C–C Bond Formation

Cross-Metathesis of Propane and Methane: A Catalytic Reaction of C–C Bond Cleavage of a Higher Alkane by Methane[**]

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In memory of Ian P. Rothwell

Natural gas is the most abundant hydrocarbon resource: reserves for 60 years of normal consumption have already been proven, and for about 200 years or greater are expected to be discovered, which makes it the probable future source

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not only for energy but also for basic chemicals. However, its main component, methane, is one of the most inert hydrocarbons. Apart from using methane for power generation the only other current methods commercially used to valorize methane are "steam reforming", "partial oxidation" (leading to "syngas", a mixture of carbon monoxide and hydrogen which is converted into fuels and chemicals, such as gasoline, methanol, and dimethyl ether), and the oxidative pyrolysis to acetylene, which also produces a syngas byproduct. The syngas processes are indirect, since they require first the chemical transformation of CH_4 to CO and H_2, which are the building blocks for further chemistry. All these processes are limited by selectivity, with formation of CO_2 as a by-product, and require high temperatures which make them relatively unattractive in terms of energy and environmental considerations.[1] Therefore, a tremendous effort has been directed at finding direct catalytic transformations of methane into more valuable and useful carbon-containing products. Transition metals have been shown to readily activate the C–H bond of methane to form metal–methyl complexes[2–6] and, in some instances, enable the reforming of this C–H bond; these reactions are, however, either stoichiometric or degenerate (these types of exchange reaction can only be detected by isotope labeling!). The transformation of methane into methanol by platinum salts in sulfuric acid is also noteworthy despite highly acidic conditions.[7] Methane has also been reported to react with olefins to give higher alkanes in the presence of superacids or organometallic catalysts[8–10] and, more recently, its coupling reaction with silanes has been disclosed.[11] The difficulty in achieving selective transformation of methane into valuable chemical products resides in the low reactivity of methane compared to co-reactants (e.g. olefins) and/or the products. However, this problem would be overcome by the reaction of methane with alkanes to produce other alkanes, which all have similar reactivity to the starting alkanes. Herein we report the successful accomplishment of this reaction through a low-temperature incorporation of methane into another alkane, propane.

Recently, we have shown that a highly electrophilic tantalum hydride supported on silica $[(\equiv SiO)_2Ta\text{-}H]$ (**1**), prepared by surface organometallic chemistry,[12] can catalytically transform a given alkane into its higher and lower homologues.[13,14] This reaction, called "alkane metathesis", involves a successive cleavage and formation of carbon–carbon bonds: hence two ethane molecules give one methane and one propane molecule. The free energy of the reaction is slightly negative ($-8.2\,kJ\,mol^{-1}$ at 150 °C, driven by the formation of methane), and the equilibrium conversion is around 87 % at 150 °C. This raises the question: is it possible to drive this reaction in the reverse direction, that is, to react methane with another alkane to give a mixture of alkanes with incorporation of methane? This reaction would correspond to the cross-metathesis of methane with a higher alkane.

To test this concept, we studied the degenerate reaction of methane with ethane [Eq.(1)] which requires ^{13}C labeling to detect the phenomenon.

$$ {}^{*}CH_4 + CH_3{-}CH_3 \rightarrow CH_4 + {}^{*}CH_3{-}CH_3 \quad \Delta G^{o}_{(T)} = 0 \tag{1} $$

A mixture of ^{13}C-labeled methane (500 equiv; 64 kPa) and ethane (10 equiv; 1.25 kPa) was heated at 165 °C over **1** (53 mg, 5 wt % in Ta (see Method of preparation in Experimental Section)) in a glass reactor (0.28 L), and the distribution of the ^{13}C isotopomers of ethane (unlabeled, mono-, and dilabeled) was monitored over time by GC/MS. Incorporation of ^{13}C labels in ethane occurred over 200 h; hydrogenolysis of ethane into methane was also detected as a competitive parallel reaction, since H_2 had been produced during the first step of C–H bond activation (formation of Ta–R from Ta–H (**1**), R=Me, Et).[15,16] Note that the initial formation of monolabeled ethane followed by the dilabeled isotopomer is in agreement with a stepwise incorporation of the label (Figure 1). Additionally, propane was also produced by the known self-metathesis of ethane and was also converted into its isotopomers. The incorporation of the label into ethane clearly shows that cross-metathesis occurs and that methane can participate in the carbon–carbon formation of higher alkanes. In the case of ethane, this reaction yields ethane, a degenerate process, which can only be detected by labeling. The reaction conditions (batch reactor, methane/ethane reaction) were designed to detect this possible phenomenon, but were not optimized to study a productive reaction.

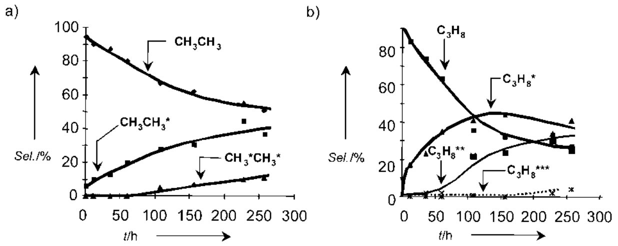


Figure 1. Evolution of the isotopomeric distribution of a) ethane {unlabeled (CH_3CH_3), monolabeled ($CH_3CH_3^*$), and dilabeled ($CH_3^*CH_3^*$)} and b) propane {unlabeled (C_3H_8), monolabeled ($C_3H_8^*$), dilabeled ($C_3H_8^{**}$), and trilabeled ($C_3H_8^{***}$)} in the cross-metathesis of ethane and ^{13}C-labeled methane.

To observe a productive cross-metathesis of methane with an alkane, the reaction with propane was investigated in a continuous-flow reactor, and the reaction conditions tuned to work at full conversion of propane. This reaction has a positive free energy ($8.2\,kJ\,mol^{-1}$ at 150 °C for a 1:1 methane/propane ratio), but its conversion can be, in principle, thermodynamically driven by a high methane to propane ratio. For example for a methane/propane ratio of 1250:1 the conversion of propane can be up to 98 % at 250 °C; the temperature and the contact time are also important parameters (kinetic). Note that the production of ethane does not guarantee that such a reaction takes place since **1** is also known to readily catalyze the hydrogenolysis of propane into a mixture of methane/ethane[17] or the self-metathesis of propane (production of ethane and butane). Nonetheless if 100 % cross-metathesis takes place, two ethane molecules are produced per propane molecule consumed [Eq. (2)], while only one ethane is produced per propane molecule in the case of hydrogenolysis [Eq. (3)], and half an ethane (and half a

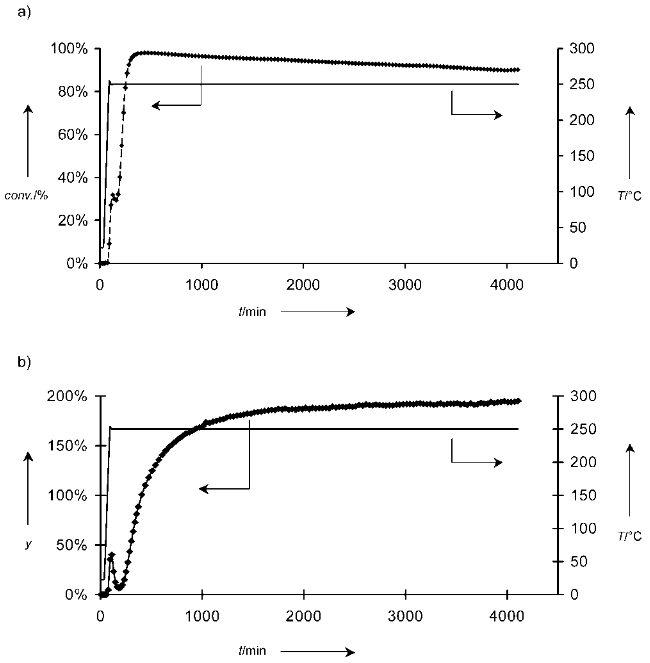


Figure 2. a) Conversion of propane as a function of time on stream. b) Number of equivalents of ethane formed by propane consumed y in% as a function of time on stream.

butane) per propane in the case of propane "self-metathesis" [Eq. (4)]. Therefore, to make a clear cut distinction between cross-metathesis and side reactions (hydrogenolysis and self-metathesis) it is critical to establish the mass balance of the overall reaction.

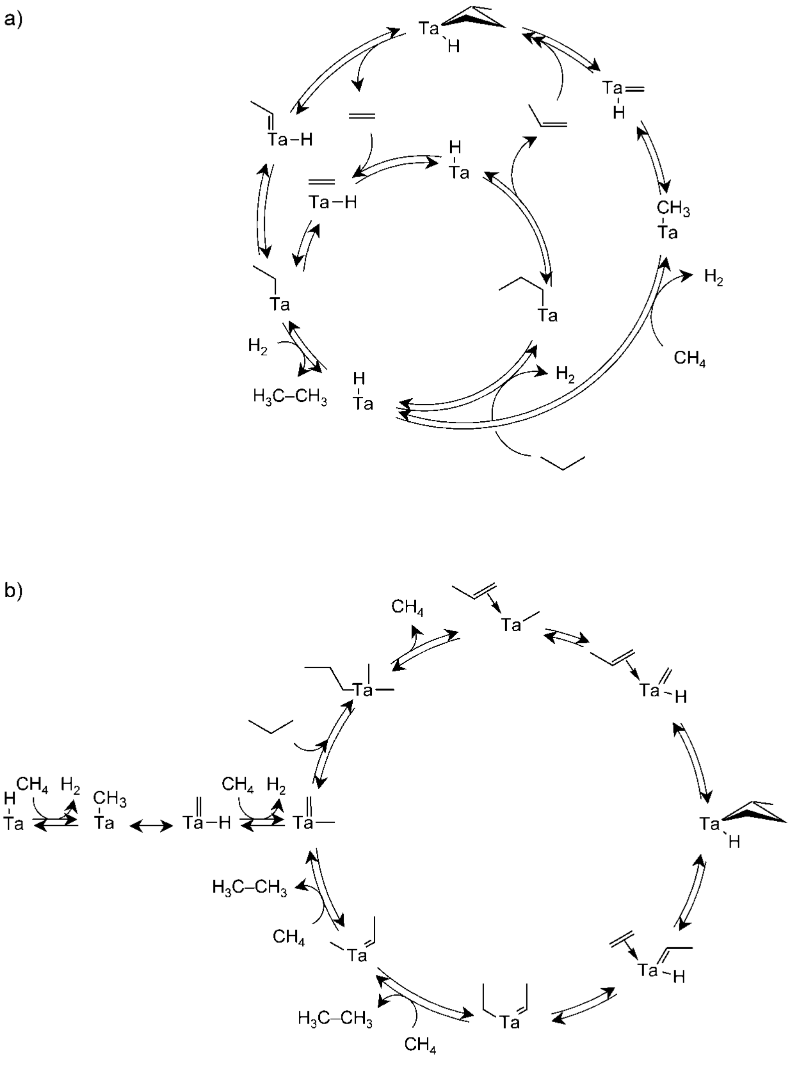
$$CH_4 + C_3H_8 \rightarrow 2\,C_2H_6 \quad (2)$$

$$H_2 + C_3H_8 \rightarrow CH_4 + C_2H_6 \quad (3)$$

$$C_3H_8 \rightarrow {}^1\!/_2\,C_2H_6 + {}^1\!/_2\,C_4H_8 \quad (4)$$

To make this distinction, the reaction is carried out by passing a 1.5 mL min^{-1} flow of a 1250:1 methane/propane mixture at 50 × 10^2 kPa over 300 mg of **1** at 250 °C. The alkane mixture was first contacted at room temperature and then a ramp of 250 °C h^{-1} was applied up to 250 °C (Figure 2). During this period a large amount of hydrogen is produced by reaction of the alkane mixture (methane and propane) with **1** to form the propagating species, surface alkyl species, which are formed by C–H activation (See Supporting Information).[15,16] Propane is partially consumed and converted into a methane/ethane mixture by hydrogenolysis.[17] After the evolution of hydrogen (produced in the activation step) has ceased, the amount of ethane in the stream increases until it reaches a plateau after 1000 min (Figure 2b); ethane is the major higher hydrocarbon detected (> 99 % of selectivity; see Supporting Information) along with residual methane. 1.9 ± moles of ethane are produced per mole of propane consumed and 95 % of the propane is converted by cross-metathesis, that is through its reaction with methane to produce two ethane molecules.

The reaction of methane with higher alkanes was further supported by running an identical reaction, in which ^{13}C-labeled methane was used in place of unlabeled methane. In this case the ethane produced at steady-state conditions is > 85 % dilabeled according to GC/MS, which confirms that ethane is produced by the reaction with methane (see Supporting Information). The multiple labeling is due to running the reaction at full conversion of propane, which implies a long contact time and secondary reactions, such as the successive degenerate reaction[14] of monolabeled ethane with labeled methane, as described above, leading finally to dilabeled ethane as the main isotopomer. Ethane produced initially ($t < 200$ min) is unlabeled, clearly showing that it comes from the hydrogenolysis of propane.



Scheme 1. Possible mechanisms via carbene intermediates: a) on two sites and b) on one site.

In summary, we have shown that **1** can catalyze the reaction of methane with a higher hydrocarbon, namely propane, and thereby incorporate methane into a higher alkane by cross-metathesis. While we earlier proposed mechanism based on cleaving the C–C bond system by either σ-bond metathesis or oxidative addition,[13] we now propose that it proceeds via carbene intermediates and olefin metathesis as suggested by previous studies.[18],[19] Since the alkane-metathesis active site can be generated from either Ta^{III} or Ta^{V} intermediates, and since olefin metathesis would require the formation of olefins, one and two-site mechanisms can be proposed (Scheme 1), which are under investigation.

The overall reaction provides a route for the direct transformation of methane into more valuable hydrocarbon materials. This reaction makes possible new processes, such as replacing expensive hydrogen by low-cost methane in the recycling of polyolefins.[20]

Experimental Section

Method of preparation of catalyst **1**: Silica (1 g), previously treated at 500 °C under vacuum, in suspension in pentane (15 mL) was treated at 25 °C with a pentane solution of $[Ta(=CHtBu)(CH_2tBu)_3]$ (0.155 g, 0.33 mol) under an inert atmosphere. The reaction mixture was stirred for 2 h at 25 °C and filtered. The remaining orange solid was then washed three times with pentane and dried under vacuo. This solid was then contacted with dry and deoxygenated H_2 (200 equiv) for 15 h at 250 °C, and the amounts of methane was monitored by GC. Typically after 3 cycles of treatment under H_2, less than 1 % of carbon (as methane) is present in the gas phase.

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