

Design and study of homogeneous catalysts for the selective, low temperature oxidation of hydrocarbons

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Abstract

The direct, low temperature conversion of hydrocarbons to functionalized products using novel, single site catalysts could lead to technological advances that redefine the landscape of the current materials and energy industries. Natural gas continues to represent a vast source of untapped hydrocarbons around the globe that has the potential to replace or augment petroleum as the raw material for materials and energy. Its abundance has garnered much interest in the scientific community as groups have focused on the catalytic conversion of its major component, methane, to functionalized products. The key requirements is to design new catalysts for the oxidative functionalization of methane that operate at lower temperatures and that also meet the basic requirements of selectivity, rate, and lifetime that characterize useful catalysts. Recent advances in the field of hydrocarbon CH activation have shown the potential for transition metal based coordination catalysts to meet these requirements. Described herein are recent advances in designing catalysts based on the CH activation reaction that address the basic requirements for practical systems with emphasis on the issues that have prevented promising reported systems from becoming commercially viable.

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1. Introduction

The conversion of fossilized hydrocarbons to energy and materials is a foundational technology. While it is important that we consider a switch to future alternatives, such as the proposed hydrogen-based economy, it is critical that as a bridge to this long term future, we develop more environmentally benign, greener technologies for these essential fossil fuel-based processes that will continue to be important in the next decade. As shown in Fig. 1, the key objectives of such greener processes must be to minimize emissions and capital while maximizing energy and materials output. Importantly, reducing dependence on petroleum and increasing use of underutilized, abundant natural gas would facilitate this movement to greener technologies while extending the lifetime of limited fossilized resources.

Alkanes from natural gas and petroleum are among the world's most abundant and low-cost feedstocks. Current petrochemical technologies to convert these feedstocks to energy, fuel and chemicals operate at high temperatures and utilize multiple steps that lead to inefficient, capital intensive processes. The development of low temperature, selective, direct alkane oxidation chemistry could lead to a new paradigm in petrochemical technology that is environmentally cleaner, economically superior and allows the large reserves of untapped remote natural gas to be valorized as primary feedstocks for fuels and chemicals [1]. Alcohols are among the highest volume commodity chemicals and most versatile feedstocks [1b]. A primary reason that new technologies for direct, selective hydroxylation of alkanes to alcohols remain important is that the current commercial catalysts for alkane oxidation (typically solid metal oxides) are not sufficiently active for the functionalization of alkane CH bonds and employ high temperatures and harsh conditions that lead to low reaction selectivity [1a].

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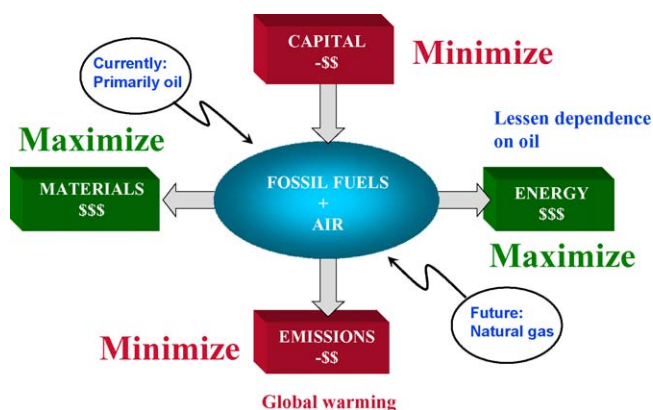


Fig. 1. Oxidative conversion of fossil fuels is a foundational technology.

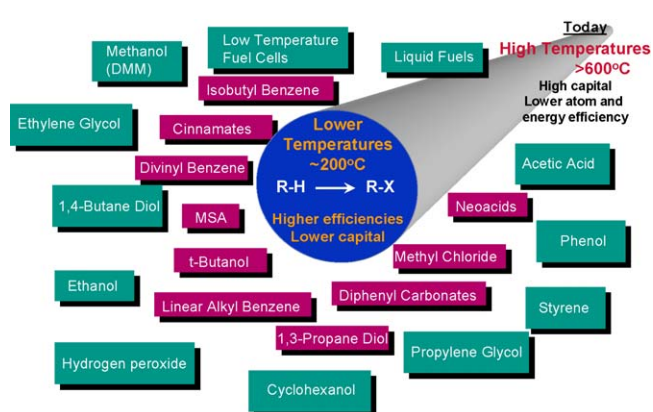


Fig. 2. Examples of products potentially impacted by next generation, low temperature, selective, hydrocarbon oxidation catalysts.

The development of next generation catalysts that would allow the selective conversion of methane and higher alkanes to alcohols or other materials at low temperatures ($\sim 200\text{--}250\text{ }^\circ\text{C}$) in inexpensive reactors, with fewer steps and in high yields could provide a basis for this paradigm change in the petrochemical industry. Examples of products that could be dramatically impacted by such low temperature conversion catalysts are shown in Fig. 2.

- **Methanol**
 - Methane \rightarrow Syn-gas \rightarrow Methanol (Current)
 - Methane \rightarrow Methanol (Next Generation)
- **Acetic acid**
 - Ethane \rightarrow Ethylene \rightarrow Ethanol \rightarrow Acetaldehyde \rightarrow Acetic acid (Past)
 - Methane \rightarrow Methanol \rightarrow Acetic acid (Current)
 - Methane \rightarrow Acetic acid (Next Generation)
- **Ethylene Glycol**
 - Ethane \rightarrow Ethylene \rightarrow Ethylene Chlorohydrin \rightarrow Ethylene Oxide \rightarrow Ethylene Glycol (Past)
 - Ethane \rightarrow Ethylene \rightarrow Ethylene oxide \rightarrow Ethylene Glycol (Current)
 - Ethane \rightarrow Ethylene Glycol (Next Generation)

Fig. 3. Direct conversion is the next step for hydrocarbon technology.

The primary basis for direct alkane conversion chemistry impacting the petrochemical industry is that, unlike the fine chemical industry, the bulk of the production costs are related to process costs, as opposed to material costs. Indeed, as much as 50–75% of the process costs can be related to the capital costs (that can be in the hundreds of millions of dollars) of the plant itself. Consequently, in addition to improvements related to environmental considerations, so-called “Green chemistry”, key improvements in developing new petrochemical processes must involve significant reductions in capital costs in order to warrant the risks involved in developing new processes. One key to reducing the capital costs in new petrochemical processes is to reduce the number of process steps since this is related to the number of process units and capital cost in the plant. This type of plant evolution involving reduction in the number of process steps is well preceded for the production of various commodities as shown in Fig. 3 for the production of methanol, acetaldehyde, acetic acid and ethylene glycol. As shown, the development of new, selective low-temperature CH conversion chemistry could enable the development of the next generation methane to methanol process.

Methane, the major component of natural gas, is an abundantly available raw material that is largely underutilized due to its inherently low reactivity. In addition to more obvious possibilities involving the direct conversion of methane shown in Fig. 3, if new, low temperature, selective, direct conversion chemistry could be developed for methane, less obvious advances (such as the one shown in Fig. 4) could be developed that reduce the number of process steps and overall costs for the production of some of the largest commodities on the planet; electricity and ammonia. Such chemistry could also allow clean materials such as hydrogen peroxide to be more widely utilized. The direct reactions of methane shown in Fig. 4 serve to illustrate that, while methane is one of the cheapest reductants on the planet, the key to unleashing the largely underutilized potential of this molecule is increasing the rate of reaction; that is, making methane a kinetically facile reductant.

The grand challenge to the direct, selective oxidation of methane and higher alkanes can be exemplified by a direct oxidation of alkanes to the corresponding alcohols, Fig. 5. The

- Electricity
 - $\text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} + \text{Heat} \rightarrow \text{Electricity (Current)}$
 - $\text{CH}_4 + \text{O}_2 \rightarrow 2 \text{H}_2 + \text{CO}_2 + \text{O}_2 \rightarrow \text{Electricity} + 2 \text{H}_2\text{O}$ (Current fuel Cells)
 - $\text{CH}_4 + 2 \text{O}_2 \rightarrow \text{Electricity} + \text{CO}_2 + 2 \text{H}_2\text{O}$ (Next Generation fuel cells)
- Hydrogen Peroxide
 - $\text{CH}_4 + \text{O}_2 \rightarrow 2 \text{H}_2 + \text{CO}_2 + 2 \text{O}_2 \rightarrow 2 \text{H}_2\text{O}_2$ (Current)
 - $\text{CH}_4 + 3 \text{O}_2 \rightarrow 2 \text{H}_2\text{O}_2 + \text{CO}_2$ $\Delta G = -132 \text{ kcal/mol}$ (50 °C) (Next Generation)
- Ammonia
 - $\text{CH}_4 + 2\text{O}_2 \rightarrow 2 \text{H}_2 + \text{CO}_2 + 2/3 \text{N}_2 \rightarrow 4/3 \text{NH}_3$ (Current)
 - $1.5 \text{CH}_4 + 1.5 \text{O}_2 + \text{N}_2 \rightarrow 2 \text{NH}_3 + 1.5 \text{CO}_2$ $\Delta G = -128 \text{ kcal/mol}$ (200 °C) (Next Generation)

Fig. 4. Thermodynamically favored pathways for the oxidation of methane.

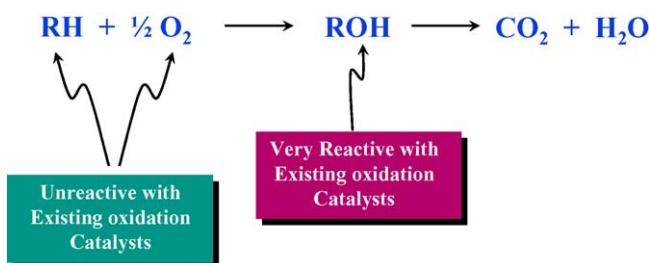
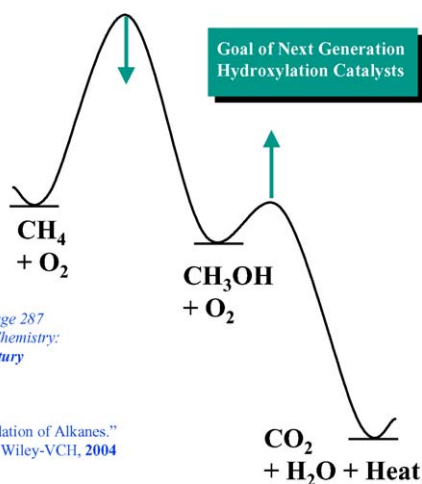


Fig. 5. Direct conversion of alkanes to alcohols demands selectivity.

primary issue is that both the alkane and oxygen are relatively un-reactive molecules with existing oxidation catalysts, whereas the alcohol products are typically quite reactive, resulting in very low alcohol yields with existing catalyst systems.

The key to developing the next generation, direct selective hydroxylation processes is shown in Fig. 6. As shown in this figure, the requirement is to reduce the activation barrier for the overall reaction of methane with oxygen, while simultaneously increasing the activation barrier for the overall reaction of methanol with oxygen. If this can be accomplished with the next-generation of oxidation catalysts, then a direct, high yield process can be developed for the conversion of methane to methanol.



C&E News: March 26, 2001, page 287
ACS 125 Years, New Voices in Chemistry:
Cool Chemistry for the 21st Century

J. Mol. Cat., 2004, 22, 7

Transition-Metal Catalyzed Oxidation of Alkanes.[™]
in Handbook of C-H Activation, Wiley-VCH, 2004

Fig. 6. Thermodynamic profile for the oxidation of methane.

There are now several known catalytic systems that directly convert methane to methanol [2]. However, none of the systems are commercially viable. This is because the existing methane to methanol process is highly evolved and very efficient (the overall carbon yield is ~70%). Significantly, the primary disadvantage of the existing methane to methanol process is the high capital of the process. The resulting relatively high production costs prevent methanol, and correspondingly natural gas, from displacing petroleum as the primary feedstocks for the production of fuels and chemicals.

Consequently, in developing the next-generation direct methane to methanol process several key guidelines, shown in Table 1, are important to consider in developing a process that is economically superior to the existing process. As a general consideration it should be expected that any new process not only substantially reduces the capital costs for the process (ideally by >50%) but also meets (and desirably exceeds) the overall yield and atom-efficiency of the existing process.

Perhaps the single most important requirement in developing a direct, air-based process that utilizes both atoms of oxygen for the conversion of methane to methanol is that the reaction be highly selective (>90%) at a minimum level of conversion (~20%) per pass through the reactor with respect to both methane and the oxidant (which, if not oxygen must be recyclable with oxygen from air) to be useful. An emphasis on the selectivity of the reaction is critical because selectivity sets

Table 1

Engineering guidelines
>20% methane conversion per pass
>90% product selectivity (overall carbon yield >70%)
>20% oxidant conversion per pass
Ultimate oxidant should be air
Few steps
Inexpensive reactors
Facile product isolation
Pressure < 500 psig
Temperature > 200 °C but < 300 °C
Reactor volumetric productivity (STY) ~ 10 ⁻⁶ mol/cm ³ s

Key catalyst guidelines

TOF ~ 1 s ⁻¹
TON > 10 ³
Catalyst concentration of 1 mM at TOF = 1 s ⁻¹ to be cost effective
At 1:1 gas:liquid should generate 2 M MeOH in ~1.5 h

the maximum yield. A less obvious consideration is that loss of selectivity typically leads to the generation of CO_2 as the major side product. This can lead to increased requirement for separations and heat management that can substantially increase the process and capital costs. Another key consideration to reducing the capital costs of a new process is to utilize lower reaction temperatures in the process as this will lead to simpler and less expensive reactors. An unobvious consideration is that whilst lower temperatures are desirable, the temperature range from 200 to 250 °C is preferred. The basis for the upper limit in this temperature range reaction systems can be maintained in the liquid phase and allow the use of simple reactor systems. The basis for the lower limit is that since the direct oxidation of methane to methanol is an exothermic process, the heat released in this temperature range can be utilized beneficially, thereby increasing the efficiency of the overall process.

Important guidelines related to the catalyst involve achieving a minimum volumetric productivity of the reaction system (typically $\sim 10^{-6}$ mol/cm³ s) and catalyst rates (turnover frequencies, TOF ~ 1 s⁻¹ for noble metal-based catalysts) in order to be cost effective (Table 1). To put these challenges in perspective, confirmation that these guidelines had been met would require an oxidation system with a 1 mM catalyst concentration that generated a ~ 2 M solution of methanol after ~ 1.5 h of reaction time. Of course, these are guidelines that are meant to *guide* rather than *restrict* research in attacking this challenge.

In considering the *de novo* design of any new catalyst it is important to note that to be *useful*, all catalysts must meet some minimum performance requirements related to catalyst stability, rate, and selectivity. Importantly, as illustrated in Fig. 7, effective catalysts must *simultaneously* meet *all three* of these performance requirements; meeting any one or two would not lead to useful catalysts. This represents a key challenge to the rational design of *any* efficient catalyst because these requirements related to catalyst rate, stability and selectivity are all interdependent on the molecular structure and composition of the catalyst and reaction system. This is an important consideration because a common approach to *de novo* catalyst design is to attempt to meet these three requirements by a sequential consideration of each requirement: e.g. focusing on meeting the rate

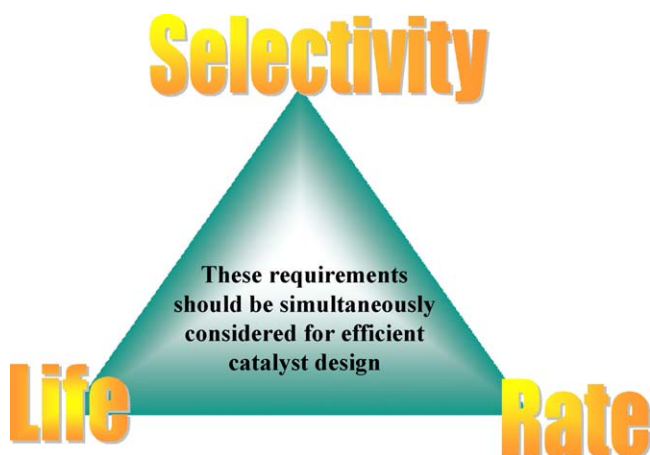


Fig. 7. Key requirements for any efficient catalyst.

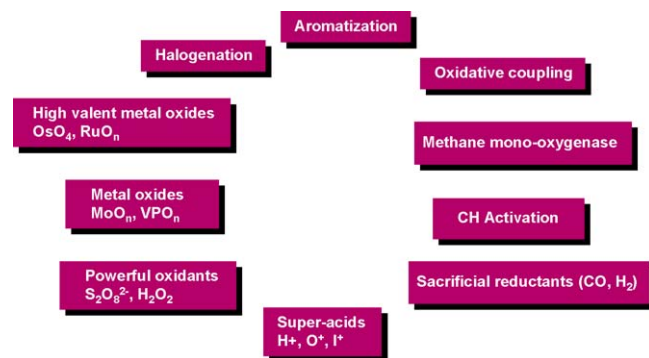


Fig. 8. Broad classification of the various approaches being examined for the direct conversion of methane.

or selectivity requirements by modifying the catalyst structure and composition and then after that target is met, attempting to modify the catalyst to meet the other two performance requirements.

Significantly, such a sequential approach to catalyst design may not be the most efficient because focused structural, compositional and reaction system modifications to meet one requirement can lead to catalyst motifs that cannot be efficiently (or indeed, at all) modified to meet the other performance requirements. This emphasizes that an effective strategy to developing useful catalysts should involve *simultaneous* consideration of all structure–function relationships that relate to stability, rate and selectivity. This can be challenging because such an approach can severely restrict the range of catalyst structures and compositions to be examined.

There has been significant effort devoted to the development of catalysts for the direct conversion of methane to useful products. A broad classification of the various approaches being examined is shown in Fig. 8. Considering the general guidelines discussed above that emphasize the need for high product selectivity (to ensure high atom efficiency) a useful method of evaluating these various approaches would be to compare the maximum yields of the products obtained at greater than 90% selectivity to methyl products. Such a comparison shown in Fig. 9. As can be seen, the approach that shows the highest yields at high selectivity are based on CH activation chemistry. CH activation is defined as a two step process in which (1) the CH bond

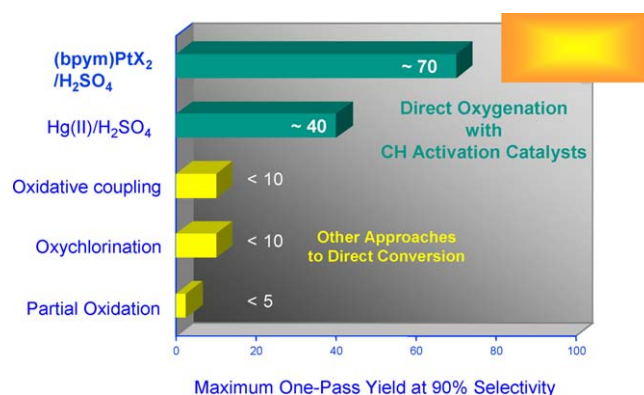


Fig. 9. Comparison of known methane functionalization systems.

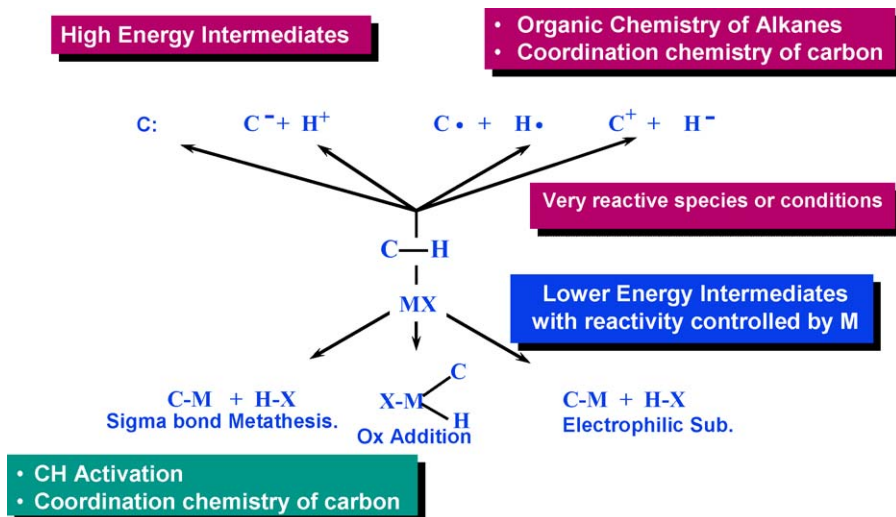


Fig. 10. A key advantage of the CH activation reaction is that, unlike classical reactions of the CH bond, the reaction can occur with moderately energetic materials and conditions.

of an unactivated hydrocarbon coordinates to an open site at a transition metal center followed by (2) cleavage of the CH bond to form a well defined metal–carbon bond. Mechanistic studies have shown that there are three predominant pathways that operate in known CH activation systems: sigma bond metathesis, oxidative addition, and electrophilic substitution.

As shown in Fig. 10, a fundamental basis for the higher efficiency of CH activation-based catalysts is that the CH activation reaction can be made to occur without the involvement of high energy intermediates. As can be seen, the classical chemistry of the CH bond typically involves the generation of intermediates such as free radicals, carbocations, carbanions or carbenes. Since these intermediates are highly energetic species, their formation

requires very reactive conditions, such as extreme temperatures or very energetic reagents (i.e. superacids or peroxides). The key advantage of the CH activation reaction is that, to our knowledge, it is the only reaction that can cleave the CH bond of alkanes using moderately energetic conditions and reagents.

The high selectivity and facile reaction conditions that are characteristic of most organic reactions arise because these processes involve atom-transfer reactions within the coordination sphere of carbon. Similarly, the facile nature of the CH activation reaction can be attributed to atom transfer within the coordination sphere of carbon and the reactant, MX, as shown in Fig. 11. As for the case for organic reactions, coordination catalysis can be facile and selective. An excellent example that

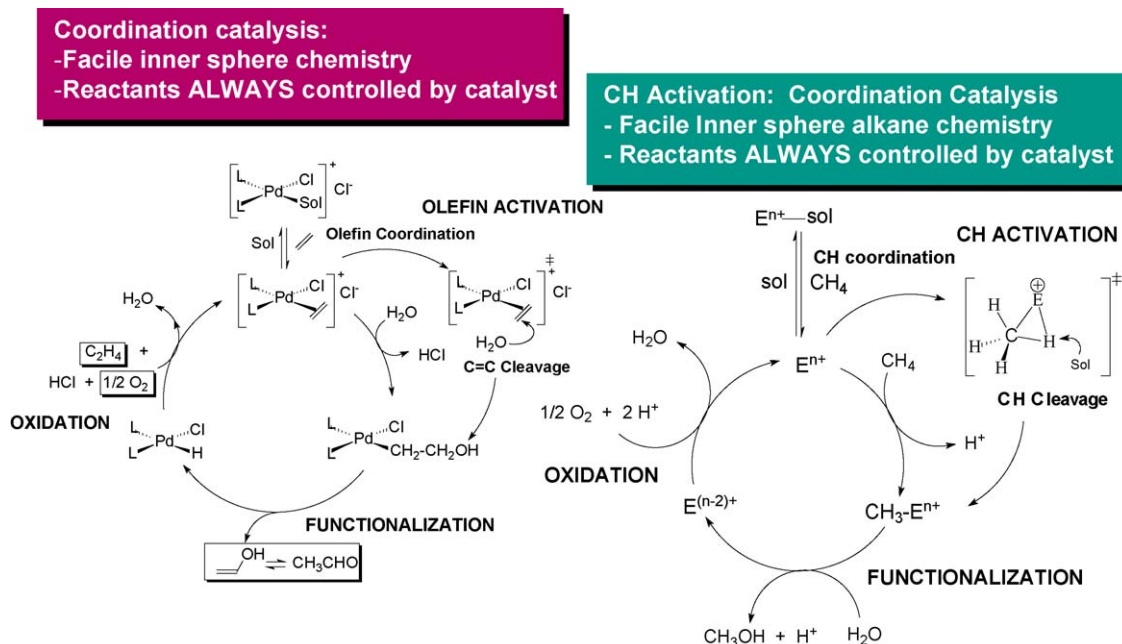


Fig. 11. Comparison showing that electrophilic CH activation-based oxidation and Wacker catalysts operate by coordination chemistry involving the formation of organometallic intermediates and an oxidative functionalization reaction.

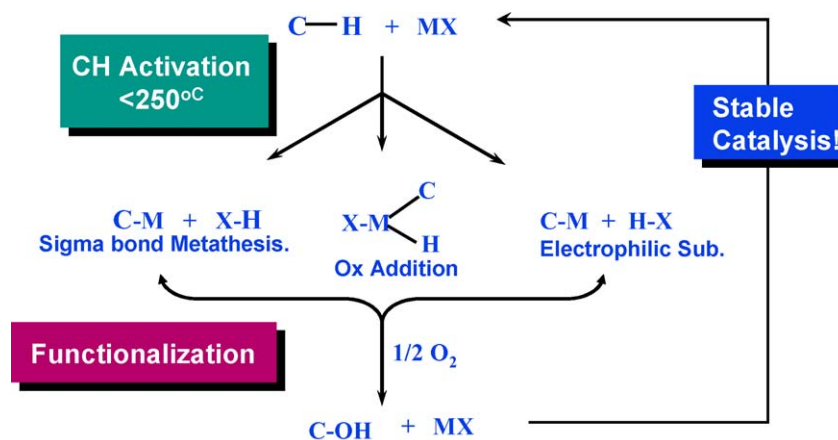


Fig. 12. Incorporating the “CH activation” reaction into a catalytic system requires integration with a functionalization reaction and stable systems.

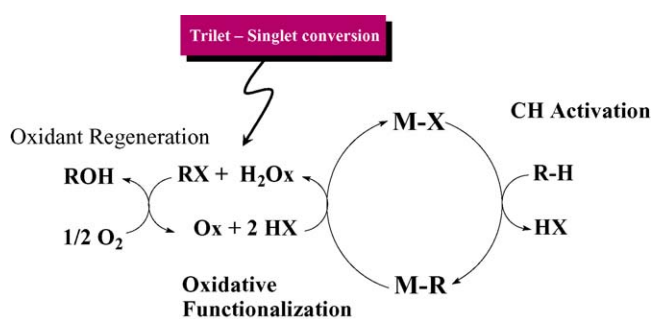


Fig. 13. Wacker type system can avoid issues with unselective free-radical reactions and likely explosive mixtures.

is relevant to the development of coordination catalysts for the selective oxidation of alkanes is the palladium catalyzed oxidation of olefins; the Wacker reaction. As shown in Fig. 11, this system involves the coordination of the olefin to the electrophilic Pd(II) center, followed by nucleophilic attack of water to generate a Pd organometallic intermediate (olefin activation)

and finally oxidative functionalization to generate the oxidized product and regenerate the catalyst. These key steps, coordination of the CH bond to an electrophilic center, nucleophilic attack to generate organometallic intermediates (CH activation) followed by oxidative functionalization have also been identified in the most efficient CH activation-based catalysts for alkane oxidation. The fundamental difference between the oxidation of olefins in the Wacker process and the oxidation of alkanes is, of course, that olefins are much more powerful nucleophiles. As such, much less powerful electrophilic catalysts are required to activate olefins as compared to alkanes.

As shown in Fig. 12, several types of CH activation reactions are known, three of which are shown; so-called sigma bond metathesis, oxidative addition and electrophilic substitution. The key to utilizing the CH activation in a catalytic reaction is to develop stable systems that can be integrated with a functionalization reaction to generate, for example, alcohols.

Many schemes could be considered for such integration. Reactions involving direct combination of the alkane and oxygen gas would be theoretically ideal. However, practical

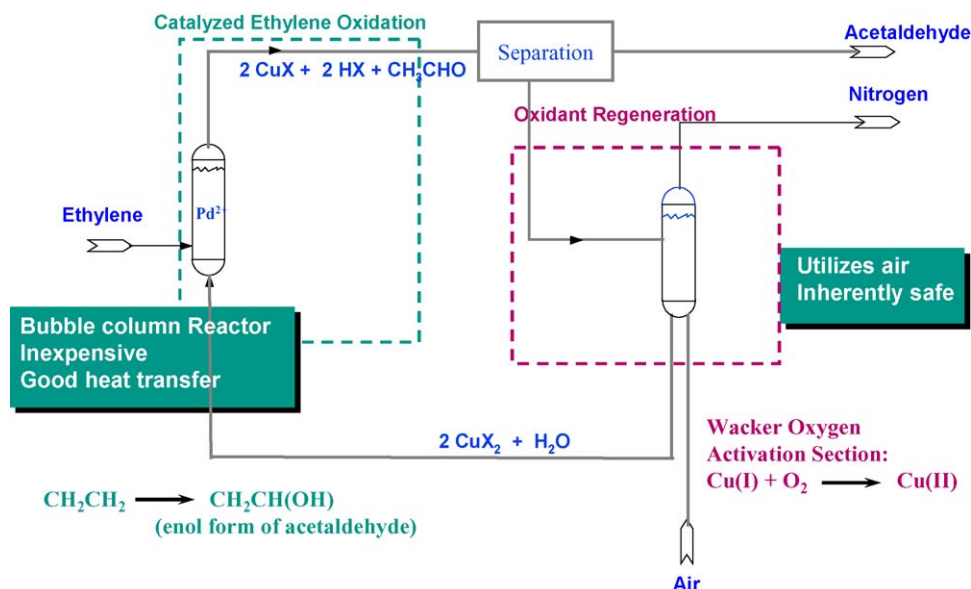


Fig. 14. Wacker system for conversion of ethylene to acetaldehyde.

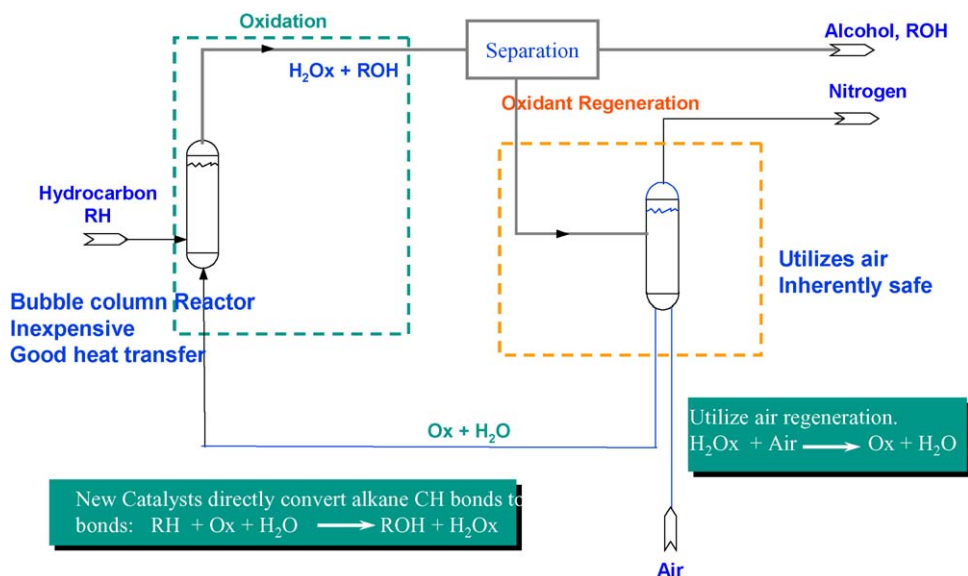


Fig. 15. Proposed Wacker type system for conversion of alkanes to alcohols.

considerations, such as avoiding explosive gaseous mixtures and minimizing free radical reactions due to the triplet ground state of oxygen, suggest that the Wacker type scheme, which employs a stoichiometric, air recyclable oxidant in a direct reaction with the alkane, could be preferred. A simplified process diagram for such a scheme is shown in Fig. 13. In the Wacker system for the oxidation of ethylene to acetaldehyde catalyzed by Pd(II), the role of this stoichiometric, air recyclable oxidant is filled by Cu(II).

A simplified schematic of the reactor design for the Wacker process is shown in Fig. 14. As can be seen, two key advantages of utilizing this process design are: (A) air, instead of pure oxygen, can be utilized for the reoxidation and (B) that simple inexpensive, gas–liquid, bubble column reactors can be

employed. Since these reactors can be designed to operate at comparable pressures and temperatures, there is no disadvantage to separating the alkane reaction from reactions with air. Significantly, as shown in Fig. 15 the Wacker process can be adapted for the conversion of alkanes to alcohols if new catalysts can be designed to convert alkanes to alcohols under these reaction conditions.

This Wacker type design has been embodied in the most effective system that has been reported to date for the oxidation of methane to methanol; the Catalytica Pt(bpym)Cl₂/H₂SO₄ system. In this case, the overall reaction is the desired reaction of methane and air to generate methanol. The reaction proceeds with >70% yield (based on added methane) and a selectivity to methanol of greater than 90% and is carried out at 220 °C,

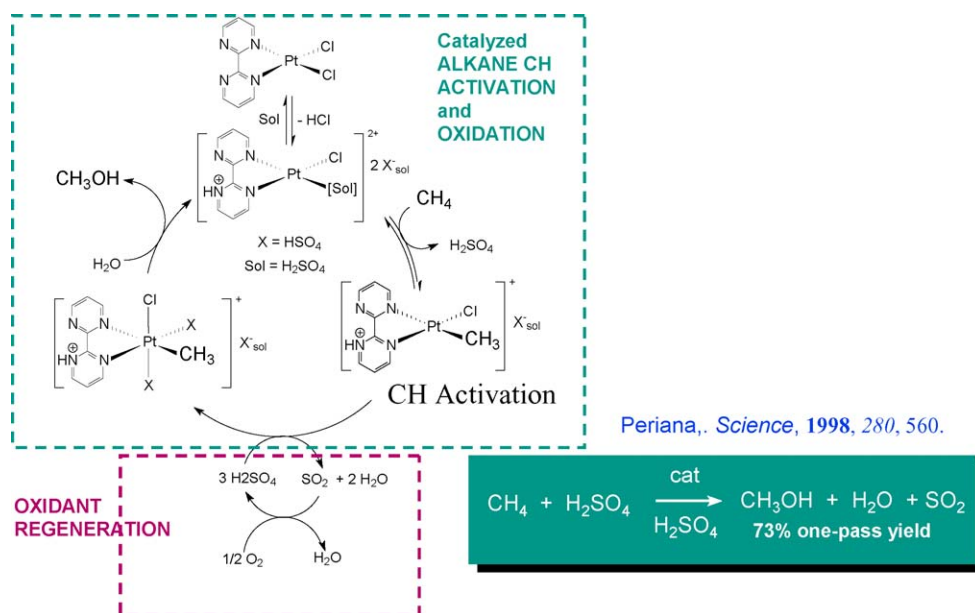


Fig. 16. Proposed reaction mechanism of the Pt(bpym)Cl₂/H₂SO₄ system for the selective oxidation of methane to methanol illustrating the use of S(VI) in H₂SO₄ as a stoichiometric, air recyclable oxidant.

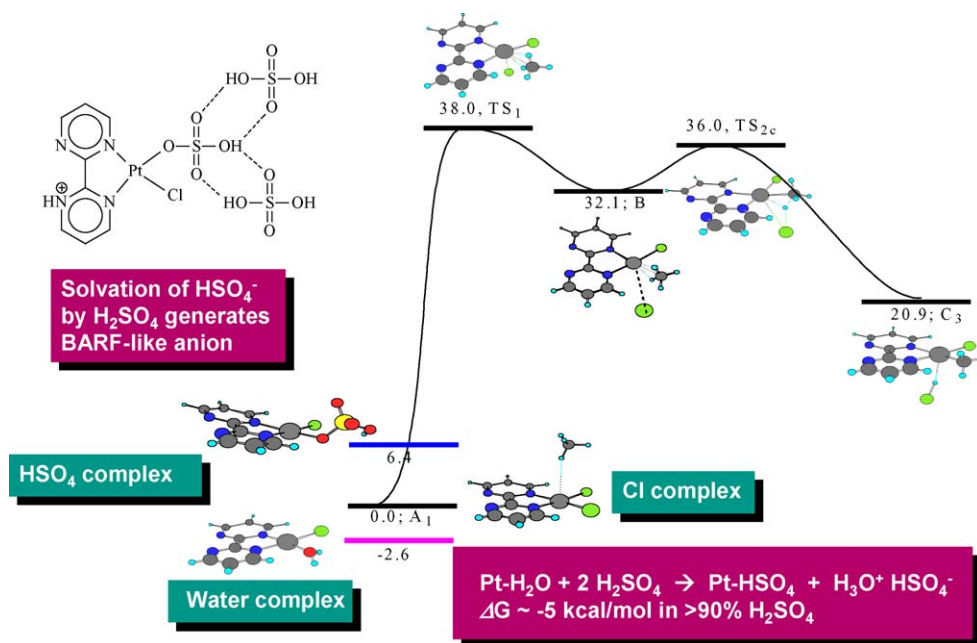


Fig. 17. Simplified energy diagram showing the inhibition of the Pt(bpy)X₂ catalyst by water.

operates at a volumetric productivity (STY of $\sim 10^{-7}$ mol/cm³ s), and meets many of the process requirements for a commercial catalyst system. As shown in Fig. 16, the role of the stoichiometric, air recyclable oxidant in this system is played by S(VI) in H₂SO₄ and the catalyst for converting methane to methanol is the Pt(bpy)Cl₂ complex. During the oxidation of methane to methanol with H₂SO₄, catalyzed by this complex, S(VI) is reduced to S(IV) in the form of SO₂. Gaseous SO₂ can then be recycled by treatment with air to generate SO₃, S(VI), which is absorbed into water. Though it adds some cost, the SO₂ reoxidation step is well-established technology based on industrially practiced sulfuric acid chemistry and is not the pri-

mary reason the system has not been commercialized. The key requirement to make the system efficient enough to be commercialized is to increase the catalyst rate from TOF = $\sim 10^{-3}$ s⁻¹ to a TOF of ~ 1 s⁻¹, while operating below 96% sulfuric acid solvent. Of course, replacing sulfuric acid with a less corrosive solvent of low or nonacidic character would also be desirable if these catalyst rates can still be achieved.

Experimental studies have shown that while the rate determining step for the system in >90% sulfuric acid solvent is the oxidation of Pt(II) to Pt(IV), this is not the case in the lower concentrations of sulfuric acid (50–80%) that are more practical. Under these conditions, the overall oxidation reaction is

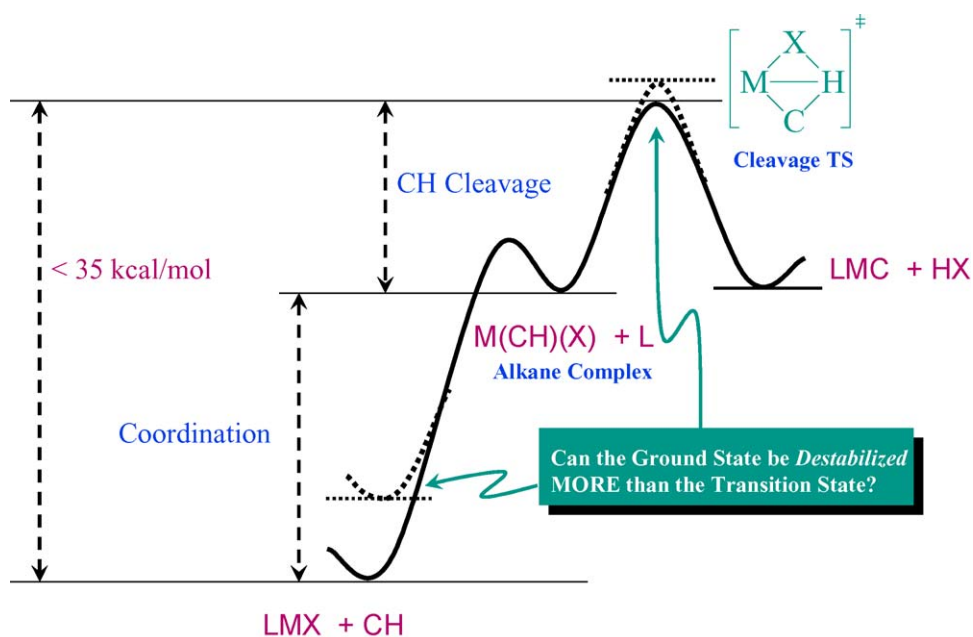


Fig. 18. Reaction profile for the CH activation reaction: ground state destabilization must be a greater than transition state destabilization to lower the overall barrier.

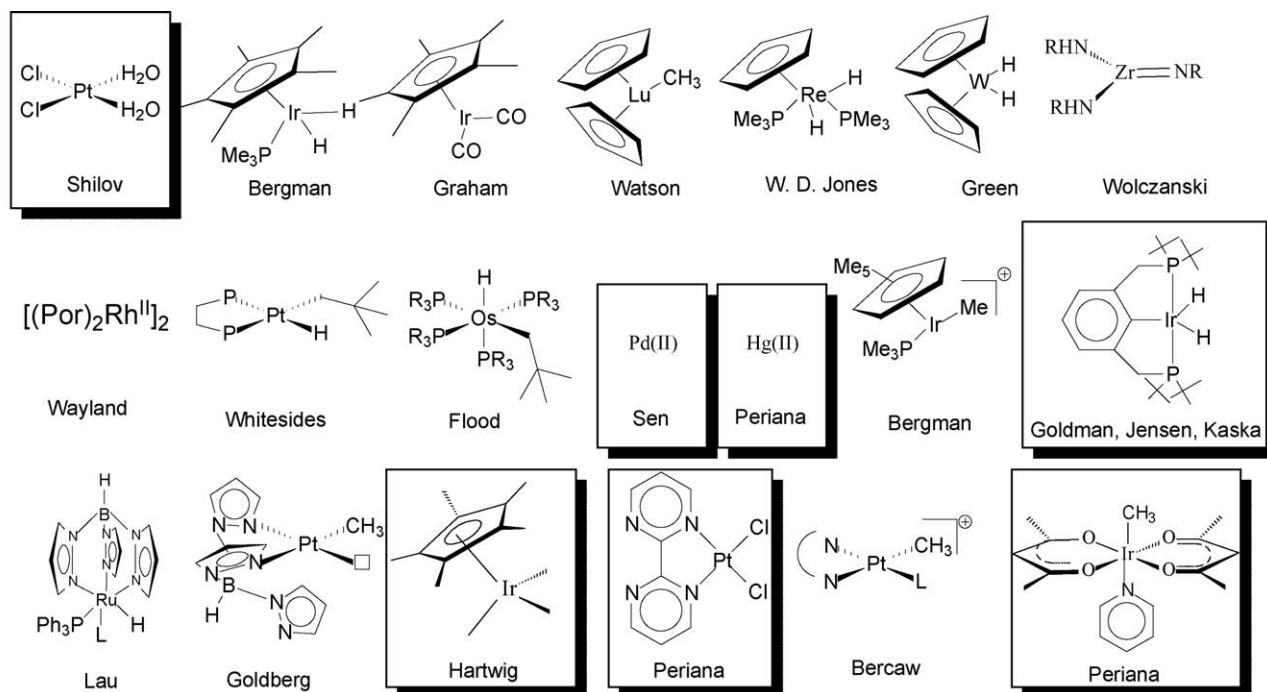


Fig. 19. Many complexes capable of CH activation have now been reported. However, relatively few have been utilized in catalytic reactions for the conversion of alkanes to useful products.

severely inhibited and the rate limiting step becomes cleavage of the CH bond; the CH activation step. Theoretical and experimental studies show, Fig. 17, that this results from the ground state stabilization (~ 10 kcal/mol relative to the HSO₄ complex) of the platinum complex by reversible binding to water or methanol. Consequently, the key to developing improved systems that could be commercially viable is to develop CH activation systems that are not inhibited by water and are also stable to the conditions required for functionalization to occur at a TOF of ~ 1 s⁻¹.

These studies indicate that while we tend to think of the CH activation reaction in the context of breaking the CH bond, it is instructive to consider the overall CH activation reaction as composed of two steps since the CH activation is a coordination reaction. This is shown schematically in Fig. 18, where the overall CH activation reaction is shown to be composed of two key steps: (A) coordination to generate an alkane complex and (B) the CH bond cleavage. Indeed, our studies have shown that in some cases (particularly in systems that activate the CH bond by electrophilic substitution), the bulk of the activation barrier for the overall CH activation step (and formation of the M–C intermediate) can be associated with the coordination of the CH bond to the metal center rather than with the actual breaking of the CH bond. Thus, in the case of the Pt(bpym)Cl₂ system, the thermodynamics associated with coordination of the alkane to the platinum center contributes approximately 32 kcal/mol while the activation barrier for cleavage from the alkane complex is only ~ 4 kcal/mol.

It is useful to distinguish between the steps because it is likely that the steric and electronic requirements are different for binding of the alkane and cleavage of the CH bond. As shown in Fig. 18, the key challenge in designing complexes that would not

be inhibited by water is to destabilize the catalyst ground state (e.g. the water complex) *without proportionately* destabilizing the transition state for the cleavage step. While this is expected to be challenging, it should be possible given the differences in bonding between the states.

As can be seen in Fig. 19, many examples of CH activation complexes have been reported. However, relatively few (those shown in boxes) have been utilized to develop catalytic systems for the conversion of alkanes to useful products [3]. We believe the primary reason for this is that most of the CH activation systems that are known are either: (A) unstable to conditions required for product formation, (B) restricted by CH activation reactions that are impractically slow under the conditions required to generate a product or (C) produce an M–C intermediate from CH Activation that cannot be functionalized under catalytic conditions.

To address these issues our focus has been on developing new CH activation catalysts that: (A) are stable to the conditions required for product formation, (B) operate at a TOF of ~ 1 s⁻¹ and not inhibited by water or desired reaction products and (C) create an M–C intermediate that would be readily functionalized to oxygenated or other functionalized products. Reasoning that O, N and C chelating ligands could be stable to the likely elevated temperatures, oxidizing, and potentially protic conditions required for functionalization of the M–C intermediates, we are designing new complexes to carry out the CH activation reaction based on new ligand motifs. Fig. 20 shows examples of some of the ligand motifs that are under investigation.

In an attempt to address the key issue of water inhibition, we have been examining modifications of the Pt^{II}(bpym)Cl₂ catalyst that increase the electron density at the platinum center, as this could be expected to destabilize the ground state by

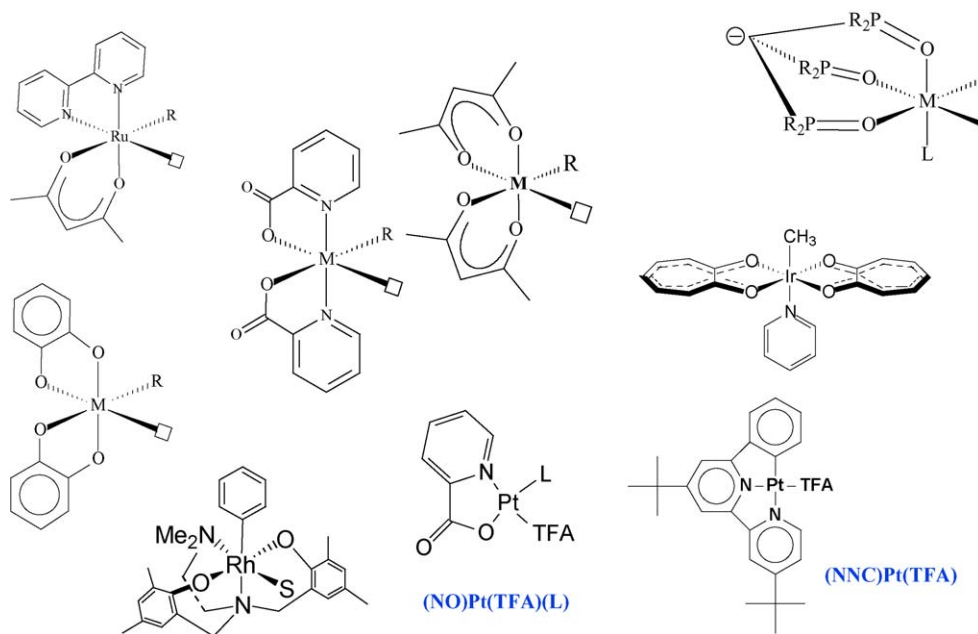


Fig. 20. Examples of ligand motifs that are being investigated for designing new CH activation complexes that could be expected to be stable to conditions required for functionalization.

decreasing the affinity for binding to water. Thus, for example, two examples of ligand motifs under consideration are the anionic $[(\text{NO})\text{Pt}^{\text{II}}(\text{TFA})_2]^-$ and neutral $(\text{NNC})\text{Pt}^{\text{II}}(\text{TFA})$ complexes shown in Fig. 21 (TFA = trifluoroacetate, CF_3COO^-). The inclusion of O- and C-donor ligands in these complexes is expected to lead to the desired increase in electron density at the platinum center and the potential for weaker binding to water.

The theoretical studies of the $[(\text{NO})\text{Pt}(\text{TFA})_2]^-$ complex show that the overall barrier for CH activation of benzene (~ 21 kcal/mol) is less than that for the $\text{Pt}(\text{bpym})(\text{TFA})_2$ com-

plex (27.3 kcal/mol) (Fig. 21). The ground state for the NO ligated complex is $[(\text{NO})\text{Pt}(\text{TFA})_2]^-$ in trifluoroacetic acid solvent (TFA-H). Our expectation that the trifluoroacetate anion should be more labile in the anionic, NO ligated complex than in the corresponding neutral bis-TFA complex, $\text{Pt}(\text{bpym})(\text{TFA})_2$, is consistent with the calculated energetics for benzene coordination. In the case of the anionic complex, $[(\text{NO})\text{Pt}(\text{TFA})_2]^-$, benzene coordination is ~ 5 kcal/mol. Coordination for the neutral complex $\text{Pt}(\text{bpym})(\text{TFA})_2$ is ~ 14 kcal/mol, a significant difference of ~ 9 kcal/mol. However, while increasing electron

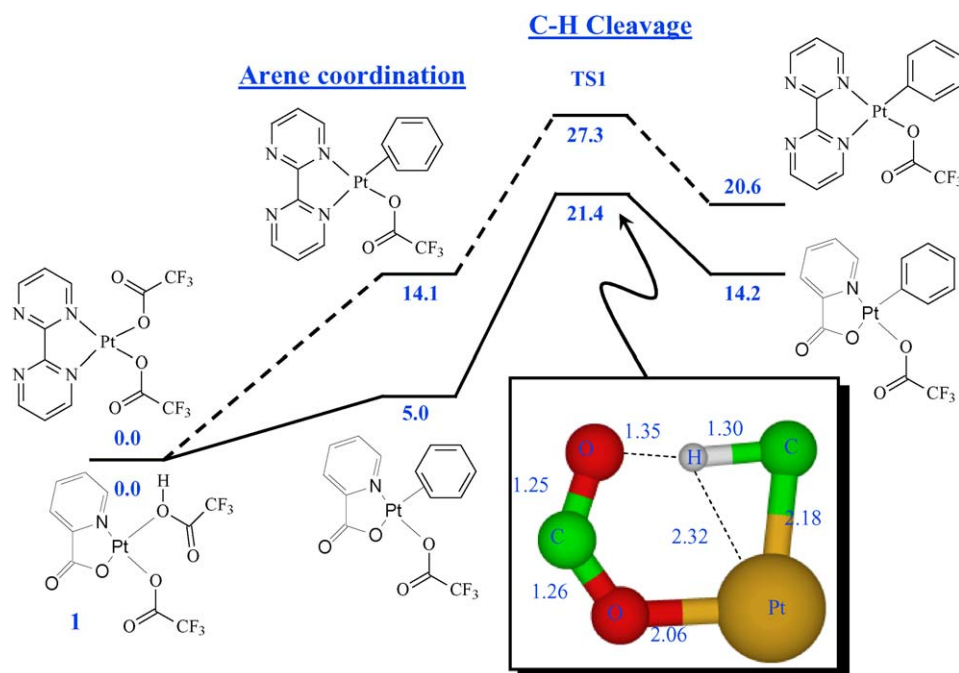


Fig. 21. Thermodynamic comparison of proposed reaction pathways shows ground state destabilization favors CH activation for $[(\text{NO})\text{Pt}(\text{TFA})_2]^-$.

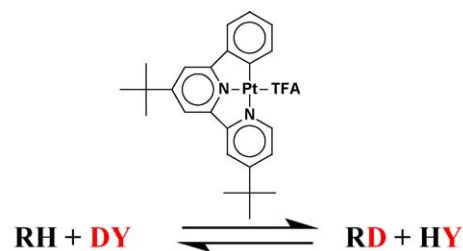
density at the metal center (the calculated Mulliken charge of the Pt centers in the $[(\text{NO})\text{Pt}(\text{TFA})_2]^-$ and $\text{Pt}(\text{bpym})(\text{TFA})_2$ complexes are $\sim +0.6$ and $+0.8$, respectively) could be expected to facilitate the loss of hard, oxygenated solvents (by ground state destabilization) and subsequent coordination of benzene, the reduced electrophilicity at the more electron rich center could be expected to increase the barrier for the CH cleavage by destabilization of the transition state, TS1 (assuming an electrophilic CH cleavage step pathway). This could potentially result in an overall barrier for CH activation that is unchanged or even higher, as the electron density at the metal is increased. Of course, there is no requirement that these changes correlate linearly. It is interesting to note that this is not the case in the two systems under study as there is an overall reduction in the calculated activation barrier.

The transition states for the CH cleavage steps with these two complexes both show that the proton-transfer from benzene occurs to the free oxygen of coordinated TFA via a six-membered ring (Fig. 21). However, since the CH cleavage transition states are similar for both NO and NN–Pt complexes this does not explain why the transition state for the CH cleavage step is not destabilized to a greater extent in the more electron rich NO–Pt complex. We considered that the more electron rich complex may switch mechanism to an oxidative addition pathway, but there is no evidence for a Pt–H bond (2.32 Å) in the transition state for the CH cleavage with the NO–Pt complex. A possible explanation is that electron density changes have a greater impact on bonding to hard species, such as oxygenated ligands, because of the greater importance of ionic bonding in the transition state compared to soft species where covalent bonding is more important.

Investigation into the ability of these complexes, $[(\text{NO})\text{Pt}(\text{TFA})_2]^-$ and $\text{Pt}(\text{bpym})(\text{TFA})_2$, to catalyze H/D exchange between C_6H_6 and $\text{CF}_3\text{CO}_2\text{D}$ solvent shows that the $[(\text{NO})\text{Pt}(\text{TFA})_2]^-$ complex is stable and ~ 300 times faster than $\text{Pt}(\text{bpym})(\text{TFA})_2$ system. This suggests that increasing electron density at the metal center, while maintaining catalyst stability, is a promising direction in which to focus our research and one that we are continuing to explore.

Emphasizing the importance that the design of efficient catalysts require simultaneous consideration of rate, selectivity and stability, we have found that though $[(\text{NO})\text{Pt}(\text{TFA})_2]^-$ is stable and more efficient than the $\text{Pt}(\text{bpym})(\text{TFA})_2$ complex in trifluoroacetic acid, it could not be studied in sulfuric acid due to thermal instability. Similarly, the NO–Pt system, but not the NN–Pt system, was found to react with methane in trifluoroacetic acid at higher temperatures ($\sim 175^\circ\text{C}$) but was also unstable under these conditions. Preliminary studies of the oxidation of benzene with added oxidant to the $[(\text{NO})\text{Pt}(\text{TFA})_2]^-/\text{TFA-H}$ system shows the formation of phenyl trifluoroacetate. The studies are ongoing in an attempt to develop an oxidation system for conversion of benzene to phenyl trifluoroacetate.

A related Pt system we have been examining is the $(\text{NNC})\text{Pt}(\text{TFA})$ complex shown in Fig. 22. This system is more electron rich than the $\text{Pt}(\text{bpym})\text{Cl}_2$ system (one Cl is substituted for a C) and it also more stable than $[(\text{NO})\text{Pt}(\text{TFA})_2]^-$ as it can be heated in $\text{CF}_3\text{CO}_2\text{H}$ up to 200°C for hours with-



RH	DY	TOF (sec^{-1})	Comments
C_6H_6	$\text{CF}_3\text{CO}_2\text{D}$	1.9×10^{-4}	170°C , stable
CH_4	$\text{CF}_3\text{CO}_2\text{D}$	no rxn	180°C , stable
CH_4	D_2SO_4	5×10^{-4}	180°C , stable Trace MeOH

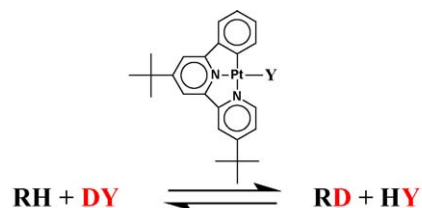
Fig. 22. TOF for H–D exchange between various acid and hydrocarbons.

out decomposition. Significantly, this complex catalyzes HD exchange between benzene and trifluoroacetic acid, Fig. 23, and also shows reactivity with methane in sulfuric acid, where trace levels (above background reaction) of methanol have been observed (Fig. 22). However, the system is not more active than the $\text{Pt}(\text{bpym})\text{Cl}_2/\text{H}_2\text{SO}_4$ system for the production of methanol.

The calculated activation barrier of ~ 34 kcal/mol for the proposed CH activation reaction of benzene, Fig. 22, compares well with experimental values of ~ 32 kcal/mol. Comparison of catalytic H/D exchange rates shows that synthesized $(\text{NNC})\text{Pt-Ph}$ and $(\text{NNC})\text{Pt}(\text{TFA})$ are comparable catalysts, which is consistent with the formation of a $(\text{NNC})\text{Pt-Ph}$ intermediate from the CH activation of benzene with the $(\text{NNC})\text{Pt}(\text{TFA})$ complex.

We are exploring the theoretical and experimental basis for the reaction of this complex with benzene under oxidizing conditions with the objective of developing catalysts for the oxidation of benzene to phenol or phenyl esters. Interestingly, no net oxidation of benzene has been observed. We are synthesizing the discrete proposed catalyst intermediates in order to understand the basis for this lack of oxidation. It is important to understand if the mechanism shown in Fig. 24 is viable (overall activation barrier < 35 kcal/mol) and, if so, which of the steps shown in the proposed mechanism is not proceeding with the oxidants under study.

An important consideration is that as the $\text{Pt}(\text{bpym})\text{Cl}_2$ complex is modified to increase the electron density of the platinum



RH	DY	Y	TOF (sec^{-1})	Comments
C_6H_6	$\text{CF}_3\text{CO}_2\text{D}$	CF_3CO_2	1.9×10^{-4}	170°C , stable
C_6H_6	$\text{CF}_3\text{CO}_2\text{D}$	Ph	1.4×10^{-4}	170°C , stable

Fig. 23. HD exchange between benzene and D-TFA.

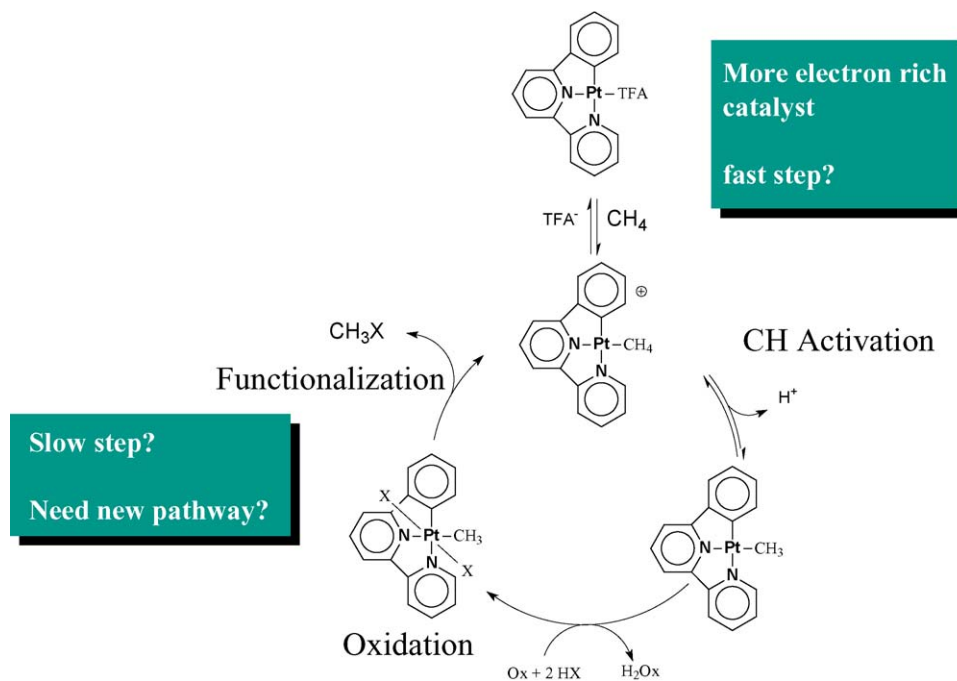


Fig. 24. Proposed mechanism for CH activation and functionalization for (NNC)Pt(TFA).

center, the rate of functionalization could decrease if the electrophilicity of the platinum center is important for the functionalization step, as was shown for the Pt(bpym)Cl₂/H₂SO₄ system [4]. Indeed, this is likely the case when using metals to the left of platinum in the periodic table. Thus, while facile CH activation is well known with more electron-rich, less oxidizing systems based on the middle or early transition metals such as Ir, Ru, Zr, etc. [5], to our knowledge, these systems have not been incorporated into catalytic cycles that generate oxy-functionalized products. This is likely because reductive heterolysis or elimination reactions of the M–R intermediates are not facile and/or the systems are not stable to the conditions required for oxy-functionalization (likely due to the increased oxophilicity of these metals). Thus, to develop single-site oxidation catalysts based on these systems it is likely that new systems that are stable and exhibit both new CH activation and oxy-functionalization reactions will be needed.

To begin to develop such systems with the middle transition metals we are investigating the development of catalytic cycles based on the reaction of O-donor metal-alkoxo complexes with CH bonds as shown in Fig. 25. This is of interest because as

shown, the reaction can lead to the simultaneous CH activation of the hydrocarbon and formation of a desired oxy-functionalized product, ROH. We have reported evidence for the first step of this conceptual catalytic cycle; facile, selective CH activation with a metal alkoxo complex (acac)₂Ir(OCH₃)(L), where L = CH₃OH or pyridine (Py) [6]. The observation of such a one step CH activation/oxy-functionalization reaction is significant since, to our knowledge, there is no precedent for this CH activation reaction [6] and because we anticipated possible complications due to: (A) decomposition of the alkoxo complexes by facile β-hydride elimination reactions or formation of inert dinuclear complexes and (B) destruction of the alcohol product during the CH activation reaction of RH. Developing reactions for the oxidation of the M–R intermediate to M–OR, for which there is precedent via free-radical as well as non-free radical reactions [7], would complete the catalytic cycle.

The (acac)₂Ir(OCH₃)(CH₃OH) complex was synthesized from the known [Ir(μ-acac-O,O,C3)(acac-O,O)(acac,C3)]₂ using sodium methoxide in methanol. Conversion to (acac)₂Ir(OCH₃)(Py) is facile with the addition of pyridine. Both complexes were shown to activate benzene,

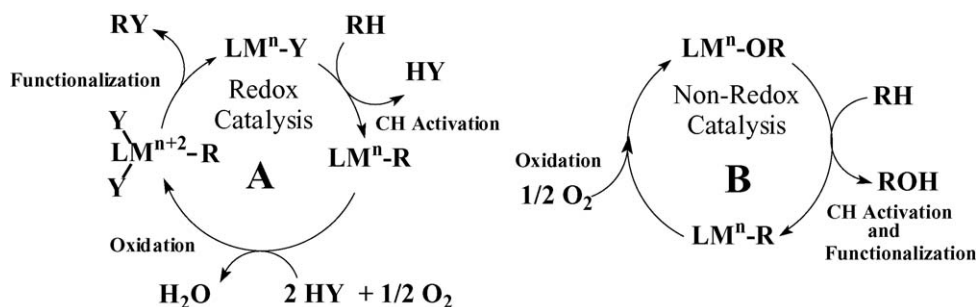


Fig. 25. Redox (A) and non-redox (B) catalytic sequences for functionalization of hydrocarbons via CH bond activation.

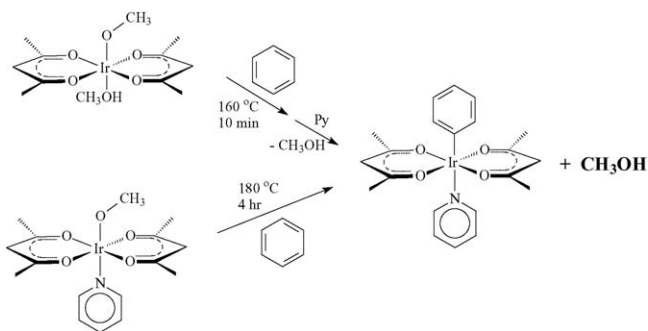


Fig. 26. CH activation of benzene by $(\text{acac})_2\text{Ir}(\text{OCH}_3)(\text{L})$.

simultaneously producing the isolable Ir–Ph compound and methanol as in Fig. 26. It is significant that this CH activation reaction is thermodynamically favorable and proceeds cleanly and in high yield given the possibility for side reactions. This suggests that the CH activation reaction of this d6, O-donor Ir(III)-methoxo is substantially different from that of d6, Ru(II)– NH_2 complexes where stoichiometric CH activation is calculated to be unfavorable and has not been observed. Possible π -type destabilizing interactions between the O-donor ligands, the d6 Ir(III) center and the –OMe group along with the increased electronegativity of the Ir in an O-donor ligand field could account for the favorable thermodynamics for this CH activation reaction. It is also likely that these properties of the Ir center in an O-donor ligand field could serve to minimize the expected irreversible side reactions of metal alkoxides such as: (A) β -hydride elimination reactions due to the reduced electron density at the metal center or (B) the formation of bridging alkoxo complexes by the *cis*-labilization effect of π -donor spectator O-ligands [8].

The theoretical calculations on this system are consistent with the reaction proceeding via the coordination pathway shown in Fig. 27. The observation that $(\text{acac})_2\text{Ir}(\text{OCH}_3)(\text{Py})$, reacts more slowly than $(\text{acac})_2\text{Ir}(\text{OCH}_3)(\text{CH}_3\text{OH})$ is consistent with the

requirement for reversible loss of L since pyridine is a less labile ligand than methanol. The calculated barrier (23.4 kcal/mol) and favorable thermodynamics (-17.1 kcal/mol) of the reaction with $(\text{acac})_2\text{Ir}(\text{OCH}_3)(\text{CH}_3\text{OH})$, are consistent with the reaction proceeding at 160°C in ~ 10 min and in good yield. Interestingly, the transition state for C–H cleavage appears to be best described as a formal σ -bond metathesis. This can be observed in the Ir–H distance of 1.98 \AA , Fig. 27, which corresponds to classical σ -bond metathesis geometry. Pathways involving oxidative addition, oxidative hydrogen migration [9], or ionization of the methoxido group were all found to be higher in energy. It is not yet clear why this system favors a σ -bond metathesis mechanism over one involving oxidative addition. Possible reasons could be that the lone pair on the methoxo oxygen facilitates the hydrogen transfer and the decreased electron-density of an Ir with five electronegative O-donor ligands disfavors a transition state with oxidative addition character.

Transition metal alkoxides are well known to decompose to metal hydrides via β -hydride elimination reactions [10] and Ir–H's are well documented to be highly active for CH activation reactions [11]. For the CH activation reaction to proceed via a mechanism involving Ir–H the formation of an Ir–H must necessarily be reversible to account for the stoichiometric formation of MeOH. To examine this possibility we investigated the reaction of $(\text{acac})_2\text{Ir}(\text{O}^{13}\text{CH}_3)(\text{Py})$ with C_6D_6 as the Ir–H pathway would be expected to lead to generation of the $\text{D}_{13}\text{CH}_2\text{OD}$ isotopomer whereas the proposed σ -bond metathesis would lead to $^{13}\text{CH}_3\text{OH}(\text{D})$. ^{13}C NMR spectroscopy of the crude reaction mixture showed that only $^{13}\text{CH}_3\text{OH}(\text{D})$ was formed [12]. Ruling out this intermediate substantiates our interest in further investigating M–OR species as part of the proposed catalytic cycle.

We have also found that $(\text{acac})_2\text{Ir}(\text{OCH}_3)(\text{L})$ catalyzes H/D exchange between D_2O and C_6H_6 at 160°C . We anticipate that the Ir– OCH_3 is converted to the related Ir–OH complex that reversibly activates the CH bonds of benzene generating Ir–Ph and water. In ongoing efforts we are examining the extension

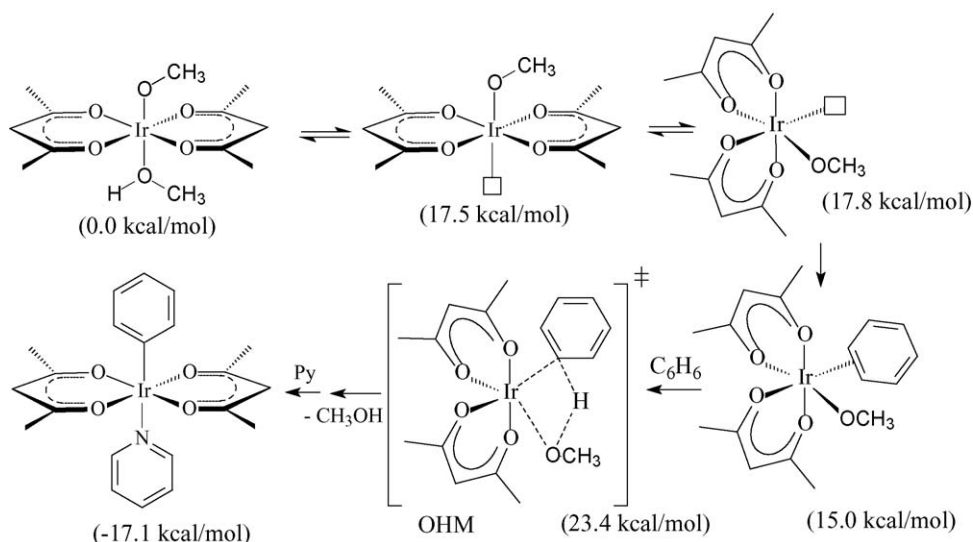


Fig. 27. Proposed mechanism for the reaction of $(\text{acac})_2\text{Ir}(\text{OCH}_3)(\text{CH}_3\text{OH})$ (values in parenthesis are calculated ΔH).

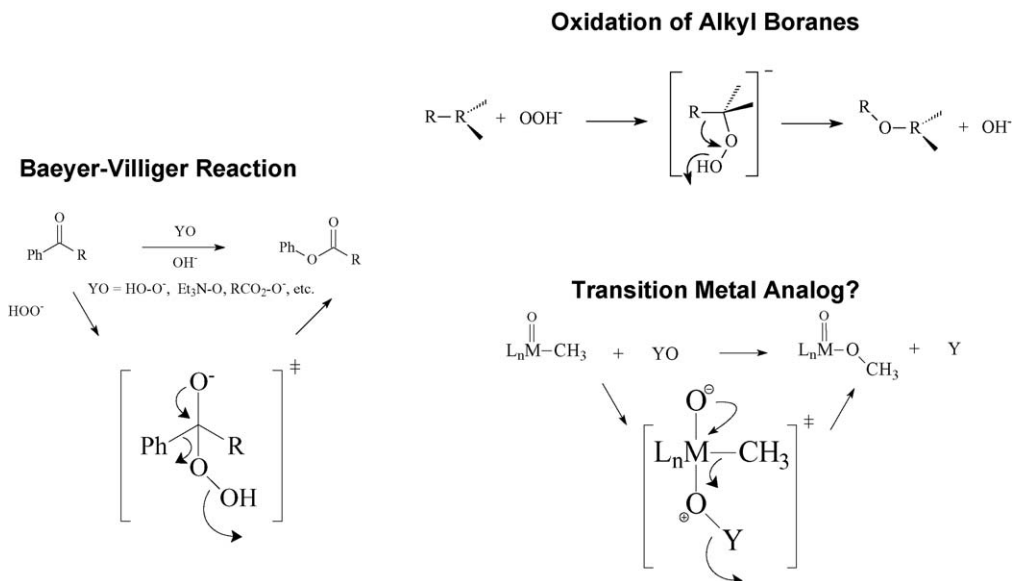


Fig. 28. Baeyer–Villiger and alkyl borane reactions and comparison to possible transition metal analog.

this chemistry to the discrete hydroxo, phenoxy and *t*-butoxy complexes as well as to the CH activation of alkanes.

In addition to working on the CH activation reaction with these metal alkoxide and related species, we have begun to develop reactions to oxidize metal hydrocarbyl complexes to the corresponding alkoxides under none free-radical conditions, a reaction that would complete the proposed catalytic cycle. Mayer has shown that well-defined $\text{Re}^{\text{V}}(\text{O})\text{R}$ species can react with O-atom donors such as dimethyl sulfoxide (DMSO) and pyridine-*N*-oxide (PyO) to generate the corresponding $\text{Re}-\text{OPh}$ complexes via metal-oxo intermediates [13]. To be incorporated into a catalytic cycle for the overall conversion of hydrocarbons to alcohols, this reaction will have to be facile. In an attempt to develop facile, new pathways for the conversion of metal hydrocarbyl complexes to metal alkoxides, we considered analogous reactions from organic chemistry; the Baeyer–Villiger reaction for the conversion of ketones to esters and the oxidation of alkyl boranes to alkyl borates, shown in Fig. 28. In the organic reaction a C–C bond is cleaved under relatively mild conditions to generate a C–O–C bond. Considering the carbonyl carbon atom analogous to the metal of a metal-oxo species suggests that the reaction of $\text{R}-\text{M}(\text{O})$ complexes with hydrogen peroxide and other O-atom donors could proceed via a Baeyer–Villiger pathway as the most facile reaction mechanism.

To examine this possibility, we have begun a study of the reaction of the well-known methyl trioxo rhenium complex, MTO, and the mechanism for its reported conversion to methanol in reactions with hydrogen peroxide and other O-atom donors. The room temperature conversion of MTO to methanol in the presence of basic hydrogen peroxide solutions has been reported in the context of studying the basis for decomposition of the MTO catalyst under conditions required for epoxidation of olefins [14]. Several pathways have been proposed, but to our knowledge the Baeyer–Villiger pathway was not considered. Additionally, only hydrogen peroxide had been examined for reactions with MTO to generate methanol.

As shown in Fig. 29, the Baeyer–Villiger or alkyl borane type pathway is the most viable for the reaction of MTO with basic hydrogen peroxide to generate methanol with an overall activation barrier of ~ 22 kcal/mol. The details of this reaction pathway shown in Fig. 30, involve coordination of HOO^- to MTO to generate a stable anionic species. This intermediate undergoes the Baeyer–Villiger type rearrangement with an activation barrier of ~ 22 kcal/mol by migration of the methyl group to the alpha-oxygen of the coordinated HOO^- anion to generate a methoxy rhenium trioxide intermediate with displacement of the hydroxide anion. Rapid hydrolysis of the methoxy rhenium trioxide intermediate leads to the observed products, methanol and the perrhenate anion, ReO_4^- .

This reaction mechanism would predict that reactions with O-atom donors that have labile leaving groups, such as iodosyl benzene (PhIO) or PyO should also readily react with MTO to generate methanol and ReO_4^- anion in basic water. As seen in Table 2, this has been observed to be the case for a variety of O-atom donors.

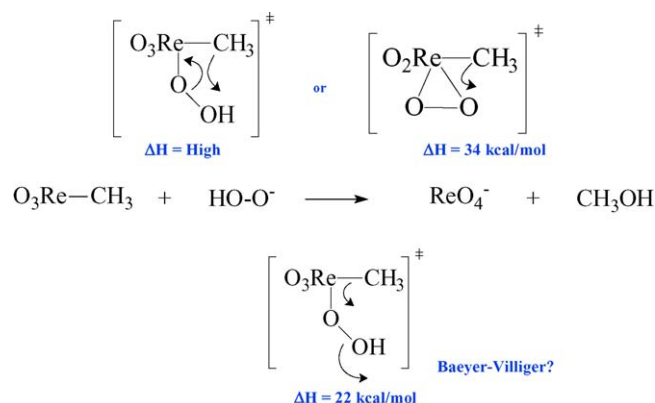
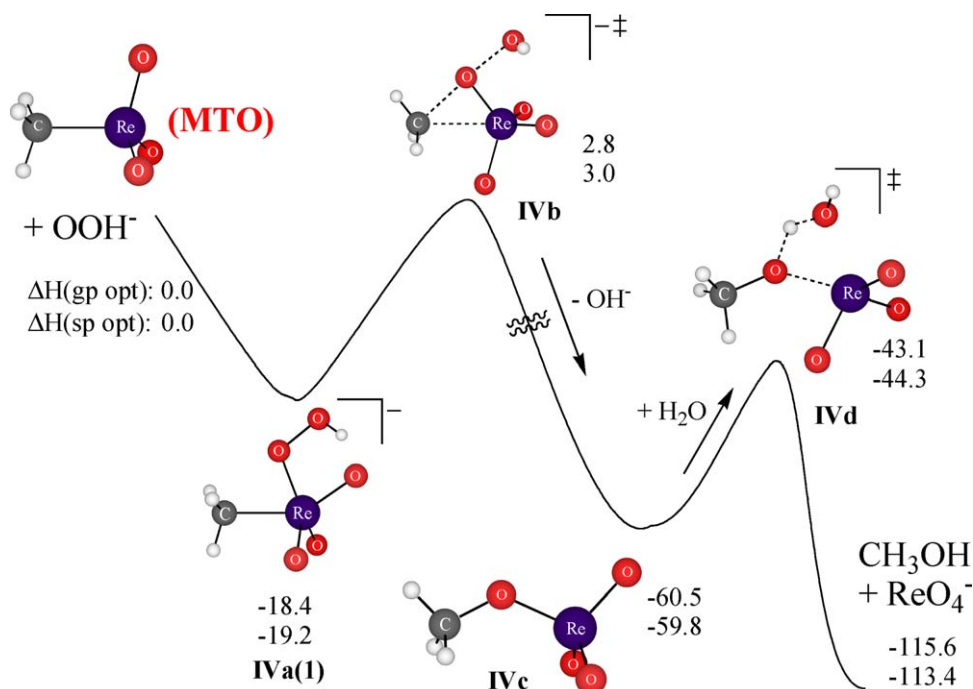


Fig. 29. Energetics of Baeyer–Villiger pathway for reaction of MTO with HOO^- .

Fig. 30. Reaction profile for Baeyer–Villiger reaction of MTO with HOO^- .Table 2
Oxidants used for conversion of MTO to methanol and perrhenate

Equivalents	Oxidant	% Methanol (3.1)	% Completion	Other species
2	H_2O_2	84%	86%	MTO:14%
2	$(\text{CH}_3)_3\text{SiOOSi}(\text{CH}_3)_3$	90%	100%	7% (2.75)
4	PhIO	85%	98%	–
4	mCPBA	30%	40%	–
2	NaIO_4	95%	100%	–
2	KIO_3/KOD	31%	100%	12% (2 ppm)
2	$\text{OsO}_4/2\text{eq KOD}$	28%	78%	No Reaction
2	$(\text{CH}_3)_3\text{NO}$	50%	99%	Species at 2.4
2	Pyridine N-oxide/KOD	No reaction	No reaction	–

2. Conclusion

Our work on the development of new molecular catalysts for the selective, low temperature, direct oxidation of hydrocarbons to useful products suggests that progress can be made with respect to key issues: (A) ground state inhibition of the CH activation reaction by water or reaction products; (B) design of catalysts that are stable to conditions required for functionalization; (C) the development of new functionalization reactions that can be utilized with facile CH activation systems.

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