Theoretical quest for the titanium-substituted hydrocarbons†

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Using theoretical calculations we predict a novel family of compounds, which might serve for hydrogen storage, and for chemical vapour deposition of titanium carbide coatings.

The electronegativity perturbation (ENP)\(^1\) has significant consequences for the thermodynamic and kinetic stability of substituted hydrocarbons. The increase of thermodynamic stability of a molecule upon ENP may be giant, as for borazine, \(\text{B}_3\text{N}_3\text{H}_6(l)\) (\(\Delta G_{f}^{0} = -392.7\ \text{kJ mol}^{-1}\)) as compared to \(\text{C}_6\text{H}_6(l)\) (\(\Delta G_{f}^{0} = +124.5\ \text{kJ mol}^{-1}\)). But another effect – an inter- or intramolecular proton-hydride interaction\(^3\) – simultaneously decreases the thermal stability of the substituted compounds. In consequence the “perturbed” compounds often solidify easily (due to electrostatic stabilization of the crystal lattice, nearly absent for hydrocarbons), and they decompose with \(\text{H}_2\) evolution at much lower temperatures than their carbon analogues. Take e.g. cyclohexane, which is thermally stable up to several hundreds °C, while cycloazagallane, \(\text{Ga}_3\text{N}_3\text{H}_{12}\), decomposes at +150 °C to yield pure GaN and \(\text{H}_2\).\(^4\)

† Electronic supplementary information (ESI) available: optimized geometries and molecular parameters, enthalpies of hydrocarbon elimination reactions and auxiliary numerical data. See http://www.rsc.org/suppdata/cc/b4/b418316a/

This paper presents the results of the DFT/B3LYP theoretical calculations;\(^5\) for hypothetical hydrocarbons in which half of the carbon atoms have been substituted by Ti in an ENP.\(^6\) This novel family of molecules will be subsequently referred to as “Titanium-Substituted Hydrocarbons” (TSHs).\(^7\) The optimized geometries of TSHs, possible transformations among them, and the calculated enthalpies of clustering and \(\text{H}_2\) elimination reactions,\(^8\) are shown in Fig. 1.\(\uparrow\)

\(\text{TiCH}_6\), the most H-rich TSH (9.6 wt% H) and an analogue of ethane, can formally be viewed as a donor–acceptor adduct of the \(\text{CH}_3\) to elusive \(\text{Ti}^{\text{IV}}(\text{H}_2)_3^+\), or alternatively as a product of the oxidative addition of methane to \(\text{Ti}^{\text{II}}\text{H}_2\). As far as we know it has not yet been isolated in bulk, or observed in noble gas matrixes, in contrast to \(\text{TiH}_4\), another hydride of tetravalent Ti.\(^9\) The calculated enthalpies of elimination of \(\text{H}_2\), \(\text{CH}_4\) and \(\text{K}_2\text{H}_4\) from \(\text{TiCH}_6\) are +0.77 eV, +0.92 eV and +1.24 eV per molecule, thus suggesting thermodynamic stability of gaseous \(\text{TiCH}_6\) at ambient temperatures (even if an entropy term is considered).\(^10\)

\(\text{Ti}_2\text{C}_2\text{H}_4\) takes a rather non-classical geometry, with all H atoms attached to C and not to Ti (the cyclobutadiene-like isomer lays +0.16 eV above in energy). The ease of H transfer from Ti to C, seen also for \(\text{TiCH}_4\) and \(\text{TiCH}_2\), is typical of small TSHs. This feature has been previously observed also for other compounds with poor π overlap, such as \(\text{H}_2\text{C} = \text{TiHF}^{11a}\) and unsaturated

Fig. 1 Selected chemical transformations of TSHs (oligomerization or clustering and \(\text{H}_2\) elimination) along with their calculated enthalpy/eV per TiC unit. Ti – black spheres, C – blue spheres, H – white spheres.
The HOMO and LUMO of Ti₄C₄H₈ are shown in Fig. 2. The HOMO is composed mainly of a σ bonding combination of d(z²) orbitals of Ti and 1s orbitals of H⁻ ions bound to Ti. The LUMO is formed from a σ* antibonding combination of d(z²) orbitals of Ti and 1s orbitals of H⁻ ions bound to Ti, with little contribution from 1s orbitals of H bound to C. The LUMO is essentially weakly bonding between Ti atoms. Donor function of a molecule is mainly hydride-centered, while acceptor function is based predominantly on Ti. Such a frontier orbital picture is representative of the majority of TSHs studied here. The Ti–H bonds are weak, long and quite ionic as compared to the Ti–C and C–H ones, and they form the uppermost σ manifold of a molecule.

For Ti₄C₄H₈ we predict the relaxed ionization potential, Iₛ, of 8.47 eV and relaxed electron affinity, Eₐ, of 2.10 eV. From these values one can calculate Mulliken electronegativity of 5.29 eV, and Pearson hardness of 3.19 eV. These parameters are comparable to those for an atom of ‘noble’ Au (9.22 eV, 2.3 eV, 5.76 eV and 3.46 eV, respectively), or of NO₂ radical (9.60 eV, 2.27 eV, 5.94 eV, 3.67 eV). Comparison indicates that (TiHCH)₄ could form moderately stable anions, by analogy to known Au⁻ and NO2⁻; these anions could occur e.g. for alkali metal salts, such as Csₙ(TiHCH)₄. (TiHCH)₄ is also expected to undergo nonoxidative addition of Lewis bases at the Ti site, e.g. with formation of (TiHCH)₄(H⁻)ₙ or (TiHCH)₄(CS)₁. The quite large electronegativity of TSHs and the interconnected substantial electrophilicity of the Ti site also explain the tendency of TSHs for dimerization through formation of Ti···H···Ti bridges. Interestingly, sharing hydride anions between Ti’s stabilizes dimer more than intermolecular CH···–I HTI interactions. The former process, and progressive oligomerization via formation of new TiC bonds, are thought to predominate solidification paths of TSHs.

TSHs are hydrogen-rich molecules. The hydrogen content decreases from 9.6 wt% for TiCH₄, via 6.4 wt% for (TiCH₄)₂, down to 3.2 wt% H for (TiCH₃)₂. The overall H content for (TiCH₄)ₙ homologues is slightly smaller than that for NaAlHₓ (7.4%), and is very close to the US DOE target of 6.5 wt%.26

There are two straightforward trends of H₂ evolution from TSHs. (i) At a constant size of the TiC core, H₂ release is least prohibited for the most H-rich TSH (analogue of alkanes), and more difficult for analogues of alkenes and alkynes.13 (ii) At a constant H content, H₂ desorption is easier from oligomeric TSHs than from the monomers. It can therefore be anticipated that enthalpy of dihydrogen release of +0.40 eV (equal to entropy factor S(H₂)T at 298 K) could be achieved for TiC clusters (‘metcars’14) of moderate size. Such species are supposed to bind and release H₂ at ambient temperatures.15 The surface of other prefabricated TiC nanostructures could also be decorated with H atoms via heterolytic splitting of H₂, as seen for related collapsed BN nanotubes.16 This process could be reversible for moderate quantities of H₂ and in a narrow temperature range if polymerization is avoided of (TiC)ₙ clusters after H₂ gas release.

Prompted by the possibility of feasible hydrogen absorption by TiC nanostructures, we have analyzed the reaction path for absorption of one H₂ molecule by Ti₄C₄H₈. This species exemplifies the smallest partially hydrogenated nanocluster with the 3D (TiC)₄ core. In Fig. 3 we show a diagram of the changes of electronic energy and HH distance along the reaction path.

It turns out that the H₂ molecule reacts exothermally with Ti₄C₄H₈ to yield the dihydrogen complex (H₂C₄). The reaction shows no energy barrier at this stage.17 Remarkably, subsequent

Fig. 2 The DFT HOMO (bottom) and LUMO (top) of Ti₄C₄H₈ cubane. Ti – big white spheres, C – big gray spheres, H – small white spheres.
This purpose.

activation of $H_2$ requires only 0.33 eV to reach the transition state on the way to product ($^{1}^{1}TiC_4H_6$), despite the necessity of highly endothermic heterolytic splitting of the $H_2$ molecule. We anticipate that other partially hydrogenated TiC nanostructures are likely to store $H_2$ on their own and serve as catalysts of $H_2$ attachment/detachment reactions from other, more stable, hydrogen stores.18

Selected TSHs could also be used for chemical vapour deposition of mechanically and thermally resistant TiC coatings (by analogy with their BN$H_2$ and GaNN$H_2$ cousins which yield BN19 and GaN20, respectively). This process requires full thermal desorption of $H_2$ from volatile material, and in consequence demands an elevated temperature. At present, mixtures of TiCl4 and CH4 are used for TiC deposition, typically at 850–1050 °C in a $H_2$ atmosphere.2 Such harsh conditions obviously eliminate thermally-sensitive materials from the substrate list. We estimate (see Supplementary Information) that TiC could be deposited under much milder conditions (300–450 °C) if TSHs are used for this purpose.

In conclusion we predict a novel family of potentially useful compounds, the Ti-substituted hydrocarbons. Many of these should be sufficiently stable towards $H_2$ and $CH_4$ elimination to survive at ambient temperatures without decomposition.20 TSHs could possibly be obtained via metathetical (halide and cyclopentadienyl for hydride) substitutions for known methyltitanium halides.5,21

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Notes and references
† We used the 6-311+G** basis set for C and H, and the 6-31G** set for Ti.
6 Compounds containing only Ti, C and H are scarce. Ti(CH3)4, which is a tetramethylenimine in which 1/5 of the C atoms have been substituted by Ti, has been obtained only in the form of THF or ether solvates, which decompose above −40 to −30 °C. For the most recent report see: S. Kleinheinz and K. Seppelt, Chem. Eur. J., 1999, 12, 3573 and references therein.
8 Some organometallic complexes of Ti are known to activate and/or eliminate methane, acetylene and $H_2$. See Ref. 6c, and (a) T. R. Cundari, J. Am. Chem. Soc., 1992, 114, 10557; (b) J. R. Hagadorn and M. J. McNeive, Organometallics, 2003, 22, 609.
10 Entropies of gaseous $H_2$, $CH_4$ and $^{1/2}C_2H_4$ translate to the following contributions to $\Delta G^\circ$ at $T = 298$ K: $0.40$ eV, $0.58$ eV, and $0.34$ eV.
12 Despite similar ENP for TSHs and for BN compounds. The differences between Pauling and Mulliken electronegativities for Ti and C (1.01 au and 2.82 eV) are very close to respective values for B and N (1.00 au and 3.00 eV). Here au stands for arbitrary units of Pauling electronegativity. These values might suggest that the Ti–C bonds should be more ionic, similar to the BN ones.
13 Similar behaviour is seen for other hydrides with substantial ENP, for example, Mulliken charges are +1.02 e and −1.09 e for Ti and C ($\text{Ti(CH}_3)\text{H}_4$), and +0.32 e and −0.54 e for B and N (BN$\text{H}_4$).
14 Similar behaviour is seen for other hydrides with substantial ENP, for which gradual thermal dehydrogenation occurs; see Ref. 36 and compare to G. Wolf, J. Baumann, F. Baitalow and F. P. Hoffmann, Thermochim. Acta, 2000, 356, 19. Also for $^{1}^{1}H_2TiC_4H_8$, a two-step reaction is anticipated, the first step leading to $^{1/2}^{1}HTiC_4H_6$ (+0.27 eV), and the second one to $^{1/2}HTiC_4H_4$ (+0.50 eV).
16 Here we discuss thermal decomposition based exclusively on thermodynamic parameters.
18 The optimization path, rather than the process taking place along the intrinsic reaction coordinate, is calculated here (note: DFT underestimates energy barriers). The effective barrier is thought to be small due to immense zero-vibrational energy of C–H and Ti–H oscillators (~ 0.5 eV per pair of H atoms). See also: I. I. Zakharov, G. M. Zhidomirov and V. A. Zakharov, J. Mol. Catal., 1991, 58, 149.
20 This is especially true for gaseous TSHs at low concentrations; under such conditions $H_2$ detachment interconnected with simultaneous oligomerization could be avoided.