Inorganica Chimica Acta, *195* (1992) 249–253

Kinetics of the oxidation of L-ascorbic acid by diaquatetraamminecobalt(III) in acidic aqueous solution. Application of the Fuoss model and the Marcus–Sutin cross-relationship for electron-transfer processes

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(Received December 31, 1991)

Abstract

The kinetics of the oxidation of L-ascorbic acid by diaquatetraamminecobalt(III) was studied as a function of pH, L-ascorbic acid concentration, ionic strength and temperature using a stopped-flow technique. The rate of the process was found to be first order with respect to both redox partners, whereas the $[H^+]$ concentration showed a retarding influence. The kinetic data are interpreted in terms of rate-determining oxidation of the deprotonated ascorbate anion, for which $k=(3.42\pm0.15)\times10^{-2}$ M^{-1} s^{-1} at 25 °C, $\Delta H^{\neq}=81\pm6$ kJ mol^{-1} and $\Delta S^{\neq}=1\pm20$ J K^{-1} mol^{-1}. The ion-pair formation theory of Fuoss and the Marcus–Sutin cross-relationship for electron transfer were applied to this redox process to estimate the ion-pair formation constant, the rate constant for electron transfer and the self-exchange rate constant for the $Co(NH_3)_4(H_2O)_2^{2+/3+}$ couple.

Introduction

The oxidation reactions of L-ascorbic acid (AH_2) are of fundamental interest in biochemical and related processes. The oxidation mechanism in weakly acidic solution (pH = 2.0–5.5) involves the formation of $AH^{\cdot}$ radicals (demonstrated by EPR measurements [1–3]), which subsequently produce L-dehydroascorbic acid (A) as oxidation product. Various groups have investigated these reactions using a wide range of oxidants [4–11]. It was in general found that these reactions exhibit a characteristic pH dependence, which is related to the acid dissociation constant of AH_2 and to the hydrolysis equilibria of the oxidant when it involves an aquated metal ion. The results have been analysed in terms of inner-sphere and outer-sphere electron-transfer mechanisms, and in a few cases it was possible to detect and to identify intermediate species [8].

Our general interest in the oxidation mechanism of L-ascorbic acid by various oxidants [8–10, 12–14], has recently resulted in a detailed study of the oxidation by $Fe(CN)_6^{3-}$ [15] and $Fe(H_2O)_6^{3+}/Fe(H_2O)_5OH^{2+}$ [16]. In continuation of these studies we have now investigated the oxidation of L-ascorbic acid by *cis*-$Co(NH_3)_4(H_2O)_2^{3+}$ as a function of various kinetic variables. In addition, we have used theoretical treatments by Fuoss and Marcus–Sutin to estimate fundamental thermodynamic and kinetic constants for the electron-transfer process.

Experimental

Materials

The oxidizing agent *cis*-$[Co(NH_3)_4(H_2O)_2](ClO_4)_3$ was prepared via the acidification of $[Co(NH_3)_4CO_3]ClO_4$ according to the method described in the literature [17]. L-Ascorbic acid and all other chemicals were of analytical reagent grade (Merck and Fluka), and used without further purification. Stock solutions were prepared with deaerated doubly distilled water and purged with N_2 for *c.* 30 min prior to use. Universal buffer solutions [18] consisting of phosphoric, acetic and boric acid, and NaOH were used to control the pH in the range 2.8–4.1. The ionic strength of the reaction medium was varied between 0.06 and 0.10 M through the addition of $NaClO_4$.

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0020-1693/92/$5.00

Measurements

pH measurements were performed with a Beckman Expandomatic SS-2 pH meter and a reference electrode filled with NaCl to prevent the precipitation of $KClO_4$. UV–Vis spectra were recorded on a Cary 17 spectrophotometer. Kinetic measurements were performed on a thermostated (±0.1 °C) Durrum D110 stopped-flow instrument at 515 nm where the *cis*-$Co(NH_3)_4(H_2O)_2^{3+}$ species exhibits an absorbance maximum. The reactions were studied under pseudo-first-order conditions by using an excess of L-ascorbic acid, and the corresponding rate constants were obtained with the aid of an on-line data acquisition and analysis system. All reported rate constants are the mean values of at least four determinations and are subjected to an average error limit of less than 5%.

Results and discussion

The oxidation of L-ascorbic acid by $Co(NH_3)_4(H_2O)_2^{3+}$ leads to the formation of L-dehydroascorbic acid according to the overall reaction (1), as also found for other oxidants, followed by the rapid equation of the Co(II) complex. The reaction

$$AH_2 + 2Co(NH_3)_4(H_2O)_2^{3+} \longrightarrow A + 2H^+ + 2Co(NH_3)_4(H_2O)_2^{2+} \qquad (1)$$

strongly depends on pH which can be due to the formation of the more reactive conjugate base species AH^- and/or $Co(NH_3)_4(H_2O)OH^{2+}$ in the studied pH range. It is furthermore safe to assume that the redox process follows an outer-sphere mechanism since the investigated reaction occurs on a stopped-flow time scale which does not permit the Co(III) complex to undergo ligand substitution prior to electron transfer. A general mechanism that can account for the observed pH dependence is given in eqn. (2), and the corresponding rate law is presented in eqn. (3), where $[AH_2]_0$ represents the total concentration of AH_2 and AH^-, $K_1 = 1.6 \times 10^{-4}$ M [15] and $K_2 = 6.3 \times 10^{-6}$ M [19]. In this mechanism it is assumed that AH_2 is significantly more redox stable than AH^-, based on our experience with earlier investigated systems. Furthermore, although the slow spontaneous *cis–trans* isomerization of $Co(NH_3)_4(H_2O)_2^{2+}$ cannot be prevented, it is not expected to affect the kinetic data significantly since both isomers will react at a very similar rate.

$$AH_2 \overset{K_1}{\rightleftharpoons} AH^- + H^+$$

$$Co(NH_3)_4(H_2O)_2^{3+} \overset{K_2}{\rightleftharpoons} Co(NH_3)_4(H_2O)OH^{2+} + H^+$$

$$Co(NH_3)_4(H_2O)_2^{3+} + AH^- \xrightarrow{k_3} Co(NH_3)_4(H_2O)_2^{2+} + AH^{\bullet} \qquad (2)$$

$$Co(NH_3)_4(H_2O)OH^{2+} + AH^- \xrightarrow{k_4} Co(NH_3)_4(H_2O)OH^{+} + AH^{\bullet}$$

$$Co(III) + AH^{\bullet} \xrightarrow{\text{fast}} Co(II) + A + H^+$$

$$k_{obs} = \frac{2[AH_2]_0(k_3 + k_4K_2[H^+]^{-1})}{(1+[H^+]K_1^{-1})(1+K_2[H^+]^{-1})} \qquad (3)$$

The pH dependence of k_{obs} (Table 1) can be used to estimate k_3 and k_4 by plotting $k_{obs}(1+[H^+]K_1^{-1})(1+K_2[H^+]^{-1})$ versus $[H^+]^{-1}$, which results in the values 3.41×10^{-2} and 3.39×10^{-2} M^{-1} s^{-1}, respectively. It follows that the rate constant for the electron-transfer process is not affected by the deprotonation of the Co(III) complex. In addition, the contribution of the k_4 reaction path is negligibly small compared to that of the k_3 path over the selected pH range, since the contribution of the aquahydroxo species is at its most 13% at pH = 4.1. It is therefore appropriate to disregard this reaction path in the subsequent treatment of the data and to simplify eqn. (3) to eqn. (4). The average value of k_3 is $(3.42 \pm 0.15) \times 10^{-2}$ M^{-1} s^{-1} at 25 °C. The observed rate constant depends linearly on $[AH_2]_0$, which results in a similar value for k_3.

$$k_{obs} = 2k_3[AH_2]_0/(1+[H^+]K_1^{-1}) \qquad (4)$$

The redox reaction exhibits a significant decrease in k_{obs} with increasing ionic strength (see Table 1). The data can be fitted with the Brönsted equation (eqn. (5)) by plotting log k_3 versus $\sqrt{\mu}$, from which it follows that $k_3^0 = 0.29$ M^{-1} s^{-1} and $Z_AZ_B = -2.9$. The latter

$$\log k_3 = \log k_3^0 + 1.02Z_AZ_B\sqrt{\mu} \qquad (5)$$

value is in good agreement with that expected on the basis of the reaction in eqn. (2), and further demonstrates that the reduction of Co(III) mainly involves AH^- in the investigated pH range. The temperature dependence of k_3 results in the activation parameters quoted in Table 1, which are compared with those for related redox processes in Table 2. The selected systems can only undergo outer-sphere electron-transfer reactions and cover a range of rate constants from 1×10^{-4} to 6×10^8 M^{-1} s^{-1}. The higher redox reactivity is characterized by a significantly smaller $\Delta H^{\neq}$, but no definite trend in $\Delta S^{\neq}$. The electron-transfer rate constant for the $Co(NH_3)_4(H_2O)_2^{3+}/AH^-$ system is significantly larger than for the $Co(NH_3)_5Cl^{2+}/AH^-$ system, which can be related to the increase in charge on the cobalt center and a stronger outer-sphere precursor formation. Both these reactions are considerably slower than for the $Co(NH_3)_6^{3+}/AH^-$ system, which may be related to the non-symmetrical nature of the substituted ammine complexes that could lead to non-adiabaticity in these systems. Similar trends seem to show up for the quoted Fe(III) systems [13]. A more

TABLE 1. Rate and activation parameters for the oxidation of L-ascorbic acid by $Co(NH_3)_4(H_2O)_2^{3+}$[a]

pH	$[AH_2]_0\times10^2$ (M)	μ (M)	Temperature (°C)	$K_1\times10^4$[b] (M)	$k_{obs}\times10^3$ (s^{-1})	$k_3\times10^2$ ($M^{-1}\ s^{-1}$)
2.8	5	0.10	25.0	1.6	0.31	3.38
3.2					0.69	3.41
3.5					1.16	3.45
3.8					1.72	3.42
4.1					2.27	3.40
3.5	5	0.10	25.0	1.6	1.16	3.45
	6				1.31	3.25
	7				1.67	3.55
	8				1.91	3.55
	9				2.01	3.32
3.5	5	0.06	25.0	1.2	1.55	5.63
		0.07		1.3	1.43	4.91
		0.08		1.4	1.30	4.24
		0.09		1.5	1.26	3.92
		0.10		1.6	1.16	3.45
3.5	5	0.10	15.0	0.5	0.18	1.32
			20.0	1.3	0.55	1.89
			25.0	1.6	1.16	3.45
			30.0	1.7	2.68	7.67
			35.0	1.8	4.09	11.28
$\Delta H^{*}=81\pm6$ kJ mol^{-1}				$\Delta S^{*}=1\pm20$ J K^{-1} mol^{-1}		

[a] $[Co(NH_3)_4(H_2O)_2^{3+}]=2.5\times10^{-3}$ M, $\lambda=515$ nm. [b] Values taken from ref. 15.

TABLE 2. Rate and activation parameters for a selected series of oxidation reactions of L-ascorbic acid

Redox partners	k at 25 °C ($M^{-1}\ s^{-1}$)	ΔH^{*} (kJ mol^{-1})	ΔS^{*} (J K^{-1} mol^{-1})	Reference
$Co(NH_3)_6^{3+}/AH^-$	2.7	36 ± 1	-116 ± 3	9
$Co(NH_3)_5Cl^{2+}/AH^-$	9×10^{-4}	81 ± 8	-29 ± 27	14
$Co(NH_3)_5Cl^{2+}/A^{2-}$	1.8×10^{2}	59 ± 1	-3 ± 5	14
$Co(NH_3)_4(H_2O)_2^{3+}/AH^-$	3.4×10^{-2}	81 ± 6	$+1\pm20$	this work
$Co(C_2O_4)_3^{3-}/AH_2$	1.2×10^{-4}	108 ± 22	$+46\pm61$	20
$Co(C_2O_4)_3^{3-}/AH^-$	4.1×10^{-3}	54 ± 4	-109 ± 15	20
$Co(C_2O_4)_3^{3-}/A^{2-}$	20	34 ± 2	-108 ± 7	13
$Fe(CN)_6^{3-}/AH_2$	0.58	35 ± 1	-133 ± 3	15
$Fe(CN)_6^{3-}/AH^-$	8.0×10^{2}	18 ± 2	-127 ± 6	15
$Fe(CN)_6^{3-}/A^{2-}$	2×10^{7}	17.4 ± 0.4	-47 ± 1	13
$Fe(phen)_3^{3+}/AH_2$	2×10^{5}	21 ± 1	-73 ± 2	20
$Fe(phen)_3^{3+}/AH^-$	6×10^{8}	7.7 ± 0.3	-50 ± 1	20
		9 ± 2	-46 ± 7	7

detailed analysis of these data will require a separation of the precursor formation constant and the electron-transfer rate constant.

We now turn to a series of theoretical calculations for the outer-sphere oxidation of AH^- by $Co(NH_3)_4(H_2O)_2^{3+}$. The electron-transfer process consists of three steps [21]; formation of the precursor (ion-pair) complex, irreversible electron transfer, and dissociation of the successor complex to the reaction products. Of these steps electron transfer is rate determining since precursor formation and successor dissociation are diffusion controlled processes. For the reaction under consideration, this can be formulated as in eqn. (6).

$$Co(NH_3)_4(H_2O)_2^{3+}+AH^- \overset{K}{\rightleftharpoons} \{Co(NH_3)_4(H_2O)_2^{3+}\cdot AH^-\} \quad (6)$$
$$\xrightarrow{k} \{Co(NH_3)_4(H_2O)_2^{2+}\cdot AH^{\bullet}\} \rightleftharpoons Co(NH_3)_4(H_2O)_2^{2+}+AH^{\bullet}$$

The measured second-order rate constant is equal to the product of the ion-pair formation constant and the electron-transfer rate constant, i.e. $k_3=Kk$. The association constant K can be obtained using the extended Fuoss equation (eqn. (7)) for ion-pair

$$K=\frac{4}{3}\pi\sigma^3 N_A \times \exp(-W_{ij}/RT) \qquad (7)$$

formation [22], where W_{ij} is the electric work term required to bring the reactants i and j at the contact distance $\sigma\,(=r_i+r_j)$ in the precursor complex. The work term, arising from the Debye–Hückel interionic potential to allow for ionic strength effects [23], can be expressed as in eqn. (8), where Z_i and Z_j

$$W_{ij}=Z_iZ_je_0^2N_A/4\pi\epsilon_0\epsilon(1+x\sigma) \qquad (8)$$

are the charges on the ions, e_0 the electronic charge, ϵ_0 the permittivity of vacuum, ϵ the bulk dielectric constant and x the reciprocal Debye–Hückel length. For aqueous solutions at 25 °C, $\epsilon=78.5$ and $x=3.29\sqrt{\mu}$ nm^{-1} with μ in mol dm^{-3} [24].

Ionic radii of 0.34 nm for AH^- [25] and 0.30 nm for $Co(NH_3)_4(H_2O)_2^{3+}$* were used to calculate at 25 °C and $\mu=0.1$ M. $W_{12}=-5.0$ kJ mol^{-1} and $K=4.9$ M^{-1}. Therefore $k=k_3/K=7.0\times10^{-3}$ s^{-1} for the electron-transfer step.

The Marcus theory for electron-transfer reactions [26] can be used to evaluate the self-exchange rate constant k_{11} of the couple C^{3+}/C^{2+} ($C=Co(NH_3)_4(H_2O)_2$), that is at present not known. In fact, a form of the Marcus theory relates the rate constant of the cross-reaction $k_{12}(C^{3+}/AH^-)=k_3$ with the rate constants of the self-exchange reactions of the implied species $k_{11}(C^{3+}/C^{2+})$ and $k_{22}(AH^-/AH^\bullet)$. The so-called cross-relation, in terms of a modification of the Marcus theory [27] with inclusion of work terms, is expressed in eqn. (9), where W_{12} and W_{21} refer to the cross-reaction and represent the electric work required to bring reactants or products together at the separation distance in the activated complex, and W_{11} and W_{22} are the electric work terms involved in the self-exchange reactions.

$$\begin{aligned}
&k_{11}=(k_{12}/U)^2/k_{22}K_{12}f\\
&\ln U=(W_{11}+W_{22}-W_{12}-W_{21})/2RT \qquad (9)\\
&\ln f=\frac{[\ln K_{12}+(W_{12}-W_{21})/RT]^2}{4[\ln(k_{11}k_{22}/A_{11}A_{22})+(W_{11}+W_{22})/RT]}
\end{aligned}$$

The term A_{11} is related to the frequency of decomposition of the activated complex and to the thickness of the reaction layer; a typical value for the product $A_{11}A_{22}$ is 10^{25} M^{-2} s^{-2} [28, 29].

The equilibrium constant for the cross-reaction is calculated with eqn. (10) from the standard redox potentials of the complex involved. The self-exchange rate constant k_{11} was determined in the following way.

$$\ln K_{12}=nF(E_{11}^0-E_{22}^0)/RT \qquad (10)$$

For the reduction potential of the couples C^{3+}/C^{2+} and $AH^-/AH^\bullet$ the values $E_{11}^0=0.33$ V [30] and $E_{22}^0=0.71$ V [31, 32] were adopted. This led to an equilibrium constant of $K_{12}=3.77\times10^{-7}$. The self-exchange rate constant for the couple $AH^-/AH^\bullet$ was found to be $k_{22}=1.6\times10^5$ M^{-1} s^{-1} [15]. To evaluate the electric work terms with eqn. (8), the radius of 0.32 nm for C^{2+} and the above indicated for C^{3+} and AH^- were employed. This resulted in (kJ mol^{-1}) $W_{11}=10.4$, $W_{22}=0$, $W_{12}=-5.0$ and $W_{21}=0$. Then, with eqn. (9) and using an iteration procedure starting with $f=1$, the consistent values $f=0.24$ and $k_{11}=1.6\times10^{-4}$ M^{-1} s^{-1} for the self-exchange rate constant of C^{3+}/C^{2+} were attained after 3–4 iterations. This result for k_{11} lies between the experimental values obtained for the self-exchange rate constant of the couples $Co(H_2O)_6^{3+/2+}$ and $Co(NH_3)_6^{3+/2+}$ as shown in Table 3. The experimental k_{ex} values for other Co^{III}/Co^{II} self-exchange reactions are also included in Table 3. The remarkable increase in k_{ex} for the $Co(NH_3)_6^{3+/2+}$ and $Co(sep)^{3+/2+}$ systems has been ascribed to the tightness of ligand binding in both oxidation states and the strain in both ground states of the latter complex [41, 42]. These factors help the cage to reach the configuration required for electron transfer. Thus relaxation of strain which occurs on extension of the Co–N bond during reduction of Co(III) contributes significantly to the driving force of the process [43]. The introduction of π conjugated ligands (bpy, phen, terpy) on the Co center also causes a significant increase in k_{ex}, which has been ascribed to the fact that such complexes are much closer to the high–low spin crossover point [39]. In the absence of such effects in the presently investigated system, it is quite reasonable that k_{ex} should be very similar to that found for the en and dien systems. The increase of three orders of magnitude on going from $Co(NH_3)_6^{3+/2+}$ to $Co(NH_3)_4(H_2O)_2^{3+/2+}$ is probably due to an increase in reduction potential (driving force) which can be expected on the basis of the correlation found between $E_{1/2}$ and the frequency of the low-energy d–d transition of the Co(III) complexes (viz. 21 000 and 19 400 cm^{-1}, respectively) [43].

As we have seen, the ion-pair formation model of Fuoss and the Marcus theory for electron-transfer processes, expressed as the cross-relation of Marcus–Sutin, lead to reasonable values for the parameters k, K and k_{11} of the investigated reaction.

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*Estimated radius by comparison with similar Co^{3+}/Co^{2+} amine complexes.

TABLE 3. Self-exchange rate constants for various Co^{III}/Co^{II} complexes at 25 °C

Reaction	μ (M)	k_{ex} (M^{-1} s^{-1})	Reference
$Co(H_2O)_6^{3+} + Co(H_2O)_6^{2+}$	0.5	3	33
$Co(NH_3)_6^{3+} + Co(NH_3)_6^{2+}$	1.0	10^{-7}	34
$Co(NH_3)_4(H_2O)_2^{3+} + Co(NH_3)_4(H_2O)_2^{2+}$	0.1	1.6×10^{-4}	this work
$Co(en)_3^{3+} + Co(en)_3^{2+}$	1.0	8×10^{-5}	35
$Co(dien)_2^{3+} + Co(dien)_2^{2+}$	1.0	1.9×10^{-4}	36
$Co(phen)_3^{3+} + Co(phen)_3^{2+}$	1.0	9.5×10^{-2}	37
$Co(bpy)_3^{3+} + Co(bpy)_3^{2+}$	2.0	3.6×10^{-2}	38
$Co(sep)^{3+} + Co(sep)^{2+}$	0.2	5	39
$Co(terpy)_2^{3+} + Co(terpy)_2^{2+}$	1.0	1.7×10^2	40

Acknowledgements

The authors gratefully acknowledge financial support from CICYT (Madrid) and the Deutsche Forschungsgemeinschaft.

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