FLASH PHOTOCHEMICAL KINETICS OF CHROMIUM CARBONYLS

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Abstract

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Chromium hexacarbonyl, $Cr(CO)_6$, has been shown to be a very effective photochemical catalyst for many reactions, such as the 1,4-hydrogenation and 1,4-hydrosilation of conjugated 1,3-dienes resulting in the formation of a cis alkene product in greater than a 99% percent yield. The catalytic power of $Cr(CO)_6$ has merited its study by many investigators, mostly with regard to the structure of the catalytic intermediates, rather than the actual kinetics of individual steps in the mechanism. The goal of this study is to construct a database of both rate and mechanistic information on the reactions of $Cr(CO)_6$ with various alkenes and hydrosilanes.

Metal carbonyls are typically very sensitive to such impurities as oxygen and water, thus it is of utmost importance that solvents be dry and degassed. The first set of experiments involved running tests on the photochemical behavior of $Mn_2(CO)_{10}$ in order to develop an efficient method for solvent purification. Many methods were tried, and it was discovered that refluxing over CaH_2 followed by a second distillation in a fractionating column (all under flowing argon) proved to be the most effective at solvent purification.

When we began flashing a system containing just $Cr(CO)_6$ in order to reproduce literature results, it was discovered that a side reaction was occurring to form an impurity complex. Attempts to identify the impurity have so far failed, however, it does not appear to be either water, O_2, or an alkene.

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Introduction

In the realm of chemical research, the study of catalysis is a subject being vigorously pursued. People are always searching for a more efficient way to run a reaction or find a procedure which results in a purer and more selective product. Photochemical catalysts are one type of catalyst which is of much interest to researchers, since photochemical catalysts often allow reactions to occur under much milder conditions than they normally would. One such catalyst which has been of interest is chromium hexacarbonyl, $Cr(CO)_6$. This photochemical catalyst is known to increase the stereoselectivity of the products in such reactions as the 1,4-hydrogenation or 1,4-hydrosilation of 1,3-dienes. Much research has been done on the reactions which $Cr(CO)_6$ catalyzes, but not much is known about the details of how $Cr(CO)_6$ actually reacts with the individual components in each system. It is the goal of our research to study the kinetics and mechanisms of the reactions of $Cr(CO)_6$ with simple alkenes, dienes, and hydrosilanes, with the goal of building a database of how organotransition metal intermediates in photocatalysis react with their substrates.

Literature Review

Section 1: $Mn_2(CO)_{10}$ Literature

We chose $Mn_2(CO)_{10}$ as a test system for solvent purification because it is a well studied system whose photochemical dissociations are thought to be understood. Some of the early studies on the photodissociation of $Mn_2(CO)_{10}$ were performed by Meyer in the mid 1970's when his group flash photolyzed solutions of $Mn_2(CO)_{10}$ in cyclohexane and THF.[1] They observed the bleaching of the solution at about 343 nm, which is the main metal-metal s --> s* absorption for $Mn_2(CO)_{10}$, thus they assumed that the primary species being formed after the flash was $Mn(CO)_5$; in the region observed, they never monitored the actual recombination of two $Mn(CO)_5$ fragments to reform $Mn_2(CO)_{10}$. They also observed the formation of an intermediate species with a maximum absorbance at about 500 nm. They did not label this species, but they found that it decayed at a rate independent of added [CO], so they wrongfully ruled out the possibility that the species was $Mn_2(CO)_9$. As will be seen, they must have made a mistake in their experiment, as subsequent investigators have convincingly shown that this species is in fact $Mn_2(CO)_9$.

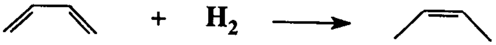
Peters and Vaida were the first people to positively identify two primary photoproducts upon flash photolysis of $Mn_2(CO)_{10}$ in ethanol.[2] By monitoring absorbance values from 400 nm to 800 nm with picosecond spectroscopy, they identified two absorption maxima at 480 nm and 780 nm. Upon comparison with previous work in solid matrices, they were able to label the peak at 780 nm as due to the formation of $Mn(CO)_5$. They concluded that the second peak at 480 nm could not be a secondary photoproduct since it was formed within 25 ps of the flash, and thus they decided that it was most likely $Mn_2(CO)_9(EtOH)$ formed by loss of a CO and coordination of the solvent, since a similar peak at 450 nm had recently been identified for $Mn_2(CO)_9$(pyridine). Another possibility which they addressed but could not confirm was that the 480 nm species could be due to $Mn_2(CO)_9$ which contained a bridging CO ligand.

The first definitive identification of the structure of the nonacarbonyl fragment was performed by Wrighton, who studied $Mn_2(CO)_{10}$ in 77K hydrocarbon matrices by using IR detection.[3] He discovered that the formation of $Mn_2(CO)_9$ by the dissociative loss of CO accounted for about 30% of the photoproducts of the reaction. By substituting ^{13}CO into the $Mn_2(CO)_{10}$ and studying the IR stretching of the molecule, he was able to determine that there was indeed a bridging CO between the two Mn metal centers. This bridged compound was not identified in solution phase experiments, however, until Grevels studied the decay kinetics of the two photoproducts in hydrocarbons by using IR detection.[4] He detected a bridging CO stretching frequency, whose position and intensity led them to believe that it was an asymmetrical bridge. In addition, Grevels noticed that the rate of recombination of $Mn_2(CO)_9$ with CO varied greatly on the solvent used for the experiment.

Studies such as this led researchers to investigate the reactivity of $Mn_2(CO)_9$ toward other potential ligands(including solvent). Yesaka *et al* were one of the early groups to study the reaction of $Mn_2(CO)_9$ toward added components such as phosphines and cyanides.[5] The absorbance maximums for $Mn_2(CO)_9$ and $Mn(CO)_5$ in hydrocarbons were reported by Yesaka to be 500 nm and 827 nm respectively, and these were the wavelengths we monitored in our $Mn_2(CO)_{10}$ experiments. The main findings of the experiment were that $Mn_2(CO)_9$ was most reactive with $P(n\text{-}Bu)_3$ and least reactive with CO, with two different cyanides being of approximately equal reactivity in-between. This was most likely due to the fact that the electrophilic manganese fragment is most likely to react with the electron rich phosphine.

Section 2: $Cr(CO)_6$ Literature

As a result of the catalytic power demonstrated by chromium carbonyl systems, researchers have been studying them for over thirty years. As is often the case, early work on catalytic systems usually does not begin with a detailed look into their mechanism, but rather an overview of the system as a whole in order to see where to begin probing deeper. Wrighton was one of the first researchers to publish data on one of these systems: the photocatalytic 1,4-hydrogenation of 1,3-dienes. What he discovered was that the 1,3-dienes which he studied were almost completely converted to their respective alkene in the presence of $H_{2(g)}$ (1atm), UV light, and $Cr(CO)_6$, via 1,4-hydrogenation.[6]



Wrighton attributed the catalytic reactions which he observed to the photochemical induced formation of a thermally active catalyst from the $Cr(CO)_6$ precursor. This reaction was novel in two ways, one being that contemporary organometallic catalysts for this reaction, such as $Fe(CO)_5$, required extreme temperatures and pressures for the reaction to proceed, while reactions catalyzed by $Cr(CO)_6$ occurred in a much more mild environment. The second and much more important point about this reaction which he reported was that the alkene product almost exclusively adopts a cis conformation. This adoption of the cis conformation was found to be the case both when the starting solution contained multiple stereoisomers of the diene and when the starting solution contained a single stereoisomer of the diene.

If $Cr(CO)_6$ is capable of catalyzing the 1,4-hydrogenation of these dienes, then it seems reasonable that it might be able to catalyze reactions similar to hydrogenation, such as the 1,4-hydrosilation of 1,3-dienes. This is the exact reaction which Wrighton studied next. He found that $Cr(CO)_6$ did indeed act as a photocatalyst for the 1,4-hydrosilation of 1,3-dienes.[7]

Wrighton also discovered that, like the hydrogenation reaction, the 1,4-hydrosilation catalysis resulted in greater than ninety percent of the products adopting the cis conformation. He also learned from this experiment that photolysis continued even after the system ceased to be irradiated, which further supported the hypothesis that a thermally active catalyst was being formed, although he did discover some results which suggested that the rate of catalysis was elevated when the system was being photolyzed.[7] Perhaps the most important result of this experiment was that when a methyl substituent was present on the 1 or 4 position of the 1,3-diene, it appeared that the hydrosilation did not occur very rapidly. This is important because it implies that there is some sort of steric effect involved with the catalyst (as implied by the stereoselectivity of the products) and thus it would be a good idea to start probing the nature of the catalyst and its precursor.

Kelly and Koerner von Gustorf were some of the first people who began to study the catalyst precursor, $Cr(CO)_6$, by using flash photolysis. Upon UV flash photolysis, they observed the formation, within 50 ns, of a species, which then decayed over a time greater than 200 ms and had an absorbance maximum at 503 nm.[8] This species then reacted to form another species which had an absorbance maximum at 445 nm and which decayed in under a second. The following is a mechanism which was proposed to explain these results:

$$Cr(CO)_6 \quad + \quad h\nu \quad \Longrightarrow \quad Cr(CO)_5 \quad + \quad CO$$

$$Cr(CO)_5 \quad + \quad CO \quad \Longrightarrow \quad Cr(CO)_6$$

$$Cr(CO)_5 \quad + \quad X \quad \Longrightarrow \quad Cr(CO)_5X$$

After the flash, $Cr(CO)_5$ is created and then either recombines with CO to form the species with $\lambda_{max}=503$ nm or reacts with some other component in the system to form the $Cr(CO)_5X$ complex, where X is neither solvent nor another chromium carbonyl fragment. It is noteworthy to mention that the impurity complex absorbance maximum shifted to 470-480 nm when the solution was subjected to several freeze, pump, thaw cycles.

The one thing that all of the previous experiments had in common is that they were conducted in hydrocarbon solvents. In solution it is more complicated to study the reaction of $Cr(CO)_5$ with other species, since the solvent molecules will obstruct the reaction by coordinating to the metal, physically being in the way, or by absorbing energy, thus it would be useful to study these reactions in either a less interfering solvent or in the gas phase. Since previous studies had suggested that $Cr(CO)_5$ would interact much weaker with a perfluorocarbon solvent molecule than with a hydrocarbon solvent molecule, Bonneau and Kelly studied the formation on the nanosecond timescale of $Cr(CO)_5$, and its subsequent recombination with CO to form $Cr(CO)_6$.[9] By studying the recombination under added CO, they were able to determine that the $Cr(CO)_5$ species reacted with CO three orders of magnitude faster in perfluorocarbon solvents than in cyclohexane, so in effect, the species was more "naked."[9] Kelly and Bonneau also observed the formation of a longer lived impurity complex which had a maximum absorbance at 485 nm. While they were also not able to identify the nature of this $Cr(CO)_5X$ complex, they were able to rule out the possibility that it was $Cr_2(CO)_{11}$, formed from the reaction of $Cr(CO)_6$ with $Cr(CO)_5$. They were able to do this based on the fact that the dissociation constant, K_d, of $Cr_2(CO)_{11}$ is greater than 10^6 s^{-1} so it is unlikely that this species is stable long enough to account for the longer lived impurity.

The identity of the $Cr(CO)_5X$ complex is thus still in question. The identity of the impurity complex was postulated by Grevels, who studied the reaction of solutions of $Cr(CO)_6$ by using flash photolysis.[10] He observed that the solvation of $Cr(CO)_5$ by hydrocarbon solvents to form $Cr(CO)_5$(solvent) occurred within 25 ps. This solvated species then reacted with CO to reform $Cr(CO)_6$; however, when water was added to the solution, it was discovered that $Cr(CO)_5$(solvent) reacted to form $Cr(CO)_5(H_2O)$ thirteen times faster than it recombined with CO to form $Cr(CO)_6$. This $Cr(CO)_5(H_2O)$ complex had an absorption maximum at 455 nm and thus it was labeled as the previously unidentified $Cr(CO)_5X$ complex. It was also noted that this water peak could be almost completely removed by performing at least three freeze, pump, thaw cycles.

Eric Weitz was the first to study the products of the photolysis of $Cr(CO)_6$ in the gas phase, namely the $Cr(CO)_x$ fragments, where x=5,4,3,2. In the gas phase there is no chance of the $Cr(CO)_5$ losing energy to a solvent, so the extra energy absorbed results in the displacement of multiple CO's, thus creating a wide range of $Cr(CO)_x$ fragments which are free to recombine with CO or other fragments. By using increasingly powerful lasers, they were able to identify by IR detection the creation of the $Cr(CO)_x$ fragments, where x=5,4,3,2. In addition, they were able to identify peaks corresponding to the recombination of $Cr(CO)_6$ with both $Cr(CO)_4$ and $Cr(CO)_5$, to afford $Cr_2(CO)_{10}$ and $Cr_2(CO)_{11}$ respectively.[11] These reactions allow the least restricted view into the actual kinetics and mechanisms of chromium carbonyl photochemistry.

As more flash photochemical experiments were conducted on $Cr(CO)_6$, where it was the only component in the system, people began to get a better understanding of how it might act as a catalyst precursor. The next step was for researchers to initiate research into the reaction of $Cr(CO)_6$ with another component in the system. Many catalysts provide a surface where the reactants are able to interact more efficiently, so if $Cr(CO)_6$ was to catalyze the hydrogenation of 1,3-dienes, then it would be useful to know if hydrogen is capable of binding to the metal and if it does, then it is necessary to know if it binds via a hydride or if it binds as molecular dihydrogen. Previous studies had implied that hydrogen did coordinate to $Cr(CO)_6$, but these studies were performed at very cold temperatures; Grevels' group at the Max Planck Institute was one of the first groups to observe the formation of a stable hydrogen complex, $Cr(CO)_5(H_2)$, at room temperature and normal pressures by using flash photolysis with infrared detection.[12] Previous studies by the same group had revealed that upon flash photolysis of solutions containing $Cr(CO)_6$ with added N_2, the bimolecular species $Cr(CO)_5(N_2)$ was formed with l_{max}=370 nm.[13] The species which they detected with added hydrogen also had an absorbance maximum at 370 nm and it so happens that the two complexes are indistinguishable by UV/Vis detection, but by infrared detection the two species were readily distinguishable. Grevels had been able to ascertain that nitrogen was coordinated to the metal as N_2 by observing the N-N stretching bands, but such identification was not possible with the hydrogen complex; however, the rate constants of the hydrogen and the nitrogen species were very similar and they both decayed within 200 ms, which suggested that the hydrogen was indeed coordinated to the metal center as dihydrogen, just as nitrogen was coordinated as dinitrogen.

Just as it is useful to understand the nature of the $Cr(CO)_6$-H_2 bond when considering the hydrogenation reaction, it is useful to understand if and how the silane coordinates to the metal during the 1,4-hydrosilation reaction. In order to hydrosilate the 1,3-diene, a silane need only contain one hydrogen, so its formula need only be $HSiR_3$, where R can be any suitable ligand, such as a phenyl group, various aliphatic hydrocarbons, or an electron withdrawing group such as a nitro group or a chlorine. The introduction of so many variables into the silane is exciting in that different groups would most likely lead to different bonding. Brown, Dobson, and Zhang have studied the nature of the metal-silane bond by varying the substituents on the silane from methyl, ethyl, and phenyl groups, to halogens and perfluoronated hydrocarbons.[14] What they discovered was that the hydrosilane can bond to the metal either by a 3-center, 2 electron bond, where the two H-Si σ electrons in the H-Si bond are shared between the H, Si, and the metal center, or by oxidative addition to the metal center, where the H-Si bond is broken and the hydrogen and silicon bind separately to the metal. The bond between a metal and a given silane is not necessarily one of these extremes, but rather lies somewhere in the continuum between them. If the hydrosilane contained simple hydrocarbon ligands such as a methyl or an ethyl group, then not surprisingly, the silane bound to the metal in a manner more indicative of a 3-center, 2 electron bond, since there is little competition for the two electrons from the relatively electron rich hydrocarbons. They found that if the hydrosilane contained electron withdrawing groups, such as a chlorine or a fluorine, however, the hydrosilane formed a bond to the metal via oxidative addition as these groups competed for the electrons in the H-Si bond. Note that binding via oxidative addition results in a much stronger bond, which could influence the rate of a hydrosilation reaction, since as the silane binds more strongly to the metal, it is less likely to leave the catalyst so that the reaction can continue. In fact, some of the $Cr(CO)_5(HSiR_3)$ species formed were very stable, with a lifetime of about 60 minutes. These long lifetimes were achieved only where R was a very electron withdrawing group such as a perfluorocarbon, but nevertheless, the silane adducts all were more stable than the dihydrogen complexes. One interesting discovery of the work done by Brown, Dobson, and Zhang was that in the case of chlorinated silanes, the hydrosilane is able to bind to the metal either through the H-Si bond or through the lone pair on the chlorine atom. These results all indicate that in the case of the 1,4-hydrosilation of 1,3-dienes, the exact nature of the hydrosilane could be very important.

Since it is important to understand the nature of the bond between the metal and either the hydrogen or the hydrosilane, it follows that it would be beneficial to investigate the bond between the metal and the diene. Before one looks at the binding of a bidentate ligand, however, it is reasonable that one would want to study how the metal binds to simple alkenes, in order to better understand how each double bond of an alkene might bind to the metal. By using infrared spectroscopy, Turner's group studied the photoproducts resulting from the photolysis of $Cr(CO)_6$ in liquid Xe spiked with added ethylene.[15] Under continued photolysis it was noted $Cr(CO)_6$ lost either one or two CO's in order to form either $Cr(CO)_5(C_2H_2)$ or cis- and trans-$Cr(CO)_5(C_2H_2)_2$ respectively. It was observed that while all three of the species proved unstable at low temperatures, the monosubstituted species proved the most stable, and the trans species proved the most stable of the disubstituted species. Turner attempted to rationalize the thermal stability difference by the

π bonding ability of the CO and ethylene groups, stating that the increased competition between CO and ethylene groups trans to one another, as is the case in cis-$Cr(CO)_5(C_2H_2)_2$, makes the complex much more unstable than if the two ethylene groups are trans to one another, as is the case in trans-$Cr(CO)_5(C_2H_2)_2$. This argument does not explain, however, why the monoethylene complex is more stable than the trans diethylene complex. If a diene was to coordinate to the metal, then it would seem that a trans arrangement of the double bonds around the metal would not be favored since it is not likely that a 1,3-diene is large enough to occupy trans positions in a complex with octahedral geometry. Perhaps the decreased stability of the cis conformation helps the diene leave once it has been converted to an alkene. This study looks at two separate "double bond units", however, whereas a 1,3-diene is a conjugated system, so perhaps the bonding is different.

In order to observe such a system, recent studies by Weitz have focused on the nature of the reaction of $Cr(CO)_4$ with both a conjugated diene and a non-conjugated diene. More specifically, he has used time resolved infrared spectroscopy to monitor the reaction of $Cr(CO)_4$ with both 1,3- and 1,4-pentadiene.[16] This work has resulted in the development of several proposed mechanisms for these reactions, but the important point for this work is that the conjugated system of 1,3-pentadiene was able to coordinate to the metal as a bidentate ligand and formed a much more stable $Cr(CO)_4$(1,3-pentadiene) complex than was possible with the non-conjugated 1,4-

pentadiene, which was apparently only able to form a weakly coordinated complex with $Cr(CO)_4$ as a result of reduced stability. It seems that the conjugated diene is able to orient itself in order to coordinate more strongly to the metal, while in the non-conjugated diene the double bonds are not able to orient themselves in a proper position.

All of this work has allowed people to better understand the photocatalysis of several reactions via the $Cr(CO)_6$ precursor. Current work by many researchers focuses on the whole catalytic cycle, which involves the coordination to the metal of both the hydrosilane (or dihydrogen) and the diene followed by the regeneration of the catalyst. The study of such a system is beyond the scope of our lab due to availability of certain equipment and resources. Many of the above experiments only focused on the structure of the reaction intermediates, and not the actual kinetics and mechanisms of the reactions, and as a result, the goal of our current research is to construct a database of the kinetics and mechanisms of the reaction of $Cr(CO)_5$ with various alkenes and hydrosilanes for use by future researchers.

Experimental

Section 1: Solvent Preparation

Since many experiments involved varying the method used for preparing the solvent, the following is a general procedure for solvent preparation. Any modifications which were made for particular experiments will be discussed in the Results section.

The solvent used for all of the experiments was n-heptane(Aldrich, 99+%, HPLC grade). The heptane was dried by refluxing over CaH_2 for 24 hours under flowing argon and then distilled into a round bottom flask. The flask filled with heptane was then transferred to a fractionating column filled with glass beads, where it was distilled a second time under flowing argon in order to remove any impurities more volatile than heptane. To ensure that no unnecessary impurities were collected, the first 10 mL(approximately) of distillate were discarded by drawing it out with a gas tight syringe. When all of the heptane was collected, 15 mL were drawn off in a gas tight syringe for solution preparation.

Section 2: Solution Preparation

All of the $Mn_2(CO)_{10}$ used was sublimed under vacuum at 40°C and stored under vacuum in a freezer. When preparing solutions, 1.2 mg of

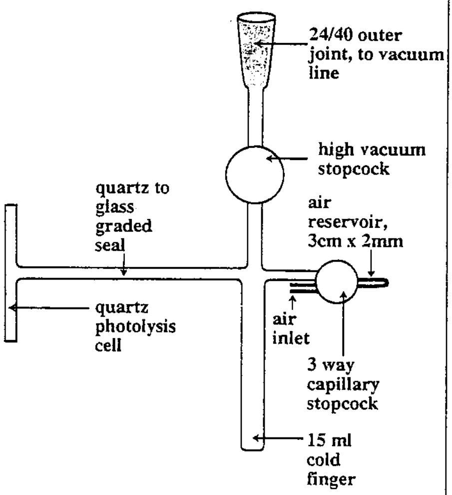
$Mn_2(CO)_{10}$ was weighed out in order to afford $Mn_2(CO)_{10}$ solutions with a concentration of 2×10^{-4} M in 15 mL of heptane.

The $Cr(CO)_6$ (Strem Chemicals, 99%) was stored under 1 atmosphere of air with no special preparation. When preparing solutions, 3.3 mg of $Cr(CO)_6$ were weighed out in order to afford $Cr(CO)_6$ solutions with a concentration of 1×10^{-3} M in 15 mL of heptane.

The solution was prepared in a sample cell assembly which is similar to the cell represented in Figure 1. There were two main differences: 1) the cell used for these experiments was constructed entirely of Pyrex and contained no quartz; 2) the cell used for these experiments did r[illegible]ve the air reservoir with a three way capillary stopcock. The cell was blown by Bill Jones at the General Electric Research and Development Center in Niskayuna, NY. The cell was placed on the vacuum line and exposed to high vacuum (about 10^{-5} torr) for approximately thirty minutes in order to remove any adsorbed water or atmospheric gases. Then it was filled to overpressure with argon and the stopcock to the atmosphere was removed so that argon was flowing out of the cell.

The respective metal carbonyl was then transferred to the cell via filter paper and then washed down into the cold finger with 15 mL of purified heptane. After a magnetic stirring bar was dropped into the cold finger, the stopcock was replaced. The solution was then stirred with a magnetic stirring plate for about five minutes until all of the metal carbonyl had dissolved.

Figure 1
Sample cell assembly



Detail of the Sample Cell Assembly

The $Mn_2(CO)_{10}$ solutions were clear with a pale yellow color, and the $Cr(CO)_6$ solutions were clear and colorless.

The solution was then degassed by performing: 1) 3 successive pump, freeze, pump, thaw cycles followed by 2) 3 successive freeze, pump, thaw cycles. The first procedure involved opening the liquid solution to vacuum while stirring until it was possible to see convection currents form, and after one minute the solution was cut off from the vacuum by closing the stopcock. Then the solution was slowly frozen by placing a glass dewar containing liquid nitrogen around the cold finger. After the solution appeared frozen, it was exposed to high vacuum for five minutes, after which it was closed off from the vacuum and thawed by placing a beaker containing room temperature water around the cold finger. Once the solution was thawed, it was stirred for five minutes and then the procedure was repeated two more times. The procedure for the last three cycles was the same as above, except the liquid solution is never exposed to high vacuum, in order to prevent too much solvent from being drawn off. After the solution was degassed, the vacuum line was flooded with argon and the sample cell was removed and placed in the flash photolysis apparatus.

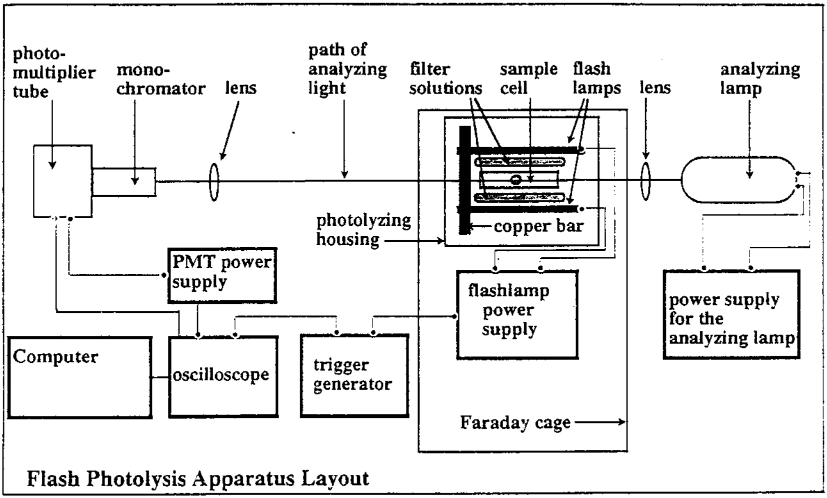
Section 3: Flash Experiment and Data Collection

A schematic of the flash photolysis apparatus is shown in Figure 2. Before the photolysis cell was placed in the flash apparatus, there were a number of steps which must be followed:

1) It was necessary to turn on the xenon analyzing lamp and the lamp water supply approximately forty minutes before flashing in order to assure that the beam was stable.
2) The LeCroy 9410 Dual Beam 150 MHz oscilloscope was turned on, the sweep rate was set to 10 ms/div, and the gain was set to 10 mV/div. Then the input signal was set to ground and the trace was aligned with the first box from the top of the screen.
3) The cover was removed from the ISA Instruments monochromator and the wavelength was set at 500 nm.
4) The correct filter solutions for the xenon flash lamps were chosen so that the lamps photolyzed into the necessary regions of the spectrum. For both $Mn_2(CO)_{10}$ and $Cr(CO)_6$, solutions of $CuSO_4$ were used.
5) Both the trigger generator and the computer were turned on.

When all of this was accomplished, the sample cell was tilted so that the solution completely filled the side arm photolysis cell; it was important to check that there were no gas bubbles in the cell, as this could affect the measured absorbance of the solution. The cell was then placed in the flash

Figure 2
Flash photolysis apparatus layout



Flash Photolysis Apparatus Layout

photolysis apparatus so that the long axis of the photolysis cell was directly in the path of the beam from the analyzing lamp. At this time the input signal on the oscilloscope was set to DC, the power supply to the photomultiplier tube (PMT) was turned on, and then the voltage on the PMT was increased until a 50 mV (5 boxes) difference existed between the DC signal and the ground on the oscilloscope. The optimum voltage on the PMT is about 400 V at 500 nm, so it was often necessary to adjust the cell housing, the lamp orientation, or the lens distances so that the beam fell directly on the monochromator detector. After the orientation of the sample cell had been optimized, the back of the Faraday cage was closed and the flash lamp power supply was turned on. After the capacitor was charged, the voltage on the power supply was set to 9000 V and the front door of the Faraday cage was closed.

$Mn_2(CO)_{10}$ experiments

Before the system was ready to be flashed, the monochromator had to be set to an appropriate wavelength. The two wavelengths of interest in the $Mn_2(CO)_{10}$ system are 827 nm for the recombination of 2 $Mn(CO)_5$ fragments and 500 nm for the recombination of $Mn_2(CO)_9$ and CO, both of which result in the reformation of $Mn_2(CO)_{10}$. Once the monochromator was set, the oscilloscope sweep setting was adjusted to an appropriate rate. The actual sweep rate varied for each experiment, but on average at 500 nm, the sweep rate was about 100-500 ms/div, and at 827 nm, the sweep rate was about 50-100 ms/div. These are good ranges to conduct an initial flash, and the actual sweep rate was adjusted after an initial flash in order to maximize the amount of data recorded. Once the sweep rate was optimized, the collection mode on the oscilloscope was changed from auto sweep to single sweep, the trace was reset to a 50 mV difference by adjusting the PMT power supply, and then the lamps were triggered. The trace was viewed on the screen and then saved on the computer by entering the 94rem directory on the C: drive, and then running the 94g program. Once in the program, 'S' was selected to store the trace, channel 1 was the selected input from the oscilloscope, and the trace on the oscilloscope was given a filename. The filename consisted of the date of the run followed by a letter representing which run of the day was being recorded(A = first run, etc.), then the filename was designated as consisting of binary information by placing a '.bin' at the end. A sample filename for the second run on May 5, 1996 would look like this:

050596B.bin

The data was now ready for data analysis.

$Cr(CO)_6$ experiments

There were two different types of experiments performed on the $Cr(CO)_6$ system, therefore the wavelength of interest varied with the experiment. The simple recombination reaction of $Cr(CO)_5$ with CO to reform $Cr(CO)_6$ was monitored at 500 nm, which is the maximum absorbance of $Cr(CO)_5$. The rest of the collection procedure followed that of $Mn_2(CO)_{10}$, except that two time scales were monitored for two different reactions, so the sweep rate was about 0.1-2 ms/div when monitoring the quick decay and about 0.5-1 seconds/div when monitoring the slower decay.

For experiments in which time resolved spectra were desired, the monochromator would be set to 370 nm and a trace was recorded and saved. Then the monochromator would be set to 380 nm and the procedure repeated. This repetition of data collection at 10 nm increments occurred until 670 nm was reached. When the letter 'Z' was reached, the lettering reset so that the next experiment filename ended in 'AA', 'AB', 'AC', etc.

Section 4: Data Analysis

In order to analyze the data it was necessary to convert it from its binary form to absorbance values. The first step involved using the 94tran program provided with the oscilloscope to convert the data from binary to ASCII format. Then the data was converted from voltage values to percent transmittance and absorbance values by using the Voltages program written in FORTRAN by Professor David Hayes. Then the file was imported into the data analysis program Axum written by Trimetrix Systems. In Axum, plots were constructed of Absorbance vs. Time, Ln Absorbance vs. Time, and Inverse Absorbance vs. Time, for kinetic analysis, and plots of Time Resolved Absorbance vs. Wavelength were constructed when a whole spectrum was required. In order to review the full procedures for the data analysis on the computer, please refer to Appendix A: Computerized Data Analysis.

Results

Section 1: $Mn_2(CO)_{10}$ Results

As stated previously, the $Mn_2(CO)_{10}$ system was initially used as a test system to determine an effective solvent purification procedure. The preferred procedure, which included refluxing over CaH_2 and a second distillation in a fractionating column, has been previously described. Please note that all of these procedures were performed under flowing argon. The first and second order kinetic plots (Ln Absorbance vs. Time and Inverse Absorbance vs. Time) of these experiments are in the laboratory notebook, but they are not presented in this thesis, since the only information which they demonstrate is that these solvent preparation steps were not successful.

Untreated heptane

In an effort to determine if any special solvent preparation was actually necessary, a solution of $Mn_2(CO)_{10}$ was prepared using heptane directly from the container. It was not necessary to even perform a flash experiment on this solution, as it changed from a pale yellow color to a dark brown color in a matter of a few minutes, indicating that the solution had been ruined.

Treatment with CaH_2

In order to dry the solvent, a solution of $Mn_2(CO)_{10}$ was prepared using heptane refluxed over CaH_2 for 24 hours. Neither first or second order kinetic reactions was observed.

Treatment with $LiAlH_4$

$LiAlH_4$ is known as a more vigorous drying agent than CaH_2, so a solution of $Mn_2(CO)_{10}$ was prepared using heptane refluxed over $LiAlH_4$ for 24 hours. The rest of the experiment proceeded as described in the Experimental. Neither first or second order kinetic reactions was observed.

Treatment with $LiAlH_4$ and fractionation

It was noted that there appeared to be a gray precipitate on the walls of the collection flask of the $LiAlH_4$ still, which was attributed to $LiAlH_4$ being distilled over by vigorous heating. In order to be certain that no $LiAlH_4$ was in our solvent, a second distillation was performed in a fractionating column. The rest of the experiment then proceeded as described in the Experimental. Neither first or second order kinetic reactions was observed.

Treatment with H_2SO_4 and CaH_2

In order to remove any potential alkene impurities, the heptane was treated with a sulfuric acid treatment as described in the literature. We added 30 mL of concentrated H_2SO_4 and 300 mL of heptane to a 500 mL round bottom flask containing a magnetic stirring bar and then stirred over a magnetic stir plate for 24 hours in order to sulfonate any alkenes present. The heptane phase was separated with a separatory funnel and then washed three times with 100 mL of water. Then 100 mL of saturated $NaHCO_3$ was added and the solution was stirred for 24 hours in order to neutralize any excess

H_2SO_4. After the heptane phase was separated, it was washed three more times with 100 mL of water. Then one tablespoon of $CaCl_2$ was added and the solution was stirred for two days in order to pre-dry the solvent, after which it was refluxed over CaH_2 for 24 hours. The rest of the experiment proceeded as described in the Experimental. Neither first or second order kinetic reactions was observed.

Treatment with H_2SO_4, $LiAlH_4$, and fractionation

In order to see if the sulfuric acid treatment was effective with $LiAlH_4$ drying, a solution of $Mn_2(CO)_{10}$ was prepared with heptane treated with the sulfuric acid wash, then refluxed over $LiAlH_4$ for 24 hours, followed by a second distillation in a fractionating column. The rest of the experiment proceeded as described in the Experimental. Neither first or second order kinetic reactions was observed.

Treatment with Na metal

Sodium metal reacts vigorously with water and O_2 to form NaOH and Na_2O, and thus is a very effective drying and degassing agent. As a result, a solution of $Mn_2(CO)_{10}$ was prepared which contained heptane that had been refluxed for 24 hours in the presence of Na metal. Before addition to the heptane, the Na metal was washed with isopropyl alcohol(IPA) and untreated heptane in order to remove any oxides. The rest of the experiment proceeded as described in the Experimental. Neither first or second order kinetic reactions was observed.

Treatment with Sodium Benzophenone Ketyl

Sodium benzophenone ketyl is known to be a more effective drying and degassing agent than just Na metal by itself, so we prepared a solution of $Mn_2(CO)_{10}$ with heptane that had been refluxed 24 hours in the presence of sodium benzophenone ketyl. The sodium was prewashed and added to the heptane as previously described, then several teaspoons of benzophenone were added. The solution was then heated to reflux and left to sit until it had changed to a blue color. The rest of the experiment proceeded as described in the Experimental. Neither first or second order kinetic reactions was observed.

Section 2: $Cr(CO)_6$ Results

Before we began performing flash experiments and monitoring the decay of $Cr(CO)_5$, we wanted to be sure there would be no interference from the absorbance spectrum of $Cr(CO)_6$, so we took an absorbance spectrum of a solution of $Cr(CO)_6$. In order to take a spectrum without exposing the solution to the atmosphere we had a special cell constructed by Bill Jones which had a quartz cuvette attached opposite the photolysis arm. The spectrum which we obtained can be seen in Figure 3. Since our photolysis cell is Pyrex, it is opaque to light below 300 nm. As a consequence, Figure 3 shows that our flash experiments only photolyzed into the long wavelength ($\lambda > 300$ nm) shoulder of the $Cr(CO)_6$ absorbance spectrum. In addition, the region of observation for all of the experiments, as marked on Figure 3, was between 370 nm to 750 nm, and thus there was no interference from absorption.

Once it was realized that observing the decay of $Cr(CO)_5$ near its λ_{max} at 500 nm would be possible, we attempted to reproduce some literature results in order to be certain that our system was behaving as expected. We flashed a solution of $Cr(CO)_6$ and monitored at 500 nm expecting to observe the simple second order recombination of $Cr(CO)_5$ with CO to reform $Cr(CO)_6$, but instead we observed two different reactions occurring on two different time scales. It was easy to see the two decays on the oscilloscope, but due to software limitations, not all of the data points from the oscilloscope could be converted to Axum, so it was not as easy to observe the two time scales on the computer. Figure 4 is an Absorbance vs. Time plot of the two decays on the same Y axis. The actual maximum absorbance of the fast decay is about 0.8 absorbance units, but in Figure 4 it is possible to see the last few points of the fast decay, which occurred in about 100 ms and thus appears almost vertical during the 2 second observation time. The slow decay begins after the first 100 ms at about 0.1 absorbance units, and then decays over the course of several seconds. Clearly the primary photochemical and secondary thermal reactions which were occurring are totally reversible.

Figure 3
Absorbance versus Wavelength spectrum of $Cr(CO)_6$

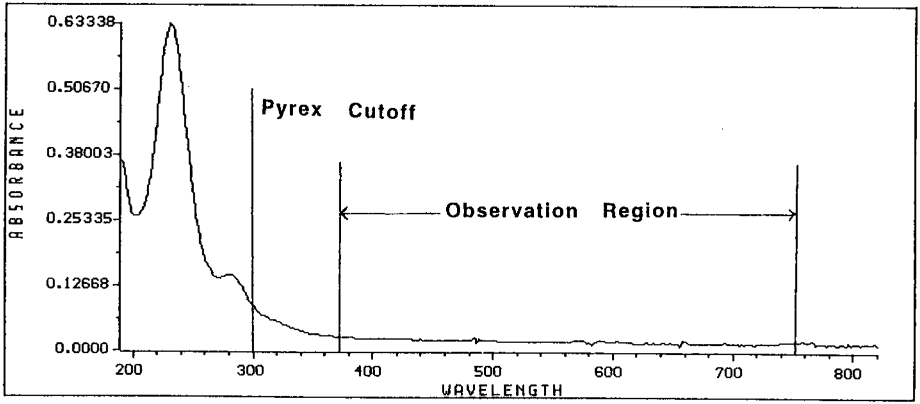
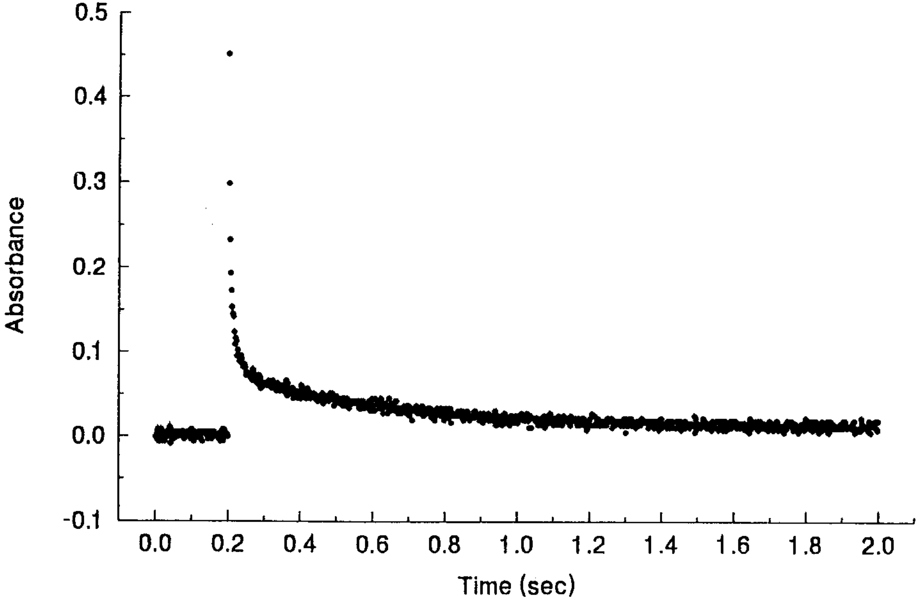


Figure 4



Absorbance vs Time Spectrum of $Cr(CO)_5$ Followed at 500 nm

It appeared that there was some unknown side reaction occurring after flashing. In order to better understand what was happening, we decided to analyzed the data in order to see what type of kinetics the decays were displaying. If the reactions were first order, then a plot of Ln Absorbance vs. Time should be a straight line; if the reactions were second order, then a plot of Inverse Absorbance vs. Time should be a straight line. Figure 5 is a plot of Ln Absorbance vs. Time for the quick decay, and it is obvious that the data does not plot up in a linear fashion. Similarly, Figure 6 is a plot of Inverse Absorbance vs. Time for the quick decay, and it is also obvious that it is not a linear plot. The same plots were constructed for the slow decay, and it turned out that neither of them were linear. Thus the $Cr(CO)_6$ system in our laboratory did not seem as simple as expected. In order to better observe what was occurring, we decided to generate time-resolved spectra.

The first time-resolved experiment which we performed was on the fast decay on a microsecond time scale(Figure 7). The time-resolved spectrum is an overlay plot of Absorbance versus Wavelength where each overlay plot is at successively later times after the initial flash, so in Figure 7, each line on the graph differs by 100 ms. The absorbance spectra in Figure 7 is what one would expect from reading the literature for the recombination of $Cr(CO)_5$ and CO in a hydrocarbon solvent; the spectra is very gaussian with an absorbance maximum at about 500 nm, and the maximum does not shift over time. Since everything appeared normal at this timescale, we decided to construct a new plot at longer times. If the fast decay was purely due to the

Figure 5

Ln Absorbance vs Time Plot of $Cr(CO)_5$ at 500nm

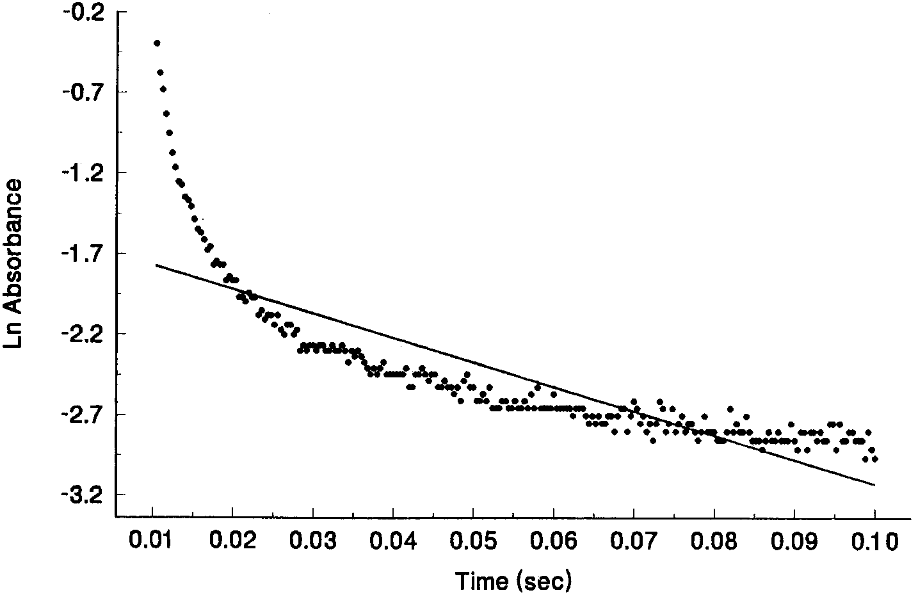


Figure 6

Inverse Absorbance vs Time Plot of $Cr(CO)_5$ at 500nm

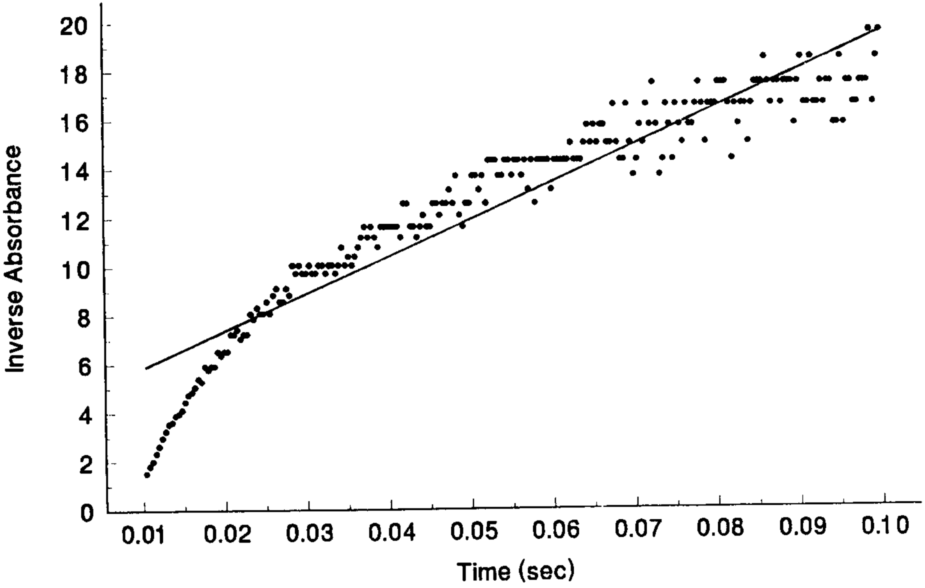
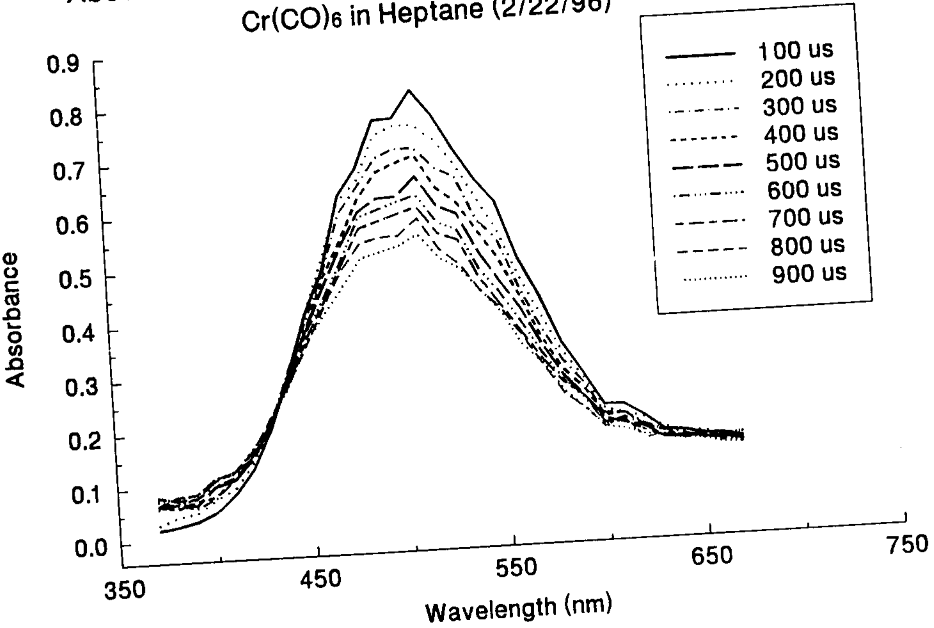


Figure 7

Absorbance vs Wavelength Time Resolved Spectrum of $Cr(CO)_6$ in Heptane (2/22/96)



recombination of $Cr(CO)_5$ and CO, then one would expect the spectra to simply decay to the baseline, but as can be seen in Figure 8, if one follows the fast decay out to about 18 ms, another absorbance maximum appears at about 450 nm. It is impossible from just observing Figure 8 to tell whether this peak grows in on the same time scale as the 500 nm peak decays or whether it forms more rapidly. At this time there is not a definitive answer to this question, but what is certain is that some species, which we will call the impurity complex $Cr(CO)_5X$, is being formed less than 20 ms after the flash.

The time-resolved spectra for the long decay is displayed in Figure 9 and follows over a range of 4.5 seconds at 0.5 second intervals. After 0.5 seconds (500 ms), the impurity peak at 450 nm has now shifted to about 430 nm and does not appear to shift any further. What is observed in this spectrum is the decay of the impurity complex, and note that the absorbance at all wavelengths monitored in this experiment return to zero, which proves that the reaction is irreversible. At this time we have developed no explanation for the apparent 'flat peak' from about 600 nm to >800 nm. Recall from the Literature section that a water impurity had been identified with an absorbance maximum at about 450 nm, so this led us to believe that the impurity complex could be due to added water in the system.[10] If so, then the following reactions could be occurring:

Figure 8

Absorbance vs Wavelength Time Resolved Spectrum of $Cr(CO)_6$ in Heptane (3/8/96)

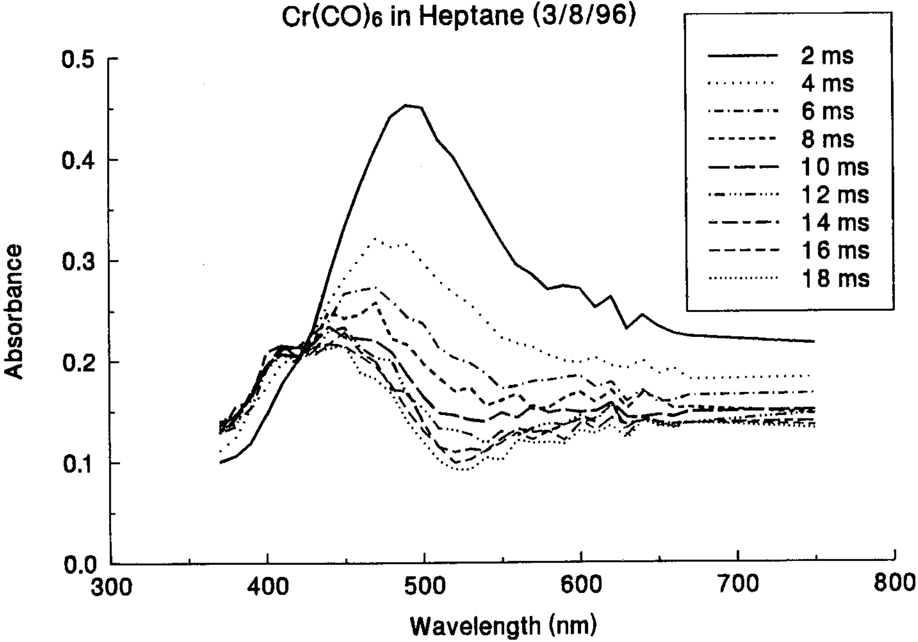
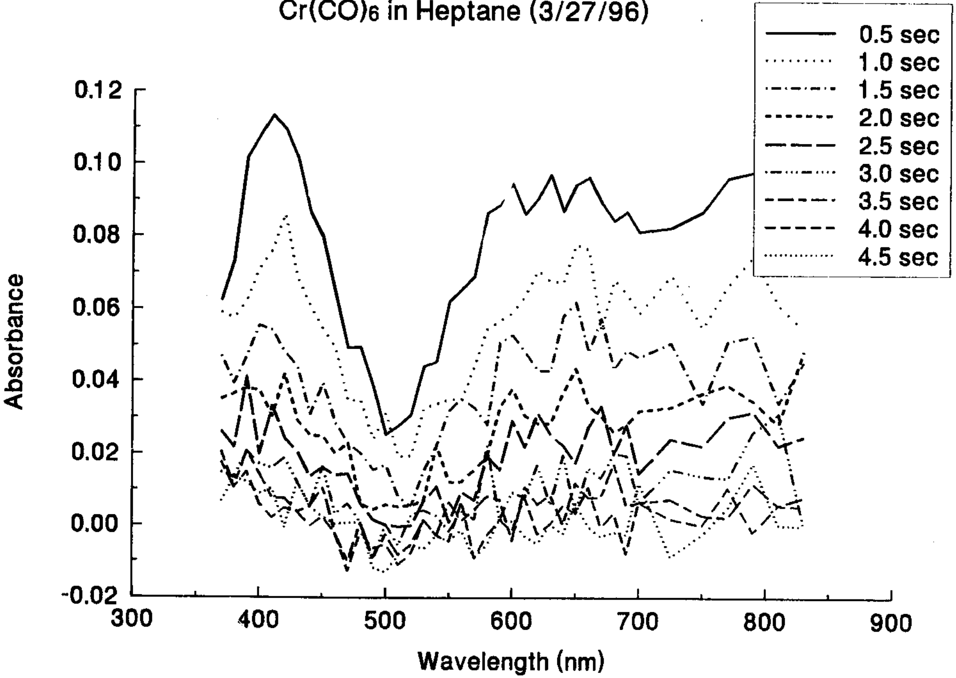


Figure 9
Absorbance vs Wavelength Time Resolved Spectrum of $Cr(CO)_6$ in Heptane (3/27/96)



$Cr(CO)_5$ + H_2O ===> $Cr(CO)_5(H_2O)$ fast

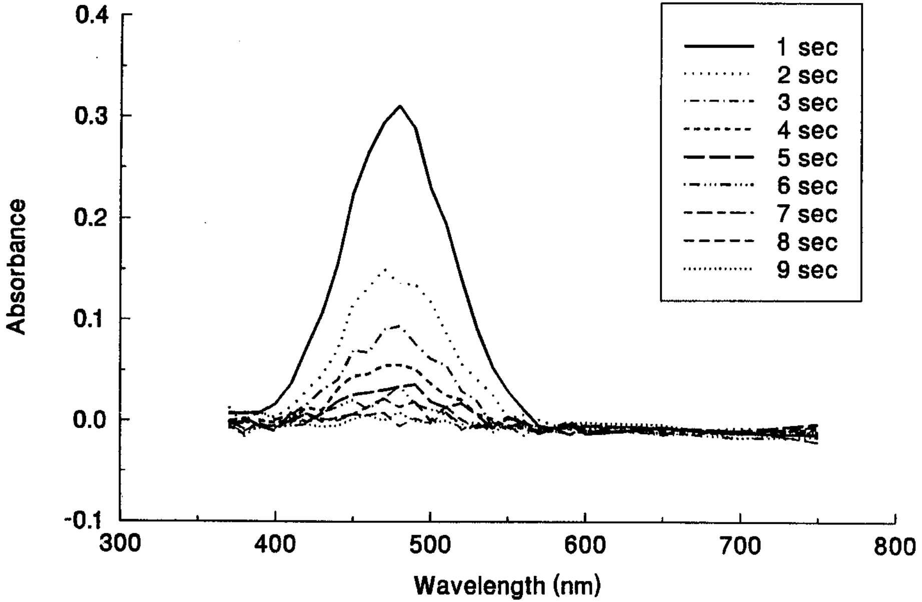
$Cr(CO)_5$ + CO ===> $Cr(CO)_6$ fast

$Cr(CO)_5(H_2O)$ + CO ===> $Cr(CO)_6$ slow

where $Cr(CO)_5$ reacts competitively with H_2O and CO in the fast decay to form either $Cr(CO)_5(H_2O)$ or $Cr(CO)_6$ respectively, and then the water complex reacts with CO in the slow reaction to form $Cr(CO)_6$. This mechanism is consistent with the literature which reported that $Cr(CO)_5$ reacts thirteen times faster with H_2O than with CO.[10]

In order to test this hypothesis, we decided to see how $Cr(CO)_5$ would react with added water, so we prepared a solution of $Cr(CO)_6$ in heptane which was spiked with 1 mM H_2O, so that $Cr(CO)_6$ and H_2O were in a 1:1 molar ratio. After flashing, there was no noticeable difference between this solution and previous solutions, so we opened the solution to the atmosphere under flowing argon and added three times the amount added previously, so that the $[H_2O]$ in solution was theoretically 4.7 mM. The fact that there was no noticeable reaction after the first addition could be due to the fact that the pump, freeze, pump, thaws effectively removed the added water, and thus we can not be certain of the actual $[H_2O]$. After degassing this solution, without pumping on the liquid, and flashing again, there appeared to be only one curve which decayed over about 10 seconds, so we constructed the time-resolved spectrum displayed in Figure 10. The species formed in the flash had an absorbance maximum at about 480 nm and had a very clean

Figure 10
Absorbance vs Wavelength Time Resolved Spectrum of $Cr(CO)_6$ in Heptane Spiked with 4.7 mM H_2O (4/3/96)



gaussian spectrum which decayed to zero after 9 seconds, implying that the reaction is reversible. Since the $[H_2O] >> [CO]$ in this system, it would seem logical that $Cr(CO)_5$ reacts almost exclusively with water to form a $Cr(CO)_5(H_2O)$ complex immediately, and thus we are observing the reaction of this water complex with CO to reform $Cr(CO)_6$. This experiment seemed to rule out the water hypothesis for two reasons: 1) the impurity in our system had an absorbance maximum at about 450 nm, while the water system had an absorbance maximum at 480 nm; 2) the 'flat peak' at wavelengths greater than 600 nm that appears in the unspiked system is not present in the system spiked with water. It was necessary to develop another hypothesis.

Since heptane is a straight chain hydrocarbon, it would not be unlikely that it contained significant quantities of simple alkene impurities, such as heptene. If this was the case, then a reaction similar to the one postulated in the water hypothesis could be occurring:

$Cr(CO)_5$ + alkene ===> $Cr(CO)_5$(alkene) fast
$Cr(CO)_5$ + CO ===> $Cr(CO)_6$ fast
$Cr(CO)_5$(alkene) + CO ===> $Cr(CO)_6$ slow

where $Cr(CO)_5$ reacts competitively with an alkene and CO in the fast decay to form either $Cr(CO)_5$(alkene) or $Cr(CO)_6$ respectively, and then the water complex reacts with CO in the slow reaction to form $Cr(CO)_6$. In order to test this second hypothesis, we spiked a solution of $Cr(CO)_6$ with enough 1-

hexene to afford a 1.0 mM solution(1:1 molar ratio of $Cr(CO)_6$:1-hexene). After flashing this solution, it appeared that two reactions were occurring on two different time scales, with the fast decay occurring over a few milliseconds and the slow decay occurring over several seconds. A time-resolved spectrum form the fast decay is displayed in Figure 11. There appears to be two absorbing species in this spectra, one with an absorbance maximum at a little less than 500 nm which is decaying, and one with an absorbance maximum at a wavelength shorter than 370 nm which is growing in. The peak around 500 nm was attributed to $Cr(CO)_5$. The small shift of this peak to shorter wavelengths is attributed to a strong overlap with the other $\lambda_{max} < 370$ nm peak. The peak with a maximum less than 370 nm was attributed to the formation of the $Cr(CO)_5$(alkene) complex. Note that there is a possible isosbestic point at about 430 nm, however it is difficult to be certain of this since the resolution of this experiment is only 10 nm. Hence, it appears that the disappearance of $Cr(CO)_5$ is accompanied by the formation of an alkene complex. The time-resolved spectrum is only followed out to 0.9 seconds in Figure 12, but the spectrum did decay completely within about 10 seconds. It is clear in this spectrum, however, that the 500 nm species has either decayed completely or is hidden in the shoulder of the < 370 nm peak after 0.9 seconds.

The fact that the alkene spiked solution appeared to have two reactions occurring on two different time scales upon flashing(see alkene reactions above), and coupled with the fact that the alkene complex appeared to have

Figure 11

Absorbance vs Wavelength Time Resolved Spectrum of $Cr(CO)_6$ in Heptane Spiked with 1.0 mM 1-hexene (4/18/96)

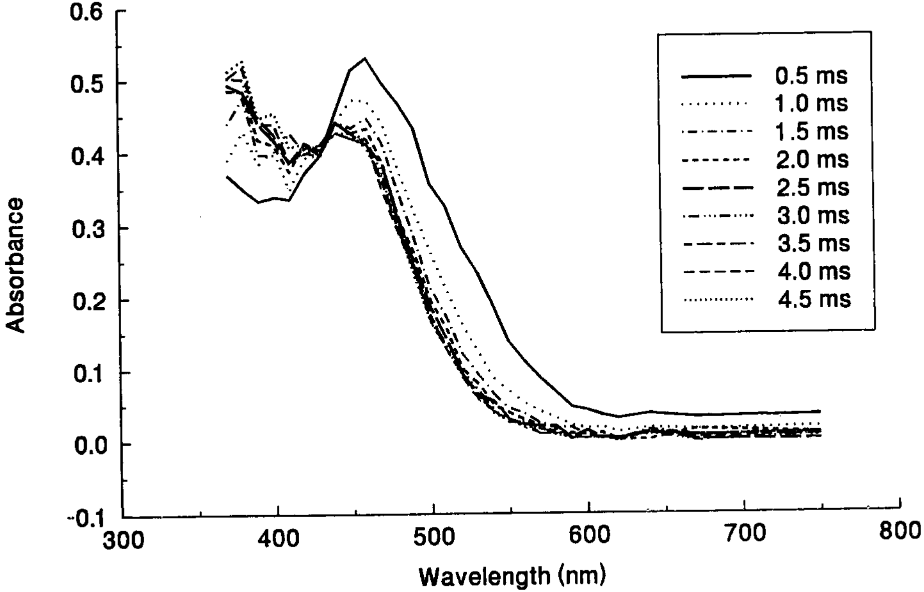
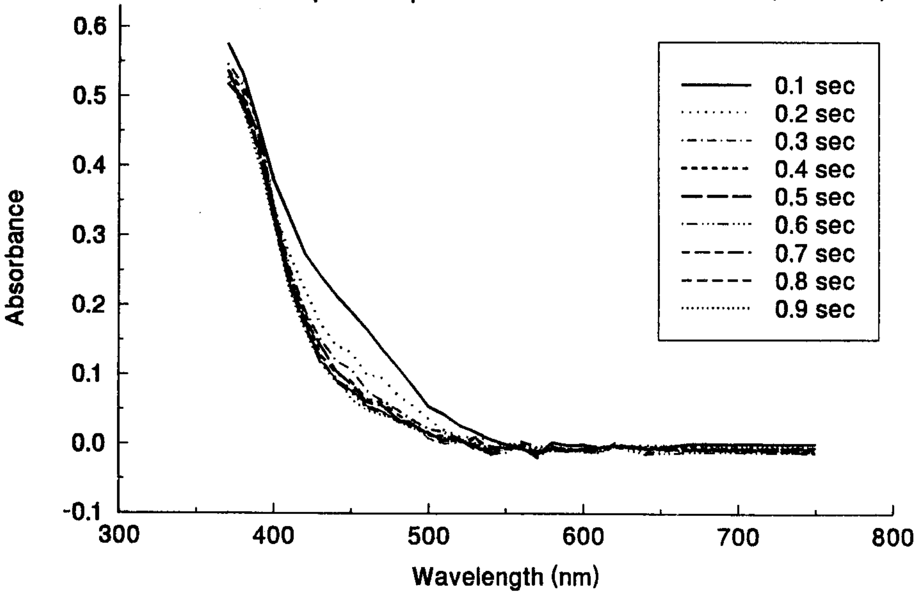


Figure 12

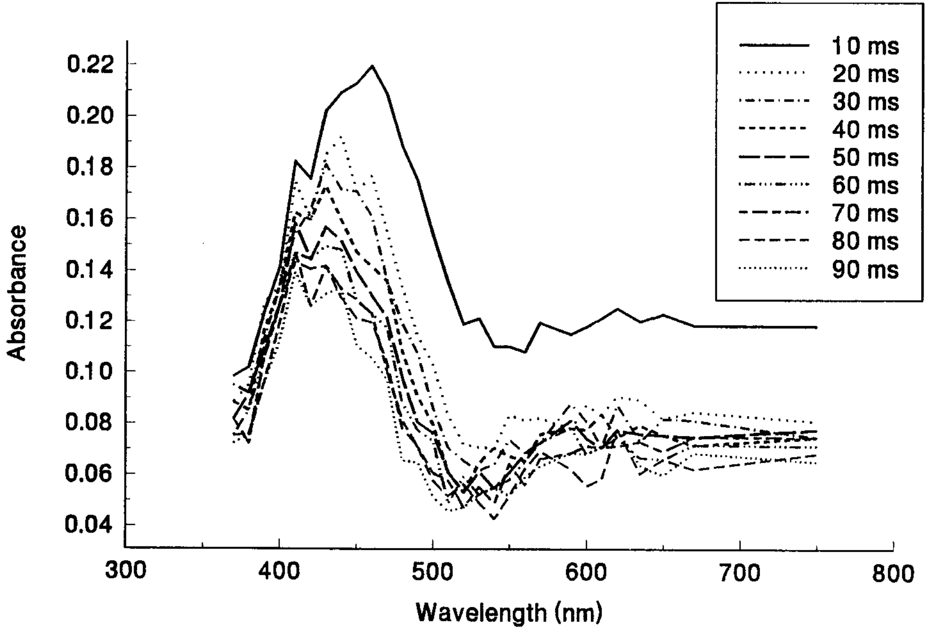
Absorbance vs Wavelength Time Resolved Spectrum of $Cr(CO)_6$ in Heptane Spiked with 1.0 mM 1-hexene (4/18/96)



an absorbance maximum at short wavelengths led us to believe that the impurity could be an alkene. Thus we attempted to perform an experiment effective at removing alkenes, similar to the one used in the $Mn_2(CO)_{10}$ experiment. In this procedure, we added 30 mL of concentrated H_2SO_4 and 300 mL of heptane to a 500 mL round bottom flask containing a magnetic stirring bar and then stirred for 7 days in order to sulfonate any alkenes present. The heptane phase was separated with a separatory funnel and then washed three times with 100 mL of water. Then 100 mL of saturated $NaHCO_3$ was added and the solution was stirred for 2 days in order to neutralize any excess H_2SO_4. After the heptane phase was separated, it was washed three more times with 100 mL of water. Then three tablespoons of $MgSO_4$ was added and the solution was shaken for several minutes in order to pre-dry the solvent, after which it was refluxed over CaH_2 for 2 days. The rest of the experiment proceeded as described in the Experimental. The time-resolved spectrum constructed from the data obtained in this experiment is displayed in Figure 13. Note that it appears very similar to Figure 8 in that a peak at about 480 nm decays on a millisecond timescale to a peak with an absorbance maximum at about 430 nm, and there is still an unexplained 'flat peak' at longer wavelengths. It would appear that either the procedure was not effective at removing alkenes, or alkenes were never present in solution at high enough concentrations to be the cause of the impurity complex observed at about 430-450 nm.

Figure 1 3

Absorbance vs Wavelength Time Resolved Spectrum of $Cr(CO)_6$ in Heptane with H_2SO_4 Treatment (4/25/96)



Discussion

When observing the kinetics of our system in heptane, we see two different decays which occur on two different timescales. There is a fast decay which initially has an absorbance maximum at 500 nm and then, as it decays over the course of about 20 ms, the maximum absorbance shifts to 450 nm. The peak at 500 nm presumably is due to $Cr(CO)_5$, formed by direct photodissociation of $Cr(CO)_6$. The absorbance at 450 nm is our impurity complex, which decays over about 10 seconds, accompanied by a further peak shift to about 430 nm. The reaction has proven to be totally reversible with no noticeable photoproduct buildup even after more than 60 successive flashes.

The impurity complex peak at 430-450 nm would seem to imply that the impurity was water, since previous studies described in the literature have discovered a $Cr(CO)_5(H_2O)$ peak at 450 nm, however, this does not seem to be the case in our system, as spiking our solution with water resulted in a single absorption maximum at 480 nm. In addition, a time resolved spectrum obtained after a solution had been prepared with added water resulted in a spectrum with an absorbance maximum at 480 nm without any of the 'flat peak' at long wavelengths which seems to be a unique characteristic of our impurity. This led us to seek another explanation for the impurity.

It is unlikely that the impurity complex is due to the presence of alkenes in our solvent. While spiking our solution with an alkene appeared to give results which were somewhat similar to our impurity, namely two different decays at two different timescales and a short wavelength absorbance maximum for the alkene complex, further experiments also seem to have disproved the presence of alkenes in our solvent. Thorough treatment of our solvent by a process which should remove alkenes showed no direct evidence that anything had drastically changed in our system. Thus, at this time the identity of our impurity complex is still unknown.

Regardless of the identity of our impurity complex, some of the results from the experiment involving the addition of alkene suggest that it will still be possible to study the reaction of $Cr(CO)_6$ with added alkenes and hydrosilanes. The apparent isosbestic point at 430 nm seems to imply that we can observe the direct formation of the $Cr(CO)_5$(alkene) complex from $Cr(CO)_5$. Since the $Cr(CO)_6$ and alkene were present in a 1:1 molar ratio, it would appear that we should be able to make the reaction with alkenes pseudo first order, and so future work would involve performing successive runs with increasing concentrations of alkene in order to better study the reaction kinetics of $Cr(CO)_5$ + alkene. Along the same line, another set of future experiments which we would like to perform would involve spiking the system with different alkenes in order to observe where the various alkene complexes have their maximum absorbances, and to study the decomposition kinetics of these complexes.

The procedure which we performed is not the only method for removing alkenes from an alkane solvent, thus it is not entirely certain that there are no alkenes present in our heptane. We would like to attempt one more purification procedure reported in the literature which involves pre-drying with $CaCl_2$. instead of $MgSO_4$ and then passing the heptane over activated silica gel prior to refluxing it over CaH_2.[14]

Another experiment which could prove interesting also would involve driving our reactions toward pseudo first order kinetics. We would like to make the recombination of $Cr(CO)_5$ pseudo first order with respect to added gases. Such an experiment would involve proving that it is possible to drive the reaction pseudo first order in the presence of added CO in preparation for looking at the reactions of $Cr(CO)_5$ with other added gases such as ethylene and propene.

It is obvious from the literature and our experiments that UV/Vis detection does not always allow good spectral resolution, so it might be profitable to conduct experiments on the new UV/Vis pulsed laser system with IR detection in the new physics spectroscopy lab. By switching to IR detection it would be possible to obtain much better spectral resolution in our solutions. In addition, the shorter pulse width of a laser flash photolysis source will allow the investigation of faster reactions involving transition metal fragments.

Even though chromium carbonyl systems have been studied for over three decades, the mechanisms of $Cr(CO)_6$ catalyzed reactions still remains somewhat of a mystery. This is not surprising when one realizes that not even all of the intermediate steps in the photochemical catalysis are understood. This study is proof to this, as we have found it difficult as of yet to study the reaction of $Cr(CO)_5$ with simple alkenes and hydrosilanes due to side reactions with an impurity. As is the case with any interesting puzzle, however, investigation into the $Cr(CO)_6$ system has led to more intriguing questions that merit deeper study, which future researchers can investigate.

Appendix A: Computerized Data Analysis

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

   - Enter the 94REM directory and run the program 94G when the trace to saved is on screen.
   - Press 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, but the .BIN is standard procedure.
   - Press E to exit the program. This should 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. The format MUST appear as shown here.

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

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

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

   - In the directory C: \FORTRAN\SOURCE\SAMPLES>, run the program 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. 0.050 V
     e. FILENAME.ABS
   - Again, the filenames should agree aside from the extensions.

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

   - From the C:\AXUM> directory, type AXUM to run the program.
   - From the MAIN menu enter the DATA menu.
   - From the DATA menu enter the FILE menu.
   - Run Import.
   - On the Import screen enter only the input file name

c:\fortran\source\samples\ FILENAME.ABS

- From the FILE menu, run Save.
- Return to the DATA menu by hitting ESC.
- Position the cursor over each column with the mouse and type a column name(Time, Percent T, Absorb)

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

- Return to the MAIN menu by hitting ESC
- Enter the graphing menu by hitting GRAPH
- Choose CREATE
- Under graph specifications make the following entries. Move from one entry to the next by hitting ENTER:

Graph Name:	FILENAME	
Plot Type:	scatter	
Data Sheet:	FILENAME	(this is the input file to be graphed)
Columns X:	TIME	
Columns Y:	Absorb	

- Type F10 or use the mouse to click on OK to leave the form and have it accepted.
- You should automatically return to the Modify menu. Choose VIEW.
- You should see a graph of your data. Before plotting it, however, you need to add a title and improve the axis labels. Begin this by hitting ESC.
- You should be in the Modify menu. Hit ESC again to get into the GRAPH menu.
- Choose Edit Screen.
- Choose Titles then Add.
- Choose Y Axis and type in Absorbance in the box provided at the bottom of the screen. Hit F10 or ENTER twice.
- Choose Main and type in a 1-line title. Hit F10 or ENTER twice.
- If you wish a second line to your title, type in SUB. Enter your subtitle and hit F10 or ENTER twice.
- The mouse can be used to drag the titles and x- and y-axis labels to any position you want.
- Hit ESC twice to return to the GRAPH menu.
- Choose File, then Save, then Graph. Then, in response to the prompt, enter a name or, if you wish to use the default name(recommended), click on OK to save the graph.
- Return to the GRAPH menu, select PRINT, and, in response to the prompt, click on OK to plot a copy of your absorbance vs. time data.

6. Using Axum for Data Analysis: Calculating Ln (Abs) and 1/Abs vs. time

- Enter the DATA menu and, if the data sheet is not already loaded, select FILE, then LOAD, enter the file name, and hit ENTER.
- Scan the data using the up and down arrow cursors looking for the row just after the firing of the flashlamps. This should be near the beginning of the decay portion of the absorbance vs. time curve. Note the row number. Continue scanning downward until you come to where the absorbance approaches zero(Abs = 0.02 will do). Note a row number in this region of the data sheet. You will use these starting and ending row numbers along with the time and absorbance column numbers to delineate a section of the datasheet which will be transferred to a new empty sheet.
- Select BLOCK, then COPY
- In the copy block form enter the appropriate column and row numbers that you wish to copy. For example, to copy columns 1 and 3 only from row 25 to row 150 type the following(use ENTER to advance from one entry to the next):

From:

Column(s): 1,3
Row(s): 25..150
Data Sheet: FILENAME

To:

Start Column: 1
Start Row: 1
Data Sheet: NEWFILE

Overwrite: YES

- Click on OK to carry out the copy.
- You should still be in the DATA menu after copying. Select DATASHEET, then CURRENT, and finally the new datasheet in order to display it.
- Type column labels over columns 3(Ln Abs) and 4(Inv Abs).
- From the DATA menu select TRANSFORM.
- In the transformation window type:

```
\3 = Ln(\2);
```

This means: "Calculate the natural logarithm of each entry in column #2 and place the result in the same row of column #3. Hit F10 to implement the calculation.

- Type TRANSFORM again, then enter:

\4 = 1/(\2);

This means: "Calculate the inverse of each entry in column #2 and place the result in the same row of column #4. Hit F10 to do the calculation.

- Select FILE, then SAVE, and save under the same name as you are currently using.

7. Graphing Ln (Absorbance) and 1/(Absorbance) vs. time.

- Follow the directions in Section #5.

8. Fitting a straight line to a set of plotted data.

- Assume the plot of Ln (Abs) vs. Time looks linear and we wish to do a linear regression fit to the data and obtain the equation of the fitted straight line.
- Go to the GRAPH menu, then select CREATE
- On the Graph Specifications sheet type:

Graph Name:	anything you want but not more than 8 alphanumeric characters
Axes Type:	XY
Plot type:	Curve Fitting (Select Linear)
Data Sheet:	The data sheet containing the numbers which you are plotting.

Columns:

X: Column number in the data sheet containing the x data.

Y: Column number in the data sheet containing the y data.

Example:

Graph name: 101095a
Axes type: XY

Plot #	Plot type	Data sheet	X	Y
line 1	Scatter	101095a	4	6
line 2	CF-linear	101095a	4	6

-Click on OK to do the plot. Go to Modify. Select Curve Fitting.
-Change symbol frequency to 0

-Change line width to 9
-Then type ESC to return to the GRAPH menu.
- Select EDIT SCREEN
- To display the equation of the straight line, select the following:

    COMMENTS
    ADD
    Hit the Insert key on the keyboard.
    F10

- Use the mouse to drag the equation to the location you wish it to be at.
- Use the directions presented in Section #5 to edit the axis labels and add a title, if you wish.
- The graph may be plotted in the usual way.

9. Organizing Time Resolved Data

-Since you will be importing a number of files, their import into Axum will be speeded up if you copy the files in DOS from the voltages directory to the Axum data directory:

```
copy c:\fortran\source\samples\filename.abs c:\axum\data
```

-Note that you can enter generic filenames so that filenames with common characters can all be copied with the same command, so for the 5th of May, 1996, all 10 runs (A-J) could be copied by (see the DOS manual for more details):

```
copy c:\fortran\source\samples\050596*.abs c:\axum\data
```

- From the MAIN menu enter the DATA menu.
- From the DATA menu enter the FILE menu.
- Run Import.
- On the Import screen enter only the input file name

```
filename.abs
```

-Press F10 to select this file
-On the data screen type in the column headings for only Time and Absorbance
-Enter the FILE menu
-Select SAVE and enter the runname (date plus run letter)
-Repeat this import procedure until all of the runs are loaded

> NOTE: Do not load more than 30 files at a time as AXUM may crash; therefore it is suggested that you import 10 at a time then

perform the next several steps before importing more.

-Enter the DATASHEET menu
-Select CREATE and name the new datasheet:

filename1(without the run letter)

-Enter the BLOCK menu
-Select COPY and fill in the following information:

From:

Column(s):	1,3
Row(s):	1...number of datapoints you converted
Data Sheet:	FILENAME(with run letter starting with A)

To:

Start Column:	1
Start Row:	variable*
Data Sheet:	FILENAME(without run letter)
Overwrite:	NO

*as you add more columns as you progress, you will need to change this to the next clear column, therefore check before you get to this step.

-As you transfer each run, label the time column 'Time' and the absorbance column:

A_(wavelength of run in nm)

-When all of the runs are transferred to the new data sheet, check each column pair against the others to be sure that the flash went off at the same time for each run.
-After this is done, choose COLUMN then DELETE and successively delete each TIME column except the first one.
-Enter the file menu and save this as:

DATENAME1(FILENAME minus run letter)

-Create a new datasheet as above and name it DATENAME2
-Label the first column WAVELENGTH and each sucessive colmun by the time you will be monitoring after the flash, so if you are monitoring every 20ms:

t_20ms	t_40ms	etc.....
Column 2	Column 3	

-Select ROW from the DATA menu
-Choose TRANSPOSE and enter the following information:

From:
    Row(s): (the row for each correct time after the flash)
    Datasheet: DATENAME1
To:
    Column(s): 2,3,4,...,10
    Datasheet: DATENAME2

-In DATANAME2 enter the ROW menu
-Choose DELETE and enter row 1(this contains times and not absorbance values)
-Save this datasheet as DATENAME2

10. Constructing a Time Resolved Plot

-From the Main menu enter the GRAPH menu
-Select CREATE and enter the following information:

Graph name: DATENAME2
Axes type: XY

Plot #	Plot type	Data sheet	X	Y
line 1	Scatter	DATENAME2	1	2
line 2	Scatter	DATENAME2	1	3
.				
.				
line 9	Scatter	DATENAME2	1	10

-Press F10 and enter the MODIFY menu.

*NOTE: It is imperative that you save after each step for the rest of the procedure as the program has a habit of crashing!!!

-Select PLOT ATTRIBUTES and for each set of data enter

symbol frequency: 0
line width: 9
line color(going down from line 1 to line 9):
black
green
magenta
blue

dark grey
red
green
cyan
light magenta

-Press F10 and then enter the FONTS/SPACING menu
-Select CHOOSE FONTS
-For FONT 1hit the INSERT key and then move the cursor to SWISS and press F10
-Select TYPE SPACING and enter:

Auto thicken all text?: YES

-Press F10 and return to the MODIFY menu
-Enter PAGE LAYOUT and enter:

Max Display Area: NO(under display colummn)

-Press F10 and return to MODIFY menu
-Enter AXES menu and then the RANGES/TICKS menu and enter:

Ticks:	Major	Minor
Line Width:	5	5

-Press F10 and return to the MODIFY menu
-Enter the TEXT/SYMBOLS menu and then the LEGEND menu and enter:

Draw Legend: YES
Auto Update: YES

-Press F10 to leave the LEGEND menu then reenter it again (this is an odd quirk in the program)
-Enter names for each set of plotted data(it automatically assigns the column names, but the column names can not start with a number, so here you can enter 20ms instead of t_20ms)
-Press F10 and return to the MODIFY menu
-Select EDIT SCREEN
-Modify the titles and axes as described above. The Axes should be labelled:

Y Axis: Absorbance
X Axis: Wavelegnth (nm)

-Print the document as described above

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