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Kinetics of oxidation of ascorbic acid and 1,4-dihydroxybenzene by semiquinone radical bound to ruthenium(II)

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In 40% (v/v) MeOH–H_2O media, containing [H^+] (0.001–0.038 mol dm^{-3}), the semiquinone (sq) radical, bound to Ru(II) in $[Ru(bpy)_2(sq)]^+$ **1**, oxidises ascorbic acid (H_2A) to dehydroascorbic acid (A), and 1,4-dihydroxybenzene (H_2Q) to *p*-benzoquinone (Q); **1** is itself reduced to $[Ru(bpy)_2(Hcat)]^+$ **2**H. The reactions are centred at sq not Ru(II). The sq/cat couple in **1** is reversible and its $E_{1/2}$ increases with increasing [H^+]; rate of chemical reduction of **1** to **2**H increases in parallel. Rate increases also with increasing mole percent of D_2O in the solvent suggesting a preliminary protonation equilibrium producing **1**H, in which a H^+ binds to the π-electron cloud of Ru(II)-bound sq. Under the experimental conditions, the kinetically significant species are **1**H, H_2Q, H_2A and HA^-. The kinetic activity of HA^- ion is only ≈200 times more than that of H_2A. This testifies against a purely outer-sphere mechanism and suggests significant electronic interaction between the redox partners. Increased percentage of MeOH in the solvent decreases λ_{max} for the LMCT band; reaction rate for ascorbic acid decreases in parallel.

The electron and proton transfer on the acceptor side of the primary photochemical reaction centre in bacterial photosynthesis involves the formation of a semiquinone as the first step in the formation of ubiquinol.[1] The semiquinone is a stable state, which remains attached to the protein pocket until the second reduction of quinol. Semiquinone related ligands attached to transition metal ions represent models for the primary photochemical donor–acceptor centre in bacterial photosynthesis and for the biological transport of iron for some enzymes.[2] They may also serve as models for ascorbate oxidase.[3] Many groups have, therefore, examined the structural characterisation, electrochemistry, spectroscopy, magnetic properties and electronic structure of transition metal complexes involving non-innocent semiquinone related ligands.[4–6] The members of the catechol–semiquinone redox series involving bis-(bipyridine)ruthenium(II/III) complexes appear particularly well characterised structurally and with respect to the metal and ligand oxidation states. However, there appears no report on the kinetics of redox reactions of coordinated semiquinone, in spite of their relevance in understanding the photochemical reaction centre.

The ESR spectra[7] of the complex $[Ru(bpy)_2(sq)]^+$ (**1**, bpy is 2,2′-bipyridine, sq is semiquinone radical) show that the unpaired electron is located primarily on the semiquinone ligand and therefore Ru(II)sq is the proper description of **1**. The redox changes in the semiquinone ligand occur at potentials well separated from those centred on ruthenium. The complex **1** therefore affords a nice chance to study the kinetics of redox changes in coordinated semiquinone without complications due to simultaneous redox changes at the metal centre.

Experimental

Materials

All solutions were prepared in double distilled, freshly boiled water. L-Ascorbic acid (H_2A, G.R., E. Merck) was stored in the dark. 1,4-Dihydroxybenzene (H_2Q, quinol, A.R., B.D.H) was recrystallised from ethanol. All reported data are at 25.0 °C, *I* 0.10 mol dm^{-3} maintained with $NaClO_4$. Crystals of $NaClO_4 \cdot H_2O$ were made by neutralising a 35% $HClO_4$ solution (made by dilution of 70% $HClO_4$, G.R., E. Merck) with solid $NaHCO_3$ (G.R., E. Merck) followed by evaporation to incipient crystallisation. All other reagents used were of reagent grade.

Microanalyses (C, H, N) were performed using a Perkin-Elmer 4100 elemental analyzer. IR spectra were recorded as KBr pellets using Perkin-Elmer Spectra GX 2000 spectrometer. Absorbance and electronic spectra were recorded with a Shimadzu (1601 PC) spectrophotometer using 1.00 cm quartz cells. Fast-atom bombardment measurement was carried out on a VG-ZAB instrument using 3-nitrobenzyl alcohol as matrix. Electrochemical experiments were performed using a CH 660A (USA) electrochemical instrument; a conventional three-electrode cell assembly was used. A saturated Ag/AgCl reference electrode and platinum working electrode were used.

$[Ru(bpy)_2(sq)]X$ ($X = PF_6^-$ or Cl^-)

The hexafluorophosphate and chloride salts of $[Ru(bpy)_2(sq)]^+$, **1** were prepared by known methods[8] with some modifications. $[Ru(bpy)_2Cl_2] \cdot 2H_2O$ (200 mg, 0.385 mmol), 1,2-dihydroxybenzene (43 mg, 0.385 mmol) and KOH (44 mg, 0.78 mmol) were refluxed in ethanol (50 cm^3) for 6 h under a dinitrogen blanket. To this resulting mixture $FcPF_6$ (0.127 mg, 0.385 mmol) was added and stirred at room temperature for 1/2 h. The volume was reduced to ≈5 cm^3 and an aqueous KPF_6 solution was added. The precipitate was filtered off, air dried and purified by column chromatography using a silica column and CH_3CN–water (98 : 2, v/v) solution of NH_4PF_6 as the eluent. The first major fraction was collected and concentrated *in vacuo* (≈5 cm^3). Excess NH_4PF_6 was removed by solvent extraction in the aqueous layer. The desired compound was collected in the CH_2Cl_2 layer and dried *in vacuo*. Yield: 155 mg, 66%. Elemental analyses: Calc. for $C_{26}H_{21}N_4O_2PF_6Ru$: C, 46.82; H, 3.15; N, 8.14. Found: C, 46.0; H, 3.18; N, 8.10%. FAB MS: *m/z* 664 (M^+, ≈5%), 519 ($M^+ - PF_6$, >25%). IR (KBr, cm^{-1}): 1610, 1580

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(C=C and C=N), 1444 (semiquinone streching), 835 (PF_6^-). For the corresponding chloride salt, the crude reaction mixture was evaporated to dryness and chromatographed on an alumina column (grade III) with acetonitrile–toluene (60 : 40, v/v) as eluent. The second major fraction was collected and found to be the desired product. Yield: 35%. Elemental analyses: Calc. for $C_{26}H_{21}N_4O_2ClRu$: C, 56.01; H, 3.77; N, 10.05. Found: C, 56.0; H, 3.80; N, 10.0%. FAB MS: *m/z* 555 (M^+, ≈10%), 519 ($M^+ - Cl$, ≈35%). IR (KBr, cm^{-1}): 1608, 1578 (C=C and C=N), 1448 (semiquinone stretching). The λ_{max} for the characteristic MLCT band of the complex in MeOH–H_2O mixed solvents of different solvent composition are given below:

%(v/v) MeOH	:	40	60	80	100
λ_{max}/nm	:	933.5	928.5	920.0	907.5
$10^{-3}\varepsilon$/dm^3 mol^{-1} cm^{-1}	:	2.6	2.0	1.94	1.9

Kinetics

Most of the kinetics were studied in 40% (v/v) MeOH–H_2O using the MeOH-soluble PF_6^- salt of **1**. The Cl^- salt was used for reactions in H_2O and H_2O–D_2O media. The Cl^- salt was otherwise avoided due to its hygroscopic nature.

Kinetics were monitored at 933.5 nm, the λ_{max} of complex **1** in 40% (v/v) MeOH–H_2O media. At this wavelength, the reducing agents and their oxidation products do not absorb, while absorbance of **2**H, *i.e.*, the reduction product of **1**, is very small. The kinetics were monitored *in situ* in the thermostatted cell housing (CPS-240A), following the decrease in absorbance with time. For ascorbic acid, kinetics were measured both under the second order and the first order conditions. Reactions of quinol were followed only under the first order conditions. For second order conditions, [**1**] : [R] = 1 : 1 was maintained. Under the first order conditions, an excess of reducing agent over complex **1** was used. All the reactions were carried out in the presence of a large excess of $HClO_4$ in the range 0.001 to 0.038 mol dm^{-3}. For a reaction 2A + B = product, under first order conditions:

$$\frac{1}{[\mathbf{1}]}\left(\frac{-\mathrm{d}[\mathbf{1}]}{\mathrm{d}t}\right) = 2k_o \qquad (1)$$

The integrated form of eqn. (1) in terms of absorbance is eqn.(2). The absorbance (A_t)–time (t) data for the reactions under the first order conditions were fitted into eqn. (2) using the nonlinear least-squares regression routine of the program package ORIGIN 4.0.[9] The values for k_0 and associated errors were thus determined.

$$\ln(A_t - A_\infty) = -2k_0t + \ln(A_0 - A_\infty) \qquad (2)$$

The A_t–t data, collected under second order conditions ([**1**] : [R] = 1 : 1) were fitted to a typical second order reaction for which,

$$-\mathrm{d}[\mathbf{1}]/\mathrm{d}t = 2k_A[\mathbf{1}][\mathrm{R}] \qquad (3)$$

Comparing eqns. (1) and (3), one gets

$$k_o = k_A[\mathrm{R}] \qquad (4)$$

For [**1**] : [R] = 1 : 1, the integrated form[10] for eqn. (3) is eqn. (5)

$$\log\left(\frac{a_o - x}{a_o - 2x}\right) = \left(\frac{2k_Aa_o}{2.303}\right)_t \qquad (5)$$

where a_o is the initial concentration of both **1** and R. The amount of complex **1** consumed at any time t is $2x$ while that for R is x.

In terms of absorbance, eqn. (5) becomes,

$$\log\left[\frac{A_o + A_t - 2A_\infty}{2(A_t - A_\infty)}\right] = \left[\frac{2k_A(A_o - A_\infty)}{2.303(\varepsilon_A - \varepsilon_B)}\right]_t \qquad (6)$$

k_A and associated errors were evaluated by least-squares analysis (ORIGIN 4.0) of the LHS of eqn. (6) against time data and using known values for A_o, A_∞, ε_A and ε_B.

Reaction stoichiometry was determined by spectrophotometric titration (λ, 933.5 nm) of a solution of complex **1** with different amounts of reducing agent in the presence of excess $HClO_4$ in 40% (v/v) MeOH–H_2O media.

Results and discussion

Reduction product of 1

The complex **1** is stable in acidic MeOH–H_2O media and its spectrum [Fig. 1A] did not change for at least 24 hours. However, the NIR absorption band gradually loses its intensity when H_2A or H_2Q is added. The reducing agents slightly affect the other spectral regions. A family of spectra changing with time after the addition of H_2A is shown in Fig. 1. The final spectrum [Fig. 1G] closely resembles those reported[7] for [Ru(bpy)$_2$(Hcat)]$^+$ **2**H, the singly protonated form of the catechol complex [Ru(bpy)$_2$(cat)]$^+$, (**2**, cat is the catecholate form of the ligand). **2**H lacks the LLCT bands characteristic of **2** and can be easily distinguished from **2**. Spectral changes similar to those in Fig. 1 are observed with H_2Q and we conclude that in $HClO_4$ media both ascorbic acid and 1,4-dihydroxybenzene reduce **1** to **2**H under the present experimental conditions. Neither **1** nor **2**H aquates or decomposes during the reactions studied here.

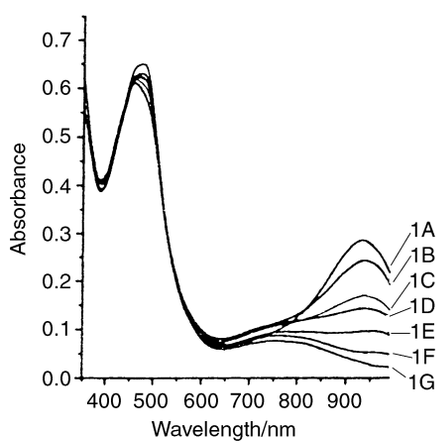


Fig. 1 Spectra of 0.05 mmol dm^{-3} solutions of **1** (A) and its mixture with 0.10 mmol dm^{-3} ascorbic acid; immediately after mixing (B) and after 2 (C), 4 (D), 7 (E), 12 (F) and 20 (G) min; [H^+] 0.01 M, *I* 0.10 M.

The break point in the absorbance *versus* total concentration of a reducing agent, T_x (X = Q for H_2Q and A for ascorbic acid) was observed at [**1**] : T_x = 2 : 1 for both H_2A and H_2Q. Fig. 2 is a typical example recorded with H_2Q. The most likely oxidation products of H_2A and H_2Q are therefore dehydroascorbic acid (A) and 1,4-benzoquinone (Q) respectively.

Kinetics and reaction scheme

With excess [R], A_t–t data followed first order kinetics in [**1**] and yielded an excellent fit to eqn. (2) for more than three half-lives (see Fig. 3). A_t–t data collected under second order conditions ([**1**] = [R]) yielded equally an good fit to the second order eqn. (6) (see Fig. 4). The k_A and k_o values have been collected in Tables 1 and 2 respectively.

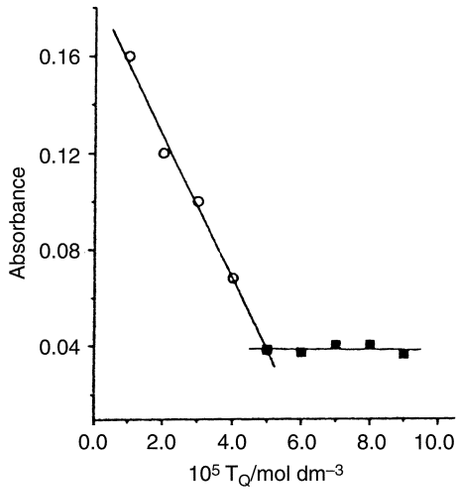


Fig. 2 Stoichiometry of the reaction between **1** and 1,4-dihydroxybenzene. [**1**] 0.10 mmol dm^{-3}; [$HClO_4$] 10 mmol dm^{-3}; T 25.0 °C; I 0.10 mol dm^{-3} ($NaClO_4$); 40% (v/v) MeOH–H_2O media. λ 933.5 nm.

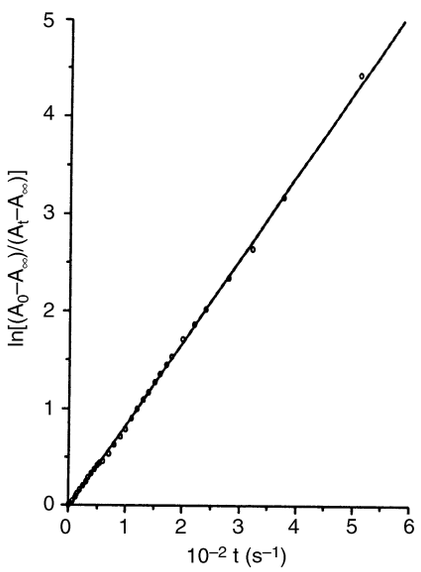


Fig. 3 A typical first order plot for the oxidation of ascorbic acid. [**1**] 0.10 mmol dm^{-3}; T_A 0.50 mmol dm^{-3}; [$HClO_4$] 2.0 mmol dm^{-3}; T 25.0 °C; I 0.10 mol dm^{-3} ($NaClO_4$); 40% (v/v) MeOH–H_2O media.

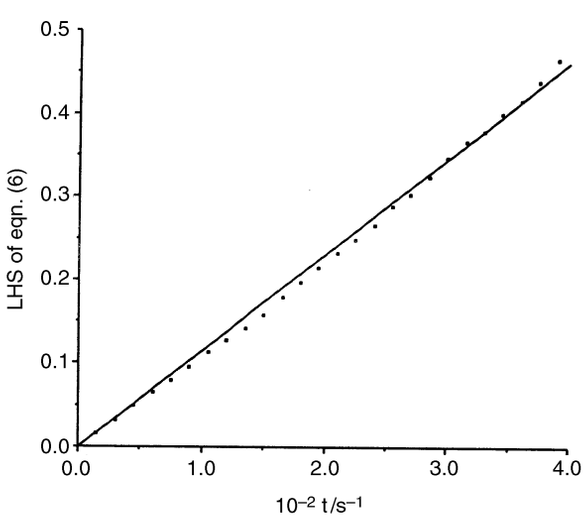


Fig. 4 A typical second order plot for the oxidation of ascorbic acid. [**1**] 0.1 mmol dm^{-3}; T_A 0.10 mmol dm^{-3}; [$HClO_4$] 20.0 mmol dm^{-3}, T 25.0 °C; I 0.10 mol dm^{-3} ($NaClO_4$); 40% (v/v) MeOH–H_2O media.

Table 1 Second order rate constants,[a] k_A, for the reduction of **1** to **2**H by ascorbic acid

[$HClO_4$]/mmol dm^{-3}	k_A/dm^3 mol^{-1} s^{-1}
1.0	9
2.0	9.4
5.0	9.2
10	9
15	10.4
20	12.3
25	13.8
30	17.5
34	19.5
38	21.2

[a] [complex] 0.10 mmol dm^{-3}; T_A 0.10 mmol dm^{-3}; T 25.0 °C; I 0.10 mol dm^{-3} ($NaClO_4$); 40% (v/v) MeOH–H_2O media. Error in k_A, 3–5%.

Table 2 First order rate constants,[a] k_o, for the reduction of **1** to **2**H

T_X/mmol dm^{-3}	[H^+]/mmol dm^{-3}	$10^4 k_o$/s^{-1}
(X = A)		
0.40	10	44
0.50	1.0	30
	2.0	40
	5.0	49
	10	50
	15	62
	20	77.5
	25	80
	30	84
0.60	10	57.5
0.70		61
0.80		65
X = Q		
1.00	3.0	0.29
	5.0	0.415
	10	0.80
	15	1.5
	20	1.65
	25	2.08
	30	2.5
	34	2.8
	38	3.15
2.0	15	2.0
3.0		2.3
5.0		2.5
10		2.5
15		2.9
20		2.8
25		2.9
30		2.9
		3.0[b]
		2.95[c]

[a] [complex] 0.10 mmol dm^{-3}; T 25.0 °C; I 0.10 mol dm^{-3} ($NaClO_4$); 40% (v/v) MeOH–H_2O media. [b] Repeated with minimum stray light. [c] Repeated after purging dinitrogen, error in k_o, 2–5%.

Some reactions were carried out avoiding ambient light as far as possible by using volumetric flasks coated on the outside with a black paint and by bringing the spectrophotometer cell to the light path only at the instance of absorbance measurements during kinetic studies. These measures minimised stray light but did not change the reaction rate significantly. The reaction rate also changed little when the medium was purged with purified dinitrogen.

Rates of oxidation of hydroquinone and ascorbic acid by transition metal complexes generally increase if [H^+] is decreased.[11a,b] This is because the conjugate base forms, HA^- and HQ^- of the reducing agents are kinetically much more active than their parent acids. Additionally, for metal cations as oxidant, the hydrolysed form of the cation dominates at

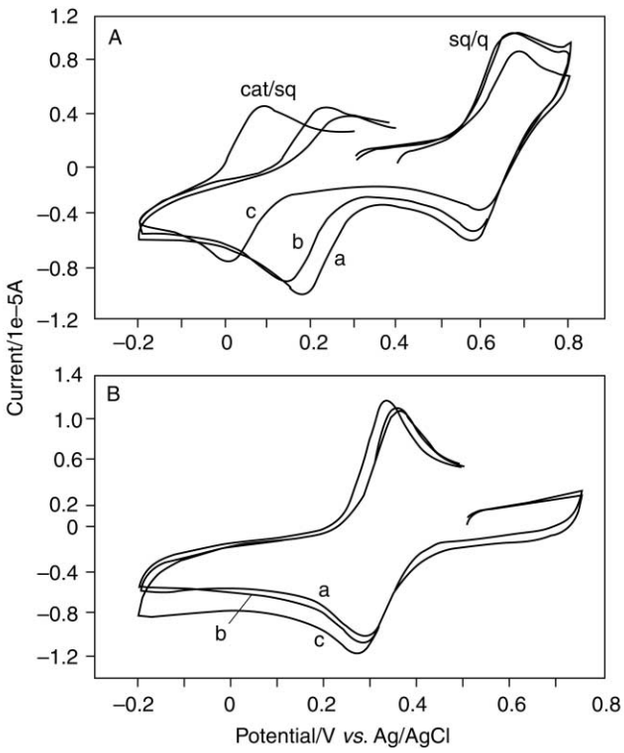


Fig. 5 (A) Cyclic voltammogram of **1** in 40% (v/v) MeOH–H_2O media with (a) 0.01 mol dm^{-3}, (b) 0.003 mol dm^{-3} and (c) 0.001 mol dm^{-3} HCl; (B) Cyclic voltammogramm of ferrocene in 40% (v/v) MeOH–H_2O media with (a) 0.0 mol dm^{-3}, (b) 0.003 mol dm^{-3} and (c) 0.01 mol dm^{-3} HCl. Scan rate 200 mV s^{-1}.

reduced [H^+] and Pellizzetti[12] noticed that hydrolysed metal cations are kinetically superior oxidants when the reductant contains a transferable hydrogen atom, as in the cases of ascorbic acid and quinol. In the present study, no indication could be obtained for increased rate on reduction of [H^+]. Rather, the rate is enhanced at higher [H^+]. Increased [H^+] also assists the electroreduction of the sq radical. The sq/cat couple of complex **1** is completely reversible. Its $E_{1/2}$ value in 40% (v/v) MeOH–H_2O is 0.281 V (NHE) at pH 4.6. The potential increases with decreasing pH (Fig. 5A) and the $E_{1/2}$ *versus* pH graph is a straight line (Fig. 6) with a slope (-0.061 ± 0.002) very close to the theoretical value, -0.059, expected when one proton per mole of **1** is involved in the electron transfer reaction at 25 °C. The potential shift with [H^+] is not due to any change in junction potential. We noted that the potential for the reversible ferrocene/ferrocenium couple (Fig. 5B) and sq/q couple of **1** (Fig. 5A) did not change with change in [H^+].

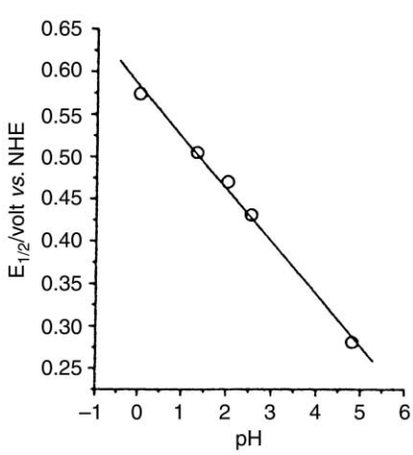


Fig. 6 Plot of $E_{1/2}$ (NHE) for the sq/cat couple *versus* pH.

The observed dependence of rate and $E_{1/2}$ on [H^+] indicates either a preliminary protonation equilibrium or a simultaneous transfer of an electron and a proton in the rate-determining step. We studied some kinetics in a H_2O–D_2O mixture to distinguish between the two possibilities. It is known that the rate increases significantly with increased percentage of D_2O in the H_2O–D_2O mixture if a preliminary acid–base equilibrium step exists,[13] but for electroprotic reactions, the rate decreases.[14–17] Such a kinetic isotope effect $k_{H_2O}/k_{D_2O} \geq 31.1$ has been reported recently by Meyer and co-workers.[18]

In contrast the rate in H_2O is closely similar to the rate in D_2O for a simple electron transfer reaction. Fig. 7 shows that in

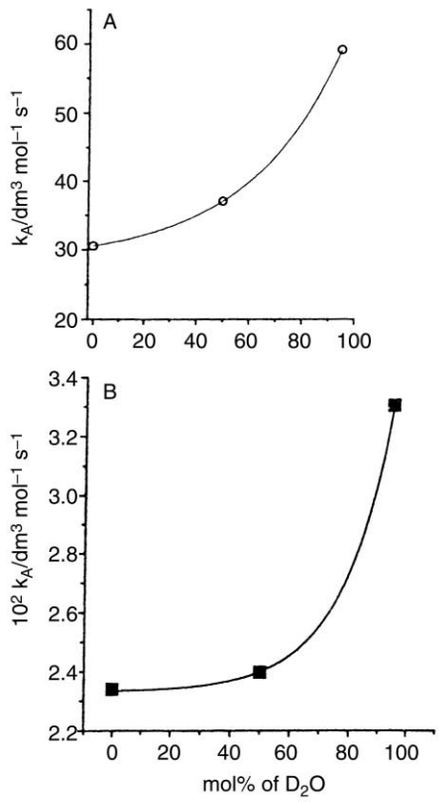
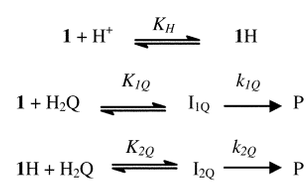


Fig. 7 k_A *versus* mol% of D_2O in a D_2O–H_2O mixture. [H^+] 1.0 mmol dm^{-3} (A) and 30 mmol dm^{-3} (B). [**1**] 0.10 mmol dm^{-3}; T_A 0.05 mmol dm^{-3}; T 25.0 °C; I 0.10 mol dm^{-3} ($NaClO_4$); 40% (v/v) MeOH–H_2O media.

the present reactions of ascorbic acid the rate increases almost exponentially with increasing mol% of D_2O. The observation strongly suggests a preliminary protonation equilibrium (Scheme 1) and refutes both a rate-determining electroprotic reaction and a simple electron transfer reaction.



Scheme 1

I_{1Q} and I_{2Q} represent preliminary adducts formed by two forms of the complex. The pK_a for H_2Q is 8.0[11a] and we assume H_2Q to be the exclusive form of 1,4-dihydroxybenzene in the experimental range of [H^+].

The scheme leads to

$$\frac{1}{[\mathbf{1}]}\left(-\frac{\mathrm{d}[\mathbf{1}]}{\mathrm{d}t}\right) = 2k_0 = \frac{2(k_{1Q}K_{1Q} + k_{2Q}K_{2Q}K_H[H^+])T_Q}{1 + K_H[H^+] + K_{1Q}T_Q + K_{2Q}K_H[H^+]T_Q} \quad (7)$$

Where T_Q ($\cong [H_2Q]$) is the total concentration of hydroquinone and the stoichiometric factor is 2.

Provided that, $(1 + K_{1Q}T_Q) \gg \{K_H[H^+](1 + K_{2Q}T_Q)\}$ and that $k_{1Q}K_{1Q} \ll k_{2Q}K_{2Q}K_H[H^+]$, the expression reduces to:

$$\frac{1}{[\mathbf{1}]}\left(-\frac{d[\mathbf{1}]}{dt}\right) = 2k_0 = \frac{2k_{2Q}K_{2Q}K_H[H^+]T_Q}{1 + K_{1Q}T_Q} \quad (8)$$

The k_0 values for different T_Q at fixed $[H^+]$ fit satisfactorily to eqn. (6) (see Fig. 8) and yields $K_{1Q} = (1026 \pm 44)$ mol^{-1} dm^3 and

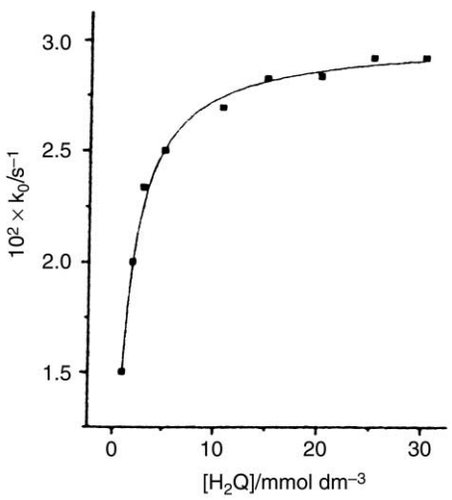
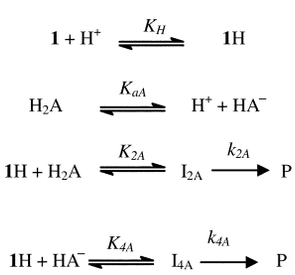


Fig. 8 k_o *versus* T_Q plot; [**1**] 0.10 mmol dm^{-3}, [$HClO_4$] 15 mmol dm^{-3}; T 25.0 °C; I 0.10 mol dm^{-3} ($NaClO_4$); 40% (v/v) MeOH–H_2O media.

$k_{2Q}K_{2Q}K_H = (20.5 \pm 1.2)$ mol^{-2} dm^6 s^{-1}. Also, as expected from eqn. (8), the k_0 *versus* $[H^+]$ plot (T_Q = 1.0 mmol dm^{-3}) is a straight line (r = 0.97) with negligible intercept. The assumptions leading to eqn. (8) thus appear justified. The slope of the line [$(9.23 \pm 1.0) \times 10^{-3}$ dm^3 mol^{-1} s^{-1}] yields $k_{2Q}K_{2Q}K_H = (18.7 \pm 1.0)$ mol^{-2} dm^6 s^{-1}.

The simplest explanation for the kinetics observed with ascorbic acid is shown in Scheme 2.



Scheme 2

Here, I_{2A} and I_{4A} represent preliminary adducts.

In **1**H, most probably the π-electron cloud on sq in **1** provides electrostatic attraction to the proton. Such a mode of protonation is closely similar to that proposed[19] for the second protonation of the free *p*-benzoquinone radical.

In Scheme 2, the reaction between **1** and HA^- has been excluded because of the nature of the dependence of rate on $[H^+]$. This path demands decreased rate with increased $[H^+]$. But, actually rate increased with $[H^+]$. Again, HA^- is well known to be kinetically much more active than H_2A; if the reaction between **1** and HA^- were insignificant, then, that between **1** and H_2A should also be insignificant. On this basis, we excluded also the reaction between **1** and H_2A from Scheme 2. Scheme 2 leads to

$$k_0 = \frac{(k_{4A}K_{4A}K_{aA}K_H + k_{2A}K_{2A}K_H[H^+])T_A}{1 + K_{4A}K_{aA}K_HT_A + [H^+](K_H + K_{2A}K_HT_A)} \quad (9)$$

where T_A ($\cong [H_2A] + [HA^-]$) is the total concentration of the ascorbic acid. Provided that, $1 \gg \{(K_{4A}K_{aA}K_HT_A + [H^+](K_H + K_{2A}K_HT_A)\}$, eqn. (9) reduces to eqn. (10):

$$k_0 = (k_{4A}K_{4A}K_{aA}K_H + k_{2A}K_{2A}K_H[H^+])T_A \quad (10)$$

Again, according to eqn. (4)

$$k_0 = k_AT_A \quad (11)$$

hence, from eqns. (10) and (11)

$$k_A = (k_{4A}K_{4A}K_{aA}K_H + k_{2A}K_{2A}K_H[H^+]) \quad (12)$$

The second order rate constants, k_A, increased linearly (r = 0.989) with $[H^+]$; The slope = (311 ± 42) and intercept = (7.7 ± 0.9), values lead to. $k_{2A}K_{2A}K_H = (311 \pm 42)$ and $k_{4A}K_{4A}K_H = (7.7 \pm 0.9) \times 10^4$ dm^6 mol^{-2} s^{-1}.

The results demonstrate overwhelming kinetic dominance of **1**H over **1**, in the oxidation of ascorbic acid and quinol. This arises from the greater oxidising power of **1**H as indicated by the higher $E_{1/2}$ value of **1** at higher $[H^+]$.

It has been shown[11a] that for a purely outer-sphere reaction, the ratio of rate constants in the HA^- path to the H_2A path is ≈10.[4] In the present case the $k_{4A}K_{4A}/k_{2A}K_{2A}$ ratio is only $\approx 2 \times 10^2$ which suggests that the reactions are not purely outer-sphere. As **1**H is substitutionally inert, we do not see any possibility for the formation of an inner-sphere adduct. However, significant electronic interaction is possible *via* a H-bond between **1**H and the reducing agents, *viz*., H_2Q, H_2A and HA^-.

In this context, it is noticed with interest that in spite of the insignificant kinetic activity of **1**, the proposed adduct, I_{1Q}, formed between **1** and H_2Q, is moderately stable. We anticipate that I_{1Q} is stabilised by interaction between the OH group of H_2Q and the π-electron cloud on the ring of Ru^{II}-bound sq in **1**.[19] The π-electron density of the sq ring in **1**H is greatly depleted and the adduct should be weak.

Product formation

In the reaction described above, **1** is ultimately reduced to $[Ru(bpy)_2(Hcat)]^+$. The complex **1** is a one electron oxidant but H_2Q and ascorbic acid are two electron reductants. Therefore, the immediate products of the first act of electron transfer should be $[Ru(bpy)_2(Hcat)]^+$ and the radical species $HQ^\bullet$ or $HA^\bullet$. We proposed above that the proton in **1**H attaches itself to the π-electron cloud of the Ru^{II}-bound sq radical. Addition of an electron to **1**H should form the catecholate anion, when the proton attached to the π-electron cloud shifts to the O^- site and thus forms complex **2**. In the next step, the radical, $HQ^\bullet$ or $HA^\bullet$, reacts rapidly with another molecule of **1**H according to eqn. (13), for example:

$$\mathbf{1}H + HQ^\bullet \longrightarrow [Ru(bpy)_2(catH)]^+ + Q + H^+ \quad (13)$$

An analogous reaction, $Q^{\bullet-} + Q^{\bullet-} + 2H^+ \longrightarrow Q + QH_2$, proceeds with a rate constant of 8×10^7 dm^3 mol^{-1} s^{-1} at pH 7.4.[19] The reaction (13) is thus expected to be very fast.

Rate constant k_A decreases with increased percentage of MeOH, in MeOH–H_2O reaction media (Table 3). It may be an effect of the expected decrease in K_H with increased percentage of the less-polar component in the solvent.[20] The increased percentage of MeOH probably also renders **1**H a weaker oxidant. The trend of change in λ_{max} of the MLCT band with solvent composition indicates this possibility.

Table 3 Effect of solvent composition in the media on the second order rate constant,[a] k_A, for the reduction of **1** to **2**H by ascorbic acid

%(v/v) MeOH	k_A/dm³ mol^{-1} s^{-1}
40	9
50	8
60	6.5
70	5
84.7	3.9

[a] [complex] 0.10 mmol dm^{-3}; T_A 0.10 mmol dm^{-3}; [$HClO_4$] 0.01 mol dm^{-3}; T 25.0 °C; I 0.10 mol dm^{-3} ($NaClO_4$); 40% (v/v) MeOH–H_2O media; error in k_A, 3–6%.

Conclusion

Reduction of sq radical bound to Ru(II) involves (a) protonation of sq in Ru(II)-sq to generate the thermodynamically stronger, and the kinetically dominant, oxidant [Ru(bpy)$_2$(Hsq)]$^{2+}$, **1**H, and (b) formation of a dead end adduct I_{1Q} between **1** and H_2Q. We could gather no evidence for simultaneous transfer of a proton and an electron in the rate-determining step though such an electroprotic mechanism has been postulated for the reduction of quinone to semiquinone to quinol in photosystem I.

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References

1 J. Lavergne, C. Matthews and N. Ginet, *Biochemistry*, 1999, **38**, 4542.
2 M. S. Graige, M. L. Paddock, J. M. Bruce, G. Fener and M. Y. Okamura, *J. Am. Chem. Soc.*, 1996, **118**, 9005.
3 (*a*) S. D. Pell, R. B. Salmonsen, A. Abelleira and M. J. Clarke, *Inorg. Chem.*, 1984, **23**, 385; (*b*) S. E. Jones, L. E. Leon and D. T. Sawyer, *Inorg. Chem.*, 1982, **21**, 360.
4 S. Arzberger, J. Soper, O. P. Anderson, A. Cour and M. Wicholas, *Inorg. Chem.*, 1999, **38**, 157.
5 J. H. Rodrignez, D. E. Wheeler and J. K. McCusker, *J. Am. Chem. Soc.*, 1998, **120**, 12051.
6 C. G. Pierpont, *Inorg. Chem.*, 1997, **36**, 19.
7 H. Masui, A. B. P. Lever and P. R. Auburn, *Inorg. Chem.*, 1991, **30**, 2402.
8 H. Haga, E. S. Dadsworth and A. B. P. Lever, *Inorg. Chem.*, 1986, **25**, 447.
9 Microcal Origin 4.0, Microcal Software Inc., Northampton, USA, 1995.
10 (*a*) K. J. Laidler, *Chemical Kinetics*, 3rd edn., Harper & Row, New York, 1987, p. 32; (*b*) C. Capellos and B. H. J. Bielski, *Kinetic System*, Wiley-interscience, New York, 1972.
11 (*a*) A. McAuley, L. Spencer and P. R. West, *Can. J. Chem.*, 1985, **63**, 1198; (*b*) D. Dixon, T. P. Dasgupta and N. P. Sadler, *J. Chem. Soc., Dalton Trans.*, 1997, 1903.
12 E. Pellizzetti, *J. Chem. Soc., Dalton Trans.*, 1980, 484.
13 (*a*) K. Wiberg, *Chem. Rev.*, 1955, **55**, 713; (*b*) R. P. Bell, *Acid–base catalysis*, Oxford University Press, London, 1941, p. 145; (*c*) E. L. Purlee, *J. Am. Chem. Soc.*, 1959, **81**, 263.
14 R. A. Binstead and T. J. Meyer, *J. Am. Chem. Soc.*, 1987, **109**, 3287.
15 W. J. Albery, in *Proton Transfer Reactions*, eds. E. Caldin and V. Gold, Wiley-Interscience, New York 1975, ch. 9.
16 W. J. Albery and M. H. Davies, *J. Chem. Soc., Faraday Trans.*, 1972, **68**, 167.
17 U. Roy Choudhury, S. Banerjee and R. Banerjee, *J. Chem. Soc., Dalton Trans.*, 2000, 589.
18 M. V. Huynh, P. S. White and T. Meyer, *Angew Chem., Int. Ed.*, 2000, **39**, 4104.
19 (*a*) V. A. Roginsky, L. M. Pisarenko, W. Bors and C. Michel, *J. Chem. Soc., Perkin Trans. 2*, 1999, 871; (*b*) S. Isaaca and R. van Eldik, *J. Chem. Soc., Perkin Trans. 2*, 1997, 1465.
20 A. Frost and R. G. Pearson, *Kinetics and Mechanism*, John Wiley & Sons, Inc., USA, 1961, 2nd edn., p. 135.