The average ratio in the first eleven analyses where the trichloride was dissolved in five molecules of sodium hydroxide is 3.25827, while the average in the remaining experiments where four molecules were used is 3.25815. The first four experiments give the average result 3.25840, while in the last thirteen where the quantity of material used was more than twice as large, the average is 3.25819, but two of the first four experiments give results essentially identical with the average of the last thirteen.

In the last four experiments the air current was passed over heated iodine pentoxide before entering the bottling apparatus, and as has been stated in these experiments the iodine pentoxide prepared for the analysis remained colorless. The average ratio found in these experiments is however only slightly lower than the average of all.

If the atomic weight of iodine is assumed to be 126.917, as recently determined by Hönigschmid,[8] the atomic weight of arsenic calculated from the average ratio obtained in all the reliable experiments is 74.916. If the first four, which may be looked upon as preliminary, are omitted, the result is 74.911, while the last four experiments yield 74.906.

This work confirms the conclusion recently reached by Baxter, Shaefer, Dorcas and Scripture[1] from analyses of arsenic trichloride and tribromide that the atomic weight of arsenic is not far from 74.91, and makes improbable the recent suggestion of Baxter and Butler[6] that iodine pentoxide does not possess normal composition.

[8] Hönigschmid and Striebel, *Z. physik. Chem.*, Bodenstein Festband, 283 (1931); *Z. anorg. Chem.*, **208**, 53 (1932).

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Anhydrous Hydrazine. VI.[1,2] Hydrazine Trinitride Monohydrazinate, $N_2H_5N_3 \cdot N_2H_4$

BY A. L. DRESSER AND A. W. BROWNE WITH MICROSCOPICAL STUDIES BY C. W. MASON

Of all the chemical elements, no other two display in their binary compounds with each other so wide a range of chemical character as do nitrogen and hydrogen in their limited series of combinations. The compounds thus far isolated may be classified as (1) basic, (2) acidic, (3) saline, and (4) solvated saline hydronitrogens. In the first of these groups

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[1] For the earlier articles of this series see (a) Hale and Shetterly, THIS JOURNAL, **33**, 1071 (1911); (b) Welsh, *ibid.*, **37**, 497–508 (1915); (c) Welsh and Broderson, *ibid.*, **37**, 816 (1915); (d) Welsh and Broderson, *ibid.*, **37**, 825 (1915); (e) Dresser and Browne, *ibid.*, **53**, 4235 (1931).

[2] The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University. The present paper is Article No. 2 under Heckscher Grant No. 158. For references to earlier articles published under Heckscher Grants No. 4 and No. 60 see THIS JOURNAL, **52**, 2799 (1930), footnote 1; 2806 (1930), footnote 2. Original manuscript received April 23, 1932.

are ammonia and hydrazine; in the second, hydronitric acid, and in the third, ammonium trinitride and hydrazine trinitride.

The first solvated saline hydronitrogen to be described is ammonium trinitride diammonate, prepared in this Laboratory by Browne and Houlehan.[3] In connection with his discussion of the ammonia system of acids, bases, and salts, E. C. Franklin[4] has declared that this "ammonia addition product of ammonium trinitride of the formula $NH_4—N{=}N{\equiv}N\cdot 2NH_3$ is isomeric with nitrogen pentamide or may even be this compound itself."

The existence of a monammonate of ammonium trinitride was noted in this Laboratory by F. Friedrichs.[5] In conformity with the Franklin system of nomenclature these compounds might be regarded, respectively, as orthoammononitric acid and triammonium normal ammononitrate.

In the present article is described a fifth solvated saline hydronitrogen, hydrazine trinitride monohydrazinate, $N_2H_5N_3\cdot N_2H_4$, first obtained in this Laboratory by H. E. Riegger.[6] This compound is empirically isomeric with normal hydrazonitrous acid (3-hydrazinopentazane), and with heptazane.

Hydrazine Trinitride

Preparation.—This substance was first prepared[7] by treatment of (a) ammonium trinitride or (b) a concentrated aqueous solution of hydronitric acid with hydrazine hydrate. Riegger[6] acidified a solution of anhydrous hydrazine in ethanol with an ethereal solution of hydronitric acid. This method was employed throughout the present research.

Analysis.—(a) Hydrazine was determined by titration in moderately concentrated hydrochloric acid with standard potassium bromate by the method of Kolthoff;[8] (b) hydronitric acid, after distillation from dilute sulfuric acid, by weighing as silver trinitride.

Anal. (a) Subs., 0.1349, 0.0848. Calcd. for $N_2H_5N_3$: N_2H_4, 42.69. Found: N_2H_4, 42.75, 42.80. (b) Subs., 0.2710, 0.2302. AgN_3, 0.5362, 0.4526. Calcd. for $N_2H_5N_3$: N_3, 57.31. Found: N_3, 56.8, 56.5.

Properties.—Hydrazine trinitride is a deliquescent white solid, extremely soluble in water, from which it is precipitated in fine needles by addition of ethanol. At 23°, 100 g. of solvent will dissolve the following weights of the compound: anhydrous hydrazine, 190 g.; methanol, 6.1 g.; ethanol, 1.2 g. The salt is not appreciably soluble in chloroform, carbon tetrachloride, benzene, carbon disulfide, ethyl acetate, or diethyl ether. It reacts readily with benzaldehyde and with acetone.

The melting point of hydrazine trinitride was first reported by Curtius[7] to be 50°,

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[3] Browne and Houlehan, (a) THIS JOURNAL, **33**, 1742 (1911), footnote 1, p. 1745; (b) *ibid.*, **35**, 649 (1913).

[4] Franklin, *Orig. Com. Eighth Intern. Congr. Appl. Chem.*, **6**, 119 (1912).

[5] Ref. 3b, p. 657; see also THIS JOURNAL, **38**, 288 (1916), footnote 1. Some evidence of the existence, at low temperatures, of a higher ammonate, at first supposed to be the tetrammonate, was also obtained by Friedrichs. More recent work in this Laboratory by D. H. Howard, Jr., has, however, conclusively demonstrated the existence of a pentammonate, of the formula $NH_4N_3\cdot 5NH_3$. An ammonate of hydrazine trinitride having the formula $2N_2H_5N_3\cdot NH_3$ has also been obtained by Howard.

[6] See Browne and Wilcoxon, *ibid.*, **48**, 682 (1926), footnote 13.

[7] Curtius, *Ber.*, **24**, 3341 (1891).

[8] Kolthoff, THIS JOURNAL, **46**, 2009 (1924).

and later by Curtius and Rissom[9] to be 65°. In a capillary tube the salt was observed by the authors to melt at 74°, and in the larger apparatus at 75.4°, which is undoubtedly the most accurate value yet obtained. Heated in a sealed, evacuated tube for ten days to 84°, a sample of hydrazine trinitride sublimed completely to the cooler end, held at room temperature. Determinations of hydrazine in the sublimate, which was obtained in the form of large, very thin plates, yielded the following results.

Anal. Subs., 0.0486, 0.0632. Calcd. for $N_2H_5N_3$: N_2H_4, 42.69. Found: N_2H_4, 42.8, 42.6.

Hydrazine trinitride in the pure state is a relatively stable substance. Heated to 110° *in vacuo* for several days, it showed only very slight decomposition. Thrown upon a hot-plate or a red hot metallic gauze, it burns with a puff, but without detonation. It appears to be entirely insensitive to ordinary mechanical shock or impact. No explosion of the substance has occurred throughout the present investigation, as the result of either accident or design.

Under the microscope, prisms and elongated tablets are obtained by evaporation of an aqueous solution of hydrazine trinitride. If the direction of the *c* axis is taken as parallel to the elongation, and that of the *b* axis as transverse of the tablets, the following forms are present: 100, 001, 110, 101; 011 faces may truncate the ends of the crystals, making terminal angles of about 85°.

All views of the crystals exhibit parallel extinction, and end views yield a biaxial positive interference figure, with $B_{x_a} = C$ and axial plane = 100. 2 *V* is about 75°.

On account of the extreme solubility and deliquescence of the material, refractive index determinations are incomplete. For vibrations crosswise of the prisms *n* is about 1.53; for vibrations lengthwise, about 1.76.

Hydrazine Trinitride Monohydrazinate, $N_2H_5N_3 \cdot N_2H_4$

Preparation.—By treatment of a nearly saturated solution of hydrazine trinitride in anhydrous hydrazine with an equal volume of absolute ethanol, hydrazine trinitride monohydrazinate was obtained in the form of white crystals. The precipitate was quickly filtered, washed with small amounts of ethanol, dried *in vacuo* over sulfuric acid, and stored over calcium chloride in an atmosphere of nitrogen.

Anal. (a) Subs., 0.0436, 0.0436. Calcd. for $N_2H_5N_3 \cdot N_2H_4$: N_2H_4, 59.83. Found: N_2H_4, 59.93, 59.93. (b) Subs., 0.2639, 0.2199: AgN_3, 0.3732, 0.3132. Calcd. for $N_2H_5N_3 \cdot N_2H_4$: N_3, 40.17. Found: N_3, 39.65, 39.93.

Properties.—Hydrazine trinitride monohydrazinate is a white, crystalline solid, extremely deliquescent, very soluble in water and in anhydrous hydrazine. Its melting point was found to be 66.4°.

Under the microscope, the monohydrazinate crystallizes as prisms the long direction of which may be taken as the *C* axis. The crystals are flattened on 010, and sometimes beveled by 110. The end face 001 is slightly oblique, making an angle of about 87° with the long edge. Occasionally the faces 011 and 101 truncate the edges of the crystals.

Double refraction is strong; parallel extinction is exhibited by prisms seen edgewise, and oblique extinction at an angle of about 6° by those seen flatwise. Multiple lamellar twinning on 100 is common in the larger crystals, and hinders the observation of interference figures and optical constants. The material is biaxial, with 2 *V* large and B_{x_a} probably parallel to *C*; optical character is probably positive. The refractive indices are approximately as follows: α (vibrations lengthwise of prisms lying flat), 1.50; β (vibrations crosswise of prisms lying flat), 1.60; γ (vibrations crosswise of prisms lying on edge), 1.67.

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[9] Curtius and Rissom, *J. prakt. Chem.*, [2] **58**, 261 (1898).

Temperature–Concentration Diagram for the System Hydrazine Trinitride, Hydrazine

In order to establish the chemical identity of the monohydrazinate and to ascertain whether or not higher solvates are capable of existence the temperature–concentration diagram for the system hydrazine trinitride, hydrazine was investigated. For this work a specially designed melting point apparatus was used. Throughout the determinations the system was thoroughly agitated by means of a motor-driven stirrer operating through a mercury seal. Whenever the thermometer was withdrawn for the purpose of introducing additional amounts of either solute or solvent the apparatus was swept out with a current of dry nitrogen gas.

The data obtained are recorded in Table I, and are plotted in Fig. 1.

TABLE I

TEMPERATURE–CONCENTRATION DATA FOR THE SYSTEM HYDRAZINE TRINITRIDE, HYDRAZINE

% N_2H_4	Temp., °C.	% N_2H_4	Temp., °C.	% N_2H_4	Temp., °C.
0.0	75.4	29.7	66.4	62.1	31.5
6.0	67.5	35.1	66.0	67.2	18.5
10.9	55.4	40.5	63.8	72.0	3.1
16.2	58.8	45.1	60.2	75.2	− 8.5
22.6	65.0	51.2	52.7	85.0	− 7.8
26.2	66.2	57.1	43.4	92.9	− 2.0
				100.0	+ 1.0

From these data it is obvious that the monohydrazinate is the only solvate formed in the system hydrazine trinitride, hydrazine. The eutectics are at 51 and −17.5°.

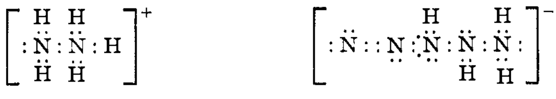
Structure.—Hydrazine trinitride and its monohydrazinate tend to dissociate in aqueous solution as follows

$$N_2H_5N_3 \rightleftharpoons N_2H_5^+ + N_3^-$$
$$N_2H_5N_3\cdot N_2H_4 + H_2O \rightleftharpoons 2N_2H_5^+ + N_3^- + OH^-$$

In the fused state both conduct the electric current readily, undergoing electrolysis, with liberation of gas at both electrodes. It is therefore probable that these substances in crystalline form are ionized lattices. Hydrazine trinitride might therefore be formulated as follows

$$\left[\begin{array}{c} \mathrm{H}\quad\mathrm{H} \\ :\ddot{\mathrm{N}}:\ddot{\mathrm{N}}:\mathrm{H} \\ \mathrm{H}\quad\mathrm{H} \end{array}\right]^{+} \qquad \left[:\dot{\mathrm{N}}::\mathrm{N}::\underset{..}{\mathrm{N}}:\right]^{-}$$

while the additional hydrazine molecule of the hydrazinate may be joined by coördinate linkage either to the hydrazinium ion or to the trinitride ion. In the latter case it is conceivable that the hydrazinated trinitride ion might be regarded as a pentazene-1 ion, and that hydrazine trinitride monohydrazinate might be formulated as the hydrazine salt of pentazene-1



$$\left[\begin{array}{c} \mathrm{H}\quad\mathrm{H} \\ :\ddot{\mathrm{N}}:\ddot{\mathrm{N}}:\mathrm{H} \\ \mathrm{H}\quad\mathrm{H} \end{array}\right]^{+} \qquad \left[\begin{array}{c} \qquad\qquad\ \mathrm{H}\qquad\ \ \mathrm{H} \\ :\ddot{\mathrm{N}}::\underset{..}{\mathrm{N}}:\underset{..}{\ddot{\mathrm{N}}}:\ddot{\mathrm{N}}:\ddot{\mathrm{N}}: \\ \qquad\qquad\qquad\ \ \mathrm{H}\quad\ \mathrm{H} \end{array}\right]^{-}$$

Whether or not the empirical isomerism of these two compounds with the ortho and normal hydrazonitrous acids is of significance in connection with their structure is a question that cannot be definitely answered until further experimental evidence is available.

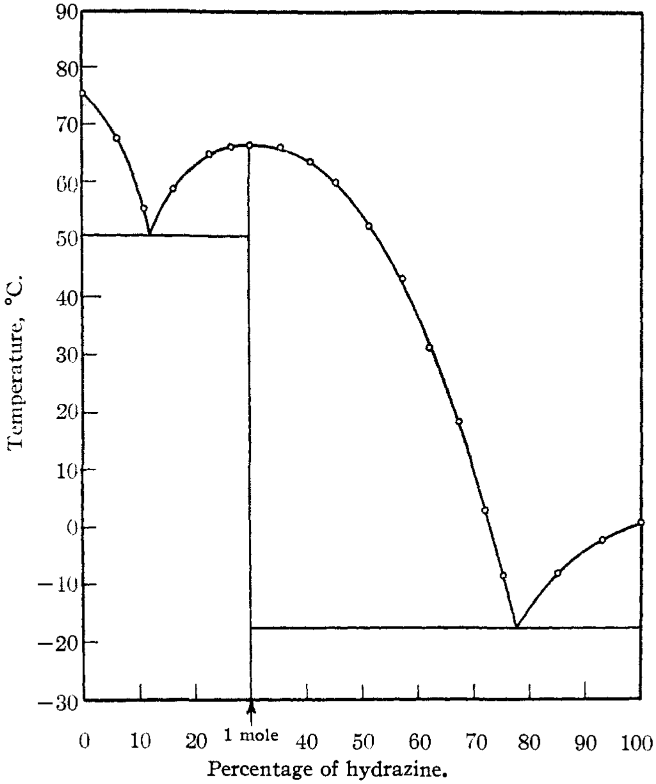


Fig. 1.—Temperature-concentration diagram for the system hydrazine trinitride, hydrazine.

Summary

Temperature-concentration relations in the binary system hydrazine trinitride, hydrazine have been investigated. One solvate, *hydrazine trinitride monohydrazinate*, $N_2H_5N_3 \cdot N_2H_4$ (m. p. 66.4°), has been isolated and described. Eutectics were located at 51 and −17.5°. Pure hydrazine trinitride was found to melt at 75.4°. Crystallographic data for both the salt and the solvate have been determined.

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