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 class of 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.[3] 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)$_5$Re radical, generated by photodissociation of the Re–Re bond of 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.[4] 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)$_5$ReCl in neat CCl$_4$ solution exhibits two CO stretching peaks at 1982 and 2045 cm^{-1}.[5] At shorter time delays (40 ns < 2.5 μs)[6] 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 *eq*-Re$_2$(CO)$_9$(CCl$_4$), in agreement

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(3) (a) Lian, T.; Bromberg, S. E.; Yang, H.; Proulx, G.; Bergman, R. G.; Harris, C. B. *J. Am. Chem. Soc.* **1996**, *118* (15), 3769–3770. (b) Yang, H.; Kotz, K. T.; Asplund, M. C.; Harris, C. B. *J. Am. Chem. Soc.* **1997**, *119* (40), 9564–9565. (c) Bromberg, S. E.; Yang, H.; Asplund, M. C.; Lian, T.; McNamara, B. K.; Kotz, K. T.; Yeston, J. S.; Wilkens, M.; Frei, H.; Bergman, R. G.; Harris, C. B. *Science* **1997**, *278*, 260–263. (d) Yang, H.; Asplund, M. C.; Kotz, K. T.; Wilkens, M. J.; Frei, H.; Harris, C. B. *J. Am. Chem. Soc.* **1998**, *120* (39), 10154–10165. (e) Asbury, J. B.; Ghosh, H. N.; Yeston, J. S.; Bergman, R. G.; Lian, T. Q. *Organometallics* **1998**, *17* (16), 3417–3419.
(4) (a) Stiegman, A. E.; Tyler, D. R. *Comments Inorg. Chem.* **1986**, *5*, 215. (b) Baird, M. C. *Chem. Rev.* **1988**, *88*, 1217–1227. (c) Tyler, D. R. *Acc. Chem. Res.* **1991**, *24*, 325–331 and references therein.
(5) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97* (8), 2065–2072.
(6) Please refer to the Supporting Information for technical details. All uncertainties reported herein represent one standard deviation.
(7) Firth, H.; Klotzbücher, W. E.; Poliakoff, M.; Turner, J. J. *Inorg. Chem.* **1987**, *26* (20), 3370–3375.
(8) Firth, S.; Hodges, P. M.; Poliakoff, M.; Turner, J. J. *Inorg. Chem.* **1986**, *25* (25), 4608–4610.
(9) The results of extensive DFT calculations for the photochemistry of Re$_2$(CO)$_{10}$ will be described in a separate publication. The interaction energies shown here are gas-phase values.
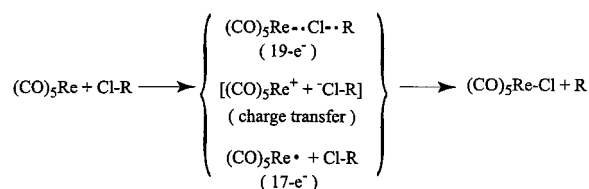(10) Kim, S. K.; Pedersen, S.; Zewail, A. H. *Chem. Phys. Lett.* **1995**, *233*, 500–508.

Figure 1.

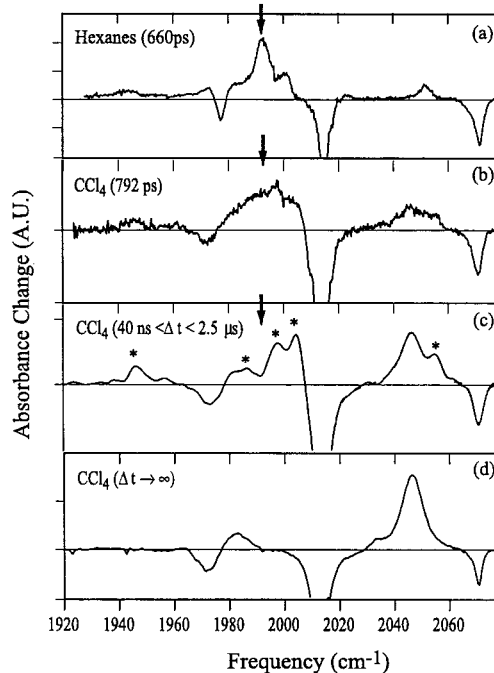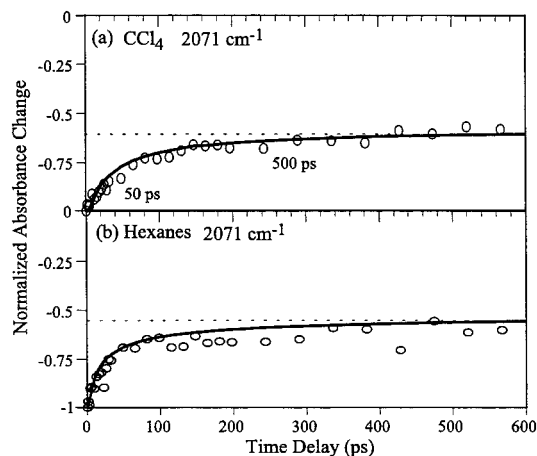**Figure 2.** Transient difference spectra in the CO stretching region for Re$_2$(CO)$_{10}$ in neat CCl$_4$ and hexanes. In panel c, peaks due to Re$_2$(CO)$_9$-(CCl$_4$) are marked with asterisks.

with low-temperature studies.[7] 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 at around 1992 cm^{-1}, assigned to the weakly solvated Re(CO)$_5$ radical in hexanes solution.[8] 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 CCl$_4$. The similar peak positions of the Re-(CO)$_5$ band in CCl$_4$ 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,[9] which provide a qualitative estimate of the interaction energies for Re(CO)$_5$/CH$_4$ (ca. −0.2 kcal/mol) and Re(CO)$_5$/CCl$_4$ (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,[4c] 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 Re$_2$(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 CCl$_4$ (Figure 3a) and hexanes (Figure 3b)

Figure 3. Representative parent bleach kinetics (open circles) of Re$_2$-(CO)$_{10}$ in (a) neat CCl$_4$ and (b) hexanes 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 CH$_n$Cl$_{4-n}$, 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.

solutions. The parent kinetics in CCl$_4$ recovers on two time scales of ~50 and ~500 ps if fitted to two exponentials. Considering that the photoinitiation step is most likely a direct dissociation (~100 fs)[10] 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 adapted to reproduce the parent bleach kinetics in all the solvents studied.[11] 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 Re$_2$-(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 (CO)$_5$ReCl in chlorinated methane solutions. By monitoring the product kinetics at 2045 cm^{-1}, the time scales for activation are found 1.33 ± 0.06 ns for CCl$_4$,[12] 128 ± 40 ns for CHCl$_3$, and 270 ± 60 ns for CH$_2$Cl$_2$. These time scales correspond to mean free-energy barriers $\Delta G^\ddagger$ of 5.35 ± 0.03, 8.03 ± 0.20, and 8.48 ± 0.13 kcal/mol, respectively.[13] 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 suggest that the reaction involves only the rate-limiting Cl-atom transfer step without the 19-e$^-$ nor the charge-transfer intermediates.

To better understand the reactivity, the transition states for the series of reactions were studied using DFT methods. As illustrated in Figure 4, the results show that each transition state can be characterized by a single imaginary frequency that involves
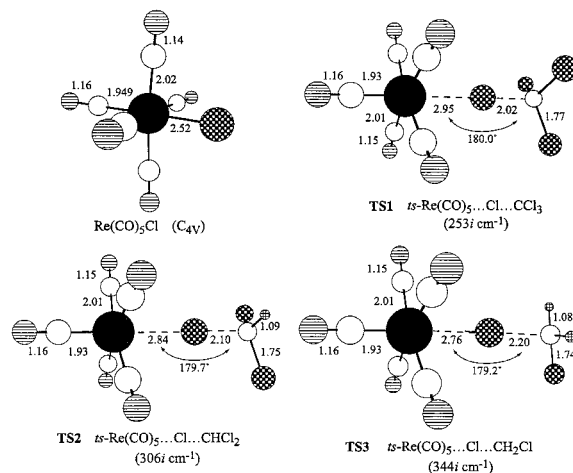
simultaneous dissociation of the C−Cl bond and formation of the Re−Cl bond. The structural variation along the series of chlorinated methanes suggests that the transition state becomes more product-like as the number of hydrogen n in CH$_n$Cl$_{4-n}$ increases. For example, the Re···Cl distance in (CO)$_5$Re···Cl···CH$_n$-Cl$_{3-n}$ 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 the product (CO)$_5$Re−Cl. The calculated energy barriers $\Delta E_0^\ddagger$ in CCl$_4$, CHCl$_3$, and CH$_2$-Cl$_2$ are respectively 0.86, 3.0, and 8.5 kcal/mol, where the solvent effects are treated self-consistently in the reaction-field approximation. The current level of theory, however, does not permit an immediate comparison of the experimental energy barriers to the calculated values. Nonetheless, comparison of the experimental trend and the qualitative trend from the theoretical calculations along the series of chloromethane provides greater insight in understanding the reactivity. The observed trends in the barrier and the transition-state structure are in agreement with Hammond's postulate,[14] which associates a later transition state with a higher energy barrier.

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−R] for this reaction.[15] For if this is the case, the positively charged (CO)$_5$Re$^+$ will exhibit a substantial ν_{CO} 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.[16]

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.

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(11) (a) Naqvi, K. R.; Mork, K. J.; Waldenstrøm, S. *J. Phys. Chem.* **1980**, *84* (11), 1315−1319. (b) Bultmann, T.; Ernsting, N. P. *J. Phys. Chem.* **1996**, *100* (50), 19417−19424. (c) Scott, T. W.; Liu, S. N. *J. Phys. Chem.* **1989**, *93*, 1393. (d) Churchill, M. R.; Amoh, K. N.; Wasserman, H. J. *J. Inorg. Chem.* **1981**, *20* (5), 1609−1611.

(12) This time scale corresponds to a reaction rate of (7.3 ± 0.4) × 10^7 M^{-1} s^{-1}, and is in good agreement with the literature value of (1.8−9.1) × 10^7 M^{-1} s^{-1}, calculated from a set of Arrhenius parameters by: Meckstroth W. K.; Reed, D. T.; Wojcicki, A. *Inorg. Chim. Acta* **1985**, *105*, 147−151.

(13) The energy barriers are calculated using $1/\tau \approx k_{TST} = (k_B T/h)$ exp$(-\Delta G^\ddagger/RT)$, T = 298 K.

(14) Hammond, G. S. *J. Am. Chem. Soc.* **1954**, *77*, 334−338.

(15) There is, however, only a limited extent of charge-transfer character in the calculated transition states (Table 1 of the Supporting Information).

(16) (a) Herrick, R. S.; Herrinton, T. R.; Walker, H. W.; Brown, T. L. *Organometallics* **1985**, *4*, 42−45. (b) Lee, K.-W.; Brown, T. L. *J. Am. Chem. Soc.* **1987**, *109*, 3269−3275.