expressions for $k_2(T)$ are given as $5.8 \times 10^{-33}(T/1000)^{-1.0}$ cm^6 molecule^{-2} s^{-1} (200 K $\leq T \leq$ 2200 K) and $1.8 \times 10^{-32}(T/300)^{-0.8}$ cm^6 molecule^{-2} s^{-1}, respectively. At 850 K, which is approximately the median temperature of the present study, Slack's expression gives a value of 6.8×10^{-33} cm^6 molecule^{-2} s^{-1} and the expression of Baulch et al.[37] yields a value of 7.8×10^{-33} cm^6 molecule^{-2} s^{-1}. In contrast, these results and that of the present study are about a factor of 3 larger than the determination of Pamidimukkala and Skinner.[11]

Very recenty, Hsu et al.[38] have undertaken a comprehensive experimental study of reaction 2. For the temperature interval 300 K $\leq T \leq$ 639 K, they report (with He as the third body):

$$k_2(T) =$$
$$(4.0 \pm 1.2) \times 10^{-33} \exp(+560 \pm 100/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$
(XIX)

It is generally accepted that the third-body efficiencies for He and Ar are about the same, and thus it is appropriate to extrapolate eq XIX to 850 K in order to make a comparison with the present value. The value computed, $k_2(\text{He}) = 7.7 \times 10^{-33}$ cm^6 molecule^{-2}

s^{-1}, is in good agreement with the present determination of k_2, $(7.1 \pm 1.9) \times 10^{-33}$ cm^6 molecule^{-2} s^{-1}.

Theoretical calculations on the limiting low-pressure third-order rate constant for reaction 2 have been discussed by Cobos et al.[39] The present result between 746 and 987 K, $k_2 = (7.1 \pm 1.9) \times 10^{-33}$ cm^6 molecule^{-2} s^{-1}, requires the following Troe model parameters at 850 K: $\beta_c = 0.03$ and $\langle \Delta E \rangle = -51.4$ cal mol^{-1}. These values for β_c and $\langle \Delta E \rangle$ are in good agreement with those reported by Cobos et al.[39] for M = Ar at 1000 K. Indeed, this agreement was expected since Cobos et al.[39] based their calculations on a value for k_2 of 6.9×10^{-33} cm^6 molecule^{-2} s^{-1} at 1000 K.

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Photodissociation of Cr(CO)$_6$ in 1-Propanol and 2-Propanol: Effect of Solvent Structure on the Mechanisms of Formation of Cr(CO)$_5$(OHR) from Photogenerated Cr(CO)$_5$(ROH)

John D. Simon[*,†] and **Xiaoliang Xie**

Department of Chemistry and the Institute of Nonlinear Studies, University of California at San Diego, La Jolla, California 92093 (Received: June 20, 1988)

Picosecond absorption spectroscopy is used to examine the dynamics of formation of Cr(CO)$_5$(OHR) from Cr(CO)$_5$(ROH) generated by the photodissociation of CO from Cr(CO)$_6$ in 1-propanol (1-Pro) and 2-propanol (2-Pro) solutions. The rearrangement process is considerably faster in 2-Pro than in 1-Pro despite the similar macroscopic properties of the two solvents. The dynamics in 2-Pro are similar to that observed in neat ethanol solution. These data show that the mechanism for formation of the more stable hydroxyl complex from an initially formed alkane complex depends on the structure of the coordinated solvent molecule. On the basis of bond strength data for the chromium–alkane bond, the rearrangement in 2-Pro is concluded to occur by a unimolecular displacement mechanism.

Introduction

The chemistry of coordinatively unsaturated metal–carbonyl complexes is of current interest due to their importance as intermediates in substitution reactions.[1] In particular, the coordinatively unsaturated complexes M(CO)$_5$ (M = Cr, Mo, W) exhibit a wide variety of reactivities. The structure and dynamics of these reaction intermediates have been studied by several spectroscopic techniques.[2] Photochemical studies in solution reveal that electronic excitation of M(CO)$_6$ results in efficient ($\Phi \approx 0.7^3$) photoelimination of a single CO ligand producing a C_{4v} M(CO)$_5$ fragment.[4] Time-resolved studies on the photolysis of Cr(CO)$_6$ in solution show that photodissociation occurs on the subpicosecond time scale and that coordination of a single solvent molecule to the site vacated by the photoeliminated CO occurs within a few picoseconds of excitation.[2a–c] Recent studies on the photodissociation of Cr(CO)$_6$ in long chain alcohols (pentanol) revealed a distribution of primary products in which either the alkane, Cr-

(CO)$_5$(ROH), or hydroxyl, Cr(CO)$_5$(HOR), part of the solvent molecule coordinates to the vacant site.[2c] These two types of complexes are easily distinguished by absorption spectroscopy; the hydroxyl and alkane species have absorption maxima at 460 and 505 nm, respectively. The thermodynamically most stable complex involves coordination of the hydroxyl end of the alcohol

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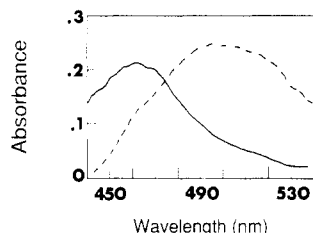
Figure 1. Absorption spectra for Cr(CO)$_5$(alkane) (—) and Cr(CO)$_5$-(propanol) (---). The alcohol spectrum reflects coordination of the hydroxyl end of the solvent molecule.

molecule; complexes that initially involve bonds between the chromium and alkane portion of the solvent molecules will undergo rearrangement to form the more stable complex. For the linear alcohols (methanol to decanol), the time scales for this restructuring process increase substantially with increasing chain length.[5]

In this paper the effect of solvent structure on the mechanism of formation of Cr(CO)$_5$(HOR) from initially formed Cr-(CO)$_5$(ROH) complexes is examined by comparing the dynamics observed in room-temperature 1-propanol (1-Pro) and 2-propanol (2-Pro) solutions. On a macroscopic level, the two solvents have several similar properties. The viscosities of 1-Pro and 2-Pro at 15 °C are 2.52 and 2.86 cP, respectively.[6] In addition, the Debye relaxation times of the two solvents are nearly identical (450 and 475 ps for 1-Pro[7a] and 2-Pro,[7b] respectively), suggesting that the time scales for the making and breaking of hydrogen bonds in the two liquids are very similar. These data might lead one to conclude that the restructuring of the initially formed alkane complex to the more stable hydroxyl complex would occur at similar rates in the two solvents.
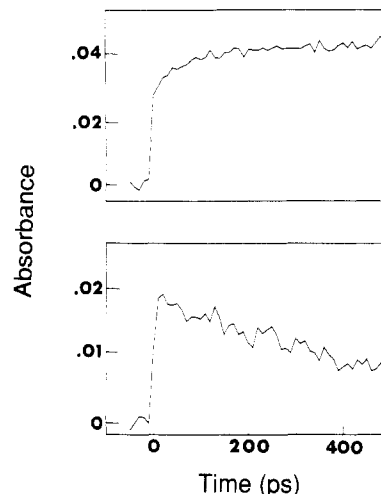
Experimental Section

Picosecond laser pulses are generated by amplifying the output of a synchronously pumped dye laser. The amplified pulses are ≈1 mJ/pulse, <1.0 ps fwhm, 600 nm, and occur at a repetition rate of 20 Hz. The laser output is frequency doubled to 300 nm by using a 2-mm KDP crystal providing the UV light which is used for photolysis. The remaining red light is focused into a cell of H$_2$O, generating a white light continuum which is used to record transient absorption data in a dual-beam configuration. Details of the experimental apparatus will be published shortly.

Cr(CO)$_6$ was purchased from Aldrich and purified by sublimation. The solvents were of spectroscopic grade and used without any further purification.

## Results and Discussion

In Figure 1, transient absorption spectra for Cr(CO)$_5$(propanol) and Cr(CO)$_5$(hexane) are plotted. The spectrum of the alcohol complex reflects coordination of the hydroxyl end of the solvent molecule to the chromium metal. The alkane complex, Cr-(CO)$_5$(ROH), and hydroxyl complex, Cr(CO)$_5$(HOR), have absorption maxima at 505 and 460 nm, respectively. The absorption spectrum of the alcohol complex is insensitive to the length of the alkane chain. Similar results are found in hydrocarbon solvents. In long chain alcohols, time-resolved studies clearly show that photodissociation produces a distribution of solvated complexes,[2e] where the vacant coordination site on the metal can be occupied by either an alkane group or the hydroxyl group of the solvent molecule. In light of the data presented in Figure 1, these complexes are easily distinguished by their respective absorption spectrum. Thus, in order to monitor the restructuring dynamics, transient absorption data at 460 and 520 nm are examined.

In Figure 2, the time dependence of the transient absorption at 520 and 460 nm is plotted as a function of time after photoexcitation of Cr(CO)$_6$ in 1-Pro. In Figure 3, the corresponding

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Figure 2. Absorption intensity at 460 nm (top) and 520 nm (bottom) for the photolysis of Cr(CO)$_6$ in 1-propanol plotted as a function of time following photoexcitation.
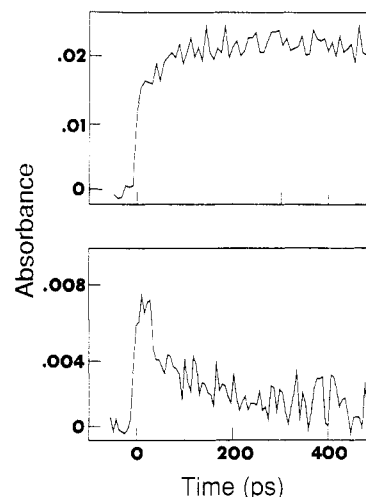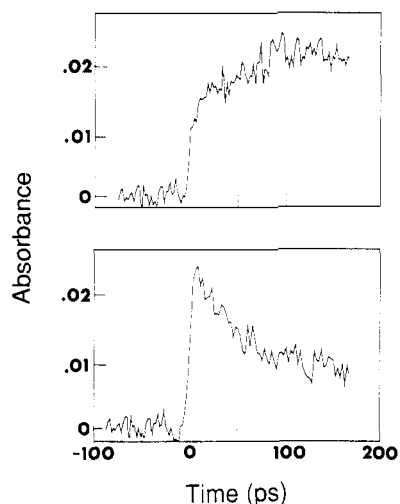

Figure 3. Absorption intensity at 460 nm (top) and 520 nm (bottom) for the photolysis of Cr(CO)$_6$ in 2-propanol plotted as a function of time following photoexcitation.

data for photolysis in 2-Pro are given. In both solvents, the transient absorption at both wavelengths rises with the laser pulse. For times longer than the laser pulse, the absorption at 460 nm continues to increase while the absorption at 520 nm decays. The initial rises correspond to formation of a distribution of alkane coordinated complexes and hydroxyl coordinated complexes, respectively. The slow rise component at 460 nm is difficult to resolve as both species absorb appreciably at this wavelength. If one uses the transient optical spectra shown in Figure 1 and assumes similar extinction coefficients for the two complexes, the relative absorbance of the Cr(CO)$_5$(OHR) to Cr(CO)$_5$(ROH) at 460 nm is ≈1.5:1. This is contrasted with a relative absorbance of ≈1:8 observed at 520 nm. It would be better to monitor the dynamics at wavelengths shorter than 460 nm (the absorption difference between the two solvated complexes is greater); however, our picosecond probe continuum is limited to wavelengths longer than 450 nm. Thus, the restructuring dynamics are more easily resolved at the green wavelength. Examination of the data at 460 nm does reveal that an appreciable concentration of Cr(CO)$_5$-(HOR) is formed immediately following photolysis. The slower rise component represents less than one-third of the transient absorption signal observed after solvent restructuring is complete. In 2-Pro, the signal increases during the first 100 ps and then is constant for the remainder of the delay examined. In 1-Pro, the signal continues to rise for the entire 400 ps studied. These results are confirmed by the dramatic changes observed at 520 nm. Comparison of the data in 1-Pro and 2-Pro clearly shows that the initially formed alkane complex with 2-Pro disappears significantly

Figure 4. Absorption intensity at 460 nm (top) and 520 nm (bottom) for the photolysis of Cr(CO)$_6$ in ethanol plotted as a function of time following photoexcitation.

faster than the corresponding complex formed with 1-Pro.

The data presented in Figures 2 and 3 indicate that despite the similar macroscopic properties of the two solvents, the restructuring of the alkane complexes to form the thermodynamically more stable hydroxyl complex is faster in the case of coordinated 2-Pro. It is generally thought that thermal ligand displacement reactions of Cr(CO)$_6$ and Cr(CO)$_5$L follow a dissociative mechanism. Recent photoacoustic measurements demonstrate that the strength of the methyl–alkane bond in cyclohexane is on the order of 10 kcal/mol.[8] Similar bond strengths would be expected for the chromium–alkane bonds formed with the alcohols. Using this value for the chromium–alkane bond strength, we can calculate the equilibrium constant between uncoordinated "Cr(CO)$_5$" and Cr(CO)$_5$(alkane). Kinetically, this equilibrium constant is simply the ratio of the solvent coordination rate to the solvent dissociation rate. From picosecond studies of solvent coordination to photogenerated Cr(CO)$_5$ in methanol and cyclohexane solutions, the solvent association rate is estimated to be on the order of 1 ps^{-1}. These data suggest a dissociation rate of $\approx 10^7$ s^{-1}. This rate

constant would represent the fastest rate allowed for displacement reactions of Cr(CO)$_5$(ROH) which occur by a dissociative process. However, the data given in Figures 2 and 3 indicate that the formation of Cr(CO)$_5$(HOR) from Cr(CO)$_5$(ROH) involves rate constants on the order of 10^{10} s^{-1}, 3 orders of magnitude faster than that predicted for a dissociative mechanism. The microscopic structure of the solvent must be important in determining the reaction rate.

Two mechanisms could be envisioned to account for the reaction dynamics observed; the displacement of the coordinated alkane group could occur by either a unimolecular or a bimolecular displacement process. From the consideration of steric effects at the coordination site, bimolecular displacement reactions should be slower for 2-Pro than 1-Pro, in contrast with the experimental data. This suggests that, in the case of 2-Pro, the rearrangement is unimolecular. Based on the structure of 2-Pro, coordination of any of the alkane groups results in a metal–solvent bond which is within close proximity to the hydroxyl group of the molecule. Thus, rapid unimolecular displacement of the alkane group by the hydroxyl group can occur. Coordination of either methylene groups of 1-Pro results in similar chromium–hydroxyl distances as those predicted for 2-Pro; in this case similar rates of rearrangement would be expected. The slower rate observed for 1-Pro suggests that the hydroxyl group is further away from the metal center in the alkane complex, supporting the conclusion that the terminal end of the linear alcohol is preferentially coordinated to chromium.

This is further confirmed by the restructuring dynamics found in ethanol solution. Coordination of the alkane part of an ethanol molecule results in structures similar to that expected for 2-Pro coordination. In Figure 4, the transient absorption dynamics at 460 and 520 nm for the photolysis of Cr(CO)$_6$ in ethanol are shown. As observed in 2-Pro, the transient absorption at 520 nm decreases to a constant value in about 100 ps. The data at 460 nm reveal an instantaneous rise followed by a slower component which also reaches a constant value in about 100 ps. These dynamics are similar to that observed in 2-Pro and argue for a unimolecular displacement mechanism in both solvents.

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