[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, OREGON STATE COLLEGE]

The Iodides of Hydrazine[1]

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A study of the unusual compound $(N_2H_4)_3(HI)_2$ is reported including its temperature and pressure stabilities, together with infrared absorption data for it and for hydrazine monoiodide. Attempts to prepare anhydrous hydrazine diiodide were not successful but led to the preparation of a new hydrate, $N_2H_6I_2 \cdot 2H_2O$.

Introduction

Among all the inorganic salts of hydrazine the compound $(N_2H_4)_3(HI)_2$ is unique in its stoichiometric proportions, having neither the simple ratio of 1–1 or 1–2 shown by all others. It was first prepared by Curtius and Schulz,[2] who proposed a rather complicated ring structure for its constitution. The present work was initiated to elucidate the structure of the compound and to examine its properties. It was extended to include also a study of the compound hydrazine diiodide, $N_2H_6I_2$ (or $N_2H_4 \cdot 2HI$) concerning which the literature references are few, conflicting or inaccurate.[3] In so doing the existence of a compound, the hydrate, $N_2H_6I_2 \cdot 2H_2O$, not previously reported, was established.

Experimental

Materials.—Hydrazine hydrate, 85 or 100%, Fisher and Kahlbaum, and hydriodic acid 50%, Merck reagent grade, were used as supplied commercially.

Fuming HI, sp.gr. 2.0, was prepared by absorption of anhydrous HI in water.

Anhydrous HI was prepared by the method of Dillon and Young,[4] using 50% HI as the starting material.

Analytical Methods.—The presence of iodide limited the analyses for hydrazine practically to one method, namely, titration with free iodine in presence of a buffer. This method has been demonstrated to give quantitative results if the buffer is Na_2HPO_4.[5] The method was standardized by the use of pure hydrazine sulfate.

Iodide was determined by titration with standard silver nitrate using dichlorofluorescein as indicator. Solutions containing free acid always were brought to neutrality before titration.

Infrared spectroscopy was used to study the structure of the $(N_2H_4)_3 \cdot (HI)_2$ in its relation to hydrazine monoiodide. A Perkin–Elmer Model 112 double pass instrument was used with NaCl prism. The iodides were incorporated in KI pressed windows.

Hydrazine Monoiodide.—This compound, N_2H_5I (or $N_2H_4 \cdot HI$), reported first by Curtius and Schulz,[2] has been prepared by various methods, many of which were repeated by us with success. In view of the ready availability of pure hydrazine and hydriodic acid, however, the direct method is simple and preferable. To hydrazine hydrate 85–100%, diluted with ethanol, is added (with cooling) concentrated HI until a *p*H of approximately 2.0 is attained.

The salt precipitates at once and upon recrystallization from absolute ethanol is pure, m.p. 124–126°. It is entirely stable over a period of months.

Anal. Calcd. for N_2H_5I: I, 79.3. Found: I, 78.8, 79.3, 78.9.

Trihydrazine Dihydriodide.—Many devious methods have been used for the preparation of this salt but direct combination of hydrazine and hydriodic acid in ethanol, at a *p*H of 8–9, gives beautiful crystals of the compound which can be recrystallized from ethanol in excellent yield, m.p. 90–92°. In a closed bottle this compound was stable, as analysis at repeated intervals showed no deterioration over a 6 month period.

Anal. Calcd. for $(N_2H_4)_3(HI)_2$: N_2H_4, 27.30; I, 72.1. Found: N_2H_4, 27.45, 27.25; I, 71.5, 72.0, 71.7, 72.7.

The compound does not exist in solution. Hydrazine hydrate and hydriodic acid were titrated potentiometrically and conductimetrically both in concentrated aqueous solution and in 80% ethanol. Only one break in the curves was observed, corresponding to the formation of hydrazine monoiodide.

The hydrazine is very strongly held in the crystalline compound. Evacuation to a pressure of 25 μ for 5.5 hr. at room temperature gave no detectable loss in weight.

Duplicate samples of the material were placed in porcelain boats in an Abderhalden pistol at 56°. After heating for 2 hr. at a pressure of about 0.05 mm. there showed a loss in weight of less than 1%. At 80.1° in the same apparatus and pressure, 5 hr. of heating caused a weight loss corresponding to conversion to hydrazine monoiodide. Analysis, and the melting point of the residue, 125–126°, confirmed the observation. On the other hand, heating for 2 hr. at atmospheric pressure at the same temperature gave no detectable loss in hydrazine and the melting point was unchanged. The temperature needed for rapid removal of the hydrazine is within 10° of the melting point of the compound showing the stability of the bonds retaining the hydrazine in the solid structure. Three samples were now evacuated at 80.1°, one being withdrawn after 30 minutes heating, one after 90 minutes and one after 135 minutes.

Analysis showed conversions of 6.1, 32.0 and 68.8% to hydrazine monoiodide. Examination of these products and of pure samples of the two separate compounds by infrared absorption further confirmed these change.

The infrared absorption maxima observed for samples of N_2H_5I and $(N_2H_4)_3 \cdot (HI)_2$ are listed in Table I and are compared with those of N_2H_5Br.[6] Although the spectra of the two iodides are readily distinguishable, they resemble one another more closely than do those of N_2H_5Br and $N_2H_6Br_2$. It is therefore possible to conclude that no $N_2H_6^{++}$ ions exist in the salt with the formula $(N_2H_4)_3 \cdot (HI)_2$. The 3:2 compound is therefore best formulated as $(N_2H_5^+I^-)_2 \cdot N_2H_4$, wherein the neutral hydrazine molecule is probably hydrogen bonded to the $N_2H_5^+$ ions. In analogy to the studies of Watt,[7] on the ammoniates of the ammonium halides it seems probable that this unusual salt is a hydrazinate.

Hydrazine Diiodide.—There are only two references in the literature indicating successful preparation of this compound.[2,3,8] Von Rothenberg reported that reaction of methyl iodide in ethanol with hydrazine hydrate gives hydrazine diiodide. He gave analyses for the product and reported a melting point of 220°.

Duplication of this method by the authors yielded a white compound which softened at 122°, the melting point of hydrazine monoiodide and decomposed at 200°. The product was found to be neutral, not acid, and contained carbon as was shown by charring, indicating that some methylation had occurred. Harries and Haga[9] reported results similar to ours.

Curtius and Schulz[2] emphasized that the desired compound could be prepared successfully only by the decomposition of benzalazin with fuming HI. These authors report analytical results and a melting point of 220°. Attempts to

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[1] Financial aid for this work was provided by the General Research Council of this College. Research paper #331, School of Science, Department of Chemistry.

[2] T. Curtius and H. Schulz, *J. prakt. Chem.*, **42**, 521 (1890).

[3] "Gmelins Handbuch der Anorganische Chemie," 8th Ed., Verlag Chemie, Berlin, 1936, System #23, p. 559.

[4] R. T. Dillon and W. G. Young, THIS JOURNAL, **51**, 2389 (1929).

[5] E. C. Gilbert, *ibid.*, **46**, 2648 (1924).

[6] J. C. Decius and D. P. Pearson, *ibid.*, **75**, 2436 (1953).

[7] G. W. Watt and W. R. McBride, *ibid.*, **77**, 1317 (1955).

[8] R. von Rothenburg, *Ber.*, **26**, 865 (1893).

[9] C. Harries and T. Haga, *ibid.*, **31**, 56 (1898), discarded the method as inaccurate.

repeat their work with HI, sp. gr. 1.60, 1.85 and 2.0, failed. At ordinary temperatures a yellow compound was formed which was not soluble in water but melted at about 165°. At high temperatures a lachrymator was formed. Attempts to extract the benzaldehyde with organic solvents gave no better success. (Extraction with alcohol is of course not feasible as it immediately precipitates hydrazine monoiodide.) This is the only hitherto undisputed method of preparation for this compound, and since it involves an aqueous medium it seems very unlikely that the compound they obtained was other than the compound we have now prepared below.

TABLE I

INFRARED ABSORPTION MAXIMA FOR SEVERAL HYDRAZINE HALIDES (CM.$^{-1}$)

$(N_2H_4)_3 \cdot (HI)_2$	N_2H_5I	N_2H_5Br
941		
958	958	965
1098	1080	1095
1118		1100
	1236	1243
	1403	1410
	1493	1491
	1573	1568
2010		
2130		
	2556	2575
	2659	2690
2945		
3075	3037	
3300	3280	3250

In the light of our other work the m.p. of 220° looks unreasonable.

Hydrazine Diiodide Dihydrate.—Addition of fuming HI, sp. gr. 2.0, to a saturated water solution of hydrazine monoiodide with cooling resulted in the immediate formation of a white compound composed of small clear prisms, distinctly different from the needle-form of hydrazine monoiodide.[10] These crystals were collected on a fritted glass filter, and pressed with a rubber dam to remove as much liquid as possible. Washing with alcohol or water will remove the second molecule of HI leaving only hydrazine monoiodide. They were placed in a desiccator over KOH pellets for about 3–4 hours and analyzed. The material is extremely hygroscopic. In a sealed capillary the compound melts at 65–66°.

Anal. Calcd. for $N_2H_6I_2 \cdot 2H_2O$: N_2H_4, 9.9; HI, 79.0; mol. wt., 324. Found: N_2H_4, 9.8, 10.6, 9.82; HI, 78.3, 81.2, 80.5; mol. wt. by titration with 0.02 *N* NaOH, 329, 332, 325.

For the determination of molecular weight, advantage was taken of the fact that in all hydrazine salts containing two equivalents of acid the second equivalent can be titrated to a neutral end-point with base.

This compound has not been reported previously in the literature but might be expected to exist by analogy to the hydrazine dibromide dihydrate.[11]

Standing for 24 hours over KOH removes both the water and second molecule of HI leaving hydrazine monoiodide.

The water of hydrazine dibromide dihydrate can be removed by standing over P_2O_5,[11] but unfortunately this is not true for the iodide. If an attempt is made to dehydrate the compound in this manner, HI and water are lost simultaneously. An anhydrous hydrazine diiodide is not obtained.

Dehydration cannot be effected with ethanol; dehydration with dioxane was also unsuccessful.

In a final attempt to synthesize anhydrous hydrazine diiodide two methods were used. (a) Gaseous dry HI was passed through a slurry of hydrazine monoiodide in benzene and also in chloroform. No formation of the diiodide took place. (b) Anhydrous HI was condensed on hydrazine monoiodide at the temperature of a Dry Ice–acetone bath. The temperature was then raised to −25° to remove excess HI. The residue proved to be unchanged hydrazine monoiodide.

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[10] If anhydrous ether is added to a cold saturated solution of hydrazine monoiodide in 50% HI, it separates first into three layers. On scratching with a rod the material crystallizes but is unfortunately a mixture of the hydrated crystals with some hydrazine monoiodide. The mixture cannot be separated.

[11] E. C. Gilbert, THIS JOURNAL, **57**, 2611 (1935).

[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS EXPERIMENT STATION, REGION II, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Heats of Formation of Niobium Dioxide, Niobium Subnitride and Tantalum Subnitride

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The energies of combustion of niobium dioxide (NbO_2), niobium subnitride (Nb_2N) and, tentatively, tantalum subnitride (Ta_2N) were determined by bomb calorimetry. The results, in conjunction with the heats of formation of the corresponding pentoxides, lead to the following standard heats of formation at 298.15°K. (kcal./mole): NbO_2, −190.9 ± 0.4; Nb_2N, −61.1 ± 1.0; and Ta_2N, −64.7 ± 3.0 (tentative).

Previous papers from this Laboratory have dealt with heats of formation of the pentoxides[2] of niobium and tantalum and the nitrides[3] of composition NbN and TaN. The present paper reports energies of combustion and heats of formation of niobium dioxide and the subnitrides of composition Nb_2N and Ta_2N. As is usually the case with refractory nitrides, the purity of the available samples of these subnitrides leaves much to be desired. This is especially true of the tantalum compound for which only tentative values are reported. No previous similar measurements exist for any of these compounds.

Materials.—Niobium dioxide was prepared by K. C. Conway of this Laboratory from high purity niobium pentoxide obtained from Fansteel Metallurgical Corp. Small patches of the pentoxide were reduced in hydrogen at 950–1000° for 4 hours. These were combined and heated again in hydrogen for another 4 hours at the same temperature. Completion of the reactions was demonstrated by heating a portion of the product to 1450° in hydrogen and observing no weight change. Analysis by reconversion to the pentoxide indicated 99.90% niobium dioxide. Analysis by dissolving, precipitating the niobium as hydroxide and igniting to constant weight showed virtually 100.00% niobium dioxide. The X-ray diffraction pattern agreed with that of Brauer.[4]

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[1] Bureau of Mines, U. S. Department of the Interior, Region II, Berkeley, California.

[2] G. L. Humphrey, THIS JOURNAL, **76**, 978 (1954).

[3] A. D. Mah and N. L. Gellert, *ibid.*, **78**, 3261 (1956).

[4] G. Brauer, *Z. anorg. allgem. Chem.*, **248**, 1 (1941).