

Femtosecond IR Studies of Alkane C–H Bond Activation by Organometallic Compounds: Direct Observation of Reactive Intermediates in Room Temperature Solutions

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The photochemistry of transition metal complexes capable of undergoing oxidative addition with carbon–hydrogen bonds has been intensely studied^{1,2} since its first discovery.^{3,4} This type of reaction is commonly thought to begin by the initial dissociation of a ligand from the metal complex to form a coordinatively unsaturated intermediate. This reactive species then forms an intermediate solvate which subsequently undergoes C–H bond oxidative addition.¹ The first step of this mechanism is supported by the observation of monocarbonyl intermediates such as Cp*Rh(CO) in the gas phase⁵ and its solvated forms in the liquefied rare gases Kr and Xe⁶ detected by microsecond time-resolved IR spectroscopy. Due to its rapid rate, the subsequent C–H bond activation step is not well understood. The low quantum yield (~1%) for loss of CO in the well-studied model compounds Cp*M(CO)₂ (M = Rh, Ir)⁷ has hindered the direct femtosecond and picosecond time-resolved studies of the bond activation in room temperature alkane solution.^{8,9} Our recent study on this system attributes the origin of the low quantum yield to the involvement of short-lived nondissociative excited states.⁹

In this communication, we report the first femtosecond time-resolved IR spectroscopic study of the C–H bond activation reaction of Tp*Rh(CO)₂ (Tp* = HB–Pz₃*, Pz* = 3,5-dimethylpyrazolyl) in room temperature alkane solution. The relatively high C–H activation quantum yield of 30%¹⁰ for this compound has enabled us to detect several very short-lived transient intermediates that are formed during the overall C–H bond activation process. These experiments were performed with our recently completed 30 Hz femtosecond IR spectrometer with 200 fs time resolution.¹¹ The sample was pumped by a 16 μJ UV pulse at 295 nm, and the subsequent changes of the IR absorption in the CO stretching mode region were probed as a function of both time and wavelength. In order to ensure that all signals were due to population dynamics, pump–probe polarizations were set at the magic angle (54.7 deg). Tp*Rh-

(CO)₂ was synthesized according to a published procedure¹² and fully characterized by conventional spectroscopic methods. The sample solution, degassed and sealed under a N₂ atmosphere, was flowed through an air-tight cell to ensure that each laser pulse probed a fresh volume of sample.

Figure 1 shows the transient difference IR spectra of Tp*Rh(CO)₂ in cyclohexane at –10, 10, 66, 200, and 660 ps. Similar spectral evolution was also observed in *n*-pentane solution. The last panel in Figure 1 is an FTIR difference spectrum of the sample in *n*-pentane after exposure to about 30 UV pulses at 308 nm from an excimer laser. The negative CO stretching bands at 1981 and 2054 cm⁻¹ indicate the depletion of the parent molecule while all positive absorption bands correspond to the creation of new species. Detailed kinetics of the spectral features in *n*-pentane were measured up to 1 ns as shown in Figure 2. A broad wavelength-independent background signal from CaF₂ windows has been subtracted from both the transient spectra and kinetics.

As shown in Figure 1, the bleaches at 1981 and 2054 cm⁻¹ partially recover within 66 ps. In addition, the detailed kinetics of the bleach at 2054 cm⁻¹ are shown in Figure 2a. About 50% of the bleach recovers with a 70 ps time constant while the other half stays constant until ca. 1 ns, the longest delay time that can be achieved with our translation stage. This partial recovery is slightly smaller than the expected 70% recovery based on the reported 30% quantum yield.¹⁰ This difference suggests that there is a fast reformation of the ground state parent molecule through the ultrafast geminate recombination of the CO and monocarbonyl species and/or radiative and radiationless decay from the excited state.¹¹ It is important to note, however, that the 70 ps recovery time is not necessarily an indication of the time scale of these processes. It can also reflect the vibrational relaxation of the rapidly formed hot ground state molecules.

The spectrum at 10 ps shows absorption bands at 1972, 1958, and 1945 cm⁻¹. These bands are assigned to the $\nu = 0-1$, $1-2$, and $2-3$ transitions, respectively, of the CO stretching mode of an intermediate. Photoproducts with vibrationally excited CO stretching modes have been observed in the photolysis of other metal carbonyls such as M(CO)₆ (M = Cr, W, Mo).^{11,13} The observed anharmonic shift of about 13 cm⁻¹ is also similar to those of other metal carbonyls.¹³⁻¹⁵ The time scale for the vibrational cooling of this intermediate in *n*-pentane is found to be about 23 ps by monitoring the rise time of the signal at $\nu = 0-1$ transition frequency as shown in Figure 2. The spectrum at 66 ps shows that the vibrationally deactivated intermediate has only one absorption band at 1972 cm⁻¹, in the spectral region from 1900 to 2075 cm⁻¹. This species decays to form a new intermediate with a single absorption band at 1990 cm⁻¹. We assign the absorptions at 1972 and 1990 cm⁻¹ to the $0-1$ transition of two subsequently formed monocarbonyl intermediates. These appear in the same spectral region as the monocarbonyl species Tp*Rh(CO) observed in low-temperature Ar and CH₄ matrices (1968 cm⁻¹).¹⁶

The Tp*Rh(CO) monocarbonyl intermediate at 1972 cm⁻¹ decays with a time constant of 200 ps to form the more stable monocarbonyl species at 1990 cm⁻¹ as shown in Figures 1 and 2b,c. The spectral shifts for the monocarbonyl species are ca. 18 cm⁻¹ in both *n*-pentane and cyclohexane. Although the detailed solvation structures of the two monocarbonyl species are not known, there are two possible explanations for the

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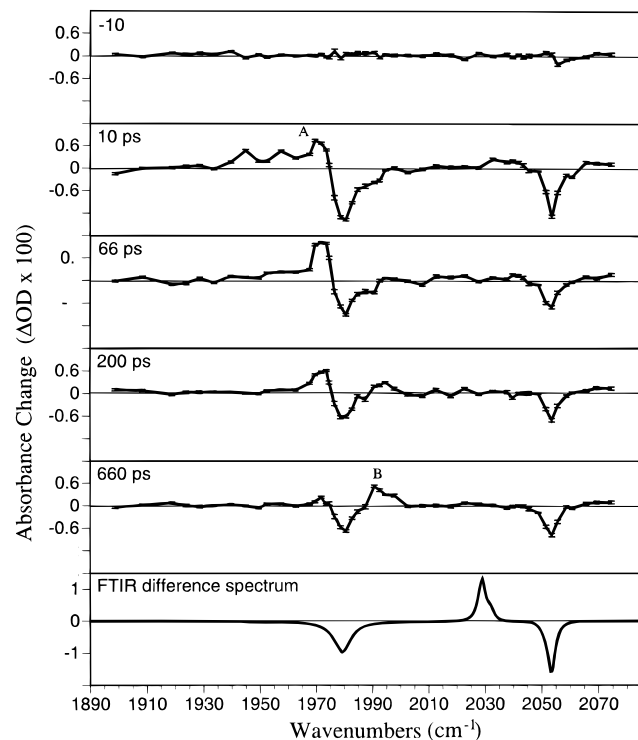


Figure 1. Transient difference spectra in the CO stretching region for $\text{Tp}^*\text{Rh}(\text{CO})_2$ in cyclohexane at -10, 10, 66, 200, and 660 ps after 295 nm UV photolysis. The last panel is a FTIR difference spectrum before and after UV photolysis at 308 nm.

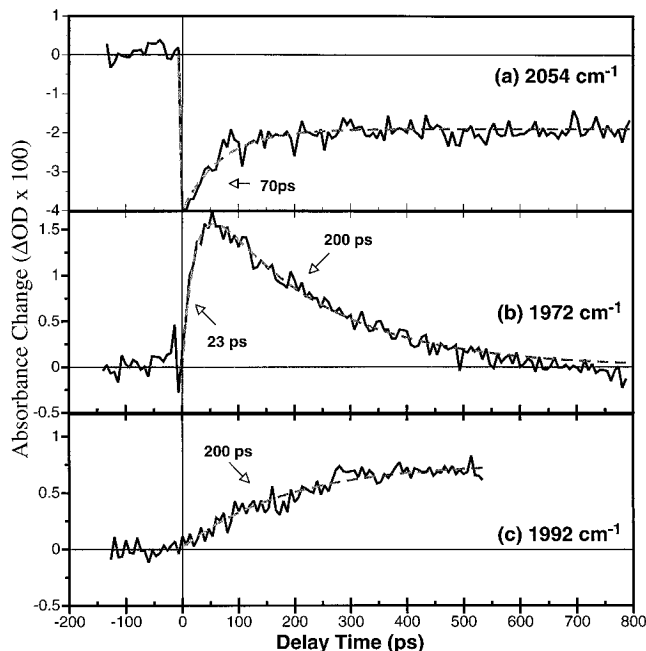


Figure 2. Kinetics of $\text{Tp}^*\text{Rh}(\text{CO})_2$ in *n*-pentane after 295 nm UV photolysis at (a) 2054 cm^{-1} , the parent molecule CO stretch, (b) 1972 cm^{-1} . The time constants for the exponential fits (the dashed line) are shown in the graphs.

observed spectral shift. One possibility is that the species at 1972 cm^{-1} is only weakly solvated, but then undergoes intramolecular rearrangement to form a more stable solvated complex at 1990 cm^{-1} . A similar time scale for the rearrangement of solvation structure was observed for $\text{Cr}(\text{CO})_5$ in alcohols, in which the initial solvation of the unoccupied site occurred within 1–2 ps,^{17–19} while the exchange from the less-stable solvation structure, $\text{Cr}(\text{CO})_5(\text{ROH})$, to the more stable one, $\text{Cr}(\text{CO})_5(\text{OHR})$, took about 100 ps in propanol.^{18,19} Another possible, although less likely, explanation is that the

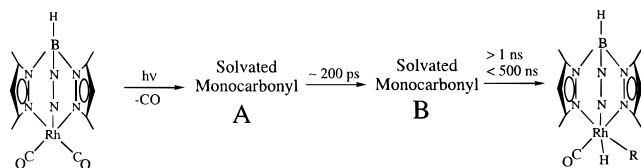


Figure 3.

initially formed species at 1972 cm^{-1} is in a triplet state which decays back to the singlet ground state (at 1990 cm^{-1}) with a 200 ps time constant. Long-lived triplet states have been observed previously in organometallic compounds of Fe^{20} and Co^{21} . We do not understand why this change in solvation results in a large blue shift in the CO stretching mode, in view of the fact that for most solvated monocarbonyls different solvents only give rise to spectral shifts of a few wavenumbers. For example, for $\text{Cp}^*\text{Rh}(\text{CO})$ in Kr and cyclohexane, a 1 cm^{-1} shift was observed.⁶ It is possible that an unknown change in solvation structures for Tp^*RhCO in alkanes results in a large decrease in electron density at the metal center.

The C–H bond activated alkyl hydride product $\text{Tp}^*\text{Rh}(\text{CO})(\text{R})(\text{H})$ ^{10,22} has a single CO stretching band at 2032 cm^{-1} as shown in the FTIR spectrum. No final C–H activated product is observed within 1 ns, although a separate experiment on a slower time scale showed that its formation was complete within the instrument response time of ca. 500 ns. On the basis of our measurement, C–H bond activation occurs between 1 and 500 ns, corresponding to a free energy of activation $\Delta G^\ddagger = 5.2\text{--}8.9$ kcal/mol using transition state rate theory for a unimolecular reaction.²³ This is similar to the ΔG^\ddagger value of 7.2 kcal/mol for the C–H activation reaction by $\text{Cp}^*\text{M}(\text{CO})_2$ ($\text{M} = \text{Ir}, \text{Rh}$) at room temperature extrapolated from the ΔG^\ddagger value determined by a low-temperature kinetics study in liquefied rare gas.⁶

Our experiment represents the first direct observation of the reactive solvated monocarbonyl intermediate species that form in the C–H oxidative addition reactions at room temperature in alkane solution. A summary of our results is shown in Figure 3. Currently, spectra after 1 ns are being measured to directly study the actual bond activation step. Measurements in other solvents are also planned to elucidate the structure of the reactive intermediates and to establish the relationship between the properties of the solvents and the rates of C–H bond activation.

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