

Methane Dehydrogenation by Ti⁺: A Cluster-Assisted Mechanism for σ -Bond Activation

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In gas phase reactions of first-row transition metal ions with simple alkanes, spontaneous C–H and C–C bond cleavage products are observed.^{1–3} Reactivity is found to increase as the size of the alkane increases.^{3b} Under single-collision conditions, all M⁺ + CH₄ reaction channels have been experimentally determined to be endoergic,⁴ a result consistent with theory.⁵ Of the second-row transition metal ions, only Zr⁺ has been reported to dehydrogenate methane spontaneously.⁶ For many third-row transition metal ions, however, multiple dehydrogenation reactions lead to the oligomerization of methane.⁷

The study of a new class of reactions was suggested when we first observed H₂ activation by Sc⁺ via a cluster-mediated σ -bond activation mechanism.⁸ Equilibrium studies of Sc⁺ in a bath of H₂ indicated that both the adduct, Sc⁺H₂, and the inserted species, HSc⁺H, were present. H₂ activation occurred only after the addition of the third H₂ ligand. At this point we questioned whether this was a general process and if we could apply it to methane activation. Experimentally, the activation of methane by ground state Ti⁺ to form the inserted species, HTi⁺CH₃, is estimated⁹ to be exothermic by 12 kcal/mol,^{10,11} but dehydrogenation at thermal energies is endothermic by 18.9 kcal/mol.¹⁰

In this communication, we suggest a mechanism for cluster-mediated σ -bond activation by Ti⁺ as the first step to the oligomerization of methane by a first-row transition metal ion. We also report binding energies, measured in equilibrium experiments, of all pertinent species involved.

Details of the experimental apparatus¹² and the ion chromatography¹³ experiment have been published. In the experiments reported here, titanium ions were formed by surface ionization of TiCl₄. The mass-selected ions were injected into a reaction cell containing $\sim 7 \times 10^{16}$ molecules/cm³ of methane (2.2 Torr at 300 K). The ions were quickly translationally and electronically¹⁴ thermalized via collisions with CH₄, and were moved through the cell with a small electric field ($E/N < 3 \times 10^{-17}$

Table 1. Experimental Enthalpies from Equilibria

Reaction	$-\Delta H_0^\circ$ ^a (kcal/mol)
Ti ⁺ + CH ₄ \rightleftharpoons Ti(CH ₄) ⁺	16.8 \pm 0.8
Ti(CH ₄) ⁺ + CH ₄ \rightleftharpoons Ti(CH ₄) ₂ ⁺	17.4 \pm 0.6
Ti(CH ₄) ₂ ⁺ + CH ₄ \rightleftharpoons Ti(CH ₄) ₃ ⁺	6.6 \pm 1.5
Ti(CH ₄) ₂ ⁺ + CH ₄ \rightleftharpoons (CH ₄) ₂ Ti ⁺ (H)(CH ₃)	~ 16 ^b
(CH ₄) ₂ Ti ⁺ (H)(CH ₃) + CH ₄ \rightleftharpoons (CH ₄) ₃ Ti ⁺ (H)(CH ₃)	9.8 \pm 0.8
(CH ₄) ₃ Ti ⁺ (H)(CH ₃) + CH ₄ \rightleftharpoons (CH ₄) ₄ Ti ⁺ (H)(CH ₃)	5.1 \pm 0.7
Ti ⁺ + CH ₂ + CH ₄ \rightleftharpoons (CH ₄)Ti ⁺ = CH ₂	> 24 ^c
(CH ₄)Ti ⁺ = CH ₂ + CH ₄ \rightleftharpoons (CH ₄) ₂ Ti ⁺ = CH ₂	19.2 \pm 1.0
(CH ₄) ₂ Ti ⁺ = CH ₂ + CH ₄ \rightleftharpoons (CH ₄) ₃ Ti ⁺ = CH ₂	7.2 \pm 0.5

a The uncertainties reflect the uncertainties in ΔH_0° in addition to the uncertainties due to the statistical mechanical modeling.

b This value is approximate because equilibrium was obtained at only two temperatures.

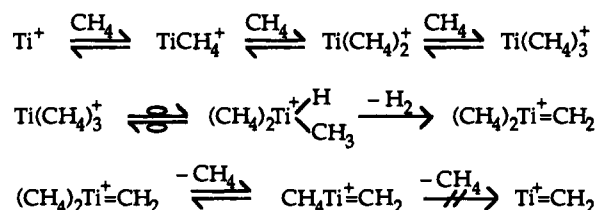
c This equilibrium could not be observed, putting a lower limit on ΔH_0° (see text).

V·cm²). Ions exiting the cell were quadrupole mass analyzed and counted.

In the equilibrium experiment,¹⁵ product/parent ion ratios were measured as a function of reaction time (i.e., $(E/N)^{-1}$). As the drift time was increased, the product/parent ion ratios became constant, indicating that equilibrium had been reached. The ratios were converted to equilibrium constants and standard free energies.¹⁵ A plot of ΔG° versus T yielded straight lines for all systems with the intercept equal to ΔH°_T and a slope equal to ΔS°_T . Standard statistical thermodynamic methods were used to obtain ΔH°_0 from ΔH°_T and ΔS°_T . The data for the present systems will be published elsewhere.¹⁶

Although first-row transition metal ions cannot dehydrogenate CH₄ at thermal energies for thermochemical reasons, when Ti⁺ is injected into a high pressure of CH₄ a strong signal corresponding to (CH₄)₂Ti⁺=CH₂ is observed. Furthermore, the formation rate for (CH₄)₂Ti⁺(H)(CH₃) is slow and exhibits a positive temperature dependence (discussed later). The mechanism which we consider most likely responsible for these interesting observations is given in Scheme 1.

Scheme 1



All the CH₄ loss/addition steps shown come to equilibrium quickly ($\ll 500$ μ s). Measured binding energies of methane to Ti(CH₄)_n⁺, $n = 0-2$, (CH₄)_nTi(H)(CH₃)⁺, $n = 2-3$, and (CH₄)_n-Ti=CH₂⁺, $n = 1-2$, are summarized in Table 1. The first methane ligand is bound to ground state Ti⁺(⁴F,4s3d²) by 16.8 \pm 0.8 kcal/mol. It is bound strongly despite the presence of the repulsive 4s electron, due to a crossing from the Ti⁺(4s3d²)-CH₄ surface (evolving from the Ti⁺(⁴F,4s3d²) ground state) to the Ti⁺(3d³)CH₄ surface (evolving from the Ti⁺(⁴F,3d³) first excited state) as shown in Figure 1. Although σ -bond activation is estimated to be exothermic by about 12 kcal/mol,⁹ statistical thermodynamics predicts the inserted species, HTi⁺CH₃, to comprise less than 0.07% of the first cluster (at 470 K) due to the presence of the more stable Ti⁺-CH₄ adduct. In addition, this insertion requires a crossing from the quartet to doublet surface which may not be facile. As shown in Figure 1, a

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(14) Surface ionization of TiCl₄ produces 36% Ti⁺(⁴F,3d³), the first excited state. Ion chromatography experiments¹³ indicate that this state is effectively quenched to ground state Ti⁺(⁴F,4s3d²) in collisions with CH₄.

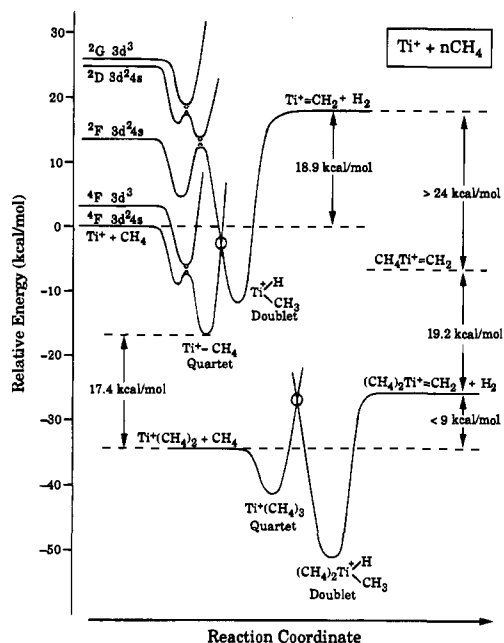
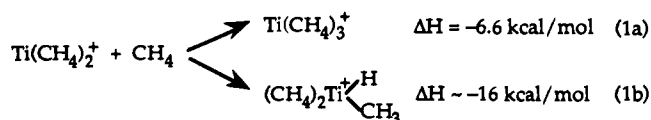


Figure 1. Reaction coordinate diagrams for $\text{Ti}^+ + \text{CH}_4$ (top part) and $\text{Ti}(\text{CH}_4)_2^+ + \text{CH}_4$ (bottom part). The state designations are for the Ti^+ atom. Spin-allowed avoided crossings are shown with crossed dashed lines and spin-orbit coupled crossings between different spin states by the open circles. The energies shown are from the literature or from the data given here (Table 1). The exact energy of the spin-orbit coupled crossings are not known, and the crossing points shown are only estimates.

component of the ^2G , 3d^3 state of Ti^+ correlates directly to the inserted HTi^+CH_3 product ion, but one avoided crossing and one spin-orbit coupled crossing are required for ground state Ti^+ to activate methane.¹⁰

The second methane is also strongly bound to Ti^+ , by 17.4 ± 0.6 kcal/mol, whereas the third methane is bound by only 6.6 ± 1.2 kcal/mol. Theoretical calculations in progress¹⁶ will provide insight into the nature of the bonding and help interpret the relative binding energies observed. With the addition of the third methane ligand, our data indicate that σ -bond activation becomes competitive with adduct formation and $\text{Ti}(\text{CH}_4)_3^+$, $(\text{CH}_4)_2\text{Ti}(\text{H})(\text{CH}_3)^+$, and $(\text{CH}_4)_2\text{Ti}^+=\text{CH}_2$ are all observed. The driving force for this σ -bond activation is the increased methane binding in the inserted products relative to the $\text{Ti}(\text{CH}_4)_n^+$ adducts. We refer to this mechanism as cluster-assisted σ -bond activation.

The $(\text{CH}_4)_2\text{Ti}(\text{H})(\text{CH}_3)^+$ and $\text{Ti}(\text{CH}_4)_3^+$ clusters are clearly distinguishable in our experiment even though they have the same mass.¹⁷ At low temperatures (255–340 K) addition of CH_4 to $\text{Ti}(\text{CH}_4)_2^+$ comes quickly into equilibrium ($t \ll 500 \mu\text{s}$), indicating that simple adduct formation is occurring (reaction 1a). At high temperatures (500–580 K) addition of CH_4 occurs very slowly and equilibrium is obtained only at very long times ($t > 3000 \mu\text{s}$), indicating that σ -bond activation is occurring (reaction 1b).



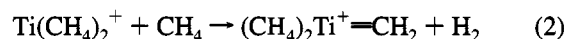
The rate of the slow approach to equilibrium has a positive energy dependence, and modeling yields a barrier to insertion of 8 kcal/mol. The fact that two distinct linear regions are observed in the ΔG° vs T plot¹⁶ allows bond dissociation

(16) van Koppen, P. A. M.; Perry, J. K.; Maitre, P.; Kemper, P. R.; Bushnell, J. E.; Bowers, M. T. (to be published).

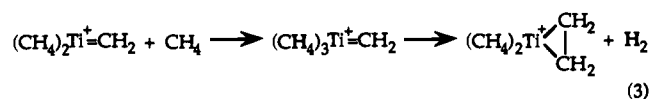
(17) Alternate structures with the same mass, such as $(\text{CH}_4)_2\text{TiCH}_2(\text{H}_2)^+$ or $(\text{CH}_4)\text{Ti}(\text{CH}_3)_2(\text{H}_2)^+$, can be excluded. H_2 loss would be facile and the reverse reaction would be negligible because the partial pressure of H_2 is 0.

energies to be obtained for both reactions 1a and 1b. This analysis indicates that σ -bond activation is favored over adduct formation by ~ 10 kcal/mol as shown in Figure 1.

Equilibrium measurements indicate a binding energy of 19.2 ± 0.8 kcal/mol for CH_4 to $\text{CH}_4\text{Ti}=\text{CH}_2^+$. Because $\text{Ti}=\text{CH}_2^+$ is not observed in these experiments even at the highest temperatures, the $\text{TiCH}_2^+-\text{CH}_4$ bond energy must be ≥ 24 kcal/mol. This binding energy seems reasonable because the net charge on Ti will be more positive for $\text{Ti}=\text{CH}_2^+$ than Ti^+ and should thus bind methane more strongly than does Ti^+ . A summary of the known thermochemistry is indicated on the reaction coordinate diagram, Figure 1. These data imply that reaction 2 is endothermic by less than 9 kcal/mol. Because formation of $(\text{CH}_4)_2\text{Ti}(\text{H})(\text{CH}_3)^+$ is observed and it has an 8 kcal/mol barrier, it is reasonable that reaction 2 is also observed in our experiment.



Reaction of $(\text{CH}_4)_2\text{Ti}=\text{CH}_2^+$ with methane initiates the oligomerization process, reaction 3, converting methane to ethylene.



Our observation of reaction 3 is in line with the reactivity we observe for the second-row transition metal Zr^+ which has the same valence electronic configuration as Ti^+ .¹⁶ In the Zr^+ case, dehydrogenation is observed for the first methane ligand, to form $\text{Zr}=\text{CH}_2^+$, which reacts with methane to form the adducts, $\text{CH}_4\text{Zr}=\text{CH}_2^+$ and $(\text{CH}_4)_2\text{Zr}=\text{CH}_2^+$. As with $(\text{CH}_4)_2\text{Ti}=\text{CH}_2^+$, reaction of $(\text{CH}_4)_2\text{Zr}=\text{CH}_2^+$ with methane leads to ethylene formation, $(\text{CH}_4)_2\text{ZrC}_2\text{H}_4^+$, which further activates methane to form $(\text{CH}_4)_2\text{ZrC}_3\text{H}_6^+$.¹⁸ Third-row metals with more than three valence electrons have been shown to convert methane to ethylene with the addition of only two methane ligands, and the observed oligomerization is more extensive.⁷ Ta^+ and W^+ , for example, lead to TaC_4H_8^+ and $\text{WC}_8\text{H}_{16}^+$.⁷

In summary, even though dehydrogenation is endothermic for first-row transition metal ions reacting with methane in the gas phase, $\text{Ti}(\text{CH}_4)_2^+$ does activate methane and dehydrogenation is observed. Further reaction with methane starts the oligomerization process converting methane to ethylene. The results presented here, along with the recently published $\text{Sc}^+ + n\text{H}_2$ results,⁸ suggest that cluster-assisted σ -bond activation by transition metal centers is a powerful and general mechanism that can efficiently activate even the most difficult bonds, those found in H_2 and CH_4 .

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Supplementary Material Available: Figure 1, plots of ΔG° vs temperature for reactions in Table 1 (1 page). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(18) Thermodynamics clearly indicates that $\text{MC}_3\text{H}_{10}^+$ corresponds to $(\text{CH}_4)_2\text{M}(\text{CH}_2)^+$ rather than $(\text{CH}_4)\text{M}(\text{CH}_3)_2^+$ for $\text{M} = \text{Ti}^+$ and Zr^+ because only reaction of $(\text{CH}_4)_2\text{M}(\text{CH}_2)^+$ with methane results in exothermic dehydrogenation and formation of an ethylene ligand bound to the metal center, $(\text{CH}_4)_2\text{M}(\text{C}_2\text{H}_4)^+$.