Ambient Temperature Preparations of Thio-, Seleno-, and Oxo-halides of Niobium, Tantalum, Molybdenum, Tungsten, and Rhenium

By GERALD W. A. FOWLES, RICHARD J. HOBSON, DAVID A. RICE, and KENNETH J. SHANTON
(*Department of Chemistry, The University, Whiteknights, Reading* RG6 2AD)

Summary The isolation of a large range of thio-, seleno-, and oxo-halides has been achieved by allowing Sb_2Y_3 ($Y = O$, S, or Se) to react with a metal halide at room temperature with carbon disulphide as solvent.

SEVERAL routes have been described for the preparation of the thio- and seleno-halides of the early transition metals.[1–4] The superior method is the reaction of a metal halide with either sulphur or Sb_2S_3 as it is relatively easy to control the extent of the reaction by careful choice of the reactant stoicheiometry.

All the routes so far described require temperatures in excess of 373 K either to promote the reaction, or to sublime out one of the reaction products. The disadvantage of this became apparent when attempts were made to synthesise $MSCl_3$ ($M = Nb$ or Ta) by allowing MCl_5 to react with Sb_2S_3 in a sealed tube, a procedure which led to the isolation of a range of tungsten and molybdenum thiohalides.[4] In reactions with the niobium(v) and tantalum(v) halides we observed a variety of colour changes and obtained non-stoicheiometric products. It is possible that the desired thiohalides were formed initially, but at the reaction temperature they underwent a disproportionation reaction similar to that undergone by $TaOCl_3$.[5]

Accordingly, MCl_5 (M = Nb or Ta) and Sb_2S_3 were allowed to react at room temperature for 1—3 days in the presence of non-co-ordinating solvents in which MCl_5 and one of the reaction products, $SbCl_3$, had sufficient solubility. CS_2 proved to be the most useful solvent of those tried and we report the first synthesis of $MSCl_3$ (M = Nb or Ta) [ν(Nb=S) 552, ν(Ta=S) 463 cm^{-1}] on a large scale. We have extended the method to prepare a range of thio- and seleno-halides: $NbSBr_3$ [(ν(Nb=S) 542 cm^{-1}] $NbSeCl_3$, $NbSeBr_3$, $TaSBr_3$ [ν (Ta=S) 448 and 437 cm^{-1}], and $TaSeBr_3$. The preparation of $TaSeBr_3$ is best effected by heating the reaction mixture to 50 °C.

For the previously reported[4] $MoSCl_3$ the synthetic route described here is preferable as the product is much more reactive towards Lewis bases. WS_2Cl_2, $WSSeCl_2$, $WOSCl_2$, and WO_2Cl_2, were isolated quantitatively by allowing $WYCl_4$ (Y = O, S, or Se) to react with $Sb_2Y'_3$ (Y' = O, S, or Se) in the presence of CS_2. With the high-temperature reaction it is difficult to prevent some $WYCl_4$ subliming out of the presence of the $Sb_2Y'_3$. For the products of the type $WYY'Cl_2$ ($Y \neq Y'$) there is a choice between two pairs of reactants. The best combination is to start with the species $WYCl_4$ where Y is the lowest member of Group VIb, because the solubility of $Sb_2Y'_3$ in CS_2 increases in the order Se<S<O.

A number of rhenium thio-[2] and seleno-halides[6] have been prepared but the routes described have usually led to a mixture of products. If $ReCl_5$ is allowed to react with Sb_2S_3 in CS_2 a material is obtained having analysis corresponding to $ReSCl_3$. Likewise, the reaction between $ReCl_5$ and Sb_2O_3 yields a species whose analysis approximates to $ReOCl_3$. The isolation of this oxo-halide has been claimed[7] although the claim was later withdrawn;[8] accordingly we are, at present, using our material in attempts to isolate some of the well characterised complexes of $ReOCl_3$[9] in order to prove its authenticity.

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