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THE ACTION OF CARBON TETRACHLORIDE ON MOLYBDENUM(IV) OXIDE. TUNGSTEN(IV) OXIDE, AND TUNGSTEN(VI) OXIDE

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The preparation of anhydrous metal chlorides by the reaction of carbon tetrachloride on the appropriate metal oxide has been studied in detail by Knox and Tyree and their coworkers (1, 2). Their method, modified from that of Michael and Murphy (3), utilizes a pressure bomb and a usual temperature of 400° C. Their data show that the oxide of highest oxidation state yields the highest chloride; thus WO_3 produces WCl_6 and MoO_3 yields $MoCl_5$. This communication is a report of attempts to synthesize chlorides of Mo(IV), W(IV), and W(VI) using the general method of Knox and Tyree but at the lower temperature of 250° C. The pressure bomb used was identical with that described in the previously cited works. Under these conditions, we find that MoO_2 is converted to $MoCl_4$ in good yield, WO_2 is partially changed to WO_2Cl_2, and WO_3 is quantitatively converted to $WOCl_4$.

Experimental

Materials: Molybdenum(IV) oxide was obtained from the Climax Molybdenum Company, tungsten(IV) oxide from the Wah Chang Corporation, and tungsten(VI) oxide from the Fisher Scientific Company; these oxides, and reagent grade carbon tetrachloride, were used without further purification.

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General Procedure: A carefully weighed amount of pulverized metal oxide was sealed in a 110-milliliter Pyrex tube together with the appropriate amount of carbon tetrachloride; eight milliliters of CCl_4 was added for each 26 milliliters of tube volume. The materials need not be rigorously dried because small amounts of water are converted to phosgene and hydrogen chloride. The sealed tube was placed in the steel bomb, and enough carbon tetrachloride was added to the bomb to balance the internal pressure of the tube at reaction temperature. The steel bomb was then securely assembled and placed in the heating jacket; the temperature was held at 250° C. for four to eight hours. The bomb was then allowed to cool and was dissembled. The reaction tube was transferred to a glove box flushed with dry nitrogen, and the crystals were recovered from the reaction mixture and washed with fresh carbon tetrachloride used sparingly to prevent loss of product. The crystals were then dried under vacuum in the glove box or in an oven at 110° C. for five minutes; the dried product thus obtained was preserved in the glove box under a nitrogen atmosphere for analysis.

Analytical: Molybdenum was determined by reduction to Mo(III) by means of a Jones reductor, oxidation with Fe(III), and titration of the Fe(II) formed with permanganate. Tungsten was determined gravimetrically as tungsten(VI) oxide, and chlorine was weighed as silver chloride. In the latter case, care must be taken to prevent coprecipitation of silver molybdate if molybdenum is present. Analytical data are given in Table I together with calculated mole ratios of metal to chlorine for four identified compounds.

TABLE I

Analytical Data for Reaction Products

Compound	Theoretical		Analysis		Ratio
	% metal	% chlorine	% metal	% chlorine	M:Cl
$MoCl_4$	40.35	59.65	39.0	57.6	1:4.0
WO_2Cl_2 (from WO_2)	64.12	24.73	62.2	22.5	1:1.87
$WOCl_4$ (from WO_2)	52.29	40.31	51.2	30.2	1:3.1
$WOCl_4$ (from WO_3)	52.29	40.31	52.8	40.7	1:3.99

Results

The reaction of Mo(IV) oxide with carbon tetrachloride under pressure at 250° C. for eight hours yielded $MoCl_4$ in 90-92 per cent yield. The amount of contaminating unreacted oxide was determined by hydrolyzing a weighed sample of product and then weighing the insoluble MoO_2 after filtration. The crystals of $MoCl_4$ are black and disproportionate before melting at 310-20° C.

The reaction of W(IV) oxide under the conditions outlined above usually yielded a yellow-brown crystalline solid identified as a mixture of WO_2Cl_2 and $WOCl_4$ with the former present in much greater amount. Less than stoichiometric quantities of the oxide produced feathery orange crystals identified as principally $WOCl_4$. The analytical results in Table I show that both tungsten and chlorine are low probably because of the presence of both oxochlorides together with some unreacted oxide. A steel-blue surface luster usually observed on the crystals could be accounted for on the basis of the presence of very small amounts of WCl_4 and WCl_6. In the case of the orange crystals of $WOCl_4$, very large surface area doubtless caused extensive hydolysis during sampling leading to very low chlorine values; the tungsten percentages indicate that $WOCl_4$ was indeed formed. These data are in agreement with those of Komandin and Tarasenkov (4) who state that the oxochlorides of tungsten(VI) always occur together. For this reason, no yield data are given here.

The reaction of W(VI) oxide with carbon tetrachloride at 250° C. yielded $WOCl_4$, and at 300° C. the conversion was essentially quantitative after four to six hours. The melting point of the scarlet needle crystals was 200-210° C. with decomposition. At 400° C. this reaction yields WCl_6.

Attempts to substitute bromoform for carbon tetrachloride were mostly unsuccessful. MoO_2 did not react at all, and WO_2 yielded a small amount of $WOBr_4$.

Conclusions

Under the conditions of this research, the method of Knox and Tyree is very useful for the preparation of tungsten(VI) oxotetrachloride and moderately useful for the synthesis of molybdenum(IV) tetrachloride. Higher temperatures yield chlorides of higher oxidation states than those reported in this paper.

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