Communication

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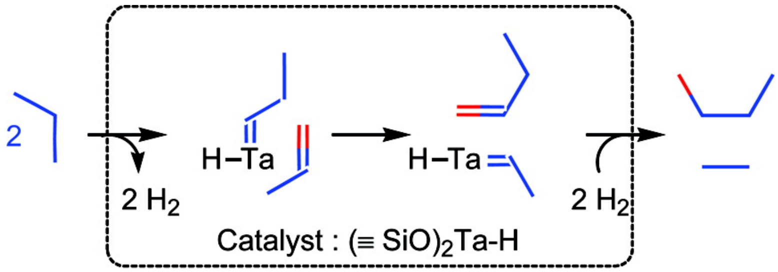

Alkane Metathesis through Olefin Metathesis

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Primary Products and Mechanistic Considerations in Alkane Metathesis

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We reported in 1997 the discovery of a new catalytic reaction: the metathesis of alkanes.[1,2] Acyclic alkanes, except methane, when contacted with the silica-supported tantalum hydride [$(\equiv SiO)_2Ta-H$], **1**, are transformed at moderate temperatures into their lower and higher homologues. For example, ethane is transformed into methane and propane along with traces of butanes. Interestingly, **1** is also able to achieve the reverse reaction, that is, the cross-metathesis of methane and propane, giving two ethanes and thereby incorporating methane into higher alkanes.[3] It is also possible to perform the cross-metathesis of ethane and toluene to give xylenes and ethylbenzene.[4] When the reaction was discovered, two mechanistic hypotheses were formulated on the basis of the d^2 configuration and the highly electrophilic character of $(\equiv SiO)_2Ta^{III}-H$, formally an eight-electron species.[5] The first one was based on successive oxidative addition and reductive elimination steps (Scheme 1a). To our knowledge, such oxidative addition of a C−C bond on early transition metals is not known at the moment.[6,7] The second one involved exchange of alkyl fragment through a four-centered transition state in which there would be a concomitant cleavage and formation of C−C and M−C bonds, a σ-bond metathesis type mechanism (Scheme 1b). Although many examples of σ-bond metathesis have been observed between the C−H bond of alkanes or aromatics and various d^0 early transition metal hydrides, alkyls or aryls, in each case, the four-centered transition state always bears a hydrogen atom in the middle position and never a sp^3 carbon (Scheme 1c).[8−13] To summarize, these mechanisms were not especially satisfactory without experimental evidence.

We wish to report a kinetic study performed in a continuous flow reactor, which shows unambiguously that olefins and H_2 are primary products and which is consistent with a mechanism based on elementary steps known in tantalum organometallic chemistry and related to that of olefin metathesis.

When propane metathesis is carried out in a continuous flow reactor, conversion goes through a maximum during time on stream, and both selectivity and turnover number (TON) after 100 h reach values comparable to those obtained under batch conditions (Figure 1a,b, Table S1, and Figure S1).[1,2,14,15] The higher selectivity in methane at short time on stream is due to hydrogenolysis of the alkane since **1** generates H_2 upon activation and catalyzes the hydrogenolysis of alkanes.[16]

After 100 h, the observed selectivities in the metathesis of propane (C_n) are: 30.5 (butane), 3.7 (isobutane), 7.3 (pentane), 1.3 (isopentane), and 2.0 (hexanes), and they can be ordered as follows: $C_{n+1} > C_{n+2} \gg C_{n+3}$. Moreover, the linear products are always favored over the branched ones. These observations are quite general if we look at the selectivities obtained during ethane, propane, butane, or isobutane metatheses (Tables S1 and S2).[1]

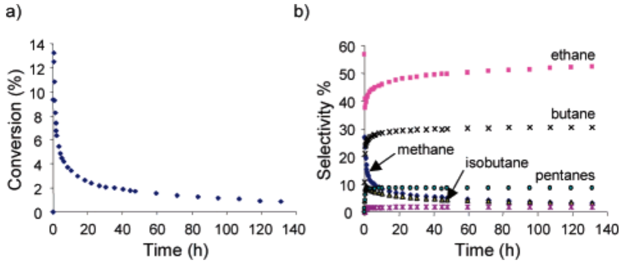
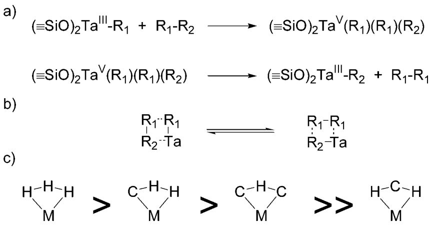


Figure 1. (a) Conversion and (b) selectivities obtained during the metathesis of propane catalyzed by [$(\equiv SiO)_2Ta-H$], **1**, (5.33% wt Ta) in a continuous flow reactor (150 °C, 1 atm, 1 mL/min, VHSV = 38 h^{-1}).

Scheme 1



The effect of inverse space velocity (proportional to contact time) on selectivity was studied using flow rates varying between 1 and 100 mL/min (or volume hourly space velocity (VHSV) of 38 to 3807 h^{-1}). During this study, the conversion increased linearly with the inverse space velocity, showing that the data determine reaction rates (Figure S2). The extrapolated selectivities at zero inverse space velocity allow a reliable determination of real primary products. Upon decreasing inverse space velocity, a strong increase in the proportion of H_2 and alkenes (from C_2 to C_5) and a parallel decrease in the production of alkanes are observed (Figure 2a−c). Interestingly the alkanes/alkenes ratio decreases when the inverse space velocity decreases and clearly reaches 0 at extrapolated zero inverse space velocity (Figure 2d). These data imply that olefins and H_2 are primary products.

These data and the known elementary steps of organometallic chemistry lead us to propose the following mechanism. The first step is the C−H bond activation of the alkane, as observed when **1** reacts with cycloheptane or methane to form the corresponding tantalum−alkyl complexes **2-R** and H_2.[5] In the case of propane, this step probably leads to linear and branched propyl fragments, **2-Pr** and **2-*i*Pr**, with liberation of H_2 as a primary product (Scheme 2a). These Ta-propyls can then undergo α-H transfer to give $Ta(H)(=C(CH_3)_2)$ and $Ta(H)(=CH-CH_2-CH_3)$,[17,18] **3**, or β-H transfer leading to $Ta(H)(\eta^2\text{-}CH_2=CH-CH_3)$.[18,19] Propene resulting

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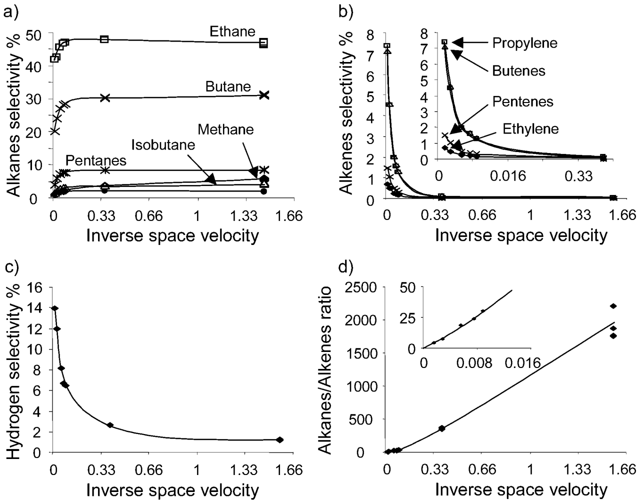
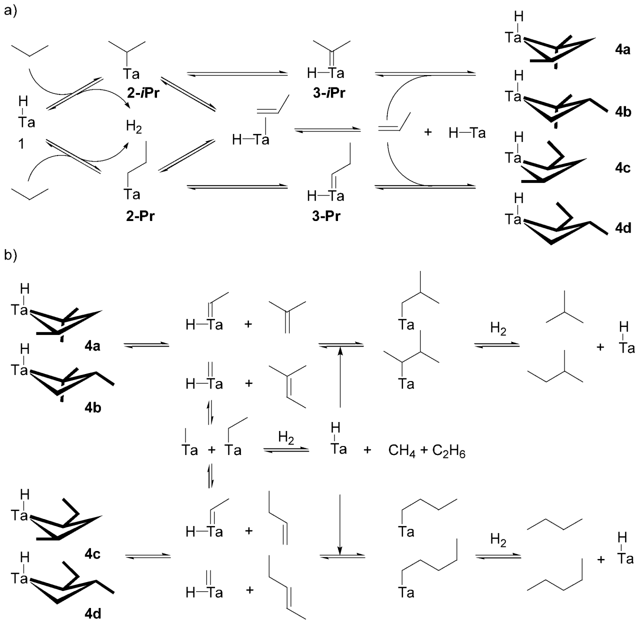


Figure 2. Metathesis of propane in a continuous flow reactor (150 °C, 1 atm, 520 mg of ($\equiv$SiO)$_2$TaH, 5.33% wt Ta). Selectivity vs inverse space velocity expressed in [(min)(volume of catalyst)/(volume of propane)] for (a) alkanes, (b) alkenes, and (c) H_2. (d) Alkanes/alkenes ratio vs inverse space velocity.

Scheme 2



from β-H transfer decoordinates (primary product) and can react with either of the hydrido-tantallacarbenes, **3**, giving four possible tantallacyclobutanes, **4**, having methyl or ethyl substituents in the [1,2]- or [1,3]-positions.[14,15,20−24] These four tantallacycles can undergo metathetical cleavage, giving back propene and carbenes or new olefins and hydrido-tantallacarbenes (Scheme 2b). The catalytic cycle ends with the insertion of the olefins into the tantalum hydride or the migration of the hydride onto the new carbene ligands. The resulting alkyl groups can be cleaved by H_2 (a primary product), a known step already observed during the hydrogenolysis of alkanes with **1**.[16] The alkyl groups could also be displaced by the incoming alkane reactant via σ-bond metathesis, but it is usually much less favored. The observed product selectivities can be understood on the basis of the stability of the key metallacyclobutane or of the facility of their formation (**4a** > **4b**; **4c** > **4d**; **4c** > **4a**; **4d** > **4b**), both of which depend on the interaction between substituents in [1,2]- or [1,3]-positions as it has been proposed in olefin metathesis.[25]

In conclusion, kinetic studies on propane metathesis, in a continuous flow reactor, have allowed primary products to be detected, namely olefins and H_2. A mechanism is proposed on the basis of known elementary steps of organometallic chemistry, which is in full agreement with all the observed selectivities. We are currently developing better catalysts on the basis of these insights.[26]

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Supporting Information Available: Experimental details, Tables S1 and S2, and Figures S1−S3. This material is available free of charge via the Internet at http://pubs.acs.org.

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