Oxo Transfer from High-Valent Totally Inorganic Oxometalloporphyrin Analogs, $[X^{n+}W_{11}O_{39}Cr^{V}O]^{(9-n)-}$ $(X^{n+} = P^{5+}, Si^{4+})$, to Hydrocarbons

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Abstract: Chromium(III) heteropolytungstate complexes or their corresponding oxygenated forms, the oxo Cr(V) complexes $[X^{n+}W_{11}O_{39}Cr^{V}O]^{(9-n)-}$ $(X^{n+} = P^{5+}$ and $Si^{4+})$, first reported by Katsoulis and Pope, can catalyze the oxidation of organic substrates (alkenes, alkanes, alcohols, and one phosphine, Ph_3P) by a variety of oxidants (OCl^-, H_2O_2, or iodosylbenzene). Many of the electronic, structural, chemical, and catalytic features of these transition metal-substituted polyoxometalate complexes parallel those in the versatile and thoroughly investigated metalloporphyrins, but the catalysts are thermodynamically resistant to oxidative degradation. The physical properties of the title oxo Cr(V) complexes confirm that all have $S = {}^1/_2$ d^1 Cr(V) ground electronic states. Of the two general processes that comprise the oxygenation cycle catalyzed by the Cr undecatungstophosphates, $Cr^{III} + DO \rightarrow Cr^{V}{=}O + D$ (eq 2 in text; DO = oxygen donor) and $Cr^{V}{=}O + Sub \rightarrow Cr^{III} + SubO$ (eq 3 in text; Sub = substrate), eq 3 is rate limiting for all the hydrocarbon substrates examined. Alkenes are oxygenated by the oxo Cr(V) complexes at 50 °C to produce epoxides, allylic alcohols and ketones, and the Cr(III) complex. Product–time curves and kinetics data are consistent with both allylic oxidation and epoxidation products arising from a common intermediate. The inherent kinetic preference of oxo Cr(V) complexes ($k_{allylicCH}/k_{epoxide}$) varies from 1.2 to 24 and depends on solvent, polyoxotungstate ligand, and countercation. The collective yields of oxygenated organic products based on oxo transfer depend on solvent (acetonitrile < benzene) and substrate (monosubstituted alkenes < disubstituted alkenes) and range from 7% (1-octene/$[(C_7H_{15})_4N]_5[SiW_{11}O_{39}$-$Cr^{V}O]$ (1a)/acetonitrile) to over 90% (cyclohexene/1a/benzene). Production of tricyclo[2.2.1.0^{2,6}]heptan-3-ol, the loss of stereochemistry in *cis*-stilbene epoxidation by 1a, and $k_{allylicCH}/k_{epoxide}$ are consistent with radical intermediates. The rate laws for production of epoxide and allylic ketone are second order overall at concentrations of cyclohexene < 0.5 M ($V = [1a][cyclohexene]$). For oxidation of cyclohexene by 1a, the activation parameters for production of epoxide are $\Delta H^{\ddagger} = 9.1 \pm 0.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -53.4 \pm 3.1$ eu. Eight lines of experimental evidence regarding the oxo-transfer step, eq 3, for alkene substrates collectively argue strongly against concerted oxo transfer, the formation of oxometallocyclobutane or the β-oxochromium carbocation, electron transfer, and other mechanisms. The mechanism most compatible with the data involves radical addition to the double bond by the oxo chromium(V) moiety. Three experiments involving the Cr(III) or oxo Cr(V) complexes and ^{18}O-labeled iodosylbenzene or water indicate that (i) the oxygen transferred to alkene substrates in eq 3 is that bound to the Cr(V) atoms, (ii) oxygen exchange between the oxo chromium(V) group and water is very slow, and (iii) the Cr(III) complexes catalyze oxygen exchange between iodosylbenzene and water. The results collectively indicate that oxygen exchange proceeds via an intermediate chromium–iodosylbenzene complex.

Introduction

Efforts on the part of investigators worldwide to design and develop catalysts for selective and sustained oxidation of hydrocarbons remain considerable.[1-10] Oxidation by oxygenation or oxo transfer, eq 1, is attractive, as the metal oxo intermediates in such processes are potentially accessible from dioxygen and exhibit reactivity that is more experimentally variable and, in the most activated forms, higher than that exhibited by other types of oxygenated transition metal species.[2,5,9,10] Nearly all the oxygenated transition metal complexes that react with unactivated carbon–hydrogen bonds under mild conditions are metal oxo species. The oxidizing intermediates and mechanisms involved in the commercially successful Halcon[2,4] and Sharpless[11-13] chiral epoxidation processes are not particularly modifiable and the intermediates not sufficiently reactive to attack unactivated carbon–hydrogen bonds unless temperatures sufficient to homolyze the peroxo moieties are used. Another continuing impetus for investigation of the kinetically potent metal-based oxygenation derives from the fact that the most versatile biological hydrocarbon oxidizing system, cytochrome P-450,[14] more than likely oxidizes its myriad of substrates by metal-facilitated oxo transfer and a

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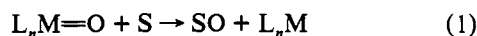(14) *Cytochrome P-450*; Ortiz de Montellano, P. R., Ed.; Plenum: New York, 1986.
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similar mechanism is probably operable in methane monoxygenase (MMO):[15-19]

$$L_nM{=}O + S \rightarrow SO + L_nM \qquad (1)$$

where L_n are the ligands of L_nM, a transition metal complex (the lower valent resting state), $L_nM{=}O$ is the metal oxo complex, and S = the organic or inorganic substrate.

Many research groups have now examined hydrocarbon oxygenation, principally by oxygen donors rather than the more desirable but less tractable dioxygen, catalyzed by metalloporphyrins and other d-electron transition metal complexes in an effort to elucidate the mechanism of cytochrome P-450 through modeling or to explore the oxidative reactivity of metal oxo species in general.[20-29] A recent comprehensive review indicates the magnitude of this effort: the number of papers with the three key words porphyrin/oxidation/catal has been increasing every year since the late 1970s, when the first papers were published, and now totals about 500.[25] Schiff-base and other complexes have also been examined as oxygenation catalysts.[30-37] Although rates and selectivities have proven satisfactory in hydrocarbon oxidations and oxygenations catalyzed by transition metal complexes including metalloporphyrins, the thermodynamic instabiltiy of the organic ligands of these complexes with respect to oxidation presents a formidable obstacle to the development of practically useful reactions. Remarkable synthetic efforts have now been put forward by several groups to stabilize metalloporphyrins with respect to oxidative degradation, including the synthesis of elegant polyhalogenated porphyrin ligands.[24,38-42] One logical end to this work has been achieved—a "Teflon porphyrin", one with all carbon–hydrogen bonds replaced with carbon–fluorine bonds.[24,43]

An alternative approach to preparing effective homogeneous oxygenation catalysts involves formulation of d-electron complexes with ligand systems that are thermodynamically, not just highly

kinetically, stable to oxidative degradation under turnover conditions and are simultaneously capable of catalyzing oxygenation with satisfactory rates and selectivities. In 1986 it was first demonstrated that d-electron-substituted derivatives of oxidatively resistant d^0 early transition metal polyoxometalates (TMSP complexes for convenience) were capable of oxygen donor activation and catalysis of oxo transfer to organic substrates in processes highly analogous to those involving metalloporphyrins that we and others had examined in considerable detail in the preceding 5 years.[21-29,31] Although it was apparent that several structural types of TMSP complexes might function as oxidatively resistant analogs of metalloporphyrins, we chose to first examine the C_s symmetry monosubstituted Keggin derivatives of the general formula $[(TM^{n+})PW_{11}O_{39}]^{(7-n)-}$ where TM^{n+} is a d-electron transition metal ion, a class of complexes first prepared 3 decades earlier by Baker,[44] as they were the best understood and most accessible class of TMSP complexes. Several features of these complexes including their extractability into nonpolar solvents such as toluene and reversible O_2 binding, reported 2 years earlier by Katsoulis and Pope,[45] indicated these particular TMSP complexes were among the most tractable. After our initial reports on alkene and alkane oxygenation catalyzed by $[(TM^{n+})PW_{11}O_{39}]^{(7-n)-}$ complexes,[46,47] several groups have collectively examined 31 TMSP type complexes as catalysts to oxidize five types of substrates with 10 oxidants in 11 different solvents (solvent systems),[10,42,46-65] and Piepgrass and Pope have reported the microscopic reverse of organic oxygenation by a high-valent TMSP, namely the deoxygenation of oxygenated organic molecules by highly reduced TMSP complexes ("heteropoly browns").[66] The TMSP complexes to date remain the only homogeneous oxygenation catalysts stable and fully active in the presence of oxygen donors or other oxidants and in the absence of any kinetically protecting organic substrate.

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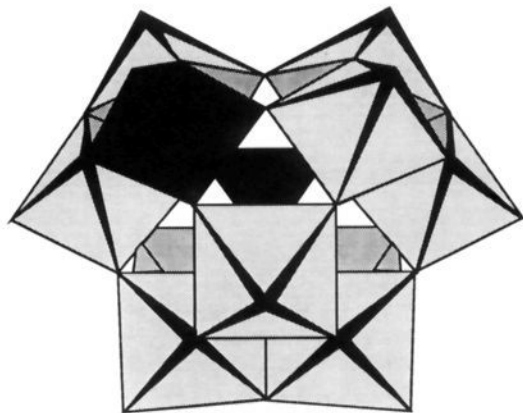
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Figure 1. Structure of the oxo Cr(V) polyoxometalates, $[X^{n+}W_{11}O_{39}Cr^VO]^{(9-n)-}$ ($X^{n+} = P^{5+}$, Si^{4+}), and their Cr(III) precursor compounds. The darker octahedron on the surface of the complex represents the location of the Cr center (chromium(III) in the precursor and oxochromium(V) in the product complexes), and the darker central tetrahedron represents the heteroatom, X^{n+}. In polyhedral notation, the vertices of the polyhedra, principally WO_6 octahedra, are the nuclei of the oxygen atoms. The metal atoms are internal to the polyhedra and not directly visible.

In this paper we examine for the first time the transfer of oxygen from kinetically active high-valent metal oxo forms of TMSP complexes to organic substrates. The oxo TMSP complexes are the oxo Cr(V) complexes $[X^{n+}W_{11}O_{39}Cr^VO]^{(9-n)-}$ (X^{n+} = P^{5+}, Si^{4+}) (Figure 1), and the substrates are a range of hydrocarbons (with an emphasis on alkenes), alcohols, and one phosphine, Ph_3P. Katsoulis and Pope described the preparation and characterization of the complexes $[SiM_{11}O_{39}Cr^VO]^{5-}$ (M = Mo^{VI}, W^{VI}) in a 1986 communication.[67] In this work they also reported that the oxo Cr(V) complexes "did not detectably cause epoxidation of *trans*-stilbene during 24 h", a point they indicated was consistent with our previously reported result[46] that $[PW_{11}O_{39}Cr^{III}]^{4-}$ was not active for epoxidation by iodosylarenes under mild conditions. Given the literature on metal-catalyzed oxo transfer from inorganic to organic centers, including the substantial metalloporphyrin literature, it was clear to us that the best experimental opportunity to examine and document the inherent reactivity of oxo transfer from oxygenated TMSP complexes to substrates involved oxo Cr(V) complexes. The high-valent d-electron oxo complexes of the TMSP complexes of other first-row transition metals and ruthenium examined to date are not directly accessible, as all are transient intermediates. That is, the catalytic turnover rates are simply too high to permit adequate examination of the oxo-transfer reactivity and this reactivity can only be inferred indirectly through product distribution, kinetics, and related studies. At the same time, the limited mechanistic information on homogeneous oxidation of substrates by d^0 polyoxometalates does not provide compelling evidence that oxo transfer is operable in these systems. In this work, we establish that oxo transfer from oxo Cr(V) TMSP complexes to substrates, including hydrocarbon substrates, is facile and we elaborate in detail the inherent reactivity of these d-electron (d^1) species toward organic substrates.

Experimental Section

General Methods. The alkene products were unambiguously identified by gas chromatography (GC; Hewlett-Packard 5890), gas chromatography–mass spectrometry (GC–MS; Hewlett-Packard 5971 A MSD), and ^1H NMR (General Electric QE-300 and Nicolet NT-360). For the last, $CDCl_3$ was used as the solvent. *cis*- and *trans*-Stilbene oxides were

quantified by the ^1H NMR method in standard use.[68] Analysis by ^1H NMR spectroscopy showed the presence of *cis*-stilbene oxide (s, δ = 4.36 ppm) and *trans*-stilbene oxide (s, δ = 3.86 ppm). Triphenylphosphine and triphenylphosphine oxide were quantified by GC. Dioxygen was rigorously excluded in all reactions involving organic substrates in order to minimize trapping of intermediate organic radicals, the initiation of radical chain autoxidation, and related problems.

Electronic absorption spectra were recorded on a Hewlett-Packard (H/P) Model 8451A diode-array UV–visible spectrometer. Infrared spectra (2% samples in KBr) were recorded on a Perkin-Elmer Model 1430 instrument. ^{31}P broad-band proton-decoupled NMR spectra were obtained on an IBM WP-200-SY spectrometer operating at a frequency of 81 MHz. Trimethyl phosphate (0.1% in CD_3CN) was used as the external reference. Magnetic susceptibilities were measured by the Evans NMR method[69] using a 360-MHz Nicolet NT-360 instrument. Pascal's constants and the value χ_g = -253×10^{-9} cgsu for $[(C_4H_9)_4N]_4Na_3$-$PW_{11}O_{39}$ (23 °C) were used in determining diamagnetic corrections.[70] EPR spectra were recorded on a Bruker ER200D-SRC X-band instrument at 80 and 20 K. Elemental analyses were performed by Atlantic Microlabs (for C, H, and N) and Galbraith (for the other elements).

Materials. The polyoxometalates $K_8SiW_{11}O_{39}$,[71] $Na_7PW_{11}O_{39}$,[72] were prepared and purified by literature procedures. The Cr(III) heteropolytungstates were prepared from $Cr(NO_3)_3$ and $K_8SiW_{11}O_{39}$ at pH 4.7 or from $Cr(NO_3)_3$ and $Na_7PW_{11}O_{39}$ at pH 4.0 according to literature procedures.[73] The hydrophobic tetraalkylammonium salts of the Cr-(III) compounds $[(C_7H_{15})_4N]_5[SiW_{11}O_{39}Cr^{III}(OH_2)]$ (2a) and $[(C_6-H_{13})_4N]_4[PW_{11}O_{39}Cr^{III}(OH_2)]$ (2b) were prepared by the extraction procedure[45,74] of Katsoulis and Pope.[67] $[(C_4H_9)_4N]_4[PW_{11}O_{39}Cr^{III}]$ (2c) was prepared by treatment of aqueous $[PW_{11}O_{39}Cr^{III}(OH_2)]^{4-}$ with tetra-*n*-butylammonium bromide. All three Cr(III) precursor compounds were judged to be pure from elemental analyses, magnetic properties, and spectroscopic data (EPR, UV–visible, and infrared). Iodometric titration of the title oxo Cr(V) complexes was carried out by a modified procedure reported by Bruice[75] which required dissolving the Cr(V) compounds in 95% ethanolic NaI containing 10% acetic acid. The reduction of Cr(V) to Cr(III) by I$^-$, as followed spectrophotometrically by the absorbance of I_3^- at 360 nm (ϵ = 3.4×10^4 M^{-1} cm^{-1}),[76] was quantitative and clean (100% of the theoretical 2 equiv of I$^-$/mol of Cr(V) was consumed). Care was taken to remove all bromide from the polyoxometalate precursor compounds, as any residual bromide could have complicated the chemistry and compromised the value of product distribution, kinetics, and other data in this study. Not only are alkenes readily oxidized by Br_2 and higher valent forms of bromide derived from Br$^-$ oxidation but also most oxidized bromine species react with organic radicals and the experimental evidence argues strongly for these intermediates (*vide infra*). Independent control experiments established that the title oxo Cr(V) complexes did not oxidize bromide within detectable limits under the conditions in the oxygen-transfer reactions described in this study.

The acetonitrile and benzene solvents (Burdick and Jackson) were glass-distilled grade. All the alkene, alkane, and triphenylphosphine substrates and the epoxide, alcohol, ketone, and triphenylphosphine oxide products were commercial reagent grade samples with a minimum purity of 97% and were used as received, except for norbornene. Norbornene (Fluka, Aldrich) was distilled in vacuo, assessed to have a purity of 99+% by gas chromatography (GC), and stored in the refrigerator at 0 °C. Iodosylbenzene was prepared by hydrolysis of iodobenzene diacetate (Aldrich) with aqueous acetonitrile, dried carefully under reduced pressure, and kept at 0 °C. The oxidants NaOCl (0.5 M aqueous solution, pH 10.2) and H_2O_2 (0.5 M aqueous solution, pH 10.8) were commercial samples and were used as received.

Synthesis of $[(C_7H_{15})_4N]_5[SiW_{11}O_{39}Cr^VO]$ (1a) by Oxidation with Iodosylbenzene. A solution of 2a (1.04 g, 0.2 mmol) in benzene or

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(76) Lee and Bruice obtained ϵ = 2.5×10^4 M^{-1} cm^{-1}, but upon calibration with different oxidants in the absence of acetic acid, we obtained ϵ = 3.4×10^4 M^{-1} cm^{-1}.

acetonitrile was stirred with a 5- to 10-fold molar excess of iodosylbenzene at room temperature for 30 min. After isolation of the unreacted iodosylbenzene by filtration, the yellow-green supernatant, containing virtually a quantitative yield of **1a**, was concentrated to a green oil and analyzed. IR (cm^{-1}): 1036 (s), 1005 (m), 793 (s). UV–visible [CH$_3$-CN; λ, nm (ϵ, M^{-1} cm^{-1})]: 650 (15). EPR (CH$_3$CN, 80 K): $g = 1.972$, $A_{Cr} = 25$ G (^{53}Cr, $I = {}^3/_2$; 9.55% natural abundance). $\mu_{eff} = 1.54$ μ_B (complex was 17 mM in benzene as for the standard Evans method determination). Anal. Calcd for [(C$_7$H$_{15}$)$_4$N]$_5$[SiW$_{11}$O$_{39}$CrVO]·[(C$_7$H$_{15}$)$_4$N]Br: C, 38.16; H, 6.81; Br, 1.51; Cr, 0.98; N, 1.59; O, 12.15; Si, 0.53; W, 38.27. Found: C, 38.89; H, 6.94; Br, 1.21; Cr, 0.92; N, 1.66; O (by difference), 12.63; Si, 0.59; W, 38.37. A solution of **1a** showed no sign of decomposition after several weeks of storage in the refrigerator (0 °C).

Synthesis of 1a by Oxidation with NaOCl or H$_2$O$_2$. A solution of **2a** (0.58 g, 0.111 mmol) in 4 mL of benzene was stirred with either a 0.5 M solution of NaOCl (adjusted to pH 10.2 by addition of 1.0 M HCl) or a 0.5 M solution of H$_2$O$_2$ (adjusted to pH 10.8 by addition of 1.0 M NaOH) in 1 mL of water. After 2 h of stirring, a yellow-green solution of the oxo Cr(V) complex was separated from the water phase and dried over anhydrous MgSO$_4$. Removal of the benzene solvent typically produced 0.51 g (95% yield based on active oxygen) of **1a** as a green oil. UV–visible [C$_6$H$_6$; λ, nm (ϵ, M^{-1} cm^{-1})]: 650 (10). EPR (20 K): $g = 1.975$, $A_{Cr} = 36$ G. As in the case for all the oxo Cr(V) preparations, EPR indicated that no residual Cr(III) was present after oxidation. The elemental analysis was satisfactory.

Synthesis of [(C$_6$H$_{13}$)$_4$N]$_4$[PW$_{11}$O$_{39}$CrVO] (1b). The procedure was identical to that used in the synthesis of **1a** from iodosylbenzene except that **2b** was in Cr(III) precursor complex. IR (cm^{-1}): 1040 (s), 1030 (m), 794 (s). UV–visible [CH$_3$CN; λ, nm (ϵ, M^{-1} cm^{-1})]: 674 (10). ^{31}P NMR (CD$_3$CN): δ 6.52 ppm.

Synthesis of [(C$_4$H$_9$)$_4$N]$_4$[PW$_{11}$O$_{39}$CrVO] (1c). To a solution of 1 g of **2c** in 60 mL of acetonitrile was added 220 mg (1 mmol) of iodosylbenzene, and the mixture was stirred 30 min. After filtration, 40 mL of toluene was added to the yellow-green supernatant. This solution was placed in a 200-mL crystallization dish until the yellow-green crystals began to form. The ratio of active oxygen (by iodometric titration) to Cr = 1 ± 0.1. IR (cm^{-1}): 1072 (s), ν_{Cr-O} 1027 (m), 963 (s), 889 (s), 816 (s). ^{31}P NMR (CD$_3$CN): δ 6.46 ppm. $\mu_{eff} = 1.53$ μ_B. EPR (solid at 20 K): $g = 1.975$, $A_{Cr} = 66$ G. Anal. Calcd for [(C$_4$H$_9$)$_4$N]$_4$[PW$_{11}$O$_{39}$CrVO]: C, 20.68; H, 3.88; Cr, 1.40; N, 1.51; O, 17.24; P, 0.83; W, 54.45. Found: C, 20.49; H, 3.82; Cr, 1.34; N, 1.44; O (by difference), 16.26; P, 1.00; W, 55.65.

PhI^{18}O Labeling Studies. PhI^{18}O was made from 85 atom % H$_2$^{18}O by the literature method.[77] Isotopic purity was checked by IR and by GC–MS analysis of triphenylphosphine oxide-^{18}O produced upon reaction of the labeled iodosylbenzene with triphenylphosphine in dichloromethane. Incorporation of ^{18}O into norbornene oxide was also determined by GC–MS analysis (the ratio of m/z 112 to 110).

Preparation of [(C$_7$H$_{15}$)$_4$N]$_5$[SiW$_{11}$O$_{39}$Cr^V=^{18}O] (1a-^{18}O). The chromium(III) complex **2a** (2 g, 0.4 mmol) in 10 mL of benzene was treated with 0.44 g (2 mmol) of ^{18}O-enriched (60 atom %) iodosylbenzene. The resulting light green mixture was stirred for 30 min at 20 °C. After separation of unreacted PhI^{18}O from the mixture, a yellow-green solution of ^{18}O-enriched (60%) **1a** was obtained. The ratio of equivalents of active oxygen (by iodometric titration) to equivalents of Cr was 1 ± 0.1. The reaction of this ^{18}O-labeled **1a** with norbornene afforded almost quantitative yields of norbornene oxide which showed 50 ± 5 atom % ^{18}O incorporation by GC–MS. The isotopic shift of the Cr^V=O stretching fundamental could not be clearly discerned due to overlap with other X—O stretching bands in this region.

Preparation of [(C$_4$H$_9$)$_4$N]$_4$[PW$_{11}$O$_{39}$Cr^V=^{18}O] (1c-^{18}O). The chromium(III) complex **2c** (20 mg, 5 mmol) in 5 mL of acetonitrile was treated with 44 mg (0.2 mmol) of ^{18}O-enriched (60 atom %) iodosylbenzene. The resulting yellow solution was stirred for 30 min at 20 °C. After filtration, 10 mL of water was added to the supernatant. The yellow solid that formed immediately was isolated by filtration, collected, and then dried in vacuo. The ratio [active oxygen]:[Cr] = 1.0 ± 0.1. In the IR spectrum of **1c-^{18}O** the 1027-cm^{-1} absorbance diminished in intensity and a new shoulder at 993 cm^{-1} appeared.

Exchange with H$_2$^{18}O. In a first experiment, a solution of 0.035 mmol of **1c** in 3 mL of acetonitrile was treated with 50 μL of ^{18}O-enriched (85 atom %) water. The solution was stirred for 14 h at 25 °C, and then the solvent was removed to recover the yellow-green **1c**. Infrared analysis

of this reisolated **1c** indicated neither significant decomposition of the complex nor significant oxygen exchange between the oxochromium(V) group and water. In a second experiment, a solution of 0.031 mmol of **1a** in 2 mL of benzene was treated with 20 μL of the same ^{18}O-enriched water. The solution was stirred for 48 h at 25 °C. On the basis of the quantitative reaction of triphenylphosphine (under the conditions given in Table I) to give triphenylphosphine oxide and isotopic analysis of the latter by GC–MS, **1a** contained 19 atom % ^{18}O. Oxygen isotope exchange between the oxochromium(V) group and water under these conditions was incomplete. A control reaction carried out with ^{16}O-labeled **1c** and cyclohexene in 1 mL of benzene plus 10 μL of 85% H$_2$^{18}O produced organic oxidation products containing only ^{16}O.

Exchange of PhI^{16}O with H$_2$^{18}O Catalyzed by 2a. The Cr(III) complex **2a** (0.067 mmol) in 1.7 mL of benzene was treated with 55 mg (0.25 mmol) of PhI^{16}O and 10 mg (0.5 mmol) of ^{18}O-enriched (85 atom %) water. The resulting solution was stirred for 24 h at 25 °C and then filtered from the resulting solid. The resulting Cr(V) complex, **1a**, contained 32 atom % ^{18}O, as indicated by reaction with triphenylphosphine followed by GC–MS analysis. The residual iodosylbenzene exhibited a substantial but incomplete oxygen exchange with water; the reisolated compound contained ~30% PhI^{18}O.

Attempted Oxygen Evolution from 1c. A solution of 0.061 g of **1c** (0.017 mmol) in 0.42 mL of acetonitrile was degassed, placed under argon, and then heated to 50 °C for 20 h. Dioxygen was analyzed directly by gas chromatography using a 5 Å molecular sieve column, argon carrier gas, nitrogen as an internal standard, and thermal conductivity detection. Within the detectability limits of the instrument (ca. 1%), no O$_2$ was generated.

Kinetics Studies. Reaction rates for epoxidation by **1a** were determined principally by monitoring the evolution of the organic oxidation products with time by GC. The most effective GC conditions involved the use of a 5% phenyl methyl silicone fused-silica capillary column, nitrogen as the carrier gas, and temperature programming. GC analysis was performed on aliquots withdrawn directly from the reaction mixture. Control experiments indicated there was negligible reaction between the residual reactants (oxo Cr(V) complex and substrate) in the hot injector port of the gas chromatograph during product analysis.

In a typical reaction, alkene (2 mmol) was added to a degassed solution (three freeze–thaw cycles) of the oxo Cr(V) complex (0.04 mmol) in 1 mL of CH$_3$CN or C$_6$H$_6$ containing trimethylacetonitrile as an internal standard. The reactions were run in a 10-mL Schlenk flask equipped with a serum stopper and a magnetic stirring bar. The reactants were stirred under argon at the appropriate temperature, usually 50 °C, and the progress of the reaction was monitored by GC. In most cases under these conditions, the reaction was nearly complete in about 6 h. In these cases, identical yields were obtained after 24 h, indicating minimal complication from subsequent reaction of initial products. Rates and rate constants were evaluated principally using initial-rate methods.

Results

Preparation and Electronic Structure of Oxo Cr(V) Inorganic Metalloporphyrin Analog Complexes, [R$_4$N]$_{9-n}$[X^{n+}W$_{11}$O$_{39}$Cr^{V}O] (X^{n+} = P^{5+}, Si^{4+}; R = n-C$_4$H$_9$, n-C$_6$H$_{13}$, n-C$_7$H$_{15}$). Treatment of hydrophobic tetra-n-alkylammonium salts of the Cr(III) complexes [X^{n+}W$_{11}$O$_{39}$Cr^{III}(OH$_2$)]$^{(9-n)-}$ (X = P^{5+}, Si^{4+}) in aprotic organic media with a second phase of an inexpensive aqueous oxidant (3.7% H$_2$O$_2$ or 1.7% NaOCl) results in production of the corresponding oxo Cr(V) complexes (e.g. eq 2). The specific

$$[PW_{11}O_{39}Cr^{III}(OH_2)]^{4-} + DO \rightarrow$$
$$[PW_{11}O_{39}Cr^VO]^{4-} + D + H_2O \quad (2)$$
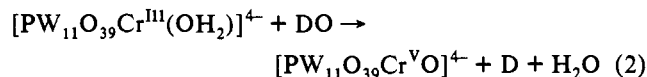
DO = oxygen donor oxidant = OCl$^-$, H$_2$O$_2$, or PhIO

complexes examined here are [(C$_7$H$_{15}$)$_4$N]$_5$[SiW$_{11}$O$_{39}$CrVO] (**1a**), [(C$_6$H$_{13}$)$_4$N]$_4$[PW$_{11}$O$_{39}$CrVO] (**1b**), and [(C$_4$H$_9$)$_4$N]$_4$-[PW$_{11}$O$_{39}$CrVO] (**1c**). The organic medium can be a polar solvent such as acetonitrile ($\epsilon = 35.94$; $Z = 71.3$) or a nonpolar solvent such as benzene ($\epsilon = 2.27$; $Z = 54.0$)[78] If a 10-fold molar excess

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Table I. Oxidation of Hydrocarbons by Oxochromium(V) Complexes[a]

complex[b]	substrate	solvent	product (yield, %)[c]	tot. yield, %[c]
[4]Q$_4$[PW$_{11}$O$_{39}$CrO] (1c)	cyclohexene	CH$_3$CN	cyclohexene oxide (1) cyclohexenol (3) cyclohexenone (21)	46
[6]Q$_4$[PW$_{11}$O$_{39}$CrO] (1b)	cyclohexene	CH$_3$CN	cyclohexene oxide (5) cyclohexenol (5) cyclohexenone (32.5)	75
[6]Q$_4$[PW$_{11}$O$_{39}$CrO] (1b)	cyclohexene	C$_6$H$_6$	cyclohexene oxide (22.5) cyclohexenol (14) cyclohexenone (23)	82.5
[7]Q$_5$[SiW$_{11}$O$_{39}$CrO] (1a)	cyclohexene	C$_6$H$_6$	cyclohexene oxide (25) cyclohexenol (9) cyclohexenone (29)	92
[7]Q$_5$[SiW$_{11}$O$_{39}$CrO] (1a)	cyclohexene	CH$_3$CN	cyclohexene oxide (3.5) cyclohexenol (12.5) cyclohexenone (37.5)	91
[7]Q$_5$[SiW$_{11}$O$_{39}$CrO] (1a)	cyclohexenol[d]	CH$_3$CN	cyclohexenone (75)	75
[7]Q$_5$[SiW$_{11}$O$_{39}$CrO] (1a)	styrene	C$_6$H$_6$	styrene oxide (14) benzaldehyde (25)	64
[7]Q$_5$[SiW$_{11}$O$_{39}$CrO] (1a)	*cis*-stilbene	CH$_3$CN	*cis*-stilbene oxide (1.5) *trans*-stilbene oxide (0.5) benzaldehyde (12.5)	27
[7]Q$_5$[SiW$_{11}$O$_{39}$CrO] (1a)	*trans*-stilbene[e]	C$_6$H$_6$	*trans*-stilbene oxide (0.5) benzaldehyde (22.5)	46
[7]Q$_5$[SiW$_{11}$O$_{39}$CrO] (1a)	1-octene	CH$_3$CN	1-octene oxide (5) octan-2-one (1.2)	7
[7]Q$_5$[SiW$_{11}$O$_{39}$CrO] (1a)	norbornene	CH$_3$CN	*exo*-norbornene oxide (52.7) norcamphor (6.8) tricyclo[2.2.1.0^{2,6}]heptan-3-ol (17.5)	87
[7]Q$_5$[SiW$_{11}$O$_{39}$CrO] (1a)	triphenylphosphine[f]	C$_6$H$_6$	triphenylphosphine oxide (100)	100
[7]Q$_5$[SiW$_{11}$O$_{39}$CrO] (1a)	cyclohexane	C$_6$H$_6$	cyclohexanone (5.5)	11

[a] Reaction conditions: [substrate] = 1.7 M, [1] = 40 mM in 1 mL of solvent at 50 °C. Reaction time: 24 h. [b] [4]Q = (C$_4$H$_9$)$_4$N$^+$; [6]Q = (C$_6$H$_{13}$)$_4$N$^+$; [7]Q = (C$_7$H$_{15}$)$_4$N$^+$. [c] Yield = (mol of product/mol of initial 1) × 100; total yield = (mol of all organic products/mol of initial 1) × 100; correction has been made for the fact that aldehydes and ketones represent four-electron oxidations while the alcohols and epoxides represent two-electron oxidations; Cr^{V}O is reduced cleanly to Cr^{III} in all cases (see text). [d] [C$_6$H$_9$OH] = 80 mM. [e] Concentration was limited by the solubility of substrate. [f] In benzene at 25 °C; [Ph$_3$P] = 60 mM.

of either H$_2$O$_2$ or NaOCl is used, the corresponding oxo Cr(V) complexes are produced with virtually quantitative selectivity. In their 1986 communication, Katsoulis and Pope reported that toluene solutions of tetra-*n*-heptylammonium salts of the Cr(III) precursor complexes stirred with a 10- to 15-fold excess of iodosylbenzene at room temperature for 30 min led to oxo Cr(V) complexes, [SiM$_{11}$O$_{39}$Cr^{V}O]$^{(9-n)-}$ (M = W(VI) (1a), Mo(VI)) (eq 2).[67] The one oxidant of greater practical interest than H$_2$O$_2$, namely O$_2$, does not effect oxidation of the Cr(III) precursor complexes to the oxo Cr(V) complexes. While this process may be thermodynamically feasible, the kinetic barriers to this effective four-electron reduction of O$_2$ to H$_2$O are significant. The reverse reaction, O$_2$ evolution from the oxo Cr(V) complexes, was attempted thermally (CH$_3$CN solvent, 20 h, 50 °C), and no O$_2$ whatsoever was produced.

Katsoulis and Pope assigned the complexes resulting from iodosylbenzene oxidation of Cr(III) TMSP precursor complexes to be the corresponding oxo Cr(V) complexes.[67] A wide variety of physical and spectroscopic properties of the oxo Cr(V) complexes 1a–c in our laboratory are in complete agreement with the oxo Cr(V) formulation. All three complexes exhibit d^1, S = $^1/_2$ systems in both solution (100% acetonitrile or 100% benzene) and the solid state: (1) The electronic absorption spectra of these complexes exhibit absorption maxima (ca. 650 nm for the Si-centered complex, 1a, and 674 nm for the P-centered complex, 1b), molar extinction coefficients (10–15 cm^{-1} M^{-1} depending on the central heteroatom and the solvent), and a number of bands (one broad feature; see Figure S1 in the supplementary material) that are all diagnostic of d–d absorption arising from d^1 Cr(V) centers.[79] (2) The complexes in both solution and the solid state exhibit magnetic moments near the spin-only value for a d^1 ion.[80]

The EPR spectra confirm the d^1, S = $^1/_2$ system with demonstrable hyperfine interactions only with the Cr nucleus. For example, for 1a (frozen CH$_3$CN, 80 K) g = 1.972 and A_{Cr} = 25 G (^{53}Cr, I = $^3/_2$; 9.55% natural abundance; see Figure S2 in the supplementary material). No hyperfine coupling is discernible with ^{17}O (I = $^5/_2$; 0.037% natural abundance), ^{1}H from protons on the polyoxometalate oxygen atoms, or ^{31}P for the phosphorus-containing complexes 1b and 1c.

The Cr^V=O stretching fundamental is readily seen in the mid-infrared as a shoulder on the asymmetric PO$_4$ stretch at 1027 cm^{-1} for 1c, a value typical of oxo Cr(V) complexes,[80–82] and it is shifted by the appropriate amount (to ca. 993 cm^{-1}) upon labeling with ^{18}O. Unlike the Cr(III) and the oxo Cr(V) undecametallosilicates examined by Katsoulis and Pope, the oxo Cr(V) undecametallophosphates 1b and 1c exhibit a splitting of the ν_3 asymmetric stretch of the central XO$_4$ unit ($\Delta\nu$ of PO$_4$). In the Cr(III) precursor compound 2c and the corresponding oxo Cr(V) compound, 1c, this splitting is 35 cm^{-1} (1051 and 1086 cm^{-1}) and 0 cm^{-1} (1072-cm^{-1} singlet), respectively. These data are consistent with the Cr(V) ion sitting more deeply in the pentadentate O$_5$ coordination polyhedron defined by the lacunary α-PW$_{11}$O$_{39}$$^{7-}$ unit in 1c than the Cr(III) ion in 2c.[83]

Transfer of Oxygen from [(C$_4$H$_9$)$_4$N]$_{9-n}$[X^{n+}W$_{11}$O$_{39}$Cr^{V}O] (X^{n+} = P^{5+}, Si^{4+}) to Organic Substrates. Product Studies. The oxo Cr(V) complexes 1a–c oxidize a range of substrates including, in order of decreasing reactivity, triphenylphosphine, a secondary alcohol (cyclohexanol), alkenes (internal, terminal, and aromatic), and even alkanes (eq 3). Representative reactions (conditions and product distributions) are given in Table I. The data in this table were collected under conditions which allowed for maximally

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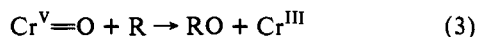
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Oxo Transfer from Oxometalloporphyrin Analogs

J. Am. Chem. Soc., Vol. 115, No. 18, 1993 8183

$$Cr^V{=}O + R \rightarrow RO + Cr^{III} \qquad (3)$$

R = organic substrate = alkene, alcohol, alkane, or Ph_3P

informative inferences to be drawn regarding the mechanism of oxidation of these substrates. Principally, the reactions were demonstrated to be under kinetic control through an analysis of the time dependence of generation of multiple products. Most reactions were purposely not taken to completion. A representative plot of the time dependence of product generation, that derived from the oxidation of cyclohexene by **1a**, is given in Figure 2. The ratios of oxidation products are constant within experimental error for even the smallest conversions for which products can be quantified ($\sim$0.1%). The degree of subsequent reaction of initial products in Table I is minimal, with the exception of the formation of cyclohexenone from intermediate cyclohexenol in the case of cyclohexene oxidation, and the relative yields are proportional in most cases to the relative rates of reaction. All the processes in Table I involve, in whole or in part, oxygen transfer from the metal to the organic substrate, and the corresponding Cr(III) form of the complex is generated cleanly in all cases (cf. eq 3).

Four lines of evidence regarding the nature of oxo transfer can be inferred from the data in Table I. First, oxidation of alkenes leads to both epoxide and allylic oxidation products. While the selectivity for epoxide during oxidation of the terminal alkene, 1-octene, is 81%, the selectivity for epoxide during oxidation of cyclohexene can be as low as 4% (the first reaction in Table I). Much higher selectivities for epoxide are observed in alkene oxidation by the Halcon and Sharpless chiral epoxidation processes and in stoichiometric epoxidation with peracids and several other electrophilic oxidants. The ratio of allylic to epoxide products seen in all the reactions in Table I is not inconsistent with several other possible mechanisms including attack by radical species. Second, the high degree of oxidative cleavage exhibited in the oxidation of *cis*- and *trans*-stilbene and styrene is uncharacteristic of electrophilic oxygenation. Third, the oxidation of norbornene by **1a** is the most informative experiment in Table I. No 7-substituted bicyclo[2.2.1]heptyl products indicative of Wagner-Meerwein rearrangement of intermediate carbocations are observed. At the same time, tricyclo[2.2.1.0^{2,6}]heptan-3-ol is formed. By far, the most reasonable formation of the tricyclo[2.2.1.0^{2,6}]-hept-3-yl skeleton is via equilibration with the bicyclo[2.2.1]heptyl radical.[84] Fourth, the generation of trans epoxide during oxidation of *cis*-stilbene indicates that epoxidation proceeds with loss of stereochemistry. The chemoselectivity exhibited collectively by the reactions in Table I [phosphine lone pairs (most reactive) > double bonds > unactivated carbon–hydrogen bonds (least reactive) and internal alkenes (more reactive) > terminal alkenes (less reactive)] is not very informative, as it is compatible with several oxidation mechanisms.

A fifth line of evidence from Table I is that the reactions in nonpolar aprotic benzene (ϵ = 2.27; Z = 54.0) were significantly faster than the same reactions in polar aprotic acetonitrile (ϵ = 35.94; Z = 71.3), consistent with a transition state of oxygenation that is as polar as or less polar than the reactants. This argues strongly against mechanisms involving rate-limiting electron transfer and β-oxy carbocation formation (see Discussion).

Although the detailed nature of oxo transfer from the metal center to the organic substrate and hence stoichiometric oxo-transfer reactions, eq 3, are the main focus of this investigation, the chromium TMSP complexes (either the Cr(III) or oxo Cr(V) forms), not surprisingly, can also function as catalysts for oxo transfer (eq 4). In an exemplary reaction, 1 equiv (1.7 μmol) of the Cr(III) complex **2a** and 24 equiv (0.04 mol) of iodosylbenzene and 1 M cyclohexene in acetonitrile at 50 °C under argon produced

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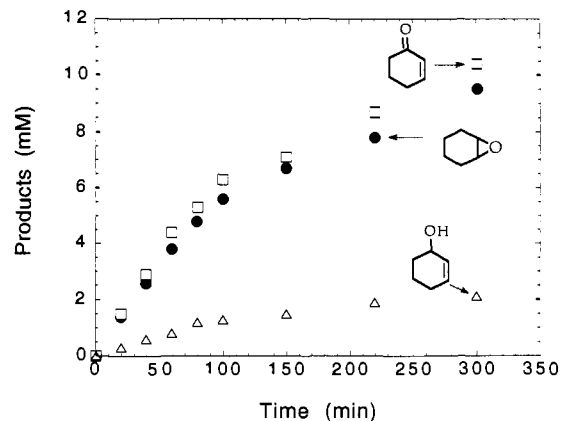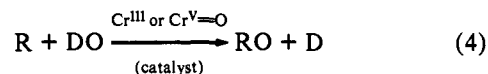

Figure 2. Time dependence of the generation of the three principal products resulting from oxidation of cyclohexene (1.7 M) by **1a** (40 mM) in benzene.
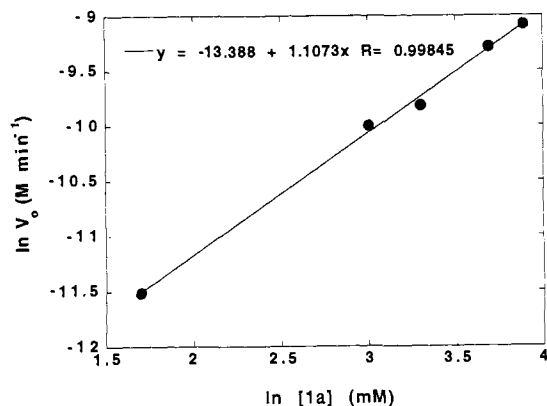
$$R + DO \xrightarrow[\text{(catalyst)}]{Cr^{III}\text{ or }Cr^V{=}O} RO + D \qquad (4)$$

R = organic substrate = alkene, alcohol, alkane, or Ph_3P

a 7.5% yield of cyclohexene oxide and a 75% yield of cyclohexenone after 6 h, representing $\sim$10.6 turnovers of **2a**. Reactions involving OCl^- and H_2O_2 as terminal oxidants in place of iodosylbenzene work equally well, and none of these reactions is extremely selective with respect to organic products.
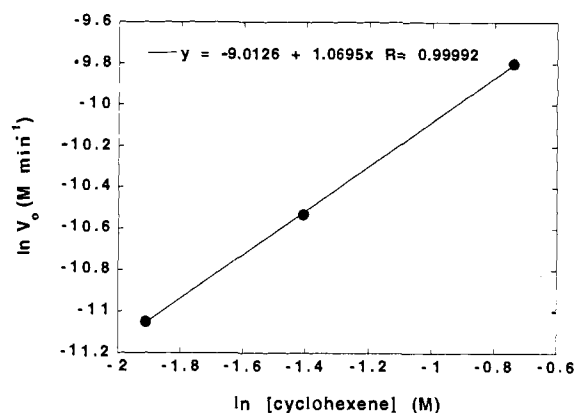
Transfer of Oxygen from $[(C_4H_9)_4N]_{9-n}[X^{n+}W_{11}O_{39}Cr^VO]$ $(X^{n+}$ = P^{5+}, $Si^{4+})$ **to Organic Substrates. Kinetic Studies.** The rate constants for the oxidation of cyclohexene and cyclohexenol in acetonitrile under the pseudo-first-order reaction conditions in Table I are 3.3×10^{-5} and 52.0×10^{-5} s^{-1}, respectively. The sixth line of evidence concerning the mechanism of oxo transfer is derived from the rate law. The rate law was determined for an exemplary reaction, the epoxidation of cyclohexene by the oxo Cr(V) complex **1a** in benzene at 50 °C. The reaction was second order overall and first order in both **1a** (Figure 3) and cyclohexene substrate (Figure 4). This simple kinetic behavior is consistent with a stepwise as well as a concerted mechanism for oxo transfer.

The seventh and eighth types of experimental evidence regarding mechanism are derived from the rate constants for cyclohexene oxidation by **1a** at different temperatures and from the kinetic isotope effects, respectively. Both the activation parameters and isotope effects can be more meaningfully assessed for production of epoxide than for production of the allylic oxidation product, cyclohexenone, as epoxide is formed more directly than the allylic oxidation product. Cyclohexenone is almost surely not produced in one concerted four-electron process from the cyclohexene and oxo Cr(V) reactants, as this would require the simultaneous cleavage of two carbon–hydrogen bonds, the removal of four electrons, the cleavage of a chromium–oxygen double bond, and the formation of a carbon–oxygen double bond. Both Eyring (or Arrhenius) plots and isotope effect plots for cyclohexenone would then represent a superposition of two or more processes. An Eyring plot, given in Figure 5, indicates simple or Arrhenius behavior for epoxidation (correlation coefficient of least-squares lines shown = 0.980), yielding the following activation parameters: $\Delta H^{\ddagger}$ = 9.1 kcal/mol, $\Delta S^{\ddagger}$ = -53.4. Note: $\Delta G^{\ddagger}$ = 25.5 kcal/mol. There is little bonding reorganization upon going to a highly ordered transition state. As the principal observed organic oxidation product involving direct cleavage of the alkene substrate bonds by the high-valent oxo Cr(V) complexes is the allylic ketone, the primary isotope effect is not readily calculated. The experimentally determined ratio of cyclohexenone-h_8 to cyclohexenone-d_8 products at 2.5% conversion is 14.7, however.

Figure 3. Plot of ln V_0 (V_0 = initial rate of cyclohexene oxidation in M min^{-1}) versus ln [1a] ([cyclohexene] = 1.7 M; T = 50 °C in benzene under an inert atmosphere). The equation is the least-squares line through the points.

**Figure 4.** Plot of ln V_0 versus ln [cyclohexene] ([1a] = 40 mM; T = 50 °C in benzene under an inert atmosphere). The equation is the least-squares line through the points.

Oxygen-18 Isotope Studies. Oxygen-Exchange Behavior of Oxo Cr(V) Complexes, Iodosylbenzene, and Iodosylbenzene-Cr Intermediates. Four experiments were conducted with ^{18}O-labeled compounds to clarify issues regarding the mechanism of oxo transfer from the oxo Cr(V) TMSP complexes to hydrocarbons and the chemistry of the high-valent oxometal moiety in general. The protocols and details of these experiments are given in the Experimental Section. The reaction of ^{18}O-labeled iodosylbenzene with cyclohexene resulted in ^{18}O-labeled epoxide. Furthermore, the reaction of ^{16}O-labeled [PW$_{11}$O$_{39}$Cr^{V}O]$^{4-}$ (1c) in the presence of ^{18}O-labeled water resulted in no incorporation of ^{18}O into the epoxide product, implying the oxygen exchange between the oxochromium(V) group and water (eq 5) was slow relative to the

$$\text{Cr}^V\!\!=\!\!O + H_2{}^*O \xrightarrow{\text{very slow}} \text{Cr}^V\!\!=\!\!{}^*O + H_2O \qquad (5)$$
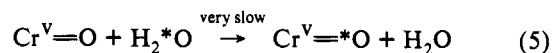
rate of substrate oxidation. The slow rate for oxo–water exchange was independently confirmed in two experiments involving isolated purified oxo Cr(V) complexes under various reaction conditions including those in Table I (see Experimental Section). These results contrast sharply with the implication of rapid oxygen exchange between oxo Cr(V) porphyrin and water.[81,82] In contrast to these experiments, oxygen exchange between PhI^{16}O and H$_2$^{18}O was catalyzed by the Cr(III) complex 2a. Both the resulting oxo Cr(V) complex, 1a, and the unreacted iodosylbenzene recovered after reaction contained ∼30–35 atom % ^{18}O. The implication of these experiments is that a complex between iodosylbenzene and the Cr atom exchanges oxygen with water on a time scale comparable to that of substrate oxygenation (eq 3), while the fully formed and freely diffusing oxo Cr(V) complex does not.
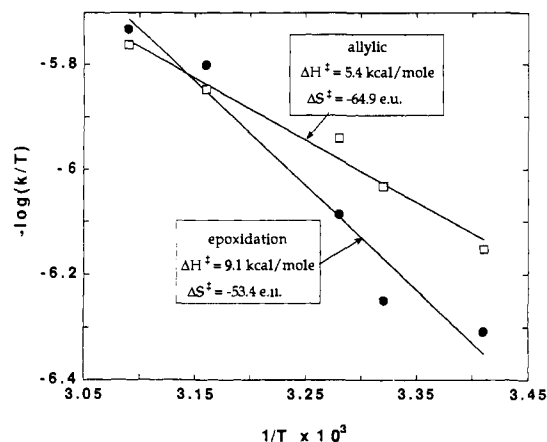
**Figure 5.** Eyring plots for allylic oxidation and epoxidation of cyclohexene by 1a at [1a] = 40 mM and [cyclohexene] = 1.7 M in benzene.
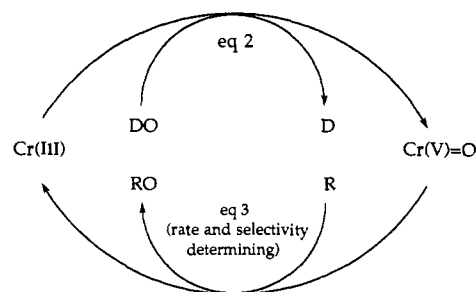
Figure 6. Cycle for oxidation of organic substrates, R = alkenes, alkanes, alcohols, and Ph$_3$P, with oxygen donor oxidants, DO = OCl$^-$, H$_2$O$_2$, and PhIO, catalyzed by Cr(III) or oxo Cr(V) heteropolytungstate complexes.

These results implicate two points of significance beyond the present study: First, high-valent d-electron transition metal oxo complexes are not always labile with respect to oxo exchange with water and indeed the oxo Cr(V) species are not labile, at least in the title polyoxometalate complexes, and second, the chemistry of iodosylarenes with transition-metal centers continues to evolve beyond a mere oxygen donor role for the iodosylarene. Research has implicated not only that iodosylarenes or iodosylarene ligands can function as substrate oxidizing centers remote from the d-metal ion "active site"[36] but also that they can play a role in oxygen exchange with water.

Discussion

Oxo Cr(V) complexes [X^{n+}W$_{11}$O$_{39}$Cr^{V}O]$^{(9-n)-}$ (X^{n+} = P^{5+}, Si^{4+}) are formed rapidly at ambient temperature upon treatment with a 10-fold molar excess of aqueous OCl$^-$, aqueous H$_2$O$_2$, or, as Katsoulis and Pope reported previously for the Si-centered complex, iodosylbenzene. The spectroscopic and magnetic properties of the oxo Cr(V) complexes indicate that the best description of the ground electronic state for all of them is a fully oxidized d^0 polyoxotungstate ligand enclosing a localized d^1 oxochromium(V) ion. These S = $^1/_2$ centers exhibit little admixing of excited states. Four features of the reactivity of these complexes derived from Table I are also consistent with an electronic ground state with localized radical character on the oxochromium(V) moiety: (1) the high ratio of allylic products to epoxides in alkene oxidation, (2) the demonstrable reactivity for unactivated carbon–hydrogen bonds under conditions comparable to those in the epoxidation reactions, (3) the loss of stereochemistry in cis-stilbene epoxidation, and (4) the radical products seen in the oxidation of norbornene.

In the overall catalytic process, oxidation of the organic substrates (alkenes, alkanes, alcohols, or Ph$_3$P) by the oxidants (OCl$^-$, H$_2$O$_2$, or PhIO) catalyzed by the Cr(III) or oxo Cr(V) compounds (Figure 6), the catalyst oxidation step, eq 2, is

Oxo Transfer from Oxometalloporphyrin Analogs

J. Am. Chem. Soc., Vol. 115, No. 18, 1993 8185
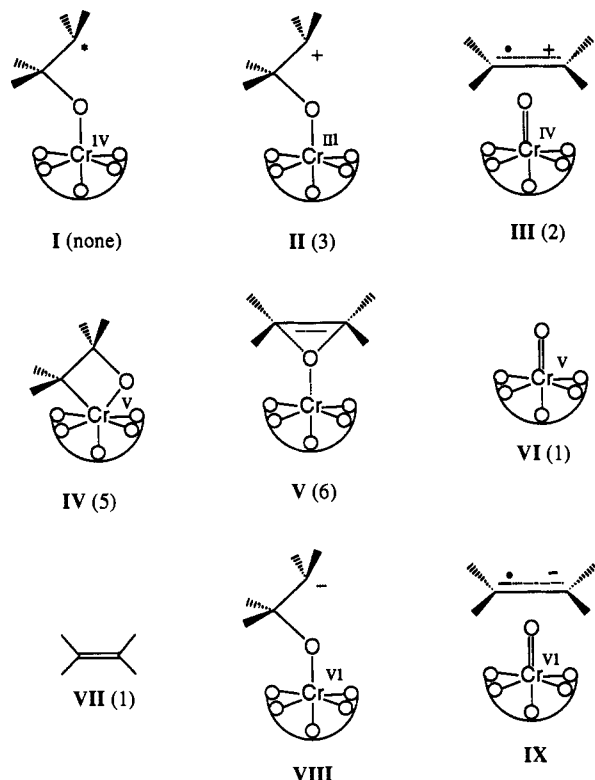
Figure 7. Possible transition states for epoxidation of alkene by the oxo Cr(V) heteropolytungstate. The numbers given in parentheses after the Roman numerals for the first seven transition states are the total unequivocal lines of experimental evidence against each particular transition state.

substantially faster than the substrate oxidation step reducing oxo Cr(V) back to Cr(III), eq 3. For alkene substrates, eq 3 is the key process that controls the overall rate of the catalytic cycle in Figure 6 and, in large part, the selectivity. The tractable rate of eq 3 for alkene substrates and the accessibility of the reactant oxo Cr(V) complexes facilitated a detailed evaluation of this reaction.

Nine possible transition states for alkene epoxidation (eq 3, where oxygen is transferred from the oxo Cr(V) heteropolytungstate to substrate alkene) are depicted in Figure 7. They are given in rough order of likelihood. In parentheses after the Roman numeral designating the particular transition state is the number of total lines of evidence inconsistent with that transition state. No number appears in parentheses after transition states **VIII** and **IX** as these do not appear to lie along any reaction coordinate involving reduction of the oxometal group and oxidation of the alkene substrate nor has either of them been generally proposed in any organic substrate oxidation by a metal center to the best of our knowledge. As a consequence, there is no body of structure–activity information defining such transition states for reference. They are included for sake of completeness, as they are possible, in principle. They are highly improbable not only because oxidation of oxochromium(V) to oxochromium(VI) and alkene reduction do not lie along the desired redox reaction coordinate but also because alkenes without electron-withdrawing substituents make them highly unlikely on thermodynamic grounds. Furthermore, they are inconsistent with higher rates of epoxidation in benzene versus acetonitrile. Transition states **VI** and **VII** represent the isolated oxo Cr(V) complex and the isolated alkene, respectively. As epoxidation is first order in both oxochromium(V) and alkene, both these transition states can be rigorously ruled out.
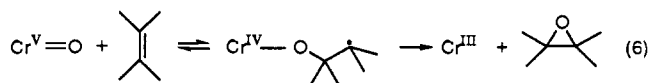
The concerted transfer of oxygen from chromium to alkene is depicted in **V** (Figure 7). This is an electrophilic process analogous to epoxidation by peracids and by the heterolytically activated

peroxide moieties bound to d^0 transition metal centers operable in the Halcon and Sharpless chiral epoxidation processes. It is compatible with the rate law but incompatible with (1) the substantial quantities of allylic products (electrophilic oxygenations of all kinds are highly selective for epoxide),[2] (2) oxidative cleavage (unusual in this type of reaction), (3) loss of stereochemistry in *cis*-stilbene oxidation (they are usually, but not always, highly stereoselective), (4) the production of tricyclo-[2.2.1.0²,⁶]heptan-3-ol, a product indicative of radical intermediates, in norbornene oxidation (concerted oxo transfer would not involve free radicals), and (5) the activation parameters. Higher enthalpies and less negative entropies of activation would probably be expected. For example, $E_a = 10.9$ kcal/mol and $\Delta S^{\ddagger} = -27.8$ eu for the epoxidation of cyclohexene by *m*-chloroperoxybenzoic acid.[85]

The oxometallocyclobutane transition state, **IV**, has been proposed in some epoxidations by oxometalloporphyrins and related complexes, but it cannot be operable to a significant extent in these epoxidations. It is inconsistent with all the lines of evidence that rule out the concerted electrophilic transition state, **V**. The observed rate behavior is consistent with **IV**, however. Transition state **III** represents the mechanism involving initial electron transfer from alkene to chromium. The principal evidence against this is the increased rates in nonpolar benzene versus polar acetonitrile. The second line of evidence against this mechanism is the activation parameters. For a rate-limiting electron transfer between these two partners, one would expect a somewhat more positive enthalpy and entropy of activation. A mechanism involving **III**, like the final transition states to be discussed below (**I** and **II**), would necessarily lie earlier along the reaction coordinate or more elementary processes away from the observed products than do transition states **IV** and **V**.

Transition state **II** is unlikely given the solvent effect and the intermediacy of radicals implicated by the product distribution data (the ratio of allylic products to epoxide and the production of tricyclo[2.2.1.0²,⁶]heptan-3-ol from oxidation of norbornene). This leaves transition state **I**, which is definitely the most consistent with all the data.

The minimal mechanism consistent with all the data for the epoxidation of alkenes by oxo Cr(V) complexes (eq 3; R = alkene) is eq 6. For sake of completeness, two points need to be made.

First, not all alkene oxidation reactions necessarily proceed by eq 6 although it is likely in view of the collective data that eq 6 is dominant in all reactions. Furthermore, more than one mechanism for the transfer of oxygen from chromium to alkene may be operable in any particular reaction.

Conclusions

(1) In our first report in 1986 on oxo transfer by polyoxometalate-based inorganic metalloporphyrin analogs, the Cr TMSP complex $[PW_{11}O_{39}Cr^{III}]^{4-}$ was reported to be almost inactive as a catalyst for the epoxidation of alkenes by iodosylbenzene at 25 °C.[46] Likewise, in the subsequent communication by Katsoulis and Pope involving the first characterization of oxo Cr(V) TMSP complexes, these high-valent forms were reported to have little or no activity for oxidation of *trans*-stilbene at room temperature.[67] In contrast to these preliminary indications, we find that at higher temperatures (at least 50 °C) both the Cr(III) and the oxo Cr(V) complexes can catalyze alkene oxygenation not only by iodosylbenzene but also by the inexpensive oxidants aqueous hypochlorite and hydrogen peroxide. Not surprisingly, alcohols and triphenylphosphine are also oxygenated and oxygenated at

(85) Shea, K. J.; Kim, J.-S. *J. Am. Chem. Soc.* **1992**, *114*, 3044–3051.

a faster rate than alkenes. Alkanes are also oxidized, but at a slower rate than alkenes.

(2) The data are consistent with the dominance of a two-step process in the oxygenation of alkenes catalyzed by Cr TMSP complexes, oxygenation of the Cr(III) center by the oxygen donor, DO (PhIO, OCl⁻, or H_2O_2) ($Cr^{III} + DO \rightarrow Cr^V{=}O + D$ (eq 2)) followed by oxo transfer from chromium to alkene ($Cr^V{=}O + alkene \rightarrow Cr^{III} + alkene$ oxidation products (eq 3)). The second process (eq 3) is rate limiting for all the hydrocarbon substrates examined.

(3) Magnetic and spectroscopic data are consistent with the title oxo Cr(V) complexes $[X^{n+}W_{11}O_{39}Cr^VO]^{(9-n)-}$ ($X^{n+} = P^{5+}$, Si^{4+}) being isolated d^1 Cr(V) ions in d^0 $X^{n+}W_{11}O_{39}^{(12-n)-}$ pentadentate ligands, the same assignments first made by Katsoulis and Pope for the corresponding Si^{4+}-centered chromium heteropolyoxometalates. The reactivity of the oxo Cr(V) complexes with alkenes is also consistent with dominant doublet or radical character at the reactive metal center: the high ratio of allylic oxidation products to epoxide, the close relative reactivities of alkenes and alkanes (actual ratio varies with alkene), the loss of stereochemistry in epoxidation of a representative alkene, *cis*-stilbene, and products directly indicative of radical intermediates in the oxidation of norbornene.

(4) The transfer of oxygen from chromium to alkenes is very clean with respect to the chromium (only Cr(III) is detected) and reasonably clean with respect to the organic products (the selectivity depends on the substrate). The rate law for a representative metal-to-substrate oxygen transfer, the reaction of $[SiW_{11}O_{39}Cr^VO]^{5-}$ (**1a**) with cyclohexene (acetonitrile solution, 50 °C, argon) ($V = k[Cr^V{=}O][alkene]$), and seven other lines of evidence including product distributions, isotope effects, and activation parameters argue strongly against concerted oxo transfer, the formation of oxometallocyclobutane and the β-oxochromium carbocation, electron transfer, and other mechanisms and are collectively most consistent with radical addition of the oxochromium(V) moiety to the double bond followed by collapse of the β-oxochromium radical to the observed products, Cr(III) and oxygenated organics (eq 6).

(5) Experiments with ^{18}O-labeled iodosylbenzene or water indicate that transfer of oxygen from oxochromium(V) to alkenes is far faster than oxygen exchange between oxochromium(V) and water. The Cr(III) complexes catalyze oxygen exchange between water and iodosylbenzene. Whereas oxygen exchange between water and oxochromium(V) is not facile, oxo exchange between these two species via a chromium–iodosylbenzene intermediate under the oxygenation reaction conditions in this study is facile.

Supplementary Material Available: Figures showing the electronic absorption spectra of **1a** and **2a** and the EPR spectrum of **1a** (2 pages). Ordering information is given on any current masthead page.