ABSTRACT

Kinetics and Mechanisms of the Oxidation of L-ascorbic Acid by Dinuclear Cobalt(III) Dioxygen Complexes.

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The kinetic measurements of the oxidation of L-ascorbic acid (H_2A) by a series of dioxygen complexes; $(NH_3)_5Co\mu(O_2)Co(NH_3)_5^{5+}$ and $LCo\mu(NH_2,O_2)CoL^{4+}$ (L = ammine, ethylenediamine, 2, 2′,2"triaminotriethylamine, 2,2′bipyridyl) have been investigated over the ranges, $0.01 \le [H^+] \le 0.10$ mol dm^{-3}, $0.005 \le [asc.] \le 0.200$ mol dm^{-3}, $20^\circ \le \theta \le 30^\circ C$ and at an ionic strength of 0.5 mol dm^{-3} maintained with lithium perchlorate.

The reaction was a two step process. The first step was a rapid one electron transfer to the μ-superoxo resulting in the formation of the μ-peroxo complex and the ascorbate radical. For the first step the experimental data for each compound conformed to the following rate law :

$$\text{rate} = \left[k_1 + \frac{k_2 K_a}{[H^+]} \right] [A]_T[\text{complex}]$$

where k_1 and k_2 corresponds to the second order rate

constants for the H_2A path and the HA^- path respectively, $[A]_T$ is the sum of the concentration of ascorbic acid and ascorbate monoanion (HA^-) and K_a is the first dissociation constant of ascorbic acid. With $K_a = 1.05 \times 10^{-4}$ at 25°C, second order rate constant k_2 for the complexes in the same order given above are $(8.5 \pm 0.01) \times 10^4$, $(1.253 \pm 0.20) \times 10^6$, $(1.554 \pm 0.30) \times 10^6$, $(1.532 \pm 0.04) \times 10^6$, and $(14.0 \pm 4.0) \times 10^8$ $dm^3 mol^{-1} s^{-1}$. $\Delta H^{\#}$ and $\Delta S^{\#}$ are 34.5 ± 4.8, 35.8 ± 6.7, 23.4 ± 2.8, 15.4 ± 1.5 kJ mol^{-1} and -35.3 ± 19.2, -8.7 ± 27.6, -47.9 ± 11.2, -75.1 ± 6.3 J mol^{-1} K^{-1} respectively.

The effect of ionic strength, chloride and copper(II) on this reaction were also investigated. This step was also analyzed by means of the Marcus cross relationship treatment for outer sphere electron transfer reactions.

The second step was a slow two electron oxidation of the ascorbic acid by the μ-peroxo complex, the single bridged complex was an exception as the μ-peroxo decomposed to cobalt(II) under these conditions. This reaction was studied under similar conditions to those used for the μ-superoxo complexes. Under these conditions, the 2, 2′ bipyridyl and 2, 2′, 2"triaminotriethylamine peroxo complexes virtually did not react. Consequently, the ethylenediamine complex was studied in most detail. The mechanism proposed involves equilibration of the μ-peroxo complex, followed by reaction of the equilibrated species with monohydroascorbate (HA^-) and ascorbic acid (H_2A) to produce the μ-hydroxo complex and the ascorbate radicals. The experimental data conforms to the following rate expression:

$$\text{rate} = \left[\frac{k_1 K_5 + k_2 K_1' K_5 [H^+]}{(1 + K_1' [H^+])[H^+]} \right] [A]_T [\text{complex}]$$

K_5 is the first acid dissociation constant of ascorbic acid, and k_1 and k_2 are the second order rate constants for the H_2A and the HA^- paths respectively. $k_1 = 0.29 \pm 0.10\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ and $k_2 = 5.36 \pm 0.32\ \text{dm}^3 \text{mol}^{-1}\ \text{s}^{-1}$ at $\theta = 25\,^{\circ}\text{C}$, $\Delta H_1^{\#} = 70.0 \pm 15.5\ \text{kJ mol}^{-1}$, $\Delta S_1^{\#} = -19.3 \pm 63.5\ \text{J mol}^{-1}\ \text{K}^{-1}$, $\Delta H_2^{\#} = 28.2 \pm 3.5\ \text{kJ mol}^{-1}$ and $\Delta S_2^{\#} = -136.9 \pm 14.5\ \text{J mol}^{-1}\ \text{K}^{-1}$.

The effect of copper(II) on the reaction was also studied. There was no apparent effect of copper(II) ion on the oxidation of L-ascorbic acid by the μ-superoxo complexes. However, the copper(II) ion catalysed the second step significantly, in fact the tren and bipy complexes reacted at measureable rates, in the pH range $0.01 \leq [H^+] \leq 0.10\ \text{mol dm}^{-3}$.

The complexes studied in most detail were the ethylendiamine and tren analogs. The mechanism proposed for these complexes involves equilibration of the μ-peroxo complex, followed by reaction of the hydroperoxo (AH) with the copper(II)-ascorbate complexes by a two electron process to generate the μ-hydroxo complex. The experimental data fits the following rate expression:

$$\text{rate} = \left[\frac{k_1 K_m K_a}{[H^+]} + k_2 K_{mH} K_a \right] [A]_T [Cu]_T [\text{complex}]$$

Where K_m and K_{mH} are the equilibrium constants for the formation of copper(II)-ascorbate complex and K_a is as defined earlier. The rate constants k_1 and k_2 for the catalyzed reactions were calculated at $\theta = 25^\circ C$ and the values reported.