The Oxidation of some Transition-metal Chlorides by Trichloroacetonitrile

By G. W. A. FOWLES,* D. A. RICE, N. ROLFE, and R. A. WALTON
(*Department of Chemistry, University of Reading, Whiteknights, Reading*, RG6 2AD)

Summary The ability of trichloroacetonitrile to oxidise (and complex with) various transition-metal chlorides is reported, and compared with the analogous reactions involving acetonitrile, in which reduction occurs.

THE ability of nitriles to reduce metal halides has been studied fairly extensively.[1-6] The organic oxidation products of the reactions of acetonitrile with rhenium(V) chloride[7] and vanadium(IV) chloride[8] have been examined and it is believed that the primary product may be trichloroacetonitrile.

We have studied the reactions of trichloroacetonitrile with a range of metal chlorides and found that certain of the lower-valent transition-metal halides are oxidised to give complexes of a higher oxidation state. These reactions, which involve the reaction of the metal chloride with the neat ligand, have been studied on an all-glass vacuum line under air and moisture-free conditions.

Both tungsten(V) and tungsten(VI) chlorides yield the same diamagnetic crystalline yellow solid $WCl_6,2CCl_3CN$. Oxidation-state titrations confirm that all tungsten is in the sexivalent state. The complex is monomeric and non-conducting in dichloromethane, indicating that the tungsten atom is probably eight-co-ordinate. This formation of sexivalent tungsten is in contrast to the reactions involving acetonitrile in which both tungsten(V) and (VI) chlorides are reduced to give tungsten(IV) adducts. Analogous reactions with molybdenum(IV) chloride yield a mixed product, the principal constituent being $MoCl_5,2CCl_3CN$, which can be made directly from molybdenum(V) chloride. Similarly niobium(IV) chloride yields a mixed product consisting largely of $NbCl_5,Cl_3CCN$, the adduct of which is formed by reaction with niobium(V) chloride.

Titanium(III) chloride is oxidised to the crystalline yellow complex $TiCl_4,CCl_3CN$ [which may also be obtained directly from titanium(IV) chloride]; preliminary *X*-ray studies show the product to have a dimeric centrosymmetric chlorine-bridged structure.[9] Reduction products of trichloroacetonitrile, which may be isolated from the solution from the titanium(III) chloride reaction, are tetrachlorosuccinonitrile and a dark coloured polymeric chlorinated nitrile.[11]

The reactions of boron tribromide and chloride with trichloroacetonitrile yield white crystalline products of the formulation BX_3,CCl_3CN. The i.r. and Raman spectra of these compounds indicate the absence of any $C{\equiv}N$ frequencies, and the presence of characteristic $C{=}N$ frequencies. Accordingly, we suggest a dimeric bridged structure for these compounds similar to that postulated for BF_3,CF_3CN.[10]

Trichloroacetonitrile is a poorer electron-donor than acetonitrile, as might be expected, in view of the electron-withdrawing power of the chlorine atoms, and the isolated complexes tend to lose the ligand easily *in vacuo*. Furthermore, treatment of the trichloroacetonitrile complexes with even a very dilute solution of acetonitrile results in replacement of the trichloroacetonitrile ligands. This indicates that even in systems in which acetonitrile is oxidised to the trichloro-species, only acetonitrile complexes would normally be isolated.

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