A computational study on the intriguing mechanisms of the gas-phase thermal activation of methane by bare [Ni(H)(OH)]⁺

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A detailed computational study on the reaction mechanisms of the thermal activation of methane by the bare complex [Ni(H)(OH)]⁺ has been conducted. The experimentally observed reaction features, i.e., the ligand exchange Ni(H) → Ni(CH₃), the H/D scrambling between the incoming methane and the hydrido ligand of the nickel complex, the spectator-like behavior of the OH ligand, and the relatively moderate reaction efficiency of 6% relative to the collision rate of the ion/molecule reaction, can be explained by considering three competing mechanisms, and a satisfactory agreement between experiment and theory has been found.

Introduction

The activation and functionalization of methane under ambient conditions remain a challenge in contemporary chemistry. 1 Among the numerous gas-phase studies aimed at elucidating mechanistic aspects of the C–H bond activation by using bare or ligated transition-metal ions or by employing small metallic cluster species, the thermal reaction of [Ni(H)(OH)]⁺ (1) with CH₄, eqn (1), 2 has received quite some attention.

\[
\text{[Ni(H)(OH)]⁺} + \text{CH}_4 \rightarrow \text{[Ni(CH₃)(OH)]⁺} + \text{H}_2 \quad (1)
\]

Pertinent findings of this ion/molecule reaction are: (1) the hydroxy group does not participate but rather acts as a spectator ligand and (2) partial H/D exchange of the hydrido ligand, the latter KIE = 1.4, thus suggesting that breaking of the nickel–hydrogen and carbon–hydrogen bonds is involved in the rate-limiting step. The electronic structure of the reagent [Ni(H)(OH)]⁺ also turned out to be of quite some interest. 3,4 For example, the doublet state of [Ni(H)(OH)]⁺ is ca. 1 eV more stable than its quartet elecrtomer and is further found to readily undergo a near barrier-free reductive elimination to afford [Ni(H₂O)]⁺; this Ni⁺–H₂O complex is thermodynamically stable and kinetically inert toward CH₄. 5 The observed gas-phase reactivity of [Ni(H)(OH)]⁺ is due to the fact that the hydroxyl group of this complex behaves actually as a redox non-innocent ligand resulting in an electronic structure which is consistent with a [(H)NiIII–(OH⁻)]⁺ species rather than a formally resonant [(H)NiII–(OH⁻)]⁺ system. As a consequence of the electronic structure mismatch there is no direct, facile way of converting this high-energy quartet elecrtomer to the ground-state doublet by a simple spin flip; rather, an insufficient combination of metal-to-ligand electron transfer followed by a spin inversion is operative 6,7 thus providing a kinetic protection of the quartet state and imparting to it a lifetime long enough to undergo the thermal ion/molecule reaction with CH₄. 2,3

Here, we will present a computational study which addresses the hitherto unknown mechanistic details of the experimentally observed partial H/D exchange between the hydrido ligand of [Ni(H)(OH)]⁺ and CH₄. The computations are confined to the quartet state of the nickel complex based on the grounds outlined above. 2,3

Computational details

All calculations were performed using the hybrid density functional theory functionals B3LYP 5 and M06 6 with triple-ζ plus polarization basis sets TZVP for the nickel atom. 7
Frequency calculations, at the same level of theory, were performed to characterize stationary points and to estimate harmonic zero-point vibrational energy (ZPVE) corrections. The latter have been included in the reported relative energies (given in eV). The TZVP basis set was supplemented with a diffuse s function, two sets of p functions (optimized by Wachters) for the excited states, one set of diffuse pure d angular momentum functions (optimized by Hay), and three sets of uncontracted pure angular momentum f functions, including both tight and diffuse exponents, as recommended by Raghavachari and Trucks. For the oxygen, carbon and hydrogen atoms, the 6-311+G(3df,2p) basis set (denoted as TZVP+G(3df,2p)) reported by Krishnan et al. was used. For selected aspects, we have also carried out CCSD(T) single-point calculations using the B3LYP optimized structures, and in very few cases, quite demanding CCSD geometry optimizations were performed. All calculations have been performed using the GAUSSIAN03 and the NWChem suite of programs. Previous studies showed that the B3LYP and M06 hybrid functionals together with a TZVP+G(3df,2p) basis set are a good choice for a qualitative description of the problem at hand in that the energetic differences between experimental and computational data in general do not exceed ±0.3 eV.

For the location of the minimum energy crossing points (MECPs), which are relevant in two-state reactivity (TSR) scenarios, we treated the present system in a pseudo-one-dimensional way; here, each of the two crossing surfaces are mapped out for several values of a given reaction co-ordinate, which is typically a bond length or a bond angle. The crossing point between the resulting one-dimensional curves is a rough approximation to the lowest energy crossing point between the surfaces. However, it is usually more accurate, and faster, to use a gradient-based method to explicitly locate the exact minimum energy crossing point between the surfaces. Several algorithms have been proposed in the literature. In this work, we have used a script program to locate and characterize the MECPs. This program (a) generates suitable input files for an electronic structure code, (b) calls the code, (c) extracts from the output the energies and gradients on two surfaces, (d) combines them to yield an effective gradient which is directed towards the MECP, and (f) uses it to update the geometry until convergence is achieved.

Results and discussion

In Fig. 1 we present the simplified potential energy surface (PES) for the ligand exchange according to eqn (1). The reaction commences with the exothermic barrier-free formation of the encounter complex 2 which is characterized by a η2-coordination of the incoming methane molecule. For 2 various conformers, e.g. rotation around the Ni–OH bond, exist which are separated by barriers much below the σ-metathesis transition state TS2/3. In this σ-complex assisted reaction the emerging H2 molecule of TS2/3 has a bond length of 1.001 Å. TS2/3 leads directly to the ion/molecule complex [H2Ni(CH3)(OH)]+ (3); here, formation of the H2 leaving group is nearly complete as indicated by the close-to-equilibrium bond length of 0.766 Å. From 3, liberation of H2 proceeds without a barrier to form the ligand-exchange product

\[
\text{[Ni(H)(OH)]}^+ + \text{CH}_4 \rightarrow \text{[Ni(CH}_3)(OH)]^+ + \text{H}_2
\]

4. The overall reaction is exothermic by −0.730 eV (B3LYP) and −0.698 eV (M06); the entropy contribution to the reaction at room temperature is not significant as indicated by ΔG = −0.647 eV (as compared to ΔE = −0.730 eV). As the crucial TS2/3 and the exit channel are located well below the entrance channel and as the reaction is not subject to a spin change its smooth occurrence under thermal conditions is expected.

However, the experimentally observed specific hydrogen exchange between the Ni–H unit of 1 and the incoming methane ligand cannot be explained in terms of Fig. 1. In a rather extensive search of the PES, we managed to locate a transition state TS2/2 (Fig. 2) in which, starting from 2, a degenerate H/H exchange is possible (2 ⇌ TS2/2); however, as this transition state is located 1.56 eV (1.30 eV with M06) above the entrance channel it cannot account for the observed thermal H/D exchange that precedes or accompanies the hydrogen/methy ligand exchange in the couples [Ni(H)(OH)]+/CD4 and [Ni(D)(OH)]+/CH4.

In our computational search for a reaction path which may account for the H/D scrambling we did not only eventually succeed but came across also an entirely unexpected route for the H/CH3 ligand exchange which is energetically even more favorable than the σ-metathesis path described in Fig. 1. In this new reaction, Fig. 3, the encounter complex 2 rearranges via TS2/5 to an almost linear dihydrogen-bridged complex 5. In 5, the bond length of the central H–H unit amounts to 1.027 Å (B3LYP), thus indicating the incipient formation of a...
Relative energies (in eV) of the various transition structures

<table>
<thead>
<tr>
<th></th>
<th>B3LYP</th>
<th>M06</th>
<th>CCSD(T)/B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>S5</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>TS2/5</td>
<td>0.21</td>
<td>0.06</td>
<td>0.18</td>
</tr>
<tr>
<td>TS5/3</td>
<td>0.24</td>
<td>0.14</td>
<td>0.11</td>
</tr>
<tr>
<td>TS5'/5'</td>
<td>0.20</td>
<td>0.08</td>
<td>0.16</td>
</tr>
<tr>
<td>TS5</td>
<td>0.38</td>
<td></td>
<td>0.25</td>
</tr>
</tbody>
</table>

"TS5/5" could not be located using M06 functional.
This coupled spin-inversion, isomerization reaction can be understood considering the electronic situation of $^{6}$[Ni(CH$_3$)(H)(H$_2$O)]$^+$, which has a spin density of 1.01 for the CH$_3$ group and 1.95 for Ni (B3LYP). In the spin-crossing process, one of the unpaired electrons of the nickel atom undergoes a spin flip while the carbon retains its single unpaired electron. Next, the methyl group behaving as a radical attacks intramolecularly the H–Ni bond leading to the formation of the doublet state of [Ni(CH$_3$)(OH)]$^+$. Thus, the presence of this MECP can explain the fact that the OH ligand remains intact along the ligand/hydrogen switch described in eqn (1).

Conclusions

We have identified computationally three reaction pathways that are relevant in the thermal activation of methane by the bare [Ni(H)(OH)]$^+$ complex. Our findings provide an explanation for the hydrogen exchange of the nickel hydrido ligand remains intact along the ligand/hydrogen switch. The bare [Ni(H)(OH)]$^+$ complex. Our findings provide an explanation for the hydrogen exchange of the nickel hydrido ligand with the hydrogen of the incoming methane ligand that precedes the actual ligand switch $^{4}$[Ni(H)(OH)]$^+$/CH$_4$ population from the reactive quartet surface to the thermochemically much more stable doublet surface to produce “inert” $^{4}$[Ni(H$_2$O)]$^+$/CH$_4$.

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References

1 For a recent, exhaustive review, see: H. Schwarz, Angew. Chem., Int. Ed., 2011, 50, 10996, and numerous references therein.
4 For a recent review on remarkable nickel-mediated gas-phase reactions, see: M. Schlangen and H. Schwarz, J. Catal., 2011, 284, 126.