[Contribution from The Norwich Pharmacal Co.]

# The Thermal Decomposition of 2-Hydrazinoethanol and 1-Hydrazino-2-propanol

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The thermal decomposition of the title compounds formed methylhydrazine in 20–30% yield.

In an earlier paper we reported our interest in hydrazino alcohols and their use in the synthesis of 3-amino-2-oxazolidones.[1]

During the attempted distillation of 2-hydrazinoethanol, brisk gas evolution occurred at about 215° and a liquid, b.p. 80–150°, distilled. The residue then charred with some violence. Purification of the liquid gave methylhydrazine in 25% yield, identified by its boiling point, acid sulfate and acid oxalate. In this and subsequent decompositions, the presence of 2-aminoethanol was established, and ammonia and hydrazine were identified in the gaseous effluent. Neutral gases were also evolved but not identified.

These results were considered to be of sufficient synthetic interest to justify a serious effort to improve the rather low yield of methylhydrazine (Table I). However, neither a nitrogen atmosphere during the decomposition, nor the addition of powdered glass (recently used with success by Newman and Caflisch[2] in the McFayden-Stevens aldehyde synthesis) had a significant effect on the yield. A free radical initiator, benzoyl peroxide, was used in an effort to lower the decomposition temperature. This was also unsuccessful; good results were achieved, however, in moderating the occasionally violent decompositions by the use of polyethylene glycol-400, although this had little effect on the yield.

TABLE I

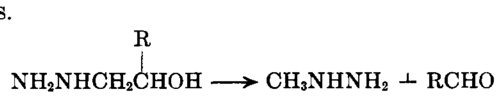
Effect of Additives on Methylhydrazine Yield

| Additive | 2-Hydrazinoethanol, g. | % Yield of Methylhydrazine |
|---|---|---|
| None | 116 | 25 |
| Nitrogen | 200 | 31 |
| Powdered glass, 4 g. | 10 | 30 |
| Benzoyl Peroxide, 105 mg. | 30 | 21 |
| Polyethylene Glycol-400, 300 g. | 200 | 30 |

We next turned our attention to the thermal decomposition of 1-hydrazino-2-propanol, $NH_2NHCH_2CHOHCH_3$. This reaction proceeded more smoothly than with 2-hydrazinoethanol, little gas was evolved and no violent decompositions occurred. The crude volatile liquid product was distilled, and the distillate, b.p. 95–108°, was dried over sodium hydroxide and redistilled. Two main fractions were obtained. Fraction A was identical with methylhydrazine in boiling point and infrared spectrum. Fraction B, b.p. 92–97°, showed more intense absorption at 7.25 $\mu$ (methyl deformation) and weaker absorption at 6.2 $\mu$ (NH deformation) than methylhydrazine. The preparation of methylhydrazine acid oxalate, and acetaldehyde 2,4-dinitrophenylhydrazone from Fraction B indicated that it might be acetaldehyde methylhydrazone. Several attempts to synthesize this compound from acetaldehyde and methylhydrazine in ether solution yielded an unstable liquid very similar to Fraction B. Satisfactory analytical data could not be obtained. That the substance was mainly acetaldehyde methylhydrazone was indicated by its conversion to acetaldehyde 2,4-dinitrophenylhydrazone and methylhydrazine oxalate.

The corrected yield of methylhydrazine from 1-hydrazino-2-propanol based on the amount isolated by distillation plus the methylhydrazine acid oxalate from Fraction B was 20%. Infrared analysis of the crude volatile product in chloroform solution indicated a total yield of 30–40%.

Although the main reaction leading to methylhydrazine may be simply described (Eq. 1), its mechanism probably involves several steps and possibly proceeds through free radical intermediates.

(1) 

$$NH_2NHCH_2\overset{R}{C}HOH \longrightarrow CH_3NHNH_2 + RCHO$$

R=H, $CH_3$

## EXPERIMENTAL[3]

*Thermal decomposition of 2-hydrazinoethanol.* (This describes Run 1, Table I; other runs summarized there were

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[1] (a) G. Gever, *J. Am. Chem. Soc.*, **76**, 1283 (1954); (b) G. Gever, C. O'Keefe, G. Drake, F. Ebetino, J. Michels, and K. J. Hayes, *J. Am. Chem. Soc.*, **77**, 2277 (1955).

[2] M. S. Newman and E. G. Caflisch, Jr., *J. Am. Chem. Soc.*, **80**, 862 (1958).

[3] The melting points were determined on a calibrated Fisher-Johns block and the infrared spectra were determined on the Perkin-Elmer Model 21 equipped with sodium chloride optics. The elemental analyses were performed by Mr. Gordon Ginther and associates of these Laboratories.

carried out by the same general method and are not individually described.) In a 200-ml. flask set up for distillation and equipped with a gas outlet tube connected to a dilute hydrochloric acid trap was placed 116 g. (1.53 moles) of 2-hydrazinoethanol, b.p. 91–98° (0.8–1.5 mm.). The flask was heated to 215–220° with an oil bath. At about 200° moderate bubbling began and gases evolved. After 1 hr. a total of 75.5 g. of distillate had collected. An attempt was made to fractionate 61.7 g. of this material at reduced pressure. At room temperature 39.2 g. distilled at 14 mm. Continued heating of the residue gave 2.3 g., b.p. 50° (3.5 mm.). This liquid was refluxed with 6.6 g. of oxalic acid dihydrate in 50 ml. of ethanol, filtered, cooled, and the crystalline precipitate recrystallized from 100 ml. of 80% ethanol. This gave 0.7 g. of ethanolamine oxalate, melting point and mixed melting point with authentic material 191–192°. Redistillation of the 39.2 g. at normal pressure gave 35.1 g., b.p. 81–104°. That this was mainly methylhydrazine was indicated by preparation of the oxalate. One gram of the distillate was refluxed with 3 g. of oxalic acid dihydrate in 85 ml. of 80% ethanol; cooling separated 1.1 g. (37%) of crystals, m.p. 162–164° (lit.[4] m.p. 166°). Preparation of authentic methylhydrazine oxalate under these conditions resulted in a 51% yield (m.p. 167–168°) after recrystallization from 80% ethanol. The boiling range for the distillate indicated it to be wet. (It is known that methylhydrazine forms a high-boiling (104°) azeotrope[5, 6]). The distillate (33.8 g.) was therefore dried on the steam bath over 35 g. of sodium hydroxide. Distillation through a Vigreux column gave 13.9 g. of methylhydrazine, b.p. 86–87° (lit. b.p. 87°). The yield corresponded to a total of 17.8 g. (25%) of methylhydrazine in the 75.5 g. of crude distillate. (The infrared spectrum of this sample was not recorded, but in other runs (Table I) the distillate gave a infrared spectrum in chloroform identical with authentic methylhydrazine). One gram of the distillate was added to 35 ml. of ethanol containing 2 g. of sulfuric acid. Cooling separated 2.2 g. (70%) of crystals, m.p. 141–142°, mixed melting point with authentic methylhydrazine acid sulfate (m.p. 141–142°) was undepressed. Titration of the dilute hydrochloric acid solution showed that 2.73 g. of alkaline gases (calculated as ammonia) were evolved. Ammonia was identified in one run by condensation of the alkaline gases, including some water, in a trap cooled with a Dry Ice–acetone mixture. Treatment with benzoyl chloride yielded benzamide, m.p. 129–130°. Mixed melting point with authentic benzamide was undepressed. Evidence proving the presence of a small quantity of hydrazine in these gases was obtained in another run by treatment of the acid solution with ethanolic 5-nitro-2-furaldehyde. A small amount of yellow solid separated; it was identified by m.p. (245–248°) and infrared spectrum as 5-nitro-2-furalazine.[7]

*Thermal decomposition of 1-hydrazino-2-propanol.* In a 500-ml. flask equipped with stirrer, thermometer, gas outlet tube leading through an acid trap, and a variable take-off distillation assembly, was placed 301 g. (3.34 moles) of hydrazino-2-propanol[1a]. The flask was heated to 210° with a mantle. After 5.5 hr. 187 g., b.p. 125–145°, had distilled. A reflux ratio of 3 to 1 was used. Near the end of the reaction some gas evolved and a yellow liquid began to distil. This fraction, b.p. 145–193°, (27 g.) showed an infrared band at 6.0 $\mu$. It was not investigated further. The bulk (164 g.) of the distillate was redistilled through a Vigreux column. The first fraction (112 g.), b.p. 95–108°, was dried over 50 g. of sodium hydroxide at room temperature for 8 hr. The organic layer was decanted and dried again over 14 g. of sodium hydroxide overnight in the refrigerator. The organic layer was then filtered through glass wool and distilled through a Vigreux column. Two fractions, A, 9.5 g., b.p. 85–86°, and B, 31.0 g., b.p. 92–97°, were collected. Fraction A was identical in boiling point and infrared spectrum with authentic methylhydrazine.

A solution of 2.0 g. of Fraction B in 10 ml. of ethanol was added to a warm solution of 5.0 g. of oxalic acid in 20 ml. of ethanol. Colorless crystals immediately separated; after cooling, these were collected, 2.83 g., m.p. 167–169°, undepressed with authentic methylhydrazine acid oxalate.

A solution of 2.0 g. of Fraction B in 10 ml. of methanol was slowly added with cooling to a solution of 6.0 g. of 2,4-dinitrophenylhydrazine prepared by dissolving the hydrazine in 10 ml. of concentrated sulfuric acid and subsequent dilution with 100 ml. of methanol. Orange crystals separated and were collected, washed with methanol and water, 3.09 g., m.p. 150–152°. Recrystallization from 50 ml. of ethanol and 10 ml. of nitromethane gave 2.2 g., m.p. 164–165° (lit.[8] m.p. 164°). Mixed melting point with authentic acetaldehyde 2,4-dinitrophenylhydrazone was undepressed.

*Attempted preparation of acetaldehyde methylhydrazone.* To 164 g. (3.57 moles) of freshly distilled methylhydrazine in 500 ml. of ether was dropwise added, with stirring and cooling, 157 g. (3.57 moles) of acetaldehyde in 200 ml. of ether. The flask was protected from carbon dioxide by a soda-lime tube, and maintained at about 20° by an ice bath. The reaction mixture consisted of two phases at the end of the addition. These were separated, and the aqueous phase was extracted with 200 ml. of ether. The combined ether extracts were dried over 100 g. of sodium hydroxide for 2 days. After removal of the drying agent the ether was distilled through a 1-ft. Vigreux column. The residue was distilled in the same way, and the distillate, b.p. 97–108°, was collected. The distillate was twice fractionated through an 8-inch Vigreux column and the fraction b.p. 105–106° (33 g.) was collected.

*Anal.* Calcd. for $C_3H_8N_2$: C, 49.97; H, 11.18. Found: C, 47.13; H, 11.03.

When exposed to the air this material quickly formed a solid (m.p. 50–60°) which slowly turned yellow even in the refrigerator. This material yielded methylhydrazine oxalate in 31% yield (m.p. 168–170°) and acetaldehyde 2,4-dinitrophenylhydrazone in 43% yield (m.p. 164–165°) after treatment with oxalic acid and 2,4-dinitrophenylhydrazine in the usual manner.

*2-Aminoethanol oxalate.* A solution of 1 g. of 2-aminoethanol, 3 g. of oxalic acid dihydrate and 100 ml. of ethanol was heated to boiling then cooled and the crystalline product collected (m.p. 134–135°) and recrystallized from 37 ml. of 75% ethanol. The yield was 0.3 g., m.p. 190–192°.

*Anal.* Calcd. for $C_6H_{16}N_2O_6$: C, 33.95; H, 7.60; N, 13.20. Found: C, 34.06; H, 7.96; N, 13.39.

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(6) G. Gever, unpublished results.

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(8) F. Challenger and L. Klein, *J. Chem. Soc.*, 1644 (1929).