DOI: 10.1002/adsc.200600438

Osmium-Catalyzed Selective Oxidations of Methane and Ethane with Hydrogen Peroxide in Aqueous Medium

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Received: August 27, 2006; Revised: February 11, 2007

Abstract: Various transition metal chlorides including $FeCl_3$, $CoCl_2$, $RuCl_3$, $RhCl_3$, $PdCl_2$, $OsCl_3$, $IrCl_3$, H_2PtCl_6, $CuCl_2$ and $HAuCl_4$ were studied for the selective oxidations of methane and ethane with hydrogen peroxide in aqueous medium. Among the metal chlorides investigated, osmium(III) chloride ($OsCl_3$) exhibited the highest turnover frequency (TOF) for the formation of organic oxygenates (mainly alcohols and aldehydes) from both methane and ethane. For the $OsCl_3$-catalyzed oxidation of methane with hydrgen peroxide, methyl hydroperoxide was also formed together with methanol and formaldehyde. The effects of various kinetic factors on the catalytic behavior of the $OsCl_3$-H_2O_2 system were investigated, and TOF values of 12 and 41 h^{-1} could be obtained for oxygenate formation during the oxidations of methane and ethane, respectively. In the presence of $OsCl_3$, NaClO, $NaClO_4$ or $NaIO_4$ as oxidant was incapable of oxidizing methane and ethane to the corresponding oxygenates, and the use of *tert*-butyl hydroperoxide (TBHP) instead of H_2O_2 provided remarkably lower rates of formation of oxygenates. UV-Vis spectroscopic measurements suggested that $OsCl_3$ was probably oxidized into an Os(IV) species by H_2O_2 in aqueous medium, and the Os(IV) species might be involved in the oxygenation of methane or ethane. The result that the conversions of both methane and ethane to oxygenates were suppressed by the addition of a radical scavenger suggested that the reactions proceeded *via* a radical pathway.

Keywords: ethane; homogeneous catalysis; hydrogen peroxide; methane; oxygenation; water solvent

Introduction

Activation and catalytic oxidation of lower alkanes into useful oxygenates have long been attractive and challenging research fields.[1–10] It is highly desirable to transform the inexpensive and abundant lower alkanes, especially methane and ethane, which are the main constituents of natural gas, into useful chemicals. The activation of lower alkanes usually requires severe conditions because of their chemical inertness, but carbon oxides (CO and CO_2) may be formed more easily than valuable oxygenates under such conditions. As compared with a heterogeneous catalytic system, which generally needs a much higher temperature (>500 °C) to oxidize methane or ethane,[7,8] a homogeneous system with a highly active catalyst or reactive species may operate under milder reaction conditions (<200 °C),[9,10] and thus may be promising for the selective oxidations of methane and ethane to the corresponding oxygenates such as alcohols and aldehydes.

Shilov and co-workers[2,3] found that methane could be converted into methanol and methyl chloride by a $PtCl_4^{2-}/PtCl_6^{2-}$ system in an aqueous medium in which Pt(II) was believed to function as an electrophile for C–H bond activation while Pt(IV) worked as an oxidant.[4,9] This earlier system has resulted in a number of subsequent studies on the selective oxidation of alkanes including methane *via* a route involving electrophilic C–H activation and subsequent oxidative functionalization.[4,9,10] Sen and co-workers[11] reported that methane was oxidized and converted to methyl trifluoroacetate (CF_3COOCH_3) by H_2O_2 in trifluoroacetic acid anhydride solvent in the presence of Pd(II). The use of highly electrophilic Pd(II) and Cu(II) complexes, which contained a strong electron-withdrawing ligand (hexafluoroacetylacetonate anion), further raised the efficiency for CF_3COOCH_3 formation, and the best turnover frequency (TOF) values reached 19.9 and 3.3 h^{-1} over the Pd- and Cu-based catalysts, respectively.[12] A Pd(II)–N-heterocyclic carbene complex provided a TOF of *ca.* 2 h^{-1} for the conversion of methane to CF_3COOCH_3 in tri-

fluoroacetic acid anhydride when potassium peroxodisulfate ($K_2S_2O_8$) was used as an oxidant.[13] Periana et al.[14,15] reported a highly efficient oxidative conversion of methane to methyl bisulfate with concentrated H_2SO_4 (SO_3) in the presence of an Hg(II) or Pt(II) complex. Periana et al.[16] recently also showed that methane could be converted to methanol or methyl bisulfate in a strong acid medium such as triflic or sulfuric acid in the presence of Au(III), but Au(III) could not act as a catalyst and was converted to Au(0) when sulfuric acid was used as the oxidant. To avoid the formation of Au(0) and to raise the turnover number (TON) to >1, a stronger oxidant, i.e., H_2SeO_4 (or SeO_3) was required. It is clear that, in all these systems, the combination of an electrophile such as Pd(II), Hg(II) or Au(III) [Au(I)] and a proper oxidant such as H_2O_2 or concentrated H_2SO_4 is very important.

On the other hand, there is another major route for the selective oxidation of lower alkanes in which the metal compounds or complexes initially activate the oxidant to generate a reactive species for the transformation of lower alkanes into organic oxygenates.[2,3] As environmentally benign and economically attractive oxidants, H_2O_2 and O_2 have attracted particular attention,[17,18] and a large number of studies on catalytic oxidation of alkanes with H_2O_2 or O_2 have been reported.[1–4,17–35] However, efficient homogeneous systems for the catalytic oxidation of methane or ethane with H_2O_2 or O_2 are not so numerous.[26–35] Shul′pin and co-workers[26] found that methane could be oxidized into methyl hydroperoxide, formaldehyde and formic acid with air and H_2O_2 catalyzed by [*n*-Bu_4N]VO_3 combined with pyrazine-2-carboxylic acid in acetonitrile at 25–75 °C, and the reaction was proposed to proceed through a radical mechanism.[27] The *n*-Bu_4N salts of polyphosphomolybdates $[PMo_{11}VO_{40}]^{4-}$ and $[PMo_6V_5O_{39}]^{12-}$ could catalyze the selective oxidation of ethane by H_2O_2 in acetonitrile.[28] At 60 °C, the TON for the oxidation of ethane to ethyl hydroperoxide, acetaldehyde and ethanol after 10 h of reaction was 14 (TOF, 1.4 h^{-1}), but it decreased significantly when water was used to replace acetonitrile, indicating the crucial role of the acetonitrile solvent.[28] The same research group[29,30] also investigated the catalytic behavior of several iron compounds and complexes in the selective oxidations of methane and ethane by H_2O_2 in acetonitrile at mild temperatures, and obtained TOF values of 4.3 h^{-1} and 23.3 h^{-1} for methane and ethane oxidations, respectively. Mizuno and co-workers[31,32] found that the Keggin-type heteropoly acids, especially vanadium-substituted polyphosphomolybdate ($H_4PV_1Mo_{11}O_{40}$), were active for the selective oxidation of methane by H_2O_2 in trifluoroacetic acid anhydride. Methyl formate and formic acid were produced as the main products with a TOF of *ca.* 11 h^{-1}. The trifluoroacetic acid anhydride solvent played a quite important role, and no products were observed when water was used as the solvent.[31] A diiron-substituted silicotungstate was capable of catalyzing the selective oxidation of methane with H_2O_2 in aqueous medium to useful oxygenates dominated by methyl formate with a TON of 8.4 after 48 h (TOF, 0.175 h^{-1}).[33] Using trifluoroacetic acid as the solvent, Yamanaka et al.[34,35] succeeded in the selective oxidation of methane with O_2 combined with Zn(0) in the presence of $EuCl_3$ catalyst. Methanol was produced from methane with a TOF of *ca.* 4 h^{-1} but the decomposition of trifluoroacetic acid to CO_2 could not be avoided.[35]

It is clear that "green" oxidation requires not only an environmentally benign oxidant such as H_2O_2 but also a non-toxic solvent.[17,18] As solvent, none can match water for many obvious reasons such as cheapness, safety and cleanness.[36] Moreover, several studies have shown that the organic solvents such as trifluoroacetic acid and acetonitrile may take part in the reaction or be converted under the conditions used for oxidation or oxidative functionalization of methane.[30,35,37–39] Thus it is highly desirable to develop effective homogeneous catalysts for the selective oxidation of methane or ethane with H_2O_2 in aqueous medium. To our knowledge, reports on such studies are very scarce and the TOF for the reported catalyst is very low.[33] Recently, we have investigated the catalytic properties of a series of transition metal chlorides for the oxidations of methane and ethane with H_2O_2 in water medium, and have found that $OsCl_3$ exhibits the best catalytic performances in the oxidations of both methane and ethane. In the present paper, we report the details of this aqueous $OsCl_3$-H_2O_2-based homogeneous catalytic system for the oxygenations of methane and ethane. The possible reactive species and the reaction mechanism for this system are also discussed.

Results and Discussion

Oxidations of Methane and Ethane with Hydrogen Peroxide Catalyzed by Various Transition Metals Chlorides

Table 1 shows the amounts of products after 1 h of oxidation of CH_4 with H_2O_2 in the presence of various transition metal chlorides at 90 °C. Under the reaction conditions shown in Table 1, C_1 oxygenates (CH_3OH, HCHO and CH_3OOH) and CO_2 were also formed in the absence of metal chloride (entry 1, blank reaction), and the total amount of C_1 oxygenates was 24 μmol, corresponding to a concentration of 2.4 mmol dm^{-3}. The presence of $RuCl_3$, $PdCl_2$, $IrCl_3$ or H_2PtCl_6 did not provide a higher total amount of C_1 oxygenates than the blank reaction. In the presence of $RuCl_3$

Table 1. Selective oxidation of CH_4 with H_2O_2 in the presence of various metal chlorides in aqueous medium.[a]

Entry	Catalyst	H_2O_2 conv. [%]	Product amount (μmol)				TOF for C_1 oxygenates [h^{-1}]
			CH_3OH	HCHO	CH_3OOH	CO_2	
1	None	23	6.0	13	5.0	10	None
2	$FeCl_3$	88	18	39	14	177	7.2
3	$CoCl_2$	62	18	11	27	22	5.6
4	$RuCl_3$	100	0	0	0	n.d.[b]	0
5	$RhCl_3$	70	28	16	2.0	n.d.	4.6
6	$PdCl_2$	44	18	5.0	0	34	2.3
7	$OsCl_3$	52	59	58	3.0	77	12.0
8	$IrCl_3$	50	14	3.0	0	30	1.7
9	H_2PtCl_6	32	7.0	8.0	0	n.d.	1.5
10	$CuCl_2$	80	29	16	2.0	162	4.7
11	$HAuCl_4$	35	39	14	48	75	10.1

[a] *Reaction conditions:* metal chloride, 1.0 mmol dm^{-3}; CH_4, 3 MPa; H_2O_2, 0.5 mol dm^{-3}; H_2O solvent, 10 cm^3; temperature, 90 °C; reaction time, 1 h.
[b] Not detected.

(entry 4), no formation of oxygenates was detected, but H_2O_2 was completely consumed, indicating the occurrence of rapid unproductive decomposition of H_2O_2 catalyzed by $RuCl_3$. On the other hand, $FeCl_3$, $CoCl_2$, $RhCl_3$, $OsCl_3$, $CuCl_2$ and $HAuCl_4$ enhanced the formation of C_1 oxygenates. Among these transition metal chlorides, $OsCl_3$ exhibited the highest activity for the formation of C_1 oxygenates, giving a TOF for the formation of C_1 oxygenates of 12 h^{-1}. CO_2 was also formed from CH_4 in the presence of $OsCl_3$, and the selectivity of C_1 oxygenates was 61%. The formation of O_2 with an amount of 1.12 mmol was detected in the gas phase in the case of using $OsCl_3$, and the oxygen balance was estimated to be ~98%. $HAuCl_4$ also showed a good enhancing effect for the oxidation of CH_4 to C_1 oxygenates, providing a TOF higher than 10 h^{-1} and a selectivity of 57%, but precipitation possibly due to the formation of Au(0) powder took place after the reaction. In other words, Au(III) is not a stable catalyst under our reaction conditions. On the other hand, such a phenomenon has not been observed for the Os-catalyzed system.

The results in Table 2 reveal that $OsCl_3$ is also an efficient catalyst for the selective oxidation of C_2H_6 to CH_3CH_2OH and CH_3CHO (entry 4). The TOF and the selectivity for the formation of C_2 oxygenates reach ~41 h^{-1} and 85%, respectively. It is of interest to note that, in the presence of a fixed catalyst, the conversions of H_2O_2 are similar during the CH_4 and C_2H_6 oxidations. This suggests that the reaction may proceed not *via* the electrophilic C–H activation (followed by oxidative functionalization) mechanism,[9,10] but *via* a mechanism in which the Os catalyst activates H_2O_2 to generate a reactive species for the oxygenation of methane or ethane. By assuming this, we can understand that the difference in C–H bond energy between CH_4 and C_2H_6 does not significantly affect the conversion of H_2O_2 but determines the rate of oxygenation of CH_4 or C_2H_6 to C_1 or C_2 oxygenates.

It is noteworthy that, although osmium compounds, especially OsO_4, are well-known catalysts for the selective oxidation of alkenes with various oxidants,[40,41] Os-catalyzed oxidations of alkanes are scarce. Shul′pin and co-workers once reported in a short commu-

Table 2. Selective oxidation of C_2H_6 with H_2O_2 in the presence of several metal chlorides in aqueous medium.[a]

Entry	Catalyst	H_2O_2 conv. [%]	Product amount (μmol)			TOF for C_2 oxygenates [h^{-1}]
			CH_3CH_2OH	CH_3CHO	CO_2	
1	None	23	23	58	13	None
2	$FeCl_3$	77	55	222	60	27.7
3	$PdCl_2$	36	46	202	110	24.8
4	$OsCl_3$	57	101	307	140	40.8
5	H_2PtCl_6	30	18	36	n.d.[b]	5.4
6	$HAuCl_4$	36	55	225	81	28.0

[a] *Reaction conditions:* metal chloride, 1.0 mmol dm^{-3}; C_2H_6, 3 MPa; H_2O_2, 0.5 mol dm^{-3}; H_2O solvent, 10 cm^3; temperature, 90 °C; reaction time, 1 h.
[b] Not detected.

nication[22] that $OsCl_3$ could catalyze the oxidation of alkanes to alcohols and aldehydes with H_2O_2 in acetonitrile in the presence of nitrogen-containing heterocyclic compounds such as pyridine. They mentioned that CH_4 and C_2H_6 could also be oxidized with this system, but no details were reported. The same research group recently reported that a carbonyl Os(0) complex with π-coordinated olefin showed high efficiency for the oxygenation of alkanes such as cyclohexane and *n*-heptane with H_2O_2 in acetonitrile.[42] Recently, Mayer and co-workers[43] showed interestingly that OsO_4 could act as a catalyst for the oxidation of isobutane with $NaIO_4$ oxidant in aqueous solution, giving a TON of *ca.* 4 to *tert*-butyl alcohol, acetic acid and isobutyric acid after 168 h of reaction at 85 °C. More recently, the same group reported that aqueous solutions of OsO_4 and $NaIO_4$ could even oxidize CH_4 to CH_3OH under very mild conditions (50 °C and 9.5 atm). The final CH_3OH concentration was 0.6 % of the starting OsO_4 and $NaIO_4$ concentrations, and 2.7 % of the starting CH_4 concentration after 120 h of reaction.[44] However, Mayer and coworkers have shown that OsO_4 cannot work using H_2O_2 because of the rapid oxidation of H_2O_2 itself.[43] Thus, our present result that $OsCl_3$ can catalyze the selective oxidations of CH_4 and C_2H_6 to the corresponding C_1 and C_2 oxygenates with H_2O_2 in aqueous solution is of significance. Furthermore, the TOF values obtained in our work, i.e., 12 and 41 h^{-1} for the selective oxidations of CH_4 and C_2H_6, respectively, are higher than those reported in other related systems such as the diiron-substituted silicotungstate-catalyzed CH_4 oxidation with H_2O_2 in aqueous solution described above.[33] The conversions of CH_4 and C_2H_6 with respect to the total amounts of CH_4 and C_2H_6 present in the system to C_1 and C_2 oxygenates catalyzed by $OsCl_3$ under the reaction conditions of Table 1 and Table 2 were estimated to be 0.15 % and 0.52 %, respectively.

Oxidations of Methane and Ethane with Other Oxidants

We have examined several other oxidants for the selective oxidations of methane and ethane in the presence of $OsCl_3$ in aqueous medium. Table 3 shows that, in addition to H_2O_2, *tert*-butyl hydroperoxide (TBHP) is also useful for the selective oxidations of CH_4 and C_2H_6 catalyzed by $OsCl_3$ (entries 4 and 9), while $NaIO_4$, $NaClO_4$ and NaClO cannot oxidize either CH_4 or C_2H_6 into the corresponding oxygenates. However, the activity for the formation of oxygenates was lower with TBHP than that with H_2O_2 in both CH_4 and C_2H_6 oxidations. Moreover, a difference in the product distribution was observed between using TBHP and H_2O_2 in the case of C_2H_6 oxidation (entries 9 and 10). The ratio of CH_3CH_2OH/CH_3CHO was significantly lower when TBHP was used instead of H_2O_2, suggesting that the nature of the reactive species might be different.

We have also investigated the catalytic behavior of several metal chlorides for the oxidation of C_2H_6 with different oxidants in aqueous medium. Similar to the result observed for $OsCl_3$, no formation of oxygenates was observed when $NaIO_4$, $NaClO_4$ or NaClO was used for $FeCl_3$, $PdCl_2$, H_2PtCl_6 and $HAuCl_4$, whereas the use of TBHP caused the occurrence of C_2H_6 oxidation (Table 4). However, the order of catalytic activity for oxygenate formation by changing catalyst in the case of using TBHP, i.e., $FeCl_3 > H_2PtCl_6 \approx PdCl_2 > HAuCl_4 \approx OsCl_3$ was much different with that

Table 3. Selective oxidations of CH_4 and C_2H_6 with different oxidants catalyzed by $OsCl_3$ in aqueous medium.[a]

Entry	Oxidant	Product amount (μmol)				TOF (h^{-1})
		CH_4 oxidation				
		CH_3OH	HCHO	CH_3OOH	CO_2	C_1 oxygenates
1	$NaIO_4$	0	0	0	n.d.[b]	0
2	$NaClO_4$	0	0	0	n.d.	0
3	NaClO	0	0	0	n.d.	0
4	TBHP	28	26	0	67	5.4
5	H_2O_2	59	58	3.0	77	12.0
		C_2H_6 oxidation				
			CH_3CH_2OH	CH_3CHO	CO_2	C_2 oxygenates
6	$NaIO_4$		0	0	n.d.	0
7	$NaClO_4$		0	0	n.d.	0
8	NaClO		0	0	n.d.	0
9	TBHP		5.0	105	38	11.0
10	H_2O_2		101	307	140	40.8

[a] *Reaction conditions:* $OsCl_3$, 1.0 mmol dm^{-3}; CH_4 or C_2H_6, 3 MPa; oxidant, 0.5 mol dm^{-3}; H_2O solvent, 10 cm^3; temperature, 90 °C; reaction time, 1 h.

[b] Not detected.

Table 4. Selective oxidation of C_2H_6 with TBHP in the presence of several metal chlorides in aqueous medium.[a]

Entry	Catalyst	Product amount (μmol)			TOF for C_2 oxygenates [h^{-1}]
		CH_3CH_2OH	CH_3CHO	CO_2	
1	$FeCl_3$	20	189	90	20.9
2	$PdCl_2$	31	112	36	14.3
3	$OsCl_3$	5.0	105	38	11.0
4	H_2PtCl_6	38	108	n.d.[b]	14.6
5	$HAuCl_4$	32	82	35	11.4

[a] Reaction conditions: metal chloride, 1.0 mmol dm^{-3}; C_2H_6, 3 MPa; TBHP, 0.5 mol dm^{-3}; H_2O solvent, 10 cm^3; temperature, 90 °C; reaction time, 1 h.
[b] Not detected.

in the case of using H_2O_2 (Table 2), i.e., $OsCl_3 > HAuCl_4 \approx FeCl_3 > PdCl_2 \gg H_2PtCl_6$. Such considerable differences may result from the different ability of the catalyst toward activation of TBHP and of H_2O_2. Although a different oxidant requires a proper catalyst, the combination of $OsCl_3$-H_2O_2 exhibits the best performances for the selective oxidation of C_2H_6.

Effects of Kinetic Factors on Oxidations of Methane and Ethane with Hydrogen Peroxide Catalyzed by $OsCl_3$

Table 5 shows the effect of the concentration of $OsCl_3$ on the formation of products during the oxidations of CH_4 and C_2H_6 with H_2O_2 in aqueous solution. As described above, the reaction could also proceed with a slow rate without catalyst (entries 1 and 5), but the presence of $OsCl_3$ significantly accelerated the reaction. The increase in the concentration of $OsCl_3$ from 0.5 to 1.0 mmol dm^{-3} remarkably increased the amount of oxygenates in the cases of both CH_4 and C_2H_6 oxidations (entries 2, 3 and 6, 7). A further increase in the concentration of catalyst from 1.0 to 2.0 mmol dm^{-3} only slightly increased the amount of oxygenates in C_2H_6 oxidation (entries 7 and 8) and rather decreased that in CH_4 oxidation (entries 3 and 4). At the same time, the formation of CO_2 increased remarkably in both cases. Thus, the high concentration of catalyst can cause over-oxidation to CO_2 and is detrimental to the selective formation of oxygenates in both CH_4 and C_2H_6 oxidations.

The effects of the concentration of H_2O_2 on performance during the oxidations of CH_4 and C_2H_6 catalyzed by $OsCl_3$ are summarized in Table 6. No products could be detected without H_2O_2 (entries 1 and 5), confirming that H_2O_2 is the only oxygen donor in the present system. The increase in the concentration of H_2O_2 up to 0.5 mol dm^{-3} caused significant increases in the amount of oxygenates (entries 3 and 7). The formation of oxygenates would drop with a further increase in H_2O_2 concentration, whereas that of CO_2 increased significantly. H_2O_2 conversions rose to $>70\%$ at the same time (entries 4 and 8). This result suggests that a too high concentration of H_2O_2 may also cause the over-oxidation to CO_2 and the decrease in the formation of oxygenates.

The effects of CH_4 and C_2H_6 pressures on catalytic results are plotted in Figure 1 and Figure 2. Both figures show that, in the absence of CH_4 or C_2H_6, the decomposition of H_2O_2 occurs rather rapidly, suggesting that $OsCl_3$ also catalyzes the unproductive decomposition of H_2O_2 under the present conditions. However, it is of interest to note that the presence of CH_4 or C_2H_6 has inhibited the conversion of H_2O_2. The decomposition of H_2O_2 must proceed *via* radical pathways, and the presence of CH_4 or C_2H_6 may affect the radical reactions and thus has exerted influences on H_2O_2 conversions. In the case of CH_4 oxidation (Figure 1), the increase in CH_4 pressure from 1 to 5 MPa slightly raised the H_2O_2 conversion. The total

Table 5. Effect of the concentration of $OsCl_3$ on the selective oxidations of CH_4 and C_2H_6 with H_2O_2 in aqueous medium.[a]

Entry	$OsCl_3$ conc. (mmol dm^{-3})	H_2O_2 conv. (%)	Product amount (μmol)				
			CH_4 oxidation				
			CH_3OH	HCHO	CH_3OOH	CO_2	Total oxygenates
1	0	25	6.0	13	5.0	10	24
2	0.5	35	32	11	1.0	59	44
3	1.0	52	59	58	3.0	77	120
4	2.0	78	37	24	0	200	61
			C_2H_6 oxidation				
			CH_3CH_2OH		CH_3CHO	CO_2	Total oxygenates
5	0	23	23		58	13	81
6	0.5	43	66		123	130	189
7	1.0	57	101		307	140	408
8	2.0	72	124		343	210	467

[a] *Reaction conditions:* CH_4 or C_2H_6, 3 MPa; H_2O_2, 0.5 mol dm^{-3}; H_2O solvent, 10 cm^3; temperature, 90 °C; reaction time, 1 h.

Table 6. Effect of the concentration of H_2O_2 on the selective oxidations of CH_4 and C_2H_6 in the presence of $OsCl_3$ in aqueous medium.[a]

Entry	H_2O_2 conc. (mol dm^{-3})	H_2O_2 conv. (%)	Product amount (μmol)				
			CH_4 oxidation				
			CH_3OH	HCHO	CH_3OOH	CO_2	Total oxygenates
1	0	-	0	0	0	0	0
2	0.3	40	32	22	19	86	73
3	0.5	52	59	58	3.0	77	120
4	0.8	82	50	54	0	140	104
			C_2H_6 oxidation				
			CH_3CH_2OH		CH_3CHO	CO_2	Total oxygenates
5	0	-	0		0	0	0
6	0.25	45	69		91	36	160
7	0.5	57	101		307	140	408
8	0.8	76	78		184	470	262

[a] *Reaction conditions:* $OsCl_3$, 1.0 mmol dm^{-3}; CH_4 or C_2H_6, 3 MPa; H_2O solvent, 10 cm^3; temperature, 90 °C; reaction time, 1 h.

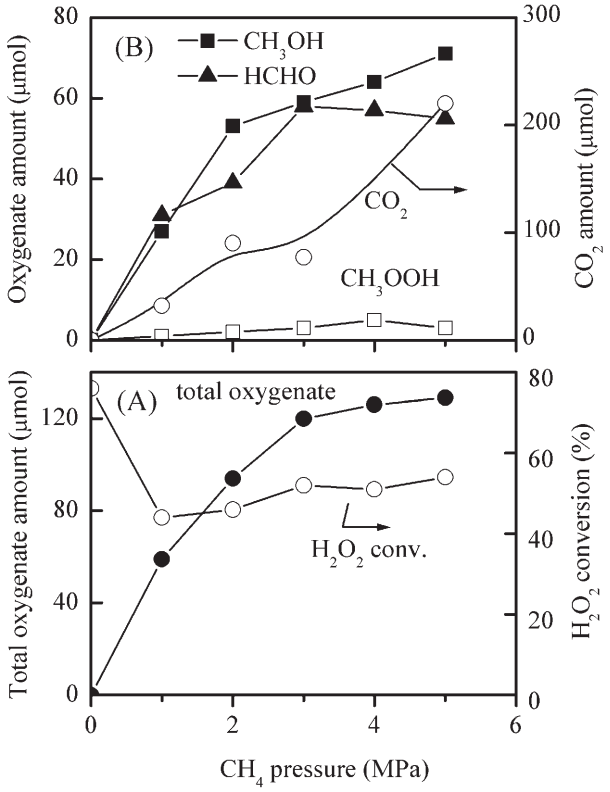

Figure 1. Effect of CH_4 pressure on catalytic performance of $OsCl_3$ for the selective oxidation of CH_4 with H_2O_2 in aqueous solutions. *Reaction conditions:* $OsCl_3$, 1.0 mmol dm^{-3}; H_2O_2, 0.5 mol dm^{-3}; H_2O solvent, 10 cm^3; temperature, 90 °C; reaction time, 1 h.

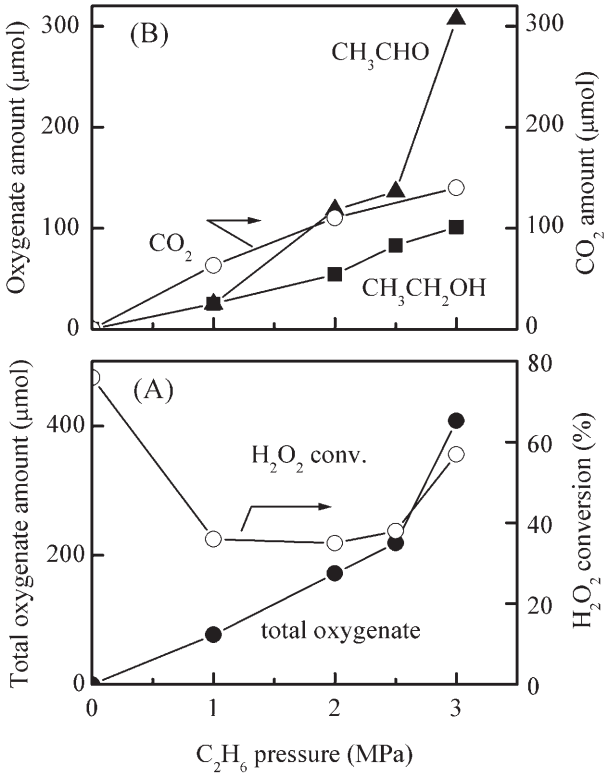

Figure 2. Effect of C_2H_6 pressure on catalytic performance of $OsCl_3$ for the selective oxidation of C_2H_6 with H_2O_2 in aqueous solutions. *Reaction conditions:* $OsCl_3$, 1.0 mmol dm^{-3}; H_2O_2, 0.5 mol dm^{-3}; H_2O solvent, 10 cm^3; temperature, 90 °C; reaction time, 1 h.

amount of all oxygenates (Figure 1 A) as well as that of each oxygenate (Figure 1 B) increased significantly with increasing CH_4 pressure to 3 MPa, and was then almost saturated. The formation of CO_2 still went up as the CH_4 pressure exceeded 3 MPa. The increase in CH_4 pressure would raise the concentration of CH_4 solubilized in water and thus increases the conversion of CH_4 into products. An estimation using solubility data of CH_4 in pure water[45] revealed that the concentration of CH_4 at 90 °C would increase almost linearly from 0.0105 mol dm^{-3} to 0.0525 mol dm^{-3} as the CH_4

pressure was raised from 1 to 5 MPa. As shown in Figure 2, in the case of C_2H_6 oxidation, the amounts of CH_3CH_2OH and CH_3CHO increased remarkably with increasing C_2H_6 pressure from 1 to 3 MPa.

Figure 3 and Figure 4 show the effects of reaction temperature on catalytic performances of $OsCl_3$ for the oxidations of CH_4 and C_2H_6 with H_2O_2. In both

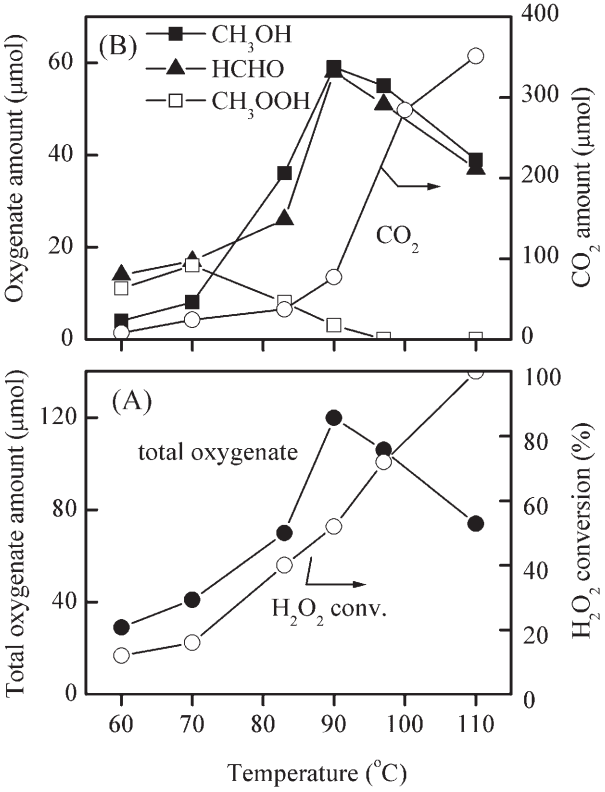

Figure 3. Effect of reaction temperature on catalytic performance of $OsCl_3$ for the selective oxidation of CH_4 with H_2O_2 in aqueous solutions. *Reaction conditions:* $OsCl_3$, 1.0 mmol dm^{-3}; H_2O_2, 0.5 mol dm^{-3}; H_2O solvent, 10 cm^3; CH_4, 3 MPa; reaction time, 1 h.

cases, the conversion of H_2O_2 went up steadily. For CH_4 oxidation (Figure 3), the total amount of C_1 oxygenates increased with increasing reaction temperature up to 90 °C, and then underwent a decrease with a further increase in temperature. The same tendency was observed for the formation of CH_3OH and HCHO (Figure 3B), whereas the amount of CH_3OOH reached a maximum at a lower temperature (70 °C), and then decreased. The result that relatively larger amount of CH_3OOH can only be obtained at lower temperatures may indicate that CH_3OOH is an intermediate product. On the other hand, the formation of CO_2 showed a steep rise as the reaction temperature rose from 90 to 100 °C. In the case of C_2H_6 oxidation (Figure 4), no formation of ethyl hydroperoxide was observed in the whole tem-

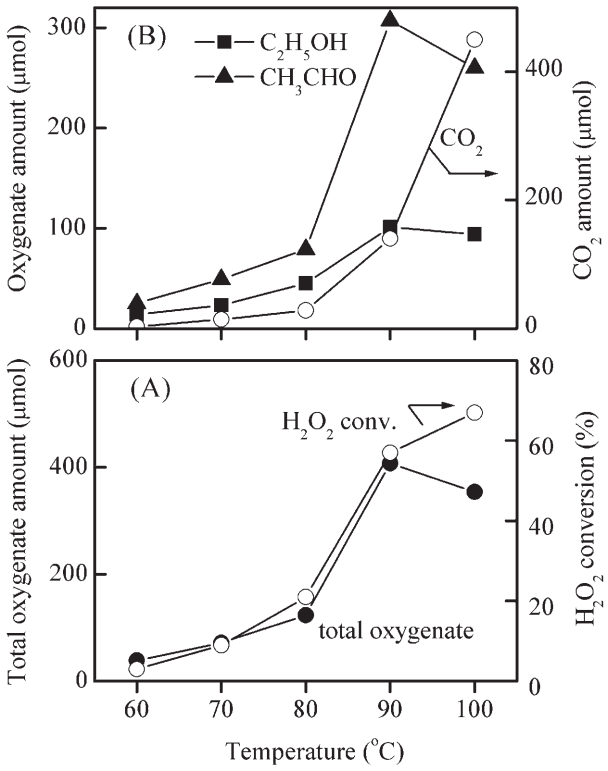

Figure 4. Effect of reaction temperature on catalytic performance of $OsCl_3$ for the selective oxidation of C_2H_6 with H_2O_2 in aqueous solutions. *Reaction conditions:* $OsCl_3$, 1.0 mmol dm^{-3}; H_2O_2, 0.5 mol dm^{-3}; H_2O solvent, 10 cm^3; C_2H_6, 3 MPa; reaction time, 1 h.

perature region. The total amount of C_2 oxygenates also arrived at a maximum at 90 °C. For both CH_4 and C_2H_6 oxidations, as the temperature exceeded 90 °C, the formation of CO_2 increased sharply, whereas that of oxygenates began to decrease, indicating that the oxygenates might undergo consecutive oxidation to CO_2 at higher temperatures.

Time courses for the oxidations of methane and ethane with H_2O_2 catalyzed by $OsCl_3$ at 90 °C are given in Figure 5 and Figure 6. Figure 5 shows that the amounts of both CH_3OH and HCHO increase almost linearly with reaction time in the initial 1 h, and then undergo decreases. However, a larger amount of CH_3OOH was obtained at a shorter reaction time. This further suggests that CH_3OOH is an intermediate product, which may be transformed to CH_3OH and HCHO. The TOF value for oxygenate formation was almost the same in the initial 1 h and began to decrease then. On the other hand, the formation of CO_2 increased steeply after the initial 1 h. This indicates that the oxygenates undergo consecutive oxidation to CO_2 at longer reaction times. Similar tendencies were observed for the oxidation of C_2H_6 except that the formation of alkyl hydroperoxide was not observed (Figure 6). The result that both alcohol

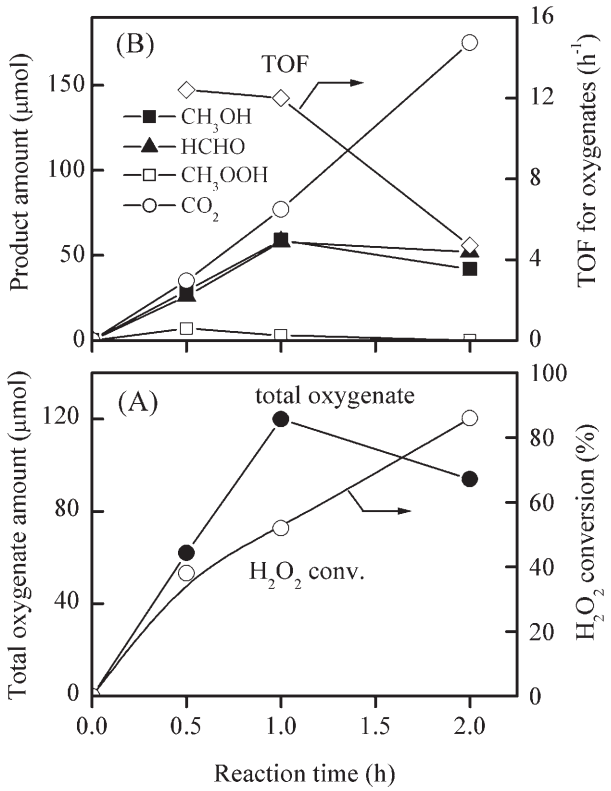

Figure 5. Time courses for the selective oxidation of CH_4 with H_2O_2 catalyzed by $OsCl_3$ in aqueous medium. *Reaction conditions:* $OsCl_3$, 1.0 mmol dm^{-3}; H_2O_2, 0.5 mol dm^{-3}; CH_4, 3 MPa; H_2O solvent, 10 cm^3; temperature, 90 °C.

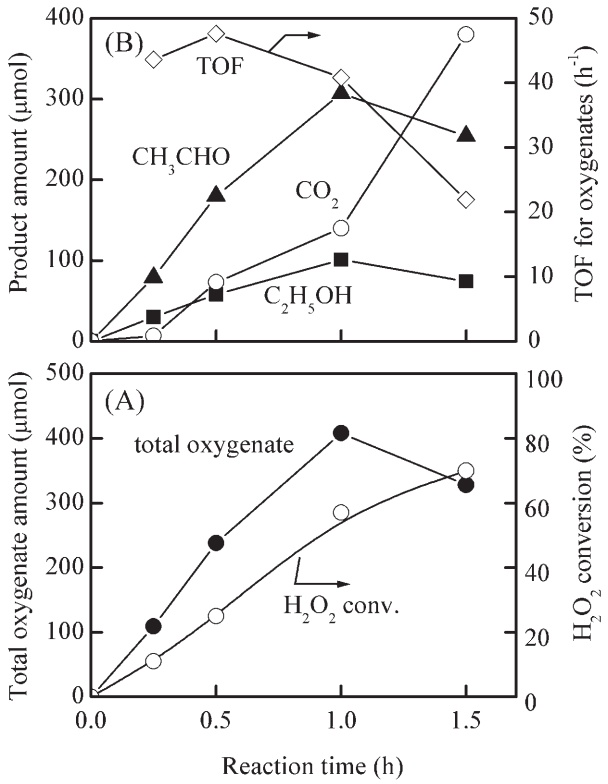

Figure 6. Time courses for the selective oxidation of C_2H_6 with H_2O_2 catalyzed by $OsCl_3$ in aqueous medium. *Reaction conditions:* $OsCl_3$, 1.0 mmol dm^{-3}; H_2O_2, 0.5 mol dm^{-3}; C_2H_6, 3 MPa; H_2O solvent, 10 cm^3; temperature, 90 °C.

and aldehyde increase almost linearly in the initial 1 h suggests that they may be formed in parallel to each other. In other words, aldehyde may not be the consecutive oxidation product of alcohol for both CH_4 and C_2H_6 oxidations in the initial 1 h.

Characterization of Os States for the Oxidation

OsO_4 is a well-known oxidant and also a catalyst for dihydroxylation of alkenes to the corresponding diols,[40,41] and it has recently been utilized for stoichiometric and catalytic oxidations of alkanes including CH_4 with $NaIO_4$ as oxidant.[43,44] On the other hand, Shul′pin et al.[42] proposed an Os(II)/Os(III) redox pair for the activation of H_2O_2 to generate hydroxyl radicals for the oxidation of alkanes such as cyclohexane catalyzed by an Os(0) complex in acetonitrile. In our experiments, when H_2O_2 was introduced into $OsCl_3$ aqueous solution, we observed a color change of the solution from dark brown to bright yellow, which may indicate a change in Os valence state after the interaction with H_2O_2.

We have characterized the possible state of Os during the oxidation of CH_4 with H_2O_2 by UV-Vis spectroscopy. Figure 7 shows UV-Vis spectra of the $OsCl_3$ aqueous solution before and after the addition of H_2O_2, and further after the CH_4 oxidation at 90 °C. The spectra of reference compounds of Na_2OsCl_6 and OsO_4 with Os in the +IV and +VIII states, respectively, are also shown in Figure 7. The $OsCl_3$ aqueous solution exhibited a strong absorption band at 371 nm with a shoulder at 298 nm and a weak band at *ca.* 500 nm (spectrum a). After the addition of H_2O_2, the spectrum changed significantly, and two bands at 337 and 370 nm were observed (spectrum b). Although the intensity was lower, these two bands were close to those mainly observed for the reference compound with Os in the +IV state, i.e., $OsCl_6^{2-}$ (spectrum e). On the other hand, the aqueous OsO_4 showed a very different spectrum in the UV region (spectrum f). Thus, it is likely that Os(III) has been oxidized to Os(IV) in the presence of H_2O_2 in aqueous medium. It is noteworthy that, in an early study, several Os(IV) ammine complexes were reported to give UV-Vis bands at lower energy positions with higher extinction coefficients as compared with the corresponding Os(III) ammine complexes.[46] However, our result for the reference compound with Os in the +IV state in Figure 7 is not consistent with this early report. We speculate that this inconsistency might arise from the ammine ligands, which do not exist in our case. Our

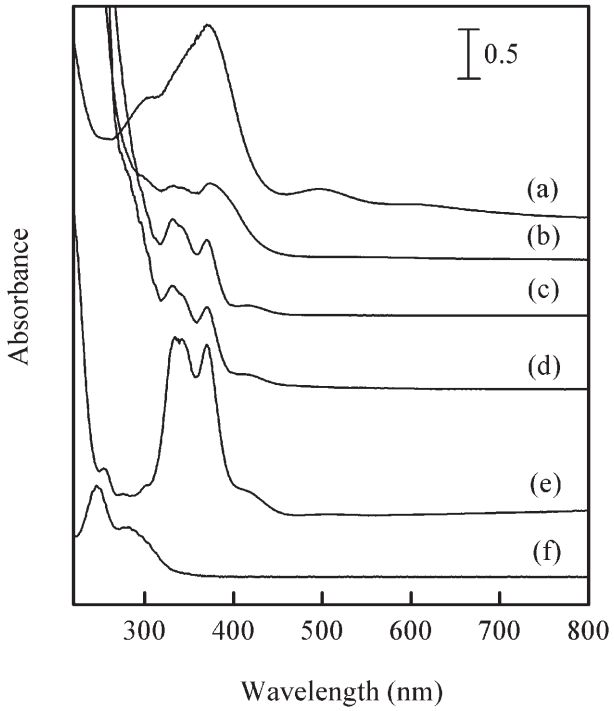

Figure 7. UV-Vis spectra of osmium-containing aqueous solutions. (a) $OsCl_3$, (b) $OsCl_3$ + H_2O_2, (c) $OsCl_3$ + H_2O_2 after CH_4 oxidation, (d) $OsCl_3$ + $NaIO_4$, (e) Na_2OsCl_6, (f) OsO_4. Reaction conditions for CH_4 oxidation: $OsCl_3$, 1 mmol dm^{-3}; H_2O_2; 0.5 mol dm^{-3}; solvent, water; CH_4, 3 MPa, temperature, 90 °C, time 1 h.

speculation that the Os(IV) species are formed after the addition of H_2O_2 to $OsCl_3$ is also reasonable if one considers that the standard electrode potential for the H_2O_2/H_2O redox pair ($E^0 = 1.78$ V) is much higher than that for the Os(IV)/Os(III) redox pair ($E^0 = 0.45$ V for $OsCl_6^{2-}/OsCl_6^{3-}$) in aqueous solution. After the oxidation of CH_4, the two bands became more distinct (spectrum c). Therefore, we conclude that osmium exists in the +IV state during the reaction. This allows us to further speculate that the Os(IV) species may be involved in the selective oxidations of CH_4 and C_2H_6 with H_2O_2.

To confirm that the Os(IV) species may play an important role in our system, we have carried out oxidations of CH_4 and C_2H_6 with H_2O_2 using Na_2OsCl_6 and OsO_4. As shown in Table 7, in the case of using OsO_4 (entries 3 and 6), no formation of oxygenates was observed for both CH_4 and C_2H_6 oxidations, but all of the H_2O_2 molecules added were consumed, indicating the rapid occurrence of unproductive decomposition of H_2O_2 to O_2. Mayer and co-workers[43] also reported the rapid oxidation of H_2O_2 by OsO_4 at a similar temperature (85 °C) in aqueous solution, and they concluded that H_2O_2 was unsuitable for the oxidation of alkanes using OsO_4 as a catalyst. On the other hand, when Na_2OsCl_6 was used (entries 2 and 5), CH_4 and C_2H_6 could be oxidized to the corresponding alcohols and aldehydes with H_2O_2. Na_2OsCl_6 exhibited lower conversions of H_2O_2 than $OsCl_3$ for both CH_4 and C_2H_6 oxidations. Simultaneously, the total amount of oxygenates for either CH_4 or C_2H_6 oxidation was also lower by using Na_2OsCl_6 than that by using $OsCl_3$. However, the product distribution patterns (the ratio of alcohol to aldehyde) by using Na_2OsCl_6 and $OsCl_3$ were similar. Thus it is likely that the oxidation catalyzed by $OsCl_3$ proceed with a similar mechanism to that by Na_2OsCl_6. As regards the higher activity of $OsCl_3$ as compared with Na_2OsCl_6, we speculate that this may result from the difference in the ligands of osmium, which may cause the difference in the coordination and activation of H_2O_2.

Possible Reaction Mechanism

Mayer and co-workers have proposed an interesting non-radical [3+2] addition of one C–H bond of the alkane molecule to two oxo groups of OsO_4 for the selective oxidation of alkanes by OsO_4.[43] For the oxi-

Table 7. Selective oxidations of CH_4 and C_2H_6 with H_2O_2 in the presence of several osmium compounds in aqueous medium.[a]

Entry	Catalyst	H_2O_2 conv. (%)	Product amount (μmol)				
			CH_4 oxidation				
			CH_3OH	HCHO	CH_3OOH	CO_2	Total oxygenates
1	$OsCl_3$	52	59	58	3.0	77	120
2	Na_2OsCl_6	33	28	21	0	50	49
3	OsO_4	100	0	0	0	0	0
			C_2H_6 oxidation				
			CH_3CH_2OH		CH_3CHO	CO_2	Total oxygenates
4	$OsCl_3$	57	101		307	140	408
5	Na_2OsCl_6	36	55		175	30	230
6	OsO_4	100	0		0	0	0

[a] *Reaction conditions:* osmium compound, 1.0 mmol dm^{-3}; CH_4 or C_2H_6, 3 MPa; H_2O_2, 0.5 mol dm^{-3}; H_2O solvent, 10 cm^3; temperature, 90 °C; reaction time, 1 h.

dation of CH_4, an unknown but very active oxidant might be formed from the $OsO_4/NaIO_4$ mixture because OsO_4 or $NaIO_4$ alone could not oxidize CH_4 to CH_3OH.[44] As described above, it has become clear that OsO_4 with Os(VIII) oxo is not the active species in our system with H_2O_2 as the oxidant. The active species is speculated to be an Os(IV) species although we still do not exactly know the coordination structure of this Os(IV) species. As shown in Figure 7, $OsCl_3$ can also be oxidized to the Os(IV) species in the presence of $NaIO_4$ (spectrum d), but $NaIO_4$ cannot function as an efficient oxidant for the oxidation of CH_4 or C_2H_6 using $OsCl_3$ catalyst (Table 3). Therefore, it is hard to consider that an Os(IV) oxo species may function for the activation and oxidation of CH_4 or C_2H_6, while H_2O_2 only acts for the oxidation of the reduced osmium [Os(II) or Os(III)] species to regenerate the Os(IV) oxo species. All the results obtained in this work allow us to speculate that the role of the osmium catalyst is to activate H_2O_2 to generate active oxygen species, which are responsible for the oxidations of CH_4 and C_2H_6.

To further uncover whether the reaction proceeds *via* a radical mechanism, we have investigated the influence of the addition of a radical scavenger (0.1 mol dm^{-3}), hydroquinone, to the reaction system under the conditions of Table 1 and Table 2 for $OsCl_3$. We found that the oxidations of both CH_4 and C_2H_6 with H_2O_2 catalyzed by $OsCl_3$ ceased after the addition of hydroquinone. This result suggests that the oxidation with H_2O_2 catalyzed by $OsCl_3$ proceeds through radical pathways. We assume that the redox of Os(IV)/Os(III) may take part in the activation of H_2O_2 to generate active oxygen species, which may be hydroxyl (·OH) or hydroperoxide (·OOH) radical. The active oxygen species may then activate methane or ethane by abstracting a hydrogen atom, forming methyl or ethyl radicals. The subsequent reactions between the radicals and/or between the radical with methane or ethane may provide the products. It is worthy of mention that an iron-based catalyst may carry out the same reactions through Fe(III)/Fe(II).[30] Under our conditions, we really found that $FeCl_3$ was also a relatively better catalyst for the oxidations of CH_4 and C_2H_6 than several other transition metal chlorides (Table 1 and Table 2). However, the unproductive decomposition of H_2O_2 was more serious in the presence of $FeCl_3$, and this resulted in lower concentrations of oxygenate products from both CH_4 and C_2H_6 as compared with $OsCl_3$.

Conclusions

Among the various transition metal chlorides investigated, $OsCl_3$ was found to be the most efficient catalyst for the oxidations of methane and ethane to the corresponding alcohols and aldehydes with H_2O_2 in aqueous medium. The turnover frequency values for oxygenate formation in methane and ethane oxidations could reach 12 and 41 h^{-1}, respectively. The formation of a small amount of methyl hydroperoxide was also observed during the oxidation of methane at the very initial stage or lower reaction temperatures. For both methane and ethane oxidations, aldehydes might mainly be formed in parallel to alcohols but not *via* the consecutive oxidation of alcohols. Carbon dioxide was also formed in both cases, and the formation of carbon dioxide became serious at higher temperatures and longer reaction times. TBHP could be used for the oxidations of methane and ethane in the presence of $OsCl_3$ catalyst but the activity for oxygenate formation was remarkably lower. On the other hand, $NaIO_4$, $NaClO_4$ or NaClO could not oxidize methane and ethane into the corresponding oxygenates by $OsCl_3$ catalyst. UV-Vis spectroscopic measurements indicated that osmium existed in the +IV state during the oxidation reactions with H_2O_2. We confirmed that OsO_4 only catalyzed the unproductive decomposition of H_2O_2 and was not the active phase in our system. The Os(IV) species was proposed for the activation of H_2O_2, generating an active oxygen species for the selective oxidations of methane and ethane probably *via* radical pathways.

Experimental Section

Catalytic Reactions

The catalytic oxidations of methane and ethane were carried out with a stainless-steel autoclave containing a Teflon vessel (75 cm^3). In a typical run, a measured amount (0.1 mol dm^{-3} aqueous solution, 0.1 cm^3) of catalyst was added into the Teflon vessel, which was pre-charged with ultrapure water. Then a certain amount of aqueous H_2O_2 (30%) was added into the reactor. The total volume of the reaction solution was 10 cm^3. The system was pressured with methane or ethane to a fixed pressure after air in the reactor was removed with the reactant. The autoclave was heated to the reaction temperature in an oil bath. The reaction solution was vigorously stirred and maintained at the reaction temperature for a fixed time. After the reaction, the autoclave was cooled with ice to room temperature.

The liquid-phase products were analyzed by gas chromatography (GC) after the addition of a known amount of liquid standards (propanol for CH_4 oxidation and acetone for C_2H_6 oxidation). Two GCs (Model SP-2100) with a capillary column (DB-5 MS) connected with an FID detector and a packed column (Porapak T) connected with a TCD detector were applied for the analyses of the products from CH_4 oxidation, and another GC (Model GC-960) equipped with a Porapak T column and an FID detector was used for the analyses of the products from C_2H_6 oxidation. Alkyl hydroperoxide was evaluated using a method proposed by Shul′pin et al.,[30] i.e., by comparing the amount of alcohol (meth-

anol or ethanol) before and after the addition of $NaBH_4$. The titration of H_2O_2 was carried out with 0.01 mol dm^{-3} $KMnO_4$ solution. Gas phase products such as O_2, CO and CO_2 were analyzed by a gas chromatograph equipped with Porapak Q and Molecular Sieve 5 A columns and TCD detectors. The gas chromatograph was directly connected to the outlet of the autoclave. The formation of CO_2 and O_2 was confirmed but no CO could be detected in all runs. We checked the oxygen balance in some runs based on the amounts of H_2O_2 consumed and products (including oxygenates, CO_2 and O_2) formed, and the oxygen balance was always better than 90%.

UV-Vis Spectroscopic Measurement

UV-Vis absorption spectroscopic measurements were performed on a Shimadzu UV-2100 UV-Vis spectrometer. The diluted aqueous solutions of Os compounds, mixtures of Os compounds and H_2O_2, and the mixtures after the reaction were measured, respectively, and each spectrum was recorded in the 200–800 nm range at room temperature.

Acknowledgements

This work was supported by the Natural Science Foundation of China (grants 20433030 and 20625310), the National Basic Research Program of China (grants 2005CB221408 and 2003CB615803), the Key Scientific Project of Fujian Province (2005HZ01–3), the Scientific Research Foundation for the Returned Oversea Chinese Scholars (grant to Q.Z.), and the Program for New Century Excellent Talents at the University of China (grant NCET-040602 to Y.W.).

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