The Photochemical Preparation of Cr^{III} Alkoxides*

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METAL ALKOXIDES[1] are typically covalent, polymeric compounds with degrees of polymerization in the range 2—6 and are generally easily hydrolysed. Publication of a recent Paper[2] concerning the methoxides and ethoxides of various first-row transition elements prompts us to communicate preliminary details of our studies of Cr^{III} alkoxides. It had been reported[3] that chromium forms a series of tetra-alkoxides, $Cr^{IV}(O{\cdot}CMe_x{\cdot}Et_{3-x})_4$, where $x = 1$—3, and that reduction of these gave the primary and secondary alkoxides of Cr^{III}, but no further mention of the latter was made. Other reports of Cr^{III} alkoxides were due to Thiessen and Kandelaky[4] [preparation of Cr^{III} ethoxide by reaction of chromium(III) chloride in absolute ethanol with sodium ethoxide], and Hornuff and Kappler[5] (formation by photolysis of alcoholic solutions of ammonium chromate). Adams and his co-workers[2] discuss the properties of $Cr^{III}(OEt)_3$ prepared by the photolysis method,[5] but do not mention the methoxide.

We report the preparation of Cr^{III} methoxide by

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the photochemical oxidative decarbonylation of the tricarbonylarenechromiums in dry methanol:

$$ArCr(CO)_3 \xrightarrow[h\nu]{MeOH} Cr^{III}(OMe)_3 + Ar + 3CO.$$

The ligands are evolved quantitatively and the methoxide is a pale green, insoluble, involatile solid (m.p. > 260°c) which is inert to hydrolysis in the cold but undergoes slow reaction in the warm. The electronic spectrum measured in KBr discs and interpreted on the basis of an octahedral environment for Cr^{III} was as follows:—
17,000 [$^4A_{2g}$—$^4T_{2g}$], 24,200 [$^4A_{2g}$—$^4T_{1g}(F)$], 47,200 cm.$^{-1}$ (charge transfer). The infrared spectrum measured in mulls and KBr discs showed a strong band at 1053 cm.$^{-1}$ due probably to both bridging and terminal C–O–M vibrations;[6] the other bands were consistent with the formulation $Cr^{III}(OMe)_3$. The reduction of observed magnetic moment† of 2·65 B.M./Cr atom compared with the spin-free moment for Cr^{III} of 3·88 B.M. is probably due to antiferromagnetic behaviour due to super-exchange *via* methoxy-bridges as suggested for the similarly reduced moment of Cu^{II} methoxide.[7] Chromium methoxide prepared by this method shows identical spectral and magnetic properties with a sample obtained by the method of Hornuff and Kappler;[5] however, elemental analyses for C and H were sometimes low (2—4%) compared with the latter preparation although correct for Cr and we believe this is due to the possibility of non-stoicheiometry arising from a layer lattice structure. Attempts to prepare chromium ethoxide by this method gave a product with correct Cr analysis but carbon analyses up to 8% low although all physical properties were consistent with the formulation, $Cr(OEt)_3$; Brubaker and Wicholas[7] encountered similar problems with $Cu(OEt)_2$. The problem becomes worse with the higher alkoxides. Adams *et al.*[2] give only Cr analysis for their product of $Cr(OEt)_3$.

X-Ray powder photographs requiring long exposure time of up to 40 hours could be indexed as a hexagonal system $a = b = 9{\cdot}91$, $c = 14{\cdot}10$Å and $z = 8$. A layer-type lattice possessing stacking defects was indicated by the presence of both sharp and diffuse lines. The two samples of $Cr(OMe)_3$ prepared as above gave very similar photographs. Further studies are in progress on these compounds.

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