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Formation of CrO_2^{2+} in the Oxidation of Chromium(II) by Molecular Oxygen

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Summary Cr^{2+} reacts with molecular oxygen with a rate constant of $(1{\cdot}6 \pm 0{\cdot}2) \times 10^8\,l\,mol^{-1}\,s^{-1}$ to give a complex, CrO_2^{2+}, with λ_{max} 245 and 290 nm, $\epsilon = 7800$ and $3200\,l\,mol^{-1}\,cm^{-1}$, and which is long lived when $[Cr^{2+}] \ll [O_2]$.

CHROMIUM(II) is rapidly oxidised by molecular oxygen according to the stoicheiometry in equation (1).[1] The

$$4Cr^{2+} + O_2 + 4H^+ = 4Cr^{3+} + 2H_2O \qquad (1)$$

final product of the reaction is known[1] to be $[Cr(OH)_2Cr]^{4+}$, although the mechanism of its formation remains uncertain.[1,2] We have studied the reaction by pulse radiolysis.

Pulse radiolysis of aerated aqueous solutions containing 10^{-2} M Cr^{3+} + 0·5M Bu^tOH produced the spectra shown in the Figure. Following the pulse there was a first order build-up, and then a much slower decay to a plateau. Under these conditions the hydrated electrons produced in the radiolysis of water, reaction (2), (concentration *ca.* 2×10^{-6} M) rapidly reduce Cr^{3+} to Cr^{2+}, reaction (3), which in turn reacts with O_2, reaction (4). Bu^tOH was added to scavenge the hydroxyl radicals and convert them into unreactive $Bu^tO{\cdot}O{\cdot}$ radicals. The pseudo-first-order build-up of absorption was linearly dependent on $[O_2]$ ($2{\cdot}6$—13×10^{-4} M), but independent of $[Cr^{3+}]$ (2—10×10^{-3} M) and pH (2·6—4·3), and is attributed, therefore, to the formation of the product of Cr^{2+} and O_2. A value of $k_4 = (1{\cdot}6 \pm 0{\cdot}2) \times 10^8\,l\,mol^{-1}\,s^{-1}$ was calculated from the pseudo-first order rate constants measured. As a check on this k_4 was also estimated by a competition method using benzoquinone. This

$$H_2O \rightsquigarrow e^-_{aq}, OH, H, H_2, H_2O_2, H^+ \qquad (2)$$

$$e^-_{aq} + Cr^{3+} \rightarrow Cr^{2+} \qquad (3)$$

$$Cr^{2+} + O_2 \rightarrow CrO_2^{2+} \qquad (4)$$

gave $k_4 = (1{\cdot}9 \pm 0{\cdot}3) \times 10^8\,l\,mol^{-1}\,s^{-1}$ taking $k[Cr^{2+} + \text{benzoquinone}] = (3{\cdot}2 \pm 0{\cdot}3) \times 10^8\,l\,mol^{-1}\,s^{-1}$.[3] The par-

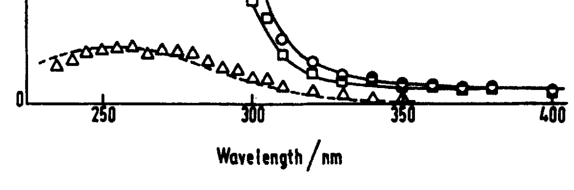

FIGURE. Spectra of transients produced by the pulse radiolysis of aerated solutions of 10^{-2} M Cr^{3+} + 0·5 M Bu^tOH, pH = 3·4, dose = *ca.* 500 rad/pulse. (○) measured 50 μs after the pulse; (□) 4·5 ms after the pulse (spectrum of CrO_2^{2+}); (△) difference spectrum, and (– – – –) spectrum of $Bu^tO{\cdot}O{\cdot}$ radical taking $G = 2{\cdot}8$, from ref. 4.

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tial decay of absorption noted at longer times is probably due to the disappearance of $Bu^tO{\cdot}O{\cdot}$ radicals. In support of this it was found that the difference of the spectra at 50 μs and of the plateau at 4·5 ms was of the same shape and magnitude (taking $G = 2{\cdot}8$) as an authentic $Bu^tO{\cdot}O{\cdot}$ radical spectrum.[4] The product of the reaction Cr^{2+} and O_2 has, therefore, λ_{max} 245 and 290 nm, ϵ 7800 and 3200 l mol^{-1} cm^{-1}, respectively, assuming it is formed with a yield of $G = 2{\cdot}8$.

The spectrum measured at 4·5 ms is assigned to the species CrO_2^{2+}. The reaction Cr^{2+} and O_2 cannot be an electron transfer resulting in O_2^-, or its protonated form, HO_2 [$pK_a(HO_2) = 4{\cdot}88$[4]] because (i) the spectrum is substantially different from that of either O_2^- or HO_2,[5] and (ii) the observation of a competition between O_2 and benzoquinone for Cr^{2+} implies that the product of reaction (4) is unreactive with benzoquinone, while O_2^- transfers an electron to benzoquinone with $k = 9{\cdot}8 \times 10^8$ l mol^{-1} s^{-1}.[6] Using the a.c. conductivity technique no post-pulse change in conductivity was found at pH 2·6—4·3 and hence reaction (4) is not accompanied by loss or uptake of protons.

No decay of CrO_2^{2+} was detected. Indeed a permanent drop in the photomultiplier current was observed in these solutions at wavelengths near 260 nm, where CrO_2^{2+} absorbs intensely, and it seems that the species is quite long lived under the conditions of our experiments. Earlier workers[1,2] have found no evidence for a long-lived intermediate such as CrO_2^{2+} probably because under their conditions ($[Cr^{2+}] \gg [O_2]$) reaction (5) occurs. Formation of the ultimate product, $[Cr(OH)_2Cr]^{4+}$, then presumably takes place

$$CrO_2^{2+} + Cr^{2+} \rightarrow CrO_2Cr^{4+} \qquad (5)$$

through further reduction of the peroxy intermediate, CrO_2Cr^{4+}, by 2 equiv. of Cr^{2+} followed by protonation.

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