

# Ru(III) analogue of model methane monooxygenase in the effective catalytic oxidation of cyclohexane by molecular oxygen

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## Abstract

The catalytic oxidation of cyclohexane to cyclohexanol by Ru(III) analogue of the model methane monooxygenase (MMO) system, involving complex  $[\text{Ru}_2\text{O}(\text{Py})_6-\mu-(\text{AcO})_2(\text{PF}_6)_2$  **1** (pyridine, Py; acetate, AcO) as a catalyst and molecular oxygen as the oxidant was investigated in a 60:40 (v/v) mixture of acetone and water. In typical experiments at 303 K and  $p\text{O}_2 = 5$  atm,  $5 \times 10^{-2}$  M of cyclohexanol was found to be formed in 7 h with  $4.54 \times 10^{-4}$  M of the catalyst from oxidation of  $8.84 \times 10^{-2}$  M of cyclohexane. Spectrophotometric, electrochemical, NMR, gas chromatographic and kinetic techniques were used to study the catalytic species and the oxidation reactions in solution. The kinetic studies indicated first order dependence in terms of the concentrations of the catalyst (complex **1**), cyclohexane and molecular oxygen. On the basis of kinetics and experimental results, a non-radical, ionic mechanism is suggested for oxidation of cyclohexane. The activation parameters for oxidation of cyclohexane evaluated from temperature dependence are:  $E_a = 33.98 \text{ kJ mol}^{-1}$ ,  $\Delta H^\ddagger = 31.48 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -215.86 \text{ J } (\text{ }^\circ \text{ mol})^{-1}$  and  $\Delta G^\ddagger = 96.90 \text{ kJ mol}^{-1}$ .

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**Keywords:** Oxidation; Cyclohexane; Kinetics; Catalysis; Methane monooxygenase

## 1. Introduction

The active site of the non-heme iron protein, hemerythrin (Hr) is  $\mu$ -oxo- $\mu$ -dicarboxylato diiron core [1]. A large number of  $\mu$ -oxo- $\mu$ -diacetato diiron(III) complexes have been synthesised to model the core in natural systems [2]. Methane monooxygenase (MMO), another such protein, has a similar core as the active site [3]. Ruthenium, the next member of the group, also forms the  $\mu$ -oxo- $\mu$ -dicarboxylato complexes and there is growing interest [4–9] in order to compare the chemistry of iron and ruthenium

complexes with the core. In spite of the role of Hr and MMO in oxygen transport and C–H activation, very few studies have been done on this aspect of  $\mu$ -oxo- $\mu$ -dicarboxylato diiron(III) complexes. Much of the reported work involves synthesis and study of magnetic [10–13] and electronic properties [14–23]. A  $\mu$ -oxo- $\mu$ -dicarboxylato diiron(III)  $[\text{Fe}_2\text{O}(\text{Hpz})_2 \mu-(\text{AcO})_2]$  (bis pyrazolyl borate, Hpz) complex has been shown to mimic MMO and to catalyse oxidation of cyclohexane and adamantane to corresponding alcohols by  $\text{O}_2$  [24]. Complex  $[\text{Fe}_2\text{O}(\text{AcO})_2\text{Cl}_2(\text{bipy})_2]$ , catalysed selective oxidation of cyclohexane to cyclohexanone by  $\text{O}_2$  is also reported [19]. A  $\mu_3$ -O ( $\text{Fe})_3$  cluster with acetato bridges is reported [25] to be the active species in GIF system, which catalyses the oxidation of hydrocarbons.

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During our studies with [Ru EDTA H (H<sub>2</sub>O)] and amino acids, it was observed that a  $\mu$ -oxo complex with acetato bridges from amino acids is formed [26]. This complex [26] catalyses oxidative deamination of amino acids. This prompted us to explore the catalytic properties of  $\mu$ -oxo- $\mu$ -carboxylato diruthenium, for the oxidation of saturated hydrocarbons by O<sub>2</sub>. In many studies oxidation of hydrocarbons are reported in presence of oxidants like H<sub>2</sub>O<sub>2</sub> [27,28], *tert*-BuOOH [19], peracids [29], by electrochemical oxidation [30], iodosyl benzene [31–33], sodium hypochlorite [34,35], and KHSO<sub>5</sub> [36,37] rather than O<sub>2</sub>. In this paper, we report the kinetic, mechanistic and catalytic studies on the oxidation of saturated hydrocarbon, cyclohexane by O<sub>2</sub> using [Ru<sub>2</sub>O(Py)<sub>6</sub>- $\mu$ -(AcO)<sub>2</sub>] (PF<sub>6</sub>)<sub>2</sub> **1** as catalyst, referred to as the ruthenium analogue of the MMO.

## 2. Experimental

### 2.1. Materials

RuCl<sub>3</sub> was purchased from Johnson Mathey. Iolar-2 grade argon (4 ppm O<sub>2</sub>), oxygen, nitrogen and hydrogen gases were purchased from Department of Special Gases, Indian Oxygen Ltd., Bombay. Nitrogen gas used was passed through vanadyl sulphate, potassium pyrogallate and dried over ascarite. Organic solvents (BDH, E.Merck) and reagents were purified prior to use by reported methods [38]. Deuterated solvents were purchased from Cambridge Isotope Laboratories. All other reagents were of AR grade and were used without further purifications.

### 2.2. Measurements

Spectrophotometric experiments were done by a temperature controlled (TCC-240) Shimadzu-160 UV–VIS spectrophotometer using matched cuvettes of quartz of 2 or 10 mm path lengths. For recording spectra under argon, solutions were transferred to cuvettes by using Schlenk technique. For conducting experiments with O<sub>2</sub>, appropriate precautions were taken to avoid evaporation of volatile solvents. Cyclic voltammetry was done by EG&G PAR electrochemical system using glassy carbon electrode and potentials were reported versus Ag/AgClO<sub>4</sub>. NMR

spectra were recorded by Bruker 500 MHz FT-NMR at Tata Institute of Fundamental Research, Bombay. Elemental analyses were carried out on Carlo Erba 1106 elemental analyser.

### 2.3. Product measurements

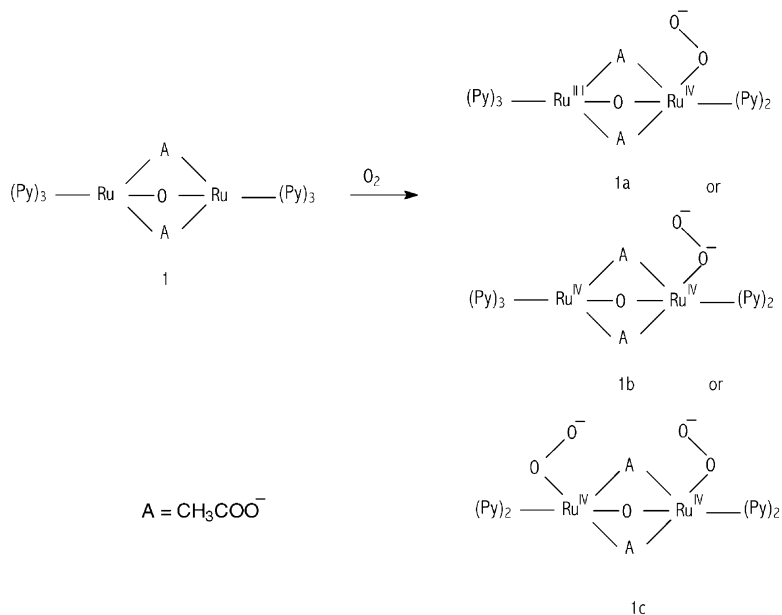
Product analysis was done by a Shimadzu gas chromatograph GC-9A assembled with programmed and computerised chromatopac CR-3A recorder and FDD 1A using a stainless steel column, 3 mm i.d.  $\times$  4 mm o.d.  $\times$  2.00 m, containing 10% carbowax 20M on 90–100 mesh Anakron on FID. A flame ionisation detector at column temperature 313–443 K, injection temperature 498 K and with nitrogen as carrier gas, was used in present investigations. Before performing the product analysis, pure samples of cyclohexane, cyclohexanol and cyclohexanone were run separately as well as in a mixture. A blank containing 1 mmol of complex and 100 mmol each of cyclohexane, cyclohexanol and cyclohexanone was also run. In these conditions cyclohexanol and cyclohexanone were easily separated at retention times 14.90 and 12.20 min, respectively. A total of 10  $\mu$ l of samples, withdrawn during the course of the oxidation, were analysed and the amount of product formed was estimated by comparing the peak areas with the blank.

### 2.4. Kinetic measurements

An appropriate quantity of the catalyst was dissolved in 60 ml of 60:40 (v/v) mixture of acetone and water, containing suitable amount of cyclohexane. Reactions were carried out at different temperatures and atmospheric pressures of molecular oxygen by using an autoclave (pressure reactor) of 300 ml capacity (M/S Parr. Inst. Co., USA) having provisions for, stirring, maintenance of temperature and sample withdrawing. The pressure reactor was evacuated and flushed with oxygen to ensure that a complete oxygen atmosphere prevails in the reactor. Molecular oxygen was directly pressurised at required pressure from the oxygen gas cylinder. Samples of 0.5 ml were withdrawn from the reactor at suitable intervals and the kinetics of the oxidation reaction was followed gas chromatographically by directly estimating the amount of product formed with time. During the reaction the oxygen gas cylinder was continuously attached with

reactor and after withdrawing the sample, the reactor was repressurised with oxygen every time. The solubility of O<sub>2</sub> in mixed solvent (60:40, acetone–H<sub>2</sub>O) was computed from the reported solubility data of O<sub>2</sub> at 1 atm in pure solvents [39,40] by using Henry's law. Rate constants ( $k_{\text{obs}}$ ) in forms of the concentration of

Ar (Fig. 1a). However, spectrum in acetone–H<sub>2</sub>O under O<sub>2</sub> exhibited an initial shift to 574 nm ( $\epsilon = 8050$ ; Fig. 1b), followed by a further shift to 556 nm ( $\epsilon = 5470$ ; Fig. 1b') and no further shift was noted even after a week. This shift in  $\lambda_{\text{max}}$  evidenced the interaction of O<sub>2</sub> with complex **1** to form dioxygen complexes as given in reaction 1.



cyclohexanol were computed from the slopes of the plots of concentration of cyclohexanol versus time.

### 3. Results and discussion

#### 3.1. Characterisation of species in solution

Complex [Ru<sub>2</sub>O(Py)<sub>6</sub>- $\mu$ -(AcO)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> **1** used as a catalyst, was prepared by a reported procedure [4]. Characterisation of species of complex **1** in suitable solvents and in presence of dioxygen were done spectrophotometrically, electrochemically, kinetically and by NMR. Absorption spectra of complex **1** in acetonitrile, acetone, acetonitrile–H<sub>2</sub>O (60:40 v/v) and acetone–H<sub>2</sub>O (60:40 v/v) under Ar are presented in Fig. 1a. All the spectra, similar to earlier report [4] exhibited a band at 581 nm ( $\epsilon = 10,000$ ). In all the above said solvents, except in acetone–H<sub>2</sub>O, absorption spectra under O<sub>2</sub> were found to be similar with those under

Formation of  $\mu$ -peroxo complex in reaction 1 can be ruled out on the basis of disposition of the facial bonds [4], while formation of **1c** was ruled out, on the basis of kinetic results which indicated interaction of 1 mol of O<sub>2</sub> as well as electrochemical studies which indicated an asymmetric structure. Since absorption spectrum under O<sub>2</sub> showed a shift to 574 nm followed by further shift to 556 nm, it is possible that formation of complex **1a** occurs firstly and then it is converted to **1b**.

As it is mentioned earlier, that the interaction of **1** takes place with O<sub>2</sub> in the acetone–H<sub>2</sub>O and not in other solvents, this may be due to the non-availability of the sites for coordination of O<sub>2</sub>. Bindings of trans to  $\mu$ -oxo pyridines with Ru, are comparatively weaker than those of cis to  $\mu$ -oxo pyridines [4]. Trans pyridines are also found to be exchanged with deuterated pyridines. Thus, the form of occurrence of equilibrium in solution is as given in

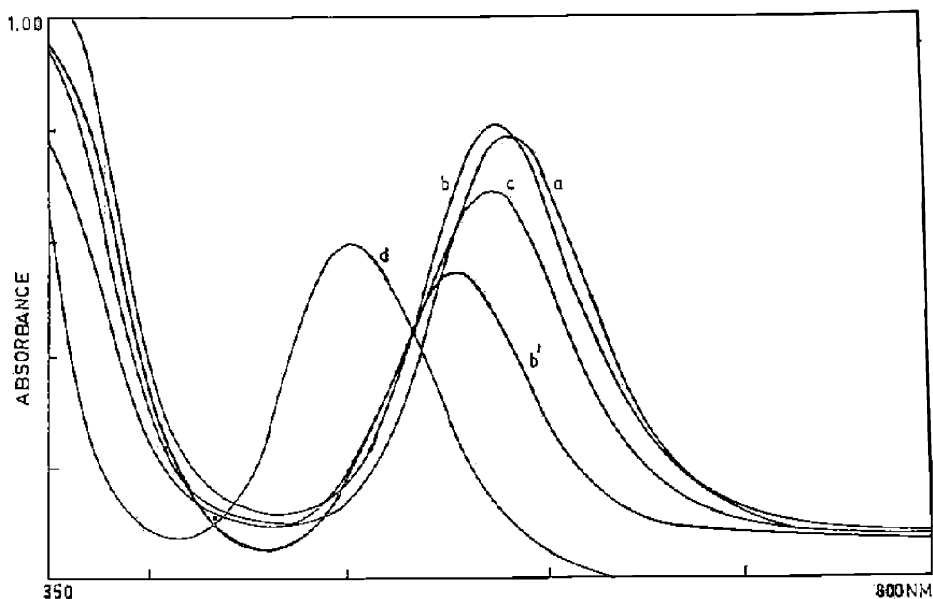
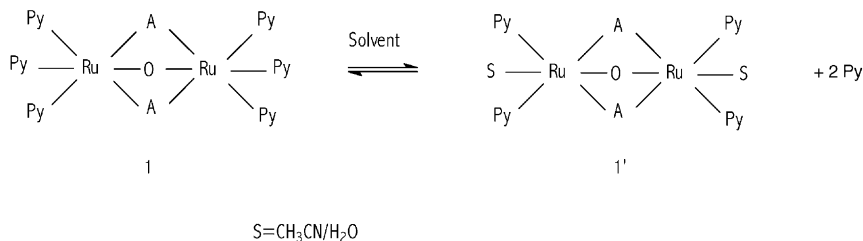


Fig. 1. Absorption spectrum of **1** (a) in  $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{CN-H}_2\text{O}$  (60:40), acetone and acetone- $\text{H}_2\text{O}$  (60:40) under Ar, (b, b') in acetone- $\text{H}_2\text{O}$  (60:40) under  $\text{O}_2$ , (c) after oxidation at 0.5 V and (d) after oxidation at 1.0 V, at 308 K,  $\mu = 0.10$  (TBAP), and  $[\mathbf{1}] = 1 \times 10^{-3}$  M.

reaction 2.



In the solvents acetonitrile and acetonitrile- $\text{H}_2\text{O}$ , trans sites available are occupied by acetonitrile and in the acetone equilibrium lies far to the left. Acetonitrile and pyridine are good donors and oxygen is unable to replace these ligands. In the solvent acetone- $\text{H}_2\text{O}$ , the sites are occupied by water molecules, and these molecules have potential to be replaced by  $\text{O}_2$  to form dioxygen complex(s) **1a/1b**. These contentions were confirmed by NMR studies. Although absorption spectral changes have been explained in terms of formation of a dioxygen complex, they can as well be accounted for, by the oxidation of ruthenium(s) without coordination of  $\text{O}_2$ . However, this was ruled out by conducting coulometric experiments by oxidising the solution at 1.0 V ( $2e^-$  oxidation) and

0.5 V ( $1e^-$  oxidation) and by comparing their absorption spectra with that of **1** under  $\text{O}_2$ . Spectra of solutions, oxidised at 1.0 V (4,4) and 0.5 V (4,3) exhibited bands at 503 nm ( $\epsilon=6250$ ; Fig. 1d) and at 567 nm ( $\epsilon=6250$ ; Fig. 1c), respectively. The spectrum of **1** under  $\text{O}_2$  showed a peak at 556 nm. Since the band at 556 nm is in between the 3,4 and 4,4 species, one may conclude that due to incomplete transfer of electrons from  $\text{Ru(III)} \rightarrow \text{O}_2$ , on formation of peroxy complex the oxidation state of two ruthenium lies between 3,4 and 4,4. If merely  $\text{O}_2$  would have oxidised the ruthenium then one would have expected the spectrum similar to that of the ruthenium species 4,4. Involvement of  $\text{O}_2$  was further confirmed by the catalytic studies,

Table 1

Electrochemical data for complex **1** under N<sub>2</sub> and O<sub>2</sub> at  $T = 303\text{ K}$ ,  $\mu = 0.10$  (TBAP: tetra butyl ammonium perchlorate) and  $[1] = 1 \times 10^{-3}\text{ M}$

Condition		$E$ versus Ag/AgClO <sub>4</sub> (V)	
CH <sub>3</sub> CN under Ar	$E_{pc}$	+0.93	−0.42 (−0.40)
	$E_{pa}$	+0.97 (+0.79)	−0.20
CH <sub>3</sub> CN under O <sub>2</sub>	$E_{pc}$	+0.92	−0.42
	$E_{pa}$	+0.97 (+0.79)	−0.19 (−0.40)
Acetone–H <sub>2</sub> O (60:40) under Ar	$E_{pc}$	+0.90	−0.43
	$E_{pa}$	+0.97 (+0.725)	−0.25 (−0.35)
Acetone–H <sub>2</sub> O (60:40) under O <sub>2</sub>	$E_{pc}$	+0.85 (+0.50)	−0.20 (−0.45)
	$E_{pa}$	+0.92	−0.275

in which oxidation of cyclohexane to cyclohexanol which was found to occur in presence of O<sub>2</sub>, could not occur when cyclohexane was electrochemically oxidised at 1.00 V.

### 3.2. Electrochemical studies

In order to substantiate the spectrophotometric results, electrochemical studies were also performed with acetonitrile and acetone–H<sub>2</sub>O and the corresponding data are given in Table 1.

The CV of complex **1** in acetonitrile (Fig. 2a) exhibited two cathodic peaks at +0.93 and −0.42 V corresponding to the reactions 4,4/4,3 and 4,3/3,3. In the oxidation cycle, CV exhibited two anodic peaks at −0.20 and +0.97 V corresponding to the oxidations 3,3/4,3 and 4,3/4,4. Two smaller anodic peaks were also observed as shoulders at −0.40 and +0.79 V. These two smaller peaks were not exhibited when scan was reversed at +0.75 V. These two smaller peaks may be due to the presence of complex **1** and its solvent complex existing in equilibrium (reaction 2). If this was so then in the reductive sweep such a behaviour was also expected. Although the cathodic peak at −0.42 V gave an indication of two peaks (more pronounced in repetitive scan between 0.0 and −0.80 V), but no such indication was found for cathodic peak at −0.93 V. Probably oxidation to 4,4 species shifted the equilibrium towards left (reaction 2). The fact that two cathodic peaks at −0.42 V became more pronounced, when scanned between 0.09 and −0.80 V, but not when scanned between 1.4 and 1.0 V, lend support to the argument. The earlier mentioned

assignments were confirmed by conducting coulometric experiments at +0.5 V (1e<sup>−</sup>) and +1.00 V (2e<sup>−</sup>).

The CV of complex **1** in acetone–H<sub>2</sub>O under Ar (Fig. 2b) was almost similar to that in acetonitrile with minor shifts in some of the peaks (Table 1), however, CV under O<sub>2</sub> was quite different (Fig. 2c). Anodic peaks were shifted towards right, while cathodic peaks were splitted. Repetitive scan showed decrease in currents of cathodic peaks only. These observations can be accounted for by considering the following sequence of reaction (Scheme 1).

Although possibility of coordination of two oxygen molecules with two ruthenium centres exist but based on kinetic experiments showing first order dependence in O<sub>2</sub>, and existence of splitted peaks in CV indicating the structure to be asymmetric, coordination of dioxygen with one of the ruthenium ion is shown in Scheme 1.

### 3.3. NMR

It had been shown that pyridines trans to  $\mu$ -oxo in complex **1** are replaceable by pyridine d<sub>5</sub> [4]. NMR indicated that the displacement of more coordinated pyridines occurred on increasing the concentration of pyridine d<sub>5</sub> and as a consequence signal corresponding to free pyridine showed an increase in the area (Fig. 3a) [4]. This enabled us to mark the free pyridine in NMR at 8.7 ppm and to use it to confirm the existence of equilibrium (reaction 2) in solution. Comparison of the area of the peak of the free pyridine, in acetonitrile d<sub>3</sub> (Fig. 3b) and acetone d<sub>6</sub> (Fig. 3c) indicated that area of the peak in acetonitrile was higher

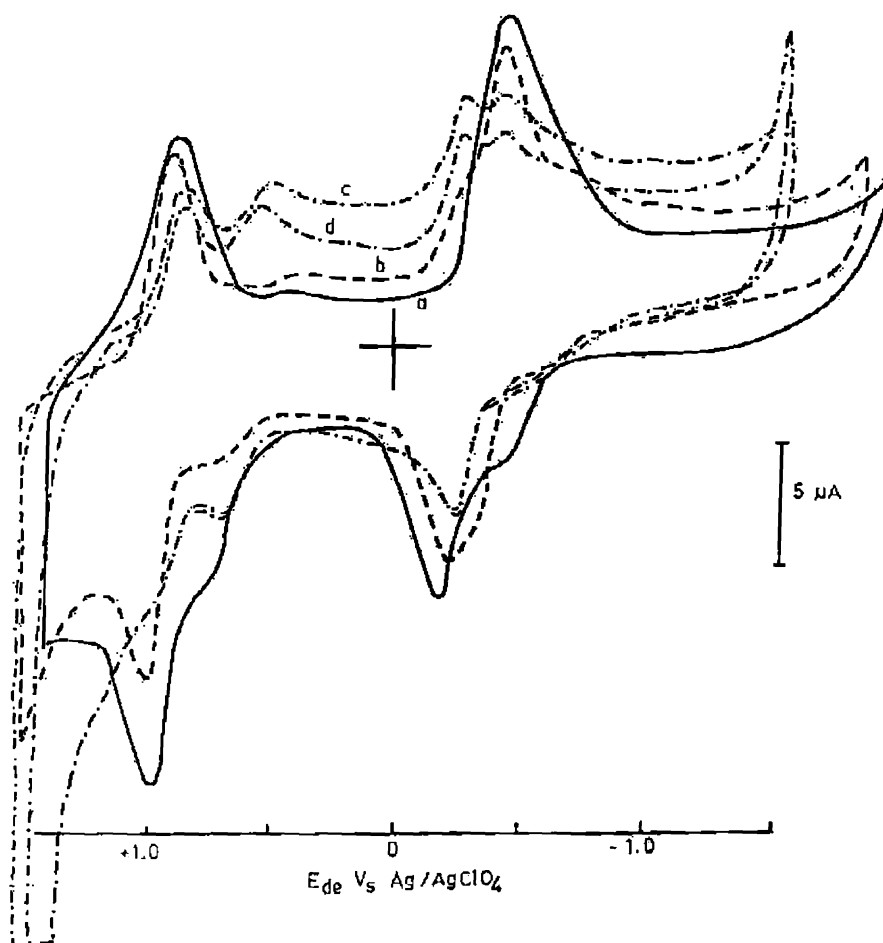
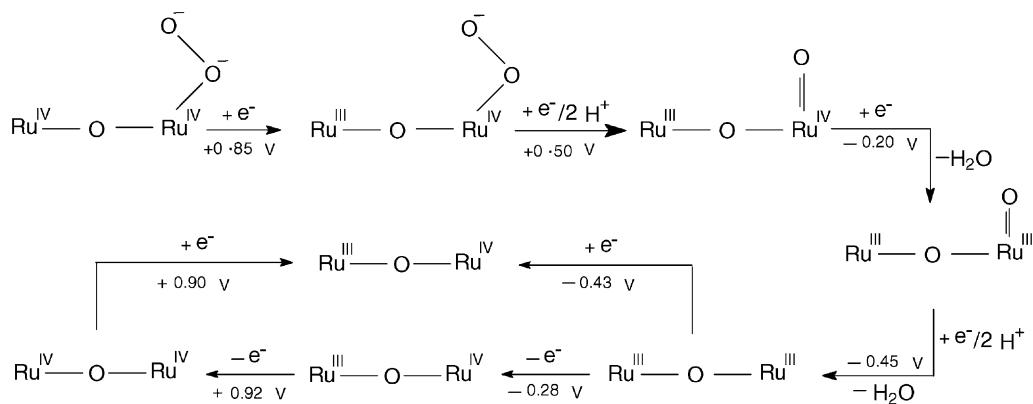


Fig. 2. Cyclic voltammogram of **1** (a) in CH<sub>3</sub>CN, under Ar, (b) in acetone–H<sub>2</sub>O (60:40) under Ar, (c) in acetone–H<sub>2</sub>O (60:40) under O<sub>2</sub> and (d) repetitive scan of (c), at 308 K,  $\mu = 0.10$  (TBAP) and  $[1] = 1 \times 10^{-3}$  M.



Scheme 1.

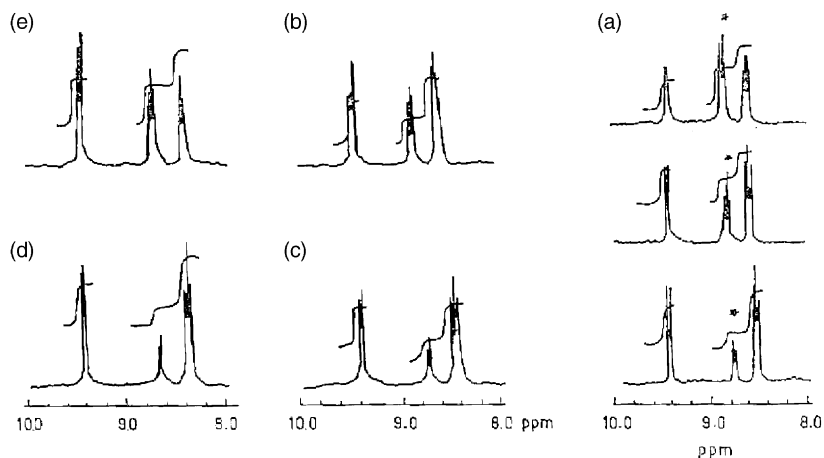


Fig. 3. 500 MHz NMR spectrum of **1**: (a) in  $\text{CD}_3\text{CN}$ : effect of increasing the concentration of pyridine  $\text{d}_5$ . The peaks marked (\*) due to free pyridine are showing an increase (lower to upper spectrum) in the area; (b) in  $\text{CD}_3\text{CN}$ ; (c) acetone  $\text{d}_6$ ; (d) acetone  $\text{d}_6$ - $\text{D}_2\text{O}$  (80:20); (e) acetone  $\text{d}_6$ - $\text{D}_2\text{O}$  (60:40).

than that of in acetone. This can be explained as due to the replacement of coordinated pyridine (reaction 2) by acetonitrile. However, in the case of poor coordinating solvent acetone in comparison to acetonitrile, the displacement of coordinated pyridine was found to be less. In acetone  $\text{d}_6$ - $\text{D}_2\text{O}$ , the area of free pyridine peak increased on increasing the  $\text{D}_2\text{O}$  content in the mixture (Fig. 3d and e). This is explained as due to the replacement of coordinated pyridine by  $\text{D}_2\text{O}$  as explained earlier. Thus, NMR experiments further supported the earlier given explanations.

#### 3.4. Product of oxidation

In typical experiments of oxidation of cyclohexane, containing  $4.54 \times 10^{-4}$  M catalyst,  $8.84 \times 10^{-2}$  M cyclohexane at 5 atm pressure of molecular oxygen and 303 K,  $5 \times 10^{-2}$  M, neat cyclohexanol (57% conversion based on initial amount of cyclohexane) was formed in 7 h. with initial rate of formation of cyclohexanol,  $12.5 \times 10^{-5}$  M  $\text{min}^{-1}$ .

#### 3.5. Kinetics of oxidation reactions

Kinetics of oxidation of cyclohexane was investigated in detail as a function of the concentration of cyclohexane, molecular oxygen, catalyst and temperature. The plots of formation of cyclohexanol from

the oxidation of cyclohexane with time (Fig. 4) was found to be linear for 7 h and after that formation slowly started attaining saturation. In the  $p\text{O}_2$  range, 2–15 atm, almost linear formation of neat cyclohexanol was observed up to  $\sim 7$  h, however, on increasing the time and analysing the samples at 24 h, formation of little cyclohexanone was also observed. In the experimental conditions of Fig. 4, at 5 atm pressure of  $\text{O}_2$ , 57% neat cyclohexanol was found to be formed

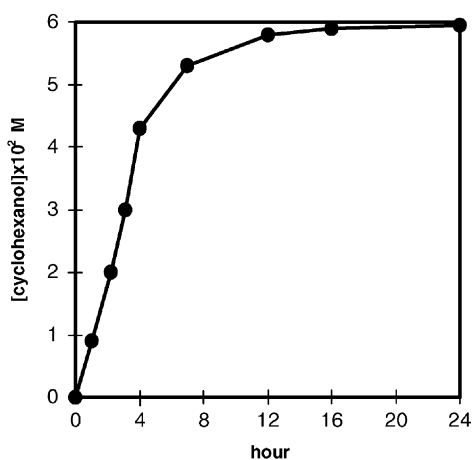


Fig. 4. Time dependent plot of the formation of cyclohexanol at 303 K,  $[\text{I}] = 4.54 \times 10^{-4}$  M,  $[\text{cyclohexane}] = 8.84 \times 10^{-2}$  M and  $\text{O}_2$  pressure = 5 atm.

in 7 h. The sample analysed at 24 h gave 67% cyclohexanol and 1.5% cyclohexanone. Based on this experimental observation of the linear formation of the cyclohexanol for  $\sim 7$  h, the rate constants  $k_{\text{obs}}$  were suitably determined by estimating the amount of cyclohexanol formed up to 8 h and for that five samples (0.5 ml) were withdrawn at suitable time intervals and were analysed by gas chromatography for all the kinetic studies.

### 3.6. Dependence of the rate on catalyst concentration

The oxidation of cyclohexane was studied by conducting the experiments at 303 K at different concentrations of the catalyst, keeping the concentrations of other reactants constant. Fig. 5 shows the first order kinetic plot of rate constant versus catalyst concentration ( $d \log k_{\text{obs}}/d \log [\text{catalyst}] = 1$ ).

### 3.7. Dependence of the rate on molecular oxygen concentration

Experiments conducted at different atmospheric pressure (2–15 atm) of molecular oxygen at 303 K with  $[\text{catalyst}] = 4.45 \times 10^{-4}$  M and  $[\text{cyclohexane}] = 8.84 \times 10^{-2}$  M and  $k_{\text{obs}}$  obtained:  $k_{\text{obs}} \times 10^5 \text{ M min}^{-1}$  ( $p_{\text{O}_2}$  in atm): 5.10 (2), 12.61 (5), 18.28 (10) and 21.82 (15) indicated that the rate of formation of cyclohexanol increased with increasing  $p_{\text{O}_2}$  up to 15 atm pressure. Further increase in oxygen pressure

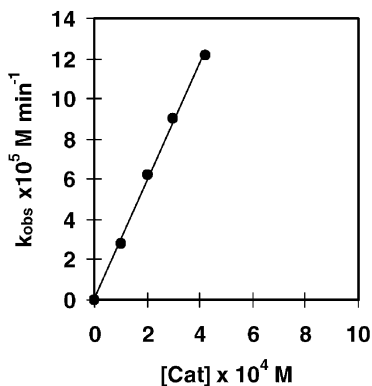


Fig. 5. Kinetic plot showing first order dependence in catalyst concentration at 303 K,  $[\text{cyclohexane}] = 8.84 \times 10^{-2}$  M and  $\text{O}_2$  pressure = 5 atm.

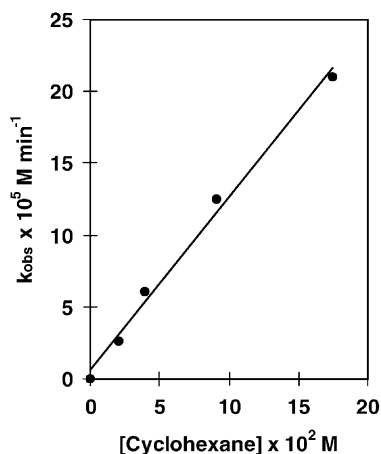


Fig. 6. Cyclohexane concentration dependence plot for the oxidation of cyclohexane at 303 K,  $[\text{I}] = 4.54 \times 10^{-4}$  M and  $\text{O}_2$  pressure = 5 atm.

did not much increase the formation of cyclohexanol. Hence towards lower pressure, the rate of formation of cyclohexanol was found to be first order dependent in molecular oxygen concentration.

### 3.8. Dependence of the rate on cyclohexane concentration

Kinetic experiments conducted at different initial concentrations of cyclohexane (Fig. 6) by keeping the concentrations of other reactants and physical conditions constant indicated a first order dependence in  $[\text{cyclohexane}]$ .

### 3.9. Dependence of the rate on temperature

In order to evaluate the activation parameters of the oxidation of cyclohexane, the experiments for the rate measurements were conducted at 293, 303 and 313 K and corresponding rates ( $k_{\text{obs}} \times 10^5 \text{ M min}^{-1}$ ) obtained were 8.00, 12.60, and 19.42, respectively. The evaluated activation parameters given in Table 2 indicated that both, the activation energy and highly negative entropy values, are favourable for activation of C–H bond of cyclohexane for its oxidation to cyclohexanol. The dissociation energy of C–H bond which is  $401.28 \text{ kJ mol}^{-1}$  at 298 K for cyclohexane [40] is highly reduced to  $33.98 \text{ kJ mol}^{-1}$



Table 2

Comparison of activation parameters for oxidation of cyclohexane with closely related reaction systems

Reaction system	Oxidant	$E_a$ (kJ mol <sup>-1</sup> )	$\Delta H^\ddagger$ (kJ mol <sup>-1</sup> )	$\Delta S^\ddagger$ (J ° mol <sup>-1</sup> )	$\Delta G^\ddagger$ (kJ mol <sup>-1</sup> )	Reference
[Ru <sub>2</sub> O(Py) <sub>6</sub> -μ-(AcO) <sub>2</sub> ] (PF <sub>6</sub> ) <sub>2</sub>	O <sub>2</sub>	33.98	31.48	-215.86	96.90	This work
Ru(III)-EDTA-ascorbate	O <sub>2</sub>	48.86	44.31	-155.92	91.55	[41]
Ru(III)-EDTA-CTAB	O <sub>2</sub>	51.41	48.91	-112.86	83.62	[42]
Ru(III)-EDTA-ascorbate	H <sub>2</sub> O <sub>2</sub>	49.32	46.82	-150.50	91.54	[43]
([EDTA Ru(V) (O)] <sup>-1</sup> ) <sup>a</sup>	-	35.95	33.44	-229.91	103.12	[44]
([PDTA Ru(V) (O)] <sup>-1</sup> ) <sup>a</sup>	-	35.95	33.44	-234.08	104.36	[44]

<sup>a</sup> Used as oxidants.

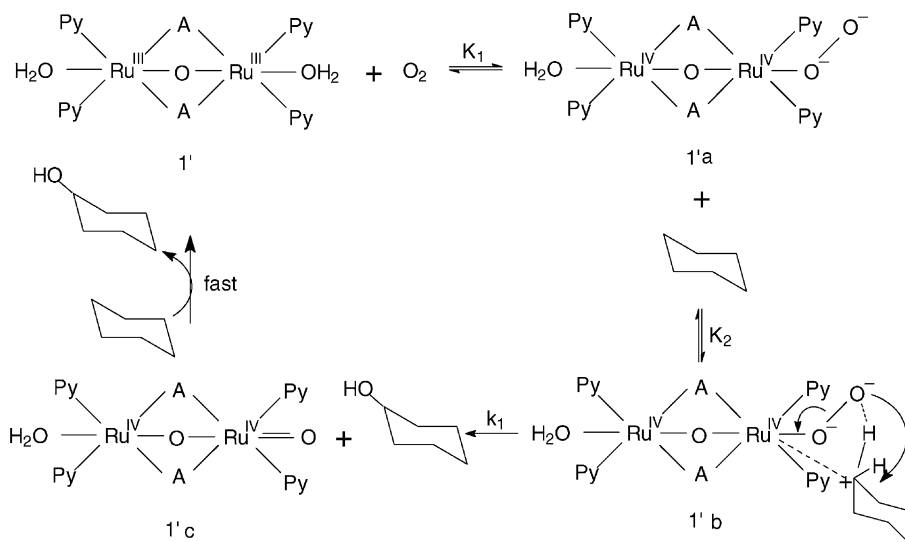
through the activation of C–H bond. Ruthenium complexes used as catalysts [41–43] as well as oxidants [44], are reported to be associated with very low activation energies during the oxidation of cyclohexane to cyclohexanol. It is of interest to compare the activation parameter of oxidation of cyclohexane to cyclohexanol with closely related reaction systems (Table 2) associated with very low activation energies.

Activation energies associated with reaction systems 2, 3 and 4 are almost comparable and their entropies are significantly low. Both, activation energies and entropies associated with reaction system 1, 5 and 6 are almost identical and lower than those associated with reaction systems 2–4.

### 3.10. Mechanism and rate expression

On the basis of kinetic results, product analysis and other experimental evidences, a mechanism proposed for oxidation of cyclohexane by molecular oxygen is given in Scheme 2.

In the proposed mechanism, molecular oxygen first co-ordinates with diaquated complex **1'** and forms complex **1'a** by replacing a water molecule in equilibrium step  $K_1$ . The formation of the complex **1'a** in solution has been characterised and substantiated on the basis of spectrophotometric and electrochemical evidences. In presence of cyclohexane, **1'a** reacts in preequilibrium step  $K_2$ , forming kinetic intermediate complex **1'b**. Formation of complex **1'b** is proposed



Scheme 2.

on the basis of first order dependence in cyclohexane concentration. In kinetic intermediate complex **1'b**, cleavage of the C–H bond takes place by forming a carbonium ion resulting from the hydride abstraction from a C–H bond. The rate determining step  $k$  involves the concerted cleavage of O–O bond and transfer of one of the oxygen atoms to the carbonium ion centre to yield cyclohexanol followed by formation of ruthenyl oxo (Ru(IV) = O) complex **1'c**. Complex **1'c** further reacts with another molecule of cyclohexane to give yet another molecule of cyclohexanol and the catalyst **1'**. The experimental value of the kinetic isotope effect  $k_H/k_D$  for oxidation of  $C_6H_{12}$  and  $C_6D_{12}$  was found to be 3.48. The kinetic isotope effect of similar order ( $\sim 3.48$ ) for the hydroxylation of cyclohexane, though lower compared to other systems [45] is also reported, for the cleavage of the C–H bond of cyclohexane by hydride abstraction in the rate determining step in the Ru(III)-EDTA-ascorbate system catalysed oxidation of cyclohexane to cyclohexanol, by molecular oxygen [41,46,47]. Non-radical, ionic mechanism via formation of carbonium ion by hydride abstraction, was also found to be more reasonable to propose in Scheme 2, as no positive evidence for formation of radical intermediate was obtained on adding a radical trapping agent, acrylonitrile in the reaction mixture. The mechanism is equivalent to oxygen atom insertion in the C–H bond by an ionic route reported by Sugimoto and Sawyer [48,49].

On the basis of kinetic observations and product formation the rate law for the oxidation of cyclohexane to cyclohexanol (Eq. (1)) was derived by considering a steady-state concentration of the catalyst.

$$\frac{[\text{Cat}]_T}{k_{\text{obs}}} = \frac{1}{k_1 K_1 K_2 [\text{C}_6\text{H}_{12}] [\text{O}_2]} + \frac{1}{k_1 K_2 [\text{C}_6\text{H}_{12}]} + \frac{1}{k_1} \quad (1)$$

$$\frac{[\text{Cat}]_T}{k_{\text{obs}}} = \frac{1}{[\text{C}_6\text{H}_{12}]} \left( \frac{1}{k_1 K_1 K_2 [\text{O}_2]} + \frac{1}{k_1 K_1} \right) + \frac{1}{k_1} \quad (2)$$

where  $[\text{Cat}]_T$  is the total concentration of the catalyst. The plots of  $[\text{Cat}]_T/k_{\text{obs}}$  versus  $[\text{cyclohexane}]^{-1}$  (Eq. (2)) and  $[\text{Cat}]_T/k_{\text{obs}}$  versus  $[\text{O}_2]^{-1}$  (Eq. (1)) depicted in Figs. 7 and 8, respectively, gave non-zero

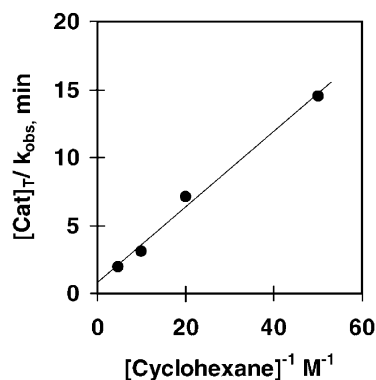


Fig. 7. Plot of  $[\text{Cat}]_T/k_{\text{obs}}$  vs.  $[\text{cyclohexane}]^{-1}$  at 303 K.  $[\text{I}] = 4.54 \times 10^{-4}$  M and  $\text{O}_2$  pressure = 5 atm verifying rate expression.

intercepts and positive slopes verifying the rate expressions.

The constants  $k_1$ ,  $K_1$  and  $K_2$  calculated kinetically from the analysis of the kinetic data with the help of slopes and intercepts of Eqs. (1) and (2), by substituting the required known concentration values are:  $k_1 = 80 \times 10^{-2} \text{ min}^{-1}$ ,  $K_1 = 762 \text{ M}^{-1}$  and  $K_2 = 47 \text{ M}^{-1}$  at 303 K.

From the preceding discussion it is clear that complex **1** activates  $\text{O}_2$  and catalyses the oxidation of cyclohexane in moderate conditions, of temperature and pressure in which cyclohexanol is selectively formed as the oxidation product. Iron and palladium based

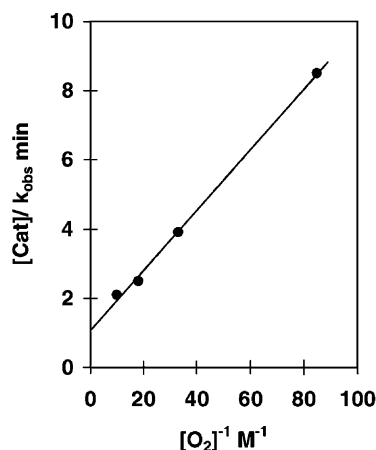


Fig. 8. Plot of  $[\text{Cat}]_T/k_{\text{obs}}$  vs.  $[\text{O}_2]^{-1}$  at 303 K.  $[\text{I}] = 4.54 \times 10^{-4}$  M and  $[\text{cyclohexane}] = 8.84 \times 10^{-2}$  M.

bimetallic catalysts are also reported [50] to be selective for oxidation of cyclohexane to cyclohexanol by molecular oxygen in the solvent, acetone.

#### 4. Conclusions

Investigations towards total oxidation of cyclohexane [51] are in progress. In present system, complex  $[\text{Ru}_2\text{O}(\text{Py})_6-\mu-(\text{AcO})_2](\text{PF}_6)_2$  **1** was found to be an efficient catalyst for oxidation of cyclohexane to cyclohexanol by molecular oxygen in moderate conditions of temperature and pressure in which 57% conversion of cyclohexane to cyclohexanol was obtained in 7 h, in 60:40 (v/v) mixture of acetone and water solvent. Complex **1** gets diaquated and first coordinates with molecular oxygen and then loosely coordinates with cyclohexane to form the final kinetic intermediate, in which cleavage of the C–H and O–O bond is observed to occur via non-radical, ionic route associated with favourably reduced activation, energy and entropy.

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