Catalytic Hydrogenolysis and Isomerization of Light Alkanes over the Silica-Supported Titanium Hydride Complex (≡SiO)$_3$TiH

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We have recently reported the hydrogenolysis of light alkanes under very mild conditions of temperature and pressure catalyzed by (≡SiO)$_3$ZrH[1] and (≡SiO)$_3$HfH.[2] This remarkable reactivity can be attributed to the fact that the active species are formally 8 e$^-$ and extremely coordinatively unsaturated. We proposed, on the basis of the primary products observed, that the hydrogenolysis proceeds by stepwise cleavage of carbon–carbon bonds by β-alkyl elimination from surface metal–alkyl intermediates. We now report that under identical conditions the reactions of neopentane and isobutane with hydrogen over (≡SiO)$_3$TiH cannot be simply described as hydrogenolysis but that alkane skeletal isomerization also occurs.

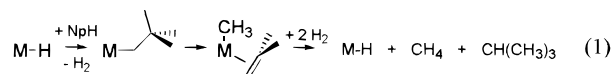The title complex, (≡SiO)$_3$TiH, is synthesized in two steps from TiNp$_4$ [Np = CH$_2$C(CH$_3$)$_3$] and silica (Degussa Aerosil, 200 m^2/g). All reactions are performed in sealed tube reactors pre-equipped with break-seal tubes for the introduction of nongaseous reactants and CaF$_2$ windows to allow aquisition of infrared spectra, as described elsewhere.[3]

A silica wafer was dehydroxylated under dynamic vacuum for 15 h at 500 °C (silica$_{500}$). The infrared spectrum indicates the presence of surface silanols free of any hydrogen bonding. Tetraneopentyl titanium[4] is sublimed (60 °C, 10^{-4} mm Hg) onto the disk at room temperature. The disk turns from white to yellow, neopentane is given off, the ν(SiO–H) band (3747 cm^{-1}) is consumed, and new bands corresponding to the neopentyl ligand ν(CH) (2956, 2905, 2867, and 2800 cm^{-1}) and δ(CH) (1466, 1393, 1365 cm^{-1}) vibrations appear. When the reaction is performed on a fully deuterated silica disk, 1 equiv of neopentane-d_1 was evolved. It should be noted that the surface complex is never isolated, per se, but rather the formulations proposed would represent the vast majority of titanium centers on the surface. Spectroscopy,[5] other chemical tests and elemental analyses[6] are consistent with a surface species in which a trineopentyl metal complex is linked to the surface by one siloxy bridge, ≡SiOTiNp$_3$ (**1**), as was the case for the analogous zirconium and hafnium reactions.

This alkyl complex (20 mg, 1 wt % Ti, 9.5 μmol) was treated under hydrogen (1 atm, 10 mmol) at 150 °C for 1 h. The solid turned from pale yellow to brownish yellow. In the infrared spectrum, the bands associated with the neopentyl ligands disappear with the formation of four bands associated with ν-

(TiH) at 1706, 1692, 1679, and 1647 cm^{-1} and two bands associated with ν(SiH) at 2263 and 2196 cm^{-1}. Methane and ethane were formed in a 1:1 ratio (total carbon given off corresponds to the release and hydrogenolysis of 3 equiv of neopentane). Reaction of this complex with deuterium gas (1 atm, 10 mmol) showed rapid disappearance of the ν(TiH) bands (within 15 min at room temperature) with no modification of ν(SiH) bands: the expected ν(TiD) bands were not observed as the silica is opaque in the region corresponding to these bands (around 1200 cm^{-1}). Subsequent reaction with hydrogen gas completely restored the ν(TiH) bands. Further characterization of this complex has been accomplished by chemical analyses[7] which leads to the tentative formulation (≡SiO)$_3$TiH (**2**).

The formation of methane and ethane rather than neopentane indicates that **2** catalyzes the hydrogenolysis of neopentane. Similar observations were made regarding the formation and reactivity of the analogous surface complexes (≡SiO)$_3$ZrH1 and (≡SiO)$_3$HfH.[2] What surprised us was the ratio of methane to ethane at completion which was 1:1 in the case of Ti, but was always observed in a strict 3:1 ratio for Zr and Hf. For these latter cases, we have proposed a mechanism in which neopentane undergoes C–H bond activation to form a metal–neopentyl complex. The carbon–carbon bond cleavage step was one of β-methyl elimination to form a metal–alkyl–olefin complex,[8] which on further reaction with hydrogen produces methane and isobutane (or a surface metal-isobutyl complex) (eq 1). The

$$M{-}H \xrightarrow[\ -H_2\ ]{+\ NpH} M \overset{}{\diagup} \longrightarrow M \overset{CH_3}{\diagup} \xrightarrow{+\ 2\ H_2} M{-}H\ +\ CH_4\ +\ CH(CH_3)_3 \qquad (1)$$

isobutane (or isobutyl fragment) is in turn converted by the same mechanism to methane and propane and then propane to methane and ethane. The carbon–carbon bond of ethane cannot be broken by this mechanism as a surface metal–ethyl fragment has no carbon–carbon bond β to the metal.

The fact that in the titanium case we observed a methane to ethane ratio at completion of 1:1 indicates that there was some skeletal rearrangement of the alkyl ligands occurring on the same time scale as the overall hydrogenolysis reaction. We have studied this by following the evolution of products in the catalytic hydrogenolysis of neopentane and isobutane with **2** at various temperatures and conversions (Figures 1 and 2).[9]

(1) (a) Lecuyer, C.; Quignard, F.; Choplin, A.; Olivier, D.; Basset, J. M. *Angew. Chem.* **1991**, *103*, 1692−1694; *Angew. Chem., Int. Ed. Engl.* **1991**, *30* (12) 1660−1661. (b) Quignard, F.; Lecuyer, C.; Choplin, A.; Olivier, D.; Basset, J. M. *J. Mol. Catal.* **1992**, *74*, 353−63. (c) Corker, J.; Lefebvre, F.; Lecuyer, C.; Dufaud, V.; Quignard, F.; Choplin, A.; Evans, J.; Basset, J.-M. *Science* **1996**, *271* (5251), 966−969.
(2) d'Ornelas, L.; Reyes, S.; Quignard, F.; Choplin, A.; Basset, J. M. *Chem. Lett.* **1993**, 1931−1934.
(3) Quignard, F.; Lecuyer, C.; Bougault, C.; Lefebvre, F.; Choplin, A.; Olivier, D.; Basset, J. M. *Inorg. Chem.* **1992**, *31*, 928−30.
(4) The complex is synthesized as decribed in: Mowat, W.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 1120−1124.
(5) Infrared spectra were obtained using a Nicolet Magna-IR 550 spectrometer with a Mid-IR (4000−400 cm^{-1}) detector at 4 cm^{-1} resolution. Solid state CP-MAS NMR were obtained on a Bruker DSX 300 spectrometer (90°, 3.8 ms ^{1}H, contact time 10 ms, recyle delay 2 s). Mass spectra were obtained on a HP-GCD GC-MS system at 120 °C (gas chromatography, Chromopack KCl/Al$_2$O$_3$, 50 m × 250 μm, isothermal at 80 °C).

(6) Elemental analyses were performed at the CNRS Central Analysis Service, Solaize. For titanium analysis, the metal is dissolved in HF/HClO$_4$/HNO$_3$, dried, taken up in HClO$_4$/HNO$_3$, and analyzed by AES. (a) ^{1}H CP-MAS NMR (300 MHz, Bruker): δ 0.46 (CH$_3$), 1.73 (CH$_2$). (b) ^{13}C CP-MAS NMR (75 MHz, Bruker): δ 36.7 (CH$_3$), 37.2 (*C*(CH$_3$)$_3$). The CH$_2$ was not observed. (c) Hydrolysis of the surface complex shows removal of all alkyl ligands in the IR: quantification of neopentane given off and elemental analysis of the solid yields a NpH/Ti ratio of 3. (d) Reaction with O$_2$ produces no gaseous product, and the elemental analysis of the solid yields a C/Ti ratio of 14.8 (expected, 15). ^{1}H CP-MAS NMR (300 MHz, Bruker): δ 1.10 (CH$_3$), 2.03 (CH$_2$). ^{13}C CP-MAS NMR (75 MHz, Bruker): δ 25.1 (CH$_3$), 33.9 (*C*(CH$_3$)$_3$), 89.1 (CH$_2$). (e) Reaction with ^{t}-BuOH produced a solid, ≡SiOTi(O^{t}Bu)$_3$ for which the elemental analysis yields a C/Ti ratio of 13 (expected, 12). ^{13}C CP-MAS NMR (75 MHz, Bruker): δ 29.6 (*C*(CH$_3$)$_3$), and no peaks at δ 36−38. The quaternary carbon of the ^{t}Bu was not observed. (f) Reaction with hydrogen at 150 °C produces methane and ethane in quantities consistent with three neopentyl ligands (vide infra).
(7) (a) Reaction with O=C(^{t}Bu)$_2$ produces a white solid (presumably ketone insertion into Ti–H bond). Microanalysis revealed C/Ti ratio of 7 (expected, 9 for the monohydride). (b) Reaction with CH$_3$I produced 0.7 equiv of methane per Ti (expected, 1.0). (c) Reaction with ^{t}BuOH converts hydrides to *tert*-butoxides. Microanalysis revealed C/Ti ratio of 5 (expected, 4).
(8) The direct observation of the β-alkyl elimination has been reported: Horton, A. D. *Organometallics* **1996**, *15*, 2675−2677. This mechanism has been implicated in a number of reactions. See refererences in the above article.
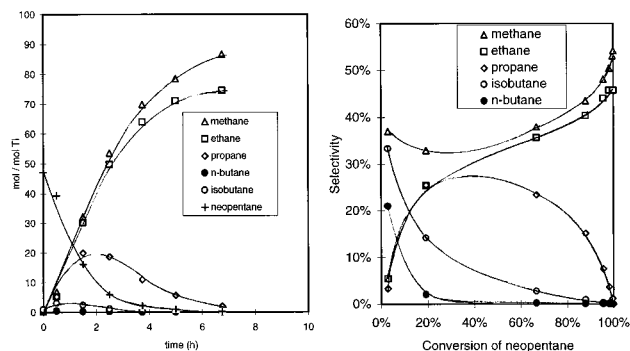
Figure 1. Evolution of products and selectivity for the reaction of neopentane with hydrogen in the presence of **2** at 150 °C.

For neopentane at low conversion, methane, isobutane, and *n*-butane are primary products. Although isopentane was not observed, the presence and importance of *n*-butane are a clear indication of carbon skeletal rearrangement prior to the formation of products. Furthermore, the fact that propane and ethane are initially formed in a 1:1 ratio can also be considered as the signature of the isomerization of surface neopentyl fragments to isopentyl fragments prior to product formation.

A similar result is obtained in the reaction of isobutane with hydrogen at 150 °C (Figure 2). Ethane is clearly a primary product, the implication being that the initially formed surface isobutyl fragment has rearranged to an *n*-butyl fragment.[10] In this case, the C_4 isomerization product *n*-butane is observed in significant quantities and the selectivity for this product increases at very low conversion, suggesting that it is indeed a primary product (although a minor one).

(9) In a typical reaction, a reactor is charged with **2** (isolated from reactants by a break-seal, ~25 mg, 1–1.7 wt % Ti, ~10 μmol Ti–H; weight of wafer and wt % Ti varies from one experiment to another), the alkane (50 mm Hg, 60–80 mol/mol of Ti) and hydrogen (1 atm, 15.2 mol/mol of alkane). The reactor was heated to the reaction temperature, and the break-seal was broken ($t = 0$). Gases were sampled by opening the reactor to a closed known volume equipped with a septum. The reactor was then reisolated, the known volume was filled to atmospheric pressure with air, and the gases were removed by syringe for quantification by gas chromatography (Chrompack KCl/Al$_2$O$_3$ column, 50 m × 250 μm, FID detector).

(10) We have previously demonstrated that the hydrogenolysis of *n*-butane catalyzed by (≡SiO)$_3$HfH[2] leads to the formation of primarily ethane by a mechanism of initial primary C–H bond activation to produce surface *n*-butyl and subsequent β-ethyl elimination to form C_2 fragments. Methane and propane are formed in a minor pathway by first-step secondary C–H bond activation to give surface Hf–CH(CH$_3$)CH$_2$CH$_3$ which then undergoes β-methyl elimination eventually leading to methane and propane.
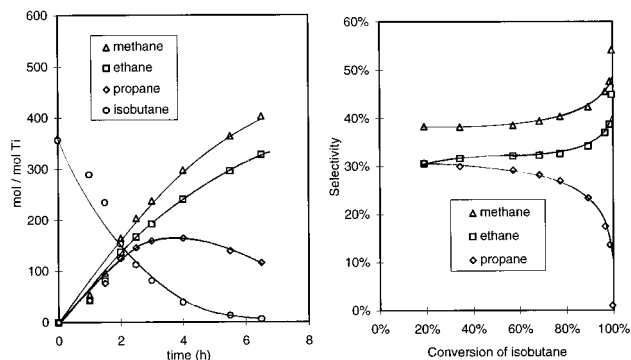

Figure 2. Evolution of products and selectivity for the reaction of isobutane with hydrogen in the presence of **2** at 150 °C.

The skeletal alkane isomerization is not difficult to explain. Following an initial step of C–H bond activation the surface alkyl fragment can undergo β-methyl elimination. For titanium, the intermediate metal–alkyl–olefin complex persists long enough (relative to olefin rotation) to undergo reinsertion of the rotated olefin into the metal–carbon bond. This isomerisation step is illustrated for the neopentyl fragment in eq 2.
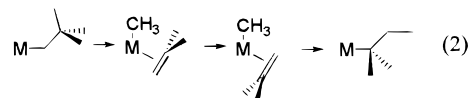
These reactions were repeated at 50 and 100 °C (see Supporting Information). For the hydrogenolysis of neopentane, this effect was clearly present at these temperatures. For isobutane, the process of isomerization is not clearly indicated.

Thus the remarkable activity of these surface complexes with respect to carbon–carbon bonds is thus more interesting given the possibility of light hydrocarbon isomerization at very mild temperatures.

Supporting Information Available: Infrared spectra (4000–1300 cm^{-1}) corresponding to the syntheses of **1** and **2**; NMR spectra cited in footnotes; graphs of the evolution of gaseous products in the reaction of neopentane and isobutane at 50 and 100 °C (equivalents of product vs time, selectivity vs neopentane conversion) (10 pages). See any current masthead page for ordering and Internet access instructions.

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