

**COMPUTATIONAL STUDY OF LOW-
TEMPERATURE CATALYTIC C-C BOND
ACTIVATION OF ALKANES FOR PORTABLE
POWER**

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Final Report

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14. ABSTRACT The development of a room temperature (<50C) fuel cell that could use a generally available fuel such as JP8 would be most valuable. However there are no known catalysts that can selectively activate the CC bonds of such fuels at such temperature. The goal of this project was to investigate the whether it is plausible to develop such a catalysts. To do this we used validated first-principles (quantum mechanics) based simulations to investigate the barriers for alkyl carbon-carbon cleavage for two prototypical systems: A metal alloy catalyst & An organometallic cluster catalyst. That might serve as an anode for electrochemical power generation. For the metal alloy catalyst we used a Top-down approach where we determined the bond energies to the alloy catalyst to various fuel fragments necessary to achieve room temperature decomposition of butane and oxidation to CO2. For organometallic cluster catalyst we used a bottom-up strategy, determining specific metals, ligand compositions, solvents and operating conditions to evaluate which conditions could lead to reasonable rates at room temperature. For the bottom up approach we the density functional theory (DFT) form of quantum mechanics to investigated homogeneous catalysts. We decided that Rh is the best metal for a low temperature oxidation of C-H and C-C bonds. We then considered a number of possible mechanisms and reaction pathways for butane oxidation. The lowest barriers we determined for these mechanisms are 30 kcal/mol, which is probably too high for reasonable rates at room temperature (probably requiring ~200C). We then began a study of Rh/O2 complexes, such as spin singlet RhCl3(O2)2- and the spin doublet RhIII superoxide complex RhCl3(H2O)(O2)1-, which we consider would be accessible under reaction conditions. We conclude that these might serve as 3- or 4-electron oxidants. Further research is needed to draw a firm conclusion about prospect of these and other possible metal complexes to provide suitable catalysts.					
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1.0 Summary

The development of a room temperature (<50C) fuel cell that could use a generally available fuel such as JP8 would be most valuable. However there are no known catalysts that can selectively activate the Carbon-carbon (CC) bonds of such fuels at such temperature. The goal of this project was to investigate whether it is plausible to develop such a catalysts. To do this we used validated first-principles (quantum mechanics) based simulations to investigate the barriers for alkyl carbon-carbon cleavage for two prototypical systems:

- A metal alloy catalyst
- An organometallic cluster catalyst;

that might serve as an anode for electrochemical power generation.

For the metal alloy catalyst, we used a Top-down approach where we determined the bond energies of the alloy catalyst to various fuel fragments necessary to achieve room temperature decomposition of butane and oxidation to CO₂.

For organometallic cluster catalyst we used a bottom-up strategy, determining specific metals, ligand compositions, solvents and operating conditions to evaluate which conditions could lead to reasonable rates at room temperature.

For the bottom up approach, we used the density functional theory (DFT) form of quantum mechanics to investigate homogeneous catalysts. We decided that Rhodium (Rh) is the best metal for a low temperature oxidation of Carbon-hydrogen (C-H) and C-C bonds. We then considered a number of possible mechanisms and reaction pathways for butane oxidation. The lowest barriers we determined for these mechanisms are 30 kcal/mol, which is probably too high for reasonable reaction rates at room temperature (probably requiring ~200C). We then began a study of Rh/O₂ complexes, such as spin singlet $\text{RhCl}_3(\text{O}_2)^{2-}$ and the spin doublet Rh^{III} superoxide complex $\text{RhCl}_3(\text{H}_2\text{O})(\text{O}_2)^{-}$, which we consider would be accessible under reaction conditions. We conclude that these might serve as 3- or 4-electron oxidants. Further research is needed to draw a firm conclusion about the prospect of these and other possible metal complexes to provide suitable catalysts.

For the Top Down studies we used ReaxFF, the bond order based reactive force field developed by our group at Caltech in reactive molecular dynamics simulations of hydrocarbon decomposition on metal surfaces. This was used to model the hydrocarbon fuel conversion on metal surfaces, where instead of modeling a specific system, say FeNi, we determined the surface-adsorbate bond energies required to operate at room temperature. These surface-adsorbate bond energies can be used to scan the periodic table to find which combinations of metals is most suitable for successful alkane oxidation at low temperature. These results show that no pure metals are suitable as catalysts for the C-C bond cleavage at room temperature. This analysis suggests metal alloy systems that might satisfy the desired parameters that could be investigated further.

Our conclusion is that there is some possibility of developing a low temperature fuel cell capable of using butane as a fuel. However, some components of JP8 would not be reactive under these conditions. We have organized a conference at Caltech to criticize this analysis and to suggest alternatives. This involves six speakers on the morning of August 9 and 13 all day on August 12. In addition there will be 3 additional experts at both sessions to provide discussion. The program is attached in section 4.

2.0 Introduction

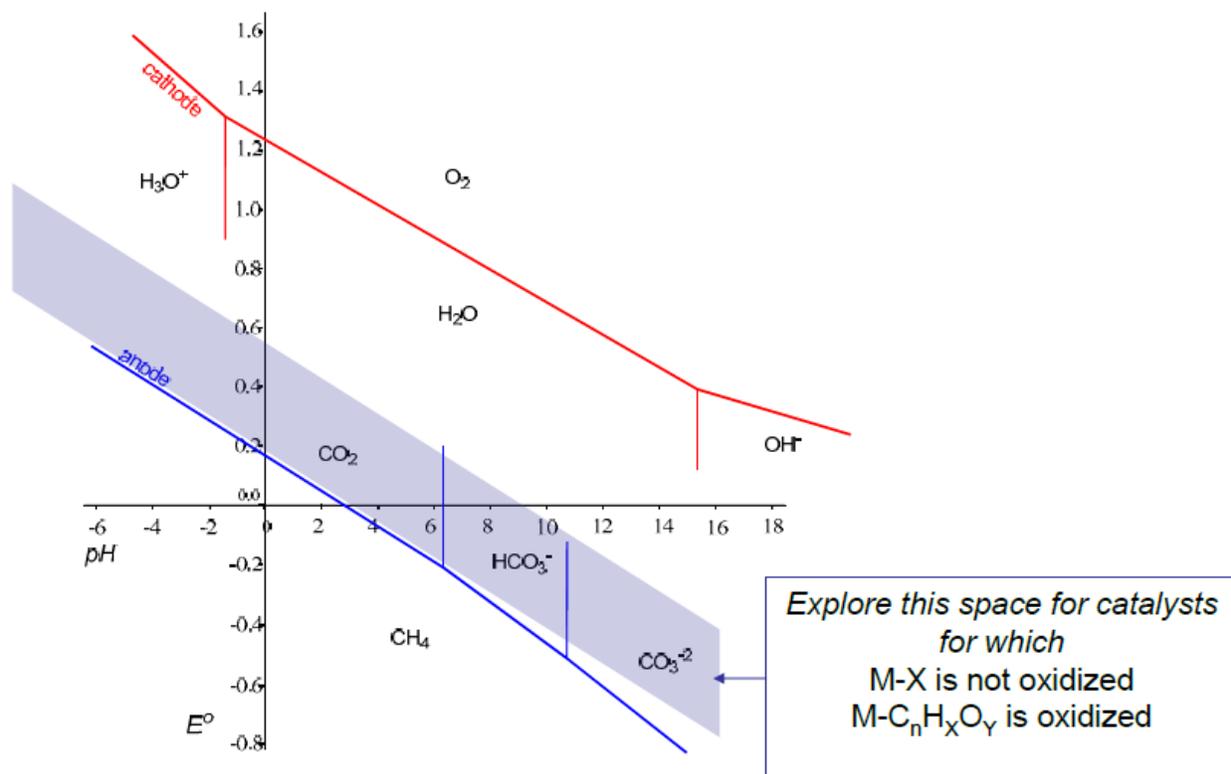
For complete electrochemical oxidation of alkanes, the prospective catalytic systems should display as many as possible of the following features:

- A low barrier (probably < 15 kcal/mol) for activating C-H bonds of saturated alkenes to form new M-CH₃ and M'-H bonds
- A low barrier (probably < 15 kcal/mol) for activating C-C' bonds of saturated alkenes to form new M-C and M'-C' bonds
- A mechanism and a low barrier (probably < 15 kcal/mol) for forming C-O bonds
- Stability against oxidation and protonation at a pH and potential corresponding to a low overpotential above the effective fuel↔CO₂ oxidation potential
- Not poisoned by CO

In addition electro/thermochemical relationships should include

- Alkane-activating catalyst ("M-X") not oxidized at operating potential *but*
- Catalytic intermediates (many electrons worth) that all can be oxidized *and*
- Catalytic intermediates (many protons worth) acidic at the operating pH.

(see Figure 1)



$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$: ΔG of -195 kcal/mol sets a maximum potential difference of 1.06 V at pH = 0.

Figure 1. Electrochemistry features of a catalyst for alkane oxidation.

We applied top-down and bottom-up strategies to evaluate compositions and structure-performance relationships that might satisfy these constraints.

3.0 QM Studies of Homogeneous Catalysts for Oxidation of C-H and C-C Bonds

3.1 Methods, Assumptions & Procedures

In order to identify catalysts relevant for the tasks of the project, we investigated computationally many possible candidates over a wide range of pH's (with roughly correlated oxidation potentials). Free energy surfaces for complete or partial catalytic cycles featuring CH or CC cleavage were computed using density functional theory (DFT) coupled to a polarizable continuum solvation model.

We took a homogeneous $(bpy)_2Ru^{II}(OH)_2$ complex as a potential catalyst that features

- a later transition metal with the ability to form strong M-C bonds and
 - oxidative stability in basic aqueous solution above the CH_4/CO_2 oxidation potential.
- To avoid oxidation of $(bpy)_2Ru^{II}(H_2O)(OH)$ to $(bpy)_2Ru^{III}(OH)_2$, the complex must operate below $-0.4V$ vs. Standard hydrogen electrode (SHE) at $pH = 14$ (Ru^{III} is incompetent for H_3C-H activation). We find that ΔG for CH_4 activation is 32.4 kcal/mol, and 13.7 kcal/mol uphill (Figure 2). This would provide reasonable rates at $200C$. Unfortunately, the calculated barrier for CH_4 activation (32 kcal/mol) was too high to permit ambient-temperature CH activation.

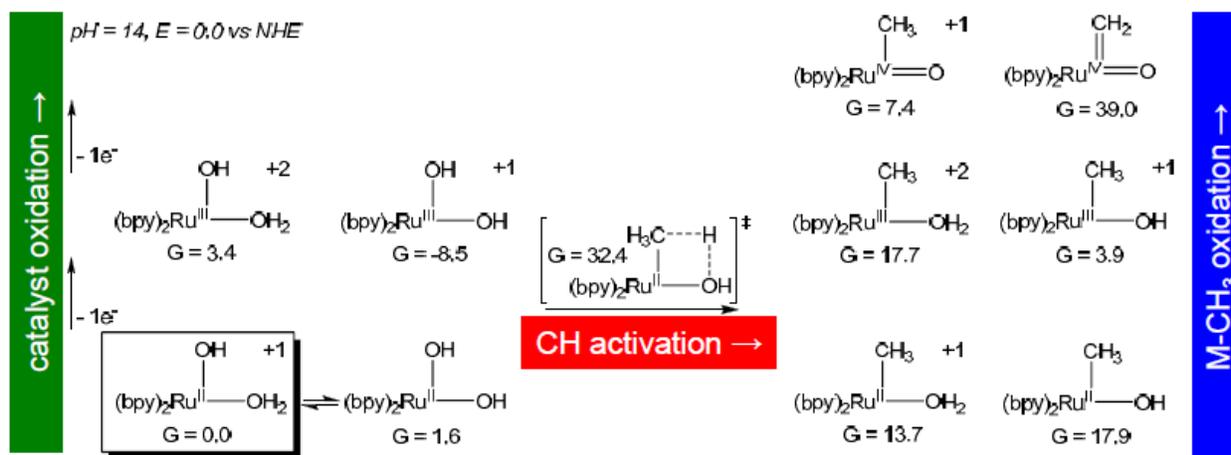


Figure 2. The free energy surface for stable intermediates as a function of pH and electrochemical potential.

A promising system, tungsten phosphine complex, was reported by Parkin et al. [1] to cleave an aromatic C-C bond in quinoxaline stoichiometrically.

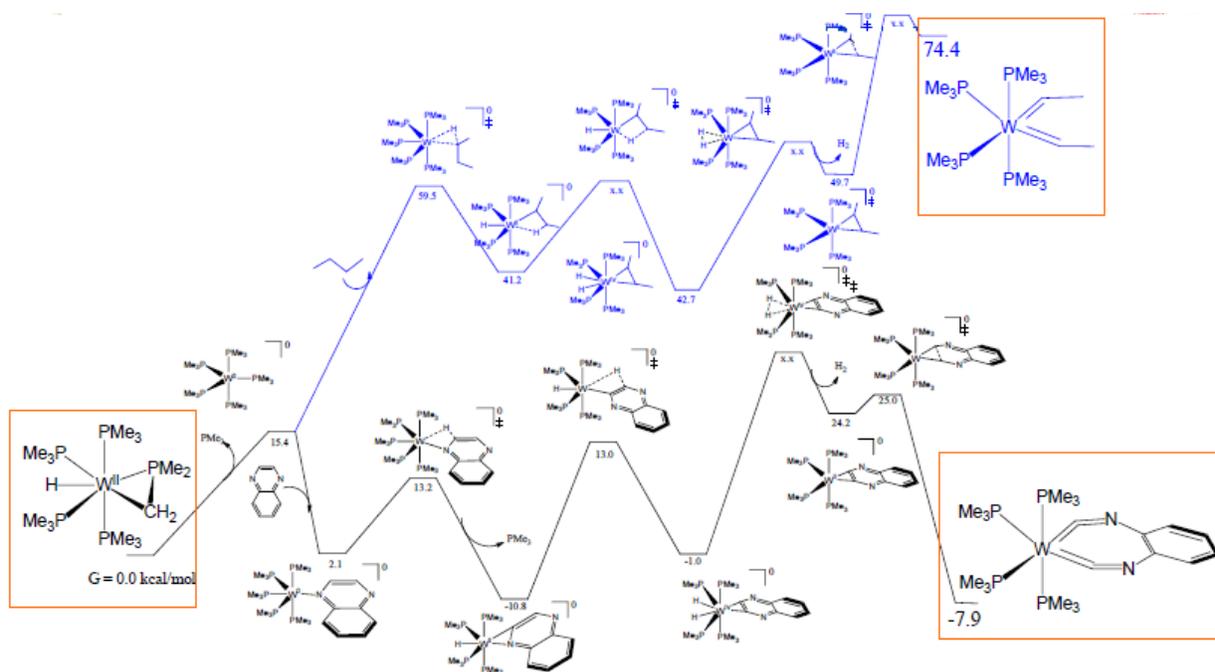
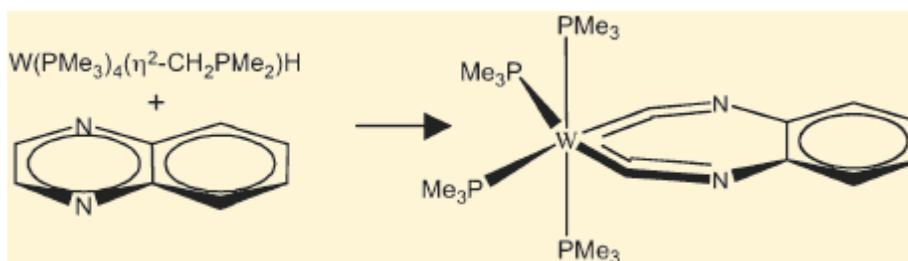


Figure 3. Low-valent organometallic tungsten.

To determine

1. whether this reaction would apply to general hydrocarbon substrates or is specific to just the quinoxaline substrate and

2. if general to hydrocarbons, whether the complex is stable with respect to oxidation and compatible with C-O bond formation,

we calculated the free energy surfaces for the interaction of the $(PMe_3)_5W^0$ complex with both quinoxaline and butane. This allows us to explore the scope of this reaction. Indeed we found that the reaction of this highly reducing tungsten complex with quinoxaline is 8 kcal/mol exergonic, but unfortunately the similar insertion of the tungsten into a C-C bond of butane is 70 kcal/mol endergonic (Figure 3).

This suggests that the reaction is not a generally viable mechanism for CC cleavage. A second problem with this catalyst is that regenerating a metal center as reducing as W^0 is likely quite unfavorable under oxidizing conditions.

As a third class of systems we considered the catalytic mixture of RhCl_3 , Cl^- , I^- , CO and O_2 in a water/fluorobutyric acid solvent. This system was reported by Sen [2] who observed that it oxidizes light hydrocarbons at 80-90°C. This system displays several attractive characteristics:

- low temperature oxidation of hydrocarbons,
- tolerance of CO , and
- a preference for CC cleavage over CH cleavage that is most unusual in higher hydrocarbons.

Drawbacks in the Sen system include

- dependence on CO ,
- the price of rhodium, and
- the dependence on O_2 , which cannot be used as a *stoichiometric* oxidant in a fuel cell setting.

We first examined the RhCl_3 system. Our initial computations regarding this system showed that

- Rh^{II} chloride salts are stable in a mixture of Rh^{I} and Rh^{III} , so that metallo-radicals may be present and have a role the catalytic cycle,
- Oxidation of the Rh^{I} chloride to Rh^{II} is exothermic even at SHE, and
- Moreover, oxidation of Rh^{II} to Rh^{III} is also exothermic (reflecting the driving force to form Rh-Cl bonds).

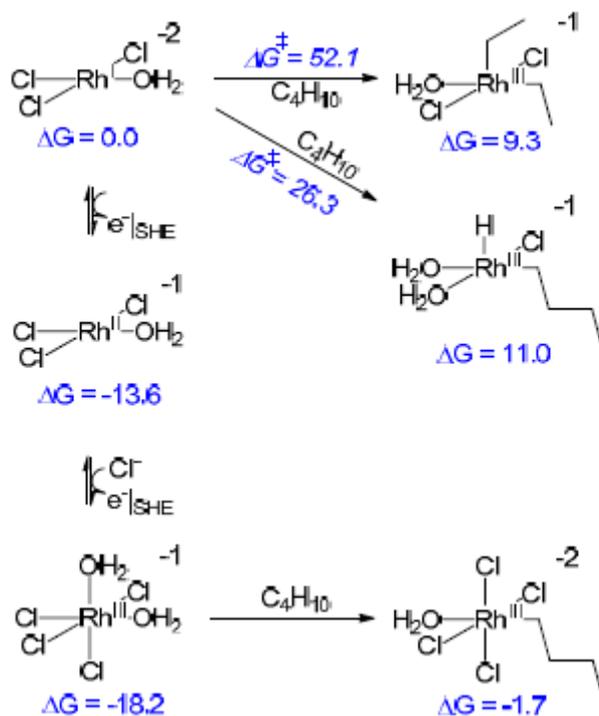


Figure 4. ΔG for some possible reactions

These free energies suggest Rh^{I} and Rh^{III} will comproportionate to two Rh^{II} 's. This would be the resting state for metallo-radicals at some low potentials, suggesting that this system could be useful for attacking strong CH and CC bonds. However in the presence of O_2 , Rh^{III} is the thermodynamic resting state.

We calculate that:

- C-H cleavage in butane by insertion of Rh^{I} chloride into a CH bond is 11.0 kcal/mol endergonic (uphill), with a 26.3 kcal/mol barrier.
- C-C cleavage by insertion of Rh^{I} is 9.3 kcal/mol endergonic (uphill), but with a 52.1 kcal/mol barrier.
- C-H cleavage by Rh^{III} is 16.5 kcal/mol endergonic (uphill) (Figure 4).
- Nonradical insertion of Rh^{I} into the $\text{C}_2\text{-C}_3$ bond of butane yielded a calculated barrier of 52 kcal/mol showing that this is not a viable pathway.

However this very complex system has a large number of potential reactions, many of which we have not yet studied. Thus the real barriers might be lower,

Since the $\text{RhCl}_3/\text{O}_2/\text{CO}/\text{I}/\text{H}_2\text{O}/\text{F}_7\text{C}_4\text{OOH}$ catalyst system described by Sen [2] displays selective methane oxidation and butane oxidation to C_2 products at moderate (90°C) temperatures, we selected this system for our further investigations. Our goal was to determine the mechanism by which C-C bonds are broken and which of these reaction steps *directly* involve O_2 and whether this might be reproduced in an anodic setting. Non-radical mechanisms explored earlier had barriers too high to be responsible for reaction. Thus we conclude that the critical reactions are concerted. There are many combinations of $\text{Rh}(\text{III})/\text{O}_2/\text{iodine}$ that could serve as a strong oxidant and several permutations of electron transfer/hydrogen abstraction/C-C cleavage reactions. Since there are a large number of combinations, investigating them exhaustively would be a major undertaking too extensive for this project. Indeed despite the very promising results there has not been a successful experiment reported that gives any suggestion of the critical catalytic steps.

Therefore we first, determined the energies of $\text{Rh}/\text{O}_2/\text{I}$ complexes and their 1-, 2-, 3-electron reduction potentials. Then, using the complexes that are the strongest oxidants, we determined transition states for C-C cleavage. Finally, we determined whether the other required steps (electron transfer, hydrogen atom transfer) are energetically favorable.

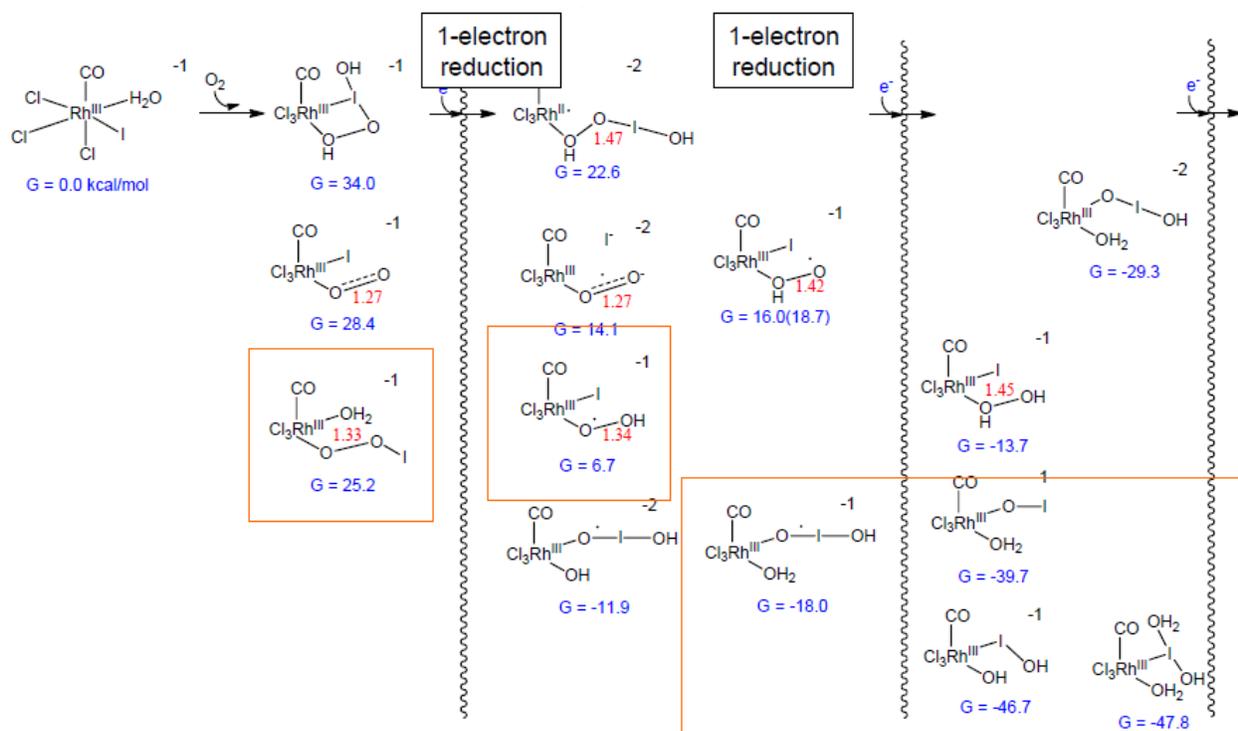


Figure 5. $\text{Rh}^{\text{III}}/\text{O}_2$ /iodine chemistry.

One possibility is that C-C cleavage in butane observed by Sen [2] involves electron transfer from alkane to an activated oxidizing complex. To determine what magnitude of oxidation potentials could be created by combining rhodium, dioxygen and iodide, we modeled $\text{Rh}/\text{O}_2/\text{I}$ -complexes with different bonding arrangements (Figure 5). We then added electrons and protons to these to predict what magnitude of oxidation potentials could be generated.

We took $\text{Rh}^{\text{III}}\text{Cl}_3\text{I}(\text{CO})(\text{H}_2\text{O})^{-1}$ as a representative starting point. The initial coordination of dioxygen to Rh^{III} in this case (and other cases we have studied) is unfavorable in free energy but required for activation. O bonds are present in both the dioxygen complex and products, suggesting a role for iodine in the O_2 activation process. The most stable of the three isomers involves stabilization of singlet- O_2 in a $\text{Rh}-\text{O}-\text{O}-\text{I}$ peroxide fragment (“ $G = 25.2$ kcal/mol). After reduction by one electron, the lowest-energy state we were able to find that keeps the O-O bond intact is $G = 6.7$ kcal/mol endergonic from O_2 . This is consistent with an oxidation potential of 0.8 V vs. SHE for the reduction of the $\text{Rh}-\text{O}-\text{O}-\text{I}$ fragment at $\text{pH} = 0$. If some bond rearrangement is allowed, a more stable hypoiodite complex can be accessed after 1- electron reduction, which is $G = 11.9$ kcal/mol downhill from O_2 . While it is feasible that the superoxide complex ($G = 6.7$ kcal/mol) can rearrange to this hypoiodite complex ($G = -11.9$ kcal/mol), it is not obvious that there is a favorable pathway. It could be that the system gets “stuck” at the superoxide state prior to further reduction. After the first reduction has generated the hydrogen superoxide complex (“ $G = 6.7$ kcal/mol), the next reduction is much more favorable. Breaking the O-O bond (and trapping a hydroxyl radical with iodide) upon reduction generates the hypoiodous acid complex (“ $G = -46.7$ kcal/mol). The reduction from $G = 6.7$ kcal/mol to $G = -46.7$ kcal/mol implies an oxidation potential of 2.3 V vs. SHE. This is formidable, and well higher than the overall $\text{O}_2 + 2\text{e}^- + 2\text{H}^+ \leftrightarrow 2\text{H}_2\text{O}$ potential of 1.23 V. Since I-O bonds are present

in both the dioxygen complex and products, this suggests a role for iodine in the O₂ activation process.

Next, we determined which C-C cleavage mechanisms are available from Rh^{III}/O₂/I mixture and found that all located pathways have inaccessible barriers (Figure 6).

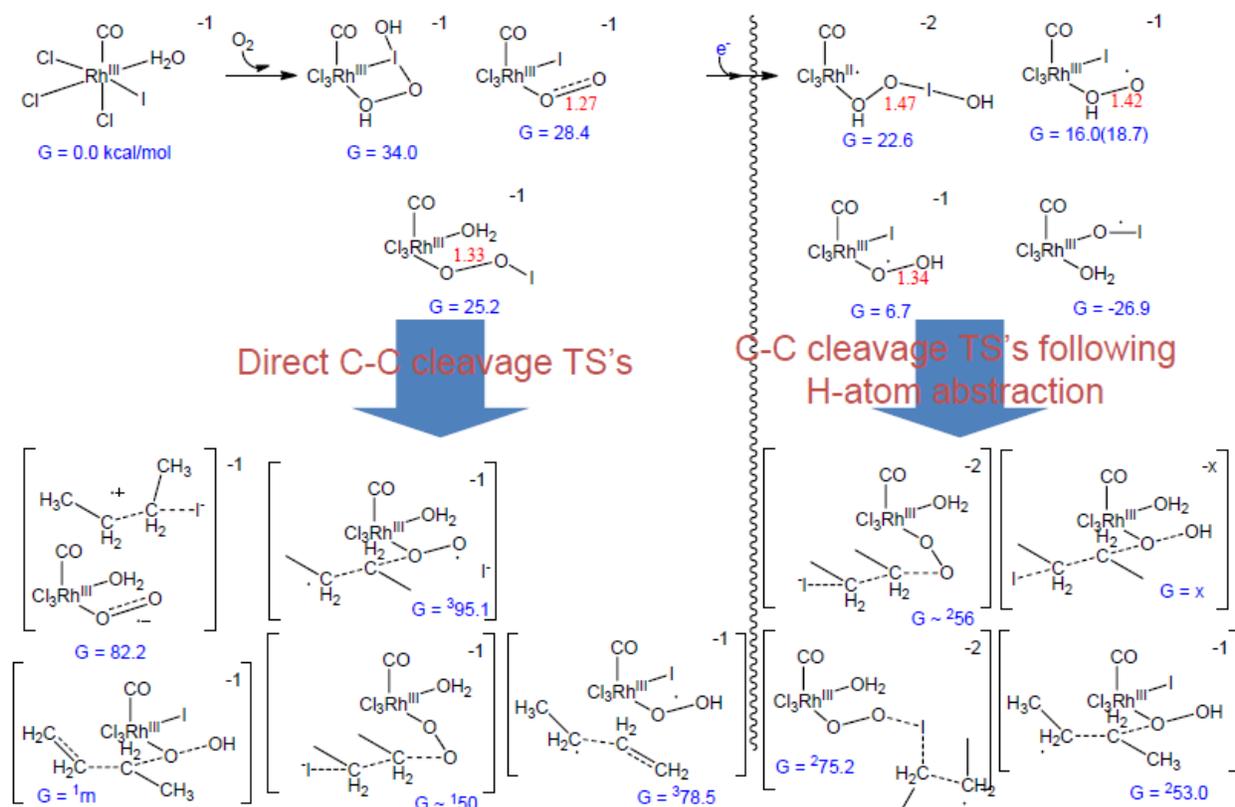


Figure 6. C-C cleavage mechanisms available from Rh^{III}/O₂/I mixture.

For this reason, we studied a similar process of O₂ coordination and reduction using a Rh^I starting point. The electron-withdrawing CO present stabilizes the Rh(I) oxidation state. The 2-electron reduction of O₂ is more than twice as favorable as the one-electron reduction of O₂ (Figure 7). Unlike Rh^{III}, Rh^I itself can provide electrons to the O₂ fragment (in addition to electrons supplied by the hydrocarbon.). Reducing the Rh^I-O₂ complexes by one electron is *more* exergonic than reducing the Rh^{III}-O₂ complexes by one electron because the Rh^I center simultaneously donates a second electron to O₂ to make the total reaction a two-electron reduction of O₂.

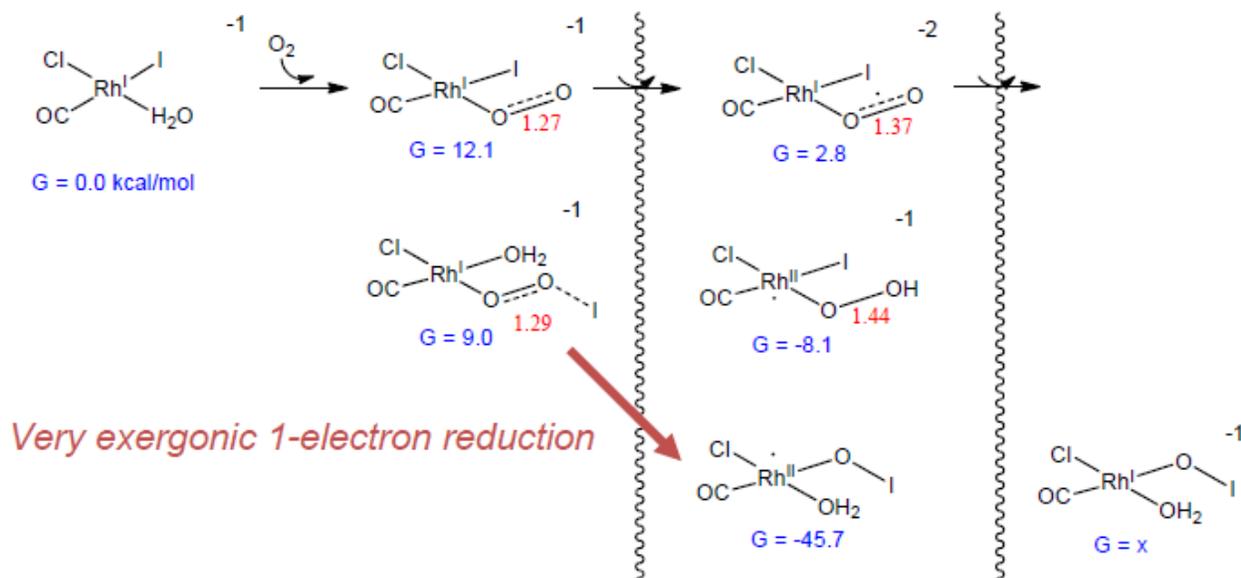


Figure 7. Thermo/electrochemistry of the oxidant $\text{Rh}^{\text{I}}/\text{O}_2/\text{I}$ mixture.

3.2 Results & Discussion

Overall, we are looking for low-barrier processes for forming alkyl peroxide intermediates, following an initial CH cleavage. We consider that a $\text{Rh}^{\text{I}}/\text{O}_2$ complex or a $\text{Rh}^{\text{II}}/\text{O}_2$ complex may be responsible for the CH cleavage, since they showed the largest reduction potentials in the previous studies. Since none of the CH cleavage transition states using the $\text{Rh}^{\text{I}}/\text{O}_2$ are consistent with such a low-temperature reaction. The best hypothesis for CH cleavage involves a radical generated by Rh and O_2 (Figure 8a) (since free radicals are not consistent with experimental observations). Since C-C cleavage barriers beginning from Rh^{III} are high, we consider that an alkyl peroxide may be formed instead. The lowest C-C cleavage barrier we have been able to find is the Acid-catalyzed Baeyer-Villiger decomposition from the alkyl peroxide (Figure 8b). However, we must show that the alkyl peroxide can be formed from $\text{O}_2 + \text{Rh}$. Electrochemical C-C cleavage is possible, but since this involves O_2 directly, it is not useful. Schulz found Co^{III} ions in acetic acid oxidized n-butane, suggesting methyl ethyl ketone as an intermediate, which is also consistent with a BV decomposition [4].

We found that the Rh^{I} complex $(\text{CO})_2\text{Rh}^{\text{I}}(\text{TFA})(\text{H}_2\text{O})$ ($\text{TFA}=\text{trifluoroacetate}$) can react with butane via activation of a secondary CH bond with a thermally accessible barrier of 24 kcal/mol.

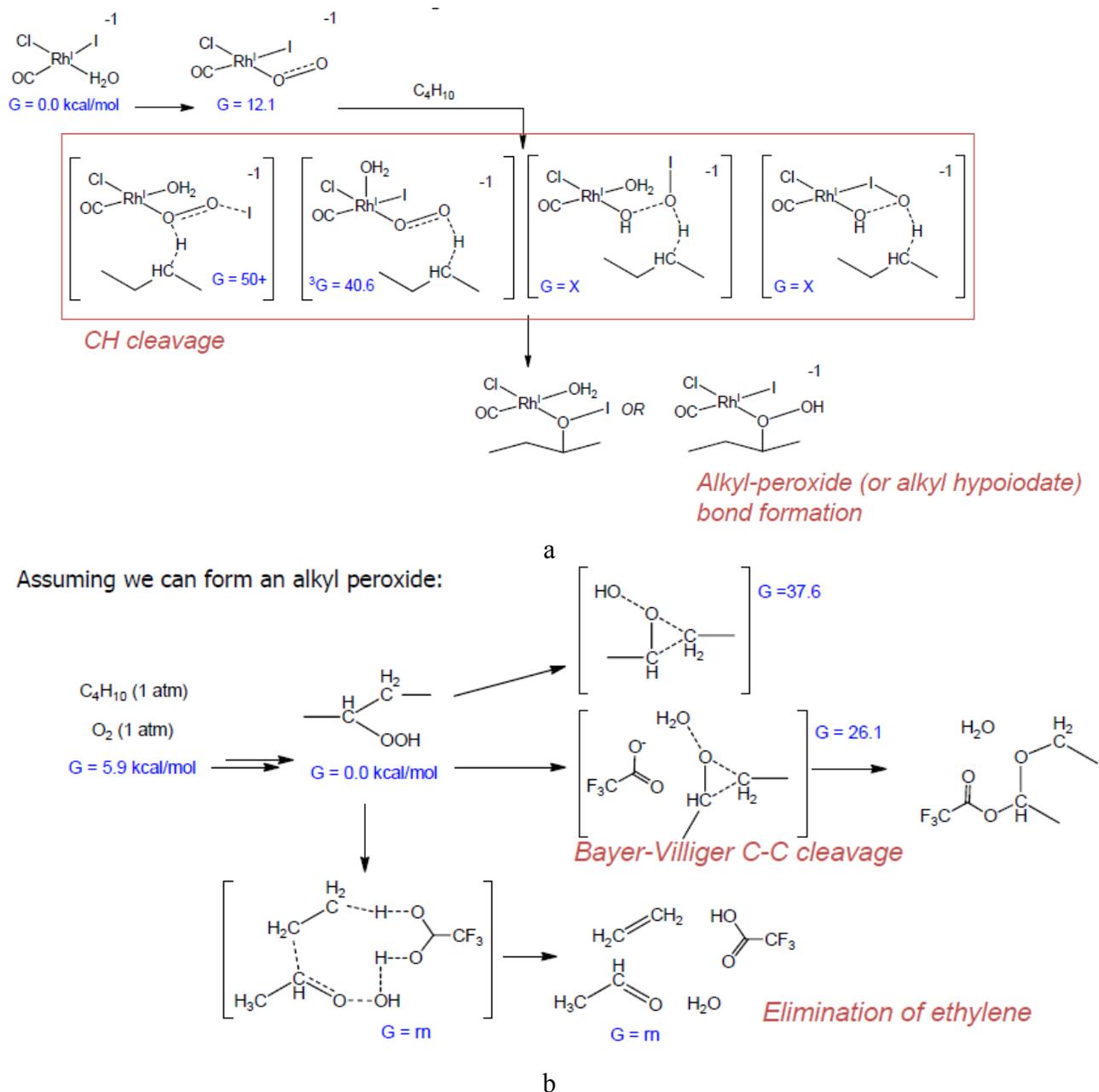


Figure 8. Possible processes involving the $\text{Rh}^{\text{I}}/\text{O}_2/\text{I}$ mixture.

Oxidation of the resulting Rh^{I} alkyl complex using O_2 is exergonic, and we identified a nonradical mechanism for C-C cleavage on the resulting Rh^{III} alkyl complex. However, depending on the ligand set, we found that the C-C cleavage reaction leads to barriers of 30-40 kcal/mol, showing that this is not the mechanism of the Sen catalyst. This mechanism, in which an ethyl group migrates 1, 2 across the C-Rh bond, would generate a Rh ethyl ethylidene

fragment. This could subsequently undergo thermally accessible nucleophilic attack by oxygen nucleophiles, resulting in the desired C-O bonds.

Comparing the Rh^{III} redox couple using different ligand sets, we found a role for carbon monoxide. The most stable Rh^I complexes contain two CO ligands and are the only Rh^I complexes whose oxidation to Rh^{III} by ½ O₂ is endergonic. Since CO is known to poison many catalysts by binding to active sites, we sought other electron-withdrawing ligands that could be bound to Rh statically to stabilize the low oxidation state without inhibiting the reaction. We found that Fluorinated phosphines are sufficiently π-accepting to satisfy this role.

In our next step, we wanted to determine the mechanism by which C-C bonds are broken in the Sen system. Non-radical mechanisms explored earlier had barriers too high to be responsible for reaction.

Since many combinations of Rh^{III}/O₂/iodine could serve as a strong oxidant and several permutations of electron transfer/ hydrogen abstraction/C-C cleavage reactions, we first determined the energies of Rh/O₂/I complexes and their 1-, 2-, 3-electron reduction potentials. Second, using the complexes that were the strongest oxidants, we looked for transition states for C-C cleavage. To date, however, the search for reactions which couple CH or C-C cleavage to reduction of the Rh/O₂/I- fragment has only yielded reactions with thermally inaccessible barriers.

Unlike Rh^{III}, Rh^I itself can provide electrons to the O₂ fragment (in addition to electrons supplied by the hydrocarbon.) Reducing the Rh^I-O₂ complexes by one electron is more exergonic than reducing the Rh^{III}-O₂ complexes by one electron because the RhI center simultaneously donates a second electron to O₂ to make the total reaction a two-electron reduction of O₂. The initial reaction of butane with the reactive state of Rh could result in direct CC cleavage or CH activation followed by C-C cleavage (Figure 9). Rebound of an alkyl radical resulting from CH cleavage (G = -6 kcal/mol) will likely form a Rh^{III} alkyl (G = -27 kcal/mol), since this rebound will have a much lower barrier (if any) than ethylene liberation (25 kcal/mol). New transition states for C-C cleavage via rearrangement of the Rh^{III}-alkyl were located (G = 12.2 and 24.5 kcal/mol), but these pose inaccessible barriers of 40 kcal/mol or higher.

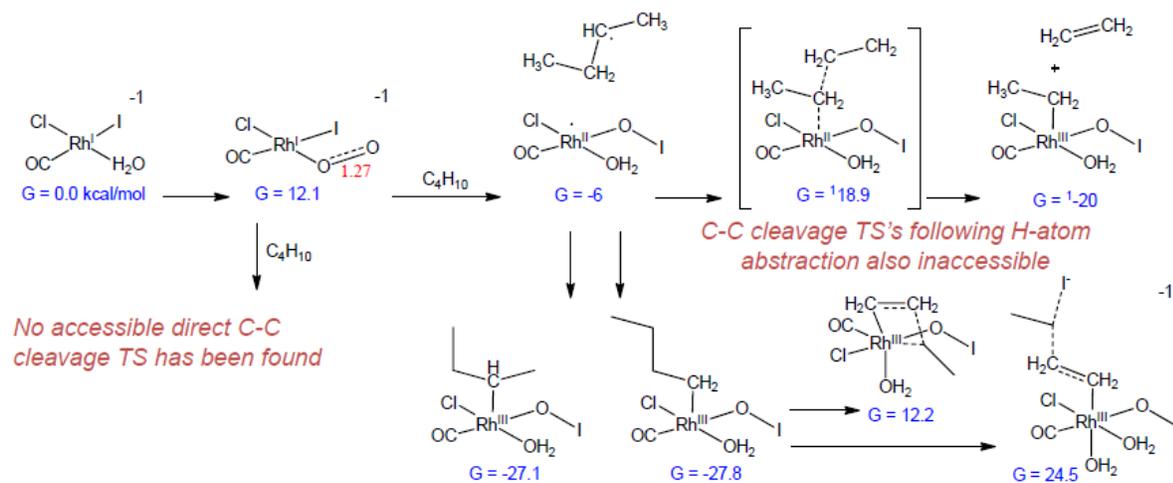


Figure 9. C-C cleavage barriers involving the Rh^I/O₂/I mixture.

Our calculations showed that if a secondary alkyl peroxide can be formed, a Bayer-Villiger migration can occur with a 26 kcal/mol activation barrier, that may be sufficiently low. In this process the C2-C3 bond is broken as an ethyl group migrates 1,2 from carbon to the peroxide oxygen. However a mechanism for forming the isobutyl peroxide must be identified,

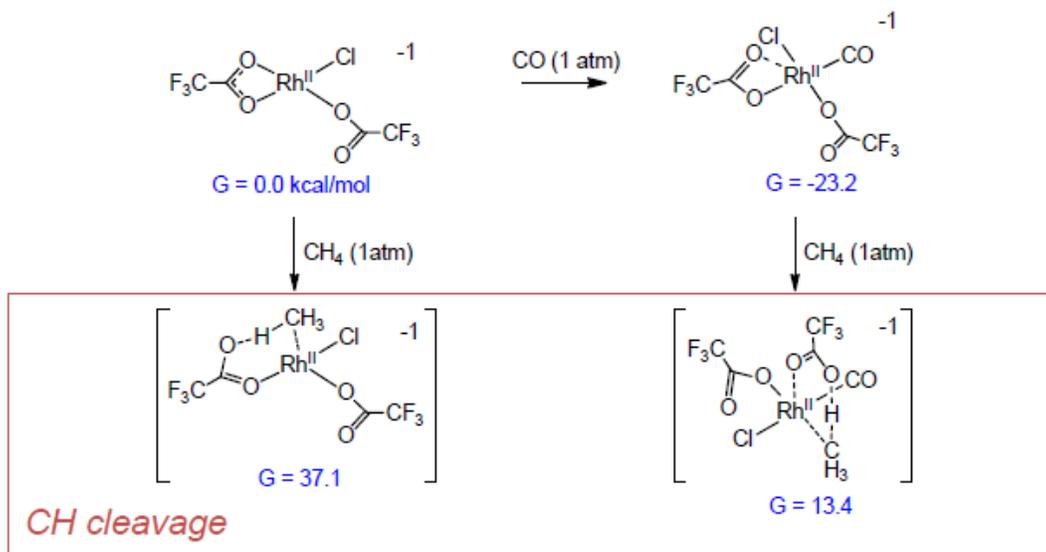


Figure 10. H₃C-H activation by Rh^{II}

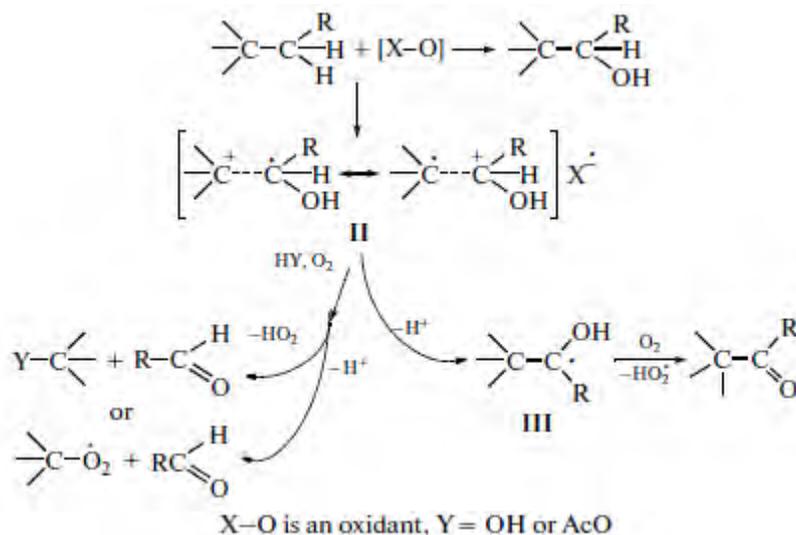


Figure 11. Multi-electron oxidation of butane.

Our computations explored possible reactions between Rh^I/O₂/I-complexes and butane. Hydrogen-atom transfer from butane to an as-yet unidentified reactive complex of oxygen could yield a butyl radical and a Rh^{II} complex exergonically. The likely fate of such a pair is simply recombination to form a Rh^{III} alkyl complex, without further bond cleavage. We did find a

competing transition state for C-C cleavage in which a primary butyl radical is attacked at the C3 position by the Rh^{II} metallo-radical, resulting in C2-C3 cleavage and release of ethylene and a Rh^{III} ethyl complex (Figure 9). The path poses an accessible barrier of ~25 kcal/mol.

We also investigated the activation of a CH bond in methane by Rh^{II} complexes (CO)Rh^{II}(TFA)₂Cl⁻ and found that Rh^{II}(TFA)₂Cl⁻ yielded inaccessible activation barriers of 37 kcal/mol which is too high to be observed thermally (Figure 10). The TOF for methane oxidation suggests a barrier ~28 kcal/mol. These barriers are similar to barriers predicted for Rh(III)-TFA complexes.

To rationalize the predominance of C-C cleavage products over CH cleavage products in the oxidation of butane by Sen's catalyst, Chepaikin et al. [5] proposed that CH cleavage occurs first. But the resulting catalyst fragment "X" is so electrophilic that it immediately abstracts an electron from the alcohol highest occupied molecular orbital (HOMO), a C-C σ -bond. The resulting radical cation "C⁺-C[•]" is susceptible to nucleophilic or oxidative attack resulting in C-C cleavage. This requires a 3- or 4-electron oxidant "X-O"(Figure 11). Thus, we propose that the initial reaction of a Rh/O₂ complex with butane involves a one- or two-electron reduction to result in another reactive complex with sufficient oxidation potential to abstract an electron from the central C-C bond of the butyl fragment present. The oxidation leads to C-C cleavage. This is consistent with the observations that O₂ (a 4-electron oxidant) is required for catalysis, while traditionally "more reactive" oxidants (H₂O₂, mCPBA, IO₄⁻, C₆H₅IO) are incompetent. The ionization potential of butanol (calculated 2.4 V vs. SHE) is lower than that of butane (calculated 3.5 V). Oxidation of butane and 2-butanol leads to a large weakening and lengthening of the C-C bond. Oxidation of the alkane (3.5 V) would be exergonic, but if the oxidant and alkane are in proximity, electron transfer coupled to bond rearrangement may be possible (Figure 12).

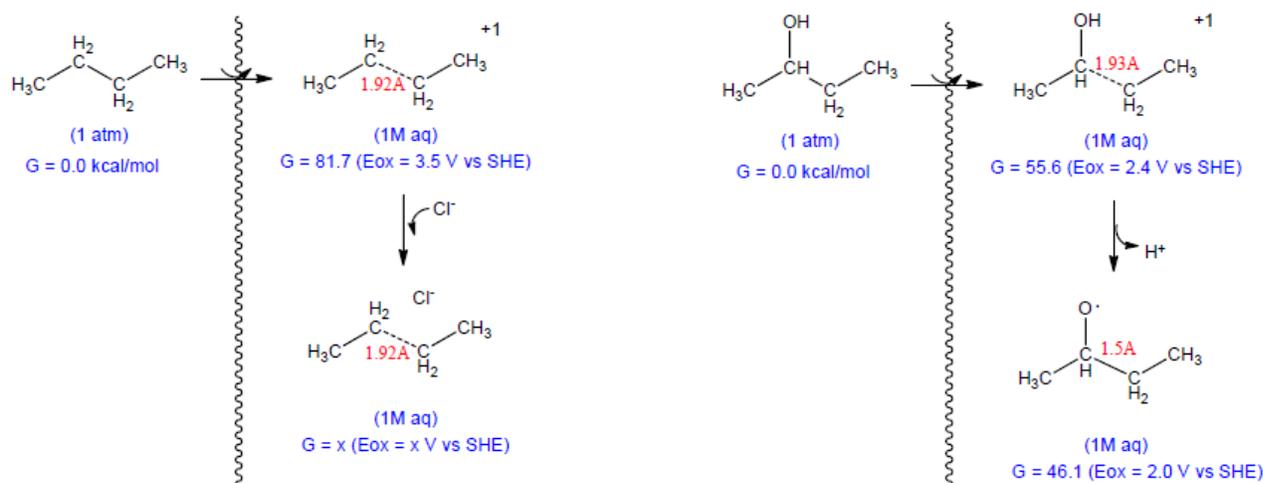


Figure 12. Alkane and alcohol ionization.

Proceeding from the above discussion, we began to seek Rh/O₂ complexes that would be accessible under reaction conditions and which could potentially serve as 3- or 4-electron oxidants. We identified one candidate as the singlet rhodium chlorides, RhCl₃(O₂)²⁻, with a singlet wavefunction similar to that in ozone (Figure 13). Its formation from O₂ and Rh^I is exergonic, and its wavefunction suggests it may be a competent oxygen-atom transfer reagent.

We assume here that the Rh(I) reactant did not “cost” any energy to form. Since Rh(I) is observed in solution in the presence of the electron-withdrawing CO, this is likely.

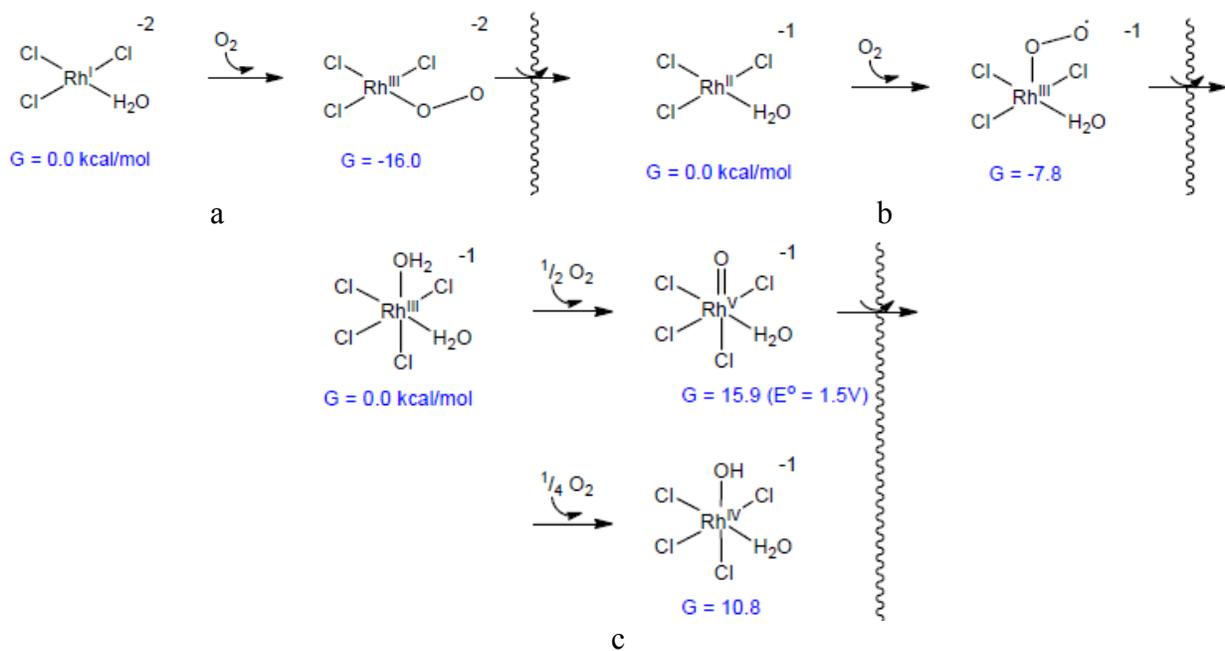


Figure 13. New oxidized Rh chemistry.

One of the 4 available reductions of O_2 is “used up” when O_2 bonds to Rh^{II} , but 3 units remain, and the radical character on the superoxide ligand is likely kinetically reactive (Figure 13b). We assume that the Rh^{II} reactant here did not “cost” any energy to form.

Neither the Rh^V nor Rh^{IV} is formed exergonically from O_2 (Figure 13c). These could be formed using the stronger oxidant H_2O_2 generated in situ. However, neither of these are 3- or 4-electron oxidants.

Another candidate might be the doublet Rh^{III} superoxide complex $RhCl_3(H_2O)(O_2)^{1-}$. The radical character of the superoxide unit may impart reactivity toward hydrogen-atom transfer reactions. The higher oxidation state complexes $Rh^VCl_4(O)(H_2O)^{1-}$ and $Rh^{IV}Cl_4(H_2O)(OH)^{1-}$ are less stable than Rh^{III} precursors.

Ultimately, $Rh-O_2$ complexes like those in Figure 13a and b are the most likely active species, being formed exergonically from the reagents present and capable of multi-electron oxidations.

3.3 Conclusions

In summary, we find that the “Sen” system [$RhCl_3/I^-/O_2/CO$ in $F_3CC(O)OH/H_2O$] is unique in oxidizing light alkanes at $85^\circ C$. C-C and C-H bonds are broken and C-O bonds are formed. In the reaction of butane, C-C cleavage is faster than C-H cleavage. Our interest is to identify the role of O_2 and CO in this mechanism. Since they will not be present at an anode they must be replaced by viable surrogates.

Phosphine ligands stabilize Rh^I (relative to Rh^{III}) so that it may continue to activate C-H bonds under oxidizing conditions. Thus phosphines can be considered as a replacement for carbon monoxide. There is no evidence that O_2 can be replaced for forming H_3C-O bonds: the

methanol produced contains only labeled oxygen if labeled O₂ is employed, and calculated barriers are high, ~30 kcal/mol. However, it can be replaced for forming bonds between oxygen and heavier alkyl groups: barriers for nucleophilic attack of anions on Rh^{III}-C₂H₅ are below 20 kcal/mol.

4.0 Top-Down determination of Metal-adatoms bond parameters suitable for low temperature fuel cells using butane as the fuel.

4.1 Methods, Assumptions & Procedures

The ReaxFF force field is a first principles based force field trained to describe energetics and reaction barriers to match an extensive set of quantum mechanics reaction pathways. To consider the parameters that a suitable metallic alloy must have to serve as the anode for a low temperature fuel cell, we used ReaxFF to model the hydrocarbon fuel conversion on metal surfaces in a top-down approach. We started with the ReaxFF already developed to describe the anode reactions of hydrocarbons for Ni/SOFC catalyst.^{9-11,12-14} Then we tuned the M-H, M-C, and M-O parameters to reduce the reaction temperature to ~100C. Then we used these parameters to suggest which elements to consider in the alloy. Note that the high temperatures are used to achieve reaction rates sufficiently high that we could get results in a day or so. More realistic temperatures would take longer and would be used for the final alloys selected.

First, we used ReaxFF to describe reactions of butane on a Ni (111) single crystal surface. Here 20 butane molecules were exposed to a Ni slab containing 480 atoms (Figure 14). The temperature was increased from 50K to 1250K over 25ps and held at 1250K (NVT) for 100ps. The cleavage of C-H bonds (with Ni-C bond formation) was observed after 87 ps, but C-C bond cleavage was not observed.

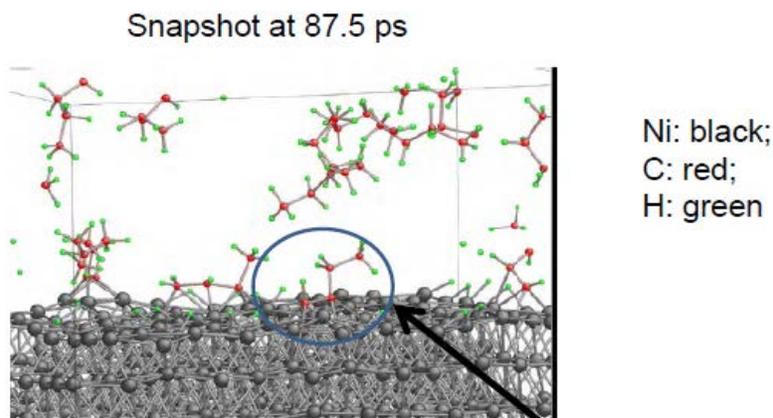


Figure 14. Butane on the Ni(111) surface.

Then we continuously heated the system from 1250 K to 1500 K over 100 ps and found two cases of C-C bond breaking: the first one was observed at 1415 K and the other at 1500 K (Figure 15).

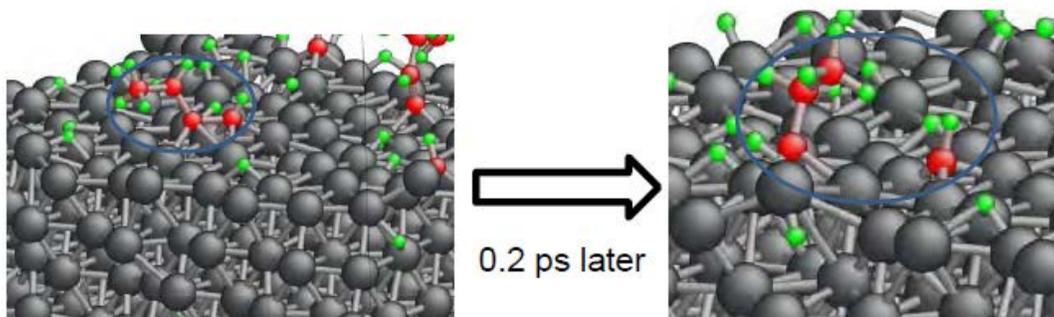


Figure 15. Reaction pathway for C-C bond breaking at $T = 1415$ K.

To determine how strong a Ni-C bond should be in order that a surface-bound butyl fragment would undergo CC cleavage spontaneously, we modified the parameters of the ReaxFF force field. The Ni-C single bond energy was increased until a butyl fragment bound to the Ni surface through C1 and C2 decomposed without a barrier into methyne and propyl fragments. A 60% increase in the Ni-C bond energy was required. This adjustment of the ReaxFF resulted in the effective increase of the Ni-CH₃ single bond from 43 to 85 kcal/mol, and in the increase of the Ni-CH bond (3 Ni-C single bonds) from 123 to 257 kcal/mol. After that, the Ni* metal with a bond energy to a methyl fragment 42 kcal/mol stronger than that of real Ni could break a dehydrogenated C-C bond with no barrier (Figure 16).

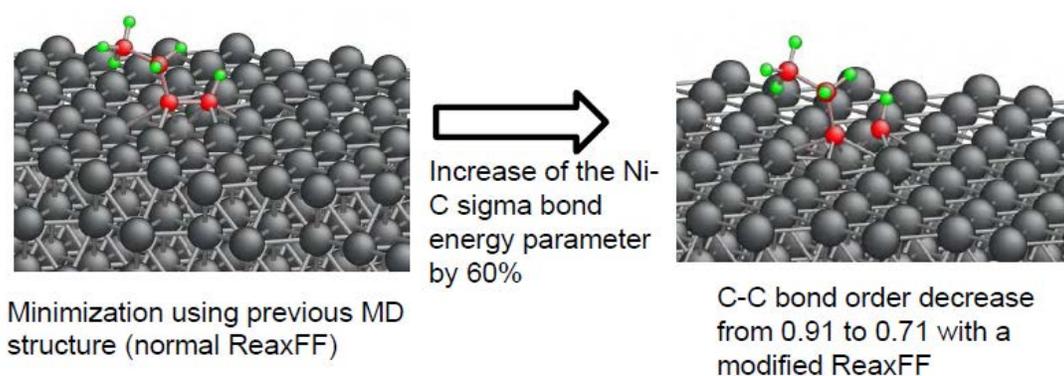


Figure 16. Influence of Ni-C bond strength on C-C bond breaking.

Using this modified ReaxFF force field, we simulated new trajectories in which butane was reacted with Ni at 500K, 600K and 700K for 50ps. In these simulations multiple CC cleavage events were observed, corroborating that the surface with the strengthened Ni-C bonds would decompose butane at room temperature (Figure 17).

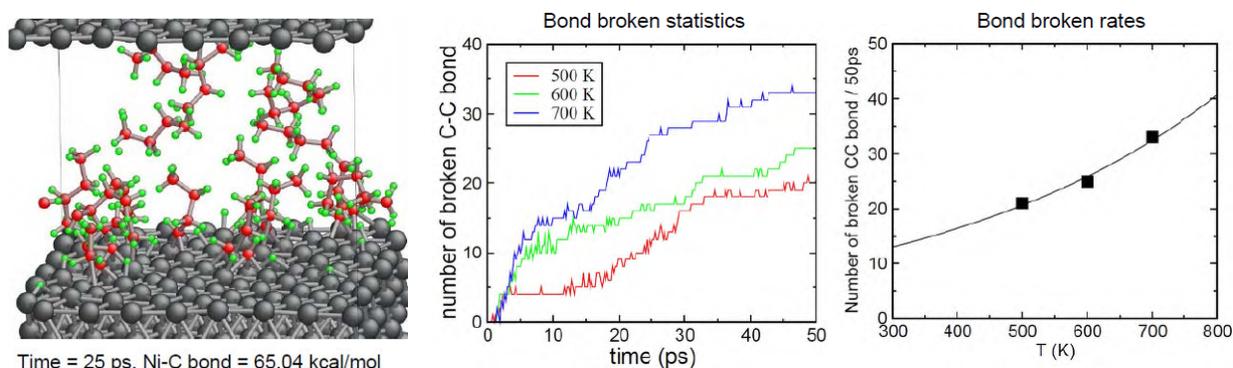


Figure 17. ReaxFF MD simulations of butane conversion on the Ni*(111) surface.

Next, we probed other metals, such as Pt and Ti which have higher metal-carbon bond strengths. Using ReaxFF, butane molecules were allowed to react with Pt and Ti surfaces (Figures 18 and 19). As the temperature over the Pt surface was increased, the first CC bond is broken at 1250K, similar to the reactions on Ni. For the Ti surface, CC cleavage is observed at 900K. Therefore, the C-C bond cleavage temperature decreases by ~ 500 K compared to that for the Ni surface and the $(\text{OH})_3\text{Ti}-\text{CH}_3$ bond energy is 55 kcal/mol according to the ReaxFF potential.

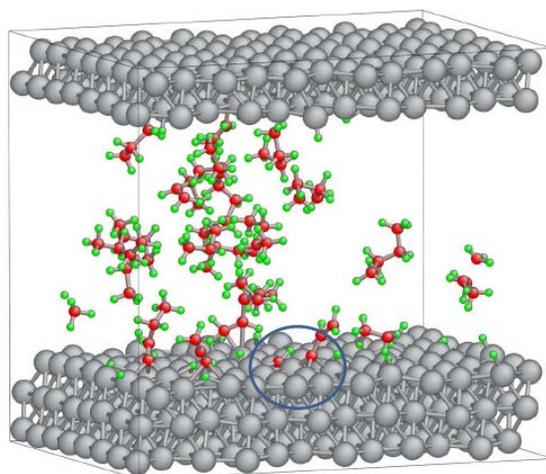


Figure 18. Butane on the Pt (111) surface, $T=1250-1500$ K.

4.2 Results & Discussion

Despite some improvement in the temperature for the catalytic reactions, neither Pt or Ti, are suitable for the alkane oxidation at low temperatures.

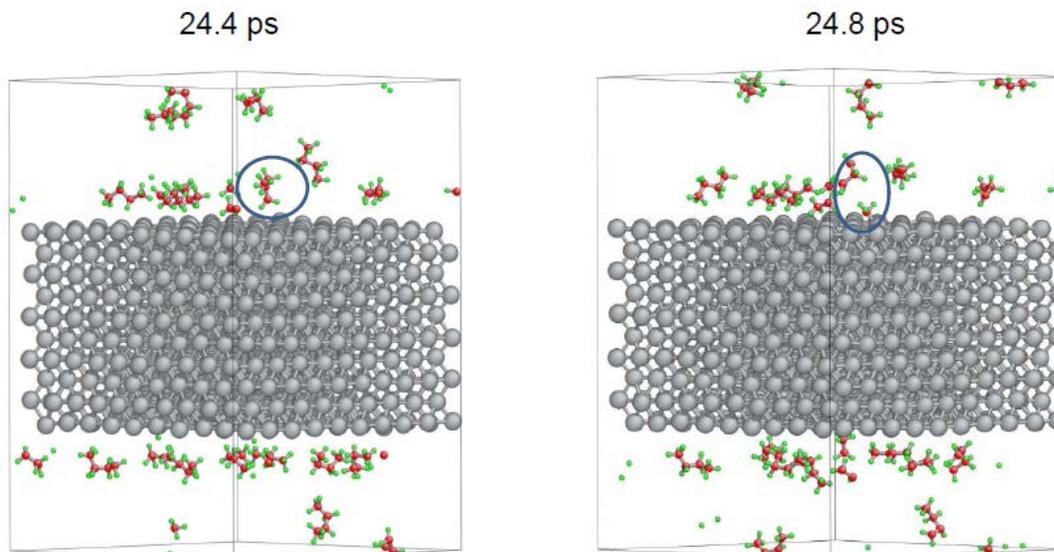


Figure 19. Butane on the Ti surface, T = 900 K.

To examine the oxidation process of the C-C cleavage products at low temperature, we simulated butane reactions on various surfaces (NiO surface and YSZ-Ni interface) using the modified ReaxFF force field (with increased Ni-C bond strength). Here we used our recently developed force-biased Monte Carlo (fbMC) to decrease the computer time to obtain reactive events. In fbMC, atoms are displaced by δ_r , a temperature-dependent component in the force direction for each step. Here α controls the temperature dependence of the jump, k_B is the Boltzmann constant, T is the temperature, F_r is the magnitude of the force, and ε is a scaling factor.

$$\delta_r = \frac{2k_B T}{F_r} \ln \left[\frac{1}{\alpha} + \left(\alpha - \frac{1}{\alpha} \right) R \right] \quad \alpha = \exp \left(\frac{|\varepsilon F_r|}{2k_B T} \right) \quad (1)$$

This gives a kick toward the transition state.

For the NiO(100) surface, we observed C-C cleavage and H₂O formation at 800 K. We also observed C-O bond formation (Figure 20).

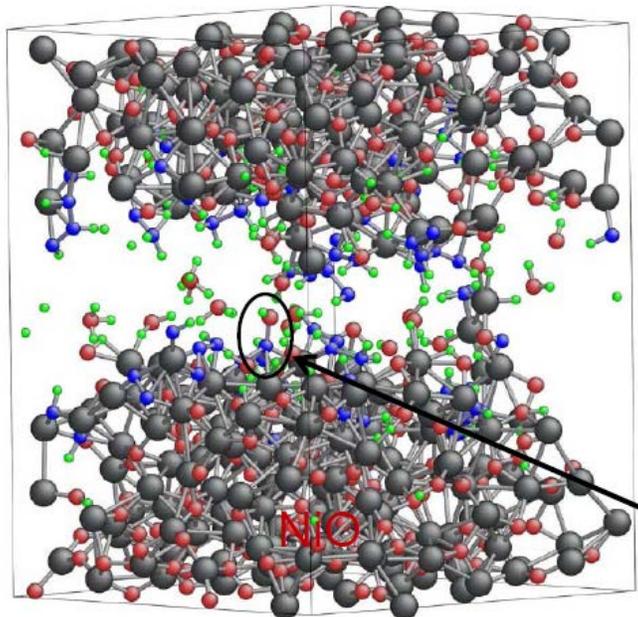


Figure 20. Butane on the Ni(100) surface.

We increased the temperature of our simulations to 900 K and did ReaxFF MD for ~2 ns on the NiO surface. C-C cleavage, H₂O and C-O bond formation were observed at this temperature. We still did not observe formation of isolated CO or CO₂. All the C species remain bonded to the Ni surface. We concluded that the Ni-C bond is too strong to form CO or CO₂. Thus, we decreased the Ni-C bond strength from 65.04 kcal/mol to 56.8 kcal/mol and then to 48.9 kcal/mol and reran the simulations. The CO bond can form on the surface and desorb to the gas phase when Ni-C bond is 48.9 kcal/mol.

To examine the CO oxidation process, 40 CO molecules were placed on the surface to perform ReaxFF MD simulations. Two chemical pathways to form CO₂ were found. In the first process, CO adsorbs on a surface Ni atom, then is oxidized by a neighboring O atom and desorbs into the gas phase. We also observe CO₂ formation via the reaction of a gas phase CO with an under-coordinated oxygen bridging two Ni atoms.

We also simulate reactions of the JP-8 logistic fuel on the Ni(111) surface (Figure 21). The mixture representing JP-8 consists of 2 isooctane C₈H₁₈; 4 methyl-cyclohexane C₇H₁₄; 3 *m*-xylene C₈H₁₀; 6 *n*-dodecane C₁₂H₂₆; 1 tetralin C₁₀H₁₂; 4 tetradecane C₁₄H₃₀ [3]. The temperature was increased from 50K to 2000K over 68ps. Similar to the butane case C-C bond breaking is observed for JP-8 molecular on Ni the (111) surface. Both for JP-8 and butane on the Ni(111) surface, the main products are H, H₂ from the hydrocarbons reaction with Ni surface.

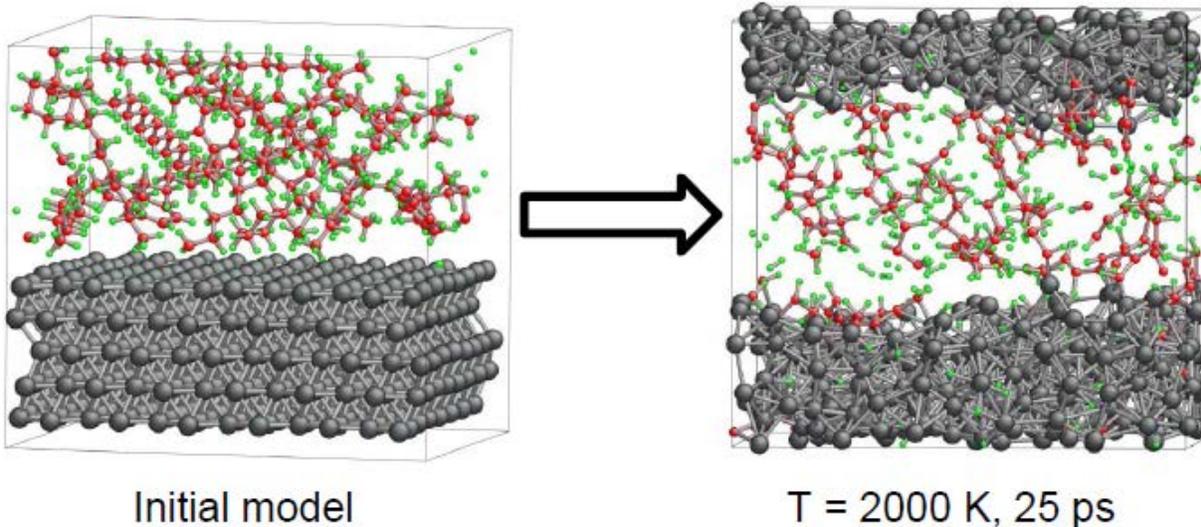


Figure 21. ReaxFF simulation of JP-8 on the Ni (111) surface.

To simulate a surface containing oxygen that could lead to C-O bond formation following hydrocarbon decomposition, the JP-8 mixture was reacted with a surface containing both Ni and yttria-stabilized zirconia (YSZ) (Figure 22). No reactions were observed below 2000K within 50ps.

We simplified the system by excluding the YSZ electrolyte, introducing oxygen atoms into simulations of butane and JP-8 decomposition on the Ni surfaces and built the models in which JP-8 constituents and O₂ molecules were separated by a Ni slab. The parameters governing Ni-C bonds were those developed earlier, in which the Ni-C bond energy was increased to 65 kcal/mol (the modified ReaxFF with Ni* metal) to accelerate hydrocarbon decomposition. The Ni (411) surface was used to provide possible oxygen diffusion to the surface after the C-C cleavage (Figure 23). Following hydrocarbon decomposition, oxygen was allowed to dissociate on one side of the slab and diffuse to the other side, where it reacted with JP-8 decomposition products.

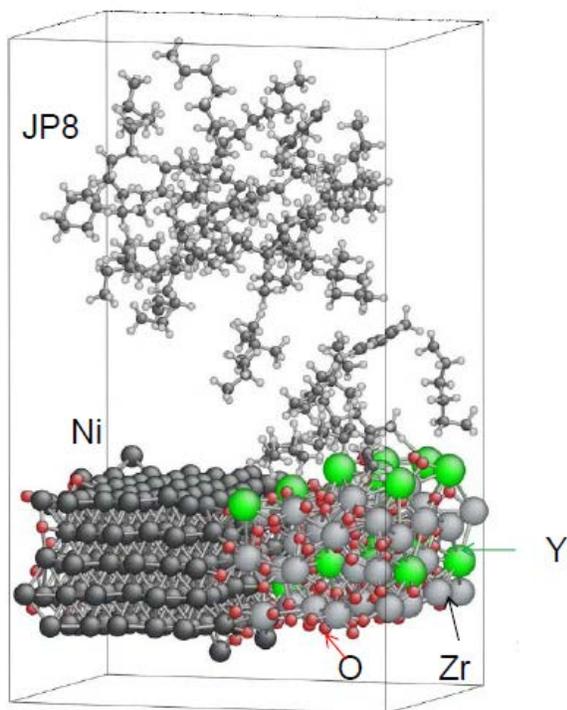


Figure 22. ReaxFF MD simulation of JP-8 on the YSZ/Ni interface.

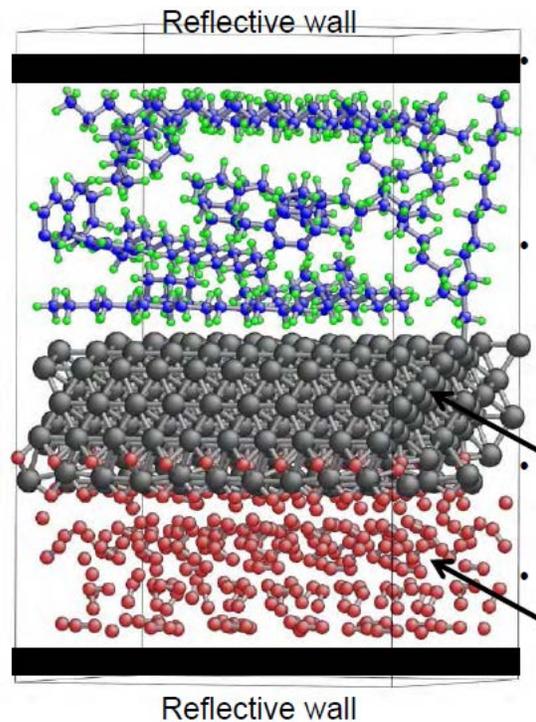


Figure 23. JP-8 on Ni (411) surface + O₂.

At 600K, oxygen atoms diffused across the Ni slab and reacted with surface-bound hydrogen to produce water. Hydrogen also diffused into the slab. The O atom reacts with one H to form OH radical and then OH was further oxidized and reacted with another absorbed H to form H₂O. CH, CH₂, C₂H₄ are formed via C-C cleavage on the Ni surface. The most abundant species are CH and CH₂.

At 500K, C-C cleavage was again observed on the slab. Oxygen reduction to H₂O similar to that at 600K was observed but in smaller amounts. Hydrocarbon species (CH, CH₂, CH₃) form via C-C cleavage on the Ni surface. Observation of CH₃ species indicates less chemistry than at 600 K. During the oxidation process, H₂O molecules and HO radicals formed on the surface and in the gas phase at T = 500 and 600 K. The H₂O forms via two oxidization steps.

At 400K, oxygen did not diffuse through the slab, so no hydrocarbon oxidation was observed.

4.3 Conclusions

Summarizing these results,

- for low temperature activation of CC bonds we require M-C bond energies of 65 kcal/mol (similar to Ni)
- for low temperature activation of CH bonds we require M-H bond energies of 62 kcal/mol (similar to Ni)

- for low temperature formation of CO and dislocation of CO₂ bonds we require M-C bond energies of 49 kcal/mol (similar to Os and Ru)⁷ and MO bond energies of 60kcal/mol

The conclusion that two different M-C bond energies are required, one for activation of the C-C bonds and the other for formation of CO and CO₂ products may be achievable. For example in the Ru-Pt catalysts for methanol fuel cells⁶ the Pt atoms preferentially break the CH bonds to form Pt-H and Pt-COH while the Ru atoms activate H₂O to form Ru-H and RuOH. The Ru-OH leads to formation of RuO_xH_y clusters on the surface that reacts with Pt-COH to form CO₂ while the RuO_xH_y conducts away the proton.

Summarizing, the top-down approach has been used to determine parameters needed to permit low temperature alkane oxidation. The next step would be ReaxFF simulations with metals possessing the above bond energies.

5.0 Conference on low temperature fuel cells for JP8

We have organized a conference on low temperature fuel cells with half a day on Aug. 9 and a full day on Aug. 12. Participants include

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Dr. Hongsen Wang, Cornell, Representing Prof. Abruna

Professor William A. Goddard, Caltech

Dr. Robert Nielsen, Caltech

Dr. Boris Merinov, Caltech

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