Oxidation of olefins catalysed by (HEDTA) Ru$^{V} = O$

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Abstract. The complex $K[Ru^{VI}(HEDTA)Cl].H_{2}O$ I and $[(HEDTA) Ru^{V} = O] 2$ were prepared and characterised by elemental analysis, IR, UV-Vis spectroscopy, conductivity, magnetic susceptibility and electrochemical studies (HEDTA = hydroxyethyl-ethylene-diaminetriaceta anion). The kinetics of oxygen atom transfer of $[Ru^{IV}(HEDTA) (H_{2}O)]$ Ia to $[(HEDTA) Ru^{V} = O] 2$ with iodosylbenzene was studied spectrophotometrically by using stopped-flow technique. The oxygen atom transfer from complex 2 to cyclohexene, cyclooctene, styrene, cis and trans-stilbene was studied by the disappearance of the characteristic oxo peak (λ$_{max}$ = 391 nm) at constant pH (3-0) and ionic strength (μ = 0.1 M NaClO$_4$) and also product analysis by gas chromatography (GC). The activation parameters for both the oxygenation of complex 1 to complex 2, and oxygen atom transfer from complex 2 to the organic substrates studied were evaluated and suitable mechanisms proposed.

Keywords. Oxidation of olefins; N-hydroxyethyl-ethylenediaminetriaceta anion (HEDTA); oxygen-transfer kinetics.

1. Introduction

Oxometal complexes have recently gained much importance in the efficient modelling of cytochrome P-450 (Ortuz de Montellario 1986) by porphyrin complexes of Fe(III) (Groves and Subramanian 1984; Ostovic and Bruice 1989; Collman et al 1990), Mn(III) (Robert and Meunier 1988; Querei and Ricci 1989; Quintana et al 1989) and Cr(III) (Geajer and Murray 1985; Garrison and Bruice 1989; Garrison et al 1989) in the presence of oxygen atom donors such as iodosylbenzene, sodium hypochlorite, potassium hydrogenpersulphate and amine-N-oxides. The oxo-complexes of Ru(IV) (Seok and Meyer 1988; Seok et al 1988; Chi et al 1989) and Ru(VI) (Chi and Long 1987; Chi and Wong 1989; Awed et al 1989) were used in the oxygen atom transfer reaction of organic substrates with varying degrees of success. Ru(V)-oxo complexes were, however, comparatively less studied. The oxidation of olefins by the Ru(III)-HEDTA complex in the presence of t-butylhydroperoxide was reported by Zhang and Shepherd (1992). The complex $[(EDTA)Ru^{V} = O]^{-}$ was isolated (Taqui Khan et al 1986b) and used in the oxidation of PPh$_3$ by molecular oxygen. In our earlier communications, we have reported the oxidation of organic compounds catalysed by Ru(III) complexes of non-porphyrinic ligands such as Schiff bases (Taqui Khan et al 1988b) and EDTA (ethylenediaminetetraacetate) (Taqui Khan and Shukla

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1986–1988; Taqui Khan and Prakash Rao 1987; Taqui Khan et al 1988a, 1989, 1990) in the presence of molecular oxygen as oxidant. We have recently extended our studies (Taqui Khan et al 1990) to Ru\textsuperscript{III}-EDTA catalysed oxidation of PPh\textsubscript{3} and organic substrates with PhIO, NaOCl and KHSO\textsubscript{3} as oxidants. In our continued efforts to search for new Ru(III) catalysts for oxidation reactions, we communicate in this paper the synthesis and characterisation of the [(HEDTA)Ru\textsuperscript{V} = O] \textsubscript{2} (HEDTA = N-hydroxyethylendiaminetriacetate anion) complex and stoichiometric oxygen atom transfer from \textsubscript{2} to unsaturated and saturated substrates in water–dioxan media.

2. Experimental

The complex K[Ru(HEDTA)Cl\textsubscript{4}]\textsubscript{2}H\textsubscript{2}O was prepared by following our earlier procedure (Taqui Khan et al 1986a) and characterised by elemental analysis and IR data. Analysis: calculated (found) (\%) C = 26·61 (26·42); H = 3·26 (3·41); N = 6·21 (6·1); vCCO\textsuperscript{−}(antisym) = 1650 cm\textsuperscript{−1}; vCCO\textsuperscript{−}(sym) = 1450 cm\textsuperscript{−1}; vCO(alcoholic) = 1080 cm\textsuperscript{−1}; vRu-N = 520 cm\textsuperscript{−1}; vRu-Cl = 310 cm\textsuperscript{−1}. Iodosylbenzene was prepared by following the literature method (Lucas and Kennedy et al 1955). All other chemicals used were of AR grade. Double-distilled water and purified dioxane were used wherever necessary.

2.1 Synthesis of [(HEDTA)Ru\textsuperscript{V} = O]\textsubscript{2}H\textsubscript{2}O

To a solution (5 ml) of complex \textsubscript{1} (1 mmol) was slowly added iodosylbenzene (1·2 mmol) dissolved in a minimum volume (10 ml) of 1:1 water–dioxane mixture. The reaction mixture was stirred for an hour (in dark) at room temperature, and the iodosobenzene so formed was extracted by ether. The solution was concentrated at room temperature under vacuum to 2–3 ml. On the dropwise addition of dry ethanol, a greenish-brown compound precipitated. The precipitate was immediately washed with alcohol–water mixture (9:1) and dried under vacuum (yield 72% based on complex \textsubscript{1} used, 65·5% based on iodosylbenzene taken). Analysis: calculated (found) (\%) C = 26·08 (25·94); N = 6·76 (6·71); H = 4·11 (4·02); magnetic susceptibility at 298 K \(\mu\textsubscript{eff} = 2·01\) BM. Molar conductivity \(\Lambda_m\) at 298 K = 80·6 ohm, mol\textsuperscript{−1} cm\textsuperscript{2}. Characteristic absorption peaks \(\lambda\textsubscript{max}(\text{nm})/\varepsilon\textsubscript{max}(\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}) = 393 (4700 ± 25).

2.2 X-ray structure

Complex \textsubscript{1} K[Ru(C10 H20 N2 O8 C11)]\textsubscript{2}H\textsubscript{2}O (figure 1) crystallises in the triclinic space group P\textsubscript{1} with \(a = 6·581(1), b = 7·107(1), c = 16·866(3)\) Å, \(\alpha = 91·35^\circ(1), \beta = 95·15^\circ(1), \gamma = 103·39^\circ(2), V = 763(3)\) Å\textsuperscript{3} and \(Z = 2\). The structure solved by direct methods is refined to the final R-index of 0·090 (\(R_w = 0·11\)) for 2458 significant \(|F\textsubscript{obs}| > 3(F\textsubscript{obs})\) reflections. The ligand HEDTA is bound to the ruthenium atom in a pentadentate manner to form four chelate rings with the CH\textsubscript{2}–CH\textsubscript{2}–OH arm uncomplexed and the sixth position on the metal ion occupied by the chloride ion. Ruthenium(III) coordination in the complex can be described as distorted octahedral. The Ru(III)-Cl bond distance of 2·397(3) Å is much longer than the sum of the van der Waals radius of the individual atoms. The free CH\textsubscript{2}–CH\textsubscript{2}–OH arm exhibits rotational disorder
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(rotation angle \(\sim 113^\circ(3)\)) about the \(\text{CH}_2 - \text{CH}_2\) bond with hydroxyl oxygen taking two distinct sites with equal probabilities in the crystal lattice.

2.3 Physical measurements

Microanalysis of complexes 1 and 2 was carried out by the use of Carlo Erba elemental analyser. Conductivity was measured at 30°C on a Digisum conductivity meter. IR spectra were recorded on a Carl Zeiss spectrophotometer. The electronic spectra were recorded on a Shimadzu UV-160 Spectrophotometer.

Cyclic voltammetric and differential pulse polarographic measurements were carried out on a Princeton Applied Research (PAR) Instruments model 174A with polarographic analyzer. The measurements were carried out with glassy carbon electrode (working) and standard calomel reference electrode (SCE) in aqueous \(\text{HClO}_4\) (0·1 M) at a fixed pH 1·0.

Magnetic susceptibilities of complex 2 were measured at room temperature (298 K) with a PAR 155 vibrating sample magnetometer. The pH measurements were carried out on a digisum pH meter with an accuracy of \(\pm 0.01\) unit.

2.4 Kinetic measurement

The kinetics of oxygenation of complex 1 with iodosylbenzene was studied spectrophotometrically by using HI-TECH Stopped-Flow Spectrophotometer
equipped with Apple IIe data analyser. The time course of the reaction was followed by monitoring the growth of the oxo-peak of complex 2 at 391 nm. For this purpose solution of iodosylbenzene was prepared by dissolving solid iodosylbenzene in 1:1 water–dioxane mixture by stirring with a magnetic stirrer in the dark. The supernatant liquid was separated and immediately titrated iodometrically with standard thiosulphate solution in presence of sodiumboreate. The iodosylbenzene (PhIO₂) if formed due to disproportionation of iodosylbenzene cannot oxidise iodide to iodine (Lucas and Kennedy et al 1955). The concentration of iodozylbenzene thus obtained is not, however, the true concentration of iodosylbenzene in solution but represents the total oxidising equivalents irrespective of the nature of different species formed due to different side reactions including disproportionation of iodosylbenzene. By this technique 2.5 × 10⁻³ M of solution of iodosylbenzene can be prepared. It is important to note that the solution of iodosylbenzene cannot be preserved, since it loses its oxidising power within a few hours. The stoichiometric oxygen atom transfer from complex 2 to organic substrates was studied by a conventional mixing technique using Shimadzu UV-160 A Spectrophotometer equipped with TCC 240 A temperature controller. For this purpose, equal volumes of complex 2 (2 × 10⁻⁴ M) and the substrate of the desired concentration (range from 2 × 10⁻³ to 2 × 10⁻⁲ M) were mixed in a spectrophotometric cell. The kinetic solutions were pre-equilibrated before mixing at the desired temperature. The time-course of the reaction was studied by following the disappearance of the oxo-peak of complex 2 at 391 nm with time.

2.5 Product analysis

The products were identified by ¹³C NMR spectra recorded on a JEOL FX-100 NMR Spectrometer and gas chromatography (Shimadzu GC-9A Gas Chromatograph) by using a stainless steel column containing 10% carbowax 20 M on 90–100 mesh Anakrom working on TCD. Authentic samples of oxidation products of the substrates were used to quantify the GC parameters. A thermal conductivity detector (TCD) at 200°C using nitrogen as carrier gas was used for product analysis. For identification of reaction products of the oxidation of cis-stilbene and trans-stilbene, the reaction mixture was extracted with diethylether and after solvent (ether) evaporation the residue was quantitatively transferred to an NMR tube using CDCl₃ as the solvent. ¹H NMR spectra of the reaction products were recorded using TMS as internal standard. Signals for epoxidic proton for cis-isomer were found at δ = 4.42 (singlet) and δ = 3.87 (singlet) for the trans-isomer. No mixture of cis- and trans-epoxide was present in any of the reactions involving the oxidation of cis- or trans-stilbene.

3. Results and discussion

The complex [Ru⁶⁺(HEDTA)Cl] 1 gets aquated rapidly to give the neutral species [Ru⁶⁺(HEDTA)H₂O] 1a at pH ( < 3) and to anionic [Ru⁶⁺(HEDTA)(OH)]⁻ 1b at high pH ( > 5), respectively (Bajaj and Eldik 1989a). The spectra of aquo- and hydroxo-complexes 1 and 1b are shown in figure 2. On addition of PhIO to a solution of Ru⁶⁺(HEDTA) (H₂O) 1 a new peak appeared at 393 nm (figure 2). The peak, which is characteristic of the oxo-complex 2, was assigned to dπ* → t₂g,Ru V charge transfer transition. The IR spectrum of complex 2 shows a peak at 895 cm⁻¹ corresponding
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Figure 2. Absorption spectra of complex 1, (a) at low pH (\(<3\)); (b) at high pH (\(>6\)) and (c) complex 2.

Table 1. Cyclic voltammogram data of \( \text{LRu}^V(\text{O})(\text{L} = \text{EDTA-H, PDTA-H and HEDTA}) \) in 0.1 M HClO4 medium, pH = 1.0. All potentials are reported in volt (V) vs SCE, working electrode was glassy carbon, scan rate 50 mV/s.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \text{E}^{1/2} \text{(Ru}^5+/\text{Ru}^4+) )</th>
<th>( \text{E}^{1/2} \text{(Ru}^4+/\text{Ru}^3+) )</th>
<th>( \text{E}^{1/2} \text{(Ru}^3+/\text{Ru}^2+) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ru}^V(\text{EDTA-H})) (\text{O}) )</td>
<td>0.99</td>
<td>0.10</td>
<td>-0.17</td>
</tr>
<tr>
<td>( \text{Ru}^V(\text{PDTA-H})) (\text{O}) )</td>
<td>0.98</td>
<td>0.20</td>
<td>-0.24</td>
</tr>
<tr>
<td>( \text{Ru}^V(\text{HEDTA})) (\text{O}) )</td>
<td>0.86</td>
<td>0.10</td>
<td>-0.24</td>
</tr>
</tbody>
</table>

to \( v(\text{Ru} = \text{O}) \) stretch. The position of the band agrees with those reported for other \( \text{Ru}^V = \text{O} \) complexes; \([\text{(EDTA)}\text{Ru}^V = \text{O}]^- \) and \([\text{PDTA}]\text{Ru}^V = \text{O}]^- \) at 890 cm\(^{-1}\), \([\text{Ru}^V = \text{O}((\text{O}_2\text{C})\text{C}\text{Et}_2)]_2 \) \(\text{2} \) (Dengel \textit{et al} 1989) at 900 cm\(^{-1}\), \([\text{Ru}^V = \text{O}((\text{N}_2\text{O})2^+ \text{N}_2\text{O} = \text{polydentate pyridylamine ligand}) \) (Chi \textit{et al} 1990) at 872 cm\(^{-1}\). The strong broad band around 1630–1640 cm\(^{-1}\) is due to coordinated carboxylate groups (Nakamoto 1970). The far-infrared spectrum of the oxo-complex 2 exhibits peaks at 530 and 410 cm\(^{-1}\) region assigned to \( v(\text{Ru-N}) \) and \( v(\text{Ru-O}) \), respectively. The absence of any band at 310 cm\(^{-1}\) confirms the complete removal of chloride ion from the coordination sphere of \([\text{(HEDTA)}\text{Ru}^{3\text{Cl}}] \) by the oxo group.

To confirm the oxidation state of ruthenium in the oxo-complex 2, electrochemical studies were carried out using glassy carbon electrode (working) and SCF (reference) electrode at \( \mu = 1.0 \) in 0.1 M HClO\(_4\) medium. The cyclic voltammograms (figure 3) of the oxo-complex 2 give \( E^{1/2} \) values at 0.86 V, 0.10 V and -0.24 V for \( \text{Ru}^5+/\text{Ru}^4+ \), \( \text{Ru}^{4+/\text{Ru}^3+} \) and \( \text{Ru}^{3+/\text{Ru}^2+} \) redox couples, respectively. The \( E^{1/2} \) values are more or less constant at different scan rates (10–100 mV sec\(^{-1}\)). The \( E^{1/2} \) values for the \( \text{Ru}^5+/\text{Ru}^3+ \) and \( \text{Ru}^{4+/\text{Ru}^3+} \) are more negative than those for \( \text{O} = \text{Ru}^V(\text{EDTA}) \) \(3\) and \( \text{Ru}^V = \text{O}(\text{PDTA}) \) \(4\) complexes (Taqi Khan \textit{et al} 1992) (table 2).
Figure 3. Cyclic voltammogram (CV) of complex 2 in 0.1 M HClO₄ medium at pH = 1.0, working electrode glassy carbon, scan rate = 50 mV/s.

Table 2. Kinetic and activation parameters for the reaction Ru²⁺(HEDTA)(H₂O) + PhIO → Ru⁺ = O(HEDTA) + PhI + H₂O [Ru²⁺(HEDTA)(H₂O)] = 1 × 10⁻⁴ M, pH = 3.0 and η = 0.1 M (NaClO₄).

<table>
<thead>
<tr>
<th>System</th>
<th>Temperature (°C)</th>
<th>k(M⁻¹s⁻¹)</th>
<th>ΔH° (k cal/mol)</th>
<th>ΔS° (cal/deg.mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru²⁺(HEDTA)(H₂O)</td>
<td>30</td>
<td>8.0</td>
<td>9.3</td>
<td>-18.8</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>12.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>22.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>*Ru²⁺(EDTA)(H₂O)⁻</td>
<td>30</td>
<td>70.1</td>
<td>8.8</td>
<td>-21.2</td>
</tr>
<tr>
<td>*Ru²⁺(PDTA)(H₂O)²⁻</td>
<td>30</td>
<td>75.8</td>
<td>8.1</td>
<td>-23.0</td>
</tr>
</tbody>
</table>

*From Taqui Khan et al (1990)

The Ru(V)-oxo complex 2 is paramagnetic with μ_eff = 2.1 BM which is slightly higher than expected for one unpaired spin (S = 1/2) system due to some orbital contribution to the magnetic moment. A μ_eff of 2.2 BM was observed for the complex [Ru⁺ = O(N₂O)²⁺]. Complex 2 is a nonelectrolyte with a molar conductivity of λ_m = 80.7 ohm⁻¹ mol⁻¹ cm² in water.
3.1 Kinetics of oxygenation of complex 1 with PhIO

The kinetics of formation of the oxo-complex 2 was studied by monitoring the appearance of the characteristic oxo-peak at 391 nm. The reaction rate was found to be first order with respect to complex 1 concentration. At the specified conditions of pH 3.0 and ionic strength \( \mu = 0.1 \text{ M NaClO}_4 \) the value of observed rate constant \( (k_{\text{obs}}) \) increases linearly with the increase in the iodosylbenzene concentration. Based on the above kinetic results, the following mechanism is proposed for the oxygenation of complex 1 to complex 2 with iodosylbenzene.

\[
[Ru^{III}(HEDTA) (H_2O)] + \text{PhIO} \rightarrow [Ru^{III}(HEDTA) (OI\text{Ph})]^{\text{fast}} \\
[(HEDTA)Ru^{V} = O] + \text{PhI.}
\] (1)

At pH 3.0, the concentration of hydroxo-species 1a can be neglected and only aquo complex 1 may be considered to be involved in the above reaction. At pH 5.0, two parallel reactions as outlined below are supposed to occur in the oxygenation process.

\[
[Ru^{III}(HEDTA)(H_2O)] + \text{PhIO} \rightarrow [HEDTA]Ru^{V} = O] + \text{PhI} + H_2O,
\] (2)

\[
[Ru^{III}(HEDTA)(OH)^- + \text{PhIO} \rightarrow [(HEDTA)Ru^{V} = O] + \text{PhI} + OH^-.
\] (3)

The rate of the formation of the oxo-complex can be expressed as:

\[
\frac{d[\text{HEDTA}]Ru^{V} = O]}{dt} = k[Ru^{III}(HEDTA)(H_2O)][\text{PhIO}] + k[Ru^{III}(HEDTA)(OH)^-][\text{PhIO}],
\] (4)

considering the following acid dissociation equilibrium

\[
[Ru^{III}(HEDTA)(H_2O)] \leftrightarrow [Ru^{III}(HEDTA)(OH)^-] + H^+ \\
K_a = 4.95 \pm 0.05 \text{ at } \mu = 0.2 \text{ M KCl, } t = 25^\circ C.
\] (5)

The following rate expression in terms of the total concentration of complex 1 \( ([Ru^{III}]_T) \) can be derived:

\[
\frac{d[[\text{HEDTA}]Ru^{V} = O]}{dt} = \frac{k[H^+] + K_a [Ru^{III}]_T[\text{PhIO}]}{[H^+] + K_a}
\] (6)
or

\[
k_{\text{obs}} = \frac{k[H^+] + K_a}{[H^+] + K_a} [\text{PhIO}].
\] (7)

At low pH \( ([H^+] > K_a) \) (7) can be reduced to \( k_{\text{obs}} = k_1[\text{PhIO}] \), which is in accord with the experimental results.
The rate of oxygenation of \([\text{Ru}^{III}\text{(HEDTA)}(\text{H}_2\text{O})]\) to \([(\text{HEDTA})\text{Ru}^{V}=\text{O}]\) is about an order of magnitude slower than those for \([\text{Ru}^{III}\text{(EDTA)}(\text{H}_2\text{O})]^- 3 \) and \([\text{Ru}^{III}\text{(PDTA)}(\text{H}_2\text{O})]^- 4 \). This trend is in general agreement with the rate of substitution of \(\text{H}_2\text{O}\) by other groups in complexes 3 and 4 where the \(\text{H}_2\text{O}\) group is very labile (Baja and Eldik 1988). The rates of oxygenation of complex 1 with PhIO at three temperatures along with the values of \(H^\#\) and \(S^\#\) are recorded in table 2. The enthalpies and entropies of the oxygenation of 1 with PhIO are tabulated in table 4 along with the corresponding values for complexes 3 and 4. The enthalpies and entropies become more positive in the order \([\text{Ru}^{III}\text{(EDTA)}(\text{H}_2\text{O})]^- > [\text{Ru}^{III}\text{(PDTA)}(\text{H}_2\text{O})]^- > [\text{Ru}^{III}\text{(HEDTA)}(\text{H}_2\text{O})]\) as per the decreasing order of rate of oxygenation of these complexes.

3.2 Kinetics of oxygen transfer from complex 2 to olefins

The kinetics of oxygen atom transfer from complex 2 to the olefins viz., cyclohexene, cyclooctene, styrene, cis- and trans-stilbenes was studied spectrophotometrically in 1:1 water–dioxane medium by monitoring the disappearance of the characteristic oxo-peak of complex 2 at 391 nm at a constant \(p\text{H} 3\) and 0 ionic strength = 0.1 M (\(\text{NaClO}_4\)). Under the pseudo-first order condition of excess substrate concentration, the reaction is first order with respect to complex 2 concentration. The value of pseudo-first order rate constant \((k_{\text{obs}})\) increases with increase in olefin concentration and at higher olefin concentrations, a limiting rate is attained. One such rate plot for the dependence of cyclohexene epoxidation is shown in figure 4. The observed

![Graph showing the dependence of \(k_{\text{obs}}\) on [cyclohexene] at different temperatures.](image)

**Figure 4.** Dependence of \(k_{\text{obs}}\) on [cyclohexene] at different temperatures [complex 2] = 1 \(\times 10^{-4}\) M, \(p\text{H} 3.0\) and \(\mu = 0.1\) M (NaClO4) (A) 30°C, (B) 40°C and (C) 50°C.

\[
\text{LRu}^{V} + \text{L} \rightleftharpoons K_1 \text{LRu}^{V}\text{O} \xrightarrow{k_1} \text{LRu}^{III}\text{(H}_2\text{O}) + \text{O} \text{C} \xrightarrow{k_1} \text{LRu}^{III}\text{(EDTA)}(\text{H}_2\text{O})\]

\(L = \text{HEDTA}, \ S = \text{Olefin}, \ SO = \text{epoxide}.

**Scheme 1.**
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saturation in \( k_{obs} \) values at high olefin concentration can be explained in terms of the mechanism outlined in scheme 1, for which the rate expression is as follows.

\[
k'_{obs} = \frac{k_1 K_1 [S]}{1 + K_1 [S]},
\]

(8)

\[
1/k'_{obs} = \frac{1}{K_1} + \frac{1}{k_1 K_1 [S]}
\]

(9)

In the proposed mechanism, it is suggested that the oxo-ruthenium complex \( 2 \) first reacts with olefins to form an oxo-alkyl intermediate (metallaaxetane)\( (Collman \ et \ al \ 1985) \). Subsequent oxygen atom transfer from ruthenium to substrate in intermediate (I) takes place in a rate-determining step. At high substrate concentration, a limiting rate was observed due to saturation of intermediate (I) with substrate. Further increase in concentration of olefins only changes its bulk concentration without effecting the rate of epoxidation. Though we have proposed a metallaaxetane intermediate in our mechanism, it is only based on the stereoselective formation of the epoxides. Radical cation intermediates \( (Castellino \ and \ Bruice \ 1988) \) or radical ion-pair intermediates \( (Ostovic \ and \ Bruice \ 1989b) \) always give small quantities of rearranged products which were not detected in our case.

The presence of resonating radical intermediates of the type \( \text{ORu}^{III}(\text{HEDTA}) \leftrightarrow \text{ORu}^{IV}(\text{HEDTA}) \leftrightarrow \text{O}^2^- - \text{Ru}^V(\text{HEDTA}) \) were proposed by Zhang and Shepherd \( (1992) \) in the oxidation of olefins by \( \text{Ru}^{III}(\text{HEDTA}) \) in the presence of \( t \)-butylhydroperoxide. This system did not epoxidize cyclohexene but rather gave 2-cyclohexene-1-one. The oxidation of \emph{cis}-stilbene by this system gave 63-5\% \emph{cis}-stilbene oxide and 11\%

\[ \text{Cyclohexene} \times 10^{-3} (M^{-1}) \]

\[ 1/k_{obs} \times 10^4 \]

\[ 0 \quad 0.1 \quad 0.2 \quad 0.3 \quad 0.4 \quad 0.5 \]

\[ \frac{1}{[\text{Cyclohexene}]} \times 10^{-3} (M^{-1}) \]

\[ 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6 \]

\[ n \]

\[ A \]

\[ B \]

\[ C \]

\[ \frac{1}{k_{obs}} \]

\[ \frac{1}{\text{Cyclohexene}} \]

\[ \text{at different temperatures (A) 30°C (B) 40°C and (C) 50°C.} \]
Table 3. Rate and activation parameters for the reaction \( \text{Ru}^{v} = \text{O(HEDTA)} + \text{S} \rightarrow \text{Ru}^{u} \text{(HEDTA)(H}_{2}\text{O)} + \text{SO} \) \( [\text{Ru}^{v} = \text{O(HEDTA)}] = 1 \times 10^{-4} \text{M}, \text{ pH} = 3.0, \) and \( \mu = 0.1 \text{ M (NaClO)}_{4}. \)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Temperature (°C)</th>
<th>( k_{\text{ex}} \times 10^{4} \text{s}^{-1} )</th>
<th>( \Delta H^{#} ) (k cal/mol)</th>
<th>( \Delta S^{#} ) (cal/deg mole)</th>
</tr>
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<tbody>
<tr>
<td>Cyclohexene</td>
<td>30</td>
<td>0.84</td>
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<td>-44.3</td>
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<td>Cis-stilbene</td>
<td>30</td>
<td>0.36</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.89</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>1.49</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trans-stilbene</td>
<td>30</td>
<td>0.28</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.68</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>1.35</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4. Oxidation of unsaturated hydrocarbon by \( \text{Ru}^{v} = \text{O(HEDTA)} \) complex.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Products formed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexene</td>
<td>Cyclohexene oxide (51)</td>
</tr>
<tr>
<td>Cyclooctene</td>
<td>Cyclooctene oxide (57)</td>
</tr>
<tr>
<td>Styrene</td>
<td>Styrene oxide (45)</td>
</tr>
<tr>
<td>Cis-stilbene</td>
<td>Cis-stilbene oxide (35)</td>
</tr>
<tr>
<td>Trans-stilbene</td>
<td>trans-stilbene oxide (33)</td>
</tr>
</tbody>
</table>

*Yield calculated on the basis of oxo-complex concentration in 1:1 stoichiometric reaction (products obtained less than 1% are neglected here).

Trans-stilbene, however, gave 65.1% of cis-stilbene oxide with no trans-product. In our system, however, trans-stilbene gave 33% trans-epoxide and cis-stilbene, 35% of cis-stilbene oxide. The epoxidation of cyclohexene and cyclooctene gave no allylic oxidation products but clear epoxides. Thus, the \( \text{Ru}^{v} = \text{O(HEDTA)} \) complex seems to have some free radical character in stilbene oxidations.

Plots of \( 1/k_{\text{obs}}^{1} \) vs \( 1/[S] \) (9) were linear in all cases. One such plot is shown in figure 3. The values of \( k_{1} \) (calculated from intercepts) at different temperatures are recorded in table 3.

The oxygen atom transfer reactions were studied at three different temperatures and the activation parameters \( \Delta H^{\#} \) and \( \Delta S^{\#} \) calculated with the help of the Eyring equation are presented in table 5.

The reaction has low values of \( \Delta H^{\#} \) and large negative values of \( \Delta S^{\#} \) supporting an associative mechanism for the formation of an olefin complex prior to the oxygen atom transfer reaction.
Oxidation of olefins catalysed by (HEDTA) RuV = O

On the basis of the rate constant values (table 3) the observed reactivities of the olefins towards epoxidation decrease in the order cyclooctene > cyclohexene > styrene > cis-stilbene > trans-stilbene. The most reactive olefins in this series is cyclooctene due to its strong nucleophilicity and flexible geometry. The aromatic olefins are less reactive than cyclooctene and cyclohexene. The least reactivity of trans-stilbene may be due to the steric effect of the bulky trans phenyl groups. The percent yield (calculated on the basis of complex 2 concentration) of the oxidation products obtained from the stoichiometric epoxidation of olefins with complex 2 are listed in table 4. The rate of epoxidation of olefins by 2 is much slower than that observed by complexes 3 and 4.

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