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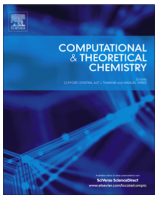

Computational insights into the mechanism of iron carbonyl-catalyzed ethylene hydrosilylation or dehydrogenative silylation

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ABSTRACT

The hydrosilylation of alkenes catalyzed by $Fe(CO)_5$ is an intricate process involving formation of alkylsilane, vinylsilane, and alkane. Herein, we represent a computational study of this reaction to determine the underlying reaction mechanism using density functional theory (DFT) techniques. On the basis of an extensive exploration of the potential energy surfaces, the modified Chalk–Harrod mechanism was found to be competitive with the Chalk–Harrod mechanism in the stoichiometric reaction of ethylene and trimethylsilane. The source of product selectivity was predicted to be determined by the relative stability of transition state **TS(4b–5b)**, which is for the ethylene-insertion into Fe—Si bond from $(H)(Me_3Si)Fe(CO)_3(C_2H_4)$ to $(H)(C_2H_4SiMe)Fe(CO)_3$, and **TS(5a–7a$_1$)** for the conversion of ethylene hydrometallation product $(Me_3Si)Fe(CO)_3(\eta^2\text{-}H)(C_2H_4)$ to $(C_2H_5)(Me_3Si)Fe(CO)_4$. The relative free energy difference of 3.27 kcal/mol between these two transition states gives a percentage ratio of 79:21 for $C_2H_5SiMe_3$ to $C_2H_4SiMe_3$, which is qualitatively in agreement with the experimental observations. The largely excessive ethylene favors not only the formation of $Fe(CO)_3(C_2H_4)(H)(SiMe_3)$ **4b** but also the release of vinylsilane from $Fe(CO)_3(H_2)(C_2H_3SiMe_3)$ or $Fe(CO)_4(C_2H_3SiMe_3)$ via the addition of another ethylene molecular to the metal center. Alternatively, in the presence of excessive R_3SiH, species $Fe(CO)_4(H)(SiR_3)$ will be dominate over $Fe(CO)_4(C_2H_4)$. In the catalytic process, $Fe(CO)_4(H)(SiR_3)$ plays the main role of active species. The experimental findings were rationalized in terms of two reaction pathways, the accessibility of which depended on the ratio of silane/alkene.

1. Introduction

Hydrosilylation of alkenes is one of the fundamental versatile synthetic reactions for manufacturing commercially important organic silicon compounds, which can construct organofunctionalized silicon monomers and cross-linked silicon polymers. These organosilicon building blocks are of importance in such diverse fields as polymer, materials, bio-organic and organometallic chemistry [1,2]. In this regard, noteworthy efforts have been devoted to the development of efficient and selective reaction of hydrosilanes to olefins employing a wide variety of transition metals [3–10]. Since iron is much less expensive and environmentally friendly compared to other transition metals like Rh, Pt and Ru [11], iron-based catalysts for hydrosilylation have received considerable interests [12–19].

Iron pentacarbonyl ($Fe(CO)_5$) has been focused on a great deal of thermally and photochemically homogeneous transition metal catalyzed reactions. The earliest report on the selective formation of vinylsilanes was obtained by the $Fe(CO)_5$-catalyzed reaction of olefins with $HSiEt_3$ under the stringent thermal conditions (100–140 °C) [20], and their experiments showed that an excess of silicon hydride (R'_3SiH) favored the silylated alkane (**A**), whereas an excess of olefin favored the unsaturated vinylsilane (**B**). However, efforts to detect the intermediates had been hindered by the hermetically sealed reaction conditions.

$$\begin{array}{c} R'_3SiH \\ + \\ CH_2{=}CHR \end{array} \xrightarrow[\text{UV,degassed solution, 25 °C}]{Fe(CO)_5} \left\{ \begin{array}{cl} R'_3SiCH_2CH_2R & (\mathbf{A}) \\ + & \\ R'_3SiCH{=}CHR & (\mathbf{B}) \\ + & \\ CH_2CH_2R & (\mathbf{C}) \end{array} \right.$$

In contrast to the thermal dissociation of CO from $Fe(CO)_5$, the Near-UV irradiation of $Fe(CO)_5$ to yield coordinatively unsaturated iron-carbonyls was very easily under mild conditions. The $Fe(CO)_5$-photocatalyzed alkene hydrosilylation was reported by Schroeder and Wrighton [21] and possible mechanisms for the normal and dehydrogenative hydrosilylation involving $(H)(SiR_3)Fe(CO)_3(\text{olefin})$ was suggested. For alkylsilane formation, their

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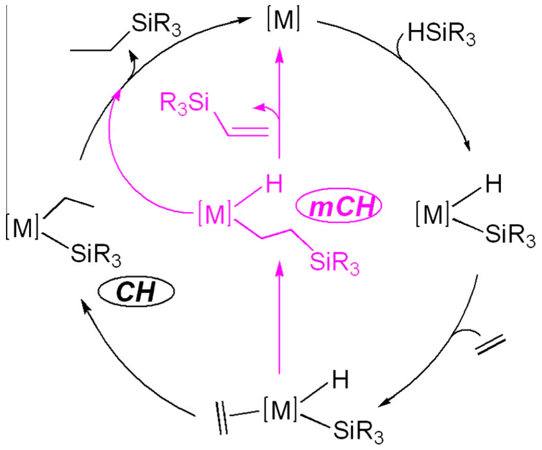
proposal is related to the typical Chalk–Harrod mechanism [22] involving the coordinated alkene C═C bond insertion into the M—H bond to form the M—C—C—**H** species followed by the Si—C reductive elimination (Scheme 1). For vinylsilane formation, they proposed the modified Chalk–Harrod mechanism involving the coordinated olefin C═C bond insertion into the M—SiR_3 bond to give an M—C—C—$\mathbf{SiR_3}$ intermediate followed by the β-H elimination (Scheme 1). Along with advanced experimental techniques (e.g., matrix isolation, time-resolved gas phase IR spectroscopy, and time-resolved resonance Raman spectroscopy), some important mechanistic explorations shedding light on the activation of silane and alkene by $Fe(CO)_5$ as well as on the reactivity of $HFe(R_3Si)(CO)_4$ have been reported. In 1971, Graham and Jetz showed that irradiation of $Fe(CO)_5$ with R_3SiH led to *cis*-$HFe(R_3Si)(CO)_4$ ($R = Cl$ and C_6H_5) with the loss of CO below 25 °C at ambient pressure in heptanes [23]. In the reaction of $HFe(Ph_3Si)(CO)_4$ with isoprene, Bellachioma et al. [24] suggested that a previous olefin coordination to the metal center is not possible under thermal conditions and a direct hydrogen transfer of the Fe—H group via a radical or an ionic process occurs as the proposal for the hydrosilylation of dienes catalyzed by $HFe(Cl_3Si)(CO)_4$ [25]. Using ultrafast UV pump/IR probe spectroscopy and quantum chemical calculations, the Si—H activation of triethylsilane with the photogenerated triplet $Fe(CO)_4$ from $Fe(CO)_5$ had been studied by Harris et al. [26]. It has been shown that triplet $Fe(CO)_4$ is stable on the ultrafast time scale and does not coordinate with the solvent. The reactivity of triplet $Fe(CO)_4$ in triethylsilane, leading to singlet silyl hydride complex $HFe(SiEt_3)(CO)_4$, was proposed to be understood in terms of spin–orbit coupling between the singlet and triplet surfaces. On the other side, $Fe(CO)_4$(alkene) species was observed by infrared spectra in the iron pentacarbonyl catalyzed olefin isomerization reactions[27].

Given above-mentioned diverse observations concerning $Fe(CO)_5$ reactivity, it is likely that multiple reaction pathways for olefin hydrosilylation controlled by reaction conditions and the subtle features of substrates are accessible. Nonetheless, due to the lack of kinetic information and direct evidences for the very short-lived intermediates involved in catalytic reaction, it is ambiguous why this reaction can take place and how the catalytic cycle proceeds. It is notable that Fe-catalyzed alkene hydrosilylation has not been investigated by theoretical modeling to date. We noticed that several theoretical studies on the transition metal mediated alkene hydrosilylation have been reported. For instance, the Pt-catalyzed ethylene hydrosilylation followed the typical Chalk–Harrod mechanism [28,29]. Sakaki et al., elucidated the $RhCl(PH_3)_3$-catalyzed hydrosilylation obey the modified Chalk–Harrod mechanism [30]. Alternatively, the σ-bond metathesis mechanism [31], in which a initial formed M—C bond is cleaved by a Si—H bond of uncoordinated silane via the four-membered transition state to afford M—H and C—Si bonds simultaneously, has been considered for the Ru-catalyzed hydrosilylation of alkenes [32,33] and the ethylene hydrosilylation catalyzed by $ZrCp_2$ [34] and bis-N-heterocyclic carbene rhodium complex [35]. In addition, Beddie and Hall [36] provided the first theoretical evidence for the Glaser–Tilley mechanism [7] involving the direct insertion of alkene into the Si—H bond of ruthenium silylene complex without direct interaction between the alkene and metal center. The activation of Si—H bond by triplet cyclopentadienylcobalt was examined without the intervention of σ-silane complex and lead to singlet silylcobalt hydride [37]. However, the aforementioned results are hardly transferable to the $Fe(CO)_5$-catalyzed reaction system. Because the detailed mechanism for hydrosilylation of olefins would to be different depending on not only the transition metals but also the nature of silanes used. Here, the Glaser–Tilley type mechanism is excluded because the model silane SiR_3H ($R \neq H$) is not possible to form the metal silylene species. Very recently, Asatryan and Ruckenstein [38] have investigated the detailed mechanism of iron carbonyl-catalyzed hydrogenation of ethylene using DFT methods. The water gas shift reaction catalyzed by $M(CO)_5$ (M = Fe, Ru, Os) has been studied by density functional theory and ab initio calculations [39].



Scheme 1. Simplified Chalk–Harrod (CH) and modified Chalk–Harrod (MCH) mechanisms for metal-catalyzed alkene hydrosilylation.

Now many interesting questions remain about the title reaction, particularly the possibility of the high-spin intermediates, the kinetics and energetics of the catalytic process. Also, which factors determine the chemo-selectivity of the process and how is it controlled? To answer these questions, we have performed a comprehensive investigation on the full catalytic cycles using density functional theory. In this work, trimethylsilane and ethylene were chosen as model substrates. All possible reaction pathways associated with the formation of alkylsilane, vinylsilane, and alkane reported in Ref. [21] have been explored and calculated. On the basis of our computations, we have elucidated the detailed reaction mechanisms of $Fe(CO)_5$-catalyzed alkene hydrosilylation and found a very different pathway from that of Pt- and Rh-catalyzed alkene hydrosilylations. Moreover, this work provides a reasonable explanation for experimental findings and clarifies why $Fe(CO)_5$-mediated alkene hydrosilylation or dehydrogenative silylation occurs competitively.

2. Computational details

All calculations were performed with the Gaussian 03 program package [40]. The geometries of reactants, intermediates and transition states were fully optimized without symmetry constraints using the BPW91 density functional theory (DFT) method [41,42] and an all-electron triple-ξ valence basis set with polarization functions on all atoms (TZVP) [43]. The harmonic vibrational frequency analysis was performed to characterize the nature of the stationary points as true minima (all positive eigenvalues) or transition states (one imaginary eigenvalue) and to provide zero-point energies (ZPE) and thermal corrections to enthalpies and Gibbs free energies. Moreover, the validity of transition states was confirmed by intrinsic reaction coordinate computations (IRC) [44] and the connectivity between stationary points was established. It is well-know that the gas-phase calculations can overestimate the entropic contributions, especially for the cases where the numbers of reactant and product molecules are different. Corrections were added to the calculated gas-phase free energies according to the free volume theory. For one-to-one or two-to-two transformation, no correction was made. For two-to-one (or one-to-two) transformation, a correction of −2.6 (or 2.6) kcal/mol was made at the temperature of 298.15 K. These corrections have been applied in