Chapter 23

Catalytic Hydrocarbon Oxidations Involving Coreductants

Joseph E. Remias and Ayusman Sen*

Department of Chemistry, The Pennsylvania State University, University Park, PA 16802

Hydrogen peroxide is a useful oxidant for selective aliphatic and aromatic hydrocarbon oxidations. Unlike dioxygen, which typically does not oxidize these molecules in a selective fashion, a wide body of research already exists reporting selective, catalytic hydrocarbon oxidations using H$_2$O$_2$. This, coupled with the fact that H$_2$O$_2$ produces only water as a byproduct and has a high percentage of active oxygen, make it an excellent choice for hydrocarbon oxidations. Consequently, great interest exists in using H$_2$O$_2$ for selective oxidations. With this has grown interest in generating H$_2$O$_2$ from dioxygen and another coreductant for its instantaneous use in organic oxidations. Efficiently doing so would significantly increase a reaction’s economic value and its environmental friendliness. In this short review, we focus on the oxidation of alkyl and aromatic hydrocarbons with H$_2$O$_2$ generated in situ using hydrogen as a coreductant. Special attention is given to the use of palladium in these reactions, and to bimetallic systems that utilize one catalyst for peroxide generation while another performs hydrocarbon oxidations. We also present some of our own data on this topic, particularly on vanadium catalyzed benzene oxidation using H$_2$O$_2$ generated in situ on a palladium catalyst. Furthermore, we compare our in situ results to an analogous system where H$_2$O$_2$ is added directly.
Introduction

Coreductants serve an important function in enzymatic oxidations. The monooxygenases such as cytochrome P-450 (1,2) and methane monooxygenase (3) perform difficult oxidations via reductive activation of dioxygen. In the oxidations, a molecule of water is produced making the maximum efficiency based on oxygen 50%. The ultimate goal of catalysis would be to use 100% of the oxidant, as in “heme” type oxygenases. However, when one considers autoxidation or free radical processes that use 100% of oxygen, they rarely show the necessary selectivity for hydrocarbon oxidations. Consequently, the use of a monooxygenase type catalyst, one involving a coreductant, provides an appealing alternative. A wealth of catalysts and oxidants are available which act in this way and provide more selective reactions. Some examples of oxidants are as follows: hydrogen peroxide, peracids, organic hydroperoxides, inorganic and metallorganic peroxides, sodium hypochlorite, iodosobenzene, and nitrous oxide. Many of these oxidants are too expensive for basic chemical production, the focus here, and find more use in fine chemical production where expensive and even stoichiometric oxidants still play a large role.

Of the oxidants listed above hydrogen peroxide shows the most promise for several reasons. First, H$_2$O$_2$ delivers the most active oxygen per molecule, 47%, when compared to those listed above. It is important to note that this is actually ca. 20%, when using H$_2$O$_2$ as an aqueous solution. The atom economy of oxidants is important to consider when trying to minimize the environmental impact of a reaction (4). It produces only water as a byproduct, a concern when one considers the need for “green” oxidants (ones that produce minimal non-toxic waste) (5). Finally, hydrogen peroxide has proven to be a strong oxidant with good selectivity for many oxidations (6).

The use of metal catalysts for the generation of hydrogen peroxide using hydrogen (the coreductant) and oxygen has generated significant interest recently as evidenced by the proliferation of publications. This desire is at least partially fueled by an interest in pursuing “greener” routes than the current anthraquinone process to make H$_2$O$_2$ (7). Also, generating the oxidant \textit{in situ} maximizes the percent of usable oxygen in the oxidant, no diluent is needed for the oxidant if generated \textit{in situ}. Furthermore, the cost associated with storing and transporting hydrogen peroxide is eliminated. Another advantage is that a bi-metallic catalyst system can be envisioned where the H$_2$O$_2$ is generated in a slow steady state amount on one catalyst while another performs the oxidation. This should maximize the selectivity and efficiency of the reaction. Finally, the cost of hydrogen peroxide versus that of hydrogen (the only consumable of cost assuming 100% catalyst recyclability and air as the oxidant) is about 5 times more. Thus, a significant cost savings can be realized per mole of oxidant used.

In this short review, we focus on the generation of hydrogen peroxide in an \textit{in situ} fashion for hydrocarbon oxidations. Specifically, we are concerned with the selective oxidation of alkanes and aromatics using H$_2$O$_2$ generated on a
noble metal catalyst. In all these cases hydrogen will serve as the coreductant either directly or indirectly. The use of bimetallic systems where one catalyst generates the \( \text{H}_2\text{O}_2 \) while another performs hydrocarbon oxidation is given particular attention. We also present some of our recent work in this area looking at the selectivity of \textit{in situ} reactions compared to when \( \text{H}_2\text{O}_2 \) is added directly, and briefly address how the two catalysts in a bimetallic system, as above, might interact.

It is worthwhile to succinctly survey some other oxidations in the presence of coreductants. Barton has developed several Gif systems using iron catalysts in the presence of zinc or iron(0) as a reductant (8). These methods were developed more to model biological monooxygenases than to serve practical industrial functionality. Ascorbic acid has also been used as a reductant to generate hydrogen peroxide (9). There has also been a substantial body of work on alternative organic species to generate hydrogen peroxide in an \textit{in situ} fashion, (10). Finally, a substantial body of research exists on the epoxidation of olefins using generated \( \text{H}_2\text{O}_2 \) (11-14).

**Metal Catalyzed Formation of \( \text{H}_2\text{O}_2 \)**

Numerous examples exist in the literature detailing the formation of hydrogen peroxide on metal catalysts. During Pd catalyzed aerobic oxidations, it is known that hydrogen peroxide is formed as a byproduct (15). In some instances this peroxide remains in solution. For instance, in the aerobic oxidation of alcohols by a combination of palladium acetate and pyridine, it was suggested that the peroxide may actually compete with the substrate for binding to the metal center and, therefore, its removal by decomposition (e. g., by molecular sieves) promoted substrate oxidation (16). Another notable example is the oxidation of alcohols via Pd(II) complexes producing a significant amount of peroxide, eq. 1 (17). These reactions were carried out in a biphasic mixture to prevent oxidation of the catalyst’s ligand; however, this methodology may also have served to prevent peroxide decomposition via the Pd catalyst. The biphasic conditions may partially explain why in other examples no peroxide was observed in alcohol oxidation (see below). The quick separation of the peroxide from the palladium catalyst via phase separation prevented its subsequent metal catalyzed decomposition. Surprisingly, considering the results below, the authors claim that equimolar amounts of ketone and peroxide are formed- a result indicative of no metal catalyzed decomposition of the latter occurring.

\[
\text{R}_2\text{CHOH} + \text{O}_2 \rightarrow \text{R}_2\text{CO} + \text{H}_2\text{O}_2 \quad (1)
\]

Additionally, several patents and papers report the palladium-catalyzed generation of hydrogen peroxide in relatively high concentrations in the absence of an oxidizable substrate (see below). These reactions involve the use of dioxygen and either carbon monoxide or dihydrogen as the coreductant. Carbon monoxide used in these conditions is an indirect source of hydrogen through the
water gas shift reaction, eq. 2. Both metallic palladium and discrete palladium compounds have been employed as catalysts for the reaction.

\[ \text{H}_2\text{O} + \text{CO} \rightleftharpoons \text{H}_2 + \text{CO}_2 \] (2)

Leading work showed that hydrogen peroxide could be formed in relatively high concentrations (10-20\% by wt.) with a palladium catalyst, hydrogen and oxygen (18). The need for acidic solution and the use of halide promoters, making purification difficult and generating a corrosive environment, have led researchers to look at variations to the above. For example, supported heteropoly acids were used to replace inorganic acids (19). Furthermore, others have found that halides can be excluded with certain catalysts but only in organic solvents (20). An interesting study recently performed sheds light on how palladium catalysts form hydrogen peroxide (21). The researchers contend that \text{H}_2\text{O}_2 formation occurs only on colloidal Pd particles regardless of their source (Pd\(^{2+}\) ions or Pd on silica support) at least under acidic aqueous conditions.

In contrast to the above report, discreet Pd\(^{2+}\) complexes have been found to catalyze the formation of \text{H}_2\text{O}_2 using CO as the coreductant (22). Here, a biphasic mixture is again employed to isolate the catalyst from the \text{H}_2\text{O}_2 formed. It was necessary to carry out the reaction with a large excess of O\(_2\) to prevent reduction to palladium metal. By carefully selecting nitrogen coordinated ligands with appropriate steric and electronic environments, the researchers were able to produce \text{H}_2\text{O}_2 in concentrations up to 8\% by wt.

Though the mechanism of hydrogen peroxide generation on noble metals is still not completely understood, particularly on surfaces in the presence of various promoters and other metals, some conclusions can be made based on discreet Pd and Pt complexes. The first step involves the formation of a metal-peroxo complex. The coordinated peroxide can then be displaced from the metal by the addition of a ligand (e. g., eq. 3) (23). More commonly, in acidic solutions, it is protonated to form hydrogen peroxide (24,25). Finally, it is worthwhile to note that while both Pd and Pt catalysts can effectively form \text{H}_2\text{O}_2 in the presence of a coreductant, Pt is faster at decomposing the oxidant (26).

\[ (\text{R}_3\text{P})_2\text{Pt(O}_2) + 2 \text{R}_3\text{P} + \text{ROH} \rightleftharpoons [(\text{R}_3\text{P})_4\text{Pt}]^{2+} + \text{HO}_2^- + \text{RO}^- \] (3)

**Metal Catalyzed Decomposition of \text{H}_2\text{O}_2**

It is pertinent to point out that while \text{H}_2\text{O}_2 can be formed in reasonable yields, significant decomposition of it once formed is also observed. For example, during olefin oxidation with palladium diacetate and hydrogen peroxide, decomposition of the oxidant was observed (27). This effect was more pronounced in the absence of the substrate. Furthermore, during the aerobic oxidation of alcohols with Pd(OAc)\(_2\), it was shown that \text{H}_2\text{O}_2 in the absence of substrate underwent rapid disproportionation to molecular oxygen and water.

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Further experiments showed that even while alcohol oxidation was occurring the addition of hydrogen peroxide to the solution resulted in only decomposition of the H$_2$O$_2$, eq. 4. No additional oxidation of the alcohol, by the peroxide, was observed, eq. 5.

\[
\begin{align*}
\text{H}_2\text{O}_2 & \rightarrow \text{H}_2\text{O} + 0.5 \text{O}_2 \tag{4} \\
\text{H}_2\text{O}_2 + \text{RCH}_2\text{OH} & \rightarrow \text{RCHO} + 2 \text{H}_2\text{O} \tag{5}
\end{align*}
\]

Figure 1: Efficiency in use of H$_2$O$_2$ generated for benzene oxidation. Calculated from total H$_2$O produced vs. amount of phenol and benzoquinone formed. Run using 3.2 µmol catalyst, 20.0 mg 5% Pd/Al$_2$O$_3$, 2 mL benzene, and 2.5 mL acetic acid, exposed to 100 psi H$_2$, 1000 psi N$_2$, and 100 psi O$_2$ for 2 h at 65°C. Each column is the average of four reactions. Abbreviations: acac = acetylacetonate, OAc = acetate, T(DBM) = tris(dibenzoylmethanato).  

* 10.0 mg of 3% Pd/Al$_2$O$_3$.


Figure 1 shows our results on the efficiency with which the dihydrogen (and H$_2$O$_2$ formed from it) is used for benzene oxidation with several catalysts. It demonstrates that only about 5.5% of the dihydrogen consumed to make peroxide is used in substrate oxidation. For comparison, under analogous conditions where H$_2$O$_2$ was added directly, an oxidant efficiency of 20% was observed. Observation that the efficiency with respect to in situ generated H$_2$O$_2$ remains constant regardless of the hydroxylation catalyst used is consistent with
the palladium catalyst causing almost all of the observed hydrogen peroxide decomposition. Recent work using palladium, gold, and amalgams of the two speculates that the decomposition on Pd may limit the amount of usable H\textsubscript{2}O\textsubscript{2} (29).

A plausible solution to decrease the rate of decomposition may involve simply decreasing the percentage of hydrogen in the media. This action would limit the availability of hydrogen for palladium catalyzed H\textsubscript{2}O\textsubscript{2} hydrogenation (eq. 6). This has been found effective in other cases (7). However, it seems unlikely that this would completely halt the unwanted reaction and will not stop the disproportionation reaction. Consequently, one must consider the rate of decomposition when seeking out catalysts for the \textit{in situ} generation of hydrogen peroxide.

\begin{equation}
\text{H}_2\text{O}_2 + \text{H}_2 \rightarrow 2\text{H}_2\text{O} \tag{6}
\end{equation}

**H\textsubscript{2}O\textsubscript{2} Generation and Hydrocarbon Oxidation at a Single Metal**

The use of palladium generated hydrogen peroxide has found use in performing hydrocarbon oxidations, Scheme 1, where Cat = Pd. An elegant example which separated the hydrogen and oxygen, preventing the potential for an explosion, showed that a palladium containing membrane could catalyze the formation of hydrogen peroxide. The formed peroxide then reacted with Pd to oxidize benzene to phenol (30). The method shows high selectivity, 96% for phenol based on benzene consumed; however, anywhere from 5 to 9 moles of H\textsubscript{2}O\textsubscript{2} disproportionate for every mole of benzene oxidized. Other work has focused on supporting palladium on highly acidic resins such as Nafion and has successfully generated phenol using H\textsubscript{2}O\textsubscript{2} from H\textsubscript{2} and O\textsubscript{2} (31). The use of a heteropolyanion with palladium or platinum catalyst has also been attempted with generated H\textsubscript{2}O\textsubscript{2} for benzene oxidation (32).

In the past we have had success in using generated H\textsubscript{2}O\textsubscript{2} for hydrocarbon oxidations using palladium. We have shown that supported Pd is effective in oxidizing methane and ethane at mild temperatures in the presence of CO and O\textsubscript{2} (33). In an effort to trap the desired oxidation products at the alcohol stage, trifluoroacetic acid (TFA) was used to generate the corresponding ester. Interestingly, while simply adding TFA did not change the product distribution, the addition of copper salts dramatically increased the selectivity of the reaction with methanol and its TFA ester being virtually the only products (34). The reactivity of the above system in water has been exploited for the deep oxidation (to carbon monoxide, carbon dioxide, and water) of a variety of hazardous organics (35). Several hundred turnovers in 24h can be achieved with numerous substrates including, benzene, phenol, substituted phenols, aliphatic and aromatic halogenated compounds, organophosphorous, and organosulfur compounds.
Other work from our group shows the functionalization of methane to methanol and acetic acid using Rh salts as catalysts (36,37). These reactions also employed CO and oxygen with the two products formed arising from competitive attack of a metal alkyl via a nucleophile or insertion of carbon monoxide (Scheme 2). It is presumed that in these reactions CO is performing a dual role: it generates H\(_2\) and thus H\(_2\)O\(_2\) via the water gas shift, and it inserts into metal alkyl bonds to form carbonylated products. Indeed, the water gas shift reaction does proceed under similar conditions (38), and the oxidation of CO to CO\(_2\) was observed in the absence of methane (36).

**Scheme 2**

**H\(_2\)O\(_2\) Generation and Hydrocarbon Oxidation Using Two Different Metals**

Utilizing another catalyst for hydrocarbon oxidations once the hydrogen peroxide was generated has also been shown effective, Scheme 1. Miyake has explored the effect of adding metal oxides to silica supported palladium catalysts (39). It was found that numerous oxides, vanadium, yttrium, and
lanthanum oxides exhibiting the best performance, increased the rate of phenol formation from benzene. Though no details are presented it is hypothesized that the metal oxides may assist in delivering activated oxygen to the palladium catalyst. A more recent paper screens numerous homogeneous metal salts with a heterogeneous palladium catalyst; it is proposed that this reaction occurs via the same pathway as above (40). Of course a pathway where hydrogen peroxide forms a catalytically active species from the metal oxide is also a plausible explanation. A comparison of Pd or Pt supported on silica and promoted with vanadium oxides has been performed (41). The authors note a significant increase in both yield and selectivity in the use of platinum over palladium; a find contrary to the body of literature on the generation of hydrogen peroxide, where palladium is highly favored (42,43). This result may indicate a mechanism not involving the simple generation of H$_2$O$_2$ with its immediate use.

The use of Pd-Cu supported on silica has been found to be effective in benzene oxidation via the path shown in Scheme 3 (44,45). It is believed that the actual C-H activation occurs by metal promoted formation of hydroxyl radicals attacking the benzene nucleus. The pathway shown in Scheme 3 has the practical advantage of separating the hydrogen and oxygen activation steps- a method eliminating the mixing of these potentially explosive gases. The reaction has been elaborated to the gas phase, which promotes higher selectivities by removing the product phenol from the reaction (46,47). Unfortunately, the high temperatures needed for gas phase oxidation also serves to reduce the efficiency of the hydrogen consumed with much of it forming water. Benzene and hexane oxidation have also been attempted with palladium supported on titanium silicates in an attempt to exploit the well known oxidations using TS-1 with generated H$_2$O$_2$ (48).

**Scheme 3**

Beyond benzene oxidation, the oxidation of alkanes using *in situ* generated H$_2$O$_2$ has also received attention. The first report of this nature involved the use of a Pd(0) and Fe(II) doped zeolite for the oxidation of alkanes with hydrogen and oxygen (49). The catalyst exhibited the remarkable shape selectivity that can be generated with zeolites showing an *n*-octane/ cyclohexane preference of >190. Furthermore, supporting noble metals on TS-1 proved effective in the oxidation of *n*-hexane and *n*-octane in the presence of H$_2$ with the product being exclusively secondary alcohols and ketones (10). The efficiency, based on oxidant used, never exceeded 57%. However, when H$_2$O$_2$ was added to the reaction from an external source an efficiency of 86% was obtained even at a
significantly higher temperature. Higher temperatures increase the rate of metal catalyzed hydrogen peroxide decomposition. Platinum heteropoly catalysts have been investigated for the oxidation of cyclohexane (50). Catalyst redox studies showed that activity is associated with both Pt$^{0}$ and Pt$^{2+}$ being present along with a redox couple of Mo$^{5+}$/Mo$^{6+}$ in the phosphomolybdate. Furthermore, the use of gold supported on titanium mesoporous materials have received some attention in the oxidation of propane and isobutanol (51). While acetone from propane yield was meager, when compared to propene oxidation, $\tau$-butanol was formed with reasonable yield and selectivity from isobutane. The GoAgg$^{II}$ system, originally developed by Barton (8), has been modified and implemented for the oxidation of cyclohexane using H$_2$O$_2$ generated on a Pd surface with an H$_2$/O$_2$ mixture (52). Based on the typical use of acidic conditions for Pd catalyzed H$_2$O$_2$ generation, acetone and acetone/ acetic acid mixtures were employed (instead of the typical basic conditions for the GoAgg$^{II}$ reaction). Under these conditions an increase in the alcohol product of over an order of magnitude was observed compared to the basic conditions. Interestingly, while the alcohol was favored in neutral or acidic conditions, the ketone showed preference under basic conditions. Otsuka has observed a very interesting increase in both methane oxidation and selectivity to methanol when hydrogen is added to certain iron catalysts (53). Experiments show that hydrogenation of CO (formed through methane oxidation) is not responsible for the formation of methanol and that similar selectivities are observed when H$_2$O$_2$ replaces the H$_2$/O$_2$ gas mixture.

Furthermore, we have recently completed work showing the persistence of palladium-generated hydrogen peroxide in solution. The oxidant, though showing marked decomposition, is formed fast enough to interact with another catalyst (e.g., vanadium or iron) and effectively oxidizes aromatic and aliphatic hydrocarbons (15). Control experiments showed that very little oxidation occurs in the absence of the second, hydroxylation catalyst (vanadium species) and that V(acac)$_3$ (acac = acetylacetonate) will catalyze the hydroxylation of benzene by hydrogen peroxide, even in the absence of metallic palladium, dihydrogen and dioxygen. Furthermore, no oxidation occurs when the vanadium hydroxylation catalyst is used without some source of hydrogen peroxide (15). Thus, metallic palladium is active in the formation of hydrogen peroxide, which in turn generates an active catalytic species from the vanadium complex.

It was of interest what, if any, selectivity advantage could be obtained by employing in situ generated H$_2$O$_2$ for hydrocarbon oxidations. One can imagine that by carefully adjusting the ratio of the two catalysts (Pd and V) present, better selectivities could be obtained since no excess of H$_2$O$_2$ would ever be present during the reaction. We have previously established the oxidations are limited by the amount of hydrogen peroxide formed (15). Tables I and II, respectively, show results on the oxidation of benzene comparing the in situ reactions to those where H$_2$O$_2$ was added directly. It is clear that in all cases a remarkable selectivity advantage can be obtained. For the vanadium-catalyzed oxidations the selectivity difference is around 20% even when the substrate is in huge excess. It is important to note that due to phase separation problems the
syringe pumped H_2O_2 reactions employed about one half the amount of oxidant as the in situ case (Fig. 1) - a condition that should favor the selectivity for the added H_2O_2 case. In the case of the iron catalyst, the selectivity advantage is nearly 30%.

Table I: Conversion and selectivity to phenol using lower initial benzene concentration in situ H_2O_2 generation

<table>
<thead>
<tr>
<th>Hydroxylation Catalyst</th>
<th>Benzene (µmol)</th>
<th>Phenol (µmol)</th>
<th>Benzoquinone (µmol)</th>
<th>Conversion to Phenol (%)</th>
<th>Selectivity to Phenol (%)^b</th>
</tr>
</thead>
<tbody>
<tr>
<td>V(acac)_3</td>
<td>1400</td>
<td>200(10)</td>
<td>tr.</td>
<td>14</td>
<td>&gt;99</td>
</tr>
<tr>
<td>V(acac)_3</td>
<td>520</td>
<td>130(10)</td>
<td>tr.</td>
<td>26</td>
<td>&gt;99</td>
</tr>
<tr>
<td>FeT(DBM)</td>
<td>1400</td>
<td>59(9)</td>
<td>1.7(0.2)</td>
<td>4.2</td>
<td>97</td>
</tr>
</tbody>
</table>

^a Performed using benzene as indicated with 3.2 µmol V(acac)_3 or FeT(DBM) = tris(dibenzoylmethanato)Fe(III) and 20.0 mg 5% Pd/Al_2O_3 in 4.5 mL acetic acid exposed to 100 psi H_2, 1000 psi N_2, and 100 psi O_2 for 2 h at 65ºC. Data is an average of 2 runs.

^b Selectivity calculated as mmol phenol/ (mmol phenol + mmol benzoquinone).


Table II: Oxidation of benzene using H_2O_2 added via a syringe pump

<table>
<thead>
<tr>
<th>Hydroxylation Catalyst</th>
<th>Benzene (µmol)</th>
<th>Phenol (µmol)</th>
<th>Benzoquinone (µmol)</th>
<th>Conversion to Phenol (%)</th>
<th>Selectivity (%)^b</th>
<th>H_2O_2 Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V(acac)_3</td>
<td>22000</td>
<td>600(30)</td>
<td>190(10)</td>
<td>2.7</td>
<td>76</td>
<td>20</td>
</tr>
<tr>
<td>V(acac)_3</td>
<td>5900</td>
<td>220(60)</td>
<td>41(2)</td>
<td>3.7</td>
<td>84</td>
<td>6.2</td>
</tr>
<tr>
<td>V(acac)_3</td>
<td>520</td>
<td>47(3)</td>
<td>12(2)</td>
<td>9.0</td>
<td>80</td>
<td>1.4</td>
</tr>
<tr>
<td>FeT(DBM)</td>
<td>5900</td>
<td>9.7</td>
<td>tr.</td>
<td>0.16</td>
<td>69</td>
<td>0.37</td>
</tr>
<tr>
<td>FeT(DBM)</td>
<td>520</td>
<td>1.7</td>
<td>1</td>
<td>0.33</td>
<td>64</td>
<td>0.075</td>
</tr>
</tbody>
</table>

^a Performed using 3.2 µmol V(acac)_3, or FeT(DBM) = tris(dibenzoylmethanato)Fe(III), benzene as indicated, and acetic acid (making total volume 4.5 mL) for 2 h at 65ºC. During this time 0.28 mL, 4.9 mmol of 50% H_2O_2 (diluted to 0.68 mL total with acetic acid) was added dropwise via a syringe pump. Data is an average of 2 runs unless indicated.

^b Selectivity calculated as mmol phenol/ (mmol phenol + mmol benzoquinone).


Another aspect needing consideration in systems where two catalysts operate simultaneously, one generating the H_2O_2 and another performing hydrocarbon oxidation, is whether the H_2O_2 generating catalyst participates in
the substrate oxidation. As described above, there are numerous examples where a Pd catalyst generates the oxidant and also uses it for substrate oxidation. In order to truly exploit the available range of catalysts for hydrocarbon oxidations with H$_2$O$_2$, it must be ensured that the H$_2$O$_2$ generator does not interfere with the catalyst doing the actual substrate oxidation. We have explored this for the vanadium catalyzed oxidation of benzene using palladium generated H$_2$O$_2$ (54). The mechanism of benzene oxidation in this system was found to be identical to that where H$_2$O$_2$ was added directly. Therefore, the role of the palladium catalyst is to generate H$_2$O$_2$ in situ, and it does not play a part in the benzene oxidation step. However, this may not be the case under all conditions. In an effort to increase the oxidant efficiency we examined the use of soluble halide salts to retard H$_2$O$_2$ decomposition by palladium (18). Rather than the desired effect, a trend was observed showing that the amount of phenol produced decreased in the order Cl$^-$ > Br$^-$ > I$^-$ tracking the coordinative ability of the halide. This result suggests that these species might be showing coordinative inhibition of the vanadium catalyst.

**Conclusion**

The oxidation of aromatic and aliphatic molecules has clearly been shown possible using *in situ* generated H$_2$O$_2$. We have also shown that a significant increase in selectivity can be achieved via the use of *in situ* generated oxidant. However, the reaction is markedly less efficient in its use of oxidant. It is also crucial to address the influence of each catalyst and components present when using bimetallic conditions. The observation that conditions promoting one reaction in the system may inhibit or form alternative products in the second reaction warrants careful scrutiny of how the two systems interact.

One particular concern in reactions generating H$_2$O$_2$ *in situ* is the concomitant decomposition or hydrogenation via the catalyst making it. Though using a large excess of oxidant can minimize hydrogenation and using a biphasic solution can slow disproportionation, it seems unlikely that these methods will completely eliminate these competitive reactions. Also, in some situations the use of a biphasic mixture is impossible or impractical, such as in a gas phase reaction. Consequently, there is currently a significant need for catalysts that are less active for the unwanted reactions. It is important to note that the efficiency in the use of generated oxidant is important due to the fact that the economics are significantly impacted by the efficiency with which the coreductant is consumed.

Performing selective hydrocarbon oxidations with H$_2$O$_2$ and generating this oxidant *in situ* are currently receiving considerable attention. The current work shows that oxidative hydrocarbon activation can be effectively carried out in this manner. However, there is still a need for H$_2$O$_2$ generators showing more efficiency in use of oxidant and a fundamental understanding of how the two parts, H$_2$O$_2$ generation and hydrocarbon oxidation, interact. The latter should
help in generating oxidation catalysts that work at their maximum rates and through mechanisms unhindered by or assisted by the presence of the H$_2$O$_2$ generating catalyst.

**Experimental**

_Caution: Due care must be taken when dealing with gas mixtures under pressure. Special attention must be paid to gas flammability limits (55). All reactions were performed in 300 mL Parr stainless steel autoclaves. Quantitation was typically done using the FID detector excepting water quantitation reactions where the TCD detector was employed. Reactions with benzene used an Alltech EC-5 30 m, ID = 0.32 mm column with 100:1 split ratio and o-dichlorobenzene internal standard. Reaction products were confirmed using comparison to known compounds and further confirmed using GC-MS._

3.2 µmol of catalyst and 20.0 mg of 5% Pd/Al$_2$O$_3$ were weighed into ca. 25 mL constricted neck glass liner. To this a small magnetic stir bar was added along with 2 mL of benzene and 2.5 mL of glacial acetic acid. The mixture was sealed in the autoclave and flushed thoroughly with hydrogen. It was then charged with 100 psi H$_2$, 1000 psi N$_2$, and 100 psi O$_2$ in that order and placed in a temperature regulated oil bath for 2 h at 65°C. Internal autoclave temperatures were determined using an autoclave equipped with a temperature sensor. At the end of the reaction, the autoclave was cooled in ice, slowly degassed, and the contents filtered through a 2 µm filter to remove the supported palladium catalyst. After internal standard addition, the liquid was analyzed with GC.

Syringe pump reactions were carried out by weighing 3.2 µmol of catalyst into a 5 mL conical vial. Substrate and solvent were added so that the total volume after hydrogen peroxide addition was 4.5 mL. A solution of acetic acid and 50% hydrogen peroxide (v/v, confirmed by permanganate titration) was made up to deliver 4.9 mmol of hydrogen peroxide in 0.68 mL of solution over 2 h at 65°C using a syringe pump (with a 1 mL syringe entirely of plastic to prevent peroxide decomposition). Reactions were chromatographed after internal standard addition.

**Acknowledgement**

JER thanks the NCER Star/ EPA fellowship for financial support. This work was funded by a grant from the NSF.
References


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