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Pt^+-mediated activation of methane: theory and experiment

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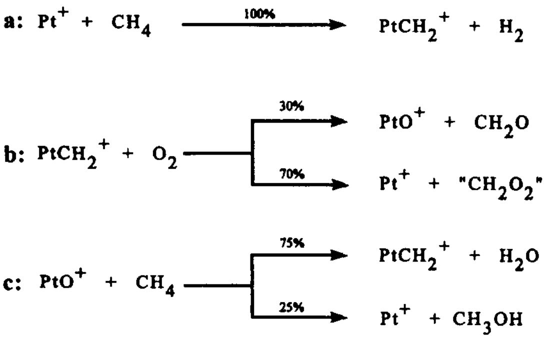
Abstract

A combined theoretical and experimental study on the Pt^+-mediated activation of methane is presented. Dehydrogenation of CH_4 by thermalized Pt^+ cations ($Pt^+ + CH_4 \rightleftarrows PtCH_2^+ + H_2$) proceeds along a doublet ground state potential energy surface and is found to be reversible under the conditions of Fourier transform ion-cyclotron resonance mass spectrometry. The recently reported oxidation of the cationic platinum carbene $PtCH_2^+$ by O_2 produces electronically excited Pt^+ cations, which are detected in the $^4F_{9/2}$ state by means of charge-transfer bracketing experiments.

1. Introduction

The transition-metal catalyzed activation of methane constitutes an important topic of research driven by both the challenging inertness of this simplest hydrocarbon molecule and the substantial industrial interest in the functionalization of natural gas resources [1–7]. The catalytic conversion of CH_4 to CH_3OH has recently been listed as one of the ten challenges for catalysis [1]. Recently, we found that platinum cations catalyze the reaction of methane with molecular oxygen in the gas phase, yielding methanol, formaldehyde, and probably formic acid as oxidation products (see Scheme 1) [8].

In our continuing efforts to correlate the gas-phase reactivity of isolated transition-metal species with their underlying electronic structures [9] this Letter presents a combined experimental and theoretical study on the mechanism of the initial step in this catalytic cycle, i.e. the activation of CH_4 by the 'bare' Pt^+ cation (a). As discovered by Irikura and Beauchamp [10–12], this reaction also occurs for other third-row transition-metal cations which may be attributed to the relativistic stabilization of the cationic methylidene complexes MCH_2^+ [13]. Detailed theoretical investigations on the potential energy surface for the reaction of Ir^+ [14,15] and other transition metal cations M^+ with methane have been published elsewhere (Co^+ [16]; Rh^+ [17]; Fe^+ [18]; Y^+–d^+ [19]). In the second part of this contribution,



Scheme 1.

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[1] See Chem. Eng. News May 31 (1993) 27.

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we communicate preliminary experimental results for the involvement of an electronically excited state of Pt^+ the second step in the catalytic cycle (b), which is hoped to guide theoretical investigations on the oxidation of $PtCH_2^+$ by molecular oxygen.

2. Theoretical and experimental procedures

Quantum-chemical calculations were carried out using a recently developed density-functional/Hartree–Fock hybrid approach [20]. While these methods proved to be successful in reproducing highly accurate thermochemical data of organic systems, promising applications to transition-metal chemistry have only recently been initiated [21,22]. These calculations are in remarkably good agreement to highly correlated electronic structure methods and experiments as far as geometries and energetics are concerned (e.g. mean absolute deviations from experiment of less than 5 kcal/mol for bond dissociation energies of cationic 3d-block metal methyl complexes MCH_3^+ [22]). In the present study, the functional used was the BECKE3LYP formula of the GAUSSIAN 92 program package [23], which is superior to the related BHANDHLYP functional for multiply bonded open-shell transition-metal systems [24]. The 60 core electrons ([Kr + $4d^{10}$ + $4f^{14}$]) of platinum were described by a relativistic effective core potential [25]. The Pt valence orbitals were expanded in the corresponding (5s5p3d)/[3s2p2d] (441|41|21) basis set, augmented by a diffuse d function with an exponent of 0.0685, and the standard Huzinaga–Dunning polarized double-ζ basis was employed for carbon and hydrogen [26]. Tight SCF convergence criteria for the solution of the unrestricted Kohn–Sham equations and fine grids for numerical integration were employed throughout. All geometries were optimized using standard gradient techniques and numerically computed harmonic frequencies served to characterize stationary points as true minima or transition states on the potential energy surface.

A description of the experimental apparatus, a Spectrospin CMS 47 X Fourier transform ion-cyclotron resonance mass spectrometer, and details of the kinetic studies have been reported elsewhere [8], so that we can restrict ourselves to the description of the single-electron transfer experiment here. The fluorinated benzenes were admitted to the cell via a leak valve at a constant pressure of 1.5×10^{-8} mbar. $PtCH_2^+$ was generated by pulsing-in methane up to a pressure of about 5×10^{-7} mbar to react with isolated $^{195}Pt^+$. After the isolation of $PtCH_2^+$, oxygen was pulsed-in for about 1.5 s up to a pressure of about 5×10^{-5} mbar as reaction partner and as buffer gas to transfer kinetic energy. The regenerated Pt^+ ions were isolated and their reaction with fluorinated benezenes measured for three different reaction times. In control experiments, the reaction of Pt^+ extracted from the ion source was probed by using exactly the same experimental sequence of pulses and isolation steps except for the methane pulse. Off-resonance excitation [27] of the Pt^+ cations during their isolation could thus be excluded.

3. Results and discussion

Figs. 1 and 2 show the calculated ground state potential energy surface corresponding to the process $Pt^+(^2D) + CH_4 \rightarrow PtCH_2^+(^2A_1) + H_2$, and the geometrical features of all relevant species involved.

The insertion of a ground state Pt^+ cation [28] into a C–H bond of CH_4 proceeds via a $\eta^2 Pt^+ – CH_4$ complex (**1**) with an almost negligible activation barrier (1.3 kcal/mol for $\mathbf{1} \rightarrow \mathbf{2}$) to generate the cationic $H–Pt^+–CH_3$ complex (**3**, $^2A'$), which represents the global energy minimum along the reaction path. Within the chosen theoretical model, this species adopts a pseudo-staggered conformation whereas the eclipsed conformer corresponds to the transition state (0.5 kcal/mol above **3**) for rotation around the Pt–C bond. All C_{2v} and C_{3v} structures for an electrostatic adduct complex between Pt^+ and methane are saddle points on the potential energy surface. Following the curvatures associated with the negative eigenvalues of the Hessian matrix leads to the η^2(C,H) structure **1** which has so far not been considered in theoretical investigations of metal–cation/methane complexes $M(CH_4)^+$. Recently, the importance of this mode of coordination in bulk-phase organometallic chemistry was demonstrated by Luo et al. who isolated the first organometallic complex containing an intact η^2-bound silane (SiH_4) ligand [29].

An α-hydrogen shift involving the transition state **4** (30.1 kcal/mol above **3**) leads to the intermediate dihydrido-methylene species **5** (^{2}A), followed by rearrangement to the dihydrogen complex of the cationic platinum carbene, (H_2)–$PtCH_2^+$ (**7**, $^2A_1$). The transition state for the latter isomerization (**6**, 9.4 kcal/mol above **5**) constitutes the highest energy structure of the overall process prior to the final dissociation to H_2 and $PtCH_2^+$ ($^2A_1$). Doublet spin multiplicity is conserved along the whole reaction pathway. While in the $6s^05d^9$ electronic ground state configuration of Pt^+ formally only one σ-bonded ligand is allowed, promotion of a 5d electron to yield the excited $6s^15d^8$ configuration enables the Pt^+ cation to form up to three covalent bonds. The platinum–carbon bond distances in the hydridomethyl complex **3** (2.050 Å) and the carbene complexes **7** (1.851 Å) and **8** (1.830 Å) indicate bond orders of 1 and 2, respectively. Thus, one valence orbital of Pt remains singly occupied in these structures. However, in the energetically unfavorable dihydridomethylene complex **5** the maximum number of three possible covalent metal–ligand bonds is established. Consequently,the spin density in **5** is mainly located on the carbon atom of the CH_2-substituent and the platinum–carbon bond distance in this species (1.934 Å) is intermediate between a singly and doubly bonded system.

In the following, we will briefly compare the results for the $[Pt,C,H_4]^+$ potential energy surface to recent calculations on the reactions of Pd^+ and Ir^+ with methane. The main difference between Pt^+ and its isoelectronic homologue Pd^+ ($5s^04d^9$ ground state) concerns the cationic hydrido-methyl species H–M–CH_3^+. While H–Pt–CH_3^+ represents the overall energetic minimum in the Pt^+/CH_4 system, Siegbahn and co-workers could not locate a stable minimum geometry for H–Pd–CH_3^+ at the Hartree–Fock level of theory [19]. Although inadequacies of their chosen method for geometry optimization cannot be excluded, we rather relate this finding to the higher $d^9s^0 \rightarrow d^8s^1$ promotion energy of Pd^+ (3.19

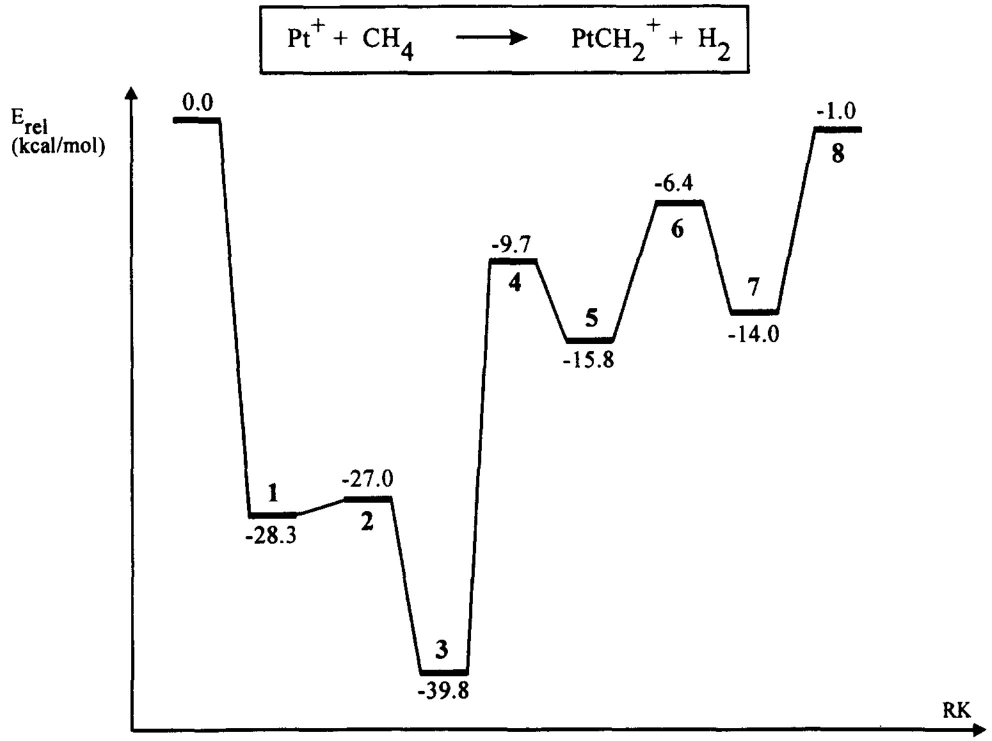


Fig. 1. Potential energy surface for the formation of $PtCH_2^+$ and H_2 from Pt^+ and CH_4. The numbering of molecular structures refers to Fig. 2. Relative energies (in kcal/mol) are reported for 0 K neglecting zero-point vibrational energies (see text and theoretical procedures).

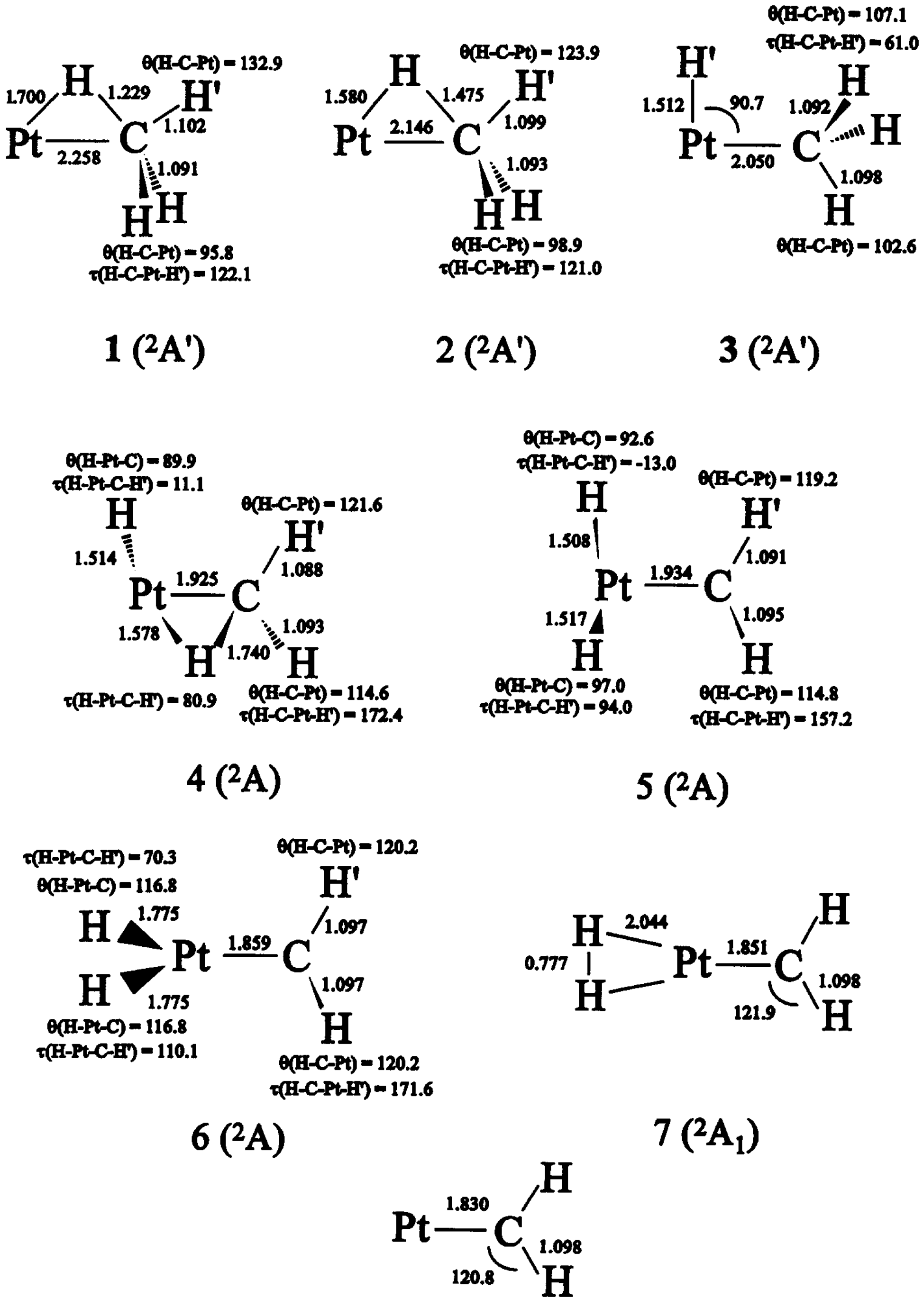
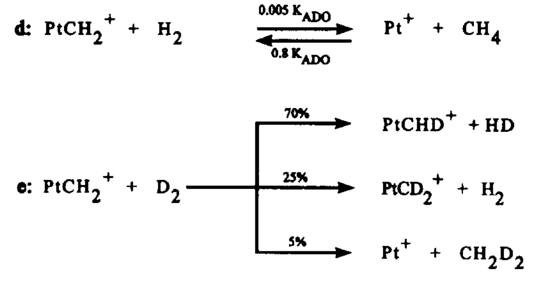


Fig. 2. Calculated structures for intermediates and transition states on the potential energy surface displayed in Fig. 1. Bond lengths are reported in Å, bond angles θ and dihedral angles τ in deg.

eV) as compared to Pt^+ (0.78 eV) [28]. Since the second covalent bond of the hydrido-methyl complex is formed upon d → s excitation, higher promotion energies will decrease its stability which may be the reason why in the case of $H\text{–}Pd\text{–}CH_3^+$, this structure no longer represents a stable minimum on the potential energy surface.

The main difference between the Pt^+/CH_4 and the Ir^+/CH_4 system consists of the relative stability of the dihydrido-methylene complex. While the singlet $Ir(H)_2(CH_2)^+$ species represents the overall energy minimum on its potential energy surface (≈ 20 kcal/mol below the hydrido-methyl complex [14]), the corresponding platinum structure **5** to be is found more than 20 kcal/mol above the hydrido-methyl complex **3**. Perry et al. have conclusively related this difference to the $5d^76s^1$ electronic ground state configuration of Ir^+ [14] and considered the doublet $Pt(H)_2(CH_2)^+$ species **5** to be unstable thus explaining why Pt^+ activates methane less efficiently than Ir^+, as reported earlier [12]. However, our results show that, albeit energetically somewhat disfavored, a distinct minimum for a cationic dihydrido-methylene complex of platinum does in fact exist on the $[Pt, C, H_4]^+$ potential energy surface. Moreover, we have recently demonstrated [13] that methane activation proceeds at the same rate (≈ 70% of the theoretical collision rate [30]) for properly thermalized Pt^+ and Ir^+ cations.

Overall, neglecting zero-point energies, the formation of $PtCH_2^+$ and H_2 from Pt^+ and CH_4 is calculated to be exothermic by 1.0 kcal/mol. The calculated adiabatic excitation energies from the $^2A_1$ ground state of $PtCH_2^+$ to electronically excited states amount to: 13.8 kcal/mol ($^2A_1 \rightarrow {}^2A_2$), 23.9 kcal/mol ($^2A_1 \rightarrow {}^2B_2$), 52.6 kcal/mol ($^2A_1 \rightarrow {}^2B_1$), 49.4 kcal/mol ($^2A_1 \rightarrow {}^4A'$) [2]. The chosen theoretical method describes the atomic $^2D(6s^05d^9) \rightarrow {}^4F(6s^15d^8)$ excitation of the Pt^+ cation reasonably well (1.16 eV, calculated [22]; 0.76 eV, experimental, averaged over all J-levels [28]). Thus, the calculations suggest that $PtCH_2^+$ in reaction (a) is most likely formed in its $^2A_1$ ground state if the reaction starts with thermalized Pt^+ cations in their electronic $5d^9(^2D_{5/2})$ ground state. Since these conditions are given in the employed FT-ICR scheme [31], we will now discuss the experimental results on the background of the potential energy surface depicted in Fig. 1.



Scheme 2.

From the observed intramolecular kinetic isotope effect in the reaction of Pt^+ with CH_2D_2 [8] it has been concluded that the rate determining step in the methane activation must involve the elimination of dihydrogen from a symmetric transition structure. The calculated energy profile (see above) suggests that oxidative insertion of Pt^+ into a C–H bond of methane (**1** → **3**) should be facile whereas there are substantial kinetic and thermodynamic restrictions for both the hydrogen shift (**3** → **5**) and the subsequent rearrangement to the dihydrogen complex of $PtCH_2^+$ (**5** → **7**). Consequently, one would expect one of these steps to be rate-determining, in agreement with the measured kinetic isotope effect.

We now consider the overall thermochemistry of methane activation by Pt^+. The formation of $PtCH_2^+$ from Pt^+ and CH_4 (**a**) proceeds at $k_r = 8.2 \times 10^{-10}$ $cm^3\ s^{-1}$ $molecule^{-1}$, i.e. 80% of the theoretical collision rate k_{ADO} [30]. Interestingly, the reverse process (**d**) can also be observed in the FT-ICR experiment. This indicates that the activation of methane by thermalized Pt^+ cations does indeed proceed close to the thermochemical threshold. The rate constant for the reverse reaction of $PtCH_2^+$ with H_2 amounts to $k_r = 0.07 \times 10^{-10}$ $cm^3\ s^{-1}$ $molecule^{-1}$ or 0.5% of the theoretical collision rate k_{ADO} [30]. Thus, one derives an equilibrium constant of

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[2] Structures of the excited states of $PtCH_2^+$: $^2A_2$: r(Pt–C): 1.876 Å, r(C–H): 1.097 Å, θ(H–C–Pt): 121.8°; $^2B_2$: r(Pt–C): 1.858 Å, r(C–H): 1.101 Å, θ(H–C–Pt): 122.2°; $^2B_1$: r(Pt–C): 2.029 Å, r(C–H): 1.098 Å, θ(H–C–Pt): 122.4°; $^4A'$: r(Pt–C): 1.986 Å, r(C–H): 1.090 Å, θ(H–C–Pt): 114.4°, τ(H–C–Pt–H): 97.9°.

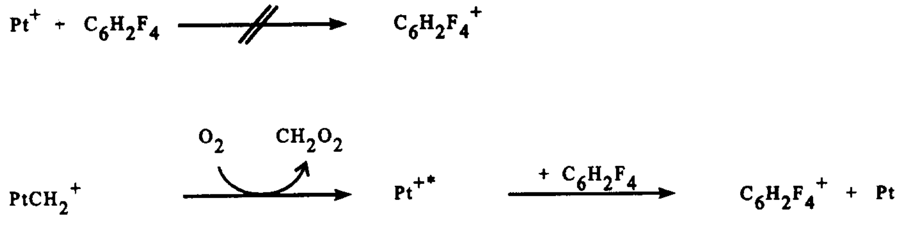
160 ± 80 for the system $Pt^+ + CH_4 \rightleftharpoons PtCH_2^+ + H_2$ assuming an error of ±30% for the measured absolute rate constants. From the correlation $\Delta G = -RT \ln K$ the free enthalpy of the reaction is calculated to be -3.2 ± 1 kcal/mol at 298 K, the assumed temperature of the experiment. This corresponds to a free enthalpy of dissociation for $Pt-CH_2^+$ to $Pt^+(^2D)$ and CH_2 $(^3B_1)$ of 114.6 ± 1 kcal/mol, in excellent agreement to previous results [8,13]. If D_2 is employed in the reaction with $Pt-CH_2^+$ (e) one observes the two primary products $PtCHD^+$ and $PtCD_2^+$ in a ratio of 2.8/1. Considering the kinetic isotope effect of 1.6 per hydrogen atom, which has been deduced from the reaction of Pt^+ with CH_2D_2 [8], one would have expected a $PtCHD^+/PtCD_2^+$ ratio of only 1.2/1. This implies that about 40% of the primary products in the $PtCH_2^+/D_2$ reaction is formed via one single sequence of insertion into the D–D bond and consecutive elimination of $H_{2-x}D_x$ ($x = 1, 2$). The remaining 60% undergo statistical H/D exchange most likely by an equilibration between the hydrido-methyl complex **3** and the adduct **1**. The analogous reaction of $PtCD_2^+$ and H_2 yields $PtCHD^+$ and $PtCH_2^+$ in a ratio of 3.8/1, which corresponds to 90% scrambling. Thus, the extent to which this process takes place in competition to a single insertion/elimination event is also affected by a kinetic isotope effect. Only 5% of the ionic products in reaction (e) derive from regeneration of Pt^+ and concomitant formation of CH_2D_2, corresponding to a branching ratio of 1:19 between both possible product channels (see Fig. 1). The observation of facile H/D exchange in $PtCH_2^+$ provides yet another experimental support for the calculated potential energy surface, implying that the kinetic bottleneck in the reverse reaction concerns the reductive elimination of Pt^+ and methane from the insertion product **3**.

Table 1
Theoretical thermochemistry (in kcal/mol) for the reaction $Pt^+(^2D) + CH_4 \rightarrow PtCH_2^+(^2A_1) + H_2$

ΔH(0 K)	−1.0
ΔH(0 K) + ZPVE	−8.0
ΔH(298 K)	−7.3
$T\Delta S$(298 K)	+1.0
ΔG(298 K)	−8.3

For an adequate comparison between theoretical and experimental thermochemistry we have included zero-point vibrational energies and temperature effects (298 K) in the calculated potential energy surface using harmonic frequencies and the harmonic-oscillator, rigid-rotor approximation [32] for an ideal gas (see Table 1). With these corrections one obtains a theoretical reaction exothermicity of −7.3 kcal/mol and a small contribution of −1 kcal/mol from entropy changes between $Pt^+(^2D)/CH_4$ and $PtCH_2^+(^2A_1)/H_2$. The overall deviation of 5 kcal/mol between the experimental and theoretical ΔG values lies within the expected accuracy of the employed quantum-chemical method [22,24].

As evident from Scheme 1, the main process for regeneration of the 'catalyst' Pt^+ within the oxidation cycle consists of the reaction of $PtCH_2^+$ with O_2. Depending on which neutral 'CH_2O_2' is formed this reaction is exothermic by 62–74 kcal/mol [8]. The large excess energy must be deposited in kinetic energy or internal degrees of freedom of the reaction products. For example, Pt^+ might be regenerated in an electronically excited state. To check this hypothesis, we monitored the electronic state of the Pt^+ ions by their charge-transfer behavior, assuming that single electron transfer (SET) is not hampered by kinetic barriers [33]. Pt^+ ions, extracted from the ion source and thermalized by at least 200 collisions



Scheme 3.

with pulsed-in oxygen gas do not undergo single-electron transfer (absence of a signal in Fig. 3a corresponding to $C_6H_2F_4^+$) towards 1,2,3,4-tetrafluorobenzene (ionization energy, IE: 9.53 ± 0.01 eV) [34]. Therefore, these Pt^+ cations must reside in their $^2D_{5/2}$ electronic ground state with an excess kinetic energy of less than 0.53 eV within the center-of-mass frame. However, Pt^+ ions generated in the reaction of $PtCH_2^+$ with pulsed-in excess of O_2 (reaction (b), Scheme 1) do indeed abstract an electron from the same substrate to yield the $C_6H_2F_4^+$ cation (Fig. 3b). Under identical conditions, no charge

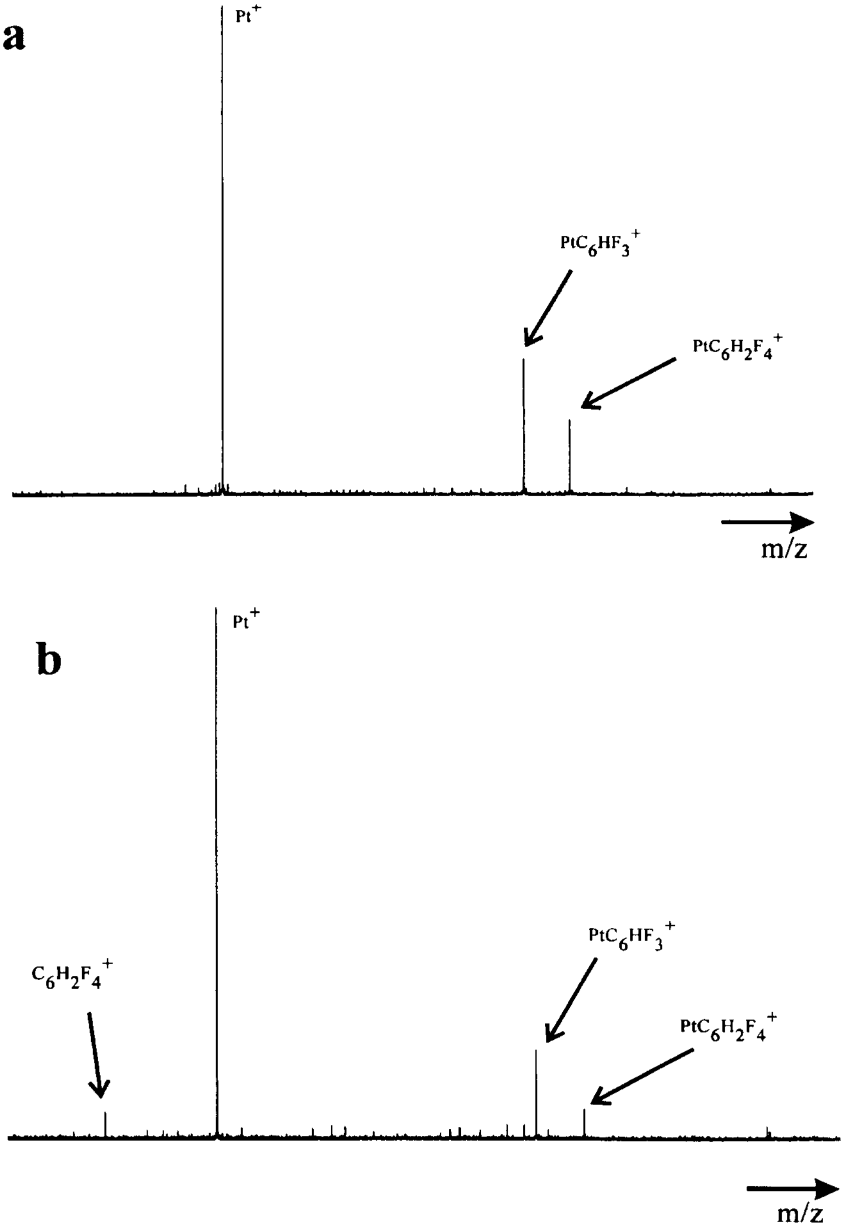


Fig. 3. ICR mass spectra recorded after 4s reaction of Pt^+ with 1,2,3,4-tetrafluorobenzene: (a) Pt^+ ions extracted from the ion source and thermalized by collisions with oxygen; (b) Pt^+ ions regenerated from $PtCH_2^+$ by reaction with oxygen.

Table 2
Low-lying electronic states of Pt^+ and excitation energies ΔE_{exc} from the $5d^9 6s^0$ $(^2D_{5/2})$ ground state (in eV) [28]

State	ΔE_{exc}	State	ΔE_{exc}
$(5d^8 6s^1)^4F_{9/2}$	0.59	$(5d^8 6s^1)^2F_{7/2}$	2.24
$(5d^9 6s^0)^2D_{3/2}$	1.04	$(5d^8 6s^1)^4P_{3/2}$	2.63
$(5d^8 6s^1)^4F_{7/2}$	1.16	$(5d^8 6s^1)^4P_{1/2}$	2.69
$(5d^8 6s^1)^4F_{5/2}$	1.65	$(5d^8 6s^1)^2F_{5/2}$	2.91
$(5d^8 6s^1)^4F_{3/2}$	1.96	$(5d^8 6s^1)^2D_{3/2}$	2.96
$(5d^8 6s^1)^4P_{5/2}$	2.09	$(5d^7 6s^2)^2D_{3/2}$	3.08

transfer occurred between regenerated Pt^+ ions and hexafluorobenzene (IE = 9.91 eV), which implies that the Pt^{+*} cations generated in reaction (b) were excited by less than 0.91 eV, thus corresponding to the $^4F_{9/2}$ state (see Table 2). In principle, the exothermicity of reaction (b) allows for the formation of up to 10 electronically excited states of Pt^+. However, higher excited states (e.g. lower spin–orbit components of the ^4F term), which can also evolve from reaction (b), are expected to undergo fast radiative stabilization on the timescale of the experiment. In contrast, the optical transition of $Pt^{+*}(^4F_{9/2})$ to its ground state $(^2D_{5/2})$ is spin and dipole forbidden, resulting in a longer lifetime of the excited $^4F_{9/2}$ state. Thus, the detection of $Pt^{+*}(^4F_{9/2})$ by charge-transfer is favored compared to other excited states. Whether the reaction of $PtCH_2^+$ with O_2 proceeds exclusively on a potential energy surface which correlates with Pt^+ cations in the ^4F state or via additional mechanisms involving different spin multiplicities is left as an open question which cannot be answered using our present experimental methods. The potential energy surface for the oxidation of $PtCH_2^+$ by O_2 remains a challenge for the predictive power of today's state-of-the-art computational methods.

4. Summary

We have theoretically and experimentally characterized the activation of methane by 'bare' Pt^+ cations in the gas phase. The reaction $Pt^+ + CH_4 \rightarrow PtCH_2^+ + H_2$ occurs as a kinetically efficient process on a doublet ground-state potential energy surface. A cationic hydrido-methyl complex $H\text{–}Pt\text{–}CH_3^+$ is formed upon the almost barrierless insertion of Pt^+ into a C,H-bond of CH_4. The final products $PtCH_2^+$ and H_2 evolve after 1,2-migration of a hydrogen atom and subsequent elimination of H_2 from the transition-metal center. Under FT-ICR conditions, also the reverse process $PtCH_2^+ + H_2 \rightarrow Pt^+ + CH_4$ can be observed. At 298 K the free reaction enthalpy for this reaction amounts to $+3.2 \pm 1$ kcal/mol. Oxidation of the cationic carbene complex $PtCH_2^+$ by O_2 proceeds, at least to some extent, along a quartet potential energy surface producing electronically excited Pt^+ cations, which can be detected in the $^4F_{9/2}$ state by electron transfer reactions.This involvement of electronically excited states may explain the previously reported kinetic irregularities [8] in the later cycles of the Pt^+-mediated oxidation of methane.

Acknowledgements

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