

Time-Resolved Studies of Solvation: The Photodissociation of $\text{Cr}(\text{CO})_6$ in Pentanol

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Time-resolved picosecond absorption spectroscopy is used to examine the dynamics of formation of $\text{Cr}(\text{CO})_5(\text{pentanol})$ generated by photolysis of $\text{Cr}(\text{CO})_6$ in a room-temperature pentanol solution. The kinetics were monitored at 460 nm, the absorption maximum of $\text{Cr}(\text{CO})_5(\text{pentanol})$, and 520 nm, near the maximum of $\text{Cr}(\text{CO})_5(\text{alkane})$ absorption. The time-resolved absorption data show that photodissociation results in the formation of a distribution of solvated $\text{Cr}(\text{CO})_5$ intermediates. The restructuring of the local environment to form the most stable hexacoordinate intermediate is examined.

Introduction

Recently, there has been a great deal of experimental¹ and theoretical² interest in the dynamics of solvation. Most of the experimental studies center around measurements of the time-resolved Stokes shift of a probe molecule in polar solvents.^{1a-f} This approach uses the fact that a molecule's charge distribution is different in the excited state than in the ground state. As the surrounding solvent adjusts to the demands of the new charge distribution of the excited state, the emission spectrum of the probe molecule will shift to lower energy. This method can provide a direct measure of the solvation kinetics occurring on the molecular level.

In a previous study on the photodissociation of $\text{Cr}(\text{CO})_6$ in methanol and cyclohexane,^{1g} we demonstrated that molecules which undergo rapid photodissociation followed by solvent coordination can also reveal details of the solvation dynamics on the molecular level. In cyclohexane, the $\text{Cr}(\text{CO})_5(\text{cyclohexane})$ complex was found to rise within the time resolution of the experiment ($\tau < 0.8$ ps). As a result, any excited-state processes (photodissociation, isomerization³) or vibrational relaxation of the photofragment must occur on a faster time scale. However, in MeOH solution, the absorption signal of the $\text{Cr}(\text{CO})_5(\text{MeOH})$ complex exhibit a 2.5-ps rise time. Comparison with the cyclohexane data supported the conclusion that the observed dynamics were a measure of the time needed for the first solvent shell to restructure, forming the Cr-S bond.

In order to examine the local solvation of the hexacarbonyl in alcohol solution, we have examined the photodissociation dynamics in pentanol. Pentanol was chosen because both hydroxyl and alkyl groups are available for coordination; the initial intermediates formed would depend on the local solvent structure around the $\text{Cr}(\text{CO})_6$ molecule. Coordination of an alkyl or hydroxyl group produces complexes which have different absorption properties (vide infra). The thermodynamically most stable complex involves coordination of the hydroxyl end of the solvent molecule. Thus, if the initial solvation produces intermediates where the alkyl group is coordinated to the chromium metal, rearrangement or exchange with solvent molecules will occur to form the most stable complex. By use of picosecond absorption spectroscopy, the details of the solvation dynamics of $\text{Cr}(\text{CO})_5$ in pentanol can be addressed.

Experimental Section

A detailed description of the picosecond absorption spectrometer will be published at a later date.⁴ Picosecond pulses are generated by a dye laser synchronously pumped by a mode-locked CW Nd³⁺:YAG laser. The dye laser pulses are amplified by a three-stage longitudinally pumped pulsed dye 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 output of the amplifier is frequency-doubled, and the resulting UV light (≈ 0.1 mJ, 300 nm) is passed down a variable delay line and focused on the sample. The remaining fundamental

radiation is focused into a cell of water in order to generate a white light continuum. The probe wavelength of interest is selected by using narrow band interference filters (5-nm fwhm). The probe beam is focused on a diffuser, collected, and collimated, producing a spatially homogeneous beam. The probe light is split into two beams of equal intensity. One beam serves as a reference beam; the other is passed down a variable stepper motor delay line before passing through the sample cell collinearly with the UV excitation beam. The light is detected by photodiodes and integrated by a track-and-hold circuit, the output of which is digitized by a lab computer. Approximately 200 laser shots are used for the collection of a single absorbance value. The sample was flowed to prevent the buildup of photoproduct.

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 of the laser pulse.

Results and Discussion

In Figure 1, the absorption spectra for the $\text{Cr}(\text{CO})_5(\text{alcohol})$ and $\text{Cr}(\text{CO})_5(\text{alkane})$ complexes are shown. The maximum absorption for the alcohol complex is observed at 460 nm. The maximum and shape of this spectrum are not dependent on the length of the alkyl chain (methanol–hexanol). In hydrocarbon solvents (hexane, cyclohexane), the absorption band shifts to lower energy, 505 nm, reflecting the weaker interaction between the bound solvent molecule and the chromium metal.⁵ The relative extinction coefficients for the absorption spectra of these two complexes have not been determined. Under conditions of similar laser power and sample concentration, the ratio of the maximum absorption of $\text{Cr}(\text{CO})_5(\text{cyclohexane})$ to $\text{Cr}(\text{CO})_5\text{MeOH}$ is similar

- (1) (a) Maroncelli, M.; Fleming, G. R. *J. Chem. Phys.* **1987**, *86*, 6221. (b) Castner, E. W. Jr.; Maroncelli, M.; Fleming, G. R. *J. Chem. Phys.* **1987**, *86*, 1090. (c) Su, S.-G.; Simon, J. D. *J. Phys. Chem.* **1987**, *91*, 2693. (d) Nagarajan, V.; Brearley, A. M.; Kang, T.-J.; Barbara, P. F. *J. Chem. Phys.* **1987**, *86*, 3183. (e) Halliday, L. A.; Topp, M. R. *J. Phys. Chem.* **1978**, *82*, 2415. (f) Anthon, D. W.; Clark, J. H. *J. Phys. Chem.* **1987**, *91*, 3530. (g) Simon, J. D.; Xie, X. *J. Phys. Chem.* **1986**, *90*, 6751. (h) Siemiarzuck, A.; Ware, W. R. *J. Phys. Chem.* **1987**, *91*, 3677. (i) Hameka, H. F.; Robinson, G. W.; Marsden, C. J. *J. Phys. Chem.* **1987**, *91*, 3150.
- (2) (a) Bagchi, B.; Oxtoby, D. W.; Fleming, G. R. *Chem. Phys.* **1984**, *86*, 257. (b) Van der Zwan, G.; Hynes, J. T. *J. Phys. Chem.* **1985**, *89*, 4181. (c) Wolynes, P. G. *J. Chem. Phys.* **1987**, *86*, 5133. (d) Yan, Y. J.; Mukamel, S. *J. Chem. Phys.* **1987**, *86*, 6085. (e) Rossky, P. J. *Annu. Rev. Phys. Chem.* **1985**, *36*, 321. (f) Calef, D.; Wolynes, P. G. *J. Chem. Phys.* **1983**, *78*, 4145. (g) Onsager, L. *J. Am. Chem. Soc.* **1936**, *58*, 1486. (h) Chandler, D.; Schweizer, K. S.; Wolynes, P. G. *Phys. Rev. Lett.* **1982**, *49*, 1100. (i) Schweizer, K. S.; Chandler, D. *J. Chem. Phys.* **1983**, *78*, 4118. (j) Loring, R. F.; Yan, Y. J.; Mukamel, S. *Chem. Phys. Lett.* **1987**, *135*, 23. (k) Mazurenko, Y. T.; Bakshiev, N. G. *Opt. Spectrosc.* **1970**, *28*, 490.
- (3) Burdett, J. K.; Gzybowski, J. M.; Perutz, R. N.; Poliakoff, M.; Turner, J. J.; Turner, R. F. *Inorg. Chem.* **1978**, *17*, 146.
- (4) Xie, X.; Simon, J. D. *J. Am. Chem. Soc.*, in preparation.
- (5) (a) Kelly, J. M.; Bent, D. V.; Hermann, H.; Schulte-Frohlinde, D.; von Gustorf, E. K. *J. Organomet. Chem.* **1974**, *69*, 259. (b) Welch, J. A.; Peters, K. S.; Vaida, V. *J. Phys. Chem.* **1982**, *86*, 1941. (c) Bonneau, R.; Kelly, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 1220. (d) Kelley, J. M.; Long, C.; Bonneau, R. *J. Phys. Chem.* **1983**, *87*, 3344.

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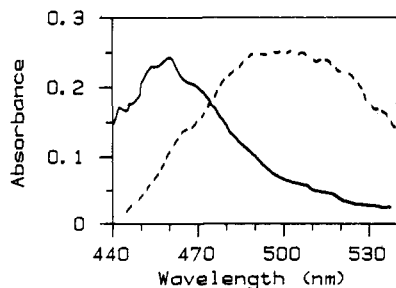


Figure 1. Transient absorption spectra of $\text{Cr}(\text{CO})_5(\text{cyclohexane})$ (---) and $\text{Cr}(\text{CO})_5(\text{pentanol})$ (—). Spectra were obtained 1 ns after photolysis of $\text{Cr}(\text{CO})_6$ in cyclohexane and pentanol, respectively. The transient spectrum observed in pentanol is identical with that observed in methanol and propanol.

to within 10%. Assuming that the quantum yield for photodissociation is the same in both solvents,⁶ the extinction coefficients of the two species are essentially identical.

As mentioned earlier, in pentanol both hydroxyl and alkyl groups are available for coordination into the site vacated by the photoelimination of a CO. It is reasonable to expect that bonding of an alkyl group will produce a species with an absorption spectrum similar to that observed in hexane or cyclohexane. If both alkyl and hydroxyl complexes are formed immediately after photodissociation, the transient spectrum will reflect a superposition of the spectra characteristic of these two complexes. In addition, with increasing delay time, complexes initially formed with alkyl groups in the coordination site would be expected to undergo rearrangement or exchange with the solvent to form the more stable hydroxyl coordinated isomer. The dynamics of solvent restructuring would be manifested by a change in the transient absorption spectrum. Examination of the data shown in Figure 1 clearly shows that the two species have regions of different absorbance. In order to address these details of the solvation process, the transient kinetics were recorded at 460 and 520 nm.

In Figure 2, the absorption dynamics observed at 460 and 520 nm are plotted as a function of time after photolysis. At 460 nm (top), an instantaneous rise in the absorption signal is observed. This is followed by a slow increase in absorption for the first ≈ 800 ps. At 520 nm (bottom), the signal also rises instantaneously. This is followed by a decay in signal to approximately 30% of its initial value. The absorption at both wavelengths is constant for delay times greater than 1 ns.

The instantaneous rise observed at 460 nm is unexpected given that the rise time in methanol was found to be 2.5 ps. However, comparison with the time-resolved data in cyclohexane¹⁸ strongly supports the conclusion that the initial rises at 460 and 520 nm reflect the formation of solvated intermediates where the alkyl chain of the pentanol molecule is coordinated to the vacant site.

In order to examine the nature of the primary intermediate in more detail, the following assumptions are made. First, the initial solvation produces species with either an alkyl group or a hydroxyl group coordinated to the vacant site. Second, the spectrum of $\text{Cr}(\text{CO})_5(\text{hexane})$ is used for the spectrum of the alkyl coordinated complex. This is consistent with the observation of similar transient spectra in pentane, hexane, and cyclohexane. Third, the relative extinction coefficients at the absorbance maximum of the hydroxyl and alkyl complexes are assumed to be equal. Finally, the constant absorption signal observed for delay time longer than 1 ns corresponds to only species where the hydroxyl group is coordinated to the vacant site. Based upon these assumptions, the transient absorption signal for a particular wavelength, λ , can be expressed as follows.

$$A^\lambda(t) = \epsilon_{\text{alkyl}}^\lambda [\text{Cr-alkyl}](t) + \epsilon_{\text{hydroxyl}}^\lambda [\text{Cr-hydroxyl}](t) \quad (1)$$

In the above expression, $\epsilon_{\text{alkyl}}^\lambda$ and $\epsilon_{\text{hydroxyl}}^\lambda$ are the extinction coefficients of the alkyl and hydroxyl complex at wavelength λ ,

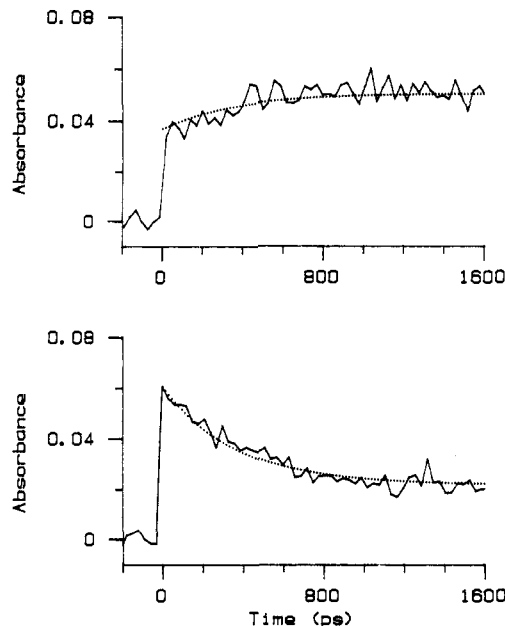
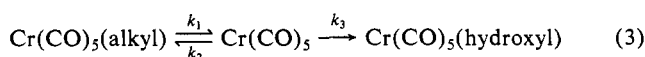
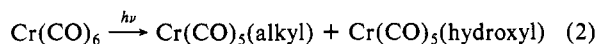


Figure 2. Transient absorption kinetics for the photolysis of $\text{Cr}(\text{CO})_6$ in pentanol. The probe wavelengths are 460 nm (top) and 520 nm (bottom). Data were collected in increments of 10 ps. The absorption at 460 nm shows an instantaneous rise followed by a slow increase in signal for the first 800 ps after photolysis. At 520 nm, an instantaneous rise followed by a slow decay is observed. Both wavelengths reveal constant signals for delays in excess of ≈ 800 ps. The dotted lines are the fit of eq 1, 4, and 5 to the data. For these calculations, the rates of alkyl and hydroxyl coordination were assumed to be the same.

respectively; $[\text{Cr-alkyl}](t)$ and $[\text{Cr-hydroxyl}](t)$ are the corresponding time-dependent concentrations of these two complexes. Using the spectra shown in Figure 1, we can determine the relative extinction coefficient for the two complexes at any wavelength. One can then use the absorption data to determine the ratio $[\text{Cr-hydroxyl}](0)/[\text{Cr-alkyl}](0)$, the initial distribution of solvated species formed immediately after photodissociation. Using the absorption data at 460 and 520 nm results in a $[\text{Cr-hydroxyl}](0)/[\text{Cr-alkyl}](0)$ ratio of $1.20 (\pm 0.3)$ and $1.22 (\pm 0.2)$, respectively. These results indicate that the vacant site of more than 50% of the photofragments are initially occupied by the hydroxyl group of the alcohol.

The preference for the coordination of the hydroxyl group for photolysis in pentanol could result from several mechanisms. First of all, in long-chain alcohols, $\text{Cr}(\text{CO})_6$ could be preferentially solvated by the hydroxyl end of the alcohol molecule. Second, the local solvent structure around the photoexcited $\text{Cr}(\text{CO})_6$ could affect which CO is photoeliminated. The details of the photodissociation mechanism in solution still remain elusive. Matrix studies show that $\text{Cr}(\text{CO})_5$ isomerizes via a square pyramid \rightarrow trigonal bipyramid \rightarrow square pyramid interconversion.³ Although this mechanism has been used to explain the small degree of geminate recombination observed upon photodissociation in solution,⁶ no unambiguous evidence supporting this mechanism has been obtained. Based on the solvation dynamics in cyclohexane, if isomerization occurs, the time scale is less than 0.5 ps. However, it is possible that interconversions between square-pyramidal isomers may preferentially open the vacant site in the vicinity of a hydroxyl group. Transient measurements on a faster time scale could help distinguish between these possibilities.

The changes in transient absorption signal observed during the first nanosecond after photolysis correspond to rearrangement of the initially formed alkyl complex to the more stable hydroxyl complex. The simplest kinetic scheme for this process can be written as a two-step process.



(6) (a) Nasielski, J.; Colas, A. *Inorg. Chem.* **1978**, *17*, 237. (b) Nasielski, J.; Colas, A. *J. Organomet. Chem.* **1975**, *101*, 215.

The first step is instantaneous ($\tau < 0.8$ ps) on the time scale of the experiment. The second step involves either rearrangement of the coordinated ligand or exchange with another solvent molecule. Studies of the ligand displacement reactions of $\text{Cr}(\text{C}-\text{O})_5\text{L}$ show that the mechanism follows a dissociative pathway.⁷ As a result, we would expect that the dissociation is rate-limiting. It is straightforward to show that the time-dependent concentrations are given by

$$[\text{Cr-alkyl}(t)] = [\text{Cr-alkyl}(0)] \left[\frac{\gamma_1 - k_2 - k_3}{\gamma_1 - \gamma_2} e^{-\gamma_1 t} + \frac{\gamma_2 - k_2 - k_3}{\gamma_2 - \gamma_1} e^{-\gamma_2 t} \right] \quad (4)$$

$$[\text{Cr-hydroxyl}(t)] = k_1 k_3 [\text{Cr-alkyl}(0)] \times \left[\frac{1}{\gamma_1 \gamma_2} + \frac{1}{\gamma_1 (\gamma_1 - \gamma_2)} e^{-\gamma_1 t} + \frac{1}{\gamma_2 (\gamma_2 - \gamma_1)} e^{-\gamma_2 t} \right] \quad (5)$$

where γ_1 and γ_2 are the negative roots to the following quadratic equation.

(7) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic: New York, 1979.

$$\gamma^2 + \gamma(k_1 + k_2 + k_3) + k_1 k_3 = 0 \quad (6)$$

From the solvation dynamics in cyclohexane and methanol, it is clear that $k_2, k_3 \gg k_1$.¹⁸ In addition, these studies show that solvent coordination can occur as fast as < 0.5 ps. If we assume that $1/k_2$ and $1/k_3$ are 0.5 ps, we obtain a half-life for the dissociation of 180 ± 50 ps. The dotted lines in Figure 2 show this fit of the above equations to the experimental data. The value of $1/k_1$ is not affected by changing the association lifetimes ($k_2 = k_3$) from 0.5 to 2.5 ps (the solvation time in methanol). However, the value for k_1 is dependent on the ratio k_2/k_3 . For example, assuming that $1/k_3 = 1$ ps, for the two cases, $k_2 = 5k_3$ and $k_2 = 0.2k_3$, the dissociation rate k_1 is 75 and 350 ps, respectively. As a result, a more detailed picture of the coordination dynamics is needed in order to be able to determine accurate time scales and activation parameters for this process.

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Diode Laser Absorption Probe of Vibration-Vibration Energy Transfer in CO_2

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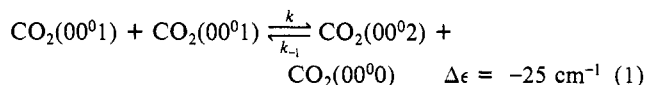
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Time domain absorption spectroscopy with a tunable diode laser has been used to measure the rate constant for vibration-to-vibration energy transfer in CO_2 via the near-resonant "collisional up-pumping" process $\text{CO}_2(00^01) + \text{CO}_2(00^01) \rightleftharpoons \text{CO}_2(00^02) + \text{CO}_2(00^00)$. The diode laser, in combination with a CO_2 discharge reference cell, is used to monitor the time-dependent population increase within the $\text{CO}_2(00^02)$ state in a 10:1 mixture of Ar and CO_2 following pulsed excitation of the $\text{CO}_2(00^01)$ level by a Q-switched CO_2 laser. The intramode relaxation rate constant, k , for this process is found to be $(5.6 \pm 0.7) \times 10^6 \text{ s}^{-1} \text{ Torr}^{-1}$ or $(1.7 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \text{ molecule}^{-1}$ at 298 K.

Introduction

The dynamics of both pulsed and CW CO_2 lasers have been the subject of extensive research for many years.¹⁻³ The behavior of these systems is now rather well understood, and kinetic models agree well with experimental results. Such models are based upon numerous rate constants for vibration-to-vibration (V-V) and vibration-to-translation (V-T) energy transfer between CO_2 , N_2 , and rare gases, values for which have been measured by infrared fluorescence and CO_2 laser double-resonance techniques.²⁻¹⁰

Perhaps the most fundamental V-V energy-transfer process in CO_2 is the near-resonant "collisional up-pumping" process



which serves as a model for how vibrational energy is distributed within the asymmetric stretch (ν_3) mode of CO_2 . The intramode relaxation rate constant, k , for this process is expected to be approximately gas kinetic and has been calculated by Pack,¹¹ but an experimental value for the room-temperature rate constant has not been published to date.¹⁰ We have recently measured this rate using the powerful combination of a tunable diode laser (TDL) spectrometer and a CO_2 discharge reference cell. The diode laser provides a high-resolution probe ($\sim 0.0003 \text{ cm}^{-1}$) for time domain absorption spectroscopy and has been recently used to probe CO_2 laser dynamics.³ The CO_2 discharge reference cell

(1) Patel, C. K. N. *Phys. Rev. Lett.* **1964**, *12*, 588; **1964**, *13*, 617; *Appl. Phys. Lett.* **1965**, *7*, 290.

(2) Gordictz, B. F.; Sobolev, N. N.; Sokovikov, V. V.; Shelepin, L. A. *IEEE J. Quantum Electron.* **1968**, *4*, 796. Moore, C. B.; Wood, R. E.; Hu, B. E.; Yardley, J. T. *J. Chem. Phys.* **1967**, *46*, 4222.

(3) Dang, C.; Reid, J.; Garside, B. K. *Appl. Phys.* **1983**, *B31*, 163; *IEEE J. Quantum Electron.* **1983**, *19*, 755. Brimacombe, R. K.; Reid, J.; Znotins, T. A. *Appl. Phys.* **1985**, *B36*, 115.

(4) Stephenson, J. C.; Moore, C. B. *J. Chem. Phys.* **1972**, *56*, 1295. Stephenson, J. C.; Wood, R. E.; Moore, C. B. *J. Chem. Phys.* **1971**, *54*, 3097. Yardley, J. T.; Moore, C. B. *J. Chem. Phys.* **1967**, *46*, 4491.

(5) Rosser, Jr., W. A.; Gerry, A. D.; Wood, E. T. *J. Chem. Phys.* **1969**, *50*, 4996. Rosser, Jr., W. A.; Sharma, R. D.; Wood, E. T. *J. Chem. Phys.* **1971**, *54*, 1196. Rosser, Jr., W. A.; Gerry, A. D. *J. Chem. Phys.* **1971**, *54*, 4131.

(6) Huddleston, R. K.; Weitz, E. *Chem. Phys. Lett.* **1981**, *83*, 174.

(7) Temple, T. A.; Suhre, D. R.; Coleman, P. D. *Appl. Phys. Lett.* **1973**, *22*, 349. Stark, Jr., E. E. *Appl. Phys. Lett.* **1973**, *23*, 335. Jacobs, R. R.; Pettipiece, K. J.; Thomas, S. J. *Phys. Rev. A* **1975**, *11*, 54.

(8) Finzi, J.; Moore, C. B. *J. Chem. Phys.* **1975**, *63*, 2285.

(9) Burak, I.; Nöter, Y.; Szoke, A. *IEEE J. Quantum Electron.* **1973**, *9*, 541.

(10) Thomason, M. D. Ph.D. Thesis, University of Virginia, Los Alamos National Laboratory, LA9420-T, 1982.

(11) Pack, R. T. *J. Chem. Phys.* **1980**, *72*, 6140. Note that Pack's rate constant, k , written in terms of the disappearance of $\text{CO}_2(00^01)$, is twice as large as that defined in eq 1 and 2.