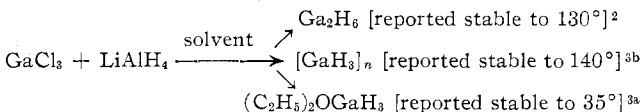two separate laboratories, have failed to provide any positive evidence for the existence of Ga_2H_6 or polymeric $[GaH_3]_n$ as separate stable molecular species, despite conscientious efforts to repeat earlier preparative procedures. Since the results from two separate laboratories lead to a common conclusion, this joint communication has been prepared.

Experimental

The Reduction of $GaCl_3$ by $LiAlH_4$ in Solvents.—The reaction between $LiAlH_4$ and $GaCl_3$ has been described in terms of three distinct processes

$$GaCl_3 + LiAlH_4 \xrightarrow{solvent} \begin{cases} Ga_2H_6 \text{ [reported stable to } 130°]^2 \\ [GaH_3]_n \text{ [reported stable to } 140°]^{3b} \\ (C_2H_5)_2OGaH_3 \text{ [reported stable to } 35°]^{3a} \end{cases}$$
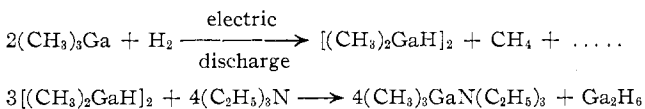
In our hands all hydridic products which could be obtained from $LiAlH_4$–$GaCl_3$–solvent systems contained relatively large amounts of chloride which could not be removed by repeated vacuum line fractionation. The chloride-containing oils decomposed even at 0°.

In a typical run a 25-mmole sample of $LiAlH_4$ was mixed with 8 mmoles of $GaCl_3$ using about 100 cc. of solvent. Diethyl ether, dimethyl ether, benzene, and isopentane were all tried as solvents; $GaBr_3$ in benzene was also tried. Reaction times ranged from 1 to 19 hr. and reaction temperatures of −45, 0, 25, and 50° were used. In diethyl ether an oily product was obtained which decomposed when an attempt was made to fractionate it on the vacuum line. H_2, Ga, ether, and a solid residue were the products. In isopentane (0 to 25°) the oily product gave 1–2 atoms of hydridic H for each Cl. At 25° the oil gave H_2, Ga, and a white solid containing Ga and Cl.

The Reduction of $GaCl_3$ by Other Reagents.—$GaCl_3$ and LiH react to give unstable $LiGaH_4$ as described by Finholt, Bond, and Schlesinger.[7] $LiGaH_4$ (6 mmoles) and $GaCl_3$ (3 mmoles) in ether (30 cc.) at 20° for 48 hr. gave no volatile products and no ether-insoluble $(GaH_3)_n$.

Attempts to reduce $GaCl_3$ with $LiBH_4$ in diethyl ether at 20° gave diborane and a trace of H_2. No Ga_2H_6 was isolated.
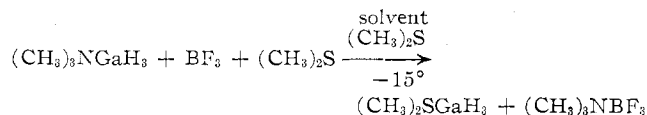
Reaction of Gallium Trimethyl and H_2 in an Electric Discharge.—The original report[1,2] on Ga_2H_6 described its preparation by the reactions

$$2(CH_3)_3Ga + H_2 \xrightarrow[\text{discharge}]{\text{electric}} [(CH_3)_2GaH]_2 + CH_4 + \ldots\ldots$$

$$3[(CH_3)_2GaH]_2 + 4(C_2H_5)_3N \longrightarrow 4(CH_3)_3GaN(C_2H_5)_3 + Ga_2H_6$$

In our hands fractionation of the products from the discharge tube gave a viscous liquid which could be condensed at −15° along with hydrocarbons separated at −196° and unreacted $Ga(CH_3)_3$ separated at −95°. The viscous liquid in the −15° trap did not correspond in properties to the compound $[(CH_3)_2GaH]_2$ reported as a product in the original paper of Wiberg.[1] Although pyrolysis of $[(CH_3)_2GaH]_2$ should give 0.75 mole of H_2 per mole of $Ga(CH_3)_3$ formed, our product, separating at −15°, gave only 0.32 mole of $H_2/Ga(CH_3)_3$. Since the reported conversion of $(CH_3)_4Ga_2H_2$ to Ga_2H_6 demanded that $(CH_3)_4Ga_2H_2$ and $N(C_2H_5)_3$ be mixed in stoichiometric quantities, it did not seem appropriate to attempt the conversion with the poorly characterized products obtained from the discharge reaction. Difficulties in the preparation of Ga_2H_6 using $N(C_2H_5)_3$ as a reagent were also indicated by the relatively high stability of $H_3GaN(CH_3)_3$ isolated in a subsequent study.[8]

Displacement of GaH_3 from its Complex.—An attempt was made to liberate Ga_2H_6 by thermal decomposition of one of its weaker adducts. The first system studied can be represented by the equation

(7) A. E. Finholt, A. C. Bond, and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 1199 (1947).

$$(CH_3)_3NGaH_3 + BF_3 + (CH_3)_2S \xrightarrow[-15°]{\substack{\text{solvent} \\ (CH_3)_2S}} (CH_3)_2SGaH_3 + (CH_3)_3NBF_3$$

The resulting $H_3GaS(CH_3)_2$ was purified by fractionation through a trap at −78°. When the excess of $(CH_3)_2S$ was removed at −70°, pure dimethyl sulfide–gallane was obtained. It decomposed quantitatively at room temperature to $(CH_3)_2S$, Ga, and $1.5 H_2$.

In an analogous reaction, in the absence of solvent, $(CH_3)_3NGaH_3$ and B_2H_6 gave no reaction below room temperature, but at 20° gave a product which decomposed immediately to gallium and hydrogen. In no case was any real evidence for Ga_2H_6 obtained.

Discussion

Recently $(CH_3)_3NGaH_3$ has been synthesized,[8] and the properties of this material can be used as an index to the stability of Ga_2H_6. For example $(CH_3)_3NBH_3$ is stable at 125°,[9] whereas B_2H_6 decomposes at these temperatures to give hydrogen and higher boron hydrides.[10] Similarly, $(CH_3)_3NB_3H_7$ is fairly stable at 25° but the parent boron hydride, B_4H_{10}, decomposes on storage at room temperature. It is then logical to postulate that Ga_2H_6 would be significantly less stable than the known $(CH_3)_3NGaH_3$ and $(CH_3)_2SGaH_3$. The relatively low stability of the latter compounds[8] and our inability to prepare Ga_2H_6 cast serious doubt on previous literature reports relative to this compound.

A similar comparison of $(CH_3)_3NBH_3$ with $(CH_3)_2OBH_3$ and $(CH_3)_3NB_3H_7$ with $(C_2H_5)_2OB_3H_7$ suggests that $(C_2H_5)_2OGaH_3$ should, if formed, be much less stable than $(CH_3)_3NGaH_3$. Such a comparison also casts serious doubt upon the reported stability of the compound $(C_2H_5)_2OGaH_3$.

(8) (a) D. F. Shriver and R. W. Parry, *Inorg. Chem.*, to be published (1963); (b) N. N. Greenwood, A. Storr, and M. G. H. Wallbridge, *ibid.*, to be published (1963).

(9) A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, **59**, 780 (1937).

(10) A. B. Burg and H. I. Schlesinger, *ibid.*, **55**, 4009 (1933).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY OF TEXAS, AUSTIN 12, TEXAS

Ammines of Osmium(I) and Osmium(0)

BY GEORGE W. WATT, E. M. POTRAFKE, AND DONALD S. KLETT

Earlier work[1–3] has provided evidence for the existence of species interpreted as ammines of platinum(0) and iridium(0), *i.e.*, $Pt(NH_3)_4$ and $Ir(NH_3)_5$. We report here similar evidence for ammines of osmium(I) and osmium(0), $[Os(NH_3)_6]Br$ and $[Os(NH_3)_6]$; these were formed by the reactions

$$[Os(NH_3)_6]Br_3 + 2K^+ + 2e^- \longrightarrow [Os(NH_3)_6]Br + 2K^+ + 2Br^- \quad (1)$$
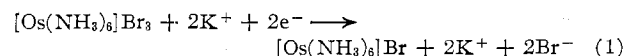
(1) G. W. Watt, M. T. Walling, Jr., and P. I. Mayfield, *J. Am. Chem. Soc.*, **75**, 6175 (1953).

(2) G. W. Watt and P. I. Mayfield, *ibid.*, **75**, 6178 (1953).

(3) G. W. Watt, E. P. Helvenston, and L. E. Sharif, *J. Inorg. Nucl. Chem.*, in press.

$[Os(NH_3)_6]Br_3 + 3K^+ + 3e^- \longrightarrow$
$$[Os(NH_3)_6] + 3K^+ + 3Br^- \quad (2)$$
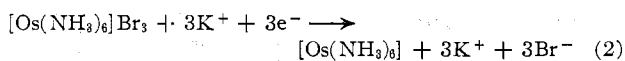
in liquid ammonia at $-33.5°$. Both $Pt(NH_3)_4$ and $Os(NH_3)_6$ are too unstable for use in experiments designed to determine whether these species involve metal–hydrogen bonds; such studies, however, are in progress using the relatively more stable $Ir(NH_3)_5$.

An improved procedure for the synthesis of hexaammineosmium(III) bromide also is described.

Experimental

Materials.—Ammonium hexabromoösmate(IV) was prepared by the method of Dwyer and Gibson.[4]

For the preparation of hexaammineosmium(III) bromide, 4.6210 g. of $(NH_4)_2OsBr_6$ was placed in a Faraday tube and maintained at 10^{-3} mm. for 12 hr. to ensure complete dryness. Forty ml. of anhydrous NH_3 was condensed on the solid and the tube was sealed and allowed to stand for 28 days at $25°$. Thereafter, the insoluble product was washed four times with 40-ml. portions of NH_3, the tube was cooled to $-78°$, opened, and the solvent evaporated. The brown NH_3-insoluble product was dissolved in 40 ml. of H_2O and the resulting solution was passed through a column (18 in. $\times$ 15 mm. i.d.) of freshly activated Al_2O_3. The column was washed with H_2O until the washings failed to produce a white precipitate when added to NH_4Br-saturated C_2H_5OH; brown impurities remained on the column. When excess NH_4Br-saturated C_2H_5OH was added to the eluate, 1.0990 g. [31.6% based on $(NH_4)_2OsBr_6$] of white solid precipitated. *Anal.* Calcd. for $[Os(NH_3)_6]Br_3$: Os, 35.8. Found: Os, 35.8. X-Ray diffraction data for this product were essentially identical with those reported earlier[5] for $[Os(NH_3)_6]Br_3$.

Preliminary Experiments.—To establish that $[Os(NH_3)_6]Br_3$ does not ammonolyze, a 0.2072-g. sample was dissolved in 125 ml. of liquid NH_3 and allowed to stand for 4 hr., after which the solvent was evaporated. The dry residue gave an X-ray diffraction pattern identical with that of the original bromide; there were no lines attributable to NH_4Br.

Using equipment and procedures described elsewhere[6,7] a solution of 0.2958 g. of $[Os(NH_3)_6]Br_3$ in 135 ml. of liquid NH_3 was titrated potentiometrically with a 0.0912 M solution of K in NH_3 at $-33.5°$ over a period of 14 hr. Significant changes in potential occurred upon addition of 1, 2, and 3 molar equivalents of the titrant. The solid phase that began to separate during the addition of the latter part of the first equivalent and that was present upon addition of 2 equivalents was a voluminous bright yellow precipitate; that present after addition of 3 equivalents was more dense and dark brown. Water-insoluble gases were not evolved during the course of the titration. The yellow-brown supernatant solution was removed by filtration and the brown solid was washed three times with 100-ml. portions of NH_3; analysis of the residue from the combined supernatant solution and washings accounted for 94.3% of the Br used as $[Os(NH_3)_6]Br_3$. The brown NH_3-insoluble product was stable at $-33.5°$ but decomposed when warmed to $25°$ to form (*only*) NH_3 and Os; the latter was identified by X-ray diffraction data.

Isolation of $[Os(NH_3)_6]Br$.—Using equipment and procedures described earlier,[8] 0.3600 g. of $[Os(NH_3)_6]Br_3$ in 130 ml. of liquid NH_3 was reduced by addition of 2 molar equivalents of K in NH_3 (13.8 ml. of 0.0905 M solution). The resulting bright yellow precipitate was separated by filtration and washed three times with 30-ml. portions of NH_3; analysis of the residue from the combined filtrate and washings accounted for 63.3% of the Br used as $[Os(NH_3)_6]Br_3$.

The yellow solid was warmed to room temperature, dried under reduced pressure for 4 hr., and removed from the reactor in an anhydrous O_2-free atmosphere. *Anal.* Calcd. for $[Os(NH_3)_6]$-Br: Os, 51.1; Br, 21.5. Found: Os, 50.5; Br, 22.0. As expected, this product was paramagnetic (1.5 B.M.). An X-ray diffraction pattern[9] led to the following d-spacings (Å.) (relative intensities in parentheses): 6.10 (0.75), 5.16 (0.20), 3.74 (1.00), 3.14 (0.05), 2.72 (0.07), 2.59 (0.15), 2.15 (0.05). Upon exposure to the atmosphere or water this product decomposed slowly.

Establishment of the Composition of $[Os(NH_3)_6]$.—Since the separation of KBr from the Os-containing product of reaction 2 had been demonstrated and because this product was too unstable for analysis at $25°$, it was necessary and possible otherwise to establish its composition without separation from KBr; this was done as follows.

In a typical experiment, 0.4534 g. of $[Os(NH_3)_6]Br_3$ in 130 ml. of liquid NH_3 was treated with 3 molar equivalents of K in NH_3 (0.111 M solution). A connection was made from the top of the reactor[8] to a trap inside a dewar flask. The trap was cooled by adding liquid nitrogen at a rate such that the solvent distilled from the reactor at a smooth controlled rate. When all of the *liquid* NH_3 was removed, the trap was maintained at liquid nitrogen temperature for 1 hr., the temperature of the reactor was lowered to $-78°$, and the pressure therein was reduced to 10^{-3} mm. for 18 hr. The brown solid showed no evidence of change during these operations. Thereafter, the reactor was connected to a gas collection system (including a Toepler pump) and the brown solid was decomposed by allowing it to warm to $25°$ followed by heating it at $100°$ for 1 hr. The solid turned black and 4.85×10^{-3} mole of NH_3 gas was collected; this corresponds to 5.71 moles of NH_3/mole of Os originally introduced as $[Os-(NH_3)_6]Br_3$. The X-ray data obtained using a sample of the black residue showed the presence of only Os and KBr.

(9) Copper Kα radiation (Ni filter), 35 kv. tube voltage, 15 ma. filament current, and 8 hr. exposure time; relative intensities were estimated visually.

CONTRIBUTION NO. 1272 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA

Rare Earth Metal–Metal Halide Systems. VI. Praseodymium Chloride[1]

BY LEONARD F. DRUDING, JOHN D. CORBETT,[2] AND BOB N. RAMSEY

The reaction of praseodymium with liquid $PrCl_3$ is of interest in relation to the behavior of the neighboring rare earth metal–metal halide systems. Lanthanum and cerium show only the phenomenon of solution in their respective molten trichlorides with no intermediate solid phases. The solubility in $LaCl_3$ has been reported to be 9 (mole) % at the eutectic ($826°$) and 11% at $920°$,[3] and in $CeCl_3$, 9.3% at the monotectic ($777°$)

(4) F. P. Dwyer and N. A. Gibson, *Nature*, **165**, 1012 (1950).
(5) G. W. Watt and L. Vaska, *J. Inorg. Nucl. Chem.*, **5**, 308 (1958).
(6) G. W. Watt and J. B. Otto, Jr., *J. Electrochem. Soc.*, **98**, 1 (1951).
(7) G. W. Watt and D. M. Sowards, *ibid.*, **102**, 46, 545 (1955).
(8) G. W. Watt and R. J. Thompson, *J. Inorg. Nucl. Chem.*, **9**, 311 (1959).

(3) F. J. Keneshea and D. Cubicciotti, *J. Chem. Eng. Data*, **6**, 507 (1961).