FeCl₃-Activated Oxidation of Alkanes by [Os(N)O₃]⁻

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Abstract: Although the ion $[Os^{VIII}(N)(O)_3]^-$ is a stable species and is not known to act as an oxidant for organic substrates, it is readily activated by FeCl₃ in CH_2Cl_2/CH_3CO_2H to oxidize alkanes efficiently at room temperature. The oxidation can be made catalytic by using 2,6-dichloropyridine *N*-oxide as the terminal oxidant. The active intermediates in stoichiometric and catalytic oxidation are proposed to be $[(O)_3Os^{VIII}{\equiv}N{-}Fe^{III}]$ and $[Cl_4(O)Os^{VIII}{\equiv}N{-}Fe^{III}]$, respectively.

Introduction

Nature has evolved reactive oxoiron species in enzymes such as cytochrome P-450 and methane monooxygenases that can oxidize alkanes under mild conditions.[1-3] The search for highly reactive metal−oxo species in chemical systems that can match the reactivities of these enzymes continues to be a challenge to chemists.[4-8] Metal−oxo species such as chromate and permanganate have long been used as oxidants for a variety of organic functional groups.[9] However, their use in the oxidation of alkanes is limited; refluxing conditions are often required to oxidize unactivated C−H bonds. Much more reactive metal−oxo species have been generated by using synthetic porphyrin ligands,[2] and a number of oxometalloporphyrins of iron,[10] chromium,[11-13] ruthenium[14,15] and manganese,[16] usually generated in situ, are capable of oxidizing a variety of organic substrates, including alkanes. Our approach is to use Lewis acids to activate metal−oxo species. The activating effects of Brønsted acids on metal−oxo species are well known; however, the use of Lewis acids to enhance the reactivity of metal−oxo species is much less studied. We recently reported that the oxidation of alkanes by oxo species of ruthenium,[17] iron,[18] manganese, and chromium[19] is greatly enhanced by Lewis acids. The Lewis-acid-assisted oxidation of various other organic substrates by permanganate was also subsequently reported by Lee and co-workers.[20,21]

We report here a study of the remarkable activating effects of FeCl₃ on the oxidation of alkanes by the nitridoosmate(VIII) ion, $[Os(N)(O)_3]^-$. Although OsO_4 is a well-established reagent for the dihydroxylation of alkenes, it does not oxidize alkanes.[22] The $[Os(N)(O)_3]^-$ ion is an even weaker oxidant than OsO_4 due to the stronger electron-donating properties of the N^{3-} ion than the O^{2-} ion, and it is not known to act as an oxidant for any organic substrates. However, the addition of just a few equivalents of FeCl₃ to $[Os(N)(O)_3]^-$ results in a system that can perform stoichiometric and catalytic oxidation of alkanes efficiently at room temperature.

Experimental Section

Materials. All chemicals were of reagent grade unless otherwise noted. $[^nBu_4N][Os(N)(O)_3]$[23] and $[^nBu_4N][Os(N)Cl_4]$[24] were synthesized according to published procedures. The purity of these complexes was determined by CHN analysis and UV−vis spectrophotometry. Anhydrous ferric chloride (98%), *cis*- and *trans*-1,2-dimethylcyclohexane, propane, isobutane, and *n*-butane were purchased from Aldrich and were used as received. Other alkanes and solvents were purified

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according to standard methods.[25] 2,6-Dichloropyridine *N*-oxide was prepared according to a literature method,[26] and its purity was determined to be >99% by NMR. $H_2^{18}O$ (95 atom % ^{18}O) was obtained from Aldrich.

Instrumentation. Gas chromatographic analyses were performed on a HP 6890 gas chromatograph with a HP-5MS (30 m × 0.25 mm i.d.) or a HP-FFAP (25 m × 0.2 mm i.d.) column. GC−MS measurements were carried out on a HP 6890 gas chromatograph interfaced to a HP 5973 mass-selective detector.

Kinetic experiments were performed by using either a HP 8452A UV−vis spectrophotometer or a Hi-Tech Scientific SF-61 stopped-flow spectrophotometer equipped with a diode-array detector. The progress of the reaction was monitored by observing absorbance changes at 450 nm (λ_{max} of the intermediate). Pseudo-first-order rate constants, k_{obs}, were obtained by nonlinear least-squares fits of A_t vs time t according to the equation $A_t = A_\infty + (A_0 - A_\infty) \exp(-k_{obs}t)$, where A_0 and A_∞ are the initial and final absorbance, respectively.

Electrospray ionization mass spectrometry (ESI-MS) was performed on a PE SCIEX API 365 mass spectrometer. The samples were dissolved in CH_2Cl_2/CH_3CN (1:1) or CH_2Cl_2/CH_3CO_2H (3:1) at 23 °C. These were continuously infused with a syringe pump at a constant flow rate of 5 μL min^{-1} into the pneumatically assisted electrospray probe with nitrogen as the nebulizing gas.

^1H NMR spectra were recorded on a Varian (300 MHz) FT NMR spectrometer. Elemental analyses were done on an Elementar Vario EL Analyser. Infrared spectra were recorded as KBr pellets on a Nicolet Avatar 360 FTIR spectrophotometer.

Stoichiometric and Catalytic Oxidation of Alkanes. All experiments were carried out under argon, unless otherwise specified. In a typical stoichiometric oxidation reaction, a light yellow solution of [$^nBu_4N$][Os(N)(O)$_3$] (5.0 × 10^{-3} M) was mixed with a yellow solution of FeCl$_3$ (2.0 × 10^{-2} M) in CH$_2$Cl$_2$/CH$_3$CO$_2$H (5:2, v/v) containing alkane (1.2 M) at 23 °C. The resulting red solution was vigorously stirred for 30 s. Chlorobenzene was then added as an internal standard, and the mixture was analyzed by GC and GC−MS.

In a typical catalytic oxidation reaction, a solution of 2,6-dichloropyridine *N*-oxide (0.1 M) was mixed with a solution of [$^nBu_4N$]-[Os(N)(O)$_3$] (1.25 × 10^{-3} M) and FeCl$_3$ (1.0 × 10^{-2} M) in CH$_2$Cl$_2$/CH$_3$CO$_2$H (5:2, v/v) containing alkane (1.2 M). For reactions at 23 °C the mixture was stirred for 16 h, while for reactions at 60 °C the reaction time was 30 min. The products were analyzed by GC and GC−MS with chlorobenzene as the internal standard.

Kinetic isotope effects for stoichiometric and catalytic oxidation of cyclohexane were investigated by using an equimolar mixture of cyclohexane and cyclohexane-d_{12} as substrate. The organic products were quantified and identified by GC and GC−MS. The KIE values were obtained by taking the ratio of the corresponding areas from GC measurement. Kinetic isotope effects for stoichiometric oxidation were also determined by comparing the rates of reactions of single-substrate experiments.

For oxidation of cyclohexane in the presence of $H_2^{18}O$, the ^{16}O and ^{18}O compositions of cyclohexanol were determined from the relative abundances of the peaks at $m/z = 100$ (^{16}O) and 102 (^{18}O) in GC−MS (EI).

Isolation and Detection of the Osmium-Containing Product from Stoichiometric and Catalytic Oxidation. The typical stoichiometric oxidation reaction was scaled up 20 times, and the resulting red solution was pumped to dryness at room temperature and then washed with water and diethyl ether. The residue was recrystallized from dichloromethane/diethyl ether to give a red crystalline solid, identified to be [$^nBu_4N$][Os^{VI}(N)Cl$_4$] (yields > 80%) by infrared spectroscopy,

Table 1. Stoichiometric Oxidation of Cyclohexane by [$^nBu_4N$][Os(N)(O)$_3$] under Various Conditions^a

entry	FeCl$_3$, molar equiv	CH$_3$CO$_2$H (mL)	CH$_2$Cl$_2$ (mL)	product yield, %^{b}			time
				c-C$_6$H$_{11}$OH	c-C$_6$H$_{10}$O	c-C$_6$H$_{11}$Cl	
1	0	0	7	nd^c	nd	nd	24 h
2	0	2	5	nd	nd	nd	24 h
3^d	0	2	5	<1	21	nd	20 min
4	2	2	5	2	63	1	30 min
5	4	2	5	15	62	1	30 s
6^e	4	2	5	15	61	1	30 s
7^f	4	2	5	17	63	1	30 s
8	4	3	4	15	55	3	10 min
9	4	4	3	15	55	3	10 min
10	4	3^g	4	2	12	1	3 h
11	8	2	5	19	51	4	30 s
12	8^h	2	5	34	38	3	30 s
13	16^i	2	5	51	26	1	30 s

^{a} [$^nBu_4N$][Os(N)(O)$_3$], 5.0 × 10^{-3} M; cyclohexane, 1.2 M; $T = 23$ °C. ^{b} The yields were calculated on the basis of the system acting as a two-electron oxidant. ^{c} Not detected. ^{d} CF$_3$CO$_2$H was used instead of CH$_3$CO$_2$H. ^{e} 0.1 M BrCCl$_3$ was added. ^{f} Reaction in air. ^{g} CH$_3$CN was used instead of CH$_3$CO$_2$H. ^{h} [$^nBu_4N$][Os(N)(O)$_3$], 1.25 × 10^{-3} M. ^{i} [$^nBu_4N$][Os(N)(O)$_3$], 6.25 × 10^{-4} M.

UV−vis spectroscopy, CHN analysis, and ESI-MS.[27] The same product was obtained from catalytic oxidation. The [Os^{VI}(N)Cl$_4$]$^-$ ion was also directly detected in the reaction mixture by ESI-MS.

Spectrophotometric Analysis of the Oxidation State of the Iron Species after Reaction. The solution after stoichiometric or catalytic oxidation was evaporated to dryness at room temperature. The residue was dissolved in 0.25 M HCl and filtered. Excess potassium thiocyanate was then added, and the resulting intensely red-colored iron(III) thiocyanate solution was analyzed by UV−vis spectrophotometry at 480 nm.[28] It was found that iron(III) thiocyanate was formed quantitatively, indicating that all the iron species remained in the 3+ oxidation state in both catalytic and stoichiometric oxidation.

Results and Discussion

Products and Stoichiometry of Cyclohexane Oxidation by [Os(N)(O)$_3$]$^-$/FeCl$_3$. In a typical reaction, a light yellow solution of [$^nBu_4N$][Os(N)(O)$_3$] (5.0 × 10^{-3} M) was mixed with a yellow solution of FeCl$_3$ (2.0 × 10^{-2} M) in CH$_2$Cl$_2$/CH$_3$CO$_2$H (5:2, v/v) containing cyclohexane (1.2 M) at 23 °C under argon. The solution immediately turned dark green and then changed to red after ca. 5 s. Analysis of the red solution by GC and GC−MS indicated the presence of cyclohexanol, cyclohexanone, and a small amount of chlorocyclohexane, with a total yield of 78% (Table 1, entry 5). The yields were calculated by assuming that the system acted as a two-electron oxidant (vida infra). In the absence of FeCl$_3$, [Os(N)(O)$_3$]$^-$ remained unchanged and no products could be detected for at least 24 h (entries 1 and 2). Addition of BrCCl$_3$ (0.1 M) to the system caused little change in the yield and product distribution, and the amount of bromocyclohexane detected was <1% (entry 6). When the reaction was carried out in air, a slightly higher yield of 81% was obtained (entry 7). Replacing CH$_3$CO$_2$H with CH$_3$CN resulted in a slower reaction and a much lower yield of 15% (entry 10). The Brønsted acid CF$_3$CO$_2$H also produced an activating effect, but the yields were much lower (entry 3). No products could be observed after 24 h when OsO$_4$ was used instead of [Os(N)(O)$_3$]$^-$.
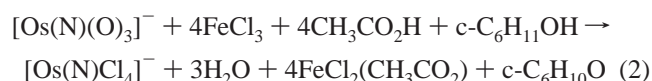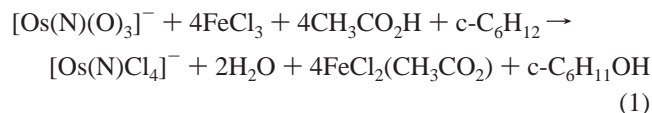
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The oxidation of cyclohexane was also carried out in the presence of $H_2^{18}O$. When $[^nBu_4N][Os(N)(O)_3]$ in CH_2Cl_2 was added to $FeCl_3$ and cyclohexane in CH_2Cl_2/CH_3CO_2H containing 0.125 M $H_2^{18}O$, the cyclohexanol was 61% ^{18}O enriched. Control experiments show that cyclohexanol does not exchange with $H_2^{18}O$ under these conditions; however, $[Os(N)(^{16}O)_3]^-$ exchanges rapidly with $H_2^{18}O$ in CH_2Cl_2/CH_3CO_2H. When $H_2^{18}O$ (0.125 M) was added to $[^nBu_4N][Os(N)(^{16}O)_3]$ $(1.25 \times 10^{-3}$ M) in CH_2Cl_2/CH_3CO_2H (3:1, v/v) at 23 °C, the ESI-MS (negative mode) taken after 3 min showed a mixture of 10% $[Os(N)(^{18}O)_3]^-$, 35% $[Os(N)(^{18}O)_2(^{16}O)]^-$, 35% $[Os(N)(^{18}O)(^{16}O)_2]^-$, and 20% $[Os(N)(^{16}O)_3]^-$. This distribution remained unchanged for at least 30 min. Substantial ^{16}O was still present in $[Os(N)(O)_3]^-$, presumably because there was trace $H_2^{16}O$ in the solvent.

The rates and product distributions in cyclohexane oxidation depend on the relative amount of $FeCl_3$ used. A higher yield and faster rate were observed when 4 equiv of $FeCl_3$ was used instead of 2 equiv (entries 4 and 5). Further increase of $FeCl_3$ to 8 equiv resulted in a slightly lower yield of 74%; however, the relative amount of cyclohexanol increased (entry 11). A significant increase in the relative amount of cyclohexanol was also observed when the concentration of $[Os(N)(O)_3]^-$ was decreased (entries 12 and 13).

From the reaction mixture the well-known osmium(VI) nitrido species, $[^nBu_4N][Os^{VI}(N)Cl_4]$, could be isolated in over 80% yield. The $[Os^{VI}(N)Cl_4]^-$ ion was also detected in the reaction mixture by ESI-MS. Spectrophotometric analysis of the iron species after reaction by forming the $[Fe(NCS)_6]^{3-}$ complex indicated that all the iron remained in the 3+ oxidation state. The $[Os(N)(O)_3]^-/FeCl_3$ system thus acts as a two-electron oxidant, and its oxidation of cyclohexane in the presence of acetic acid can be represented by eqs 1 and 2.

$$[Os(N)(O)_3]^- + 4FeCl_3 + 4CH_3CO_2H + c\text{-}C_6H_{12} \rightarrow$$
$$[Os(N)Cl_4]^- + 2H_2O + 4FeCl_2(CH_3CO_2) + c\text{-}C_6H_{11}OH \quad (1)$$

$$[Os(N)(O)_3]^- + 4FeCl_3 + 4CH_3CO_2H + c\text{-}C_6H_{11}OH \rightarrow$$
$$[Os(N)Cl_4]^- + 3H_2O + 4FeCl_2(CH_3CO_2) + c\text{-}C_6H_{10}O \quad (2)$$

The alkane is first oxidized to the alcohol, which is then further oxidized to the ketone. Since the concentration of the alcohol is much lower than that of the alkane, the observation of a substantial amount of ketone product suggests that the alcohol is oxidized at a much faster rate than the alkane. This is substantiated by an experiment on the competitive oxidation of a mixture of cyclopentanol and cyclohexane (in a mole ratio of 1:168), in which the products contained 81% cyclopentanone, 6% cyclopentyl acetate, 2% cyclohexanol, and 2% cyclohexanone.

Kinetic Isotope Effects (KIEs). KIE (k^H/k^D) values were determined from the competitive oxidation of cyclohexane and cyclohexane-d_{12}. KIEs for cyclohexanol, cyclohexanone, and chlorocyclohexane are 2.4 ± 0.3, 6.0 ± 0.6, and 2.6 ± 0.3, respectively; the overall KIE is 4.2 ± 0.5.

Stability of the Active Oxidant. To investigate the stability of the active oxidant generated in the $[Os(N)(O)_3]^-/FeCl_3$ system, a mixture of $[^nBu_4N][Os(N)(O)_3]$ (5×10^{-3} M) and $FeCl_3$ (2×10^{-2} M) in CH_2Cl_2/CH_3CO_2H (5:2, v/v) was allowed

to stand for 5 min at room temperature before the addition of cyclohexane. It was found that the total yield was reduced from 78% (with no delay) to 11% (6% cyclohexanol, 3% cyclohexanone, and 2% chlorocyclohexane). This suggests that the active oxidant is highly unstable. If the $[Os(N)(O)_3]^-/FeCl_3$ mixture was allowed to stand for 10 min at room temperature before addition of cyclohexane, no products could be detected within 1 h. In a separate experiment, a $[Os(N)(O)_3]^-/FeCl_3$ mixture was again allowed to stand for 10 min at room temperature, and then *cyclohexene* (1.4×10^{-2} M) was added. It was found that 10% of *trans*-1,2-dichlorocyclohexane and 20% of *trans*-2-chlorocyclohexanol were produced, indicating the presence of Cl_2 in the system. Thus, at least one of the decomposition pathways of the active oxidant is via oxidation of chloride derived from $FeCl_3$ to Cl_2.

Involvement of Chlorine Species in the Oxidation. Since Cl_2 is detected in the absence of cyclohexane, an important question is whether Cl_2 is also produced in the presence of cyclohexane and whether it is involved in the oxidation. In principle, it is possible that Cl atom derived from Cl_2 or directly from $FeCl_3/[Os(N)(O)_3]^-$ may be responsible for the formation of the observed products. $Cl^{\bullet}$ is thermodynamically capable of abstracting a $H^{\bullet}$ from $c\text{-}C_6H_{12}$ to produce $c\text{-}C_6H_{11}^{\bullet}$, which could then react with $[Os(N)(O)_3]^-$ to produce $c\text{-}C_6H_{11}OH$ and $c\text{-}C_6H_{10}O$, or with $FeCl_3$ or Cl_2 to produce $c\text{-}C_6H_{11}Cl$.

However, as discussed above, if the $[Os(N)(O)_3]^-/FeCl_3$ mixture was allowed to stand for *10 min* at room temperature before addition of cyclohexane, no products could be detected. Chlorine was present in the mixture, since it forms *trans*-1,2-dichlorocyclohexane with cyclohexene, but it was not able to oxidize cyclohexane, as least within 1 h at room temperature. Moreover, if Cl_2 (1×10^{-3} M) was added before mixing $FeCl_3$ and $[Os(N)(O)_3]^-$, the total yield and product distribution for the oxidation of cyclohexane remained unchanged.[29] Additional experiments using *cyclohexene* as the substrate were also performed, but in this case it was added before mixing $FeCl_3$ and $[Os(N)(O)_3]^-$. In a typical experiment, $[^nBu_4N]$-$[Os(N)(O)_3]$ (5×10^{-3} M) was added to a solution of $FeCl_3$ (2×10^{-2} M) and *cyclohexene* (1.2 M) in CH_2Cl_2/CH_3CO_2H (5:2, v/v). Analysis of the reaction mixture after 30 min indicated the formation of *cis*-1,2-cyclohexanediol in 95% yield.[30] In the absence of $FeCl_3$, the yield of *cis*-1,2-cyclohexanediol was 3%. No other product, such as 1,2-dichlorocyclohexane, was found. The observation of *cis*-diol formation is fully consistent with oxidation by an active osmium species with a *cis*-dioxo moiety, and not by Cl_2 or Cl atom. There is also no difference between oxidations carried out in the dark or in daylight.

We conclude from the above evidence that significant amounts of Cl_2 are not produced by $FeCl_3/[Os(N)(O)_3]^-$ in the

(29) After the solution was left to stand for 1 h, the yield of cyclohexanone decreased from 63% to 54%, while 9% of 2-chlorocyclohexanone appeared. Control experiments showed that this is due to an uncatalyzed reaction between Cl_2 and cylohexanone.
(30) *cis*-1,2-Cyclohexanediol was first converted to *cis*-1,2-diacetoxycyclohexane with acetic anhydride and 1-methylimidazole and then analyzed by GC and GC−MS.[31,32] *cis*-1,2-Cyclohexanediol does not react with $FeCl_3$ for at least several hours at room temperature.
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Table 2. Stoichiometric Oxidation of Alkanes by [^{n}Bu$_4$N][Os(N)(O)$_3$]/FeCl$_3$[a]

entry	alkane	product (yield, %)[b]	total yield (%)
1	cyclohexane	cyclohexanol (15), cyclohexanone (62), chlorocyclohexane (1)	78
2	cyclooctane	cyclooctanol (6), cyclooctanone (69)	75
3	cyclopentane	cyclopentanol (4), cyclopentanone (66)	70
4	*n*-pentane	2-pentanol (5), 3-pentanol (3), 2-pentanone (39), 3-pentanone (19)	66
5	*n*-hexane	2-hexanol (3), 3-hexanol (3), 2-hexanone (27), 3-hexanone (29)	62
6	*n*-heptane	2-heptanol (3), 3-heptanol (3), 4-heptanol (2), 2-heptanone (22), 3-heptanone (23), 4-heptanone (12)	65
7	*n*-octane	2-octanol (3), 3-octanol (3), 4-octanol (2), 2-octanone (21), 3-octanone (19), 4-octanone (19)	67
8	adamantane[c]	1-adamantanol (39), 1-chloroadamantane (48), 2-adamantanol (1), 2-adamantanone (9)	97
9	2,2-dimethylbutane	3,3-dimethyl-2-butanol (2), 3,3-dimethyl-2-butanone (35)	37
10	3-methylpentane	3-methyl-3-pentanol (10), 3-methyl-2-pentanone (21), 3-chloro-3-methylpentane (9)	40

[a] [^{n}Bu$_4$N][Os(N)(O)$_3$], 5.0×10^{-3} M; FeCl$_3$, 2.0×10^{-2} M; alkane, 1.2 M. All reactions were carried out in CH$_2$Cl$_2$/CH$_3$CO$_2$H (5:2, v/v). $T = 23$ °C. Time = 30 s. [b] The yields were calculated on the basis of the system acting as a two-electron oxidant. [c] [adamantane] = 0.1 M.

presence of a hydrocarbon substrate; even if some Cl$_2$ is formed, it does not play any noticeable part in the oxidation of the substrate.

Stoichiometric Oxidation of Other Alkanes. Oxidation of other alkanes by [Os(N)(O)$_3$]$^-$/FeCl$_3$ was also investigated (Table 2); yields are typically over 70% for cycloalkanes, and around 60% for linear alkanes. For 2,2-dimethylbutane and 3-methylpentane, which have fewer secondary C−H bonds compared with linear alkanes, the yields are around 40%. In all cases, no products arising from the oxidation of primary C−H bonds were observed. In the oxidation of secondary C−H bonds, the corresponding ketones are the predominant products for the concentrations of [Os(N)(O)$_3$]$^-$ (5.0×10^{-3} M) and FeCl$_3$ (2.0×10^{-2} M) used. However, as mentioned above, the alcohol/ketone ratio increases when the relative amount of FeCl$_3$ increases. In the oxidation of adamantane, the yield is almost quantitative, and the ratio of tertiary/secondary products is 26 (after statistical correction). A large amount of 1-chloroadamantane is produced, however, which probably comes from the reaction of 1-adamantanol with FeCl$_3$. Independent experiments show that 1-adamantanol is rapidly converted to 1-chloroadamantane by FeCl$_3$ under these conditions. Thus, when 1-adamantanol (4.3×10^{-3} M) and FeCl$_3$ (2.0×10^{-2} M) were mixed together in CH$_2$Cl$_2$/CH$_3$CO$_2$H (5:2, v/v) at 23 °C, 1-chloroadamantane (3.4×10^{-3} M) was produced in 80% yield after 30 s. However, under similar conditions, secondary alcohols such as cyclohexanol are not converted to the corresponding chloroalkanes by FeCl$_3$.

Kinetic Studies. The kinetics of the oxidation of cyclohexane by [Os(N)(O)$_3$]$^-$/FeCl$_3$ in CH$_2$Cl$_2$/CH$_3$CO$_2$H have been investigated by UV−vis spectrophotometric methods. In a typical experiment, [^{n}Bu$_4$N][Os(N)(O)$_3$] (1.2×10^{-3} M) was mixed with FeCl$_3$ (5.8×10^{-3} M) in CH$_2$Cl$_2$/CH$_3$CO$_2$H (3:1, v/v) containing cyclohexane (1.2 M) in a stopped-flow spectrophotometer equipped with a diode-array detector. Repetitive scanning revealed the rapid formation of an intermediate (**A**) with λ_{max} at around 450 nm, which then decayed at a slower rate (Figure 1). Upon addition of cyclohexane, the rate of formation of the intermediate was unchanged but the decay was accelerated. Figure 2 shows the absorbance changes with time at 450 nm at various cyclohexane concentrations.

Although the concentration of FeCl$_3$ was only about 5 times that of [Os(N)(O)$_3$]$^-$, the formation of **A** (k_{for}) followed reasonable pseudo-first-order kinetics. Pseudo-first-order plots were linear to 2 half-lives, and the rate constants k_{for} were found to be independent of the concentration of cyclohexane ($k = 104$−111 s^{-1} at 298 K, Table S1, Supporting Information). The
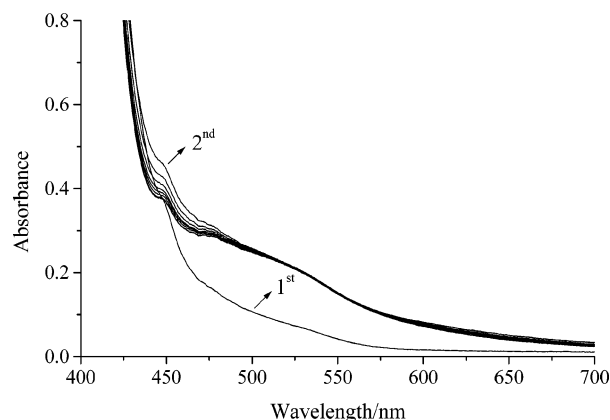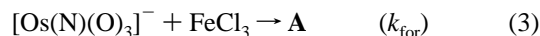

Figure 1. Spectral changes during the reaction of [^{n}Bu$_4$N][Os(N)(O)$_3$] (1.2×10^{-3} M) with FeCl$_3$ (5.8×10^{-3} M) and cyclohexane (1.2 M) in CH$_2$Cl$_2$/CH$_3$CO$_2$H (3:1, v/v) at 298 K. Time between consecutive runs, 20 s.
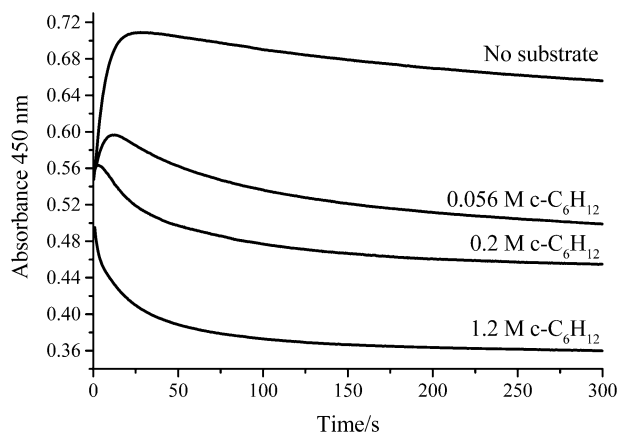
Figure 2. Absorbance changes versus time at 450 nm after mixing [^{n}Bu$_4$N][Os(N)(O)$_3$] (1.2×10^{-3} M) with FeCl$_3$ (5.8×10^{-3} M) in CH$_2$Cl$_2$/CH$_3$CO$_2$H (3:1, v/v) in the presence of cyclohexane at 298 K.

decomposition of the active intermediate also obeyed first-order kinetics, but the pseudo-first-order plots were linear to only about 2 half-lives. The rate constant (k_{dec}) was found to increase with cyclohexane concentration, and it reached saturation at high cyclohexane concentration (Figure 3). These results are consistent with the reaction scheme shown in eqs 3−5.

$$[Os(N)(O)_3]^- + FeCl_3 \rightarrow \mathbf{A} \qquad (k_{for}) \qquad (3)$$

$$\mathbf{A} + RH \rightleftharpoons [\mathbf{A}, RH] \qquad (K) \qquad (4)$$

$$[\mathbf{A}, RH] \rightarrow products \qquad (k) \qquad (5)$$

The observed rate constant for the decay of the intermediate
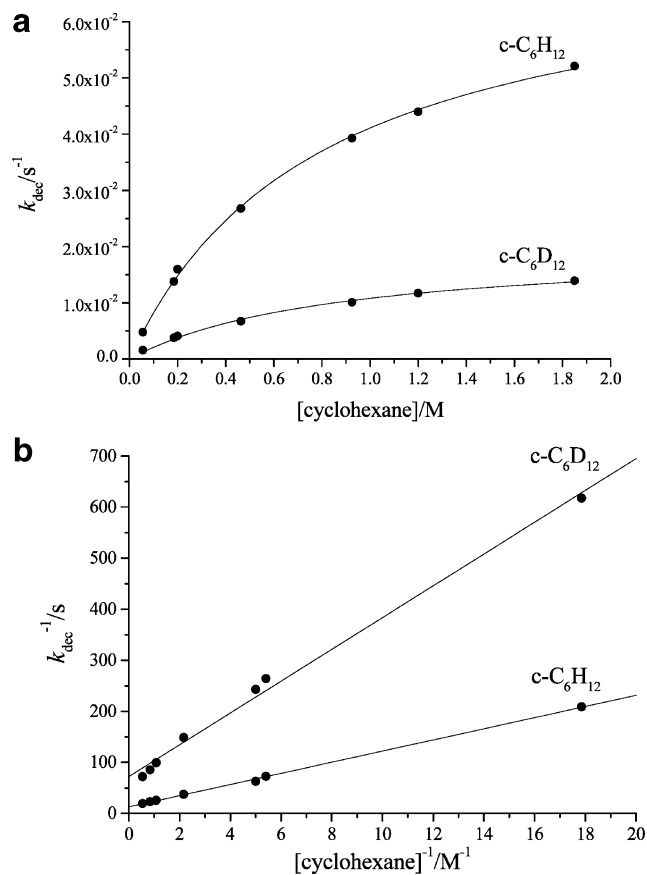
Figure 3. (a) Plot of k_{dec} vs [cyclohexane] at $T = 298$ K. (b) Plot of $1/k_{dec}$ vs $1/$[cyclohexane].

(k_{dec}) is related to K and k by eq 6. A nonlinear least-squares

$$k_{dec} = \frac{kK[RH]}{1 + K[RH]} \qquad (6)$$

fit of the data to eq 6 gives $k = (7.38 \pm 0.37) \times 10^{-2}$ s⁻¹, $K = 1.3 \pm 0.1$ M⁻¹ for c-C₆H₁₂ at 25.0 °C. Similar kinetic behavior was observed when c-C₆D₁₂ was used as substrate and $k^D = (2.01 \pm 0.08) \times 10^{-2}$ s⁻¹, $K^D = 1.2 \pm 0.2$ M⁻¹ at 25.0 °C. The KIE obtained, $k/k^D = 3.7 \pm 0.4$, is in reasonable agreement with the value of 4.2 ± 0.5 obtained from competition experiments.

Nature of the Active Intermediate. Kinetic studies suggest that the active intermediate is a binuclear species formed from FeCl₃ and [Os(N)(O)₃]⁻. Since Fe^III is a rather labile center, several species may be present in a solution of FeCl₃ in CH₃CO₂H/CH₂Cl₂, and it is not a trivial problem to find out the actual species that activates [Os(N)(O)₃]⁻. Using electrospray ionization mass spectrometry (ESI-MS), we have detected the species [Os(N)(O)₃·FeCl₃]⁻ in both CH₃CN/CH₂Cl₂ and CH₃CO₂H/CH₂Cl₂. Figure 4 shows a typical ESI mass spectrum (negative mode) of [^nBu₄N][Os(N)(O)₃] (5 × 10⁻⁴ M) and FeCl₃ (2 × 10⁻³ M) in CH₂Cl₂/CH₃CN (1:1, v/v) obtained ca. 5 min after mixing at 23 °C. There are two major osmium-containing species, [Os(N)(O)₃]⁻ at $m/z = 254$ and [Os(N)(O)₃·FeCl₃]⁻ at $m/z = 415$. There is excellent agreement between the experimental and calculated osmium isotopic mass distributions for each peak. MS/MS of [Os(N)O₃·FeCl₃]⁻ produced the ion [Os(N)O₃]⁻ due to the loss of FeCl₃. Upon addition of acetic
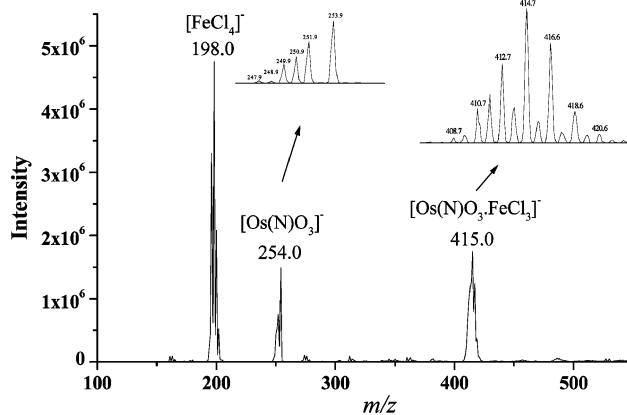
Figure 4. ESI-MS (negative mode) of a mixture of [^nBu₄N][Os(N)(O)₃] (5 × 10⁻⁴ M) and FeCl₃ (2 × 10⁻³ M) in CH₂Cl₂/CH₃CN (1:1, v/v). Insets show isotopic distributions of osmium-containing peaks.
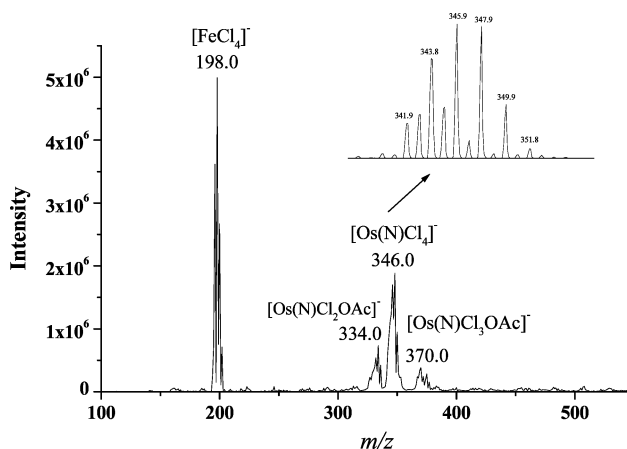
Figure 5. ESI-MS (negative mode) obtained after addition of acetic acid (1.5 M) to a mixture of [^nBu₄N][Os(N)(O)₃] (5 × 10⁻⁴ M) and FeCl₃ (2 × 10⁻³ M) in CH₂Cl₂/CH₃CN (1:1, v/v). Inset shows isotopic distribution of [Os(N)Cl₄]⁻.

acid (1.5 M), the peaks at $m/z = 254$ and 415 disappeared and a new peak at $m/z = 346$ appeared, which is due to [Os(N)Cl₄]⁻ (Figure 5). There were also two minor peaks at $m/z = 334$ and 370, which are due to [Os(N)Cl₂(CH₃CO₂)]⁻ and [Os(N)Cl₃(CH₃CO₂)]⁻, respectively. These peaks are also present in the same relative amounts in the ESI-MS of an authentic sample of [^nBu₄N][Os(N)Cl₄] in CH₂Cl₂/CH₃CO₂H. At −20 °C, [Os(N)(O)₃·FeCl₃]⁻ can also be detected in CH₃CO₂H/CH₂Cl₂, although the peak has a much lower relative intensity.

An intermediate with λ_{max} at around 450 nm has been detected when FeCl₃ and [Os(N)(O)₃]⁻ were mixed in CH₃CO₂H/CH₂Cl₂, and based on information from ESI-MS, this species could be [Os(N)(O)₃·FeCl₃]⁻. However, attempts to detect a similar intermediate in CH₃CN/CH₂Cl₂ were unsuccessful due to the relatively large absorption of FeCl₃ in CH₃CN/CH₂Cl₂ around 450 nm. When lower concentrations (ca. 0.5 mM) of [Os(N)(O)₃]⁻ and FeCl₃ were used, there was little spectral change upon mixing; in this case the equilibrium concentration of the intermediate was probably too low.

Since CH₃CO₂H was used as solvent, species such as FeCl_x(CH₃CO₂)₃₋ₓ may be formed in solution and act as the activating agent. The UV−vis absorption spectra of FeCl₃ in CH₃CO₂H/CH₂Cl₂ and CH₃CN/CH₂Cl₂ are quite similar (except

Table 3. Catalytic Oxidation of Alkanes by [^{n}Bu$_4$N][Os(N)(O)$_3$]/FeCl$_3$/2,6-Dichloropyridine *N*-Oxide^a

entry	alkane	*T*, °C	product (yield, %)	turnovers
1	cyclohexane	23	cyclohexanol (57), cyclohexanone (20), chlorocyclohexane (5), 2-chlorocyclohexanol (tr), cyclohexyl acetate (tr)	66
2	cyclohexane^b	23	cyclohexanol (2), cyclohexanone (tr), chlorocyclohexane (tr)	2
3	cyclohexane^c	23	cyclohexanol (56), cyclohexanone (19), chlorocyclohexane (5), 2-chlorocyclohexanol (tr), cyclohexyl acetate (tr)	64
4	*cis*-1,2-dimethylcyclohexane	23	*cis*-1,2-dimethylcyclohexanol (44), *trans*-1,2-dimethylcyclohexanol (<1), 2,3-dimethylcyclohexanol (3), 3,4-dimethylcyclohexanol (6), 2,3- and 3,4-dimethylcyclohexanone (10)	50
5	*trans*-1,2-dimethylcyclohexane	23	*trans*-1,2-dimethylcyclohexanol (20), *cis*-1,2-dimethylcyclohexanol (<1), 2,3-dimethylcyclohexanol (18), 3,4-dimethylcyclohexanol (18), 2,3- and 3,4-dimethylcyclohexanone (10)	53
6	cyclohexane	60	cyclohexanol (62), cyclohexanone (18), chlorocyclohexane (5), 2-chlorocyclohexanol (3), cyclohexyl acetate (2)	72
7	cyclohexane^d	60	cyclohexanol (63), cyclohexanone (18), chlorocyclohexane (5), 2-chlorocyclohexanol (3), cyclohexyl acetate (2)	73
8	cyclohexane^e	60	cyclohexanol (16), cyclohexanone (8), chlorocyclohexane (4), cyclohexyl acetate (30)	930
9	cyclooctane	60	cyclooctanol (65), cyclooctanone (19)	67
10	*n*-hexane	60	2-hexanol (20), 3-hexanol (21), 2-hexanone (13), 3-hexanone (14)	54
11	*n*-heptane	60	2-heptanol (17), 3-heptanol (17), 4-heptanol (8), 2-heptanone (11), 3-heptanone (11), 4-heptanone (6)	56
12	adamantane^f	60	1-adamantanol (77), 1-chloroadamantane (10), 2-adamantanol (6), 2-adamantanone (2)	76
13	2,2-dimethylbutane	60	3,3-dimethyl-2-butanol (18), 3,3-dimethyl-2-butanone (35), 2-chloro-3,3-dimethylbutane (tr)	42
14	*n*-butane (1.3 atm)	60	2-butanol (21), 2-butanone (49), 2-chlorobutane (2)	58
15	isobutane (2.5 atm)	60	2-methyl-2-propanol (38), 2-chloro-2-methylpropane (10)	38
16	propane (2.5 atm)	60	2-propanol (12), 2-propanone (42)	43

^{a} [^{n}Bu$_4$N][Os(N)(O)$_3$], 1.25×10^{-3} M; FeCl$_3$, 1.0×10^{-2} M; alkane, 1.2 M; Cl$_2$pyO, 0.1 M. For *T* = 23 °C, reactions were carried out in CH$_2$Cl$_2$/CH$_3$CO$_2$H (5:2, v/v) and time = 16 h. For *T* = 60 °C, reactions were carried out in ClCH$_2$CH$_2$Cl/CH$_3$CO$_2$H (5:2, v/v) and time = 30 min. A quantitative amount of Cl$_2$py was detected at the end of each reaction. ^{b} No FeCl$_3$ was added. ^{c} 0.1 M BrCCl$_3$ was added. ^{d} [^{n}Bu$_4$N][Os(N)Cl$_4$] was used as the catalyst instead of [^{n}Bu$_4$N][Os(N)(O)$_3$]. ^{e} [^{n}Bu$_4$N][Os(N)(O)$_3$], 1.25×10^{-4} M; FeCl$_3$, 4.0×10^{-2} M; cyclohexane, 1.2 M; Cl$_2$pyO, 0.2 M. ^{f} [adamantane] = 0.28 M.

around 450 nm, Figure S1, Supporting Information), suggesting that the iron species present in the two solutions are similar, and hence FeCl$_x$(CH$_3$CO$_2$)$_{3-x}$ is at least not a major species in acetic acid solution. We have not been able to unambiguously synthesize or generate Fe(CH$_3$CO$_2$)Cl$_2$ in solution; however, refluxing FeCl$_3$ in net CH$_3$CO$_2$H for 1 h produces quantitatively Fe(CH$_3$CO$_2$)$_2$Cl,[33] which has quite a different UV−vis spectrum from that of FeCl$_3$. Moreover, this species is unable to activate [Os(N)(O)$_3$]$^-$ toward alkane oxidation. Another species that may be present in FeCl$_3$ solution is [FeCl$_2$(CH$_3$CO$_2$H)$_x$]$^+$. The following equilibrium is believed to occur when FeCl$_3$ is dissolved in a solvent (S):[34]

$$2FeCl_3 \rightleftharpoons [FeCl_2(S)_x]^+ + FeCl_4^- \qquad (7)$$
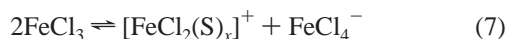
The equilibrium constant is expected to increase with increasing polarity and donor properties of the solvent. Although we have not measured the equilibrium constant in CH$_3$CO$_2$H/CH$_2$Cl$_2$, it is not expected to be very large since acetic acid is not a good donor solvent.

We conclude from the above discussions that, although FeCl$_3$ is likely to be the activating species, other possibilities cannot be ignored. Hence, in subsequent discussions the activating species will be denoted as "Fe^{III}".
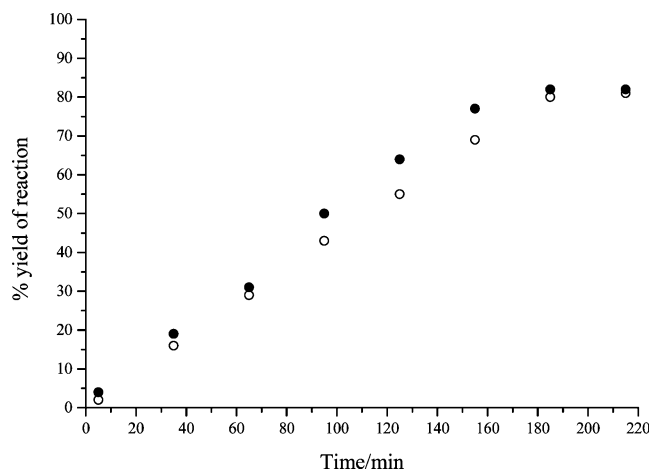
Catalytic Oxidation of Alkanes. The oxidation of alkanes by [Os(N)(O)$_3$]$^-$/FeCl$_3$ can be made catalytic by using 2,6-dichloropyridine *N*-oxide (Cl$_2$pyO) as the terminal oxidant

(Table 3). At 23 °C the yield for cyclohexane oxidation is >80%, although the reaction requires 16 h (entry 1). However, at 60 °C the reaction is completed within 30 min and the yield is 90%, although the reaction becomes somewhat less selective (entry 6). There is no difference between reactions carried out in air or under argon, indicating that O$_2$ does not play a significant role in the reaction. Addition of BrCCl$_3$ to the catalytic system also produces no effect. This catalytic reaction requires the presence of both [Os(N)(O)$_3$]$^-$ and FeCl$_3$ to function. In the absence of FeCl$_3$, only 2% of cyclohexanol was detected, while in the absence of [Os(N)(O)$_3$]$^-$, no products could be detected under our experimental conditions. Also, FeCl$_3$ alone does not catalyze the oxidation of alcohol to ketone by Cl$_2$pyO; however, alcohol is oxidized much more rapidly than alkane using [Os(N)(O)$_3$]$^-$/FeCl$_3$. The [Os(N)(O)$_3$]$^-$ catalyst can be substituted with [Os(N)Cl$_4$]$^-$ with the same results. Turnover numbers of >900 can be achieved for the oxidation of cyclohexane. The KIE (k^H/k^D) values for cyclohexanol, cyclohexanone, and chlorocyclohexane are 3.3 ± 0.3, 8.7 ± 0.8, and 2.7 ± 0.3, respectively; the overall KIE is 3.8 ± 0.4.

The catalytic oxidation of cyclohexane was also run in the presence of H$_2$^{18}O using the following procedure. [^{n}Bu$_4$N]-[Os(N)(O)$_3$] (1.25×10^{-3} M) was added to FeCl$_3$ (1×10^{-2} M) in CH$_2$Cl$_2$/CH$_3$CO$_2$H containing cyclohexane at 23 °C, and the mixture was stirred for 3 min. H$_2$^{18}O (0.125 M) was then added to the reaction mixture, followed by Cl$_2$pyO (1.25×10^{-2} M). The cyclohexanol, analyzed after 16 h, was found to be only 8% ^{18}O-enriched, in contrast to the 61% enrichment in

(33) Anal. Calcd for C$_4$H$_6$O$_4$ClFe: C, 22.95; H, 2.89. Found: C, 22.89; H, 2.78. Fe^{III} content was also analyzed spectrophotometrically after conversion to iron(III) thiocyanate. Acetate and chloride contents were also analyzed by ion chromatography.

(34) Drago, R. S.; Carlson, R. L.; Purcell, K. F. *Inorg. Chem.* **1965**, *4*, 15−17.

Figure 6. Plot of % yield versus time in catalytic oxidation. ●, c-C₆H₁₂; ○, c-C₆D₁₂. Reaction conditions: [ⁿBu₄N][Os(N)(O)₃], 1.25×10^{-3} M; FeCl₃, 1.0×10^{-2} M; cyclohexane, 1.2 M; 2,6-dichloropyridine *N*-oxide, 0.10 M. Reactions were carried out in ClCH₂CH₂Cl/CH₃CO₂H (5:2, v/v). $T = 40 \pm 1$ °C.

stoichiometric oxidation. The same result was obtained by using [ⁿBu₄N][Os(N)Cl₄] instead of [ⁿBu₄N][Os(N)(O)₃]. These observations strongly suggest that the reactive intermediate in catalytic oxidation is different from that in stoichiometric oxidation, since the former intermediate exchanges much more slowly with H₂¹⁸O than [Os(N)(O)₃]⁻. Control experiments show that Cl₂pyO does not exchange with H₂¹⁸O for at least 24 h under the same conditions.

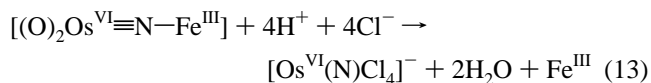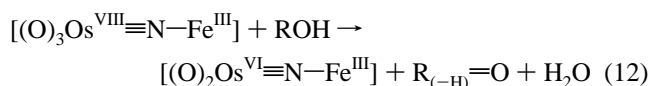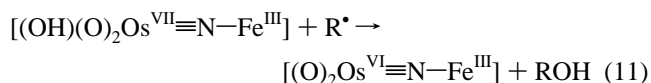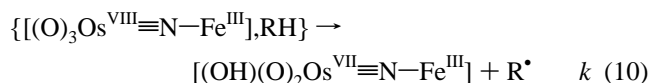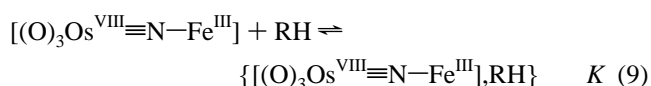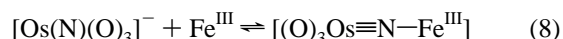The oxidation of various other alkanes was also investigated. This system is efficient in oxidizing both linear and cyclic alkanes. As in stoichiometric oxidation, no products arising from the oxidation of primary C−H bonds were observed. Oxidation of secondary C−H bonds produces both the corresponding alcohols and ketones. In the oxidation of adamantane, the ratio of tertiary/secondary products is 32 (after statistical correction). Similar to stoichiometric oxidation, a large amount of 1-chloroadamantane is produced. The oxidations of *cis*- and *trans*-1,2-dimethylcyclohexane are highly stereospecific: <1% of epimerized products were observed. Similar stereospecificity was also observed in oxidation by systems involving iron−oxo intermediates.[35,36]

Notably, the alcohol/ketone ratios in the catalytic oxidation of secondary C−H bonds are higher than those in stoichiometric oxidation. In stoichiometic oxidation, the [FeCl₃]/[Os(N)(O)₃⁻] ratio used was usually 4, because it gave the highest yield. On the other hand, in catalytic oxidation the optimum [FeCl₃]/[Os(N)(O)₃⁻] ratio is 8. As noted above, the alcohol/ketone ratio increases with the [FeCl₃]/[Os(N)(O)₃⁻] ratio in stoichiometric oxidation. However, even with the same [FeCl₃]/[Os(N)(O)₃⁻] ratio, catalytic oxidation results in a higher alcohol/ketone ratio than stoichiometric oxidation. These results again suggest that the active intermediate in catalytic oxidation is different from that in stoichiometric oxidation.

Kinetic studies for cyclohexane oxidation were performed at 40 °C. The plot of % yield of products versus time for c-C₆H₁₂ is linear, indicating zero-order kinetics (Figure 6). Significantly, although there is a large KIE of 3.8, c-C₆D₁₂ is oxidized nearly

(35) Chen, K.; Que, L., Jr. *J. Am. Chem. Soc.* **2001**, *123*, 6327−6337.
(36) Nam, W.; Park, S.-E.; Lim, I. K.; Lim, M. H.; Hong, J.; Kim, J. *J. Am. Chem. Soc.* **2003**, *125*, 14674−14675.

at the same rate as c-C₆H₁₂ and with a similar overall yield when it is used as a single substrate. This suggests that the active intermediate is formed in the rate-limiting step. Similar observations were also found in the Cl₂pyO oxidation of alkanes catalyzed by ruthenium porphyrins;[15] presumably in all these cases cleavage of the Cl₂py−O bond is rate-limiting. Addition of 5 molar equiv of Cl₂ (relative to the osmium catalyst) has no effect on the kinetics profile, other than that 1% of cyclohexanone is converted to 2-chlorocyclohexanone, which is due to the uncatalyzed action of Cl₂. As in stoichiometric oxidation, there is no evidence for the formation and involvement of Cl₂ in the catalytic oxidation.

Mechanism of Stoichiometric Oxidation of Alkanes. A proposed mechanism for the stoichiometric oxidation of alkanes by FeCl₃/[Os(N)(O)₃]⁻/CH₃CO₂H is shown in eqs 8−13 (the charge of the binuclear species is not specified).

$$[Os(N)(O)_3]^- + Fe^{III} \rightleftharpoons [(O)_3Os\equiv N-Fe^{III}] \quad (8)$$

$$[(O)_3Os^{VIII}\equiv N-Fe^{III}] + RH \rightleftharpoons$$
$$\{[(O)_3Os^{VIII}\equiv N-Fe^{III}],RH\} \quad K \ (9)$$

$$\{[(O)_3Os^{VIII}\equiv N-Fe^{III}],RH\} \rightarrow$$
$$[(OH)(O)_2Os^{VII}\equiv N-Fe^{III}] + R^\bullet \quad k \ (10)$$

$$[(OH)(O)_2Os^{VII}\equiv N-Fe^{III}] + R^\bullet \rightarrow$$
$$[(O)_2Os^{VI}\equiv N-Fe^{III}] + ROH \quad (11)$$

$$[(O)_3Os^{VIII}\equiv N-Fe^{III}] + ROH \rightarrow$$
$$[(O)_2Os^{VI}\equiv N-Fe^{III}] + R_{(-H)}=O + H_2O \quad (12)$$

$$[(O)_2Os^{VI}\equiv N-Fe^{III}] + 4H^+ + 4Cl^- \rightarrow$$
$$[Os^{VI}(N)Cl_4]^- + 2H_2O + Fe^{III} \quad (13)$$

According to the above mechanism, the first step is the formation of the active intermediate (eq 8) by coordination of the tetrahedral [Os(N)(O)₃]⁻ to Feᴵᴵᴵ. As discussed above, the activating species is denoted as Feᴵᴵᴵ. Although FeCl₃ is likely to be the activating species, other iron(III) species are also possible. In principle, [Os(N)(O)₃]⁻ could bond to Feᴵᴵᴵ via either an oxo ligand or the nitrido ligand. Attempts to isolate the active intermediate and further characterize it have so far been unsuccessful because of its instability. However, a number of heterobimetallic complexes formed between [Os(N)(O)₃]⁻ and low-valent metal centers, including those of Ruᴵᴵ, Rhᴵ, Irᴵ, Ptᴵᴵ, and Auᴵ, have been prepared and structurally characterized by Leung and co-workers.[37,38] In all these complexes the [Os(N)(O)₃]⁻ is N-bonded to the metal centers; thus, it is reasonable to assume that in this case the active intermediate is also a *μ*-nitrido species, [(O)₃Os≡N−Feᴵᴵᴵ].

The second step in the mechanism is the oxidation of alkanes by the active intermediate. The observation of saturation kinetics

(37) (a) Leung, W. H.; Chim, J. L. C.; Wong, T. W. *J. Chem. Soc., Dalton Trans.* **1996**, 3153−3154. (b) Leung, W. H.; Chim, J. L. C.; Wong, W. T. *J. Chem. Soc., Dalton Trans.* **1997**, 3277−3282. (c) Leung, W. H.; Chim, J. L. C.; Lai, W.; Lam, L.; Wong, W. T.; Chan, W. H.; Yeung, C. H. *Inorg. Chim. Acta* **1999**, *290*, 28−35. (d) Zheng, H.; Leung, W. H.; Chim, J. L. C.; Lai, W.; Lam, C.-H.; Williams, I. D.; Wong, W. T. *Inorg. Chim. Acta* **2000**, *306*, 184−192.
(38) These complexes, however, are not active oxidants.

suggests that there is a preassociation step (eq 9). The relatively large KIE ($k^H/k^D = 3.7-4.2$ for cyclohexane) is consistent with a hydrogen-atom abstraction mechanism that is commonly observed in the oxidation of C−H bonds by metal−oxo species. The attachment of an electrophilic Fe^{III} center to $[Os(N)(O)_3]^-$ would increase the redox potential of the Os^{VIII}/Os^{VII} couple in the same way that the attachment of a H^+ to a metal−oxo species would increase its redox potential. This would in turn increase the ability of $Os^{VIII}=O$ to abstract a H atom from a C−H bond.[39] H-atom abstraction is followed by rapid attack of the hydroxyl group by the alkyl radical (eq 11). The lack of significant effects of O_2 or $BrCCl_3$ means that the alkyl radicals are efficiently trapped while in the solvent cage. The alcohol formed is then further oxidized by $[(O)_3Os\equiv N-Fe^{III}]$ to the corresponding carbonyl compound. Control experiments indicate that alcohols are oxidized much more rapidly than alkanes.

The final step in the mechanism consists of protonation of the basic oxo ligands in $[(O)_2Os^{VI}\equiv N-Fe^{III}]$, followed by Cl^- (from $FeCl_3$) substitution to produce the stable $[Os^{VI}(N)Cl_4]^-$. This reaction is probably only slightly slower than the H-atom abstraction step and would therefore be responsible for the deviation from pseudo-first-order kinetics for k_{dec} after ca. 2 half-lives. Acetic acid plays a key role in the protonation step. If acetic acid is replaced with CH_3CN, protons would have to come from trace water in the solvent, and this would decrease the reaction rate and the product yield. Acetic acid also helps to dissolve the $FeCl_3$.

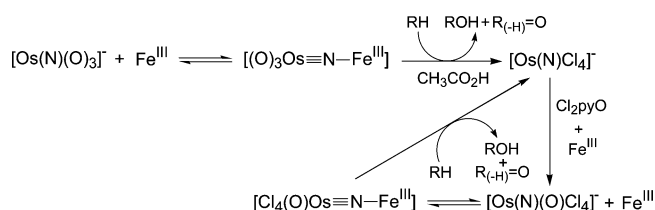The [alcohol]/[ketone] ratio increases with the $[FeCl_3]/[Os(N)(O)_3^-]$ ratio, presumably because at higher $[FeCl_3]/[Os(N)(O)_3^-]$ the concentration of the active oxidant increases, and this would increase the rate of oxidation of alkane to alcohol, and hence also the relative amount of active oxidant consumed in the production of alcohol.

Mechanism of Catalytic Oxidation of Alkanes. ^{18}O-labeling experiments strongly suggest that the active intermediate in catalytic oxidation is different from that in stoichiometric oxidation; i.e., the active intermediate in catalytic oxidation is not $[(O)_3Os\equiv N-Fe^{III}]$. This is also supported by the observation of significant differences in alcohol/ketone ratios for the two oxidations. However, there are also a number of similarities between the reactivity patterns of stoichiometric and catalytic oxidation. The KIEs for cyclohexane are around 4, the ratios of tertiary/secondary products for adamantane are around 30, and $BrCCl_3$ and O_2 have little effects. These results suggest that the active intermediate in catalytic oxidation is also an Fe^{III}-activated osmium−oxo species. The observation of high stereospecificity in the oxidation of 1,2-dimethylcyclohexanes is also consistent with oxidation by a metal−oxo species. We propose that, in catalytic oxidation, an octahedral osmium(VIII) species is generated according to eq 14. Such an O-atom transfer

$$[Os^{VI}(N)Cl_4]^- + Cl_2pyO \rightarrow [Os^{VIII}(N)(O)Cl_4]^- + Cl_2py \quad (14)$$
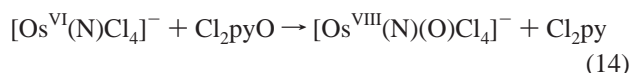
from Cl_2pyO to the metal catalyst to generate a metal−oxo species has also been proposed in the catalytic oxygenation of hydrocarbons by ruthenium porphyrins.[14,15] It is not un-

(39) Mayer, J. M. In *Biomimetic Oxidations Catalyzed by Transition Metal Complexes*; Meunier, B., Ed.; Imperial College Press: London, 2000; pp 1−43.

Scheme 1

reasonable to assume that such an osmium(VIII) species would have a stronger and less basic $Os=O$ bond than that in $[Os(N)(O)_3]^-$, and hence would exchange more slowly with $H_2^{18}O$. Since the presence of $FeCl_3$ is required for catalytic activity, the active oxidant in catalytic oxidation is proposed to be $[Cl_4(O)Os^{VIII}\equiv N-Fe^{III}]$. This species oxidizes C−H bonds by H-atom abstraction, followed by OH rebound to generate ROH and $[Os(N)Cl_4]^-$. The absence of any effects of $BrCCl_3$ and O_2 suggests that the alkyl radicals are efficiently trapped while in the solvent cage. Either $[Os(N)(O)_3]^-$ or $[Os(N)Cl_4]^-$ can be used as the catalyst with essentially the same results. If $[Os(N)(O)_3]^-$ is used as the catalyst, then it would first stoichiometrically oxidize alkane to generate $[Os(N)Cl_4]^-$, which then enters the catalytic cycle. Attempts to detect $[Cl_4(O)Os^{VIII}\equiv N-Fe^{III}]$ by oxidizing $[Os(N)Cl_4]^-$ with Cl_2pyO in the presence and in the absence of $FeCl_3$ have not been successful; the only osmium-containing species that could be detected by ESI-MS or UV−vis spectroscopy is $[Os(N)Cl_4]^-$. This species is expected to be very unstable and would decompose rapidly, even in the absence of organic substrates.

The proposed mechanism for stoichiometric and catalytic oxidation is summarized in Scheme 1.

Concluding Remarks

The ion $[Os(N)(O)_3]^-$ is not known to be an oxidant for organic substrates. However, addition of just a few equivalents of $FeCl_3$ to $[Os(N)(O)_3]^-$ in CH_2Cl_2/CH_3CO_2H produces a system that can perform stoichiometric and catalytic oxidation of alkanes.[40,41] The active oxidants in stoichiometric and catalytic reactions are proposed to be $[(O)_3Os^{VIII}\equiv N-Fe^{III}]$ and $[Cl_4(O)Os^{VIII}\equiv N-Fe^{III}]$, respectively. The attachment of an electrophilic iron(III) center to an osmium−oxo species would increase its redox potential and make it a stronger oxidant. There are numerous examples of binuclear species that are much better oxidants than the corresponding mononuclear species. Apart from being able to act as multielectron-transfer agents, these binuclear species also have higher redox potentials as a result of one metal acting as a Lewis acid on the other. For example, the oxo-bridged ruthenium(V) dimer, $[(bpy)_2(O)Ru^V(\mu-O)Ru^V(O)(bpy)_2]^{4+}$, has been suggested as the active intermediate in the catalytic oxidation of H_2O to O_2 by $[(bpy)_2(H_2O)Ru^{III}(\mu-O)Ru^{III}(OH_2)(bpy)_2]^{4+}$, whereas the corresponding monomeric ruthenium−oxo species are ineffective catalysts.[43] Nature also utilizes binuclear and polynu-

(40) This system can also catalyze the oxidation of alkanes by other oxidants such as H_2O_2 and TBHP. Yiu, S. M.; Lau, T. C., manuscript in preparation.
(41) The oxidation of alkanes catalyzed by lower-valent osmium species such as $OsCl_3$ and Na_2OsCl_6 has also been reported.[42]
(42) (a) Shul'pin, G. B.; Süss-Fink, G.; Shul'pina, L. S. *Chem. Commun.* **2000**, 1131−1132. (b) Shul'pin, G. B.; Nizova, G. V.; Kozlov, Y. N.; Cuervo, L. G.; Süss-Fink, G. *Adv. Synth. Catal.* **2004**, *346*, 317−322.
(43) Binstead, R. A.; Chronister, C. W.; Ni, J.; Hartshorn, C. M.; Meyer, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 8464−8473.

clear species to oxidize highly inert substrates. The active site of water evolution in the photosystem II protein complex is a tetranuclear oxo-bridged manganese cluster.[44] Methane monooxygenase (MMO), which catalyzes the oxidation of methane to methanol by dioxygen, is believed to involve a bis(μ-oxo)-diiron(IV) species as the active oxidant.[45]

Supporting Information Available: Table of rate data and UV–vis spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(44) Vrettos, L. S.; Brudvig, G. W. Oxygen Evolution. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. J., Eds.; Elsevier: Oxford, 2004; Vol. 8, pp 507–547.
(45) Lee, D.; Lippard, S. J. Nonheme Di-iron enzymes. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. J., Eds.; Elsevier: Oxford, 2004; Vol. 8, pp 309–342.