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# Computational study of the highly efficient conversion of methane to methanol with mercury(II) catalysts

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## Abstract

The highly efficient activation of methane by a homogeneous mercury(II) catalyst has been investigated by an ab initio computational study of the interaction of methane with the $HgF^+$ ion. The key steps in the activation were found to be the formation of a loose adduct between methane and the $HgF^+$ ion followed by abstraction of a proton by a solvent molecule. The efficiency of the methane activation is enhanced by the high solvation energy of the proton and the formation of the strong Hg–$CH_3$ bond.

## 1. Introduction

The efficient conversion of methane to a readily transportable liquid, such as methanol, is a problem of great economic importance. However, due to the inertness of methane it has proved difficult to obtain the desired liquid products in high yield. The products are usually more reactive than methane itself under the conditions required for significant methane conversion.

A promising approach to methane conversion is the homogeneous electrophilic activation of methane to form a 'protected' intermediate that is less reactive than methane towards the electrophile. Recently, Periana et al. [1] have reported the conversion of methane to methanol in high yield using mercury(II) bisulfate as the catalyst for an electrophilic displacement reaction that produces a methyl bisulfate ester intermediate. The net reaction is:

$$CH_4 + 2H_2SO_4 \rightarrow CH_3OSO_3H + 2H_2O + SO_2$$

The methyl bisulfate is readily converted to methanol by hydrolysis. This system gives 85% selectivity to the intermediate at 50% methane conversion with a turnover frequency of $10^{-3}$ per second.

Nuclear magnetic resonance and deuterium isotope studies [1] indicate that methane initially reacts with the mercury(II) bisulfate to produce the species methyl mercury bisulfate. The active mercury species is probably the cation $Hg(OSO_3H)^+$ produced by autoionization of $Hg(OSO_3H)_2$.

$$CH_4 + Hg(OSO_3H)^+ \rightarrow CH_3HgOSO_3H + H^+$$

This activation of methane by mercury bisulfate is highly efficient: the equilibrium constant, $[CH_3HgOSO_3H][H_2SO_4]/[Hg(OSO_3H)_2][CH_4]$ is in the range 0.1–1.

In order to understand how the mercury system can convert methane to methyl bisulfate so efficiently it is first necessary to understand why the

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initial methane activation is so efficient. We report here the results of an ab initio computational study of the initial steps in the activation of methane by mercury(II) catalysts. In order to simplify the calculations the bulky $Hg(OSO_3H)^+$ cation was replaced by the $HgF^+$ cation. The $HgF^+$ cation would be produced by dissolving $HgF_2$ in HF:

$$HgF_2 + (HF)_n \rightarrow HgF^+ + H_nF_{n+1}$$

## 2. Computational

Calculations were carried out with the TURBOMOLE quantum chemistry program package [2] and the Gaussian 92 quantum chemistry program [3]. For the mercury atom relativistic effective core potentials were used to represent the electrons outside the valence region. The calculations with Gaussian 92 used the Los Alamos LANL1MB and LANL1DZ basis sets [4]. The LANL1MB basis consists of a STO-3G basis for the first row atoms and an effective core potential plus a minimal basis of STO-3G quality for the valence electron region in heavy atoms. The LANL1DZ basis set is of double zeta quality. The TURBOMOLE calculations used a split-valence plus polarization (SV+P) basis set for the first row atoms [5]. The SV+P basis is a (7s4p)/[3s2p] + 1d gaussian basis for first row atoms and a (4s)/[2s]+1p basis for hydrogen. In the SV+P calculations the effective core potential and the valence region basis set for mercury were those published by Ross et al. [6]. The valence region basis for mercury was a (5s5p4d)/[4s3p3d] Gaussian basis. Calculations of solvation energies were carried out using the COSMO method of Klamt and Schuurmann [7] with AM1 charge distributions obtained with MOPAC [8].

## 3. Results

We first examined the interaction of methane with an isolated $HgF^+$ ion in order to clearly distinguish solvent effects from other types of interaction. Methane was found to form a loosely-bound adduct with the unsolvated $HgF^+$ ion. With the SV + P basis the $\eta^2$ complex shown in Fig. 1 had the lowest energy. The binding energy of this complex was calculated to be − 23.3 kcal/mol with respect to the separate $CH_4$ and $HgF^+$ species. However, the $\eta^3$ complex was calculated to lie only 2.3 kcal/mol higher in energy than the $\eta^2$ complex. The complex would therefore be fluxional at the reaction temperature. Similar loosely-bound adducts have been found in computational studies of the interaction of methane with ions and transition metal complexes [9–12]. In some cases the calculated binding energies of these complexes approach the calculated binding energy for methane and $HgF^+$. Blomberg et al. [9] found that methane binding energies were significantly higher for metal ions with the $s^0$ ground state configuration. The $s$ orbitals are the most diffuse so $s$ electrons give the largest repulsion terms. The high binding energy for the $(HgF^+)$–$CH_4$ complex can be attributed partly to the $s^0$ configuration of $Hg^{II}$, which allows close approach of the methane to the mercury atom.

A significant part of the binding energy between the methane molecule and the Hg–$F^+$ ion arises from an electrostatic interaction of the ion-induced dipole type. However, there are indications that some of the binding energy can be attributed to weak chemical bonding arising from a donor–acceptor interaction between the $\sigma_{CH}$ bonds of the methane and the empty orbitals of the mercury. The calculated (double zeta) stretching frequency for the C–H bonds adjacent to the mercury atom is 3010 $cm^{-1}$, while the calculated

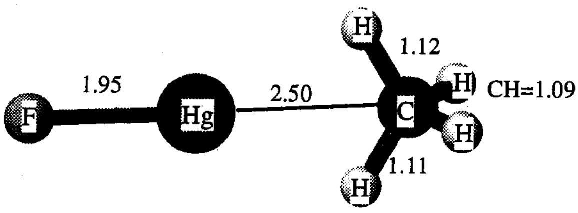

Fig. 1. Geometry of adduct between $CH_4$ and $HgF^+$. Bond lengths are in Ångström.

stretching frequency for the C–H bonds on the other side of the methane molecule is 3286 $cm^{-1}$. The significantly lower frequency for the C–H bonds closest to the mercury atom indicates that these bonds are weaker than the remaining C–H bonds. The bond weakening is attributed to $\sigma_{CH}$ donation into the empty orbitals of Hg. The weakening of the C–H bonds adjacent to the Hg is also indicated by their slightly longer bond length, 1.11 Å vs. 1.08 Å for the remaining C–H bonds. Weak donor–acceptor bonds have also been indicated by C–H frequency and bond length changes in calculations on methane adducts with $d^0$ transition metal imido complexes [11] and with 14-electron $Ir(PH_3)_2(X)$ complexes [12].

Weak $\sigma_{CH}$ donor–acceptor bonds with metal complexes are well-known and have been termed 'agostic' interactions [13]. This type of interaction is usually observed only in ligands that are already covalently attached to the metal center. However, Wasserman et al. [14] have recently obtained evidence that loosely-bound alkane adducts of the species CpRh(CO) are intermediates in C–H oxidative addition reactions. Methane adducts have been implicated as intermediates in methane elimination from $Cp_2W(CH_3)(H)$ [15] and $[Cp_2Re(H)(CH_3)]^+$ [16]. We propose that a methane adduct with the $HgOSO_3H^+$ species (in the experimental system) is a precursor to the electrophilic activation of methane by the $Hg^{II}$ catalyst.

In the case of the mercury system the methane adduct is not a precursor to a C–H oxidative addition reaction. This pathway is ruled out because it would involve the formation of $Hg^{IV}$ and the participation of the Hg 5d shell in the bonding. The Hg 5d electrons lie well below the 6s electrons in energy and no compound of $Hg^{IV}$ has ever been observed.

In HF solution the $HgF^+$ ion will be solvated by one or more solvent molecules. The methane binding to the solvated ion will be effected by the presence of the coordinated solvent molecules and formation of the adduct may even be prevented if the approach of the methane is blocked by more strongly bound solvent molecules. With the split valence basis the binding energy of a single HF molecule to the $HgF^+$ ions was calculated to be 32 kcal/mol. The calculated geometry for the $HgF^+(HF)$ species is shown in Fig. 2a.

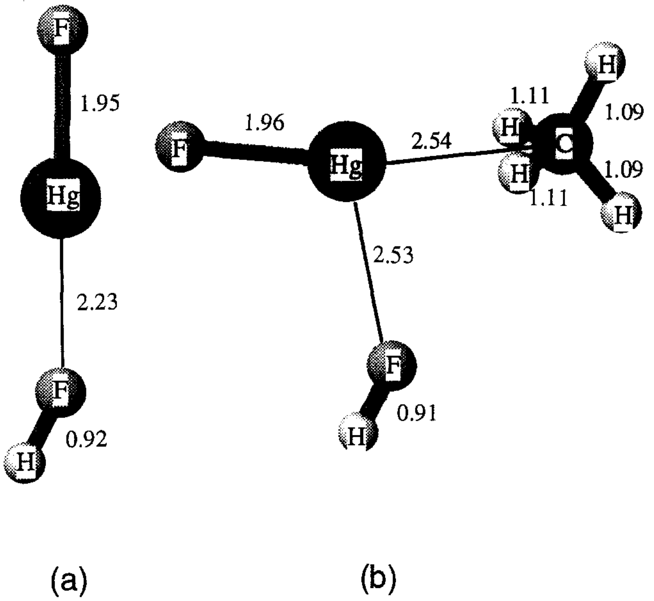

Fig. 2. (a) Geometry of complex between HF and $HgF^+$. (b) Geometry of adduct between $CH_4$ and $HgF^+$ solvated by one HF. Bond lengths are in Ångstrom.

Calculations with the split valence basis set indicate that methane also forms an adduct with the $HgF^+(HF)$ species. The calculated geometry of the adduct is shown in Fig. 2b. Note that the coordinated HF has moved away from the mercury atom by about 0.25 Å, i.e. the solvation has become weaker in response to the additional 'solvation' of the $HgF^+$ by the methane. The binding energy of the methane adduct was calculated to be 9.5 kcal/mol with the split valence basis set. However, the binding energy of a second HF solvent molecule to the $HgF^+(HF)$ species is calculated to be 19.5 kcal/mol. Therefore the methane will not tend to displace an HF ligand bound to the $HgF^+$ ion. This suggests that HF may not be a suitable solvent for activation of the methane with the mercury catalyst.

The results of the calculations on the solvated $HgF^+$ ion highlight the importance of the solvent in the formation of the proposed methane adduct. Methane conversion proceeds rapidly at 180°C in sulfuric acid [with $Hg(HSO_4)_2$] and triflic acid [with $Hg(CF_3SO_3)_2$], where the solvating species are only weakly coordinating. The methane conversion reaction does not take place, however, in the more strongly coordinating acetic acid solvent.

The coordination of triflic acid and sulfuric acid to metal ions appears to be significantly weaker than the coordination of HF. A study of the UV-visible spectrum of $Co^{II}$ ions in various solvents [17] showed that the main *d–d* transition is shifted to longer wavelengths in sulfuric acid and triflic acid compared to its position in HF. It is possible that the binding energy of methane to the $HgX^+$ ion is comparable to the binding energy of sulfuric acid or triflic acid ligands, in which case the methane will 'solvate' the ion to the same extent as do the acid ligands.

Although in reality coordinated HF molecules may block the approach of the methane to the $HgF^+$ ion, we assume for the sake of convenience that an $HgF^+$–methane adduct is formed in order to investigate the methane activation using this relatively simple model system. The most probable reaction pathway following formation of the methane–$HgF^+$ adduct is removal of a proton from the adduct by a solvent molecule:

$$[HgF\ldots CH_4]^+ + HF \rightarrow CH_3HgF + H_2F^+$$

The potential energy surface for the reaction of a single HF molecule with the adduct was scanned using the LANL1MB minimal basis. The HF molecule was made to approach one of the hydrogens adjacent to the mercury atom along the C–H bond axis, as in Fig. 3. The weakening of the C–H bond caused by the agostic interaction with the mercury should make the hydrogen atoms adjacent to the mercury easier to remove than the more distant hydrogens.

Minimal basis calculations cannot, of course, provide more than qualitative accuracy. Moreover, the coordinated solvent molecules were regarded as 'spectators' and were not included in the calculation. However, the aim of the calculation was simply to determine whether any large energy barrier exists on the reaction pathway for proton transfer. Such a barrier, if it exists, should be predicted even at this level of calculation.

The departing hydrogen atom was moved away from the adduct in increments of 0.2 Å in the C–H distance. For each C–H distance the HF molecule was moved stepwise towards the departing hydrogen atom with a step size of 0.2 Å. All other bond lengths and bond angles were optimized for each calculation. A contour map of the region of the potential energy surface that was scanned in this way is shown in Fig. 4. It can be seen that the reaction is endothermic, and that the energy rises steadily from the reactants to the products, i.e. there is no transition state and no energy barrier other than the endothermicity.

Note that as the HF molecule approaches the adduct the calculated energy for the system initially falls below the energy of the separated reactants. This is due to the coordination of the HF molecule by the $HgF^+$. Such a coordination would be prevented in reality by the presence of HF solvent molecules that surround the $HgF^+$. Alternatively, the reacting HF molecule can be regarded as being one of the molecules that solvates the $HgF^+$ ion. The close proximity between the coordinated HF molecules and the coordinated $CH_4$ would certainly tend to favor reaction between them.

Starting from the adduct the removal of the proton is calculated to be endothermic by 23.9 kcal/mol with the minimal basis and 46.6 kcal/mol with the split valence basis. Relative to the separate $HgF^+$ and $CH_4$ reactants, however, the reaction is endothermic by only 12.4 kcal/mol with the minimal basis and 23.3 kcal/mol with the split valence basis. The overall energy barrier is therefore fairly modest, and could be reduced further by solvation effects. We have made some preliminary estimates of the solvation energies of the reactants and products based on a dielectric continuum model of the solvent. A simple spherical cavity approach does not appear to be appropriate for these molecules, so we used the COSMO method of Klamt and Schuurmann [7], which is based on a realistic shape for the solvent accessible surface. The COSMO method has so far only been implemented with the MOPAC semiempirical

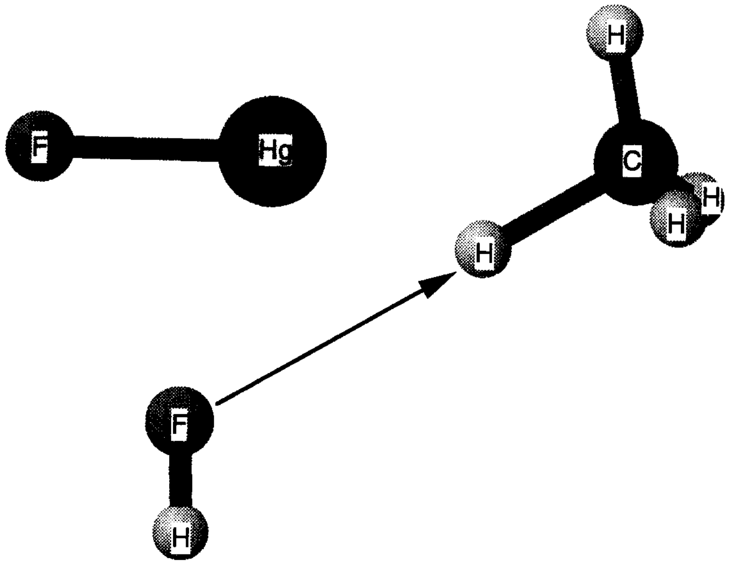

Fig. 3. Approach of HF molecule to $[HgF–CH_4]^+$ adduct.

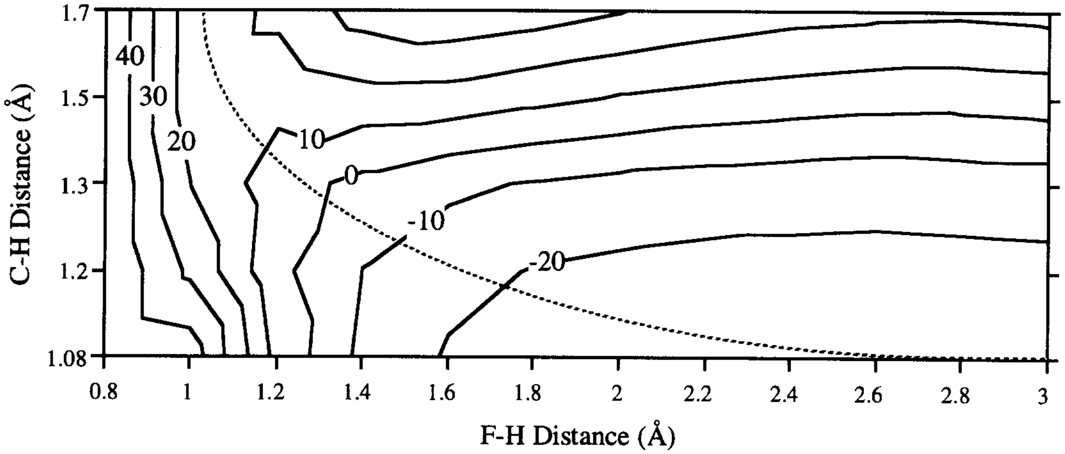

Fig. 4. Contour map of potential energy surface scan for reaction $[HgF–CH_4]^+ + HF \rightarrow FHgCH_3 + H_2F^+$ corresponding to approach of HF molecule shown in Fig. 3. Contour values are in kcal/mol and are relative to the energy of the separate reactants. (– – –) Minimum energy path.

program package [8], so the AM1 method was used to obtain the necessary charge distributions. The total solvation energies for the products ($H_2F^+ + CH_3HgF$) were 28 kcal/mol larger than the solvation energies for the reactants ($HgF^+ + CH_4 + HF$), due to the high solvation energy of the compact $H_2F^+$ ion and the solvation energy contributed by the dipolar $CH_3HgF$ molecule. The results from the potential energy surface scan taken together with the solvation energy estimates indicate that the energy barrier for the deprotonation reaction in solution could be fairly small. An accurate estimate of this energy barrier must await more detailed, high-level calculations, perhaps including explicit treatment of solvent molecules.

## 4. Discussion and conclusions

Ab initio and semiempirical MO calculations have provided some insight into the very efficient methane activation by the mercury(II) catalyst. Three factors appear to be of importance:

(i) Formation of an adduct between methane and a solvated $HgX^+$ ion; the solvent must be weakly coordinated to the $HgX^+$ so that solvent molecules can be displaced by the methane.

(ii) The absence of any significant energy barrier along the reaction pathway for deprotonation of the adduct.

(iii) The stability of the products; this can be attributed largely to the strength of the $CH_3$–Hg bond and the high solvation energy of the $H_2X^+$ ion.

These factors are all favorable for the $Hg^{II}/H_2SO_4$ system, but may not be so favorable for other combinations. For example solvents that coordinate more strongly to the $HgX^+$ ion than do sulfuric acid or triflic acid may prevent formation of the adduct. Thus solvents such as acetic acid are not favorable for this reaction. The calculations indicate that HF may also coordinate too strongly to the $HgF^+$ ion to be a suitable solvent. Similarly, it is not possible to obtain $CH_3MgOSO_3H$ from methane and the corresponding $Mg^{II}/H_2SO_4$ system because (a) the small magnesium ion will bind the sulfuric acid solvent more strongly than will the mercury ion and (b) the Mg–$CH_3$ bond is significantly weaker than the Hg–$CH_3$ bond. The latter factor is perhaps more important in the case of magnesium: the deprotonation reaction:

$$[MgF...CH_4]^+ + HF \rightarrow CH_3MgF + H_2F^+$$

is calculated to be endothermic by 82.1 kcal/mol with the split valence basis, compared to an endothermicity of 46.6 kcal/mol for the corresponding mercury ion.

Our highly simplified treatment of solvent effects has led to important insights, but further progress in understanding the mercury system will require an accurate treatment of solvation effects in the formation of the adduct and in the deprotonation step. Such calculations now appear to be within the bounds of possibility [18].

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