was recrystallized from methanol and sublimed *in vacuo* to give a white crystalline product, m.p. 50–51°.

Anal. Calcd. for $C_6H_5ClN_2O_2$: N, 16.2. Found: N, 16.2.

5-Methyl-3-nitro-2-pyridinethiol.—To a solution of 10 g. of potassium hydroxide in 100 ml. of methanol and saturated with hydrogen sulfide, 10 g of 2-chloro-5-methyl-3-nitropyridine was added in portions. After the vigorous reaction had subsided, the mixture was allowed to stand for five minutes, cooled, treated with 100 ml. of water, acidified with acetic acid, and thoroughly chilled. The product which separated at this point was contaminated with sulfur and hence was dissolved in hot, dilute ammonium hydroxide, filtered, and reprecipitated with acetic acid to give 2.5 g. of a yellow powder. The filtrate slowly deposited 0.1 g. of an orange substance melting at 240°, presumably the disulfide (see below). Recrystallized from 95% ethanol, the thiol appeared as fine yellow needles which decomposed slowly above 170°. On rapid heating, it was completely melted at about 200°.

Anal. Calcd. for $C_6H_6N_2O_2S$: N, 16.5; S, 18.8. Found: N, 16.5; S, 19.0

Five tenths of a gram of this disulfide was dissolved in 10 ml. of 5% sodium hydroxide and treated with a solution of 0.4 g. of iodine in alcohol to form 0.2 g. of **bis-(5-methyl-3-nitro-2-pyridyl) disulfide** an orange compound melting at 246° with decomposition after crystallization from benzene.

Anal. Calcd. for $C_{12}H_{10}N_4O_4S_2$: N, 16.6; S, 18.7. Found: N, 16.6; S, 18.9.

5-Methylpyrido[3,2-d]thiazole.—A suspension of 400 mg. of 5-methyl-3-nitro-2-pyridinethiol in 12 g. of 85% formic acid containing 3 g. of iron filings was boiled vigorously for 1.5 hours, cooled, made basic, and extracted with ether.

The ether was evaporated and the residue sublimed *in vacuo* to yield 90 mg. of pale yellow crystals melting at 85–87°. A solution of the compound in methanol after treating with Norite, evaporating, and resubliming gave rise to white crystals melting at 85.5–87.5°. The compound had an odor resembling that of quinoline and turned yellow after standing for a few days.

Anal. Calcd. for $C_7H_6N_2S$: N, 18.7; S, 21.3. Found: N, 18.6; S, 21.4.

2,5-Dimethylpyrido[3,2-*d*]thiazole.—The reduction of 5-methyl-3-nitro-2-pyridinethiol with iron or zinc or of bis-(5-methyl-3-nitro-2-pyridyl) disulfide with iron followed by treatment with acetic anhydride apparently gave rise to the desired compound, but repeated crystallization and sublimation failed to give a product of satisfactory melting point or analysis. Thus, 1.0 g. of 5-methyl-3-nitro-2-pyridinethiol, 25 g. of acetic acid, 1.0 ml. of concentrated hydrochloric acid and 3 g. of iron filings were refluxed for 1.5 hours. After adding 11 g. of acetic anhydride, the mixture was boiled for an additional 15 minutes. The product was obtained by making the solution basic, distillation with steam, and extraction of the distillate with ether. Sublimation afforded 0.1 g. of white crystals which softened at 55° and melted from 63 to 66°. The most pure product obtained after resublimation softened at 63° and melted at 67.5–69.5° and retained an odor resembling that of quinoline.

Anal. Calcd. for $C_8H_8N_2S$: N, 17.1; S, 19.5. Found: N, 16.9; S, 18.9.

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RECEIVED MARCH 9, 1951

The Nature of the Vapor State of Hydrazine Monohydrate and Ethylenediamine Monohydrate

BY LOWELL V. COULTER

Experimental investigations of the vapor state of hydrazine monohydrate have led to contradictory conclusions regarding the extent of association in the vapor phase. Scott[1] has reported vapor densities at 99°, 367 mm. pressure and 138°, 744 mm. pressure that correspond to molecular weights of 31.8 and 25.0, respectively. These observations have been explained by Yost and Russell[2] by the dissociation equilibrium

$$N_2H_4\cdot H_2O(g) \rightleftarrows N_2H_4(g) + H_2O(g)$$

Infrared absorption spectrum measurements[3] indicate, however, that no monohydrate species is present since the spectrum consists of the superposition of the spectra of hydrazine and water.

In view of the opportunity this system might afford for a study of the energy of a gaseous N······H-O hydrogen bond system, an exploratory study of vapor densities was conducted. Within the limits of error of these measurements it appears that the earlier observation, indicating association of water and hydrazine in the gas phase, was in error because of adsorption of vapors on the walls of the apparatus or the lack of complete volatilization of the sample in the Victor Meyer procedure. The results of this research indicate no appreciable association between hydrazine and water or ethylenediamine and water in the gas phase. The latter system was also selected for investigation because of the similarity of the two systems.

Experimental

Hydrazine monohydrate was prepared from the commercial product (National Biochemical Co.) by high vacuum distillation at room temperature and the addition of water to give an equimolecular solution of hydrazine and water. Analysis by acid titration and the iodate method[4] indicated 64.54 and 64.25% hydrazine, respectively (64.01% theoretical). The freezing point of the hydrazine monohydrate was −51.1°, which we compare with −51.7° reported by Mohr and Audrieth[5] for the freezing point. The ethylenediamine monohydrate was prepared from a purified commercial product by the quantitative addition of water. Anhydrous ethylenediamine was obtained by drying over calcium oxide both before and after fractional distillation. The anhydrous product froze at 11.1°, to be compared with 11.0° reported by Wilson.[6] By acid titration the monohydrate analyzed 0.5013 mole fraction diamine.

The experiments involved the determination of pressure-temperature relationships at constant vapor densities. The apparatus consisted of a calibrated glass bulb with an attached Bodenstein gage,[7] sensitivity 0.2 mm., that was employed as a null instrument for pressure measurements with a mercury manometer and cathetometer. The glass bulb and attached gage were completely thermostated in an oil-bath with temperature control usually better than 0.01°.

Samples of the hydrates were transferred to the apparatus with the aid of high vacuum techniques and inert protective gases thereby avoiding exposure of the preparations to atmospheric oxygen, water and carbon dioxide. In each isochore determination the vapor pressure of the liquid was determined prior to complete vaporization in order to ascertain the sharpness of the discontinuity at the point of complete vaporization. The $P-T$ curves are presented in Fig. 1 for hydrazine monohydrate at two different pressure ranges and for ethylenediamine monohydrate at one pressure range. In drawing the vapor pressure curves of the liquid the steepness of the slope near the saturation pressure has been exaggerated in order to reveal the maximum deviation possible of observed pressures from the extrapolated curves (dotted portions).

On the basis of the pressure temperature curves it appears unlikely that any association between hydrazine or

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(1) A. Scott, *J. Chem. Soc.*, **85**, 919 (1904).

(2) D. M. Yost and H. R. Russell, "Systematic Inorganic Chemistry," Prentice Hall, Inc., New York, N. Y., 1944, p. 115.

(3) P. A Giguère, *Trans. Roy. Soc. Can.*, **35**, 1 (1941), citing E. Eyster, Thesis, Calif. Inst. Tech., Pasadena, 1938.

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

(5) P. H. Mohr and L. F. Audrieth, *J. Phys. Chem.*, **53**, 901 (1949).

(6) A. L. Wilson, *Ind. Eng. Chem.*, **27**, 867 (1935).

(7) W. E. Vaughan, *Rev. Sci. Inst.*, **18**, 192 (1947).

ethylenediamine and water occurs in the vapor phase. Over the major portion of the temperature range the pressure shows a linear dependence on the temperature in both pressure ranges studied. The only deviations to be noted are those occurring within five degrees of the saturation pressure where surface adsorption effects are likely to be important. This was demonstrated experimentally by determining the influence of an increase in the surface–volume ratio on the pressure–temperature relationship. This is illustrated by a comparison of curves III and IV of Fig. 1, in which a more pronounced deviation of the pressure is apparent near the saturation region of curve IV. The data represented by curve IV were obtained with the same sample employed in obtaining the data represented by curve III but with a 2.5-fold increase in the surface–volume ratio. The deviation of the observed pressures in the liquid range from the extrapolated vapor pressure curve appears to be a vapor pressure lowering effect resulting from the accumulation of solute in the basic solutions. Silica residues were observed in the bottom of the vapor bulb following the removal of each sample by vacuum distillation.

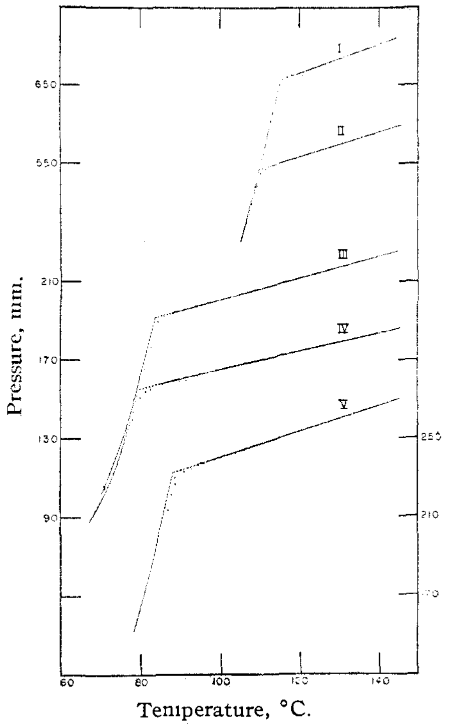

Fig. 1.—Pressure–temperature curves for hydrazine and ethylenediamine monohydrates: Curves I, II, III and IV hydrazine monohydrate; (ordinate on left); curve V ethylenediamine monohydrate (ordinate on right).

Molecular weights calculated from the observed vapor densities by means of the ideal gas law are presented in column 5 of Table I. We have included in column 6 the calculated molecular weights to be expected for the samples used in this research assuming no association of water and hydrazine in the vapor phase.

TABLE I

MOLECULAR WEIGHTS

Curve	Temperature range, °C.	Sample wt., g.	Volume, cc.	Molecular weight Obsd.	Calcd.
		Hydrazine Monohydrate			
III	92–140	0.0740	335.1	25.6 ± 0.3	25.1
IV	86–140	.7040	399.7	26.1 ± .3	25.1
I	118–140	.2376	335.2	26.1 ± .3	25.1
II	116–140	.2376	399.8	26.1 ± .3	25.1
		Ethylenediamine Monohydrate			
V	94–140	0.1343	335.1	38.7 ± .3	39.0

To what extent the 4% deviation of the molecular weight of the hydrate may be accounted for by usual non-ideal behavior is uncertain. Its constancy, however, appears to exclude the possibility of appreciable polymerization in the gas phase of the usual type.

A comparison of Scott's data with the vapor pressure curve of Fig. 1 indicates that his vapor density measurements suggesting association were probably made without complete volatilization of the sample or were accompanied by a significant surface adsorption effect.

Acknowledgment.—The author is indebted to the American Philosophical Society for financial assistance in support of this research. The technical assistance of Mr. Richard Blair is also acknowledged.

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RECEIVED FEBRUARY 5, 1951

The Effect of Aluminum Chloride on *n*-Propyl Chloride

BY THOMAS I. CROWELL AND GEORGE L. JONES, JR.

Anhydrous aluminum chloride is known to convert liquid *n*-propyl chloride to isopropyl chloride with evolution of hydrogen chloride and polymerization.[1] We have found that when small portions of aluminum chloride are added to *n*-propyl chloride, the degree of isomerization is less than 100% and depends on the proportions of the reactants. The equilibrium mixture was shown to contain 100% *i*-propyl chloride (within 0.8%), in agreement with the vapor phase data.[2] The incomplete reaction is, therefore, due to inactivation of the catalyst by the reaction products. Since amylene markedly inhibits the isomerization while hydrogen chloride has no effect, we assume that propylene forms with aluminum chloride a complex which does not promote isomerization.

A clear nitrobenzene solution of aluminum chloride also reacted with *n*-propyl chloride. This shows that solid aluminum chloride, believed necessary for chlorine exchange in carbon tetrachloride,[3] is unnecessary here.

Experimental

Anhydrous aluminum chloride was added to *n*-propyl chloride in a dry-box. Hydrogen chloride was copiously evolved and isomerization ceased within five minutes, though polymerization slowly continued. The mixture was shaken with concd. H_2SO_4 followed by water, and dried over K_2CO_3. The chlorine content of this product was 98.8% of the theoretical for propyl chloride. The samples were

TABLE I

Mole per cent. $AlCl_3$ added	Product composition *n*-PrCl, %	*i*-PrCl, %
0.10	98.0	2.0
.20	94.4	5.6
.35	91.5	8.5
.54	74.2	25.8
.90	54.6	45.4
.33[a]	0	100
.65[b]	96.9	3.1

[a] Started with 95% *i*-PrCl, 5% *n*-PrCl. [b] Added 10% amylene.

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[1] E. Wertyporoch and T. Firla, *Ann.*, **500**, 295 (1933).

[2] (a) W. Nagai, *J. Chem. Soc. Japan*, **61**, 864 (1940); (b) L. M. Nash, T. I. Taylor and W. v. E. Doering, THIS JOURNAL, **71**, 1516 (1949).

[3] See C. H. Wallace and J. E. Willard, *ibid.*, **72**, 5275 (1950).