Multiple-Timescale Photoreactivity of a Model Compound Related to the Active Site of [FeFe]-Hydrogenase


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Ultraviolet (UV) photolysis of (μ-S(CH₂)₃S)Fe₂(CO)₆ (1), a model compound of the Fe-hydrogenase enzyme system, has been carried out. When ultrafast UV-pump infrared (IR)-probe spectroscopy, steady-state Fourier transform IR spectroscopic methods, and density functional theory simulations are employed, it has been determined that irradiation of 1 in an alkane solution at 350 nm leads to the formation of two isomers of the 16-electron complex (μ-S(CH₂)₃S)Fe₂(CO)₆ within 50 ps with evidence of a weakly associated solvent adduct complex. 1 is subsequently recovered on timescales covering several minutes. These studies constitute the first attempt to study the photochemistry and reactivity of these enzyme active site models in solution following carbonyl ligand photolysis.

The Fe-only hydrogenases reversibly catalyze the reduction of protons to molecular hydrogen. Understanding the chemical basis of this process is of significance to the design of new technological systems for hydrogen production and utilization, and considerable advances have been made in studies of the biochemistry of these enzymes and of synthetic active site models;¹ these have been extensively reviewed.²,³

X-ray crystallographic studies of the active site of an Fe-only hydrogenase show a {4Fe4S} cubane structure linked via a cysteinyl bridge to a diiron subsite, a structure previously unprecedented in nature.⁴,⁵ One important facet of the chemistry of the enzyme is the inhibition of catalysis by CO bound to the active site. Studies using irradiation of the CO-inhibited state at cryogenic temperatures have shown evidence for a structure identical with that of the oxidized form of the enzyme, as well as the loss of the infrared (IR) band associated with the bridging carbonyl ligand.⁶ Photolysis of diiron carbonyl analogues is thus important in the context of the photolability of CO in the biological hydrogenase system and provides a vital basis for future studies of the enzyme; however, the ultrafast dynamics of these species remains unexplored. Ultraviolet (UV)–Fourier transform IR (FTIR) studies of iron carbonyl sulfide, Fe₂(CO)₆(μ-S₂), in a Nujol matrix show that the two lowest-energy transitions correspond to Fe=Fe bond activation at 450 nm, resulting in a change of the geometry, while higher-energy absorptions (285 nm < λ < 420 nm) correspond to metal-to-ligand charge-transfer transitions and result in the loss of a carbonyl ligand.⁷ The role of CO loss in the enzyme mechanism makes the latter transition the most pertinent to this study.

To establish the general photochemical behavior of diiron carbonyl dithiolate systems related to the subsite of Fe-only hydrogenase in solution, results of the photolysis of 1 under ambient conditions using ultrafast UV-pump IR-probe techniques and continuous photolysis are presented. UV-pump IR-probe spectroscopy is a well-established technique. Briefly, UV-pump pulses (60 fs duration, λ = 330 nm) were incident upon the sample, where they were overlapped spatially and temporally with mid-IR pulses (100 fs) with a wavelength resonant with the carbonyl ligand stretching vibrations of 1 (ca. 2000 cm⁻¹). The time delay between pump and probe pulses was variable up to 1 ns using an

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optical delay line. Thus, the IR spectrum of the sample was recorded before and after UV irradiation with ultrafast time resolution. Steady-state UV–FTIR measurements were performed by recording FTIR spectra before, during, and after irradiation by a continuous UV light source. A band-pass filter placed in the UV beam restricted the wavelengths used to 350 ± 50 nm to emulate the ultrafast experiments. The samples were heptane solutions of 1, produced using established methods,2 with a peak optical density in the CO sample.

The results of the ultrafast photolysis of 1 are shown in Figure 1. Parts a and b of Figure 1 show UV–IR difference spectra recorded at pump–probe delay times of 50 ps and 1 ns. It was observed that, at all positive time delays, negative bleach signals appeared at 2076, 2035, 2006, and 1991 cm⁻¹, corresponding to the expected IR absorption frequencies of the parent complex1,11,12 (the small peak expected at 1982 cm⁻¹ was not clearly resolved because of overlap with product bands; see below), indicating the loss of this complex following irradiation. At short pump–probe time delays (<100 ps), a broad-band transient absorption was observed in the range 1940–2075 cm⁻¹ attributable to heating effects and vibrational excitation following UV irradiation. No evidence for electronically excited products was observed on any timescales, indicating rapid relaxation to the electronic ground states of parent and photoproduct complexes, whereupon vibrational cooling occurred. The latter manifests itself as a loss of the broad-band transient absorption; the blue trace in Figure 1c shows the temporal dependence of this absorption well away from any observed bleach or photoproduct bands. At pump–probe delay times longer than ~50 ps, positive peaks due to the appearance of photoproducts were resolved. These appeared at 2064, 2052, 1999, 1977, and 1944 cm⁻¹ (Figure 1a,b) and persisted to the experimental time limit of 1 ns. The temporal dependence of these peaks is shown in Figure 1c (red trace). By 1 ns, evolution of the spectrum such as the narrowing and blue-shifting of photoproduct transitions caused by vibrational cooling was complete, allowing separation of parent bleaches and photoproduct bands. These are shown as red and blue dashed lines in Figure 1b and were obtained by fitting Gaussian profiles to the observed lines. These functions were scaled and added to Figure 1a in order to better show the effects of vibrational heating such as the increased amplitude observed near 2025 and 1960 cm⁻¹. No absorptions at frequencies corresponding to bridging CO groups were observed.

When the temporal dynamics are examined in more detail, Figure 1c shows that excitation of the parent complex leads to the immediate appearance of bleach signals (black and green lines in Figure 1c), all of which recover to around 30% of the initial value. This data were recorded with magic-angle pump–probe polarization geometry in order to negate the effects of molecular rotation. Fitting to a biexponential function revealed two timescales, one of ~150 ps and a longer value of ~5 ns. The broad-band transient absorption due to hot photoproducts decayed with a single-exponential timescale of 30 ps (blue trace), identical with the rise time observed for each of the photoproduct bands. It is interesting to note the different timescales for recovery of 1 in comparison to photoproduct formation. This suggests that UV excitation leads to rapid relaxation to a photoproduct state following carbonyl photolysis, while molecules not undergoing photolysis relax more slowly to the ground state of the parent complex possibly because of the need to shed excess energy through vibrational cooling. This also accounts for the slower rate of loss of the transient absorption near 2025 cm⁻¹ (Figure 1b) in comparison to the broad-band absorption. The former is red-shifted from the parent complex bleach at 2035 cm⁻¹ and is attributable to hot parent complex molecules.

Examination of the anisotropy parameter of the bleach signals of the parent complex showed a molecular rotation time of 17 ps, consistent with previous ultrafast 2D-IR studies following the 2D-IR profiles to the observed lines. These functions were scaled and added to Figure 1a in order to better show the effects of vibrational heating such as the increased amplitude observed near 2025 and 1960 cm⁻¹. No absorptions at frequencies corresponding to bridging CO groups were observed.

When the temporal dynamics are examined in more detail, Figure 1c shows that excitation of the parent complex leads to the immediate appearance of bleach signals (black and green lines in Figure 1c), all of which recover to around 30% of the initial value. This data were recorded with magic-angle pump–probe polarization geometry in order to negate the effects of molecular rotation. Fitting to a biexponential function revealed two timescales, one of ~150 ps and a longer value of ~5 ns. The broad-band transient absorption due to hot photoproducts decayed with a single-exponential timescale of 30 ps (blue trace), identical with the rise time observed for each of the photoproduct bands. It is interesting to note the different timescales for recovery of 1 in comparison to photoproduct formation. This suggests that UV excitation leads to rapid relaxation to a photoproduct state following carbonyl photolysis, while molecules not undergoing photolysis relax more slowly to the ground state of the parent complex possibly because of the need to shed excess energy through vibrational cooling. This also accounts for the slower rate of loss of the transient absorption near 2025 cm⁻¹ (Figure 1b) in comparison to the broad-band absorption. The former is red-shifted from the parent complex bleach at 2035 cm⁻¹ and is attributable to hot parent complex molecules.

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of this complex in heptane.\textsuperscript{13} Further study of the anisotropy parameters of the CO stretching modes of \textsuperscript{1} revealed, by comparison with IR transition dipole moment angular relationships measured by 2D-IR,\textsuperscript{13} that the transition dipole moment for the electronic transition lies along the Fe–Fe internuclear bond; this is discussed in more detail in the Supporting Information.

Figure 2 shows the results of 60-s-duration UV irradiation on the FTIR spectrum of \textsuperscript{1}. The bleach and photoproduct bands observed are in good agreement with those observed via ultrafast spectroscopy, suggesting that no further chemistry occurs beyond 1 ns. It is interesting to note that turning off the UV source leads to bleach recovery and disappearance of photoproduct peaks, suggesting that the products of the photoreaction are not stable and that the parent complex is recovered. This would be consistent with a CO ligand loss mechanism with no ensuing photochemistry. It can be shown through analysis of the peak integrals that the bleach recovery can be fit using established second-order kinetics,\textsuperscript{14} consistent with recombination following photolysis (see the Supporting Information).

To establish the identity of the photoproducts, DFT simulations were used to calculate the structure and IR spectra of three candidate species. These were selected to be (μ-S(CH$_2$)$_3$S)Fe$_2$(CO)$_5$ with an axial or equatorial carbonyl ligand removed and the solvent adduct (μ-S(CH$_2$)$_3$S)Fe$_2$-(CO)$_5$(solvent). To increase the computational efficiency, a propane molecule was used for the latter, though it has been shown that the size of the alkane adduct has little effect upon the IR spectrum of the complex.\textsuperscript{15}

The results are shown in Figure 3 (for detailed results, see the Supporting Information). It is clear that the IR spectra of the three photoprodut candidates are similar and in good agreement with the observed photoproduct bands. The broad bands observed experimentally near 1950 and 1970 cm$^{-1}$ and multiple bands between 2030 and 2070 cm$^{-1}$ suggest that photolysis leads to a mixture of these three products; this is supported by their similar calculated energies, with approximately equal contributions from all candidate photoproducts (see the Supporting Information), the structures of which are also shown in Figure 3. It is noteworthy that contributions to the FTIR results (Figure 2a) at 2043 cm$^{-1}$ and below 1970 cm$^{-1}$ contrast slightly with the ultrafast data, which show slightly higher frequency contributions. The calculated spectra (Figure 3) suggest that the lower-frequency bands in each region are due to the solvent adduct, and this may imply a shift in the equilibrium toward these on longer timescales in keeping with the greater calculated stability of this species. It is interesting to note, however, that use of a heptanol solvent resulted in similar photoproduct band positions, though resolution was reduced by the broader associated line widths, which suggests weak solvent coordination with the model compound, possibly arising from steric effects.

In summary, irradiation of \textsuperscript{1} at 330 nm leads to carbonyl photolysis and the formation of 16-electron photoproducts along with evidence for a weakly associated solvent adduct species (Figure 3), laying the groundwork for future studies of the reactivity of these models of the hydrogenase system.

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Supporting Information Available: Experimental details and further details relating to analysis procedures as referred to in the main text. This material is available free of charge via the Internet at http://pubs.acs.org.

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