Dialkyl Sulphoxides as Starting Materials for the Preparation of Alkyl–Transition-metal Complexes. Formation of Penta-aquamethylchromium(III) and Pentacyanomethylcobaltate(III) Salts, and the Reduction of Methyl Radicals by Vanadium(II)

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The penta-aquamethylchromium(III) ion is formed in high yield from the chromium(II)–hydrogen peroxide–dimethyl sulphoxide system in aqueous solution. The methyl-deuteriated analogue has been prepared by the corresponding reaction with [$^2H_6$]dimethyl sulphoxide. The secondary kinetic deuterium isotope effect for the acid-catalysed aquation has been measured. The analogous 'Fenton reagents' with pentacyanocobaltate(II) and with vanadium(II) yield the pentacyanomethylcobaltate(III) ion and methane, respectively.

ORGANIC σ-bonded complexes of chromium(III) have been prepared by procedures involving the reaction of the corresponding radicals with chromium(II) ions in aqueous solution.[1-5] The approach seems to be quite general, and rate constants have been determined for a number of radical–Cr^{II} reactions.[6] However, the application to the preparation of simple alkyl complexes, as exemplified by the methyl complex, is relatively inefficient because the commonly used methods and conditions for the generation of such radicals do not lead to high yields of the product of the trapping reaction. For example, it has been shown in a slightly different context that the generation of the methyl radical by the reaction of t-butyl hydroperoxide with chromium(II) ions[2] proceeds in poor yield because the intermediate t-butoxyl radicals are themselves intercepted by chromium(II),[4,5] and their preparation from methyl halides[7,8] suffers from the low solubility of the substrates in water. It has been known for some time that methyl radicals are readily formed[9] in a synthetically useful yield[10,11] *via* the reaction of hydroxyl radicals with dimethyl sulphoxide (Me_2SO), and that other alkyl radicals can similarly be generated from the corresponding dialkyl sulphoxides.[9,11-13] In a study of the methylation of organic substrates by solutions in which the methyl radicals were generated from Me_2SO and 'Fenton reagents' with various metal ions it was noted that chromium(II) was an unsuitable metal ion to use.[10] The inference to be drawn from this observation is not that methyl radicals are not formed but rather that their reaction with chromium(II) ions is much more rapid than that with the organic substrate to be methylated, and suggests that this system might be an efficient source for the formation of the penta-aquamethylchromium(III) complex. In the present work we have successfully applied this reaction to the formation of the methylchromium(III) complex. The 'Fenton reagent' hydrogen peroxide–chromium(II) in the presence of Me_2SO is used as the source of methyl radicals, with an excess of the substitution-labile hexa-aquachromium(II) ion to act as scavenger for the radicals. The use of an excess of scavenger and relatively low concentrations is designed to optimise the efficiency of the capture of the radicals to form the desired product. The sequence of reactions (1)—(4) accounts for the products. It has been suggested[11] that this may be an over-simplification of the mechanism (*cf.* Gilbert *et al.*[14]).

The success of this preparation (coupled with the known formation of other radicals from various sulphoxides)[9,11-13] leads us to the view that the method may be equally useful with other alkyl groups.

$$[Cr(OH_2)_6]^{2+} + H_2O_2 \longrightarrow [Cr(OH_2)_6]^{3+} + HO\cdot + OH^- \quad (1)$$

$$HO\cdot + (CH_3)_2SO \longrightarrow (CH_3)_2S(O\cdot)OH \quad (2)$$

$$(CH_3)_2S(O\cdot)OH \longrightarrow CH_3\cdot + CH_3SO_2H \quad (3)$$

$$CH_3\cdot + [Cr(OH_2)_6]^{2+} \longrightarrow [Cr(OH_2)_5(CH_3)]^{2+} + H_2O \quad (4)$$

The preparation has been applied to the formation of the corresponding [$^2H_3$]methyl complex, and to a study of related reactions of pentacyanocobaltate(II) and vanadium(II) ions with methyl radicals.

EXPERIMENTAL

Solutions of chromium(II) (*ca.* 1.5 mol dm^{-3}) were prepared by dissolution, in a limited amount of perchloric acid (3 mol dm^{-3}) under nitrogen, of excess electrolytic chromium metal (BDH), activated by immersion in 5 mol dm^{-3} hydrochloric acid. The solution was warmed (*ca.* 60 °C) near the end of the reaction until gas evolution ceased. Vanadium(II) perchlorate was obtained by the zinc-dust reduction of vanadium(IV) perchlorate under nitrogen, and was used within 2 h of preparation. Vanadium(IV) perchlorate solutions were prepared from vanadyl sulphate (BDH) by ion-exchange chromatography. A solution of vanadyl sulphate (*ca.* 1 mol dm^{-3}) was transferred to an ion-exchange column (15 × 1 cm; Dowex 50 W-X8). The column was washed with $HClO_4$ (0.1 mol dm^{-3}, 200 cm^3) to remove sulphate ions, and vanadium(IV), typically at a final concentration of 0.15 mol dm^{-3}, was eluted with $HClO_4$ (1 mol dm^{-3}). Solutions of the potassium salt of pentacyanocobaltate(II), $[Co(CN)_5]^{3-}$, were prepared by mixing stoicheiometric amounts of deoxygenated solutions of cobalt(II) perchlorate [obtained by neutralising cobalt(II) carbonate with perchloric acid] and potassium cyanide under nitrogen.

Hydrogen peroxide (AR, Fisons) was standardised against potassium permanganate. Dimethyl sulphoxide was distilled under reduced pressure from calcium hydride, and was stored over molecular sieve 4A. Deuterium-substituted Me_2SO was used as received (Aldrich, 99.5% D).

Cr^{2+}–H_2O_2–Me_2SO.—Hydrogen peroxide (0.010 cm^3, 0.015 mmol, corresponding to an initial concentration of *ca.* 5×10^{-3} mol dm^{-3}) was injected into a serum-capped spectrophotometric cell containing a deoxygenated acidic (0.5 mol dm^{-3} $HClO_4$) solution (2.9 cm^3) of chromium(II) (0.05 mol dm^{-3}) and either Me_2SO or $(CD_3)_2SO$ (0.5 mol dm^{-3}). The ionic strength of the solution was maintained at 1 mol dm^{-3} with lithium perchlorate. The absorbance of the solution was followed as a function of time at 390 nm on a Pye-Unicam SP8-100 spectrophotometer with a thermostatted cell holder.

$[Co(CN)_5]^{3-}$–H_2O_2–Me_2SO.—The cobalt(III) products formed in the reaction of hydrogen peroxide (3.8 mmol) with $[Co(CN)_5]^{3-}$ (7.5 mmol in 50 cm^3) and Me_2SO (70 mmol) in a nitrogen atmosphere were precipitated as the potassium salts by the method of Kwiatek and Seyler.[15] The i.r. spectrum of the products was recorded as a KBr disc.

V^{2+}–H_2O_2–Me_2SO.—The gas evolved on the addition of hydrogen peroxide (2.42 mmol, corresponding to an initial concentration of 0.044 mol dm^{-3}) to a deoxygenated acidic (0.3 mol dm^{-3} $HClO_4$) solution (55 cm^3) of vanadium(II) (0.13 mol dm^{-3}) and Me_2SO (0.8 mol dm^{-3}) was collected. Mass spectrometric analysis indicated $CH_4 \geqslant 98\%$, $C_2H_6 \leqslant 2\%$. The volume of gas (*ca.* 15 cm^3) corresponds to a yield of *ca.* 25% calculated as methane and based on the initial amount of hydrogen peroxide.

RESULTS AND DISCUSSION

The product of the reaction of Cr^{2+} with hydrogen peroxide and dimethyl sulphoxide is the penta-aquamethylchromium(III) ion, formed as shown in reactions (1)—(4). The identity of the product is confirmed by the observed absorption maximum, characteristic of a chromium–carbon bonded species,[2,6a] and by the excellent agreement of the second-order rate constant for the reaction (5) with H_3O^+ in 0.5 mol dm^{-3} $HClO_4$ ($5.00 \pm 0.06 \times 10^{-3}$ dm^3 mol^{-1} s^{-1}) with the reported value for $[Cr(OH_2)_5(CH_3)]^{2+}$ prepared by a different method.[5]

$$Cr(CH_3)^{2+} + H_3O^+ \longrightarrow Cr^{3+} + CH_4 + H_2O \quad (5)$$

The yield of complex, determined spectrophotometrically, was 80%. This is to be compared with a yield of $Cr(CH_3)^{2+}$ of *ca.* 15% reported for the reaction of Cr^{2+} with t-butyl hydroperoxide.[2,5] If the radical $(CH_3)_2S(O\cdot)OH$ reacts rapidly with Cr^{2+}, as has been reported for organic radicals ($k \geqslant 3 \times 10^7$ dm^3 mol^{-1} s^{-1}),[6] hydroxyl radicals ($k = 1.2 \times 10^{10}$ dm^3 mol^{-1} s^{-1}),[16] hydrogen atoms ($k = 1.5 \times 10^9$ dm^3 mol^{-1} s^{-1}),[17] and $\cdot CO_2H$ ($k = 1.1 \times 10^9$ dm^3 mol^{-1} s^{-1}),[6b] then the decay of $(CH_3)_2S(O\cdot)OH$ is in competition with its reaction with Cr^{2+}. It is the latter reaction (6) to which the formation of by-products is attributed. This

$$(CH_3)_2S(O\cdot)OH + [Cr(OH_2)_6]^{2+} \longrightarrow \longrightarrow \text{by-products} \quad (6)$$

scheme is consistent with known values or estimates of rate constants for the various processes involved. For example, as the yield of the main product exceeds 80%,

$$k_3/k_6[Cr^{2+}]_{average} = [Cr(CH_3)^{2+}]/[\text{by-products}] \geqslant 4 \quad (7)$$

a lower limit for the rate constant of reaction (3) can be evaluated from equation (7). Taking $k_6 \geqslant 3 \times 10^7$ dm^3 mol^{-1} s^{-1} and $[Cr^{2+}]_{average} = 0.04$ mol dm^{-3}, then $k_3 \geqslant 4.8 \times 10^6$ s^{-1}. This value is consistent with the lower limit of $k_3 \geqslant 10^5$ s^{-1} as estimated by Gilbert *et al.*[14]

The Cr^{2+}–H_2O_2–Me_2SO system has also been used by us in the investigation of the secondary α-deuterium effect in the protonolysis of $Cr(CD_3)^{2+}$, which was obtained from $(CD_3)_2SO$ by a sequence of reactions analogous to (1)—(4).

TABLE 1

Observed rate constants for reaction of $Cr(CH_3)^{2+}$ and $Cr(CD_3)^{2+}$ with 0.5 mol dm^{-3} perchloric acid

Ion	$10^3\ k_{obs}$*/s^{-1}	k_H/k_D
$[Cr(OH_2)_5(CH_3)]^{2+}$	2.50 ± 0.03	1.055 ± 0.030
$[Cr(OH_2)_5(CD_3)]^{2+}$	2.37 ± 0.04	

* At 25 °C, $I = 1.0$ mol dm^{-3} (0.5 mol dm^{-3} $HClO_4$, 0.5 mol dm^{-3} $LiClO_4$); $[Cr^{2+}]_0 = 5 \times 10^{-2}$, $[Me_2SO] = 0.5$, $[H_2O_2]_0 = 5 \times 10^{-3}$ mol dm^{-3}.

Rate constants for the reaction (5) of $Cr(CH_3)^{2+}$ and of $Cr(CD_3)^{2+}$ with oxonium ions are given in Table 1. The corresponding secondary isotope effect per deuterium atom $[(k_H/k_D)^{\frac{1}{3}} = 1.018 \pm 0.010]$ is significantly smaller than the calculated effect per deuterium atom in the co-ordinated water molecules (1.05).[18] The former effect relates to deuterium substitution in the nucleofugic moiety of the heterolysed complex (the portion that carries away the electron pair of the broken bond), whereas the latter refers to the electrofugic moiety.

The activation parameters for the reaction of the methyl complex are shown in Table 2, and are similar to those reported for the corresponding reaction of $Cr(CH_2OH)^{2+}$.[2a]

TABLE 2

Temperature effect on the reaction of $Cr(CH_3)^{2+}$ with aqueous perchloric acid

Temp./K	10^3k_2*/dm^3 mol^{-1} s^{-1}	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}
314.75	22.6 ± 0.2		
298.15	5.58 ± 0.08	64 ± 4	-74 ± 6
286.95	1.81 ± 0.03		

* $I = 1.5$ mol dm^{-3} (0.5 mol dm^{-3} $HClO_4$, 1.0 mol dm^{-3} $LiClO_4$); $[Cr^{2+}]_0 = 5 \times 10^{-2}$, $[Me_2SO] = 0.5$, $[H_2O_2]_0 = 5 \times 10^{-3}$ mol dm^{-3}.

The solid product of the reaction of $[Co(CN)_5]^{3-}$ with hydrogen peroxide and Me_2SO, pressed into a KBr disc, gave two absorptions of equal intensity in the CN stretching-frequency region, at $2\,125 \pm 5$ and at $2\,095 \pm 5$ cm^{-1}. The former is due to $[Co(CN)_5(OH_2)]^{2-}$ (lit.[7] $2\,128 \pm 2$ cm^{-1}) and the latter is in agreement with the value previously reported[7] for $[Co(CN)_5(CH_3)]^{3-}$

($2\,094 \pm 2$ cm^{-1}). These products are consistent with the sequence of reactions (8)—(11).

$$[Co(CN)_5]^{3-} + H_2O_2 \longrightarrow [Co(CN)_5(OH)]^{3-} + OH\cdot \tag{8}$$

$$OH\cdot + (CH_3)_2SO \longrightarrow CH_3\cdot + CH_3SO_2H \tag{9}$$

$$[Co(CN)_5]^{3-} + CH_3\cdot \longrightarrow [Co(CN)_5(CH_3)]^{3-} \tag{10}$$

$$[Co(CN)_5(OH)]^{3-} + H_2O \longrightarrow [Co(CN)_5(OH_2)]^{2-} \tag{11}$$

The reaction of $[Co(CN)_5]^{3-}$ with H_2O_2 has been reported before,[19] but it has not previously been utilised as part of a route to pentacyano-organocobaltate(III) ions.

In the reaction of V^{2+} with hydrogen peroxide and Me_2SO, methane is formed together with traces of ethane ($\leqslant 2\%$). By analogy with the above systems, the formation of methane is thought to occur as in reactions (12)—(14).

$$V^{2+} + H_2O_2 \longrightarrow V^{3+} + OH\cdot + OH^- \tag{12}$$

$$OH\cdot + (CH_3)_2SO \longrightarrow CH_3\cdot + CH_3SO_2H \tag{13}$$

$$V^{2+} + CH_3\cdot + H^+ \longrightarrow V^{3+} + CH_4 \tag{14}$$

The reaction of vanadium(II) with hydrogen peroxide has been examined by Swinehart [20] who concluded that a significant portion of the overall reaction involves a one-electron path, which presumably implies the formation of hydroxyl radicals. Our results strongly suggest that hydroxyl radicals are in fact formed in this reaction and show that organic radicals can be reduced by vanadium(II). The low yield of methane (*ca.* 25% based on the amount of H_2O_2 used) is attributed to the non-quantitative yield of hydroxyl radicals in the reaction of hydrogen peroxide with vanadium(II), *e.g.* through the intervention of competing reaction paths,[20] and also to the solubility of methane in the solution (containing 5.5% of Me_2SO by volume). The rapid reduction of radicals by $[V(py)_4Cl_2]$ (py = pyridine) (by a more complicated mechanism) has been postulated in a related system.[21]

The low yield of ethane in this reaction implies that the reduction of methyl radicals by vanadium(II) must be very rapid to compete so efficiently with their dimerisation ($k = 1.6 \times 10^9$ dm^3 mol^{-1} s^{-1}).[22] Substitution (involving displacement of water ligands) at vanadium(II) is a relatively slow reaction ($k = 80$ s^{-1}),[23] and reduction of $CH_3\cdot$ by vanadium(II) *via* an outer-sphere electron-transfer mechanism is not thought to be energetically possible.[24] It is therefore concluded that the reduction involves the rapid formation of a seven-co-ordinate methylvanadium(III) species [17,25] as an intermediate in reaction (14), or, as a referee has suggested, an unusual hydrogen-atom abstraction by the methyl radical from a water ligand co-ordinated to vanadium(II), according to reactions (15) and (16).

$$[V(OH_2)_6]^{2+} + CH_3\cdot \longrightarrow [V(OH_2)_5(OH)]^{2+} + CH_4 \tag{15}$$

$$H_3O^+ + [V(OH_2)_5(OH)]^{2+} \longrightarrow [V(OH_2)_6]^{3+} + H_2O \tag{16}$$

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