*p*H 10–13. According to the Brönsted–Bjerrum rule,[20] this indicates a reaction between negative and positive ions in acidic solution and leads to the conclusion that the rate is catalyzed by hydrogen (hydronium) ion. Apparently at low values of the *p*H, the P–O–P linkage reacts with a $(H_3O)^+$ ion; but, as the *p*H is raised, this reaction plays a less important role with the reaction with neutral $H_2O$ or hydrated cations becoming predominate at high *p*H.

At *p*H values of 4 and above, the case with sodium ion is just the reverse, as can be seen in Table I. When sodium was substituted for tetramethylammonium as the cation for either the pyro- or triphosphate at *p*H 4 and above, the ratio of the rate without swamping electrolyte to that with becomes a fraction (0.7 to 0.8), the value of which does not appear to depend on *p*H. Also, either with or without the presence of swamping electrolyte, the substitution of sodium for tetramethylammonium ion at *p*H 4 and above causes an increase in degradation rate—an effect which is more noticeable in the presence of the swamping electrolyte. As was pointed out in the communication[21] which preceded this paper, these effects must be considered as additional evidence for the formation of polyphosphatosodium complexes, which have been shown to exist by other experiments.[13] The reports in the literature (*e.g.*, Watzel[6]) that there is a minimum rate of hydrolysis at *p*H 10, with an acceleration as the alkalinity is increased, do not show that the degradation is catalyzed by hydroxyl ion. Rather, the observed increase in rate on going to very strongly alkaline solutions is attributable to the sodium ion being added as NaOH.

In highly acidic solutions, the hydrogen ion seems to displace the sodium ion as a catalyst, so that addition of a sodium salt as swamping electrolyte results in a diminution in reaction rate in opposition to its accelerating action under less acidic conditions. This is borne out by the data in Table I for sodium pyrophosphate at *p*H 1 and 60°. The work by Friess[19] and by Campbell and Kilpatrick[5] describes this effect in more detail; but these authors do not show the accelerating action of sodium salts in mildly acidic, neutral and basic solutions, since the pertinent part of their work was done under conditions (strong acid) where the hydrogen ion was dominant.

Although we did not experimentally find its exact value, there must be a *p*H, perhaps varying with concentration, at which the addition of a sodium salt to a sodium pyro- or triphosphate solution has no effect on the rate of degradation of the phosphate. At this *p*H, the catalysis attributed to complex formation would be exactly balanced by the shielding effect of the type due to non-catalytic swamping electrolytes.

Our data for sodium pyrophosphate at *p*H 4 and 60° indicate that there is little difference between the effect of sodium bromide and sodium chloride swamping electrolytes. This agrees with the data of Campbell and Kilpatrick[5] and indicates that these anions are not involved in the hydrolysis process except indirectly by affecting activities.

DAYTON, OHIO

[20] J. N. Brönsted, *Z. physik. Chem.*, **102**, 109 (1922); *ibid.*, **115**, 337 (1925); and N. Bjerrum, *ibid.*, **108**, 82 (1924).

[21] J. R. Van Wazer, E. J. Griffith and J. F. McCullough, THIS JOURNAL, **74**, 4977 (1952).

---

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CATHOLIC UNIVERSITY OF AMERICA]

# The Hydrazino Radical and Tetrazane[1]

BY FRANCIS OWEN RICE AND FLOYD SCHERBER[2]

RECEIVED AUGUST 16, 1954

When hydrazine is thermally decomposed at low pressures (~0.5 mm.) and high temperatures (~850°) in a flowing system and the gases leaving the furnace are quickly brought in contact with a liquid nitrogen-cooled finger, a deposit is formed of a bright yellow material, stable indefinitely at −195°; on warming to −178° it decomposes suddenly giving off almost pure nitrogen. Since the material is not paramagnetic, we think it is tetrazane, $H_2NNHNHNH_2$, rather than the hydrazino radical, $NH_2NH$. The decomposition is probably represented by the equation $H_2NNHNHNH_2 \rightarrow 2NH_3 + N_2$. Preliminary experiments with $H_2N^{15}N^{14}H_2$ indicated that there was at least some randomization of the $N_2$ formed in the furnace as well as the $N_2$ formed by decomposition of the yellow substance.

The thermal decomposition of gaseous hydrazine has been studied by several investigators[3] most of whom agree that the thermal decomposition proceeds by a free radical mechanism and is, at least in part, heterogeneous. The homogeneous free radical steps may be represented by the equations

$$N_2H_4 \longrightarrow 2NH_2$$

$$NH_2 + N_2H_4 \longrightarrow NH_3 + NH_2NH$$

We assume that the hydrazino radical decomposes on the wall according to the equation

$$2NH_2NH \longrightarrow 2NH_3 + N_2$$

although collision of $NH_2NH$ either with itself or with $NH_2$ may be followed by interaction. The intermediate formation of the hydrazino radical in the photochemical decomposition of hydrazine[4] in presence of nitric oxide is strongly suggested by the formation of nitrous oxide as a major product presumably according to the equation

$$NH_2NH + NO \longrightarrow NH_3 + N_2O$$

---

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

[2] Taken from the dissertation presented by Floyd Scherber for the degree of Doctor of Philosophy in The Catholic University of America.

[3] M. Szwarc, *J. Chem. Phys.*, **17**, 505 (1949); P. J. Askey, THIS JOURNAL, **52**, 970 (1930); C. H. Bamford, *Trans. Faraday Soc.*, **35**, 1239 (1939).

[4] C. H. Bamford, *ibid.*, **35**, 568 (1939); see also E. O. Wiig and G. B. Kistiakowsky, THIS JOURNAL, **54**, 1817 (1932).

## Experimental

Anhydrous hydrazine was prepared by refluxing 95% hydrazine with barium oxide for six hours and distilling the dry hydrazine at reduced pressure in a hydrogen atmosphere.[5] Hydrazine purified in this way was used for all experimental work other than the anhydrous hydrazine containing $N^{15}$.

The dry hydrazine vapor at low pressures (~0.5 mm.) was passed through a furnace at 850° and the condensable products were frozen out suddenly on a cold finger at −195°. The condensate prepared in this way has a bright yellow color and appears to be stable indefinitely at −195°. If the finger is slowly warmed by replacing the liquid nitrogen by methane, the yellow color suddenly disappears at −178° and the smooth condensate blisters and cracks over the entire surface. The change is strongly exothermic as shown by the vigorous boiling of the methane in the cold finger. Furthermore, a gas is given off and when analyzed on the mass spectrometer was found to be almost pure nitrogen. As the cold finger was warmed from −178 to −100°, more nitrogen was given off, as well as ammonia. This additional nitrogen appears to have been formed at −178° and trapped in interstices in the condensate; our evidence for this is that a heating curve of the condensate showed no abnormalities and a separate experiment showed that nitrogen is not trapped when a mixture of nitrogen, hydrazine and ammonia is passed over the finger at −195°.

The coating on the cold finger may be as thin or thick as one desires up to certain limits, depending on the temperature of the furnace and the distance of the cold finger from the end of the furnace. If the coating is made too heavy, radiation may cause the change to occur while the experiment is in progress.

Although the change of the yellow substance to white at −178° is strongly exothermic, we did not observe any emission of visible light when the change occurred. We made a qualitative test for paramagnetism with a powerful permanent magnet but did not observe any effect.

We then performed an experiment in which pure hydrazine was condensed on the finger at −195° and irradiated for 20 minutes with a quartz mercury lamp. There was no formation of yellow material and no formation of permanent gas although hydrazine commences to absorb at about 2800 Å.

In order to find the composition of the permanent gas we warmed the yellow deposit on the cold finger to −80° and then cooled the finger with liquid nitrogen. A sample of the permanent gas was analyzed on the mass spectrometer and the results of four typical experiments are shown in Table I. In these experiments we also pumped off separately and measured both the nitrogen and ammonia on the cold finger and give the results in the third line of Table I. More accurate determinations, which will be described later, show the ratio to be almost exactly six.

TABLE I

ANALYSIS OF GAS EVOLVED WHEN YELLOW MATERIAL DECOMPOSES AT −178°

| | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| $N_2$, % | 98.5 | 98.5 | 98.8 | 97.0 |
| $H_2$, % | 1.5 | 1.5 | 1.2 | 3.0 |
| $NH_3/N_2$[a] | 6.8 | 5.6 | 6.8 | 6.0 |

[a] This is the ratio of total moles of ammonia on the cold finger to moles of nitrogen evolved when the yellow material decomposes. We think that part of the ammonia was formed when the yellow material decomposed and part was formed in the furnace and frozen out on the cold finger.

**Half-life Determinations.**—In order to determine the half-life of the yellow material, we constructed a special apparatus consisting of a quartz tube about 60 cm. long fitted with a sliding furnace kept at 875°. We then made a series of runs with the furnace at different distances from the cold finger, a fixed amount of hydrazine vapor under fixed conditions passing through the furnace. The quartz tubing between the end of the furnace and the cold finger was kept at room temperature by running water. A measure of the amount of yellow material reaching the cold finger was obtained by warming it and measuring the amount of nitrogen obtained.

The rate of flow of vapor through the 60-cm. tube was obtained as follows. The time was determined for a weighed amount of hydrazine to pass through the tube under run conditions, and knowing the temperature and pressure at points along the tube, it was found that the rate of flow under our conditions was 2900 cm./sec. During runs it is necessary to agitate the liquid hydrazine in order to prevent surface cooling by evaporation. If this is not done, very erratic results are obtained. The data are listed in Table II and show that the concentration decreases to half its value in a distance of 27.3 cm. Since the flow rate is 2900 cm./sec., the half-life is $9.2 \times 10^{-3}$ sec.

TABLE II

HALF-LIFE MEASUREMENT OF YELLOW SUBSTANCE

| A[a] | B[b] | A[a] | B[b] |
|---|---|---|---|
| 25 | 0.55 | 30 | 0.47 |
| 25 | .60 | 32 | .45 |
| 25 | .54 | 32 | .44 |
| 25 | .55 | 32 | .45 |
| 25 | .45 | 32 | .46 |
| 30 | .47 | 35 | .42 |
| 30 | .45 | 35 | .40 |
| 30 | .48 | 35 | .42 |
| 30 | .48 | 35 | .41 |

[a] This column lists the distance in cm. from the end of the furnace to the cold finger. [b] This column lists the pressure of $N_2$ in mm. formed in each experiment by decomposition of the yellow material.

The yellow material has a much longer life (approximately a factor of 10) than NH[6] or $CH_3$[7] or $CH_2$,[8] being ~0.01 sec. We confirmed this qualitatively by showing that when hydrazoic acid was decomposed in our apparatus, no blue material at all was obtained under conditions that gave a considerable deposit of the yellow compound.

**Experiments with Labeled Nitrogen.**—When hydrazine is decomposed under our conditions, nitrogen is produced in the furnace as well as by the yellow substance on the cold finger when warmed to −178°. By preparing $H_2N^{15}N^{14}H_2$ and analyzing the nitrogen gas in the mass spectrometer, it would be possible to tell whether each $N_2$ molecule came from the same or different molecules of hydrazine. We made labeled hydrazine and used it in three types of experiments. First the nitrogen formed when the yellow substance changed was analyzed, second the nitrogen formed in the furnace (and pumped off) while the yellow substance was frozen on the cold finger was analyzed and third all the nitrogen was analyzed in a run made without the cold finger. Some preliminary results indicated, in all three cases, that the gaseous nitrogen, whether formed in the furnace or formed by decomposition of the yellow substance at −178°, contained $N^{14}N^{14}$, $N^{14}N^{15}$, $N^{15}N^{15}$ in proportions that showed at least partial randomization; we have not yet however established whether or not complete randomization occurred in any of the three cases. Since, however, at least some randomization of $N_2$ occurs even in the furnace it appears unlikely that further experiments with labeled nitrogen will help to establish the constitution of the yellow solid.

We found that the following is a satisfactory way to prepare anhydrous hydrazine containing one of the nitrogen atoms enriched with $N^{15}$. Enriched ammonium nitrate (only the ammonium nitrogen is enriched) was heated with an aqueous solution of sodium hydroxide and the enriched ammonia was collected in water. One equivalent of sodium hypochlorite was added to the aqueous ammonia according to the method of Raschig[9]; a little gelatin and a large excess of ordinary ammonia was then added and the mixture was heated to about 80°. The solution was neutralized with sulfuric acid, concentrated by evaporation and cooled to precipitate the rather insoluble $N_2H_4 \cdot H_2SO_4$ which could be

---

(5) T. W. B. Welsh, THIS JOURNAL, **37**, 497 (1915).

(6) F. O. Rice and M. J. Freamo, *ibid.*, **73**, 5529 (1951).

(7) F. O. Rice and W. R. Johnston, *ibid.*, **56**, 214 (1934).

(8) F. O. Rice and A. L. Glasebrook, *ibid.*, **55**, 4329 (1933).

(9) F. Raschig, *Z. anorg. Chem.*, **20**, 2068 (1907).

filtered off and dried. Anhydrous hydrazine was obtained by shaking this with liquid ammonia at −45°, filtering and evaporating off the ammonia.

**Weight Balance.**—In an attempt to establish unequivocally the nature of the yellow material we made an over-all weight balance by taking a known amount of pure anhydrous hydrazine, decomposing it according to the method described and as far as possible accounting for the undecomposed hydrazine and all the products.

During the run, the gases not condensed on the liquid nitrogen-cooled finger were pumped out of the apparatus, measured and analyzed on the mass spectrometer. This gas consisted of 50% $N_2$ and 50% $H_2$. The material on the cold finger was then slowly warmed to room temperature and condensable material was frozen out by re-cooling the finger back to −195°. The almost pure nitrogen formed by decomposition of the yellow material was pumped off and measured. The material now left on the cold finger ($N_2H_4$ + $NH_3$) was determined in the following way. Dry air was admitted to the apparatus, the condensate was washed out and the total base (hydrazine and ammonia) was determined[10] by titrating with 0.5 *N* HCl to a brom cresol green end-point. The hydrazine in the solution was determined by oxidation with $KIO_3$[11] and the ammonia was calculated by difference. The results are shown in Table III.

TABLE III

THERMAL DECOMPOSITION OF HYDRAZINE

Weight balance (expressed in mmoles).

| $N_2H_4$ | | | | Products | | | | |
|---|---|---|---|---|---|---|---|---|
| Used | Recov. | % decomp. | Decomp. | $NH_3$ | Gas A[a] $N_2$ + $H_2$ | Gas B[b] $N_2$ | Total $H_2$ | Total $N_2$ |
| 22.43 | 21.55 | 3.9 | 0.88 | 1.05 | 0.36 | 0.19 | 0.18 | 0.37 |
| 23.70 | 22.10 | 6.8 | 1.60 | 1.90 | .60 | .29 | .30 | .59 |
| 29.76 | 28.53 | 4.1 | 1.23 | 1.47 | .49 | .25 | .25 | .50 |
| 11.77 | 11.03 | 6.3 | 0.74 | 0.88 | .30 | .15 | .15 | .30 |
| 10.54 | 9.80 | 9.3 | 0.74 | 0.90 | .34 | .17 | .17 | .34 |
| 10.40 | 9.85 | 9.5 | 0.55 | 0.65 | .23 | .11 | .12 | .22 |
| Mean | | | 1 | 1.2 | | | 0.21 | 0.41 |

[a] Gas A was formed in the furnace and consisted of 50% $H_2$ and 50% $N_2$. [b] Gas B was formed by decomposition of the yellow material at −178°.

## Discussion and Conclusions

We have not been able to establish with any degree of certainty either the constitution of the yellow material or the mechanism of the decomposition in the furnace. The following stoichiometric equation expresses the over-all reaction after decomposition of the yellow substance

$$5N_2H_4 \longrightarrow 6NH_3 + 2N_2 + H_2$$

In the circumstances we propose the following mechanism which we believe is reasonable and in accord with the over-all stoichiometric reaction[12]

$$N_2H_4 \longrightarrow NH_2 \qquad (1)$$

$$NH_2 + N_2H_4 \longrightarrow NH_3 + NH_2NH \qquad (2)$$

$$NH_2NH \longrightarrow NH_2NHNHNH_2 \qquad (3)$$

$$NH_2NHNHNH_2 \longrightarrow 2NH_3 + N_2 \qquad (4)$$

$$NH_2 + HNNH_2 \longrightarrow NH_3 + N_2 + H_2 \qquad (5)$$

The first two steps very probably represent the initial part of the homogeneous thermal decomposition of hydrazine. We have not been able to establish unequivocally the fate of the hydrazino radical. It may reach the liquid nitrogen cooled surface and be frozen there as the radical or it may combine, at the surface, with itself to form tetrazane. The absence of paramagnetism would favor the second hypothesis. There is also the possibility that hydrazino radicals may, at least in part, combine in the gas phase to form tetrazane which would be frozen out on the liquid nitrogen cooled surface. The rather long life of the hydrazino radicals might be due to this effect.

The evolution of practically pure nitrogen when the yellow compound decomposes at −187° makes it certain that the nitrogen formation is accompanied by ammonia production[13] and the most reasonable explanation is that the nitrogen originates from two hydrazino radicals either directly or indirectly through the intermediate formation of tetrazane. While we cannot rule out the possibility that the yellow material is condensed $NH_2$, we think this is unlikely because of (1) the difficulty of finding a plausible explanation for the production of almost pure nitrogen when the yellow material decomposes at −178° and (2) because $NH_2$ radicals are very probably largely removed in the furnace by the reaction $NH_2 + N_2H_4 \rightarrow NH_3 + NH_2NH$.

Our experiments with hydrazine containing $N^{15}$ were directed toward finding whether or not the nitrogen formed in the decomposition of the yellow compound came from two different molecules of hydrazine. Actually we did not succeed in doing this because we found that nitrogen formed in the furnace in the thermal decomposition of $N^{15}H_2N^{14}H_2$ was, at least partly, randomly mixed. We think that the mixing is due to some such radical reaction as

$$N^{15}H_2 + HNN^{14}H_2 \longrightarrow N^{15}H_2NH + N^{14}H_2$$

According to our experiments the yield of yellow material, based on the hydrazine decomposed, is quite high. In the six experiments listed in Table III, the percentage of hydrazine decomposed varied from 4 to 10 and the amount of yellow material collected on the cold finger varied from 36 to 46% of the hydrazine decomposed. In making this calculation we assumed that each atom of nitrogen in gas B corresponded to one molecule of hydrazine decomposed.

WASHINGTON, D. C.

---

[10] R. A. Penneman and L. F. Audrieth, *Anal. Chem.*, **20**, 1058 (1948).

[11] I. M. Kolthoff, THIS JOURNAL, **46**, 2009 (1924).

[12] The elementary steps add up to the stoichiometric equation if reactions 1 and 3 are multiplied by 2 and reaction 2 is multiplied by 3.

[13] At −178°, the ammonia would remain frozen on the cold finger.