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Thermodynamic fitness of an $Ru^{III}(EDTA)/Ru^{V}=O(EDTA)$ couple in the oxygen atom transfer reactions

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Abstract. The complex $[Ru^{III}(EDTA-H)(H_2O)]$ 1 (EDTA–H = protonated ethylenediaminetetraacetic acid) catalyzes the epoxidation of cyclohexene and the oxidation of PPh_3 to $OPPh_3$ with molecular oxygen or NaOCl as the oxidant. In both the cases, the active catalytic species is the $[Ru^{V}=O(EDTA)]^-$ ion 2 characterized by elemental analyses, UV-vis, infrared spectra and cyclic voltammograms.

When oxygen is used as an oxidant in the reaction, oxidation of the substrates proceeds through a μ-peroxo-Ru(IV) intermediate $[Ru^{IV}(EDTA)(S)]_2O_2^{2-}$ 3 (S = olefin, PPh_3) which undergoes a fast homolytic cleavage of the O–O bond to form $[Ru^{V}=O(EDTA)(S)]$ 4 and a rate determining transfer of O atom to S to form SO and 1. The cleavage of the O–O bond in 3 and O-atom transfer to S proceed in a concerted step.

With NaOCl as an oxidant (excess), oxidation of 1 to 2 proceeds through a unimolecular decomposition of the $[Ru^{III}(EDTA)(OCl)]^{2-}$ intermediate. The transfer of the O-atom from 2 to S proceeds by an associative (*Ia*) pathway involving a concerted cleavage of the Ru=O bond and formation of an SO bond. The free energy (ΔG) values for various steps are computed and the thermodynamic fitness of 2 as an oxidant discussed.

Keywords. Thermodynamic fitness; $Ru^{III}(EDTA)/Ru^{V}=O(EDTA)$ couple; oxygen atom transfer reactions.

1. Introduction

There has been a recent upsurge of interest in oxygenation reactions of organic substrates through metal oxo (Moyer *et al* 1981; Nee and Bruice 1982; Groves and Meyers 1983; Groves and Nemo 1983; Groves and Subramanian 1984; Harlan *et al* 1986; Roecker and Meyer 1987) and metal peroxo (Groves *et al* 1981; Groves and Watanabe 1986) intermediates because of their relevance to reactions catalyzed by cytochrome P-450 oxidase (Collman *et al* 1986) and xanthine oxidase (Holm and Berg 1986). In these model-oxygenase reactions, the catalytically active metal-oxo species is generated by the oxidants H_2O_2, iodosylbenzene, peroxy acids (Groves *et al* 1981; Moyer *et al* 1981; Nee and Bruice 1982; Groves and Meyers 1983; Groves and Nemo 1983; Groves and Subramanian 1984; Groves and Watanabe 1986; Harlan *et al* 1986; Roecker and Meyer 1987) and amine oxides (Woon *et al* 1986).

The complexes of ruthenium in the + 3 oxidation state have evinced a great deal of interest in recent years in view of their use in homogeneous catalysis (Halpern *et al*

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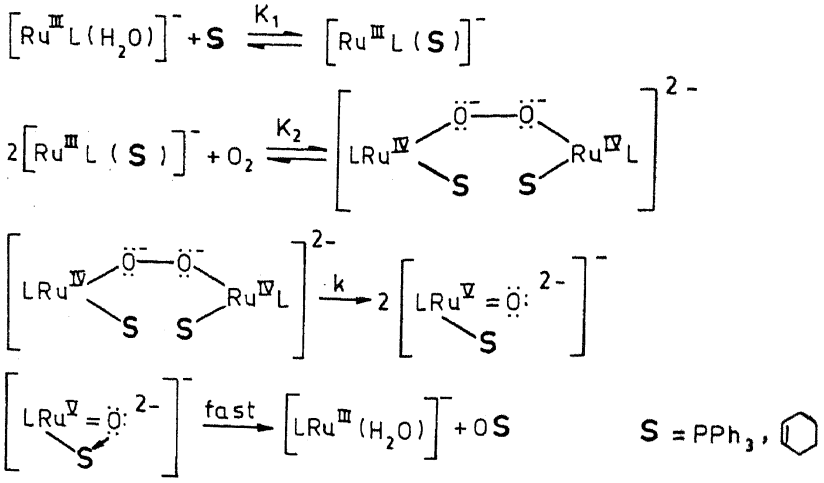

Scheme 1.

1961; Harrod *et al* 1961; Gore 1983; Taqui Khan 1983, 1986). Ru(III)–EDTA has been used as a catalyst in the epoxidation of olefins (Taqui Khan and Prakash Rao 1987; Taqui Khan *et al* 1987), oxidation of PPh_3 (Taqui Khan *et al* 1986) and saturated hydrocarbons (Taqui Khan and Shukla 1988) by molecular oxygen. Ruthenium(III) chloride was employed as a catalyst in the oxidation of allyl alcohol (Taqui Khan and Prakash Rao 1986), cyclohexene (Taqui Khan and Prakash Rao 1989) and 1-hexene (Taqui Khan and Prakash Rao 1988) by molecular oxygen. We have recently reported the oxidation of PPh_3 to $OPPh_3$ (Taqui Khan *et al* 1990b) and cyclohexene to epoxide (Taqui Khan *et al* 1990a) with NaOCl as an oxidant. In the present paper we describe the thermodynamic fitness of $[Ru^{III}EDTA\text{–}H)(H_2O)]$ as a catalyst by computing the ΔG for various steps involving the oxidation of PPh_3 and cyclohexene with molecular oxygen and NaOCl as oxidants. Complex 1 is a much better oxidant than the molybdenum oxo complexes (Harlan *et al* 1986) with a ΔG of -7 kcal/mol as compared to the ΔG of the latter complexes in the range -30 to -35 kcal/mol.

2. Experimental

2.1 *Materials*

Cyclohexene (AR) was distilled and purified before use to remove trace impurities. Triphenylphosphine (AR) was used as such. A fresh solution of cyclohexene was prepared in distilled 1,4-dioxane. The complex $K[Ru(EDTA\text{–}H)Cl]\cdot 2H_2O$ was synthesized by the method reported by Diamantis and Dubrawski (1981). The complex gets rapidly aquated in aqueous solution to give the neutral complex $[Ru^{III}(EDTA\text{–}H)(H_2O)]$ 1. A solution of NaOCl was prepared and titrated with standard thiosulphate (Vogel 1961). AR grade potassium perchlorate was used as supporting electrolyte to maintain the ionic strength (0·1 M) of the solution.

2.2 *Product identification*

The oxidation-product of cyclohexene, the epoxide, was analysed by GLC, IR and NMR measurements. Gas chromatography was done on a Shimadzu Gas Chromatograph GC-9A using a dual flame ionization detector. The IR and proton

NMR of the product were recorded on a Beckman IR-12 spectrophotometer and Jeol FX-100 NMR spectrometer, respectively. The oxidation product of PPh_3, viz. $OPPh_3$ was identified by an ^{31}P NMR spectrum recorded using a Jeol FX-100 NMR spectrometer.

2.3 *Kinetic measurements*

2.3a *Oxidations with molecular oxygen:* Kinetics of the oxidation of cyclohexene and PPh_3 was followed by the oxygen absorption manometric technique in water–dioxan (1:1) mixture at a desired pH and temperature (Taqui Khan and Prakash Rao 1987). Oxygen used in the investigation was 99% pure and was passed through an ascarite tube to remove CO_2 and was pre-saturated with water vapour by streaming through a wash bottle containing the same electrolyte as the reacting solution. As the rate of the reaction is slower than the rate of dissolution of O_2, the reacting solution is considered to be saturated with respect to molecular oxygen at all times and that Henry's law is obeyed. In order to obtain the desired partial pressure of O_2, a mixture of O_2 and N_2 varying in composition from 20–100% was employed. The concentration of the catalyst was in the range 10^{-4}–$2{\cdot}5 \times 10^{-3}$ M and that of the substrate in the range 0·05–0·25 M. The rate of O_2 absorption was obtained from the tangent of the plot of the moles of O_2 absorbed versus time. The rate of oxidation was also measured by measuring the concentration of the epoxide by GLC and that of $OPPh_3$ by ^{31}P NMR spectroscopy.

2.3b *Oxidation with NaOCl:* The kinetics of the oxygenation of $[Ru^{III}(EDTA–H)(H_2O)]$ 1 was studied by following the development of the absorption peak at 393 nm, characteristic of the oxo-complex $[Ru^{V}=O(EDTA)]^-$ by using a Shimadzu UV–vis spectrophotometer equipped with TCC-240A temperature controller. The oxygen atom transfer reaction from $[Ru^{V}=O(EDTA)]^-$ to PPh_3 or to the olefin, cyclohexene, was studied by following the disappearance of the characteristic peak of the oxo-complex at 393 nm. Pseudo first-order conditions were employed for both the oxygenation reaction of $[Ru^{III}(EDTA)(H_2O)]$ (excess of NaOCl) and oxygen atom transfer to PPh_3 or cyclohexene (excess of substrate). The plots of log $(A_\infty - A_t)$ against time were linear upto three half-lives.

2.4 *Synthesis and characterization of* $K[Ru^{V}=O(EDTA)]\cdot 3H_2O$

The oxo-complex 2 was synthesized by adding iodosylbenzene dissolved in 1:1 water–dioxan mixture to a solution of complex 1 in H_2O. The reaction mixture was stirred for 7 h (in the dark) at room temperature and the iodobenzene so formed was extracted with ether. The solution was concentrated at room temperature under vacuum to 2–3 ml. On addition of ethanol (8 ml) dropwise, a greenish brown compound was precipitated. The compound was filtered, washed with alcohol and dried under vacuum. Analysis: C–24·3 (24·1), H–3·3 (3·6), N–5·1 (5·6) (percentages, calculated value in parentheses). The compound absorbs at 393 nm ($\varepsilon_{max} = 8000 \pm 20$). The infrared spectrum of the complex shows an intense band at 860 cm^{-1} corresponding to νRu=O stretch. A cyclic voltammogram of the oxo-complex taken in $HClO_4$–$NaClO_4$ medium at pH 3·0 with a glassy carbon electrode gives $E_{1/2}$ values for the Ru^{5+}/Ru^{4+} couple at + 0·77, Ru^{4+}/Ru^{3+} at + 0·53, Ru^{3+}/Ru^{2+} at 0·01 and

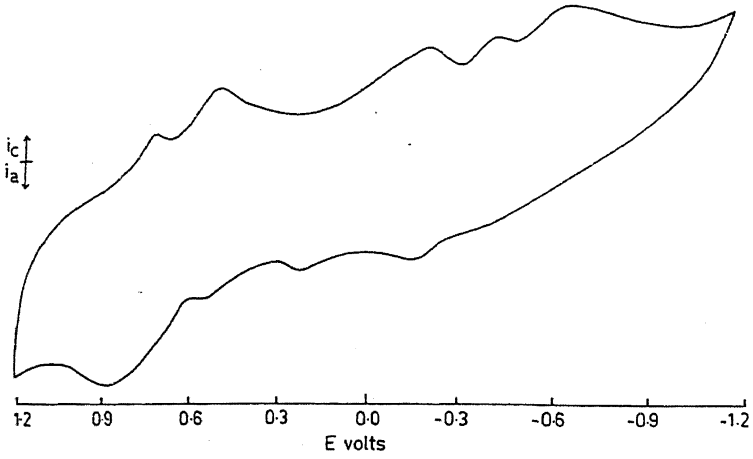

Figure 1. Cyclic voltammogram of the oxo-complex taken in $HClO_4$–$NaClO_4$ medium (pH 3·0) with a glassy carbon electrode.

Ru^{2+}/Ru^{+} at $-0{\cdot}4$ V (figure 1). The $E_{1/2}$ values as reported earlier (Taqui Khan *et al* 1986), are nearly constant at different scan rates.

3. Results and discussion

3.1 *Oxidation with molecular oxygen*

The rate of oxidation of cyclohexene and PPh_3 catalyzed by 1 was found to be first order with respect to the catalyst and substrate and $\frac{1}{2}$-order with respect to O_2 concentration. Saturation kinetics were observed in both the cases at higher concentrations of the olefin or PPh_3. The proposed mechanism is shown in scheme 1.

In the proposed mechanism, the first step involves the formation of a mixed ligand 1:1:1 Ru(III)–EDTA–substrate (olefin, PPh_3) complex 1 in solution. This is followed by the combination of two molecules of the 1:1:1 mixed ligand substrate complex with one molecule of O_2 to yield an intermediate μ-peroxo complex $[Ru^{IV}(EDTA)(S)]_2O_2$. Concerted cleavage of the O–O bond and transfer of O to the substrate take place in the rate determining step to form the oxygenated product, epoxide or $OPPh_3$ with the regeneration of the catalyst 1. The rate constant k for the oxygenation of phosphine was found to be an order of magnitude higher than that for the olefin as expected from the higher π-acidic nature of PPh_3 as compared to the olefin. An important and most interesting feature of the reaction is the transfer of both the O atoms to the substrate in a homo-dioxygenation reaction without the use of a reducing agent. The thermodynamic parameters corresponding to the equilibrium and rate steps in the two reactions are presented in scheme 2.

The ΔG values corresponding to the equilibrium constants K_1 and K_2 are more exothermic for PPh_3 as compared to cyclohexene, reflecting the higher stability of the 1:1:1 complexes involving the phosphine. The ΔG value for the rate-determining O-atom transfer in phosphine is about 2 kcal/mol more exothermic than the olefin.

3.2 *Oxidations with NaOCl*

3.2a *Oxygen atom transfer from NaOCl to 1*: Under the pseudo first-order condition of an excess of NaOCl, a rapid displacement of (H_2O) in $[Ru^{III}(EDTA)(H_2O)]^{-}$ by

Reaction	ΔG (cal/mole) at 298 K
$[Ru^{III}(EDTA\text{-}H)(H_2O)]+\bigcirc \overset{K_1}{\rightleftharpoons} [\bigcirc\text{-}Ru^{III}(EDTA\text{-}H)]$	-2·0
$2[\bigcirc\text{-}Ru^{III}(EDTA\text{-}H)]+O_2 \overset{K_2}{\rightleftharpoons} [\bigcirc\text{-}Ru^{IV}(EDTA\text{-}H)]_2O_2$	-4·3
$2[\bigcirc\text{-}Ru^{IV}(EDTA\text{-}H)]_2O_2 \xrightarrow{k} 2[Ru^{III}(EDTA\text{-}H)(H_2O)]+2\bigcirc\!\!>O$	24·0
$[Ru^{III}(EDTA\text{-}H)(H_2O)+PPh_3 \overset{K_1}{\rightleftharpoons} [Ph_3PRu^{III}(EDTA\text{-}H)]$	-3·12
$2[Ph_3PRu^{III}(EDTA\text{-}H)]+O_2 \overset{K_2}{\rightleftharpoons} [Ph_3PRu^{IV}(EDTA\text{-}H)]_2O_2$	-4·6
$2[Ph_3PRu^{IV}(EDTA\text{-}H)]_2O_2 \xrightarrow{k} 2[Ru^{III}(EDTA\text{-}H)(H_2O)]+2OPPh_3$	22·0

Scheme 2.

NaOCl gives rise to an intermediate $[Ru^{III}(EDTA)(OCl^-)]^{2-}$ complex which transfers an O-atom to 1 in a rate-determining step according to scheme 3.

$$[Ru^{III}(EDTA)(H_2O)]^- + OCl^- \xrightarrow{\text{fast}} Ru^{III}(EDTA)(OCl^-)]^{2-} + H_2O \quad (1)$$

$$[Ru^{III}(EDTA)(OCl^-)]^{2-} \xrightarrow{k} [ORu^{V}(EDTA)]^- + Cl^-. \quad (2)$$

The ΔG value for reaction (2) is 19·0 kcal/mol at 298 K.

3.2b *Oxygen atom transfer from 2 to PPh_3 and cyclohexene*: Under the pseudo first-order condition of excess of the substrate (olefin phosphine) the oxidation of the substrate proceeds according to

$$[Ru^{V}=O(EDTA)]^- + S \xrightarrow{k} SO + [Ru^{III}(EDTA)(H_2O)]^- \quad (3)$$

In the case of the olefin there is evidence (Taqui Khan *et al* 1990a) for the formation of a mixed ligand complex $[Ru^{V}=O(EDTA)(olefin)]$ but for the phosphine there is no evidence of this intermediate as supported by the lack of saturation kinetics in the oxidation of PPh_3 by 2 (Taqui Khan *et al* 1990b). This is in contrast to the reaction with molecular oxygen as oxidant. The ΔG values corresponding to k in reaction (3) for PPh_3 and cyclohexene are 21 and 23 kcal/mole at 298 K. The oxidation of phosphine is, thus, more exothermic by about 2 kcal/mol as compared to that of cyclohexene, a trend similar to that observed in the reaction with molecular oxygen. The ΔG for the rate-determining step k for reactions with molecular O_2 are about 1 kcal/mol more endothermic than the reaction with NaOCl. This reflects on an almost instantaneous cleavage of the O–O bond in the mixed ligand μ-peroxo

complexes of cyclohexene and PPh_3 to give the $Ru^V = O$ species (scheme 2). The slow step in both the mechanisms is, thus, the transfer of an O-atom from an $Ru^V = O$ species to the substrate.

3.3 *Thermodynamic fitness of the (Ru^{III}/Ru^V) oxidation couple*

In order to compute the ΔG value for the reaction

$$[Ru^{III}(EDTA{-}H)(H_2O)] + \tfrac{1}{2}O_2 \rightarrow [Ru^V(EDTA{-}H)(O)], \quad (4)$$

one has to consider the ΔG values for the component steps as shown in scheme 3.

Reaction	ΔG (cal/mole) at 298 K	
$Cl^- + O \longrightarrow ClO^-$	22·6	(5)
$[Ru^{III}(EDTA\text{-}H)(H_2O)] \longrightarrow [Ru^{III}(EDTA)(H_2O)]^- + H^+$	3·5	(6)
$[Ru^{III}(EDTA)(H_2O)]^- + ClO^- \longrightarrow [Ru^V(EDTA)(O)]^- + Cl^-$	19·0	(7)
$[Ru^{III}(EDTA\text{-}H)(H_2O)] + ClO^- \longrightarrow [Ru^V(EDTA\text{-}H)(O)] + Cl^-$	15·5	(8)

Scheme 3.

ΔG for (4) is thus, $\Delta G_{(5)} - \Delta G_{(2)} = -7{\cdot}1$ kcal/mole. The ΔG values for the epoxidation of the olefin and the oxidation of phosphine were reported as (Harlan *et al* 1986).

$$C_6H_{10} + \tfrac{1}{2}O_2 \rightarrow C_6H_{10}(O) \quad -19\,\text{kcal/mole} \quad (9)$$

$$PPh_3 + \tfrac{1}{2}O_2 \rightarrow OPPh_3 \quad -62\,\text{kcal/mole.} \quad (10)$$

Thus, complex 2 with a more positive ΔG value of $-7{\cdot}0$ kcal/mole can transfer the O-atom very readily to an olefin or a phosphine. In the case of $MoO_2(X)$ complexes (Harlan *et al* 1986), the ΔG values are about -30 to -35 kcal/mole. Thus, these complexes can transfer O-atoms to a phosphine but not to an olefin. The ruthenium complex 2 is, thus, a versatile oxidant for any couple with ΔG values more negative than -7 kcal/mole.

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