The Mechanism of a C–H Bond Activation Reaction in Room-Temperature Alkane Solution

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Chemical reactions that break alkane carbon-hydrogen (C–H) bonds are normally carried out under conditions of high temperature and pressure because these bonds are extremely strong (∼100 kilocalories per mole), but certain metal complexes can activate C–H bonds in alkane solution under the mild conditions of room temperature and pressure. Time-resolved infrared experiments probing the initial femtosecond dynamics through the nano- and microsecond kinetics to the final stable products have been used to generate a detailed picture of the C–H activation reaction. Structures of all of the intermediates involved in the activation reaction of Tp*Rh(CO)(5) (Tp* = HB–Pz3*, Pz* = 3,5-dimethylpyrazolyl) in alkane solution have been identified and assigned, and energy barriers for each reaction step from solvation to formation of the final alkyl hydroxy product have been estimated from transient lifetimes.

Since the initial discovery that the strong C–H bonds in alkanes undergo oxidative addition to certain transition metal complexes, the quest to understand and utilize this “C–H activation” reaction (Fig. 1, A and B) has been the focus of intense research effort (1). Insights into the individual steps involved in metal-mediated C–H activation reactions have been obtained from spectroscopic techniques with microsecond time resolution, with the goal of identifying the reaction intermediates (2, 3). However, the extremely rapid reaction rate prevents these established methods from monitoring the earliest kinetics at room temperature and requires that the experiments be performed in the gas phase (4), in liquefied noble gases (5), or in low-temperature matrices (2, 6) to slow down the reaction.

In the gas phase, photoysis of CpRh(CO)2(Cp = C5H5) yields the highly reactive CpRhCOC, which reacts with alkanes at rates close to the gas kinetic values (Fig. 1A) (4). Low-temperature matrix work also showed the formation of CO-loss products (2, 6). In liquid krypton solution, the solvated complex Gp*Rh(CO)5Kr (Gp* = C5Me5, Me = methyl) is the first species observed. The alkane must then displace Kr before the final activation step can take place (5). These experiments established that the first step involves loss of a CO ligand to generate a coordinatively unsaturated intermediate. It is difficult, however, to generalize the results to room-temperature neat alkane solution because of the extreme changes in reaction conditions. In contrast to earlier work, our goal has been to study the reaction under the most relevant conditions, room-temperature alkane solution. To accomplish this, and to overcome the reaction-rate measurement limitations inherent in microsecond spectroscopy, we used ultrafast spectroscopy with picosecond (7) and femtosecond (8) time resolution, which allows access to the intramolecular processes that take place on time scales faster than diffusion.

The relatively low quantum yield of ∼1% (9) for activation in the CpM(CO)2 (M = Rh, Ir) system made ultrafast infrared (IR) observation of the reactive intermediates in this reaction impossible (10). To better understand the origin of the low quantum yield, we recently investigated the ultraviolet-visible spectroscopy of a C–H activating complex (7). In cyclohexane and n-pentane, ∼99% of the molecules were directly promoted to a nondissociative excited state. As a result, relaxation back to the ground state was a much more favorable process than CO loss.

Identification and subsequent understanding of the reaction intermediates are required to build a detailed picture of the overall bond-activation reaction. In our initial study of the photochemistry of C–H activation, we used ultrafast IR spectroscopy to monitor the reaction with Tp*Rh(CO)(5) (Tp* = HB–Pz3*, Pz* = 3,5-dimethylpyrazolyl) (Fig. 1B), taking advantage of its relatively high quantum yield (∼30%) for the formation of activated product (11). In cyclohexane, Tp*Rh(CO)2 shows peaks at 1981 and 2054 cm−1 due to the antisymmetric and symmetric stretching modes of the two CO ligands. Upon irradiation, the static Fourier transform IR (FTIR) spectrum exhibits only a decrease in the intensity of the parent peaks and the corresponding formation of the final C–H activated product at 2032 cm−1 [see figure 1 of (8)]. On the
picosecond time scale, two different monocarbonyl transient species were produced in the reaction in alkane solution. The CO absorption peak associated with the first intermediate was to the red of the 1981 cm\(^{-1}\) parent peak, whereas the second was shifted to the blue. In our earlier work, we reported that the energies of these peaks are 1972 and 1990 cm\(^{-1}\) in cyclohexane.

The first intermediate (herefore denoted A) has a CO absorption at 1972 cm\(^{-1}\) and has been assigned to Tp*Rh(CO)-RH (RH = alkane solvent), a complex between the monocarbonyl and the solvent (8). The time scale for formation of the intermediate is consistent with those associated with solvent complex generation observed in previous studies of CpCo(CO)\(_2\) (12), (acac)Rh(CO)\(_2\) (acac = acetyl acetonate) (10), and M(CO)\(_6\) (M = Cr, Mo, and W) (13, 14). After the CO dissociated from the metal center, the solvent moved in to occupy the empty site on the metal and formed a complex that vibrationally relaxed in 10 to 20 ps (10). The Tp*Rh(CO)\(_2\) molecule shows similar reactivity and forms a new complex that vibrationally cools on a time scale of 23 ps (8). This monocarbonyl solvent complex then converts to the second intermediate, B, on a time scale of 200 ps.

The identity of B is more difficult to assign. There is some experimental and preliminary theoretical evidence to support the postulate that one of the pyrazolyl arms in the Tp*Rh(CO)-RH complex detaches from the metal center after photoexcitation (2, 6). In the Tp*Rh(CO)\(_2\), the three pyrazolyl arms are coordinated to the Rh center to form an \(\eta^3\) complex (Fig. 1B), whereas the dechelated complex would be \(\eta^1\) (Fig. 1C) (15). In room-temperature solution, the Tp*Rh(CO)\(_2\) complex exists as a mixture of \(\eta^1\) and \(\eta^2\) isomers, with equilibrium constant \(K_{eq} = 100\) favoring the \(\eta^1\) species (16). In addition, recent density functional theory calculations (17) indicate that the closely related monocarbonyl complex TpRhCO (Tp = HB-Pz\(_2\), Pz = pyrazolyl) may be stable in an \(\eta^2\)-bound configuration. Static low-temperature matrix studies (2, 6) and ab initio calculations support the blue-shifted position of the CO stretch in \(\eta^2\)-Tp* complexes. Thus, the second intermediate observed in the ultrafast IR spectrum may be an \(\eta^2\)-Tp*RhCO-RH complex. Despite this support, there has been no experimental evidence for the involvement of an \(\eta^2\) species in the early time dynamics of the C-H bond activation reaction at room temperature.

A model chemical system for probing the effect of dechelation on CO stretching frequencies and testing whether intermediate B is an \(\eta^2\) solvent complex is Bp*Rh(CO)\(_2\) (Bp* = H\(_3\)B-Pz\(_2\*)) (Fig. 1D) (2, 6). This complex, with only two pyrazolyl rings attached to the boron atom, is a known stable \(\eta^3\) species. Because it has only two Rh-N bonds instead of three, the CO stretches of this compound are blue-shifted at the \(\eta^1\)-Tp*Rh(CO)\(_2\) complex. Photoinduced loss of CO from Bp*Rh(CO)\(_2\) should produce a monocarbonyl species whose coordination environment is similar to that of the proposed \(\eta^1\)-Tp*Rh(CO)\(_2\) intermediate. Briefly, the Bp*Rh(CO)\(_2\) compound was prepared according to the literature (18) and dissolved in dry cyclohexane (~1.4 mM). The solution was sealed under a nitrogen atmosphere and flowed through a 1-mm IR cell. After irradiation at 295 nm, the spectrum was collected from 1960 to 2090 cm\(^{-1}\) at time delays of ~10, 100, 660 ps (13). The ultrafast IR spectra of Bp* in cyclohexane (Fig. 2) show that at 10 ps, the bleaching of the parent peaks at 2010 and 2080 cm\(^{-1}\) coincides with the growth of another peak at 1992 cm\(^{-1}\). Thus, the spectrum of the \(\eta^2\)-Bp*RhCO matches that of the second intermediate in the Tp*Rh(CO)\(_2\) system. There is, however, no peak at 1972 cm\(^{-1}\) as there is in the Tp*Rh(CO)\(_2\) system, which suggests that the second intermediate in the reaction scheme is an \(\eta^1\)-Tp*RhCO-RH complex in which one of the Rh-N bonds is broken. With this proposed structure for the second intermediate, we have assigned all of the observable species in the ultrafast spectra and can focus on the bond-activation process.

In the Tp*Rh(CO)\(_2\) system, the newly assigned second intermediate was stable to ~1 ns, the longest time we could measure with our ultrafast system, so we could not observe the formation of the final C-H activated product. In order to understand the complete reaction and establish whether other intermediates are involved, we must observe the final bond activation step and link this with the ultrafast dynamics. Previous studies with microsecond...
We then performed nanosecond IR experiments to probe C–H activation of Tp*Rh(CO)₂ in alkane solvents. The nanosecond FTIR system used in this study has been previously reported in detail (20). It consists of a pulsed Nd: yttrium-aluminum-garnet laser to initiate the photochemistry and a modified Bruker IFS88 Step-Scan FTIR spectrometer to record the transient absorptions. Samples in cyclohexane were excited at 355 nm, and their spectra were collected from 1600 to 2300 cm⁻¹. Kinetic traces for transients formed upon UV photolysis, there is no bleach and was not affected.

For the Bp*Rh(CO)₂ system, nuclear magnetic resonance (NMR) and IR studies showed that upon UV photolysis, there is no formation of C–H activated product, consistent with previous work (11). Time-resolved FTIR measurements showed only one peak at 1992 cm⁻¹ due to the monocarbonyl solvent complex and no evidence for the formation of an alkyl hydride (Fig. 5). The solvent complex was stable for longer than 1 ms, but static FTIR spectra showed that it eventually recombined with CO or decomposed into unknown products. The inability of Bp*Rh(CO)₂ to activate C–H bonds suggests that not only is dechelation necessary to provide reactivity at the metal center, but recrrelation is required to stabilize the product that results from the reaction.
Kr–cyclohexane experiments to room temperature (24).

We can combine these data with our earlier ultrafast result to assemble a comprehensive reaction coordinate diagram (Fig. 6). The rhodium dicarbonyl is initially in formal oxidation state I. Upon UV irradiation, the compound loses one CO in less than 100 fs (25) to form a vibrationally hot, coordinatively unsaturated (16-electron) complex, also in oxidation state I. The reactive species generated is quickly solvated in a barrierless reaction and then vibrationally cools in 20 ps (12, 26). All subsequent processes that take place at the Rh center are thermal and do not depend on either the absorption of additional photons or residual photon energy in the complex. The CO stretching absorption of the first detectable solvated intermediate A could be observed at 1972 cm⁻¹, red-shifted from the lowest frequency peak of the parent complex at 1981 cm⁻¹.

Loss of one CO substantially reduces back-bonding from Rh and increases the electron density at the metal center. This change weakens the bonds between the Rh center and the σ-donating Tp* pyrazole ligands and eventually breaks a Rh-N bond. The complex traverses a 4.2 kcal/mol barrier [with \( k = 5.0 \times 10^9 \text{s}^{-1} \) or 1/(200 ps)] and forms the \( \eta^2-\text{Tp}^* \) mono-carbonyl complex B. Removal of the electrons formerly donated to the metal by the now detached arm of the Tp* ligand reduces the electron density at the metal again, shifting the CO absorption to higher frequency (1990 cm⁻¹). Detachment of the pyrazole ring in B increases the coordinative unsaturation of the solvate, making it more reactive toward C–H oxidative addition. The bond-breaking step occurs with a time constant of 230 ns, corresponding to a barrier of ~8.3 kcal/mol, and forms the unstable \( \eta^1 \) C–H-activated complex C. This complex now has the metal center in formal oxidation state III, which reduces its electron density, providing the driving force for rechelation of the dangling pyrazole ring to form the final product, Tp*Rh(CO)(R)(H) (complex D).

Monitoring the C–H bond activation reaction in the nanosecond regime with IR detection has made it possible to establish directly the time scale for C–H bond-activation in room-temperature solution. The final breaking of the C–H bond occurs during the last step of the reaction, 230 ns after photolysis in cyclohexane. Before this bond can be broken, the Tp*Rh(CO)₂ complex must dissipate its initial excess vibrational energy and then break one of the Rh-N bonds. Immediately following the rate-limiting C–H bond-activation step, the Rh-N bond reforms to stabilize the final product. These steps before and after activation provide the structural and electronic environment around the metal center that allows the reaction to occur.

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**Fig. 6.** Proposed mechanism and energy diagram for the C–H activation reaction of Tp*Rh(CO)₂ in alkaline solution. These energy differences are estimates from separate ultrafast and nanosecond experiments. The stabilities of the intermediates are shown relative to each other and are not intended to be absolute.

**REFERENCES AND NOTES**


15. In multidentate organometallic systems such as Tp*Rh(CO)₂, the number of bonds between the ligand and metal is denoted by \( \eta \).


17. S. Zaric and M. B. Hall, personal communication.


23. Using \( k = \frac{1}{\tau} = \frac{1}{(k_BT/\hbar)\text{exp}(\Delta G/k_BT)} \), where \( k_B \) is the rate constant, \( \Delta G \) is the free energy of activation, \( R \) is the gas constant, and \( T \) is temperature.


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