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Direct Observation of a Picosecond Alkane C−H Bond Activation Reaction at Iridium

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The use of metals to cleave (“activate”) alkane carbon−hydrogen bonds holds significant promise for the selective conversion of petroleum into higher-value-added organic compounds.[1−2] Our current understanding of C−H bond activation reactions[3] has benefitted greatly from recent ultrafast kinetics studies on the irradiation of Cp′Rh(CO)$_2$ complexes.[4−11] However, it has proven difficult to study the C−H activation reaction at iridium carbonyl centers using ultrafast infrared spectroscopic techniques. In this paper we report the application of a new, more highly sensitive femtosecond infrared spectrometer that has allowed us to study C−H activation reactions at an iridium center in room-temperature cyclohexane solution. As expected from the selectivity studies and recent theoretical calculations (see below), and in dramatic contrast to the observations made earlier with rhodium, the Ir-mediated C−H activation is exceptionally rapid. It occurs with a time constant in the 2 ps range, suggesting a negligible barrier for C−H activation.

A flowing cell (250 μm path length) containing CpIr(CO)$_2$ (Cp = η^5-C_5H_5) in cyclohexane was excited by a 3 μJ photolysis pulse at 267 nm, and the subsequent IR spectral changes in the CO stretching-mode region were recorded as a function of time ranging from a few tens of femtoseconds to 1 ns.[12] Shown in Figure 1 are the averaged transient IR difference spectra at 0.5−1, 1−5, 5−10, 30−70, 130−300, and 700−1000 ps. Each curve is the average of about 5−10 spectra within that delay time interval to improve the signal-to-noise ratio. For clarity, we have displayed only a few averaged spectra at selected delay time intervals. These spectra have been displaced vertically to facilitate comparison; the dashed lines indicate the zero absorbance change at each delay time. The top panel in Figure 1 shows the static FTIR difference of CpIr(CO)$_2$ in cyclohexane after UV photolysis.

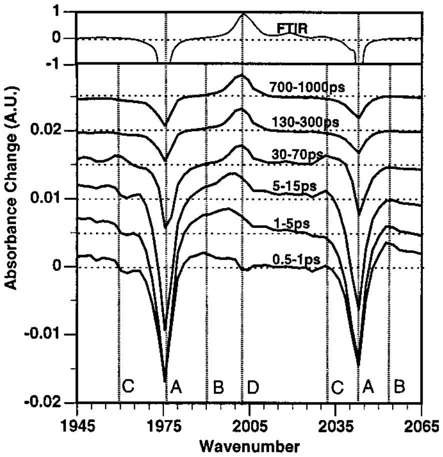
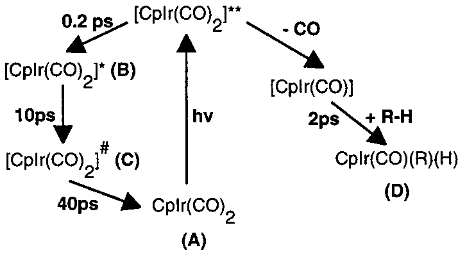


Figure 1. Average transient IR difference spectra for CpIr(CO)$_2$ in cyclohexane at selected delay time intervals after 267 nm excitation.-

The negative peaks (bleach) at the CO stretching positions (1976 and 2043 cm^{-1}; feature A) correspond to the depletion of ground-state parent molecules due to photoexcitation. The spectra at delay times longer than 30−70 ps show a single final product peak (see Scheme 1) at 2002 cm^{-1}(feature D), which is also observed in the static FTIR difference spectrum. This long-lived product is assigned to the C−H bond activated complex CpIr(CO)(R)(H). This assignment is consistent with a previously measured frequency of about 2005−2009 cm^{-1} for CpIr(CO)(CH$_3$)(H) in low-temperature matrices.[13,14] Before that, there are additional peaks at 1991 and 2050 cm^{-1} (feature B) as well as 1958[15] and 2030 cm^{-1} (feature C) on the higher- and lower-frequency side of the parent CO stretching bands, respectively. As discussed below, these observations are consistent with the operation of the two-channel photochemical process illustrated in Scheme 1. One pathway leads to an electronically excited, non-dissociative state of dicarbonyl (B), which returns to the ground state to form vibrationally excited parent molecules (C) and eventually parent molecules (A). The other leads to a CO-dissociative state that ultimately gives C−H activation product D.

Scheme 1. A Schematic for Different Processes Resulting from 267 nm Excitation of CpIr(CO)$_2$ in Cyclohexane



To facilitate the assignment of these intermediates, their formation and decay kinetics were also compared (see Figure 2

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(3) It is now well established that C−H bond activation involves the initial fragment, Cp′Rh(CO) (Cp′ = Cp or Cp*, Cp = η^5-C_5H_5, Cp* = η^5-C_5Me_5), generated on irradiation of the corresponding dicarbonyl complex. In room-temperature cyclohexane solution, the solvate, CpRh(CO)(cyclohexane), is formed with a time constant of less than 1 picosecond (ps),[10] which, once vibrationally cooled, undergoes conversion to CpRh(cyclohexyl)(H) on the nanosecond to microsecond time scale.[9,10] The barrier for C−H bond activation in Cp*Rh(CO)(alkane) complex in liquid rare gas was found to depend on the nature of the alkane[11] and contains significant contribution from both enthalpy (2.7−4.6 kcal/mol) and entropy (−9 to −16 cal/mol/K).[5,11]

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in Supporting Information). The bleach (feature A) recovery kinetics at 2043 and 1976 cm^{-1} (not shown) were well-fit to a single-exponential recovery time of 40 ± 5 ps. The band at 1991 cm^{-1} (feature B) has an approximately 0.2 ps rise time and a decay time of about 12 ps. The absorption at 2031 cm^{-1} (feature C) increased with a 9ps time constant to become an absorption peak and subsequently decayed to 0 with a time constant of 40 ps. The final product absorption band at 2002 cm^{-1} (feature D) was formed with a rise time of 2 ps.

We first consider the nondissociative channel, since that is the one for which transient intermediates are detectable. As shown in Figure 1 about 82% of the bleach at 1976 and 2043 cm^{-1} was recovered within 200 ps with a 40 ps time constant. The recovery of bleach on this time scale suggested that 82% of the excited molecules proceeded through a nondissociative pathway. This recovery time contains the contributions of both electronic relaxation to the ground state as well as the subsequent vibrational relaxation of the hot ground-state molecules. The measured 40 ps recovery time of the bleach is identical to the decay of intermediate C, the red-shifted peaks at 2031 cm^{-1} and 1958 cm^{-1} (result not shown). We propose that these peaks are due to vibrationally hot parent molecules generated through decay of the nondissociative excited state.[10,12,16,17] Similar spectral evolution was observed in our previous study of the photolysis of CpRh(CO)$_2$ in cyclohexane, in which a 60 ps bleach recovery was observed.[10]

The hot ground-state molecules (intermediate C) were formed with a 10 ps time constant. This formation time corresponded well with the decay of intermediate B, suggesting that B is the immediate precursor. As shown in Figure 1, intermediate B, with absorption peaks at around 2050 and 1991 cm^{-1}, blue-shifted from the ground-state CO stretch peaks, was formed promptly (about 0.2 ps) after the excitation of the parent molecules. We believe that this is an electronically excited (nondissociated) state of CpIr(CO)$_2$. The detailed nature of this excited state is not known, but its blue-shifted CO stretching bands relative to those of the ground state indicate strengthened CO bonds.

The remaining 18% loss of the parent molecules can be attributed to the CO extrusion channel, since no long-lived nondissociative excited states were present after 200 ps. This result indicated a quantum yield of 0.18 for CO dissociation and photoconversion from CpIr(CO)$_2$ to CpIr(CO)(R)(H) at 267 nm excitation. A previous study reported a much smaller quantum yield of a few percent for the same molecule at 366 nm excitation.[18] These results suggest an excitation wavelength-dependent quantum field for CO dissociation, which has been reported for CpRh(CO)$_2$.[19]

The reactive channel led to the final CpIr(CO)(R)(H) product that exhibited only one new metal carbonyl IR stretching band at 2002 cm^{-1}. The formation of the product peak is well fit by a 2 ps exponential rise, suggesting that the coordinatively unsaturated CpIr(CO)(RH) alkane solvate, produced by photolysis and formed on the subpicosecond time-scale, can undergo conversion to the C−H activation product CpIr(CO)(R)(H) with almost no activation barrier. This formation time corresponds to only a few collisions at room temperature in solution. In a previous study of the photolysis of CpIr(CO)$_2$ in matrices, a CO stretching band at 1954 cm^{-1} was assigned to naked η^5-CpIr(CO), and a band at 1985 cm^{-1} was attributed to the methane-solvated η^5-CpIr(CO)(CH$_4$) intermediate.[13] We have not identified the analogous precursors to the final products in our system because of broadened spectra, spectral overlap, and poor data quality at early time.[20]

To our knowledge, the observed 2 ps formation time of the C−H bond activated product CpIr(CO)(cyclohexyl)(H) is the first report of a picosecond alkane C−H bond activation reaction in room-temperature solution. In our recent study of alkane C−H bond activation by CpRh(CO), no bond activated products were observed on the less than 1 ns time scale.[10] Consistent with this, a recent study of a related Rh complex, Tp*Rh(CO)$_2$ (Tp* = HB-Pz$_3$*, Pz* = 3,5-dimethylpyrazolyl), reported that the C−H activation at Rh takes place even more slowly, with a time constant of about 200 ns and a free energy of activation of 8.8 kcal/mol in room-temperature cyclohexane.[9] Therefore, the rate of the C−H activation reaction at iridum reported here is at least 3 (and possibly 5) orders of magnitude faster than that for C−H activation by corresponding Rh complexes.[9,10]

Our results are consistent with a large body of theoretical calculations on the reaction between CpM(L) and various molecules X−H.[21−25] In two recent calculations,[24,25] the reactivity of CpM(CO) (M = Rh, Ir) toward a C−H bond in CH$_4$ was compared. Both calculations predicted a much smaller activation barrier for CpIr(CO) than for CpRh(CO). Ziegler et al.[24] predicted a 8.8 and 2.4 kcal/mol for CpRh(CO) and CpIr(CO), respectively. Su et al.[25] predicted an activation barrier of 10 kcal/mol and −0.6 kcal/mol for CpRh(CO) and CpIr(CO), respectively. It should be noted a picosecond Si−H bond activation by CpMn(CO)$_2$ was reported recently,[26,27] consistent with an earlier prediction of barrierless Si−H bond activation.[21]

In summary, we have studied the photolysis of CpIr(CO)$_2$ in room-temperature cyclohexane solution. The overall reaction process can be summarized by Scheme 1. The excited CpIr(CO)$_2$ molecules after absorption of a 267 nm photon react through two pathways. About 80% of the molecules relax to a nondissociative excited-state B with a 10 ps lifetime while 20% undergo dissociation to lose a CO ligand, leading to CpIrCO or a solvate of this species. The nondissociative excited state decaysecules (A) with a time constant of 40 ps. The activation of a cyclohexane C−H bond in the CO-dissociative pathway was found to occur with a rate constant of 2 ps, suggesting a negligible activation.

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Supporting Information Available: (1) Kinetics at selected wavelengths and (2) experimental methods (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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