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Electron-transfer reactions in $[Ru(edta)(pyz)]^-$ (edta = ethylenedinitrilotetraacetate, pyz = pyrazine)

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The kinetics of reduction of $[Ru^{III}(edta)(pyz)]^-$ (edta = ethylenedinitrilotetraacetate, pyz = pyrazine) with L-ascorbic acid (H_2A) and catechol(H_2cat) was studied spectrophotometrically as a function of $[H_2A]$ or $[H_2cat]$, pH, ionic strength and temperature (25–45 °C). The reduction was found to be first order in both the complex and reductant concentrations. The pH dependence of the process(for H_2A) was ascribed to the deprotonation of H_2A. Kinetic data and activation parameters are interpreted in terms of a mechanism involving outer-sphere electron transfer.

The chemistry of ruthenium ethylenedinitrilotetraacetate (edta) complexes is my present research interest.[1–6] Although most previous work published by various groups involves substitution[7–10] and catalytic reactions[11–15] of such complexes, their electron-transfer reactions have been almost totally neglected (apart from a brief report[7]). This prompted me to initiate a programme of study of these reactions. To begin with some aromatic N-heterocyclic ligands (L) *viz.* pyrazine, isonicotinamide, *etc.* were chosen which can form mixed-ligand complexes of the type $Ru^{III}(edta)L^-$ through a very rapid and straightforward aqua-substitution reaction.[7] The $Ru^{II}(edta)L^{2-}$ complexes exhibit a strong m.l.c.t. (metal-to-ligand charge transfer) band in the visible region (460–474 nm) and this offers an amenable way to monitor the electron-transfer reaction spectrophotometrically as the spectra of the ruthenium(III) analogues are featureless in the visible region. The present paper reports the kinetics and mechanism of the reduction of $[Ru^{III}(edta)(pyz)]^-$ (pyz = pyrazine) with L-ascorbic acid and catechol in aqueous solution.

Experimental

The salt $K[Ru^{III}(Hedta)Cl]\cdot 2H_2O$ was prepared by following the published procedure[16] and characterised. It is rapidly aquated when dissolved in water and exists predominantly in its most labile form $[Ru^{III}(edta)(H_2O)]^-$ in the range pH 5–6. All other chemicals used were of A.R. grade. Doubly distilled water was used throughout the experiments. The absorption spectra of the experimental solutions were recorded on a Shimadzu-160 UV/VIS spectrophotometer equipped with a TCC-240A temperature controller. Electrochemical studies were carried out with Princeton Applied Research (PAR) electrochemical instruments. Kinetic measurements were carried out on a Hi-Tech(SF-51) stopped-flow spectrophotometer attached to an on-line data analyser (Apple IIe) with which kinetic traces could be evaluated. All the reactions were monitored at the absorbance maximum of the ruthenium(II) complex (λ_{max} = 463 nm). The instrument was thermostatted at ±0.1 °C. Rate constant data were measured under pseudo-first-order conditions of an excess (10–100 fold) of reductant. Acetic acid–acetate and phosphate buffers were used to maintain the pH of kinetic solutions, whereas KCl was used to control the ionic strength. The pH measurements were carried out with a Digisun pH meter. Rate constant data represented as an average of several kinetic runs (at least five to six) are reproducible within ±4%.

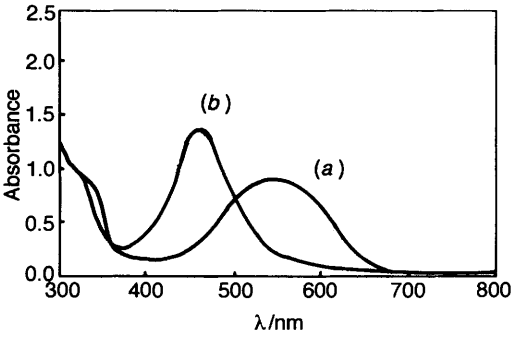

Fig. 1 Spectra of (*a*) $[Ru^{II}(edta)(Hpyz)]^-$ and (*b*) $[Ru^{II}(edta)(pyz)]^{2-}$ in aqueous solution

Results and Discussion

The $[Ru^{III}(edta)(pyz)]^-$ complex can be readily prepared by mixing equimolar amounts of $[Ru^{III}(edta)(H_2O)]^-$ and pyrazine in aqueous solution. This straightforward procedure is a result of the high lability of $[Ru^{III}(edta)(H_2O)]^-$ towards aqua substitution with nitrogen heterocycles.[7] A cyclic voltammogram of $[Ru^{III}(edta)(pyz)]^-$ in water showed a quasi-reversible cathodic and anodic peak with ΔE_p (peak separation) 70 mV. The value of the $[Ru^{III}(edta)(pyz)]^-$–$[Ru^{II}(edta)(pyz)]^{2-}$ couple estimated as an average of the cathodic and anodic peak potentials is +0.01 V (*vs.* saturated calomel electrode, SCE). Cyclic voltammetric results reveal that the $[Ru(edta)(pyz)]^-$ complex would be a good system for redox studies.

The absorption spectrum of $[Ru^{III}(edta)(pyz)]^-$ does not show any peak above 390 nm,[7] whereas that of the ruthenium(II) complex is characterised by a strong m.l.c.t. band at 463 nm (ε_{max} = 11 000 ± 5000 $dm^3\ mol^{-1}\ cm^{-1}$). The position of this band, however, changes with the pH of the solution and a red shift (Fig. 1) is observed at very low pH due to protonation of the remote aromatic N atom of the co-ordinated pyrazine. The proton dissociation constant (pK_a) of $[Ru^{II}(edta)(Hpyz)]^-$ [equation (1)] estimated spectrophoto-

$$[Ru^{II}(edta)(Hpyz)]^- \overset{K_a}{\rightleftharpoons} [Ru^{II}(edta)(pyz)]^{2-} + H^+ \quad (1)$$

metrically (by measuring the absorbance at 463 nm at different pH) is 2.63 at 25 °C.

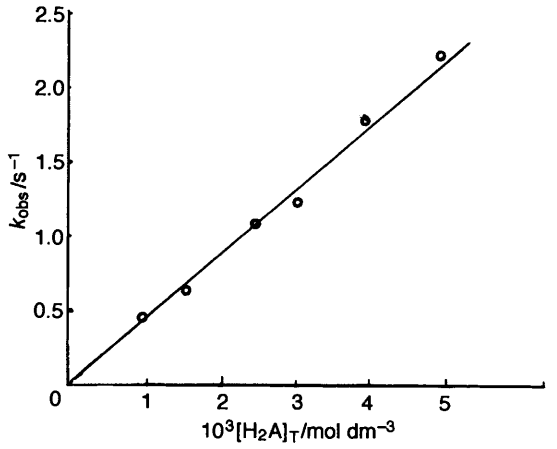

Fig. 2 Plot of k_{obs} *vs.* $[H_2A]_T$ at 25 °C, pH 6.0, I = 0.23 mol dm^{-3} and $[Ru^{III}]$ = 5 × 10^{-5} mol dm^{-3}

Table 1 Rate and activation parameters for the reduction of $[Ru^{III}(edta)(pyz)]^-$ (5 × 10^{-5} mol dm^{-3}) with L-ascorbic acid (1 × 10^{-3} mol dm^{-3})

pH	I/mol dm^{-3}	T/°C	k_{obs}/s^{-1}
2.1	0.23	25	0.02
2.9			0.06
3.8			0.16
4.5			0.29
5.3			0.43
6.0			0.67
7.1			0.84
8.2			1.1
6.0	0.13	25	0.49
	0.23		0.67
	0.33		0.77
	0.5		0.97
6.0	0.23	25	0.67
		30*	0.89
		35	1.11
		45	1.87

* $\Delta H^{\ddagger}$ 38 ± 3 kJ mol^{-1}, $\Delta S^{\ddagger}$ = −122 ± 11 J K^{-1} mol^{-1}.

Reduction of $[Ru^{III}(edta)(pyz)]^-$ with L-ascorbic acid

Addition of L-ascorbic acid (H_2A) to a solution of $[Ru^{II}(edta)(pyz)]^-$ resulted in an immediate change from pale yellow to orange-red and the spectrum displayed an intense band at 463 nm due to formation of $[Ru^{II}(edta)(pyz)]^{2-}$. The stoichiometry of the reaction determined spectrophotometrically (at 463 nm) under a nitrogen atmosphere at pH 6.0 is outlined in equation (2) where A (dehydroascorbic acid)[17–20] denotes the oxidation product of L-ascorbic acid.

$$2[Ru^{III}(edta)(pyz)]^- + HA^- \longrightarrow 2[Ru^{II}(edta)(pyz)]^{2-} + A + H^+ \quad (2)$$

In a typical kinetic experiment a solution of $[Ru^{III}(edta)(pyz)]^-$ was allowed to mix with L-ascorbic acid in the stopped-flow mixing chamber and corresponding kinetic traces (growth at 463 nm) were found to be single exponential in all cases. At a constant pH of 6.0 the pseudo-first-order rate constant (k_{obs}) increased linearly (Fig. 2) with increase in $[H_2A]_T$ (throughout this paper the total concentration of ascorbic acid is represented by $[H_2A]_T$ and equals the sum of $[H_2A]$, $[HA^-]$ and $[A^{2-}]$). Considering that the monoprotonated ascorbate (HA^-) is the dominant reacting species at pH 6.0 (pK_1 and pK_2 values of H_2A are 4.1 and 11.4, respectively)[18,21,22] and comparing the present kinetic observations to those reported for the reduction of $[Ru^{III}(NH_3)_5(pyz)]^{3+}$[23] and other transition-metal complexes[24] with L-ascorbic acid, the following mechanism involving sequences of two one-electron transfer steps (3) and (4) is proposed for the present reaction.

$$[Ru^{III}(edta)(pyz)]^- + HA^- \xrightarrow{k_r} [Ru^{II}(edta)(pyz)]^{2-} + HA \quad (3)$$

$$[Ru^{III}(edta)(pyz)]^- + HA \xrightarrow{fast} [Ru^{II}(edta)(pyz)]^{2-} + A + H^+ \quad (4)$$

The rate-determining step (3) proposed in the above mechanism involves a one-electron transfer [from HA^- to ruthenium(III) complex] in an outer-sphere manner. The subsequent and kinetically inconsequential step (4) is a rapid electron transfer from the ascorbate radical (HA) to another molecule of the complex. Though the presence of the ascorbate radical (a highly reactive species)[25] could not be demonstrated (acrylonitrile polymerisation), its formation cannot be disregarded. The rate of its (HA) disappearance through reaction with the ruthenium(III) complex [equation (4)] is perhaps much faster than the rate of initiation of polymerisation of acrylonitrile.

In order to substantiate the proposed rate-determining step (3) the ionic strength dependence of the rate constant at 25 °C was studied and the experimental results (Table 1) are in consonance with the Bronsted–Bjerrum equation.[26] A plot of log k_{obs} *versus* $I^{\frac{1}{2}}$ gave a straight line with a positive slope (0.84) as expected for a reaction between two similarly charged ions. Expressing the activity coefficients of the reactants and the transition-state complex in terms of ionic strength [equation (5)] (f_i = ionic

$$\log f_i = -AZ_i^2 I^{\frac{1}{2}} \quad (5)$$

activity coefficient, A = Debye–Hückel constant, Z_i = ionic charge, I = ionic strength), the Bronsted equation for the present case [equation (3)] can be expressed as in equation (6).

$$\log k = \log k_0 - AZ_{Ru^{III}}{}^2 I^{\frac{1}{2}} - AZ_{HA^-}{}^2 I^{\frac{1}{2}} + AZ_T{}^2 I^{\frac{1}{2}} \quad (6)$$

By using the charges on the reactants ($Z_{Ru^{III}} = Z_{HA} = -1$) and the transition-state species ($Z_T = -2$) and taking the value of A as 0.509, equation (6) can be expressed as (7) where k_0 =

$$\log k = \log k_0 + 1.02\, I^{\frac{1}{2}} \quad (7)$$

rate constant at infinite dilution. A plot of log k *versus* $I^{\frac{1}{2}}$ should be a straight line with a positive slope equal to 1.02. In practice a linear plot with a slope of 0.84 was obtained. This suggests the validity of the proposed rate-determining step (3).

The pH dependence of the rate constant was studied in the range pH 3.8–8.2 using appropriate buffers. The rate of the reaction was found to be pH dependent (Table 1) since the reducing power of ascorbic acid greatly differs from that of its conjugate bases HA^- and A^{2-}. In general, reactivity decreases in the order $A^{2-} \gg HA^- > H_2A$.[22] The values of the observed rate constant at various pH are summarised in Table 1. Considering that the pK_2 (corresponding to the second proton dissociation of H_2A) of ascorbic acid is 11.4,[22] it is expected that the rate of reaction would be almost pH independent in the range pH 6.0–8.0 (more than 95% of L-ascorbic acid is present as HA^-). However as reported earlier[27,28] the present results (sharp increase in rate constant in the range pH 6–8) suggest the participation of the highly reactive species A^{2-}, though present in very small concentration, in the reduction process.

The reduction of $[Ru^{III}(edta)(pyz)]^-$ with HA^- was studied at three different temperatures. The rate and activation

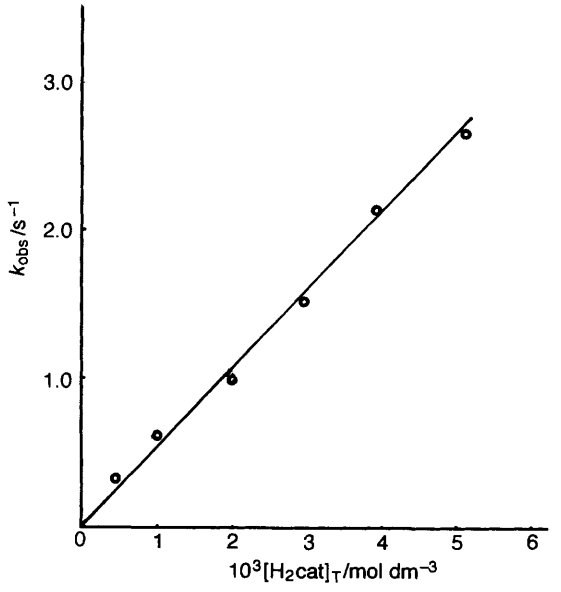

Fig. 3 Plot at k'_{obs} *vs.* [H_2cat] at 25 °C, pH 6.0, I = 0.23 mol dm^{-3} and [Ru^{III}] = 5 × 10^{-5} mol dm^{-3}

parameters (determined by using an Eyring plot, *i.e.* log (k/T) *vs.* $1/T$), are summarised in Table 1. The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are quite comparable to those reported[21,24,27] for other relevant reactions and consistent with the proposed outer-sphere electron-transfer process. The large negative value of $\Delta S^{\ddagger}$ is probably due to an increase in electrostriction around the negatively charged reacting species during the electron transfer. An attempt was made to correlate the cross-reaction data by a modification of the Marcus relationship[29] (neglecting the work terms for two similarly charged reactants), which correlates [equations (8)–(10)] the rate constants k_{11} (self-

$$k_{12} = (k_{11}k_{22}K_{12}f)^{\frac{1}{2}} \quad (8)$$

$$\log K_{12} = \Delta E^{\circ}/0.059 \quad (9)$$

$$\log f = (4 \log K_{12})^2/4 \log (k_{11}k_{22}/Z^2) \quad (10)$$

exchange rate constant for HA–HA$^-$ couple) and k_{22} [self-exchange rate constant for the [Ru(edta)(pyz)]$^{1-/2-}$ couple] for the component self-exchange reactions and the equilibrium constant, K_{12}, for the cross-reaction. By utilising the values of k_{11} = 1 × 10^6 dm^3 mol^{-1} s^{-1},[24] k_{22} = 8 × 10^5 dm^3 mol^{-1} s^{-1},[30] E°_{HA/HA^-} = 0.71 V (*vs.* normal hydrogen electrode, NHE)[23] and $E^{\circ}_{Ru^{III}/Ru^{II}}$ {for [Ru(edta)(pyz)]$^{1-/2-}$ couple} = 0.24 V (*vs.* NHE), the value of k_{12} calculated is 477 dm^3 mol^{-1} s^{-1}. The close agreement between the calculated and experimentally obtained (k_r = 450 ± 30 dm^3 mol^{-1} s^{-1} at 25 °C) values further substantiates the arguments in favour of the proposed outer-sphere electron-transfer mechanism.

Reduction of [Ru^{III}(edta)(pyz)]$^-$ with catechol

Oxidation of catechol to semiquinone to quinone (catecholase activity) is a reaction of biochemical importance.[31,32] In order to assess the feasibility of [Ru^{III}(edta)(pyz)]$^-$ to serve as an oxidant in the oxidation of catechol (H_2cat) to quinone (Q) brief spectral and kinetic studies of the interaction of [Ru^{III}(edta)(pyz)]$^-$ with catechol were performed. Spectral measurements revealed the formation of [Ru^{II}(edta)(pyz)]$^{2-}$ (as characterised by its strong metal-to-ligand charge-transfer band at 463 nm) in the reaction between [Ru^{III}(edta)(pyz)]$^-$ and catechol. However, spectrophotometric evidence for a slow subsequent reaction was also observed. This is probably related to the removal of co-ordinated pyrazine from [Ru^{II}(edta)(pyz)]$^-$ in the presence of an excess of catechol.

The kinetics of the reduction of [Ru^{III}(edta)(pyz)]$^-$ with catechol was studied as a function of [Ru^{III}], [H_2cat] and ionic strength at a constant pH of 6.0. The rate of reaction was found to be first order both with respect to [Ru^{II}(edta)(pyz)$^-$] and [H_2cat]. The observed rate constant (under pseudo-first-order conditions of an excess of catechol) increased linearly with increasing [H_2cat] (Fig. 3) in the concentration range studied. Based on the above experimental observations the mechanism in equations (11) and (12) is proposed for the reduction of

$$[Ru^{III}(edta)(pyz)]^- + H_2cat \xrightarrow{k'_r} [Ru^{II}(edta)(pyz)]^{2-} + bsq + H^+ \quad (11)$$

$$[Ru^{III}(edta)(pyz)]^- + bsq \xrightarrow{fast} [Ru^{II}(edta)(pyz)]^{2-} + bq + H^+ \quad (12)$$

[Ru^{III}(edta)(pyz)]$^-$ with catechol where bsq and bq represent benzosemiquinone (one-electron oxidation product of catechol) and benzoquinone (two-electron oxidation product of catechol) respectively. The value of k'_r estimated from the plot of k'_{obs} *vs.* [H_2cat] (Fig. 3) is 570 ± 30 dm^3 mol^{-1} s^{-1} at 30 °C. The observed rate constant (k'_{obs}) values are independent of the ionic strength of the medium. The lack of ionic strength effect in the present reaction is consistent with the proposed rate-determining step with reference to the Bronsted equation[26] for a reaction between a charged and a neutral reactant.

In conclusion, the present study revealed that the [Ru^{III}(edta)(pyz)]$^-$ complex can effectively and readily be reduced to the corresponding ruthenium(II) complex by L-ascorbic acid or catechol. Reoxidation of the ruthenium(II) to the ruthenium(III) species can be effected by $S_2O_8^{2-}$ on a stopped-flow scale regardless of the mechanistic uncertainty.[30] The present redox studies of Ru–edta complexes containing the aromatic N-heterocyclic ligand pyrazine is definitely an instructive beginning in ascertaining the electron-transfer reaction in the Ru(edta)–DNA adduct as DNA binds to the metal complex through the aromatic N heteroatoms of its purine or pyrimidine base units.[33]

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References

1 D. Chatterjee and H. C. Bajaj, *J. Chem. Soc., Dalton, Trans.*, 1993, 1065.
2 D. Chatterjee, H. C. Bajaj and A. Das, *Inorg. Chem.*, 1993, **32**, 4049.
3 D. Chatterjee, H. C. Bajaj and A. Das, *Inorg. Chim. Acta*, 1994, **224**, 189.
4 D. Chatterjee, H. G. Bajaj and A. Das, *Polyhedron*, 1995, **14**, 3585.
5 D. Chatterjee, H. C. Bajaj and A. Das, *J. Chem. Soc., Dalton Trans.*, 1995, 2497.
6 D. Chatterjee and H. C. Bajaj, *J. Chem. Soc., Dalton Trans.*, 1995, 3415.
7 T. Matsubara and C. Creutz, *Inorg. Chem.*, 1979, **18**, 1956.
8 H. E. Toma, P. S. Santoz, M. P. D. Mattioli and L. A. A. Oliveira, *Polyhedron*, 1987, **6**, 603.
9 H. C. Bajaj and R. van Eldik, *Inorg. Chem.*, 1988, **27**, 4052.
10 H. Ogino, T. Katsuyama and S. Ito, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 1370.
11 M. M. Taqui Khan, M. R. H. Siddiqui, A. Hussain and M. A. Moiz, *Inorg. Chem.*, 1986, **25**, 2765.
12 M. M. Taqui Khan, R. S. Shukla and A. P. Rao, *Inorg. Chem.* 1989, **28**, 452.
13 M. R. Rhodes, M. H. Barby and T. J. Meyer, *Inorg. Chem.*, 1991, **30**, 629.

14 M. M. Taqui Khan, D. Chatterjee, R. R. Merchant, P. Paul, S. H. R. Abdi, D. Srinivas, M. A. Moiz, M. M. Bhadbhade and K. Venkatasubramanian, *Inorg. Chem.*, 1992, **37**, 711.
15 S. Zhang and R. E. Shepherd, *Inorg. Chim. Acta*, 1992, **193**, 217.
16 A. A. Diamantis and J. V. Dubrawski, *Inorg. Chem.*, 1981, **20**, 1142.
17 G. P. Laroff, R. W. Fessenden and R. H. Schuler, *J. Am. Chem. Soc.*, 1972, **94**, 9062.
18 M. M. Taqui Khan and A. E. Martell, *J. Am. Chem. Soc.*, 1969, **91**, 4668.
19 E. Pelizzetti and E. Mentasti, *J. Chem. Soc., Dalton. Trans.*, 1978, 61.
20 U. S. Mehrotra and S. P. Mushran, *Can. J. Chem.*, 1970, **48**, 1148.
21 M. Kimura, M. Yamamoto and S. Yamabe, *J. Chem. Soc., Dalton Trans.*, 1982, 423.
22 N. H. Williams and J. K. Yandell, *Aust. J. Chem.*, 1983, **36**, 2377.
23 M. J. Akhtar and A. Haim, *Inorg. Chem.*, 1988, **27**, 1608.
24 C. Cruetz, *Inorg. Chem.*, 1981, **20**, 4449.
25 B. H. J. Bielski, A. O. Allen and H. A. Schwarz, *J. Am. Chem. Soc.*, 1981, **103**, 3516.
26 J. H. Espenson, *Chemical Kinetics and Reaction Mechanism*, McGraw-Hill, New York, 1981, p. 172.
27 P. Martinez, J. Zuluaga and D. Uribe, *Z. Phys. Chem. Neue Folge*, 1983, **137**, 43.
28 P. Martinez, J. Zuluaga, J. Kraft and R. van Eldik, *Inorg. Chim. Acta*, 1989, **146**, 9.
29 R. A. Marcus, *J. Phys. Chem.*, 1963, **67**, 853.
30 M. S. Ram and A. Haim, *Inorg. Chem.*, 1991, **30**, 1319.
31 R. H. Heistand, R. B. Lauffer, E. Fikrig and L. Que, *J. Am. Chem. Soc.*, 1982, **104**, 2789.
32 D. E. Wilcox, A. G. Porras, Y. T. Hwang, K. Lerch, M. E. Winkler and E. I. Solomon, *J. Am. Chem. Soc.*, 1985, **107**, 4015.
33 R. B. Martin, *Acc. Chem. Res.*, 1985, **18**, 32.

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