REACTIONS OF METAL CHLORIDES AND CHLOROMETALLATE SALTS WITH RED PHOSPHORUS

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SUMMARY

The use of red phosphorus as a reducing agent for $NbCl_5$, $TaCl_5$, and $MoCl_5$ has been investigated by heating mixtures of red phosphorus and the metal chloride in a closed tube. By this method, $NbCl_4$ and $MoCl_3$ are obtained as products, while $TaCl_5$ undergoes little or no reduction under these conditions. Similarly, upon heating mixtures of red phosphorus, CsCl, and $CsNbCl_6$ or $CsTaCl_6$, purple Cs_2NbCl_6 or Cs_2TaCl_6 were obtained. Mixtures of red phosphorus, CsCl, and $MoCl_5$ or WCl_6 yielded Cs_2MoCl_6 or $CsWCl_6$, respectively, upon heating.

INTRODUCTION

The behavior of red phosphorus as a reducing agent toward tungsten(VI) chloride was reported by Novikov *et al.*[1], and has been used in this laboratory routinely to synthesize tungsten(V) chloride[2]. The method involves the reaction of red phosphorus with solid tungsten(VI) chloride, phosphorus(III) chloride being evolved, and tungsten(V) chloride remaining as a residue. It was decided to explore the application of the reaction to other metal chlorides and hexachlorometallate salts. The following reactions have been investigated:

$$nP + 3MCl_5 \rightarrow nPCl_3\uparrow + 3MCl_{(5-n)} \quad (1)$$

$$P + 6CsCl + 3MCl_5 \rightarrow PCl_3\uparrow + 3Cs_2MCl_6 \quad (2)$$

where M = Nb, Ta, or Mo

$$P + 3CsMCl_6 + 3CsCl \rightarrow PCl_3\uparrow + 3Cs_2MCl_6 \quad (3)$$

where M = Nb or Ta

$$P + 3CsCl + 3WCl_6 \rightarrow PCl_3\uparrow + 3CsWCl_6 \quad (4)$$

EXPERIMENTAL

All handling of starting materials and products was done in a dry nitrogen atmosphere.

The red phosphorus used has been washed with dry CCl_4, and dried *in vacuo* at 110°.

Reaction of red phosphorus with niobium(V) chloride. Approximately 20 g of commercial niobium(V) chloride (Alfa Inorganics) first was dissolved in 75 ml of thionyl chloride. The solvent was removed in an inert atmosphere. The foregoing procedure converted possible oxides and oxychlorides of niobium(V) to niobium(V) chloride[3].

Approximately 0.04 mol (10–12 g) of the resulting $NbCl_5$ was ground intimately for 5–10 min in an agate mortar with 0.01 mol (0.25–0.30 g) or red phosphorus. The mixture was placed in one end of a 14 mm o.d. pyrex tube which was closed either with a joint and stopcock or a tightly-fitting rubber stopper. The end of the tube containing the mixture was placed in a tube furnace pre-heated to 165°C. The mixture melted almost immediately to a black liquid, from which phosphorus trichloride and the excess niobium(V) chloride distilled, collecting in the cool portion of the tube. After several hours or overnight, the black melt slowly solidified as niobium(V) chloride distilled out, leaving a black crystalline residue, often in a matrix of brown powdery material. On grinding in a mortar, the black crystals turned to a brown powder identical in appearance, solution properties, and analysis with the non-crystalline portion of the residue.

The product was remarkably sensitive to air and moisture, dissolving violently in water to give a blue solution which turned green rapidly. The products of some of the preparations were contaminated with residual unreacted red phosphorus in amounts from 0–6%. This residue was removed prior to analyses by filtration and analytical results were corrected for the red phosphorus content.

Anal. Calcd. for $NbCl_4$: Nb, 39.58; Cl, 60.42%. Found on several different preparations: Nb, 40.38, 40.12, 39.47, 40.15; Cl, 59.71, 60.19, 60.03, 59.23%.

Reaction of red phosphorus with molybdenum(V) chloride. Approximately 0.04 mol (10–12 g) of commercial molybdenum(V) chloride (Alfa Inorganics) was ground with 0.01 mol (0.25–0.30 g) of red phosphorus. The resulting mixture was placed in one end of a closed tube heated at 200°C, or, alternatively, under vacuum at 175°C. After heating 2–3 days, the mixture was re-ground and re-heated 2–3 days.

Excess molybdenum(V) chloride and product phosphorus(III) chloride sublimed to the cool portion of the tube, but no appreciable liquefaction of the reaction mixture was observed during heating. The residue which had been subjected to vacuum at 175°C was pinkish-red in color, while the residue from the reaction at 200°C was pinkish-red with some remaining black coating. The product residues were insoluble in water in all cases, although hydrolyzed by strong base to a brownish-black flocculent hydroxide.

Anal. Calcd. for $MoCl_3$: Mo, 47.42; Cl, 52.58%. Found: Mo, 46.85; Cl, 53.16 (results corrected for 1.9% residual red phosphorus). Another preparation which apparently contained negligible residual red phosphorus contained 46.62% Mo.

Reaction of red phosphorus with tantalum(V) chloride. Approximately 0.015 mol (5.2 g) of commercial tantalum(V) chloride (Alfa Inorganics), after treatment with thionyl chloride in a manner similar to that used for niobium(V) chloride, was ground intimately with approximately 0.005 mol (0.15 g) of red phosphorus. The mixture was placed in one end of a closed tube heated at 200°C for 1 h. The mixture melted to a black liquid, from which most of the tantalum(V) chloride sublimed to the cool portion of the tube. On cooling, the reddish-black residue was determined to be 72% red phosphorus, with the soluble portion of the residue having a Cl:Ta ratio of approximately 4.5.

A similar mixture of tantalum(V) chloride and red phosphorus was placed in a sealed tube, and the entire tube heated at 220°C. The mixture formed a black melt, which was heated for 6 days. At the end of this time, one end was cooled to room temperature, and unreacted tantalum(V) chloride sublimed to the cool end. Approximately 95% of the original tantalum(V) chloride was recovered unreacted. The dark red residue was 60% red phosphorus, the soluble portion of the residue having a Cl:Ta ratio of 3.3.

An identical sealed-tube experiment was carried out at 320°C for 6 days. The black liquid formed was observed to contain particles of a dark red material. After cooling one end of the tube to permit sublimation of unreacted tantalum(V) chloride out of the hot zone, approximately 90% of the initial tantalum(V) chloride was recovered unchanged, the residue again being largely red phosphorus.

Reaction of red phosphorus with $CsNbCl_6$ *and* $CsTaCl_6$. Approximately 3 g of yellow $CsNbCl_6$, prepared from ICl–$SOCl_2$ solution as described by BAGNALL AND BROWN[4], was ground with an equimolar quantity of dried CsCl and with a proportional one-third molar quantity of red phosphorus. The mixture was heated in one end of a closed tube placed in a furnace at 250°C. After three days, the mixture remained solid, and had turned purple. After re-grinding and heating at 250°C for another day, the purple product residue was removed and analyzed. A light coating of yellow powder was observed to have sublimed to the cool portion of the tube, together with a considerable amount of colorless phosphorus trichloride liquid.

Anal. Calcd. for Cs_2NbCl_6: Nb, 16.26; Cl, 37.23%. Found: Nb, 16.70; Cl, 35.35%.

A similar procedure was carried out using cream-colored $CsTaCl_6$, also prepared by the method of BAGNALL AND BROWN[4]. The reaction temperature was 235°C. Phosphorus trichloride was observed in the cool portion of the tube, while a reddish-purple residue remained as a product in the hot zone.

Anal. Calcd. for Cs_2TaCl_6: Ta, 27.44; Cl, 32.26%. Found: Ta, 27.07; Cl, 32.34%.

Reaction of red phosphorus with cesium chloride and niobium(V) chloride, tantalum(V) chloride, molybdenum(V) chloride, and tungsten(VI) chloride. A mixture made up in the molar ratios 1/3 P to 2 CsCl was ground with niobium(V) chloride, tantalum(V) chloride or molybdenum(V) chloride. In each case an amount of metal chloride was used in excess of the quantity required for conversion to Cs_2MCl_6. A ratio 1/3 P to 1 CsCl was ground with excess tungsten(VI) chloride.

The niobium(V) chloride-containing mixture was heated to 200°C and 250°C in different preparations, re-ground with excess niobium(V) chloride and re-heated. The tantalum(V) chloride-containing mixture was heated to 210°C and 230°C in different preparations. In all cases a purple residue was obtained, with excess MCl_5 (where M=Nb, Ta) and an additional black sublimate collected in the cool portion of the tube. Analyses of the purple residues corresponded to mixtures of Cs_2MCl_6 and CsCl.

The molybdenum(V) chloride-containing mixture was heated to 200°C several days, and re-ground and re-heated twice with excess molybdenum(V) chloride. A green-black residue was obtained from which excess black molybdenum(V) chloride and colorless phosphorus(III) chloride had sublimed to the cool portion of the tube.

Anal. Calcd. for Cs_2MoCl_6: Mo, 16.70; Cl, 37.02%. Found: Mo, 16.88; Cl, 36.87.

The WCl_6-containing mixture was heated to 105°C for several days, and was re-ground and re-heated with excess WCl_6. A dark green residue was obtained, while colorless PCl_3 and excess WCl_6 sublimed to the cool end of the tube.

Anal. Calcd. for $CsWCl_6$: W, 34.72; Cl, 40.18%. Found: W, 34.72; Cl, 39.26, 38.09% (last one uncorrected for slight red phosphorus content).

On heating the green $CsWCl_6$ to 220°C for several days it exhibited the behavior reported earlier[5,6], forming a red-purple solid (the color reported for Cs_2WCl_6) and a black sublimate (the color of WCl_6).

Analyses

Removal of red phosphorus. In preparations where it was present in more than trace amounts, red phosphorus was removed by filtration from a solution of the sample which had been dissolved in dilute aqueous nitric acid, and subsequently made basic with potassium hydroxide. The insoluble phosphorus was dried and weighed to correct the orginal weight of the sample.

Analyses of niobium and tantalum compounds. Acidification with nitric acid of the solution from which phosphorus had been removed, and subsequent addition of ammonium hydroxide precipitated the hydrous oxide of niobium or tantalum. The precipitate was filtered, ignited at 800–850°C, and weighed. Chloride was determined gravimetrically on the filtrate.

Analyses of tungsten compounds. Prolonged hydrolysis (1–2 days) at slightly above room temperature of the sample in 10% aqueous nitric acid effected the precipitation of tungsten(VI) oxide which was filtered, ignited to 900°, and weighed. Chloride was determined gravimetrically on the filtrate.

Analyses of molybdenum compounds. Molybdenum was determined by reduction in a Jones Reductor after decomposition of the sample in fuming sulfuric acid. The reduced molybdenum was titrated with Ce(IV). Chloride was determined gravimetrically after basic hydrolysis and acidification of a separate sample.

X-ray powder patterns. Powder patterns were determined for representative samples using a 114.59 mm Norelco powder camera and CuKα radiation.

RESULTS AND DISCUSSION

The use of red phosphorus as a reducing agent seems promising for the reduction of transition metal halides and hexahalometallate salts. Quite simple equipment is required. The products are contaminated occasionally with small amounts of unreacted red phosphorus. The quantity of red phosphorus contamination can usually be reduced by successive grindings and re-heatings with excess metal chloride.

The reduction of $NbCl_5$ by red phosphorus constitutes a direct route to crystalline niobium(IV) chloride. Attempts to carry the reduction further to produce niobium(III) chloride failed. In a reaction run at 300°C with sufficient phosphorus to reduce the niobium(V) chloride to niobium(III) chloride, the residue in the hot end of the tube was found to be 84% red phosphorus, with amounts of niobium and chloride too small for analysis. The total weight of the residue was equal to approximately half of the weight of red phosphorus initially used. The cool end of the tube contained sublimed yellow niobium(V) chloride, and a black sublimate which reacted violently with water to give a blue solution, typical behavior for niobium(IV) chloride. Thus at high temperatures in the presence of niobium(V) chloride vapor, the niobium(IV) chloride formed in the reduction sublimes out of the hot zone without reacting further with red phosphorus. The stability of niobium(IV) chloride is well-known, the disproportionation temperature of niobium(IV) chloride having been estimated by SCHAFER[7] as about 420°C. Powder patterns of niobium(IV) chloride formed at 165°C were identical to that of a product formed at 200°C, the latter with a slightly lower Cl : Nb ratio. These patterns were different from those obtained for molybdenum(III) chloride.

Attempts to stop the reduction of $MoCl_5$ at $MoCl_4$ were unsuccessful. Attempts to effect reduction at 145°C, both with and without vacuum, resulted in partial conversion to water-insoluble, pinkish-red molybdenum(III) chloride, the remainder of the product being unreacted $MoCl_5$. For example, one reaction mixture was held at 140°C for several days with regrinding and was finally heated to 110°C *in vacuo* overnight to attempt removal of excess molybdenum(V) chloride. About 20% of the latter black product residue was insoluble in water, the remainder dissolving to give a red solution. Analyses on the soluble portion showed it to be unreacted molybdenum(V) chloride, while the insoluble material exhibited the color and properties of molybdenum(III) chloride. Its decomposition to a flocculent hydroxide in strong base further indicated the insoluble material to be molybdenum(III) chloride and not residual red phosphorus. It must be concluded that, if the reduction of molybdenum(V) chloride does proceed stepwise through molybdenum(IV) chloride, the molybdenum(IV) chloride is immediately reduced further to non-volatile molybdenum(III) chloride.

The results of the attempts to reduce tantalum(V) chloride with red phosphorus indicate that some reduction does occur, but the yields of reduced tantalum chlorides are negligibly small. When one end of the reaction tube is maintained at room temperature, tantalum(V) chloride sublimes out of the hot zone before undergoing appreciable reduction, although some slight reduction is indicated by the formation of the black melt. Even after prolonged heating of the entire sealed tube containing a reaction mixture, the greater portion of the tantalum(V) chloride did not undergo reduction. It must be concluded that very small amounts of tantalum(IV) and/or tantalum(III) chloride, depending upon reaction conditions, can be formed by the reduction of tantalum(V) chloride with red phosphorus. However, the method is not useful for producing isolatable quantities of the lower tantalum chlorides.

The reduction of the cesium hexachlorometallate salts of these metals gave products similar to those described by MCCARLEY[8] from the reaction of cesium chloride with niobium(IV) chloride and tantalum(IV) chloride. They were also identical in color, powder patterns, and analyses to the products obtained by using cesium iodide as a reducing agent both on WCl_6[5] and on $CsNbCl_6$ and $CsTaCl_6$[9].

As noted above, attempts to prepare Cs_2NbCl_6 and Cs_2TaCl_6 from the correct molar ratios of MCl_5 (where M = Nb, Ta), cesium chloride, and red phosphorus always gave residues contaminated with cesium chloride. Apparently the solid-phase reaction proceeds so slowly, even at the temperatures involved, that (1) MCl_5 sublimes unreacted out of the hot zone, and/or (2) MCl_5 reacts first with the phosphorus, forming black MCl_4, which, in turn, sublimes out to some extent before fitting itself into the lattice of the complex cesium salt. Both (1) and/or (2) above contribute to loss of niobium or tantalum halide from the salt and enrichment of the residue with cesium chloride.

Such a problem was not encountered for salts of molybdenum and tungsten. The $CsWCl_6$ forms at temperatures too low for appreciable sublimation of tungsten(VI) chloride; indeed, as reported earlier[5,6], $CsWCl_6$ disproportionates readily into Cs_2WCl_6 and tungsten(VI) chloride at temperatures much above 160°C. It has been shown by FOWLES and coworkers[10] that Cs_2MoCl_6 will form simply by the reaction of molybdenum(V) chloride with cesium chloride, evolving chlorine. So it is not surprising that Cs_2MoCl_6 formed cleanly with the present phosphorus reduction technique, since excess molybdenum(V) chloride was present.

Powder patterns of all metal(IV) hexachlorometallates were similar to those of the Cs_2NbCl_6, Cs_2TaCl_6[9], and Cs_2WCl_6[5] reported earlier, which have the K_2PtCl_6 cubic structure. The powder pattern of $CsWCl_6$ was similar to that observed for $CsWCl_6$[5], $CsTaCl_6$ and $CsNbCl_6$[9] reported earlier. The application of the method of phosphorus reduction to similar compounds of other transition metals currently is being investigated.

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