NOTES

Vapor Pressure of Boron Triiodide and Silicon Tetraiodide[1]

By Holger C. Andersen and Lawrence H. Belz

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Vapor pressures of BI_3 and SiI_4 were measured in the 5–730 mm. range, using the static isoteniscope method of Smith and Menzies.[2]

Table I

BI_3: $\log P_{mm} = 24.3125 - (3{,}342.3/T, {}^\circ K.) - 5.4058 \log T{}^\circ K.$; (336–480°K.)

t, °C.	P_{mm} Obsd.	P_{mm} Calcd.	$P_{obsd.} - P_{calcd.}$
206.7	711.3	714.8	−3.1
189.8	485.9	483.2	+2.7
173.7	321.0	321.4	−0.4
153.7	183.8	183.7	+0.1
131.7	91.4	91.9	−0.5
113.6	49.2	48.3	+0.9
98.1	27.0	26.3	+0.7
80.9	12.7	12.1	+0.6
63.4	5.3	5.3	0

Calcd. b.p. at 760 mm., 209.5°. B.p. (ref. 3), 210°.

Table II

SiI_4: $\log P_{mm} = 23.3809 - (3{,}862.7/T, {}^\circ K.) - 4.9934 \log T{}^\circ K.$; (399–573°K.)

t, °C.	P_{mm} Obsd.	P_{mm} Calcd.	$P_{obsd.} - P_{calcd.}$
299.4	732.4	731.1	+1.3
285.2	559.4	558.3	+1.1
267.3	385.8	387.6	−1.8
244.6	232.3	233.5	−1.2
220.0	126.6	126.4	+0.2
201.9	77.3	76.6	+0.7
187.4	48.5	49.7	−1.2
169.4	26.9	27.7	−0.8
148.3	13.1	12.8	+0.3
126.4	5.3	5.3	0

Calcd. b.p. at 760 mm., 301.5°. B.p. (ref. 4), 290°.

Experimental

Temperatures were measured with a copper–constantan thermocouple and calibrations of the Bureau of Standards.[5] Pressures were measured with a mercury manometer-cathetometer and are corrected for temperature, latitude (elevation correction negligible) and difference in liquid level in the isoteniscope at moment of reading. This last correction required liquid density, which was determined on the SiI_4 as

$$\rho = 3.40 - 2.5 \times 10^{-3}(t - 120) \text{ g./cc. } t = {}^\circ\text{C.}$$

The density of the BI_3 was assumed to be the same for this correction, which was always small. The equipment was filled with dry helium instead of air, to prevent hydrolysis and oxidation of the iodides. Mineral oil and molten salt constant temperature baths were used. Best reproducibility was achieved by measuring the vapor pressure at the highest temperature first and "boiling out" the last traces of contaminating volatiles, followed by measurement at the lower temperatures.

The SiI_4 was prepared by passing iodine and argon through ground silicon (30 × 80 mesh) held in a quartz reactor at 850°. The product was condensed and purified by distillation in a 4-step still at 200 mm. The white crystalline material had a melting point of 122–122.5° (m.p. 120.5°[6]). The BI_3 was prepared by the method of Schumb, Gamble and Banus[7] where sodium borohydride reacts with iodine and the resulting BI_3 is extracted by sublimation, dissolution and reduction of the excess iodide. About 15 g. of BI_3 was obtained from 1000 ml. of CS_2 liquor after reduction and removal of the iodine. The over-all material balance was 15 g. of BI_3 from 64 g. of sodium borohydride and 1054 g. of iodine. The BI_3 was resublimed twice before being deposited in the isoteniscope. The white crystalline solid had a melting point of 49.6° (m.p. 49.9 ± 0.5°[7]).

Research and Development Laboratories
Foote Mineral Company
Berwyn, Penna.

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[2] A. Smith and A. W. C. Menzies, This Journal, **32**, 1412 (1910).

[3] H. Moissan, *Compt. rend.*, **112**, 717 (1891).

[4] C. Friedel, *Liebigs Ann. Chem.*, **149**, 96 (1868).

[5] W. F. Roeser and A. I. Dahl, *J. Research Natl. Bur. Standards*, **20**, 337 (1938), RP 1080.

[6] R. Schwartz and A. Pflugmacher, *Ber.*, **75B**, 1062 (1942).

[7] W. C. Schumb, E. Gamble and M. Banus, This Journal, **71**, 322 (1949).

The System Aluminum Triethyl–Ethyl Ether[1]

By Evelyn Blust Baker and Harry H. Sisler

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Krause and Wendt[2] reported some three decades ago the formation of an etherate of aluminum triethyl to which they assigned the formula $4Al(C_2H_5)_3 \cdot 3(C_2H_5)_2O$. This formula is difficult to rationalize, particularly in view of the well known tendency for aluminum trimethyl to form 1:1 complexes with such Lewis bases such as dimethyl ether, trimethylamine, trimethylphosphine and dimethyl sulfide. The present study was undertaken to determine conclusively the composition of the etherate of aluminum triethyl by careful analysis and by cryoscopic studies of the binary system $Al(C_2H_5)_3$–$(C_2H_5)_2O$.

Preparation of Aluminum Triethyl.—The procedure used was an adaptation of that of Grosse and Mavity.[3] The process is represented essentially by the equations

$$2Al + 3C_2H_5Br \longrightarrow Al(C_2H_5)_2Br + Al(C_2H_5)Br_2$$

$$Al(C_2H_5)_2Br + Al(C_2H_5)Br_2 + 3Na \longrightarrow Al(C_2H_5)_3 + 3NaBr + Al$$

Granular aluminum (20 mesh) and Eastman Kodak ether-free ethyl bromide were used. The sodium was added directly to the mixture without previous distillation of the halides. The product was a colorless, clear liquid, b.p. 76° at 2.5 mm. and 69° at 1.5 mm. A hydrolyzed and acidified sample gave no precipitate with silver nitrate.

Purification of Ethyl Ether.—Anhydrous reagent grade ethyl ether was dried over sodium wire. Iron wire and copper powder were added to minimize peroxide formation. The ether was outgassed with nitrogen.

Apparatus for Cryoscopic Measurements.—Temperatures were measured with a recording potentiometer (Leeds and Northrup Micromax) using a copper–constantan thermo-

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[1] Taken from the Ph.D. dissertation of E. B. Baker, The Ohio State University, 1953.

[2] E. Krause and B. Wendt, *Ber.*, **56B**, 466 (1923).

[3] A. V. Grosse and J. M. Mavity, *J. Org. Chem.*, **5**, 106 (1940).

couple. The apparatus was calibrated at the freezing points of water, carbon tetrachloride and chloroform.

The freezing point cell contained a glass spiral with an enclosed iron slug at the upper end.[4] Stirring was effected by applying an intermittent current to an air-cooled solenoid placed around the neck of the cell. A thermocouple well was built into the cell. Petroleum ether (30–60° fraction) was used as a heat transfer medium in the thermocouple well to minimize convection effects within this well.

The system $Al(C_2H_5)_3$–$(C_2H_5)_2O$.—The aluminum triethyl was vacuum-distilled into the cell and then nitrogen was admitted. The cell was weighed to determine the amount of aluminum triethyl. Additions of ether were made by a hypodermic syringe through a serum bottle stopper, the amounts being determined by weighing the cell.

Cooling was effected by either a Dry Ice–acetone slurry or liquid nitrogen. Single, double or evacuated jackets were used to control the rate of cooling to around 0.5 to 2° per minute.

While the method is capable of accuracy within ±1.5°, the extreme reactivity of aluminum triethyl and consequent difficulty in obtaining and keeping it pure, the apparent low heats of fusion which make it difficult to obtain sharp changes of slope in the cooling curve, and the tendency of the mixtures to supercool make the freezing points obtained from 0 to 80 mole % ether probably accurate to within ±2°. From 80 mole % to 100 mole % it was necessary to determine most of the freezing points visually, as the formation of solid did not affect the slope of the time–temperature curve enough to be detected.

The freezing point–composition curve for the system is shown in Fig. 1. The values obtained for the freezing point of aluminum triethyl were -50.3 and $-50.7°$, as compared with a melting point of $-52.5°$ reported by Pitzer and Gutowsky[5] using a pentane thermometer. The formation of a compound between aluminum triethyl and diethyl ether is indicated by the maximum in the curve at about $-65°$ and 50 mole %. There are eutectics at 34 mole % ether, $-71°$, and at 96 mole % ether, $-119°$.

The results of the cryoscopic studies indicate that the addition compound has the formula $Al(C_2H_5)_3 \cdot (C_2H_5)_2O$. However, the maximum in the freezing point curve is rather flat, and, in view of the experimental difficulty encountered in determining portions of the curve, the results though reasonably convincing cannot be considered to be completely conclusive. To remove any remaining doubt the following additional evidence was obtained: 1. Samples of the etherate of aluminum triethyl prepared by the method of Krause and Wendt[2] and purified as carefully as possible gave freezing points ($-64°$, $-64.5°$) agreeing well with the maximum in the freezing point curve ($-65°$). 2. Changes in the freezing points of these prepared samples produced by the addition of known quantities of ethyl ether fit the freezing point curve closely if it is assumed that the prepared samples contain the metal alkyl and ether in a 1:1 mole ratio. The freezing points do not lie upon the curve if it is assumed that the prepared samples contain metal alkyl and ether in a 4:3 ratio. 3. Carefully purified samples of the etherate of aluminum triethyl were analyzed for aluminum by hydrolysis and precipitation of the aluminum as the 8-hydroxyquinolate. Found: Al, 14.31, 14.46 (two different preparations). Calcd. for $4Al(C_2H_5)_3 \cdot 3(C_2H_5)_2O$: Al, 15.89. Calcd. for $Al(C_2H_5)_3 \cdot (C_2H_5)_2O$: Al, 14.33.

Conclusion.—In consideration of the evidence presented it must be concluded that the composition of the etherate of aluminum triethyl is correctly represented by the formula $Al(C_2H_5)_3 \cdot (C_2H_5)_2O$ and that the earlier report of Krause and Wendt[2] is in error.

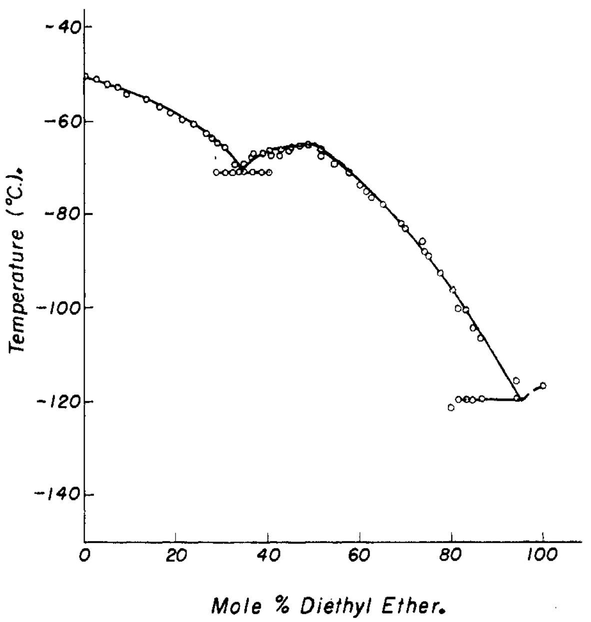

Fig. 1.—The system aluminum triethyl–ethyl ether.

DEPARTMENT OF CHEMISTRY
OHIO STATE UNIVERSITY
COLUMBUS 10, OHIO

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[4] B. Rubin, H. Sisler and H. Shechter, THIS JOURNAL, **74**, 877 (1952).

[5] K. S. Pitzer and H. S. Gutowsky, *ibid.*, **68**, 2204 (1946).

Tetraalkyloxamides and their Reduction to N,N,-N',N'-Tetraalkylethylenediamines[1]

BY BERNARD H. ARMBRECHT, LEONARD M. RICE, CHARLES H. GROGAN AND E. EMMET REID[2]

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In recent notes the preparation of N,N'-dialkyloxamides and their reduction to N,N'-dialkylethylenediamines have been reported.[3,4] It was shown for the first time that the adjacent carbonyls of the dialkyloxamides as well as isolated carbonyls could be reduced by lithium aluminum hydride.

It was of interest to find out whether this applied as well to the tetrasubstituted oxamides. This note deals with the preparation and reduction of several tetraalkyloxamides.

Since, as is well known, secondary amines react only slowly and incompletely with ethyl oxalate the tetraalkyloxamides were prepared from the amines and oxalyl chloride in the presence of a tertiary amine. From pyrrolidine and piperidine only tars could be obtained in spite of wide variations in operating conditions. These tars did not yield to chromatography over fluorosil. The oxamides prepared are in Table I and their reduction products in Table II.

The lithium aluminum hydride reduction of three representative tetraalkyloxamides went smoothly

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[1] Supported in part by the Geschickter Fund for Medical Research, Inc.

[2] Professor Emeritus, Johns Hopkins University, Baltimore, Maryland.

[3] L. M. Rice, C. H. Grogan and E. E. Reid, THIS JOURNAL, **75**, 242 (1953).

[4] L. M. Rice, B. H. Armbrecht, C. H. Grogan and E. E. Reid, *ibid.*, **75**, 1750 (1953).