Femtosecond Infrared Studies of a Prototypical One-Electron Oxidative-Addition Reaction: Chlorine Atom Abstraction by the Re(CO)5 Radical

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Oxidative-addition is one of the fundamental reactions of organometallic complexes. A comprehensive understanding of the mechanism requires knowledge of the dynamics of all the intermediates. The extremely fast reaction rates, however, have made it experimentally challenging to elucidate the reaction scheme. Femtosecond infrared (fs-IR) spectroscopy, which is capable of “real-time” observation and characterization of the reactive intermediates down to hundreds of femtosecond, offers the possibility of deducing the elementary steps of a photochemical reaction in room-temperature solutions. Recently, this technique has been successfully used to unravel the reaction dynamics on a time scale faster than that of diffusion in the photoinitiated two-electron oxidative-addition reactions of C=H and Si=H bond activation. This communication reports the use of fs-IR spectroscopy to study a prototypical one-electron oxidative-addition. The transition-metal complex under study is the 17-e− (CO)5Re radical, generated by photodissociation of the Re−Re 2 (CO) 10. The 17-e− radical reacts to extract a Cl atom from a chlorinated methane solvent. The reaction may proceed through a strongly solvated 19-e− intermediate, through a charge-transfer intermediate, or through a weakly solvated 17-e− intermediate as shown in Figure 1. This aspect is examined directly for the first time by following the reaction from initiation to completion with 300-fs time resolution. To study the nature of the reaction barrier, the rates are measured along a series of chlorinated methane solutions under ambient conditions. The transition states are studied using density-functional theoretical (DFT) methods.

As shown in the static FTIR in Figure 2d, the final product (CO)5ReClI in neat CCl4 solution exhibits two CO stretching peaks at 1982 and 2045 cm−1. At shorter time delays (40 ns < 2.5 ps) in Figure 2c, there appear five additional bands at 1945, 1985, 1998, 2005, and 2055 cm−1 that are assigned to the equatorially solvated nonacarbonyl species eg-Re(CO)5(CCl4) in agreement with low-temperature studies. On the hundreds of picosecond time scale (Figure 2b), one sees a broad feature centering at around 1990 cm−1, marked by a down-pointing arrow. This spectrum is to be compared with that taken in the chemically inert hexanes solution (Figure 2a), which also exhibits a broad band centering around 1992 cm−1, assigned to the weakly solvated Re(CO)5 radical in hexanes solution. It follows that the broad feature at 1990 cm−1 on the third panel can be attributed to the weakly solvated Re(CO)5 in CCl4. The similar peak positions of the Re(CO)5 band in CCl4 and hexanes solutions suggests that the Re(CO)5/solvent interactions are of similar magnitude in these two solutions. This conclusion is supported by DFT calculations, which provide a qualitative estimate of the interaction energies for Re(CO)5/CH4 (ca. −0.2 kcal/mol) and Re(CO)5/CCl4 (ca. −0.6 kcal/mol). Furthermore, the calculated weak interaction energy indicates that the mean thermal energy ~0.6 kcal/mol at the room temperature is sufficient to disrupt the formation of a stable complex of the form Re(CO)5(solvent). In other words, a dynamic equilibrium is established for Re(CO)5(solvent) ⇌ Re(CO)5 + solvent, the time scale of which is on the order of collision in liquids (ca. a few picoseconds). This allows the chemically active Re center to undergo recombination reaction with another Re(CO)5 radical to reform the parent Re2(CO)10 molecule. As will be shown later, the aforementioned processes in general occur on a time scale orders of magnitude faster than that of the C−Cl bond activation step, which is in the nanosecond regime.

Figure 3 shows the ultrafast kinetics for the parent molecule at 2071 cm−1 in CCl4 (Figure 3a) and hexanes (Figure 3b).
solutions. The parent kinetics in CCl₄ recovers on two time scales of ~50 ps if fitted to two exponentials. Considering that the photoinitiation step is most likely a direct dissociation (~100 fs) and the fact that no other transient intermediate is observed, the most likely origin for the biphasic recovery is geminate recombination of the Re(CO)₅ pairs. To account for such dynamics, a diffusion model is adopted to reproduce the parent bleach kinetics in all the solvents studied. According to the model, the fast 50 ps component is attributed to a convolution of vibrational relaxation and the probability of reactive collision of the Re(CO)₅ pair within the solvent cage to form the parent Re₂(CO)₁₀. On a longer time scale, the mean separation of the two Re(CO)₅ fragments increases as a result of diffusive motion, thus diminishing the probability of recombination.

In the nanosecond time regime, the Re(CO)₅ radicals that have not undergone geminate recombination (>50%), indicated by the parent kinetics shown in Figure 3, or from the asymptotes of the diffusion model may activate the C–Cl bond to form the final product ReCl(CH₂Cl₂). By monitoring the product kinetics at 2045 cm⁻¹, the time scales for activation are found 1.32 ± 0.06 ns for CCl₄, 128 ± 40 ns for CHCl₃, and 270 ± 60 ns for CH₂Cl₂. These time scales correspond to mean-free-energy barriers ΔG⁰ of 5.35 ± 0.03, 8.03 ± 0.20, and 8.48 ± 0.13 kcal/mol, respectively. The fact that no other intermediates were detected prior to the product formation and that no appreciable CO stretch frequency shift for Re(CO)₅ was observed suggests that the reaction involves only the rate-limiting Cl-atom transfer step without the 19-e⁻ transfer intermediate [(CO)₅ ReCl]. Nor do the results support the idea of a charge-transfer intermediate. Nor do the results support the idea of a charge-transfer intermediate [(CO)₅ Re⁺ Cl⁻] for this reaction. For if this is the case, the positively charged (CO)₅ Re⁺ will exhibit a substantial νCO shift, which was not observed. With the above evidence and the fact that no other intermediates were observed, it is suggested that the reaction be considered as involving only the C–Cl bond activation process. More studies are needed to arrive at a model that is capable of predicting, even qualitatively, the reaction rates from macroscopic parameters such as the strength or electron affinity of the carbon–halogen bond.

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Supporting Information Available: Details of the experiments, the DFT calculations, and the diffusional model for geminate recombination (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

Figure 3. Representative parent bleach kinetics (open circles) of Re₂(CO)₁₀ in (a) neat CCl₄ and (b) hexane solution. Fits to a diffusion model to account for geminate recombination are shown as solid lines. Except for the macroscopic viscosity, identical molecular parameters are used for all the solvents studied (hexanes, and CH₃Clₙ, n = 0, 1, 2).

Figure 4. DFT structures for the final product and transition-state structures. Geometrical parameters are in angstroms for bond lengths and degree for bond angles. Also shown are the imaginary vibrational frequencies associated with each transition state.

simultaneous dissociation of the C–Cl bond and formation of the Re–Cl bond. The structural variation along the series of chlorinated methanes suggests that the transition state becomes more product-like as the number of hydrogen n in CH₃Clₙ increases. For example, the Re–Cl distance in (CO)₅ ReCl(CH₂Cl₂) decreases monotonically from 2.95 (n = 0) to 2.84 (n = 1) to 2.76 (n = 2), and to 2.52 Å for the final product (CO)₅ ReCl. The calculated energy barriers ΔE_p in CCl₄, CHCl₃, and CH₂Cl₂ are respectively 0.86, 3.0, and 8.5 kcal/mol, where the solvent effects are treated self-consistently in the reaction-field approximation.

In summary, femtosecond IR spectroscopy that allows for direct assessment of the roles of the transient intermediates during a reaction continues to demonstrate its ability to elucidate otherwise intricate chemical reaction mechanisms. The present work provides experimental and theoretical evidence that one-electron oxidative-addition of a Cl atom (from chlorinated methanes) to the Re(CO)₅ radical does not involve an appreciable 19-e⁻ intermediate. Nor do the results support the idea of a charge-transfer intermediate [(CO)₅ Re⁺ Cl⁻] for this reaction. For if this is the case, the positively charged (CO)₅ Re⁺ will exhibit a substantial νCO shift, which was not observed. With the above evidence and the fact that no other intermediates were observed, it is suggested that the reaction be considered as involving only the C–Cl bond activation process. More studies are needed to arrive at a model that is capable of predicting, even qualitatively, the reaction rates from macroscopic parameters such as the strength or electron affinity of the carbon–halogen bond.

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