

Catalytic Activity of Iron and Ruthenium Complexes of *Bis*(2,3-dihydroxy benzaldehyde)pyridine diimine towards Oxidation of Cyclohexene, Cyclohexane, THF and Alcohols Using O₂, H₂O₂, *t*-BuOOH

MINU GUPTA BHOWON*, SABINA JHAUMEER-LAULLOO, HENRI LI KAM WAH, ANISHA MEETUN and KARISHMA MUDHOO

Department of Chemistry, Faculty of Science, University of Mauritius, Reduit, Mauritius

*Corresponding author: Tel: +230 4037502; E-mail: mbhowon@uom.ac.mu

Received: 2 July 2016;

Accepted: 19 September 2016;

Published online: 29 October 2016;

AJC-18117

The oxidation of primary alcohols, cyclohexene, cyclohexane and tetrahydrofuran (THF) was studied using the catalysts [Fe(L)ClH₂O] (1) and [Ru(LH₂)PPh₃Cl₂H₂O] (2) where L = *bis*(2,3-dihydroxy benzaldehyde)pyridine diimine in various solvents and co-oxidants. Primary aromatic alcohols gave better yields compared to aliphatic alcohols. Both catalysts oxidized cyclohexene into cyclohexene-1-ol and cyclohexene-1-one in almost 1:1 ratio with negligible epoxide formation. The conversion of cyclohexane into cyclohexanol and cyclohexanone was most effective with *t*-BuOOH as co-oxidant. For THF, iron complex 1 gave better results than ruthenium complex 2.

Keywords: Catalytic, Cyclohexene, Cyclohexane, Alcohols, Co-oxidant.

INTRODUCTION

The development of catalytic method for the selective oxidation of organic substrates remains a challenge in modern chemistry. Iron [1-4] and ruthenium [5-10] complexes of Schiff bases have been reported to be active catalyst for oxidation of hydrocarbons/THF/alcohols in the presence of O₂, H₂O₂, *t*-BuOOH, PhIO, NaOCl, NMO as co-oxidants. In recent times, more environmental-friendly processes for the oxidative transformation of organics have gained considerable interest. The increased environmental concerns call for benign oxidation including recoverable catalyst and clean oxidant such as oxygen, hydrogen peroxide and *t*-butyl hydrogen-peroxide to provide means for enhanced economics and greener processes.

In our previous work, the synthesis of *bis*(2,3-dihydroxy benzaldehyde)pyridine diimine (LH₂) and [Fe(L)ClH₂O] (1) have been reported [11]. In the present study, we are reporting the synthesis of [Ru(LH₂)PPh₃Cl₂H₂O] (2) and the catalytic properties of LH₂, 1 and 2 for the oxidation of cyclohexene, cyclohexane, THF and alcohols with regards to various solvents and terminal oxidants such as O₂, H₂O₂ and *t*-BuOOH.

EXPERIMENTAL

All chemicals were purchased from either Aldrich or BDH Chemicals and were used without purification. Infrared spectra (KBr pellets) were recorded on an AVARTAR 1000 FT IR spectrometer in the range of 4000-400 cm⁻¹. ¹H and ¹³C spectra were obtained from a Bruker Spectrospin 250. UV-visible

spectra were recorded on a PV8700 series UV-visible spectrometer. The melting point of all samples was determined using a Stuart Scientific Electric Melting point apparatus. Magnetic susceptibility of the metal complexes was carried out on a Sherwood Scientific magnetic balance. Carbon, hydrogen, nitrogen and sulphur contents were obtained using a LECO 932 CHNS Mattson 1000 spectrophotometer. Gas chromatographic analyses were performed with a UNICAM GC 610 series instrument on a 30 m long DB-1 column with an FID detector.

Synthesis of [Fe(L)ClH₂O] (1): To a solution of diimine (0.5779 g, 1 mmol) in ethanol (20 mL), FeCl₃·3H₂O (0.261 g, 1 mmol) was added and the reaction mixture was stirred for 24 h at room temperature. The green compound was filtered, washed with ethanol, ether and dried. m.p. > 350 °C. Yield: 62 %. Anal. found: (calc.) for C; 49.8 (49.9), H; 3.1 (3.3), N; 9.2 (9.2), Cl; 8.2 (7.8). IR (KBr pellets, cm⁻¹): 1605, 1545, 1457, 1267, 1379; magnetic moment (μ_{eff}): 5.63 BM. UV-visible (DMSO, λ_{max}, nm): 263 (ε = 7480 M⁻¹cm⁻¹), 324 (ε = 14156 M⁻¹cm⁻¹), 351 (ε = 2667 M⁻¹cm⁻¹), 609 (ε = 4372 M⁻¹cm⁻¹).

Synthesis of [Ru(LH₂)PPh₃Cl₂H₂O] (2): To a solution of *bis*(2,3-dihydroxy benzaldehyde)pyridine diimine LH₂ (0.349 g, 1 mmol) in ethanol (20 mL), RuCl₃·3H₂O (0.261 g, 1 mmol) and triphenylphosphine (PPh₃) (0.3934 g, 1.5 mmol) were added and the resulting solution was refluxed for 3 h. The black solid formed was filtered, washed with ethanol and diethyl ether and dried. m.p. > 300 °C. Yield 68.8 %. Anal. found: (calcd.) for Ru(LH₂)PPh₃Cl₂H₂O: C; 52.8 (53.1), N;

5.4 (5.0), H; 4.1(4.3), Cl; 8.7 (8.9). IR (KBr pellets, cm^{-1}) 3451, 1608, 1538. ^1H NMR (DMSO, δ ppm): 10.14-10.47 (s, 4H); 9.82 (s, 1H); 11.01 (s, 1H, HC=CN); 6.77-8.24 (m, 24H). UV-visible (DMSO, λ_{max} , nm): 257 ($\epsilon = 21604 \text{ M}^{-1} \text{ cm}^{-1}$), 325 ($\epsilon = 20112 \text{ M}^{-1} \text{ cm}^{-1}$) 478 ($\epsilon = 19074 \text{ M}^{-1} \text{ cm}^{-1}$), 628 ($\epsilon = 1697 \text{ M}^{-1} \text{ cm}^{-1}$).

Oxidation of alcohol: To a solution of the corresponding primary alcohol (1 mmol) in dichloromethane (20 mL), O_2 or 30 % H_2O_2 (2 mL, or *t*-BuOOH (1 mL) was added followed by the complex (0.02 g). The solution was stirred for 3 h at room temperature. The mixture was filtered, concentrated and extracted with ether. The ether extract was concentrated and quantified with 2,4-dinitrophenylhydrazine.

Oxidation of cyclohexene, cyclohexane and THF: The synthesized metal complex (0.03 mmol) was dissolved in 5 mL of CH_2Cl_2 or CH_3CN or ethyl acetate and substrate (10 mmol) was added to the solution together with *n*-octane (about 0.089 g) as an internal standard for GC analyses. The resulting solution was stirred using oxygen or H_2O_2 (1.7 mL, 15 mmol) or *t*-BuOOH (1.8 mL, 10 mmol) at room temperature. The oxidation products were monitored by GC at different time intervals (3, 24, 48 and 72 h) and were identified by comparison with authentic samples.

RESULTS AND DISCUSSION

Bis(2,3-dihydroxy benzaldehyde)pyridine diimine (LH_2) was prepared by the reaction of 2,3-diaminopyridine and 2,3-dihydroxy benzaldehyde in 1:2 molar ratio in ethanol. A green solid, iron(III) complex (**1**) was formed by the reaction of iron(III) chloride with LH_2 in 1:1 ratio while ruthenium(III) complex (**2**) was formed by Ru(III) chloride, LH_2 and PPh_3 in the molar ratio 1:1:1.5 in ethanol.

In IR spectra of the ligand (LH_2), the imine band appeared at 1614 and 1558 cm^{-1} , which on complexation showed a red shift of $\approx 8\text{-}10 \text{ cm}^{-1}$ indicating the coordination of the metal ion (Ru, Fe) with imine nitrogen. The pyridine imine at 1589 cm^{-1} in LH_2 showed no shift in the complexes indicating no involvement in coordination of ring nitrogen with the metal.

In ^1H NMR spectra of complex **2**, the imine protons move downfield at δ 9.02 and 11.01 ppm compared to δ 8.85 and 9.41 ppm in the free ligand. The phenolic OH in LH_2 appeared at δ 13.01, 12.44, 9.32, 9.27 ppm. The appearance of peaks at 10.14-10.47 ppm corresponding to 4 protons indicated no deprotonation of hydroxyl protons in complex **2**.

Both complexes exhibit well-resolved intraligand and ligand to metal charge transfer bands in the region of 257-263 and 325 nm. In the free ligand LH_2 , the band at 293 and 339 nm was observed indicating a blue shift after coordination. The metal to ligand charge transfer in the visible region was at 609 and 478 nm for complexes **1** and **2**, respectively. An additional band at 628 nm in complex **2** was due to the *d-d* charge transfer.

The iron complex (**1**) was paramagnetic with 5 unpaired electrons (5.363 BM) which is consistent with + 3 oxidation state of the metal while the ruthenium complex (**2**) was diamagnetic hence containing the Ru(II) acceptor center.

Based on these observations, in complex **2**, ruthenium is octahedrally coordinated with two imine nitrogens, two

terminal chlorine atoms, one triphenyl phosphine and one water molecule while in complex **1**, iron is octahedrally coordinated with two imine nitrogens, two deprotonated oxygen atoms, one chlorine atom and one water molecule.

Catalytic evaluation: The oxidation of alcohols and hydrocarbons are reported to occur using different catalysts in the presence of different co-oxidants such as NMO, iodosylbenzene, H_2O_2 , O_2 and *t*-BuOOH [8,12-15]. The ability of complexes **1** and **2** to catalyze the oxidations of primary alcohols, cyclohexene, cyclohexane and THF were systematically studied in different solvents such as CH_3CN , CH_2Cl_2 , EtOAc in the presence of environmental-friendly terminal oxidants such as H_2O_2 , O_2 or *t*-BuOOH. The results of the different oxidation reactions are summarized in Tables 1-4.

Primary alcohols: The primary alcohols were converted into their corresponding aldehydes in 21-94 % yield with turnover 9-33 (Table-1). For **1**, the highest yield for oxidation products for the alcohols was obtained with H_2O_2 as oxidant while for complex **2**, *t*-BuOOH gave better results. The product formation using complex **1** was in the order $\text{H}_2\text{O}_2 > t\text{-BuOOH} > \text{O}_2$ while for complex **2** the order was *t*-BuOOH $> \text{H}_2\text{O}_2 > \text{O}_2$. Aromatic benzyl alcohols gave better yields with both complexes compared to the aliphatic alcohols due to the fact that the aromatic product is a non-enolisable aldehyde thus reducing the number of possible side products [13].

TABLE-1
OXIDATION OF PRIMARY ALCOHOLS
USING COMPLEXES **1** AND **2**

Substrate	Co-oxidant	Catalyst	Yield (%)	TON
Benzyl alcohol	H_2O_2	1	67	16
		2	60	25
	O_2	1	56	13
		2	35	15
	<i>t</i> -BuOOH	1	63	14
		2	76	32
4-Methoxy benzyl alcohol	H_2O_2	1	94	21
		2	66	28
	O_2	1	82	19
		2	42	18
	<i>t</i> -BuOOH	1	87	20
		2	80	33
Heptan-1-ol	H_2O_2	1	68	16
		2	47	20
	O_2	1	55	12
		2	29	13
	<i>t</i> -BuOOH	1	66	15
		2	57	12
Octan-1-ol	H_2O_2	1	57	13
		2	44	19
	O_2	1	43	10
		2	21	9
	<i>t</i> -BuOOH	1	39	9
		2	50	21

TON = Turnover = No of moles of product/No of moles of catalyst.

Cyclohexane: The oxidation of cyclohexane gave cyclohexanol and cyclohexanone as a mixture and the response factor was determined by assuming the formation products in a 1:1 ratio (Table-2). When complexes **1** and **2** were used with O_2 as co-oxidant, no appreciable conversion of cyclohexane

Catalyst	Optimum co-oxidant	Time (h)	Yield (%) (TON)		
			CH ₃ CN	CH ₂ Cl ₂	EtOAc
1	<i>t</i> -BuOOH	3	–	0.4 (1)	–
		24	6.8 (16)	0.6 (1)	4.7 (11)
		48	20.7 (47)	0.6 (1)	5.0 (12)
		72	21.5 (49)	1.3 (3)	5.0 (12)
2	<i>t</i> -BuOOH	3	14.5 (17)	10.0 (12)	6.3 (7)
		24	16.7 (19)	21.0 (24)	11.7 (10)
		48	20.8 (24)	27.0 (31)	11.9 (14)
		72	29.1 (33)	35.0 (40)	12.0 (14)
1	H ₂ O ₂	3	0.9 (2)	–	–
		24	2.1 (5)	–	–
		48	13.2 (30)	–	–
		72	15 (32)	0.1 (–)	0.7 (2)

–: not detected

was observed. With H₂O₂ as co-oxidant, complex **2** gave negligible yield while complex **1** gave the yield of the products in 15 % yield after 72 h. In the presence of *t*-BuOOH, the % yield of products was found in the range of 0.4–21 % for complex **1** and 12–35 % for complex **2**. For the oxidation of cyclohexane, *t*-BuOOH was a better co-oxidant for both catalysts and complex **2** was found to be a better catalyst than complex **1**. Higher conversion of cyclohexane was observed with catalyst **2** in dichloromethane (Fig. 1).

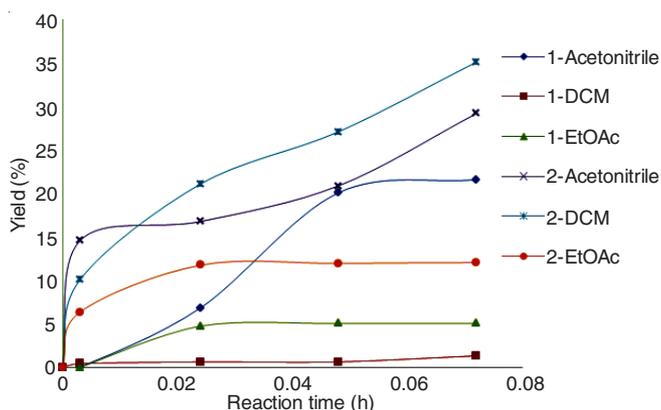


Fig. 1. Oxidation of cyclohexane using complexes **1** and **2** with *t*-BuOOH

Oxidation of tetrahydrofuran: The oxidation of tetrahydrofuran with the iron complex (**1**) gave no appreciable yield of α -butyro-lactone with O₂ and *t*-BuOOH. However, the 28.8 % yield was noted with the combination of **1**/H₂O₂/ethyl acetate after 24 h, which decreases considerably with time. Compared to iron complex (**1**), ruthenium complex (**2**) gave *a*-butyrol-

actone with only *t*-BuOOH but in poor yield (0.7–2.2 %) (Table-3).

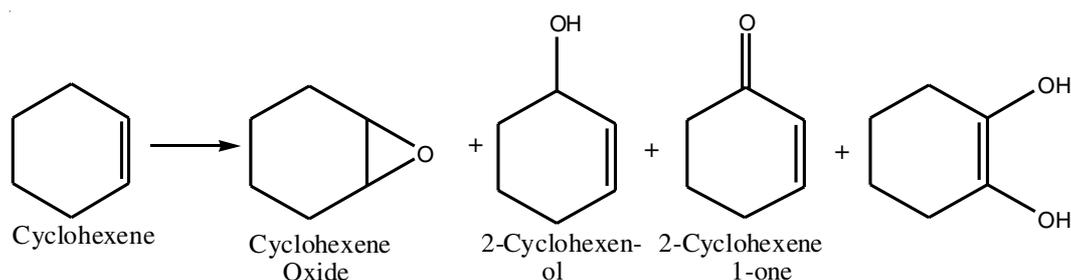
Catalyst	Optimum co-oxidant	Time (h)	Yield (%) (TON)		
			CH ₃ CN	CH ₂ Cl ₂	EtOAc
1	H ₂ O ₂	3	0.3 (1)	0.2 (1)	9.7 (22)
		24	0.4 (0.8)	0.4 (1)	28.8 (65)
		48	0.9 (2)	0.4 (1)	7.1 (16)
		72	1.3 (3)	0.5 (1)	2.2 (5)
1	<i>t</i> -BuOOH	3	0.1 (–)	0.9 (2)	1.9 (4)
		24	1.0 (2)	0.8 (7)	0.6 (1)
		48	1.0 (2)	0.8 (2)	0.5 (1)
		72	–	–	–
2	<i>t</i> -BuOOH	3	0.91 (2)	0.8 (2)	1.3 (3)
		24	2.0 (5)	0.7 (2)	1.5 (3)
		48	2.2 (5)	0.6 (1)	1.3 (3)
		72	1.9 (4)	0.5 (1)	1.2 (3)

Oxidation of cyclohexene: The oxidation of cyclohexene is reported to give four products 2-cyclohexene-1-ol, 2-cyclohexene-1-one, cyclohexene-oxide and cyclohexene-diol [16] (Scheme-I).

In the present work, three products 2-cyclohexene-1-ol (cy-ol), 2-cyclohexene-1-one (cy-one), cyclohexene-oxide (cy-oxide) were clearly identified using gas chromatography by comparison with the standards. The nature and relative yields of the products formed by catalytic oxidation of cyclohexene using complexes **1** or **2** vary considerably depending on the catalyst, oxidant and the solvents used (Table-4).

When molecular O₂, H₂O₂, *t*-BuOOH were used as co-oxidant with iron complex, complex **1** in CH₂Cl₂ and CH₃CN, 2-cyclohexene-1-ol was obtained in higher yield than 2-cyclohexene-1-one while in EtOAc, 2-cyclohexene-1-one was the predominant product. The product formation for O₂ and H₂O₂ decreased in the order acetonitrile > ethyl acetate > CH₂Cl₂ while for *t*-BuOOH the order is ethyl acetate > acetonitrile > CH₂Cl₂.

While using ruthenium complex **2** as catalyst in the presence of O₂ and H₂O₂, the formation of the cyclohexene-1-ol was more than the cyclohexene-1-one. However, in *t*-BuOOH as co-oxidant the % yield obtained for 2-cyclohexene-1-one was higher than cyclohexene-1-ol with different solvents used. The product formation in the presence of ruthenium complex **2** for O₂ and H₂O₂ decreased in the order acetonitrile > CH₂Cl₂ > ethyl acetate while for *t*-BuOOH the order was ethyl acetate > CH₂Cl₂ > acetonitrile. It is reported that CH₃CN suppresses the co-ordination of *t*-BuOOH with substrate and compete for



Scheme-I: Oxidation products for cyclohexene

TABLE-4
OXIDATION OF CYCLOHEXENE IN DIFFERENT SOLVENTS, CO-OXIDANTS USING COMPLEXES 1 AND 2

Catalyst	Co-oxidant	Time (h)	Yield (%) (TON)								
			CH ₃ CN			CH ₂ Cl ₂			EtOAc		
			Cy-ol	Cy-one	Oxide	Cy-ol	Cy-one	Oxide	Cy-ol	Cy-one	Oxide
1	O ₂	3	–	–	–	0.5(1)	0.4(1)	–	0.8(2)	2.0(5)	–
		24	4.5(10)	4.2(10)	–	0.7(2)	0.6(1)	–	2.0(4)	3.5(8)	–
		48	7.6(17)	5.6(13)	2.1(5)	1.2(3)	0.9(2)	0.3(1)	2.5(6)	4.4(10)	0.4(1)
		72	19.7(44)	13.7(31)	3.4(8)	1.2(3)	1.0(2)	0.4(1)	3.6(8)	6.4(14)	0.5(1)
2	O ₂	3	2.2(6)	1.5(4)	–	1.8(4)	0.6(1)	0.4(1)	1.5(4)	1.5(4)	–
		24	8.1(22)	4.6(13)	–	2.1(5)	0.9(2)	0.5(1)	2.1(5)	1.6(4)	0.7(2)
		48	17.8(48)	12.6(34)	–	6.4(15)	2.5(6)	1.6(4)	4.1(9)	3.4(8)	1.3(3)
		72	–	–	–	–	–	–	4.1(9)	3.8(9)	1.4(3.1)
1	H ₂ O ₂	3	5.6(13)	3.4(8)	–	0.8(2)	0.9(2)	0.2(0.4)	1.0(2)	1.0(2)	0.2(0.4)
		24	32.8(74)	20.1(45)	–	0.9(2)	1.0(2)	0.3(1)	1.7(4)	1.2(3)	0.3(1)
		48	29.9(68)	19.1(43)	–	1.0(2)	1.0(2)	0.1(0.3)	2.8(6)	2.7(6)	–
		72	15(30)	6.9(16)	–	1.1(2)	1.2(3)	–	2.6(6)	2.0(4)	–
2	H ₂ O ₂	3	2.3(6)	1.7(5)	0.2(10)	1.5(4)	1.1(3)	0.2(1)	1.7(4)	1.5(3)	–
		24	2.4(6)	2.0(5)	0.3(1)	2.8(7)	1.8(5)	0.7(2)	2.2(5)	1.7(4)	–
		48	6.3(17)	6.0(16)	–	5.7(15)	5.7(15)	–	4.1(9)	3.3(8)	–
		72	7.5(20)	7.1(19)	0.5(1)	2.1(6)	2.2(6)	–	1.9(5)	1.4(4)	–
1	<i>t</i> -BuOOH	3	0.9(2)	0.9(2)	0.3(1)	1.9(4)	0.6(1)	0.6(1)	0.9(2)	0.3(1)	0.7(1)
		24	3.8(9)	1.3(3)	0.9(2)	2.1(5)	1.3(3)	0.3(1)	0.8(2)	6.7(15)	0.4(1)
		48	1.4(3)	2.8(6)	1.0(2)	2.4(5)	0.8(2)	–	0.7(2)	7.0(16)	0.4(1)
		72	1.3(3)	4.0(9)	0.2(1)	2.8(6)	0.5(1)	–	0.6(1)	7.5(17)	0.3(1)
2	<i>t</i> -BuOOH	3	4.7(10)	2.1(5)	0.4(1)	6.2(14)	9(21)	2.1(5)	2.4(5)	6.4(15)	1.2(3)
		24	2.8(6)	10.3(24)	2.3(5)	6.6(15)	10.9(25)	1.4(3)	2.9(7)	8.8(20)	2.0(5)
		48	1.0(2)	12.0(28)	1.1(3)	6.5(15)	10.5(24)	1.2(2.7)	3.6(8)	11.2(26)	2.1(5)
		72	1.2(1)	8.0(19)	0.8(2)	6.4(15)	9.0(21)	0.8(1.8)	4.3(10)	11.4(26)	2.1(5)

Ru(IV)=O moiety [5]. Inert solvent like EtOAc and chlorinated solvent like CH₂Cl₂ were found to be good solvents for the oxidation in the presence of *t*-BuOOH as there is less competition between solvent and substrate molecules for coordination with metal active site.

Fig. 2 shows the relative % yield of the different products obtained using 1/H₂O₂ and 2/*t*-BuOOH in acetonitrile.

The oxidation of cyclohexene using ruthenium complex 2 showed the formation of 2-cyclohexene-1-ol and 2-cyclohexene-1-one more compared to the epoxide formation. This is due to the formation of Ru(IV)=O or Fe(IV)=O in the solution which is more selective towards hydroxylation of C-H bond rather than epoxidizing the C=C bond as reported earlier [5,9].

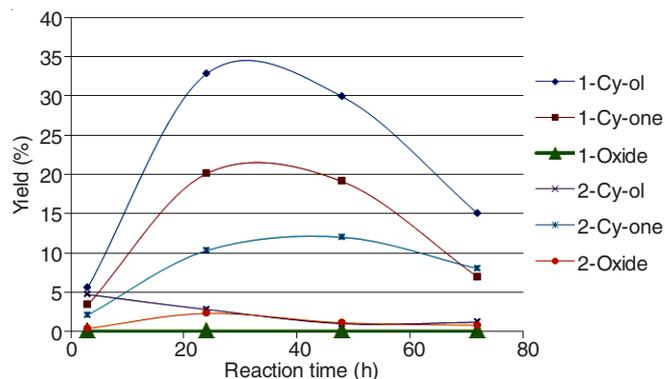
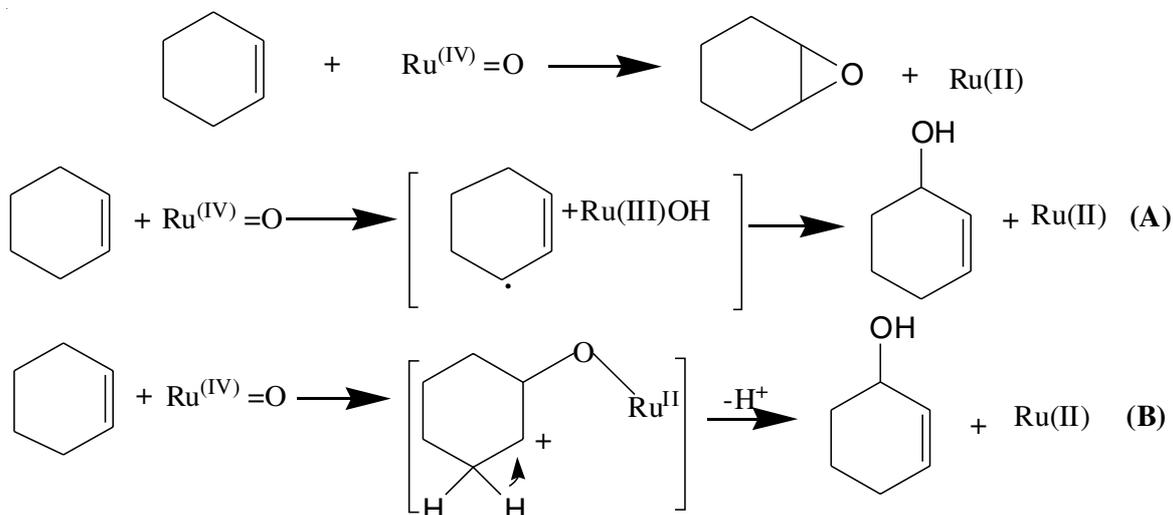


Fig. 2. Oxidation of cyclohexene using 1(H₂O₂) and 2(*t*-BuOOH) in acetonitrile



Scheme-II: Proposed mechanism for oxidation of cyclohexene using ruthenium complex 2

The mechanism of formation of products may be suggested to proceed in two ways either in heterolytic manner or radical pathways (**Scheme-II**).

The oxidation reaction for ruthenium complex **2** is believed to proceed *via* Ru(IV)=O intermediate which supported by the spectral studies. The IR spectrum of the solid mass obtained by evaporation of reaction mixture of ruthenium complex **2** taken after 30 min exhibited a characteristic Ru(IV)oxo band [5] at 877 cm⁻¹ and which was not found in the IR spectrum of the pre-cursor ruthenium complex **2**. However, the other bands in the IR remained same, which indicated no change in the structure of ruthenium complex **2** during oxidation.

Catalyst recycling: A preliminary study of the recycling efficiency of complexes **1** and **2** using *t*-BuOOH or H₂O₂ and benzyl alcohol as model substrate was undertaken. The catalyst was separated from the reaction mixture after each experiment by filtration, washed with solvent and dried before using it in the subsequent run. It was inferred that the catalyst could be recycled about three times. However, there is a progressive loss of activity accompanied by diminished yield of 5-20 %. The IR and elemental analysis of used complexes indicated that the complexes did not undergo major oxidative degradation during catalysis.

Conclusion

In summary, both catalysts **1** and **2** were successfully used for the catalytic oxidation of primary alcohols, cyclohexane,

cyclohexene and THF in the presence of environmentally friendly co-oxidants.

REFERENCES

1. E. Balogh-Hergovich and G. Speier, *J. Mol. Catal. Chem.*, **230**, 79 (2005).
2. S. Khare and S. Shrivastava, *J. Mol. Catal. Chem.*, **217**, 51 (2004).
3. A.G.J. Ligtenbarg, P. Oosting, G. Roelfes, R.M.L. Crois, R. Hage, B.L. Feringa, M. Lutz and A.L. Spek, *Chem. Commun.*, 385 (2001).
4. K.C. Gupta and A.K. Sutar, *Coord. Chem. Rev.*, **252**, 1420 (2008); S. Zhou and W. Chen, *Molecules*, **20**, 8429 (2015); A. Aggarwal, S. Singh, J. Samson and C.M. Drain, *Macromol. Rapid Commun.*, **33**, 1220 (2012).
5. D. Chatterjee and A. Mitra, *J. Coord. Chem.*, **57**, 175 (2004).
6. C.-M. Che, W.-P. Yip and W.-Y. Yu, *Chem. Asian J.*, **1**, 453 (2006).
7. R. Karvembu, S. Hemalatha, R. Prabhakaran and K. Natarajan, *Inorg. Chem. Commun.*, **6**, 486 (2003).
8. T.D. Thangadurai and S.-K. Ihm, *Transition Met. Chem.*, **29**, 189 (2004).
9. A.S. Kanmani and S. Vancheesan, *J. Mol. Catal. Chem.*, **125**, 127 (1997).
10. D. Chatterjee, *Coord. Chem. Rev.*, **252**, 176 (2008).
11. H. Li Kam Wah and S. Bangarigadu-Sanasy, *Asian J. Chem.*, **25**, 9221 (2013).
12. M.G. Bhowon, H.L.K. Wah and R. Narain, *Polyhedron*, **18**, 341 (1998).
13. Z.Q. Lei, Q.X. Kang, X.Z. Bai, Z.W. Yang and Q.H. Zhang, *Chin. Chem. Lett.*, **16**, 846 (2005).
14. R. Karvembu and K. Natarajan, *Polyhedron*, **21**, 1721 (2002).
15. J. Hu, L. Chen, K. Zhu, A. Suchopar and R. Richards, *Catal. Today*, **122**, 277 (2007).
16. N. Sehlotho and T. Nyokong, *J. Mol. Catal. Chem.*, **209**, 51 (2004).