Ruthenium catalysed Oxidation of Alkanes with Alkylhydroperoxides

Tai-Chu Lau, Chi-Ming Che,* Wai-On Lee, and Chung-Kwong Poon
Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong

The cis-$[Ru^{II}(L)_2(OH_2)_2]^{2+}$ complexes (L = substituted 2,2'-bipyridines or 1,10-phenanthrolines) catalyse oxidation of saturated hydrocarbons to alcohols and ketones by t-butylhydroperoxide; the low values of kinetic isotope effect (k_H/k_D = 3.5 for cyclohexane) and tertiary to secondary C–H bond relative reactivities (k_{tert}/k_{sec} ca. 6.5 for adamantane) are in a range expected for hydrogen atom abstraction by radical species.

The use of alkyl hydroperoxides as terminal oxidants of organic substrates is of current interest due to the recent utilization of t-butyl alcohol coproduct as a gasoline octane improver.[1] A variety of transition metal complexes (e.g. Mo^{VI}, V^V, Ti^{IV}, Mn^{III}) catalyse the epoxidation and allylic oxidation of alkenes.[2—4] In contrast, few systems are effective for oxygenation of alkanes.[2,5—7] In recent years ruthenium complexes containing polypyridyl ligands have proved to be very useful catalysts for the oxidation of organic substrates using oxygen,[8—10] iodosylbenzene,[8] and hypochlorite[11] as

Table 1. Catalytic oxygenation of alkanes with t-butyl hydroperoxide (TBHP).[a]

Catalyst	Substrate	Products[b], (% yield)[c]						Turnover of catalyst
	Cyclohexane	Cyclohexanol			Cyclohexanone			
(1)		(24)			(37)			420
(2)		(20)			(37)			400
(3)		(10)			(17)			180
(4)		(13)			(23)			235
(5)		(7)			(8)			75
(1)[d]		(nil)			(ca. 0.6)[d]			ca. 4
	Hexane	3-ol	3-one	2-ol	2-one + 1-al	1-one		
(1)		(2)	(9)	(2)	(11)	(<0.1)		160
	Heptane	4-ol + 3-ol	4-one	3-one	2-ol	2-one + 1-al	1-ol	
(1)		(1)	(2)	(6)	(1)	(8)	(0.1)	115

[a] Reaction conditions: temperature, 20 °C; time, 3h; alkane, 9.2 mmol; TBHP, 1.4 mol; catalyst, 0.002 mmol; acetone (solvent), 2 ml [substrate : TBHP : catalyst (mol) 4600 : 700 : 1]. [b] Products quantified and identified by g.c. and g.c.–m.s. [c] Yields based on TBHP consumed. The ketone yields are molar yields multiplied by 2, since 2 moles of TBHP are required to make 1 mole of ketone. [d] In 0.2 ml acetonitrile and 1.8 ml acetone as solvent.

terminal oxidants. We are thus concerned with the use of this class of compounds for the catalytic oxidation of hydrocarbons with alkyl hydroperoxides. We report here that substituted 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen) complexes of ruthenium(II)† are highly active catalysts for oxygenation of alkanes with t-butyl hydroperoxide (TBHP). Turnover numbers of over 1000 can be readily achieved at room temperature.

The following ruthenium(II) complexes were used in this study: cis-[Ru(6,6-Cl$_2$bpy)$_2$(OH$_2$)$_2$](CF$_3$SO$_3$)$_2$ (1),[12] cis-[Ru(2,9-Me$_2$phen)$_2$(OH$_2$)$_2$](CF$_3$SO$_3$)$_2$ (2),[13] cis-[Ru(phen)$_2$(OH$_2$)$_2$](ClO$_4$)$_2$ (3),† cis-[Ru(5,5'-Me$_2$bpy)$_2$(OH$_2$)$_2$](ClO$_4$)$_2$ (4),† and trans-[Ru(bpy)$_2$(OH$_2$)$_2$](ClO$_4$)$_2$ (5).[14] Addition of a catalytic amount of complexes to a solution of TBHP and cyclohexane in acetone at room temperature led to the production of cyclohexanol and cyclohexanone. Product distribution and reaction conditions are shown in Table 1. No oxidised products could be detected in the absence of either the ruthenium catalyst or TBHP. Examination of the catalysts by u.v.–visible spectroscopy after alkane oxygenation indicated that over 97% of complex (1) was regenerated while the other complexes underwent various degrees of degradation.‡ The stability of (1) enables higher turnover numbers to be achieved by using more substrate and TBHP. For example, combining 0.002 mmol of (1) with 46 mmol of cyclohexane and 14 mmol of TBHP in 5 ml acetone produced 1.56 mmol of cyclohexanol and 3.24 mmol of cyclohexanone after 24 h; corresponding to a combined yield of 57% and a catalyst turnover number of 4000. Good yields of oxygenated products were also obtained from linear-chain alkanes such as n-hexane using (1) as catalyst.

The oxidations are almost completely inhibited by the addition of π-acid ligands such as MeCN (Table 1), which are known to have high affinities for Ru^{II}.[15] This suggests that substitution of TBHP on Ru^{II} is required for activating the oxidant. This is further supported by the finding that complexes (1) and (3), which are substitutionally more labile than the other catalysts due to the presence of sterically bulky ligands, give the best yields and fastest reaction rates (Table 1).

Evidence suggests that the oxidation reactions have radical character. With (1) as catalyst, cyclohexyl chloride was formed in 6% yield when the oxidation of cyclohexane was carried out in a Me$_2$CO/CCl$_4$ (9:1) mixture, indicating that cyclohexyl radicals are produced. The low values of kinetic isotope effect (k_H/k_D = 3.5 for cyclohexane) and tertiary to secondary C–H bond relative reactivities (k_{tert}/k_{sec} ≃ 6.5 for adamantane) with (1) as catalyst in the TBHP oxidations of cyclohexane and adamantane are in a range expected for hydrogen atom abstraction by radical species.[6,16]

The similarities between the reactivity patterns of the

ruthenium/TBHP systems and the VO(dipic)(Bu^{t}OO)(H$_2$O)/TBHP (dipic = pyridine-2,6-dicarboxylate) system[6,16] led us to speculate that the active immediate is likely to be a Ru–O(Bu^t)–O· radical species. Another alternative is a dioxoruthenium(VI) intermediate, cis-[Ru(L)$_2$O$_2$]$^{2+}$, which we consider less likely for the following reasons. Firstly, addition of TBHP to complex (1) or (5) in acetone does not generate cis-[Ru(6,6'-Cl$_2$bpy)$_2$O$_2$]$^{2+}$ (ref. 12) or trans-[Ru(bpy)$_2$O$_2$]$^{2+}$.[17] Secondly, although trans-[Ru(bpy)$_2$O$_2$]$^{2+}$ does oxidize alkanes under stoicheiometric conditions, the rate is too slow compared to the catalytic reaction.[18] Thirdly, under the same reaction conditions, the catalytic oxygenation of cyclohexane by PhIO has been found to occur with (1) as catalyst but with very low turnovers and efficiency.[18] However, with complex (3) or (4), no oxidation of cyclohexane by PhIO was found and the ruthenium catalyst had been found to decompose rapidly in presence of PhIO.[18] Since PhIO oxidation usually proceeds through a metal-oxo intermediate, the result could be interpreted as due to the instabilities of cis-[Ru(L)$_2$O$_2$]$^{2+}$ (L = phen, 5,5'-Me$_2$bpy) in fluid solutions when compared to cis-[Ru(6,6'-Cl$_2$bpy)$_2$-O$_2$]$^{2+}$.[12] The difference in reactivity patterns between PhIO and TBHP oxidations suggest that the active intermediates in these two cases are different.

References

1 R. Landau, G. A. Sullivan, and D. Brown, Chemtech., 1979, 602.

2 R. A. Sheldon and J. K. Kochi, in 'Metal Catalysed Oxidation of Organic Compounds,' Academic Press, New York, 1981.

3 K. B. Sharpless and T. R. Verhoeven, Aldrichimica Acta, 1979, 12, 63.

4 H. Mimoun, in 'Comprehensive Coordination Chemistry,' vol. 6, ed. G. Wilkinson, Pergamon Press, 1987, p. 317.

5 M. Faraj and C. L. Hill, J. Chem. Soc., Chem. Commun., 1987, 1487.

6 H. Mimoun, P. Chaumette, M. Mignard, L. Saussine, J. Fisher, and R. Weiss, Nouv. J. Chim., 1983, 7, 467.

7 D. Mansuy, J.-M. Bartoli, J.-C. Chottard, and M. Lange, Angew. Chem., Int. Ed. Engl., 1980, 19, 909.

8 C. M. Che, W. H. Leung, and C. K. Poon, J. Chem. Soc., Chem. Commun., 1987, 173.

9 C. L. Bailey and R. S. Drago, J. Chem. Soc., Chem. Commun., 1987, 179.

10 R. A. Leising and K. J. Takeuchi, Inorg. Chem., 1987, 26, 4391.

11 J. C. Dobson, W. K. Seok, and T. J. Meyer, Inorg. Chem., 1986, 25, 1514.

12 C. M. Che and W. H. Leung, J. Chem. Soc., Chem. Commun., 1987, 1376.

13 J. P. Collin and J. P. Sauvage, Inorg. Chem., 1986, 25, 135.

14 B. Durham, S. R. Wilson, D. J. Hodgson, and T. J. Meyer, J. Am. Chem. Soc., 1980, 102, 600.

15 See for example, H. Taube, Coord. Chem. Rev., 1978, 26, 23.

16 H. Mimoun, L. Saussine, E. Daire, M. Postel, J. Fischer, and R. Weiss, J. Am. Chem. Soc., 1983, 105, 3101.

17 C. M. Che, K. Y. Wong, W. H. Leung, and C. K. Poon, Inorg. Chem., 1986, 25, 345.

18 C. M. Che and W. H. Leung, unpublished result.

19 P. A. Lay, A. M. Sargeson, and H. Taube, Inorg. Synth., 1986, 24, 291.

---

† Abbreviations: 5,5'-Me$_2$bpy = 5,5'-dimethyl-2,2'-bipyridine; 2,9-Me$_2$phen = 2,9-dimethyl-1,10-phenanthroline; 6,6'-Cl$_2$bpy = 6,6'-dichloro-2,2'-bipyridine. Complexes (1) and (2) were characterised by elemental analyses, u.v.–visible spectroscopy, and cyclic voltammetry. Cis-[Ru(5,5'-Me$_2$bpy)$_2$Cl$_2$] was prepared the same way as cis-[Ru(bpy)Cl$_2$].[19] The dichloro compound was converted to complex (4) by treatment with AgClO$_4$. Treatment of cis-[Ru(phen)$_2$(CO$_3$)][18] with dilute HClO$_4$ (0.1 M) afforded cis-[Ru^{II}(phen)$_2$(H$_2$O)$_2$][ClO$_4$]$_2$.

‡ The solutions usually turned green or brown after oxidation and the activities of the ruthenium catalysts were found to diminish greatly upon further addition of TBHP.