The Reduction of Iron(III) by Ascorbic Acid
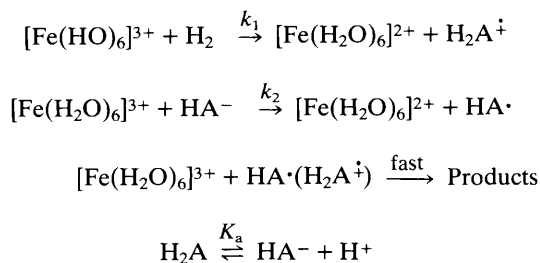
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The kinetics of the reduction of iron(III) with ascorbic acid have been investigated in aqueous solution at an ionic strength of 0.5 mol dm^{-3} NaClO$_4$ using the stopped-flow technique; the nature of the reaction observed is sensitive even to small concentrations of added chloride.

The oxidation of ascorbic acid by iron(III) and its complexes has been the subject of a number of investigations.[1—9] In general, it is believed that oxidation of the ascorbic acid takes place by an outer-sphere process. In most of the systems investigated to date, the rate law was of the form shown in equation (1), where Fe^{III} represents the oxidant, thus confirming that the HA$^-$ anion was the active reducing species. Martinez and Uribe have recently investigated the kinetics and mechanism of the reaction of iron(III) with ascorbic acid in aqueous solution.[6] They claim that k_{obs} has the form of equation (1). However, careful examination of the data shows

that this is not strictly true, and a plot of k_{obs} against [H$_2$A]$_{total}$ at constant [H$^+$] has a small positive intercept. Martinez and Uribe used FeCl$_3$ as the source of iron(III) and observed a relatively rapid reaction which they monitored at 330 nm.[6] However, when we used Fe(ClO$_4$)$_3$ (0.001 mol dm^{-3}, I = 0.5 mol dm^{-3} NaClO$_4$) as the source of iron(III) a different behaviour was observed. A much slower reaction is observed at 300 nm. There is no reaction corresponding to the reaction observed by Martinez and Uribe at 330 nm. However, when solutions of Fe(ClO$_4$)$_3$ (0.001 mol dm^{-3}) to which NaCl has been added (0.003—0.010 mol dm^{-3}) are reacted with

$$[Fe(HO)_6]^{3+} + H_2 \xrightarrow{k_1} [Fe(H_2O)_6]^{2+} + H_2A^{\dot{+}}$$

$$[Fe(H_2O)_6]^{3+} + HA^- \xrightarrow{k_2} [Fe(H_2O)_6]^{2+} + HA\cdot$$

$$[Fe(H_2O)_6]^{3+} + HA\cdot(H_2A^{\dot{+}}) \xrightarrow{fast} Products$$

$$H_2A \overset{K_a}{\rightleftharpoons} HA^- + H^+$$

Scheme 1

ascorbic acid, *two* reactions are observed. The faster of these reactions is best monitored at 330 nm and has a rate constant similar to that obtained by Martinez and Uribe[6] while the slower reaction, which can be monitored at 300—310 nm, has a rate constant similar to that obtained using $Fe(ClO_4)_3$ in the absence of added chloride. Only small quantities of chloride need be added to obtain this effect, the addition of further quantities has no effect on the magnitude of the rate constants. However, the amplitude of the faster step increases with increasing chloride concentration while that of the slower step decreases.

$$k_{obs} = (k[Fe^{III}][H_2A])/[H^+] \tag{1}$$

Under our experimental condition, the concentration of $[Fe_2(OH)_2]^{4+}$ is negligible so that any contribution from this species can be neglected. The equilibrium constant for reaction of Cl^- with Fe^{3+} is approximately 5 mol^{-1} dm^3 at an ionic strength of 0.5 mol dm^{-3}.[10] Concentration jump experiments carried out by reacting a solution containing 3 × 10^{-3} mol dm^{-3} of $FeCl_3$ at 0.5 mol dm^{-3} $HClO_4$ with 0.5 mol dm^{-3} $HClO_4$ in the stopped flow apparatus gave k_{obs} = 16.2 s^{-1}. This can be equated to the rate of dissociation of chloride from $[FeCl(H_2O)_5]^{2+}$. Consequently, the rate of formation of $[FeCl(H_2O)_5]^{2+}$ is 81 dm^3 mol^{-1} s^{-1}. The extinction coefficient of $[FeCl(H_2O)_5]^{2+}$ at 335 nm is 1.3 × 10^3,[10] while that of $[Fe(H_2O)_6]^{3+}$ is *ca.* 6.7. Thus, although only a small percentage (*ca.* 2.5%) of the iron(III) is present as $[FeCl(H_2O)_5]^{2+}$ when $FeCl_3$ (0.001 mol dm^{-3}) is used as the source of iron(III), nevertheless owing to the large difference (×200) in the extinction coefficients of the two species, virtually all the absorption at 330—335 nm derives from the

$[FeCl(H_2O)_5]^{2+}$ present. The disappearance of this absorbance when aqueous solutions of $FeCl_3$ (0.001 mol dm^{-3}) are reacted with ascorbic acid accounts for the reaction observed by Martinez and Uribe.[6] The rate constants they derived measure the rate of reduction of $[FeCl(H_2O)_5]^{2+}$ and not $[Fe(H_2O)_6]^{3+}$. The slower reaction measured by us at 300 nm and for which k_{obs} has the form of equation (2) is the reduction of $Fe[(H_2O)_6]^{3+}$ by ascorbic acid. Both H_2A (acid independent term) and HA^- (inverse acid term) contribute to the reduction under our experimental conditions. The fact that two separate reaction steps can be observed at 330 nm is caused by the slow rate of reaction of iron(III) with chloride.

$$k_{obs} = (14.6 + 9.65/[H^+])[H_2A] \tag{2}$$

$$k_{obs} = 2(k_1 + k_2K_a/[H^+])[H_2A] \tag{3}$$

The mechanism proposed for the reaction is shown in Scheme 1. This mechanism predicts that when ascorbic acid is in pseudo-first-order excess, k_{obs} has the form of equation (3), with $K_a = 7.94 \times 10^{-5}$ mol dm^{-3}. Thus from equation (2), k_1 = 7.3 s^{-1} and $k_2 = 6.07 \times 10^4$ dm^3 mol^{-1} s^{-1}. The value of k_2 is approximately thirty times smaller than that reported by Martinez and Uribe.[6]

References

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