ABSTRACT

Mechanistic studies of the reduction of the trinuclear complex cation, \([\text{Fe}^{III}_3\text{O(CH}_3\text{COO)}_6(\text{H}_2\text{O})_3]^+\), by ascorbic acid.

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The reduction potential of the \(\text{Fe}^{III}_3/\text{Fe}^{II}_2\text{Fe}^{II}\) 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 \(\text{Fe}^{III}_3\) 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, \(K_{b,1}\), of \(6.4 \pm 3.4\) mol\(^{-1}\) dm\(^3\) for the \(\text{Fe}^{III}_3\text{O(CH}_3\text{COO)}_6(\text{H}_2\text{O})_3]^+\) complex. The values of the first-order rate constant for the spontaneous hydrolysis step, \(k_0\), were \((3.89 \pm 0.91) \times 10^{-3}\) (25 °C), \((5.34 \pm 0.86) \times 10^{-3}\) (30 °C) and \((6.17 \pm 0.62) \times 10^{-3}\) (35 °C) s\(^{-1}\). The values of the rate constants for the first stage of the hydrolysis, \(k_1\), were \((4.2 \pm 1.7) \times 10^{-2}\) (25 °C), \((4.9 \pm 2.2) \times 10^{-2}\) (30 °C) and \((5.9 \pm 2.8) \times 10^{-2}\) (35 °C) s\(^{-1}\). The values of \(\Delta H^+_0\) and \(\Delta S^+_0\) for the spontaneous hydrolysis step were \(32.8 \pm 5.7\) kJ mol\(^{-1}\) and \(-181 \pm 19\) J K\(^{-1}\) mol\(^{-1}\) respectively, while for the adduct formation step, the values of \(\Delta H^+_1\) and \(\Delta S^+_1\) are \(22.6 \pm 2.1\) kJ mol\(^{-1}\) and \(-195 \pm 7\) 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, $K_{b2}$, decreased slightly with increasing temperature, that is $8.9 \pm 2.4$ (25 °C), $7.4 \pm 2.2$ (30 °C) and $5.7 \pm 4.6$ (35 °C) mol$^{-1}$ dm$^{-3}$. The values of the first-order rate constant for the spontaneous hydrolysis step, $k'_0$, were $(3.66 \pm 0.16) \times 10^{-4}$ (25 °C), $(5.07 \pm 0.30) \times 10^{-4}$ (30 °C) and $(7.20 \pm 0.97) \times 10^{-4}$ (35 °C) s$^{-1}$, while the values of the first-order rate constant for the second adduct formation step, $k_2$, were $(1.88 \pm 0.56) \times 10^{-3}$ (25 °C), $(2.75 \pm 0.85) \times 10^{-3}$ (30 °C) and $(4.16 \pm 3.37) \times 10^{-3}$ (35 °C) s$^{-1}$. $\Delta H^+_0$ and $\Delta S^+_0$ values for the spontaneous hydrolysis step were found to be $48.2 \pm 3.4$ kJ mol$^{-1}$ and $149 \pm 11$ J K$^{-1}$ mol$^{-1}$ respectively, while $\Delta H^+_2$ and $\Delta S^+_2$ values for the adduct formation step were found to be $57.2 \pm 4.7$ kJ mol$^{-1}$ and $-105 \pm 16$ 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$^{-3}$, $3.35 \leq \text{pH} \leq 4.35$, $15.2 \leq \theta \leq 30.1$ °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 $61 \pm 16$ mol$^{-1}$ dm$^{-3}$. The values of the first-order rate constants, $k_1$, were found to be $5.7 \pm 1.2$ (15.2 °C), $12.2 \pm 1.9$ (19.9 °C) $15.0 \pm 1.6$ (25.1 °C) and $37.9 \pm 4.5$ (30.1 °C) s$^{-1}$. The value of $\Delta H^+_1$ was found to be $82 \pm 16$ kJ mol$^{-1}$ and that of $\Delta S^+_1$ found to be $56 \pm 53$ 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 Δ\(H^\dagger\)_2 and Δ\(S^\dagger\)_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 Δ\(H^\dagger\)_3 and Δ\(S^\dagger\)_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 Δ\(H^\dagger\)_3 and Δ\(S^\dagger\)_3 were found to be 51.9 ± 6.2 kJ mol\(^{-1}\) and −74 ± 21 J K\(^{-1}\) mol\(^{-1}\) respectively.