ABSTRACT

Mechanistic studies of the reduction of the trinuclear complex cation, $[Fe^{III}_3O(CH_3COO)_6(H_2O)_3]^+$, by ascorbic acid.

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The reduction potential of the $Fe^{III}_3/Fe^{III}_2Fe^{II}$ couple was found to be –0.184 V versus the standard calomel electrode. The pK value of the second proton dissociation of the complex was determined to be 4.90.

The kinetic measurements of the hydrolysis of the Fe^{III}_3 complex were investigated over the ranges $0.01 \leq [H^+] \leq 0.15$ mol dm^{-3}, $25 \leq \theta \leq 35$ °C at an ionic strength of 1.0 mol dm^{-3} ($NaClO_4$). Acid hydrolysis studies gave a value for the first protonation constant, $K_{h,1}$, of 6.4 ± 3.4 mol^{-1} dm^3 for the $Fe^{III}_3O(CH_3COO)_6(H_2O)_3]^+$ complex. The values of the first-order rate constant for the spontaneous hydrolysis step, k_0, were (3.89 ± 0.91) x 10^{-3} (25 °C), (5.34 ± 0.86) x 10^{-3} (30 °C) and (6.17 ± 0.62) x 10^{-3} (35 °C) s^{-1}. The values of the rate constants for the first stage of the hydrolysis, k_1, were (4.2 ± 1.7) x 10^{-2} (25 °C), (4.9 ± 2.2) x 10^{-2} (30 °C) and (5.9 ± 2.8) x 10^{-2} (35 °C) s^{-1}. The values of $\Delta H^{\ddagger}_0$ and $\Delta S^{\ddagger}_0$ for the spontaneous hydrolysis step were 32.8 ± 5.7 kJ mol^{-1} and –181 ± 19 J K^{-1} mol^{-1} respectively, while for the adduct formation step, the values of $\Delta H^{\ddagger}_1$ and $\Delta S^{\ddagger}_1$ are 22.6 ± 2.1 kJ mol^{-1} and –195 ± 7 J K^{-1} mol^{-1} respectively.

The second slower stage, under the same conditions as the first, revealed that the values of the adduct formation constant, $K_{h,2}$, decreased slightly with increasing temperature, that is 8.9 ± 2.4 (25 °C), 7.4 ± 2.2 (30 °C) and 5.7 ± 4.6 (35 °C) mol^{-1} dm^3. The values of the first-order rate constant for the spontaneous hydrolysis step, k'_0, were (3.66 ± 0.16) x 10^{-4} (25 °C), (5.07 ± 0.30) x 10^{-4} (30 °C) and (7.20 ± 0.97) x 10^{-4} (35 °C) s^{-1}, while the values of the first-order rate constant for the second adduct formation step, k_2, were (1.88 ± 0.56) x 10^{-3} (25 °C), (2.75 ± 0.85) x 10^{-3} (30 °C) and (4.16 ± 3.37) x 10^{-3} (35 °C) s^{-1}. $\Delta H'^{\ddagger}_0$ and $\Delta S'^{\ddagger}_0$ values for the spontaneous hydrolysis step were found to be 48.2 ± 3.4 kJ mol^{-1} and 149 ± 11 J K^{-1} mol^{-1} respectively, while $\Delta H^{\ddagger}_2$ and $\Delta S^{\ddagger}_2$ values for the adduct formation step were found to be 57.2 ± 4.7 kJ mol^{-1} and –105 ± 16 J K^{-1} mol^{-1} respectively.

The reduction of the Fe^{III}_3 complex by L-ascorbic acid occurred in three stages resulting in the formation of aqueous iron(II) perchlorate solution. The first stage was studied over the ranges $0.005 \leq [H^+] \leq 0.20$ mol dm^{-3}, $3.35 \leq pH \leq 4.35$, $15.2 \leq \theta \leq 30.1$ °C at an ionic strength of 1.0 mol dm^{-3} ($NaClO_4$). The value of the adduct formation constant, K_1, over the temperature range studied was found to be 61 ± 16 mol^{-1} dm^3. The values of the first-order rate constants, k_1, were found to be 5.7 ± 1.2 (15.2 °C), 12.2 ± 1.9 (19.9 °C) 15.0 ± 1.6 (25.1 °C) and 37.9 ± 4.5 (30.1 °C) s^{-1}. The value of $\Delta H^{\ddagger}_1$ was found to be 82 ± 16 kJ mol^{-1} and that of $\Delta S^{\ddagger}_1$ found to be 56 ± 53 J K^{-1} mol^{-1}.

For the second stage, under the same condition as the first, the values of the second-order rate constants, k_2, were found to be

41 ± 1 (15.2 °C), 65 ± 2 (19.9 °C), 119 ± 2 (25.1 °C) and 136 ± 5 (30.1 °C) mol^{-1} dm^3 s^{-1}. The values of $\Delta H^{\ddagger}_2$ and $\Delta S^{\ddagger}_2$ were found to be 59.2 ± 8.0 kJ mol^{-1} and –8 ± 27 J K^{-1} mol^{-1} respectively.

The third stage proceeded via two steps where the values of the rate constants for the spontaneous decomposition step, k'_3, were found to be (0.341 ± 0.134) x 10^{-2} (15.2 °C), (0.73 ± 0.06) x 10^{-2} (19.9 °C), (2.12 ± 0.17) x 10^{-2} (25.1 °C) and (3.40 ± 0.30) x 10^{-2} (30.1 °C) s^{-1}. The values of $\Delta H'^{\ddagger}_3$ and $\Delta S'^{\ddagger}_3$ were found to be 114 ± 9 kJ mol^{-1} and 104 ± 29 J K^{-1} mol^{-1} respectively. The values of the rate constants, k_3, for electron transfer step for this stage were found to be (3.33 ± 0.18) x 10^{-1} (15.2 °C), (5.17 ± 0.11) x 10^{-1} (19.9 °C), (8.38 ± 0.26) x 10^{-1} (25.1 °C) and (9.72 ± 0.38) x 10^{-1} (30.1 °C) mol^{-1} dm^3 s^{-1}. The values of $\Delta H^{\ddagger}_3$ and $\Delta S^{\ddagger}_3$ were found to be 51.9 ± 6.2 kJ mol^{-1} and –74 ± 21 J K^{-1} mol^{-1} respectively.