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Oxidation of Alcohols by Hexanuclear Cluster Ions

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Introduction

A diverse activation chemistry of organic substrates may be accomplished with transition metal complexes that are powerful oxidants. Most activation schemes usually rely on the electrochemical[1] or photochemical[2] generation of the metal oxidant. We have been studying one class of transition metal oxidants derived from the hexanuclear metal halide complexes, $[M_6X_8]Y_6^{2-}$ (M = Mo, W; X = Cl, Br, I; Y = donor ligand including halide), which comprise eight metal atoms arranged in an octahedral metal core ligated by eight face-bridging halides and six axial donor ligands. A facile one-electron-oxidation and -reduction chemistry of the cluster ions is derived from the metal-based orbitals of the octahedral core.[3] The ability to generate stable $[M_6X_8]Y_6^-$ ions at high potentials (1.0–1.3 V vs SCE)[4] suggested to us that their oxidation chemistry with a variety of organic substrates may be explored. Indeed, during our studies of the electrogenerated chemiluminescence of these cluster ions,[3a,5] we noticed that orange-red solutions of the electrogenerated $[M_6X_8]Y_6^-$ ions turned to the characteristic yellow of $[M_6X_8]Y_6^{2-}$ solutions upon the addition of alcohols.

We now report the oxidation chemistry of alcohols by electrochemically generated $M_6X_{14}^-$ ions. The $Mo_6Cl_{14}^{2-}$ parent cluster was chosen as the transition metal reactant because its monoanion is the most potent oxidizing agent of this series. In addition, benzyl alcohol and 2-propanol were chosen as prototypic organic substrates because their reactivity with transition metal oxidants is well understood.[6] We also present the reaction of these alcohols with $W_6Br_{14}^{2-}$, which provides insight into the role that the terminally coordinated halide ligands play in the oxidation process.

Experimental Section

Materials. The tetrabutylammonium salts of the hexanuclear molybdenum chloride and tungsten bromide cluster ions were prepared by previously described methods.[4a] The salts were recrystallized three times by evaporation from CH_2Cl_2, and product purity was determined by electrochemistry, emission lifetime measurements, and fast atom bombardment mass spectrometry (FABMS). The purity of the cluster system was confirmed by the presence of a single parent ion cluster peak in the FABMS spectrum with the typical fingerprint pattern.[3a]

Benzyl alcohol, 2-propanol, (Aldrich Gold Label), *tert*-butyl alcohol, and triphenylcarbinol (Aldrich HPLC grade) were used as received. Cumene was distilled from sodium under an argon atmosphere, prior to use. Tetrabutylammonium hexafluorophosphate (Southwestern Analytical Chemicals) was dissolved in ethyl acetate, and the solution was dried over $MgSO_4$. The salt was recrystallized from pentane–ethyl acetate solution and dried in vacuo for 12 h at 60 °C. Dichloromethane, obtained from Burdick and Jackson (Distilled-in-Glass grade), was subjected to seven freeze–pump–thaw cycles and distilled on a high-vacuum manifold into a flask containing activated 4-Å molecular sieves.

Methods and Instrumentation. The direct oxidation of organic substrates was accomplished with $M_6X_{14}^-$ ions produced by bulk electrolysis of the tetrabutylammonium salts of $M_6X_{14}^{2-}$ in CH_2Cl_2 at 22 ± 1 °C. Controlled-potential electrolysis experiments were performed by using standard methods and instrumentation.[3a] Procedures enabling experiments to be performed under rigorously dry and oxygen-free conditions have been described.[5] A standard three-compartment H-cell specially adapted for high-vacuum manipulations was equipped with Pt mesh working and auxiliary electrodes; the reference was a Ag wire quasi-reference electrode. Initial concentrations of cluster ions were 6.5×10^{-3} and 1.25×10^{-3} M for $Mo_6Cl_{14}^-$ and $W_6Br_{14}^-$, respectively). The current during bulk electrolysis decayed exponentially to 91% of its initial value. Normally, bulk electrolysis required ~0.5 h, depending upon electrode area, stirring efficiency, and the solubility of the cluster. Cyclic voltammograms were obtained before and after bulk electrolysis in order to determine if any side reactions accompanied the electrolysis process. Oxidized solutions were charged with a 10-fold excess of alcohol from a side arm isolated from the main body of the cell with a high-vacuum Teflon stopcock and allowed to react for ~0.5 h. Sample analysis was facilitated by isolating organic products from the cluster species by vacuum transfer of bulk-electrolyzed solutions. Organic products were determined by ^1H NMR spectroscopy (Bruker WM-250) and GC/MS, the instrument for which consisted of a Hewlett-Packard 5980 GC modified for coupling to a JEOL JMS-AX505H MS. The GC column was a 15-m Carbowax Foxboro capillary. Once identified, the formation of organic oxidation products during reaction was monitored with a 5890 Hewlett-Packard GC equipped with a flame ionization detector, a 15-m Carbowax Foxboro capillary column, and integrator. Hexadecane was used as an internal standard.

The apparent current efficiency (Φ_e) for reaction was calculated on the basis of a two-electron oxidation of the alcohol to aldehyde with the relation

$$\Phi_e = \frac{2FN}{Q - Q'} \times 100 \qquad (1)$$

where N is the number of moles of product analyzed, F is 96 485 C/mol, and Q and Q' are the charges passed during electrolysis in the presence and absence of the cluster, respectively.

Sample irradiations for photochemical experiments were accomplished by using a Hanovia 1000-W Hg/Xe high-pressure lamp. Photolysis experiments were performed in two-arm evacuable cells equipped with Kontes quick-release Teflon valves. Sample temperatures were thermostated at 15.0 ± 0.5 °C in all photoreactions. Photolyses were accomplished by using Schott color glass high-energy cutoff filters to eliminate the unwanted higher energy light. For quantum yield measurements, the 436-nm excitation wavelength was isolated by using interference filters purchased from Oriel Corp. Photochemical quantum yields were measured by using a ferrioxalate actinometer.

Results and Discussion

Yellow solutions of $Mo_6Cl_{14}^{2-}$ turn bright orange when a Pt electrode is held at a potential 100 mV positive of the formal potential of the cluster ion ($E_{1/2}(Mo_6Cl_{14}^{-/2-})$ = 1.38 V vs SCE[5a]). Absorption spectra of bulk-electrolyzed solutions are dominated by the intense LMCT absorption band of $Mo_6Cl_{14}^-$ at 480 nm. The red shift in this transition results from the introduction of a hole in the metal-based HOMO of $Mo_6Cl_{14}^-$.[7] During controlled-potential electrolysis (CPE), the anodic current was observed to decay exponentially to 91% of its initial value and

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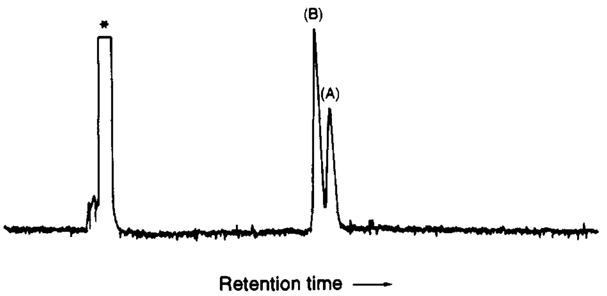

Figure 1. Gas chromatogram of the organic products from the reaction of benzyl alcohol with electrolyzed solutions of $Mo_6Cl_{14}^{2-}$. The solvent peak is designated by an asterisk, and the benzyl alcohol reactant, which elutes from the column after 30 min, is not shown.

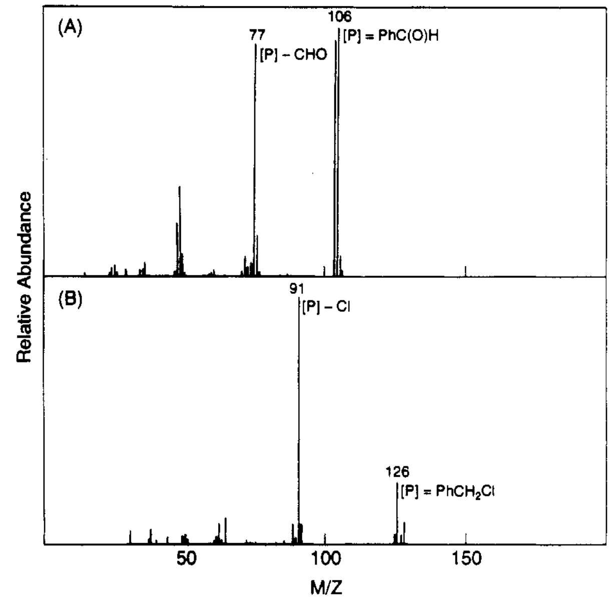

Figure 2. Mass spectra of (A) peak A and (B) peak B in Figure 1. [P] denotes parent ion peak; assignments of selected mass fragments are shown.

coulometry showed that 1.05 ± 0.10 equiv of charge was passed into solution, thereby confirming a one-electron process. Cyclic voltammograms recorded before and after bulk electrolysis were identical, indicating that no cluster was destroyed and no new electroactive species was formed during the electrolysis process.

Even though direct oxidation of benzyl alcohol ($PhCH_2OH$) occurs at potentials >2 V vs SCE,[8] we observed vestiges of anodic current at a platinum electrode poised at potentials between 1.3 and 1.4 V. Consequently, the alcohol was reacted with the cluster monoanion upon the completion of CPE. Introduction of the alcohol caused the yellow solutions of $Mo_6Cl_{14}^{2-}$ to reappear, as was confirmed by the absorption spectrum of the reacted solution.

The organic products resulting from the reaction of $PhCH_2OH$ with $Mo_6Cl_{14}^-$ were analyzed by gas chromatography and mass spectrometry. Figure 1 shows a typical gas chromatogram of the $PhCH_2OH/Mo_6Cl_{14}^-$ system. In addition to the solvent, two products are observed to elute promptly from the GC column; $PhCH_2OH$ elutes from the column after ~30 min and is not shown. The identity of these organic products is established unequivocally with the GC/MS shown in Figure 2. Peak A yields a mass spectrum identical to that of benzaldehyde (PhC(O)H), and peak B produces the mass spectrum of benzyl chloride ($PhCH_2Cl$). Production of the former is selective with no formation of the carboxylic acid. The stoichiometry of the reaction is 0.92 mol of benzaldehyde and 1.8 mol of benzyl chloride formed/2 mol of $Mo_6Cl_{14}^-$ with an apparent current efficiency for reaction to product of 87 ± 6%.

We account for the production of benzaldehyde with the following scheme

$$2Mo_6Cl_{14}^{2-} \rightarrow 2Mo_6Cl_{14}^- \qquad (2)$$

$$Mo_6Cl_{14}^- + PhCH_2OH \rightarrow Mo_6Cl_{14}^{2-} + Ph\dot{C}(O)H + H^+ \qquad (3)$$

$$Mo_6Cl_{14}^- + Ph\dot{C}(O)H \rightarrow Mo_6Cl_{14}^{2-} + PhC(O)H + H^+ \qquad (4)$$

This reaction sequence is consistent with the 2:1 $Mo_6Cl_{14}^-$:PhC(O)H stoichiometry and the complete lack of reactivity for alcohols that do not possess an α-hydrogen atom. We observe no reaction when *tert*-butyl alcohol or triphenylcarbinol is the organic reactant. The lack of reactivity of tertiary substituted alcohols in the presence of strong one-electron oxidants is a typical hallmark of an α-hydrogen abstraction mechanism;[6] and our results are similar to those for the reactions of Ru(IV) oxo compounds with alcohols,[9] which have also been postulated to react according to an α-hydrogen abstraction mechanism. Whereas eqs 2–4 account for the overall reaction sequence, the intimate details of this mechanism remain undefined. We have no data to differentiate between discrete hydrogen abstraction and electron transfer followed by proton loss.[1a,9,10]

Equations 2–4 incompletely describe the observed reaction chemistry, as they do not account for benzyl chloride formation. A 2:1 benzyl halide:benzaldehyde stoichiometry is consistent with the subsequent reaction of the protons, produced by eqs 3 and 4, and benzyl chloride as follows

$$PhCH_2OH + H^+ \rightarrow Ph\overset{+}{C}H_2 + H_2O \qquad (5)$$

$$Ph\overset{+}{C}H_2 + Mo_6Cl_{14}^{2-} \rightarrow PhCH_2Cl + Mo_6Cl_{13}^- \qquad (6)$$

In nonaqueous solution, the activity of H^+ is significant and it is capable of attacking a hydroxyl group to produce the carbocation.[11] Subsequent trapping by chloride yields the observed product benzyl chloride. In support of reactions 5 and 6, the ^{13}C resonance for the benzyl carbon of the alcohol (59 ppm) disappears with the concomitant appearance of a benzyl resonance for the chloride (42 ppm) upon the addition of CF_3SO_3D to benzyl alcohol solutions containing the cluster anion $Mo_6Cl_{14}^{2-}$.

A noteworthy difference between the cluster reactivity and that of other transition metal oxidants is the chemistry derived from the incipient proton. Typically the side reaction of protons released in alcohol oxidation with substrate is circumvented by the presence of Lewis basic sites on the oxidation catalyst. For instance, protons generated from benzyl alcohol oxidation by electrocatalysts such as $[py(bpy)_2Ru(O)]^{2+}$ and *trans*-$Os(\eta^4$-DHBEt$)(py)_2$ (DHBEt = 1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane) are rendered inactive upon their reaction with the oxo ligand to produce a hydroxo ligand.[9,12] In our case, no such basic site exists on the transition metal reactant, thereby leaving H^+ for reaction with substrate. In order to test this hypothesis, we performed the oxidation reaction in the presence of a proton scavenger. Most common homogeneous bases such

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Table I. Product Yields for the Oxidation of Benzyl and Tertiary Alcohols by Electrogenerated $M_6X_{14}^-$

	benzyl alcohol products[a]			R_3COH reactants[a]	
parent cluster ion, soln	Ph-CH_2Cl	Ph-C(O)H	Ph-CH_2Br	R = Ph	R = CH_3
$Mo_6Cl_{14}^{2-}$, CH_2Cl_2	1.8[b]	0.92	0	0	0
$Mo_6Cl_{14}^{2-}$, CH_2Cl_2/Na_2CO_3	0.95[c]	0.87	0	0	0
$W_6Br_{14}^{2-}$, CH_2Cl_2	0.10	0.83	1.7[d]	0	0

[a] Equiv of product/2 equiv of $M_6X_4^-$ ion. [b] Produced with a current efficiency of 87 ± 16%. [c] Produced with a current efficiency of 95 ± 5%. [d] Produced with a current efficiency of 101 ± 2%.

as pyridines and alkyl- or arylamines either react with the cluster (by substitution of the axial halide ligands[13]) or do not possess sufficiently positive oxidation potentials to be inert to our electrochemical conditions. Accordingly, we adopted the commonly used strategy of employing a heterogeneous base, Na_2CO_3, as a proton scavenger in chlorinated solvents.[12] As summarized in Table I, a reduction in the benzyl halide:benzaldehyde stoichiometry from 2:1 to nearly 1:1 is observed when the reaction is performed in the presence of a 15-fold molar excess of solid base. Benzyl halide formation is not completely precluded because, as previously observed,[12] solid Na_2CO_3 is an inefficient trap of H^+. Nevertheless the attenuation of benzyl chloride production in the presence of a proton scavenger is clearly in line with the overall reaction chemistry described by eqs 5 and 6. Further support for eqs 5 and 6 is provided when the oxidation is carried out in the presence of the free-radical scavenger cumene. The reaction of the chlorine radical with cumene is diffusion controlled ($k_{Cl} = 6.9 \times 10^9\ M^{-1}\ s^{-1}$) as is the dimerization of cumyl radicals to produce dicumene ($k_{dim} = 8.0 \times 10^9\ M^{-1}\ s^{-1}$).[14] Nevertheless, gas chromatographic analysis of solutions in which the oxidation was performed in the presence of cumene showed no formation of dicumene or cumyl chloride, thereby indicating the absence of radical pathways.

The cluster ion is an ideal source of chloride ion in eq 6. Previous studies of the molybdenum chloride system show that the axial chloride ligands are labile and subject to substitution.[15] Evidence that the cluster functions as a halide source for the carbocation is provided with the substitution of $W_6Br_{14}^{2-}$ for $Mo_6Cl_{14}^{2-}$ in eqs 2–4. Addition of benzyl alcohol to bulk-electrolyzed solutions of $W_6Br_{14}^-$ yields 1.7 mol of $PhCH_2Br$/2 mol of $W_6Br_{14}^-$ with no appreciable formation of $PhCH_2Cl$.[16] These results indicate that the source of the halide ion present in the halogenated organic products is the cluster ion.

The oxidation of alcohols by the $M_6X_{14}^{2-}$ cluster system is not necessarily restricted to electrochemical strategies. The ability to produce $M_6X_{14}^-$ ions by oxidative quenching of the $M_6X_{14}^{2-}$ excited state offered the opportunity to design a photochemical scheme for alcohol oxidations. On the basis, the oxidized cluster may be produced photochemically in the presence of acceptor A

$$Mo_6Cl_{14}^{2-} \rightarrow Mo_6Cl_{14}^{2-*} \qquad (7)$$

$$Mo_6Cl_{14}^{2-*} + A \rightarrow Mo_6Cl_{13}^- + A^- \qquad (8)$$

Parallel to the electrochemical results, once formed, alcohol oxidation may be achieved by eqs 3 and 4. However these photochemical experiments were not successful. Although $M_6X_{14}^{2-*}$ is efficiently quenched by chloranil and tetracyanoethylene to produce $M_6X_{14}^-$,[17] only negligible amounts of ketone and aldehyde were produced when this excited-state chemistry was investigated in the presence of 2-propanol or benzyl alcohol, respectively. After 24 h of irradiation, oxidation products were detected at the sensitivity limit of GC. The quantum yield for the photoreaction is less than 10^{-6}. The low yield for product formation (6–20%), in addition to this low quantum yield, suggests that the generation of products by photochemical means is unlikely. Indeed, in light of the recent observation that reduced quenchers of the type used in the our photochemical studies react with organic substrates,[18] a photochemical side reaction involving the quencher radical anion and alcohol is possible. The negligible yields for benzaldehyde and acetone production likely result from the very efficient back electron transfers between $M_6X_{14}^-$ and the radical anions of TCNE and chloranil, which proceed near the diffusion-controlled limit.[17] Thus hydrogen abstraction by $M_6X_{14}^-$ (eq 3) is circumvented by simple recombination of the photogenerated electron/hole pair.

In summary, the $M_6X_{14}^-$ clusters are powerful oxidants that are capable of effecting the oxidations of organic substrates. The ability to modify the cluster core with the substitution of a variety of ligands at its axial coordination sites while maintaining the clusters' electrochemical and photochemical properties permits these species to be specially tailored to oxidation reactions. This may be a key to the future development of photochemical cycles based on these reagents. One unique approach, which these clusters offer to circumvent the back-electron-transfer problem, is the coordination of the alcohol directly to the cluster core. Alcohol and alkoxide derivatives of these clusters have been previously reported.[19] In an axial coordination site, the α-hydrogen is situated over the face of the metal octahedron and thus predisposed to abstraction. To this end, the kinetics of abstraction should be enhanced relative to the kinetics of the bimolecular back-reaction. Photochemical studies on such modified clusters would be welcome.

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