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Dinetic and mechanistic investigations of photocatalysis : photoreactions of $\text{Cr}(\text{CO})_6$ with alkenes

Aaron E. Dietrich

Union College - Schenectady, NY

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KINETIC AND MECHANISTIC
INVESTIGATIONS OF PHOTOCATALYSIS:
PHOTOREACTIONS OF $\text{Cr}(\text{CO})_6$ WITH
ALKENES

By

Aaron E. Dietrich

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ABSTRACT

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Flash photolysis has proven to be an effective technique for determining reaction mechanisms. Upon photolysis, a CO ligand is removed from $\text{Cr}(\text{CO})_6$ forming the reactive molecular fragment $\text{Cr}(\text{CO})_5$. In the presence of alkene, L, $\text{Cr}(\text{CO})_5$ can react to form the meta-stable intermediate $\text{Cr}(\text{CO})_5\text{L}$. At high L concentrations, $\text{Cr}(\text{CO})_5\text{L}$ decays by pseudo-first-order kinetics with an observed rate constant, k_{obs} , which is dependent on the concentration of both L and added CO. The exact nature of the dependence provides insight into the mechanism of the decay of $\text{Cr}(\text{CO})_5\text{L}$ and a plot of $1/k_{\text{obs}}$ vs. [L] will give the rate constants for both the dissociation and formation of this complex.

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Introduction

Organotransition metal compounds have a long history and participate in a wide variety of reactions from synthesis to catalysis, as well as many others.

Zeise's salt, $K[PtCl_2(C_2H_4)]H_2O$, discovered in 1827 by the Danish chemist W. C. Zeise, was the first organotransition metal compound synthesized. Another major discovery that increased the attention on organotransition metal compounds was that of Ziegler's catalyst. In 1953 Karl Ziegler discovered that a mixture of $TiCl_4$ and $AlEt_3$ could be used to catalyze the polymerization of ethylene. The discovery of Ziegler's catalyst was closely followed by another industrially important discovery, the Wacker process. The Wacker process, discovered in 1956 can be used to convert ethylene to acetaldehyde via a palladium-ethylene intermediate. These discoveries illustrated the usefulness of organotransition metal compounds and encouraged research towards acquiring a more thorough understanding of the types of reactions in which organotransition metal compounds participate.

A common use for organotransition metal compounds is as catalysts and catalytic precursors. A requirement of any reaction is that the reacting molecules be near each other. Often an organotransition metal compound can be used to facilitate the bringing together of two species spatially. For example, by coordinating an olefin to an organotransition metal compound a wide range of reactions previously unlikely to occur can be facilitated. One such reaction involves Wilkinson's catalyst, $RhCl(PPh_3)_3$, which can be used to catalyze the hydrogenation of alkenes. In this reaction, the rhodium atom is used to bring

together the alkene and a hydrogen molecule. Wilkinson's catalyst and Ziegler's catalyst are just two examples of the usefulness of organotransition metal compounds as catalysts.

Ziegler's catalyst and Ziegler-type catalysts have proven to have many industrial uses. In addition to catalyzing the polymerization of ethylene they have been shown to catalyze the polymerization of propylene, cyclic olefins, and other alkene systems. Olefin metathesis, a ligand exchange reaction, which has been acquiring more attention recently, has also been shown to be catalyzed by Ziegler-type catalysts.

Another class of reactions that also commonly plays a role in the catalytic cycle is that of insertion, or ligand substitution, reactions. Insertion reactions, whereby a molecule is inserted into a transition metal-substituent bond, is often an elementary step in the reaction of organotransition metal catalysts. Subsequent elimination, or deinsertion, is commonly a final stage in the catalytic cycle and leads to the regeneration of a coordinatively unsaturated organotransition metal complex. Along with studies on the catalytic applications of organotransition metal complexes, work has also been done on their kinetic and mechanistic behavior. Through a more thorough knowledge of the mechanism, steps can be taken towards improving the efficacy of catalysts by making them more efficient, selective, and cost effective.

One experimental method commonly used for elucidating reaction mechanisms is flash photolysis. Upon absorption of a photon many organotransition metal compounds convert to energetically excited molecular

fragments, often by loss of one or more ligands. These highly reactive fragments can often act as excellent catalysts or precursors to catalysts. The photochemistry of chromium hexacarbonyl, $\text{Cr}(\text{CO})_6$, has been studied extensively for over twenty years. Photolysis of $\text{Cr}(\text{CO})_6$ has been shown to catalyze 1,4-hydrogenation and 1,4-hydrosilylation of 1,3-dienes, and to catalyze many other reactions as well.

The photoinitiated reactions of $\text{Cr}(\text{CO})_6$ with alkenes has been an active area of research. Typically, the first step in these reactions is loss of one or more CO ligands from $\text{Cr}(\text{CO})_6$ to produce $\text{Cr}(\text{CO})_{6-n}$ ($n = 1, 2, 3, 4$). The ability of $\text{Cr}(\text{CO})_{6-n}$ to coordinate one or more alkenes via the alkene's π -bond allows for many types of interesting reactions, as stated earlier. Upon coordination, a meta-stable organotransition metal-alkene complex is typically formed. In addition to studying the reactions of these complexes with other molecules, information about the nature of the activated complex itself can be obtained by monitoring the decay of these complexes with various alkenes.

Extensive work has been done on the photolysis of $\text{Cr}(\text{CO})_6$ in the presence of olefins in the gas phase. In each case, the mechanism for the decay of the meta-stable organotransition metal complex has been found to be dissociative. It is the goal of this research to carry out a similar study on photolysis of $\text{Cr}(\text{CO})_6$ *in the solution phase* in the presence of a number of alkenes to determine the effect of olefin size and electron donating ability on the kinetic lability of $\text{Cr}(\text{CO})_5$ -alkene complexes. Our kinetic studies to date suggest that a dissociative mechanism is present and preliminary rate constants for the dissociation and

formation of the meta-stable organotransition metal-alkene complex have been obtained.

Literature

Use of Cr(CO)₆ as a photocatalyst

Organotransition metal compounds have many uses as catalytic precursors and as catalysts. They can typically be used under mild reaction conditions and typically bind with high selectivity. These favorable properties have stimulated much research on organotransition metal compounds. Wrighton and Schroeder presented two of the earliest papers on the use of Cr(CO)₆ as a photocatalyst. First, in 1973 they published a paper on the use of Cr(CO)₆ as a catalyst in the hydrogenation of 1,3-dienes.¹ Secondly, in 1974 another paper was published describing a process by which Cr(CO)₆ could be used to catalyze 1,4-hydrosilylation of 1,3-dienes.²

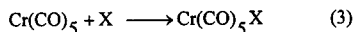
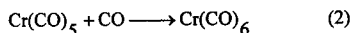
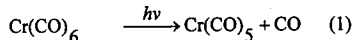
An important result of their work was the discovery that the diene must be able to adopt the *s-cis* conformation in order for catalysis to be successful.² They found their product to be greater than 99% isomerically pure using gas chromatography. It is probable that the diene must bond as a bi-dentate ligand and thereby bring both double bonds spatially close to the chromium atom. This facilitates electron transfer from both double bonds via the chromium atom. This requirement leads to a high degree of stereoselectivity and thereby allows one to have a large amount of control over the structure of the products.

Another discovery was that the reaction is truly photocatalytic as opposed to photoassisted.¹ In a photocatalytic reaction light is initially used to generate the catalytically active species but is not required as the catalyst is reformed during

the catalytic cycle. In a photoassisted reaction product generation would shut down when the light was shut off.

Photolysis of naked $\text{Cr}(\text{CO})_6$

An important step in understanding the role organotransition metal compounds play in catalysis lies in understanding their reactivity in the absence of added ligands. It is generally accepted that the primary photoproduct of $\text{Cr}(\text{CO})_6$ is $\text{Cr}(\text{CO})_5$. However, it was not until 1973 that a detailed mechanism describing the fate of $\text{Cr}(\text{CO})_5$ was presented. Kelly and co-workers presented a mechanism whereby $\text{Cr}(\text{CO})_6$ expels a CO ligand upon photolysis and generates the coordinatively unsaturated $\text{Cr}(\text{CO})_5$. $\text{Cr}(\text{CO})_5$ then adds to either CO or X, an impurity in the system.³ That mechanism is outlined below.



Kelly and co-workers also report a derived rate constant for reaction 2, the recombination of CO with $\text{Cr}(\text{CO})_5$, of $3 \pm 1 \cdot 10^6 \text{M}^{-1} \text{s}^{-1}$.

Using UV/VIS detection, a peak was observed at $503 \pm 5 \text{nm}$ immediately after the flash. This peak decayed with a lifetime of more than $200 \mu\text{s}$. In the presence of 1atm of CO however, this peak disappears with a half-life of $25 \mu\text{s}$. A peak was also observed at 445nm and assigned to $\text{Cr}(\text{CO})_5\text{X}$. This peak disappeared due to ensuing substitution by CO and had a half-life of 25s . Their

work demonstrated the high reactivity of coordinatively unsaturated $\text{Cr}(\text{CO})_5$ and the importance of removing all impurities from the system.

Solvation of photo-generated $\text{Cr}(\text{CO})_5$

An important consideration when dealing with such a highly reactive species in solution is its interaction with the solvent. In 1983 Kelly and co-workers investigated this issue by photolyzing $\text{Cr}(\text{CO})_6$ in both a coordinating and a non-coordinating solvent.⁴ They selected perfluoromethylcyclohexane, C_7F_{14} , as their non-coordinating solvent based on previous matrix studies⁵ and cyclohexane, C_6H_{12} , as their coordinating solvent. The use of cyclohexane is important since it is a very common solvent in organometallic photochemistry and most likely behaves similarly to other common hydrocarbon solvents.

Immediately after laser flash photolysis in C_7F_{14} a peak assigned to "naked" $\text{Cr}(\text{CO})_5$ was observed at 620nm at a time of 5ns. However in a $\text{C}_7\text{F}_{14}/\text{C}_6\text{H}_{12}$ (0.25M) mixture an absorbance maxima was observed at $485 \pm 10\text{nm}$. This is consistent with what was observed by Kelly in 1973 when $\text{Cr}(\text{CO})_6$ was photolyzed in cyclohexane.³

Once again in 1983 Kelly and co-workers had difficulty with impurities. They found it difficult to reproduce data and found that a method of performing freeze-pump-thaw cycles on the solution to remove dissolved gases was successful in improving their reproducibility. The impurity complex they observed prevented them from investigating the $\text{Cr}(\text{CO})_5-(\text{C}_6\text{H}_{12})$ complex further since they both have a maximum absorbance around 500nm. They were able to compare the reaction of CO with $\text{Cr}(\text{CO})_5$ in both the coordinating and non-

coordinating solvent. They found that CO reacts 3 orders of magnitude faster in C_7F_{14} than in C_6H_{12} , thus illustrating the important role the solvent plays in the kinetics of these coordinatively unsaturated organotransition metal complexes.

Reactions of Solvated $Cr(CO)_5$ (Non-Alkene Ligands)

In addition to research into the solvation of coordinatively unsaturated $Cr(CO)_5$, work has also been done on the mechanism of desolvation of $Cr(CO)_5S$. Zhang and co-workers performed flash photolysis studies on the displacement of benzene from $Cr(CO)_5(\eta^2\text{-Benzene})$ in the presence ligand, L (L = piperidine, 1-hexene, pyridine).⁶ Upon displacing benzene the ligand, L, reacts with $Cr(CO)_5$ to form $Cr(CO)_5L$ whose subsequent decay could also be studied. $Cr(CO)_5(\eta^2\text{-Benzene})$ is formed in less than $5\mu s$ under their experimental conditions, and has a maximum absorption at $458\pm 10nm$. By performing experiments over a wide range of benzene and L concentrations, they were able to show that the decay of $Cr(CO)_5(\eta^2\text{-Benzene})$ is pseudo-first-order and follows a dissociative mechanism. A dissociative mechanism is analogous to an organic S_N1 reaction in that the outgoing ligand dissociates from the complex prior to the attack of the incoming ligand. The outgoing ligand plays no role in the bonding of the incoming ligand. An alternative would be an associative mechanism. This is analogous to an organic S_N2 reaction in which the outgoing ligand remains bound to the complex until the incoming ligand is coordinated.

Using Xenon flash photolysis and IR detection, Grevels and co-workers found evidence for the presence of $Cr(CO)_5N_2$ in N_2 flushed solutions of $Cr(CO)_6$ at room temperature.⁷ Upon photolysis they observed the solvated form of

$\text{Cr}(\text{CO})_5$ and upon its disappearance five new bands in the infrared were observed. These bands, only observed in N_2 flushed solution, were attributed to $\text{Cr}(\text{CO})_5\text{N}_2$. They obtained a rate constant for the first order formation of $\text{Cr}(\text{CO})_5\text{N}_2$ of $18,000\text{s}^{-1}$. Monitoring the disappearance of $\text{Cr}(\text{CO})_5\text{N}_2$ at 1978cm^{-1} , they obtained a rate constant of 1.7s^{-1} . While Grevels and co-workers do not provide conclusive evidence for the mechanism of $\text{Cr}(\text{CO})_5\text{N}_2$ disappearance, they suggest that a simple dissociation into $\text{Cr}(\text{CO})_5$ and N_2 is a probable first step in light of the observed first order behavior.

Grevels and co-workers reported similar findings in 1985 for a $\text{Cr}(\text{CO})_5\text{H}_2$ complex.⁸ Upon disappearance of $\text{Cr}(\text{CO})_5\text{S}$ they observed two new bands at 1974cm^{-1} and 2092cm^{-1} which they attributed to a $\text{Cr}(\text{CO})_5\text{H}_2$ complex. A rate constant of $19,000\text{s}^{-1}$ for the formation of $\text{Cr}(\text{CO})_5\text{H}_2$ was obtained. They also found evidence that the decay of $\text{Cr}(\text{CO})_5\text{H}_2$ proceeds via a dissociative pathway with a first order rate constant of 2.5s^{-1} . It is interesting to note that the rate constants for formation of $\text{Cr}(\text{CO})_5\text{N}_2$ and $\text{Cr}(\text{CO})_5\text{H}_2$, $18,000\text{s}^{-1}$ and $19,000\text{s}^{-1}$ respectively, as well as those for dissociation, 1.7s^{-1} and 2.5s^{-1} respectively, suggesting that these two species have similar stability's.

Work has also been done on the dissociation of various phosphine ligands from $\text{Cr}(\text{CO})_5$. Wovkulich and Atwood studied the dissociation of $\text{Cr}(\text{CO})_5\text{L}$ ($\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$, $\text{P}(\text{OC}_6\text{H}_5)_3$, $\text{P}(\text{OCH}_3)_3$, and $\text{As}(\text{C}_6\text{H}_5)_3$) and found that it followed a first order dissociative mechanism as well.⁹

The reactions of photolyzed $\text{Cr}(\text{CO})_6$ with silanes has been an active research area due to $\text{Cr}(\text{CO})_6$'s importance in catalysis, as noted earlier. In an

attempt to better understand the role $\text{Cr}(\text{CO})_6$ plays in the catalytic cycle, Zhang and co-workers measured the kinetic stability of many $\text{Cr}(\text{CO})_5(\text{silane})$ complexes with silanes that have widely varying steric and electronic properties.¹⁰ Much of their work was carried out under pseudo-first-order conditions with an excess of CO and silane. Under these conditions, it was found that the mechanism of silane displacement from $\text{Cr}(\text{CO})_5(\text{silane})$ follows a dissociative mechanism. They also found that the rate of dissociation of $\text{Cr}(\text{CO})_5(\text{silane})$ decreased with increasing electron-donor ability in the silane.

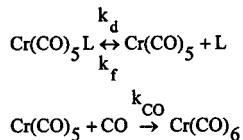
Reactions of Solvated $\text{Cr}(\text{CO})_5$ with Alkenes

Our own interests are with the kinetic and thermodynamic stability of transition metal-alkene complexes. As stated earlier, these can be prepared by photolytic cleavage of a metal-CO bond followed by addition of alkene. It is thought that the alkene bonds to the transition metal via its π -bond.

Photolyzing $\text{Cr}(\text{CO})_6$ in liquid xenon doped with C_2H_4 , Poliakoff and co-workers, using IR detection, found evidence for both mono and di-substituted ethene-chromium carbonyl complexes.¹¹ Interestingly, they found that the di-substituted $\text{cis-Cr}(\text{CO})_4(\text{C}_2\text{H}_4)_2$ complex which has both ethene ligands in adjacent equatorial positions on the chromium did not isomerize to $\text{trans-Cr}(\text{CO})_4(\text{C}_2\text{H}_4)_2$. Instead, a pseudo-first-order decay to $\text{Cr}(\text{CO})_5(\text{C}_2\text{H}_4)$ was observed and again the results indicate that the reaction occurs via a dissociative pathway.

In 1995, McNamara and co-workers reported on work they performed on the decomposition of various $\text{Cr}(\text{CO})_5\text{L}$ complexes in the gas phase.¹² The

ligands they used were: ethylene, propylene, 1-butene, cis-2-butene, trans-2-butene, and isobutene. They found that the decay kinetics in all cases were pseudo-first-order at high L and CO concentrations. Once again, the decay was shown to follow a dissociative mechanism:



They found that the rate of substitution of L by CO increased with increasing ligand size.

We took an approach similar to that of McNamara et. al. except that we focused on the dissociation of $\text{Cr(CO)}_5\text{L}$ (L = alkene) in *solution*. Given the consistency of previous mechanistic findings, it was not surprising that the reaction proceeds via a dissociative pathway. Unlike McNamara, however, we were able to obtain values for both k_d and k_f . The goal of this work is to obtain values of k_d and k_f for many different transition metal-alkene complexes in solution and to characterize the influence of the electronic and steric properties of the alkene and the transition metal on the overall stability of these complexes.

Experimental

Organotransition metal complexes are very sensitive to air and must be handled with extreme care. All solvent purification and solution preparation is therefore carried out under purified flowing argon. The solution is prepared under argon inside the photolysis cell, and other than for the addition of 1-hexene, is not exposed further to air. Each step in the process from solvent purification to flashing the solution, is presented below. Instructions on using the computer programs for data analysis are presented in Appendix A.

Argon Purification

All solvent and all reagent handling is done under flowing. Argon gas (Air Products Inc.) is purified by passing it through 13X molecular sieves (Aldrich) and an oxygen scavenging column (Aldrich) to remove water, organics, and oxygen. We have conducted experiments illustrating that even after taking these measures to purify the argon the kinetic behavior of the highly reactive organotransition metal molecular fragments is affected by something introduced via the argon stream.

Solvent Purification

Due to the sensitivity of $\text{Cr}(\text{CO})_6$ to water in the solvent, 99+% heptane (Aldrich) is subjected to an exhaustive three step drying procedure. In the first step the solvent is refluxed over CaH_2 for 12 hours under flowing argon. It is then transferred to another still and refluxed for an additional 12 hours over NaK . Lastly, the solvent is distilled in a fractionating column to remove any traces of CaH_2 . The first 10mL distilled through the fractionating column is discarded.

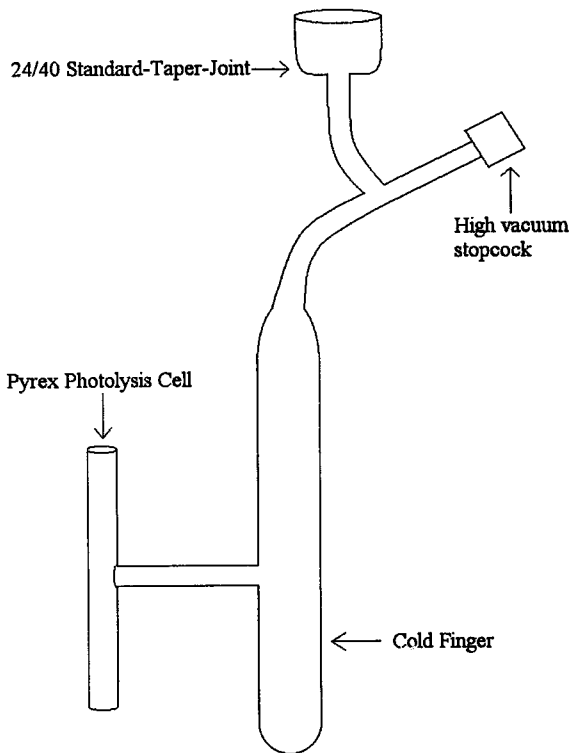
Then 20mL of heptane is removed with a gas tight syringe for transfer to the sample cell where the solution is prepared.

Solution Preparation

The empty photolysis cell (Figure 1) is attached to the vacuum line and exposed to high vacuum for five minutes to remove air and water from the cell. All solution preparation is done in the cold finger portion of the photolysis cell where the solution remains until it is flashed. Under flowing argon, 1.0 mg of 99% $\text{Cr}(\text{CO})_6$ (Aldrich) is added to the cell. Experiments have also been performed using $\text{Cr}(\text{CO})_6$ which had been purified by sublimation; however, the results showed that this had no effect on the reaction. At this point, it is necessary to add the desired amount of ligand, 1-hexene in our current study. Using a 1:1 1-hexene:heptane diluted stock solution, the desired amount is added using a micro-syringe. Using this stock solution and 20mL of solvent, 1 μ L of the 1:1 1-hexene:heptane solution corresponds to a concentration of 1mM. The 20mL of purified heptane is then added to the cell and can be used to wash the $\text{Cr}(\text{CO})_6$ and 1-hexene down the walls of the cell. A magnetic stirring bar is also added to permit agitation of the solution while it is attached to the vacuum line. The concentration of $\text{Cr}(\text{CO})_6$ in all our runs is $2.0 \cdot 10^{-4}$ M.

After the sample is prepared, it is subjected to four Freeze-Pump-Thaw cycles to remove dissolved gases. This is accomplished by freezing the solution with liquid nitrogen for ten minutes, pulling high vacuum on it for an additional ten minutes, closing the stopcock which connects the sample cell to the vacuum line, allowing the solution to thaw, and finally agitating the solution with a

Figure 1 : Photolysis Cell



magnetic stirring bar for an additional five minutes. After the four Freeze-Pump-Thaw cycles have been completed, CO is added to the cell.

CO Addition

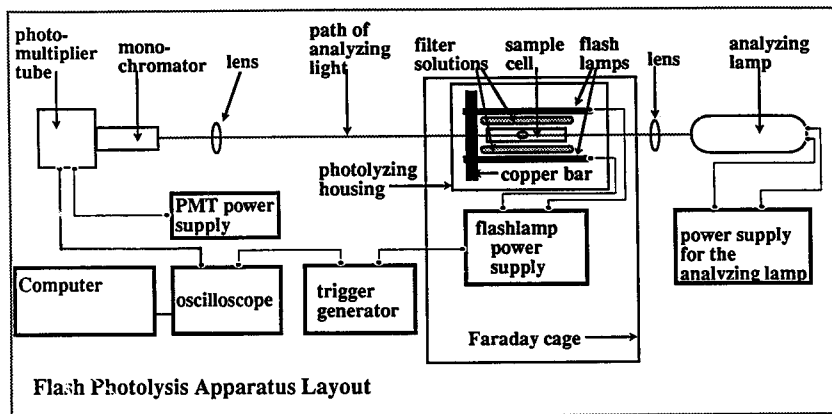
All of the reactions we study are run under pseudo-first order conditions with an excess of CO and ligand (1-hexene). Doing this will minimize the reaction of $\text{Cr}(\text{CO})_5$ with impurity. The reactions are run under 500 torr of CO. The CO gas (Matheson) is purified via a two-step process. First, it is passed through a column of activated charcoal to remove $\text{Fe}(\text{CO})_5$ which may be carried over from the walls of the steel gas canister. Secondly, the CO is passed through a dry-ice/ethanol bath (-77°C) to remove condensibles. The CO pressure is monitored using a simple manometer. In order to obtain an accurate measure of the CO pressure, the vapor pressure of the solvent must be suppressed. All but the upper 0.25" of the sample was frozen with liquid nitrogen prior to addition of CO. If the upper portion of the solution is frozen then it would become possible for some CO gas to freeze thereby preventing an accurate pressure measurement. The vapor pressure of the partially frozen solution was found to be negligible.

Flash Experiment and Data Collection

A schematic of the flash apparatus is presented in Figure 2. After placing the sample cell in the photolyzing housing the solution is ready to be flashed.

A xenon UV/VIS analyzing lamp shines white light down the long axis of the photolysis cell. When the solution is flashed the concentration of $\text{Cr}(\text{CO})_5\text{L}$ increases, as $\text{Cr}(\text{CO})_5$ combines with L, causing a proportional increase in the absorbance at 380nm. Using Beer's Law, absorbance can be related to

Figure 2 : Flash Photolysis Apparatus Layout



concentration, thereby allowing us to monitor $\text{Cr}(\text{CO})_5\text{L}$ concentration by tracking the intensity of the light transmitted by the photolysis cell.

The flashlamps are located on each side of the photolysis cell. The light from the flashlamps is blocked with CoCl_2 filter solutions which block light in the range 340-500nm. The Pyrex photolysis cell also blocks light below 310nm. These are in place to (1) reduce the scattered light from the flashlamps at the wavelength (380nm) we are using to track $[\text{Cr}(\text{CO})_5\text{L}]$ and (2) to block high energy light at $\lambda < 300\text{nm}$ that would create other forms of chromium carbonyls that would react in parallel with the chemistry we are investigating.

The change in absorbance after the solution is flashed is monitored with a photomultiplier tube (PMT). We selectively monitor the absorbance at 380nm, a wavelength near the peak absorbance of $\text{Cr}(\text{CO})_5(1\text{-hexene})$ ($\lambda_{\text{max}} = 370\text{nm}$) using a monochromator (ISA Instruments) located directly in front of the PMT.

The output of the PMT is a current proportional to the intensity of the light entering the PMT. This current is converted to a proportional voltage by passing it through a simple resistor. The oscilloscope is connected in parallel across the resistor. Therefore, the change in the absorbance of the solution over time can be monitored as voltage versus time.

The data is collected on a LeCroy 9410 Dual Beam 150MHz digital oscilloscope as change in voltage versus time. Using computer software the data is transferred from the oscilloscope to a computer and then using a program developed in-house the data is converted to absorbance versus time.

Data Analysis

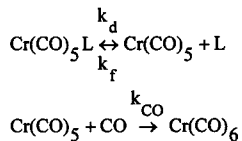
A detailed set of instructions on how to transfer the data from the oscilloscope to the computer and also how to use the programs to analyze the data is presented in Appendix A. However a brief overview is presented here.

The data is transferred from the oscilloscope to the computer using 94g, a program developed by the oscilloscope manufacturer. Another program, 94tran, is used to convert the data from binary to ASCII. Voltages, a program developed in-house, is used to convert the ASCII voltage versus time data to an ASCII absorbance versus time format.

After the data is converted to absorbance versus time it is imported into Axum 5.0 (Mathsoft, Inc.) for analysis and plotting. Plots of absorbance versus time, \ln absorbance versus time, and inverse absorbance versus time are generated. From these plots data can be gathered as to whether or not the reaction returned to the baseline, indicating that no stable products were formed that absorb at 380nm, as well as information about the order of the reaction. If the \ln plot is linear then we know the reaction followed pseudo-first order kinetics as we expected based on similar studies by others.

Mechanism and Kinetic Equations

The mechanism presented by McNamara et al. in 1995 for the dissociation of $\text{Cr}(\text{CO})_5\text{L}$ (L = alkene) is restated below.



They showed that this mechanism is correct for alkenes in the gas phase that vary in size from ethylene to iso-butene. The work we are doing currently involves studying the dissociation of $\text{Cr}(\text{CO})_5(1\text{-hexene})$. Using flash photolysis with UV/VIS detection we wish to determine whether the mechanism presented by McNamara and co-workers holds true for 1-hexene and other alkenes *in solution*.

In order to correctly interpret the kinetic data collected during the experiment the necessary rate equations need to be derived. The following rate equation can be derived from the above mechanism.

$$\frac{d[\text{Cr}(\text{CO})_5\text{L}]}{dt} = -k_d[\text{Cr}(\text{CO})_5\text{L}] + k_f[\text{Cr}(\text{CO})_5][\text{L}]$$

The lifetime of $\text{Cr}(\text{CO})_5$ in the absence of added CO in solution has been reported to be approximately $200\mu\text{s}^3$. Therefore the steady-state approximation can be applied to $\text{Cr}(\text{CO})_5$. Substituting and simplifying gives the following rate equation.

$$\frac{d[\text{Cr}(\text{CO})_5\text{L}]}{dt} = \left[\frac{-k_d k_{\text{CO}}[\text{CO}]}{k_f[\text{L}] + k_{\text{CO}}[\text{CO}]} \right] \bullet [\text{Cr}(\text{CO})_5\text{L}]$$

At high L and CO concentrations the quantity in brackets is approximately constant and the reaction becomes pseudo-first order with an observed rate constant (k_{obs}) of :

$$k_{\text{obs}} = \left[\frac{k_d k_{\text{CO}} [\text{CO}]}{k_f [\text{L}] + k_{\text{CO}} [\text{CO}]} \right]$$

The rate equation can therefore be simplified and written as :

$$\frac{d[\text{Cr}(\text{CO})_5\text{L}]}{dt} = -k_{\text{obs}} [\text{Cr}(\text{CO})_5\text{L}]$$

Upon integration the following is obtained :

$$\ln [\text{Cr}(\text{CO})_5\text{L}] = -k_{\text{obs}} \cdot t + \ln [\text{Cr}(\text{CO})_5\text{L}]_0$$

The concentration of $\text{Cr}(\text{CO})_5\text{L}$ cannot be measured directly. However, the Beer-Lambert law can be used to relate the absorbance of $\text{Cr}(\text{CO})_5\text{L}$ at 380nm to it's concentration.

$$A_{380} = a \cdot b \cdot [\text{Cr}(\text{CO})_5\text{L}]$$

Using the Beer-Lambert law the integrated rate equation can be written as follows :

$$\ln A_{380} = -k_{\text{obs}} \cdot t + \ln A_{380,0}$$

A linear plot of the natural log of the absorbance of $\text{Cr}(\text{CO})_5\text{L}$ at 380nm versus time will have a slope of $-k_{\text{obs}}$. Upon obtaining this data at various L concentrations one can use a plot of $1/k_{\text{obs}}$ versus [L] to find k_f and k_d from the slope and y-intercept. We use the value of k_{CO} provided by Kelly et al.³ of $3 \pm 1 \cdot 10^6 \text{M}^{-1} \text{s}^{-1}$.

$$\frac{1}{k_{\text{obs}}} = \left[\frac{k_f}{k_d k_{\text{CO}} [\text{CO}]} \right] \bullet [\text{L}] + \frac{1}{k_d}$$

Moreover, a linear plot of $\ln A_{380}$ vs. time combined with a linear plot of $1/k_{\text{obs}}$ vs. $[\text{L}]$ strongly supports our proposed mechanism.

Results

A significant amount of time in the summer of 1997 was devoted to reproducing the work of Kelly et al.³ This reaction involved simple photolysis of $\text{Cr}(\text{CO})_6$ in the absence of added CO. Figure 3 is a typical absorbance versus time plot for one of these experiments. The absorbance of the solution from time 0 to 0.05s corresponds to the initial absorbance of the solution. The sharp jump at $t = 0.05\text{s}$ is caused by the firing of the flashlamps and represents the absorbance of $\text{Cr}(\text{CO})_5$ or a $\text{Cr}(\text{CO})_5$ complex at 500nm. Figures 4 and 5 are natural log of absorbance versus time and inverse absorbance versus time plots for the data in Figure 3. From Figure 5 it can be seen that the reaction is approaching second-order behavior but that there is still a competing reaction analogous to the reaction mentioned by Kelly that formed $\text{Cr}(\text{CO})_5\text{X}$.³

Further examination of Figure 3 shows that there is measurable absorbance all the way out to 500ms. This is in contrast to the data quoted by Kelly stating that $\text{Cr}(\text{CO})_5$ has a lifetime on the order of 200 μs in the absence of added CO.³ In order to further probe the identity and influence of this impurity, the time resolved spectrum in Figure 6 was generated.

It was reported by Kelly and co-workers that the absorbance of solvated $\text{Cr}(\text{CO})_5$ has a peak at $485 \pm 10\text{nm}$ in a mixture of cyclohexane and perfluoromethylcyclohexane.⁴ Perfluoromethylcyclohexane was used as a non-coordinating solvent to investigate the effect of cyclohexane on $\text{Cr}(\text{CO})_5$, a common solvent in $\text{Cr}(\text{CO})_6$ photochemistry. The absorbance maximum, in Figure 6, at short times is at approximately 480nm but shifts to the left as it

Figure 3 : Cr(CO)5 followed at 500 nm

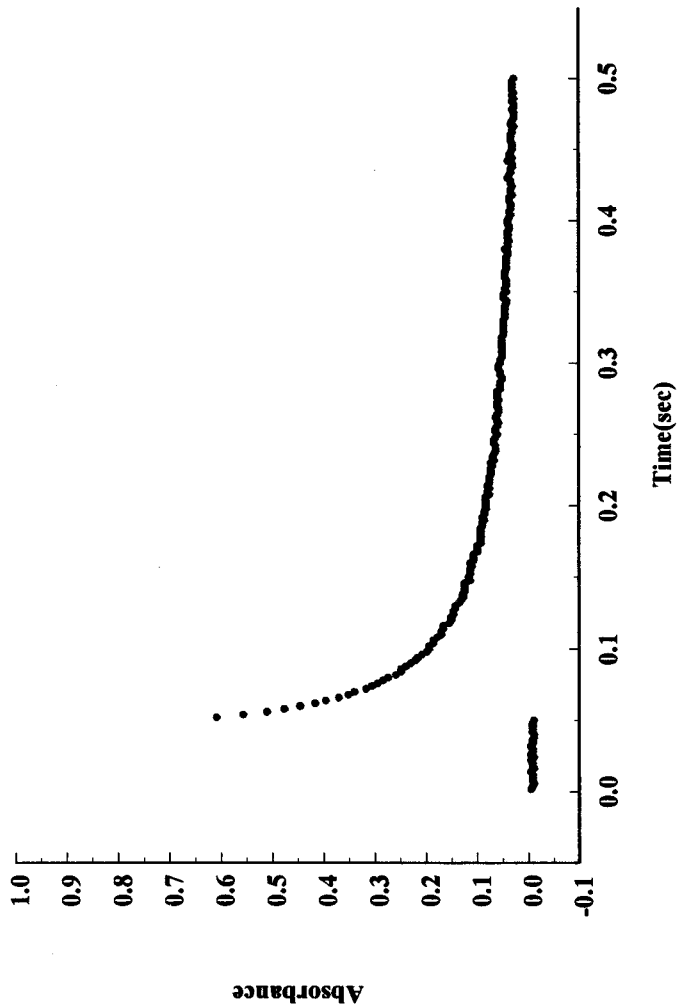


Figure 4 : Cr(CO)₅ followed at 500 nm

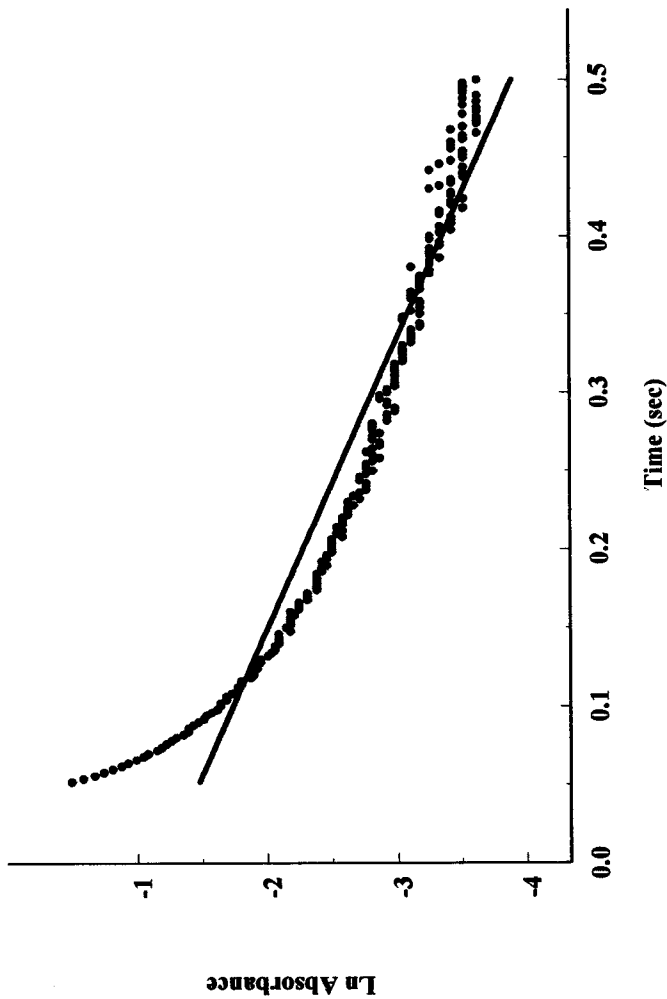


Figure 5 : Cr(CO)5 followed at 500 nm

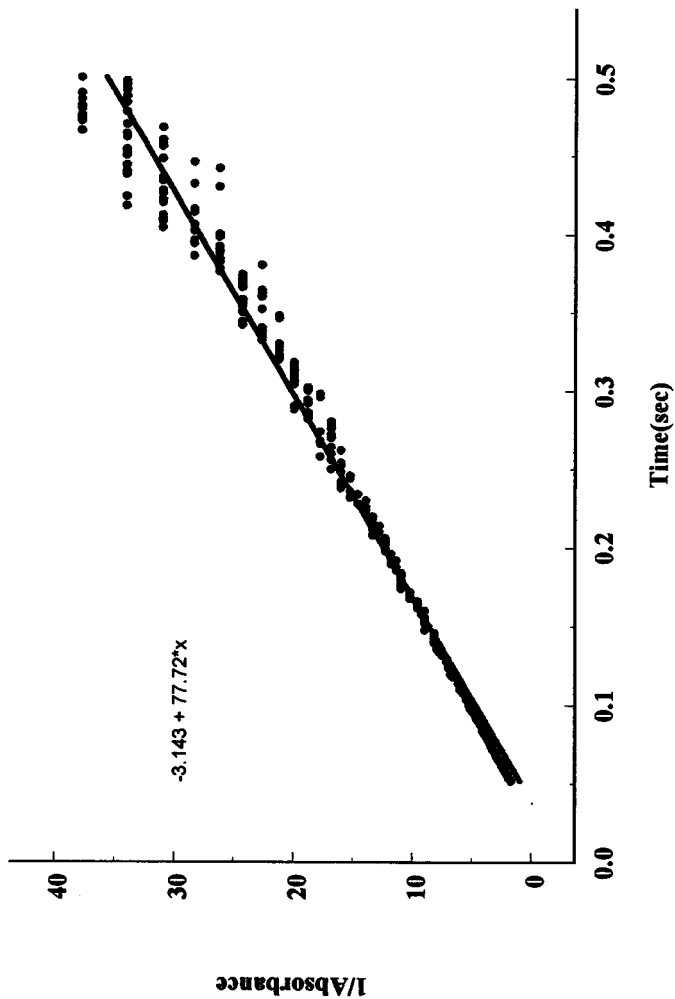
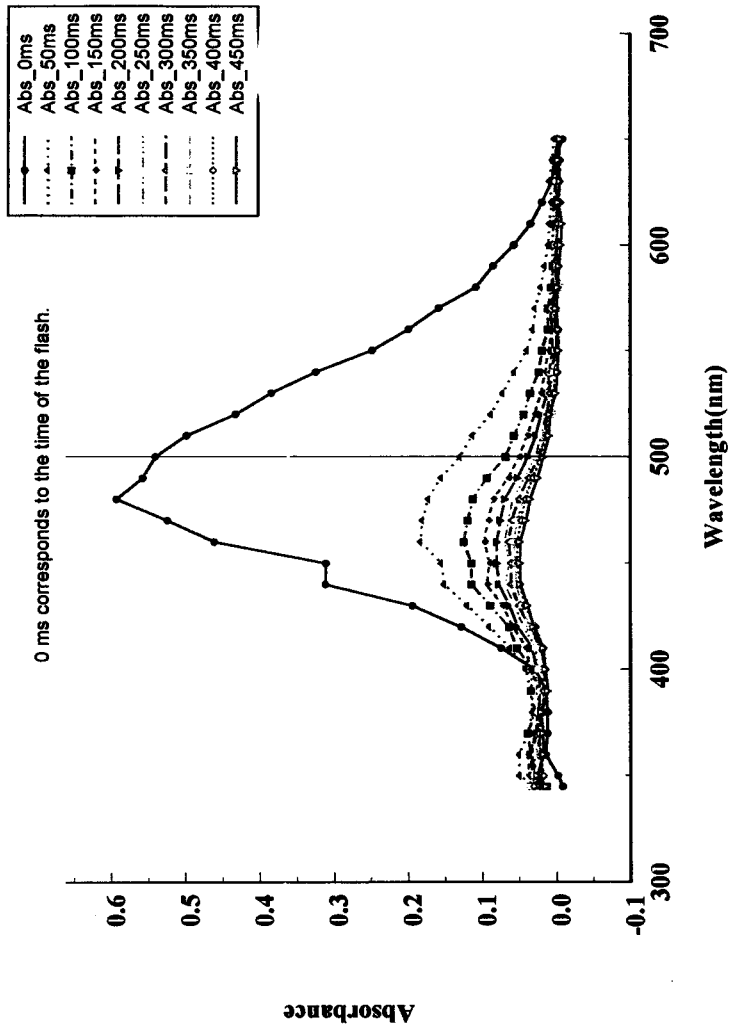


Figure 6 : Time Resolved Spectrum of Cr(CO)₅



decays. This drift represents the formation of $\text{Cr}(\text{CO})_5\text{X}$. As stated in the literature section a common impurity with a peak absorbance less than 480nm is a $\text{Cr}(\text{CO})_5$ -water complex. However, many possible impurities also have a peak absorbance in the same area. One such species is benzene, a common impurity in cyclohexane. Fortunately, this does not have a large impact on our project because $\text{Cr}(\text{CO})_5$ -alkene complexes are known to have a peak absorbance at wavelengths less than 400nm and the reactions are run in an excess of alkene. These results led us to pursue methods of solvent purification as our top priority. The following is a list of some methods tried and their effect.

- Drying of solvent by refluxing with NaK for 12 hours. A time resolved spectrum showed that this gave better results as the long time absorbance was shifted closer to 485nm. However, the impurity was still clearly present and having an effect on the kinetics.
- Passing the solvent through activated silica gel before refluxing with CaH_2 and NaK. This did not have an effect on the impurity.
- Running the reaction in the presence of additional CO. Adding CO will force the reaction to follow pseudo-first-order kinetics and hopefully minimize the effect of the impurity by forcing $\text{Cr}(\text{CO})_5$ to reaction with CO. This did not remove the effect of the impurity and also had the effect of reducing the maximum absorbance of $\text{Cr}(\text{CO})_5$ because of its fast reaction with CO.
- Using different grades of solvent and moving from cyclohexane to heptane. Due to the issue of the presence of benzene in cyclohexane and the preferred use of heptane in IR work we decided to switch to using heptane. A time resolved spectrum showed that this did not have an effect on the impurity.

After devoting two months to the aforementioned experiments, we gave up trying to further purify our solvents and moved on to doing experiments in which low

levels of impurity would not affect the outcome of the reaction. Reactions with impurities can be minimized by running the reactions we wish to investigate under pseudo-first-order conditions. This was accomplished by running all reactions under 500 torr of CO and in the presence of high concentrations of added ligand, in this case 1-hexene. As shown in the kinetic equations derived earlier, when the concentration of CO and 1-hexene are both high they can be considered constant and the proposed mechanism becomes pseudo-first-order. Figure 17 is a time resolved spectrum of $\text{Cr}(\text{CO})_5(1\text{-hexene})$ in the presence of 496.5 torr CO. It is clear that the impurity that was altering the kinetics of our previous study is not having an effect on the kinetics of the dissociation of $\text{Cr}(\text{CO})_5\text{L}$. The maximum absorbance, due to $\text{Cr}(\text{CO})_5(1\text{-hexene})$ occurs at 370nm and remains there throughout the life of the species. The reaction is monitored at 380nm rather than 370nm because there is less absorbance by $\text{Cr}(\text{CO})_6$ at 380nm and therefore the signal-to-noise ratio is much higher at 380nm than at 370nm.

After eliminating the interference due to the impurity, a series of runs could be performed on the dissociation of $\text{Cr}(\text{CO})_5\text{L}$ at various L concentrations. Figures 7 through 16 are plots of absorbance versus time and natural log of absorbance versus time for 1-hexene concentrations over the range of 0.004M to 0.032M. As the concentration of 1-hexene increases the maximum absorbance also increases as does the lifetime of the $\text{Cr}(\text{CO})_5(1\text{-hexene})$ complex. It should be noted that in some of the experiments the absorbance of the solution does not return to its initial value. Also, the natural log of absorbance versus time plots are

Figure 7 : Cr(CO)₅L followed at 380 nm (496.5 torr CO)

L = 0.004M 1-hexene

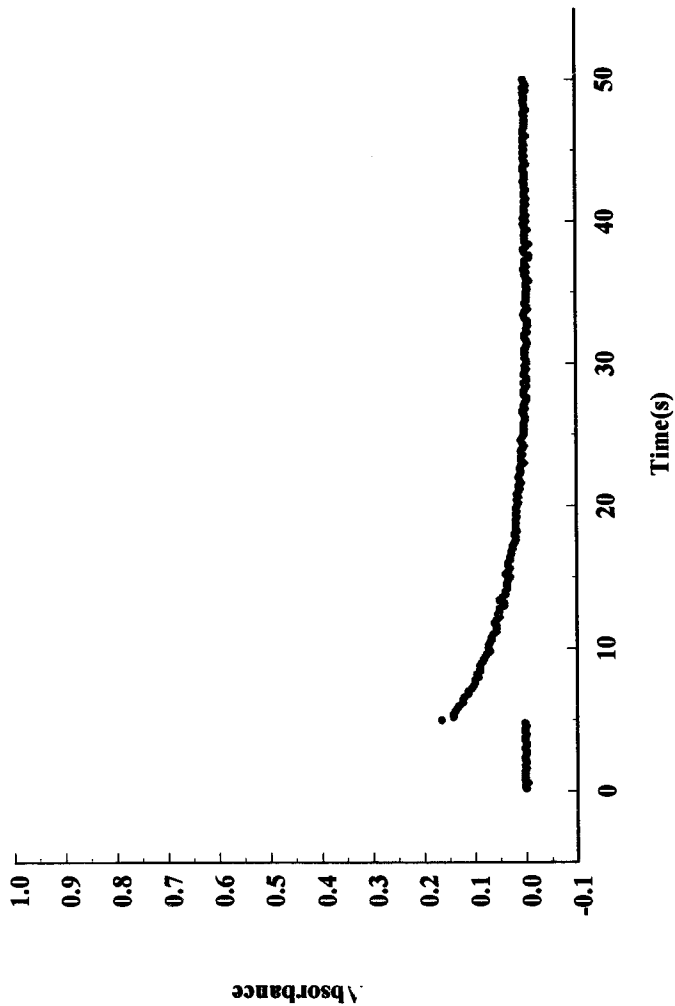


Figure 8 : Cr(CO)5L followed at 380 nm (496.5 torr CO)

L = 0.004M 1-hexene

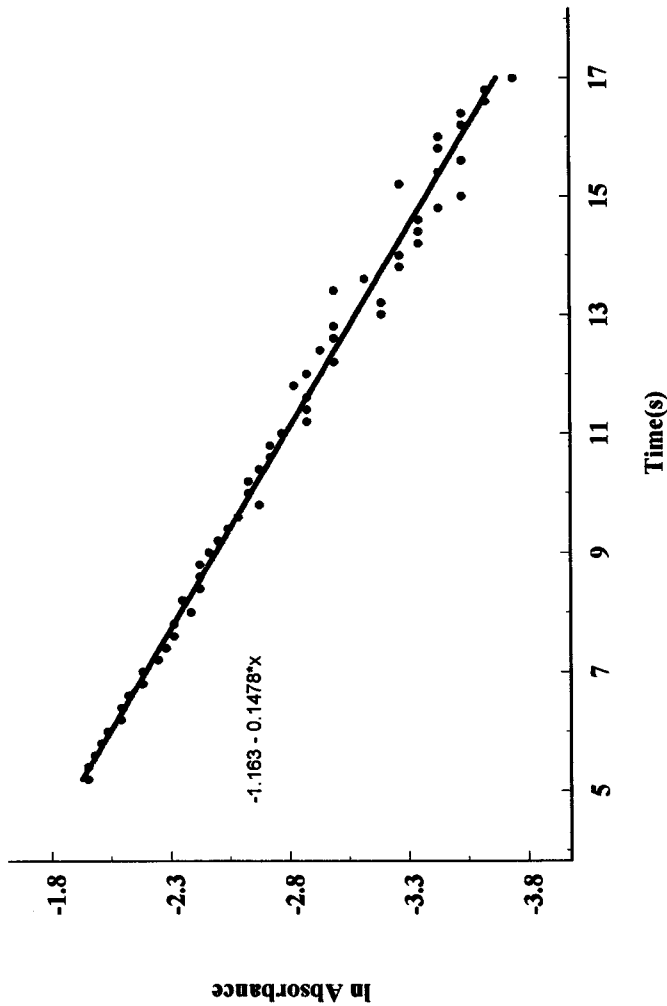


Figure 9 : Cr(CO)₅L followed at 380 nm (505.8 torr CO)

L = 0.008M 1-hexene

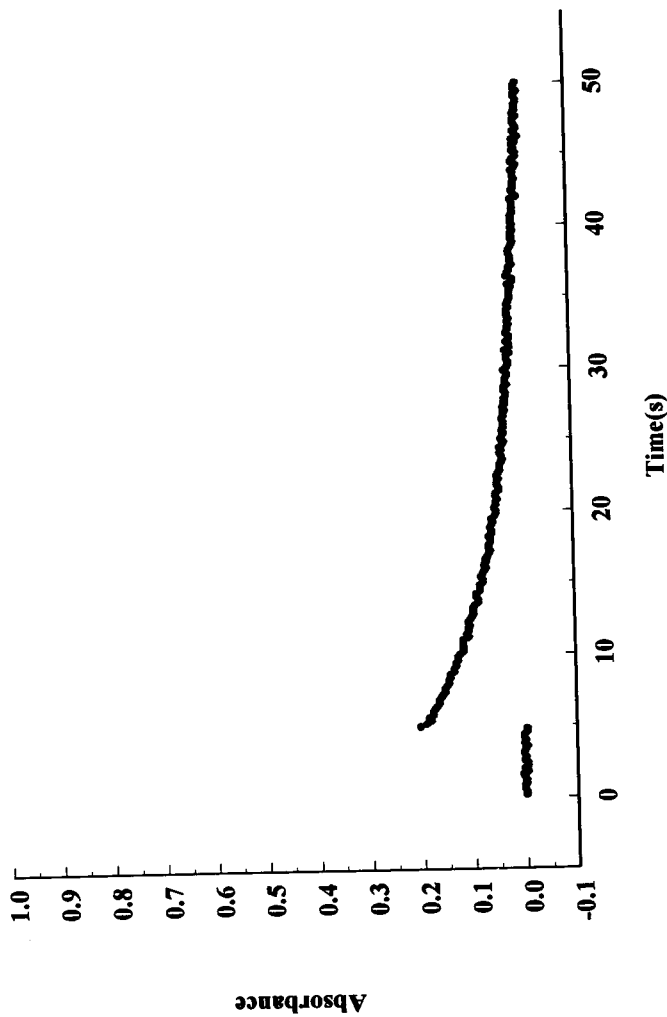


Figure 10 : Cr(CO)₅L followed at 380 nm (505.8 torr CO)

L = 0.008M 1-hexene

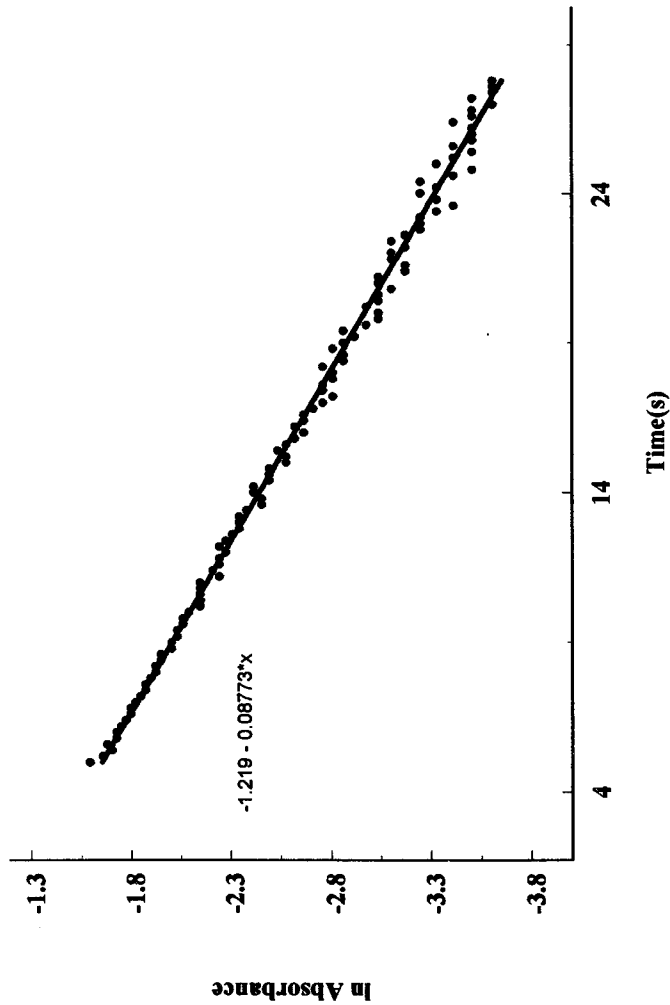


Figure 11 : Cr(CO)₅L followed at 380 nm (502.1 torr CO)

L = 0.016M 1-hexene

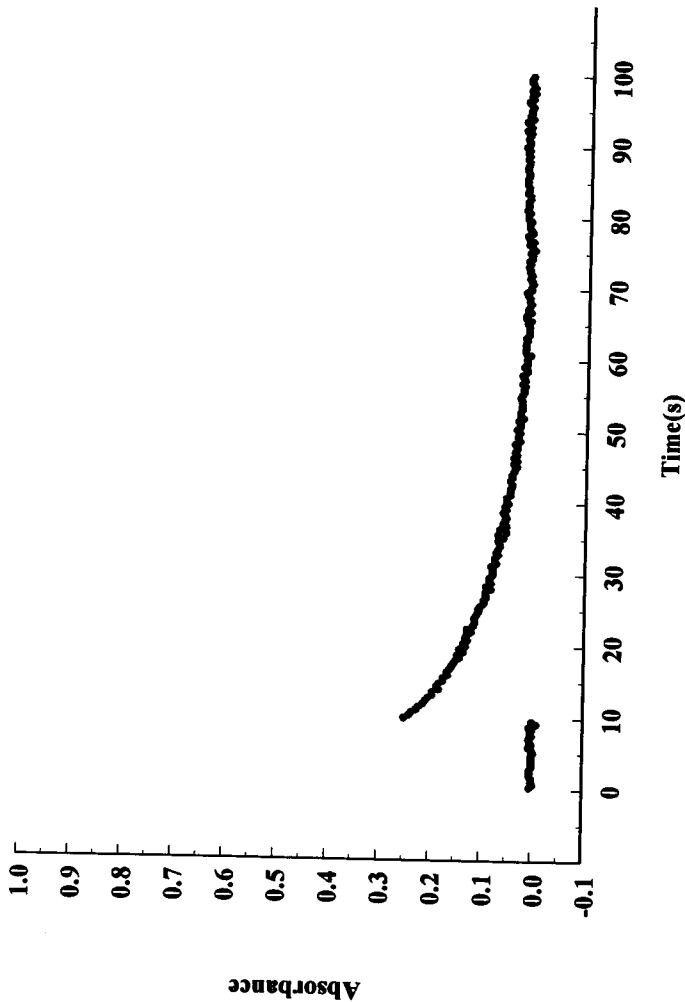


Figure 12 : Cr(CO)5L followed at 380 nm (502.1 torr CO)

L = 0.016M 1-hexene

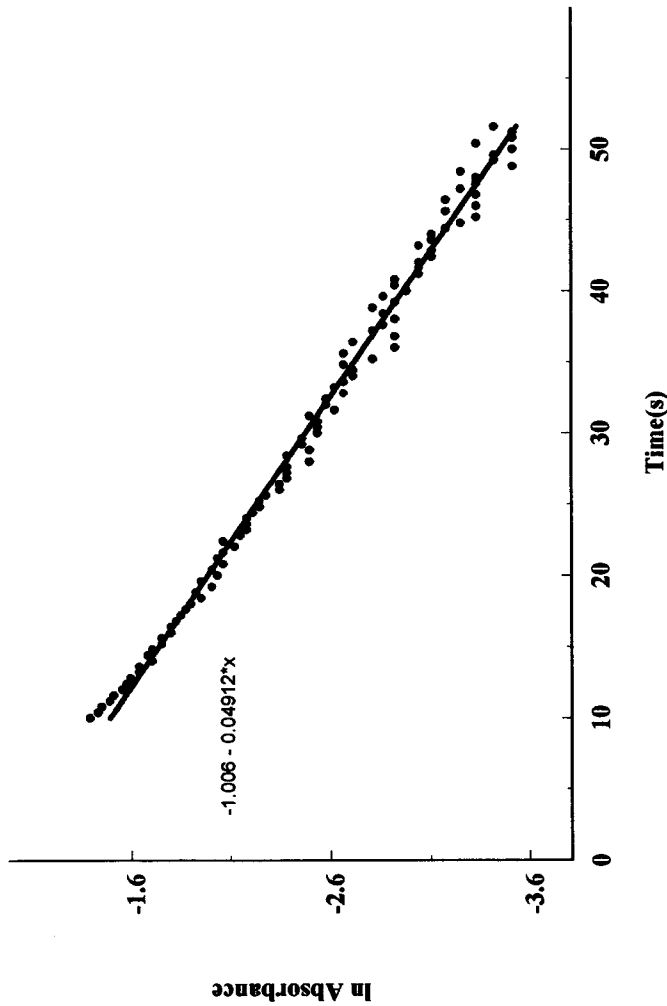


Figure 13 : Cr(CO)₅L followed at 380 nm (501.5 torr CO)

L = 0.024M 1-hexene

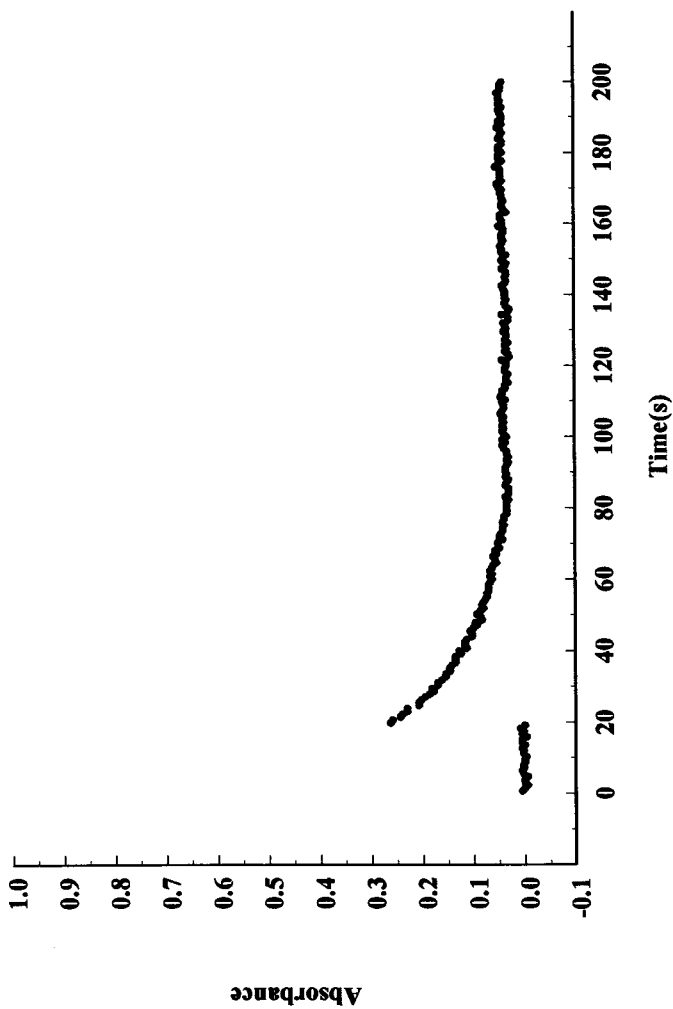


Figure 14 : Cr(CO)₅L followed at 380 nm (501.5 torr CO)

L = 0.024M 1-hexene

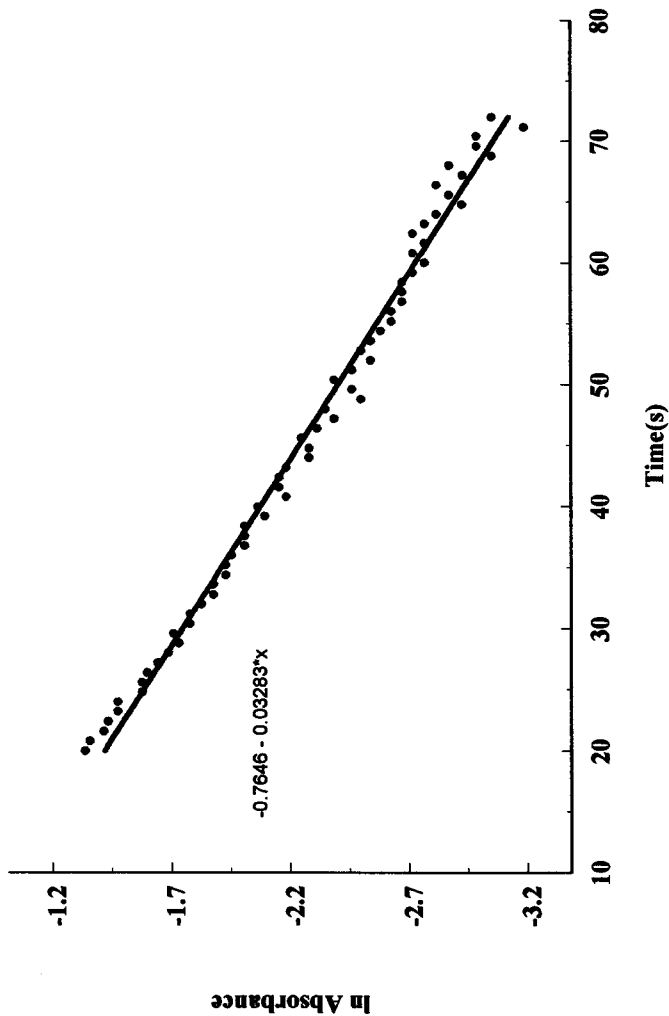


Figure 15: Cr(CO)₅L followed at 380 nm (500.8 torr CO)

L = 0.032M 1-hexene

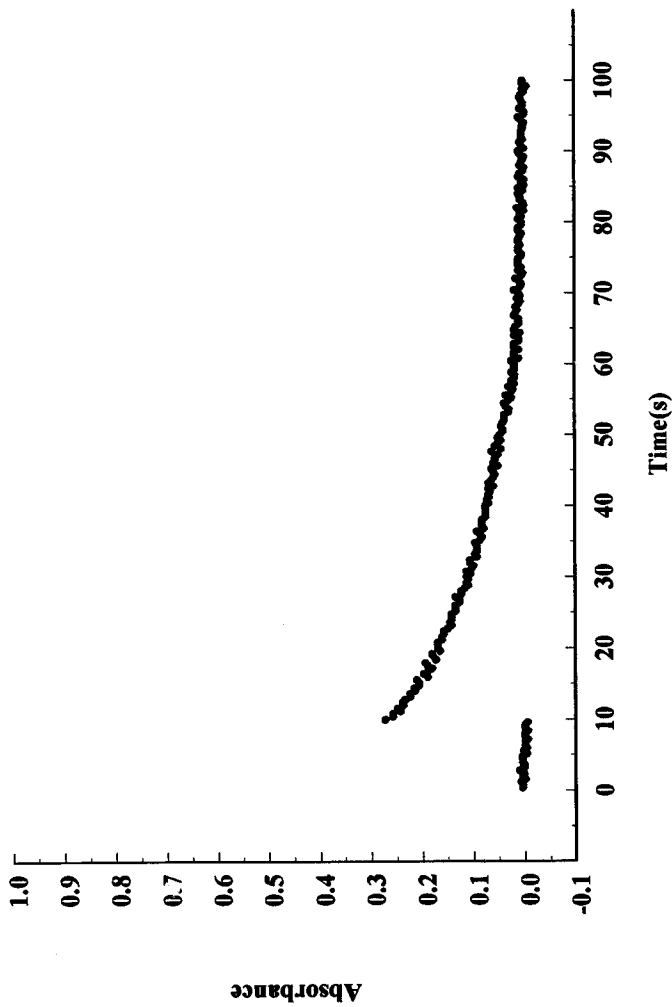


Figure 16 : Cr(CO)5L followed at 380 nm (500.8 torr CO)

L = 0.032M 1-hexene

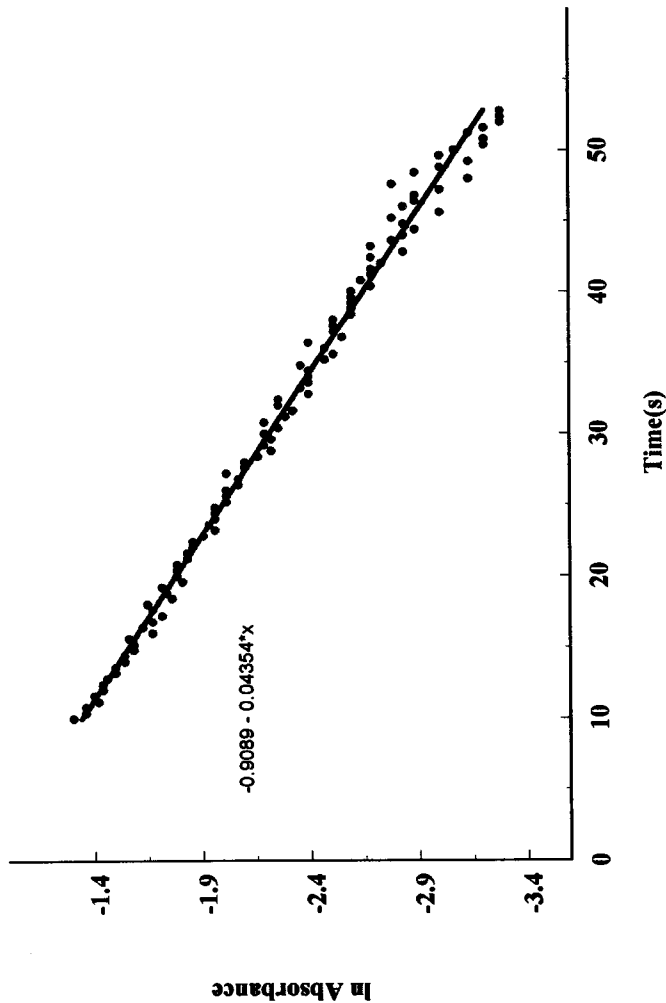


Figure 17 : Time Resolved Spectrum of Cr(CO)5L

L = 0.050M 1-hexene / 496.5 torr CO

0s corresponds to the time of the flash.

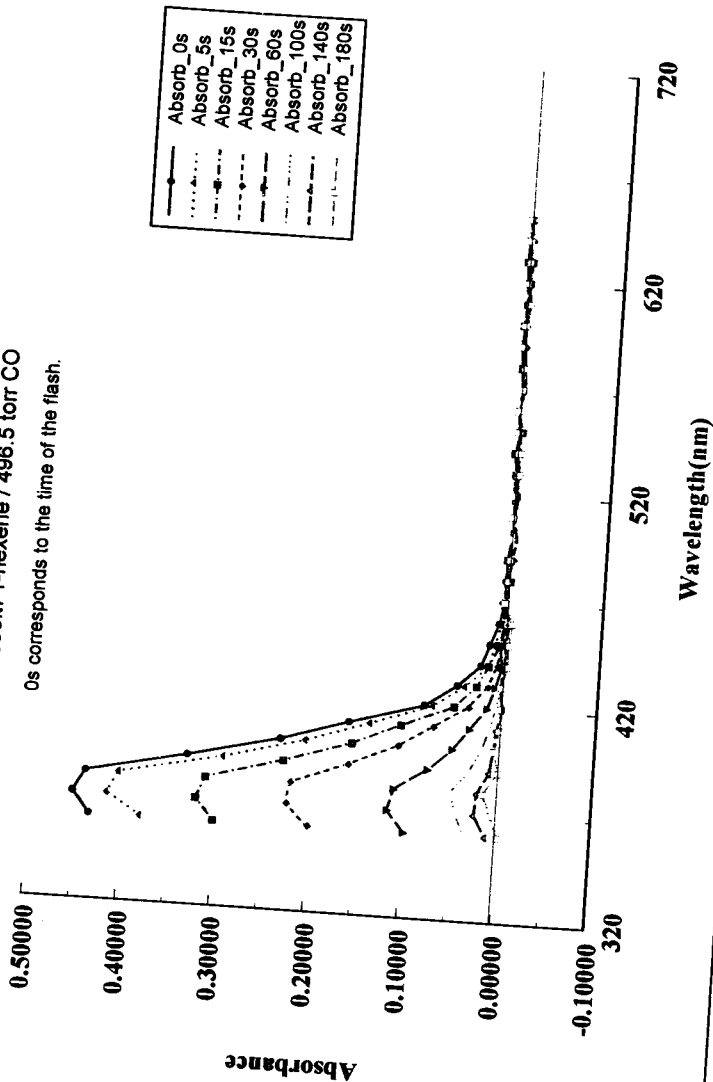
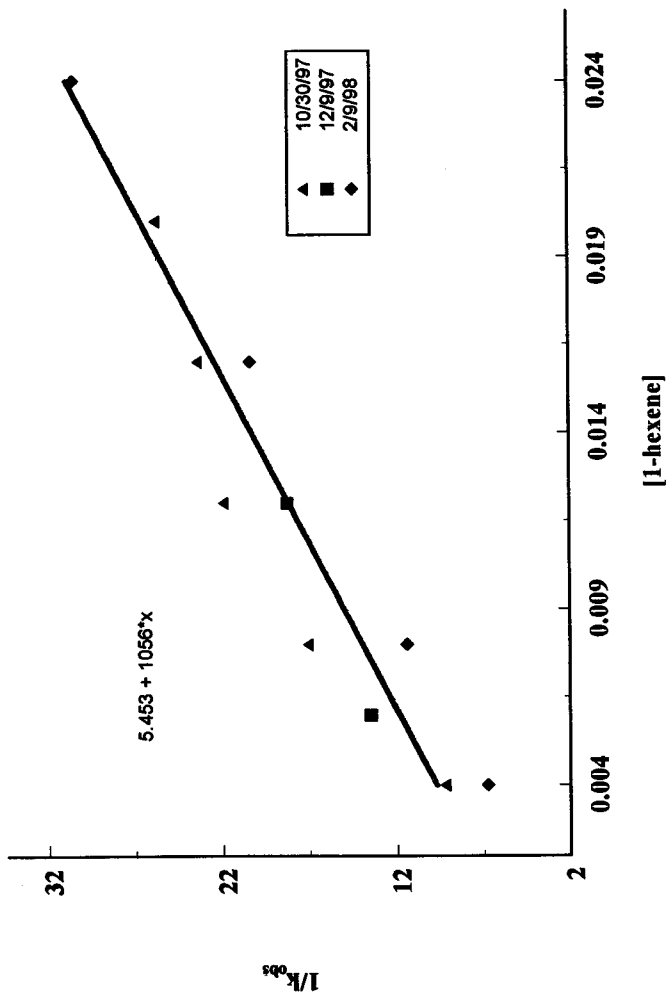


Figure 18 : $1/k_{\text{obs}}$ vs. [1-hexene] (≈ 500 torr CO)



not perfectly linear in all cases. This is suggestive of a competing process. The likely cause of this has been identified and addressed. It is discussed further in the Discussion section.

In the Kinetic Equations section, the slope of the natural log plots of Figures 7 through 16 were shown to be $-k_{\text{obs}}$. As was also described in the Kinetic Equations section, a plot of $1/k_{\text{obs}}$ versus 1-hexene concentration should be linear and can give us values for k_f and k_d from the slope and intercept. Data from the runs presented in Figures 7 through 16, as well as experiments from other days, are presented in the $1/k_{\text{obs}}$ vs. [1-hexene] plot in Figure 18. There is an obvious trend which suggests that the proposed mechanism does have merit. However, the scattering about the best fit line suggests other reactions are also occurring.

Discussion

As was mentioned in the Results section, there is evidence in the studies performed on the dissociation of $\text{Cr}(\text{CO})_5(\text{1-hexene})$ that a process is occurring that is competing with the dissociation of $\text{Cr}(\text{CO})_5\text{L}$. We discovered this problem after sending the UV/VIS analyzing light out for repair. During the repair process the lens of the lamp housing was cleaned. This allowed a much higher light intensity to reach the photolysis cell. This, in turn, is now causing significant photolysis of $\text{Cr}(\text{CO})_6$ prior to the firing of the flashlamps. This was obvious by observing the oscilloscope. A change in voltage, and therefore absorbance, could be seen at 380nm as the cell was exposed to the analyzing light before photolysis. In light of what is present in the photolysis cell this process likely involves formation of $\text{Cr}(\text{CO})_5(\text{1-hexene})$. Possible remedies to the interference and the direction we took are discussed later in this section.

Although the data collected on the dissociation of $\text{Cr}(\text{CO})_5(\text{1-hexene})$ must be refined, some qualitative statements can be made. Table 1 contains the k_d and k_f for both our experiment and for other $\text{Cr}(\text{CO})_5\text{L}$ complexes discussed in the Literature section.

As would be expected solution, the dissociation rate constant we obtained is less than those obtained by McNamara et al. for a series of alkenes in the gas phase.¹² Rapid energetic quenching by the solvent accounts for this lower value in the solution phase. It is also interesting to note that the solution phase k_f we obtained for

1-hexene is similar to that for CO obtained by Kelly and co-workers³ indicating that $\text{Cr}(\text{CO})_5$'s affinity for alkene π electrons is similar to the lone σ -electron pair on CO.

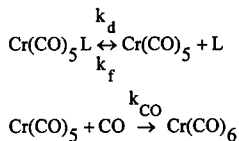


Table 1 : Rate Constants for Reactions of $\text{Cr}(\text{CO})_5\text{L}$

Solvent	L	T/°C	k_d/s^{-1}	$k_f/M^{-1}s^{-1}$	Ref.
C_7H_{16}	1-hexene	R.T.	0.183	$3.8 \cdot 10^6$	Our Data
C_6H_{12}	CO	R.T.		$3 \cdot 10^6$	3
Gas Phase	C_2H_4	40°C	0.641		12
Gas Phase	C_3H_6	40°C	2.6		12
Gas Phase	1- C_4H_8	40°C	5.18		12
Gas Phase	cis-2- C_4H_8	40°C	5.2		12
Gas Phase	trans-2- C_4H_8	40°C	22.2		12
Gas Phase	i- C_4H_8	40°C	22.8		12
C_7F_{12}	N_2	R.T.		$1.3 \cdot 10^9$	4
C_6H_{14}	HSiEt_3	21°C		$1.33 \cdot 10^7$	10
C_6H_{14}	HSiCl_3	21°C		$1.54 \cdot 10^6$	10
C_6H_{14}	HSiEt_3	25°C	2.6		10
C_6H_{14}	HSiCl_3	25°C	143		10

The most immediate problem that needs to be addressed is that of photolysis of the sample by the analyzing light. Two methods to handle this problem are: A) Filter the analyzing light to block all light below 380nm. B) Use an IR source instead of UV/VIS. We have elected to use an IR source.

Using an IR source provides many advantages. Peaks are much sharper in the IR and will make characterizing meta-stable alkene-transition metal complexes such as $\text{Cr}(\text{CO})_5(1\text{-hexene})$ easier. The other benefit is the much lower energy of the infrared light. This will eliminate the problem of photolysis by the analyzing light completely, since an IR photon carries insufficient energy to break a Cr-CO bond in $\text{Cr}(\text{CO})_6$.

Another advantage of using the IR source lies in the type of photolysis cell we will be using. It is a flow through cell and this allows us to replenish the reaction mixture after each experiment. Due to the short cell path length in an IR cell, 1mm in our case, a large volume of solution is not required to perform a series of experiments.

Converting to an IR source also has disadvantages. Fortunately, the necessary equipment is on hand and therefore the large cost of this equipment is not an issue for us. However, altering the procedure of the experiment this much will require that a significant amount of time be put into setting up and working the bugs out of the system. The last two months of this project have been devoted to this task.

Chromium hexacarbonyl photochemistry has a short history but has been the focus of much work. Due to its use in both catalytic and synthetic

applications the body of data on $\text{Cr}(\text{CO})_6$ photochemistry has grown rapidly. A major goal of this project is to relate the dissociation kinetics of $\text{Cr}(\text{CO})_5$ -alkene in the solution phase to that of $\text{Cr}(\text{CO})_5$ -alkene in the gas phase. While falling short of this goal, due to problems with the analyzing light, essential preliminary work has been done. In this project we have laid the groundwork necessary for definitive results to be obtained on the dissociation $\text{Cr}(\text{CO})_5$ -alkene complexes in the solution phase. Future work will be targeted towards obtaining data on the dissociation of various $\text{Cr}(\text{CO})_5$ -alkene complexes with alkenes of varying steric and electronic properties.

Appendix A

1. Transfer the waveform from the LeCroy 9410 oscilloscope to the IBM computer:

- Click on the Start button, go to Programs and then choose MS-DOS prompt.
- Type "cd\94rem" to change to the 94rem directory.
- When the trace is on the oscilloscope type "94g".
- Enter "s" to store the trace.
- Enter "c1" to save the trace from channel 1.
- A generic filename would be FILENAME.BIN. The actual filename is unimportant, however, it is typically the date. The .BIN is standard.
- Enter "e" to exit the program. This must be done after each trace is saved, as exiting the program returns control to the oscilloscope.

2. Convert the stored trace on the computer from binary to ASCII format:

- While in the "94rem" directory, use the following command.

```
94tran -a -oFILENAME.ASC FILENAME.BIN
```

- The filenames should be identical, aside from the .ASC and .BIN extensions.

3. Calculate %T and Absorbances from the .ASC file:

- Type "cd\fortran\source\samples"
- Type "voltages"
- The list of responses to prompts from the program should be as follows:
 - a. "c:\94rem\FILENAME.ASC"
 - b. 200 (if the time/div is a two) or 250 (if it isn't)
 - c. The time/div setting on the oscilloscope in seconds.
 - d. 1.0V
 - e. FILENAME.ABS

4. Using Axum for data processing: Importing the data from FILENAME.ABS:

- Type "exit" (this will return you to windows 95)
- Click on Start, go to programs, click on Axum 5.0 and then choose Axum (if you run Axum from MS-DOS you will get an old version of Axum).

- Go to the FILE menu and click on IMPORT DATA
- For the file name type "c:\fortran\source\samples\FILENAME.ABS".
- Position the cursor over each column number and type a column name (Time, PercentT, and Absorb) respectively.
- For column 1 change the precision to 6.

5. Using Axum for Data Analysis: Calculating ln A and 1/A:

- Label column 4 as Time2 (change precision to 6).
- Label column 5 as Absorb2
- Label column 6 as lnAbsorb2
- Label column 7 as InvAbsorb2
- Scan the data looking for the row **just after** the firing of the flash lamps (a sudden drop in PercentT will be present).
- Highlight only the Time and Absorbance columns from just after the lamps were fired until A = 0.02.
- Copy each column and paste the Time column into Time2 and the Absorb column into Absorb2.
- Click the Transform toolbar button (it is a capital X).
- In the window type :

$$\begin{aligned} \backslash 6 &= \text{Ln}(\backslash 5); \\ \backslash 7 &= 1/(\backslash 5); \end{aligned}$$

The first line means: "Calculate the natural logarithm of each entry in column 5 and place the result in the same row of column 6."

The second line means: "Calculate the inverse of each entry in column 5 and place the result in the same row of column 7."

- Save the data sheet.

6. Using Axum for Data Graphing: Plotting Absorbance vs. Time:

- Holding down the control key, click on the Time and Absorb columns.
- Click on the 2-D plot option (it is located on the top toolbar next to the transform option).
- From the graph menu click on the Scatter option (top left).
- A plot of the data will appear.

Adding a Title:

- Go to the Insert menu and click on Titles.
- Choose Main and type in a one line title.
- If a second line is needed select Sub from the Titles menu. Typically this is used for the date and run number.

Labeling the Axes:

- Click on the label of the axes you wish to change.

- The label will be editable. Enter the new label and click out of the editing area.

7. Graphing ln A and 1/A vs. Time:

- Hold down the control key and select the Time2 and either lnAbsorb or InvAbsorb column.
- Click on 2-D plot.
- Click on the Linear fit option.
- To name and change axes labels follow the directions in part 6.
- To display the equation of the best fit line do the following:
 - a. Go to the Insert menu.
 - b. Click on Curve Fit Equation
 - c. Use the mouse to drag the equation to the desired location.
- Save the plot.

8. Opening an existing data sheet or graph:

- Go to the File menu.
- Choose Open
- Choose Union Chem (C:)
- Choose Fortran
- Choose Source
- Choose Samples
- Choose or type in the desired file.

9. Constructing a Time Resolved Spectrum:

- Do steps 1, 2, and 3 from above first.
- Open Axum and make a new worksheet.
- Label the first column Time and change the precision to 6.
- Label the next column Absorb_Xnm where X is the wavelength. Initially give this column the same number as your greatest wavelength, then label successive columns with the lower wavelengths.
- Save the worksheet.
- Select Import Data from the File menu.
- Open the Absorbance file that corresponds to your first reading (highest wavelength).
- Copy the Time column from this worksheet and paste it into the Time column of the other worksheet.
- Now copy the absorbance column and paste it into the first worksheet in the Absorb_Xnm column that corresponds to that wavelength.

- Close the file that you copied from and open the file of the next lowest wavelength.
- Copy and paste the absorbance as you did before. Do this for every wavelength. Only copy the Time from the first worksheet.
- Now after all the wavelengths are in place save the worksheet again and also create and save a new worksheet.
- Label the first column in the new worksheet Wavelength. Enter each wavelength you observed into this column
- Label the remaining columns with Absorb_X where X is a time division. For example, if you had 1ms/div. your first column would be Absorb_0ms, followed by Absorb_1ms, and so on until you had as many points as you desired (10 max.).
- Now go back to the old worksheet and highlight the row that corresponds to your first time.
- Select transpose from the Data menu and select row. Then on the right side of the window change the worksheet field to display the "new" worksheet and change the column field to display the appropriate column (i.e. for time = 1ms change to Absorb_1ms).
- The first row of your Absorbance columns will contain the entry in the Time column from the "old" worksheet b/c Axum transposes the entire row. Highlight the first row of every column except for the Wavelength column and then select Clear from the edit menu. This will clear the data and move the data in every column except for the Wavelength column up one row.
- Once you have transposed all the times save the worksheet again.
- To create the spectrum, highlight all of the columns and select Scatter/Line from the graphing toolbar. This will construct the plot.

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