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Activation of Molecular Oxygen in Systems Containing Methyltrioxorhenium and Its Derivatives

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Introduction

Methyltrioxorhenium (CH_3ReO_3, abbreviated as MTO) catalyzes selective oxidation reactions with hydrogen peroxide as the oxygen source; this has been extensively documented.[1−3] Peroxide activation arises from the O-atom donating capacity of the two catalytically active forms of the rhenium catalyst, which are the η^2-peroxo complexes termed **A** [$MeRe(O)_2(\eta^2\text{-}O_2)$] and **B** [$MeRe(O)(\eta^2\text{-}O_2)_2(H_2O)$]. This system does not activate molecular oxygen; indeed, the catalyzed peroxide reactions are customarily carried out without the exclusion of air.

Nonetheless, the MTO catalysis of molecular oxygen reactions would be advantageous, and so we set out to investigate some of the relations in such systems. We have used tri(*p*-methylphenyl)phosphine, Tol_3P, as the test compound to explore how molecular oxygen and MTO might be used to form tri(*p*-tolyl)phosphine oxide (Tol_3PO) in the absence of any peroxide. Observations relating to this system were reported previously;[4] we have now identified the kinetic and thermodynamic parameters that control the reaction. This study involves the chemistry of oxorhenium(V) species, of which several examples have been reported.[5−10]

Results and Interpretation

Speciation of MTO and MDO. The intermediate forms of rhenium present during the catalytic cycle were defined experimentally. Tri(*p*-methylphenyl)phosphine was chosen because it provides a sharp singlet for precise ^1H NMR experiments. The aromatic region of the spectrum was also well-resolved and was sometimes used. The equilibrium constants for coordination of Tol_3P and Tol_3PO to MTO were evaluated by ^1H NMR procedures. Titrations of MTO were performed in d_6-benzene under argon by adding small aliquots of Tol_3P or Tol_3PO stock solution to the MTO solution, carefully thermostated at 298 K. After each addition the ^1H spectrum was recorded, noting the change in the chemical shift of the MTO-CH_3. In the case of Tol_3P, it was necessary to work quickly so that the slow reaction between it and MTO, described later, remained unimportant. The coordination equilibria between MTO and these adducts are fast on the NMR scale, so only one resonance was detected at the concentration-weighted average of the positions of MTO•$PTol_3$ and MTO or MTO•$OPTol_3$ and MTO. The chemical shift values, fitted by eq 1

$$\delta_{obs} = \frac{\delta_{MTO} + K[L]\delta_{MTO\cdot L}}{1 + K[L]} \qquad (1)$$

using a nonlinear least-squares calculation, gave $K = 2.0 \pm 0.2$ L mol^{-1} for Tol_3P and $K = 53 \pm 2$ L mol^{-1} for Tol_3PO in C_6D_6 at 298 K, where the uncertainty represents 2σ.

The phosphine oxide, being a harder Lewis base, coordinates more strongly to MTO, whereas the phosphine poses a more severe steric interaction. Evidently both the inherent acid−base interactions and the steric demands contribute to the measured values of *K*.

The next series of experiments used methyldioxorhenium (CH_3ReO_2, abbreviated as MDO), formed in benzene by reactions between MTO and an O-atom acceptor such as PAr_3, PR_3, Sn(octoate)$_2$, or $NBu_4{}^+H_2PO_2{}^-$. In these experiments MDO was generated in the presence of Tol_3P to avoid formation of a fairly soluble purple material. This species has not been fully characterized, although it seems likely to be $(MeReO)_2(\mu\text{-}O)_2$, in view of the well-characterized compound $(Cp^*ReO)_2(\mu\text{-}O)_2$.[11] The Re−C bond of this species certainly remains intact, since aqueous hydrogen peroxide converts this intensely colored species to **B**, and *tert*-butyl hydroperoxide converts it to MTO. The interaction of MDO and Tol_3P was evaluated according to eq 1, giving $K = (2.3 \pm 0.2) \times 10^3$ L mol^{-1} in C_6D_6 at 298 K. Only one tritolylphosphine was coordinated according to the ^1H data, although these experiments employed but a small excess of the phosphine. Our studies did not define the value of *K* for the coordination of MDO by Tol_3PO, but we noted that the interaction was weak.

Tol_3P coordinates more strongly to Re(V) than to Re(VII). This may reflect the greater steric requirements of MTO. Perhaps an even greater factor has to do with the extent of Re−O multiple (double, triple) bonding in each oxidation state. The d^0 center should more readily participate in π-bonding than the d^2, a factor which lowers the Lewis acidity of Re(VII) more than Re(V). A crystalline derivative of MDO, MTO•MDO•2PPh_3,[9] has been reported. In this structure Re(V) is five-coordinate, with a methyl group, two oxo oxygens, and two trans-disposed phosphines. This structure illustrates the considerable affinity of Re(V) for these ligands. We have used the same method to prepare MTO•MDO•2$PTol_3$(s).

Reactions Involving Oxygen. The buildup of Tol_3PO in reactions between Tol_3P and O_2, without and with MTO, is shown in Figure 1. These slow reactions were followed for over 2 weeks. The comparison shows that MTO, at a concentration 1% of that of the phosphine, catalyzes the reaction significantly, in terms of both initial rates and overall production of Tol_3PO. MTO is stable in benzene throughout this experiment. The rising concentration of Tol_3PO seems to level off at ~50% conversion, or after ~50 catalytic cycles. The failure of this reaction to proceed to completion suggests to us that the rhenium catalyst

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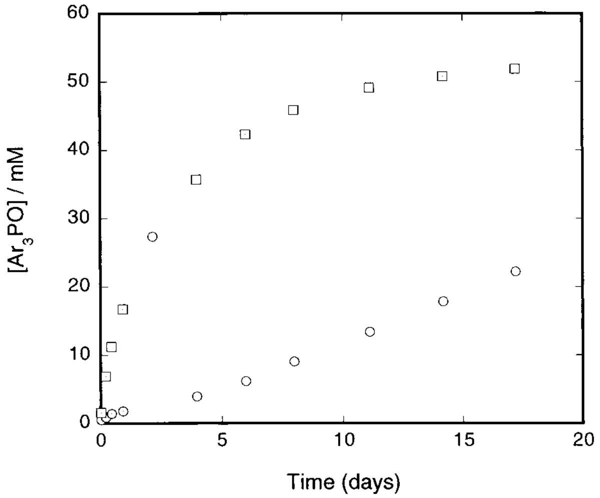

Figure 1. Buildup of Tol_3PO in an experiment with $[Tol_3P]_0 = 102$ mM and saturated (9.1 mM) oxygen in benzene with MTO (1.1 mM) and without.

is being deactivated over time, perhaps but not necessarily by coordination of Tol_3PO.

An outline of the reactions, ignoring coordination equilibria, is given in Scheme 1. We use this form to present the observed phenomena. In the first reaction, independently documented using air-free experiments, MTO oxidizes Tol_3P; similar results were obtained with $Sn(octoate)_2$. The second reaction, in which O_2 is converted to an η^2-peroxorhenium compound or a close relative, is especially interesting. The third reaction is known independently and occurs quite rapidly, $k_3 = 8 \times 10^5$ L mol^{-1} s^{-1} at 298 K in aqueous acetonitrile.[12]

Scheme 1

$$CH_3ReO_3 + Tol_3P \rightarrow CH_3ReO_2 + Tol_3PO$$

$$CH_3ReO_2 + O_2 \rightarrow CH_3Re(O)_2(\eta^2\text{-}O_2)\ [= \mathbf{A}]$$

$$\mathbf{A} + Tol_3P \rightarrow CH_3ReO_3 + Tol_3PO$$

Experiments were performed within these concentration ranges 1.5−152 mM MTO, 2.2−290 mM Tol_3P, 9.1 (and 0) mM O_2. Figure 2 presents the results of one such run. The concentration value at each time was obtained from the NMR data. Each acquisition represents one 16-transient spectrum taken from −1 to 14 ppm; each spectrum required 1 min to acquire. The NMR signals, integrated relative to the solvent peak, were then converted to concentrations. 1,2-Dichloroethane was sometimes used as an internal standard; otherwise the initial concentrations were used to scale the integrations. The sum of the tolyl-CH_3 signals (conservation of total phosphorus) was calculated at each time, and all the sums for a given experiment gave an average with a standard deviation of 3−5%, indicating that the data are internally consistent.

With excess Tol_3P, much more Tol_3PO was produced when O_2 is present, and it was formed more rapidly than in the uncatalyzed reaction. We conclude that most of the oxygen found in Tol_3PO derives from molecular oxygen rather than from MTO itself. With excess MTO the reaction went to completion under Ar or O_2; without O_2 it was stoichiometric, not catalytic, and the MTO was not recovered (see Scheme 1).

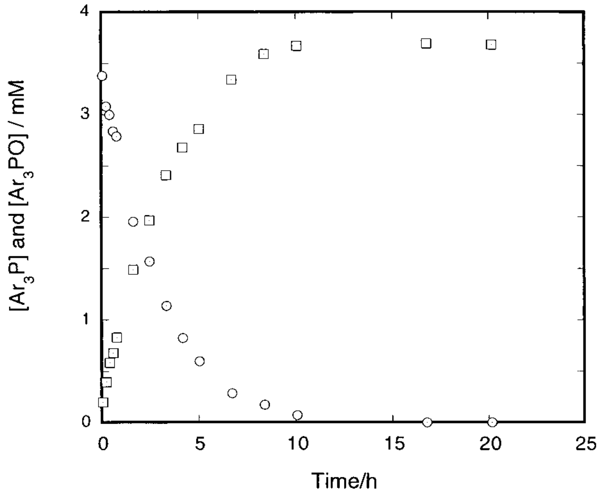

Figure 2. Data from an experiment with $[Tol_3P]_0 = 3.39$ mM, 9.1 mM O_2, and 19.4 mM MTO in benzene at 298 K, showing the loss of the phosphine and the buildup of its oxide. The experiment required some time, and evaporation of the solvent was carefully prevented.

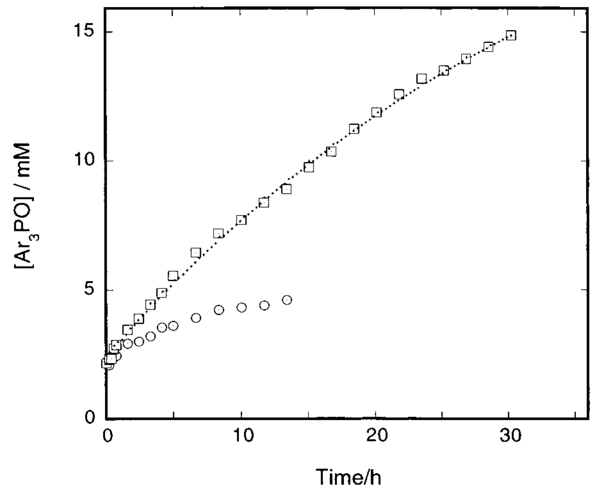

Figure 3. Plots of $[Tol_3PO]$ against time for experiments with 1.5 mM MTO, 440 mM Tol_3P, and $[O_2] = 0$ or 9.1 mM in benzene at 298 K. The dotted line shows the kinetic simulation of the experiment with oxygen using the values (refer to Scheme 1) $k_1 = 3.7 \times 10^{-4}$ L mol^{-1} s^{-1} and $k_2 = 8.3 \times 10^{-3}$ s^{-1}.

A yellow/orange color was formed immediately from Tol_3P and MTO, due to MTO·$PTol_3$. Depending on the concentrations of MTO and Tol_3P, the final color was dark brown or amber with limiting or absent O_2, due to formation of an MDO derivative. The broad NMR singlets at 8.0 ppm (arom.) and 3.6 ppm (Re^V-CH_3) and the sharp one at 1.985 ppm (Tol-CH_3) are due to MTO·MDO·2$PTol_3$. This compound, obtained as a brown powder by the reported procedure,[9] has an NMR spectrum that matches the one found in the reaction. When $Bu_4N^+H_2PO_2^-$ and MTO reacted under Ar, the MDO was complexed as MTO·MDO·2$PTol_3$; it was then converted to Tol_3PO by bubbling with oxygen for 43 min. With limiting Tol_3P and excess MTO, the oxygen reaction went to completion, giving a colorless solution. Only MTO remained; the catalytic loop had been closed.

Further ^1H NMR experiments with very low $[MTO]_0$ and $[Tol_3P]_0$ showed that MDO·$PTol_3$ also was formed under Ar and disappeared in the presence of O_2. Significant yields of Tol_3PO, well in excess from those in anaerobic experiments, were seen after just 15 min of O_2 bubbling. The spectrum of this compound, MDO·$PTol_3$, is similar to that of MTO·MDO·

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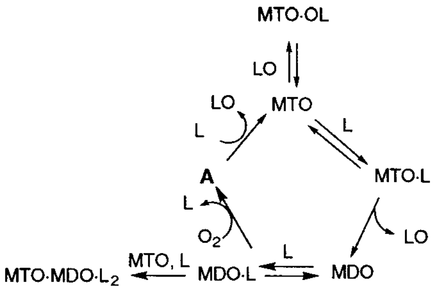
[12] Abu-Omar, M. M.; Espenson, J. H. *J. Am. Chem. Soc.* **1995**, *117*, 272.

Scheme 2



2PTol$_3$ in that it has a tolyl-CH_3 singlet at 1.985 ppm, but lacks the broad Re(V) resonances at 8.0 and 3.6 ppm. Thus MDO•PTol$_3$ is the active intermediate, but under most experimental conditions it is bound further to inactive MTO•MDO•2PTol$_3$. The buildup of Tol$_3$PO was examined by kinetic modeling of Scheme 1 with the program KinSim,[13−15] using the rate constants presented previously. The simulated concentration vs time profiles for one experiment are shown in Figure 3. It is clear there is close agreement between this model and the experimental data, though we have not perfomed an analysis of all experiments.

A more detailed view of the catalytic system is depicted in Scheme 2. The sacrificial reagent in the initial step must have a bond strength to oxygen in excess of MTO's: MTO(aq) = MDO(aq) + O(g) has $\Delta G° = 111$ kcal mol^{-1}.[16] This requirement imposes a substantial limitation, such that only reagents like Sn(octoate)$_2$ and phosphines can participate. Otherwise the reactions cannot get started nor can the cycle continue. Another step in the scheme depicts a reaction between O$_2$ and MDO•PTol$_3$ (likely, in view of its large binding constant) or MDO.

The product of the reaction between MDO•PTol$_3$ and O$_2$ is written in Scheme 2 as **A**, but **A** may form indirectly via a short-lived but unobserved end-on η^1-OO complex.[17] The most concrete statement about the intermediate is this: like **A**, it transfers an oxygen rapidly to the phosphine.[18] Given our current knowledge of the system, however, this level of detail is excessive and was not included in the model.

The slowness of the first step, in which MTO reacts with a sacrificial oxygen acceptor (Ar$_3$P or R$_3$P or Sn(octoate)$_2$), poses a significant barrier. If the peroxorhenium compound **A** formed in the second step is to react with a different reducing agent, only half of the product would derive from O$_2$, the balance coming from the first reaction. As the cycle repeats, more and more oxygen atoms in MTO are derived from oxygen; eventually almost all of the oxygen in the product will be from O$_2$. If different oxygen acceptors were used for steps 1 and 3, mixed products would result. Regardless of the implication for O$_2$ activation with MTO, the data establish that a reaction occurs between molecular oxygen and the rhenium(V) species MDO and/or MDO•PTol$_3$, and that it yields **A**. To our knowledge it is the first example of such a reaction.

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(17) As noted by a reviewer, this reaction may instead involve (a) MDO + $O_2 \rightarrow (\eta^1\text{-}O_2)Re(O)_2CH_3$ or (b) $(MeReO)_2(\mu\text{-}O)_2 + O_2 \rightarrow (MeReO_2)_2(\mu_2\text{-}O_2)$. Our results cannot distinguish among these, and we have elected to use the simplest representation in the text.

(18) A direct determination of the rate of reaction between MDO and O$_2$ was attempted, but the onset of dimerization/oligomerization of MDO at the concentrations of rhenium(V) needed to follow the reaction precluded such determinations.