

From Femtosecond Excited-State and Dissociation Dynamics to Nanosecond Reaction Kinetics: Following C-H Bond Activation with X-rays

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Abstract: Using ultrafast X-ray absorption spectroscopy, we observe how a rhodium carbonyl catalyst is formed on femtosecond timescales and reveal the decisive orbital interactions which facilitate the efficient cleavage of an alkane C-H bond from solution. © 2022 The Author(s)

Understanding the activation of inert bonds is considered one of the “holy grails” of chemistry [1,2]. Consequently, homogeneous catalysis for C-H activation with metal complexes in solution has evolved into an important field. Of particular interest is photochemical C-H bond activation using Rhodium (Rh) carbonyl complexes (see Figure 1). Photo-excitation of these complexes in the UV regime is believed to trigger femtosecond dynamics, which lead to the population of dissociative excited states and subsequent loss of a carbonyl (CO) group. Due to the resulting coordinatively unsaturated metal center, these transient fragments are highly reactive. The metal is thought to act as a catalyst by binding C-H groups of alkane solvents on picosecond timescales and inserting itself between the C and H atoms to ultimately break the C-H bond on a nanosecond timescale [3-5]. Ultrafast infrared spectroscopy with its sensitivity to molecular structure has been very successful in identifying certain reactants and intermediates for C-H bond activation on pico- to nanosecond timescales [5-8]. With its limited sensitivity to the electronic structure, though, and due to its inability to detect and characterize the initially excited vibrationally hot species on femtosecond timescales, insight into the mechanism of C-H activation has remained elusive to date. It is unclear, in particular, how reactivity towards metal-ligand dissociation and association is determined by sub-picosecond frontier orbital interactions between the metal catalyst and the ligand [9]. Here we used time-resolved X-ray spectroscopy to access the local electronic structure with elemental specificity and sensitivity to the decisive valence orbitals [10] all the way from initial femtosecond excited-state dynamics to nanosecond bond activation to find what it is that ultimately governs the formation of the catalyst and determines its reactivity towards C-H activation.

We have performed time-resolved X-ray absorption spectroscopy (XAS) experiments at the Rh L₃-edge in the femtosecond regime (at the Alvra experimental station of the SwissFEL X-ray laser) as well as in the pico- to nanosecond regime (at the PHOENIX beamline of the Swiss Light Source synchrotron) to probe metal-ligand bonding in the initially photoexcited states and in the decisive transient intermediates of a Rh-carbonyl catalyzing C-H activation. The Rh 2p → 4d core-excitation of the XAS process directly probes the essential valence orbitals, which determine metal-ligand bonding during the femtosecond formation of the photo-activated catalyst and as the covalent interactions of the Rh center with incoming C-H groups evolve. This approach allowed us to identify hitherto undetected species on ultrafast timescales and to determine, at the level of metal-ligand orbital interactions, how their varying covalency modulates reactivity and functionality for C-H activation.

Specifically, we have studied CpRh(CO)₂ (Cp = cyclopentadienyl), a prototypical complex for photochemical C-H bond activation, in an octane solution. We find that photo-excitation of the complex with 266 nm results in the appearance of transient intensity in the pre-edge region (see Figure 2), whose temporal evolution within the first 10 ps can be modeled with a biexponential decay. We tentatively assign the first time constant to the decay of an electronic excited state of CpRh(CO)₂, which transforms into the free CpRh(CO) fragment via CO dissociation on a timescale of ~400 fs. The second time constant of ~2.5 ps then corresponds to the formation of the essential metastable CpRh(CO)-alkane complex where a C-H group binds to the reactive Rh center. Finally, this species proceeds to cleave off the alkane C-H bond by forming a new species of the form CpRh(CO)-H-R on a timescale of 13 ns (see

Figure 1) in agreement with previous infrared measurements [7]. Our preliminary calculations (not shown) indicate that the pre-edge intensity can be assigned to Rh 2p \rightarrow LUMO transitions, which directly correlate with the orbital interactions of the unsaturated Rh center. Our approach therefore allows to directly probe what Nobel-laureate R. Hoffmann called “the hole on the metal”, an empty d orbital localized on the metal that is formed upon ligand dissociation and that determines the bonding capability of the metal [11]. Once an alkane molecule attaches to the free fragment formed by CO dissociation, the pre-edge is observed to shift to higher energies due to the interactions of Rh and C-H orbitals. The degree with which the hole on the Rh center interacts with the occupied orbitals of incoming C-H groups, has been hypothesized by theory to ultimately facilitate C-H bond cleavage because charge is transferred to antibonding C-H orbitals [9]. We directly probe this here via the Rh 2p \rightarrow LUMO transitions with femtosecond Rh L-edge XAS.

In summary, we have used time-resolved X-ray spectroscopy to reveal the mechanism of photo-induced C-H bond activation with a Rh metal complex. We find previously undetected species and characterize their catalytic properties on ultrafast timescales. With the sensitivity of metal L-edge XAS to the valence electronic structure, we directly reveal, to the best of our knowledge for the first time, the essential frontier-orbital interactions, which make the Rh-carbonyl catalyst reactive and which determine how it activates incoming C-H bonds.

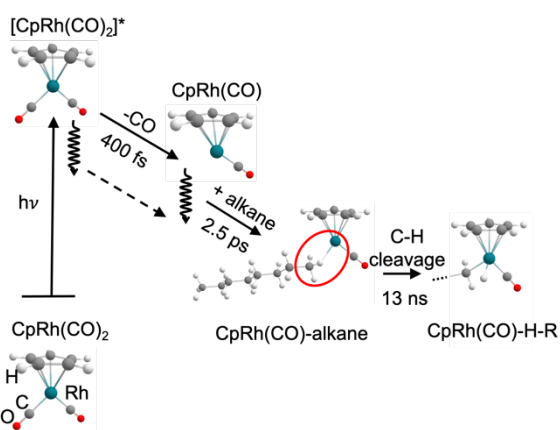


Figure 1 Schematic representation of the C-H activation reaction pathway of photo-excited $\text{CpRh}(\text{CO})_2$ in alkane solution.

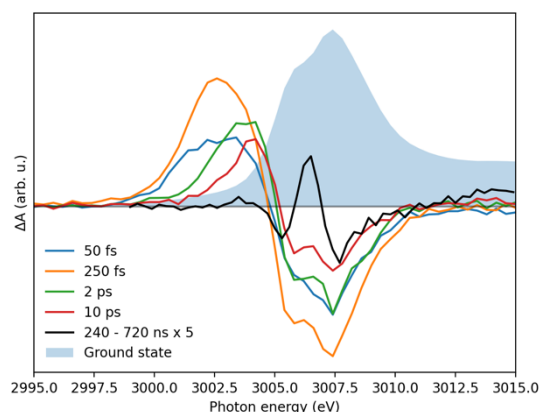


Figure 2 Transient Rh L_3 -edge X-ray absorption spectra of 20 mM $\text{CpRh}(\text{CO})_2$ in octane solution as measured at various delays from the femto- to the nanosecond regime (steady-state spectrum of the ground-state species in shaded grey).

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