ABSTRACT

Some oxo-centred trinuclear transition metal complexes—mechansim of acid catalyzed hydrolysis and electron transfer reaction in aqueous *L*-ascorbic acid.

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A detailed kinetic study of the acid assisted hydrolysis of a series of complexes of the general formula $[Cr_2Fe(\mu_3\text{-}O)(\mu_2\text{-}RCO_2)_6(H_2O)_3]^+$ (where R = H, CH_3, CH_3CH_2 or $(CH_3)_2CH$) in aqueous perchloric acid over the ranges $0.01 \leq [H^+] \leq 0.17$ mol dm^{-3} and $25.0 \leq \theta \leq 35.0$ °C, at an ionic strength of 0.50 mol dm^{-3} ($NaClO_4$) was performed using UV/Vis spectrophotometry (diode array and stopped flow). An associative (I_a) mechanism is postulated and involves an equilibrium between the protons and the complex cation, where the oxygen atoms of the carboxylate coordinated to the metal centre are protonated, followed by Fe—O bond cleavage and rapid decomposition to produce aqueous iron(III), a dinuclear chromium(III) species (which is further hydrolyzed), and carboxylate ions. The negative values for the entropy of activation calculated for these species are consistent with the I_a mechanism proposed, and an imperical relation between the pK_a of the parent acid of the complexes and the rate constant for the hydrolysis was established.

Using the same spectroscopic techniques, a detailed kinetic study of the oxidation of *L*-ascorbic acid by this $[Cr_2Fe(\mu_3\text{-}O)(\mu_2\text{-}RCO_2)_6(H_2O)_3]^+$ series, as well as other oxo-centred trinuclear complexes with the formulae $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3CO_2)_6(H_2O)_3]^+$ and $[Ru_2M(\mu_3\text{-}O)(\mu_2\text{-}RCO_2)_6(H_2O)_3]^+$ (where M = Cr(III) or Ru(III)), over the ranges $2.44 \leq pH \leq 4.83$, $15.0 \leq \theta \leq 35.0$ °C and at an ionic strength of 0.50 mol dm^{-3} ($NaClO_4$) was performed under pseudo first order reaction conditions with respect to *L*-ascorbic acid in aqueous carboxylic acid-carboxylate buffer. A mechanism involving two species of the complexes—a triaqua and a diaquahyrdoxo, is proposed.

The reactions of the $[Cr_2Fe(\mu_3\text{-}O)(\mu_2\text{-}RCO_2)_6(H_2O)_3]^+$ and $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3CO_2)_6(H_2O)_3]^+$ complexes with *L*-ascorbic acid occur with the formation of an adduct between the complex and the diprotic form of *L*-ascorbic acid (H_2A). The adduct formation is followed by an inner-sphere one-electron transfer process at the iron(III) centre. The electron transfer yields a highly unstable $Fe^{II/}M_2^{III/III}O$ core (where M = Cr(III) or Fe(III)), that decomposes immediately upon formation in the aqueous environment, to yield an aqueous mixture consisting of free iron(II) and a dinuclear chromium(III) species in the case of the mixed metal complexes. The dinuclear chromium(III) species suffers a similar fate as in the acid hydrolysis.

The reactions between *L*-ascorbic acid and the $[Ru_2M(\mu_3\text{-}O)(\mu_2\text{-}RCO_2)_6(H_2O)_3]^+$ (where M = Cr(III) or Ru(III)) complexes do not involve an adduct and the complexes react with both the diprotic (H_2A) and monoprotic (HA^-) forms of *L*-ascorbic acid. The mechanism occurs by an inner-sphere electron transfer process at a Ru(III) centre. The product of the first electron transfer is the $Ru_2^{II/III}M^{III}O$ core. The immediate fate of this mixed valent species is not clear, however the final solution consists of aqueous Ru(II) and Cr(III) when M = Cr(III).

Keywords: Mark A. W. Lawrence, trinuclear, oxo-centred, iron(III), chromium(III), ruthenium(III), acid hydrolysis, *L*-ascorbic acid, oxidation, kinetics, mechanism.