either a conformational change mechanism (Brudvig) or an electron-transfer process (Vanngard). The dual center, conformational change mechanism incorporates a mononuclear manganese center that acts solely as an electron-transfer intermediate between $P680^+$ or Z^+ and the trinuclear cluster. Both the multiline and $g = 4$ features would result from conformationally distinct clusters. Alternatively, in the dual-center, electron-transfer mechanism, a mononuclear center would be involved in a redox equilibrium between a mononuclear center with an Mn(III)/Mn(IV) couple and a trinuclear center with an Mn(III)Mn(III)Mn(III)/Mn(III)Mn(III)Mn(IV) couple. The mononuclear Mn(IV) would result in the $g = 4$ signal while the multiline signature could be generated by the $S = {}^1/_2$ excited state of the Mn(III)Mn(III)Mn(IV) cluster. The Mn(III) and Mn(III)Mn(III)Mn(III) states would be EPR-silent.

In this context, the new structural class of trinuclear acetates described for this contribution provides an interesting model for a trinuclear formulation for the OEC. However, it must be noted that **1** does not fulfill many of the requirements for the spectroscopically observable S_2 state. There is no evidence for the multiline feature over the temperature range 4–30 K. The S_2 state probably consists of three Mn(III) ions and one Mn(IV) ion while **1** would best represent the S_0 level, which may be composed of three Mn(III) ions and one Mn(II) ion. Finally, recent EXAFS results[32] suggest that there is a short manganese-manganese vector at 2.7 Å, a longer distance at 3.3 Å, and a very short Mn–(C,N,O) distance of 1.79 Å ascribed to a μ-oxo or μ-hydroxo bridge. Clearly, **1** cannot mimic these distances.

With these caveats in mind, **1** can still provide useful information toward structural proposals for the OEC. The complex **1** is the first reported multinuclear manganese species that has an $S = {}^3/_2$ ground state and a low-lying $S = {}^1/_2$ excited state and gives rise to a low-field EPR sigal. This illustrates that trinuclear formulations can generate the magnetic behavior reported by Brudvig for the OEC. Furthermore, Brudvig has suggested that the $g = 4.1$ signal originates from a cluster rather than a mononuclear Mn(IV) center. Clearly, **1** demonstrates that certain conformations of multinuclear manganese clusters can result in such a low-field EPR component.

Acknowledgment. We thank Dr. W. E. Hatfield for magnetic susceptibility data, Dr. G. T. Babcock for EPR measurements, and Dr. W. Butler for X-ray structure refinement. V.L.P. thanks the G. D. Searle Family/Chicago Communty Trust for a Biomedical Research Scholarship. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Horace H. Rackham Foundation (University of Michigan), and an NIH Biomedical Research Support Grant to the Vice-President for Research.

Supplementary Material Available: Fractional atomic coordinates (Table I), thermal parameters (Table II), fit of variable-temperature magnetic data (Table III), and numbering scheme (Figure 4) for **1** (9 pages). Ordering information is given on any current masthead page.

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Received January 20, 1987

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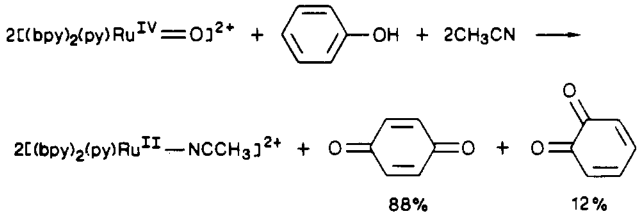
Mechanisms of Oxidation of Phenol and Cyclohexene by an Oxo Complex of Ruthenium(IV)

Sir:

In the oxidation of olefins by epoxidation or allylic oxidation or in the oxidations of phenols to quinones or hydroquinones there is a net O atom demand. Discovering how such reactions occur is important in the design of models for biological oxidations or of catalytic reagents for the oxidative activation of hydrocarbons, but detailed mechanistic insight is often lacking.[1] The substitutionally inert polypyridyl and related oxo complexes of Ru(IV), e.g., $[(bpy)_2(py)Ru^{IV}(O)]^{2+}$ (bpy = 2,2′-bipyridine; py = pyridine), have an extensive stoichiometric and/or catalytic chemistry as oxidants.[2-10] Their reactions have proven to be especially amenable to mechanistic investigations based on a variety of techniques including kinetics, ^{18}O labeling, H/D kinetic isotope effects, and the appearance of reaction intermediates. We describe here in preliminary detail the results of a series of studies that illustrate the mechanistic versatility of the $Ru^{IV}{=}O^{2+}$ oxidant in the allylic oxidation of cyclohexene and the oxidation of phenol to quinone.

In acetonitrile or water the oxidation of phenol by $[(bpy)_2(py)Ru^{IV}(O)]^{2+}$ is rapid. By integration of appropriate resonances in the ^1H NMR spectrum of the final product solution at 25 °C, the reaction stoichiometry in CH_3CN is as shown in reaction 1.



(1)

Further, by use of ^{18}O-labeled $[(bpy)_2(py)Ru^{IV}(O)](ClO_4)_2$[11] (~85% as ^{18}O) and IR monitoring of the quinone product, $\nu(C{=}^{16}O) = 1660\ cm^{-1}$ [12,13] and $\nu(C{=}^{18}O) = 1646\ cm^{-1}$, it was seen that the transfer of one O atom from the $Ru^{IV}{=}O^{2+}$ oxidant to phenol is quantitative, as shown by the integration of relative peak areas in the product

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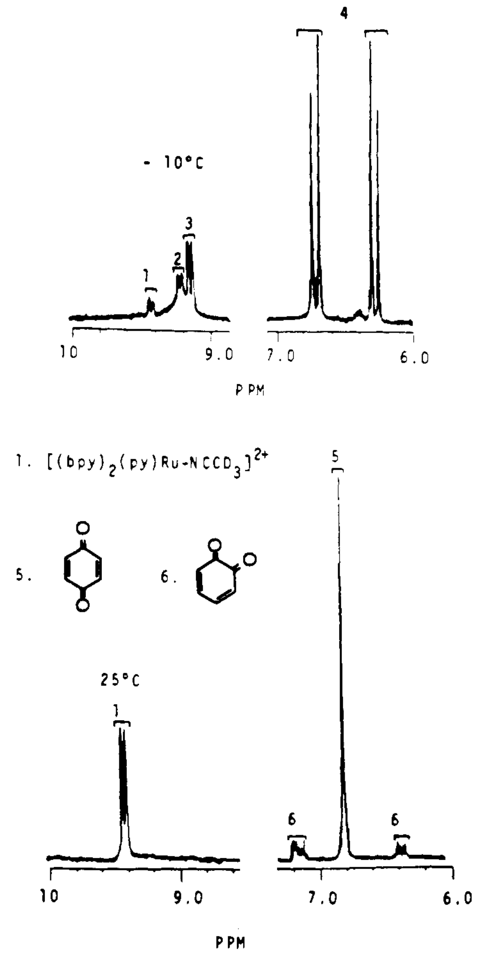
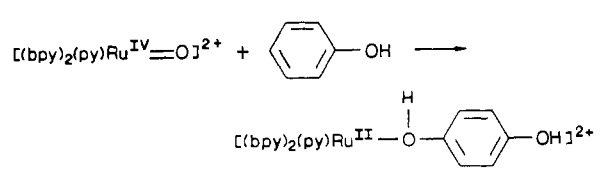


Figure 1. Portions of the ^{1}H NMR spectrum (vs TMS) of a reaction mixture containing initially phenol (9.56×10^{-3} M) and [(bpy)$_2$(py)-Ru^{IV}(O)]$^{2+}$ (1.91×10^{-2} M) in CD$_3$CN at −10 °C (20 min after mixing) and after warming to 25 °C. The origins of the resonances labeled as 1, 5, and 6 are shown on the figure. Others are as follows: 2 and 4, the intermediate with λ_{max} = 675 nm; 3, [(bpy)$_2$(py)Ru–OH$_2$]$^{2+}$. The protons that appear from 9 to 10 ppm are assignable to the 6′-position of the bpy ligand in the Ru(II) complexes whose 6′-proton lies adjacent to the sixth ligand rather than to pyridine.[18] The protons from 6 to 7.5 ppm are assignable to the aromatic ring protons of the oxidized phenol.

From the results of ^{1}H NMR studies at −10 °C (Figure 1) and stopped-flow kinetics at a variety of temperatures, the oxidation of phenol by [(bpy)$_2$(py)Ru^{IV}(O)]$^{2+}$ in CH$_3$CN or H$_2$O occurs via a detectable intermediate. In CH$_3$CN the intermediate has a characteristic low-energy λ_{max} at 675 nm and, from ^{1}H NMR (Figure 1) and IR data (ν(C=^{16}O) = 1647, 1652 cm^{-1}) and by analogy with a known literature example,[14] appears to be the bound quinone complex. Kinetic studies show that the rate law for the appearance of the intermediate, monitored at either λ_{max} = 470 or 675 nm, is first order in phenol and first order in [(bpy)$_2$(py)Ru^{IV}(O)]$^{2+}$ with k(25 °C, CH$_3$CN) = 3.9×10^2 M^{-1} s^{-1}.

The available experimental facts are consistent with initial attack on phenol by Ru^{IV}=O^{2+} to give a hydroquinone intermediate



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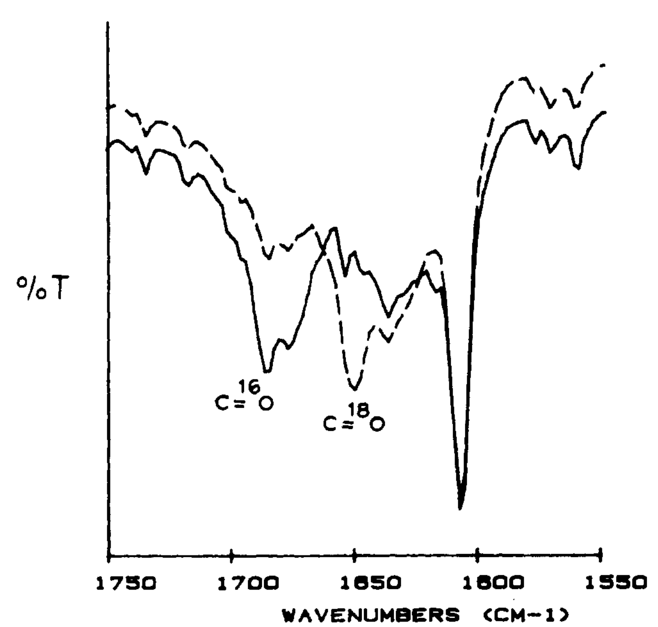
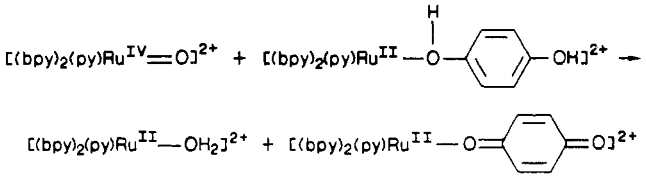


Figure 2. FT-IR spectra in CD$_3$CN of the solutions that result from the oxidation of cyclohexene (7.05×10^{-3} M) by [(bpy)$_2$(py)Ru(^{16}O)]-(ClO$_4$)$_2$ (—, 1.41×10^{-2} M) and ~85% [(bpy)$_2$(py)Ru(^{18}O)](ClO$_4$)$_2$ (- - -, 1.41×10^{-2} M).

followed by rapid oxidation by a second Ru^{IV}=O^{2+} to give the bound quinone

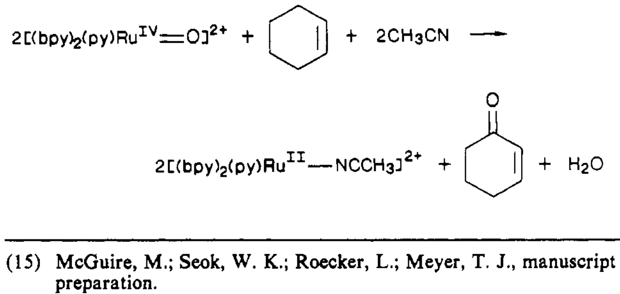


(3)

Under these conditions the oxidation of free hydroquinone to quinone is known to be rapid; k(25 °C, CH$_3$CN) = 5×10^5 M^{-1} s^{-1}.[15] The solvolysis of the intermediate to give [(bpy)$_2$(py)Ru-(NCCH$_3$)]$^{2+}$, which completes the mechanism, occurs with k(25 °C, CH$_3$CN) = 3.5×10^{-1} s^{-1}.

Separate kinetic studies on C$_6$H$_5$OH and C$_6$D$_5$OD show that at 25 °C in CH$_3$CN k_H/k_D = 5.5 ± 0.2 while in water k_H/k_D = 1.2 ± 0.2. One possible mechanism for the initial redox step is electrophilic attack on the aromatic ring by the Ru^{IV}=O^{2+} group, by analogy with the attack on phenol by Br$^+$.[16] If electrophilic attack does occur, the solvent dependence of the isotope effect suggests that the rates of initial electrophilic attack at the ring and subsequent H$^+$ loss from the resulting intermediate must be closely balanced.[17]

The oxidation of cyclohexene by [(bpy)$_2$(py)Ru^{IV}(O)]$^{2+}$ in CH$_3$CN under stoichiometric conditions was shown to occur as in reaction 4. Stoichiometry was established by UV-vis mea-



(4)

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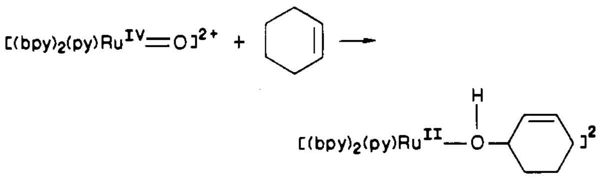
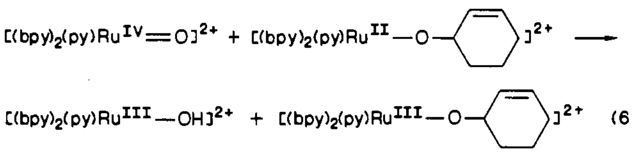
surements using $\epsilon = 8000\ M^{-1}\ cm^{-1}$ at $\lambda_{max} = 440$ nm for the nitrile complex and relative integrated peak areas for the 6′ bipyridine proton of the nitrile complex[18] ($\delta = 9.42$ (d) ppm, vs TMS) and the olefinic protons of the ketone product ($\delta = 5.91$ (m) and 7.05 (m) ppm, vs TMS) in the ^1H NMR spectrum in CD_3CN. From the product studies, epoxidation[3] is *not* competitive with allylic oxidation nor is the 2-e product 2-cyclohexen-1-ol observed as an intermediate. ^{18}O-labeling experiments (Figure 2) show that within experimental error, O atom transfer to give the ketone product is quantitative. With excess oxidant the ketone undergoes further oxidation.

From spectrophotometric studies on solutions containing 5×10^{-5} M $Ru^{IV}{=}O^{2+}$ and 5×10^{-3} M cyclohexene in CH_3CN, the reaction occurs in a stepwise manner with the initial formation of Ru^{III} (isosbestic point at $\lambda = 347$ nm) followed by slower formation of Ru^{II} as the solvento complex $[(bpy)_2(py)Ru^{II}(NCCH_3)]^{2+}$ with $\lambda_{max} = 440$ nm. The rate law for the initial formation of Ru(III) is first order in $Ru^{IV}{=}O^{2+}$ and first order in cyclohexene with $k(25\ °C, CH_3CN) = 0.5\ M^{-1}\ s^{-1}$. The second stage of the reaction is slower by a factor of ~200 at 25 °C and under stoichiometric conditions gives rise to the ketone and the solvento complex products shown in reaction 4, quantitatively.[19]

The available evidence is consistent with a mechanism involving initial attack on the olefin by $Ru^{IV}{=}O^{2+}$


(5)

followed by a rapid comproportionation

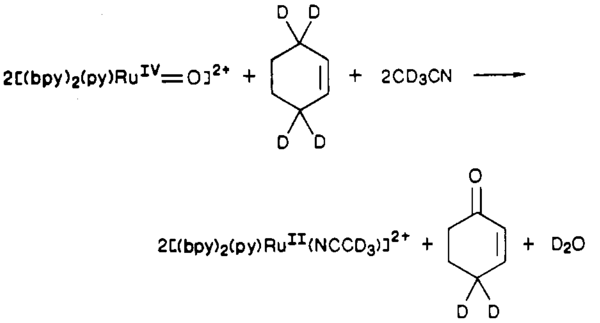

(6)

The appearance of Ru^{III} via the comproportionation reaction between the bound alcohol complex[20] and $Ru^{IV}{=}O^{2+}$ is expected to be rapid; the analogous comproportionation involving the aqua complex

$$[(bpy)_2(py)Ru^{IV}(O)]^{2+} + [(bpy)_2(py)Ru{-}OH_2]^{2+} \longrightarrow 2[(bpy)_2(py)Ru^{III}(OH)]^{2+} \quad (7)$$

occurs with $k(25\ °C) = 1 \times 10^3\ M^{-1}\ s^{-1}$ in CH_3CN.[21] In the final step in the mechanism, slow oxidation of the bound alkoxide complex by Ru^{III} occurs followed by solvolysis to give $[(bpy)_2(py)Ru^{II}(NCCH_3)]^{2+}$ and 2-cyclohexen-1-one as the final products.

The the deuterium-labeled olefin cyclohexene-*3,3,6,6-d₄* (MSD isotopes) occurs with net retention of the label adjacent to the double bond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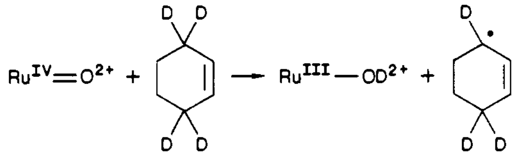
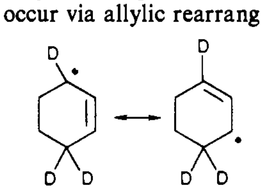
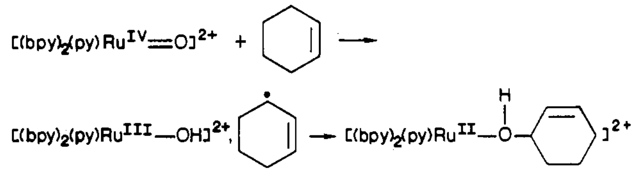
as shown by the relative integration and splitting patterns of the olefinic proton resonances in the ketone product (supplemental Figure 3). If the initial redox step involves a 1-e or H atom transfer to give the intermediate radical free in solution



deuterium scrambling to other positions on the ring would have been expected to occur via allylic rearrangement, e.g.



which is known to be rapid.[22] The initial redox step occurs with a H/D kinetic isotope effect (k_H/k_D) of 18 at 25 °C in CH_3CN for cyclohexene compared to cyclohexene-*3,3,6,6-d₄*. Given the magnitude of the isotope effect, the mechanism may involve H atom transfer and oxidative, inner-sphere capture of the intermediate radical before it can rearrange or separate in solution



rather than direct insertion into the C–H bond.

Acknowledgements are made to the National Science Foundation under Grant CHE-8601604 for support of this research and to Professor M. Brookhart for helpful discussions.

Supplementary Material Available: Figure 3, Portions of the ^1H NMR spectrum resulting from the oxidation of cyclohexene-*3,3,6,6-d₄* by *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ in CD_3CN (1 page). Ordering information is given on any current masthead page.

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Received September 30, 1987

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[18] The primed notation refers to those two of the four pyridyl groups of the cis bpy ligands that are trans to one another. See: Roecker, L.; Dobson, J. C.; Vining, W. J.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 779.

[19] The product distribution shown in reaction 4 is only valid with an excess of the initial olefin near stoichiometric conditions. With excess $Ru^{IV}{=}O^{2+}$, further oxidation of the ketone occurs. With a large excess of initial olefin, the rate of direct oxidation of the olefin by $[(bpy)_2(py)Ru(OH)]^{2+}$ formed in reaction 6 becomes competitive.

[20] Complexes of Ru^{III} containing bound alkoxide ligands have recently been prepared and characterized as products of the reactions between *trans*-$[Ru^{IV}Cl(O)(py)_4]^+$ and the corresponding alcohol: Aoyagi, K.; Nagao, H.; Yukawa, Y.; Ogura, M.; Kuwayama, A.; Howell, F. S.; Mukaida, M.; Kakihana, H. *Chem. Lett.* **1986**, 2135–2138.

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Chemical, Structural, and Electrical Property Studies on the Fluorination of the 90 K Superconductor $YBa_2Cu_3O_{6.8}$

Sir:

Following the breakthrough discoveries of high-T_c superconductivity in $La_{1.85}Ba_{0.15}CuO_4$[1,2] (LBCO) and $YBa_2Cu_3O_{6.8}$[3,4]