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Methane Activation

Vacuum Ultraviolet Photoionization Studies of $PtCH_2$ and H-Pt-CH_3: A Potential Energy Surface for the Pt + CH_4 Reaction[**]

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Activation of methane is a long-standing goal of catalysis, owing to its potential industrial utility as an inexpensive hydrocarbon feedstock, and is of interest as the most fundamental C–H bond activation reaction.[1] The observation that several gas-phase third-row transition metal cations M^+ efficiently dehydrogenate methane at room temperature[2]

$$M^+ + CH_4 \rightarrow [MCH_2]^+ + H_2 \quad (1)$$

has led to extensive gas-phase studies of reactions of metal atoms, ions, and clusters with methane (see references [1–3] and references therein). These studies provide valuable information regarding reaction mechanisms, the energetics and structures of intermediates and of critical barriers. These results inform the choice of metal, cluster size, support, and ligand properties in a potential catalyst. Furthermore, they serve as a benchmark against which the accuracy of computational studies can be assessed. Owing to its importance as an industrial catalyst, reactions of Pt and Pt^+ with methane have received particular attention. At thermal energies, Pt^+ reacts at $\geq 50\%$ of the collision rate, producing $[PtCH_2]^+$.[2,3c,4] Guided ion beam (GIB) experiments have measured the overall exothermicity of the reaction, as well as the stability of the $[\text{H-Pt-CH}_3]^+$ insertion intermediate.[5] Neutral metal atoms are much less reactive than the cations. This has been attributed to the absence of long-range ion-induced dipole attraction, and the lack of low-lying reactive (low-spin d^n or $d^{n-1}s$) electronic states. Carroll et al. find that platinum is unique in activating methane at thermal energies.[6] Campbell confirms the reactivity of Pt, at approximately 3% of the collision rate.[7] These kinetics studies monitor Pt by using laser-induced fluorescence, but do not observe products. As a result, it is difficult to determine to what extent loss of Pt is due to a true bimolecular reaction, producing $PtCH_2 + H_2$, and to what extent it is due to termolecular formation of the H-Pt-CH_3 insertion intermediate, which is stabilized by collisions with the buffer gas. These kinetics studies do not determine the reaction mechanism or provide much information on the potential energy surface. A number of questions remain outstanding. How endothermic is dehydrogenation of methane by atomic platinum? How stable is the insertion intermediate, and is there a barrier to its formation? This study addresses these questions, by determining the energetics of H-Pt-CH_3 and $PtCH_2$ by coupling photoionization measurements of their ionization energies with GIB measurements of the thermodynamics of the corresponding cations.[5] In addition, spin-orbit DFT (SODFT) calculations are used to characterize other intermediates and the barriers that separate them. Comparison of the potential energy surfaces for the reactions of Pt and Pt^+ with CH_4 shows that charge has surprisingly little effect on the potential energy surface for this most fundamental C–H activation reaction.

The laser ablation experiments are performed using tunable vacuum UV (VUV) light accessed at a synchrotron (Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory). The molecules of interest are produced by using a pulsed laser ablation source and ionized with VUV light.[8] The resulting ions are extracted into a reflectron time-of-flight mass spectrometer and tallied with a fast counter. Photoionization efficiency (PIE) curves are measured by integrating the area under the signal corresponding to the photoion of interest and normalizing to ALS current and VUV flux. Further details are available in the Supporting Information.

Figure 1 shows the PIE curves of $PtCH_2$ and H-Pt-CH_3 near the ionization onset. The figures also show simulated PIE spectra. They are calculated by computing the geometries and vibrations of the neutral species and the cation, and calculating Franck–Condon factors for each vibration. The products of the Franck–Condon factors are then integrated and convolved with the 25 meV VUV Gaussian linewidth to generate the PIE spectrum.[9] The electronic structure calculations are described in more detail below. For these two molecules, there is little geometry change upon ionization, thus leading to a sharp onset in the PIE. The ionization energy is determined by shifting the energy origin of the simulation until it provides the best match to the PIE spectrum. This procedure determines the ionization energy (IE) of $PtCH_2$ to be (8.78 ± 0.03) eV. The IE(H-Pt-CH_3) is slightly higher: (8.89 ± 0.03) eV. These values are very slightly lower than $IE(Pt) = 8.9588$ eV.[10]

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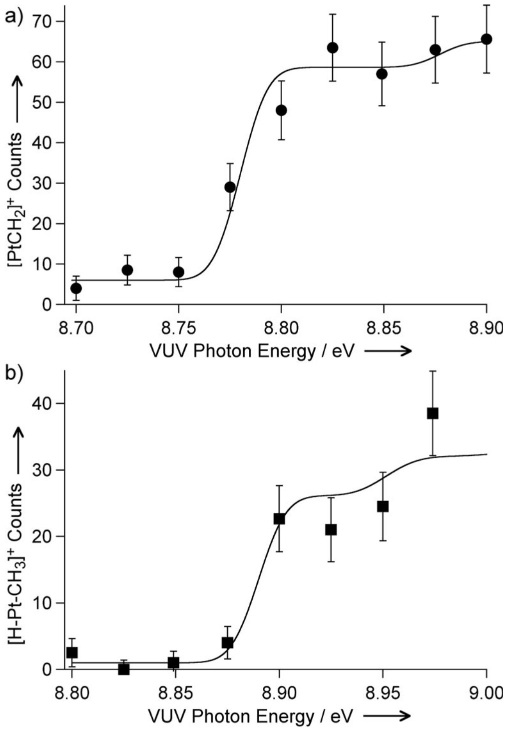

Figure 1. Photoionization efficiency spectra for $PtCH_2$ (a, ●) and H-Pt-CH_3 (b, ■) and simulations (——). The VUV line width is 25 meV. Each point includes data from 10000 ablation laser pulses.

The PIE spectrum clearly shows that the $[Pt,C,H_4]^+$ ion is formed by photoionization of the H-Pt-CH_3 insertion intermediate and is not due to a $Pt(CH_4)$ entrance channel van der Waals complex. First, in an entrance channel complex, CH_4 would interact much more strongly with Pt^+ than it does with neutral Pt, owing to the strong ion-induced dipole force. We calculate that, at the geometry of the triplet $Pt(CH_4)$ entrance channel complex, the vertical ionization energy of $Pt(CH_4)$ is 0.4 eV lower than that of Pt. In addition, the large change in geometry between the neutral and cation entrance channel complexes would lead to a very gradual onset in the PIE. Furthermore, the calculations predict that, once spin-orbit effects are included, there is no barrier to Pt insertion into the C–H bond in methane, so there is no stable entrance channel complex.

Bond dissociation energies for neutral, platinum-containing molecules are calculated by combining our ionization energies with the bond dissociation energies of the corresponding cations measured in the GIB experiments of Zhang et al.[5] All thermodynamic values are at 0 K. The bond dissociation energy of $PtCH_2$ is

$$D_0(\text{Pt-CH}_2) = D_0(\text{Pt}^+\text{-CH}_2) + \text{IE}(\text{PtCH}_2) - \text{IE}(\text{Pt}) \qquad (2)$$

Zhang et al. determined $D_0(\text{Pt}^+\text{-CH}_2) = (4.80 \pm 0.03)$ eV.[5] In conjunction with $\text{IE(Pt)} = (8.9588 \pm 0.0001)$ eV[10] and the measured $\text{IE}(\text{PtCH}_2) = (8.78 \pm 0.03)$ eV, this gives $D_0(\text{Pt-CH}_2) = (4.62 \pm 0.04)$ eV $(446 \pm 4\ \text{kJ mol}^{-1})$.

This can then be used to calculate the energetics of dehydrogenation of methane by the platinum atom. Formation of $CH_2 + H_2$ from CH_4 is endoergic by $(454.7 \pm 2.5)\ \text{kJ mol}^{-1}$.[5] Thus, the bimolecular $Pt + CH_4 \rightarrow PtCH_2 + H_2$ reaction is endoergic, but only by $(9 \pm 5)\ \text{kJ mol}^{-1}$. A second key finding in our work is the energy of the H-Pt-CH_3 insertion intermediate. GIB studies of collisions of $[\text{H-Pt-CH}_3]^+$ with Xe determine that it lies (1.77 ± 0.08) eV below $Pt^+ + CH_4$.[5] Combining this result with $\text{IE(H-Pt-CH}_3) = (8.89 \pm 0.03)$ eV means that insertion of neutral Pt into CH_4 to form H-Pt-CH_3 is exoergic by (1.70 ± 0.09) eV $(164 \pm 9\ \text{kJ mol}^{-1})$.

Is there a barrier to insertion of platinum into the C–H bond in methane? The B3LYP calculations of Xiao and Wang predict that there is a $116\ \text{kJ mol}^{-1}$ barrier for the ^3D (d^9s) ground state of Pt to insert into methane, while insertion is barrierless for the ^1S (d^{10}) excited state.[11] Although they did not calculate the energy of the singlet–triplet crossing, an earlier calculation predicts it to occur at an energy of $5\ \text{kJ mol}^{-1}$.[6] Second-order spin-orbit coupling causes these two states to interact and repel. We carried out electronic structure calculations that include this effect using spin-orbit density functional theory (SODFT)[12] in the NWChem[13] electronic structure package. Structures and vibrational frequencies of intermediates and transition states are in the Supporting Information.

Figure 2 shows a potential energy surface for the $Pt + CH_4$ reaction calculated using SODFT. Also, the dashed lines show the result of conventional B3LYP calculations, without spin-orbit coupling. Approach of the ground (^3D, d^9s^1) state of Pt to methane leads to a weakly bound entrance channel complex. C–H bond insertion by triplet Pt involves a substantial barrier, agreeing with previous calculations.[6,11] In contrast, insertion of the lowest singlet state (^1S, d^{10}) of Pt into the C–H

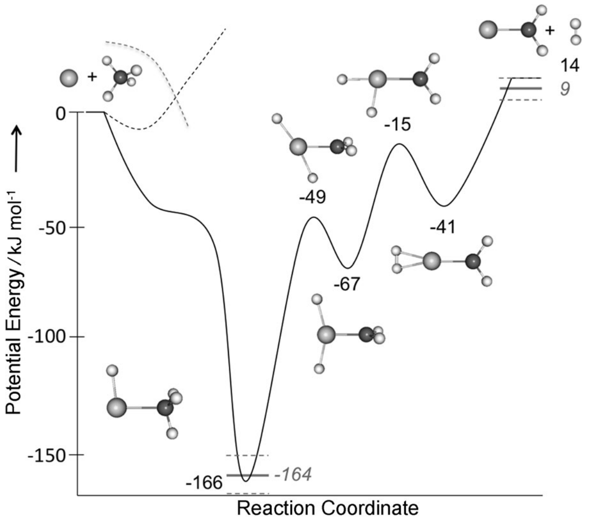

Figure 2. Potential energy surface for the $Pt + CH_4$ reaction. The solid curve and corresponding structures of intermediates and transition states are calculated using spin-orbit DFT with the B3LYP functional and aug-cc-pVTZ basis set. The lower and upper dashed lines are the result of conventional B3LYP calculations for the ground triplet state and lowest singlet state. Horizontal lines and values in italics indicate experimentally determined energies and uncertainties.

bond is barrierless. After the triplet–singlet crossing, the minimum energy path for the reaction occurs exclusively on the singlet surface. The SODFT calculations show that the spin-orbit interaction between the triplet and singlet pathways in the entrance channel is so strong that there is no barrier to insertion of platinum into the C–H bond. Despite a careful search, no transition state for this insertion could be located. On the minimum energy path, there is no local minimum corresponding to the Pt(CH_4) entrance channel complex. The insertion intermediate is calculated to lie 166 kJ mol^{-1} below reactants. This is in excellent agreement with the experimental value of (164 ± 9) kJ mol^{-1}. As proposed by Xiao and Wang,[11] on the minimum energy path the reaction proceeds by sequential H transfer to produce dihydrido H,H-PtCH_2 and (H_2)PtCH_2, which then dissociates to form PtCH_2 ($^1A_1$) + H_2. Recently, vibrational spectra of H-Pt-CH_3 and, perhaps, H,H-PtCH_2 formed by reaction of laser-ablated Pt atoms with CH_4 have been measured in a cryogenic Ar matrix.[14] The SODFT calculations predict that the overall reaction is 14 kJ mol^{-1} endoergic, which is in excellent agreement with the experimental result, (9 ± 5) kJ mol^{-1}. Our calculations predict that the barriers all lie well below the PtCH_2 + H_2 products.

A comparison of the SODFT results with conventional B3LYP calculations with the same basis set gives very similar results for the relative energies of H-Pt-CH_3, the later intermediates, and the products (all of which are singlets). The two calculations differ significantly, however, in the energies of the reactants and entrance channel complex. This agrees with the assertion by Carroll et al.[6] that spin-orbit effects are most significant for the bare atom and noncovalent complexes and that they are largely quenched by formation of covalent bonds. In addition, the previous calculations[6,11,15] predicted intermediates, transition states, and products that are at least 20 kJ mol^{-1} less stable than reactants compared to our calculations. This is primarily due to the use of the larger, more flexible aug-cc-pVTZ-PP basis set for Pt[16] in our work and, to a lesser extent, the inclusion of spin-orbit effects.

The kinetics of the reactions of neutral and cationic platinum atoms with methane are quite different. At 300 K, reaction of the neutral species is quite inefficient, with an observed bimolecular rate that corresponds to 3 % of the collision rate.[7] This has been interpreted as being due to formation and efficient termolecular stabilization of the H-Pt-CH_3 intermediate, with negligible formation of bimolecular products PtCH_2 + H_2. This view was partly due to calculations done in conjunction with the kinetics study, which predicted that conversion of H-Pt-CH_3 to the (H_2)PtCH_2 exit channel complex involves a 129 kJ mol^{-1} barrier, as it occurs through a concerted pathway involving a four-center intermediate.[6] The kinetics results were thus interpreted as being solely due to the termolecular pathway, operating near the high pressure limit. However, an estimate of the reaction rate, using $k/k_{\text{collision}} = \exp(-E_a/RT)$ with E_a set to the (9 ± 5) kJ mol^{-1} reaction endothermicity, gives a 300 K rate constant 2.7 % of the collision rate (with a range of 0.4 to 20 %). Thus, all of the observed reaction could be bimolecular. The Pt^+ cation, under single-collision conditions and at 300 K, reacts with CH_4 at ≥ 50 % of the collision rate, thereby forming $[PtCH_2]^+ + H_2$.[2,4] In the presence of buffer gas, the insertion intermediate is also observed.[5] The kinetics studies[6] concluded that charge matters: the attractive ion-induced dipole interaction stabilizes all adducts relative to reactants. This lowers the energies of intermediates and reduces barriers, thereby facilitating the reaction. Our study turns the aforementioned conclusion on its head. For activation of methane by platinum, charge matters very little! The mechanisms and energetics of the reactions of Pt and Pt^+[5] with methane are very similar. In both cases insertion of the metal into the C–H bond is barrierless, and leads to insertion intermediates with high, and very similar, stabilities. Subsequent hydrogen transfer from the methyl group to the metal is sequential, with calculated barriers that lie below the energy of the dehydrogenation products. The major difference in the observed kinetics is likely due to the (18 ± 3) kJ mol^{-1} difference between the Pt^+-CH_2 and Pt-CH_2 bond strengths. As a result, dehydrogenation of methane by Pt^+ is slightly exoergic, while reaction with neutral Pt is slightly endoergic.

The energetics of two key species involved in methane activation by platinum atom—the H-Pt-CH_3 insertion intermediate and PtCH_2 + H_2 products—have been determined by combining measured ionization energies with bond dissociation energies for the corresponding cations obtained in guided ion beam experiments. Coupled with kinetics experiments and high-level electronic structure calculations, these findings provide unprecedented insight into the mechanistic details of this most fundamental C–H bond activation reaction.

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