

C–H activation in strongly acidic media. The co-catalytic effect of the reaction medium†

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Quantum mechanical (QM) results are used to establish the role of sulfuric acid solvent in facilitating the reaction between Pt^{II}(bpym)Cl₂ (bpym = 2,2'-bipyrimidinyl) and methane; coordination of methane to the platinum catalyst is found to be catalyzed by the acidic medium.

Selective low temperature conversion of methane to methanol remains as a grand challenge for chemical technology.¹ The top five highest yielding systems utilize Pt^{2a}, Hg^{2b}, Au^{2c}, I^{2d}, and Pd^{2e} catalysts and a concentrated sulfuric acid reaction medium (acetic acid in the case of Pd). The most promising system to date uses Pt(bpym)Cl₂ as the catalyst and concentrated H₂SO₄ as both the solvent and the oxidant (Fig. 1).^{2a} The oxy-functionalized product is a mixture of methyl bisulfate, protonated methanol and methanol depending on the concentration of the sulfuric acid solvent. The methyl bisulfate and protonated methanol can be readily hydrolyzed to methanol. Despite excellent one pass yields of >70% and selectivity of >90% at 220 °C, this reaction [developed^{2a} at Catalytica by Periana *et al.* in 1998] has not been commercialized (Scheme 1). It was shown by Periana *et al.* that the methanol yield and selectivity were excellent in highly concentrated sulfuric acid (102% = 9% SO₃ dissolved in H₂SO₄) but as the reaction proceeded the water product led to dramatically decreased rates^{2a} for concentrations lower than 96%. H–D exchange of CH₄ in D₂SO₄ (Fig. 2) was found to proceed at lower temperature (150 °C) than methanol formation, and the rate of the H–D exchange was found to be strongly dependent on the acidity of the solvent.^{1,3} Most interesting was that under conditions where H–D exchange was observed without formation of methanol, the methane reactant molecules became multiply deuterated.^{2a} This observation implies that there is a barrier to coordinating CH₄ with the catalyst to form an ion pair complex, followed by a smaller barrier for activating this complex to form a M–CH₃ adduct, as suggested by Kua *et al.*⁴ Herein we use QM to show how the acid plays an integral part of the reaction mechanism,‡ explaining the strong acid dependence of the catalyst.

Prior studies⁴ proposed that the role of the strong acid solvent is to generate the bisulfate platinum complex **1**, from which the bisulfate is more readily replaced by methane. At

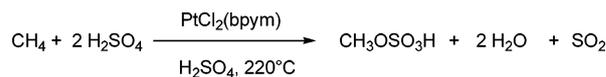
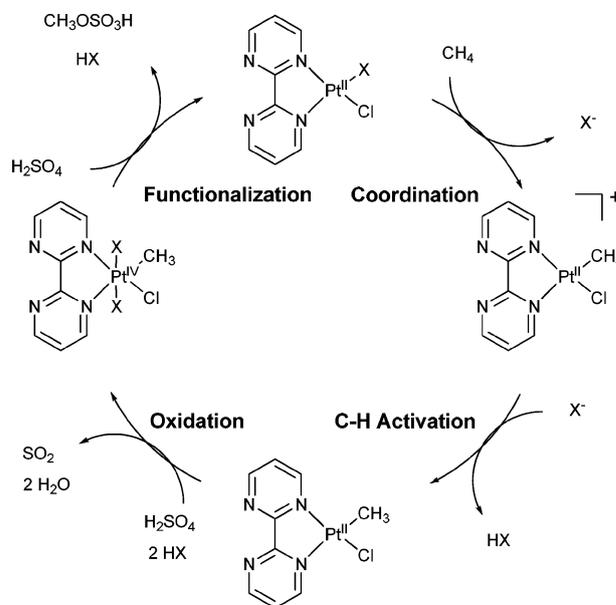


Fig. 1 Catalytica system by Periana *et al.* (ref. 2a).



Scheme 1 Proposed mechanism of the Catalytica system at 220 °C in concentrated sulfuric acid. At 150 °C, in D₂SO₄, incorporation of multiple D in the CH₄ but no conversion to oxygenated products has been observed. This indicates that reversible methane coordination and C–H cleavage occurs at a temperature lower than that required for oxidation.

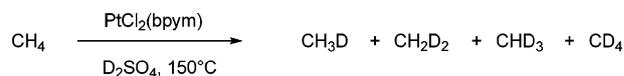


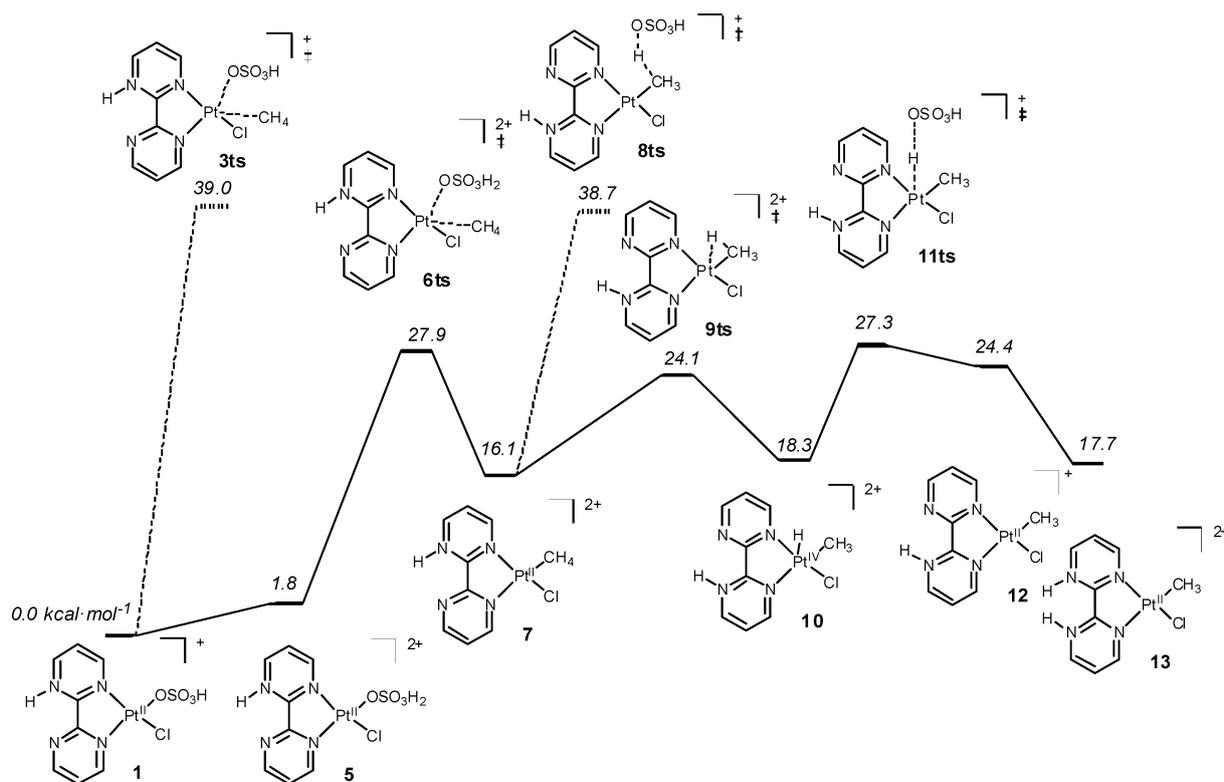
Fig. 2 At lower temperature H–D exchange of CH₄ in D₂SO₄ is observed. Multiple deuteration is observed.

lower solvent acidities, the higher concentrations of water would replace the bisulfate with H₂O, leading to a new, more stable, ground state **2**, which would increase the barrier to reach the uptake transition state. This original proposal assumed that the aquo complex reacts *via* the same transition state as the bisulfate complex. Since this assumption was not tested, we used QM to calculate the barriers for displacing bisulfate and water, respectively. We find that replacing water (**4ts**) has a barrier 1.8 kcal mol⁻¹ lower than replacing bisulfate (**3ts**) (Fig. 3). This means that the sulfuric acid must be involved in some other way than in the previous explanation.

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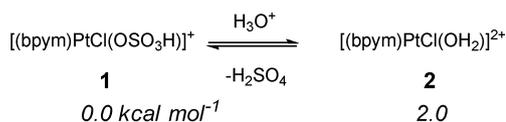


Scheme 2 Relative G (450 K) for acid-catalyzed C–H activation. All species are calculated at 1 M except CH_4 30 atm and H_2SO_4 18 M.

We calculate that the stability of the aquo complex **2** in sulfuric acid is very dependent on the water concentration. Indeed Fig. 4 shows that the bisulfate complex is more stable at high H_2SO_4 concentrations (where most water is present as H_3O^+). However in more dilute acid (1 M free H_2O) the aquo complex **2** is significantly more stable than **1**, leading to an uptake barrier of $37.2 \text{ kcal mol}^{-1}$ of **2**.

Protonation of the bisulfate leaving group of **1** would produce a sulfuric acid solvent complex **5** (Scheme 2). This complex is likely to coordinate methane more readily than the bisulfate complex **1**. We calculate the protonation to be endergonic by merely $1.8 \text{ kcal mol}^{-1}$, which means that if the barrier for methane uptake at **5** is more than $1.8 \text{ kcal mol}^{-1}$ lower than uptake at **1** the reaction will be catalyzed by acid.

In concentrated acid:



In dilute acid:

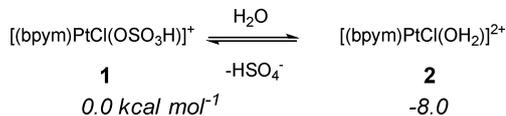


Fig. 4 Formation of the platinum aquo complex **2** is unfavorable in concentrated sulfuric acid (1 M H_3O^+). In dilute acid (1 M non-protonated H_2O) it is significantly more favorable to form **2**.

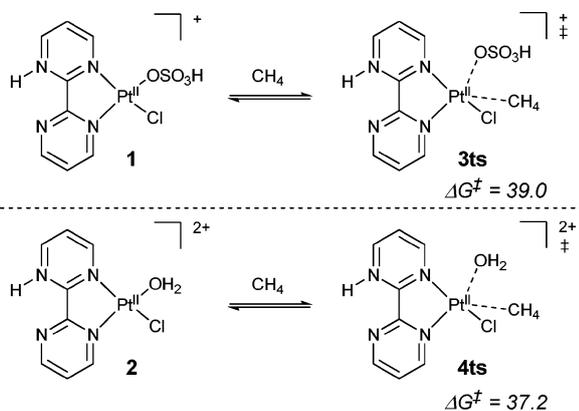


Fig. 3 ΔG^\ddagger (450 K) for direct methane coordination by **2** is calculated to be more facile than the corresponding reaction by **1**.

Indeed we find that the uptake barrier is significantly lower at **5**. We calculate that the overall uptake barrier from the bisulfate complex *via* the sulfuric acid complex **5** to the transition state **6ts** is $27.9 \text{ kcal mol}^{-1}$, compared to the 39.0 for direct reaction between **1** and methane! Thus the acid leads to a most dramatic acceleration of the uptake. Since the nucleophile is methane, whose activity is not changed by the acid concentration, the more acidic the better.

Acid-catalyzed ligand exchanges are known in coordination chemistry. Pearson *et al.* found that acetic acid, boric acid and nitric acid increased the rate of chloride exchange at Pt^{II} complexes.⁵ They proposed that the acids interacted with the metal center as Lewis acids. However, it was not completely clear if that was the case, especially since their proposed mechanism assumed a 5-coordinate platinum(II) intermediate with no strongly π -accepting ligands, which is unlikely.⁶

Once the methane complex is formed, there are two possible paths to form a Pt–C bond (Scheme 2). We calculate that the previously proposed electrophilic substitution where the coordinated methane is deprotonated by a bisulfate has a transition state barrier of 38.7 kcal mol⁻¹ higher in energy than the starting complex **1**, making it inaccessible. The other possibility is oxidative addition to cleave the C–H bond *via* insertion of the metal into the C–H bond to create a platinum(IV) methyl hydride species. This complex could then be reductively deprotonated to give the platinum(II) methyl. We calculate the transition state for the insertion to be only 8.0 kcal mol⁻¹ higher than the methane complex **7** in free energy, which is 3.8 kcal mol⁻¹ lower in energy than the uptake transition state.⁴ The resulting Pt^{IV} intermediate **10** is 2.2 kcal mol⁻¹ above **7**. We found that reductive deprotonation of **10** by bisulfate is relatively difficult and the energy of the transition state **11ts** only 0.6 kcal mol⁻¹ lower than the methane uptake transition state **6ts**. This is consistent with the experimental results suggesting that reactions between D₂SO₄ and CH₄ catalyzed by Pt(bpym)Cl₂ lead to multiple H–D exchange events for every coordination of methane to the Pt(II) center.^{2a} Yet, since all the isotopologues were present there would have to be two barriers in the H–D exchange reaction with very similar energy transition states. A mechanism with high uptake and a low cleavage/deprotonation path would produce only fully deuterated product, while a path with facile uptake and rate limiting cleavage/deprotonation would yield only mono-deuterated product. Similar results were observed by Labinger *et al.* on model systems where they observed that platinum(II) alkane complexes undergo rapid and reversible C–H cleavage followed by slow displacement of the alkane by solvent.⁷

We present the first results establishing the mechanism by which the strongly acidic medium facilitates the activation of methane. The protonation of one of the ligands on platinum reduces the barrier for displacement of that ligand by 11.1 kcal mol⁻¹. We expect that this effect of acid found here for platinum also operates for catalysis by other electron-deficient metals (*e.g.*, Hg, Au) in sulfuric acid. Such understanding of the role of the reaction medium is crucial, since the medium acts as solvent, oxidant, and co-catalyst, and

it provides protection of the methanol product. Thus to achieve high selective yields and low temperature conversion of CH₄ to CH₃OH it is essential to consider the reaction medium and its interaction with the catalyst is required, rather than only focusing on the catalyst. We also show here that the C–H cleavage goes *via* a platinum(IV) methyl hydride species followed by reductive deprotonation, and not *via* direct deprotonation of the platinum(II) methane complex.

Notes and references

‡ These quantum mechanical calculations use the B3LYP flavour of density functional theory (DFT) as described in the ESI†. We use the Hay and Wadt small core angular momentum projected effective core potential while treating the H, C, N, O, S and Cl atoms as all electron and using a triple zeta quality basis set. Most important is the use of the PBF continuum solvent method of Jaguar (using a solvent radius of 2.205 Å and a dielectric constant of 98), which we find leads to accurate pK_a values and solvation energies. Some ions required explicit solvation, which is discussed more in the ESI†.

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