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Photooxidation of alkane under visible light irradiation catalyzed by ruthenium complexes

Motowo Yamaguchi *, Miki Tomizawa, Kazuhiro Takagaki, Masayoshi Shimo, Dai Masui, Takamichi Yamagishi

Department of Applied Chemistry, Tokyo Metropolitan University, Tokyo, Japan

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Abstract

Photoreactions of chloro(Me_2SO)bis(bipyridine)ruthenium(II) complex and the MeCN ruthenium(II) complexes having both a tridentate ligand, such as a tris(1-pyrazolyl)methane (=tpm), a tris(1-pyrazolyl)ethane (=tpe), or a 2,6-bis(1-pyrazolyl)pyridine (=bpp), and a bidentate ligand, bipyridine, have been investigated in Me_2SO, MeCN, or 1,2-dichloroethane. A ligand, such as Me_2SO or MeCN, dissociated and/or substituted by a solvent molecule selectively under irradiation. Furthermore, alkane oxidation catalyzed by ruthenium complexes in the presence of 2,6-dichloropyridine *N*-oxide under visible light irradiation (>385 nm) has been examined. Tertiary carbon(s) of adamantane was oxidized selectively to give 1-adamantanol and 1,3-adamantanediol. It was found that dicholorobis(bipyridine)ruthenium(II) complex was also an efficient catalyst on photooxidation of adamantane in the presence of 2,6-dichloropyridine *N*-oxide.

Keywords: Photooxidation; Ruthenium catalyst; Alkane oxidation; Visible light irradiation

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1. Introduction

Development of the efficient oxidation catalyst for saturated hydrocarbons is a challenging goal for chemists. Photocatalysts have drawn much attention, since they are capable of activating the unreactive C–H bonds to functionalize saturated hydrocarbons [1]. Dissociation of a ligand is often a trigger to initiate the reaction catalyzed by transition metal complexes [2]. Photochemical ligand exchange reactions of ruthenium complexes have been well known. A ligand, such as pyridine derivatives, nitriles, and sulfoxides, coordinated to ruthenium(II) polypyridine complexes is selectively substituted under light irradiation [3]. Photoactivated epoxidation of alkene catalyzed by (nitrosyl)ruthenium complex in the presence of 2,6-dichloropyridine *N*-oxide has been reported [4], however, the studies on catalytic oxidation of alkanes using metal complex under irradiation has been rare. Homogeneous alkane oxidation under irradiation catalyzed by polyoxotungstate [5], Fe(III)-porphyrins [6], U(VI)-oxide [7], transition metal chlorides [8] have been reported. Recently, we have found a new ruthenium-catalyzed oxidation reaction of alkanes utilizing 2,6-dichloropyridine *N*-oxide under visible light irradiation [9,10]. Tertiary carbon(s) of alkane was oxidized selectively to give the corresponding tertiary alcohol. The hydroxylation proceeded with complete retention of the configuration. The chloro(Me_2SO)ruthenium(II) complex having a tetradentate ligand, tris(pyridylmethyl)amine (TPA) derivative *trans*-$[RuCl\{(5\text{-}MeOCO)_3\text{-}TPA\}(Me_2SO)]Cl$ (**1**), was an effective catalyst. Photodissociation of a ligand triggered by irradiation at MLCT absorption is considered to be an initial step of the photoreaction. Since the reaction slowed down considerably when the irradiation was turned off, it is assumed that the irradiation may play a significant role not only in the initiation of the catalytic reaction but also in generating the active species for alkane oxidation [9]. In the present study, the light-driven alkane oxygenation reaction catalyzed by ruthenium complexes of bis(bipyridine)ruthenium complexes or mixed-ligand type ruthenium complexes having a tridentate and a bidentate ligand in the presence of 2,6-dichloropyridine *N*-oxide has been investigated (Scheme 1).

2. Experimental

Ligands such as tris(1-pyrazolyl)methane (=tpm) [11], 1,1,1-tris(1-pyrazolyl)ethane (=tpe) [12], and 2,6-bis(1-pyrazolyl)

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* Corresponding author. Tel.: +81 426 77 2849.
E-mail address: yamaguchi-motowo@c.metro-u.ac.jp (M. Yamaguchi).

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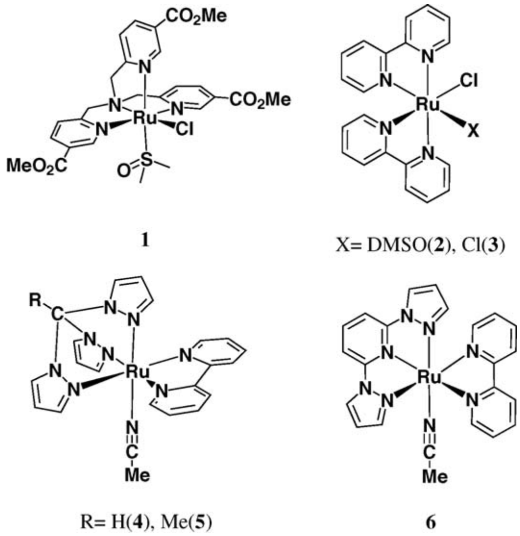


Scheme 1.

pyridine (=bpp) [13] and the complexes, chloro(Me$_2$*S*O)bis(bpy)ruthenium(II) chloride (**2**) [3], dicholorobis(bpy)ruthenium(II) (**3**) [14], (MeCN)(bpy)(tpm)ruthenium(II) (PF$_6$)$_2$ (**4**) [16], (MeCN)(bpy)(tpe)ruthenium(II) (PF$_6$)$_2$ (**5**) [15], and (MeCN)(bpy)(bpp)ruthenium(II) (PF$_6$)$_2$ (**6**) [15] were prepared by the method similar to the literature procedures. As for the photodissociation or photosubstitution reaction, the solution of the complex in MeCN or 1,2-dichloroethane was irradiated by a ultra-high pressure mercury lamp (Ushio USH500D 500 W) through Pyrex® filter (>300 nm) and monitered by UV–vis absorption or NMR spectra. FAB-MS spectra of the ruthenium complexes obtained by photoreaction were measured using *m*-nitrobenzylalcohol (*m*-NBA) as matrix. Quantum yields for photodissociation of the ligand was measured and estimated by actinometry on irradiation at 415 nm (Xe lamp) in 1,2-dichloroethane. The photooxidation of alkane was carried out under visible light irradiation using a ultra-high pressure mercury lamp with a cut-off filter (>385 nm) and an IR-cut filter in 1,2-dichloroethane in the presence of 2,6-dichloropyridine *N*-oxide under nitrogen atmosphere at room temperature. The product analyses were carried out by GC–MS. Typical procedure was as follows: 0.2 mmol (0.027 g) of adamantane and 1×10^{-3} mmol of the ruthenium complex were dissolved in 5 ml of chloroform containing 1,2-dichlorobenzene as an internal reference under nitrogen atmosphere and stirred at ambient temperature. 0.3 mmol (0.049 g) of 2,6-dichloropyridine *N*-oxide was added and stirred. The solution in the Schlenk tube was irradiated by a ultra-high pressure mercury lamp with a cut-off filter (>385 nm) and an IR-cut filter and the reaction was monitored by GC–MS.

3. Results and discussion

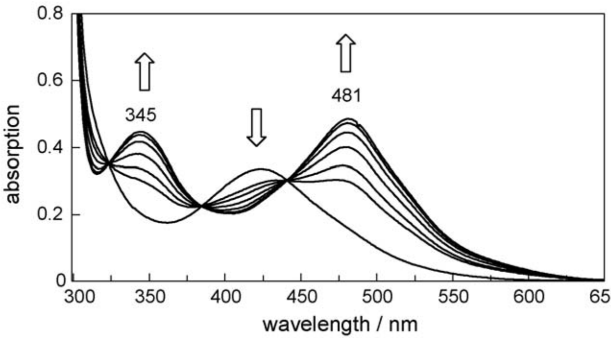


Fig. 1. UV–vis spectral changes of [RuCl(Me$_2$*S*O)(bpy)$_2$]Cl (**2**) under irradiation (>300 nm) in MeCN (irradiation time: 0, 3, 9, 18, 33 s; 1, 3 min; concentration: 6.1×10^{-5} mol/L).

Photosubstitution reactions of [RuCl(Me$_2$*S*O)(bpy)$_2$]Cl (**2**) in MeCN [3(c)] and [Ru(MeCN)(bpy)(tpm or tpe)] (PF$_6$)$_2$ (**4**, **5**) in Me$_2$*S*O have been investigated. A Me$_2$*S*O or MeCN ligand was selectively substituted to a solvent molecule due to the excitation at MLCT band. Fig. 1 shows that the UV–vis spectral changes of [RuCl(Me$_2$*S*O)(bpy)$_2$]Cl (**2**) under irradiation in MeCN. The spectra changed with isosbestic points at 325, 385, and 441 nm to the new spectrum having absorption maxima at 345 and 481 nm. The cation peak corresponding to the [RuCl(MeCN)(bpy)$_2$]$^+$ ($m/z = 490$) was observed by FAB–MS measurement of the product.

NMR spectra of [Ru(MeCN)(bpy)(tpm or tpe)] (PF$_6$)$_2$ (**4**, **5**) in CD$_3$CN before and after irradiation (3 min and 10 min, respectively) revealed that a peak assigned to a coordinated MeCN ligand disappeared and a peak of free MeCN appeared. FAB–MS spectra of the photoproducts showed the cations 3 *m*/*z* greater than those observed before irradiation, which corresponded to the CD$_3$CN complexes. Dissociation of a ligand was also observed in 1,2-dichloroethane. Formation of the pentacoordinated complex is tentatively postulated. The quantum yields for the dissociation of **5** and **6** by irradiated at 415 nm in 1,2-dichloroethane were found to be 7.2 and 1.4%, respectively. The quantum yields for photodissociation of a MeCN ligand from the tpe complex **5** was considerably higher than that of the bpp complex **6**. On the other hand, irradiation of [RuCl(Me$_2$*S*O)(bpy)$_2$]Cl (**2**) in 1,2-dichloroethane gave dichloro complex, [RuCl$_2$(bpy)$_2$] (**3**), which showed the dissociation of a Me$_2$*S*O

Table 1
Catalytic oxidation of adamantane catalyzed by complex with 2,6-dichloropyridine *N*-oxide under visible light irradiation (>385 nm)[a]

Catalyst	Time (h)	1-Adamantanol (%)	Adamantane-1, 3-diol (%)	TON
1[b]	24	67	24	230
2	16	10	0	20
3	12	47	11	138
4	24	11	0	22
5	24	43	0	86
6	24	9	0	18
1[c]	24	0	0	0
Blank[d]	6	0	0	0

[a] Conditions: [adamantane] = 0.04 mol/L. The ratio of adamantane/2,6-dichloropyridine *N*-oxide/catalyst was 200/300/1.

[b] Ref. [9].

[c] The reaction without irradiation.

[d] The reaction with irradiation in the absence of the catalyst.

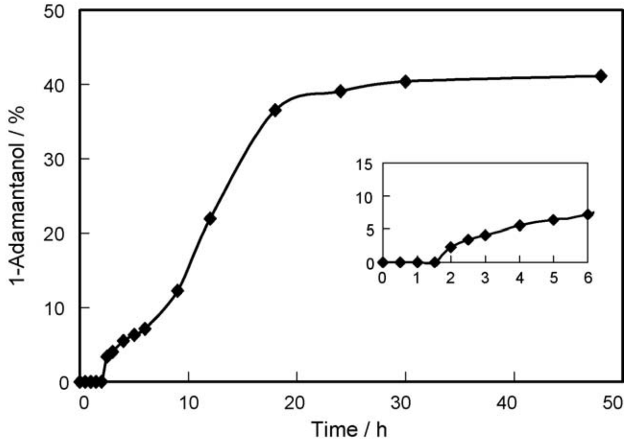


Fig. 2. Time profile of oxidation of adamantane catalyzed by [Ru(MeCN)(bpy)(tpe)] $(PF_6)_2$ (**5**) in the presence of 2,6-dichloropyridine *N*-oxide under irradiation (>385 nm) in 1,2-dichloroethane. Inset: the initial stage of the reaction.

ligand and the successive coordination of a counter-anion, chloride ion. The spectrum of $[RuCl(Me_2SO)(bpy)_2]Cl$ (**2**) changed with isosbestic points at 343, 418, and 470 nm to the new spectrum having absorption maxima at 383 and 561 nm, which was identical to that of dicholorobis(bpy)ruthenium(II) (**3**). Since the dichloro complex (**3**) is generated in situ under irradiation, catalytic activity of **3** was also examined.

Catalytic alkane oxidation catalyzed by ruthenium complexes **2–6** in the presence of 2,6-dichloropyridine *N*-oxide under irradiation in 1,2-dichloroethane has been examined (Table 1). Visible light (>385 nm) was employed, since 2,6-dichloropyridine *N*-oxide decomposed by UV-irradiation. 1-Adamantanol was selectively obtained using catalysts **3** or **5** in moderate yields (43–47%). Tertiary carbon(s) of adamantane was oxidized selectively. Almost no oxidation at the secondary carbon occurred. Adamantane-1,3-diol was also obtained (11%) in the reaction with **3**. High TON of the oxidation reaction up to 138 was observed. The diol was possibly the oxidation product of 1-adamantanol, judging from the time profile of the catalytic oxidation. No oxidation reaction took place in the absence of catalyst or without irradiation. As for the ruthenium catalysts, $[RuCl_2(bpy)_2]$ (**3**) and [Ru(MeCN)(bpy)(tpe)] $(PF_6)_2$ (**5**) were found to be the efficient catalysts for alkane oxidation. A significantly long induction period was observed as shown in Fig. 2: 4 h for **3** and 1.5 h for **5**, respectively. Catalytic oxidation of phosphine has been examined, either. Moderate activity was observed to give phosphine oxide (29% yield at 1.5 h) as shown in Fig. 3. In a control experiment without the catalyst, only a trace amount of phosphine oxide was obtained even after 3-h irradiation. In contrast to the alkane oxidation, no induction period was observed. It suggests that the different active species were responsible for the oxidation of alkane and phosphine.

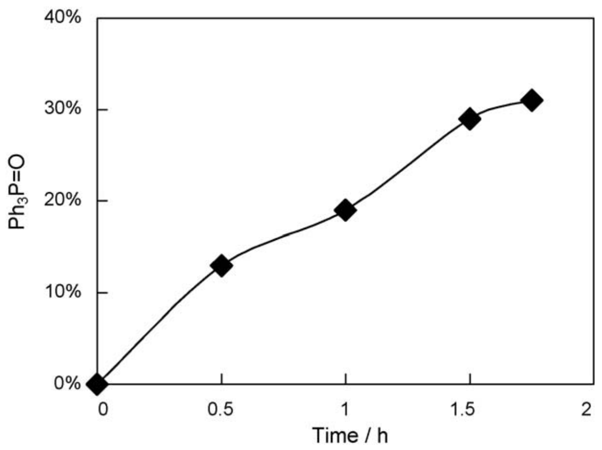
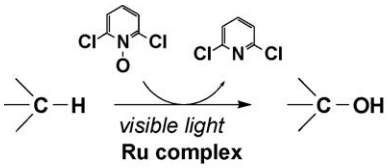


Fig. 3. Time profile of oxidation of triphenylphosphine catalyzed by [Ru(MeCN)(bpy)(tpe)] $(PF_6)_2$ (**5**) in the presence of 2,6-dichloropyridine *N*-oxide under irradiation (>385 nm) in 1,2-dichloroethane.



Scheme 2.

4. Conclusions

We have developed stereospecific and photoregulative catalytic alkane oxidation reactions using ruthenium(II) complexes in the presence of 2,6-dichloropyridine *N*-oxide under visible light irradiation. The tertitary carbon(s) is selectively oxidized to give tertiary alcohol. Although the catalytic system reported here is less reactive than the non-photochemical catalytic systems employing ruthenium porphyrin complexes as the catalyst in the presence of 2,6-dichloropyridine *N*-oxide without light irradiation [10], the photochemical system employing several non-heme type ruthenium complexes including bis(bipyridine) complexes and mixed-ligand type complexes showed similar reactivity on the oxygenation of adamantane to those catalyzed by TPA type complexes [9] (Scheme 2).

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References

[1] R.H. Crabtree, Photosensitization and Photocatalysis Using Inorganic and Organometallic Compounds, Kluwer Academic Publishers, Dordrecht, 1993, 391.

[2] (a) M. Tanaka, T. Sakakura, Homogeneous Transition Metal Catalyzed Reactions, American Chemical Society, Washington, DC, 1992, 181;
(b) M. Yoshizawa, S. Miyagi, M. Kawani, K. Ishiguro, M. Fujita, J. Am. Chem. Soc. 126 (2004) 9172.

[3] (a) A. Vlček Jr., Coord. Chem. Rev. 177 (1998) 219;
(b) D. Hasek, Y. Inoue, S.R.L. Everitt, H. Ishida, M. Kunieda, M.G.B. Drew, J. Chem. Soc. Dalton Trans. (1999) 3701;

(c) D. Hasek, G.A. Hembury, M.G.B. Drew, S. Taniguchi, Y. Inoue, Inorg. Chem. 40 (2001) 2478;
(d) J.-P. Collins, D. Jouvenot, M. Koizumi, J.-P. Sauvage, Inorg. Chem. 44 (2005) 4693.

[4] T. Takeda, R. Irie, Y. Shinoda, T. Katsuki, Synlett (1999) 1157.

[5] R.F. Renneke, C.L. Hill, J. Am. Chem. Soc. 110 (1988) 5461.

[6] A. Maldotti, C. Bartocci, R. Amadelli, P. Battioni, D. Mansuy, J. Chem. Soc. Chem. Commun. (1991) 1487.

[7] W.-D. Wang, S. Bakac, J.H. Espenson, Inorg. Chem. 34 (1995) 6034.

[8] (a) G.B. Shul'pin, G.V. Nizova, Y.N. Kozlov, New J. Chem. 20 (1996) 1243;
(b) K. Takaki, J. Yamamoto, K. Komeyama, T. Kawabata, K. Takehira, Bull. Chem. Soc. Jpn. 77 (2004) 2251.

[9] M. Yamaguchi, T. Kumano, D. Masui, T. Yamagishi, Chem. Commun. (2004) 798.

[10] High performance of catalytic alkane oxidation catalyzed by (porphyrin)ruthenium complexes without irradiation in the presence of 2,6-dichloropyridine N-oxide has been reported:
(a) H. Ohtake, T. Higuchi, M. Hirobe, J. Am. Chem. Soc. 114 (1992) 10660;
(b) J.T. Groves, M. Bonchio, T. Carofiglio, K. Shalyaev, J. Am. Chem. Soc. 118 (1996) 8961.

[11] S. Julia, J.M. del Mazo, L. Avila, J. Elgureo, Org. Prep. Proc. Int. 16 (1984) 299.

[12] (a) A.R. Katrizky, A.E. Abdel-Rahman, D.E. Leahy, O.A. Schwarz, Tetrahedron 39 (1983) 4133;
(b) M.A. Esteruelas, L.A. Oro, R.M. Claramunt, C. Lopez, J.L. Lavandera, J. Elguero, J. Organomet. Chem. 366 (1996) 245.

[13] (a) D.L. Jameson, K.A. Goldsby, J. Org. Chem. 55 (1990) 4992;
(b) P. Manikandan, B. Varghese, P.T. Manoharan, J. Chem. Soc. Dalton Trans. (1996) 371.

[14] P.A. Lay, A.M. Sargeson, Inorg. Synth. 58 (1986) 291.

[15] M. Yamaguchi, K. Takagaki, T. Yamagishi, unpublished results.

[16] N.E. Katz, F. Fagalde, N.D. Lis de Katz, M.G. Mellace, I. Romero, A. Llobet, J. Benet-Buchholz, Eur. J. Inorg. Chem. (2005) 3019.