Electron Spin Resonance Spectra of the Perruthenate(VII) Ion, $[RuO_4]^-$

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Electron spin resonance spectra of the $[RuO_4]^-$ ion {as $A[RuO_4]$, where A = NPr^n_4, $N(PPh_3)_2$ or PPh_4} in frozen glasses of dichloromethane at *ca.* 90 K have been recorded; for A = NPr^n_4, $g_x = 1.93$, $g_y = 1.98$ and $g_z = 2.06$. The spectrum of $[RuO_4]^-$ (and its electronic spectrum) have been interpreted and compared with those of an alkaline aqueous solution containing ruthenium(VII) species. The ESR spectrum of powdered potassium ruthenate(VI), *trans*-$K_2[RuO_3(OH)_2]$, at *ca.* 90 K was also recorded, and the preparation of $[PPh_4][RuO_4]$, a new salt of $[RuO_4]^-$, is described.

Salts of the perruthenate(VII) ion were first made by Debray and Joly,[1] and the X-ray crystal structure of $K[RuO_4]$ showed this to contain a slightly flattened tetrahedral anion (Ru–O 1.73 Å).[2] The electronic,[3] Raman and infrared[4,5] spectra of the ion have been measured, and organic soluble salts of it have recently found application as mild and selective organic oxidants.[6] However, no ESR spectra of this d^1 tetraoxo species have been reported. In this note we report such spectra measured in dichloromethane glasses at low temperature, using the organic soluble salts $[NPr^n_4][RuO_4]$, $[N(PPh_3)_2][RuO_4]$ and $[PPh_4][RuO_4]$, and compare these with ESR spectra of alkaline solutions of RuO_4, in which d^1 ruthenium(VII) species are thought to exist. We also report the low-temperature ESR spectrum of powdered potassium ruthenate(VI), *trans*-$K_2[RuO_3(OH)_2]$, and find it to agree with that of sodium ruthenate in an alkali glass reported by Carrington *et al.*[7]

Results and Discussion

(*a*) *ESR Spectra of Near-tetrahedral* $[RuO_4]^-$.—The ESR spectrum of $[NPr^n_4][RuO_4]$ in a frozen glass of dichloromethane at *ca.* 90 K is shown in Fig. 1. Three features are clearly discernible, corresponding to $g_x = 1.93$, $g_y = 1.98$ and $g_z = 2.06$. Similar spectra were recorded for the other perruthenate(VII) salts $[N(PPh_3)_2][RuO_4]$ and $[PPh_4][RuO_4]$, for which the g_y and g_z values were almost identical and the g_x values slightly lower (*ca.* 1.89).

The ESR spectra of other d^1 tetraoxo anions have been reported: $[CrO_4]^{3-}$ (refs. 8–10) (typical *g* values: $g_x = 1.87$, $g_y = 1.85$, $g_z = 1.94$[8]); $[MnO_4]^{2-}$ (refs. 11–14) (typical *g* values: $g_x = 1.98$, $g_y = 1.97$, $g_z = 1.94$[13]); $[ReO_4]^{2-}$ ($g_{\parallel} = 1.85$, $g_{\perp} = 1.72$).[15] In all of these the *g* values lie below 2.00, yet our g_z value for $[RuO_4]^-$ is considerably above 2.00. In order to help rationalise this and interpret the spectrum we measured the electronic spectrum of $[NPr^n_4][RuO_4]$ in dichloromethane; its general features closely resemble those found for aqueous $[RuO_4]^-$ by Connick and Hurley.[3]

The d^1 species in CH_2Cl_2 is almost certainly $[RuO_4]^-$. The electronic spectra of several tetrahedral oxyanions have been described by Viste and Gray[16] and in keeping with their assignments we would expect our transition at 386 nm to be of d–d character ($2e \longrightarrow 4t_2$) while the band at higher energy (318 nm) should be charge transfer in character ($t_1 \longrightarrow 2e$). The ESR spectrum of $[NPr^n_4][RuO_4]$ indicates a distinct lowering from T_d symmetry, and we can assume that g_z is raised above 2.0 by contributions from the filled $t_1{}^6$ orbitals. The d_{z^2} ground state has been claimed for $[CrO_4]^{3-}$ in host lattices K_2SO_4[8] or Li_3PO_4,[9] for $[MnO_4]^{2-}$ in $BaSO_4$[11] or $BaSeO_4$,[12] and for $[ReO_4]^{2-}$ in $CaWO_4$;[15] however the d_{xy} ground state has been implicated for $[CrO_4]^{3-}$ in $KH_2[AsO_4]$[10] and for $[MnO_4]^{2-}$ in K_2SO_4[13] or K_2CrO_4.[14] There appears to be no simple distortion which adequately explains all the geometries of the known near-tetrahedral d^1 tetraoxo anions. Our spectrum could be said to be consistent with that of a compressed tetrahedron having a d_{z^2} ground state. We note that this in fact is the geometry reported for $[RuO_4]^-$ in the solid $K[RuO_4]$.[2]

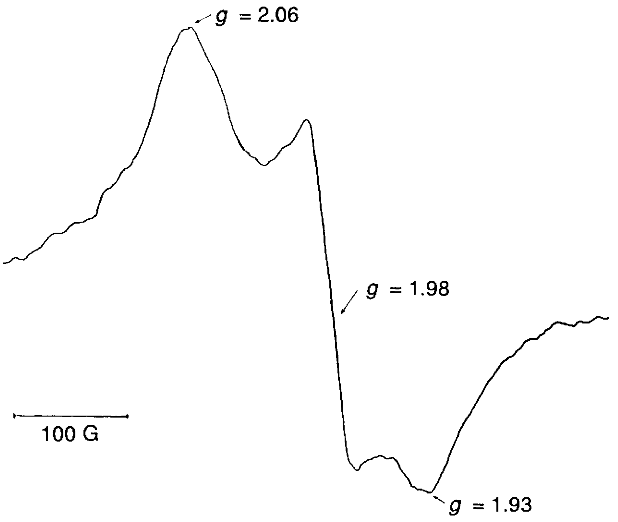

Fig. 1 Low-temperature (*ca.* 90 K) X-band ESR spectrum of $[NPr^n_4][RuO_4]$ in CH_2Cl_2; G = 10^{-4} T

(*b*) *ESR Spectra of Ruthenium*(VII) *Species in Aqueous Solution.*—Marov *et al.*[17] have reported ESR spectra of alkaline solutions of RuO_4 and proposed that the signals obtained ($g_{\parallel} = 1.84$, $g_{\perp} = 1.95$) were due to the octahedral ruthenium(VII) species $[RuO_4(OH)_2]^{3-}$. We find that an aqueous solution of RuO_4 in 1 mol dm^{-3} KOH as a frozen glass at around 90 K gives a spectrum similar to that of Marov *et al.*

and that this spectrum shows a marked diminution with increasing temperature. We have also measured the electronic spectrum of the green solution obtained by passing RuO_4 into 1 mol dm^{-3} KOH, which is very similar to that of $[NPr^n{}_4][RuO_4]$ in CH_2Cl_2, except for the presence of a weak band at 466 nm *which* we assign to ruthenate(VI)[3] (solutions of the latter species do not show an ESR signal at 90 K, see below). If the green solution is left for 12 h or more it turns deep orange due to the exclusive presence of ruthenate(VI), as confirmed by the electronic spectrum.

Our results for the d^1 system are intriguing in that the frozen-solution ESR spectra show the presence of two different species, yet the room-temperature electronic spectra are almost identical. Assuming that no change in structure occurs in cooling and freezing, it appears that different structures exist in the dichloromethane and aqueous solutions but that the electronic spectrum does not distinguish between them.

In an aqueous alkaline environment, $[RuO_4]^-$ might be expected to increase its co-ordination number to become $[RuO_4(OH)]^{2-}$ or $[RuO_4(OH)_2]^{3-}$. The latter ion was proposed as an intermediate in the alkaline decomposition of perruthenate(VII) to ruthenate(VI) by Carrington and Symons,[18] and ESR evidence for this formulation was proposed by Marov *et al.*,[17] who indeed further postulated an elongated-octahedral structure for this anion. The similarity between the electronic spectra of $[RuO_4]^-$ and $[RuO_4(OH)_n]^{(1+n)-}$ ($n = 1$ or 2) implies that the flattened tetrahedral arrangement of the four oxygen ions of $[RuO_4]^-$ is left relatively unperturbed by the approach of OH^-. We suggest therefore that the d^1 species in the aqueous environment is better described as a mono- or bi-capped tetrahedron with very long Ru–OH bond distances, and if the latter its geometry is more akin to *cis*-$[RuO_4(OH)_2]^{3-}$ (C_{2v}) rather than to *trans*-$[RuO_4(OH)_2]^{3-}$ (D_{4h}) as proposed by Marov *et al.*[17] It is not easy to see how the almost axial g anisotropy and strong temperature dependence are predicted by these structures however, and we suggest that the monocapped $[RuO_4(OH)]^{2-}$ is the most likely dominant species; both the axial ESR signal and its behaviour with temperature are consistent with this suggestion. In this connection we note that salts of $[Os^{VIII}O_4(OH)]^-$ have recently been prepared: although they were not structurally characterised, a single-crystal X-ray study of the binuclear anion in $Cs[O_4Os(\mu\text{-}OH)OsO_4]$ shows the co-ordination about the osmium to be that of a flattened OsO_4 tetahedron with an axial, long, bridging OH group.[19]

(*c*) *The ESR Spectrum of Ruthenate*(VI).—The ESR spectrum of powdered sodium ruthenate(VI), *trans*-$Na_2[RuO_3(OH)_2]$, shows what is best described as two broad overlapping lines with effective g values of 2.04 and 1.98. Bearing in mind the lower frequency of our spectrometer and the consequently smaller separation between the two lines expected from a d^2 system with small zero-field splitting, our findings would appear to agree quite well with those of Carrington *et al.*[7] at the lower temperature ($g_{eff} = 2.05$; $g_{eff} = 2.00$ at 20 K and at a frequency of *ca.* 15 000 MHz). There was an additional sharp line in our spectrum at $g = 1.99$ which we presume to arise from some other ruthenium species in the fusion melt. Frozen solutions of potassium ruthenate in dilute alkali gave no ESR signals at 90 K.

Experimental

Ruthenium tetraoxide was generated by the action of sodium periodate (2.75 g, 12.9 mmol) on hydrated ruthenium dioxide (0.75 g) in water (a method based on that of Nakata[20]) and swept into a solution of 1 mol dm^{-3} KOH (20 cm^3) to give the green solution for the ESR experiment. Potassium ruthenate was prepared by the fusion of KOH (3 g, 53.5 mmol), KNO_3 (1 g, 9.9 mmol) and $RuCl_3\cdot 3H_2O$ (1 g, 3.8 mmol) in a nickel crucible. The cooled melt was crushed to a brick red powder for ESR spectroscopy [the electronic spectrum of this powder dissolved in water showed ruthenate(VI) to be present: a strong band at 466 nm and a weaker one at 380 nm as observed by Connick and Hurley[3]].

The $[NPr^n{}_4][RuO_4]$ and $[N(PPh_3)_2][RuO_4]$ salts were prepared as reported by us previously.[21] UV–VIS spectrum of $[NPr^n{}_4][RuO_4]$: λ_{max} (CH_2Cl_2) 318 (2623) and 386 nm (ε 2268 dm^3 mol^{-1} cm^{-1}). ESR spectrum of $[N(PPh_3)_2][RuO_4]$ (CH_2Cl_2, *ca.* 90 K): $g_x = 1.88$, $g_y = 1.98$, $g_z = 2.07$. The new tetraphenylphosphonium salt was prepared by the passage of RuO_4 vapour (generated as above) in nitrogen carrier gas into an ice-cold solution of PPh_4Cl (1.87 g, 5.0 mmol) in 0.25 mol dm^{-3} K_2CO_3 (20 cm^3). The olive-green precipitate was filtered off, washed with cold water (3 × 10 cm^3) and dried *in vacuo* (Found: C, 56.6; H, 3.8; P, 8.0. Calc. for $C_{24}H_{20}O_4PRu$: C, 57.1; H, 4.0; P, 7.8%). ESR spectrum (CH_2Cl_2, *ca.* 90 K): $g_x = 1.90$, $g_y = 1.98$, $g_z = 2.07$. IR spectrum: ν_{max}/cm^{-1} 830s [ν_{asym}(RuO_2)]. UV–VIS spectrum: λ_{max} (CH_2Cl_2) 318 (2610) and 385 nm (ε 2252 dm^3 mol^{-1} cm^{-1}).

The ESR spectra were recorded on a Varian E12 X-band spectrometer (9.5 GHz), at low temperature with flowing cooled nitrogen gas, IR spectra on a Perkin-Elmer 1720 (FTIR) instrument and UV–VIS spectra on a Philips PU 8740 spectrometer using quartz glass cells. Elemental analyses were performed by the Imperial College Micro-analytical Department.

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