Complex Formation followed by Internal Electron Transfer: the Reaction of [Ethylenebis(biguanide)]silver(III) with Ascorbic Acid

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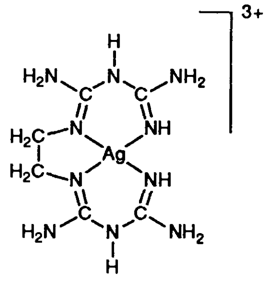
[Ethylenebis(biguanide)]silver(III) $[Ag(H_2L)]^{3+}$ **1** has been found to oxidize ascorbic acid (H_2asc) in acidic aqueous solution *via* an inner-sphere mechanism to give dehydroascorbic acid, silver(I) and free ethylenebis(biguanide). The 1 : 1 adduct formed as an intermediate between **1** and ascorbic acid decomposes after a non-separable two-electron-transfer reaction. The decomposition of the three complexes actually formed, co-ordinating different numbers of protons, occurs through two parallel pathways: one *via* decomposition of the unprotonated adduct $[Ag^{III}(H_2L)(H_2asc)]$, another *via* the deprotonated adduct $[Ag^{III}(H_2L)(Hasc)]$, while the protonated adduct $[Ag^{III}(H_3L)(H_2asc)]$ appears to be rather stable. The equilibrium constant for the adduct formation has been found to be 4.08 ± 0.45 dm^3 mol^{-1}, whereas the acid and base constants of this complex are 0.41 mol dm^{-3} and 2.86 dm^3 mol^{-1}, respectively. The two rate constants for the decomposition are 25 ± 3 and 220 ± 25 s^{-1} for $[Ag^{III}(H_2L)(H_2asc)]$ and $[Ag^{III}(H_2L)(Hasc)]$, respectively. The possibility of an outer-sphere mechanism is discussed.

The silver(III) complex **1** is one of the very few examples of a water-soluble silver(III) compound. This diamagnetic compound is well characterized[1–6] as square planar, low spin ($4d^8$) Ag^{3+} and extensively stabilized ($\log K \approx 52$)[6] by the strong-field acyclic ligand ethylenebis(biguanide). At ambient temperature this complex is reasonably stable in acidic media and may act as a two-electron acceptor. For example, studies with hydrogen peroxide[7] and alcohols[8] have shown the formation of an intermediate silver(III) complex prior to a simultaneous two-electron transfer. The reaction of hydrogen peroxide is strongly catalysed by Ag^+ which itself forms redox-labile complexes with the substrate. In case of formic acid[9] and hydrazine[10] Ag^0 is formed, which is further oxidized by the silver(III) complex. However, a thermodynamically stable metal complex is commonly a milder oxidant than the respective aquametal cation and may yield different reaction mechanisms.

Our earlier investigations on co-ordination intermediates[11–14] occurring in electron-transfer reactions encouraged us to probe into the mechanism of oxidation of ascorbic acid by this silver complex. Ascorbic acid is known to undergo outer-sphere one-electron-transfer reactions with both solvated metal ions[15] and complex ions[16–23] although it has been found that iron(III) and copper(II) ions seem to prefer inner-sphere oxidation paths.[24,25] Inner-sphere complex formation should be strongly pH-dependent. However, the lower limit of the investigated acidity range was determined by the decomposition of the silver complex itself which takes place at acidities lower than 0.02 mol dm^{-3}.[26]

Experimental

Materials.—The silver(III) complex was prepared according to the literature.[27,28] The orange-red crystals are diamagnetic and give a satisfactory elemental analysis (Found: C, 13.60; H, 3.10; Ag, 20.90; N, 34.30. Calc. for $C_6H_{16}AgN_{13}O_9$: C, 13.80; H, 3.10; Ag, 20.65; N, 34.85%). Ascorbic Acid (Loba, Austria), sodium perchlorate (Fluka, p.a.) and perchloric acid (Merck) were used as obtained. Solutions were prepared by accurately weighing the reagents and diluting them immediately before use with an aliquot of titrated 1.00 mol dm^{-3} $HClO_4$ and making up the volume with 1.00 mol dm^{-3} $NaClO_4$ solution to maintain the ionic strength. No special care to exclude light or oxygen was taken since preliminary results showed that they do not have any influence on the observed rate constants. Double distilled water was used throughout for preparing the solutions.



$[Ag(H_2L)]^{3+}$ **1**

Instruments.—Kinetic data were obtained by means of a Tracor Northern 1710 stopped-flow spectrophotometer, coupled with a Commodore PC 10 microcomputer. Since the apparatus is limited to wavelengths above 410 nm, the reaction was followed at 435 nm where a shoulder of the longest-wavelength UV band of complex **1** is found. The spectral performance of the spectrophotometric unit is only satisfactory at these low wavelengths. Rate constants and absorption data obtained are within the limits of ±7–10%. The temperature was kept constant within ±0.05 K with a Lauda cryostat.

Microanalytical data (C,H,N) were obtained with a Perkin Elmer model 240C elemental analyser. Silver was determined gravimetrically. Solution UV spectra were taken with an Hitachi UV-2000 spectrophotometer.

Traces of silver(I), which show catalytic activity in the oxidation of hydrogen peroxide, formic acid and hydrazine *via* complex formation, were prevented by precipitation of silver(0) due to reduction by the ascorbic acid. However, test-tube experiments suggest the absence of a marked catalytic effect suggesting that not enough silver(I) ($[Ag^{III}]_0 = 2.0 \times 10^{-4}$ mol dm^{-3}) was formed during the reaction to show a significant effect.

Table 1 Typical rate constants for the oxidation of ascorbic acid by complex **1** at I = 1.00 mol dm^{-3} ($NaClO_4$–$HClO_4$), 298.15 ± 0.05 K and $[Ag^{III}]_0$ = 2.0 × 10^{-4} mol dm^{-3}

$[H^+]$/mol dm^{-3}	$[asc]_T$/mol dm^{-3}	k_{obs}/s^{-1}
0.05	0.003	5.54
0.05	0.007	13.1
0.05	0.014	21.8
0.05	0.020	29.1
0.1	0.003	4.05
0.1	0.007	8.39
0.1	0.010	12.7
0.1	0.020	17.0
0.1	0.030	23.9
0.15	0.007	6.40
0.15	0.014	12.1
0.15	0.020	16.5
0.2	0.003	2.18
0.25	0.007	6.98
0.25	0.014	9.07
0.25	0.020	11.8
0.3	0.003	1.98
0.3	0.007	4.80
0.3	0.010	7.04
0.3	0.020	12.7
0.3	0.030	14.7
0.35	0.007	4.77
0.35	0.050	20.4
0.5	0.003	3.22
0.5	0.007	3.84
0.5	0.001	4.37
0.5	0.020	9.72
0.5	0.030	12.2
0.7	0.010	4.85
0.7	0.020	7.81
0.7	0.030	10.95
0.7	0.050	13.9
0.7	0.070	17.0
0.7	0.100	23.1
0.9	0.010	4.20
0.9	0.030	9.37
0.9	0.050	12.6
0.9	0.070	15.3
0.9	0.100	18.4

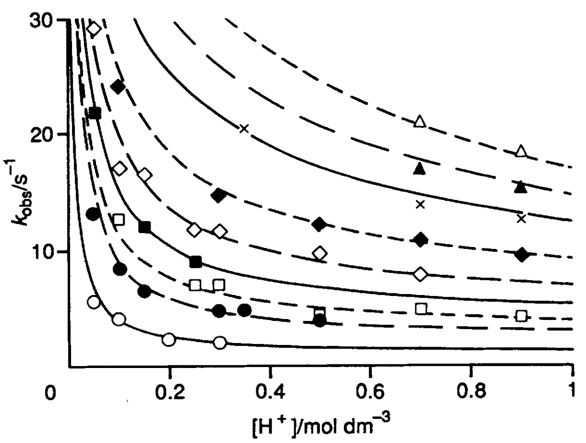


Fig. 1 Dependence of k_{obs} on $[H^+]$ at $[Ag^{III}]_0$ = 2.0 × 10^{-4} mol dm^3, I = 1.0 mol dm^{-3} $Na(ClO_4)$ and 298.15 K. Lines are drawn according to equation (16) using the values given in the text and refer to the experimental points. $[asc]_T$ = 0.003 (○), 0.007 (●), 0.01 (□), 0.014 (■), 0.02 (◇), 0.03 (◆), 0.05 (×), 0.07 (▲) and 0.1 mol dm^{-3} (△)

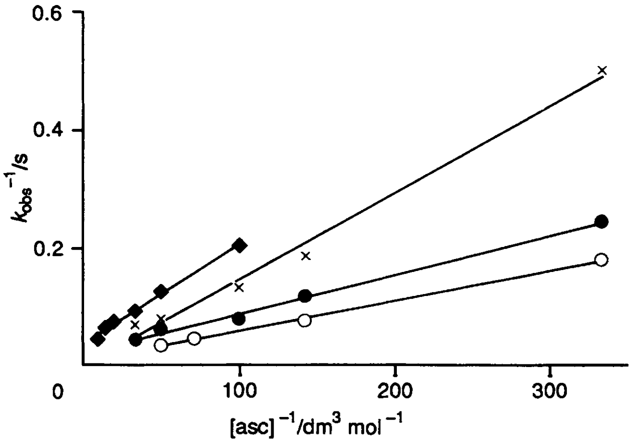


Fig. 2 A Lineweaver–Burke plot (*viz.* $1/k_{obs}$ *vs.* $1/[asc]_T$) of the rate of disappearance of complex **1**. Conditions as in Fig. 1. $[H^+]$ = 0.05 (○), 0.1 (●), 0.3 (×) and 0.7 mol dm^{-3} (◆)

Results

Stoichiometry.—To a solution of ascorbic acid H_2asc (1 mmol dm^{-3}) a slight excess of silver(III) complex was added. The remaining Ag^{III} was estimated spectrophotometrically at 380 nm. The result confirms a 1 : 1 stoichiometry as in equation (1) (dha = dehydroascorbic acid).

$$[Ag^{III}(H_2L)]^{3+} + H_2asc \longrightarrow Ag^+ + H_2L + dha + 2\,H^+ \qquad (1)$$

The Kinetics at 298 K.—In the presence of large amount of substrate (ascorbic acid) the disappearance of the complex follows strictly first-order kinetics for at least three to four half-lives, as in equation (2). The rate constant was independent of

$$-d[Ag^{III}]_T/dt = k_{obs}[Ag^{III}]_T \qquad (2)$$

the initial silver(III) concentration. Typical values for the observed rate constants are given in Table 1. It can be seen that the reaction is accelerated by increasing $[asc]_T$, but is retarded by increasing $[H^+]$. The dependence of k_{obs} on $[H^+]$ is shown in Fig. 1.

The dependence of k_{obs} on $[asc]_T$ shows a saturation effect and indeed a plot of $1/k_{obs}$ *vs.* $1/[asc]_T$ is linear with regression coefficients greater than 0.99, as can be seen in Fig. 2, indicating complex formation prior to electron transfer. However, no spectral changes occurred in the visible range. The above observations suggest that at constant $[H^+]$ the rate obeys the relationship (3) which gives after comparison with (2), as indicated, (4). The reciprocal slopes are linearly dependent on

$$\frac{d[Ag^{III}]_T}{dt} = \frac{A[asc]_T}{B + [asc]_T}[Ag^{III}]_T \qquad (3)$$

$$1/k_{obs} = \text{slope} \times [asc]_T^{-1} + \text{intercept} \qquad (4)$$

the reciprocal proton concentration whereas the intercepts are linearly dependent on the acidity, as can be seen in Figs. 3 and 4, respectively. This can be expressed as equations (5) and (6).

$$1/\text{slope} = a[H^+]^{-1} + b \qquad (5)$$

$$\text{intercept} = c[H^+] + d \qquad (6)$$

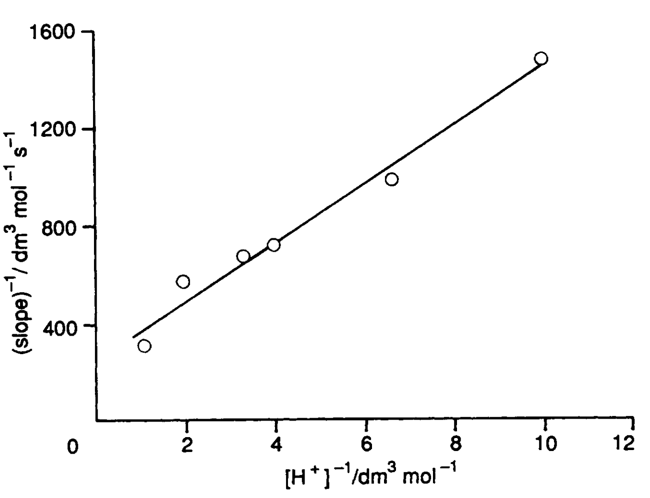


Fig. 3 Dependence of reciprocal slopes from equation (4) on $1/[H^+]$

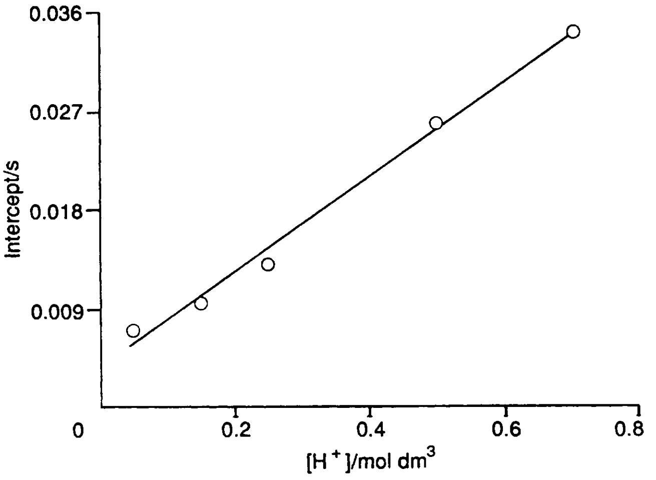


Fig. 4 Dependence of intercepts from equation (4) on $[H^+]$

Table 2 Influence of the ionic strength I on k_{obs} at 298.15 K, $[H^+] = 0.5$, $[Ag^{III}]_T = 2 \times 10^{-4}$ and $[asc]_T = 7 \times 10^{-3}$ mol dm^{-3}

I/mol dm^{-3}	k_{obs}/s^{-1}
0.5	6.85
1	3.84
1.5	2.71
2	1.92
3	1.44

Inserting (5) and (6) into (4) leads after some rearrangement and redefinition of the parameters to equation (7). The final

$$k_{obs} = \frac{(\alpha + \beta[H^+])[asc]_T}{[H^+] + (\gamma[H^+]^2 + \delta[H^+] + \varepsilon)[asc]_T} \qquad (7)$$

parameters α, β, γ, δ and ε were obtained by a least-squares fit, using the parameters from the straight-line relationships as starting parameters, yielding 365 ± 50 s^{-1}, 102 ± 11 dm^3 mol^{-1} s^{-1}, 11.7 ± 3.4 dm^6 mol^{-2}, 4.08 ± 0.45 dm^3 mol^{-1} and 1.66 ± 0.49, respectively.

The influence of the ionic strength is quite marked: halving the ionic strength almost doubles k_{obs}. The rate constants found are given in Table 2. The k_{obs} is linearly related to $I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})$ ($r = 0.9983$) indicating complex formation prior to decomposition,[29] but the slope equals -3.13, the product of the charges of an outer-sphere mechanism (see below). It is also linearly related to $I^{\frac{1}{2}}$ itself ($r = 0.9988$), except at very high ionic strength, but the slope of -0.77 is totally unexpected for our reactions. Therefore no information about the actual charges of the reacting species can be gained.

Discussion

The simplest mechanism that satisfies the rate equation (7) is given in equations (8)–(12). The adduct can either associate or

$$[Ag^{III}(H_2L)] + H_2asc \underset{}{\overset{K_c}{\rightleftharpoons}} [Ag^{III}(H_2L)(H_2asc)] \qquad (8)$$

$$[Ag^{III}(H_2L)(H_2asc)] \overset{K_a}{\rightleftharpoons} [Ag^{III}(H_2L)(Hasc)] + H^+ \qquad (9)$$

$$[Ag^{III}(H_2L)(H_2asc)] + H^+ \overset{K_b}{\rightleftharpoons} [Ag^{III}(H_3L)(H_2asc)] \qquad (10)$$

$$[Ag^{III}(H_2L)(H_2asc)] \xrightarrow{k_1} \text{products} \qquad (11)$$

$$[Ag^{III}(H_2L)(Hasc)] \xrightarrow{k_2} \text{products} \qquad (12)$$

dissociate one proton. Both the unprotonated and the deprotonated forms can react simultaneously to give the products. Under these conditions the total silver(III) concentration is given by equation (13), since the pK_a of the silver(III) complex

$$[Ag^{III}]_T = [Ag^{III}(H_2L)] + [Ag^{III}(H_2L)(H_2asc)] + [Ag^{III}(H_2L)(Hasc)] + [Ag^{III}(H_3L)(H_2asc)] \qquad (13)$$

(3.8)[9] rules out the presence of the deprotonated silver(III) complex at these high acidities.

Using equations (8)–(10) and the fact that ascorbic acid is present in great excess (and due to its pK_a of 4.17[30] exclusively in the undissociated form), (13) becomes (14). The rate is given by equation (15) which when combined with (14) gives after comparison with (2) equation (16), which is of the desired form.

$$[Ag^{III}]_T = [Ag^{III}(H_2L)]\{1 + (K_c + K_cK_a[H^+]^{-1} + K_cK_b[H^+])[asc]_T\} \qquad (14)$$

$$-d[Ag^{III}]_T/dt = k_1[Ag^{III}(H_2L)(H_2asc)] + k_2[Ag^{III}(H_2L)(Hasc)] = k_1K_c[asc]_T[Ag^{III}(H_2L)] + k_2K_cK_a[asc]_T[Ag^{III}(H_2L)][H^+]^{-1} \qquad (15)$$

$$k_{obs} = (k_1K_c[H^+] + k_2K_cK_a)[asc]_T/\{[H^+] + (K_cK_b[H^+]^2 + K_c[H^+] + K_cK_a)[asc]_T\} \qquad (16)$$

Through comparison of equation (16) with (7), the values of the equilibrium and rate constants can be extracted: $K_a = 0.41 \pm 0.05$ mol dm^{-3}, $K_b = 2.86 \pm 2.86$ dm^3 mol^{-1}, $K_c = 4.08 \pm 0.45$ dm^3 mol^{-1}; $k_1 = 25 \pm 3$ s^{-1}, $k_2 = 220 \pm 25$ s^{-1}. The rate constants for the electron transfer are different because of different charges and because the adduct is a strong acid (pK_a = 0.39), suggesting that major electronic rearrangement takes place.

In the light of the results obtained for the oxidation of 3,4-dihydroxyphenylalanine (dopa) and cysteine with iron(III) it is quite surprising, that there exists a 'stable' protonated adduct of the silver(III) complex with ascorbic acid, *i.e.* $[Ag^{III}(H_3L)(H_2asc)]$. We explain this as follows. Since the ethylenebis(biguanide) ligand is acyclic, it may be protonated and leave the co-ordination sphere of silver. At this co-ordination site the ambidentate ascorbic acid may now attack with its second hydroxy group and form a chelate. This adduct reacts only slowly to give the electron-transfer products, compared with the other adducts, which are in equilibrium with this bichelate.

However, as one of the referees has pointed out, the outer-sphere oxidation of ascorbic acid by $[Ag(H_2L)]^{3+}$ cannot completely be ruled out. In this case, the reaction scheme would consist of equations (8)–(10) and (17) and (18). The small

$$[Ag^{III}(H_2L)] + H_2asc \xrightarrow{k_1^{os}} \text{products} \tag{17}$$

$$[Ag^{III}(H_2L)] + Hasc^- \xrightarrow{k_2^{os}} \text{products} \tag{18}$$

concentration of the ascorbate monoanion can be compensated by an enhanced reactivity, but the adducts are to be redox inactive. This scheme leads to a rate equation in complete analogy to (16), the numerator being $(k_1^{os}[H^+] + k_2^{os}K_a^{H_2asc})$-$[asc]_T$. This yields values for k_1^{os} and k_2^{os} of 102 and 3.26×10^6 dm^3 mol^{-1} s^{-1}, respectively, using $K_a^{H_2asc} = 1.12 \times 10^{-4}$ dm^3 mol^{-1} from Kimura *et al.*[18] The ratio k_2^{os}/k_1^{os} is high (3.2×10^4:1), but of the same order of magnitude as for the oxidation by nickel(III) macrocycles.[20] The ionic strength dependence does not give conclusive hints. However, simultaneous two-electron transfer in outer-sphere mechanisms is improbable and silver(II) species were not detected in previous studies.[7–10] We therefore favour the inner-sphere mechanism.

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