The Reactivity of Tetrathioperrhenate

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Over the past 70 years, chemists have amassed a wealth of knowledge regarding the controlled oxidation of organic compounds. In particular the metal catalyzed oxidation of alkenes has, through the use of OsO_4, permitted the selective formation of oxidized products, e.g. diols, in high enantiomeric excess.[1-3] The mechanism of the addition of alkenes to OsO_4 in this dihydroxylation reaction has been a matter of contention for many years.[4,5] In particular, whether the addition proceeds through a concerted [3+2] or an initial [2+2] cycloaddition has been widely discussed.[6-9] The investigations of complexes that are structurally related to OsO_4 have more recently been used to argue the [3+2] and [2+2] mechanistic pathways.[10-13] While the mechanism is still poorly understood.[14,15]

Isoelectronic and isostructural with the metal tetroxides, the tetrathioperrhenate anion, ReS_4^-, displays reactivity reminiscent of OsO_4. We have shown that ReS_4^- reversibly reacts with alkenes (C_2R_4 = norbornene, norbornadiene, ethylene, and dimethyl maleate) to yield complexes with the general formula $ReS_2(S_2C_2R_4)^-$. The binding constant for this reaction varies over a wide range depending on the alkene, for norbornene K_{eq} = 9400 M^{-1}, while for dimethyl maleate K_{eq} = 0.3 M^{-1}. In the case of norbornene, the activation parameters were measured, ΔS=-98 J/mol. The solid state structure of two alkene adducts were obtained. The structures of ReS_4(norbornene)$^-$ and $(ReS_4)_2$(norbornadiene)$^{2-}$ reveal slightly distorted tetrahedral Re centers. The ReS_4(norbornene)$^-$ adduct displays electrochemical-chemical behavior upon reduction, that is the reduction of the adduct (-1.7 V vs. Ag/AgCl) causes the dissociation of ReS_4^{2-} and norbornene (Figure 1).
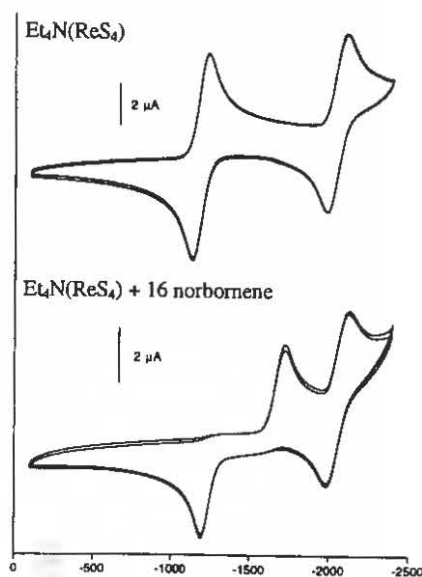

Figure 1.

Alkynes react with ReS_4^-, though the addition is irreversible. The products from the reaction of diphenylacetylene (C_2Ph_2) and bis(trimethylsilyl)acetylene ($C_2(tms)_2$) with ReS_4^- were crystallographically characterized. Their solid state structures reveal d^2- d^2 dimers based on the addition of one alkyne to a ReS_4^- moiety, i.e. $ReS_2(S_2C_2R_2)^-$, and dimerization. The

reaction of dimethylacetylenedicarboxylate (DMAD) with ReS_4^- initially yields a yellow complex that has the stoichiometry 2 ReS_4 to 1 DMAD, as determined by optical spectroscopy. The substoichiometric addition of $C_2(tms)_2$ to ReS_4^- causes the 4 electron reduction of two Re centers and yields the tetranuclear complex $\{Re_2S_6[S_2C_2(tms)_2]\}_2^{4-}$ (Figure 2). The Re_4 complex is formed reversibly; addition of alkyne to solutions containing $\{Re_2S_6[S_2C_2(tms)_2]\}_2^{4-}$ show formation of a proposed $ReS_2[S_2C_2(tms)_2]^-$ adduct followed by formation of the $Re_2S_4[S_2C_2(tms)_2]\}_2^{2-}$ dimer, as determined by ^1H NMR spectroscopy.[16]
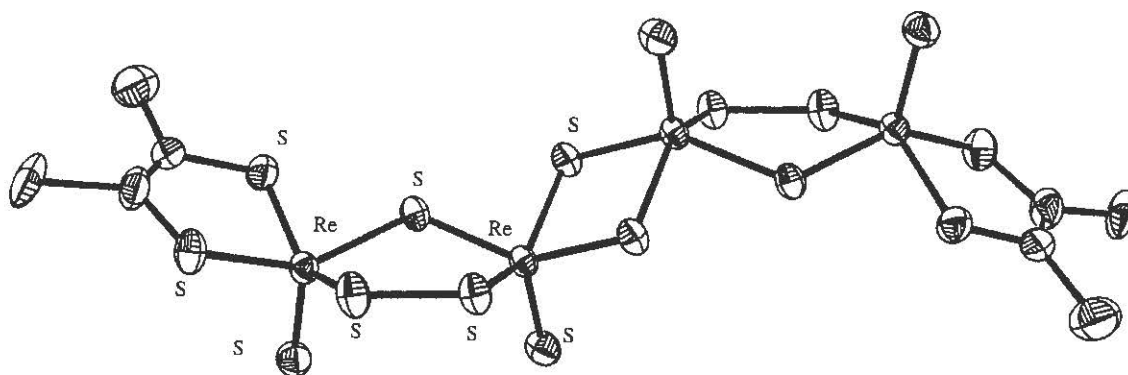

Figure 2.

The addition of oxidants, e.g. Me_3NO and S_8, to solutions containing ReS_4^- and alkyne yield reactive Re(VII) complexes, as suggested by the reaction products. The reaction of ReS_4^- with 2 C_2Ph_2 and 1/8 equiv S_8 yields $ReS(S_2C_2Ph_2)_2^-$.[17] The reaction of ReS_4^- with 1 C_2Ph_2 and 1/8 equiv S_8 yields a mixture of products that are competent precursors for the formation of $ReS(S_2C_2Ph_2)_2^-$. The reaction of ReS_4^- with excess C_2Ph_2 and Me_3NO yields a mixture of products that contain $ReO(S_2C_2Ph_2)(S_2NCMe)^-$, as determined by mass spectroscopy.[18]

The reactivity of ReS_4^- toward alkenes and alkynes is reminiscent of the proposed intermediates in the OsO_4 catalyzed oxidation of alkenes. The very reactive, as suggested by the formation of the azadithiolene ligand (S_2NCR), Re(VII) intermediate generated via the addition Me_3NO to solutions thought to contain $ReS(S_2C_2Ph_2)^-$ suggests that an Os(VIII) complex in the proposed mechanism for dihydroxylation may be unrealistic. Further studies focus on the fundamental chemistry of ReS_4^-, the addition of protic reagents to the Re(V) monomeric complexes, e.g. $PhSH+ReS_2(S_2C_7H_{10})^-$ and $ReS_2[S_2C_2(tms)_2]^-$, and the oxidation of the Re(V) complexes.

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