Methane Activation by Tantalum Carbide Cluster Anions Ta$_2$C$_4^-$

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ABSTRACT: Methane activation by transition metals is of fundamental interest and practical importance, as this process is extensively involved in the natural gas conversion to fuels and value-added chemicals. While single-metal centers have been well recognized as active sites for methane activation, the active center composed of two or more metal atoms is rarely addressed and the detailed reaction mechanism remains unclear. Here, by using state-of-the-art time-of-flight mass spectrometry, cryogenic anion photoelectron imaging spectroscopy, and quantum-chemical calculations, the cooperation of the two Ta atoms in a dinuclear carbide cluster Ta$_2$C$_4^-$ for methane activation has been identified. The C–H bond activation takes place predominantly around one Ta atom in the initial stage of the reaction and the second Ta atom accepts the delivered H atom from the C–H bond cleavage. The well-resolved vibrational spectra of the cryogenically cooled anions agree well with theoretical simulations, allowing the clear characterization of the structure of Ta$_2$C$_4^-$ cluster. The reactivity comparison between Ta$_2$C$_4^-$ cluster and the carbon-less analogues (Ta$_2$C$_3^-$ and Ta$_2$C$_5^-$) demonstrated that the cooperative effect of the two metal atoms can be well tuned by the carbon ligands in terms of methane activation and transformation.

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methylene activation, which further suggests that the cooperative
effect of two or more metal atoms may play an important role
in the activation and conversion of methane on metal-based
catalysts like metal carbides and metal nanoparticles.

The time-of-flight (TOF) mass spectra for the interactions of
laser ablation generated, mass-selected, and thermalized Ta$_2$C$_4^-$
cluster anions with CH$_4$, CD$_4$, CH$_2$D$_2$, or $^{13}$CH$_4$ are shown in
Figure 1. As shown in Figure 1a, Ta$_2$C$_4^-$ can react with a trace

![Figure 1. TOF mass spectra for the reactions of mass-selected Ta$_2$C$_4^-$
(a) with CH$_4$ (b), CD$_4$ (c), CH$_2$D$_2$ (d), and $^{13}$CH$_4$ (e) for 2.0 ms. The
reactant gas pressures are shown. The label + X denotes Ta$_2$C$_x$X$^-$ (X =
CH$_2$, CH$_4$, etc.).](image)

amount of water impurity in the gas-handling system to
generate Ta$_2$C$_4$O$^-$ (Ta$_2$C$_4^-$ + H$_2$O → Ta$_2$C$_4$O$^-$ + H$_2$), which
indicates that Ta$_2$C$_4^-$ is very reductive. Upon the interaction of
Ta$_2$C$_4^-$ with 0.23 Pa CH$_4$ in a linear ion trap (LIT) reactor for
~2.0 ms (Figure 1b), a strong product peak assigned as Ta$_2$C$_4$H$_2^-$
was observed, suggesting the following dehydrogenation channel

\[
\text{Ta}_2\text{C}_4^- + \text{CH}_4 \rightarrow \text{Ta}_2\text{C}_4\text{H}_2^- + \text{H}_2
\]

(1)

The isotopic labeling experiments with CD$_4$ (Figure 1c),
CH$_2$D$_2$ (Figure 1d), and $^{13}$CH$_4$ (Figure 1e) confirmed the
above reaction. In addition to reaction 1, minor molecular
association channels generating Ta$_2$C$_4$H$_2^-$ (8%), Ta$_2$C$_3$D$_2^-$
(16%), Ta$_2$C$_2$H$_2$D$_2^-$ (13%), and Ta$_2$C$_4$($^{13}$)CH$_4^-$ (4%) were
also observed.

The experimentally generated atomic clusters can have
different structural isomers with very different reactivity,$^{27}$
which can be characterized with the reactant-gas-pressure-
dependent experiments (Figure S1). It turns out that (83 ±
1)% of the experimentally generated Ta$_2$C$_4^-$ ions were reactive
toward CH$_4$ while the remaining component (17 ± 1)% was inert.
The pseudo-first-order rate coefficient $k_1$ of the reactive
component of Ta$_2$C$_4^-$ was determined to be $1.5 \pm 0.5 \times 10^{-11}$
cm$^3$ molecule$^{-1}$ s$^{-1}$. The theoretical collision rate
($k_{coll}$) between Ta$_2$C$_4^-$ and CH$_4$ is calculated to be $9.3 \times 10^{-10}$
cm$^3$ molecule$^{-1}$ s$^{-1}$, so the reaction efficiency ($\Phi = k_1/k_{coll}$) is

~1.6%. The kinetic isotopic effect (KIE)$^{32}$ defined as $k_1$
(Ta$_2$C$_4^-$ + CH$_4$)/$k_1$ (Ta$_2$C$_4^-$ + CD$_4$) amounts to 5.8 ± 1.7.

Density functional theory (DFT) calculations were carried
out to investigate the structures of Ta$_2$C$_4^-$ cluster and the
reaction mechanism with methane. With the 6-311+G (d) basis
set$^{43}$ for C as well as H atoms and the effective core potential
(ECP)$^{44}$ combined with the polarized triple-$\zeta$ valence (Def2-
TZVP) basis set$^{45}$ for Ta atom, the bond dissociation energies
($D_b$) of Ta$^+$$^-$CH$_4$, Ta$^+$$^-$H, C$^-$C, C$^-$H, CH$_4$$^-$H, H$^-$H, Ta$^-$
Ta, and Ta$^-$C were computed by various functionals and
compared with available experimental data (Table S1). The
TPSS functional$^{18}$ is found to be the overall best, and the
computed $D_b$ values agree with the experimental results with an
average deviation of ±0.32 eV, and anything containing Ta has
an average deviation of ±0.21 eV. The assessment of the
performance of DFT against the thermochemistry on 135 data
and barrier of 38 chemical reactions$^{47}$ demonstrated that the
uncertainties of TPSS predicted thermochemistry and kinetics
(bariers) are 0.06 and 0.22 eV, respectively. To determine
reliable relative energies of low-lying isomeric structures of
Ta$_2$C$_4^-$ cluster, the single-point energy calculations at the high-
level quantum chemistry method of coupled-cluster method
with single, double, and perturbative triple excitations$^{48}$
[CCSD(T)] were performed at the TPSS-optimized geo-
metries. Two low-lying isomers (within 0.1 eV) with doublet
electronic states were determined (Figure 2 and Figure S2). An
open-book structure with a Ta−Ta distance of 246 pm and two
C$_2$ ligands symmetrically bound to their respective Ta atoms

![Figure 2. (a) Raw photoelectron image performed at 11 K and 636
nm. The double-headed arrow indicates the laser polarization. (b)
DFT calculated structures of isomers 1 and 2 with doublet electronic
states. The dihedral (open-book) angle in isomer 1 is 119.6°. The
bond lengths are in pm and the relative energies at the TPSS
[CCSD(T)] levels are in eV. (c) The photoelectron spectrum
transformed from (a) and Franck–Condon simulated spectrum of
the electronic transition $^1$A $\leftrightarrow$ $^3$A for isomer 1 shown as green and purple
traces, respectively. The simulated spectrum is blue-shifted by 0.175
eV to align with the experimental vibrational origin (see details in
Figure S4).](image)
Figure 3. DFT-calculated potential-energy profile for reaction of Ta₂C₄⁻ (isomer 1) with CH₄ in doublet spin state. The relative energies (ΔHₑ in eV) of the reaction intermediates, transition states, and products with respect to the separated reactants are given. Bond lengths are given in pm. The structures of the transition states 4/5–10/11 are shown in Figure S5.

(1, Figure 2b) is slightly more stable than the asymmetric quasi-planar isomer (2, Figure 2b). This result well supports the experimental suggestion that the generated Ta₂C₄⁻ clusters do not have a uniform structure populated in the LIT reactor.

Cryogenic anion photoelectron imaging spectroscopy was employed to study the vibrational and geometric structures specific to the Ta₂C₄⁻ cluster at 11 K (Figure 2c). A well-resolved vibrational progression with a peak spacing of 222 ± 4 cm⁻¹ has been observed (green spectrum). This spectrum is in agreement with the Franck-Condon simulated profile of the ¹A ← ¹A transition for isomer 1 (a peak spacing of 224 ± 1 cm⁻¹, purple spectrum). When the typical peak spacing is compared with the calculated frequencies of the neutral Ta₂C₄ (Table S2), the best agreement comes with a 225 cm⁻¹ for an in-plane vibration of the two C₂ ligands (Figure S3). The resolved vibrational transitions are then assigned to the 11₁₁₁₁₁₁₁₁₁₁₁ progression. The adiabatic detachment energy (ADE) of isomer 1 is experimentally given to be 1.76 ± 0.01 eV, which is the onset of the one-photon detachment from Ta₂C₄⁻.

Isomer 2 is calculated to have a congested spectrum with ADE of 2.02 eV. In the photoelectron spectrum recorded at a wavelength of 420 nm, due to the weak transition of ¹A ← ²A for isomer 2 and low abundance of this species, there is no discernible vibrational band to feature this structure at the high electron binding energy region (see more details in Figure S4). Considering the high abundance (83%) of the active Ta₂C₄⁻ in the reactivity experiments, it is concluded that the lowest-lying structure of Ta₂C₄⁻ cluster corresponds to isomer 1.

The DFT-calculated reaction mechanism for the reaction of Ta₂C₄⁻ (isomer 1) with methane is shown in Figure 3 along the doublet potential energy surface. Either of the equivalent Ta atoms (0.36 e, natural charge) in Ta₂C₄⁻ can trap methane to form the encounter complex 3. In this process, one C–H bond of methane is cleaved around two Ta atoms via a transition state (3/4), leading to barrier-free formation of 4. The resulting intermediate 4 with a smaller Ta–Ta Wiberg bond order of 1.6 has a longer Ta–Ta bond length of 257 pm when compared with the values for the methane adduct 3 (2.1 and 245 pm of Ta–Ta bond order and bond length, respectively).

The subsequent step requires activation of a second C–H bond of CH₄ to generate a metal carbene complex 5 (4 → 5). After C–C bond coupling (5 → 6), the consecutive cleavages of two other C–H bonds (6 → 7 and 8 → 9) lead to the formation of intermediate 9 with four H atoms coordinated to two metal sites from which a H₂ unit can be formed by combining two H atoms (H₁ and H₂, 9 → 10). The resulting intermediate 10 can easily evaporate the formed H₂ moiety to produce the experimentally observed Ta₂C₄H₂⁻ product (Figure 1, see the detailed discussion about the relative energies of 10, 10/11, and 11+H₂ in Figure S5). All of the reaction intermediates and transition states shown in Figure 3 are lower in energy than the separated reactants, indicating that methane dehydrogenation by isomer 1 is thermodynamically and kinetically favorable if the first C–H bond is cleaved around two metal atoms.

Molecular orbital (MO) analysis for the interaction between Ta₂C₄⁻ (isomer 1) and CH₄ has been performed (Figure S6) to obtain further insight into the detailed reaction mechanism of methane activation. The symmetry matching between MOs of CH₄ and a single-Ta atom in Ta₂C₄⁻ demonstrates that the C–H bond activation of methane primarily occurs at a single-metal center in the initial stage of the reaction, which is supported by the geometrical characteristics of transition state 3/4 that the C–H bond being broken is not located over the Ta–Ta bond, rather it is centered over a single Ta atom (Figure 3). Despite the fact that the single-Ta atom plays a crucial role in the initial stage of methane activation, the importance of the second Ta atom in cleavage of the C–H bond should also attract attention because the second Ta atom allows the H atom formed to...
migrate away from the single-Ta center driven by the thermodynamics. The important role of the second Ta atom can be further confirmed by the reaction kinetics for C–H bond cleavage occurring at a single-metal center. On the basis of orbital analysis, all valence electrons of the Ta atom have been used to bond with C atoms and the other Ta atom. As a result, no lone electron pair locates at any of the Ta atoms, and the oxidative addition\(^{51,52}\) of one C–H bond to a single-Ta center is subject to a positive barrier of 0.62 eV (3/12, Figure 3), indicating that this pathway can be excluded under thermal collision conditions.\(^{53}\) It is noteworthy that thermal C–H activation by the Ta–C centers is also kinetically unfavorable (Figure S7). Thus methane activation facilitated by the cooperation of the two Ta atoms is identified for the reaction with Ta\(_2\)C\(_4\)-cluster (isomer 1). The reaction of isomer 2 with methane is subject to positive barriers for C–H bond cleavage around either one or two Ta atoms (≥0.21 eV, Figure S8), implying that isomer 2 could be the unreactive component of Ta\(_2\)C\(_3\)-cluster in the experiments.

To explore the excellent ability of the cooperative two metal atoms in the reactive Ta\(_2\)C\(_3^-\)isomer to promote methane activation, the reactions of one- and two-carbon-less clusters, Ta\(_2\)C\(_2\) and Ta\(_2\)C\(_2^-\), with methane have also been studied. No reactivity (\(k_1 < 10^{-14}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), the detection limit) was observed in the experiments, and the DFT calculations also predicted overall positive barriers for C–H bond activation by the cooperation of the two Ta atoms in the two clusters (≥0.27 eV, Figures S9 and S10). The electronic nature of the two metal atoms has been analyzed at DFT level by means of topological analysis of the electron localization functions (ELFs).\(^{54}\) ELF shows a significant decrease in electron density among the two Ta atoms in Ta\(_2\)C\(_2^-\) after C–H bond cleavage (Figures 4a, b), implying that both of the two Ta atoms participate in the overall C–H bond cleavage of methane (3 \(\rightarrow\) 3/4 \(\rightarrow\) 4, Figure 3). The donation of two electrons from the metal d orbitals to the C–H antibonding orbital is the driving force for the C–H bond cleavage of methane.\(^{55,56}\) As a result, the two electrons in the reactive Ta\(_2\)C\(_4^-\)are stored in the two metal atoms, and the process of C–H bond cleavage is accompanied by a formal one-electron oxidation\(^{55,57}\) of each Ta atom with a corresponding reduction in the Ta–Ta bond order from 2.1 to 1.6. The comparison of the ELF distributions in Figure 4a,c,e shows that the electron density stored in the two Ta atoms of the reactive Ta\(_2\)C\(_4^-\)isomer is significantly greater than that in both the unreactive Ta\(_2\)C\(_3^-\)isomer and carbon-less analogues. The trend of the decrease in the electron density stored in the two Ta atoms in Ta\(_2\)C\(_4^-\), Ta\(_2\)C\(_3^-\), and Ta\(_2\)C\(_2^-\)clusters correlates well with an increase in activation barriers when the clusters are reacted with methane (−0.10, 0.27, and 0.65 eV for Ta\(_2\)C\(_4^-\), Ta\(_2\)C\(_3^-\), and Ta\(_2\)C\(_2^-\), respectively). These results clearly indicate the reactivity difference of the cooperative two metal atoms surrounded by different ligands.\(^{58}\)

The symmetrical C\(_2\) ligands in Ta\(_2\)C\(_4^-\)cluster afford an electron-rich dinuclear metal center over which the C–H bond of methane is cleaved in a homolytic manner. However, when one or both of the two C\(_2\) ligands is replaced with the C\(_1\) ligands to form Ta\(_2\)C\(_3\) or Ta\(_2\)C\(_2\), the cooperative effect of the two Ta atoms decreases quickly toward methane. Similarly, the two Ta centers coordinated with one C\(_1\) and one C\(_2\) ligand in the unreactive Ta\(_2\)C\(_4^-\) (isomer 2) are also identified to be inert. These results suggest that the presence of symmetrical C\(_2\) ligands (bond order of ~2) with \(\pi\)-donating ability\(^{59}\) can facilitate the cooperative effect of the two Ta atoms mediated in C–H bond activation.

In conclusion, complementary mass spectrometry, photoelectron imaging spectroscopy, and first-principles calculations allowed us to identify the mechanism of methane activation by the cooperation of the two Ta atoms in a tantalum carbide cluster Ta\(_2\)C\(_4\). Symmetrical C\(_2\) ligands play an important role in enhancing the reactivity of the dinuclear metal species. This study has provided important insight regarding the activation and conversion of methane on metal carbides and metal nanoparticles.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.6b02568.

Details regarding experimental and theoretical methods, TOF mass spectra, experimental reaction kinetics, photoelectron spectroscopy, computational results, and data analysis. (PDF)

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