[Contribution from the National Bureau of Standards]

Mass Spectrometric Study of the Decomposition of Hydrazoic Acid by the Electric Discharge[1]

By J. L. Franklin,[2] John T. Herron, Paul Bradt and Vernon H. Dibeler

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Hydrazoic acid at low pressure has been decomposed by a Tesla discharge and the products sampled and analyzed continuously by mass spectrometer. The discharge products were condensed at 77°K. giving a blue deposit which changed to white and subsequently vaporized upon warming. The products of reaction were H_2, N_2, NH_3 and undecomposed HN_3. The NH_3/HN_3 ratio before and after condensation was very nearly the same, indicating that very little reaction occurred in the solid. Attempts to identify NH, N_3 and excited HN_3, which might serve as active intermediates in the reaction, were unsuccessful, indicating that the proportion of these materials was very small.

Introduction

Rice and Freamo[3,4] found that when hydrazoic acid was decomposed thermally, or in an electric discharge, a blue paramagnetic deposit was obtained when the decomposition products were condensed on a cold surface at 77°K. The blue color changed irreversibly to white at 148°K. The white material was identified as ammonium azide, NH_4N_3. It was concluded that the blue material was possibly due to the imine radical NH. This was in accord with their further observation that if a mixture of NH_3 and CO was passed through a furnace, cyanic acid, HNCO, was obtained as a product.

Other workers, using spectroscopic techniques, have shown that the concentration of free radicals in the blue solid probably is quite small. Mador and Williams,[5] from a study of the infrared absorption spectra of the blue solid found it to be made up principally of undecomposed HN_3 and smaller amounts of NH_4N_3. Furthermore, the concentration of NH_4N_3 did not change at the transition temperature, 148°K. Absorption bands at 3500 and 6500 Å. were attributed to NH and NH_2 radicals, respectively.

They also drew similar conclusions from photolysis experiments. In this case the quantum yields indicated that a chain mechanism was involved in the formation of NH_4N_3.

Dows, Pimentel and Whittle,[6] from similar experiments, concluded that NH_3 may have been formed in the gas phase and then reacted with excess HN_3 to form NH_4N_3 condensing at 77°K. As active species they suggested NH, N_2H_2 and $(NH)_x$, and that the latter rearranges to NH_4N_3 at higher temperatures as originally suggested by Rice and Freamo.[3,4]

More recently, Becker, Pimentel and Van Thiel[7] have carried out photolysis experiments in solid HN_3 using the matrix isolation technique. They conclude that NH and NH_2 radicals are present, in addition to N_3.

In the present study, mass spectrometric techniques were applied in an effort to determine the origin of the previously reported decomposition products of HN_3 and to observe any active intermediates resulting from the decomposition. This paper deals with the decomposition of HN_3 with an electric discharge. A similar study of the products of thermal decomposition is to follow.

Experimental

Apparatus.—The mass spectrometer was a 60° sector field instrument having a 6″ radius of curvature. The spectrum was scanned by varying the magnetic field at a constant electric field of 2500 volts. Gas samples from the system under study entered the mass spectrometer through a 0.6 mil diameter hole in a thin glass diaphragm. The Nier type ion source was separated from the leak by a 20 cm. length of Pyrex tubing, tapered at one end to enter the ion source.

The flow system was constructed of 10 mm. i.d. glass tubing. The hydrazoic acid was passed through the discharge, over the sampling leak of the mass spectrometer, past a "cold finger" 10 cm. from the leak, which could be filled with liquid nitrogen, and then to the pump. A gas sample also could be drawn off into a sample bulb just ahead of the pump.

The discharge was obtained by wrapping several turns of copper wire around the tube, about 10 cm. from the leak, and connecting this to a carefully shielded Tesla coil (leak tester).

Materials.—The hydrazoic acid was prepared *in vacuo* by treating 80% H_2SO_4 with sodium azide. The preparation was carried out behind safety screens as HN_3 has a propensity to explode under certain circumstances. However, it seems quite safe at pressures below 50 mm. The cold finger on which the blue discharge products were deposited also was shielded as on several occasions it spontaneously exploded.

Procedure.—Hydrazoic acid at pressures of 0.04 to 0.20 mm. was allowed to flow through the reactor system. The mass spectrum was determined both with the discharge on and off. The products of the decomposition were analyzed by the standard methods of mass spectrometry. Experiments were carried out only after it was demonstrated in each case, that the blue material could be trapped out on the cold finger at 77°K.

In several experiments a sample of the decomposed NH_3 was withdrawn just ahead of the pump, with no refrigerant in the cold finger.

Appearance potential measurements were made to aid in the identification of various active species. For this purpose, argon was mixed with the HN_3 and both gases passed through the discharge. The spectroscopic value of the ionization potential of argon (15.76 e.v.) was used to calibrate the ionizing electron energy scale.

Mass spectrometric analyses were also made of the trapped materials vaporized from the cold finger. A heavy deposit of the blue material was laid down at 77°K. The supply of HN_3 was then cut off and the direction of flow in the system altered so that materials evolved at the cold finger would pass over the leak and then to the pump. Mass spectral scans of 100 sec. duration were made between masses 43 and 14 during the warm up period. These measurements were correlated with visual observations on the trapped materials.

The use of conventional mass spectrometers in free radical studies depends to a great extent on the ability of the radical to withstand collisions with the walls of the ion source. It

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(2) Guest Scientist on leave from Humble Oil and Refining Co., Daytown, Texas.

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has been estimated that in a Nier type ion source a molecule entering the source has only a 1 in 50 chance of being ionized without first colliding with the wall.[8] Thus, failure to detect a radical may be due to radical destruction in the ion source.

The instrument used in this work had an ion source made of stainless steel and platinum. An experiment was carried out to determine the effect of these materials on the formation of the blue deposit. HN_3 was decomposed thermally and the products passed through stainless steel and platinum gauzes and then condensed on a cold finger at 77°K. The appearance and quantity of blue material obtained under these conditions were apparently identical to deposits obtained in the absence of the gauzes.

Results and Discussion

When the discharge was operating a glow was visible throughout the flow system, even considerably upstream from the copper winding where the discharge was initiated. This visible glow strongly suggested that reaction was occurring throughout the system. This inference was substantiated by the fact that a blue deposit formed on the cold finger even when the discharge was initiated down stream from it. Further, samples were taken 50 cm. down stream from the leak (in the absence of a cold surface) and analyzed separately. These samples invariably showed more decomposition than did those taken at the leak, as will be seen in Table I. The only products that we were ever able to identify were NH_3, N_2 and H_2, in addition to undecomposed HN_3. Thus our results are similar to those of Franklin, Dibeler and Morris,[9] who decomposed HN_3 thermally under very mild conditions. The composition of the products in the two studies differed only in that the Tesla discharge products contained hydrogen whereas the thermal product did not.

TABLE I

Conditions	Sample	P HN_3 (mm.)	% decom.	(mole %)			
				N_2	H_2	NH_3	HN_3
Strong disch.	Leak	0.09	50	31.7	6.2[a]	3.3	58.7
	Grab			66.8	16.1[a]	4.6	12.7
Weak disch.	Leak	.07		9.3	2.2[a]	0.7	87.3
	Grab			19.3	5.1[a]	1.0	74.4
Weak disch.	Leak	.04	10	10.8	2.2	1.1	85.9
Weak disch.	Leak	.10	15	36.7	6.7	2.9	53.8
Weak disch.	Trapped at 4°K.	.20	1	0.23	0.03	0.02	99.7

[a] Calculated assuming N/H = 3 in products.

Although the mechanism by which HN_3 decomposes is not known, it seems very probable that the process is initiated by the reaction

$$HN_3 \longrightarrow NH + N_2$$

as has been proposed by Rice and Freamo.[3,4] Accordingly we have made every effort to ascertain whether NH was present in the reacting gas.

If NH radicals were present in appreciable concentration in the decomposed HN_3, they would presumably be ionized to NH^+ in the ion source and contribute to the ion current at m/e 15. Both HN_3 and NH_3 make contributions to the m/e 15 ion current due to dissociative ionization. When these contributions are subtracted from the spectra observed with the discharge "on," the remainder is of the same magnitude as the uncertainty in the measurement, *i.e.*, about 1%. This sets an upper limit of about 1% to the NH concentration, on the assumption that the sensitivity of NH is not dissimilar to that of N_2.

Similar conclusions can be drawn from the appearance potential measurements. The ionization potential of NH probably differs from the appearance potential of NH^+ from HN_3 by 0.4 e.v.[10] Thus there would probably have to be at least 1% NH present for any difference in appearance potential to be detected.

It has been suggested[11] that the decomposition of HN_3 is initiated by the formation of an excited molecule which subsequently reacts with other non-excited ones. Accordingly we measured the ionization potential of HN_3 with the discharge operating, in the hope that, if excited molecules were present in considerable numbers they might be observed by a reduction in ionization potential. However, the discharge did not alter the ionization potential, the value obtained being always the same as that determined by Franklin, Dibeler, Reese and Krauss.[10] Thus any excited molecules present were either in very small concentration or very short lived. Either conclusion suggests that, if this were the source of the blue color of the solid, very little material is required to account for the phenomenon.

Thrush[12] reported the formation of N_3 radicals by flash photolysis of HN_3. We searched for this radical by observing the appearance potential and the ion-abundance curve of N_3^+ with and without the discharge. Again the discharge had no detectable effect, thus showing that any N_3 must have been present in very low concentration.

The possibility of $(NH)_2$ being a product of the decomposition led us to examine the mass spectrum from m/e 29 to 32 very carefully. It was found that the very small ion current at m/e 30 increased by a factor of about 10 when the discharge was turned on. The ion current at 32 remained unchanged. This peak at mass 30 also has been observed in discharges in N_2H_4 and NH_3.

In the presence of an electric discharge, NO must always be considered a possible product. Although the spectrum of $(NH)_2$ would be expected to have a peak at m/e 29, it is masked by the 29 isotope peak of N_2^+. It was thus impossible to distinguish between NO and $(NH)_2$ in this system.

Foner and Hudson[13] have carried out a study very similar to ours, which led to the same general conclusions. However, they were able to assign unambiguously the m/e 30 peak to N_2H_2 and in fact have been able to isolate this compound in relatively large amounts.

The ratio of ammonia to hydrazoic acid in the accumulated gases vaporized from the cold trap was found in all cases to be comparable to, but slightly smaller than, that observed by leaking a small amount of the reacting stream into the mass spectrometer. The small decrease observed is

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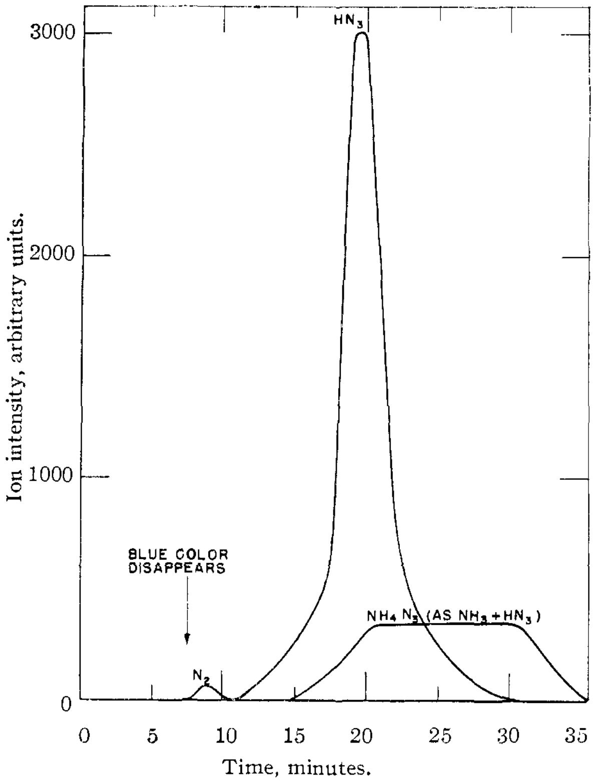

Fig. 1.—Gases evolved on warming the blue solid.

undoubtedly due to a small amount of NH_4N_3 remaining on the cold finger. Visual observation showed this to be quite small, however. If an extensive amount of reaction had occurred on warming the blue solid, the NH_3/HN_3 ratio should have been appreciably greater in the warm-up gases than during deposition. This was not the case and so we must conclude that very little reaction took place upon warming the solid, by far the greatest amount having occurred in the gas prior to or during deposition on the cold surface.

When the blue solid was allowed to warm up, the color transition was observed to occur very sharply, either the entire solid changing color at once, or separate patches changing rapidly. The mass spectrometer showed no gases evolved until the transition point, at which time a very small amount of nitrogen gas (less than 0.2% of the total trapped material) was given off. As warm up continued HN_3 appeared, followed by NH_3 which no doubt resulted from the decomposition of NH_4N_3. The evolution of nitrogen at the transition point was checked by focusing the mass spectrometer on mass 28 during the warm up in several experiments. Each time the current at mass 28 increased suddenly at the same time that the blue color disappeared. A typical set of warm-up curves is shown in Fig. 1. These curves are not corrected for pressure or pumping speed. These corrections cannot be made exactly, but when the approximate corrections are applied the ratio $N_2:NH_3:HN_3$ is found to be 0.0025:0.38:1.0.

The proportion of nitrogen in the warm up products is thus found to be very small and its origin was not certain. It might have been formed by chemical reaction or it might have been either adsorbed on or trapped in the solid and released upon warming. In an effort to ascertain whether the nitrogen had been adsorbed or trapped, a large concentration of N_2 was added to the warm-up products and the mixture recycled through the system without the discharge but with the cold trap in the stream. A white solid of course accumulated on the cold surface, but when this was allowed to warm up there was no evolution of N_2. Although this is not complete proof, it strongly implies that the N_2 released at the transition point had not been physically trapped but, rather, that it was formed by chemical reaction.

We already have shown that the reaction occurs principally in the gas phase. The evolution of N_2 at the transition temperature indicated that a very small amount of reaction occurs during warm up. This reaction corresponds to less than 1% of the NH_3 in the products. The nature of this reaction is not known. However, it must be a process capable of evolving N_2. This might involve the attack of a free radical upon HN_3; for example

$$NH + HN_3 \longrightarrow N_2H_2 + N_2$$

Alternatively, it might involve reaction of excited HN_3 with elimination of N_2. It does not seem possible, however, that this could result from the polymerization of NH or the rearrangement of $(NH)_4$ to NH_4N_3, both of which have been proposed to account for the reaction in the solid phase. Of course, the polymerization or rearrangement reaction might occur simultaneously. This would require that we have two or more mechanisms occurring simultaneously and yielding identical products. Although this explanation is not impossible, it seems unnecessarily elaborate to account for the facts observed.

To recapitulate, then, we find the following: 1. By far the greater part of the final products of the gas phase decomposition of HN_3 are formed in the gas phase. 2. Free radicals or other unstable species are present in, at most, very small proportions. 3. A very small amount of reaction seems to occur at the solid transition from blue to white. The nature of this reaction is not known but it probably is not a polymerization of NH or a rearrangement of NH polymer.

Unfortunately we cannot account for the blue color of the solid although it may well be attributable to small amounts of a free radical or other excited species present. It seems very clear, however, that any excited species can be present in only very small amounts and that it can account for only a small portion of the products.

WASHINGTON, D. C.