Homogeneous Conversion of Methane to Methanol. 1. Catalytic Activation and Functionalization of Methane by *cis*-Platin in Sulfuric Acid: A Density Functional Study of the Thermochemistry

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Abstract: The recent announcement by Periana et al. (*Science* **1998**, *280*, 560) of 70% one-pass homogeneous catalysis of methane-to-methanol conversion with high selectivity in sulfuric acid solution under moderate conditions represents an important advance in the selective oxidation of alkanes, an area of considerable current interest and activity. The conversion is catalyzed by bis(2,2′-bipyrimidine)Pt(II)Cl$_2$. In this work, the thermodynamics of the activation and functionalization steps of the related *cis*-platin-catalyzed process in H$_2$SO$_4$ are calculated using density functional techniques, including the calculation of solvation free energies by a dielectric continuum method. It is concluded that electrophilic attack by CH$_4$ on an intermediate which may be regarded as a tetracoordinate solvated analogue of a gas-phase, T-shaped, three-coordinate Pt(II) species, followed by oxidation of the resulting methyl complex to a methyl bisulfate ester, is thermodynamically feasible. This is in general accord with the mechanism proposed by Periana et al., but now, on the basis of the computational predictions, the nature of the active catalyst, as well as that of the intermediates, can be more precisely defined. While the alternative mechanism of oxidative addition does not appear to be thermodynamically feasible when using Pt(II) catalysts, catalysis by a Pt(IV) species is predicted to be, on thermodynamic grounds, a viable alternative pathway.

Introduction

The selective oxidation of methane to methanol or other efficiently transportable material represents one of the outstanding challenges of the chemical industry. Methane, being the dominant component of natural gas, is an abundant resource, yet in comparison with petroleum products it is currently underutilized, mainly because the transportation of a gas with a very low boiling point is expensive. The situation could change drastically if a simple, efficient, and economical method were found to convert methane to a readily transportable material such as methanol. A promising avenue for this appears to be homogeneous catalysis in solution,[1−10] where the first step is the *activation* of methane, whereby it becomes bound to the catalyst as CH$_3$. In a subsequent *functionalization* step, methanol is formed, with the subsequent regeneration of the catalyst.

Following their successful work utilizing mercuric salts as catalysts,[11] Periana et al.[12] recently reported the direct, low-temperature, oxidative conversion of methane to methanol catalyzed by platinum salts such as dichloro(η-2-{2,2′-bipyrimidyl})platinum(II) [Pt(bpym)Cl$_2$] at greater than 70% one-pass yield with 80% selectivity. Given their earlier observations that the inorganic salts of Tl, Au, Pd, and Pt promote the oxidation of methane in strong oxidizing acids such as concentrated sulfuric acid, the studies using [Pt(bpym)Cl$_2$] were also carried out in concentrated H$_2$SO$_4$ at temperatures of ∼200 °C and pressures of 500 psi (34 atm). The net chemical reaction that takes place is

$$CH_4 + 2H_2SO_4 \rightarrow CH_3OSO_3H + 2H_2O + SO_2 \quad (1)$$

whereby methane is oxidized to methyl bisulfate. A very important feature of the overall process is that the methyl ester is considerably less reactive with the catalyst than methane. This is attributed to greater inhibition of the presumed electrophilic reaction of the C−H bonds of methylbisulfate in comparison with methane as a result of the greater electron-wihdrawing ability of the bisulfate group. *cis*- and *trans*-[Pt(NH$_3$)$_2$Cl$_2$] were also found to be effective catalysts, although from a practical point of view [Pt(bpym)Cl$_2$] is preferred since it is much more stable than the diammine complexes, which lose NH$_3$ by protonation that results in the formation of insoluble PtCl$_2$ and ammonium bisulfate.

The proposed reaction mechanism of Periana et al.,[12] shown in Figure 1, postulates an equilibrium between the precursor [Pt(bpym)Cl$_2$] and a "T-complex" which is the actual active

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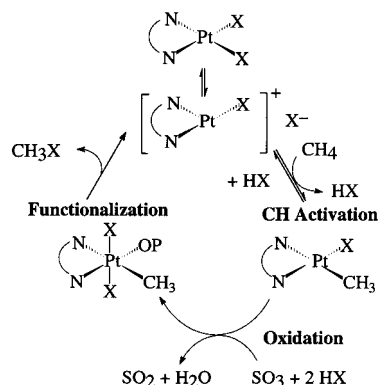(5) Shilov, A. E.; Karasevich, E. I. *Catal. Met. Complexes* **1994**, *17*, 87.

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Figure 1. Proposed reaction mechanism of Periana et al.[12] for the oxidation of methane.

catalyst. The exact chemical identity of the T-complex is uncertain, although it is believed to be a bisulfate complex, possibly a $[Pt(bpym)_2HSO_4]^+HSO_4^-$ ion pair, the chloride ions of the original *cis*-platin molecule having been completely replaced. The reaction of this catalyst with methane activates one of its CH bonds, binding the resulting methyl (formally as an anion) to Pt. This step is, in effect, an electrophilic substitution process, where the T-complex acts as an electrophile and is substituted for a proton in methane. Oxidation of this methyl complex by bisulfate results in a hexacoordinate complex, possibly $[Pt(bpym)_2(HSO_4)_3CH_3]$, from which, in the final functionalization step, methyl bisulfate is eliminated, regenerating the catalyst. An alternative to the electrophilic activation step is the oxidative addition of methane to a Pt(II) complex, although Periana et al.[12] strongly favor the former mechanism. Apart from the additional complexity introduced by the susceptibility of the ammonia ligands to protonation and dissociation, it is a reasonable supposition that the somewhat more rapid catalysis observed with the analogous ammines proceeds by an essentially similar mechanism.

Given our interest in the general problem of methane activation and functionalization by homogeneous catalysis, we decided to carry out a quantum chemical study on the above process. Our initial aim has been to compute the thermochemical parameters, viz., enthalpies, entropies, and Gibbs free energies, of the individual reactions in the catalytic process studied by Periana et al.,[12] partly as a test of our computational strategies but also with a view to verifying the proposed mechanism. However, to reduce the complexity of the calculations, we study *cis*-diammine complexes rather than the bipyrimidine complexes on which the experimental work was done. (As remarked above, the *cis*-diammine analogue of $[Pt(bpym)Cl_2]$ has been found to have a high catalytic activity.) Given the level of uncertainty with regard to the mechanism of the catalysis and nature of the actual catalyst, we undertook an explorative study where we consider several different reaction schemes as well as a number of different complexes as possible catalysts, in addition to the ion pair type T-complex proposed by Periana et al.[12] The mechanisms considered are the electrophilic substitution reaction scheme of Periana et al., the CH activation by oxidative addition of methane to a Pt(II) complex, and one involving the formation of a Pt(IV) catalyst.

Computational Methods

The calculations reported in this paper were performed using density functional theory (DFT), utilizing the B3LYP hybrid functional.[13–16]

The effective core potentials (ecp) and basis sets of Stoll et al.[17,18] were used for the heavy atoms. Thus, the valence basis for Pt is a [6s5p3d] set to accommodate the valence 5s, 5p, and 5d electrons, while for C, N, O it is [2s2p], for S and Cl it is [2s,3p], and for H it is a [2s] set.[19] For each molecular species studied, the geometries were fully optimized and the harmonic vibrational frequencies also computed. The partition functions and hence thermal corrections to the electronic and zero-point energies as well as molecular entropies were obtained using the standard formulas for quantum harmonic oscillators and classical rotors as well as classical translation. Solvation free energies were calculated using the isodensity polarized continum model (IPCM)[20] and, in some instances, by the self-consistent multipole moment reaction field (SCMMRF) method.[21] In the SCMMRF method, the solute occupies a fixed cavity of radius a_0 within the solvent field, which is obtained from the multipole moments (up to hexadecapole) and the dipole polarizability of the solute. In the IPCM model, the cavity is defined by an isodensity surface of the molecule, determined by an iterative self-consistent process. Application of the IPCM method has, however, necessitated all electron calculations; these were performed at the ecp-optimized geometries, the core orbitals of each atom expanded in terms of Huzinaga's minimal basis sets.[22] The methods and basis sets discussed above were used with a good degree of success in our previous work on molecular hydrogen complexes of osmium(II).[23,24] While it would be instructive to extend the basis sets and to experiment with other functionals, the majority of the molecules considered here are so large as to make such studies very expensive and too time-consuming at this stage.

The treatment of solvation (by H_2SO_4) in terms of a uniform dielectric approach is the least satisfactory feature of these calculations. Solvation always involves specific effects arising from chemical interaction between the solute and neighboring solvent molecules to a greater or lesser extent, and these are not explicitly taken into account by the above methods. We shall see, indeed, that in order to characterize the catalyst involved in the functionalization step, it will be necessary to go beyond the continuum approximation.

In our previous work[24] on ligand exchange reactions in molecular hydrogen complexes of osmium(II) in aqueous solution, we found that, for a series of neutral and charged ligands, the calculated solvation free energies, as obtained by the SCIPCM method (which is closely related to the IPCM technique used here), were in reasonable agreement with experiment. Understandably, the largest discrepancies were noted for the charged species, where the computed values were systematically lower than those observed by $\sim$7$-$27 kcal mol^{-1}, viz., 10$-$30%. Consequently, in our view, the assumption of a 20% maximum error in the computed solvation free energy changes of the reactions studied is reasonable, especially since we may expect some error cancellation when calculating free energy changes. As will be seen, allowing for such an error will not alter the conclusions regarding the thermochemical feasibility of the key reactions. (In the ligand exchange studies discussed above, the discrepancies in the calculated solvation energy changes were found to be $\sim$10 kcal mol^{-1} at most). In more recent work by Barone et al.,[25] using a new definition of cavities (UAHF), a significantly higher level of accuracy has been demonstrated, where the solvation free energies of 28 ions were predicted within 1$-$2 kcal mol^{-1} of experiment.

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Table 1. Pt Complexes, Ligands, and Other Species Studied: Total Electronic Energies, Solvation Energies, Zero-Point Vibrational Energies, Thermal Contributions to Enthalpies, Standard Entropies, and Thermal Contributions to Gibbs Free Energies[a]

molecule	E^{el}/E_h	$E_{solv}{}^{b}$/kcal mol^{-1}	E_{ZPE}/kcal mol^{-1}	H_{298}^{therm}(g)/kcal mol^{-1}	S_{298}^{0}(g)/cal K^{-1} mol^{-1}	G_{298}^{therm}(g)/kcal mol^{-1}
I	−172.968 831	−9.5	50.5	56.7	95.4	28.2
II	−292.299 365	−59.9	79.3	91.0	134.9	50.7
III	−217.295 340	−89.7	63.5	71.9	113.1	38.1
III′	−292.624 616	−96.6	86.0	98.2	140.8	56.3
IV	−217.335 299	−113.6	64.5	72.7	110.8	39.7
V	−292.276 741	−70.2	77.2	89.6	147.5	45.6
VI	−225.048 862	−50.4	85.8	95.8	126.0	58.2
VII	−374.391 933	−56.4	117.2	135.2	182.2	80.9
VIII	−300.286 356	−72.1	107.5	120.6	143.8	77.7
IX	−322.280 336	−67.3	80.6	95.2	159.3	47.7
X	−255.094 516	−55.7	89.3	100.7	132.8	61.1
XI	−255.092 253	−54.8	89.2	100.8	134.1	60.8
XII	−300.605 199	−108.5	113.6	127.5	150.1	82.7
XIII	−180.958 595	−11.4	78.8	86.4	103.9	55.4
H$_2$SO$_4$	−75.2392 65	−15.9	19.6	24.4	79.1	0.8
HCl	−15.587 892	−3.5	3.9	5.9	44.8	−7.4
CH$_4$	−8.064 546	−0.1	28.0	30.4	46.7	16.4
SO$_2$	−42.092 463	−9.5^{c}	3.1	5.7	62.2	−12.8
H$_2$O	−17.217 666	−7.2	12.3	14.7	45.2	1.2
CH$_3$OSO$_3$H	−82.100 710	−9.8	37.7	43.4	88.3	17.1
HSO$_4{}^{-}$	−74.759 273	−52.5	13.0	17.4	76.1	−5.3

[a] Total enthalpies and Gibbs free energies (including solvation) are obtained as follows: H_{298}^{0}(soln) $= E^{el} + E_{solv} + H_{298}^{therm}$(g), and G_{298}^{0}(soln) $= E^{el} + E_{solv} + G_{298}^{therm}$(g). H_{298}^{therm}(g) and G_{298}^{therm}(g) include the zero-point energy, E_{ZPE}. [b] Computed by IPCM method unless indicated otherwise. [c] Computed by SCMMRF method.

The computations were carried out using the Gaussian94[26] and 98[27] programs using the DEC alpha workstations of the Theoretical Chemistry group at Sydney University.

Results and Discussion

The geometric structures of the Pt complexes (B3LYP optimized in the gas phase) which are reactants and intermediates in the catalytic cycles considered in this work are shown in Figure 2, along with the numbering code used for them. The tetracoordinate Pt(II) complexes **I**, **II**, **III′**, **IV**, **V**, and **VI** are effectively square planar, as expected, while the hexacoordinate Pt(IV) complexes are approximately octahedral. The tricoordinate T-complex, viz. [Pt(NH$_3$)$_2$(OSO3H)]$^+$ (**III**), is indeed T-shaped. **IV** is an isomer of **III**, where a bisulfate anion acts as a bidentate ligand, while in **V**, described as an ion pair, a second bisulfate is hydrogen bonded to the bisulfate in the inner coordination shell. H-bonding between bisulfate ligands is evident in **II** and **V**, as well as between bisulfate and sulfuric acid in **III′** and **XII**. The metal−ligand and H-bond distances are also shown in Figure 2. The Pt−O and Pt−N distances are 2.0−2.1 Å, while the Pt−Cl distances are 2.35−2.45 Å. The H-bond distances (defined as the distance between H and the proton acceptor) typically range from 1.54 to 1.68 Å. By

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comparison, in the sulfuric acid dimer molecule, the analogous distance has been calculated to be 1.55 Å. In **V**, however, the H-bond length is much shorter, at 1.24 Å, corresponding to the H-bonding proton being almost equally shared by the two bisulfates.

The energies of the complexes as well as those of the various ligands and reaction products are summarized in Table 1, quoting for each species the total electronic energy and zero-point vibrational energy (computed in the gas phase), along with the solvation (free) energy. The thermodynamic quantities derived, viz., standard gas-phase entropies at 298 K and the (thermal) corrections to the total energies (electronic + solvation) to yield enthalpies and Gibbs free energies at 298 K, are also given in Table 1.

Each of the reaction schemes studied consists of three or four distinct steps that comprise an initialization step that results in the formation of the actual catalyst, followed by CH activation, oxidation (in the case of Scheme 1), and functionalization steps, although in reality each of these steps may involve additional intermediates and more than one reaction barrier. In this work, the detailed mechanisms of the reactions are not explored, and in particular, no activated complexes are identified; only the thermochemistry associated with the steps identified is studied. The (thermodynamic) feasibility of a given scheme is judged by whether the individual steps considered are thermodynamically favored. In other words, the tacit assumption is made that, after each step, thermodynamic equilibrium occurs and chemical activation is not invoked.

The stable Pt(II) catalyst for oxidative conversion of methane to methanol reported by Periana et al.[12] contains a reversibly coordinated bidentate ligand, bis(2,2′-bipyrimidine). This has significant chemical differences from ammonia: in particular, it functions as a π-acid, while ammonia behaves as a σ-donor. However, on considering the hypothetical gas-phase exchange,

$$(bpym)Pt(II)Cl_2 + 2NH_3 \rightarrow (NH_3)_2Pt(II)Cl_2 + bpym \quad (2)$$
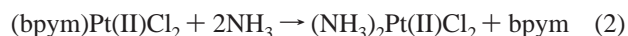
the change in the gas-phase electronic energy ΔE of this reaction, calculated at the B3LYP level, is quite small, ∼−7 kcal mol^{-1}, which suggests that the thermochemistry of the
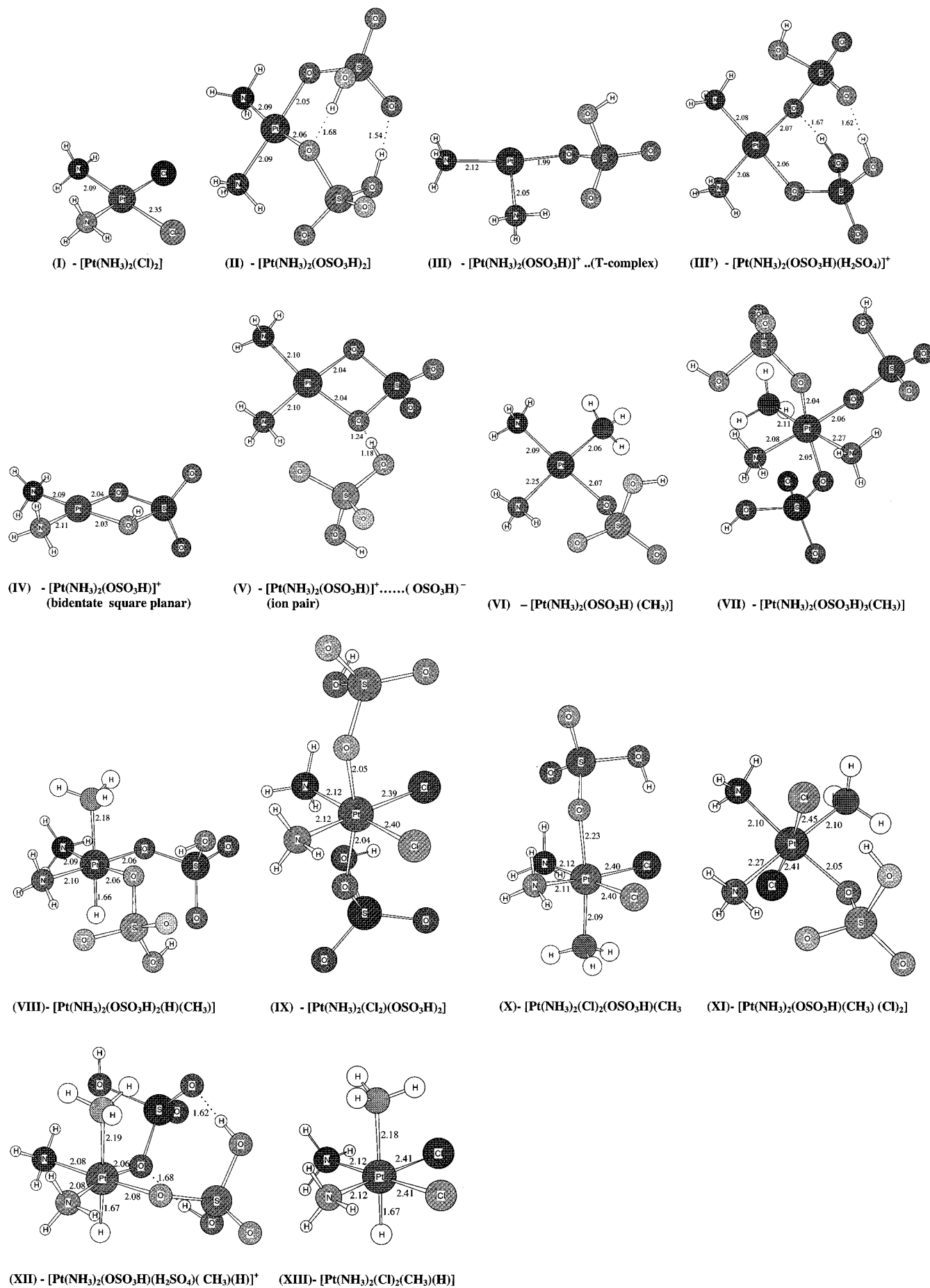
(I) - [Pt(NH₃)₂(Cl)₂]

(II) - [Pt(NH₃)₂(OSO₃H)₂]

(III) - [Pt(NH₃)₂(OSO₃H)]⁺ ..(T-complex)

(III') - [Pt(NH₃)₂(OSO₃H)(H₂SO₄)]⁺

(IV) - [Pt(NH₃)₂(OSO₃H)]⁺
(bidentate square planar)

(V) - [Pt(NH₃)₂(OSO₃H)]⁺......(OSO₃H)⁻
(ion pair)

(VI) – [Pt(NH₃)₂(OSO₃H) (CH₃)]

(VII) - [Pt(NH₃)₂(OSO₃H)₃(CH₃)]

(VIII)- [Pt(NH₃)₂(OSO₃H)₂(H)(CH₃)]

(IX) - [Pt(NH₃)₂(Cl₂)(OSO₃H)₂]

(X)- [Pt(NH₃)₂(Cl)₂(OSO₃H)(CH₃)

(XI)- [Pt(NH₃)₂(OSO₃H)(CH₃) (Cl)₂]

(XII) - [Pt(NH₃)₂(OSO₃H)(H₂SO₄)(CH₃)(H)]⁺   (XIII)- [Pt(NH₃)₂(Cl)₂(CH₃)(H)]

Figure 2. Structures and metal−ligand and intramolecular hydrogen bond distances of the Pt complexes **I−XIII**.

Table 2. Reaction Scheme 1: Computed Reaction Energies, Enthalpies, Entropies, and Gibbs Free Energies at 298.15 K and 1 atm, and at 473.15 K and 500 psi (All Energies in kcal mol^{-1}, Entropies in cal K^{-1} mol^{-1})

reaction	ΔE^{el} (g)	ΔE^{el} (soln)	ΔH^0_{298} (soln)	ΔS^0_{298}	ΔG^0_{298} (soln)	ΔH_{473} (soln)^a	ΔS_{473}^{a}	ΔG^0_{473} (soln)^a
Formation of Catalyst
I + 2H$_2$SO$_4$ → **II** + 2HCl	−17.4	−43.0	−45.6	−29.1	−36.9	−45.5	−28.9	−31.9
I + 2H$_2$SO$_4$ → **III** + HSO$_4^-$ + 2HCl	136.2	28.3	23.9	25.2	16.4	23.9	18.1	15.3
I + 3H$_2$SO$_4$ → **III'** + HSO$_4^-$ + 2HCl	79.7	−19.2	−21.6	−26.3	−13.7	−21.3	−25.8	−9.1
I + 2H$_2$SO$_4$ → **IV** + HSO$_4^-$ + 2HCl	111.1	−20.7	−24.2	22.9	−31.0	−24.2	15.9	−31.7
I + 2H$_2$SO$_4$ → **V** + 2HCl	−3.2	−39.1	−43.1	−16.6	−38.1	−42.7	−15.7	−35.3
CH Activation
II + CH$_4$ → **VI** + H$_2$SO$_4$	47.6	41.3	40.1	23.5	33.1	40.7	25.2	28.8
III + HSO$_4^-$ + CH$_4$ → **VI** + H$_2$SO$_4$	−106.0	−30.0	−29.5	−30.8	−20.3	−28.7	−21.8	−18.4
III' + HSO$_4^-$ + CH$_4$ → **VI** + 2H$_2$SO$_4$	−49.6	17.5	16.0	20.7	9.8	16.5	22.1	6.1
IV + HSO$_4^-$ + CH$_4$ → **VI** + H$_2$SO$_4$	−81.0	19.0	18.7	−28.5	27.2	19.4	−19.6	28.7
V + CH$_4$ → **VI** + H$_2$SO$_4$	33.4	37.4	37.5	11.0	34.3	37.9	12.0	32.2
Oxidation
VI + 3H$_2$SO$_4$ → **VII** + SO$_2$ + 2H$_2$O	−96.1	−78.3	−76.8	−28.5	−68.3	−76.6	−28.0	−63.4
VI + 2HCl + H$_2$SO$_4$ → **XI** + SO$_2$ + 2H$_2$O	−98.0	−103.4	−99.5	−8.0	−97.2	−100.0	−9.1	−95.6
Functionalization
VII → **II** + CH$_3$OSO$_3$H	−5.1	−18.4	−19.3	41.0	−31.5	−20.4	30.9	−35.0
VII → **III** + HSO$_4^-$ + CH$_3$OSO$_3$H	148.5	52.9	50.3	95.2	21.9	49.0	77.9	12.2
VII + H$_2$SO$_4$ → **III'** + HSO$_4^-$ + CH$_3$OSO$_3$H	92.0	5.4	4.8	43.8	−8.2	3.8	34.0	−12.3
VII → **IV** + HSO$_4^-$ + CH$_3$OSO$_3$H	123.4	3.9	2.2	93.0	−25.6	0.9	75.6	−34.9
VII → **V** + CH$_3$OSO$_3$H	9.1	−14.5	−16.7	53.5	−32.7	−17.6	44.1	−38.5
XI + 2H$_2$SO$_4$ → **II** + CH$_3$OSO$_3$H + 2HCl	−3.2	6.7	3.4	20.5	−2.7	2.9	12.1	−2.8
XI + 3H$_2$SO$_4$ → **III** + CH$_3$OSO$_3$H + 2HCl + HSO$_4^-$	150.4	78.0	73.0	74.8	50.7	72.4	59.1	44.4
XI + 3H$_2$SO$_4$ → **III'** + CH$_3$OSO$_3$H + 2HCl + HSO$_4^-$	93.9	30.5	27.5	23.3	20.6	27.1	15.1	20.0
XI + 2H$_2$SO$_4$ → **IV** + CH$_3$OSO$_3$H + 2HCl + HSO$_4^-$	125.3	29.0	24.9	72.5	3.3	24.2	56.8	−2.7
XI + 2H$_2$SO$_4$ → **V** + CH$_3$OSO$_3$H + 2HCl	11.0	10.6	6.0	33.0	−3.8	5.7	25.3	−6.2

^{a} p/psi = 500.

catalytic cycle involving bpym complexes would not be too dissimilar from that obtained here for the diammines. Indeed, the experimental rates of oxidative conversion obtained with these catalysts are comparable, as noted in the Introduction.

Reaction Scheme 1: Electrophilic Substitution. In this scheme, we consider the initial reaction of *cis*-platin (**I**) with sulfuric acid, which could give rise to a range of bisulfate complexes (**II**−**V**) which are then considered as the catalysts in the subsequent reaction with methane. The byproduct of this initialization is, of course, HCl. The activation step results in the formation of [Pt(NH$_3$)$_2$(OSO$_3$H)CH$_3$] (**VI**) from one of the above catalysts, which is followed by oxidation, viz., the formation of [Pt(NH$_3$)$_2$(OSO$_3$H)$_3$CH$_3$] (**VII**), with the evolution of sulfur dioxide. In the final (functionalization) step, the catalysts **II**−**V** re-form as **VII** decomposes, yielding methyl-bisulfate, the desired product. The computed energetics of these reactions are summarized in Table 2. In addition to standard enthalpies, entropies, and free energies of reactions at 298 K and 1 atm, these quantities were also computed at 473 K and a pressure of 500 psi, which correspond to the experimental conditions used by Periana et al.[12] The catalytic cycles, along with the corresponding free energy changes at 298 K, are also summarized in Figure 3.

All the initiation reactions, with the exception of the one producing the T-complex **III**, are exothermic and exergonic, i.e., have negative free energies of reactions, under both standard and experimental conditions. On the basis of enthalpy, the most favorable reactions are the ones that result in **II** and **V**, but when entropic effects are also considered, the reactions yielding **II**, **IV**, and **V** are almost equally probable. Given that **III** is a species with a reduced tricoordination, it is not surprising that the reaction that leads to its formation is endothermic. However, since **III'** may be considered as solvated **III**, with one solvent molecule explicitly included in the calculation, it is instructive to compare the energetics of the reactions that yield **III** and
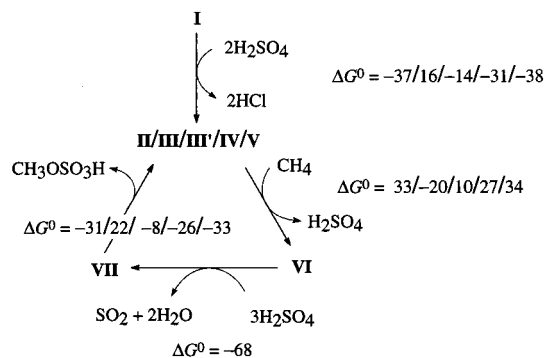
Figure 3. Electrophilic substitution mechanism utilizing **II**, **III**, **III'**, **IV**, and **V** as catalysts. (Note that, in the case of **III**, **III'**, and **IV**, HSO$_4^-$ is also a product in the initiation step, as indicated in Table 2.)

III'. The latter is fairly exothermic in solution, whereas the former is endothermic, and even after the inclusion of entropy, the production of **III'** is significantly more favorable. In fact, although **III** is calculated to be a stable species in the gas phase, it is most unlikely that it would exist in solution as an independent species. The calculated free energy change of the conversion of **III** to **III'**, i.e.,

$$\textbf{III} + H_2SO_4 \rightarrow \textbf{III'} \tag{3}$$

is, from the data of Table 1, −30.1 kcal mol^{-1} at 298 K. This value can be, therefore, regarded as the contribution of specific solvation effects to the stability of **III**, which is not accounted for by the dielectric continuum method. Alternatively, we note that the sulfuric acid molecule in **III'** is effectively a ligand, which is chemically bound to **III**, rather than as a solvent molecule, which might be reasonably incorporated into the polarizable continuum that represents the solvent in our calculations.

Table 3. Reaction Schemes 2 and 3: Computed Reaction Energies, Enthalpies, Entropies, and Gibbs Free Energies at 298.15 K and 1 atm, and at 473.15 K and 500 psi (All Energies in kcal mol^{-1}, Entropies in cal K^{-1} mol^{-1})

| reaction	ΔE^{el} (g)	ΔE^{el} (soln)	ΔH^0_{298} (soln)	ΔS^0_{298}	ΔG^0_{298} (soln)	$\Delta H_{473}{}^a$ (soln)	ΔS_{473}	$\Delta G^0_{473}{}^a$ (soln)
Scheme 2: Formation of Catalyst								
$I + 2H_2SO_4 \rightarrow II + 2HCl$	−17.4	−43.0	−45.6	−29.1	−36.9	−45.5	−28.9	−31.9
$I + 3H_2SO_4 \rightarrow III' + HSO_4^- + 2HCl$	79.7	−19.2	−21.6	−26.3	−13.7	−21.3	−25.8	−9.1
Scheme 2: CH Activation								
$II + CH_4 \rightarrow VIII$	48.7	36.6	35.8	−37.8	47.1	36.3	−29.7	50.3
$III' + CH_4 \rightarrow XII$	52.7	40.9	39.7	−37.4	50.9	40.3	−29.1	54.0
$I + CH_4 \rightarrow XIII$	46.9	45.1	44.4	−38.2	55.8	44.9	−30.1	59.1
Scheme 2: Functionalization								
$VIII + 2H_2SO_4 \rightarrow II + SO_2 + 2H_2O + CH_3OSO_3H$	−102.3	−92.0	−91.8	73.8	−113.8	−92.6	57.8	−119.9
$XII + 2H_2SO_4 \rightarrow III' + SO_2 + 2H_2O + CH_3OSO_3H$	−106.3	−96.3	−95.7	73.3	−117.6	−96.6	57.2	−123.6
$XIII + 2H_2SO_4 \rightarrow I + SO_2 + 2H_2O + CH_3OSO_3H$	−100.5	−100.5	−100.4	74.1	−122.5	−101.2	58.2	−128.7
Scheme 3								
$I + 3H_2SO_4 \rightarrow IX + SO_2 + 2H_2O$	−76.3	−110.3	−109.7	−20.8	−103.5	−109.4	−20.0	−99.9
$IX + CH_4 + X + H_2SO_4$	7.0	2.8	2.2	5.0	0.4	2.1	5.6	−0.6
$X + 3H_2SO_4 \rightarrow IX + SO_2 + 2H_2O + CH_3OSO_3H$	−60.6	−58.2	−58.2	30.1	−67.1	−58.4	22.6	−69.0

^{a} p/psi = 500.

Given the above choices of catalyst, the activation step is uniformly endothermic, with the exception of the reaction with **III** as reactant. While in some cases the entropic contributions would make some of the reactions less unfavorable, the results strongly suggest that **II**, **IV**, and **V** are not viable as catalysts. Irrespective of the temperature and pressure, the three reactions that utilize the above complexes are strongly endergonic. The reaction utilizing **III'** is mildly endothermic, but the entropic contributions would make it more favorable, especially at higher temperatures, with the end result that the reaction is endergonic by only ∼6 kcal mol^{-1}. The only exergonic reactions of those considered utilize the hypothetical T-complex **III** as catalyst, the formation of which was computed to be endergonic by ∼16 kcal mol^{-1}. Therefore, on the basis of these reactions, as well as on simple chemical grounds, **III'** is considered to be an excellent candidate as catalyst. It can, of course, be also regarded as the product of protonation of **II**.

The oxidation of **VI**, yielding **VII**, is a highly exothermic as well as exergonic reaction. However, as the experimental work has been carried out on closed systems, there is a possibility of **VI** being oxidized via HCl that is produced in the initialization step, leading to the formation of [Pt(NH$_3$)$_2$(OSO$_3$H)CH$_3$(Cl)$_2$] (**XI**). While such a process appears to be highly exergonic, the subsequent functionalization steps involving **XI**, leading to the formation of **III** and **III'**, appear to be quite unfavorable. By contrast, the functionalization step involving **VII**, where it is reduced to **II**, **III**, **III'**, **IV**, or **V** with the production of methyl bisulfate, is exergonic in all cases except the one resulting in **III**. Thus, the preference of **III'** over **III** as catalyst is confirmed by the energetics of the functionalization step.

On the basis of these results, we conclude that the above catalytic cycle appears to be quite feasible on thermochemical grounds, with **III'** as the catalyst and where the oxidation step produces [Pt(NH$_3$)$_2$(OSO$_3$H)$_3$(CH$_3$)] (**VII**). Each step in this pathway is exergonic, except the activation, which is predicted to be mildly endergonic. Therefore, subject to the assumption that there is a common dominant underlying mechanism in H$_2$SO$_4$ solution for both *cis*-platin and [Pt(bpym)Cl$_2$], we expect that an electrophilic mechanism for the conversion of methane to methyl bisulfate and subsequently to methanol is thermodynamically feasible with [Pt(bpym)Cl$_2$] as catalyst.

From the results of Table 2, it can be seen that, with the exception of the oxidation step, solvation plays a critically important role in each of the above reactions. Allowing for a
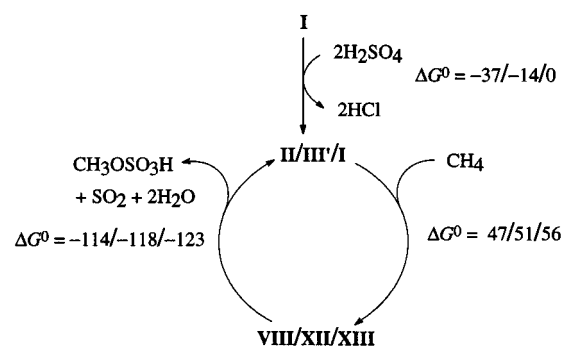

Figure 4. Oxidative addition mechanism utilizing **II**, **III'**, and **I** as catalysts. (Note that, in the case of **III'**, HSO$_4^-$ is also a product in the initiation step, while in the case of **I** there is no initiation step, as indicated in Table 3.).

20% error in the solvation free energy changes, the CH activation and functionalization reactions could become slightly endergonic or uniformly more exergonic. Such an error in solvation energies, while possibly quite large in absolute terms, does not alter the conclusions reached above concerning the thermochemical feasibility of the overall reaction scheme.

Reaction Scheme 2: C−H Activation by Oxidative Addition. In this scheme, we consider the oxidative addition of methane to a Pt(II) complex that would result in a hexacoordinate complex of methyl hydrido Pt(IV) complex. Such a mechanism has been proposed and found to be a viable alternative to σ-metathesis for several Shilov type Pt(II) systems.[28] Siegbahn and Crabtree,[29] in their theoretical studies of methane activation by *trans*-[PtCl$_2$(H$_2$O)], also found that oxidative addition is competitive with the σ-metathesis mechanism. Choosing the catalyst as **I**, **II**, or **III'**, the thermodynamics of the activation steps (which moreover are largely unaffected by solvation) are found to be quite unfavorable in our study, as indicated by the computed results summarized in Table 3. We have thus concluded that the oxidative mechanism involving one of these catalysts (Figure 4) is unlikely to be important in the systems considered in this work.

Reaction Scheme 3: C−H Activation by a Pt(IV) Catalyst. Given the highly oxidizing environment in sulfuric acid and

(28) Holtcamp, M. W.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1997**, *119*, 848 and references therein.
(29) Siegbahn, P. E. M.; Crabtree, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 4442.
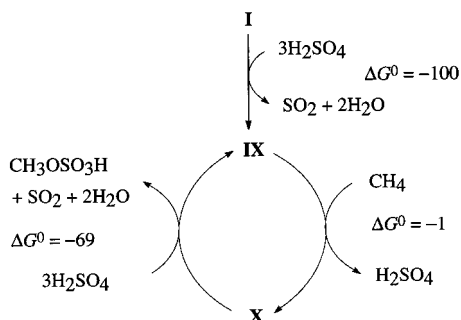
Figure 5. Activation and functionalization by [Pt(IV)(NH$_3$)$_2$(Cl)$_2$-(OSO$_3$H)$_2$] (**IX**).

the strong binding of bisulfate ligands to platinum, we have considered the possibility that the active catalyst may be a Pt-(IV) complex, namely [Pt(NH$_3$)$_2$(Cl)$_2$(OSO$_3$H)$_2$] (**IX**), formed by the oxidative addition of bisulfate to *cis*-platin (**I**). The results of the computations are summarized in Table 3. The formation of **IX** is a highly exothermic process, and the large enthalpy change completely dominates the thermochemistry. The C−H activation step, where methane is exchanged for a H$_2$SO$_4$, is largely energy neutral, while the functionalization step that produces methylbisulfate and regenerates the catalyst **IX** is again strongly exothermic as well as exergonic. Note that in this scheme, the actual catalytic steps, viz., activation and functionalization, are hardly affected by solvation since the reactions occur between neutral species. Thus, on thermochemical grounds, this reaction mechanism (Figure 5) also appears to be quite viable and certainly competitive with the electrophilic substitution scheme of Periana et al.[12] Of course, here as in the preceding discussion, in considering the thermochemistry, we

are concerned with the necessary conditions for feasibility of a particular reaction mechanism. Actual rates will crucially depend on the relative magnitudes of the activation energies and the associated Arrhenius *A*-factors.

Conclusion

On the basis of the calculations reported in this paper, we conclude that, on thermochemical grounds, the electrophilic substitution mechanism proposed by Periana et al.[12] appears feasible. The computations suggest that a solvated complex of the form [Pt(NH$_3$)$_2$(OSO$_3$H)(H$_2$SO$_4$)]$^+$ (**III′**) is a good candidate for the role of an active catalyst. The activation step is predicted to be only mildly endergonic. Given the implicit uncertainties in the predicted energetics, especially in the solvation energies, in reality this step may well be more favorable than indicated by our calculations. However, in the case of the oxidative addition scheme, the calculations are considerably less unequivocal, and in our view the mechanism is effectively ruled out on the basis of the CH activation being far too endergonic. An alternative scheme, where the catalyst is a Pt(IV) complex, viz., [Pt(NH$_3$)$_2$(Cl)$_2$(OSO$_3$H)$_2$]$^+$ (**IX**), also appears to be feasible on the basis of thermodynamics. It must be emphasized, however, that the definitive proof of feasibility requires the computation of the activation energies, viz., barriers to the reactions that make up a specific pathway. We plan to undertake such work in our future, further studies on catalytic activation and functionalization of methane.