of an oxidation of the manganese to the permanganate form by means of potassium periodate, followed by electrolysis in a specially designed cell in which magnesium hydroxide deposits in a cathode-containing compartment and the permanganate in an anode-containing compartment. An essential feature of this cell is an arrangement whereby hydrogen from the cathode is kept out of contact with the permanganate.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

GERMANIUM. XXXIV. TRIMETHYL GERMANIUM BROMIDE[1]

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Halogenated aryl compounds of germanium of the type R_3GeX have been prepared by several investigators.[2] These compounds are solids which can readily be purified by crystallization from organic solvents. Comparatively little work has been done on the germanium alkyl compounds, and no halogenated alkyl of the above type has been announced. Trimethyl germanium bromide was chosen as a typical representative of this class. It was to be expected that the compound would be somewhat more difficult to prepare and purify than the corresponding aryl compounds since it probably would be a liquid that is rapidly attacked by atmospheric moisture. Consequently, the method of halogenation developed by Dennis and Judy[3] was used.

Materials.—Germanium tetrachloride was converted to germanium tetramethyl by the method of Dennis and Hance.[4] Hydrogen bromide was prepared by the reduction of bromine by hydrogen sulfide.

Procedure.—The apparatus was similar to that used by Dennis and Judy[3] for the halogenation of monogermane. Anhydrous aluminum bromide was introduced into the reaction bulb in the manner there described. About 15 g. of germanium tetramethyl was distilled into one of the smaller bulbs of the vacuum chain, after its purity had been established by determination of its vapor tension at 0°. Slightly less than the theoretical amount of hydrogen bromide required by the equation

$$HBr + Ge(CH_3)_4 = Ge(CH_3)_3Br + CH_4$$

was condensed in another bulb of the apparatus, and was then distilled over into the bulb that contained the germanium tetramethyl. The two

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[1] The work 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.

[2] Morgan and Drew, *J. Chem. Soc.*, **127**, 1760 (1925); Kraus and Foster, THIS JOURNAL, **49**, 457 (1927); Orndorff, Tabern and Dennis, *ibid.*, **49**, 2512 (1927).

[3] Dennis and Judy, *ibid.*, **51**, 2321 (1929).

[4] Dennis and Hance, *J. Phys. Chem.*, **30**, 1055 (1926).

substances in vapor phase were then passed over into the reaction bulb which contained the catalyst. As soon as the vapors came in contact with the aluminum bromide on the walls of this bulb, reaction took place, as was evidenced by the formation of drops of liquid around the crystals of the catalyst. To insure thorough mixing of the two reacting substances, liquid air was alternately applied to and removed from the smaller bulb, which throughout the reaction remained in connection with the reaction bulb. The action was allowed to continue during a period of two days.

The volatile products were then distilled over into the smaller bulb by cooling it with liquid air, and the liquid was separated by distillation into two fractions, one volatile below $-100°$ and the other volatile above that temperature. The sample volatile below $-100°$ was analyzed by combustion, was found to be pure methane, and was discarded. The other portion was separated into three fractions by distillation, following the general method described by Dennis, Corey and Moore.[5] The greater part of the liquid showed a vapor tension at 0° of from 4.7 to 5.1 mm. This portion was again fractionated, the middle fraction was separated by further fractional distillation into small portions, and the vapor tension of each at 0° was determined. A constant value of 4.9 mm. was obtained and consequently these several small fractions were combined.

Analysis.—A sample was distilled over into a tube that was provided at its upper end with a wide slip-joint carrying a stopcock and a normal slip-joint above that for attaching it to the chain. This tube was detached and weighed to determine the weight of the sample, the liquid in it was then frozen and the large slip-joint was removed. Water and a few drops of nitric acid were added and the mixture was allowed to warm up while being gently shaken. The substance rapidly dissolved. A solution of silver nitrate was then added in excess and the silver bromide was collected on a filter and weighed.

Carbon and hydrogen were determined by the combustion method devised by Dennis and Hance,[4] the bromine in the sample being stopped by a plug of silver turnings.

Germanium was determined by slowly dropping a sample of the liquid from a pipet onto a warm mixture of 90 parts of sodium peroxide and 10 parts of sodium carbonate. The mass was allowed to cool, was then heated with dilute hydrochloric acid, and the solution was made 6 *N* with respect to hydrochloric acid. The germanium in this solution was now determined by the method of Johnson and Dennis.[6]

Analyses

Bromine.—Subs., 0.1943, 0.3141. Calcd. for $Ge(CH_3)_3Br$: Br, 0.0785, 0.1270, 40.44%. Found: Br, 0.0786, 40.45%, 0.1274, 40.54%.

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[5] Dennis, Corey and Moore, This Journal, **46,** 657 (1924).

[6] Johnson and Dennis, *ibid.*, **47,** 790 (1925).

Germanium.—Subs., 0.4101, 0.1437. Calcd. for $Ge(CH_3)_3Br$: Ge, 0.1506, 0.0528, 36.74%. Found: Ge, 0.1532, 37.35%, 0.0525, 36.52%.

Carbon and Hydrogen.—Subs., 0.8214, 0.2749. Calcd. for $Ge(CH_3)_3Br$: C, 0.1497, 0.0501, 18.23%; H, 0.0377, 0.0126, 4.59%. Found: C, 0.1485, 18.09%, 0.0503, 18.29%; H, 0.0380, 4.74%, 0.0125, 4.55%.

Physical Properties

Melting Point.—The melting point of trimethyl germanium bromide, determined by the dropping ring method of Dennis, Corey and Moore,[5] is $-25°$.

Liquid Density.—The liquid density of trimethyl germanium bromide is 1.544 g./cc. at 18°.

Vapor Density and Molecular Weight.—The vapor density was determined by the method of Victor Meyer using the apparatus as modified by Weiser.[7] The tube was heated by the vapor of boiling ethylene glycol contained in the outer jacket, and the displaced air was measured in a Hempel gas buret. Wt. 1 liter (corr.) 8.963, 9.220. Mol. wt. (av.), 203.6. Calcd., 197.6.

Refractive Index.—The refractive index of trimethyl germanium bromide is 1.4705 at 18°.

Vapor Tension.—The vapor tension curve was determined by the method of Laubengayer and Corey.[8]

Temp., °C.	−25.0	−6.2	+3.7	23.4	32.2	41.5	46.0	52.5	
Press., mm.	0.1	2.9	7.1	21.4	32.8	50.9	62.3	82.5	
Temp., °C.	58.4	63.8	66.0	74.2	77.8	80.5	85.4	89.0	94.4
Press., mm.	108.8	131.8	150.6	195.0	222.7	245.6	301.1	337.0	398.1
Temp., °C.	95.5	98.5	101.1	105.5	108.9	113.2	115.7	119.7	
Press., mm.	415.5	447.0	495.5	555.9	619.5	711.2	787.1	881.0	

The general equation as determined from the above data is

$$\log_{10} p = -1956 \times \frac{1}{T, °K.} + 7.912$$

Boiling Point.—The boiling point as taken from the vapor tension curve is 113.7°.

The material is a colorless oily liquid with a characteristic odor resembling turpentine and onions. It is soluble in the usual organic solvents.

Chemical Properties

Trimethyl germanium bromide is hydrolyzed by water. Silver bromide can be precipitated from this solution by the addition of a solution of silver nitrate. The product of hydrolysis is a volatile liquid. Germanium disulfide is not precipitated when an aqueous solution of trimethyl germanium bromide is acidified and treated with hydrogen sulfide. This is presumably due to the formation of a non-polar hydroxyl compound.

[7] Weiser, *J. Phys. Chem.*, **20**, 532 (1916).

[8] Laubengayer and Corey, *ibid.*, **30**, 1043 (1926).

$$Ge(CH_3)_3Br + HOH = Ge(CH_3)_3OH + HBr$$

This hydroxyl derivative may or may not condense with itself with the elimination of a molecule of water. The corresponding phenyl compound does, however.[9] Trimethyl germanium bromide is rapidly oxidized by sodium peroxide and by hot chromic acid, but only slowly by ammoniacal 30% hydrogen peroxide. Hot, concentrated sulfuric acid liberates bromine.

When a sample was dissolved in benzene and dry ammonia gas was bubbled through the solution, a white crystalline precipitate appeared. This was shown by analysis to be ammonium bromide. The filtrate from this precipitate was allowed to evaporate at room temperature. When only a few drops remained, the material had an odor similar to that of the original material. However, when a drop on a stirring rod was brought in contact with a drop of water, the odor of ammonia was noticed. This liquid fumed strongly when concentrated hydrochloric acid was added. It is assumed from this experiment that trimethyl germanium bromide reacts with ammonia to form an amine which is volatile and readily hydrolyzed by water.

Summary

The preparation, purification and some chemical and physical properties of trimethyl germanium bromide are described.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE SEPARATION OF EUROPIUM BY ELECTROLYTIC REDUCTION. OBSERVATIONS ON THE RARE EARTHS. XXXV

BY L. F. YNTEMA

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The existence of a bivalent europium chloride was announced by Urbain and Burion[1] who prepared it by reduction of the anhydrous trichloride with hydrogen at 400–450°. Jantsch, Alber and Grubitsch[2] extended the study of the bivalent compounds of europium. They found that europium bichloride is quite stable in solution. The bi-iodide was found to be still more stable. The sulfate is a fine, white crystalline compound, insoluble in water and difficultly soluble in acids. The bichloride of samarium, described by Matignon and Cazes[3] and by Jantsch, Rüping and Kunze,[4] reacts with water and, more rapidly, with acids, evolving hydrogen and undergoing oxidation to the trivalent state. The bivalent sulfate is a red compound, sparingly soluble.

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[9] Morgan and Drew, *J. Chem. Soc.*, **127**, 1760 (1925).

[1] Urbain and Burion, *Compt. rend.*, **153**, 1155 (1911).

[2] Jantsch, Alber and Grubitsch, *Monatsh.*, **53, 54,** 305 (1929).

[3] Matignon and Cazes, *Compt. rend.*, **142**, 83 (1906).

[4] Jantsch, Rüping and Kunze, *Z. anorg. allgem. Chem.*, **161**, 210 (1927).