Product Protection, the Key to Developing High Performance Methane Selective Oxidation Catalysts

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Abstract: Selective, direct conversion of methane to methanol might seem an impossible task since the C−H bond energy of methane is 105 kcal mol^{-1} compared to the C−H bond energy for methanol of 94. We show here that the Catalytica catalyst is successful because the methanol is protected as methyl bisulfate, which is substantially less reactive than methanol toward the catalyst. This analysis suggests a limiting performance for systems that operate by this type of protection that is well above the Catalytica system.

Introduction

Selective, direct conversion of methane to methanol might seem an impossible task since the C−H bond energy of methane is 105 kcal mol^{-1} compared to the C−H bond energy for methanol of 94. We show here that the Catalytica[1] catalyst (1) developed by Periana is successful because the methanol is protected as methyl bisulfate, which is substantially less reactive than methanol toward the catalyst. The analysis presented in this work suggests a limiting performance for systems that operate by this type of protection that is well above the Catalytica system.

$$CH_4 + 2H_2SO_4 \xrightarrow[\text{H}_2\text{SO}_4,\ 220\,°\text{C}]{\text{PtCl}_2(\text{bpym})} CH_3OSO_3H + 2H_2O + SO_2$$

(1)
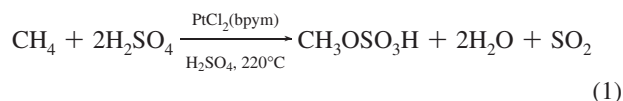
The Catalytica system was reported in 1998,[1] but was not found to be commercially competitive. Despite significant efforts to develop new systems, the Catalytica system remains the most efficient system to date for direct and selective conversion of methane to methanol. Interesting developments include the one by Tang et al.[2] where the inclusion of ionic liquids allowed for reactions at lower acid concentrations, and the heterogenization of the catalyst by Schüth et al.[3] which facilitates the recycling of the catalyst.

The Catalytica reaction is performed in neat sulfuric acid, which acts both as the solvent and as the stoichiometric oxidant. The immediate product in the reaction is the ester methyl bisulfate. It was found experimentally that reaction of the methyl bisulfate with the catalyst was >100× slower than the reaction

of methane.[1] The formation of the ester has been proposed[1] to be important in protecting the product. Indeed studies by Bercaw and Labinger[4] of similar platinum complexes showed that the reactivity of methane and methanol is close to identical. Hence, it is clear that protection is an important issue, but it is not clear how the protection functions. Herein, we present a theoretical study (B3LYP flavor of Density Functional Theory, DFT) of the reactivity of the possible products and find that the difference in reactivity is explained in terms of the difference in the electronic properties of the C−H bonds of the various species. We use these theoretical results to develop a simple kinetic model for product protection.

Results and Discussion

Recently, we reported the acid catalyzed reaction path for the methane activation.[5] We found that protonation of the bisulfate ligand on platinum activates it toward methane coordination. Recalculating this barrier assuming a 1 mM concentration of methane in solution,[6] we find the reaction barrier for methane coordination to be 27.5 kcal mol^{-1} relative to the bisulfate complex **1**, which is followed by insertion of the platinum atom into the C−H bond and reductive deprotonation to give the platinum(II) methyl intermediate (Figure 1).

The C−H bond has been cleaved, but the C−O bond needs to form for the reaction to be complete. Here we present a path to product in which the platinum(II)-methyl complex **8** is oxidized directly by sulfuric acid. It has previously been proposed that platinum(II) intermediates can react with SO$_3$,[7] to form a penta-coordinate Pt-SO$_3$H complex **9** (Figure 2). We

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(6) The exact solubility of methane in H$_2$SO$_4$ at 220 °C is not known. The value of 1 mM is picked as a reasonable value derived from the solubility in water and the fact that the solubility in sulfuric acid is similar. Lutsyk, A. I.; Rudakov, E. S.; Akopov, A. V.; Mochalin, V. N. *Russ. J. Phys. Chem.* **2002**, *76*, 1962.

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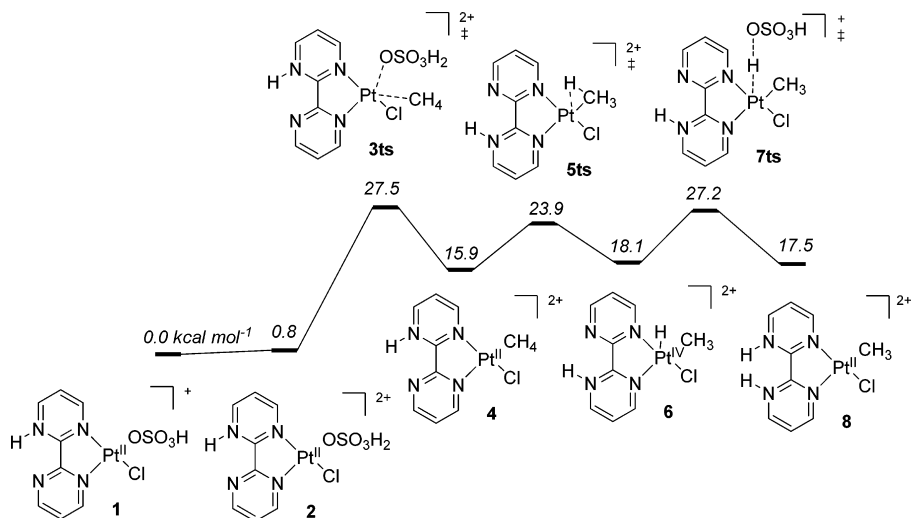
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Figure 1. Mechanism for the C−H activation of methane by the Periana−Catalytica catalyst. Free energies (kcal/mol) at 500 K including solvation by H_2SO_4.
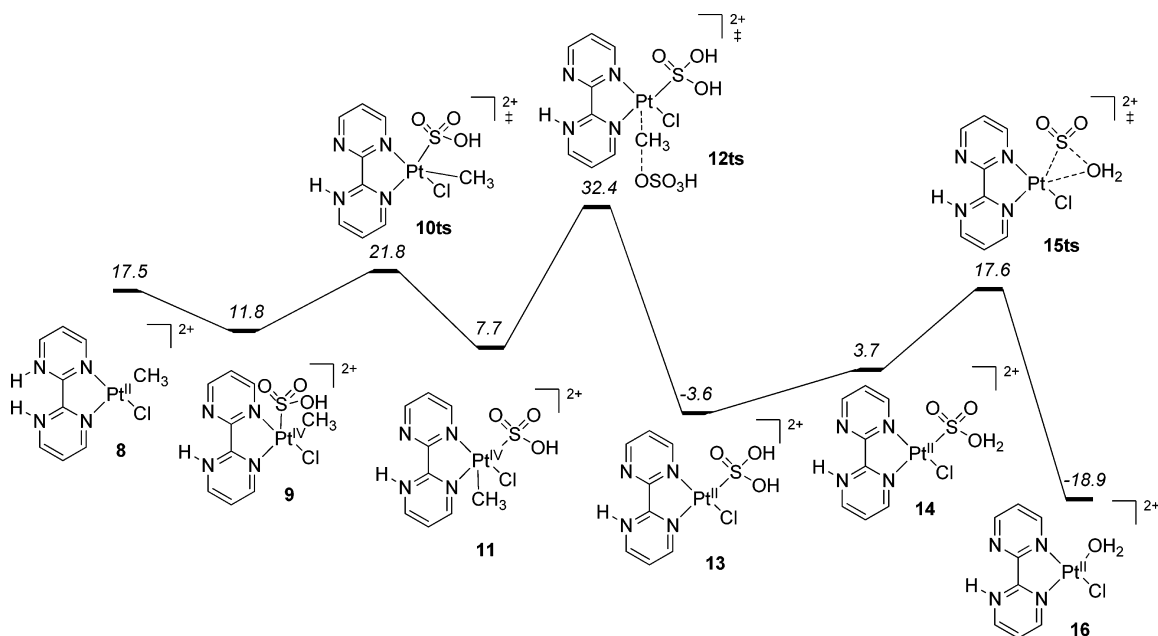

Figure 2. Oxidation of the Pt^{II}-Me intermediate **8** by sulfuric acid. Free energies (kcal/mol) at 500 K including solvation by H_2SO_4.

also find the formation of the platinum S-sulfite complex to be favorable, although we find that the energetics for the process differs considerably from previous estimates since we include the unfavorable energy for formation of SO_3 and H_3O^+ from H_2SO_4 and a proton.

The next step previously proposed[7] was a migratory extrusion of SO_2 to form a $Pt^{IV}(SO_2)OH$ intermediate. However, we find that this step has too a high barrier, 39.9 kcal mol^{-1}. Instead, we find that **9** can rearrange to **11** which has the methyl group is situated in the axial position and that **11** can react with sulfuric acid via first protonation of the S-sulfite group, followed by nucleophilic functionalization **12ts** to give the product methyl bisulfate and a platinum(II)-S-sulfurous acid complex **13**. We calculate the energy of **12ts** to be 32.4 kcal mol^{-1} relative to the starting complex **1**. Complex **13** can then rearrange to **14** where both protons are on the same oxygen atom. Extrusion of SO_2 takes place via **15ts**, which has a barrier of 21.2 kcal mol^{-1} relative to **13**. The product is the aquo complex **16**, which can exchange water for bisulfate to give **1**.

For the selectivity to be high, the oxy-functionalized product must react less readily with the catalyst. First, we examine the direct reaction of methyl bisulfate with **1** (Figure 3). The concentration of methyl bisulfate was assumed to be 1 mM to facilitate comparison with methane. The initial step is the exchange of the bisulfate ligand of **1** for the methyl bisulfate to give **18**. We calculate this reaction is to be endergonic by 12.3 kcal mol^{-1}. We calculate a barrier for this reaction of 20.1 kcal mol^{-1}, which proceeds via initial protonation of the bisulfate ligand, just as for methane coordination. However, since the coordination barrier is not the rate limiting step, vide infra, we expect that the acid dependence is less pronounced for the reaction of methyl bisulfate. For C−H activation to occur the product methyl group must coordinate to the platinum, leading to a calculated barrier for **18** to **20** of 22.0 kcal mol^{-1} (34.3 relative to **1**). We find the C−H cleavage barrier in **20** to be 13.4 kcal mol^{-1}, compared to 8.0 kcal mol^{-1} for the corresponding reaction of the methane complex **3**. Thus, the overall
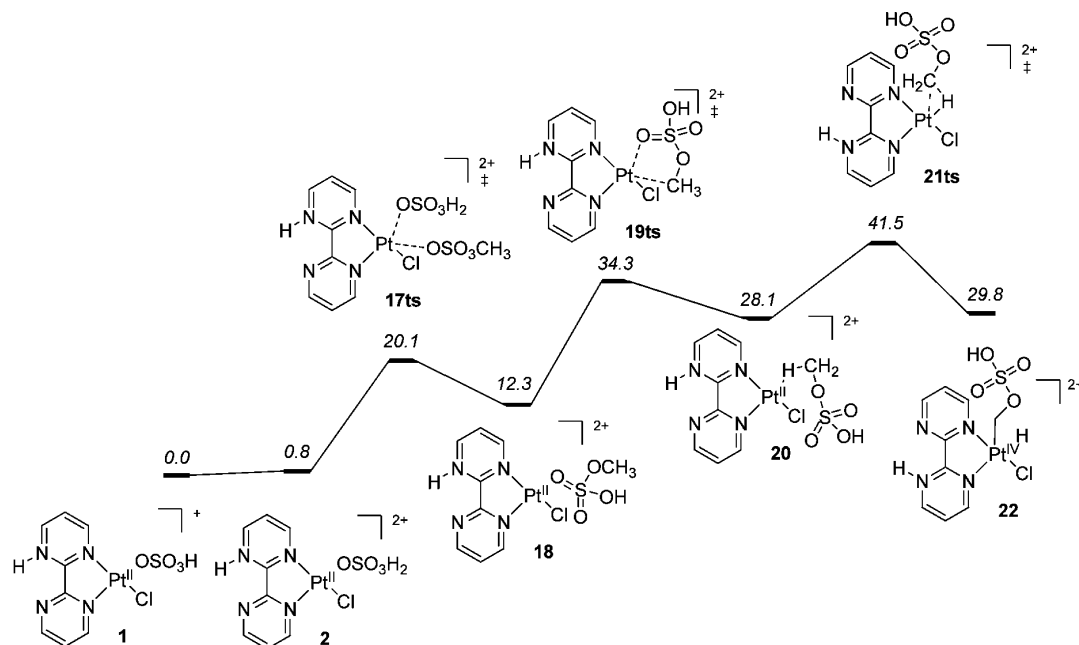
Figure 3. Proposed reaction path for C−H activation of methyl bisulfate by the Periana−Catalytica catalyst. Free energies (kcal/mol) at 500 K including solvation by H_2SO_4.

barrier relative to **1** is 41.5 kcal mol^{-1} (**19ts**), substantially higher than the 27.5 kcal mol^{-1} calculated for the methane reaction.[5]

This difference is expected from the electrophilic nature of the Catalytica catalyst.[8] To quantify that the C−H bonds of bisulfate ester are less nucleophilic than the C−H bonds of methane we calculated the natural bond orbitals[9] (NBOs) of the reactants and the catalyst with a free coordination site. The bonding C−H orbital of methane was found to have an energy quite close to the empty accepting orbital of the platinum fragment, −0.506 Hartree and −0.058 Hartree, respectively (Figure 4). (Note 1 Hartree = 27.2116 eV = 627.51 kcal/mol.) The antibonding C−H orbital was found to have an energy of 0.395, and the highest energy lone pair on platinum has an energy of −0.303 Hartree, leading to a difference in energy of 0.666 Hartree. Hence, the interaction between the bonding C−H orbital and the empty orbital on Pt is likely much stronger than the interaction between the antibonding C−H orbital and a filled orbital on Pt.

The bonding C−H orbital of methyl bisulfate was calculated to −0.546 which is 0.040 Hartree lower than the corresponding orbital of methane. Thus, the interaction is likely weaker between the C−H bond of methyl bisulfate and the platinum moiety than that of methane. The antibonding C−H orbital is lower in energy in methyl bisulfate than in methane; however, since the interaction of the antibonding C−H orbital with the platinum fragment is much weaker, the overall interaction is weaker with the electron deficient methyl bisulfate.

Once the C−H bond is broken, the platinum(IV) alkyl hydride complex **22** is formed. Rearrangement to **24** with the hydride in the axial position is calculated to have a barrier of 1.8 kcal mol^{-1} and to be exergonic by 5.5 kcal mol^{-1} (Figure 5). Reductive deprotonation gives the platinum(II) alkyl species **26**

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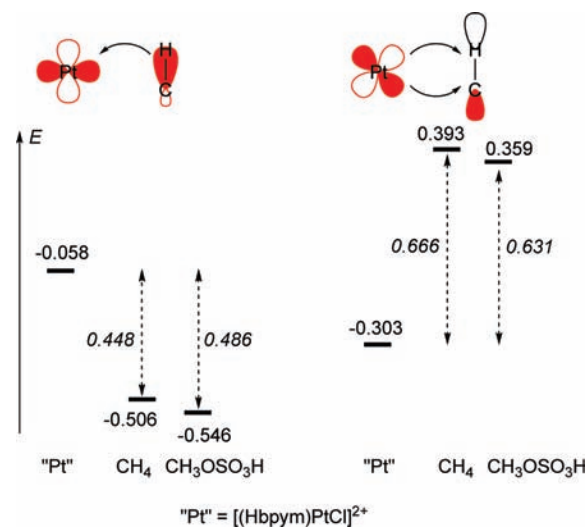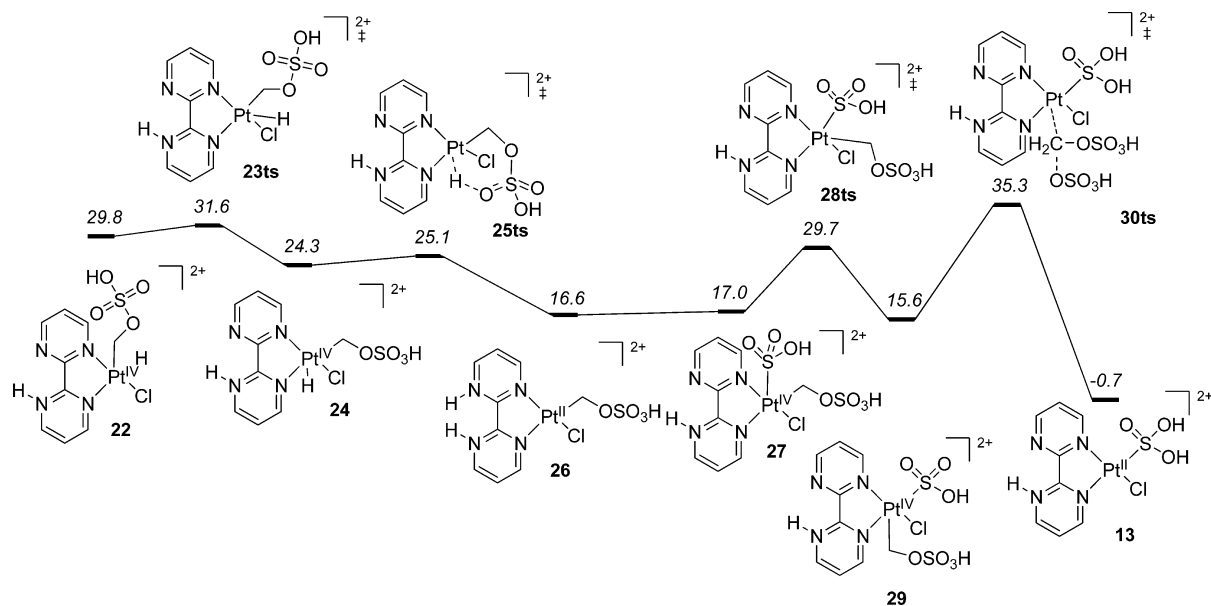
Figure 4. NBO energies (Hartree) of the catalyst moiety "Pt", methane, and methyl bisulfate.

which we calculate to have a barrier of 0.8 kcal mol^{-1}. Once the alkyl species is formed, the platinum center can be oxidized by the same mechanism as the methyl platinum complex **8**, via initial formation of the S-sulfite complex followed by rearrangement to **29** where the alkyl group is in the axial position. The highest energy point at 35.3 kcal mol^{-1} in the oxidation part of the mechanism was calculated to be the functionalization where the alkyl group reacts with a sulfuric acid molecule to form the platinum(II) S-sulfurous acid complex **13** and methylene bisbisulfate which hydrolyzes to formaldehyde. The rate limiting step in the oxidation of methyl bisulfate is thus the C−H cleavage rather than the oxidation as in the oxidation of methane.

We also investigated the possibility that methyl bisulfate could be in equilibrium with sulfuric acid and methanol (Figure 6). Methanol can coordinate to the platinum to give **31**. Assuming 1 mM concentration for methanol, we calculate that formation

Figure 5. Oxidation of the alkyl intermediate formed in the C−H activation of methyl bisulfate. Free energies (kcal/mol) at 500 K including solvation by H_2SO_4.
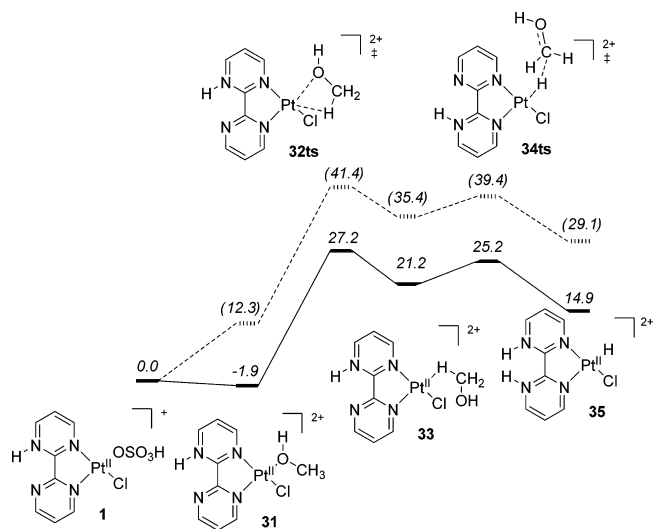

Figure 6. C−H activation of methanol by the Periana−Catalytica catalyst. The numbers in parentheses include the energy for formation of free methanol from methyl bisulfate, which illustrates the importance of the protection. Free energies (kcal/mol) at 500 K including solvation by H_2SO_4.

of **31** is exergonic by 1.9 kcal mol^{-1} relative to **1** and that the rearrangement barrier from **31** to the agostic complex **33** is 29.1 kcal mol^{-1}. The agostic complex formed with methanol **33** coordinates via the hydrogen, whereas the methane complex **3** clearly coordinates with the C−H bond (see Figure 7 for the different binding modes). Also, the subsequent C−H cleavage transition state is quite different, with the methanol providing hydride donation to platinum. The product is then a platinum(II) hydride **35** plus formaldehyde.[5] The mechanism can be viewed as a one site β-hydride elimination. We also found a two-site elimination transition state where the chloride and the proton of methanol were predissociated. The barrier is 2.0 kcal mol^{-1} higher than the one-site elimination, but could be more important under low chloride conditions. The highest barrier for methanol activation is only 1.6 kcal mol^{-1} higher than the methane C−H activation barrier, and the overall oxidation has a lower barrier

for methanol than methane oxidation. A similar observation was made by Bercaw and co-workers when methane and unprotected methanol were reacted with platinum complexes.[6] However, we calculate that the formation of methanol from methyl bisulfate is endergonic by 14.2 kcal mol^{-1}, showing that product protection is crucial to the high selectivities of these systems. This protection effectively raises the barrier from 27.2 to 41.4 kcal mol^{-1}.

Again the oxidation of the electron rich intermediate, here **35**, starts with the formation of an S-sulfite complex, which we calculate to be favorable by 5.3 kcal mol^{-1}. Rearrangement via **37ts** to the axial hydride complex **38** followed by reductive deprotonation and protonation of the S-sulfite ligand gives the platinum(II) complex **13**, as outlined in Figure 8. Just as for the methyl bisulfate oxidation, we find that oxidation is not rate limiting. Instead the formation of the agostic complex **33** has the highest barrier.

To understand how these issues combine to determine the overall selectivity, we developed a simple model for product protection that relates the maximum selectivity at a given product concentration to the barriers calculated above. Scheme 1 relates selectivity and product concentration for a given set of kinetic parameters. This model is general enough to accommodate different microscopic mechanisms and would allow various systems to be compared quantitatively. In a batch process with no removal of product, constant acid concentration and constant methane pressure, selectivity drops in time from 100% to 0 (Figure 9). Simultaneously, product concentration ([prod] = [CH$_3$OH] + [CH$_3$P]) increases from zero and approaches its quasi steady state value of $k_1 P_{CH4}/k_{ox}$ at long times, when methane and products are oxidized at equal rates. With no protection (curve $K_P = 0$), the concentration approached at long times is $k_1 P_{CH4}/k_2 \approx 8 \times 10^{-6}$ M in Figure 9. As a mechanism for methanol protection is "turned on" ($K_P > 0$), more product is sequestered in the protected form and the product concentration present at a given selectivity increases. However, as K_P increases to the point where the rate of oxidation of protected product ($k_3 K_P$) exceeds that of CH$_3$OH oxidation (k_2), increasing K_P has no further benefit and performance is
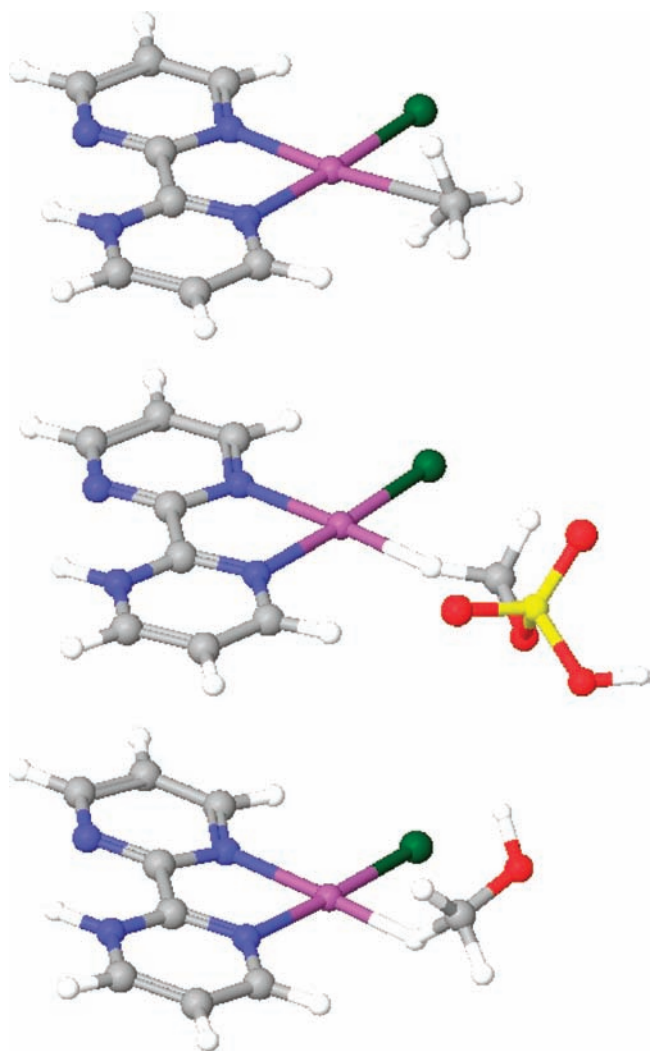
Figure 7. Top: Pt-CH4 complex **4**. Bond distances: Pt−H 1.877 Å Pt−C 2.491 Å C−H 1.147 Å. Middle: Pt-CH3OSO3H complex **20**. Bond distances: Pt−H 1.890 Å Pt−C 2.869 Å C−H 1.157 Å. Bottom: Pt-CH3OH complex **33**. Bond distances: Pt−H 1.758 Å Pt−C 2.734 Å C−H 1.233 Å.
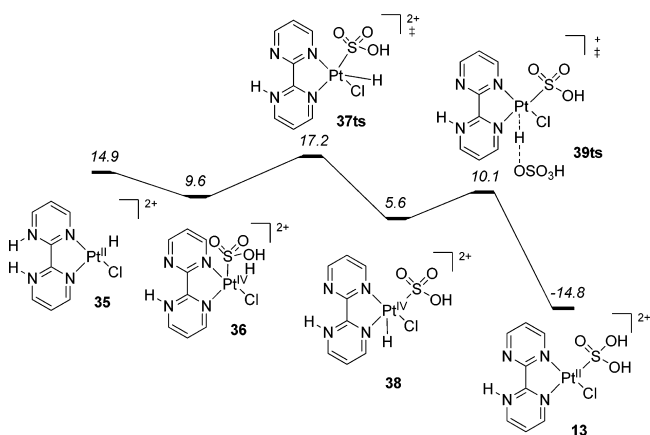

Figure 8. Oxidation of the Pt^{II}−H intermediate **35** by sulfuric acid. Free energies (kcal/mol) at 500 K including solvation by H_2SO_4.

bounded by $K_P \rightarrow \infty$. The limiting case for the parameters in Figure 9 is ~4 M, which leads to 81% selectivity, while 1 M leads to 95% selectivity.

Values for the four parameters used in Scheme 1 were estimated as functions of acid concentration from the perfor-

Scheme 1. Kinetic Model Relating Product Protection and Selectivity for the Periana−Catalytica Catalyst
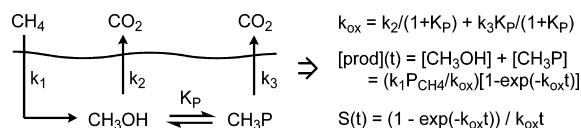
mance of the Catalytica catalyst and our calculated relative rates of methanol and methyl bisulfate oxidation. The curves "99%" and "100%" represent the progress of reactions assuming that the concentration of sulfuric acid is kept constant. The coincidence of lines "100%" and $K_P \rightarrow \infty$ show that the performance of the Catalytica catalyst in 100% sulfuric acid cannot be improved by increasing K_P above its calculated value of 2×10^7. Since the net reaction 1 generates two moles of water for each turnover, the acidity (and thus K_P) decreases as the batch reaction proceeds. Thus, a Catalytica reaction begun in 102% H_2SO_4 yields the selectivity and product concentration marked by the oval in Figure 9.

On the basis of our kinetic analysis, we suggest two approaches for achieving higher yields simultaneously with high selectivity.

Maintain High Acidity. It is well-known that a concentrated medium is needed for high activity, and here we show above that it is also crucial for selectivity. The analysis in Figure 9 shows that a highly acidic medium is key to achieving high yields and selectivities. We want to move from the oval describing the Catalytica catalyst toward the 100% line, which would lead to a ~4-fold increase in product concentration from the current value of ~1 M, while maintaining the same 80% selectivity. Alternatively, we could attain 95% selectivity while maintaining the current product concentration of 1 M. *Suggestion:* Since use of H_2SO_4 as the oxidant will always lead to lower acidity as the reaction proceeds, we suggest using an alternative oxidant that produces fewer equivalents of water, e.g., Cu^{II} or Fe^{III}.[10]

Promote Product Separation. By removing product continuously, the product concentrations could be kept low, putting us to the left on the line in Figure 9, leading to higher selectivity. Any change that increases the volatility of the protected product could facilitate this separation. *Suggestion:* Since removal of methyl bisulfate from sulfuric acid is not feasible, we suggest using a monoprotic solvent, e.g., triflic acid or trifluoroacetic acid, whose methyl ester interacts more weakly with the solvent through fewer hydrogen bonds. This would lead to a higher vapor pressure for the product and hence lower concentration, higher selectivity, and faster rates. Alternatively, addition of HCl to sulfuric acid could give methyl chloride which is easily separated. The levels of HCl would have to be set carefully since excess amounts of chloride could inhibit the catalyst.

Conclusions

We have determined mechanisms for C−H activation of methane, methyl bisulfate, and methanol, as well as the subsequent steps of oxidation of the alkyl intermediates by sulfuric acid. We show that the high performance of the Catalytica catalyst results from the formation of a product,

(10) CuCl2 is used in the Wacker process where it oxidizes the Pd catalyst. The reduced copper is the continuously reoxidized in another reactor by O2. In sulfuric acid the solubility of these oxidants is low. Addition of a ligand could change that equilibrium to favor the solvated form of the oxidant.
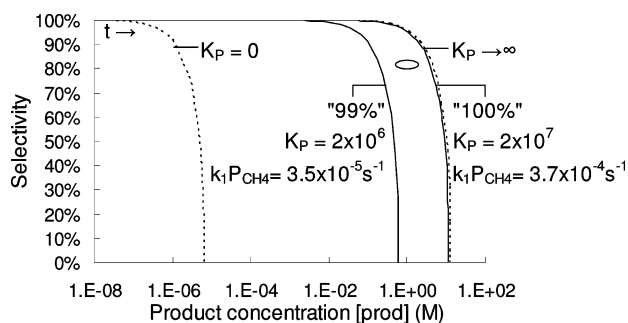
Figure 9. Effect of product protection on selectivity and maximum product concentration for the Periana−Catalytica catalyst. $K_P = 0$ represents no protection and $K_P = 10^\infty$ represents maximum protection. In 100% sulfuric acid, the protection is close to the maximum, while it drops significantly already at 99%. The oval represents the experimental result of the Catalytica system.[1]

methyl bisulfate, that is stable under reaction conditions. From an NBO analysis, we conclude that the bisulfate group protects the C−H bonds of the product by making them less nucleophilic and, hence, decreases the interaction with the electrophilic platinum. The protection of the product allows production of molar quantities of product. In contrast, if methanol had been the direct product, then the limiting concentration would be determined by the $K_P = 0$ line, leading to micromolar product concentrations. Figure 9 shows that the performance of the Catalytica catalyst system lies below the theoretical maximum, suggesting room for improvements toward an industrially viable process.

Computational Details

All calculations were performed with the hybrid density functional B3LYP[11] as implemented in the Jaguar 7.0 package.[12] Geometry optimizations included solvation using the self-consistent Poisson−Boltzmann reactive field (PBF)[13] with a dielectric constant of 98.0 and a probe radius of 2.205 to simulate sulfuric acid. For solvation of smaller ions, two explicit solvent molecules were included. For geometry optimizations, the LACVP** basis set[14] was augmented with an additional compact d-function on sulfur.[15] For single point energies, we used the LACV3P**++ basis set

augmented with one f-function on platinum[16] and two d-functions and an f-function on sulfur.[15] Frequency calculations were performed numerically including the self-consistent PBF-solver at the B3LYP/LACVP**(+d on S) level. Free energies were calculated as the sum $G = E(\text{lacv3p}\text{**}++ \text{ 2df(S) f(Pt)}) + G_{solv} + ZPE + \Delta H(500)$. Reactions such as **14 → 16** (where an SO_2 molecule is released) lead to product molecules with 6 additional translational−rotational degrees of freedom that in solution become librational modes. We estimate the entropy of these librational modes as 60% of the gas phase values.[17] All species are calculated at 1 M or 1 atm unless stated otherwise in the text, and sulfuric acid is corrected to 18 M to reflect typical experimental conditions. The sum of uncertainties contributed by the electronic energy, solvation energy, and entropy estimation is multiple kcal mol^{-1}, though we find energy changes for analogous reactions typically display cancellation of error. For comparison, the H/D exchange activation free energy calculated as (27.5 kcal mol^{-1}) matches the activation free energy of 28−30 kcal mol^{-1} experimentally measured.[18]

Supporting Information Available: Cartesian coordinates and energies of the calculated geometries, and the full kinetic analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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