support afforded by the National Science Foundation (1955–1956) and by the Allied Chemical and Dye Corporation (1957–1958) in the form of graduate fellowships. This work was performed under the auspices of the United States Atomic Energy Commission.

---

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CATHOLIC UNIVERSITY OF AMERICA, WASHINGTON, D. C.]

# The Imine Radical and the Thermal Decomposition of Hydrazoic Acid[1]

BY F. O. RICE[2] AND THOMAS A. LUCKENBACH

RECEIVED NOVEMBER 4, 1959

In the present work, we have performed experiments in which we have thermally decomposed measured amounts of hydrazoic acid in a flowing system and passed the products over a liquid nitrogen cooled finger. All the products were collected and analyzed so that a complete mass balance was obtained. We think that the imine radical is formed in the primary step $HN_3 \rightarrow NH + N_2$, but we do not know either the mechanism of formation of ammonium azide or the nature of the blue material; possibly a small fraction of the NH may reach the cold finger and form a colored polymer, $(NH)_n$.

## Introduction

Although the blue material formed by cooling suddenly the thermal decomposition products of hydrazoic acid was discovered about ten years ago[3] and has been extensively investigated in several laboratories,[4] neither its composition nor the nature of the substance causing the blue color are known. The following facts have been established: the material has an intense blue color and is stable indefinitely at liquid nitrogen temperatures; on warming to about −125° it changes irreversibly to a white material without any appreciable evolution of gas. The blue material is paramagnetic and has a broad absorption band in the visible with its center at about 6400 Å. One of the difficulties in studying the blue material is that all work must be done below its transition point −125°. It does not dissolve in any of the rather limited number of substances that are liquid below −125° and we have not succeeded in making it react with anything on the cold finger; even atomic hydrogen had no effect.[4a] The present work is the first step in a larger program to determine the nature of the blue material and the mechanism of the reaction.

## Experimental

Hydrazoic acid was generated in small quantities, as required, by slow mixing of concd. sulfuric acid with dry sodium azide. Hydrazoic acid can be kept safely and indefinitely as a gas at about 100 mm. pressure. It was purified by freezing the gas to −125° and pumping on it to remove any nitrogen or carbon dioxide. The mass spectrometer pattern compared favorably with one obtained at the Bureau of Standards.[5]

Hydrazoic acid from a small storage reservoir was led through a quartz tube about 12 mm. i.d., surrounded by a sliding furnace and fitted with a thermocouple well. The length of the furnace and its position on the quartz tube could be varied. The gases leaving the quartz tube passed over a liquid nitrogen cooled finger and then through a series of traps so that the various products could be collected and analyzed. The gas entering the furnace was at a pressure of about 0.5 mm. and the pressure at the cold finger was less than 0.1 mm.

The most volatile products of the decomposition are nitrogen and hydrogen and their collection and estimation proved a difficult problem. It was solved finally by arranging the apparatus so that the pumping system could be bypassed and replaced by a bulb immersed in a storage tank of liquid helium. At the end of the run, the bulb was removed from the liquid helium and the contents analyzed on the mass spectrometer after the pressure, temperature and volume had been measured. We have found this method to be vastly superior to all others that we tried and recommend its use for the collection and measurement of permanent gases under conditions similar to ours whenever liquid helium is available. In all our runs, the permanent gases consisted of nitrogen containing 5 to 10% of hydrogen.

At the end of a run, the cold finger was allowed to warm slowly to about −40°. During this part of the experiment, the blue material changed to white at about −125° and at a little higher temperature either undecomposed hydrazoic acid or ammonia came off. The gas was collected in a bulb at liquid nitrogen temperatures and when all the gas was cooled, it was allowed to warm to room temperature; after the pressure, temperature and volume were measured, it was analyzed on the mass spectrometer. The white residue, which is solid at room temperature, has a small vapor pressure and was sublimed into a small weighing bottle and weighed directly. The substance was tested frequently for hydrazine which was found to be absent and a mass spectrometer analysis gave a pattern characteristic of a one to one mixture of ammonia and hydrazoic acid.[6]

On the average, about 2 mmoles (about 0.1 g.) of $HN_3$ was used in each of our experiments. Work with larger quantities is exceedingly hazardous and even with these small quantities occasional explosions occurred. Needless to say, all work should be done behind a shatterproof glass screen.

## Experimental Results

We have made preliminary runs in which we obtained complete mass balances and studied the effect of changing the length of the furnace, changing the temperature and changing the distance of the end of the furnace from the cold finger.

---

[1] The major portion of this investigation was supported by the United States Atomic Energy Commission, Contract No. AT-(40-1)-1305.

[2] Chemistry Department, Georgetown University, Thirty-seventh and O Streets, Washington 7, D. C.

[3] F. O. Rice and M. Freamo, THIS JOURNAL, **73**, 5529 (1951).

[4] (a) F. O. Rice and M. Freamo, *ibid.*, **75**, 548 (1953); (b) I. L. Mador and M. C. Williams, *J. Chem. Phys.*, **22**, 1627 (1954); (c) D. A. Dows, G. C. Pimentel and E. Whittle, *ibid.*, **23**, 1606 (1955); (d) L. Baum, H. Graff, E. I. Hormats and G. Moe, "Research on Ultra-Energy Fuels for Rocket Propulsion," Report No. 1149 (Final) ASTIA Document No. AD 95432; (e) B. A. Thrush, *Proc. Rcy. Soc.* (*London*), **235A**, 143 (1956); (f) E. D. Becker, G. C. Pimentel and M. Van Thiel, *J. Chem. Phys.*, **26**, 145 (1957); (g) F. O. Rice and C. Grelecki. THIS JOURNAL, **79**, 1880 (1957); (h) M. Van Thiel, E. D. Becker and G. C. Pimentel, *J. Chem. Phys.*, **27**. 95, 489 (1957); (i) J. Franklin, V. H. Dibeler, R. M. Reese and M. Krauss, THIS JOURNAL, **80**, 298 (1958); (j) H. A. Papazian, *J. Chem. Phys.*, **29**, 448 (1958); (k) S. N. Foner and R. L. Hudson, *ibid.*, **28**. 719 (1958); (l) F. O. Rice and R. B. Ingall, THIS JOURNAL, **81**, 1856 (1959); (m) L. H. Bolz, F. M. Mauer and H. S. Peiser, *J. Chem. Phys.*, **30**, 349 (1959).

[5] J. Franklin, C. H. Dibeler, R. M. Reese and M. Krauss, THIS JOURNAL, **80**, 298 (1958).

[6] Additional confirmation of the identity of the white residue was provided by H. S. Pieser and coworkers, National Bureau of Standards, who showed that the solid gave an X-ray diffraction pattern identical with $NH_4N_3$.

TABLE I

EFFECT OF CHANGING FURNACE LENGTH

In all experiments, the end of the furnace was 0.5″ from the cold finger, the furnace temperature was 1000° and the flow rate was constant. In our experiments 10 cc. of gas measured at 30° and 760 mm. passed through the furnace per min.

| Run no. | Furnace length[b] | Moles of product per mole of $HN_3$ consumed[a] $N_2$ | $H_2$ | $NH_4N_3$ | $NH_3$ | Color deposit | % decomp. |
|---|---|---|---|---|---|---|---|
| 25 | 3 | 1.11 | 0.16 | 0.164 | ... | Deep blue | 52.2 |
| 26 | 6 | 1.15 | .16 | .165 | ... | Deep blue | 72.6 |
| 23 | 9 | 1.22 | .15 | .139 | 0.029 | Very pale blue | 86.5 |
| 11 | 12 | 1.26 | .19 | .087 | 0.099 | White | 91.3 |

[a] This is the amount of $HN_3$ entering the furnace minus the sum of the amounts of free and combined $HN_3$ frozen on the cold finger. [b] Length in inches.

## Discussion

It is very tempting to ascribe the following mechanism to the thermal decomposition of hydrazoic acid

$$HN_3 \longrightarrow NH + N_2$$

This represents the primary process. The imine radical is then carried to the cold finger where it condenses to form the blue solid. Since ammonium azide has the empirical formula $(NH)_4$, it would not be surprising to find ammonium azide as the product. It would be reasonable to expect that a large part of the NH would form ammonium azide on collision with the cold surface and only a small portion would form the blue substance which might be either the monomer or a polymer of NH.

Unfortunately, this simple picture is not in accord with our experimental results, particularly the formation of ammonia. We think now that the primary formation of NH is followed by reaction with $HN_3$ in steps leading finally to ammonia. The ammonium azide formed on the cold finger would then result from the combination of ammonia and undecomposed hydrazoic acid. We do not know the mechanism whereby NH became $NH_3$ although the experiments of Foner and Hudson[4k] indicate that di-imide is an intermediary; nor do we know the extent to which ammonium azide originates from the reaction either of ammonia with hydrazoic acid or of NH with itself.

As a second stage of our investigations we plan to repeat this work by decomposing hydrazoic acid electrically and also photochemically, in each case making complete mass balances.

TABLE II

EFFECT OF DISTANCE BETWEEN THE END OF FURNACE AND COLD FINGER

In all experiments, the furnace length was 3″ and the furnace temperature was 1000°. The flow rate was constant and the same as in Table I.

| Run no. | Dist. from finger (inch) | Moles of product per mole of $HN_3$ consumed $N_2$ | $H_2$ | $NH_4N_3$ | $NH_3$ | Color deposit |
|---|---|---|---|---|---|---|
| 37 | 0.5 | 1.20 | 0.14 | 0.148 | .. | Intense blue |
| 38 | 3.5 | 1.10 | .11 | .182 | .. | Deep blue |
| 41 | 6.5 | 1.07 | .12 | .183 | .. | Pale blue |
| 42 | 9.5 | 1.09 | .11 | .183 | .. | White |

TABLE III

EFFECT OF CHANGING FURNACE TEMPERATURE

In all experiments the furnace length was 12″ and the end of the furnace was 0.5″ from the cold finger. The flow rate was constant and the same as in Table I.

| Run no. | Temp., °C. | Moles of product per mole of $HN_3$ consumed $N_2$ | $H_2$ | $NH_4N_3$ | $NH_3$ | Color deposit |
|---|---|---|---|---|---|---|
| 4 | 850 | 1.05 | 0.10 | 0.188 | .... | Pale blue |
| 5 | 850 | 1.03 | .10 | .191 | .... | Pale blue |
| 6 | 900 | 1.09 | .11 | .190 | .... | Deep blue |
| 7 | 900 | 1.09 | .11 | .198 | .... | Deep blue |
| 8 | 900 | 1.11 | .11 | .194 | .... | Deep blue |
| 10 | 900 | 1.09 | .12 | .192 | .... | Deep blue |
| 15 | 950 | 1.23 | .15 | .128 | 0.0066 | Very pale blue |
| 16 | 950 | 1.22 | .14 | .114 | .094 | Very pale blue |
| 11 | 1000 | 1.26 | .19 | .087 | .099 | White |
| 12 | 1000 | 1.19 | .19 | .134 | .028 | White |
| 14 | 1000 | 1.32 | .18 | .052 | .156 | White |
| 21 | 1000 | 1.31 | .18 | .067 | .127 | White |
| 19 | 1050 | 1.39 | .21 | ... | .177 | White |

---

[CONTRIBUTION FROM THE ENERGY DIVISION, OLIN MATHIESON CHEMICAL CORPORATION, NEW HAVEN, CONNECTICUT]

# The Kinetics of the Homogeneous Gas Phase Thermal Decomposition of Ozone[1]

BY J. A. ZASLOWSKY, H. B. URBACH, F. LEIGHTON, R. J. WNUK AND J. A. WOJTOWICZ

2682 - 2686
AID · 007

RECEIVED AUGUST 20, 1959

The homogeneous gas phase decomposition of concentrated ozone was studied manometrically over the pressure range 11.3 to 51.8 mm. at temperatures of 115, 120, 125 and 130°. The observed second order reaction rate constant is expressed as $k_{\text{obsd.}} = 1.6 \times 10^{13} (\exp - 24{,}300/RT)$ l./mole sec. Little variation in the reaction rate constant was noted over the initial 35 to 40% reaction. The results are consistent with previous[15,16] measurements in the temperature range of 70 to 110°.

## Introduction

A survey of the literature[2–21] indicates that considerable disagreement exists among various investigators concerning the thermal decomposition of ozone. Jahn[4] postulated the following

---

[1] Work was performed under Air Force Contract AF-04(645)-72.

[2] Ozone Chemistry and Technology, Advances in Chemistry Series, No. 21, American Chemical Society, 1959, pp. 388–409.

[3] E. Warburg, *Ann. physik*, **9**, 1286 (1902).

[4] S. Jahn, *Z. anorg. Chem.*, **4B**, 260 (1906).

[5] O. R. Wulf and R. C. Tolman, THIS JOURNAL, **49**, 1183, 1202, 1650 (1927).

[6] H. E. Clarke and D. L. Chapman, *J. Chem. Soc.*, **93**, 1638 (1908).

[7] E. P. Perman and R. H. Greaves, *Proc. Roy Soc. (London)*, **80A**, 353 (1908).

[8] R. O. Griffith and A. McKeown, *J. Chem. Soc.*, **127**, 2086 (1925).

[9] D. L. Chapman and H. E. Jones, *ibid.*, **97**, 2463 (1910).

[10] K. J. Clement, *Ann. physik*, **14**, 341 (1904).

[11] J. W. Belton, R. O. Griffith and A. McKeown, *J. Chem. Soc.*, **129**, 3153 (1926).

[12] E. H. Riesenfeld and W. Bohnholtzer, *Z. physik. Chem.*, **130**, 241 (1927).

[13] E. H. Riesenfeld and H. J. Schumacher, *ibid.*, **138A**, 268 (1928).