

Catalytic oxidation of alkenes with ruthenium(II) perchlorate complexes

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Received 14 February 1997; accepted 22 April 1997

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**, $[\text{Ru}(\text{dpa})_3(\text{ClO}_4)]\text{ClO}_4$, **3**, catalyse the oxidation of cyclohexene in the presence of cumene hydroperoxide (CHP) under homogeneous liquid phase. The products of oxidation are 2-cyclohexen-1-ol and 2-cyclohexenone. Linear alkenes like 1-heptene and 1-octene are not efficiently oxidised under these conditions. Solvent influences the rate of oxidation considerably. *N*-methylmorpholine-*N*-oxide (NMO) and CHP are compared for their oxidising ability. © 1997 Elsevier Science B.V.

Keywords: Ruthenium(II) perchlorate; Homogeneous; Catalyst; Cyclohexene; Oxidation

1. Introduction

In the last few decades much interest has been directed to the oxidation of olefins in chemical industries [1]. The oxidation and epoxidation of alkenes are important synthetic processes. Several hormones and mutagens involve an oxirane moiety in their structure [2]. Transition metal catalyzed oxidations have recently attracted considerable interest and a number of reactions have been explored in order to develop methods for mild and selective oxidations [3]. The discovery of group VIII transition metal mediated olefin oxidations with hydroperoxides and other oxidising agents have presented a major breakthrough in this area of chemistry.

But there are only a few industrially and preparatively useful liquid phase catalytic oxidation processes which do not compromise on the selectivity. Various synthetic porphyrins have been widely used as model catalysts for oxidation of olefins and saturated hydrocarbons to understand the details of the enzymatic oxidation reaction mechanism [4,5]. Not only metalloporphyrins of the transition metal ions but also other transition metal complexes with simple ligands have been used for the catalytic oxidation of alkenes [6,7]. The oxygenation of organic substrates through metal-oxo and metal peroxo intermediates have become important class of reactions in chemistry. In these oxygenation reactions involving organic substrates the catalytically active metal-oxo species is generated by oxidants such as alkylhydroperoxides, hydrogen peroxide, peracids, iodosylarenes,

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molecular oxygen, amine *N*-oxides, hypochlorites (commercial bleach), periodate and other oxidizing agents [8–11].

Among the second row transition metal ions ruthenium complexes are well known to catalyse oxidation reactions under mild conditions [12–15]. Ruthenium catalysts promote the oxidative cleavage of double bonds into ketones, aldehydes and carboxylic acids. In this paper we report the catalytic oxidation of cyclohexene, 1-heptene and 1-octene catalysed by ruthenium complexes under mild reaction conditions with cumene hydroperoxide (CHP) and *N*-methylmorpholine-*N*-oxide (NMO) as oxidising agents.

2. Experimental

Products were analysed on a 5700 Nucon gas chromatograph fitted with an OV 17 column and FID mode and Oracle-1 computing integrator. Qualitative analyses were done on a QP 1000 EX Shimadzu GCMS spectrophotometer. UV-visible spectra were recorded on a Perkin Elmer Lambda 17 UV-visible spectrophotometer. IR spectra were recorded on a Shimadzu IR 470 spectrophotometer. Cyclic voltametric studies were done on a BAS 101A instrument with platinum wire, platinum foil and silver wire as working, counter and reference electrodes, respectively. Tetraethylammonium perchlorate was used as the supporting electrolyte. Solvents were purified by standard procedures [16]. Ruthenium chloride trihydrate (Arora Mathey India), 1-octene and 1-heptene (Fluka) were used as such. Cyclohexene was prepared by the standard procedure [17]. The purity of the alkenes was checked by gas chromatograph before starting the reaction. Cumene Hydroperoxide (Merck) was used as an 80% solution in cumene. *N*-methylmorpholine-*N*-oxide monohydrate (Aldrich) was used as such. The bis phosphine ligands (Lancaster) were recrystallized before use. Other chemicals and reagents were commercial samples and were purified before use [16]. Tris[1,2-bis(diphenylphosphino)methane]-

perchloratoruthenium(II)perchlorate, $[\text{Ru}(\text{dppm})_3(\text{ClO}_4)]\text{ClO}_4$ (**1**), tris[1,2-bis(diphenylphosphino)ethane]perchloratoruthenium(II)perchlorate, $[\text{Ru}(\text{dppe})_3(\text{ClO}_4)]\text{ClO}_4$ (**2**) and tris[1,2-bis(diphenylarsino)ethane]perchloratoruthenium(II) perchlorate, $[\text{Ru}(\text{dpae})_3(\text{ClO}_4)]\text{ClO}_4$ (**3**), were prepared as reported in the literature [18]. The complexes dichloro(benzoato)bis(triphenylphosphine)ruthenium(III), $[\text{RuCl}_2(\text{O}_2\text{CC}_6\text{H}_5)(\text{PPh}_3)_2]$ (**4**), dichloro(*p*-methoxybenzoato)bis(triphenylphosphine)ruthenium(III) $[\text{RuCl}_2(\text{O}_2\text{CC}_6\text{H}_4\text{X})(\text{PPh}_3)_2]$ (**5**) ($\text{X} = p\text{-OCH}_3$) and dichloro(*m*-methoxybenzoato)bis(triphenylphosphine)ruthenium(III), $[\text{RuCl}_2(\text{O}_2\text{CC}_6\text{H}_4\text{X})(\text{PPh}_3)_2]$ ($\text{X} = m\text{-OCH}_3$) were prepared as reported [19].

3. Procedure for catalytic oxidation

Reactions between the ruthenium complexes and organic substrates were performed either by dissolving the reactants in the solvent to form a homogeneous solution or by suspending the ruthenium complex in the solvent. The reaction mixture was stirred with a magnetic bar and the temperature was maintained constant. The catalytic oxidation of cyclohexene, 1-heptene and 1-octene were carried out in the presence of ruthenium complexes with cumene hydroperoxide (CHP) and *N*-methylmorpholine-*N*-oxide (NMO) as oxidising agents. Chlorobenzene was added as the internal standard.

4. Results and discussion

Catalytic oxidation of cyclohexene with ruthenium complexes **1**, **2** and **3** gave 2-cyclohexen-1-ol and 2-cyclohexenone, respectively, with no appreciable yield of cyclohexene oxide. In cyclohexene there is a preferential attack of the activated C–H bond over the C=C bond. Fig. 1 shows the time course of the oxidation of cyclohexene with cumene hydroperoxide and $[\text{Ru}(\text{dppe})_3(\text{ClO}_4)]\text{ClO}_4$ as cata-

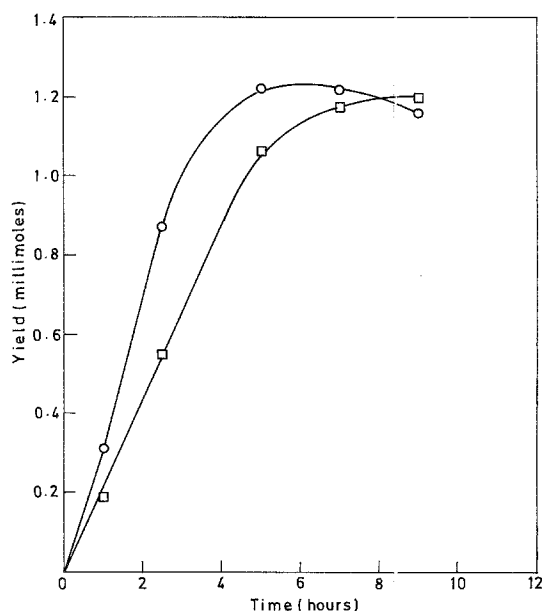


Fig. 1. Time course of the oxidation of cyclohexene in the presence of $[\text{Ru}(\text{dppe})_3(\text{ClO}_4)_4]\text{ClO}_4$ as catalyst. (○) 2-cyclohexen-1-ol; (□) 2-cyclohexenone. Conditions: temperature = 50°C , $\text{CHCl}_3 = 5 \text{ ml}$, catalyst = $1.2 \times 10^{-5} \text{ mol}$, substrate = $9.9 \times 10^{-3} \text{ mol}$, CHP = $5.3 \times 10^{-3} \text{ mol}$.

lyst. In 1 h the turnover numbers for the formation of 2-cyclohexen-1-ol and 2-cyclohexenone were 25 and 15, respectively. In 3 h the yield of 2-cyclohexen-1-ol was greater than that of 2-cyclohexenone. There was no epoxide formation. After 2 h the yield of 2-cyclohexenone and 2-cyclohexen-1-ol increased rapidly. After 5 h there was a marginal decrease in the yield of 2-cyclohexen-1-ol while there was a significant rise in the yield of 2-cyclohexenone. This trend suggests that 2-cyclohexen-1-ol is formed first

in the catalytic oxidation. During the course of the reaction the product 2-cyclohexen-1-ol formed gets further oxidised to 2-cyclohexenone under the reaction conditions [20,21]. The formation of the ketone is due to the secondary oxidation of the alcohol. Similar oxidation of cyclohexene to 2-cyclohexenone has also been reported by Meyer's reagent [22]. The oxidation of secondary alcohols to ketones by ruthenium catalysts are well known from previous studies [23,24]. When the same reaction was carried out at room temperature (27°C) the yield of 2-cyclohexen-1-ol and 2-cyclohexenone were 3.6 and 4.8 percentage, respectively. The selectivity for formation of 2-cyclohexen-1-ol decreases with time while that for 2-cyclohexenone increases with time. Percentage conversion increases with time and levels off after 9 h.

5. Effect of catalyst concentration

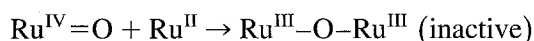
Addition of cumene hydroperoxide to a solution containing the ruthenium complex darkened the initial yellow solution to brownish red in some cases and black in other cases. The change in colour probably arises due to the change in the oxidation state of ruthenium. On addition of the oxidant the ruthenium(II) complexes are converted to the corresponding ruthenium-oxo species. Table 1 shows the effect of catalyst concentration on the oxidation of cyclohexene by cumene hydroperoxide. Increasing the catalyst concentration increases the percentage con-

Table 1
Effect of catalyst concentration on the oxidation of cyclohexene with cumene hydroperoxide (CHP) as the oxidising agent

No.	Catalyst concentration (mol)	Yield $\times 10^{-3} \text{ mol}$			% conversion
		epoxide	2-cyclohexen-1-ol	2-cyclohexenone	
1	6.8×10^{-6}	—	0.86 (58.8)	0.541 (36.2)	14.9
2	1.02×10^{-5}	—	1.233 (53.8)	1.075 (45.9)	23.3
3	1.42×10^{-5}	—	1.206 (50.0)	1.141 (46.3)	23.9
4	1.7×10^{-5}	—	1.120 (56.4)	0.816 (40.2)	20.3
5	2.11×10^{-5}	—	0.760 (50.4)	0.900 (39.3)	17.4

Catalyst = $[\text{Ru}(\text{dppe})_3(\text{ClO}_4)_4]\text{ClO}_4$ (2); temperature = 50°C ; duration = 5 h; $\text{CHCl}_3 = 5 \text{ ml}$; substrate = $9.9 \times 10^{-3} \text{ mol}$; CHP = $5.26 \times 10^{-3} \text{ mol}$. Values in parentheses indicate percentage selectivity. Percentage conversion was calculated based on olefin.

version of the products initially, but after reaching a maximum it drops significantly. The same trend was observed in the yield of 2-cyclohexen-1-ol. At catalyst concentrations greater than 1.4×10^{-5} mol the yield of product decreases. Lower activity of the catalyst is due to the formation of green paramagnetic compounds, the μ -oxo derivatives of ruthenium(III) of various molecular complexities which are completely inactive and inhibit the catalytic cycle [25]:



Other side reactions like the formation of phosphine oxide have also been reported to occur. The mono-oxo complexes of ruthenium(IV) are often unstable and undergo either disproportionation to give ruthenium(II) and ruthenium(IV) dioxo species or converted to μ -oxo ruthenium(III) derivatives [26]. The slight negative effect at a higher concentration of catalyst is attributed to the diversion of the catalytically active oxo metal species that may be dependent on the concentration of the catalyst.

6. Effect of solvent

Table 2 shows the effect of various solvents on the catalytic oxidation of cyclohexene with

different complexes. Oxidation reactions were carried out in protic, polar and nonpolar solvents. With $[\text{Ru}(\text{dppe})_3(\text{ClO}_4)]\text{ClO}_4$ (**2**) as catalyst the yield of product decreases in the order chloroform > benzene > acetonitrile > methanol > tetrahydrofuran. The reaction is retarded by strong coordinating solvents like tetrahydrofuran. In tetrahydrofuran competing side reactions occur as evidenced by the lower selectivity in the formation of the products. The reactivity pattern for formation of 2-cyclohexen-1-ol is chloroform > benzene > methanol > acetonitrile > tetrahydrofuran while that for 2-cyclohexenone is benzene > chloroform > acetonitrile > methanol > tetrahydrofuran. Halogenated hydrocarbon solvents like chloroform and inert solvents like benzene are suitable for the formation of the products. The formation of 2-cyclohexen-1-ol is inhibited by Π -acidic ligands like acetonitrile which are known to have high affinity for ruthenium(II) [27]. The oxidation reactions are also retarded in hydroxylic solvents like methanol due to the competing coordination of the hydroxyl solvent with the active metal species. In hydroxyl solvents selectivity for epoxide was significant. However the oxidation of the solvent also occurs and a small amount of formaldehyde was detected when methanol was used as the solvent. The selectiv-

Table 2
Effect of solvent on the oxidation of cyclohexene with CHP

No.	Catalyst	Solvent	Yield $\times 10^{-3}$ mol			% selectivity			Total yield $\times 10^{-3}$ mol
			epoxide	2-cyclohexen-1-ol	2-cyclohexenone	epoxide	2-cyclohexen-1-ol	2-cyclohexenone	
1	2	CHCl_3	—	1.233	1.075	—	53.8	45.9	2.308
2	2	THF	—	0.472	0.168	—	44.7	15.6	0.64
3	2	CH_3OH	0.18	0.51	0.45	9.92	37.2	32.0	1.14
4	2	C_6H_6	—	0.946	1.349	—	40.1	56.1	2.295
5	2	CH_3CN	—	0.4854	0.9077	—	24.7	45.1	1.393
6	3	CHCl_3	—	1.613	1.8103	—	45.6	50.1	3.423
7	3	CH_3OH	no reaction			—	—	—	—
8	1	CHCl_3	0.03	0.447	0.403	1.0	49.6	43.8	0.88
9	1	CH_3CN	—	0.3604	0.617	—	32.2	53.97	0.977
10	1	CH_3OH	no reaction			—	—	—	—

Solvent = 5 ml; catalyst = 1.02×10^{-5} mol; duration = 5 h, temperature = 50°C ; substrate = 9.89×10^{-3} mol; CHP (oxidant) = 5.26×10^{-3} .

ity for the formation of 2-cyclohexen-1-ol was the highest in chloroform while in acetonitrile it was the lowest. Selectivity for formation of 2-cyclohexenone was maximum in benzene. In the case of catalysts **1** and **3** there was no product formation when methanol was used as a solvent. In solvents like benzene and chloroform, there is less competition between the solvent and substrate molecules for coordination with the metal active species.

7. Activity of bisphosphine complexes

A comparison between the bisphosphine cationic complexes with chloroform as solvent (Table 2) shows that complex **3** is the most active catalyst. The order of reactivity of the catalysts are: $[\text{Ru}(\text{dpae})_3(\text{ClO}_4)]\text{ClO}_4$ (**3**) > $[\text{Ru}(\text{dppf})_3(\text{ClO}_4)]\text{ClO}_4$ (**2**) > $[\text{Ru}(\text{dppm})_3(\text{ClO}_4)]\text{ClO}_4$ (**1**).

The selectivity for the formation of 2-cyclohexen-1-ol is greater than that for 2-cyclohexenone for catalysts **1** and **2**. Catalyst **3** showed a higher selectivity for the formation of 2-cyclohexenone. The difference in activity among the three catalysts could be attributed to the steric and chelating effect of the ligands. Complexes containing a four membered ring are less stable than those with a five membered ring due to the greater effect of the chelating catalyst. When complex **3** was used as catalyst, a negligible amount of epoxide was detected.

8. Activity of ruthenium(III) carboxylate complexes

Table 3 shows the catalytic activity of the ruthenium(III) carboxylate complexes with methoxy groups substituted at different positions in the benzene ring. Methoxy substitution in the para position increases the catalytic activity. The reactivity for 2-cyclohexenone formation is meta > para > unsubstituted > ortho while that for 2-cyclohexen-1-ol is para > unsubstituted > ortho > meta. However the catalysts are not stable to oxidation and undergo decomposition after 2 to 4 h.

9. Catalytic oxidation of linear alkenes

The oxidation of 1-heptene and 1-octene with catalysts **1**, **2** and **3** with cumene hydroperoxide as the oxidant gave very low yields of the products. 1-heptene gave only traces of 1-heptene oxide. In the case of 1-octene, a negligible quantity of epoxide was formed.

10. Mechanistic studies

The oxidation of cyclohexene gave mainly the allylic oxidation products 2-cyclohexen-1-ol and 2-cyclohexenone. The formation of the allylic oxidation products strongly suggests that to some extent the oxidation proceeds either by the radical path (reaction A) or the stepwise cationic

Table 3
Ruthenium(III) carboxylate catalysed oxidation of cyclohexene in the presence of CHP

No.	Complex $\text{RuCl}_2(\text{O}_2\text{CC}_6\text{H}_4\text{-X})(\text{PPh}_3)_2$	Yield $\times 10^{-3}$ mol			% selectivity		
		epoxide	2-cyclohexen-1-ol	2-cyclohexenone	epoxide	2-cyclohexen-1-ol	2-cyclohexenone
1	X = H	—	1.078	0.936	—	51.6	43.9
2	X = <i>o</i> -OCH ₃	—	1.071	0.766	—	54.5	38.2
3	X = <i>m</i> -OCH ₃	—	0.269	1.027	—	43.2	53.2
4	X = <i>p</i> -OCH ₃	0.138	1.17	0.970	—	39.4	31.8

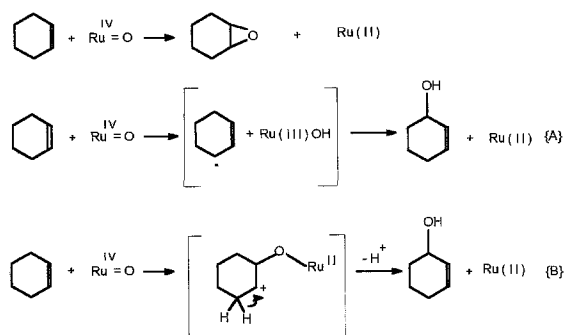
Catalyst = 1.2×10^{-5} mol; substrate = 9.9×10^{-3} mol; oxidant (CHP) = 5.26×10^{-3} , CHCl_3 = 5 ml.

Table 4
Effect of radical scavenger on the reactivity

No.	Complex	Yield $\times 10^{-3}$ mol			% selectivity		
		epoxide	2-cyclohexen-1-ol	2-cyclohexenone	epoxide	2-cyclohexen-1-ol	2-cyclohexenone
1	1	0.03 (0)	0.447 (0.792)	0.403 (0.374)	1	49.6 (62.3)	43.8 (28.8)
2	2		1.233 (1.184)	1.075 (1.214)		53.8 (47.8)	45.9 (48.1)
3	3		1.613 (1.124)	1.8103 (0.932)		45.6 (50.3)	50.1 (40.8)

Values in parentheses give the yield in the presence of radical scavenger, 2,6-di-*tert*-butyl-*p*-cresol (50 mg), catalyst = 1.02×10^{-5} mol, CHP = 5.26×10^{-3} mol; cyclohexene = 9.9×10^{-3} mol; temperature = 50°C; duration = 5 h.

mechanism (reaction B). In cyclohexene there is a preferential attack of the activated bond C–H bond over the C=C bond which is attributed to the Ru–O bond distance. This may result in allylic oxidation or epoxide formation [28].

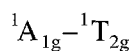
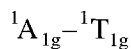


To investigate the possibility of a free radical mechanism operating in the above reactions, oxidations were carried out in the presence of free radical traps such as benzoquinone and 2,6-di-*tert*-butyl-*p*-cresol. Table 4 shows the effect of radical scavenger, 2,6-di-*tert*-butyl-*p*-cresol, in the catalytic oxidation of cyclohexene with the ruthenium complexes. In complexes **1** and **2** the combined yield of the two products, 2-cyclohexen-1-ol and 2-cyclohexenone increases on addition of 2,6-di-*tert*-butyl-*p*-cresol. However, in complex **3** a significant decrease in yield was observed. The slight increase in yield in complexes **1** and **2** on the addition of the radical trap may be due to the suppression of the radical species formed in the homolytic decomposition of the organic hydroperoxide [29].

The cyclic voltametric studies show a re-

versible peak for the cathodic reduction and anodic oxidation (Fig. 2). The peak-to-peak potential separation of the oxidation and reduction waves are 90 mV which can be assigned to a Ru(II)/Ru(III) interconversion.

The course of the reaction was followed by in situ UV at different intervals of time (Fig. 3). On the addition of CHP to catalyst **1**, there was an increase in the intensity of the peak at 400 and 715 nm. On the addition of the substrate, the intensity of the band at 715 nm decreases (Fig. 4). The band at 400 nm undergoes a blue shift to 370 nm. This band may be attributed to the ruthenium(IV) oxo species [30]. The band at 715 nm is due to the charge transition from the metal to ligand. A low spin d^6 system such as ruthenium(II) can have the following d–d transitions in addition to charge transfer transitions:



On the basis of these observations, a catalytic

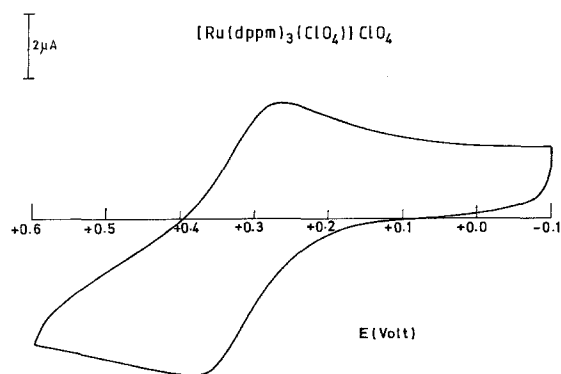


Fig. 2. Cyclic voltammogram of $[\text{Ru}(\text{dppm})_3(\text{ClO}_4)_4]\text{ClO}_4$ with tetraethylammoniumperchlorate as the supporting electrolyte.

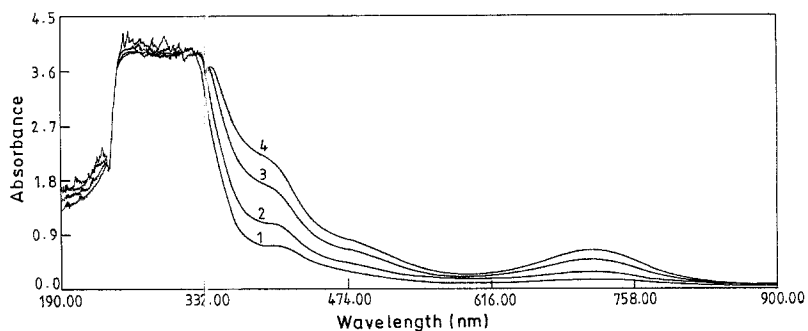


Fig. 3. UV spectrum of catalyst **2** in CHCl_3 . 1 to 4 is the spectrum recorded at intervals of 10 min after the addition of CHP to **2**. $[\mathbf{2}] = 1.2 \times 10^{-5}$ mol.

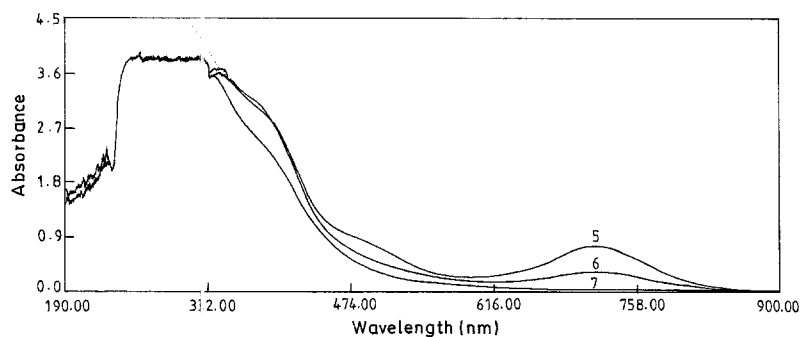


Fig. 4. UV spectrum of catalyst **2** in CHCl_3 . 5, 6 and 7 are recorded after the addition of cyclohexene to CHP and **2** at intervals of 20 min. $[\mathbf{2}] = 1.2 \times 10^{-5}$ mol, substrate = 9.9×10^{-3} mol.

cycle has been proposed. The catalytic cycle for the oxidation process is similar to that observed in the case of the iron porphyrin system [31,32].

11. Catalytic oxidation with NMO as the oxidising agent

Catalytic oxidation of cyclohexene with NMO as the oxidising agent gave mainly 2-cyclo-

hexenone. In complexes **1** and **4**, 2-cyclohexen-1-ol was also formed. However, the percentage conversion product yield was much less compared to that of CHP as the oxidising agent. Table 5 shows the catalytic activity of different complexes with NMO as the oxidising agent. Complex **2** has a high selectivity for 2-cyclohexenone formation. 1-heptene is not oxidised under the reaction conditions. 1-octene gave small amounts of 1-octene oxide.

Table 5
Catalytic oxidation of cyclohexene with NMO as the oxidising agent

No.	Complex	% Yield		% Selectivity		% Conversion
		2-cyclohexen-1-ol	2-cyclohexenone	2-cyclohexen-1-ol	2-cyclohexenone	
1	1	< 1.1	5.431	12.3	82.2	6.7
2	3	—	1.82	—	93.03	2.9
3	2	—	4.16	—	67.2	6.2
4	4	3.1	5.6	35.7	64.2	8.7

Substrate = 1×10^{-2} mol; catalyst = 1.02×10^{-5} mol; NMO (oxidant) = 3.41×10^{-3} mol; solvent = CHCl_3 ; duration = 5 h; temperature = 50°C . Conversion is based on cyclohexene.

12. Summary and conclusions

Catalytic oxidation of cyclohexene with cumene hydroperoxide gave 2-cyclohexen-1-ol and 2-cyclohexenone while oxidation with NMO gave mainly 2-cyclohexenone. CHP was a better oxidant than NMO. The active catalyst in these reactions is the $\text{Ru}^{\text{IV}}=\text{O}$ species. Linear alkenes are not reactive. The yield of products change significantly on modifying the solvents.

Acknowledgements

One of us (A.S.K) thanks the Indian Institute Of Technology, Chennai, for the award of a research fellowship.

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