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Kinetics and mechanism of oxo-transfer from pyridine *N*-oxide to dimethyl sulfide catalysed by $[Ru^{III}(edta)(H_2O)]^-$ complex (edta = ethylenediaminetetraacetate)

Debabrata Chatterjee *

Chemistry Section, Central Mechanical Engineering Research Institute, Mahatma Gandhi Avenue, Durgapur, 713209, India

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Abstract

The kinetics of the oxidation of $[Ru^{III}(edta)(H_2O)]^-$ (edta = ethylenediaminetetraacetate) (complex-**1**) with pyridine *N*-oxide (PyO) to $[Ru^{V}(edta)O]^-$ (complex-**2**) and subsequent oxo-transfer from complex-**2** to dimethylsulfide (dms) leading to the formation of dimethylsulfoxide (dmso) have been studied spectrophotometrically. The rate of formation of oxo-complex (**2**) in the reaction of complex-**1** with PyO was found to be substitution controlled and first order both in complex-**1** and PyO concentrations. The rate of oxo transfer from complex-**2** to dms was found to be first order with respect to [complex-**2**] and [dms]. Kinetic data and activation parameters are found to be consistent to the proposed mechanism.

Keywords: Oxo-transfer; Ru-edta complex; Dimethylsulfide; Pyridine *N*-oxide; Kinetics; Mechanism

1. Introduction

In the past couple of years, catalytic ability of Ru- polyaminopolycarboxylate (Ru-pac) ligands towards oxo-functionalisation of organic substrates in the presence of single oxygen atom donors like PhIO, NaOCl, $KHSO_5$, *t*-BuOOH, etc., has been decisively established [1]. Very recently, we had reported [2] selective air-oxidation of dimethylsulfide (dms) to dimethylsulfoxide (dmso) catalysed by $[Ru^{III}(edta)(H_2O)]^-$ (complex-**1**). The present work stems from our interest to explore the possibility of oxygenation of $[Ru^{III}(edta)(H_2O)]^-$ to $[Ru^{V}(edta)O]^-$ (complex-**2**) by pyridine *N*-oxide (PyO) which has not been attempted so far in Ru-pac system, to make comparision with kinetic and mechanistic results reported earlier [2] and to attempt to provide some mechanistic insight about Ru-edta catalysed oxidation of dms to dmso. The present paper reports the results of kinetic and mechanistic investigations of the formation of complex-**2** in the reaction of complex-**1** with PyO and oxo-transfer from complex-**2** to dms to produce dmso in water–dioxan medium.

* Tel.: +91-343-546818; Fax: +91-343-546745.

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2. Experimental

The complex $K[Ru^{III}(Hedta)Cl]$ was prepared and characterised by following the procedure reported earlier [3]. $K[Ru^{III}(Hedta)Cl]$ rapidly gets aquated when dissolved in water [4] and exists predominantly in its most labile form $[Ru^{III}(edta)(H_2O)]^-$ (complex-**1**) in the pH range 5–6. Synthesis and characterisation of the oxo-complex $K[Ru^{V}(edta)O]$ (complex-**2**) were achieved by following the method reported elsewhere [5]. All other chemicals used were of A.R. grade. Double-distilled water was used through the experiment. Kinetics of the reactions were studied spectrophotometrically by using a GBC Cintra 10 spectrophotometer. Formation of complex-**2** in the reaction of complex-**1** with PyO was studied by following the growth of the characteristic oxo-peak (at 390 nm) of complex-**2** [5]. Similarly oxo-transfer from complex-**2** to dms was studied by following the decay of the oxo-peak of complex-**2**. All solutions for kinetic studies were preequilibrated at the experimental temperature before mixing. Rate constant data represented as an average of several kinetic runs are reproducible within $\pm 4\%$. Oxidation product of dms was identified by following the procedure described earlier [2].

3. Results and discussion

3.1. Oxidation of complex-*1* with PyO

Addition of PyO to a solution of complex-**1** resulted in the spectral changes (Fig. 1) owing to the formation of complex-**2** as identified by spectral and electrochemical analysis of the resultant solution and comparing the results with that of reported for complex-**2** [5]. The rate of formation of complex-**2** was found to be first order both at [complex-**1**] and [PyO]. The value of observed rate constant (k_{obs}) under pseudo-first order conditions of excess PyO increased linearly with the increase in [PyO]. Based on the above observation and on general considerations

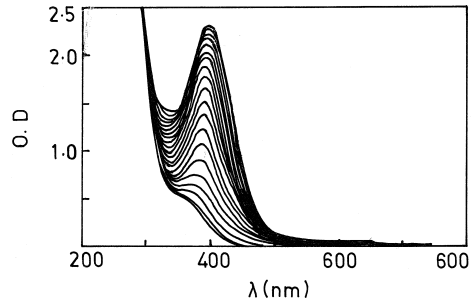

Fig. 1. Formation of complex-**2** in the reaction of complex-**1** with PyO at 25°C [complex-**1**] = 5×10^{-4} M, [PyO] = 1×10^{-3} M, pH = 5.0.

regarding formation of complex-**2** with various single oxygen atom donors [5], the following mechanism is proposed for the formation of complex-**2** in the reaction of complex-**1** with PyO:

$$\left[Ru^{III}(edta)(H_2O)\right]^- + PyO \xrightarrow{k} \left[Ru^{III}(edta)(PyO)\right]^- (\mathbf{1a}) + H_2O, \quad (1)$$

$$\left[Ru^{III}(edta)(PyO)\right]^- (\mathbf{1a}) \xrightarrow{\text{fast}} \left[Ru^{V}(edta)O\right]^- + Py. \quad (2)$$

In the proposed mechanism, PyO reacts with complex-**1** to give an O-bonded intermediate (**1a**) in a rate-determining aquo-substitution step (Eq. (1)). The subsequent and kinetically inconsequential step is the conversion of **1a** to oxo-complex (**2**) involving two electron transfer process through innersphere manner. Additional support in favour of the proposed rate-determining step comes from the observation that the formation of complex-**2** is extremely slow in 50% water–acetonitrile medium. This is because of the fact that in the presence of CH_3CN catalyst complex, $[Ru^{III}(edta)(H_2O)]^-$ converts into a stable and substitution inert $[Ru^{III}(edta)(CH_3CN)]^-$ complex species for which substitution of coordinated CH_3CN with PyO would be very slow as CH_3CN is stronger nucleophile than PyO.

The rate of formation of complex-**2** was studied at three different temperatures and the rate and activation parameters are summarised in Table 1. The small value of $\Delta H^{\neq}$ and a large

Table 1
Rate and activation parameters for the formation of complex-**2** in the reaction of complex-**1** with PyO, [complex-**1**] = 5×10^{-4} M, pH = 5.0

Temperature (°C)	k (M^{-1} s^{-1})	$\Delta H^{\neq}$ (kcal/mole)	$\Delta S^{\neq}$ (cal/deg. mole)
25	1.62×10^{-1}		
35	2.73×10^{-1}	9 ± 2	-29 ± 8
45	4.73×10^{-1}		

negative value of $\Delta S^{\neq}$ are consistent with the proposed mechanism.

3.2. Oxidation of dms by complex-2

The intensity of the oxo-peak of complex-**2** at 390 nm decreases upon addition of dms to the solution of complex-**2**. The final spectrum of the solution was found to be identical with that of complex-**1**. Dmso was to shown be the oxidation product (in the reaction mixture) by product analysis. The rate of reaction was found to be first order both in [complex-**2**] and [dms]. The values of observed rate constant (k'_{obs}) under pseudo-first order conditions of excess dms increased linearly (Fig. 2) with the increase in [dms]. On the basis of the above experimental results, the following working mechanism is proposed for the oxidation of dms (to dmso) by complex-**2**:

$$\left[Ru^{V}(edta)O\right]^{-} + Me_2S \xrightarrow{k'} \left[Ru^{III}(edta)OSMe_2\right]^{-}, \quad (3)$$

$$\left[Ru^{III}(edta)OSMe_2\right]^{-} \xrightarrow[H_2O]{fast} \left[Ru^{III}(edta)(H_2O)\right]^{-} + Me_2SO. \quad (4)$$

It is assumed that the Me_2S (dms) first attacks the oxo-atom of complex-**2** in a rate-determining step involving two electron transfer process to yield an O-bonded $[Ru^{III}(edta)OSMe_2]^{-}$ intermediate, which is unstable and rapidly undergoes hydrolysis to produce Me_2SO (dmso) as oxidation product and complex-**1** back in the reacting mixture. The lability of O-bonded $[Ru^{III}(edta)OSMe_2]^{-}$ towards hydrolysis was reported earlier [2]. Oxidation of dms with complex-**2** was carried out at three different temperatures. The rate and activation parameters summarised in Table 2 seem to be in good agreement to the proposed mechanism. The kinetic and activation parameters include overall demands of O atom transfer step. Though activation parameters are often not discriminating factors to recognise the reaction pathway, the negative entropy of activation ($\Delta S^{\neq}$), however, clearly indicates the operation of an associative mode of activation in the present reaction.

The stoichiometric oxidation of complex-**1** with PyO to complex-**2** and the formation of dmso in the oxidation of dms by complex-**2** both occurred by oxygen atom transfer provides a basis for a catalytic oxidation of sulfide to sulfoxide. However, in practice, the catalytic

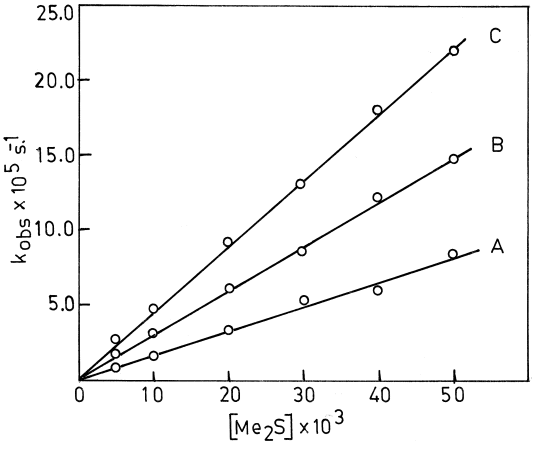

Fig. 2. Effect of [dms] on the observed rate constant (k'_{obs}) values at different temperatures, [complex-**2**] = 5×10^{-4} M, pH = 5.0, (A) 10°C, (B) 20°C and (C) 30°C.

Table 2
Rate and activation parameters for the oxidation of dms by complex-**2**, [complex-**2**] = 5×10^{-4} M, pH = 5.0

Temperature (°C)	$k\times10^3$ (M^{-1} s^{-1})	$\Delta H^{\neq}$ (kcal/mole)	$\Delta S^{\neq}$ (cal/deg. mole)
10	1.69		
20	2.95	11 ± 3	-40 ± 11
30	4.30		

efficiency of the $[Ru^{III}(edta)(H_2O)]^-$/PyO/dms system appeared not to be encouraging in comparison to the results obtained in the oxidation of dms by molecular oxygen [2]. Accumulation of pyridine (Py), which is a strong nucleophile, as the end-product of the reaction of complex-**1** with PyO (Eq. (1)) results in the formation of substitution inert $[Ru^{III}(edta)(Py)]^-$ complex. This problem is not encountered with other oxidants viz. PhIO, NaOCl, $KHSO_5$ as the decomposition products (PhI, Cl^-, HSO_4^-) of these oxidants are not strong nucleophile to substitute aquo molecule from complex-**1**. The picture that emerges for the $[Ru^{III}(edta)(H_2O)]^-$ (**1**) catalysed oxidation of dms to dmso in the presence of single oxygen atom donating agents (XO) comprises of two processes in which the first step involves the formation of high valent Ru(V)-oxo complex (**2**) in the reaction of complex-**1** with XO followed by the oxygen atom transfer from complex-**2** to substrate dms resulting in the formation of end-product, dmso. The ultimate oxygen atom transfer occurs from Ru to S. Interestingly, a different sequence of mechanism is operative when dioxygen (O_2) is the oxygenating source in which the initial step is involved in the formation of an identifiable $[Ru^{III}(edta)(dms)]^-$ intermediate species through the aquo-substitution of $[Ru^{III}(edta)(H_2O]^-$. This $[Ru^{III}(edta)(dms)]^-$ intermediate subsequently interact with O_2 to yield dmso and complex-**1** as final reaction products. The conversion of coordinated dms to end-product dmso in the presence O_2 probably takes place, though a kinetically proposed $\{[Ru^{IV}(edta)(dms)]_2O_2\}^{2-}$ peroxo-intermediate in resemblance with that of reported for $Co(acac)_2$ catalysed oxidation of phosphines [6]. The kinetic parameters include overall contributions arising from homolytic cleavage of peroxo-intermediate and orientational demand within the intermediate to effect O atom transfer coupled with the redox step itself. Now, comparing the kinetic results obtained for complex-**1** catalysed oxidation of dms, it appears unambiguously that the coordination of dms to Ru is the first step when O_2 is the oxidant, whereas, direct attack on the oxo ligand of the high valent oxo-intermediate (2) takes place when terminal oxidants (XO) are used for dms oxidation.

4. Conclusion

In conclusion, the present studies reveal the fact that PyO can also react with complex-**1** to produce Ru(V)-oxo complex (**2**), however, using it in the catalytic oxidation of dms to dmso would not be much effective like other oxidants as catalyst complex (**1**) gets deactivated through the ligation of Py as a side product of the reaction. A comparison of the mechanistic results obtained for various oxidants (XO) [5] and molecular oxygen (O_2) suggests that the oxidation of dms to dmso catalysed by Ru-edta complex in the presence of O_2 [2] is governed by the coordination of dms to Ru. Whereas, oxo transfer from complex-**2** (produced by the interaction of complex-**1** with XO) to dms is associated with the direct attack of dms to the oxo atom of complex-**2**. The former system [2] appears attractive in view of its effectiveness. Further, O_2 is cheap and a clean oxidant for which no side product is formed to deactivate the catalyst, and hence the number of catalytic cycles can be repeated.

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References

[1] D. Chatterjee, Coord. Chem. Rev. 113 (1998) 273.
[2] D. Chatterjee, J. Mol. Catal. A 127 (1997) 57.
[3] A.A. Diamantis, J.V. Dubrawski, Inorg. Chem. 20 (1981) 1142.
[4] T. Matsubara, C. Creutz, Inorg. Chem. 18 (1979) 1956.
[5] D. Chatterjee, H.J. Padhiyar, Ind. J. Chem. A 36 (1997) 956.
[6] R.P. Hanzlih, D. Williamson, J. Am. Chem. Soc. 98 (1976) 6570.