had only one explosion out of several hundred experiments, it was extremely violent and completely demolished the apparatus. After this experience we used very small deposits on the cold finger and found that under these conditions the transition from blue to white occurs at about −150 instead of −125°. We also measured the absorption spectra of the blue material produced thermally, electrically and photochemically. All three show strong absorption in the ultraviolet characteristic of ammonium azide and all three show a broad absorption band with its center at about 6500 Å. The blue material that is produced electrically and photochemically shows a second absorption band with its center at about 3500 Å. Both bands disappear at the transition temperature.

Introduction

In two earlier papers[2] are described the conditions necessary for the preparation and stabilization of the intermediate formed during the thermal, electrical or photochemical decomposition of hydrazoic acid. Thus when hydrazoic acid vapors at low pressure are drawn through a hot tube at 1000°, a portion of the products may be frozen out as a blue solid on a surface cooled with liquid nitrogen. The blue solid may also be frozen out of the exit gases leaving the tube in which hydrazoic acid has been subject to an electrical discharge and may also be prepared by illuminating solid hydrazoic acid at −196° with the 2537 mercury line.

In our previous papers it was reported that the evidence available indicated that the composition of the blue solid is $(NH)_n$ so that it might be the imine radical or diimide or a mixture of both. Mador and Williams[3] have recently attributed the blue color to the presence of the NH_2 radical which in the vapor state has a broad absorption band near 6300 Å. We have been unable to confirm this, but rather are presenting new evidence which strongly suggests that the intermediates stabilized at low temperatures are NH and a higher polymer of NH.

The present investigation is concerned with the quantitative study of the thermal reaction and an evaluation of the absorption spectra of the blue solid prepared by three different methods.

Experimental

The Thermal Reaction.—Small quantities of hydrazoic acid were prepared immediately prior to each experiment by allowing concentrated sulfuric acid to react drop by drop with solid sodium azide *in vacuo*. The gas was then allowed to expand into an evacuated reservoir of known volume.

In a typical experiment about 0.5–1.0 g. of hydrazoic acid was passed through a quartz tube heated to 1000°. The rate of flow was adjusted so that the pressure at the inlet end of the furnace was about 0.1 mm. The products of the reaction which are condensable at −196° are frozen out onto the surface of a liquid nitrogen cooled tube which is located about 3 cm. from the exit end of the furnace. The non-condensable gases which were formed at this stage were removed from the reaction chamber by means of a high speed pumping system and passed into a gas measuring buret. Use then was made of the mass spectrometer as an analytical tool for the determination of the composition of these gaseous products. This fraction consisted mainly of nitrogen with some hydrogen.

Anal. N_2, 88.2, 87.4; H_2, 11.8, 12.6.

All other products were condensed on the surface cooled to −196°. After the flow of hydrazoic acid stopped, this section of the apparatus was isolated from the pumping system by means of a stopcock and the deposit was allowed to warm up to −125° at which temperature the blue solid undergoes a transition to a white solid. An important observation at this point is that there is no gas evolution during the transition. Warming to room temperature results in the evaporation of undecomposed hydrazoic acid; the amount was determined from pressure, volume and temperature measurements.

Finally the amount of white solid which remains at room temperature was determined by direct weighing. The results of the analysis of this white solid which prove that it is pure ammonium azide have been reported earlier.[2] Table I gives the complete mass balance obtained in duplicate experiments.

The Absorption Spectra.—In all experiments the same amount of hydrazoic acid was decomposed either thermally, photochemically or in an electrical discharge. In the cases of the thermal decomposition and the reaction in the electrical discharge the blue material was frozen out of the vapors leaving the exit end of the furnace and the discharge tube,

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(1) This work was supported in part by the United States Atomic Energy Commission, contract No. AT-(40-1)-1305.

(2) F. O. Rice and M. Freamo, This Journal, **73**, 5529 (1951); **75**, 548 (1953).

(3) I. L. Mador and M. C. Williams, *J. Chem. Phys.*, **22**, 1627 (1954); see also D. A. Dows, G. C. Pimentel and E. Whittle, *ibid.*, **23**, 1606 (1955); H. P. Broida and J. R. Pelham, *Phys. Rev.*, **95**, 845 (1954).

TABLE I

MASS BALANCE FOR THE THERMAL DECOMPOSITION OF HYDRAZOIC ACID AT 1000°

	Exp. 1	Exp. 2	Moles of products produced per mole of HN_3 consumed			
			Exp. 1	Exp. 2	Av.	Cal.[a]
HN_3 used, g.	0.4988	0.9374				
HN_3 recovered, g.	.0260	.0559				
HN_3 consumed, g.	.4728	.8815	1	1	1	1
Non-condensable gases, g.	.3601	.6698	1.32	1.33	1.32	1.33
N_2, g.	.3584	.6664	1.16	1.16	1.16	1.17
H_2, g.	.0017	.0034	0.157	0.167	0.162	0.167
NH_4N_3 measured after the transition, g.	.1081	.2110	0.164	0.171	0.168	0.167

[a] Based on the reactions

$$6HN_3 \longrightarrow 4[NH] + 7N_2 + H_2$$
$$4[NH] \longrightarrow NH_4N_3$$

respectively. In the photochemical experiments the hydrazoic acid was decomposed with the mercury light after it had been deposited on a surface at −196°.

Optical density measurements were obtained on a Beckman quartz spectrophotometer, Model DU. All measurements were made at −196° in a quartz cell specially adapted for use at low temperatures. The cell which must also serve as the reaction vessel is designed as follows: Two optically flat quartz plates, 2 cm. diam., are fused exactly parallel to opposite sides of a quartz tube, 2.5 mm. i.d. and 20 cm. long. One end of this tube is sealed off, the other end terminates in a male 34/45 ground joint. A quartz cold finger 10 mm. i.d., which also contains two optically flat quartz plates 15 mm. diam., fused to opposite sides of the tube fits concentrically into the outer jacket. The cold finger is adapted to the main body of the apparatus by means of a female 34/45 ground joint to which it is attached by means of a Dewar type seal. The outer jacket is also equipped with two sidearms fused to opposite sides of the tube at the same level as the optical plates but at an angle of 90° from them. One of these arms serves to attach the system to a vacuum line while the other, which is wrapped with a resistance wire heating element, serves as the furnace for the thermal reaction. This arm is attached to the hydrazoic acid reservoir by means of a calibrated capillary. When the cold finger is properly aligned, the condensable vapors leaving the furnace are frozen out on the flat optical plate, after the reaction is complete, rotation of the inner tube through 90° aligns all four plates. Stopcocks judiciously placed allow the evacuated cell to be removed from the rest of the system. The over-all dimensions of the cell including the stopcocks are 4 cm. thick, 25 cm. high and 40 cm. wide; the cell chamber of the spectrophotometer was easily modified to accommodate this cell. By making permanent markings on the glass and on the clamps which hold the cell in place, good reproducibility was obtained from day to day. The readings were made with liquid nitrogen in the cold finger. A blank experiment was run to ascertain that there were no impurities in the nitrogen which absorb in the region in which the measurements were made.

To serve as a discharge tube the apparatus was slightly modified. The heating element was removed and two aluminum electrodes were sealed into the side arm. The distance between the terminals was 20 cm.

Results and Discussion

It has been established definitely that hydrazoic acid, when decomposed thermally under the conditions described, produces one mole of hydrogen and seven moles of nitrogen for each six-mole quantity of the acid consumed. Therefore the equation for the decomposition after the initial stage of the reaction may be written as

$$6HN_3 \longrightarrow 7N_2 + H_2 + 4(NH)$$

The parenthesized quantity represents the empirical formula of the material required to complete the mass balance. At this stage it is in the form of a blue solid at −196°. It has further been established that this material on warming to room temperature converts completely and irreversibly to ammonium azide. Quantitatively the required amount of ammonium azide is found and no other products are detected.

The spectrum of the blue metastable solid formed in the thermal reaction shows a broad absorption band whose maximum is at 6500 Å. The blue solid formed by the photochemical reaction and by the decomposition of hydrazoic acid in the electrical discharge exhibits, besides this characteristic band, another band whose maximum is between 3400 and 3500 Å. Figure 1 shows the absorption curves obtained in typical experiments.

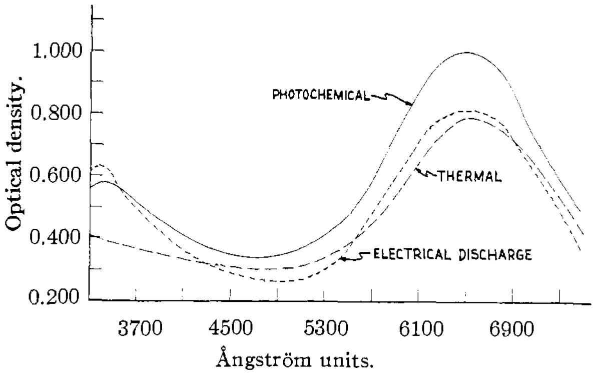

Fig. 1.—Absorption spectra of the blue solid formed by freezing the decomposition products of hydrazoic acid on a surface cooled by liquid nitrogen.

If the band at 3500 Å. is due to the imine radical, then the absence of this band in the absorption spectrum of the blue material formed during the thermal reaction can be accounted for by the fact that the deposit is being collected about 3 cm. from the end of the furnace which is at 1000° and the surface of the deposit is constantly exposed to strong thermal radiation. Under these conditions the cooling may not be sufficiently effective to stabilize NH and it may react to form diimide or ammonium azide. During the photochemical reaction and the decomposition in the electrical discharge the cooling is sufficiently effective to stabilize the imine radical. Since both bands disappear after the transition, the one at 6500 Å. must also be due to a highly reactive intermediate which may be diimide (N_2H_2).

What has not yet been definitely established is the amount of active species which is stabilized on the cold finger. Heavy deposits have an exceedingly intense blue color and it would be very surprising if the deposit was predominantly ammonium azide.

In one experiment during the transition at −125°, the blue deposit exploded violently, completely shattering the apparatus. After this experience, we did a few experiments to test the sensitivity of the blue deposit. At −195° rubbing or sparking it produces small local explosions. In no experiment did we succeed in exploding the whole of the deposit when it was at −195°.

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