Temperature-Dependent Studies of the Rearrangement Dynamics of Photogenerated Solvated Complexes of Chromium Pentacarbonyl in Linear Alcohol, Alkyl Bromide, and Nitrile Solvents

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Abstract: Picosecond absorption spectroscopy is used to study the formation of $Cr(CO)_5(XR)$ from photogenerated $Cr(CO)_5(RX)$ in alcohol, alkyl bromide, and alkanenitrile solvents. The data are discussed in terms of a unimolecular migration model recently published by Xie et al.[1e] Similar reaction dynamics are observed in alcohol and alkyl bromide solvents in accord with the predictions of the unimolecular reaction mechanism. Temperature studies show that this rearrangement process is activated; the activation energies obtained are similar to those reported for the syn rotational barrier in alkanes. The reaction dynamics in nitrile solvents are faster than that observed in the corresponding length alcohol or alkyl bromide solvent. By using the unimolecular model, the data can be accounted for by proposing that coordination of the solvent to photogenerated pentacarbonyl occurs preferentially to the end of the solvent molecule containing the CN group. These data suggest that $Cr(CO)_6$ is preferentially solvated by the dipolar end of the solvent molecule, while solvation in either linear alcohol or alkyl bromide solvents is not characterized by any preferential interactions.

Introduction

The photodissociation of $Cr(CO)_6$ and the subsequent solvation of the coordinatively unsaturated pentacarbonyl has been the subject of numerous recent time resolved electronic absorption[1-4] and infrared[5] studies. These experimental studies demonstrate that several important molecular processes contribute to the observed spectral dynamics. By using femtosecond time resolution, Nelson and co-workers[2] have demonstrated that bond cleavage occurs in less than 250 fs, suggesting that excitation directly populates a dissociative state. Transient infrared experiments reported by Spears and co-workers,[5] transient absorption studies reported by Harris and co-workers,[2] and transient Raman studies reported by Hopkins and co-workers[6] all demonstrate that the primary photoproduct, the coordinatively unsaturated pentacarbonyl, is vibrationally hot following photodissociation. Relaxation times ranging from tens of picoseconds to a hundred picoseconds have been reported depending on the particular experimental technique used. It is still unclear when the solvent molecule attaches to the vacant coordination site; however, transient absorption studies following photolysis in methanol[1a,2] and cyclohexane[3] would suggest that coordination competes with vibrational cooling. Spears and co-workers have also suggested that unsolvated D_{3h} and D_{4v} isomers are in equilibrium and remain bare for about a hundred picoseconds;[4a] however, the implications of these intermediates on the interpretation of the transient absorption measurements on this time scale has not been definitively addressed.

The dynamics of photodissociation have also been extensively studied in rare gas matrices. By using polarized light, Turner and co-workers[7] established that photogenerated $Cr(CO)_5$ can isomerize via a $C_{4v} \rightarrow D_{3h} \rightarrow C_{4v}$ mechanism, moving the vacant coordination site. This mechanism has been invoked to account for the large quantum yield of dissociation reported for this system.[8] Infrared and visible absorption studies of photogenerated $Cr(CO)_5$ in neon matrices indicate that only C_{4v} isomer is present and that a neon atom is weakly bonded to the metal center. These conclusions are consistent with calculations reported by Hay[9] in which the C_{4v} isomer is predicted to be the lowest energy geometry of $Cr(CO)_5$ with the D_{3h} isomer estimated to be less stable by ~10 kcal/mol. However, the transient infrared studies by Wang et al.[5] indicate that the energy gap between these two isomers may be considerablely smaller than these calculations suggest.

In a recent paper, we established that following photodissociation, coordination of a solvent molecule to $Cr(CO)_5$ in alcohol solution results in formation of a distribution of solvent-coordinated complexes,[1] in which either an alkane moiety (C–H group) of the molecule or the hydroxyl group is coordinated to the photogenerated coordination site. Furthermore, with increasing delay time, initially formed alkane complexes are observed to thermally rearrange to the more stable hydroxyl species. The time scale for the evolution of the alkane to the hydroxyl coordinated complexes is hundreds of picoseconds to several nanoseconds. Comparisons with the data available from transient infrared[5] and Raman[6] studies, indicates that this rearrangement reaction involves vibrationally relaxed intermediates. Various mechanistic models for the interconversion between alkane coordinated complexes and the hydroxyl species were examined.[1e] By using bond strength data and activation parameters reported for various ligand substitution reactions,[10] it was demonstrated that the observed dynamics were inconsistent with both a dissociative and an associative substitution mechanism. To account for the kinetics, a unimolecular migration model was developed.[1e] By using this model, the dynamics observed for the entire series of linear alcohols studied (methanol–decanol) could be quantitatively accounted for.

In the present paper, we examine the dynamics of formation of $Cr(CO)_5(XR)$ from photogenerated $Cr(CO)_5(RX)$ in alcohol,

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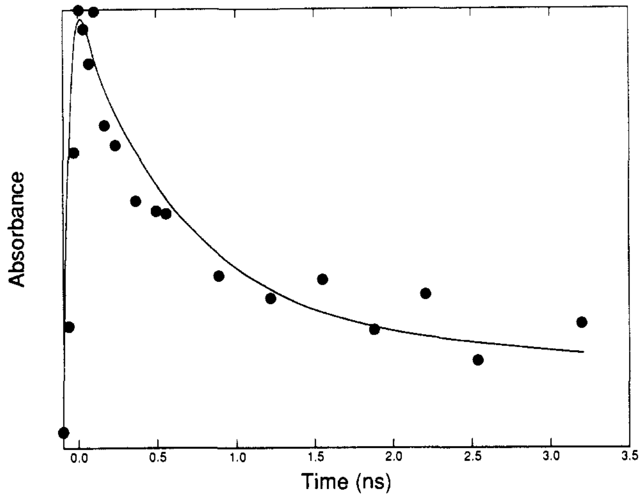

Figure 1. Transient absorption at 532 nm following photolysis of $Cr(CO)_6$ in *n*-bromobutane at room temperature. The solid line is a calculated decay using the unimolecular migration model and the kinetic parameters derived from studies in alcohol solutions.

alkyl bromide, and alkane nitrile solvents. Activation parameters for the thermal rearrangement process, $Cr(CO)_5(RX) \rightarrow Cr(CO)_5(XR)$, are determined by using the unimolecular migration model previously reported.[1e] Analysis of the reaction dynamics in alcohols and alkyl bromides reveal identical rate constants and activation parameters for the migration process. This result demonstrates that the dynamics of restructuring in alcohol solutions are not dependent on the breaking of intermolecular hydrogen bonds. Furthermore, this observation supports the conclusion that rearrangement occurs by a unimolecular migration process. On the basis of the activation parameters determined and geometric constraints of the solvent–chromium complex, a molecular mechanism for the rearrangement process is proposed. Finally, in nitrile solvents, the dynamics of formation of the cyano complex from photogenerated alkane complexes is greatly accelerated in comparison with the same chain length alcohol of alkyl bromide solvent. By using the unimolecular migration model and the rate constants obtained from studies in alcohol (or alkyl bromide) solvents, the reaction dynamics in nitriles is accounted for by proposing that initial coordination of the metal to the solvent occurs preferentially to carbons near the cyano end of the solvent molecule. These results suggest that in nitrile solvents, chromium hexacarbonyl is preferentially solvated by the dipolar end of the solvent molecule, while solvation in either alcohol or alkyl bromide solvents is not characterized by any preferential orientation.

Experimental Section

Transient absorption data were obtained by using picosecond laser pulses generated from a commercial Quantel picosecond laser system. Photolysis and probing were carried out by using the third harmonic (355 nm) and the second harmonic (532 nm) of the laser, respectively. The temperature of the sample cell was regulated by using a brass block connected to a closed cycle circulator. The sample was stirred constantly during photolysis, and at most 5% of the sample is photolyzed during an experiment. The detection system used is similar to that recently described.[11] The relative polarization of the probe and pump beams was found to have no effect on the observed dynamics.

$Cr(CO)_6$ was obtained from Aldrich and used without further purification. The alcohol solvents were dried over 3Å molecular sieves. The alkyl bromide and nitrile solvents were dried and purified immediately prior to use. All solutions were saturated ($\cong$1 mM).

Results

In Figure 1, the absorption dynamics at 532 nm following photodissociation of $Cr(CO)_6$ in *n*-bromobutane is shown. Absorption at this wavelength reflects the time-dependent population of photogenerated $Cr(CO)_5(RBr)$ complexes. The transient signal rises within the instrument response and decays to a constant value within $\cong$3 ns. The constant tail in the absorption dynamics arises from the absorption of the more stable $Cr(CO)_5(BrR)$ complex.[3b] In Figure 2, the temperature dependence of the time-dependent absorption at 532 is examined for the photolysis of $Cr(CO)_6$ in butanol solution. The transient absorption signal decreases with time, and the rate of decay increases with increasing temperature. Temperature-dependent dynamics are observed in all the linear alcohols and alkyl bromides; within experimental error, the dynamics observed in the same chain length alcohol and alkyl bromide are identical.

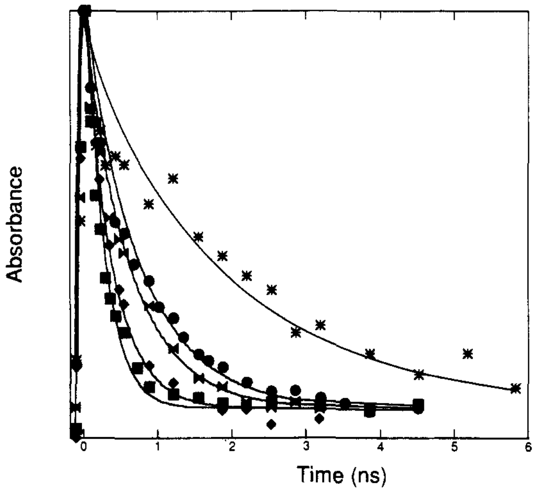

Figure 2. The temperature dependence of the transient absorption dynamics at 532 nm for the photolysis of $Cr(CO)_6$ in butanol are plotted. The temperatures studied are 7 °C (✱), 25 °C (●), 38 °C (⋈), 56 °C (♦), and 75 °C (■). The solid curves are fits of the unimolecular migration model assuming that random coordination to the possible solvent sites occurs at all temperatures studied.

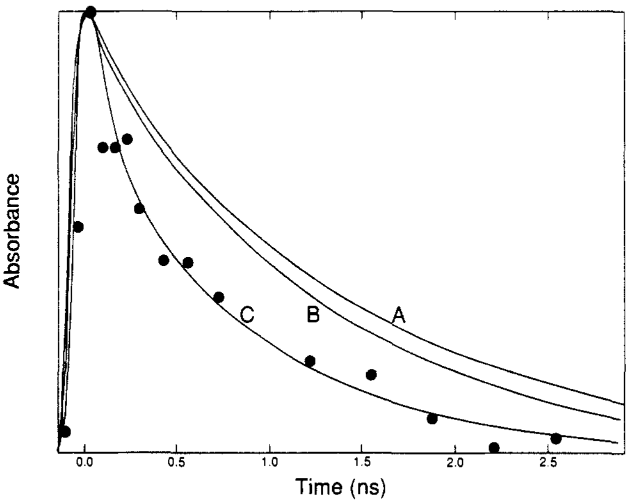

Figure 3. Transient absorption at 532 nm following photolysis of $Cr(CO)_6$ in hexanenitrile at room temperature. (A) The simulated curve using the unimolecular migration model and assuming random coordination and the rate constants derived from the alcohol study. (B) The simulated curve using the unimolecular migration model and assuming random coordination and the rate constant for $k_{C\text{-}C}$ derived from the alcohol/alkyl bromide study and $k_{C\text{-}X}$ of 1×10^{11} s^{-1}. (C) The simulated curve using the unimolecular migration model assuming the rate constants derived from the alcohol study and preferentially coordinated to the solvent chain in the vicinity of the terminal CN group.

In Figure 3, the absorption dynamics at 532 nm following photolysis of $Cr(CO)_6$ in hexanenitrile are plotted. As observed in alcohol and alkyl bromide solvents, the absorption intensity at this wavelength decreases with increasing delay time, reflecting the formation of CN coordinate complexes from initially formed alkane-coordinated species. In the nitrile solvents, the transient signal decays to zero, consistent with previous observations tht

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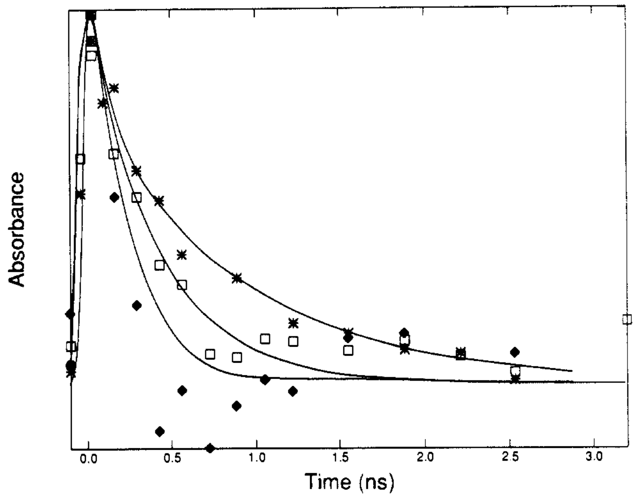

Figure 4. The temperature dependence of the transient absorption dynamics at 532 for the photolysis of $Cr(CO)_6$ in hexanenitrile is plotted. The temperatures studied are 25 °C (✱), 56 °C (□), and 75 °C (♦). The solid curves are fits of the unimolecular migration model assuming the preferential distribution for solvent coordination determined from the room-temperature study. The changes in the calculated curves arise from varying the k_{C-C} rate constant.

the $Cr(CO)_5(NCR)$ complex does not absorb at 532 nm.[7,12] However, for all chain lengths studied (n = 3–6), the dynamics of the absorption decays are faster in the nitrile solvents than in the corresponding length alcohol or alkane bromide system. In Figure 4, the temperature dependence of the population decays of $Cr(CO)_5(RCN)$ complexes formed by photolysis of $Cr(CO)_6$ in hexanenitrile are shown. Similar to that observed in the alcohol and alkyl bromides solvents, the decay of the absorption intensity at 532 nm is temperature dependent, with increased decay rates observed with increasing temperature.

Discussion

In the following sections, the restructuring of initially formed alkane complexes, $Cr(CO)_5(RX)$, to the more stable hexacoordinated complex in which the functional group of the solvent molecule occupies the metal coordination site, $Cr(CO)_5(XR)$, is examined in alkyl bromide and nitrile solvents. The data are compared with our previous results reported for photolysis of $Cr(CO_6$ in alcohol solutions. The results from these analyses provide additional evidence that the reaction proceeds by a unimolecular mechanism and also indicates that specific solvation effects are important in the photolysis studies in nitrile solvents. Before analyzing the data, the details of the unimolecular migration model are reviewed.[1e]

A. The Unimolecular Migration Model. In modeling the unimolecular rearrangement process, two rate constants are used, k_{C-C} and k_{C-X}, corresponding to migration between any two adjacent alkane groups and migration to the carbon which is attached to the functional group (X = OH, CN, Br), respectively. In addition, it is assumed that when the metal coordinates to the functional group, no further migration occurs, i.e., the OH, CN, or Br group is considered to be a trap. This assumption is consistent with both the expected difference between the metal-(C-H) and metal-X strengths and the lack of transient absorption in the regions of the alkane complex absorption band observed for the long delay times.

The migration kinetics of a linear molecule containing n carbons can then be represented by n coupled differential equations. The numbering of the carbon atoms in the alkane is sequential with C^1 being bonded to the functional group. For $n > 3$ we have

$$\frac{d[C^1]}{dt} = k_{C-X}[C^2] \qquad (1)$$

$$\frac{d[C^2]}{dt} = -k_{C-X}[C^2] - k_{C-C}([C^2] - [C^3]) \qquad (2)$$

$$\frac{d[C^m]}{dt} = k_{C-C}([C^{m+1}] + [C^{m-1}] - 2[C^m]);\ (2 < m < n) \qquad (3)$$

$$\frac{d[C^n]}{dt} = k_{C-C}([C^{n-1}] - [C^n]) \qquad (4)$$

Simplification of eq 2–4 to model shorter chain solvent molecules is straightforward.

In interpreting the meaning of $[C^m]$, the chromium metal is assumed to be bonded to the most stable substituent of the referenced carbon atom. Thus, the population $[C^1]$ represents the population of OH-, CN-, or Br-coordinated species. Given a set of initial conditions which describes the distribution of complexes formed immediately following photolysis, the series of coupled differential equations can be simultaneously solved by using the Runge–Kutta algorithm.[13] The solutions provides the time-dependent populations of various types of solvent-coordinated complexes. From these data, the time dependence of the transient absorption signals at the various wavelengths which are probed experimentally can be calculated as previously described.[1e] In the present study, the instrument response is approximately 30 ps, thus, in comparing calculated curved to the experimental data, the calculated absorption signal is convoluted with a Guassian instrument response function.

Previous analyses of the absorption dynamics in alcohols revealed two important conclusions.[1e] First, coordination of the solvent to the vacant coordination site of metal occurs randomly along the solvent chain. Second, by simultaneously fitting the absorption dynamics observed for the linear alcohols ethanol through decanol, the rate constants k_{C-X} and k_{C-C} were determined to be 2×10^{10} and $4 \times 10^9\ s^{-1}$, respectively.[1e]

B. Photodissociation and Solvation in Alkyl Bromides. The transient absorption dynamics at 532 nm following photolysis of $Cr(CO)_6$ in n-bromobutane is shown in Figure 1. The solid curve is a calculation of the expected time-dependent signal assuming a random coordination along the solvent chain by using the rate constants derived from the alcohol study. Excellent agreement is observed. Similar results are observed in all alkyl bromide solvents studied. The similarity of the alkyl bromide and alcohol data indicates that the rate of motion along the carbon chain is insensitive to the functional group. These results also strongly support the conclusion that the solvation dynamics in alcohols is not controlled by the breakage of intermolecular hydrogen bonds and that in both solvent systems the initial distribution of hexacoordinated complexes involves random coordination of the pentacarbonyl to the various binding sites of the solvent molecule.

In stimulating the data shown in Figure 1, identical rates are assumed for k_{C-Br} and k_{C-O}. This is probably not realistic due to the difference in bond strength for the Cr–X bonds.[10] In particular, as the alcohol complexes are more stable, one would expect that $k_{C-Br} < k_{C-O}$. However, assuming that coordination occurs randomly along the solvent chain, motion along the carbon chain is rate limiting for chain lengths greater than two carbons and dominates the kinetics. Thus, the simulation is relatively insensitive to the magnitude of k_{C-X}. This is clearly demonstrated in Figure 5, where data is simulated for the absorption dynamics at 532 nm, following random coordination to a four-carbon system varying the magnitude of k_{C-X}. For all the solvents studied, binding to the functional group is more stable than coordination of an alkyl group, indicating $k_{C-X} > k_{C-C}$. The differences in the calculated curves generated for values of k_{C-X} between 1×10^{11} and $1 \times 10^{10}\ s^{-1}$ are within the noise level of the experiment and

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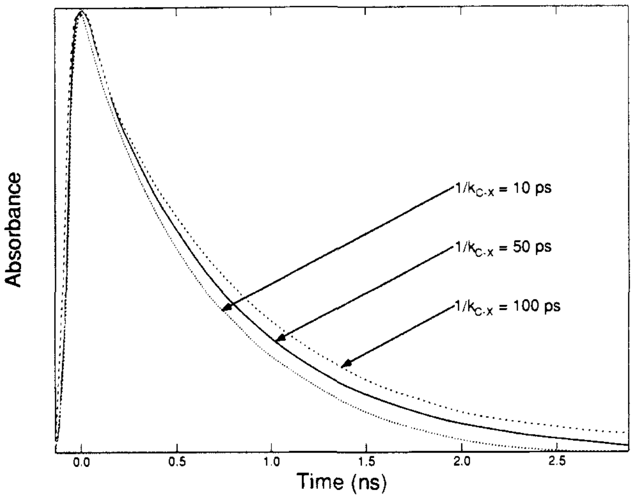


Figure 5. The effect of varying $k_{C\text{-}X}$ on the calculated transient absorption dynamics at 532 is examined for the case of random coordination to a solvent with an *n*-butyl alkyl chain. The data demonstrated that by fixing $k_{C\text{-}C}$ at 4×10^9 s^{-1} and varying $k_{C\text{-}X}$ from 1×10^{11} to 1×10^{10} s^{-1}; there is a negligible effect on the transient absorption decay.

encompass all reasonable values of $k_{C\text{-}X}$.

These data suggest that the dynamics of restructuring in alkyl bromide and alcohol solvents are identical. If the evolution in this region of the optical spectrum reflected vibrational relaxation in either a bare pentacarbonyl fragment or a solvated photoproduct, different dynamics are expected due to the changes in solvent vibrational frequencies. Furthermore, studies in chloroalkanes suggest that vibrational relaxation is complete within a few tens of picoseconds,[14] several orders of magnitude faster than the dynamics observed in Figure 3 and previous studies in alcohols. Thus, we conclude that these data are monitoring the rearrangement reaction of relaxed hexacoordinated complexes.

C. Activation Parameters for Migration Steps in Alcohol and Alkyl Bromide Solvents. By varying the temperature, activation parameters for the formation of $Cr(CO)_5(XR)$ from photogenerated $Cr(CO)_5(RX)$ can be obtained. In analyzing the temperture-dependent data, we used the unimolecular migration model summarized in section A. The temperature-dependent decays at 532 nm observed for the photolysis of $Cr(CO)_6$ in butanol between 7 °C and 75 °C are shown in Figure 2. The rate of population decay of the $Cr(CO)_5(RX)$ complex increases with increasing temperature, indicating that the rearrangement process is activated. In determining the activation energy, the following assumptions were made. First, for all temperatures examined, coordination was assumed to occur randomly along the solvent chain, as concluded for the room-temperature studies. Second, under these conditions, the reaction dynamics are insensitivity to small changes in $k_{C\text{-}X}$ (Figure 5), thus only the value of $k_{C\text{-}C}$ was adjusted in fitting the temperature-dependent data. If these assumptions are correct, the derived values of $k_{C\text{-}C}$ as a function of temperature should be the same for various chain length solvents. Temperature-dependent data are obtained for photolysis in both pentanol and butanol, and the resulting values for $k_{C\text{-}C}$ are plotted in Figure 6. As expected, the values obtained are similar for the two alcohol solvents, supporting both the assumptions made in obtaining the temperature-dependent rate constants as well as the applicability of the unimolecular model for describing the reaction process. A least-squares fit to the data shown in Figure 6 gives an activation barrier of 6.4 (±1.5) kcal/mol. Within experimental error, an identical value is obtained from analysis of temperature-dependent data in the alkyl bromides. This value is less than the metal–alkane bond strength of 9.8 kcal/mol reported by Yang et al.[9] and supports the conclusion that as migration occurs, the bond between the chromium metal and an alkane group does not completely break before a new bond on the adjacent alkane substituent is formed.

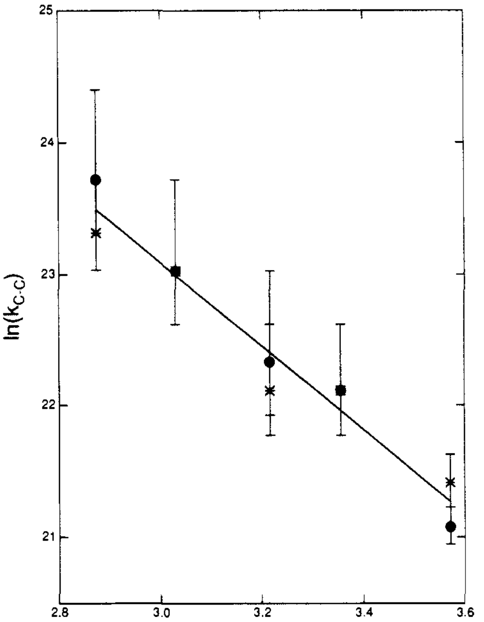
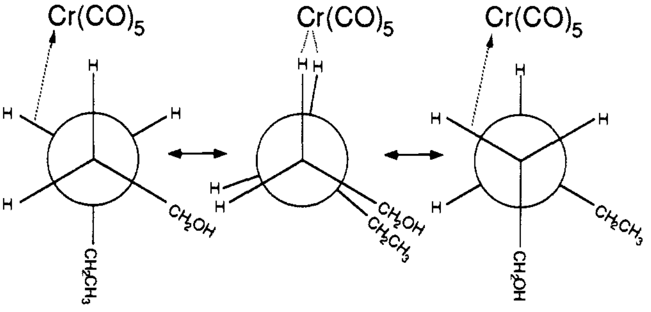


Figure 6. The log of the rate constant $k_{C\text{-}C}$ is plotted as a function of the inverse of the solvent temperature. The values of $k_{C\text{-}C}$ were obtained by using the unimolecular migration model assuming random coordination and a value of 2×10^{10} s^{-1} for $k_{C\text{-}X}$. Data are plotted for butanol (●) and pentanol (✱).

Scheme I



By using these data, one can propose a molecular picture for the migration process. The details are shown in Scheme I for the particular case of pentanol; however, the general features apply to other chain lengths and functional groups. Coordination of the alkane group to the metal center involves donation from the σC–H bond into the metal d-orbital.[15] In order for the solvent to occupy the vacant site and enable this type of interaction, the alkane chain at the coordinated site must be in a gauche configuration, directing the bulky alkane substituents which are not bonded to the chromium away from the metal center. The activation energy obtained from the temperature-dependent study indicates that during the migration process, the new bond to the metal is formed without complete breakage of the existing metal–alkane interaction. Given the distances between the metal center and the adjacent alkyl groups of the solvent in the gauche configuration, one would expect complete dissociation to occur unless there is a change in geometry. The data suggest that complete dissociation does not occur. Rotation around the C–C bond would create an intermediate in which the metal could be

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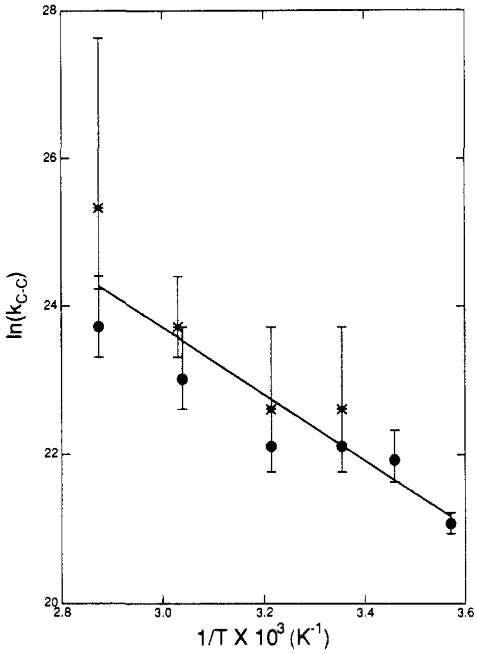

Figure 7. The log of the rate constant, k_{C-C}, is plotted as a function of the inverse of the solvent temperature. The values of k_{C-C} were obtained by using the unimolecular migration model assuming the preferential coordination distribution derived from the room-temperature studies and that k_{C-C} and k_{C-X} at this temperature are 4×10^9 and 2×10^{10} s^{-1}, respectively. Data are plotted for pentanenitrile (●) and hexanenitrile (✱).

simultaneously bonded to two C–H groups. The structure of this complex, also shown in Scheme I, is similar to calculated geometries for the lowest energy structure of a $Cr(CO)_5H_2$ complex.[16] As the alkane continues to rotate around the C–C bond, the chromium can migrate between adjacent carbon groups. It is interesting to compare the activation parameters obtained in the present study to those reported for rotation through the syn barrier for a neat alkane. In the case of *n*-butane, reports of this barrier range in the vicinity of 5 kcal/mol,[17] within experimental error of that obtained from our temperature-dependent data.

D. Photodissociation and Solvation in Nitrile Solvents. Data observed at 532 nm following photolysis of $Cr(COe)_6$ in hexanenitrile is shown in Figure 3. The absorption signal decays to zero with increasing delay time. This is consistent with the observation that the CN-coordinated complex does not absorb in this spectral region. Unfortunately, the cyano complex is characterized by a narrow absorption band which has a maximum of 390 nm[7,12] and is outside the spectral window accessible with the white light continuum probe. The data in Figure 3 are compared to three simulated curves. Curve A is the expected population decay assuming a random coordination and rate constants derived from the studies in alcohols and alkyl bromides. The observed population decay of the $Cr(CO)_5(RX)$ complex is faster than that predicted by this model. Due to the increased stability of the Cr–CN bond relative to that formed in the alcohol, it is likely that the rate for migration to the terminal carbon is faster in the case of nitrile solvents. To account for this, curve B is simulated by using a rate constant of 1×10^{11} s^{-1} for k_{C-X}. As expected from the simulations shown in Figure 5, this has a small effect on the predicted decay and results in a calculated curve which still deviates significantly from the experimental data.

The observation that the extracted values of k_{C-C} are identical in alkyl bromide and alcohol solvents suggests that there are no static solvent effects on the barrier to migration. As a result, since the dielectric properties of the nitrile solvents fall between those of the alcohols and the alkyl bromides, one would expect that the rate constant for migration between adjacent carbons in the alkyl chain should be the same in all three solvent systems. As a result, by using a rate constant of 4×10^9 s^{-1} for k_{C-C}, the initial distribution of solvent sites which are coordinated to the metal following photolysis was varied in an attempt to fit the experimental data. Optimal agreement between the experimental data and simulations was obtained by postulating that 25%, 25%, and 50% of the photogenerated complexes involved initial coordination to the first three carbons of the chain, respectively, given by curve C in Figure 3. The simulations suggest that less than 5% of the complexes generated are bound to the terminal CH_2CH_3 moiety of the solvent. This conclusion is consistent with a similar analysis of the dynamics in pentanenitrile where the initial distribution involves coordination of the metal to the first three carbon atoms in a ratio of 1:3:2, respectively, with a negligible population involving coordination of the terminal CH_3 group. These results suggest that solvent coordination to the metal center occurs preferentially to the end of the solvent molecule containing the CN group. It is possible that this results from an electrostatic interaction between the CO groups on the metal and the terminal CN dipole of the solvent, which causes the parent metal hexacarbonyl to be preferentially solvated by the dipolar end of the solvent molecule. This conclusion can be tested by examining the dynamics at 390 nm (the maximum of the $Cr(CO)_5(NCR)$ complex[12]), an experiment which cannot be carried out with the present laser apparatus.

Finally, in Figure 7, the temperature-dependent values for k_{C-C} obtained from analysis of experimental data in pentanenitrile and hexanenitrile are presented. In determining the values for k_{C-C}, the room-temperature rate constant was set equal to 4×10^9 s^{-1}, and the distribution obtained (given above) was assumed to be valid over the entire temperature range, 7–75 °C. It is likely that this assumption is not correct and that the distribution of solvent-coordinated complexes formed is probably temperature dependent. However, it is interesting to note that within these assumptions, the activation barrier is calculated to be 9 (±2) kcal/mol, reasonably close to that obtained from the temperature-dependent studies in alcohol and alkyl bromide solvents.

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