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Facile Functionalization of a Metal Carbon Bond by O-Atom Transfer

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A key challenge to developing selective, low-temperature hydrocarbon oxidation catalysts based on the CH activation reaction is integration with a compatible functionalization reaction.[1,2] We recently reported a CH activation reaction (Figure 1) with an alkoxo complex, M−OR, that simultaneously generates a functionalized product, ROH, and a metal alkyl, M−R, where M is Ir(III).[3a,b] As shown in Figure 1, a catalytic cycle for the conversion of RH to ROH could be possible by regeneration of M−OR from M−R with O-atom donors, YO. Pt(IV) or Hg(II) alkyls are $M{-}C^{\sigma+}$ polarized and readily undergo reductive functionalization with O-nucleophiles.[1b,4] However, M−Rs of more electropositive metals, such as Ir or Re, in the lower oxidation states useful for C−H activation do not undergo facile reductive functionalizations and are likely $M{-}C^{\sigma-}$ polarized. Consequently, functionalization of these M−Rs may be more facile in *non*redox, *insertion* reactions with electrophilic YOs (Figure 1) if free-radical pathways or formal oxidation of the metal centers could be minimized.[5] Conversion of Y to YO with O_2 could complete the overall catalytic cycle for the overall oxidation of RH with O_2.

The conversion of M−R to M−OR is not well-known, and the few reported examples proceed with O_2 by free-radical pathways[6] or by slow redox reactions involving alkyl to metal oxo migration.[7] Consequently, identification of a facile pathway for this reaction, especially with non-peroxo[8] YOs that could potentially be recycled with O_2, could be useful. We report here combined experimental and theoretical evidence for a facile Re−R to Re−OR bond conversion with non-peroxo YOs that proceeds via a low-energy, Baeyer−Villiger (BV)-type, electrophilic O-atom insertion.

BV and alkyl borane oxidation reactions to generate oxyesters and alkoxy boranes, respectively, are well-known organic reactions involving electrophilic O-insertions with YOs. Significantly, both peroxo and non-peroxo YOs can be utilized, and the reactions proceed without free radicals or formal redox changes.[9] Methyltrioxorhenium, MTO, with peroxo YOs is well-known to catalyze olefin epoxidation and other oxidation reactions likely via Re η^2-peroxo intermediates.[10] A reported observation that attracted our attention was that an undesirable side reaction is the decomposition of a MTO catalyst to methanol at room temperature.[11] We were intrigued because, despite the high Re(VII) oxidation state, unlike Pt(IV) alkyls,[1b,4] treatment of MTO in basic or acidic water does not generate Re(V) and methanol. Consistent with the observations of the initial investigators,[11] we find that the formation of methanol from MTO in water requires added H_2O_2 as the oxidant. The reaction is facile, selective, quantitative, and significantly proceeds without a change in oxidation state of the Re to generate the ReO_4^- anion.

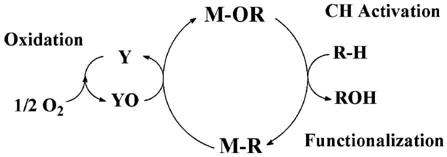

Figure 1. Proposed nonredox catalytic cycle for functionalization of hydrocarbons via CH bond activation.

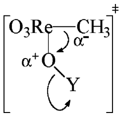

Figure 2. BV-type transition state for O-insertion into the $Re{-}CH_3$ bond.

Table 1. Reaction Yields[a] and Overall Calculated Barriers[b]

YO	% MeOH	BV TS	μ-peroxo TS
H_2O_2	80	20	13
PyO	0	32	47
IO_4^-	100	17	25
PhIO	90	8	18

[a] Yields based on added MTO (0.1 mM) with 2 equiv of YO at 25 °C for 1 h under air or argon. [b] B3LYP/LACVP/6-311G**++ enthalpies in kcal/mol, implicitly solvated in water.

In the initial studies on decomposition of MTO to methanol, only H_2O_2 was investigated and two non-BV-type mechanisms proposed: reaction via a η^2-peroxo intermediate or by direct methyl migration to the hydroxo of Re-coordinated OOH^-. We considered that since Nature tends to conserve low-energy pathways the reaction may proceed via the BV-type pathway shown in Figure 2, where the leaving group, Y, could be OH^- or H_2O. More significantly, given the ease of functionalization of the $Re{-}CH_3$ bond and the d^0 electron configuration, this system could be a useful model to determine if a BV-type pathway was viable without complication from metal-centered oxidations. Establishing that a BV-type pathway is feasible with M−Rs would be useful because, to our knowledge, this functionalization pathway has not been reported, it should be lower energy than η^2-peroxo pathways[8] and accessible with a broader range of potentially more practical, non-peroxo YOs.

To investigate this possibility, we compared the reaction of MTO with H_2O_2 and three non-peroxo YOs: PhIO, PyO, and IO_4^- in water. As can be seen in Table 1, PhIO and IO_4^- are as efficient as H_2O_2 for generation of methanol. Controls show that the selectivities and yields are independent of added O_2, and free radicals are likely not involved. Facile methanol formation with the non-peroxo YOs is consistent with a low-energy BV-type pathway and would rule against direct methyl migration to the β-atom of coordinated YO since the β-atom is not O. However, these observations alone cannot

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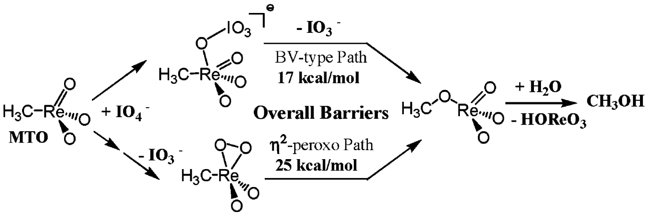
Scheme 1. B3LYP/LACVP** Calculated Low-Energy Pathways for Methanol Formation from MTO and IO_4^- in H_2O[12]



rule out a η^2-peroxo pathway with non-peroxo YOs. Significantly, calculations[12] show that a BV-type pathway is both viable and, as shown in Table 1, lower in energy than the η^2-peroxo pathways for all the non-peroxo YOs.

For IO_4^-, the BV-type and η^2-peroxo pathways shown in Scheme 1 have calculated barriers of 17 and 25 kcal/mol, respectively. The products of the BV pathway are IO_3^- and the methoxo species, $MeORe(O)_3$, which readily hydrolyzes to methanol and $Re(O)_3OH$. The BV-type transition state involves concerted methyl migration and IO_3^- loss as observed by stretching of the C−Re bond from 2.168 to 2.516 Å and the I−O bond from 1.803 to 2.399 Å. Similar to BV or alkyl borane oxidation reactions in organic chemistry, this transition state can be described as a formal insertion of an electrophilic O into the $Re-CH_3$ bond. While it is possible that a more exhaustive investigation could lead to alternative low-energy pathways, these results emphasize that a BV-type pathway can be particularly facile for M−R functionalizations.

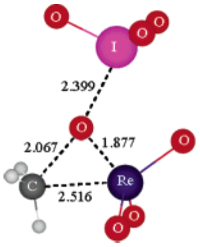


Figure 3. B3LYP/LACVP/6-311G**++ BV-type transition state for MTO + IO_4^- (bond length values in angstroms, Å).[12]

The 17 kcal/mol activation energy calculated for IO_4^- is remarkably low for a M−C to M−O−C transformation given the significant change in electronic configurations. However, this value is consistent with the facile reaction observed at room temperature. As the BV-type transition state is calculated to be significantly favored over a η^2-peroxo pathway, the O in the MeOH product should be derived almost exclusively from YO and not from MTO. Consistently, the reaction of ^{16}O-MTO with $[I^{18}O_4]^-$,[13] followed by GC−MS analysis of the reaction mixture at low conversion of MTO, showed that only $CH_3{}^{18}OH$ was formed. While this observation supports a BV pathway, it does not rule out reaction proceeding via an unsymmetrical η^2-peroxo species.

The relatively high calculated BV barrier for PyO of 32 kcal/mol is consistent with the observation that methanol was not formed at room temperature. Anticipating that the known $MeOReO_3$ complex[14] should be generated but not hydrolyzed in aprotic media at moderate temperature, we examined the reaction of MTO with 1 equiv of PyO in THF-d_8 at 125 °C in the presence of excess pyridine-d_5 by ^{1}H NMR. It is known[11] and we observe that MTO is quantitatively converted to the MTO−Py-d_5 adduct[15] (s, 1.70 ppm) at room temperature. Upon heating, clean conversion of this adduct to $MeOReO_3$−Py-d_5 (s, 4.48 ppm) and free pyridine-h_5 is observed based on comparison to the chemical shift of the known $MeOReO_3$−amine adduct.[14] While these results taken individually do not prove a specific mechanism, it is our belief that the convergence between the experimental and theoretical results strongly supports a BV-style mechanism for the functionalization of MTO by non-peroxo YOs.

Calculations of the reaction of MTO with H_2O_2 in water were found to be considerably more complicated than the reaction with non-peroxo YOs due to the multiple possible H and O rearrangements. Nevertheless, the calculations show two low-energy pathways: one via an η^2-peroxo and the other via a BV-type pathway (Table 1). While the complete mechanism for MTO−H_2O_2 will be addressed in a more thorough study, it is clear that the BV mechanism is also feasible even for peroxo YOs, such as H_2O_2.

These results are encouraging and may point to a facile pathway for heteroatom functionalization of M−R intermediates of more electron-rich metals via a BV-type pathway with electrophilic, heteroatom−atom donors, such as YO. However, there are some key considerations that must be addressed before we can determine if this pathway will be broadly applicable for M−R functionalizations. In MTO, rhenium is pseudotetrahedral and formally a d^0 metal. Consequently, competitive oxidation of the metal center versus O-atom insertion is not an issue in reactions of MTO with YO. Thus, a key question we are investigating is whether this type of concerted, low-energy, BV-type transition state can be extended to a range of YOs and M−Rs with other geometries and electronic configurations as well as the feasibility of incorporating this type of oxy-functionalization reaction into catalytic cycles of the type shown in Figure 1.

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Supporting Information Available: Synthetic procedures and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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