# Part II

# PHYSICAL PROPERTIES

# EVALUATION OF COMPOUNDS AND MATERIALS

## Preparation and Storage Stability of High-Purity Hydrazine

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HYDRAZINE of high purity was necessary for recent thermal decomposition studies. Several procedures for concentrating aqueous solutions of hydrazine and for obtaining the anhydrous product have been described (*1, 7*). To avoid certain hazards, low yields, and time consuming aspects of most of these methods (*1, 8, 9*), a new procedure was adopted in which a commercial grade of anhydrous hydrazine was treated with calcium hydride in an inert atmosphere. Calcium hydride has been previously used to dry alkyl hydrazines (*4*). The method used in this work was relatively simple and did not require heating or refluxing of the hydrazine. The purity and stability of hydrazine obtained by the calcium hydride method were similar to the respective values found for hydrazine derived from the ammonolysis of hydrazine sulfate. The latter product was obtained by a procedure reported by Browne and coworkers (*2, 3*).

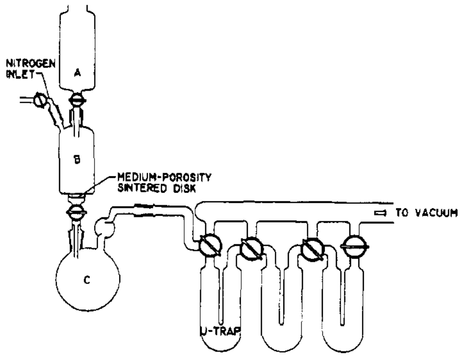

Figure 1. Apparatus used to purify commercial hydrazine

### EXPERIMENT

**Materials.** The hydrazine used was a commercial grade assaying at 95% or better. The other principal component was water. Oil-pumped nitrogen was purified by flow through the following train: copper oxide at 575° C. to destroy organic matter, Drierite and Ascarite to remove water and carbon dioxide, phosphorus pentoxide on glass beads to remove water, and copper on silica gel at 300° C. to remove oxygen.

**Apparatus and Procedure.** The apparatus used to purify commercial hydrazine with calcium hydride is shown in Figure 1. Approximately 8 grams of calcium hydride was placed on the sintered glass disk of the filtering assembly *B*. The opening was then fitted with the dropping funnel *A*, which contained 25 ml. of commercial hydrazine. The filtering assembly *B*, the bulb *C*, and the *U*-traps were then evacuated to a pressure of 1 micron of mercury. The filtering assembly was then filled with purified nitrogen, and the hydrazine was added to the hydride. The addition of hydrazine (about 25° C.) to calcium hydride resulted in an increase in temperature of 1.5° C. in the vicinity of the hydride. The temperature decreased to its initial value within 45 minutes of mixing. Gaseous products from the mild reaction were vented through the open stopcock of the dropping funnel *A*. The reaction was protected from atmospheric gases by a constant flow of purified nitrogen. After 4 hours, the hydrazine was filtered into the bulb *C*, which was isolated from the *U*-traps and immersed in an ice-water bath. The bulb *C* was evacuated to a pressure of about 5 mm. of mercury, and the ice-water bath was replaced by a bath at 30°, ± 2° C. The contents of bulb *C* were then allowed to fractionate into the *U*-traps, which were maintained at −20°, ± 3° C., −60°, ± 5° C., and −196° C. The hydrazine fraction which collected in the −20° C. trap was immediately transferred in vacuum to a storage bulb which had been baked at 300° C. and $10^{-5}$ mm. of mercury. The fraction weighed approximately 18 grams and was determined to be 99.99, ± 0.03%, pure by the method of Penneman and Audrieth (*6*). The intermediate trap contained about 0.2 gram of hydrazine, and the −196° C. trap contained a similar quantity of ammonia.

**Stability of Purified Hydrazine.** Borosilicate glass ampules were attached to the vacuum line and outgassed at 300° C. and a pressure of $10^{-5}$ mm. of mercury. Freshly distilled hydrazine in the storage bulb was transferred under its vapor pressure at room temperature to the ampules, which were cooled to liquid-nitrogen temperature. The ullages were approximately 50% (approx. 2 ml. of sample). The ampules were isolated from the hydrazine vapors, sealed, and removed from the vacuum line. The hydrazine stored in this manner deteriorated to what appeared to be an equilibrium composition. Similar samples of hydrazine from the ammonolysis of hydrazine sulfate were used for comparison. Table I shows the change in composition of these samples with time at room temperature.

Refractionation of samples 3 or more days old yielded 99.9% hydrazine and traces of ammonia. The ammonia was identified on the basis of vapor pressure (5) and molecular weight. The values in the literature for the vapor pressure of ammonia are 10 and 1 mm. of mercury at −91.9° and −109.1° C., respectively; the calculated molecular weight is 17.03. The values obtained in this experiment are 11 and 1.1 mm. of mercury at −91° and −110° C. and molecular weights of 17.01 and 17.04.

No attempts was made to search for or identify products which could not be trapped with liquid nitrogen.

Experience in this laboratory has shown that decomposition rates for hydrazine are meaningless unless the history of the material decomposed is defined, and the material is decomposed in equipment where hydrazine is exposed to a unique surface. For example, for a given sample of hydrazine, the rate of decomposition in a mixed glass-metal system will differ from that of a system of one particular metal.

Table I. The Effect of Two Procedures on the Purity of Hydrazine

| Sample | Time After Fractionation, Days | $N_2H_4$, % Calcium hydride | Ammonolysis |
|---|---|---|---|
| 1 | 0 | 99.99 ± 0.03 | 99.99 ± 0.03 |
| 2 | 1 | 99.95 | 99.93 |
| 3 | 2 | 99.92 | 99.91 |
| 4 | 3 | 99.89 | 99.90 |
| 5 | 10 | 99.90 | 99.90 |
| 6 | 30 | . . . | 99.90 |
|  | 184 | 99.90 | . . . |
| 7 | 300 | 99.90 | 99.90 |

## LITERATURE CITED

(1) Audrieth, L.F., Ogg, B.A., "The Chemistry of Hydrazine," Chap. 3, Wiley, New York, 1951.

(2) Browne, A.N., Houlehan, A.E., *J. Am. Chem. Soc.* **33**, 1734 (1911).

(3) Browne, A.W., Welsh, T.W.B., *Ibid.*, 1728 (1911).

(4) Class, J.B., Aston, J.G., Oakwood, T.S., *J. Am. Chem. Soc.* **75**, 2937 (1953).

(5) Overstreet, Roy, Giauque, W.F., *J. Am. Chem. Soc.* **59**, 254 (1937).

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

(7) Rice, F.O., Sherber, F., *J. Am. Chem. Soc.* **77**, 291 (1955).

(8) Scott, A., *J. Chem. Soc.* **85**, 913 (1904).

(9) Stolle, P., *J. Prakt. Chem.* **83**, 200 (1911); *Ber.* **37**, 454 (1904).

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# 1-Benzyl-4,5-bis(chloromethyl)-1*H*-1,2,3-triazole

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WE HAVE prepared the title compound by the reaction of benzyl azide and 1,4-dichloro-2-butyne.

## EXPERIMENTAL

To 100 ml. of toluene was added 5.6 grams (0.045 mole) of 1,4-dichloro-2-butyne (commercial sample) and 6.0 grams of benzylazide (*1*). The solution was refluxed 8 hours and the product was precipitated by addition of petroleum ether. After two recrystallizations from a mixture of petroleum ether and ethyl acetate, 5.7 grams (49%) of product was obtained, m.p. 54.5°–55°.

Anal. Calcd. for $C_{11}H_{11}Cl_2N_3$: C, 51.58; H, 4.33; Cl, 27.68; N, 16.40. Found: C, 51.69; H, 4.20; Cl, 27.96; N, 16.57.

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## LITERATURE CITED

(1) Curtius, T., Erhart, G., *Ber.* **55**, 1565 (1922).

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