

Ultrafast Chelation Dynamics of a Manganese Tricarbonyl Derivative in Solid Polyacrylonitrile

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Received: April 23, 2007; In Final Form: June 5, 2007

Ultraviolet pump, infrared probe transient absorption studies of the chelatable compound **1**, $\text{Mn}\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{C}(\text{SCH}_3)_3\}(\text{CO})_3$, dispersed in room temperature, spin-coated polyacrylonitrile (PAN) films ($\sim 25 \mu\text{m}$ thick on a CaF_2 surface) are reported for the first time. Irradiation of **1** at 289 nm induces CO loss with high yield and generates the Mn–S bound chelate within 160 ps. There is no evidence for undesirable matrix cage CO recombination or secondary competing solvation pathways for this system, which may serve as the basis for future solid-state photoswitches.

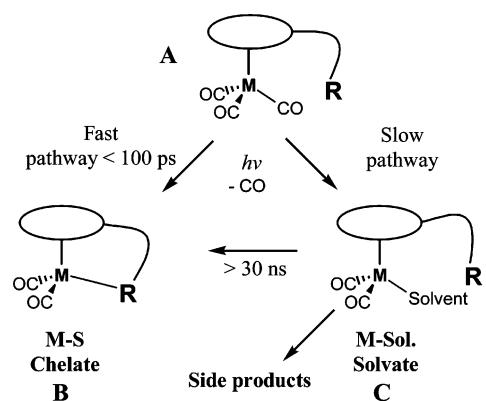
Introduction

There is great interest in developing novel photochromic materials for photonic devices such as recordable media and reversible optical switches.¹ Fast conversion rates, high quantum yields, and low fatigue are desirable features for such systems. The current challenge for the design and application of photochromic materials is that their desirable properties can be hindered by cage processes such as recombination and transitory solvation. These cage processes are well documented for many coordinatively unsaturated metal centers that are so reactive that they even bind to alkanes and noble gases.²

In the current and previous studies we examined fundamental processes relevant to the function of ultrafast photochromic organometallics based on linkage isomerization of complexes with a bifunctional, nonchelating ligand³ or intramolecular ligand exchange of organometallic chelates with tethered functional groups.⁴ We investigated several new model compounds capable of chelation to determine how cage processes might be eliminated in liquid-phase environments. For instance, following ultraviolet (UV) irradiation, the pendant sulfides of **1** (unlike for **2** and **3**; see Scheme 1) undergo chelation to the exclusion of ultrafast alkane solvent coordination or cage recombination of the photodissociated CO ligand.⁵ Chelation rates and reaction paths are significantly affected by variation of the reaction environment, metal center, or multidentate ligand. Although only **1** completely eliminates the solvation pathway in heptane, all three complexes (**1–3**) eliminate the solvation pathway in the more reactive solvent acetonitrile (ACN).⁶ Furthermore, though **1–3** yield the Mn–S chelate (**7–9**, respectively) immediately after UV irradiation in acetonitrile, **4–6** partially form the Cr–ACN solvate (**16–18**, respectively), instead.⁷

In this Letter, we report the first known study of room-temperature ultrafast molecular chelation dynamics in a solid polymer film, which is of direct relevance for optical switching in devices. We investigated **1** embedded in a new reaction

SCHEME 1



A	M	L	R	B	C
1	Mn	C ₅ H ₄	C(O)C(SCH ₃) ₃	7	13
2	Mn	C ₅ H ₄	C(O)CH(SCH ₃) ₂	8	14
3	Mn	C ₅ H ₄	C(O)CH ₂ (SCH ₃)	9	15
4	Cr	C ₆ H ₅	C(O)C(SCH ₃) ₃	10	16
5	Cr	C ₆ H ₅	C(O)CH(SCH ₃) ₂	11	17
6	Cr	C ₆ H ₅	C(O)CH ₂ (SCH ₃)	12	18

environment: solid polyacrylonitrile (PAN) films coated on an infrared transparent CaF_2 surface. Although solid-phase, steady-state CO photodissociation was previously reported for poly-(vinylcyclopentadienyl)(tricarbonyl)manganese,⁸ it was postulated that embedding the chelatable species in a solid matrix appropriate for future device conditions could present new dynamical pathways such as preferred direct molecular chelation or undesirable permanent polymer bonding. Though reduced quantum yield could also ensue because of dissociative CO geminate recombination matrix cage effects, this is apparently not the case for this investigated system.

Experimental Section

The time-resolved infrared (TRIR) apparatus used in this work was reported in previous publications.^{5,6} For the present study,

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a typical 289 nm UV excitation pulse (ca. 120 fs pulse duration with 4–6 μJ energy, 20 Hz repetition rate) was focused to approximately 100 μm diameter on the front surface of a 3 mm thick CaF_2 window spin-coated with PAN containing **1** (see below). To generate a single difference spectrum at a specific pump–probe time delay, an average of 500 laser shots was collected as the sample was mechanically raster-scanned through the excitation and probe beams to present fresh film for investigation between shots. Two to three of these combined TRIR difference spectra were averaged to obtain the final presented results. Time-resolved spectra from different films coated onto various CaF_2 windows obtained over separate days were of similar quality. Analysis of averaged spectra (typically three) yielded an intensity uncertainty from the baseline of less than ± 0.003 optical density (OD) units ($k = 1$; type B analysis).

The molecular design and the synthetic procedures of **1** were previously published.⁵ To prepare samples for time-resolved infrared experiments, the compound **1** (30 mg) was dissolved in 2 mL of dimethyl sulfoxide (DMSO, Aldrich) then polyacrylonitrile (PAN, powder, 300 mg, 150 000 molecular weight from Polysciences, Inc.) was added.⁹ The resulting mixture was warmed to 323–333 K with stirring. One surface of a 50.8 mm diameter CaF_2 window was spin-coated with the transparent yellow amorphous viscous mixture to produce a uniform film of approximately 25–35 μm thickness. DMSO was removed by gently blowing warm air across the film before UV-pump/IR-probe experiments. Obtaining the appropriate optical density of **1** in these cast PAN films (OD ~ 0.8) and subsequent removal of DMSO was checked by Fourier transform infrared (FTIR) spectroscopy. From the optical density and film thickness, we estimate the concentration of **1** to be ca. 0.26 molar.

Results and Discussion

The major result of this work is that UV irradiation of **1** in PAN efficiently dissociates a carbonyl ligand from the metal center, allowing for direct formation of the Mn–S chelate photoproduct within 160 ps. There is no evidence for competing solvation or polymer reaction pathways from these TRIR results.

As shown in Figure 1, a bleach feature arising from the parent molecule's double CO-stretching bands is clearly observed near 1940 cm^{-1} and appears within 27 ps immediately after UV irradiation of **1** at delay time $t = 0$. The spectrum obtained at $t = -13$ ps demonstrates the baseline noise of the instrument is ca. ± 0.003 OD units for only 2000 total laser shots. The second bleach feature of this molecule is found near 2024 cm^{-1} but is not examined in this study. A broad, red-shifted absorption feature relative to the doublet bleach feature is observed at early time delays (< 25 ps), which has been interpreted previously as arising from cooling of vibrationally hot species.⁵ A new CO-stretching band near 1874 cm^{-1} becomes resolved beginning at 93 ps time delay. Identical bleach and absorption features are also obtained during steady-state irradiation of these same films (Figure 1, bottom panel: FTIR difference spectrum taken before and after UV irradiation with a Hg–Ar pen lamp placed 10 cm away from the film for approximately 60 s). Except for being approximately 4 cm^{-1} red-shifted compared to absorptions in liquid-phase acetonitrile (ACN), the positions and intensities of the bleach and newly formed absorption features of **1** in PAN are also nearly identical to the previously obtained results for **1** in acetonitrile solvent in which it was determined that only the Mn–S chelate formed.⁶ Therefore, we assign the new CO-stretching band near 1874 cm^{-1} to arise from the Mn–S chelate. The second CO-stretching band of the Mn–S chelate is obscured by the parent's spectrally wide, ca. 30 cm^{-1} FWHM (full-width

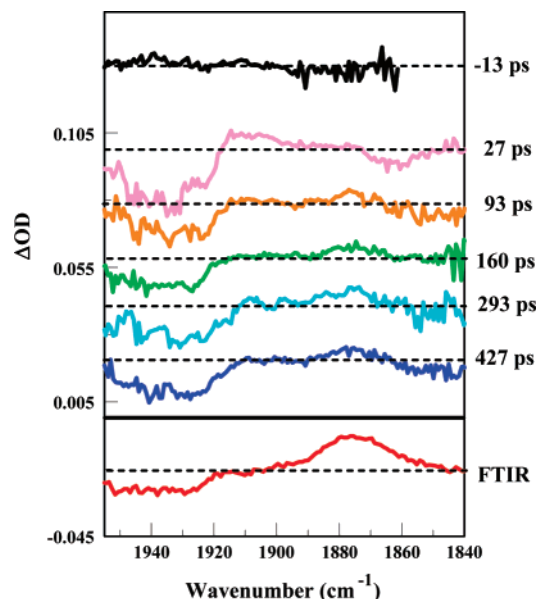


Figure 1. Transient TRIR difference spectral changes acquired after 289 nm irradiation of **1** in PAN. Spectra at different time delays are offset vertically by 0.017 OD units for clarity and dashed lines correspond to $\Delta\text{OD} = 0$ for each spectrum. The bottom panel shows the difference FTIR spectra of **1** in PAN before and after UV irradiation (OD amplitude divided by two for comparison).

at half-maximum), double band bleaching feature found near 1940 cm^{-1} . Comparison of the difference spectral bleach and absorption intensities to those obtained for **1** in liquid *n*-heptane^{5a,6} and ACN⁶ (as well as species **2–6** in other solvents yielding $\Delta\text{OD} \sim 0.02$ signals under the same experimental conditions) suggest the quantum yield for CO-dissociation leading to chelate formation is not severely affected by the solid-state environment.

In acetonitrile, the two metal–CO-stretching bands of the transient Mn–ACN solvate were previously assigned to be 20 cm^{-1} red-shifted relative to the CO-stretching bands of the Mn–S chelate.⁶ The higher frequency band of these two bands was also at least 20 cm^{-1} red-shifted relative to the parent's double bleach feature. The absence of these red-shifted features during TRIR irradiation of **1** in PAN indicates that coordination of the unsaturated Mn metal center with cyano groups in PAN does not occur. We therefore conclude that UV irradiation of **1** in solid PAN effectively dissociates a CO group to immediately yield the fully stable Mn–S chelate without an intermediary or slow (typically with lifetimes of many ns)^{5–7} transient solvation or polymer binding step. This result is extremely important for developing future highly quantum efficient, ultrafast devices for optical switching applications.

Summary

For the first time, to our knowledge, ultrafast solid-phase dynamics of a tethered organometallic capable of chelation has been investigated on the picosecond time scale using UV-pump/IR-probe transient absorption spectroscopy. The ultrafast photoinduced chelation of **1** to the exclusion of other competing cage processes, such as coordination with alkane solvent molecules,⁵ more reactive polar acetonitrile solvent,⁶ or the cyano side groups of PAN demonstrates the robust and desirable features of this newly synthesized structure in a controlled solid-state reaction environment. This study also demonstrates that efficient chelation, with little or no apparent interference or degradation from cage CO-recombination, can be used as a mechanistic platform for the development of ultrafast solid-state

optical molecular devices. We are now investigating the possibility of measuring similar reaction behavior with photo-switchable species in polyethylene films.

Acknowledgment. This work was supported by internal NIST Scientific, Technical and Research Services funding (T.T.T. and E.J.H.). Compound **1** was prepared during previous NIST supported investigations. We also like to thank Dr. I. J. Heilweil for suggesting the use and source of PAN and Professor Theodore J. Burkey at the University of Memphis for insightful discussions and providing a quantity of **1** for use in this study.

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(9) Certain commercial equipment, instruments, or materials are identified in this paper to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by NIST, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.