SYNTHESIS OF ANHYDROUS METAL CHLORIDES BY THE ACTION OF CHLOROCARBON SOLVENTS ON SOME METAL OXIDES AND SULFIDES*

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SUMMARY

Anhydrous metal chlorides have been prepared by the action of chlorocarbon solvents on some metal oxides and metal sulfides. Octachlorocyclopentene converted Nb(V), Fe(III), Ti(IV), and V(V) oxides to anhydrous Nb(V), Fe(III), Ti(IV), and V(III) chlorides, respectively, at the normal boiling point of the solvent (285°C). This solvent converted W(VI), V(V), and Mo(IV) oxides to $WOCl_4$, $VOCl_3$, and $MoOCl_3$, respectively, whereas MoO_3 gave a mixed product. Iron pyrite, FeS_2, and FeS gave $FeCl_3$ when reacted with octachlorocyclopentene. A number of other metal oxides and sulfides proved to be unaffected by this chlorinating agent at its normal boiling point.

Hexachlorocyclopentadiene converted WO_3 to $WOCl_4$ but gave little or no metal chloride with Fe_2O_3, FeS, and FeS_2. Hexachloropropene also showed no reaction with certain metal sulfides.

INTRODUCTION

In the method of KNOX AND TYREE[1], carbon tetrachloride proved to be an effective agent in converting metal oxides[1] and certain metal sulfides[2] to anhydrous metal chlorides at elevated temperature (400°C) and pressure (order of 100 atm). On the other hand, hexachloropropene converted metal oxides to anhydrous metal chlorides by simple refluxing at the normal boiling point of the solvent[3,4].

In this work, octachlorocyclopentene, hexachlorocyclopentadiene, and hexachloropropene were refluxed with some metal oxides and sulfides, at the normal boiling points of the solvents, to form anhydrous metal chlorides or oxochlorides.

EXPERIMENTAL

Materials

Niobium(V) oxide, ignited (Fairmount Co.), Fe_2O_3 (J. T. Baker Chemical Co.), TiO_2 freshly precipitated and dried at 110°C for 24 h, V_2O_5 (Fisher Scientific Co.),

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WO_3 (Fisher Scientific Co.), MoO_2 (S. W. Shattuck Chemical Co.), Al_2O_3 (Merck), ZrO_2, Ta_2O_5, ignited (Fisher Scientific Co.), iron pyrite, FeS_2 (Staley Consolidated Mine, Staley, N. C.), FeS (Baker and Adamson), and MoS_2 (Climax Molybdenum Co.) were used without further purification. Reagent grade $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (Baker and Adamson) was ignited in air at 700°C to give MoO_3, while tungstic acid (Matheson Colman and Bell) was converted to WS_2 and WS_3 by literature methods[5-7]. $Na_2MoO_4 \cdot 2H_2O$ (Merck), rhenium metal (Department of Chemistry, University of Tennessee), and TiO_2 (Baker and Adamson Co.) were converted to MoS_3, Re_2S_7 and TiS_2, respectively[8-10]. Octachlorocyclopentene (m.p. 38°C, b.p. 285°C) and hexachlorocyclopentadiene (m.p. 9.9°C, b.p. 239°C) were gifts from Hooker Chemical Corporation while hexachloropropene (b.p. 213°C) was purchased from Columbia Organic Chemicals Co., Inc.

General procedure

Two to three grams of the metal oxide or sulfide were refluxed, at the normal boiling point, with 20–30 g of the solid chlorocarbon solvent (or about 25 ml of the liquid chlorocarbon solvent) in a 100 ml round bottom flask attached to a water condenser with a Drierite-filled drying tube at the top, for a period varying from 5 min to 60 h as needed. After cooling, the reaction mixture was transferred to the dry box where it was filtered through a fritted glass crucible using suction. The solid product was washed with small portions of dry CCl_4 and pumped dry. Samples of the dry solid product were loaded into weighing pigs and, after removal from the dry box, were weighed and hydrolyzed by admitting water slowly through the ground glass stoppers of the weighing pigs. Alternatively, liquid products were fractionally distilled from the mixture using a vacuum jacketed Vigreaux Column. The distilled liquid product was transferred to the dry box where samples were loaded into weighing bottles which, after removal from the dry box and weighing, were immersed in water in glass-stoppered Erlenmeyer flasks. The latter were shaken to open the weighing bottles and to permit hydrolysis.

In the case of the iron-octachlorocyclopentene reactions, the solid product was separated by sublimation.

Analyses

Tungsten, Ti, and Nb were determined gravimetrically as WO_3, TiO_2, and Nb_2O_5, respectively. Chlorine was determined as AgCl, and rhenium as $(C_6H_5)_4AsReO_4$. Iron was reduced in the Jones reductor and titrated with Ce(IV), while Mo was determined by reduction to Mo(III) in the Jones reductor, oxidation with Fe(III), and back titration of the iron Fe(II) formed with Ce(IV). Vanadium was determined by reduction to V(II) in the Jones reductor, oxidation to V(III) with Fe(III), and back titration of the iron Fe(II) and the vanadium V(III) formed with Ce(IV).

REACTIONS YIELDING SINGLE METAL CHLORIDES

Reactions of oxides with octachlorocyclopentene

(a) *$NbCl_5$*. 1.3 g of Nb_2O_5 gave 2.4 g of yellow microcrystalline $NbCl_5$ (90% yield) when refluxed with the solvent for about 5 min.

Anal. Calc. for $NbCl_5$: Nb, 34.4%; Cl, 65.6%. Found: Nb, 34.0 ± 0.1%; Cl, 65.0 ± 0.1%; Cl/Nb, 5.01.

(b) *$FeCl_3$ (the short treatment)*. 2.0 g of Fe_2O_3 were refluxed with the solvent for

15 min. The solid reaction product gave, on sublimation, 2.4 g of green flake-like crystals of $FeCl_3$ (70% yield).

Anal. Calc. for $FeCl_3$: Fe, 34.4%; Cl, 65.6%. Found: Fe, 34.4 ± 0.1%; Cl, 65.6 ± 0.1%; Cl/Fe, 3.00.

(c) *$TiCl_4$*. 3.0 g of TiO_2 were refluxed with the solvent for 30 h. 3.4 g of light yellow $TiCl_4$ (70% yield) which distilled over at 135–136°C, were obtained.

Anal. Calc. for $TiCl_4$: Ti, 25.2%; Cl, 74.8%. Found: Ti, 24.5 ± 0.1%; Cl, 74.2 ± 0.1%. Cl/Ti, 4.09.

(d) *VCl_3*. 3.0 g of V_2O_5 gave 3.5 g of violet crystals of VCl_3 (70% yield) when refluxed with the solvent for 6–8 h.

Anal. Calc. for VCl_3: V, 32.4%; Cl, 67.6%. Found: V, 32.4 ± 0.1%; Cl, 67.6 ± 0.1%; Cl/V, 3.00.

(e) *$WOCl_4$*. 2.0 g of WO_3 gave 2.7 g of orange needles of $WOCl_4$ distributed throughout the red solution and also collected at the neck of the reaction flask (91% yield), when refluxed with the solvent for 2 h.

Anal. Calc. for $WOCl_4$: W, 53.8%; Cl, 41.5%. Found: W, 53.6 ± 0.1%; Cl, 41.5 ± 0.1%; Cl/W, 4.02.

(f) *$VOCl_3$*. 2.0 g of V_2O_5 were refluxed with the solvent for 15 min. 3.0 g of yellow-orange $VOCl_3$ (80% yield) which distilled over at 126–127°C, were obtained.

Anal. Calc. for $VOCl_3$: V, 29.3%; Cl, 61.4%. Found: V, 29.1 ± 0.1%; Cl, 61.2 ± 0.1%; Cl/V, 3.03.

(g) *$MoOCl_3$*. 1.5 g of MoO_2 gave 2.0 g of green crystals of $MoOCl_3$ (80% yield) when refluxed with the solvent for 15 min.

Anal. Calc. for $MoOCl_3$: Mo, 43.7%; Cl, 48.7%. Found: Mo, 43.7 ± 0.1%; Cl, 48.5 ± 0.1%; Cl/Mo, 3.00.

Reactions of sulfides with octachlorocyclopentene

(a) *$FeCl_3$*. 2.0 g of FeS was refluxed with the solvent for 20 min. The solid reaction product gave, on sublimation, 2.8 g of green flake-like crystals of $FeCl_3$ (80% yield).

Anal. Calc. for $FeCl_3$: Fe, 34.4%; Cl, 65.6%. Found: Fe, 34.4 ± 0.1%; Cl, 65.7 ± 0.1%; Cl/Fe, 3.00.

(b) *$FeCl_3$*. 1.5 g of iron pyrite, FeS_2, was refluxed with the solvent for 15 min. The solid reaction product gave, on sublimation, 1.5 g of $FeCl_3$ (75% yield).

Anal. Calc. for $FeCl_3$: Fe, 34.4%; Cl, 65.6%. Found: 34.3 ± 0.1%; Cl, 65.8 ± 0.1%; Cl/Fe, 3.01.

Reaction of WO_3 with hexachlorocyclopentadiene

$WOCl_4$. 2.0 g of WO_3 gave 2.6 g of orange needles of $WOCl_4$ (88% yield) when refluxed with 25 ml of the solvent.

Anal. Calc. for $WOCl_4$: W, 53.8%; Cl, 41.5%. Found: W, 53.6 ± 0.1%; Cl, 41.5 ± 0.1%; Cl/W, 4.02.

REACTIONS YIELDING MIXED METAL CHLORIDES

Reaction of MoO_3 with octachlorocyclopentene

Several experiments were carried out by reacting 2.0 g of MoO_3 with the solvent for different intervals of time. In all of these experiments, the products isolated were

TABLE I

RESULTS OF ANALYSIS FOR Mo AND Cl ON THE SOLID REACTION PRODUCT

% Mo	*% Cl*	*Cl/Mo*	*Time of Reaction*
43.8	53.5	3.31	15 min
42.5	53.5	3.40	1 h
42.5	52.8	3.37	12 h

found to be nonstoichiometric. Changing the ratio of the reactants did not change the nature of the product. Results are shown in Table I.

Reaction of MoO_2 with octachlorocyclopentene

1.5 g of MoO_2 was refluxed with the solvent for 14 h. The solid reaction product, when analyzed, gave Mo, 45.5%; Cl, 55.1%; Cl/Mo, 3.28.

Reaction of Fe_2O_3 with octachlorocyclopentene (the prolonged treatment)

2.0 g of Fe_2O_3 was refluxed with the solvent for 5 h. The solid reaction product, after extraction with CCl_4 for 18 h, analyzed for Fe, 39.3%; Cl, 58.0%; Cl/Fe, 2.32.

Reaction of $FeCl_3$ with octachlorocyclopentene

0.5 g of anhydrous $FeCl_3$ was refluxed with 10 g of the solvent for 5 h. The solid reaction product, when analyzed, gave Fe, 38.6%; Cl, 52.0%; and Cl/Fe, 2.12.

NONREACTIVE COMPOUNDS

With octachlorocyclopentene. Al_2O_3, ZrO_2, Ta_2O_5, WS_2, TiS_2, Re_2S_7, MoS_2, and MoS_3 showed little or no reaction with the solvent even after prolonged refluxing.

With hexachlorocyclopentadiene. Fe_2O_3, FeS, and FeS_2 showed little or no reaction with the solvent. Decomposition of the solvent was observed.

With hexachloropropene. Re_2S_7, MoS_3, MoS_2, TiS_2, FeS_2, and FeS showed little or no reaction with the solvent.

DISCUSSION

From the results obtained it is seen that the solvent, octachlorocyclopentene, is an effective and convenient chlorinating agent. Simple refluxing of the metal oxide with octachlorocyclopentene was found, in several instances, as in the cases of Nb_2O_5, V_2O_5, WO_3, and MoO_2, to be one of the best known methods of preparing the metal chlorides (or oxochlorides, as the case may be). The products, $NbCl_5$, VCl_3, $WOCl_4$, and $MoOCl_3$ were found to be prepared pure and in a good yield by this method, requiring only to be washed with CCl_4. With an additional simple step, like distillation or sublimation, other anhydrous metal chlorides and oxochlorides, as $VOCl_3$, $TiCl_4$, and $FeCl_3$, were also prepared by this method. With the exception of $TiCl_4$, all of these products were prepared within 4 h of reaction time. The chlorination of metal oxides with this solvent proved to be more often successful than the chlorination of metal sulfides. Of the metal sulfides tried, only FeS, and FeS_2 yielded a metal chloride when reacted with octachlorocyclopentene.

Octachlorocyclopentene was found to exhibit properties other than chlorinating action on the metal. It is (a) a dehydrating agent, (b) an oxidizing agent, and (c) a reducing agent: (a) in the presence of metal chloride it consumes water, most likely by a reaction producing HCl and replacing Cl with oxygen in the organic molecule so that the mixture is in a sense "self-drying" towards small quantities of water; (b) in the reaction of MoO_2 with the solvent, Mo was oxidized to the pentavalent state, while in the reaction of FeS and FeS_2 with the same solvent, Fe was oxidized from (II) to (III); (c) on the other hand, vanadium, in the reaction of V_2O_5 with the solvent, was converted to $VOCl_3$ with no change in its valence, but, then, on prolonged heating, was reduced from (V) to (III) as proved by the formation of VCl_3. This particular reaction was studied more closely by allowing a separately-prepared sample of $VOCl_3$ to react with octachlorocyclopentene under reflex conditions. In a few hours, VCl_3 was formed and the $V{=}O$ stretching frequency, observed in the i.r. spectrum of the reaction mixture progressively diminished until it disappeared completely. When a mixture of V_2O_5-solvent was allowed to react a short time and was then subjected to distillation, the liquid distilling at 136°C had a strong, sharp peak at 1035 cm^{-1}, which corresponds to the $V{=}O$ stretching frequency in $VOCl_3$[11,12]. This peak was absent from the i.r. spectrum of the remaining solution. On the other hand, when the reaction was allowed to proceed under reflux for a longer time, the sharp peak in the i.r. spectrum of the reaction mixture at 1035 cm^{-1} was found to diminish gradually as the violet solid, VCl_3, increased in quantity, until after about 18 h, the peak disappeared completely. Furthermore, the i.r. spectrum of the reaction mixture at this point was identical to that of the reaction mixture remaining after distilling off the $VOCl_3$ produced in the reaction in the separate experiment described above.

Reduction of the metal ion to a lower oxidation state was also observed in the reactions of FeS, FeS_2, and Fe_2O_3 with this same solvent. In all of these reactions, $FeCl_3$ was formed in the early stages of the reaction. On prolonged heating, Fe(III) was reduced to Fe(II). This was confirmed by reacting a separately-prepared sample of anhydrous $FeCl_3$ with octachlorocyclopentene. After a few hours of refluxing, the reaction was stopped and the reaction product was found, on analysis, to contain a Cl/Fe ratio equal to 2.32. The spectrum of the liquid reaction mixture was different from that of pure octachlorocyclopentene, or octachlorocyclopentene which has been refluxed alone, indicating solvent participation in the reaction.

Hexachlorocyclopentadiene has been found to be inferior to octachlorocyclopentene as a chlorinating agent because of its lower boiling temperature and slower reaction rates, as well as incompleteness of conversions and tendency to decompose on prolonged heating under these conditions.

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