ABSTRACT

Mechanistic Studies of the Oxidation of Dinuclear Cobalt(III) Dioxygen Complexes with Peroxodisulfate.

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The kinetics of the oxidation of a series of dinuclear cobalt(III) dioxygen complexes; $LCo(\mu\text{-}O_2)CoL^{4+}$; (L = 2,2',2"triaminotriethylamine(ammine), tetraethylene-pentamine, ethylenediamine(diethylenetriamine)) and $LCo(\mu\text{-}NH_2)(\mu\text{-}O_2)CoL^{3+}$ (L = ethylenediamine, 2,2',2"-triaminotriethylamine, 2,2'bipyridyl) by aqueous acidic peroxodisulfate solution have been extensively studied. The reaction was carried out over the ranges, $0.01 \leq [H^+] \leq 0.5$ M, $0.002 \leq [S_2O_8^{2-}] \leq 0.026$ M, $16 \leq \theta \leq 35$ °C and at an ionic strength of 0.25 M maintained with lithium perchlorate or lithium nitrate.

The μ-peroxo complex reacted with one mole of the peroxodisulfate to form the corresponding μ-superoxo complex, a sulfate ion and a sulfate radical anion. The mechanism of this reaction involved the formation of an ion-pair within which the electron transfer process occurs to form the products. A generalized rate law can be written;

$$\text{Rate} = \frac{k\,K\,[S_2O_8^{2-}][\text{comp}]}{1 + K\,[S_2O_8^{2-}]}$$

where K is the pre-equilibrium constant for the formation of the complex-peroxodisulfate ion-pair and k is the rate constant for the internal electron transfer process. The k and K values for the single-bridged complexes with L = tren(NH_3), tetren and en(dien) were (2.6 ± 0.2) x 10^{-2} sec^{-1} , 1.41 ± 0.[illegible] sec^{-1}, 4.42 ± 0.4 sec^{-1}; 131 ± 5 M^{-1}, 23 ± 1 M^{-1}, and 17.7 ± 2 M^{-1} respectively. The $\Delta H^{\#}$ and $\Delta S^{\#}$ values were found to be 39.9 ± 1.5, 67 ± 0.4, 82 ± 4 kJ mol^{-1} and -142 ± 11, -15 ± 1, and 42 ± 7 J mol^{-1} K^{-1} respectively.

The effect of ionic strength and silver(I) on the reaction were investigated. The above thermodynamic data for the dibridged complexes fitted the linear free energy relationship well.

The dibridged complexes with L = $(en)_2$, tren, and $(bipy)_2$ were also oxidized using the peroxodisulfate ion. The mechanism of these reactions also conformed to the general mechanism given above. The reactions however showed differences mainly due to the tendency to form protonated species in solution. The corresponding k and K values were found to be (1.1 ± 0.05) x 10^{-2} sec^{-1} for the ethylenediamine complex,

$(4.98 \pm 0.4) \times 10^{-3}$ sec^{-1} for the tren complex, $(7.4 \pm 1) \times 10^{-5}$ sec^{-1} for the bipy complex and 33 ± 2 M^{-1}, 19.4 ± 1 M^{-1}, and 8.4 ± 1 M^{-1} respectively. The $\Delta H^{\#}$ and $\Delta S^{\#}$ values were found to be 29 ± 1, 42.2 ± 1, 57.8 ± 5 kJ mol^{-1} and -186 ± 6, -147 ± 4, and -131 ± 19 J mol^{-1} K^{-1} respectively.

The effect of ionic strength and silver(I) on the reaction of the dibridged complexes were also investigated. The reaction was also analyzed by means of the Marcus Cross relationship treatment for outer sphere electron transfer reactions.

A detailed examination of the effect of silver(I) on the oxidation of $[(bipy)_2Co(\mu\text{-}NH_2)(\mu\text{-}O_2)Co(bipy)_2]^{3+}$ complex by peroxodisulfate was undertaken. The rate of the reaction was found to be zero-order in [complex], and first-order in both $[Ag^+]$ and $[S_2O_8^{2-}]$. The rate law obtained was

$$\text{Rate} = (k_u + k_1[Ag^+])[S_2O_8^{2-}]$$

where k_u is the rate constant for the uncatalysed reaction and k_1 is the rate for the catalysed reaction. The k_u and k_1 values at 25°C were found to be 4.3×10^{-6} sec^{-1} and 9.31×10^{-3} M^{-1} sec^{-1}.