Thermal Activation of Methane by [HfO]·+ and [XHfO]+ (X = F, Cl, Br, I) and the Origin of a Remarkable Ligand Effect

Shaodong Zhou, Jilai Li, Maria Schlangen, and Helmut Schwarz

Dedicated to Professor Donald Hilvert, ETH Zürich, on the occasion of his 60th birthday

Abstract: *The thermal reactions of methane with [HfO]·+ and [XHfO]+ (X = F, Cl, Br, I) were investigated by using FT-ICR mass spectrometry complemented by high-level quantum chemical calculations. Surprisingly, in contrast to the inertness of [HfO]·+ towards methane, the closed-shell oxide ions [XHfO]+ (X = F, Cl, Br) activate the H_3C-H bond to form the insertion products $[Hf(X)(OH)(CH_3)]^+$. The possible origin of this remarkable ligand effect is discussed.*

As a consequence of large relativistic effects,[1] most of the third-row transition-metal cations, such as atomic Ta+, W+, Os+, Ir+, and Pt+, are able to dehydrogenate CH_4[2] under ambient conditions in the gas phase.[3] In contrast, atomic Hf+ does not react with CH_4. This inertness has been attributed to the doubly-occupied 6s orbital of its ground state,[4] resulting in an insurmountable barrier for the oxidative insertion of Hf+ into a C−H bond and a relatively low bond-dissociation energy [BDE(Hf+−CH_2) = 435 kJ mol−1].[5] For other Hf-containing species, only a few were found to activate methane at room temperature. For example, the dication Hf2+ is able to dehydrogenate CH_4[6] owing to an empty 6s orbital in the triplet ground state of Hf2+, which can accept electron density from the σ(H_3C-H) bond.[7] By contrast, the reactivity of Hf-oxo clusters $[HfO_2]_n^+$ (n = 1, 2) towards CH_4 can be traced back to the presence of an oxyl radical "O·".[8] It is now agreed that the latter plays a crucial role in bringing about thermal hydrogen-atom transfer (HAT) from inert hydrocarbons, including CH_4.[9] The reactivity of the most simple hafnium oxide, diatomic [HfO]·+ with hydrocarbons, however, has never been examined, either experimentally or theoretically. According to our recent observations, [HfO]·+ does not react with CH_4 under thermal conditions; in contrast to the higher oxides $[HfO_2]_n^+$, the required feature of an unpaired electron located at a terminal oxygen atom is missing in [HfO]·+ (see below). However, quite surprisingly, the introduction of a halogen atom X (X = F, Cl, Br) as a ligand to form the closed-shell cluster [XHfO]+ results in the generation of an active species, in that these closed-shell ions [XHfO]+ activate

methane spontaneously. Herein, we describe the [XHfO]+/CH_4 and [HfO]+/CH_4 systems in more detail and discuss the role of the halogen ligand with respect to methane activation under ambient conditions.

When mass-selected and properly thermalized [XHfO]+ (X = F, Cl, Br, I) are exposed to CH_4 (for details, see the Supporting Information), [Hf,C,O,X,H_4]+ ions were generated as the only products (more details are listed in Table 1).

Table 1: Reaction rate constants (k, ×10−13 cm3 molecule−1 s−1), intermolecular kinetic isotope effect (KIE) values, and reaction efficiencies ($\phi = k/k_{ADO}$) relative to the collision rate[10] for the thermal reactions of [XHfO]+ (X = F, Cl, Br, I) with methane.

X	k [×10−13 cm3 molecule−1 s−1]		KIE	ϕ [%]
	CH_4	CD_4		
F	2	5	0.4	0.03
Cl	0.8	1.5	0.5	0.01
Br	0.5	0.8	0.6	< 0.01
I	–	–	–	–

Compared to the other [XHfO]+ ions, the fluoro-containing cluster ion [FHfO]+ exhibits the highest reactivity in generating the adduct complex [Hf,C,O,F,H_4]+ with methane, and [Hf,C,O,I,H_4]+ species were not observed at the detection limit, which correlates with the electron-withdrawing character of the halogen atoms. In addition, a common feature for the [XHfO]+/CH_4 (X = F, Cl, Br) couples is that an inverse kinetic isotope effect is operative. Considering the similarities of the [XHfO]+/CH_4 (X = F, Cl, Br) couples with respect to the reaction pattern and the kinetics, similar mechanistic scenarios probably hold true for all systems. Further experimental/theoretical investigations to obtain mechanistic insight into the reaction were thus confined to the [FHfO]+/CH_4 couple, which we regard as a prototypical example.

When the mass-selected product ion [Hf,C,O,F,H_4]+ is subjected to collisional activation (CA) with argon,[11] the fragmentation pattern depends crucially on the collision energy, E_{coll}. For $E_{coll} < 2$ eV, the only process corresponds to the loss of CH_4 with regeneration [FHfO]+. Upon increasing E_{coll}, the fragment ion [Hf,O,F,H]+ is co-generated with the concomitant elimination of CH_3, and this fragmentation pathway gains importance at higher collision energies as shown in Figure 1 d. At $E_{coll} > 5$ eV, the branching ratio of [Hf,O,F,H]+:[FHfO]+ already amounts to 0.7.[12] Furthermore, collision-induced dissociation of [Hf,C,O,F,D_4]+ generates [Hf,O,F,D]+ with concomitant loss of CD_3 (Figure 1 e).

[*] Dr. S. Zhou, Dr. J. Li, Dr. M. Schlangen, Prof. Dr. H. Schwarz
Institut für Chemie, Technische Universität Berlin
Straße des 17. Juni 135, 10623 Berlin (Germany)
E-mail: helmut.schwarz@tu-berlin.de
Dr. J. Li
Institute of Theoretical Chemistry, Jilin University
Changchun, 130023 (P.R. China)

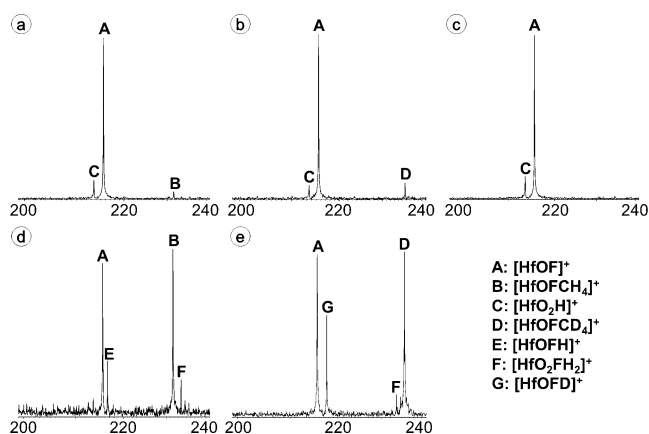Supporting information for this article can be found under:
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Figure 1. Mass spectra for the reactions of [FHfO]+ with a) CH4, b) CD4, and c) argon ($p = 5 \times 10^{-7}$ mbar; reaction delay 3 s). The signals labeled as **C** and **F** are the result of the reaction of the mass-selected ions with background water. CA spectra for d) [FHfOCH4]+ and e) [FHfOCD4]+ with argon at $E_{coll} = 4.1$ eV are also shown.

Figure 2. PESs and selected structural information for the reactions of [HfO]•+ and [FHfO]+ with CH4 as calculated at the CCSD(T)/BSI// B3LYP/BSI level of theory. Zero-point-corrected energies are given in kJ mol^{-1}, and bond lengths in Å; charges are omitted for clarity.

The structural characteristics of the [Hf,C,O,F,H4]+ species were interrogated by high-level electronic structure calculations, which also provide mechanistic insight into the reactions of the [FHfO]+/CH4 and [HfO]+/CH4 couples (Figure 2) and thus help to unravel the role the fluorine atom plays in this process.

The most favorable pathways for the [FHfO]+/CH4 system was located on the singlet potential-energy surface (PES). Since the triplet PES is much higher in energy (see below), the discussion will be confined to the singlet surface. The transformations start from the encounter complex **1a**, in which CH4 is strongly bound to the Hf atom. By passing the metathesis-like transition state **TS1a/2a**, which is located 38 kJ mol^{-1} below the entrance channel, the insertion intermediate **2a** is generated. The latter species corresponds to the global minimum on the PES; its dissociation to liberate a methyl radical through breaking of the Hf–CH3 bond requires the supply of external energy. Furthermore, as shown in the Supporting Information (Figure S1), a rebound step to convert **2a** into the complex [Hf(F)(CH3OH)]+ (**5a**) is not possible, since the related transition structure **TS2a/5a** is energetically too demanding to be accessed. Furthermore, while the formation of HF corresponds to the driving force in the reactions of methane with the fluorine-rich cluster ions CrF$_n^+$ ($n = 3$, 4) or with diatomic NiF+,[13] this process is thermally unavailable for [FHfO]+/CH4 since it is also heavily endothermic (Figure S1). So, what is the fate of the ro-vibrationally hot intermediate **2a**? 1) **2a** may be trapped in a deep potential well provided that radiative stabilization through IR photon emission is efficient, or 2) **2a** could dissociate back into [FHfO]+ and CH4. The observed, rather low reaction efficiency (0.03%) points to an inefficient radiative stabilization of **2a**. This is somewhat in contrast to the behavior of the couple [TaO2]+/CH4, for which the formation of the long-lived insertion intermediate [Ta(O)-(OH)(CH3)]+ under Fourier-transform ion-cyclotron-resonance mass spectrometry (FT-ICR-MS) conditions is significantly more efficient (0.25%).[14] However, when introducing
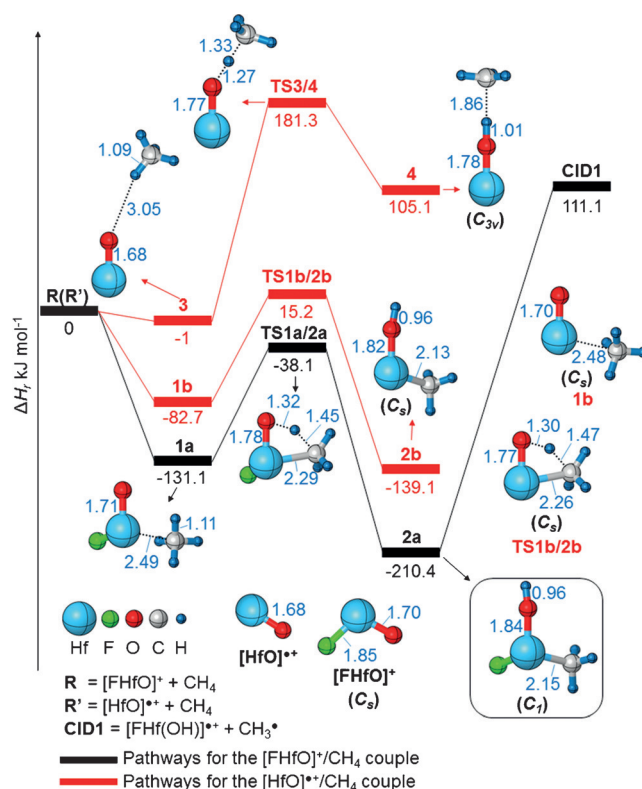
argon through a pulse valve during the reaction delay, considerably more adduct [HfCOFH4]+ is generated as a result of collisional cooling, thus preventing the back reaction to **R**.

While there is so far no spectroscopic support to assign **2a** as the structure of [Hf,C,O,F,H4]+, circumstantial evidence is indeed in favor of **2a**: 1) If only the encounter complex **1a** were generated, upon collisional activation, on both energetic and entropic grounds, [FHfO(CH4)]+ would dissociate exclusively back into [FHfO]+ and CH4 over a wide range of collisional energies; 2) if [Hf,C,O,F,H4]+ corresponded to a mixture of **1a** and **2a**, the branching ratio for generating [FHfO]+ versus [FHf(OH)]+ would not depend heavily on the collision energy; and 3) assuming that **2a** constitutes the major (if not only) product, a reasonable explanation for the experimental findings is at hand. When E_{coll} is low, only the path **2a→TS1a/2a→1a→R** is accessible. Upon increasing the collision energy, the energetically favored but entropically disfavored path back to **R** will face competition with the energetically more demanding but entropically favored process **2a→[FHf(OH)]+ + CH3**. In addition, the observed inverse kinetic isotope effect most likely results from an increased lifetime of the ro-vibrationally excited complex [FHf(OD)(CD3)]+ compared with the unlabeled system. This probably also holds true for the other [XHfO]+/CH4 (X = Cl, Br) couples that exhibit similar kinetic features. An inverse KIE has also been found for the couples [TaO2]+/CH4 and [TaO2]+/CD4.[14]

For the reaction of diatomic [HfO]$^{•+}$ with CH$_4$, two possible pathways were located on the doublet PES. The first corresponds to an insertion (**R′→1b→2b**), and the second describes a hydrogen-atom transfer (**R′→3→4**). However, the transition states for both channels, that is, **TS1b/2b** and **TS3/4**, are higher in energy than the reactant **R′** and are thus inaccessible under thermal conditions, which is in line with the experimental results mentioned above. The unavailability of the HAT pathway is due to the low spin density at the O atom of [HfO]$^{•+}$ (0.01) and unfavorable thermochemistry. The role of the fluoro ligand in [FHfO]$^+$ with respect to insertion of the cluster ion into the C−H bond of CH$_4$ will be described in the following section.

According to our calculations, the BDE[(HO)Hf$^+$−CH$_3$] and BDE[(HO)(F)Hf$^+$−CH$_3$] amount to 278 kJ mol^{-1} and 321 kJ mol^{-1}, respectively, thus pointing to a significantly strengthened Hf−C interaction induced by adding a fluoro ligand to the metal center. As a consequence, both **TS1a/2a** and intermediate **2a** are pulled down in energy relative to the entrance channel. In contrast, the calculated BDE(FHf$^+$−O) (651 kJ mol^{-1}) is considerably lower than BDE(Hf$^+$−O) (726 kJ mol^{-1}). The strengthening of the Hf−C interaction upon the addition of a fluoro ligand has its origin in the different electronic structures of [Hf(OH)]$^+$ and [Hf(F)-(OH)]$^{•+}$. The electron pair at the Hf atom in closed-shell [Hf(OH)]$^+$ thus has to be uncoupled to bind to a CH$_3$$^•$ radical. In contrast, this "promotion energy" is not necessary for the open-shell doublet [Hf(F)(OH)]$^{•+}$. As a consequence, BDE-[(HO)Hf$^+$−CH$_3$] < BDE[(HO)(F)Hf$^+$−CH$_3$]. Furthermore, according to our calculations, the singlet–triplet gap of [FHfO]$^+$ amounts to 263 kJ mol^{-1}, which is much smaller than the doublet–quartet gap of [HfO]$^+$ (387 kJ mol^{-1}). The fluoro ligand thus also affects the strength of the π(Hf−O) bond, the cleavage of which is involved in the insertion process. Related to this, natural bond orbital (NBO) analysis indicates that the charge on the HfO moiety of [FHfO]$^+$ amounts to 1.57 | e |, that is, the electronegative fluoro ligand decreases the electron density of the Hf−O bond and favors the transfer of electron density from the σ(H$_3$C−H) bond to the HfO unity. These effects taken together enable the activation of CH$_4$ by [FHfO]$^+$ under ambient conditions. Moreover, both effects are likely also operative for the [HfCOXH$_4$]$^+$ (X = Cl, Br, I) couples, however, the electron-withdrawing effect decreases in the order F > Cl > Br > I, and weakening of the Hf=O bond is insufficient for the inert [IHfO]$^+$ to activate CH$_4$.

In summary, this combined experimental/computational study of methane activation by the open-shell oxide [HfO]$^{•+}$ versus the closed-shell clusters [XHfO]$^+$ (X = F, Cl, Br, I) reveals a remarkable ligand effect; while [HfO]$^{•+}$ is thermally unreactive towards CH$_4$, [XHfO]$^+$ (X = F, Cl, Br) exhibits unexpected reactivity. This is caused by strengthening of the Hf−C bond and weakening of the π(Hf−O) bond in the halogenated cluster ions, thereby favoring insertion into the C−H bond of CH$_4$. Interestingly, in the structurally related closed-shell systems [MO$_2$]$^+$/CH$_4$ (M = V, Nb, Ta), owing to the operation of strong relativistic effects on the Ta−C bond, it is only the [TaO$_2$]$^+$/CH$_4$ couple that is able to undergo thermal insertion into a C−H bond to form [Ta(O)(OH)-

(CH$_3$)]$^+$.[14] Finally, in closed-shell [HTiO]$^+$, liberation of H$_2$ in the thermal reaction of [HTiO]$^+$ with CH$_4$ to form [Ti-(OCH$_3$)]$^+$ is the result of a metathesis process.[15]

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