

# Selective oxidation of alkenes catalysed by ruthenium(II) complexes containing coordinated perchlorate

A.S. Kanmani, S. Vancheesan \*

Department of Chemistry, Indian Institute of Technology, Madras, 600 036 India

Received 16 December 1998; accepted 14 April 1999

## Abstract

Ruthenium(II) perchlorate complexes,  $[\text{Ru}(\text{dppm})_3(\text{ClO}_4)]\text{ClO}_4$  **1**,  $[\text{Ru}(\text{dppe})_3(\text{ClO}_4)]\text{ClO}_4$  **2**, and  $[\text{Ru}(\text{dpae})_3(\text{ClO}_4)]\text{ClO}_4$  **3**, catalyse the selective homogeneous oxidation of alkenes with TBHP and  $\text{H}_2\text{O}_2$  as oxidizing agents. Oxidation of cyclohexene with TBHP gave 2-cyclohexene-1-ol, 2-cyclohexenone and 1-(*tert*-butylperoxy)-2-cyclohexene. The homogeneous liquid phase oxidation of cyclohexene with TBHP shows appreciable solvent effect. Styrene on oxidation with TBHP gave benzaldehyde as the major product and styrene oxide as the minor product. Oxidation with  $\text{H}_2\text{O}_2$  is radical-initiated and gives low conversion to products. TBHP and  $\text{H}_2\text{O}_2$  are compared for their oxidizing ability and TBHP is more effective than  $\text{H}_2\text{O}_2$  as an oxidizing agent. Linear and long chain alkenes are not efficiently oxidized. Cyclooctene and *trans*-stilbene are oxidized to the corresponding epoxides. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Ruthenium(II) perchlorate; Homogeneous oxidation; Catalyst; Alkenes; TBHP;  $\text{H}_2\text{O}_2$

## 1. Introduction

Transition metal catalysed oxidation reactions find wide chemical and biological applications [1]. Asymmetric oxidation reactions have synthetic applications in chemical and pharmaceutical industries. Among these reactions the catalytic oxidation of alkenes has potential industrial applications since the selective oxidation products serve as starting materials for the production of many fine chemicals and polymers [2,3].

The oxidation and epoxidation of alkenes is important from the synthetic point of view be-

cause several types of hormones and mutagens involve an oxirane moiety in their structure [4]. There has been considerable interest in the nature of selective olefin oxidation by alkyl hydroperoxides catalysed by group VIII transition metal complexes. Homogeneous reaction systems of the transition metals and those of group VIII, especially ruthenium have been developed to explore new ways for the mild and selective oxidation of hydrocarbons [5,2]. In the transition metal-mediated oxidation of olefins with alkyl hydroperoxides the catalytically active species in most cases is the metal in the higher oxidation state which is generated by oxidants such as amine *N*-oxides [6], alkyl hydroperoxides [7], hydrogen peroxide [8], peracids, hypochlorites [9], and other oxidizing agents [2].

\* Corresponding author. Tel.: +91-44-235-1365; fax: +91-44-235-0509; E-mail: v1143@hotmail.com

Ruthenium complexes are potent oxidant systems for mild and selective oxidation reactions at ambient conditions. The upsurge in the catalytic oxidation reactions catalysed by ruthenium complexes are due to their broad utility for the oxidation of a variety of substrates such as olefins, alcohols, alkanes, aldehydes, phosphines, sulphides and sulphoxides [10]. The oxidation of organic substrates mediated by high valent ruthenium-oxo species evokes much interest in the modelling of cytochrome P-450 [11]. Because of the periodic relationship of the metal with iron, these oxidation reactions are of significance and interest as the iron systems are widely used in biomimetic oxidation reactions. Ruthenium complexes are versatile catalysts for the oxidation of alkenes and they often promote the oxidative cleavage of the double bond into aldehydes or ketones [12]. However, selective epoxidation has been achieved by modification of the ligand moiety. In the transition metal catalysed oxidation reactions under homogeneous conditions, the nature of the coordinative environment around the metal plays a significant role in catalytic activity, which can lead to different product formation, depending on the reaction conditions.

The cationic complexes of ruthenium(II) containing phosphines and arsines are of interest in view of their catalytic activity for a variety of homogeneous reactions. We have previously reported the catalytic activity of the ruthenium(II) perchlorate complexes for the oxidation of alkenes with CHP and NMO as the oxidizing

agents [13]. In this paper we report the catalytic oxidation of alkenes with ruthenium(II) perchlorate complexes under mild and homogeneous conditions in the liquid phase with TBHP and  $H_2O_2$  as oxidizing agents.

## 2. Experimental

Products were analyzed on a Nucon 5700 gas chromatograph with a carbowax and an OV-17 column and ORACLE-1 computing integrator in the FID mode. TBHP (Lancaster) was obtained as a 70% aqueous solution. Hydrogen peroxide (Ranbaxy, India) was used as a commercial 30% aqueous solution. Other experimental procedures were similar to those previously reported [13]. The complexes  $[Ru(dppm)_3(ClO_4)]ClO_4$  **1**,  $[Ru(dppe)_3(ClO_4)]ClO_4$  **2**, and  $[Ru(dpae)_3(ClO_4)]ClO_4$  **3** were prepared as reported [14]. Products were identified by a QP 1000 EX Shimadzu GC-MS spectrophotometer. UV-visible spectra were recorded on a Perkin-Elmer Lambda 17 UV-visible spectrophotometer. IR spectra were recorded on a Shimadzu IR 470 spectrometer.

## 3. Results and discussion

### 3.1. Oxidation of alkenes with TBHP

#### 3.1.1. Oxidation of cyclohexene with TBHP

The homogeneous oxidation of cyclohexene catalysed by ruthenium complexes **1**, **2** and **3**

Table 1  
Oxidation of cyclohexene with TBHP: effect of solvent

Number	Solvent	Yield (mol%)				Conversion (mol%)
		Epoxide	2-Cyclohexen-1-ol	2-Cyclohexenone	1-( <i>tert</i> -Butylperoxy)-2-cyclohexene	
1	CHCl <sub>3</sub>	–	5.2 (22.7)	8.8 (38.4)	8.9 (39.0)	22.9
2	C <sub>6</sub> H <sub>6</sub>	–	5.7 (21.4)	10.4 (38.1)	10.9 (40.4)	27.0
3	CH <sub>3</sub> CN	–	1.4 (9.7)	3.4 (24.0)	9.2 (66.3)	14.0
4	THF	–	1.3 (15.3)	1.9 (25.2)	4.6 (59.5)	7.90
5	CH <sub>3</sub> OH	2.7 (17.8)	2.7 (18.1)	4.4 (29.9)	5.0 (40.4)	14.8

Conditions: solvent = 2 ml; catalyst  $[Ru(dppm)_3(ClO_4)]ClO_4 = 9.7 \times 10^{-6}$  mol, cyclohexene =  $1 \times 10^{-2}$  mol, TBHP =  $4.54 \times 10^{-3}$  mol, time = 5 h, 50°C. Percentage conversion was based on olefin. Values in parenthesis indicate percentage selectivity.

Table 2  
Oxidation of cyclohexene with TBHP: variation of catalyst concentration

Number	Catalyst concentration (mol%)	Yield (mol%)			Conversion (mol%)
		2-Cyclohexen-1-ol	2-Cyclohexenone	1-( <i>tert</i> -Butylperoxy)-2-cyclohexene	
1	$5.40 \times 10^{-6}$	7.3 (30.7)	7.4 (31.6)	8.9 (37.7)	23.6
2	$9.40 \times 10^{-6}$	5.5 (19.8)	11.1 (39.7)	11.2 (40.4)	27.8
3	$1.34 \times 10^{-5}$	3.3 (13.5)	10.6 (42.4)	10.9 (44.1)	24.8
4	$2.01 \times 10^{-5}$	2.6 (11.4)	9.3 (41.6)	10.6 (47.0)	22.5

Conditions: cyclohexene =  $1 \times 10^{-2}$  mol; solvent =  $\text{CHCl}_3$ , temperature =  $50^\circ\text{C}$ , 5 h, TBHP =  $5.8 \times 10^{-3}$  mol, catalyst =  $\text{Ru}(\text{dppm})_3(\text{ClO}_4)\text{ClO}_4$ .

gave 2-cyclohexene-1-ol, 2-cyclohexenone and 1-(*tert*-butylperoxy)-2-cyclohexene. Cyclohexene oxide was not formed. In cyclohexene a preferential attack of the C–H bond occurs over the C=C bond to give mainly the allylic oxidation products over the expected epoxide [15,16].

### 3.1.2. Effect of solvent

The effect of various solvents for the oxidation of cyclohexene with TBHP was studied

with ruthenium catalysts (Table 1). The oxidation reactions were carried out in polar, non-polar, coordinating and protic solvents. In the oxidation of cyclohexene with catalysts **1**, **2** and **3** with TBHP as oxidant, 1-(*tert*-butylperoxy)-2-cyclohexene was formed as the major product. The selectivity for 1-(*tert*-butylperoxy)-2-cyclohexene formation was almost 60% while the selectivity for 2-cyclohexenone and 2-cyclohexen-1-ol was less than 45%. Coordinat-

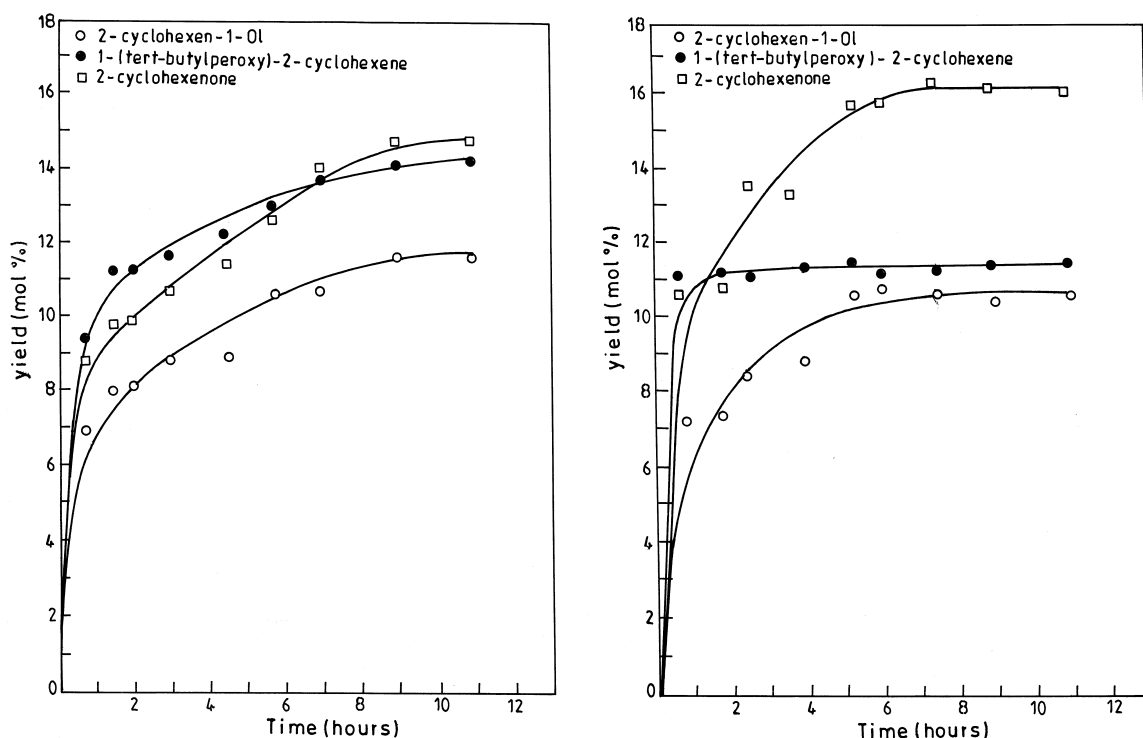


Fig. 1. Time scan for the oxidation of cyclohexene with TBHP catalysed by  $[\text{Ru}(\text{dppm})_3(\text{ClO}_4)]\text{ClO}_4$ . (a) Time scan for the oxidation of cyclohexene with TBHP catalysed by  $[\text{Ru}(\text{dppm})_3(\text{ClO}_4)]\text{ClO}_4$  in the presence of radical scavenger 2,6-di-*tert*-butyl-*p*-cresol.

ing solvents give low yield of the products. In THF percentage yield of 2-cyclohexen-1-ol and 2-cyclohexenone was less than 4%. The formation of the peroxy species is reported with other metal complexes [17]. In solvents like acetonitrile, the peroxy species was obtained as the major product and the yield of 2-cyclohexen-1-ol and 2-cyclohexenone was less than 5%. Since ruthenium(II) has a high affinity for  $\pi$ -acidic donor ligands, the yield of the products were low in  $\pi$ -acidic solvents like acetonitrile [18]. In protic solvents like methanol significant amount of cyclohexene oxide was formed. The selectivity for the peroxy species decreases in methanol, benzene and chloroform. In benzene and chloroform the yield of 2-cyclohexen-1-ol and 2-cyclohexenone was higher and lower yield of the peroxy species was obtained as compared to the other solvents. The efficiency of the catalysts for oxidation of cyclohexene in different solvents are of the order: benzene > chloroform > methanol > acetonitrile > tetrahydrofuran.

The metal complexes catalysed oxidation reactions with alkyl hydroperoxides under homogeneous reaction conditions show appreciable solvent effect [19]. In the oxidation of cyclohexene, the allylic hydrogen is more reactive than the C=C double bond towards the tertiary butyl peroxy or tertiary butyl alkoxy radical and the reaction proceeds to give mainly the allylic oxidation products [20].

### 3.1.3. Effect of catalyst concentration

The effect of varying the catalyst concentration for the oxidation of cyclohexene with TBHP and  $[\text{Ru}(\text{dppm})_3(\text{ClO}_4)]\text{ClO}_4$  as catalyst is shown in Table 2. With increase in the concentration of the catalyst, a decrease in the yield of 2-cyclohexen-1-ol was observed, while there was an increase in the yield of 2-cyclohexenone. The yield of 1-(*tert*-butylperoxy)-2-cyclohexene remained almost constant. The yield of 2-cyclohexen-1-ol decreases with increase in the concentration of the catalyst. The yield of 2-

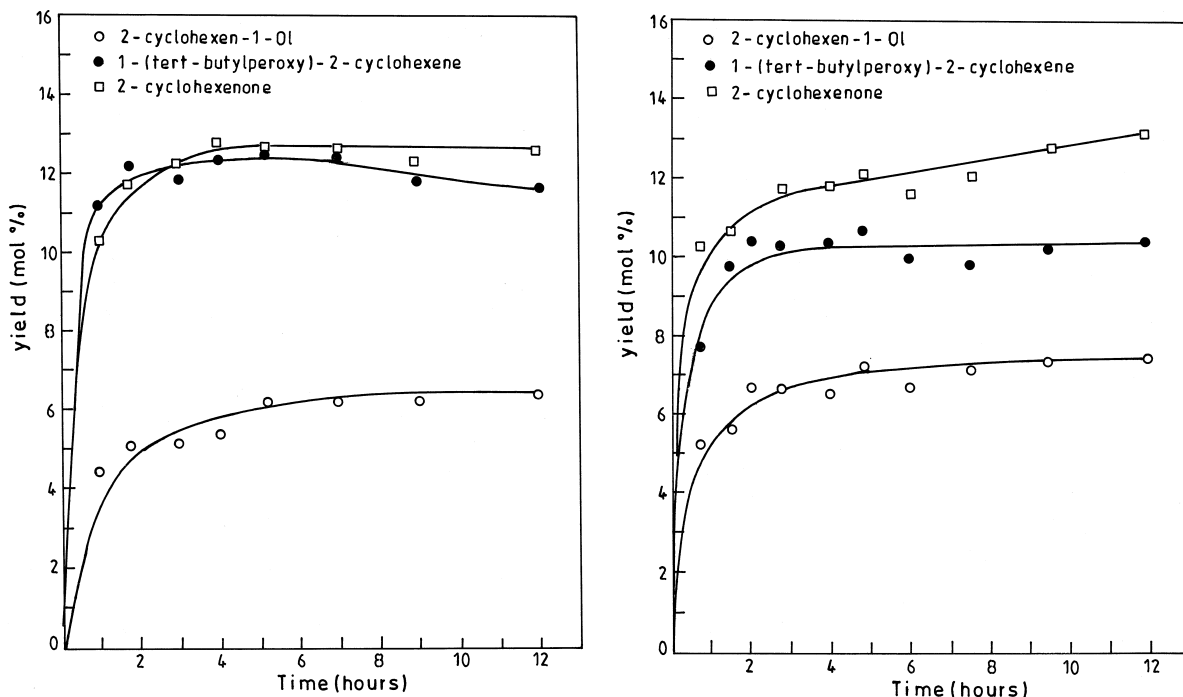
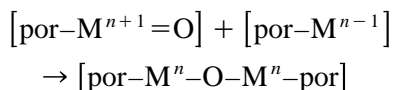


Fig. 2. Time scan for the oxidation of cyclohexene with TBHP catalysed by  $[\text{Ru}(\text{dppm})_3(\text{ClO}_4)]\text{ClO}_4$ . (a) Time scan for the oxidation of cyclohexene with TBHP catalysed by  $[\text{Ru}(\text{dppm})_3(\text{ClO}_4)]\text{ClO}_4$  in the presence of radical scavenger 2,6-di-*tert*-butyl-*p*-cresol.

cyclohexenone increases up to a concentration of  $9.4 \times 10^{-6}$  mol and a slight decrease in the percentage conversion was observed beyond this concentration. The decrease in percentage conversion at higher catalyst concentrations is attributed to the formation of  $\mu$ -oxo dimers, which inhibit the catalytic cycle. This type of  $\mu$ -oxo dimer formation is observed with many transition metal systems. In transition metal porphyrin complexes, steric and cage effects have been developed to avoid the formation of these catalytically inactive  $\mu$ -oxo dimers [21].



### 3.1.4. Mechanistic studies

The formation of the allylic oxidation products 2-cyclohexen-1-ol and 2-cyclohexenone shows the preferential attack of the activated

C–H bond over the C=C bond. The formation of 1-(*tert*-butylperoxy)-2-cyclohexene shows that this product arises from a radical pathway [20]. To investigate the mechanism of the reaction the reactions were carried out in the presence of radical scavenger 2,6-di-*tert*-butyl-*p*-cresol. Fig. 1 shows the time scan for the oxidation of cyclohexene with TBHP catalysed by  $[\text{Ru}(\text{dppm})_3(\text{ClO}_4)]\text{ClO}_4$ . The yield of the allylic oxidation products parallels the yield of the peroxy species and the yield of 2-cyclohexenone is higher than that of 2-cyclohexen-1-ol. The yield of 2-cyclohexen-1-ol and 2-cyclohexenone are independent of each other. The oxidation of cyclohexene catalysed by  $[\text{Ru}(\text{dppm})_3(\text{ClO}_4)]\text{ClO}_4$ , in the presence of radical scavenger, 2,6-di-*tert*-butyl-*p*-cresol is shown in Fig. 1a. In the presence of radical trap the yield of 1-(*tert*-butylperoxy)-2-cyclohexene remained almost constant suggesting that this

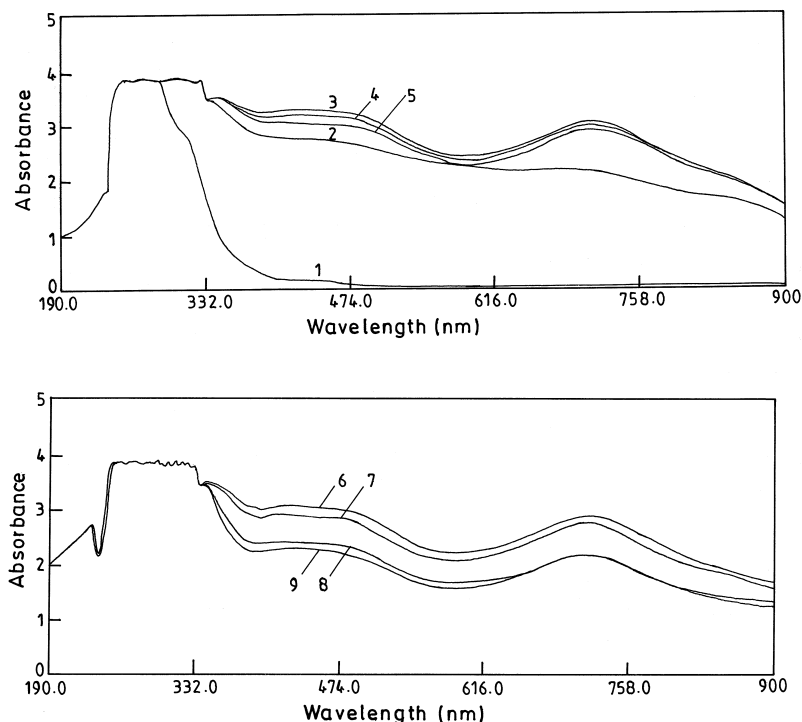


Fig. 3. In situ UV spectra of the catalyst  $[\text{Ru}(\text{dppe})_3(\text{ClO}_4)]\text{ClO}_4$  recorded at time intervals of 5 min. One spectrum of the catalyst. Two to six spectra of the catalyst recorded after the addition of TBHP at time intervals of 5 min. Seven to nine spectra recorded after the addition of cyclohexene to the above.

product was formed through a radical pathway. However, in the presence of radical trap the yield of 2-cyclohexenone increases significantly which suggests that the formation of this product occurs through the ruthenium(IV)-oxo intermediate.

The time scan for the oxidation of cyclohexene with TBHP and  $[\text{Ru}(\text{dppe})_3(\text{ClO}_4)]\text{ClO}_4$  as catalyst is shown in Fig. 2. In the presence of radical trap 2,6-di-*tert*-butyl-*p*-cresol the yield of 2-cyclohexenone was greater than that of 1-(*tert*-butylperoxy)-2-cyclohexene (Fig. 2a) while in the absence of radical trap the yield of these two products were nearly equal (Fig. 2). On the addition of the radical trap to the reaction there was a significant rise in the yield of 2-cyclohexen-1-ol (Fig. 2a). If the formation of this product occurs through a radical intermediate, then the opposite trend, namely, a decrease in the yield of cyclohexen-1-ol would be observed. The formation of 2-cyclohexen-1-ol and

2-cyclohexenone occurs probably through a higher valent ruthenium-oxo species as the intermediate.

With TBHP as terminal oxidant a radical chain type of reaction mechanism is inhibited by ionol (2,6-di-*tert*-butyl-*p*-cresol). In the epoxidation of alkenes the metal complex serves as an initiator by generation of radicals [22]. In the presence of a reactive substrate like cyclohexene, metal complexes catalyse the introduction of a peroxy group into the substrate [17]. The oxidation of cyclohexene to the peroxy product occurs through a radical intermediate. The yield of the peroxy species decreases in the presence of a radical scavenger [22]. The shuttling of the metal complex between the two oxidation states formally correspond to an oxidative-addition–reductive-elimination sequences and the metals which are capable of undergoing two electron changes like iron and ruthenium are effective in this catalysis [23].

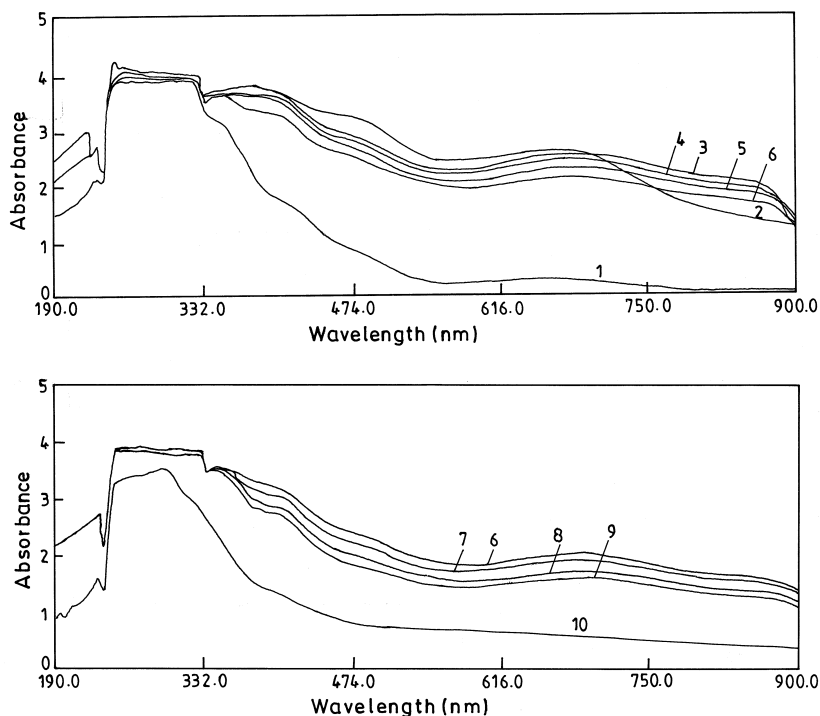


Fig. 4. In situ UV spectra of the catalyst  $[\text{Ru}(\text{dppm})_3(\text{ClO}_4)]\text{ClO}_4$  recorded at time intervals of 5 min. One spectrum of the catalyst. Two to six spectra of the catalyst recorded after the addition of TBHP at time intervals of 5 min. Seven to nine spectra recorded after the addition of cyclohexene to the above. Ten spectra recorded after 20 h indicate loss of catalytic activity.

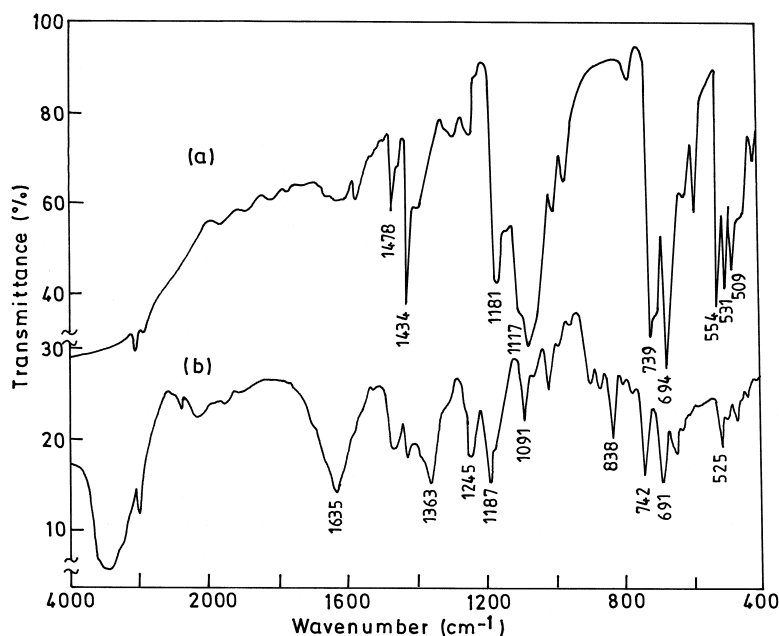
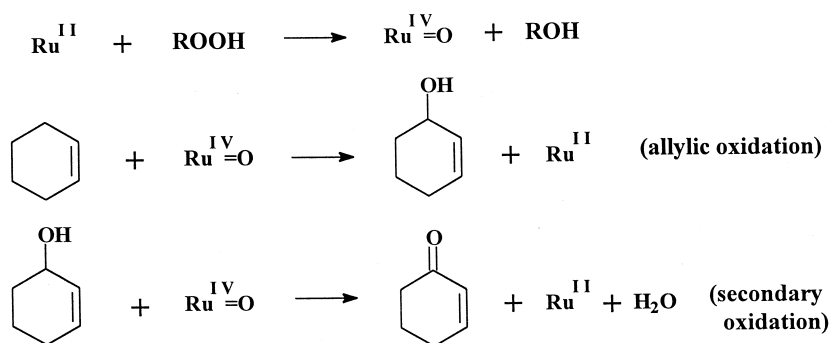


Fig. 5. (a) IR spectra of the catalyst  $[\text{Ru}(\text{dppe})_3(\text{ClO}_4)]\text{ClO}_4$ , (b) IR spectra of the catalyst  $[\text{Ru}(\text{dppe})_3(\text{ClO}_4)]\text{ClO}_4$  recorded after the addition of TBHP.

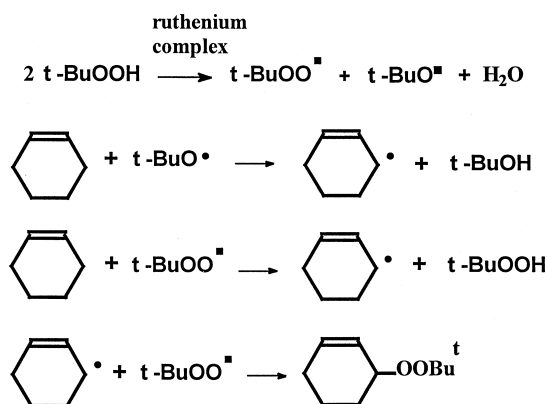
### 3.1.5. UV-visible studies

The in situ UV-visible studies for the catalysts **1** and **2** at different time intervals were carried out (Figs. 4 and 3). The spectra were recorded after the addition of TBHP to the complex at intervals of 5 min. The UV-visible spectra of complex  $[\text{Ru}(\text{dppe})_3(\text{ClO}_4)]\text{ClO}_4$  changes on the addition of TBHP and new bands are observed at 496 and 714 nm (Fig. 3).

On the addition of cyclohexene the intensity of the bands at 425 and 714 nm decrease and the disappearance of the bands was observed with time. The band at 425 nm may be due to the ruthenium(IV)-oxo species. The absorption band at 714 nm is due to the ligand to metal charge transfer from the peroxide to the metal. There are two types of electronic transition in the  $\text{Ru}=\text{O}$  systems, the ligand field ( $d_{xy} \rightarrow d_{\pi}^*$ ) and



Scheme 1.



Scheme 2.

ligand to metal  $P_{\pi}(\text{O}) \rightarrow d_{\pi}(\text{M})$  charge transfer (LMCT) [24].

Fig. 4 shows the UV–visible spectral studies carried out for  $[\text{Ru}(\text{dppm})_3(\text{ClO}_4)]\text{ClO}_4$  during the catalytic oxidation of cyclohexene with TBHP. On the addition of TBHP to the catalyst new bands were observed at 692, 490 and 388 nm. After the addition of cyclohexene to the above reaction the band at 388 nm is red-shifted to 364 nm and the intensity of the bands at 692 and 490 nm decrease rapidly. The absorption in the region 450 to 500 nm is due to the ruthenium(IV)-oxo species [25,26].

The IR spectra of the catalyst before and after the addition of the oxidant are shown in Fig. 5. On the addition of TBHP to the complex **2**, a new peak was observed at  $838 \text{ cm}^{-1}$  which corresponds to  $\text{Ru}(\text{IV})=\text{O}$  species formation. The reaction mechanism for the formation of

the allylic oxidation products 2-cyclohexene-1-ol and 2-cyclohexenone is more related to the cage controlled metal-oxo chemistry rather than to free radical chemistry.

The oxidation of cyclohexene to the allylic oxidation products 2-cyclohexene-1-ol and 2-cyclohexenone proceeds through a ruthenium(IV)-oxo intermediate (Scheme 1). The formation of 1-(*tert*-butylperoxy)-2-cyclohexene occurs through a radical intermediate (Scheme 2) [20].

### 3.1.6. Oxidation of cyclic and linear alkenes

The oxidation of linear alkenes like 1-heptene, 1-hexene, 1-dodecene and 1-pentene by TBHP is catalysed by ruthenium complexes **1**, **2** and **3** (Table 3). Long chain alkenes like 1-dodecene gave less than 3% yield. Linear alkenes are less reactive than cyclic alkenes. Cyclooctene gave moderate yields of cyclooctene oxide. Oxidation of *trans*-stilbene gave stereoselectively *trans*-stilbene oxide. In the case of *trans*-stilbene, the oxidative cleavage product namely benzaldehyde was formed in less than 3% yield. The yield of *trans*-stilbene oxide was greater than 67% as determined from proton NMR. No isomeric products such as *cis*-stilbene oxide was detected. The conversion of *trans*-stilbene to *trans*-stilbene oxide denotes the high stereospecificity of the reaction.

### 3.1.7. Oxidation of styrene with TBHP

In the oxidation of electrophilic substrates such as styrene preferential oxidative cleavage

Table 3  
Oxidation of alkenes with TBHP

Number	Catalyst	Alkene	Yield (mol%)	Product
1	<b>2</b>	cyclooctene	17.3	epoxide
2	<b>1</b>	1-dodecene	2.5	epoxide
3	<b>2</b>	1-dodecene	2.1	epoxide
4	<b>1</b>	1-octene	3.2	epoxide
5	<b>1</b>	1-hexene	< 1	epoxide
6	<b>3</b>	1-pentene	< 1	epoxide
7	<b>1</b>	<i>trans</i> -stilbene <sup>a</sup>	67 (3)	<i>trans</i> -stilbene oxide <sup>a</sup> (benzaldehyde)

Conditions: alkene =  $1 \times 10^{-2}$  mol, TBHP =  $5.8 \times 10^{-3}$  mol, catalyst =  $1.2 \times 10^{-5}$  mol, temperature =  $50^\circ\text{C}$ , 5 h.

<sup>a</sup>Yield determined by  $^1\text{H}$  NMR. *Trans*-stilbene = 500 mg, solvent =  $\text{CHCl}_3$  (3 ml).



Table 4  
Oxidation of styrene with TBHP

Number	Complex	Solvent	Additive	Yield (mol%)		Conversion (mol%)
				Benzaldehyde	Styrene oxide	
1	<b>2</b>	CHCl <sub>3</sub>	–	18.7	4.0	22.7
2	<b>2</b>	C <sub>6</sub> H <sub>6</sub>	–	12.8	5.0	17.9
3	<b>2</b> <sup>a</sup>	CHCl <sub>3</sub>	CPC	49.6	–	49.6
4	<b>1</b>	CHCl <sub>3</sub>	–	5.7	1.6	7.3
5	<b>1</b>	CHCl <sub>3</sub>	CPC	5.8	< 1%	6.8
6	<b>3</b>	CHCl <sub>3</sub>	–	6.0	< 1%	7.0
7	<b>3</b>	CHCl <sub>3</sub>	CPC	11.1	< 1%	12.4

Conditions: temperature = 50°C, time = 5 h, catalyst =  $1.2 \times 10^{-5}$  mol, styrene =  $1 \times 10^{-2}$  mol, TBHP =  $7 \times 10^{-3}$  mol, CPC = cetyl pyridinium chloride (30 mg).

<sup>a</sup>In the presence of oxygen.

of the C=C bond occurs rather than epoxide formation [27]. The oxidation of styrene with TBHP catalysed by **1**, **2** and **3** gave benzaldehyde as the major product and styrene oxide as the minor product (Table 4). Other oxidation products such as phenyl acetaldehyde were detected in less than 2% yield. Reactions were carried out in the presence and absence of oxygen. The yield of benzaldehyde increases in the presence of oxygen while the yield of styrene oxide decreases in the presence of oxygen. The effect of phase transfer additive cetyl pyridinium chloride on the oxidation of styrene was studied. In benzene significant amount of styrene

oxide was formed. The yield of benzaldehyde was the highest in chloroform. In the presence of phase transfer additive, the yield of benzaldehyde increases whereas the yield of styrene oxide decreases.

### 3.2. Oxidations with H<sub>2</sub>O<sub>2</sub>

The use of hydrogen peroxide as an oxidant is related to environmental considerations. Hydrogen peroxide has been used for many transition metal catalysed oxidation reactions and the main reaction pathway is the homolytic cleavage of the O–O bond, in which only 50

Table 5  
Oxidation of alkenes with H<sub>2</sub>O<sub>2</sub>

Number	Complex	Alkene	Additive	Yield (mol%)	Product
1	<b>1</b>	styrene	–	5.4	benzaldehyde
2	<b>1</b>	styrene	CPC	9.4	benzaldehyde
3	<b>2</b>	styrene	–	1.6	benzaldehyde
4	<b>2</b>	styrene	CPC	7.8	benzaldehyde
5	<b>2</b>	styrene	CTMAB	9.7	benzaldehyde
6	<b>3</b>	styrene	–	2.1	benzaldehyde
7	<b>3</b>	styrene	CPC	8.7	benzaldehyde
8	<b>2</b>	1-octene	no reaction		
9	<b>1</b>	cyclooctene	no reaction		
10	<b>2</b>	cyclohexene	CPC	3.5	2-cyclohexen-1-ol
				5.7	2-cyclohexenone

Conditions: temperature = 50°C, time = 5 h, catalyst =  $1.2 \times 10^{-5}$  mol, alkene =  $1 \times 10^{-2}$  mol, H<sub>2</sub>O<sub>2</sub> =  $1.7 \times 10^{-2}$  mol, solvent (CHCl<sub>3</sub>) = 2 ml, CPC = cetyl pyridinium chloride, CTMAB = cetyl trimethyl ammonium bromide.

kcal/mol are involved for the generation of hydroxy radical (OH). The rate of decomposition of hydrogen peroxide increases with temperature in the presence of certain metal complexes and metal salts. Table 5 shows the catalytic oxidation of cyclohexene with  $H_2O_2$ . The reactions were carried out in the presence and absence of phase transfer additives like cetylpyridinium chloride and cetyl trimethylammonium bromide. Cyclooctene and linear alkenes such as 1-octene, 1-heptene and 1-hexene did not react. Cyclohexene on oxidation with  $H_2O_2$  gave the allylic oxidation products, 2-cyclohexenone and 2-cyclohexene-1-ol. Styrene gave selectively benzaldehyde in less than 10% yield in all the reactions. The yield of benzaldehyde increases in the presence of phase transfer additives. In the presence of phase transfer additive and a ruthenium catalyst, styrene yields mainly benzaldehyde or acetophenone and no styrene oxide was formed [28,29].

#### 4. Summary and conclusions

The oxidation of cyclohexene with catalysts **1**, **2**, and **3** gave 2-cyclohexen-1-ol, 2-cyclohexenone and 1-(*tert*-butylperoxy)-2-cyclohexene. The reactions show appreciable solvent effect. The formation of 2-cyclohexen-1-ol and 2-cyclohexenone occurs through the higher valent ruthenium(IV)-oxo species as evidenced from UV-Visible and IR studies. The formation of 1-(*tert*-butylperoxy)-2-cyclohexene occurs through a radical pathway. TBHP is a better oxidant than  $H_2O_2$  with these catalysts. Hydrogen peroxide is a poor oxidant and the yield of the products increase significantly in the presence of phase transfer additives. Linear alkenes are oxidized to a lesser extent than cyclic and branched alkenes. Styrene undergoes a C=C bond cleavage preferentially over epoxide formation to give benzaldehyde rather than styrene oxide which is formed as the minor product.

#### References

- [1] R.A. Sheldon, J.K. Kochi, *Metal Catalysed Oxidations of Organic Compounds*, Academic Press, New York, 1981.
- [2] K.A. Jorgensen, *Chemical Reviews* 89 (1989) 431.
- [3] R.A. Sheldon, *Studies in Surface Science and Catalysis* 60 (1991) 573.
- [4] Y. Watanabe, J.T. Groves, in: D.S. Sigman (Ed.), *The Enzymes*, Vol. 20, Academic Press, San Diego, 1992.
- [5] B.R. James, *Studies in Surface Science and Catalysis* 66 (1991) 195.
- [6] H. Ohtake, T. Higuchi, M. Hirobe, *Journal of the American Chemical Society* 114 (1992) 10660.
- [7] K.A. Jorgensen, *Journal of the American Chemical Society* 109 (1987) 698.
- [8] L.T. Kist, M.J.F. Trujillo, B. Szpoganicz, M.A. Manez, M.G. Basallote, *Polyhedron* 16 (1997) 3827.
- [9] H. Yoon, J.R. Wagler, K.J. O'Connor, C.J. Burrows, *Journal of the American Chemical Society* 112 (1990) 4568.
- [10] D. Riley, J. Lyon, *Journal of Chemical Society, Dalton Transactions* (1991) 157.
- [11] B. Meunier, *Chemical Reviews* 92 (1992) 1411.
- [12] M.H. Robbins, R.S. Drago, *Journal of Chemical Society, Dalton Transactions* (1996) 105.
- [13] A.S. Kanmani, S. Vancheesan, *Journal of Molecular Catalysis A: Chemical* 125 (1997) 127.
- [14] M.M. Taqui Khan, H.C. Bajaj, R.H. Siddiqui, B. Taqui Khan, M.S. Reddy, K.V. Reddy, *Journal of Chemical Society, Dalton Transactions* (1985) 2603.
- [15] E.G. Samsel, K. Srinivasan, J.K. Kochi, *Journal of the American Chemical Society* 107 (1985) 7606.
- [16] C. Ho, W.H. Leung, Chi Ming Che, *Journal of Chemical Society, Dalton Transactions* (1991) 2933.
- [17] J.D. Koola, J.K. Kochi, *Inorganic Chemistry* 26 (1987) 908.
- [18] H. Taube, *Coordination Chemistry Reviews* 26 (1978) 33.
- [19] R.A. Sheldon, J.A. Van Doorn, C.W.A. Schram, A.J. De Jong, *Journal of Catalysis* 31 (1973) 438.
- [20] J.D. Koola, J.K. Kochi, *Journal of Organic Chemistry* (1987) 4545.
- [21] J.A. Gilbert, D.S. Eggleston, W.R. Murphy Jr., D.A. Geselowitz, S.W. Gersten, D.J. Hodgson, T.J. Meyer, *Journal of the American Chemical Society* 107 (1985) 3855.
- [22] G. Scott, *Chemistry in Britain* 21 (1985) 648.
- [23] K.B. Sharpless, *Aldrichimica Acta* 12 (1979) 63.
- [24] C.-M. Che, T.F. Lai, K.Y. Wong, *Inorganic Chemistry* 26 (1987) 2289.
- [25] K. Vijayashri, J. Rajaram, J.C. Kuriacose, *Proceedings of the Indian Academy of Sciences, Chemical Sciences* 97 (1986) 125.
- [26] K. Vijayashri, J. Rajaram, J.C. Kuriacose, *Inorganica Chimica Acta* 117 (2) (1986) 133.
- [27] J.E. Lyons, J.O. Turner, *Tetrahedron Letters* 29 (1972) 2903.
- [28] E.V. Dehmlow, S.S. Dehmlow, *Phase Transfer Catalysis*, Verlag, Weinheim, 1983.
- [29] G. Barak, Y. Sasson, *Journal of Chemical Society, Chemical Communications* (1987) 1266.