wave[3] and high-voltage dc discharge[4] have been reported as have alternate electrode materials such as copper.[5] Thus the effects of design, construction, and operating conditions for the discharge reactor have been fairly well investigated.

Since the products of the reaction (B_2Cl_4, B_4Cl_4, etc.) are considerably less volatile than BCl_3, it is reasonable to remove them *via* a low-temperature trap (usually −78°) and recirculate the BCl_3 in a closed system. Urry, Wartik, and Moore[6] contrived a Toepler type pump employing a moving piston of mercury to draw BCl_3 vapor back and forth through the discharge zone. Massey, Urch, and Holliday[7] later described a mercury diffusion pump to move the BCl_3 in a circular loop. While continuous operation with little attention is possible compared to trap-to-trap distillation of BCl_3 described elsewhere,[5] these do require specialized equipment, switches, and relays or sources of heating and cooling.

We report the design and use of a novel pump for the vapor of volatile liquids such as BCl_3, providing both circulation and fractionation and eliminating the need for auxiliary equipment except as required for the discharge cell.

Referring to Figure 1, the pump is constructed of four concentric tubes. Dimensions are given but are not considered critical. Operation is convenient at −78° where the vapor pressure of BCl_3 is 4 Torr. The long, slender design allows one to place a Dry Ice-alcohol bath around the pump.

Principle of Operation

By vaporizing BCl_3 from a liquid reservoir, condensing it in another, and then returning the liquid BCl_3 to the first, circulation of the vapor through a discharge reactor is maintained.

In this apparatus the reserviors are concentric. The outer well is kept at −78° by the cold bath. Liquid BCl_3 in the inner section is warmed by contact with a glass wall, warmed by passage of dry air *via* the fourth concentric tube G, thus locally increasing the vapor pressure. The liquid lock at F prevents equilibration except by forcing the BCl_3 vapor through the discharge zone to condense on the outermost wall along with the products from the reactor.

Experimental Section

The pump was tested using a modified mercury discharge cell (also shown in Figure 1) similar to that described by Massey,[7] *et al.* Commercial BCl_3 (10 ml), purified by pumping through a −78° trap and into a −196° trap, was transferred to the system. HCl was removed by pumping on BCl_3 at −78°. Occasional buildup of materials more volatile than BCl_3 necessitated venting the system to the vacuum line for 30-60 sec while the BCl_3 pump was held at −78°.

The cell was maintained at 20-30° by a water bath after discharge was initiated with a power supply delivering about 1 kV and about 0.4 mA. The rate of conversion as indicated by a typical experiment was 100-300 mg of B_2Cl_4/hr along with small amounts of B_4Cl_4. The B_2Cl_4 was purified by rapid fractionation through a −44° trap (trichloroethylene slush) and into a −78° (Dry Ice) trap and the purity was verified by infrared and mass spectra and vapor pressure (43 Torr (0°)).[5] In addition, B_4Cl_4 was recovered from the −44° trap and identified by its mass spectrum.

The driving pressure of the system, as indicated by the difference of level of BCl_3 between inner and outer reservoirs of the pump (see Figure 1 at the area marked F), is estimated to be 0.25 Torr.

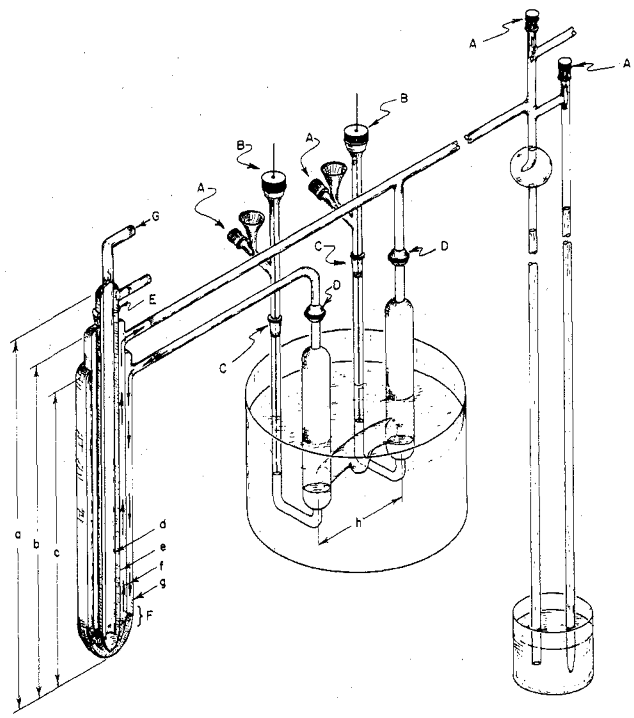

Figure 1. Diboron tetrachloride apparatus. The lower case letters correspond to dimensions (in mm) as follows: a, 370; b, 300; c, 240; d, 8; e, 16; f, 38; g, 50; h, 100. The stopcocks labeled A are Kontes No. 826600-0004. The valves are of Teflon. The electrode wire seals labeled B are Ace Glass Co. No. 5037-03. Joints D (standard taper 18/9) and E (standard taper 24/40) were sealed with wax (available from Fisher Scientific Co., Catalog No. 15-530). Joints C (standard taper 10/30) do not contact BCl_3 vapor and may be sealed with any vacuum grease.

Results and Discussion

The yield of B_2Cl_4 and production rate closely parallel those cited by Massey,[7] *et al.* With a suitable power supply, the improved production reported[5] for the multiple Cu-electrode cell should be possible using this pump instead of trap-to-trap distillation.

Most probably, vapors of other volatile liquids may be circulated by selection of appropriate baths in conjunction with this pump.

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Registry No. B_2Cl_4, 13701-67-2; BCl_3, 10294-34-5.

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Chemistry of the Polynuclear Metal Halides. XII. Preparation of Molybdenum and Tungsten $M_6X_8^{4+}$ Clusters by Reduction of Higher Halides in Molten Sodium Halide-Aluminum Halide Mixtures

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Although compounds containing the molybdenum and tungsten halide cluster units $M_6X_8^{4+}$ have been known for many years,[1] more convenient preparative routes to these basic cluster units are needed. In general the methods which have been used involve disproportionation of intermediate halides,[2] *viz.*, $MoCl_3$, $MoBr_3$, WCl_4, and WBr_4, at elevated temperatures to produce the solid halides $(M_6X_8)X_4$ and gaseous higher halides. These reactions suffer from the necessity of preparing the intermediate halides and from the reduced yields resulting from loss of the higher halides upon disproportionation. Direct reduction of WCl_6 and WBr_5 to $(W_6Cl_8)Cl_4$ and $(W_6Br_8)Br_4$ by aluminum has been reported,[2] but these reactions require carefully controlled temperature gradients in order to prevent excessive $AlCl_3$ or $AlBr_3$ pressures during reduction.

The use of sodium tetrahaloaluminate melts for preparing and stabilizing reduced species is well documented.[3] Also, when aluminum is used as the reducing agent, these melts prevent excessive pressures of $AlCl_3$ or $AlBr_3$ through the reactions[3]

$$NaX(s) + AlX_3(g) = NaAlX_4(l)$$

$$NaAlX_4(l) + AlX_3(g) = NaAl_2X_7(l)$$

In the present paper, the aluminum reduction of the higher molybdenum or tungsten halides in the appropriate sodium tetrahaloaluminate melt is reported as a convenient and safe procedure for the preparation of the corresponding molybdenum and tungsten(II) chlorides and bromides in good yields.

Experimental Section

Equipment. All syntheses, of starting materials and products, were carried out in evacuated Pyrex or Vycor glass systems. All air-sensitive reactants and products were stored and handled in a drybox under an atmosphere of argon or prepurified nitrogen maintained at a dew point of *ca.* −75°.

Materials. Molybdenum metal, with a nominal purity of 99.9%, was obtained from the Rembar Corp. as 4 × 8 in. sheets with a thickness of 15 mils. Prior to reaction, the metal was cut into small strips. Tungsten metal, as 200-mesh powder, was obtained from General Electric Co. The tungsten was purified in a stream of hydrogen at 1000° to remove tungsten oxides and then stored in the drybox until used. Aluminum round of 99.999% nominal purity was obtained from laboratory stock and shaved with a tungsten carbide bit to provide turnings suitable for the reaction. All other chemicals, used in syntheses and separations, were of reagent grade purity and used as obtained.

Analyses. Analyses for chlorine and bromine were carried out by potentiometric titrations with standard silver nitrate solution. Analysis for tungsten metal was performed by a standard gravimetric method where the oxide was precipitated, ignited, and weighed as WO_3. Acidified solutions containing molybdenum were passed down a column of amalgamated zinc, which reduced the molybdenum quantitatively to Mo(III), and then into a solution containing an excess of iron(III), and the resulting iron(II) was titrated potentiometrically with a standard solution of ceric sulfate.

Syntheses. High-purity aluminum chloride was obtained either by resubliming reagent grade aluminum chloride or by passing electronic grade (99.99%, from Air Products and Chemicals, Inc.) hydrogen chloride over turnings of high-purity aluminum metal at 300°.

The molybdenum(V) chloride, tungsten(VI) chloride, and tungsten(V) bromide were prepared by direct reaction of the elements at 450, 550, and 550°, respectively, as described previously.[4]

Preparation of $(H_3O)_2[(Mo_6Cl_8)Cl_6]\cdot 6H_2O$. In a typical reaction, 13.65 g of $MoCl_5$, 1.38 g of Al, 8.2 g of NaCl, and 13.33 g of $AlCl_3$ were loaded into a 45 × 140 mm Pyrex reaction tube fitted with an 18/9 ball or socket joint. The tube and contents were attached to the vacuum line, evacuated to *ca.* 10^{-5} Torr, and sealed off. The reaction tube was fitted with a thermocouple, wrapped in aluminum foil, wrapped with a 6-ft heating tape, and insulated with 2-in. asbestos tape, leaving thermocouple leads and heating tape plug exposed. The reaction vessel was placed on a wrist-action shaker and the heating tape leads were attached to a variable-power supply. In order to prevent too rapid initial reaction the temperature was raised to only 200° and the reaction was allowed to equilibrate for 6 hr. Then the temperature was raised carefully over a 3-hr period to 450° and the reaction allowed to proceed with shaking for 48 hr. Upon cooling, the products were removed from the tube in air, ground in a mortar, and carefully poured into *ca.* 200 ml of 1 *M* HCl. This solution was stirred for about 15 min and centrifuged, and the residue was washed with 1 *M* HCl until the washings showed no further yellow color of the $Mo_6Cl_8{}^{4+}$ cluster; the filtrate then contained the major portion of the molybdenum cluster plus the dissolved sodium and aluminum chlorides. The residue then was extracted with ethanol to dissolve any remaining molybdenum(II) chloride. The respective water and ethanol solutions were reduced in volume until solids began separating from solution. Addition of concentrated HCl to these solutions so as approximately to triple their volumes resulted in precipitation of both the cluster compound and NaCl. The mixtures were cooled and filtered, and the precipitates were washed with cold concentrated HCl. Further product was obtained after the filtrates were combined and reduced in volume, and the above procedure was repeated. Again the solids were filtered away, and at this time the filtrate was discarded. The solids were combined and extracted with dry ethanol, which dissolved the molybdenum(II) chloride away from the insoluble NaCl. This ethanol solution then was carefully reduced in volume, and the molybdenum chloride cluster, as the acid hydrate $(H_3O)_2[(Mo_6Cl_8)Cl_6]\cdot 6H_2O$, was precipitated after addition of cold concentrated HCl. The product thus obtained was washed with concentrated HCl and dried in air. Based on the initial quantity of $MoCl_5$ a yield of 98% was obtained. Prior to analysis the compound was heated *in vacuo* at 200° to produce the dihydrate $(Mo_6Cl_8)Cl_4\cdot 2H_2O$. *Anal.* Calcd for $Mo_6Cl_{12}\cdot 2H_2O$: Mo, 55.51; Cl, 41.02. Found: Mo, 55.5; Cl, 41.0.

Preparation of $(H_3O)_2[(Mo_6Br_8)Br_6]\cdot 6H_2O$. In a typical reaction, 13.65 g of $MoCl_5$, 1.38 g of Al, 14.55 g of NaBr, and 26.68 g of $AlBr_3$ were loaded and sealed in a Pyrex reaction tube. Subsequently a reaction procedure identical with that of the chloride synthesis was followed. The products then were opened to the air, ground in a mortar, and stirred for about 15 min in cold 1 *M* HBr. Thereafter the respective solutions were treated in the same manner as in the chloride synthesis, using concentrated HBr instead of HCl. However in order to dissolve the molybdenum bromide cluster from the insoluble residue, it was necessary to extract the mixture for 48 hr in boiling ethanol (50%) and HBr(aq). At the end of this period, the solution was filtered, the volume was reduced, and the cluster compound was precipitated with cold saturated HBr(aq). The products then were combined and recrystallized from ethanol. The crystalline final product, obtained in 96% yield based on the initial quantity of $MoCl_5$, was identified as the acid hydrate $(H_3O)_2[(Mo_6Br_8)Br_6]\cdot 6H_2O$. Prior to analysis this solid was heated *in vacuo* at 200° for 8 hr, which provided the dihydrate $(Mo_6Br_8)Br_4\cdot 2H_2O$. *Anal.* Calcd for $Mo_6Br_{12}\cdot 2H_2O$: Mo, 36.63; Br, 61.08. Found: Mo, 36.5; Br, 61.0.

Preparation of $(H_3O)_2[(W_6Cl_8)Cl_6]\cdot 6H_2O$. The syntheses of the tungsten compounds follow very closely the corresponding molybdenum(II) halide preparations. Thus, 19.85 g of WCl_6, 1.81 g of Al, 9.0 g of NaCl, and 13.33 g of $AlCl_3$ were loaded into a Vycor reaction tube as described previously. After sealing, the reaction vessel was then mounted inside a rocking furnace whose temperature was regulated by a thermocouple attached to the vessel. The reaction vessel was heated to 200° and maintained at this temperature for 2 hr while the furnace rocked from an upright position through an angle of *ca.* 100°. The reaction mixture then was heated carefully over a 9-hr period, including a 6-hr pause at 450°, to the reaction temperature of 550° where it was held for a 24-hr period. After cooling, the reaction vessel was opened in the drybox to allow for an examination of some products that had sublimed from the melt. The bulk of the product was ground in a mortar, removed from the drybox, and treated in a manner identical with that for the preparation of the molybdenum(II) chloride. A small portion of acid hydrate $(H_3O)_2[(W_6Cl_8)Cl_6]\cdot 6H_2O$, obtained in 54% yield, was heated to 325° *in vacuo* to produce the anhydrous $(W_6Cl_8)Cl_4$ for analysis. *Anal.* Calcd for W_6Cl_{12}: W, 72.19; Cl, 27.81. Found: W, 72.0; Cl, 27.8.

Preparation of $(H_3O)_2[(W_6Br_8)Br_6]\cdot 6H_2O$. The preparations of

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(2) R. D. Hogue and R. E. McCarley, *Inorg. Chem.*, 9, 1354 (1970), and references contained therein.

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(4) R. E. McCarley and T. M. Brown, *Inorg. Chem.*, 3, 1232 (1964).

tungsten(II) bromide and its derivatives are exactly analogous to the preparation of tungsten(II) chloride and the separation techniques of molybdenum(II) bromide. Thus, 29.20 g of WBr_5, 1.38 g of Al, 14.55 g of NaBr, and 26.68 g of $AlBr_3$ were loaded into a Vycor reaction tube and subjected to a reaction procedure as described for the tungsten chloride preparation. After reaction, the tube was opened in the drybox and a sample of the sublimed products was taken for an X-ray powder pattern. Subsequent treatment of the reaction mixture, which provided the acid hydrate $(H_3O)_2[(W_6Br_8)Br_6]\cdot 6H_2O$ in 45% yield, was exactly the same as that to obtain the corresponding molybdenum(II) bromide. The acid hydrate was decomposed to $(W_6Br_8)Br_4$ *in vacuo* at 350°, prior to analysis. *Anal.* Calcd for W_6Br_{12}: W, 53.49; Br, 46.51. Found: W, 53.74; Br, 46.49.

Discussion

In all of the reduction reactions given in this work the relative proportions of reactants were governed by eq 1 for

$$6MoCl_5 + 6Al = Mo_6Cl_{12} + 6AlCl_3 \tag{1}$$

$MoCl_5$ and WBr_5 and by eq 2 for WCl_6. Because the initial

$$6WCl_6 + 8Al = W_6Cl_{12} + 8AlCl_3 \tag{2}$$

reaction between Al and the higher halides may be quite vigorous and time must be permitted for formation of the fused salt $NaAlCl_4$ from NaCl and $AlCl_3$, it is very important that the temperature not be raised above 200° until after a few hours (*ca.* 6 hr at 200° generally was found to be adequate). In a few cases when the temperature was increased above 200° too rapidly, excessive pressures developed and the reaction tubes exploded. Also it is necessary to ensure that the ratio $AlCl_3$:$NaAlCl_4$ remains at less than 1.0 during the reaction; otherwise excessive pressure of $AlCl_3$ will result at the higher temperatures of 450–550°. Generally in the reactions given here, sufficient NaCl was added to the mixtures such that the molten $NaAlCl_4$ contained no more than 10–20 mole % $AlCl_3$ upon completion of the reaction. As noted below mixtures which contained excess NaCl were unsatisfactory because they resulted in reduced yields of the cluster compounds.

The results obtained here indicate that the molybdenum and tungsten cluster species $M_6Cl_8^{4+}$ or $M_6Br_8^{4+}$ are stable in the acidic fused salts $NaAlX_4$–AlX_3 (X = Cl or Br). However the reaction conditions required to obtain optimum yields of the cluster compounds were initially unknown. In the course of establishing the optimum reaction conditions given above it was found that at temperatures less than 450° for reduction of the molybdenum halides, or 550° for reduction of the tungsten halides, relatively poor yields of the cluster compounds were obtained. Furthermore, reaction times less than those given above also resulted in reduced yields.

In all cases good yields of the cluster compounds were obtained only from melts containing excess aluminum halide. At least in the case of the tungsten chloride reductions, when a melt containing excess NaCl was used, the yield of $(W_6Cl_8)Cl_4$ was nil. Thus, attempted conversion directly to the salt $Na_2W_6Cl_{14}$ failed, and the inference is made that the cluster species $W_6Cl_8^{4+}$ is not stable in the basic, sodium chloride rich melts.

In the $AlCl_3$-rich melts it is not obvious why the yields of $(W_6Cl_8)Cl_4$ and $(W_6Br_8)Br_4$ are low (*ca.* 50%) compared to those of the corresponding molybdenum compounds (>90%). That $(W_6Cl_8)Cl_4$ is stable in these acid melts is indicated by the following evidence. A sample of $(W_6Cl_8)Cl_4$ was dissolved in molten $NaAlCl_4$–$AlCl_3$ mixture and held for 48 hr at 450°. During this time no change in the yellow color of the melt was noticed, which indicated that no decomposition of the $W_6Cl_8^{4+}$ cluster had resulted. After further heating at 500° for 24 hr, the mixture was cooled and most of the $(W_6Cl_8)Cl_4$ was recovered unchanged from the mixture.

It is likely that there is a larger kinetic barrier to formation of the tungsten cluster species than for the corresponding molybdenum clusters. This is evidenced by the higher reaction temperature (550°) required to obtain substantial yields of the tungsten compounds as opposed to the molybdenum compounds (450°). In the case of both molybdenum and tungsten no evidence for unreacted aluminum metal was found in the mixtures resulting from reactions at lower temperatures. This suggests that reduction to molybdenum(II) or tungsten(II) species is complete but that conversion of these species to the $M_6X_8^{4+}$ cluster compounds is a much slower process. Evidently the kinetic barrier in the formation of the cluster compounds stems from the hindered conversion of the precursor, reduced species to the $M_6X_8^{4+}$ cluster units. If this is the case other interesting compounds possibly could be isolated from the fused-salt solutions, and further work on the nature of the precursor species in the solutions is indicated.

Registry No. $(Mo_6Cl_8)Cl_4$, 21057-59-0; $(Mo_6Br_8)Br_4$, 43140-50-7; $(W_6Cl_8)Cl_4$, 43140-51-8; $(W_6Br_8)Br_4$, 43140-52-9; $MoCl_5$, 10241-05-1; WCl_6, 13283-01-7; Al, 7429-90-5.

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Electronic Structure of Some Cubane-Like Fe_4S_4 Clusters. Magnetic Field Mossbauer Results

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A series of polynuclear iron–sulfur cluster compounds was first prepared by Balch.[2] By successive one-electron reductions the neutral dithiolene complex was converted to the mono- and dianions of the following composition

$$\underset{\substack{\mathbf{1}\\ \text{neutral complex}}}{\mathrm{Fe_4S_4\{S_2C_2(CF_3)_2\}_4}} \xrightarrow{1e^-} \underset{\substack{\mathbf{2}\\ \text{monoanion}}}{[\mathrm{Ph_4As}][\mathrm{Fe_4S_4\{S_2C_2(CF_3)_2\}_4}]} \xrightarrow{1e^-}$$

$$\underset{\substack{\mathbf{3}\\ \text{dianion}}}{[\mathrm{Ph_4As}]_2[\mathrm{Fe_4S_4\{S_2C_2(CF_3)_2\}_4}]}$$

Balch deduced the quadrameric nature of the clusters from a variety of physiochemical results. The actual structure of the dianion has recently been determined by an X-ray study which shows the quadramer to consist of a distorted Fe_4S_4 cube formed by interpenetration of S_4 and Fe_4 tetrahedra.[3] In addition, unperturbed Mossbauer spectral studies[2,3] show all of the iron atoms of these cluster systems to be equivalent and indicate that the three compounds are very similar in

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[1] Supported by the National Science Foundation.

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