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Structurally Selective Geminate Rebinding Dynamics of Solvent-Caged Radicals Studied with Nonequilibrium Infrared Echo Spectroscopy

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As two reacting partners approach, kinetic control of intermediate formation and asymmetric branching ratios are governed by subtle interactions that pose significant challenges to experiment and theory. Understanding geminate recombination reactions has been of paramount importance in developing a full mechanistic view of bimolecular processes including ligand rebinding after photodissociation in heme proteins[1] and radical pair rebinding in a solvent cage.[2] More generally, bimolecular reaction dynamics are driven by and are sensitive to both the details of interpair interactions and the complex role of the surrounding solvent, protein, or surface. This communication reports the direct observation—using ultrafast transient nonlinear infrared spectroscopy—of nonequilibrium structural selectivity, thus providing a model for asymmetric chemical reaction dynamics in solution.

Cyclopentadienylmolybdenum(II) tricarbonyl dimer is a dimetal carbonyl complex that exists in two different isomeric forms in polar solvents, *trans* and *gauche* (Figure 1), which slowly exchange on a millisecond time scale.[3] The relative ratios of the two isomers depend on the solvent polarity; the *trans* isomer predominates in nonpolar liquids, whereas polar liquids support both isomers.[4] Similar to other dimetal carbonyl complexes, 400-nm photoexcitation induces a $\sigma-\sigma^*$ transition, leading to homolytic cleavage of the metal−metal bond, generating [CpMo(CO)$_3$] radicals.[5] Bimolecular recombination of these radicals typically shows biexponential behavior, with a fast picosecond component attributed to rebinding inside the solvent cage, and a slow, microsecond component due to diffusion in the bulk solution.[3] Recent ultrafast transient absorption studies in the ultraviolet and visible have examined the fast geminate recombination process. The effects of the size and mass of the radicals on the recombination dynamics, as well as the nature of the solvent, have been extensively studied, and the experimental results have been modeled in terms of solvent-caged radical pairs.[2,6,7] In contrast to electronic spectroscopy, transient IR spectroscopy affords structural specificity, thus offering valuable insight into the rebinding processes lacking in electronic spectroscopy. We present our results on the geminate recombination process obtained using nonequilibrium three-pulse photon echo spectroscopy to monitor the picosecond bleach recovery of infrared bands assigned to the *trans* and *gauche* isomers in a polar solvent. To the best of our knowledge, this is the first ultrafast spectroscopic study of a geminate rebinding reaction using multidimensional infrared spectroscopy.[8,9] Interpretation of the recombination process is facilitated by computing the potential energy along the Mo−Mo bond and rotation angle using electronic structure methods.

Detailed descriptions of the experimental methods and models are provided in the Supporting Information (SI). Briefly, equilibrium 2DIR spectra of [CpMo(CO)$_3$]$_2$ in ethyl acetate were collected using a Fourier-transform 2DIR setup.[10] *UV-pump/2DIR-probe*: Transient-2DIR spectra were collected by applying a 400-nm UV pulse to cleave the Mo−Mo bond before the 2DIR measurement.[11] *UV-pump/DVE-probe*: Transient dispersed vibrational echo (DVE) signals were collected by time-overlapping all three infrared pulses and measuring the homodyne echo spectrum with and without the UV pulse. The transient-DVE measurement is a projection of the transient 2DIR spectrum but benefits from a much faster acquisition time.[12] A full potential energy surface along the Mo−Mo bond distance and the orientation angle that connects the *trans* and *gauche* configurations was computed using electronic structure methods (see SI).

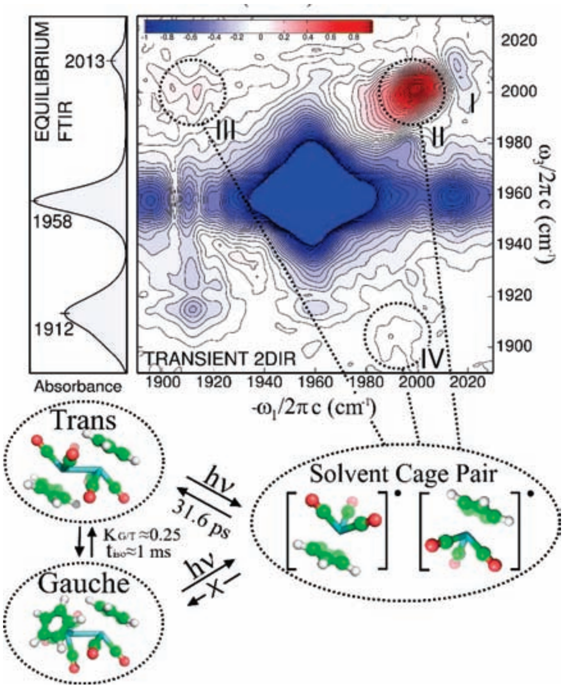

Figure 1. Reaction scheme and transient-2DIR spectrum of [CpMo(CO)$_3$]$_2$ in ethyl acetate at zero waiting time and a UV/IR delay of 5 ps. The red features (circled) are due to the photoproduct radicals.

The linear absorption spectrum of [CpMo(CO)$_3$]$_2$ shows three peaks at 1913, 1958, and 2013 cm^{-1}, with the two low-frequency transitions having contributions from the *trans* and *gauche* isomers with the high-frequency 2013 cm^{-1} peak arising from the *gauche* configuration. This peak assignment was made using the equilibrium 2DIR spectrum as described in the SI. The transient-2DIR spectrum (Figure 1) shows three main diagonal bleaches with corresponding cross peaks and a large diagonal positive peak centered near 1995 cm^{-1}. In this case, cross peaks in the spectrum appear because the transitions share a common ground state (i.e., reside on the same molecule; see SI). Similar to one-dimensional transient-absorption spectroscopy, the bleaches arise from the depletion of parent molecules, and the positive peaks are due to the nascent product species. The high-frequency positive peak (**II**), slightly distorted due to spectral overlap with the 2013 cm^{-1} bleach (**I**), has been assigned to the 17-electron CpMo(CO)$_3$ radical species, obtained by photocleavage of the metal−metal bond. A low-frequency peak centered near 1912 cm^{-1} has also been observed in infrared transient

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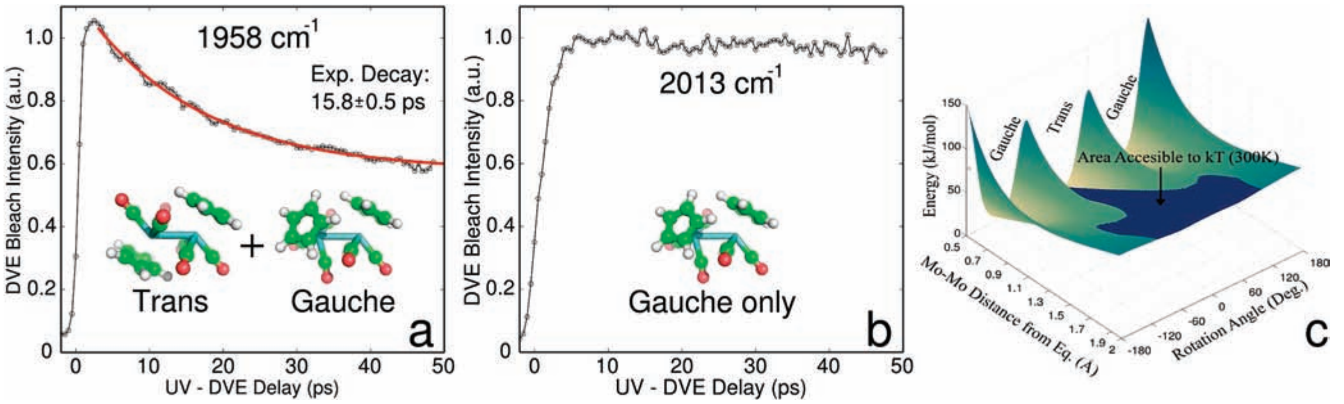

Figure 2. Transient DVE bleach recovery, due to geminate rebinding of the radical fragments, at 1958 cm^{-1} (a) corresponding to the *trans* and *gauche* conformations and 2013 cm^{-1} (b) corresponding to the *gauche* isomer. The red curve represents a single-exponential fit to the data. The insets show the chemical structures of the *trans* and *gauche* conformations obtained from electronic structure computations. (c) Potential energy surface (PES) computed along the Mo−Mo bond and the orientation angle. The blue area shows the range of angles accessible by the system at each point along the bond coordinate.

absorption; however due to the experimental detection bandwidth in our experiments, we are not able to observe this peak on the diagonal. The positive features **III** and **IV** correspond to a cross peak between the high-frequency and low-frequency peaks, indicating that both transitions arise from the product molecule.

The rebinding was tracked using UV-pump/DVE-probe, where the bleach recoveries of the peaks at 1958 and 2013 cm^{-1} were measured as a function of the UV-IR delay as shown in Figure 2. The bleach onset is instrument-limited, in agreement with previous experiments. The 1958 cm^{-1} peak is observed to recover with a time constant of 15.8 ± 0.5 ps, whereas the high-frequency peak corresponding to the *gauche* isomer does not recover significantly in the time scale of the experiment. These observations are clear indications that the geminate rebinding process favors exclusively the *trans* isomer. Because the DVE signal intensity scales with the square of the number of molecules (see SI), the actual rebinding time constant is twice the observed bleach recovery time or 31.6 ± 1 ps. UV-pump/IR-probe transient absorption (TA) experiments (not shown) yielded a 27 ± 5 ps bleach recovery rate, consistent with the DVE experiments. The background-free detected DVE signal greatly improves the experimental signal-to-noise ratio over TA, while providing enhanced spectral resolution (see SI).[12] Previous TA studies using 515-nm-pump/400-nm-probe reported a rebinding time constant of 5.9 ps in cyclohexane,[6] which is markedly more rapid than what is observed in ethyl acetate (see SI for further discussion). The recombination efficiency, which describes the number of molecules that undergo geminate recombination inside the solvent cage, can be computed from the exponential fit to the DVE bleach recovery. Our extracted value of 32% is in agreement with previous results of 30% (*n*-hexane)[13] and 48% (Cp′ derivative in cyclohexane),[14] and we further expect the recombination efficiency to depend on solvent viscosity and polarity as well as the size and mass of the radicals.

A molecular-level interpretation of the experimental results is aided by the *ab initio* energy surface for the reaction shown in Figure 2. This plot shows the potential energy as a function of the bond distance and orientation angle about the Mo−Mo bond. Multiple observations can be made from this figure: (1) The geminate rebinding is a barrierless process for both isomers, and thus the time scale for recombination is likely dominated by the diffusion of the fragments inside the solvent cage and not necessarily by the potential itself. (2) The large torsional energy barrier to isomerization remains high even at metal−metal bond distances far from the equilibrium configuration, indicating that the rebinding process preselects a specific isomer channel long before reaching the equilibrium bond distance. (3) The blue area shows the orientational angle-coordinate space thermally accessible (at 300 K) from the minimum energy at each point in the metal−metal bond distance coordinate. The preferred channel for recombination is clearly the one leading to the *trans* configuration, in agreement with the experimental observations. This is a kinetic effect where the molecules are “steered” toward the *trans* conformation as they approach each other.

In conclusion, the photochemistry of $[CpMo(CO)_3]_2$ was studied using equilibrium and nonequilibrium 2DIR spectroscopy and transient IR echo spectroscopy with particular attention to the fast rebinding of the radicals following photodissociation. The experimental data support the conclusion that fast geminate rebinding specifically favors the *trans* isomer over the slightly higher-energy *gauche* isomer. A molecular level picture of the branching is supported by the *ab initio* derived potential energy surface. These results highlight the promise of ultrafast nonlinear vibrational spectroscopy to elucidate complex many-body reaction dynamics that underlie asymmetric chemical processes central to catalysis and mechanistic determination.

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Supporting Information Available: Temperature dependent absorption spectra, Description of experimental methods and theoretical models, Electronic structure energies and geometries, and Discussion of the current results in the context of previous work. This material is available free of charge via the Internet at http://pubs.acs.org.

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