

S-Dealkylation by Tungsten Halides

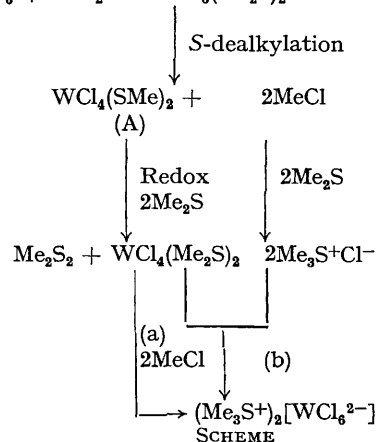
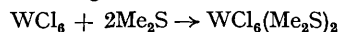
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Summary Tungsten hexa- or penta-chloride react with dialkyl sulphides to give $(R_3S^+)_2(WCl_6^{2-})$ [R = Me, Et] via an S-dealkylation-redox sequence.

IN the context of contemporary interest in S-dealkylation reactions,¹ and of the potential biological significance of redox reactions of co-ordinated sulphur ligands, we report that the interaction of WCl_6 or WCl_5 with dialkyl sulphides to give $(R_3S^+)_2(WCl_6^{2-})$ occurs via S-dealkylation of these ligands under unusually mild conditions.

Previous work² has shown that WCl_6 or WCl_5 react with dialkyl sulphides in carbon tetrachloride to give complexes of the type WCl_6L , $WCl_6 \cdot 2L$, and WCl_5L_2 . Polymeric WCl_4 will only react with the neat refluxing ligands to give $WCl_4 \cdot 2L$.³ We now find that the interaction of WCl_6 or WCl_5 with an excess of dimethyl or diethyl sulphide occurs exothermically *in vacuo* to give orange-brown crystals with the unexpected composition $(R_3S^+)_2(WCl_6^{2-})$. The identity of these products was established by elemental analysis, spectroscopic measurements, and alternative syntheses

(see below). I.r. spectra were typical of R_3S^+ cations, while a single broad band *ca.* 290 cm^{-1} , together with the



characteristic magnetic moments (1.45 B.M.), and solid state visible spectra confirmed the presence of the hexachlorotungstate(IV) anion.⁴

The Scheme is proposed to explain the typical reaction, $WCl_6 + 2Me_2S \rightarrow (Me_3S^+)_2(WCl_6^{2-})$, which must involve both dealkylation and alkylation of sulphur.

The evidence supporting this mechanism is as follows: (1) Me_2S_2 has been identified (¹H n.m.r.) as a reaction product. (2) The reaction of $WCl_4(Me_2S)_2$ with MeCl at 30° *in vacuo* yields $(Me_3S^+)_2(WCl_6^{2-})$ [route (a)]. (3) The reaction of $Me_3S^+Cl^-$ with $WCl_4(Me_2S)_2$ in carbon tetra-

chloride also produces $(Me_3S^+)_2(WCl_6^{2-})$, thus route (b) is a viable, but less likely, alternative. (4) Attempted synthesis of (A) from WCl_6 and Me_3SiSR in a 1:2 ratio gives R_2S_2 .

The combination of S-dealkylation and a metal-sulphur redox reaction under mild conditions in these systems is unique and of potentially broad interest and significance.

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³ M. A. Schaefer King and R. E. McCarley, *Inorg. Chem.*, 1973, **12**, 1972.

⁴ R. V. Parish, *Adv. Inorg. Chem. Radiochem.*, 1966, **9**, 315.