The appearance of voltammetric waves due to both $[(TPP)Fe]_2O$ and the fluoride-bound species at low fluoride ion concentrations (less than 2 equiv) implies the change in potential is not due to removal of oxidized $[(TPP)Fe]_2O$ by fluoride ion cleavage but instead is probably due to a concerted electron-transfer–fluoride ion coordination by a weakly associated fluoride ion. The irreversibility and the cathodic shift in the oxidation wave for the new species relative to $[(TPP)Fe]_2O$ indicate the possibility that the initial oxidation is metal centered with generation of a transient iron(IV)–iron(III) mixed-valent dimeric species.

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Department of Chemistry
University of Iowa
Iowa City, Iowa 52242

Alaganandan Nanthakumar
Harold M. Goff*

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Oxygen Atom Transfer Catalyzed by an Oxo-Bridged Molybdenum(V) Compound

We would like to report the catalysis of an oxygen atom transfer reaction by a μ-oxo Mo(V) dimer. The potential use of these dimers as catalysts in such reactions has largely been ignored because of the emphasis in oxo–molybdenum chemistry on the modeling of active sites in oxo-transfer enzymes such as xanthine oxidase and nitrate reductase.[1] These enzymes are believed to catalyze oxygen atom transfer using MoO_2^{2+} and MoO^{2+} as the oxidized and reduced forms of the active sites.[2] Early attempts to model these enzymes were hindered by the formation of μ-oxo Mo(V) dimers through reaction of freshly made MoO^{2+} with unreacted MoO_2^{2+} according to reaction 1.[3] Reaction 1 is usually

$$MoO_2^{2+} + MoO^{2+} \rightarrow Mo_2O_3^{4+} \qquad (1)$$

considered to be capable of breaking any catalytic cycle if the oxo-bridged dimer is formed irreversibly.[3] Catalysis is still possible if reaction 1 is in equilibrium provided that sufficient quantities of MoO_2^{2+} and MoO^{2+} are available to the substrate.[4] However, the oxo-bridged dimer itself has been considered to be unreactive to oxygen atom transfer.

We have previously reported the structure of $Mo_2O_3(dtc)_2I_2(THF)_2$ (I) (Figure 1).[5] Two features make I a viable candidate for oxygen atom transfer catalysis. First, its THF ligands are weakly associated with the metal atoms, as indicated by the long Mo–O(THF) bond lengths (2.448 (4) Å), the equivalence of the THF ^{1}H NMR lines from the complex with those of free THF, and the facile loss of THF from the complex upon dissolution in acetonitrile and acetone solvents. In fact a detailed ^{1}H NMR study indicates that the solvent molecules from $Mo_2O_3(dtc)_2I_2(solv)_2$ species, where solv = THF, tetrahydrothiophene and dioxane, are completely dissociated in solutions of noncoordinating solvents such as the dichloromethane used in this study.[6] Second, I does not exist in equilibrium with its MoO_2^{2+} and MoO^{2+} counterparts,

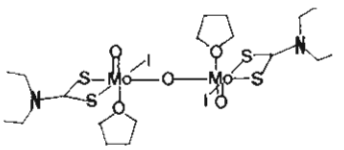

Figure 1. Structure of $Mo_2O_3(dtc)_2I_2(THF)_2$ (I).

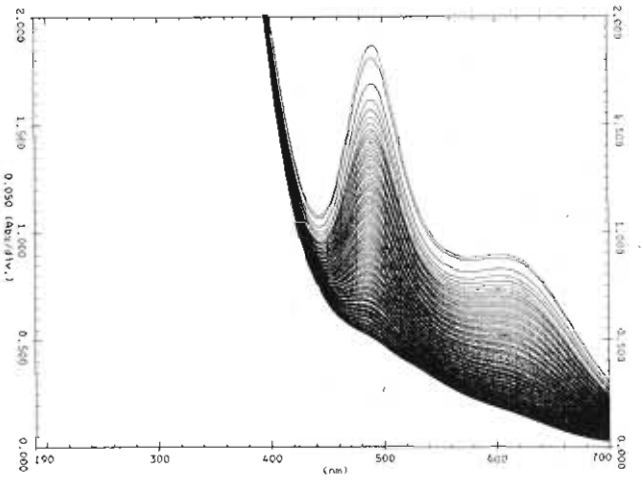

Figure 2. Changes in the electronic spectrum of $Mo_2O_3(dtc)_2I_2(THF)_2$ (I) during reaction with biotin *S*-oxide.

as indicated by obedience to the Beer–Lambert law over a wide concentration range (2.68×10^{-5} to 5.3×10^{-4} M) in methylene chloride and THF. These points indicate that the THF molecules in I are largely, if not completely, dissociated from the complex in solution. As a result each molybdenum atom should have an empty coordination site available where reduction by oxygen atom transfer could take place.

We have now shown that $Mo_2O_3(dtc)_2I_2(THF)_2$ can be used to reduce a variety of oxygen atom donating heterocyclic amine oxides and sulfoxides, including pyridine *N*-oxide, nicotinamide *N*-oxide, dimethyl sulfoxide, diphenyl sulfoxide, and biotin *S*-oxide, in either CH_2Cl_2 or THF. In these reactions oxygen atom transfer to I results in the appropriate heterocyclic amine or sulfide and an MoO_2^{2+} compound. This process can be followed spectrophotometrically by observing the disappearance of the bands characteristic of I at 614 and 490 nm (Figure 2). Upon completion of the reaction, a spectrum characteristic of an MoO_2^{2+} compound is observed with no apparent bands in the visible region.[7] The molybdenum product of this reaction can be further characterized as an MoO_2^{2+} compound by infrared spectroscopy. The complex can be formed by reaction of I with excess pyridine *N*-oxide in methylene chloride. Its isolation is then accomplished by evaporating the solvent and subliming the excess pyridine *N*-oxide. The infrared spectrum of the MoO_2^{2+} compound exhibits a band characteristic of the Mo=O stretching frequency which is shifted to 939 cm^{-1} as compared to 975 cm^{-1} in I. This is consistent with the trend usually observed for series of homologous oxo–molybdenum species in which the Mo=O stretching frequency varies in the order $MoO^{2+} > Mo_2O_3^{4+} > MoO_2^{2+}$.[8]

Samples of the MoO_2^{2+} compound that have been isolated in the manner described above can be used to oxidize triphenylphosphine to triphenylphosphine oxide, TPPO, in CH_2Cl_2 or THF with concomitant reformation of I. This reaction is evidenced by the reappearance of the electronic spectrum of I. The reformation of I is apparently the result of the rapid and irreversible reaction, according to reaction 1, of the immediate product of oxo transfer to TPP, probably an MoO^{2+} complex, with the MoO_2^{2+} remaining in solution. We have not observed any spectroscopic evidence of the existence of MoO^{2+} in our reaction systems.

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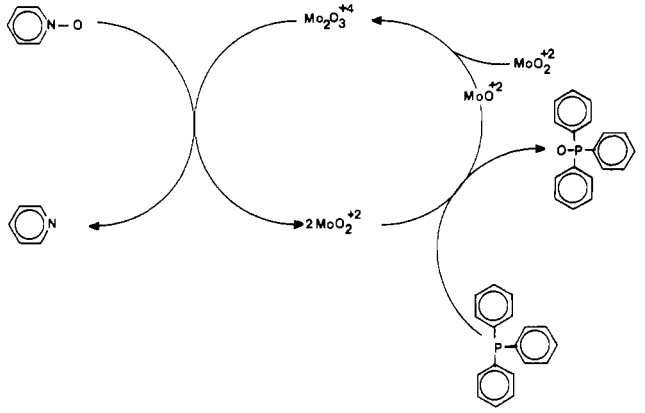
Scheme I



The above oxidation and reduction reactions can be coupled to produce catalytic oxygen atom transfer processes. For example, oxygen atom transfer from pyridine *N*-oxide to TPP to produce pyridine, py, and TPPO can be catalyzed if small quantities of I are added to the reaction mixture.

With high-performance liquid chromatography, HPLC, used to monitor the progress of this reaction system,[9] it was verified that there was little or no reaction between py-O and TPP in the absence of I. A solution was made that contained 4.12×10^{-4} mol of py-O and 2.13×10^{-4} mol of TPP in 100 mL of dry, degassed THF that had been freshly distilled from Na/benzophenone under argon. After 24 h, HPLC analysis of the mixture indicated that no TPPO or py had formed. On the other hand, if 1.73×10^{-5} mol of I was added to a freshly prepared mixture of 4.12×10^{-4} mol of py-O and 2.13×10^{-4} mol of TPP in 100 mL of dry, degassed THF, the HPLC analysis showed that 100% of the starting TPP had been converted to TPPO in an 18-h period. An equivalent amount of pyridine was also formed in the same period of time. This corresponds to 12.3 turnovers and clearly demonstrates the catalytic nature of this process.

To verify the catalytic role of I, it was reacted with a large excess of dimethyl sulfoxide, DMSO, in the presence of a 35-fold excess of TPP (based on the quantity of I). Under these conditions, the TPP was quantitatively coverted to TPPO and an equivalent amount of DMSO was converted to dimethyl sulfide, DMS. The production of DMS was followed by the method outlined by Holm and Berg.[10] In the absence of I, no DMSO was converted to DMS in a 24-h period.

Thus, for the first time, catalysis of oxygen atom transfer has been accomplished by using an oxo-bridged Mo(V) complex as an active participant in the catalytic cycle. This is apparently due to the presence of an empty or at least accessible coordination site on the molybdenum atoms where an oxygen-donating substrate may approach the Mo(V) atom. The entire process can be summarized in Scheme I. This shows that significant catalytic chemistry may be built around oxo-bridged Mo(V) complexes. It also suggests that the role of oxo-bridged Mo(V) complexes in oxygen atom transfer reactions of systems designed to model enzyme behavior cannot necessarily be ignored. This is particularly true in those cases where significant quantities of oxo-bridged Mo(V) species are present due to reaction 1.

Note Added in Proof. During the course of manuscript preparation Craig and co-workers reported the oxygen atom transfer reactions of a series of Schiff base complexes, $Mo_2O_3L_2(solv)_2$ and their Mo(VI) analogues.[11]

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Registry No. $Mo_2O_3(dtc)_2I_2(THF)_2$, 103817-70-5; pyridine *N*-oxide, 694-59-7; nicotinamide *N*-oxide, 1986-81-8; dimethyl sulfoxide, 67-68-5; diphenyl sulfoxide, 945-51-7; biotin *S*-oxide, 7553-42-6; triphenylphosphine, 603-35-0.

Department of Chemistry
Florida Atlantic University
Boca Raton, Florida 33431

D. M. Baird*
S. Falzone
J. E. Haky

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Conversion of Long-Chain Terminal Alcohols and Secondary Amines into Tertiary Amines Using Dichlorotris(triphenylphosphine)ruthenium(II) as Catalyst

The catalyzed synthesis of amines having long-chain alkyl groups is of potential commercial value because of the use of these compounds in the production of detergents. A plausible preparative route involves the condensation reaction between long-chain terminal alcohols and secondary amines (eq 1). The reaction

$$CH_3(CH_2)_nOH + R_2NH \rightarrow CH_3(CH_2)_nNR_2 + H_2O \quad (1)$$

between alcohols and amines has been previously catalyzed by metal oxides and by ruthenium phosphine complexes.[1] Furthermore, it has been recently reported that ethylene glycol can be converted into both monoamines and diamines by using solutions of ruthenium phosphine complexes as catalysts.[2] We now report that ruthenium triphenylphosphine complexes are also homogeneous catalysts for the conversion of long-chain terminal alcohols and secondary amines to tertiary amines.

The complex chosen for this study is $RuCl_2(PPh_3)_3$.[3] We find that this complex acts as a homogeneous catalyst for the conversion of terminal alcohols $CH_3(CH_2)_nOH$ (n = 9, 13, 15, 17) and secondary amines R_2NH (R = Me, Et, 1-Pr, Ph) into tertiary amines $CH_3(CH_2)_nNR_2$. The tertiary amine formed has been identified by GC–MS, and the yield of $CH_3(CH_2)_nNR_2$ after a 2.5-h reaction time at 120 °C is measured by comparison with an internal reference. The data obtained for four alcohols ROH (R = 1-$C_{10}H_{21}$, 1-$C_{14}H_{29}$, 1-$C_{16}H_{33}$, 1-$C_{18}H_{37}$) and amines $R'NH_2$ (R′ = Me, Et, 1-Pr, Ph) are collected in Table I. The catalyst to reagent mole ratio is 1:200:200 for $RuCl_2(PPh_3)_3$–alcohol–secondary amine at the beginning of the reaction. A typical loading of the reaction vessel is given in Table I. The data in Table I show that yields in the 14–82% range are obtained. For diphenylamine the yield is relatively constant in the 47–52% range, but for diethylamine and dipropylamine the yields are lower (14–28%). The highest yield is observed for dimethylamine, with an 82% yield of $C_{18}H_{37}NMe_2$ being formed from $C_{18}H_{37}OH$. Longer reaction times do not give any significant increases in yield. Adding triphenylphosphine to the reaction mixture increases the yield of tertiary amine; the addition of 1, 2, and 4 mol of triphenylphosphine to $RuCl_2(PPh_3)_3$ causes the yield of $C_{16}H_{33}NEt_2$ to increase from 21%, in the absence of excess triphenylphosphine, to 30, 35, and 42%, respectively, with the added moles. Triphenylphosphine itself is not a catalyst for the reaction. Carrying out the reaction under 1300 psig of hydrogen rather than under

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