

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

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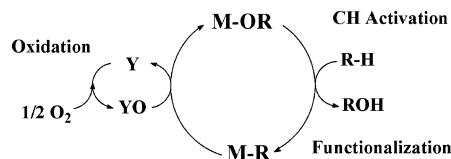
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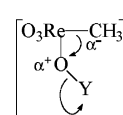
A key challenge to developing selective, low-temperature hydrocarbon oxidation catalysts based on the CH activation reaction is integration with a compatible functionalization reaction.<sup>1,2</sup> We recently reported a CH activation reaction (Figure 1) with an alkoxo complex, M–OR, that simultaneously generates a functionalized product, ROH, and a metal alkyl, M–R, where M is Ir(III).<sup>3a,b</sup> 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<sup>σ+</sup> polarized and readily undergo reductive functionalization with O-nucleophiles.<sup>1b,4</sup> 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<sup>σ−</sup> polarized. Consequently, functionalization of these M–Rs may be more facile in *nonredox, insertion* reactions with electrophilic YO (Figure 1) if free-radical pathways or formal oxidation of the metal centers could be minimized.<sup>5</sup> Conversion of Y to YO with O<sub>2</sub> could complete the overall catalytic cycle for the overall oxidation of RH with O<sub>2</sub>.

The conversion of M–R to M–OR is not well-known, and the few reported examples proceed with O<sub>2</sub> by free-radical pathways<sup>6</sup> or by slow redox reactions involving alkyl to metal oxo migration.<sup>7</sup> Consequently, identification of a facile pathway for this reaction, especially with non-peroxo<sup>8</sup> YO that could potentially be recycled with O<sub>2</sub>, could be useful. We report here combined experimental and theoretical evidence for a facile Re–R to Re–OR bond conversion with non-peroxo YO 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 YO. Significantly, both peroxo and non-peroxo YO can be utilized, and the reactions proceed without free radicals or formal redox changes.<sup>9</sup> Methyltrioxorhenium, MTO, with peroxo YO is well-known to catalyze olefin epoxidation and other oxidation reactions likely via Re  $\eta^2$ -peroxo intermediates.<sup>10</sup> 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.<sup>11</sup> We were intrigued because, despite the high Re(VII) oxidation state, unlike Pt(IV) alkyls,<sup>1b,4</sup> treatment of MTO in basic or acidic water does not generate Re(V) and methanol. Consistent with the observations of the initial investigators,<sup>11</sup> we find that the formation of methanol from MTO in water requires added H<sub>2</sub>O<sub>2</sub> 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<sub>4</sub><sup>−</sup> 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<sub>3</sub> bond.

**Table 1.** Reaction Yields<sup>a</sup> and Overall Calculated Barriers<sup>b</sup>

YO	% MeOH	BV TS	$\mu$ -peroxo TS
H <sub>2</sub> O <sub>2</sub>	80	20	13
PyO	0	32	47
IO <sub>4</sub> <sup>−</sup>	100	17	25
PhIO	90	8	18

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

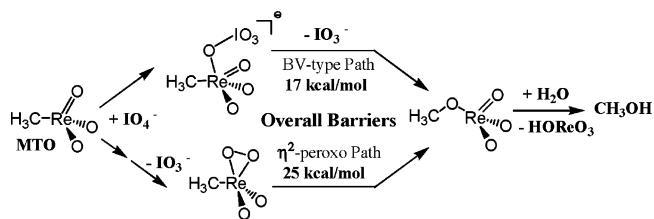
In the initial studies on decomposition of MTO to methanol, only H<sub>2</sub>O<sub>2</sub> was investigated and two non-BV-type mechanisms proposed: reaction via a  $\eta^2$ -peroxo intermediate or by direct methyl migration to the hydroxo of Re-coordinated OOH<sup>−</sup>. We considered that since 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<sup>−</sup> or H<sub>2</sub>O. More significantly, given the ease of functionalization of the Re–CH<sub>3</sub> bond and the d<sup>0</sup> 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  $\eta^2$ -peroxo pathways<sup>8</sup> and accessible with a broader range of potentially more practical, non-peroxo YO.

To investigate this possibility, we compared the reaction of MTO with H<sub>2</sub>O<sub>2</sub> and three non-peroxo YO: PhIO, PyO, and IO<sub>4</sub><sup>−</sup> in water. As can be seen in Table 1, PhIO and IO<sub>4</sub><sup>−</sup> are as efficient as H<sub>2</sub>O<sub>2</sub> for generation of methanol. Controls show that the selectivities and yields are independent of added O<sub>2</sub>, and free radicals are likely not involved. Facile methanol formation with the non-peroxo YO is consistent with a low-energy BV-type pathway and would rule against direct methyl migration to the  $\beta$ -atom of coordinated YO since the  $\beta$ -atom is not O. However, these observations alone cannot

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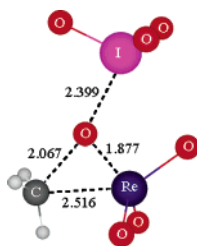
<sup>†</sup> California Institute of Technology.

**Scheme 1.** B3LYP/LACVP\*\* Calculated Low-Energy Pathways for Methanol Formation from MTO and  $\text{IO}_4^-$  in  $\text{H}_2\text{O}$ <sup>12</sup>



rule out a  $\eta^2$ -peroxo pathway with non-peroxo YOs. Significantly, calculations<sup>12</sup> show that a BV-type pathway is both viable and, as shown in Table 1, lower in energy than the  $\eta^2$ -peroxo pathways for all the non-peroxo YOs.

For  $\text{IO}_4^-$ , the BV-type and  $\eta^2$ -peroxo pathways shown in Scheme 1 have calculated barriers of 17 and 25 kcal/mol, respectively. The products of the BV pathway are  $\text{IO}_3^-$  and the methoxo species,  $\text{MeORe}(\text{O})_3$ , which readily hydrolyzes to methanol and  $\text{Re}(\text{O})_3\text{OH}$ . The BV-type transition state involves concerted methyl migration and  $\text{IO}_3^-$  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<sub>3</sub> 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 +  $\text{IO}_4^-$  (bond length values in angstroms, Å).<sup>12</sup>

The 17 kcal/mol activation energy calculated for  $\text{IO}_4^-$  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  $\eta^2$ -peroxo pathway, the O in the MeOH product should be derived almost exclusively from YO and not from MTO. Consistently, the reaction of  $^{16}\text{O}$ -MTO with  $[\text{I}^{18}\text{O}_4]^-$ ,<sup>13</sup> followed by GC–MS analysis of the reaction mixture at low conversion of MTO, showed that only  $\text{CH}_3^{18}\text{OH}$  was formed. While this observation supports a BV pathway, it does not rule out reaction proceeding via an unsymmetrical  $\eta^2$ -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  $\text{MeOReO}_3$  complex<sup>14</sup> should be generated but not hydrolyzed in aprotic media at moderate temperature, we examined the reaction of MTO with 1 equiv of PyO in  $\text{THF}-d_8$  at 125 °C in the presence of excess pyridine-*d*<sub>5</sub> by <sup>1</sup>H NMR. It is known<sup>11</sup> and we observe that MTO is quantitatively converted to the MTO–Py-*d*<sub>5</sub> adduct<sup>15</sup> (s, 1.70 ppm) at room temperature. Upon heating, clean conversion of this adduct to  $\text{MeOReO}_3$ –Py-*d*<sub>5</sub> (s, 4.48 ppm) and free pyridine-*h*<sub>5</sub> is observed based on comparison to the chemical shift of the known  $\text{MeOReO}_3$ –amine adduct.<sup>14</sup> 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  $\text{H}_2\text{O}_2$  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  $\eta^2$ -peroxo and the other via a BV-type pathway (Table 1). While the complete mechanism for MTO– $\text{H}_2\text{O}_2$  will be addressed in a more thorough study, it is clear that the BV mechanism is also feasible even for peroxo YOs, such as  $\text{H}_2\text{O}_2$ .

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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