Heteropolyanions in Non-polar Solvents. Metalloporphyrin-like Oxidation of Chromium(III) to Chromium(V) by Iodosylbenzene

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Solutions of $[SiMo_{11}O_{39}Cr(OH_2)]^{5-}$ and $[SiW_{11}O_{39}Cr(OH)]^{6-}$ in toluene, benzene, or acetonitrile react with iodosylbenzene to yield the corresponding oxochromium(V) species.

We have previously demonstrated that heteropolyanions are readily transferable into non-polar solvents such as benzene and toluene and that, with appropriate metal cation-substituted species, metalloporphyrin-type chemistry is possible in such solutions.[1,2] A major advantage of the heteropolyanions over porphyrins is their stability against oxidation and we have therefore been exploring the oxidation (and oxygenation) chemistry of a variety of substituted polyanions in nonpolar solvents. The oxidation of Cr^{III} porphyrins[3] and Cr^{III}–salen (salen = salicylideneaminato) complexes[4] to oxochromium(V)

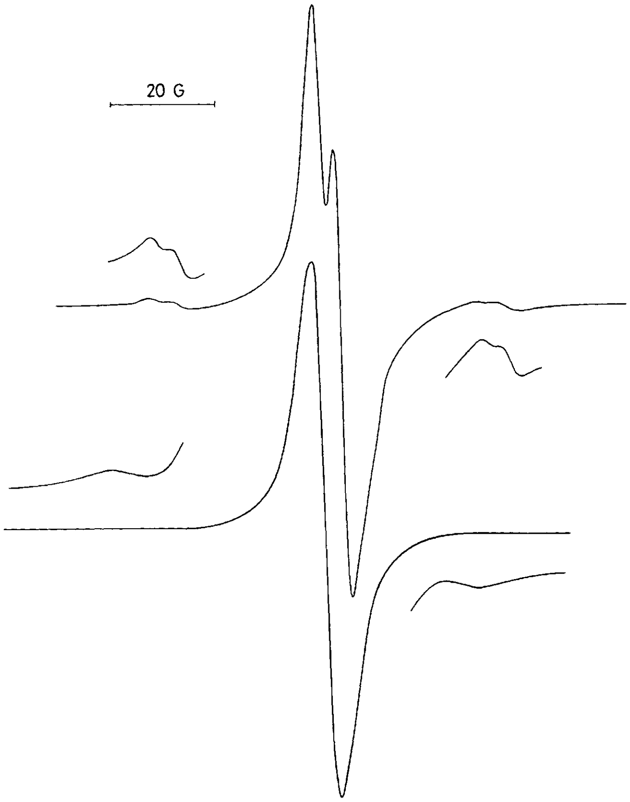

Figure 1. *X*-band e.s.r. spectra at ambient temperature: upper: $[HSiMo_{11}O_{39}CrO]^{4-}$ in acetonitrile; lower: $[SiMo_{11}O_{39}CrO]^{5-}$ in toluene.

species by the use of iodosylbenzene suggests that similar chemistry might be exhibited by heteropolyanions.

Aqueous solutions of the substituted Keggin anions $[SiMo_{11}O_{39}Cr^{III}(OH_2)]^{5-}$ (**1**)[5] and $[SiW_{11}O_{39}Cr^{III}(OH)]^{6-}$ (**2**)† were treated with solutions of tetra-n-heptylammonium bromide (*ca.* 5:1 molar excess) in benzene or toluene as described previously.[1] The heteropolyanions were thereby completely transferred into the organic layer. The resulting solutions had absorption spectra that were identical to those of the heteropolyanions in aqueous solution, indicating that the Cr^{III} ions remained six-co-ordinate with a terminal aquo or hydroxo ligand. Subsequent procedures were carried out with the solutions as extracted or with solutions that had been 'dried' by passage of argon for 2 h;‡ no difference in behaviour between 'wet' and 'dry' solutions was observed. The polyanion solutions were stirred with iodosylbenzene (10- to 15-fold excess) at room temperature for 30 min. After separation of the unreacted material, the resulting solutions [brown-green for (**1**), yellow-green for (**2**)] showed intense e.s.r. spectra (Figure 1) with clearly resolved hyperfine structure (^{53}Cr, $I = 3/2$, 9.55% abundant). Isotropic parameters, $g = 1.988$, $a = 22.8$ G; and $g = 1.963$, $a = 21.3$ G (1 G = 10^{-4} T) respectively, are attributed to the oxochromium(v) anions $[SiMo(W)_{11}O_{39}CrO]^{5-}$ (**1a**), (**2a**). The solutions show no sign of decomposition after several days storage at room temperature, and did not detectably cause epoxidation of *trans*-stilbene during 24 h.§ Addition of a solution of tetra-n-propylammonium bromide in dichloromethane to the toluene solution of (**1a**) yielded a pale brown microcrystalline precipitate. The latter had an i.r. spectrum that was virtually identical to that of the ammonium salt of (**1**) (thereby demonstrating the retention of a Keggin polyanion structure) and a rhombic e.s.r. spectrum similar to that shown by a frozen solution of (**1a**) at 77 K.

$[SiMo_{11}O_{39}Cr^{III}(OH_2)]^{5-}$ (**1**) $[SiW_{11}O_{39}Cr^{III}(OH)]^{6-}$ (**2**)

$[SiM_{11}O_{39}CrO]^{5-}$

(**1a**), M = Mo
(**2a**), M = W

The oxidation of (**1**) was also carried out in acetonitrile solution. The tetra-n-butylammonium salt of (**1**), $(Bu_4N)_4H[SiMo_{11}O_{39}Cr(OH)_2]$ (satisfactory elemental analyses were obtained) was prepared by metathesis. Treatment of an acetonitrile solution of this salt with iodosylbenzene yielded a solution with the e.s.r. spectrum shown in Figure 1. The secondary hyperfine splitting ($a = 4.0$ G) is attributed to the presence of a relatively nonlabile proton attached to one of the $Cr^V \cdots O \cdots Mo$ bridging oxygens.[6] Addition of 1 equiv. of tetra-n-butylammonium hydroxide removes the doublet pattern. The e.s.r. spectrum remained unchanged as long as the solution was stored at −5 °C. During such storage pale brown $(Bu_4N)_4H[SiMo_{11}O_{39}CrO]$ (satisfactory elemental analyses were obtained) was deposited. The solid material had an i.r. spectrum similar to that of the original tetrabutylammonium salt of the chromium(III) anion and, when dissolved in acetonitrile, an e.s.r. spectrum identical to that shown in Figure 1. Cyclic voltammograms of solutions of the solid in acetonitrile (pyrolytic graphite electrode, tetra-n-butylammonium perchlorate supporting electrolyte) were also identical to those of the freshly oxidized polyanion solutions.¶ When these solutions were kept at room temperature, or when tetrabutylammonium hydroxide was added in excess of that required for neutralization of the acidic proton, new hyperfine features appeared in the e.s.r. spectrum at $g = 2$. These correspond to the formation of currently unidentified radicals and attest to the instability of the chromium(v) complex in the

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† Synthesized by the addition of Cr^{II} (prepared by dissolving Cr metal in 20% HCl) to a well buffered solution of $SiW_{11}O_{39}^{8-}$ at pH 4.7. After aerobic oxidation of the resulting heteropoly blue, the guanidinium salt of (**2**) was precipitated and recrystallized twice from water. It gave satisfactory elemental analyses. Characterization: i.r., u.v.-visible spectra ($\lambda_{max.}$ 648 nm), cyclic voltammogram (two reversible two-electron features at −0.79 and −1.10 V *vs.* Ag/AgCl; pH 4.7).

‡ We have shown elsewhere[1b,1d] that *ca.* 25 mol water/mol heteropolyanion are transferred into the organic layer. Since these quantities exceed the solubility of water in benzene or toluene, the water molecules are probably enclosed in inverse micelles formed by the phase-transfer agent. Such water is readily removed by aspiration of dry inert gas for 1—2 h.

§ This observation is consistent with the recent report[2] that a Cr^{III} derivative of $PW_{11}O_{39}^{7-}$ was catalytically inactive for epoxidations with iodosylbenzene and pentafluoroiodosylbenzene.

¶ Voltammograms of the Cr^V polyanions show two new irreversible features at +0.1 and −0.4 V in addition to the reversible molybdenum reductions that begin at −0.75 V.

presence of acetonitrile. The oxidative ability of these and analogous complexes is under investigation.

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