Femtosecond Infrared Studies of Silane
Silicon—Hydrogen Bond Activation

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Cleavage, or activation, of the silicon—hydrogen bond of a silane by a metal center has been the focus of many recent studies. Knowledge of this type of reaction is relevant to the central ideas of chemical bonding in general and is essential to the development of catalytic reactions such as hydrosilation. It is commonly accepted that the photochemical reaction for the oxidative addition of Et3SiH (Et = C2H5) to CpMn(CO)3 (Cp = C5H5) begins with the loss of a CO ligand as the result of UV irradiation, producing a coordinatively unsaturated dicarbonyl species which further reacts to activate the Si—H bond to form CpMn(CO)2(H)(SiEt3).** Due to the fast reaction rates, however, the detailed reaction mechanism including the initial solvation of the nascent photogenerated chemical species has remained unclear. With the advent of ultrafast spectroscopy, especially in the infrared, it is now possible to identify such events which occur on a time scale shorter than diffusion to reveal the underlying elementary reaction steps. In this communication, we report the first ultrafast infrared study on silicon—hydrogen bond cleavage by CpMn(CO)3.

As a result of photodissociation one CO ligand, the kinetics of the parent molecule recorded at 2028 cm−1 (A, Figure 1) shows an instrument limited bleach, 31% of which recovers in 32 ± 7.4 ps (Figure 2A).** This rapid recovery of the parent bleach is due to vibrational relaxation in the ground electronic manifold of the parent molecule, and the new intermediate through the ethyl group of Et3SiH. Subsequent spectral evolution suggests that photolysis of the parent molecules leads to two transient species including η5-CpMn(CO)3 and a previously unreported intermediate. These reactive intermediates are solvated within a few picoseconds. The initial solvation of the nascent species through either the ethyl moiety or the Si—H bond of the solvent partitions the reaction into two channels of

Figure 1. Transient difference spectra in the CO stretching region for CpMn(CO)3 in neat triethylsilane at −10, 33, 66, 200, and 660 ps following 295-nm UV photolysis. The weak, broad bleaches in the regions 1900−1937 and 2010−2015 cm−1 can be attributed to the dissociation of naturally abundant 13CO ligands from CpMn(CO)3 (ref 33). The last panel is an FTIR difference spectrum before and after UV photolysis at 308 nm. Notice that the absorption cross-section of the product (B) is much smaller than that of the parent molecule (A). The large absorption cross-section of the parent CO bands and the solvent Si—H band (∼2100 cm−1) made it very difficult to access some regions of the spectrum under the experimental conditions. A broad, wavelength independent background signal from CaF2 windows has been subtracted from the transient spectra and kinetics.

Figure 2. Kinetics (solid lines) of CpMn(CO)3 in neat triethylsilane after 295-nm UV photolysis at (A) 2028 cm−1, the parent molecule CO stretch, (B) 1977 cm−1, the CO stretch of the silyl adduct CpMn(CO)2(H)(SiEt3), (C) 2002 cm−1, and (D) 1892 cm−1. The wavelengths were chosen to minimize overlap with adjacent peaks. The time constants for the exponential fits (dashed lines) are shown in the graph.

Figure 3. A proposed reaction mechanism for the photochemical Si—H bond activation of Et3SiH by CpMn(CO)3. Suggestive chemical structures are in brackets.

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† Disparate time scales. One channel involves a dissociative rearrangement to form the final adduct (pathway II, Figure 3), while the other channel includes a direct addition of the Si—H bond to the new intermediate, possibly a ring-slipped η4 dicarbonyl (pathway I, Figure 3). Solution of η5-CpMn(CO)3 and the new intermediate through the ethyl group of Et3SiH gives rise to a pair of bands at 1892 and 1957 cm−1 (D, Figure 2A).
are kinetically coupled (pathway IIb, Figure 3). The identity of the constant is greater than the bleach recovery time of A it is very likely that the with the second CO stretching band buried in the weak, broad (Figure 2D), and maintains the intensity up to ∼1 ns. On the other hand, the new transient species C shows a rise time of 23 ± 2.3 ps and a decay time of 90 ± 6.7 ps (Figure 2C). While the 23-ps component of both C and D is consistent with vibrational relaxation, the similarity between the decay of C (90 ps) and the rise time of D (89 ps) indicates that C and D are kinetically coupled (pathway Iib, Figure 3). The identity of C cannot be a vibrationally excited A since the latter time constant is greater than the bleach recovery time of A. However, it is very likely that the C band is due to a dicarbonyl species with the second CO stretching band buried in the weak, broad bleach (1900–1937 cm⁻¹). Considering its ∼45 cm⁻¹ blue-shift from the higher energy band of D and the chemical reactivity of the electron donating C₃ ligand, we tentatively assign C as an ethyl-solvated η⁵ dicarbonyl. This assignment is consistent with the observed 30 cm⁻¹ blue-shifting of the CO stretching frequency resulting from lowering of the hapticity of η⁵-Tp*Rh(CO)₂ (Tp⁺ = tris-(3,5-dimethylpyrazolyl)borato) to form η⁵-Tp*Rh(CO)₂.Cl₄. With this assignment, the ∼90-ps component can be related to re-chelation from an η⁵ to an η⁶ species (pathway Iib, Figure 3).

Eventually, on a time scale > 1 ns as indicated by the absence of D in the static difference FTIR spectrum (bottom panel, Figure 1), D must further rearrange to form the product. For this rearrangement, two mechanisms have been proposed which are the “chain-walk” mechanism and the “dissociative” mechanism. The chain-walk mechanism was first proposed to account for the observed ∼100-ps rearrangement from an alkyl-solvated Cr(CO)₅(ROH) to the more stable hydroxyl-solvated Cr(CO)₅(HOR), where ROH is 1-propanol. If this is the case in our study, assuming that complexed Et₃SiH migrates from the terminal carbon of one ethyl group to the silicon atom, one would expect the rearrangement to be complete within 100 ps. However, the observed decay time of D is longer than 100 ps, suggesting that a “dissociative” mechanism is dominant. In such a pathway, CpMn(CO)₂(Et₃SiH) thermally dissociates slowly into a loosely bound CpMn(CO)₂Cl⁺(Et₃SiH) complex, allowing the metal center to interact with the Si–H bond of possibly another solvent molecule. The minimum activation energy for such a dissociative process is then expected to be determined by the complexation enthalpy of a CpMn(CO)₂Cl⁺ and an alkyl group, which is estimated to be ∼8 kcal/mol. At room temperature, this barrier height corresponds to a reaction time scale of ∼120 ns. The observed rearrangement time (> 1 ns) in this study therefore supports the “dissociative” mechanism (pathway II, Figure 3).

Potentially, the bare η⁵ species may also be solvated through the Si–H bond of the solvent and lead to the product η⁵-CpMn(CO)₂(H)(SiEt₃) on a time scale similar to the decay of C, when the complex changes its hapticity from η⁵ to η⁶ thus providing sufficient electron density for the activation process. Indeed, the product band (B, Figure 1) exhibits a rise time of 71 ± 5.4 ps (Figure 2B), indicating that the Si–H bond may be activated by direct solvation through the Si–H bond of the solvent (pathway I, Figure 3). Furthermore, if the activation barrier of a Si–H bond is comparably small, the apparent rate determining step would be the dissociative rearrangement from D to B. Our measured rates for the formation of B are also consistent with the observation that the overall enthalpy of activation is dominated by the enthalpy of dissociating the solvent from the reaction site, and that the transition state consists of a loosely bound R₂SiH.

In the light of the above discussion, the overall reaction mechanism is summarized in Figure 3. Upon UV excitation, A may lose one CO ligand to form η⁵-CpMn(CO)₂, or lose one CO ligand and at the same time undergo a change in its hapticity to η⁶ species; both dicarbonyls are solvated within a few picoseconds. Solvation of the nascent η⁶ species via the Si–H bond of the solvent leads to the activated product on a time scale of 71 ps (pathway I). Solvation of the η⁵ and η⁶ dicarbonyls through the ethyl groups of the solvent results in C and D, respectively, where C evolves to form D on a time scale of 90 ps (pathway II). Finally, D rearranges dissociatively to form the product on a time scale greater than 1 ns.

This work represents the first study of Si–H bond activation at room temperature with ultrafast infrared spectroscopic methods, which are proving to be general and powerful means for studying complex chemical reaction dynamics in condensed phases. Our results suggest that the formation of η⁵-CpMn(CO)₂(H)(SiEt₃) is partitioned by the initial solvation into two possible pathways: (1) formation through a new intermediate, possibly a photogenerated ring-slippped species, which decays to form the product on a time scale of about 71 ps; and (2) formation through an ethyl-solvated dicarbonyl species CpMn(CO)₂(Et₃SiH), which eventually dissociatively rearranges to form the product on a time scale greater than 1 ns. This observation is consistent with the low reaction barrier for Si–H bond activation, in sharp contrast to the ∼10 kcal/mol barrier in activating an isoelectronic C–H bond.

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(17) Hill, R. H.; Wrighton, M. S. Organometallics 1987, 6, 632.
(18) The gas-phase CO stretch frequency of the monocarbonyl CpMn(CO) (CO) has been reported to be 1948 cm⁻¹. Zheng, Y.; Wang, W.; Lin, J.; Shen, Y.; Fu, K.-I. J. Phys. Chem. 1992, 96, 7650.
(20) Presently, we do not know the detailed structure of this intermediate C. Nevertheless, in a separate experiment on CpMn(CO) (CO) in neat n-pentane, a transient absorption at 2000 cm⁻¹ with similar kinetic behavior was observed, which supports our assigning C as an ethyl solvate. With these data, however, we cannot exclude possible involvement of other electronic states in explaining the intermediate C. Metastable triplet states have been observed for Fe and Co complexes (refs 21 and 22), and experimental evidence as well as theoretical modeling (ref 23) suggests that transition metal complexes in electronic states of different multiplicity may assume different geometry, which in turn may affect the vibrational frequencies.
(24) Generally, the CO stretching frequency of a metal carbonyl complex reflects the charge density on the metal center: the less charge the metal center has to back donate to CO π* orbitals, the higher the CO stretching frequency will be. Therefore, the 45 cm⁻¹ blue-shift implies an electron deficient metal center for C.