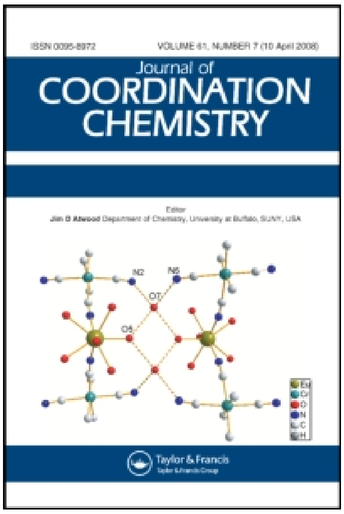

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Kinetics and mechanism for oxidation of $[Ru^{III}(edta)(H_2O)]^-$ with peroxydisulfate in aqueous medium

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Kinetics and mechanism for oxidation of $[Ru^{III}(edta)(H_2O)]^-$ with peroxydisulfate in aqueous medium

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The kinetics of oxidation of $[Ru^{III}(edta)(H_2O)]^-$ ($edta^{4-}$ = ethylenediaminetetraacetate) with peroxydisulfate ($S_2O_8^{2-}$) was studied spectrophotometrically as a function of $[S_2O_8^{2-}]$ at pH 6.0. Oxidation was found to be first order in both ruthenium complex and $S_2O_8^{2-}$ concentrations. The effect of alkali cations (K^+, Na^+, and Li^+) is attributed to triple-ion formation through an alkali cation bridging between two negatively charged reactants, facilitating the electron-transfer process. Kinetic data and activation parameters are indicative of an outer-sphere electron-transfer process. A detailed mechanism in agreement with the rate and activation parameters is presented, and the results are discussed in reference to data reported for the $[Ru^{III}(edta)(H_2O)]^-$/XO (XO = H_2O_2, t-BuOOH, and $KHSO_5$) systems.

Keywords: Ruthenium; edta; $S_2O_8^{2-}$; Kinetics; Electron transfer; Outer-sphere process

1. Introduction

The chemistry of ‘‘edta’’ complexes of ruthenium (figure 1) is intriguing in many ways [1–3]. The ‘‘edta’’ ligands are similar in donor character to many metallo-enzymes, which utilize carboxylate or amine of amino acids to bind to the metal center. A major mechanistic impetus toward the development of the chemistry of Ru–edta complexes arose from Prof. Rudi van Eldik of Erlangen University, Germany. Some articles contributed from van Eldik’s group, exploring the potential of such ruthenium complexes in biological applications, are referred herein [4–6]. As there are certain overlaps between work in van Eldik’s group and mine, we have been in collaboration for quite a long period. Our longstanding collaboration has resulted in some significant publications on kinetic and mechanistic studies of Ru–edta complexes [7–12], exploring their potential in various biochemical processes.

The present work stems from our continued interest in kinetic and mechanistic studies of the interaction of Ru–edta complexes with various oxidants, namely NaOBr [9], H_2O_2 [10], ^{t}BuOOH, $KHSO_5$ [11], with the objective of acquiring mechanistic knowledge regarding the formation of the high-valent $[(edta)Ru^V{=}O]^-$ species which

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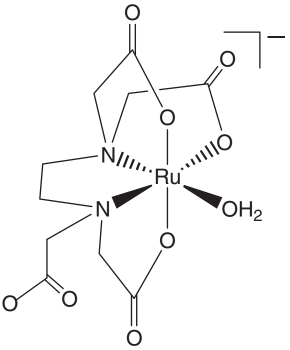

Figure 1. Structural representations of $[Ru^{III}(edta)(H_2O)]^-$ (**1**).

had been proposed earlier [13] as catalytic active intermediate in oxygen-transfer processes. In the present article, we describe the kinetic results together with detailed mechanistic studies of the reactions of $[Ru^{III}(edta)(H_2O)]^-$ with $S_2O_8^{2-}$. Although the reaction of Ru(II)–edta complex with $S_2O_8^{2-}$ leading to the formation of Ru(III)–edta complex had been reported earlier [14], we for the first time report the peroxydisulfate oxidation of Ru(III)–edta complex to Ru(V)–oxo complex. The mechanism of the overall oxidation process is discussed in reference to the previously reported data for the reaction between $[Ru^{III}(edta)(H_2O)]^-$ and ROOH (R = H, ^{t}Bu, and SO_4^-) [10, 11].

2. Experimental

2.1. *Materials*

$K[Ru^{III}(Hedta)Cl] \cdot 2H_2O$ was prepared using a published procedure [15] and characterized by elemental analysis and spectral data, which were in agreement with data reported in the literature [13]. Anal. Calcd (%) for $C_{11}H_{16}ClKN_2O_9Ru$: C, 24.8, 3.94, 5.26. Found (%): C, 24.5; H, 3.98; N, 5.19. IR, ν (cm^{-1}): 1730 (COOH), 1652 (COO^-). UV-Vis: λ_{max} (nm) (ε_{max} $(mol\,L^{-1})^{-1}\,cm^{-1}$) in H_2O: 285 (2650 ± 60), 366s (630 ± 15). The complex rapidly hydrolyzes to the aqua complex when dissolved in water, and thus exists predominantly in its most labile form $[Ru^{III}(edta)(H_2O)]^-$ (**1**) in the pH range 4–6 [4, 16]. The $[Ru^{III}(edta)(H_2O)]^-$ species undergoes rapid aqua-substitution affording facile and straight-forward binding of incoming ligand [4, 16]. All chemicals used were of reagent grade obtained from Aldrich Chemical Company and were appropriately degassed before use. Multi-distilled water was used throughout the studies.

2.2. *Instrumentation*

A Perkin-Elmer 240C elemental analyzer was used to collect microanalytical (C, H, N) data. The UV-Vis and IR spectra were recorded on Perkin-Elmer Model Lambda 35 and Model 783 spectrophotometers using KBr pellets. The kinetics of the reaction was studied spectrophotometrically adopting conventional mixing technique. A tandem

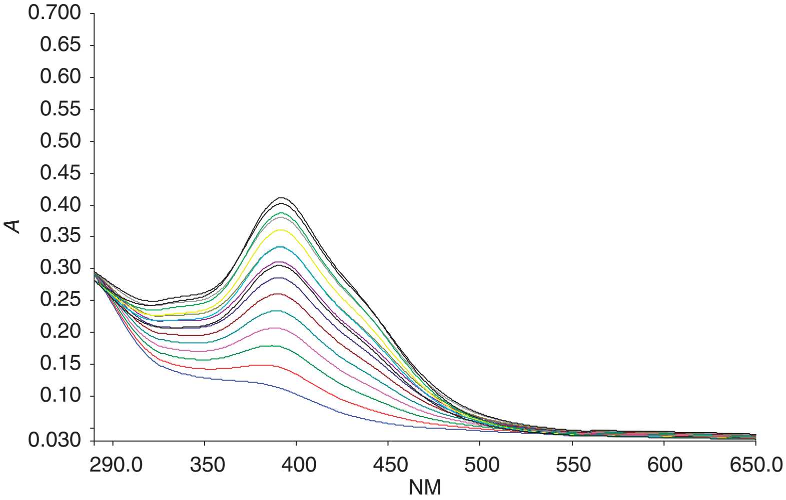

Figure 2. Spectral changes that occurred in the reaction of **1** (1×10^{-4}) with $S_2O_8^{2-}$ ($1 \times 10^{-2}\,mol\,L^{-1}$) at 35°C, pH = 6.0 ($0.2\,mol\,L^{-1}$ NaOAc/AcOH buffer), [NaCl] = $0.2\,mol\,L^{-1}$. Spectra recorded after every 900 s.

cuvette was used for this purpose. The solution temperature was maintained to within ±0.1°C using a circulating water bath. The pH of solutions was measured with a Mettler Delta 350 pH meter. Acetic acid–acetate buffer was used to maintain the pH of the kinetic solutions, whereas NaCl was used to control the ionic strength. LiCl and KCl were used to investigate the effect of varying the alkali metal cations. An excess of peroxydisulfate (10–100 fold excess) was used in all cases to ensure pseudo-first order conditions. The pseudo-first-order rate constants (k_{obs}) were determined from the slope of plots of $\ln(A_\propto - A_t)$ *versus* time ($A_\propto$ and A_t are the absorbance at the completion of reaction and at time t, respectively), which were linear over at least first three-half lives of the reaction. Observed rate constants (k_{obs}) were presented as an average of several kinetic runs (at least 3–5) and were reproducible within ±4%. Reaction product, sulfate was identified through $BaCl_2$ test.

3. Results and discussion

The spectral changes that occurred upon mixing **1** with $S_2O_8^{2-}$ are shown in figure 2. Formation of $[(edta)Ru^V(=O)]^-$ in the reaction of $[Ru^{III}(edta)(H_2O)]^-$ with $S_2O_8^{2-}$ was followed spectrophotometrically. The product solution exhibited the characteristic peak of $[(edta)Ru^V(=O)]^-$ at 391 nm ($\varepsilon_{max} = 8000 \pm 20\,(mol\,L^{-1})^{-1}\,cm^{-1}$) [13]. The stoichiometry of the reaction determined spectrophotometrically (at 391 nm) under a nitrogen atmosphere at pH 6.0 is outlined in equation (1) as follows:

$$\left[Ru^{III}(edta)(H_2O)\right]^- + S_2O_8^{2-} \longrightarrow \left[Ru^V(edta)(O)\right]^- + 2HSO_4^- \qquad (1)$$

The rate constants of the reaction were measured spectrophotometrically; as the reaction proceeded, the peak at 390 nm characteristic of $[Ru^V(edta)O]^-$

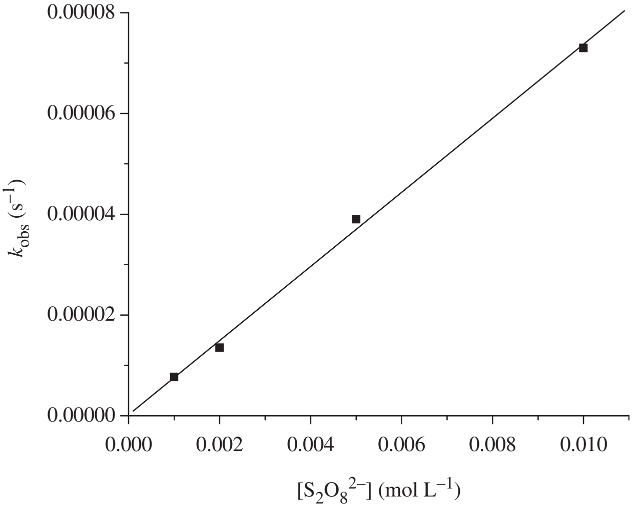

Figure 3. Plot of k_{obs} *vs.* [$S_2O_8^{2-}$] at 35°C. [1] = 1×10^{-4} mol L^{-1}, pH = 6.0 (0.2 mol L^{-1} NaOAc/AcOH buffer), [NaCl] = 0.2 mol L^{-1}.

steadily increased. The rate of oxidation was found to be first order with respect to **1**. At a constant pH 6.0, the values of the pseudo-first order rate constant (k_{obs}) increased linearly with increasing $S_2O_8^{2-}$ concentration (figure 3). The plot of k_{obs} *versus* [$S_2O_8^{2-}$] (figure 3) did not exhibit an appreciable intercept, suggesting negligible reversibility of the reaction. The effect of alkali cations on oxidation of **1** with $S_2O_8^{2-}$ was studied at pH 6.0 in presence of 0.2 mol L^{-1} M^+ ($M^+ = K^+$, Na^+, and Li^+). The increase in the reaction rate in the order: $k_{obs}^{(LiCl)}$ ($=5.87 \times 10^{-5}\,s^{-1}$) > $k_{obs}^{(NaCl)}$ ($=7.35 \times 10^{-5}\,s^{-1}$) > $k_{obs}^{(KCl)}$ ($=8.17 \times 10^{-5}\,s^{-1}$) at 35°C provides evidence that the specific effect of alkali metal cations is operative in the present case. It had been reported earlier [17, 18] that in electron transfer of two negatively charged reacting species occurring through an outer-sphere manner, the cation acts as a bridge or as a means of allowing two negatively charged reacting ions close enough for the electron transfer through the solvent. Considering the size of hydrated cations which is in the order: $Li^+ > Na^+ > K^+$, the K^+ would be more effective than Na^+ or Li^+ in forming triplet-ion species and thus contributing toward an increase in the reaction rate as observed in the present study.

On the basis of a pre-equilibrium approach, and by considering peroxydisulfate is stable and is involved in two-electron-transfer reactions [14, 19], the above kinetic results for the formation of $[(edta)Ru^{V}(=O)]^-$ in the reaction of $[(edta)Ru^{III}(H_2O)]^-$ with $S_2O_8^{2-}$ can be accounted for in terms of the suggested mechanism outlined in scheme 1.

In scheme 1, it is suggested that reaction (2) involves the formation of the $\{[Ru^{III}(edta)(O)]^- \cdots M^+ \cdots S_2O_8^{2-}\}$ intermediate species (as represented by "**I**" in scheme 1) in a rapid pre-equilibrium step. The rate-determining step proposed in the above mechanism involves one-electron transfer from ruthenium(III) complex to $S_2O_8^{2-}$ in an outer-sphere manner to yield the ruthenium(IV) complex (equation (3)) and the $SO_4^{-\bullet}$ radical. However, the presence of the $SO_4^{-\bullet}$ radical (a highly reactive species) could not be evidenced by acrylonitrile polymerization. The highly reactive $SO_4^{-\bullet}$ radical affects further oxidation of Ru(IV)-species to Ru(V)-oxo complex in a much

$$[\mathrm{Ru^{III}(edta)(H_2O)}]^{-} + \mathrm{S_2O_8^{2-}} \underset{}{\overset{K}{\rightleftharpoons}} \mathbf{I} \qquad (2)$$

$$\mathbf{I} \xrightarrow{k} [\mathrm{Ru^{IV}(edta)(OH)}]^{-} + \mathrm{SO_4^{-}} + \mathrm{HSO_4^{-}} \qquad (3)$$

$$[\mathrm{Ru^{IV}(edta)(OH)}]^{-} + \mathrm{SO_4^{-}} \xrightarrow{\text{fast}} [\mathrm{Ru^{V}(edta)(O)}]^{-} + \mathrm{HSO_4^{-}} \qquad (4)$$

Scheme 1. Mechanism of formation of $[\mathrm{Ru^{v}(edta)(O)}]^{-}$ in the oxidation of $[\mathrm{Ru^{III}(edta)(H_2O)}]^{-}$ with $\mathrm{S_2O_8^{2-}}$.

Table 1. Rate and activation parameters for reaction of $\mathrm{Ru^{III}(edta)}$ with $\mathrm{KHSO_5}$.

Temperature (°C)	$k \times 10^3$ ((mol L^{-1})$^{-1}$ s^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (JK^{-1} mol^{-1})
20	0.97 ± 0.005	104 ± 4	50 ± 11
25	1.73 ± 0.06		
30	3.75 ± 0.05		
35	7.35 ± 0.04		
40	15.3 ± 0.1		

$[\mathrm{Ru^{III}}] = 1 \times 10^{-4}$ mol L^{-1}, pH = 6.0 (0.2 mol L^{-1} NaOAc/AcOH buffer), [NaCl] = 0.2 mol L^{-1}.

faster and kinetically inconsequential step (equation (4)) than the rate of initiation of polymerization of acrylonitrile.

The linear $[\mathrm{S_2O_8^{2-}}]$ dependence of the observed rate constant and the lack of any kinetic saturation effect even at a 100-fold excess of $[\mathrm{S_2O_8^{2-}}]$ (figure 3) are suggestive of *K* not being appreciably larger. The above kinetic observations can be accounted for in terms of the rate expression outlined in equation (5).

$$k_{\mathrm{obs}} = kK[\mathrm{S_2O_8^{2-}}] \qquad (5)$$

The values for *Kk* determined from the slope of the plot of k_{obs} *versus* $[\mathrm{S_2O_8^{2-}}]$ at different temperatures are summarized in table 1 and used to construct the Eyring plot (figure 4), from which values for $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were determined (table 1). The reported activation parameters are composite values and include important contributions from the pre-equilibrium step (Equation 2) and electron-transfer step (Equation 3) involving reductive homolytic cleavage of the –O–O–bond [18] in intermediate (**I**) to form $[\mathrm{(edta)Ru^{IV}(OH)}]^{-}$ as shown in scheme 1. The interpretation of large positive $\Delta H^{\neq}$ and $\Delta S^{\neq}$ is complicated by this fact; however, it perhaps indicates that the activation barrier for electron transfer in the reduction of peroxy bond of $\mathrm{S_2O_8^{2-}}$ in **I** is higher as the solvent rearrangement to produce a highly negatively charged transition state is high to facilitate electron transfer. Furthermore, positive $\Delta S^{\neq}$ was also reported earlier [18] in the reaction of two negatively charged species, $\mathrm{CoW_{12}O_{40}^{5-}}$ and $\mathrm{X(CN)_8^{4-}}$ (X = Mo, W).

Although $[\mathrm{(edta)Ru^{V}{=}O}]^{-}$ is the common major product in the reaction of **1** with $\mathrm{S_2O_8^{2-}}$ and other precursor oxidants, $\mathrm{H_2O_2}$, ^{t}BuOOH, and $\mathrm{KHSO_5}$, above results rule out the possibility of a common mechanism. The reaction of **1** with ROOH (R = H, ^{t}Bu, and $\mathrm{SO_3^{-}}$) proceeds *via* aquo-substitution leading to the formation of $[\mathrm{(edta)Ru^{III}(OOR)}]^{2-/3-}$, which subsequently undergo heterolytic cleavage of the O–O bond resulting in the formation of Ru(V)-oxo species [10, 11]. The formation of

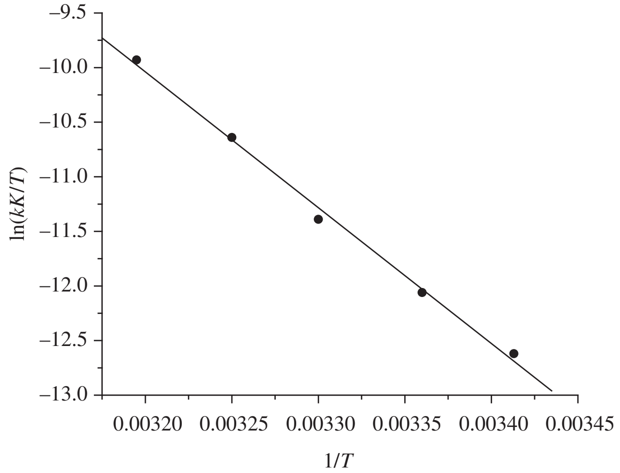

Figure 4. Plot of ln(kK/T) *vs.* $1/T$ for the data in table 1: [Ru^{III}] = 1×10^{-4} mol L^{-1}, pH = 6.0 (0.2 mol L^{-1} NaOAc/AcOH buffer), [NaCl] = 0.2 mol L^{-1}.

$[(\mathrm{edta})\mathrm{Ru}^{III}(\mathrm{OOR})]^{2-/3-}$ (R = H, ^{t}Bu, and SO_3^-) is governed by the nucleophilicity of the above oxidants. Despite having higher $E_{1/2}$ value (1.43 V for $S_2O_8^{2-}/SO_4^{2-} \cdot SO_4^-$ couple [19]) than ^{t}BuOOH ($E^0 = 1.15$ V [20]), $S_2O_8^{2-}$ appears to be a very weak nucleophile toward aqua-substitution of **1** under specified conditions. A proton-coupled electron-transfer mechanism involving the reduction of peroxy bond of $S_2O_8^{2-}$ seems to be operative in formation of Ru(V)-oxo species in the reaction of **1** with $S_2O_8^{2-}$.

4. Conclusion

In this work detailed kinetic and mechanistic study of the reaction of $[\mathrm{Ru}^{III}(\mathrm{edta})(H_2O)]^-$ with peroxydisulfate resulting in the formation of $[(\mathrm{edta})\mathrm{Ru}^{V}(=O)]^-$ as end product is presented. The findings of this work, together with those for the reaction of $[\mathrm{Ru}^{III}(\mathrm{edta})(H_2O)]^-$ with ROOH (R = H, ^{t}Bu, and SO_4^-), strongly suggests that the formation of $[(\mathrm{edta})\mathrm{Ru}^{V}(=O)]^-$ species in the reaction of **1** with $S_2O_8^{2-}$ takes place through an alkali-cation-assisted outer-sphere electron-transfer process not *via* oxo-transfer as observed for ROOH [10, 11].

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References

[1] D. Chatterjee. *Coord. Chem. Rev.*, **16**, 273 (1998), and references therein.
[2] D. Chatterjee, A. Mitra, G.S. De. *Platinum Met. Rev.*, **50**, 2 (2006), and references therein.
[3] W.H. Ang, P.G. Dyson. *Eur. J. Inorg. Chem.*, 4003 (2006).
[4] H.C. Bajaj, R. van Eldik. *Inorg. Chem.*, **27**, 4052 (1988).
[5] H.C. Bajaj, R. van Eldik. *Inorg. Chem.*, **28**, 1980 (1989).
[6] H.C. Bajaj, R. van Eldik. *Inorg. Chem.*, **29**, 2855 (1990).
[7] D. Chatterjee, A. Mitra, M.S.A. Hamza, R. van Eldik. *Dalton Trans.*, 962 (2002).
[8] D. Chatterjee, M.S.A. Hamza, M.M. Shoukry, A. Mitra, S. Deshmukh, R. van Eldik. *Dalton Trans.*, 203 (2003).
[9] D. Chatterjee, A. Mitra, R. van Eldik. *Dalton Trans.*, 4691 (2006).
[10] D. Chatterjee, A. Mitra, R. van Eldik. *Dalton Trans.*, 943 (2007).
[11] D. Chatterjee, A. Mitra, R. van Eldik. *Dalton Trans.*, 3851 (2008).
[12] D. Chatterjee, K.A. Nayak, E. Ember, R. van Eldik. *Dalton Trans.*, 1695 (2010).
[13] M.M. Taqui Khan, D. Chatterjee, R.R. Merchant, P. Paul, S.H.R. Abidi, D. Srinivas, M.R.H. Siddiqui, M.A. Moiz, M.M. Bhadbhade, K. Venkatasubramanian. *Inorg. Chem.*, **31**, 2711 (1992).
[14] M.S. Ram, A. Haim. *Inorg. Chem.*, **30**, 1325 (1996).
[15] A.A. Diamantis, J.V. Dubrwaski. *Inorg. Chem.*, **20**, 1142 (1981).
[16] T. Matsubara, C. Creutz. *Inorg. Chem.*, **18**, 1956 (1979).
[17] A. Rodriguez, S. Lopez, M.C. Carmona-Guzyman, F. Sanchez, C. Piazza. *J. Chem. Soc., Dalton Trans.*, 1265 (1986).
[18] S.K. Saha, M.C. Ghoshand, P. Banerjee. *J. Chem. Soc., Dalton Trans.*, 1301 (1986).
[19] U. Furholz, A. Haim. *Inorg. Chem.*, **26**, 3243 (1991).
[20] S.Y. Shin, R.E. Marquis. *Arch. Microbiol.*, **161**, 184 (1994).