Observation of a V^{II}–V^{IV} Oxo-bridged Transient in the Reduction of $[VO(hedta)]^-$ by $[V(hedta)]^-$

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Summary Precursor complexes of oxidation state assignment V^{II}–O–V^{IV} prior to intramolecular electron transfer have been detected in the $[VO(edta)]^{2-}$, $[V(edta)]^{2-}$ and $[VO(hedta)]^-$, $[V(hedta)]^-$ cross-reactions (H_4edta = ethylenediaminetetra-acetic acid; H_3hedta = hydroxyethylenediaminetriacetic acid).

Twenty years ago Taube and Myers were able to infer the existence of the inner-sphere activated complex in the electron transfer between $[Cr(H_2O)_6]^{2+}$ and $[(NH_3)_5CoCl]^{2+}$ in their classic experiment.[1] The precursor complex which retains the oxidation states of the reactants has often been sought in various redox systems. Only recently Isied and Taube were able to generate the intermediate, $[(NH_3)_5Co(O_2CC_6H_4N)\text{-}Ru(NH_3)_4(H_2O)]^{4+}$, which preceeds electron transfer between Ru^{II} and Co^{III}.[2] Haim has observed the precursor complex by bridging $[(NH_3)_5Co]^{3+}$ and $[(CN)_5Fe]^{3-}$ by 4,4′-bipyridine[3] or pyridine-3- and -4-carboxylate.[4] Hurst has observed a π-complex of Cu^+ with olefin species of $[(NH_3)_5Co(O_2CCHCHCO_2)]^+$ and $[(NH_3)_5RuNC_6H_4CHCH_2]^{3+}$ prior to intramolecular electron transfer.[5,6] In each of these cases, where the bridging ligand participates in an electron transfer role, the metal centres are separated by many atoms through conjugated bifunctional ligands. We report the novel observation of a precursor complex containing V^{II} and V^{IV} bridged only by one oxygen atom in the cross-reactions of $[V(edta)^{2-}$–$[VO(edta)]^{2-}$ and $[V(hedta)]^-$, $[VO(hedta)]^-$. The reactions of these species are similar to the $[V(H_2O)_6]^{2+}$ –$[VO(H_2O)_5]^{2+}$ system in which the V^{III} successor complex, $[VOV]^{4+}$, is detected in 65% of the electron transfer events.[7] Analogous bridged dimers of V^{III}, $[(hedta)VOV(hedta)]^{2-}$, and $[(edta)VOV(edta)]^{4-}$ have been characterized.[8] These complexes are in pH-dependent equilibria with $[LV(H_2O)]^{1-n}$, $[LV(OH)]^{n-}$, and $[LV(OH)_2]^{(n+1)-}$ complexes (L = edta^{4-}, $n = 2$; L = hedta^{3-}, $n = 1$). The edta dimer is stable and predominant in the pH range 9·5—10·5 while the hedta dimer is predominant in the pH range 4·0—10·5. The dimers are similar to $[(hedta)FeOFe(hedta)]^{2-}$, the spectra and kinetics of which have been studied by Gray, *et al.*[9,10] and Wilkins[11] respectively.

A transient red species is detectable to the eye when $[V(edta)]^{2-}$ and $[VO(edta)]^{2-}$ or $[V(hedta)]^-$ and $[VO(hedta)]^-$ are mixed under N_2 in a glass vessel throughout the pH range 6·33—9·86. The bleaching of the intermediate may be observed at 450 nm for the $[V(edta)]^{2-}$–$[VO(edta)]^{2-}$ system and 557 nm for $[V(hedta)]^-$, $[VO(hedta)]^-$. Stopped-flow recordings of the transmittance or absorbance *vs.* time reveal that the intermediates formed in both the $[V(hedta)]^-$, $[VO(hedta)]^-$ and $[V(edta)]^{2-}$, $[VO(edta)]^{2-}$ systems decay by first-order processes which are complete in 0·25 s with 22 and 12% changes in % transmittance (T), respectively. The highly absorbing red intermediate (0% T, $A > 3{\cdot}0$, 2·0 cm pathlength, $[V^{II}] = [V^{IV}] = 9{\cdot}0 \times 10^{-3}$ M) which is formed within 20 ms after mixing has an extinction much too large to be attributed to any monomeric complex of V^{II}, V^{III}, or V^{IV} or to the V^{III} dimers.[8] The bleaching of the red intermediate is acid dependent (at pH 9·86, 8·38, 6·81, and 6·33, k/s^{-1} = 12·6, 17·3, 23·1, and 46·2, respectively; cross-reaction: μ 0·20M; temp. 25·0 °C, three or more superimposed reaction traces) with $k = 14{\cdot}3\ s^{-1} + (6{\cdot}7 \times 10^7\ l\ mol^{-1}\ s^{-1}).[H_3O^+]$ in the $[V(edta)]^{2-}$, $[VO(edta)]^{2-}$ case. The bleaching reaction is the intramolecular electron transfer step. The fate of the successor complex, identical with the V^{III} dimers previously characterized, is predictable from the hydrolytic equilibria of the resultant complex. The V^{II}–O–V^{IV} unit of the edta cross-reaction bleaches, together with dissociation into V^{III}edta monomeric species below pH 9. The $[(hedta)V^{II}\text{-}OV^{IV}(hedta)]^{2-}$ intermediate is converted into the acid stable $[(hedta)V^{III}OV^{III}(hedta)]^{2-}$ complex. An additional growth of absorbance is observed during 2·0 s after the end of the bleaching reaction for the $[V(hedta)]^-$, $[VO(hedta)]^-$ case. The reaction after bleaching is second order in V^{III}. This reaction establishes the existence of a parallel outer-sphere reaction which forms monomeric $[V^{III}(hedta)]$ directly, in analogy with $[V(H_2O)_6]^{3+}$ formed by the outer-sphere path in the $[V(H_2O)_6]^{2+}$, $[VO(H_2O)_5]^{2+}$ reaction. From the rate of the slower dimerization reaction, which has been studied independently with authentic $[V(hedta)]$,[8] we have found the inner-sphere component to be slightly hydrogen ion dependent: 45% inner-sphere, pH = 7·49; 57%, pH = 7·01; and 62%, pH = 6·54.

Any $V^{III} - V^{IV}$ mixed oxidation state intermediate has been ruled out by the lack of formation of such a species by mixing $[VO(edta)]^{2-}$ and $[V(edta)]^-$; trace amounts of Fe^{II} or Cu^{II} which might be present owing to syringe manipulations cannot be the cause of the transient. Equivalent concentrations of $[VO(edta)]^{2-}$ with $[Fe(edta)]^{2-}$ or $[Cu(edta)]^{2-}$ formed no red transient species.

We are currently examining the factors which cause reorganization to be slow within the activated complex. The reasons are certain to be of theoretical interest. The precursor complexes observed in these systems have a duration of at least 5×10^4 times as long as the Co^{III}–O–Cr^{II} transition state.[12]

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