Selective Activation of the C−H Bond in Methane by Single Platinum Atomic Anions

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Abstract: *Mass spectrometric analysis of the anionic products of interaction between platinum atomic anions, Pt⁻, and methane, CH_4 and CD_4, in a collision cell shows the preferred generation of [PtCH₄]⁻ and [PtCD₄]⁻ complexes and a low tendency toward dehydrogenation. [PtCH₄]⁻ is shown to be H−Pt−CH₃⁻ by a synergy between anion photoelectron spectroscopy and quantum chemical calculations, implying the rupture of a single C−H bond. The calculated reaction pathway accounts for the observed selective activation of methane by Pt⁻. This study presents the first example of methane activation by a single atomic anion.*

Converting methane into high value chemicals requires it first to be chemically activated. However, because the dissociation energy of the C−H bond is high, i.e., 440 kJ mol⁻¹,[1] activation is challenging. Typically, either elevated reaction temperatures or high activity catalysts are required,[2,3] but these inevitably compromise selectivity.[4] Industrially, the end product of methane conversion is usually the generation of syngas, but this process consumes large amounts of energy. Clearly, it would be advantageous to functionalize methane through the selective and energy-efficient activation of the thermodynamically strong C−H bond. This goal is therefore among the greatest challenges in catalysis.

Gas-phase studies of methane activation by metal atoms and clusters have provided insight into methane functionalization at the molecular level.[5–42] In the case of platinum the reactivities of its cationic, neutral, and anionic atoms and clusters with methane have been widely investigated.[36–49] For its atoms, in particular, both cationic and neutral platinum atoms have been shown to activate methane, yielding both dehydrogenation and C−H insertion products, whereas anionic platinum atoms were found in FT-ICR mass spectrometric experiments to exhibit only negligible reactivity toward methane.[36]

Here, we show that under our experimental conditions, platinum atomic anions, Pt⁻, activate methane, and that due

to their preference for activating only one C−H bond, they do so with significant selectivity. This study represents the first observation of methane activation by single atomic anions.

Our experimental apparatus has been described previously.[50–52] Briefly, Pt⁻ was prepared in a laser vaporization source and interacted with methane introduced into a reaction cell downstream. The resultant anionic products were identified by time-of-flight mass spectrometry. Anions of interest were mass-selected and then characterized by anion photoelectron spectroscopy, which involves crossing a mass-selected beam of anions with a fixed-frequency photon beam and energy-analyzing the resultant photodetached electrons. The photodetachment process is governed by the energy-conserving relationship, $h\nu = \text{EKE} + \text{EBE}$, where EKE is the electron kinetic energy and EBE is the electron binding (transition) energy.

Figure 1 presents mass spectra with or without the addition of methane. With no methane in the reaction cell, only Pt⁻ and weak intensities of PtC⁻ and PtO⁻ were observed (Figure 1 A). The formation of PtC⁻ and PtO⁻ was likely due to trace amounts of carbon and oxygen present on the platinum metal surface. When methane or deuterated methane was added to the reaction cell, prominent mass series of [PtCH₄]⁻ and [PtCD₄]⁻ anionic complexes appeared

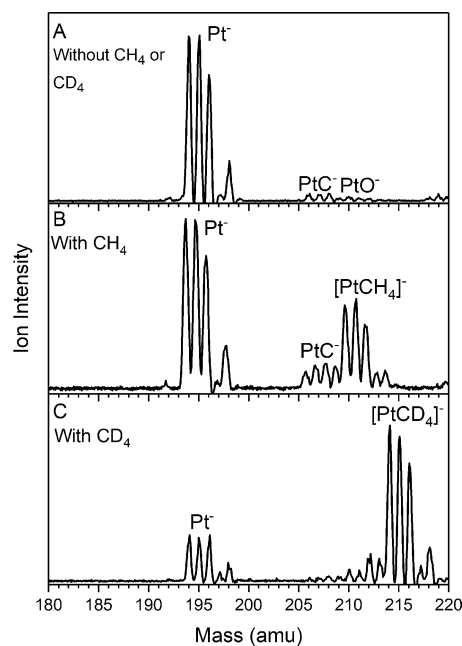[*] G. Liu, Z. Zhu, S. M. Ciborowski, Prof. Dr. K. H. Bowen
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Figure 1. The mass spectra of Pt⁻ without methane (A), with methane (B), and with deuterated methane (C).

(Figure 1 B,C). The presence of strong $[PtCH_4]^-$ and $[PtCD_4]^-$ ion intensities shows that Pt^- interacts efficiently with methane under our experimental conditions. The much weaker intensity peaks on the low mass side of the $[PtCH_4]^-$ or $[PtCD_4]^-$ peaks are due to PtC^-, $[PtCH_2]^-$ or $[PtCD_2]^-$. The presence of reaction products, $[PtCH_2]^-$ and $[PtCD_2]^-$, is indicative of relatively weak dehydrogenation of methane by Pt^-. By contrast, dehydrogenation and the formation of platinum-carbene complexes were the dominant outcomes of reactions between neutral and cationic platinum atoms and methane.[43–46]

Figure 2 presents the anion photoelectron spectra of Pt^-, $[PtCH_4]^-$, and $[PtCD_4]^-$, all measured with 3.496 eV photons. The photoelectron spectrum of Pt^- shows no transitions originating from excited-state Pt^- (Figure 2 A), confirming that the reaction occurs between ground-state Pt^- and methane. The anion photoelectron spectra of $[PtCH_4]^-$ and $[PtCD_4]^-$ are presented in Figures 2 B and 2 C, respectively. Potentially, these spectra could be due to physisorbed complexes, activation species, or both. In the physisorbed case, Pt^- and methane would be weakly bound together to form $Pt^-(CH_4)$ and $Pt^-(CD_4)$. Typically, when an anion is solvated by another molecule, the anion photoelectron spectrum of the resulting physisorbed anionic complex closely resembles that of the anion alone, except for its spectral pattern having been shifted to higher electron binding energies (EBE) and its features slightly broadened.[53] In the activation case, one or more C−H/C−D bonds would be broken, leading to the formation of H_n−Pt−$CH_{4-n}{}^-$ and D_n−Pt−$CD_{4-n}{}^-$. The anion photoelectron spectrum of such activation species would be drastically different to that of the anion due to changes in the electronic structure. The photoelectron spectra of $[PtCH_4]^-$ and $[PtCD_4]^-$ bear no resemblance to the spectrum of Pt^-, and in fact their lowest EBE peaks lie below the EBE of the lowest EBE peak in the Pt^- spectrum. Therefore the spectroscopic evidence strongly

supports that $[PtCH_4]^-$ and $[PtCD_4]^-$ are activation species rather than physisorbed complexes. Thus, within each of these entities, methane activation has occurred; chemistry has taken place. The fact that Figures 2 B and 2 C have essentially identical features confirms that the activation species, $[PtCH_4]^-$ and $[PtCD_4]^-$, have the same geometries and electronic structures.

The lowest EBE feature in the photoelectron spectra of both $[PtCH_4]^-$ and $[PtCD_4]^-$ has its maximum spectral intensity centered at EBE = 1.93 eV. Thus, 1.93 eV is their common vertical detachment energy (VDE). The VDE is defined as the photodetachment transition energy at which the Franck-Condon overlap is at its maximum between the anion's vibrational wave function and that of its neutral counterpart with both in their ground electronic states. The other peaks in the spectra are due to vertical photodetachment transitions from the ground state anion to its neutral counterpart in its various excited electronic states. All of the experimental vertical photodetachment transition energies values are tabulated in Table 1.

Table 1: Experimental and calculated vertical photodetachment transition energy values for the GM structure, H−Pt−$CH_3{}^-$.

Peak	Final neutral state	Vertical photodetachment transition energy	
		Expt.	Theory[a]
X	$^1A'$	1.98	1.95
A	$^3A'$	2.27	2.34
B	$^3A''$	2.46	2.52
C	$^1A'$	2.56	2.64
D	$^3A'$	2.75	2.73
E	$^3A''$	2.88	2.78
F	$^1A''$	3.07	2.99
G	$^1A'$	3.18	3.15
H	$^1A''$	3.28	3.49

[a] CCSD(T) calculated VDE plus MRCI + Q calculated excitation energies; see the Supporting Information.

Density functional theory (DFT) calculations were performed to find the most thermodynamically stable isomer of $[PtCH_4]^-$, which was expected to be the main contributor of the photoelectron spectrum. The energetics of the low-energy isomers were then refined at the CCSD(T) level of theory. The computational details are given in the Supporting Information (SI). Figure 3 presents the structures of different $[PtCH_4]^-$ isomers along with their relative energies. All energies are zero-point energy corrected. The global minimum (GM) of $[PtCH_4]^-$ features C_s symmetry and one activated C−H bond, i.e., H−Pt−$CH_3{}^-$. The physisorbed complex, $Pt^-(CH_4)$, is 0.62 eV above the GM. Two isomers corresponding to the breakage of two C−H bonds, the hydrogen-Pt-carbene complex (H_2)−Pt−$CH_2{}^-$ and the dihydrido-Pt-carbene complexes H_2−Pt−$CH_2{}^-$, are, respectively 0.63 and 0.69 eV higher than the GM. Note that the H−H bond length (0.99 Å) in (H_2)−Pt−$CH_2{}^-$ is significantly longer than that in the free H_2 molecule (0.74 Å). Such elongation suggests H_2 activation due to back-donation from the Pt−$CH_2{}^-$ moiety to the H_2 σ* antibonding orbital (Figure S2). This back-donation strengthens the interaction between H_2
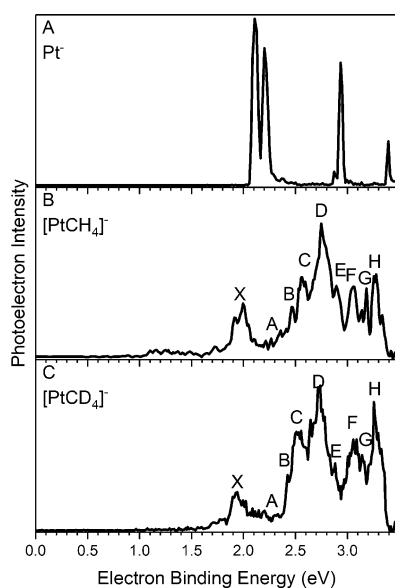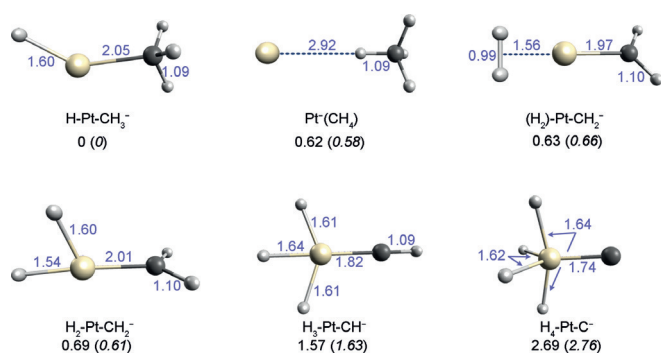

Figure 2. Photoelectron spectra of Pt^- (A), $[PtCH_4]^-$ (B), and $[PtCD_4]^-$ (C), all measured with 355 nm (3.496 eV) photons.

Figure 3. Optimized structures for [PtCH$_4$]$^-$ and their relative energies compared to its GM. The relative energies of [PtCD$_4$]$^-$ are shown in parenthesis. Energies are given in eV. Bond lengths are given in Å.
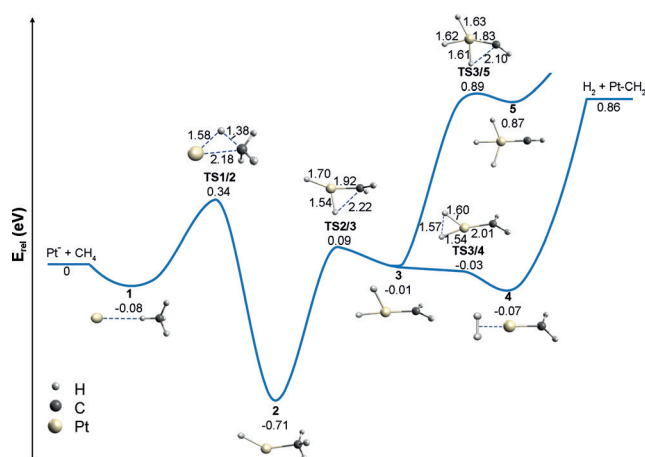

Figure 4. Calculated reaction pathway for methane activation by Pt$^-$. Zero-point energy corrected energies are given in eV. Bond lengths of the transition states are given in Å.

and Pt−CH$_2$$^-$ moieties and can lead to a high dehydrogenation energy.[54] The two structures that resulted from activating three and four C−H bonds have relative energies of 1.57 and 2.69 eV, respectively, making them unlikely to form under our experimental conditions. The isomers of [PtCD$_4$]$^-$ have the same structures as [PtCH$_4$]$^-$; their relative energies are provided in Figure 3 in parenthesis. To verify that the calculated GM of [PtCH$_4$]$^-$ describes the experimental spectrum, its vertical photodetachment transition energies values were computed at the multi-reference configuration interaction (MRCI + Q) level of theory and compared with the observed experimental values (Table 1). The calculated values accurately reproduce all the transitions observed in the photoelectron spectrum of [PtCH$_4$]$^-$, thus providing unambiguous validation of the GM structure, H−Pt−CH$_3$$^-$, as the major reaction product. Therefore, the combined results from mass spectroscopy, anion photoelectron spectroscopy, and ab initio quantum calculations have confirmed that atomic Pt$^-$ readily activates methane, and that such activation process leads to H−Pt−CH$_3$$^-$ with high selectivity.

To provide mechanistic insight into the highly selective C−H bond cleavage and low dehydrogenation tendency observed when Pt$^-$ activates methane, the reaction pathway was investigated with quantum calculations. The reaction pathway energy diagram is presented in Figure 4. The reaction occurs entirely on a doublet potential energy surface. Initially, CH$_4$ physisorbs onto Pt$^-$ and forms the van der Waals complex **1**, Pt$^-$(CH$_4$), with a binding energy of 0.08 eV. This solvation complex then passes over a transition state **TS1/2** in which one C−H bond is weakened and elongated. The activation barrier is 0.42 eV above local minima **1**. Such a moderate barrier can be overcome under the multi-collision conditions in the reaction cell, where translational energy is provided by collisions with the supersonically-expanded He carrier gas.[12] After overcoming **TS1/2**, Pt$^-$ is inserted into the C−H bond and methane is activated, yielding the GM structure **2**, H−Pt−CH$_3$$^-$, the major activation product observed in the current experiments. The activation complex would next need to overcome **TS2/3** with a barrier of 0.80 eV, in order for a second H atom to migrate from the methyl group to Pt to form **3**, H$_2$−Pt−CH$_2$$^-$. The subsequent H transfer over **TS3/5** to form H$_3$-Pt-CH$^-$ (structure **5**) is not favored, since it is quite endothermic with a large barrier of

0.89 eV above the entrance channel. Instead, H$_2$−Pt−CH$_2$$^-$ (structure **3**) can pass over the negligible barrier of **TS3/4** to form (H$_2$)−Pt−CH$_2$$^-$ (structure **4**), where the two H atoms have combined to form a H$_2$-like molecule attached to the Pt-carbene moiety. Its subsequent dissociation into H$_2$ and PtCH$_2$$^-$ is quite endothermic by 0.93 eV, which is consistent with the previous analysis of a strong binding between H$_2$ and Pt−CH$_2$$^-$. The overall reaction of Pt$^-$ + CH$_4$→PtCH$_2$$^-$ + H$_2$ is thus endothermic by 0.86 eV. Note that this is significantly different from the cases of methane reacting with Pt$^+$ or Pt^0, where dehydrogenation is exothermic or only slightly endothermic.[43,44] Our computed reaction pathway thus gives a quantitative rationale for the highly selective C−H bond cleavage and the low dehydrogenation tendency that occurs when Pt$^-$ activates methane. It also explains the lack of an efficient hydrogen dissociation channel, and especially the fact that the H−Pt−CH$_3$$^-$ is trapped in the minimum on the potential energy surface, resulting in its highly selective formation.

The ground state of Pt$^-$, ^{2}D(6s^{2}5d^9), has one unpaired electron, allowing the formation of only one σ-bond. In order for Pt$^-$ to form the GM H−Pt−CH$_3$$^-$ structure, one electron is promoted from the 5d to the 6p orbital to generate the ^{4}G(6s^{2}5d^{8}6p^1) excited state with three available unpaired electrons. Two of them can couple with the unpaired electrons of the H(^{2}S) and CH$_3$(^{2}A$_2''$) fragments to form the two Pt−H and Pt−C σ-bonds. The formations of these two σ-bonds stabilizes the H(^{2}S)/Pt$^-$(^{4}G)/CH$_3$(^{2}A$_2''$) interaction, resulting in the formation of the GM. The remaining one electron occupies a 5d-6p hybrid orbital that couples with the CH$_4$ anti-bonding orbital during the activation process (Figure 5), fulfilling the accepted donor–acceptor model for σ-bond activation.[43]

To summarize, we have demonstrated that Pt$^-$ is able to selectively activate only one C−H bond in methane, representing the first example of methane activation by atomic anions. Mass spectrometric analysis of the reaction products between Pt$^-$ and CH$_4$ shows the preferred generation of [PtCH$_4$]$^-$ and a low tendency toward dehydrogenation.
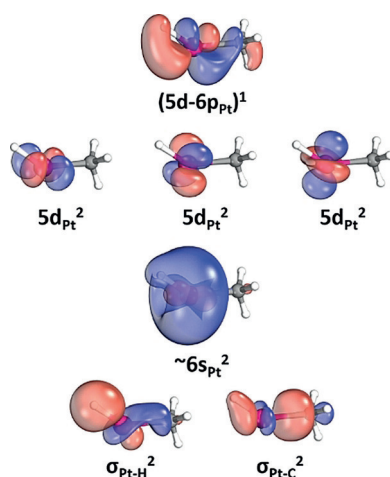
Figure 5. Selected molecular orbitals of the GM H−Pt−CH₃⁻ depicting the Pt−C and Pt−H bonds and the nearly intact valence Pt orbitals.

$[PtCH_4]^-$ is confirmed as H−Pt−CH₃⁻ by anion photoelectron spectroscopy and quantum chemical calculation, suggesting a selective rupture of just one C−H bond. The single unpaired electrons in ground-state Pt⁻ necessitates electron promotion to the 6p orbital in order to facilitate the reaction over a moderate barrier. The demonstration of methane activation by atomic anions has opened a new route for designing novel catalysts for C−H bond functionalization.

Acknowledgements

Conflict of interest

The authors declare no conflict of interest.

Keywords: ab initio calculation ·
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