

Photodissociation of $\text{Cr}(\text{CO})_6$ in Solution: Direct Observation of the Formation of $\text{Cr}(\text{CO})_5(\text{MeOH})$

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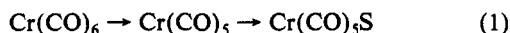
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Time-resolved picosecond absorption spectroscopy has been used to examine the dynamics of formation of $\text{Cr}(\text{CO})_5(\text{solvent})$ generated by photolysis of $\text{Cr}(\text{CO})_6$ in methanol and cyclohexane solutions. The kinetics were monitored at the absorption maximum of $\text{Cr}(\text{CO})_5\text{S}$, 460 ± 5 and 500 ± 5 nm for methanol and cyclohexane, respectively. In methanol, a rise time of 2.5 ps is observed. This is compared to the instrument response of 0.8 ps, measured by determining the rise of the $\text{S}_1 \rightarrow \text{S}_0$ absorption of *trans*-stilbene. In cyclohexane, the transient is found to rise within the time resolution of the experiment. The longer rise observed in methanol is discussed in terms of the solvent restructuring leading to the formation of the Cr-S bond.

Introduction

Understanding the interactions between solvent molecules and reacting systems has been an active area of research for several decades.¹ However, to date, most theoretical models describing solvent effects only incorporate static properties of the fluid. Only in the past decade has the coupling between solvent dynamics and reaction kinetics been addressed.² With the availability of picosecond and subpicosecond techniques, time-resolved studies of reaction dynamics on the same time scale as solvent motion can be probed. Such experiments clearly indicate that the role of the solvent cannot be completely described in terms of bulk properties, e.g. viscosity, dielectric constant, etc.³ A complete description of the role of the solvent in chemical reactions must contain a molecular picture of the solvating medium.

One approach to studying the role of solvent dynamics on chemically reacting systems involves choosing a process which can produce reaction intermediates in an environment of nonequilibrium solvation. Once produced, the dynamics associated with the restructuring of the solvent shell could provide insight into the details of the solvation process. Toward this goal we have chosen a photochemical reaction whose first step involves photodissociation, the photodissociation of CO from chromium hexacarbonyl:



Chromium hexacarbonyl was chosen for four major reasons. First of all photodissociation proceeds with a high quantum yield, $\Phi \approx 0.7$.⁴ Thus, complications resulting from geminate recombination of the $\text{Cr}(\text{CO})_5$ and CO fragments will be reduced. Second, the maximum of the absorption spectrum of the primary intermediate, " $\text{Cr}(\text{CO})_5\text{S}$ ", is very sensitive to the solvent ligand S.⁵ Considering the three group VI (group 6)¹⁴ metal carbonyls, the absorption spectra of the substituted $\text{Cr}(\text{CO})_5\text{S}$ span the largest wavelength region, 620 nm for perfluoromethylcyclohexane to 385 nm for pyridine. Mixed matrix and mixed solvent studies clearly show that the absorption arises from a hexacoordinate species in which a solvent molecule is bound to the site vacated by the photoeliminated CO. Third, the photofragment, $\text{Cr}(\text{CO})_5\text{S}$, is stable onto the nanosecond time scale. Thus, thermal reactions (recombination of bimolecular reactions between two metal species) of the photoproduct will not be important on the time scale of our measurements. Fourth, matrix isolation work as well as theoretical calculations show that the photogenerated $\text{Cr}(\text{CO})_5$ retains a C_{4v} geometry.⁶ Recently, the transient absorption spectrum of gas-phase $\text{Cr}(\text{CO})_5$ was reported.⁷ The spectrum was similar to both $\text{Cr}(\text{CO})_5(\text{perfluoromethylcyclohexane})$,^{5d} formed by the photolysis of $\text{Cr}(\text{CO})_6$ in perfluoromethylcyclohexane, and $\text{Cr}(\text{CO})_5\text{Ne}$ observed in neon matrices (known to be of C_{4v} symmetry by IR analysis⁶).

To date, there has been no direct observation of the time scale associated with the formation of $\text{Cr}(\text{CO})_5\text{S}$. Earlier picosecond studies⁸ show that the solvated complex is formed in less than 50 ps for both cyclohexane and THF solutions. In this paper picosecond absorption spectroscopy is used to examine the formation kinetics of $\text{Cr}(\text{CO})_5\text{S}$ in methanol and cyclohexane solutions.

Experimental Section

A detailed description of the experimental apparatus will be published at a later date. Briefly, a mode-locked CW Nd³⁺:YAG (Quantronix Model 116 mode-locked at 38 MHz) is used to synchronously pump a Rhodamine 6G/DQOCI dye laser producing visible pulses whose autocorrelation trace is at most 0.8 ps fwhm. These pulses are amplified by a three-stage amplifier pumped by a Quanta-Ray DCR-20 Nd³⁺:YAG laser. Amplified spontaneous emission (ASE) is controlled by saturable absorber jets (Crystal Violet) between successive stage of the amplifier. After amplification, the pulses are less than 1 ps, approximately 1–2 mJ/pulse, 600 nm, and have a repetition rate of 20 Hz. The pulse energy:ASE ratio is better than 100:1.

The output of the amplifier is frequency doubled by using an angle-tuned KDP crystal (Quantum Technologies) and the resulting UV light, ≈ 0.1 mJ, 300 nm, is passed down a variable delay line and focussed on the sample. The remaining fundamental radiation is focussed into a cell of water in order to generate a white light continuum. This broad band of light, 350 to 900 nm, serves as the light source for recording transient electronic absorption spectra. Kinetics are probed by performing narrow-band absorption spectroscopy experiments. Interference filters (ESCO,

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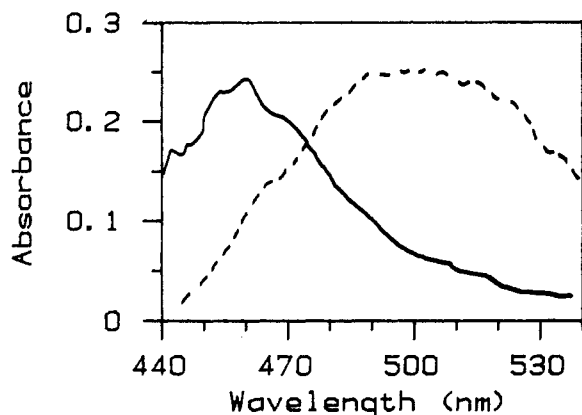


Figure 1. Continuum absorption spectrum of $\text{Cr}(\text{CO})_5(\text{cyclohexane})$ (---) and $\text{Cr}(\text{CO})_5(\text{MeOH})$ (—) recorded 50 ps after the photolysis of $\text{Cr}(\text{CO})_6$ in cyclohexane and methanol, respectively.

fwhm ≈ 5 nm) are used to select the desired probe wavelength. In this manner, the frequency chirp associated with the probe continuum is negligible. The continuum beam is focussed on a diffuser (Hamamatsu) and collected and collimated through a 0.25-in. aperture located 3 in. away from the diffuser. This produces a homogeneous probe beam which has no "spatial hopping". This beam is split into two beams of equal intensity. One beam serves as a reference beam, I_0 ; the other serves as the probe, I , and is focussed collinearly with the UV excitation beam through the sample. Both white light beams are detected by large-area photodiodes (DT110, E.G.G.), connected to a track-hold circuit (Stanford Research Systems, Model 248). The output of the track-hold circuit is directly digitized by a lab computer (LSI-11/23⁺). With a resolution of 40 fs/step on our computer driven delay line (Velmex), dynamic processes on the 1–10-ps time scale can easily be measured. A computer-controlled shutter in the UV beam enables the collection of absorbance with and without UV excitation. The transient absorbance signal is then calculated by using the following expression:

$$\Delta A = \log \left[\frac{I_0}{I} \right]_{\text{with excitation}} - \log \left[\frac{I_0}{I} \right]_{\text{without excitation}} \quad (2)$$

Approximately 400 laser shots are used for the collection of a single absorbance value.

The instrument response was determined by measuring the rise of the $S_1 \rightarrow S_N$ absorption of *trans*-stilbene. The signal is found to rise with a $1/e$ time of 0.8 ps. This is consistent with autocorrelation measurements. The experimental apparatus used to record the continuum absorption spectra has been previously described.⁹

$\text{Cr}(\text{CO})_6$ was purchased from Aldrich and used without purification. In order to prevent the buildup of stable photoproducts, the sample was prepared in the dark and flowed through a 1-cm flow cell. Approximately 300 mL of a saturated $\text{Cr}(\text{CO})_6$ solution was used for each experiment. The flow rate used ensured that new sample was in the focal volume for each laser shot.

Results and Discussion

In Figure 1, transient absorption spectra are shown 50 ps after the photolysis of $\text{Cr}(\text{CO})_6$ in room temperature methanol and cyclohexane solutions. In methanol, an absorption band with a maximum of 460 nm is observed. In cyclohexane, a broad band centered at 505 nm is observed. These spectra agree with previously reported spectra for the $\text{Cr}(\text{CO})_5(\text{MeOH})$ and $\text{Cr}(\text{CO})_5(\text{cyclohexane})$ complexes.⁵ As no change in band position is observed from 50 ps to several nanoseconds after photolysis, the dynamics associated with the photodissociation and formation of the $\text{Cr}(\text{CO})_5\text{S}$ complex must occur on a faster time scale.

In Figure 2, the kinetics observed at 460 nm for photolysis of $\text{Cr}(\text{CO})_6$ in methanol are presented. For this data a time step

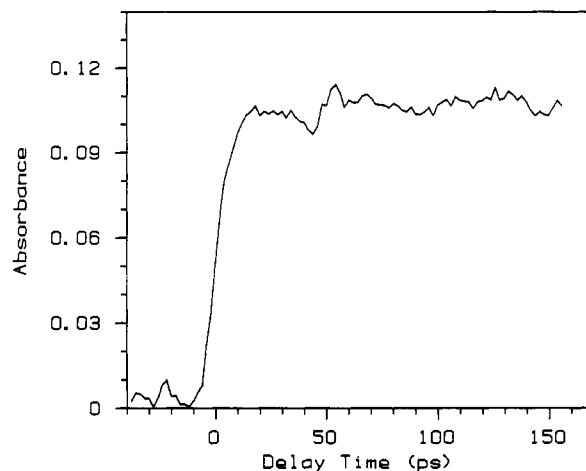


Figure 2. The absorption kinetics for the photolysis of $\text{Cr}(\text{CO})_6$ in methanol. The probe wavelength is 460 ± 5 nm, the maximum of the absorption of $\text{Cr}(\text{CO})_5(\text{MeOH})$. The data shows that the transient appears rapidly and remains constant for up to 150 ps after photolysis. The time between successive steps is 2.0 ps.

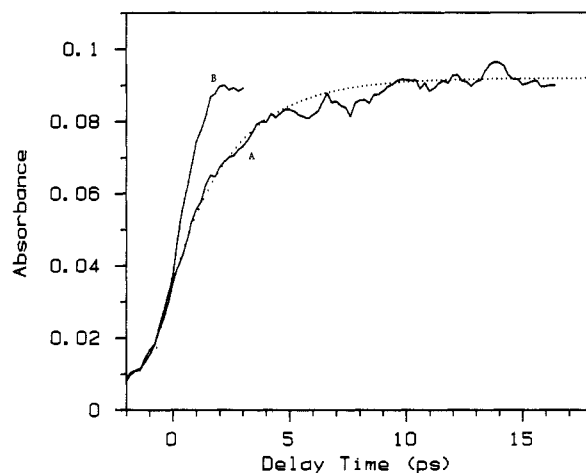


Figure 3. A detailed study of the rise of the $\text{Cr}(\text{CO})_5(\text{MeOH})$ transient absorption observed for the photolysis of $\text{Cr}(\text{CO})_6$ in methanol. (A) The experimentally measured absorbance as a function of delay time between the excitation and 460-nm probe. The dotted points represent an exponential rise of 2.5 ps. Data was collected in increments of 0.2 ps. (B) The rise of the $S_1 \rightarrow S_N$ transient absorption *trans*-stilbene in methanol. The signal rises to $1/e$ of the full intensity in 0.8 ps. This data clearly establishes that the $\text{Cr}(\text{CO})_5(\text{MeOH})$ transient rises slower than the resolution of the instrument.

of 2.0 ps between successive measurements of the transient absorption was used. These data reveal a rapid rise for the $\text{Cr}(\text{CO})_5(\text{MeOH})$ complex and a constant signal for the duration of the scan. In order to examine the dynamics of the rise of this absorption transient, the region around $t = 0$ was scanned with a time step of 0.2 ps (Figure 3). The absorption data in Figure 3 clearly show the dynamics associated with the formation of $\text{Cr}(\text{CO})_5(\text{MeOH})$. The dotted line represents an exponential rise of 2.5 ps. The rise of the $S_1 \rightarrow S_N$ absorption of *trans*-stilbene is shown for comparison. The rise of the metal carbonyl complex is clearly slower than the resolution of the experiment. The small absorption signals observed before the main rise in the absorption signals result from structure on the base of the laser pulses.

Two possible origins of the observed rise time in methanol can be envisioned. If solvent motion is rapid compared to the rate of dissociation of the Cr–CO bond and formation of ground-state $\text{Cr}(\text{CO})_5$, the rise time would correspond to the lifetime of the excited state of $\text{Cr}(\text{CO})_6$. On the other hand, if dissociation were rapid compared to solvent motion, the rise would reflect the motion of the solvent to reorganize and coordinate to the vacant coordination site.

The enthalpy change associated with the reaction

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has been measured by photoacoustic calorimetry and found to be 37 kcal/mol.¹⁰ This combined with an excitation energy of 300 nm leaves enough energy that the photofragment $\text{Cr}(\text{CO})_5$ could be formed in the excited state. Theoretical treatments support the conclusion that $\text{Cr}(\text{CO})_5$ is initially formed in the excited state.¹¹ Rapid coordination of a solvent molecule could then be followed by vibration energy relaxation, resulting in a time-dependent blue shift in the absorption spectrum of the $\text{Cr}(\text{CO})_5\text{MeOH}$ complex.

However, matrix photolysis work on $\text{Cr}(\text{CO})_6$ using polarized light indicates that, upon dissociation, the $\text{Cr}(\text{CO})_5$ fragment can isomerize via a square pyramid \rightarrow trigonal bipyramid \rightarrow square pyramid interconversion.^{6b} This isomerization pathway is believed to be the major deactivation pathway for electronically excited $\text{Cr}(\text{CO})_5$. This interconversion mechanism has been used to explain the small degree of geminate recombination in this system. The maximum production of $\text{Cr}(\text{CO})_5\text{S}$ by such a mechanism would be 67%, in close agreement with the observed quantum yields for photosubstitution.⁴ These observations support the conclusion that the observed rise does not correspond to solvent coordination to electronically excited $\text{Cr}(\text{CO})_5$, followed by vibrational relaxation of a hexacoordinate complex. Electronic relaxation occurs prior to solvent coordination and the observed rise in the methanol is a reflection of both the solute isomerization and solvent coordination.

In order to address the relative rates of solute and solvent dynamics, the rise time of $\text{Cr}(\text{CO})_5(\text{cyclohexane})$ was measured for the photolysis of $\text{Cr}(\text{CO})_6$ in cyclohexane. This solvent was chosen for several reasons. The absorption spectrum of the $\text{Cr}(\text{CO})_5\text{S}$ species has been shown to reflect the degree of bonding between the chromium center and the solvent molecule.^{5,6} The lower energy the absorption maximum, the weaker is the interaction. If one were interested in determining the time associated with the dissociation of the CO from $\text{Cr}(\text{CO})_6$ and the subsequent isomerization of $\text{Cr}(\text{CO})_5$, it is desirable to use a noninteracting, inert solvent. Cyclohexane, with its broad absorption centered around 505 nm, represented such a solvent.

The kinetics of the rise of the 505-nm absorption was also measured by using a 0.2-ps time step. Once again the data was compared with that observed for the rise of the excited-state absorption spectrum of *trans*-stilbene. In this case, the signal was found to rise within the temporal resolution of the experiment. The kinetics associated with the formation of this intermediate could not be resolved.

It is reasonable to assume that the rate of isomerization of the solute (if indeed isomerization does occur in solution) would be

independent of the solvent. The lack of any observable rise time in cyclohexane suggests that the dissociation dynamics are rapid compared to the time resolution of the experiment. From the comparison of the cyclohexane and methanol studies, we interpret the rise time observed in methanol to correspond to the time required for the local solvent to reorganize and coordinate to the ground state of the $\text{Cr}(\text{CO})_5$ fragment. For methanol, dielectric relaxation studies show that the Debye relaxation time for hydrogen-bonded methanol molecules is ≈ 50 ps.¹² If solvation of the photofragment required the breaking of solvent hydrogen bonds to free a methanol molecule for coordination, dynamics on this time scale would be expected. In addition, the coordination time is faster than the rotational diffusion time of the solute.¹³ The observed kinetics seem to support the conclusion that only a small change in the local solvent environment is necessary for solvent coordination to occur.

Conclusions

Picosecond absorption spectroscopy has been used to measure the formation kinetics of $\text{Cr}(\text{CO})_5(\text{MeOH})$ and $\text{Cr}(\text{CO})_5(\text{cyclohexane})$ generated by the photolysis of $\text{Cr}(\text{CO})_6$ in methanol and cyclohexane, respectively. The transient absorption characteristic of $\text{Cr}(\text{CO})_5(\text{cyclohexane})$ is observed to rise within the instrument response ($\tau < 0.8$ ps). In contrast, in the alcohol solution, a 2.5-ps rise time is observed. The rise time observed in MeOH solutions is concluded to reflect solvent reorganization resulting in the coordination of a solvent molecule to the vacant site of the reactive $\text{Cr}(\text{CO})_5$ intermediate.

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