Kinetics and Mechanism of Oxidation of Ascorbic Acid by Manganese(III) in Aqueous Acidic Perchlorate Media

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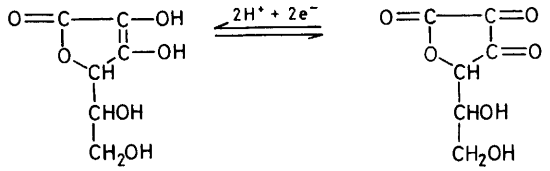
The kinetics and mechanism of oxidation of ascorbic acid (H_2A) by Mn^{III} in aqueous acidic perchlorate media have been investigated by means of stopped-flow spectrophotometry. The rate law is of the form $-\frac{1}{2}d[Mn^{III}]/dt = (k_a + k_b[H^+]^{-1})[Mn^{III}][H_2A]$ where the two terms have been assigned to reactions involving the undissociated form of ascorbic acid with Mn^{3+}(aq) and $[Mn(OH)]^{2+}$(aq) respectively. Comparison with similar reactions involving benzenediols suggests some conclusions on the reduction potentials and the oxidation mechanism of ascorbic acid.

A CONSIDERABLE amount of data concerning the oxidation of diol derivatives is now available in the literature. In particular, oxidations of catechols, quinols, and biphenyldiol by aquametal ions [such as Co^{III}, Mn^{III}, Tl^{III}, and V^V] [1] and by complexes such as $[Fe^{III}L_3]$ (L = phenanthroline or bipyridyl derivative) [2] or hexachloroiridate(IV) [3] have been studied. L-Ascorbic acid, which is a well known compound of biological interest, exhibits a vicinal diol structure which can be oxidized to the corresponding dehydroascorbic acid according to equation (i). The oxidation of ascorbic acid by several oxidizing ions has been investigated,[4] and recently we studied the reaction between ascorbic acid and a series of $[Fe^{III}L_3]$ derivatives [5] in order to estimate some of the characteristic parameters of this compound. Richman *et al.*[6] investigated the reaction of ascorbic acid with Co^{III} in perchlorate media, and some conclusions have been drawn by comparison with data concerning oxidation of aromatic diols by Co^{III}.



(i)

In this paper we present the results of an investigation of the oxidation of ascorbic acid by Mn^{III} in perchlorate media in order to achieve additional information on these systems.

EXPERIMENTAL

Reagents.—Manganese(III) was prepared by anodic oxidation of manganese(II) perchlorate (obtained by dissolution of $Mn[CO_3]$ in aqueous perchloric acid). Ascorbic acid (E. Merck) solutions were prepared immediately before use. Perchloric acid and sodium perchlorate were used for adjusting the acidity and ionic strength ($I = 3.0$ mol dm^{-3}); twice distilled water was used.

Procedure.—Manganese(III) and Mn^{II} were estimated as previously described.[7] The reaction rates were followed at 470 nm (wavelength of maximum absorption of Mn^{III}) with a Durrum–Gibson stopped-flow spectrophotometer. Rate constants were calculated by a weighted-least-squares method. The acidity range investigated was 0.50—2.00 mol dm^{-3} ($HClO_4$) and the kinetic runs were carried out at $[Mn^{III}] = 2.0 \times 10^{-4}$ and $[H_2A] = 2 \times 10^{-4}$—$4 \times 10^{-4}$ mol dm^{-3}. A large excess of Mn^{II} over Mn^{III} (>100-fold) was present in order to avoid disproportionation of Mn^{III}. The experiments were carried out at 6.0, 20.0, and 35.0 °C.

RESULTS

Stoicheiometry.—The stoicheiometric measurements were carried out by adding an excess of Mn^{III} to a solution of ascorbic acid and estimating the Mn^{III} remaining. The results indicate that the overall reaction can be represented as in (1) where A = dehydroascorbic acid.

$$2\,Mn^{III} + H_2A \longrightarrow 2\,Mn^{II} + A + 2\,H^+ \qquad (1)$$

Kinetics.—Plots of $\log\{(2[H_2A]_0 - [Mn^{III}])/([Mn^{III}]_0 - [Mn^{III}])\}$ against time were linear for at least three half-lives, indicating that the overall order of the reaction is two,

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and the order with respect to the concentration of each reagent is unity. Second-order rate constants, k_0, calculated from $2.303(\text{gradient})/(2[H_2A]_0 - [Mn^{III}]_0)$, are collected in Table 1. The dependence of the reaction rate on acidity can be interpreted in terms of the manganese(III) species $\{Mn^{3+}(aq)$ and $[Mn(OH)]^{2+}(aq)\}$ and the ascorbic acid species (H_2A and HA^-) present in solution. Thus reactions (2)—(8) can be taken into account. In reactions

$$Mn^{3+}(aq) \overset{K_h}{\rightleftharpoons} [Mn(OH)]^{2+}(aq) + H^+ \qquad (2)$$

$$H_2A \overset{K_a}{\rightleftharpoons} HA^- + H^+ \qquad (3)$$

$$Mn^{3+}(aq) + H_2A \xrightarrow{k_1} Mn^{2+}(aq) + \text{Radical} \qquad (4)$$

$$[Mn(OH)]^{2+}(aq) + H_2A \xrightarrow{k_2} Mn^{2+}(aq) + \text{Radical} \qquad (5)$$

$$Mn^{3+}(aq) + HA^- \xrightarrow{k_3} Mn^{2+}(aq) + \text{Radical} \qquad (6)$$

$$[Mn(OH)]^{2+}(aq) + HA^- \xrightarrow{k_4} Mn^{2+}(aq) + \text{Radical} \qquad (7)$$

$$Mn^{III} + \text{Radical} \xrightarrow{\text{fast}} Mn^{2+}(aq) + A \qquad (8)$$

(4)—(8) protons are omitted since the radical can exhibit different degrees of protonation. Application of the steady-state assumption to the radical concentration leads to the rate law (9). Since $K_a[H^+]^{-1} \ll 1$ in equation (10),[5] and a

$$-\tfrac{1}{2}\,d[Mn^{III}]/dt = -d[H_2A]/dt = k_0[Mn^{III}][H_2A] \qquad (9)$$

where

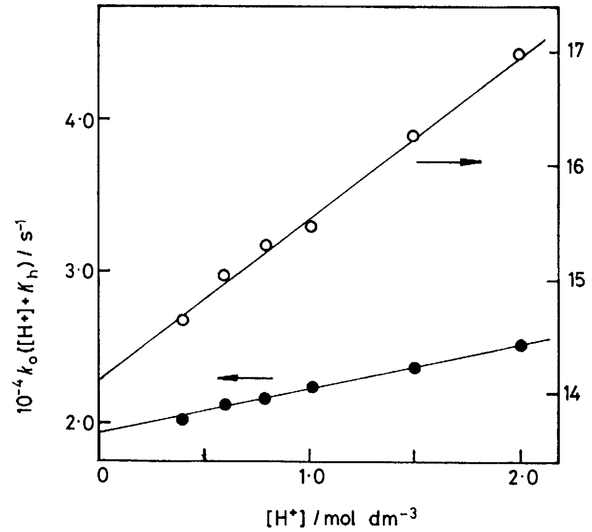
$$k_0 = \frac{(k_1 + k_2K_h[H^+]^{-1} + k_3K_a[H^+]^{-1} + k_4K_hK_a[H^+]^{-2})}{(1 + K_h[H^+]^{-1})\,(1 + K_a[H^+]^{-1})} \qquad (10)$$

plot of $k_0([H^+] + K_h)$ against $[H^+]$ gives a satisfactory straight line, it is suggested that path (7) is negligible (K_h was calculated from literature data);[8] thus k_1 and $(k_2K_h + k_3K_a)$ can be obtained from the gradient and intercept (see Figure and Table 2 where the activation parameters are also reported).

TABLE 1

Second-order rate constants, $10^{-4}k_0/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$, at different acidities and temperatures ($I = 3.0$ mol dm^{-3}) for the oxidation of ascorbic acid by Mn^{III}

	$[H^+]$/mol dm^{-3}					
θ_c/°C	0.40	0.60	0.80	1.00	1.50	2.00
6.0	2.1	1.8_5	1.6	1.4_5	1.2	1.0_5
20.0	3.7	3.3	3.0	2.7	2.3_5	2.0_5
35.0	9.1	8.3	7.5	6.9_5	6.0	5.3



Plot of $k_0([H^+] + K_b)$ against $[H^+]$ for reaction of ascorbic acid with Mn^{III} at 6.0 (●) and 35 °C (○)

DISCUSSION

In recent papers [1-3] the mechanism of redox reactions involving organic substrates and metal-ion complexes have been discussed in terms of Marcus theory,[9] although in some cases the relation between the free energy of activation and the free energy of reaction does not allow a definite choice to be made between an inner- or an outer-sphere mechanism.[10] The functional form of the Marcus theory is as in equations (11) and (12) where Z is

$$\Delta G^{\ddagger} = w_r + \lambda[1 + (\Delta G^{\ominus\prime}/\lambda)]^2/4 \qquad (11)$$

$$k = Z\exp(-\Delta G^{\ddagger}/RT) \qquad (12)$$

the collision number in solution (assumed to be 10^{11} dm^3 mol^{-1} s^{-1}) and $\lambda = 2(\Delta G_{11}^{\ddagger} + \Delta G_{22}^{\ddagger})$ where $\Delta G_{11}^{\ddagger}$ and $\Delta G_{22}^{\ddagger}$ are the free energies of activation of the self-exchange reactions for the individual reactant couples; $\Delta G^{\ominus\prime} = \Delta G^{\ominus} + w_p - w_r$, where $\Delta G^{\ominus}$ is the standard free energy of reaction for the prevailing medium and temperature and w_r and w_p are the coulombic terms for bringing together the reactants and products. (Owing to the high ionic strength, these work terms have been

TABLE 2

Rate constants and activation parameters for the reaction of ascorbic acid with Mn^{III}

	θ_c/°C			$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
	6.0	20.0	35.0	kcal mol^{-1}	cal K^{-1} mol^{-1}
$10^{-3}k_1$/dm^3 mol^{-1} s^{-1}	3.0 ± 0.6	6.0 ± 1.1	13 ± 3	8.6 ± 1.8	−12 ± 6
$10^{-4}(k_2K_h + k_3K_a)$/s^{-1}	1.9 ± 0.1	4.2 ± 0.3	14 ± 1	12.0 ± 0.7	3 ± 2
$10^{-4}k_2$/dm^3 mol^{-1} s^{-1}	3.4 ± 0.2	5.3 ± 0.4	11.5 ± 1	7.1 ± 0.7	−12 ± 2

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neglected.) Application of equation (11) to the oxidation of ascorbic acid by [$\mathrm{Fe^{III}L_3}$], which involves a reaction with the dissociated form of ascorbic acid and where an outer-sphere mechanism is operating, allowed an estimate of the reduction potential of the couple $\mathrm{HA^{\bullet}}$–$\mathrm{HA^-}$ (*ca.* 0.93 V).[5]

In the present study, there is an ambiguity in the assignment of the acid-dependent term since both paths (5) and (6) agree with the experimental dependence. If path (5) is the relevant one, a comparison with the activation parameters and rate constants of other systems, such as thioureas and catechols (with different structures and reduction potentials), suggests a substitution-controlled mechanism.[11] Also, in the reaction between ascorbic acid and $\mathrm{Co^{III}}$, the acid-dependent path has been assigned to the interaction between the undissociated form of the organic substrate and the hydrolyzed metal-ion species, that is $[\mathrm{Co(OH)}]^{2+}$(aq).[6] However, in previous kinetic studies the dependence on acidity has been attributed to the dissociated species of ascorbic acid ($\mathrm{HA^-}$).[4] If path (6) is responsible for the reaction progress, $k_3 = 4.5 \times 10^8$ dm^3 mol^{-1} s^{-1}, and because this value exceeds the usually accepted rate of water exchange in the co-ordination sphere of $\mathrm{Mn^{3+}}$(aq),[12] an outer-sphere mechanism should be operating and equation (11) could be applied. For the $\mathrm{HA^{\bullet}}$–$\mathrm{HA^-}$ couple, values * of $E^{\ominus} = 0.93$ V and $\Delta G_{11}^{\ddagger} = 4$ kcal mol^{-1} (that is *ca.* 10^8 dm^3 mol^{-1} s^{-1} for the self-exchange rate, similar to the exchange rates of other radicals with their parent molecules)[13] can be adopted;[5] for the $\mathrm{Mn^{3+}}$–$\mathrm{Mn^{2+}}$ a value of $E^{\ominus} = 1.51$ V has been reported, while the self-exchange parameter is rather uncertain.[14] If $\Delta G_{22}^{\ddagger}$ is derived from the reaction with [$\mathrm{Fe^{II}L_3}$] (an outer-sphere reaction), a value of *ca.* 26 kcal mol^{-1} is obtained [assuming $\Delta G^{\ddagger}$ ($\mathrm{Fe^{III}L_3}$–$\mathrm{Fe^{II}L_3}$) = 4 kcal mol^{-1} and neglecting the work terms that in this case must be substantial]. This leads to a value of $k_3 = 2.2 \times 10^4$ dm^3 mol^{-1} s^{-1}, that is four orders of magnitude lower than the experimental value. The possibility that a too large value for $\Delta G_{22}^{\ddagger}$ has been adopted must be taken into account, but only a value of $\Delta G_{22}^{\ddagger} = ca.$ 14 kcal mol^{-1} could justify the experimental findings; this value would in turn give dramatically high rates for $\mathrm{Mn^{III}}$–[$\mathrm{Fe^{II}L_3}$] reactions, if equation (11) holds. In conclusion, (5) seems to be the major path of the acid-dependent reaction.

The presence of an acid-independent path is rather unusual, although similar behaviour has also been observed in the oxidation by $\mathrm{Co^{III}}$ (ref. 6) and by $[\mathrm{CoW_{12}O_{40}}]^{5-}$.[15] Also the oxidation by tris(5-nitro-1,10-phenanthroline)iron(III) can be interpreted in terms of a mechanism involving acid-independent and acid-dependent paths.

The reaction rates of the paths involving $\mathrm{Mn^{3+}}$(aq) and $\mathrm{Co^{3+}}$(aq) with ascorbic acid in the form $\mathrm{H_2A}$ are similar to those observed in the oxidation of adrenaline with the same oxidants (Table 3).[1a,b] However, the reactivity of [$\mathrm{Fe^{III}L_3}$] toward $\mathrm{H_2A}$ and adrenaline differs by two orders of magnitude and the reaction rates toward $\mathrm{H_2A}$ are comparable with those of 3,4-dihydroxybenzonitrile (this suggests a reduction potential of *ca.* 1.3—1.4 V for the $\mathrm{H_2A^{\bullet +}}$–$\mathrm{H_2A}$ couple).[2a] Since the reactions with [$\mathrm{Fe^{III}L_3}$] are outer-sphere electron transfers, a different mechanism is probably operating in the oxidations by $\mathrm{Mn^{3+}}$(aq) and $\mathrm{Co^{3+}}$(aq). Further work is necessary in order to test the validity of the present hypotheses.

TABLE 3

Comparison of kinetic data (dm^3 mol^{-1} s^{-1}) for the oxidation of ascorbic acid and benzenediols with different oxidizing agents

	Substrate		
Oxidizing agent	Ascorbic [a] acid	Adrenaline	3,4-Dihydroxybenzonitrile
$\mathrm{Mn^{3+}}$(aq)	6.0×10^3 [b]	2.7×10^3 [c]	
$[\mathrm{Mn(OH)}]^{2+}$(aq)	5.3×10^4 [b]	2.0×10^4 [c]	
$\mathrm{Co^{3+}}$(aq)	2.8×10^2 [d]	1.6×10^2 [e]	*ca.* 15 [e]
$[\mathrm{Co(OH)}]^{2+}$(aq)	7.3×10^5 [d]	2.0×10^5 [e]	1.2×10^5 [e]
$[\mathrm{Fe(phen)_3}]^{3+}$ [f]	$\leqslant 2 \times 10^4$ [g]	$1.1_5 \times 10^6$ [h]	1.2×10^4 [h]
$[\mathrm{Fe(5Me\text{-}phen)_3}]^{3+}$	$\leqslant 3 \times 10^3$ [g]	4.2×10^5 [h]	3.2×10^3 [h]
$[\mathrm{Fe(5NO_2\text{-}phen)_3}]^{3+}$ [f]	4×10^6 [g]	$>10^7$ [h]	3.1×10^6 [h]

[a] The values refer to the reaction path involving the undissociated form of ascorbic acid. [b] This work. [c] Ref. 1*b*. [d] Ref. 6. [e] Ref. 1*a*. [f] phen = 1,10-Phenanthroline, 5Me-phen = 5-methyl-1,10-phenanthroline, and 5$\mathrm{NO_2}$-phen = 5-nitro-1,10-phenanthroline. [g] Ref. 5. [h] Ref. 2*a*.

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* Throughout this paper: 1 cal = 4.184 J.

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