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KINETICS AND MECHANISM OF CHROMIUM HEXACARBONYL PHOTOCHEMISTRY USING FLASH PHOTOLYSIS

By

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ABSTRACT

ZAYDMAN, MARINA Kinetics and Mechanism of Chromium Hexacarbonyl, $Cr(CO)_6$, Photochemistry Using Flash Photolysis. Department of Chemistry, June 1997

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 99% yield. Although much research has been done on the reactions which $Cr(CO)_6$ catalyzes, not much data exists on the reactions of photochemically created fragments of $Cr(CO)_6$, such as $Cr(CO)_5$. This study focuses on the reactivity of organotransition metal intermediates with the goal of contributing to the growing database of the reactions involving the photochemistry of $Cr(CO)_6$. Particular emphasis will be given to the kinetics and mechanism of these reactions.

Experiments with $Cr(CO)_6$ require the use of an extremely pure solvents. Since it has been found that metal carbonyls are very sensitive to such impurities as water and oxygen, solvents must be dried and degassed. This is done by refluxing the solvent over CaH_2 for 12 hours under flowing purified argon, followed by a second distillation in a fractionating column. Argon is purified by passing through one 13x molecular sieves column and one O_2 scavenging column to remove water, oxygen and organic impurities. The chromium hexacarbonyl solution was degassed by six freeze-pump-thaw cycles.

Chromium hexacarbonyl solutions have been flashed and the subsequent thermal reaction was found to follow second order kinetics.

$$Cr(CO)_5 + CO \Rightarrow Cr(CO)_6 .$$

The solution was then saturated with CO and the reaction kinetics changed to pseudo-first order. Plots of k_{obs} vs. [CO] are linear with the slope equal to the second-order rate constant. The value of this constant was found to be $1.7 \times 10^6 \ M^{-1} s^{-1}$, which is two times smaller than the literature value of $3.6 \times 10^6 \ M^{-1} s^{-1}$.

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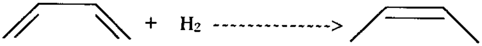
Introduction

The photochemistry of organometallic complexes is an area of vigorous research because these substances have been shown to be effective photochemical catalysts. Researchers have been very interested in this type of catalysis because using UV light to initiate reactions involves much milder conditions, with corresponding greater control over product specificity, than when done thermally. Chromium hexacarbonyl, $Cr(CO)_6$, is one example of a photochemical catalyst which has been extensively studied. It has been shown to be very effective in catalyzing the 1,4-hydrogenation and 1,4-hydrosilation of conjugated 1,3-dienes resulting in the stereoselective formation of a cis alkene product in greater than 99% yield. Although much research has been done on the reactions which $Cr(CO)_6$ catalyzes, not much data exists on the reactions of photochemically created fragments of $Cr(CO)_6$, which is important for an understanding of the detailed mechanism of photocatalysis. Thus, it is the goal of this study to focus on the reactivity of organotransition metal intermediates with the intention of contributing to the growing database of reactions involving the photochemistry of $Cr(CO)_6$ and other transition metal carbonyl complexes. Particular emphasis will be placed on the kinetics and mechanism of these reactions.

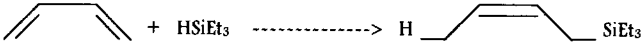
$Cr(CO)_6$ Literature Review

The photochemistry of chromium carbonyls has been studied extensively due to the wide variety of catalysts that can be generated by the photolysis of these species. While early studies did not focus on the detailed mechanism of the catalytic process, they gave an overview of the system and laid the foundation for future work. Wrighton was one of the first researchers to publish investigations of the photocatalysis of $Cr(CO)_6$. During his studies, he made several interesting discoveries. For example, he found that 1,3-dienes were hydrogenated to their corresponding alkenes in the presence of UV light, $Cr(CO)_6$, and $H_{2(g)}$ via 1,4-hydrogenation.[1] Wrighton also reported that the alkene product almost exclusively adopts a cis conformation. This appears to be the case both when the starting solution contained a mixture of diene stereoisomers and when only one stereoisomer was present.



The observed catalytic reaction was attributed to the formation of the thermally active catalyst via photolysis of the precursor, $Cr(CO)_6$. Using UV light to initiate reactions involves much milder conditions than when done thermally. For example, catalysis, by $Fe(CO)_5$, of the hydrogenation of olefins in the absence of UV radiation, requires both elevated temperatures and high H_2 pressures to promote the reaction.

After Wrighton determined that 1,4-hydrogenation of 1,3-dienes takes place in the presence of $Cr(CO)_6$, it seemed reasonable that $Cr(CO)_6$ might also catalyze reactions similar to hydrogenation, such as 1,4-hydrosilation of 1,3-dienes. He indeed found that this was the case. $Cr(CO)_6$ acts as a photocatalyst for the 1,4-hydrosilation of 1,3-dienes with greater than ninety percent of the products adopting the cis conformation.[2]



Wrighton's experiments revealed several important facts, one being that it was not necessary to continuously photolyze the $Cr(CO)_6$-1,3-diene-silane mixture to ensure product formation. This evidence supported the hypothesis that the reaction was catalytic with respect to photons, where the role of the light is to generate a thermally active catalyst but was not necessary to maintain the reaction. He did, however, see some results which suggested that continuous photolysis increased the rate of the reaction.[2] The second, and perhaps more important result is that hydrosilation of 1,3-dienes which have a methyl substituent at the 1 or 4 position, does not proceed readily. Wrighton attributed this effect to the steric restrictions created by the methyl groups and, thus, suggested that the catalyst was sterically sensitive.[2] This prompted researchers to study the nature of the catalyst and its precursor in order to gain a better understanding of how it interacts with other species.

Kelly and Koerner von Gustorf were the first researchers to do a flash photolysis study on $Cr(CO)_6$. After the solution was flash photolyzed, they observed the formation of a species within 50 ns with a maximum absorbance at 503 nm.[3] This species decayed over a period of greater than 200 μs and reacted further to form a species with an absorbance maximum at 445 nm and a decay time of under a second. After the solution was saturated with CO, the reaction was induced to follow pseudo first order kinetics and $Cr(CO)_6$ was reformed within 50 μs. The second order rate constant was found to be $3 \pm 1 \times 10^{6}\ M^{-1}\ s^{-1}$. The following mechanism was proposed:

$$Cr(CO)_6 \xrightarrow{h\nu} Cr(CO)_5 + CO$$

$$Cr(CO)_5 + CO \xrightarrow{\qquad} Cr(CO)_6$$
$$k = 3 \pm 1 \times 10^{6}\ M^{-1}\ s^{-1}$$

$$Cr(CO)_5 + X \xrightarrow{\qquad} Cr(CO)_5X\ (\lambda_{max} = 445\ nm)$$

After the solution is flashed, and the $Cr(CO)_5$ intermediate is created, it recombines either with CO to reform $Cr(CO)_6$, or with some impurity to form $Cr(CO)_5X$. It was found that X was neither solvent nor another chromium carbonyl fragment. Rather it was believed that X was an impurity present in the solvent.[3] Kelly and Koerner von Gustorf also noted that when the solution was degassed using a freeze-pump-thaw method, the absorbance maximum for the impurity complex shifted from 445 nm to 470-480 nm. No explanation, however, was given for this effect.

Up until now, all of the studies on the $Cr(CO)_6$ system have been done in hydrocarbon solvents. It has been found, however, that the reactivity of the $Cr(CO)_5$ intermediate with other species is significantly suppressed in hydrocarbon solvents since the solvent molecules hinder the reaction by either binding to the metal and thus blocking the reaction surface, or by absorbing the energy of the intermediate and thus increasing its stability. It would be interesting, therefore, to study reactions with $Cr(CO)_5$ in less interfering solvents or in the gas phase. Since it was suggested in previous studies that $Cr(CO)_5$ interacts more weakly with perfluorocarbon solvents, Kelly and Bonneau studied the flash photolysis of $Cr(CO)_6$ system in perfluoromethylcyclohexane (C_7F_{14}). They observed the formation of a transient species with a maximum absorbance at 620 nm. This peak was attributed to $Cr(CO)_5$ and the wavelength was found to be close to that (624 nm) reported for $Cr(CO)_5$ in neon matrices, where $Cr(CO)_5$ is presumably "naked".[4] By introducing CO to the solution, Kelly and Bonneau were able to determine that $Cr(CO)_5$ reacted with CO three orders of magnitude faster in perfluorocarbon solvent than in cyclohexane.[4] They also observed the formation of another species at ~485 nm with the disappearance of the $Cr(CO)_5$. Kelly and Bonneau, however, were also unable to shed light on the identity of this impurity complex.

The identity of the impurity complex was addressed by Church and Grevels who studied interactions of $Cr(CO)_5$ with hydrocarbon solvents. After excitation of $Cr(CO)_6$ in cyclohexane solvent, they observed the formation of the

$Cr(CO)_5$•solvent complex within 25 ps. Church and Grevels found that $Cr(CO)_5$•solvent complex reacted thirteen times faster with added water than with CO. The $Cr(CO)_5$•H_2O complex had an absorbance maximum at 455 nm.[5] The λ_{max} for the water complex was found to be close to the λ_{max} of the unidentified impurity complex found in previous studies. Therefore, $Cr(CO)_5$•H_2O was proposed as the impurity complex, $Cr(CO)_5X$. It was also found that water can be removed from the system by performing three freeze-pump-thaw cycles on the liquid solution.

Several studies, it addition to those of Kelly and Bonneau, have shown that the reactivity of the $Cr(CO)_5$ intermediate increases substantially in weakly coordinating solvents. Tumas, Gitlin, Rosan and Yardley provided the first evidence that the gas-phase photochemistry of $Cr(CO)_6$ is different from that in solution. Upon KrF laser photolysis they observed the formation of several peaks which they identified as $Cr(CO)_x$ fragments with x=5,4,3,2.[6] Moreover, they found that irradiation of $Cr(CO)_6$-1-butene mixtures in the gas phase resulted in the isomerization of 1-butene to 2-butene with much higher efficiency than was achieved in the solution phase. Tumas's group attributed this to the significant difference in the photofragmentation pattern in the gas phase. They believed that the active species involved in isomerization were either $Cr(CO)_3$ or $Cr(CO)_2$ fragments, rather than $Cr(CO)_5$.

Stephen Church and Eric Weitz further studied the reactivity of the primary products of the photolysis of $Cr(CO)_6$ in the gas phase.[7] After laser photolysis, they observed displacement of multiple CO's. This was attributed to the fact that in the gas phase $Cr(CO)_5$ does not lose energy in the collision with surrounding solvent molecules, and thus the extra energy is used for further CO displacement. This creates $Cr(CO)_x$ fragments, where x=5,4,3,2, which are then free to recombine with CO or other chromium carbonyl fragments. Church and Weitz were able to identify peaks corresponding to the reaction of $Cr(CO)_6$ with $Cr(CO)_5$ and $Cr(CO)_4$ to produce $Cr_2(CO)_{11}$ and $Cr_2(CO)_{10}$, respectively, and thus showing that chromium carbonyl fragments can react not only with other species, but with each other as well.[7]

Initially, researchers focused mostly on the nature of the products formed during photolysis of $Cr(CO)_6$. As more studies were conducted on this system, interest shifted to the reactivity of the products with other molecules. For example, it has been shown that $Cr(CO)_6$ can act as a catalyst precursor, providing the surface on which the reactants are able to interact more efficiently. The question was raised regarding how would $Cr(CO)_x$ coordinate with other species. For example, if $Cr(CO)_x$ were to catalyze hydrogenation of 1,3-dienes, how would hydrogen bind to the metal -- via hydride or as molecular hydrogen. Church and Grevels were one of the first researchers to present evidence for the formation of the binary molecular hydrogen complex at room temperature and normal pressure.[8] Previous studies by the same group had shown that a stable dinitrogen complex, $Cr(CO)_5N_2$, forms at room temperature with maximum absorbance at 370 nm.[9] It is worth noting that both the hydrogen and the nitrogen complexes have the same maximum absorbance --

370 nm, and so are virtually indistinguishable with UV/Vis detection. $Cr(CO)_5H_2$ and $Cr(CO)_5N_2$, however, can be distinguished using infrared spectroscopy. The $Cr(CO)_5N_2$ complex was definitively identified by observation of the N-N stretching frequency.[9] This method of identification was not possible for the hydrogen complex because the study was restricted to the CO stretching region of the IR spectrum. However, it was found that the rate constants for the nitrogen and hydrogen reactions were very similar with both species decaying within 200 ms. Thus, it is reasonable to conclude that hydrogen and nitrogen coordinate to the metal as diatomic species.

Understanding how hydrosilanes coordinate to the metal during 1,4-hydrosilation reactions is another interesting and useful piece of the puzzle. Silanes with many different substituents on Si, such as phenyl groups, different types of hydrocarbons, or electron withdrawing groups, will all bind to chromium in $Cr(CO)_x$, $x \leq 5$. Depending on the type of ligand attached, different types of bonding to the metal can be achieved. Zhang, Dobson and Brown studied the nature of the metal silane bond by varying substituents on the silane from methyl, ethyl, and phenyl groups, to halogens and perfluoronated hydrocarbons.[10] They found that depending on the nature of the ligand, hydrosilane coordinated to the metal either by a three-center, two-electron bond, where the two H-Si σ electrons are shared among the hydrogen, silane and the metal center, or by an oxidative addition, where the H-Si bond is broken and hydrogen and silane attach to the metal separately. Hydrosilanes containing a hydrocarbon substituent on Si, such as methyl or ethyl, were found to coordinate to the metal via three-center, two-electron bonds since there is little competition for the H-Si σ-electrons from the electron rich hydrocarbon substituents. This, however, was not the case with hydrosilanes containing an electron withdrawing group such as chlorine or fluorine. These groups competed for the electrons in the H-Si bond and led to the oxidative addition of hydrosilanes. Zhang, Dobson, and Brown discovered that when substituents on hydrosilanes become more electron-withdrawing, the stability of H-Si complexes decreased. This was attributed to the importance of σ donation to the metal while bonding to the more electrophilic Cr metal center.[10] Another interesting fact observed was that chlorinated hydrosilanes coordinated to the metal through either the H-Si, three-center, 2-electron bond, or Cl-Si bonds. It is not clear for the latter bonding whether the interaction with Cr occurs by means of oxidative addition or through a lone pair of electrons on the chlorine atom.

The fact that alkene and diene complexes of transition metals play an important role in many catalytic and photocatalytic reactions, such as hydrogenation and hydrosilation of 1,3-dienes, has been known for some time. However, the detailed mechanism of how these ligands coordinate to the metal has not been well studied. Before looking at the binding of dienes, it makes sense to examine the binding of the transition metal complex to simple alkenes. Turner's group studied the formation of three previously unknown ethene complexes generated by the photolysis of $Cr(CO)_6$ in liquid Xe doped with C_2H_4

at -78 °C.[11] After the photolysis, they noted that $Cr(CO)_6$ lost one or two CO, affording either $Cr(CO)_5(C_2H_4)$ or cis- and trans- $Cr(CO)_4(C_2H_4)_2$ complexes. While it was discovered that all of the generated complexes were unstable under the experimental conditions, the monosubstituted species proved to be most stable while the cis-isomer of the disubstituted species was found to be the least stable. Turner's group rationalized the greater thermal stability of the trans-isomer relative to the cis-isomer in terms of "d orbital sharing".[11] A CO group is known to have two π^* acceptor orbitals while C_2H_4 has only one. This will lead to competition for the π-bonding d electrons between the ethylene and CO group trans to it which will result in weakening of the M-alkene bond. No competition, however, is present if the two ethylene groups are trans to one another, explaining the greater stability of the trans-isomer. The above argument contradicts the fact that the monoethylene complex has higher stability than the trans-diethylene complex; no explanation for this behavior was provided. If a diene was to coordinate to the metal, then it would seem that a trans arrangement of the double bonds would not be favored since the trans-1,3-diene might not be large enough to occupy trans positions in a complex with octahedral geometry. The decreased stability of the cis conformation could, perhaps, help the diene leave once it has been converted to an alkene. Furthermore, since the above study looked at coordination of two separate double bonds, bonding of conjugated systems to the metal might be different.

The binding of both conjugated and non-conjugated dienes was addressed in recent studies by Weitz and Gravelle.[12] They used time-resolved infrared spectroscopy to look at the reactions of 1,3- and 1,4-pentadiene with the coordinatively unsaturated $Cr(CO)_4$. Several reaction mechanisms for the diene coordination to the metal were proposed. The addition of both 1,3- and 1,4-pentadiene results in the formation of highly vibrationally excited complexes which then relax as a result of collisions.[12] The highlight of this work was in determining that the conjugated system of 1,3-pentadiene was able to coordinate to the metal as a bidentate ligand, forming a much more stable $Cr(CO)_4$(1,3-pentadiene complex), while the non-conjugated 1,4-pentadiene appeared to form only a weakly coordinated complex with $Cr(CO)_4$. One could explain this by speculating that the conjugated diene was able to orient itself in order to bind more strongly to the metal, while the non-conjugated pentadiene failed in achieving the favored orientation.

As reported earlier by Church and Grevels, chromium pentacarbonyl, $Cr(CO)_5$, binds rapidly to hydrocarbon solvents. This prompted researchers to look into reactions of $Cr(CO)_5$ with various alcohols solvents. Simon and Xie used time-resolved picosecond absorption spectroscopy to examine the dynamics of $Cr(CO)_5S$ complex formation, where S is methanol.[13] After photolysis of $Cr(CO)_6$ in room temperature methanol, they observed a band with an absorption maximum at 460 nm. The kinetic analysis showed a rapid formation of the transient, $Cr(CO)_5(MeOH)$, with a rise time of 2.5 ps, and then a constant signal for up to 150 ps. The rise time was attributed to the solvent reorganization needed for the formation of the Cr-S bond.

In their later studies, Simon and Xie looked at a series of long-chain alcohol solutions in an attempt to remove the ambiguity of how solvents coordinated to the metal. Performing photolysis in long-chain alcohol solutions revealed that solvent coordinated to the $Cr(CO)_5$ transient either by means of an alkane ($Cr(CO)_5(ROH)$ or a hydroxyl group ($Cr(CO)_5(HOR)$.[14] Simon and Xie discovered that with increasing delay time, initially formed alkane complexes rearranged to the more stable hydroxide species. Several rearrangement mechanisms were proposed: solvent exchange by a dissociative mechanism where the dissociation of the solvent molecule was followed by coordination of the hydroxyl group of the same or different solvent molecule; an associative substitution reaction, and unimolecular migration between different solvent binding sites. Experiments revealed that the solvent rearrangement occurs according to the unimolecular solvent migration model where migration between adjacent methylene groups continues until the metal coordinates to a hydroxyl group, after which no further migration occurs. The hydroxyl group, in a sense, acts as a trap.

Erin O'Driscoll and John Simon further studied solvation reactions with unsaturated chromium pentacarbonyl. In addition to looking at alcohol solvents, they looked at the reactions with alkyl bromide and alkanenitrile solvents.[15] Analysis of the reaction dynamics in alcohols and alkyl bromides revealed identical rate constants ~1 x 10^{10} s^{-1}. This suggested that both alcohols and alkyl bromides had similar rearrangement dynamics in that they migrated from $Cr(CO)_5(RX)$ to $Cr(CO)_5(XR)$ according to a unimolecular solvent migration model. This result demonstrated an important fact that restructuring in alcohol solvents does not involve breaking of intermolecular hydrogen bonds. Very different results were obtained in nitrile solvents. Driscoll and Simon found that the reaction dynamics of the formation of the cyano complex from the alkane complex was significantly faster in comparison with alcohol and alkyl bromide solvents. Using the unimolecular migration model, the difference in reaction dynamics was explained by proposing that the initial metal-solvent coordination occurred to carbons that are near the cyano end of the solvent molecule. In conclusion, while there is no preference in initial solvent-metal coordination in alcohol and alkyl bromide solvents, $Cr(CO)_5$ will be preferentially solvated by the more polar end of the solvent molecule such as a nitrile.

For a number of years researchers have been studying the solvation of the chromium pentacarbonyl transient; however, the detailed mechanism of solvent displacement has been studied less thoroughly. Zhang et al. were one of the first researchers to report kinetic studies of Lewis base, (L = 1-hexene, piperidine, and pyridine), displacement of benzene from photogenerated $Cr(CO)_5(C_6H_6)$ to afford $Cr(CO)_5L$ products.[16] After flash photolysis of $Cr(CO)_6$/benzene/L solutions, a peak was formed at ~ 470 nm and, based on previous studies, was assigned to $Cr(CO)_5(C_6H_6)$. This peak decayed within 134.5 μs. It was noticed, however, that with disappearance of the benzene transient, another species was formed with λ_{max} at 410 nm, when L was piperidine, and 344 nm when L was 1-hexene.[16] It is important to note that the time resolved spectra for both solvents exhibited isosbestic points, indicating the conversion of the benzene transient to a single product. The kinetic studies of the reactions revealed that displacement of benzene from $Cr(CO)_5(C_6H_6)$ in 1-hexene, piperidine and pyridine took place by means of the reversible formation of the $Cr(CO)_5$ intermediate via a transition state. While it was found that in the $Cr(CO)_5(C_6H_6)$ complex benzene coordinates to Cr via an isolated double bond, in the transition state of the reaction of $Cr(CO)_5(C_6H_6)$ with L, agostic C-H-Cr bonding, which involves 3-center, 2-electron interaction, or formation of the σ-complex in which C-H σ-bond, from C_6H_6, interacts with the metal, takes place.[16]

This chapter has given an overview of the research that has been done on the chromium hexacarbonyl system. Much interest is now focused on the catalytic aspect of $Cr(CO)_6$, where it acts as a catalyst precursor for reactions such as hydrogenation, hydrosilation and olefin rearrangement. This type of research is, however, beyond our experimental capabilities because of the difficulty of removing more than one CO ligand from $Cr(CO)_6$ by means of flash photolysis in solution. In our research, therefore, we are focusing on the kinetic and mechanistic behavior of chromium hexacarbonyl intermediates, formed by the removal of one ligand, in order to contribute to the growing database of reactions involving the photochemistry of this molecule.

Experimental

There are many steps involved in performing $Cr(CO)_6$ experiments. First of all, argon gas and cyclohexane solvent must be purified in order to avoid reactions with impurities. The $Cr(CO)_6$ solution is then prepared inside a photolysis cell, and is subjected to CO additions when necessary. When the solution is ready, it is flash photolyzed, % transmittance data is collected which is then sent to a computer for further analysis. Each of the steps is described in greater detail below.

Argon Purification

$Cr(CO)_6$ solutions are prepared and handled either under vacuum or argon. Argon gas is purified by passing it through one 13x molecular sieves column (Aldrich, Labclear gas filter) and one oxygen scavenging column (Aldrich, Model 1000 oxygen trap) to remove water, oxygen and organic impurities all of which could react with $Cr(CO)_5$ and change the reaction kinetics. The molecular sieves and oxygen scavenging columns were installed into the copper tubing which carries argon to the solvent stills and to the vacuum line.

Solvent Preparation

Experiments with $Cr(CO)_6$ require the use of extremely pure solvents, otherwise, $Cr(CO)_5$ will react with impurities.

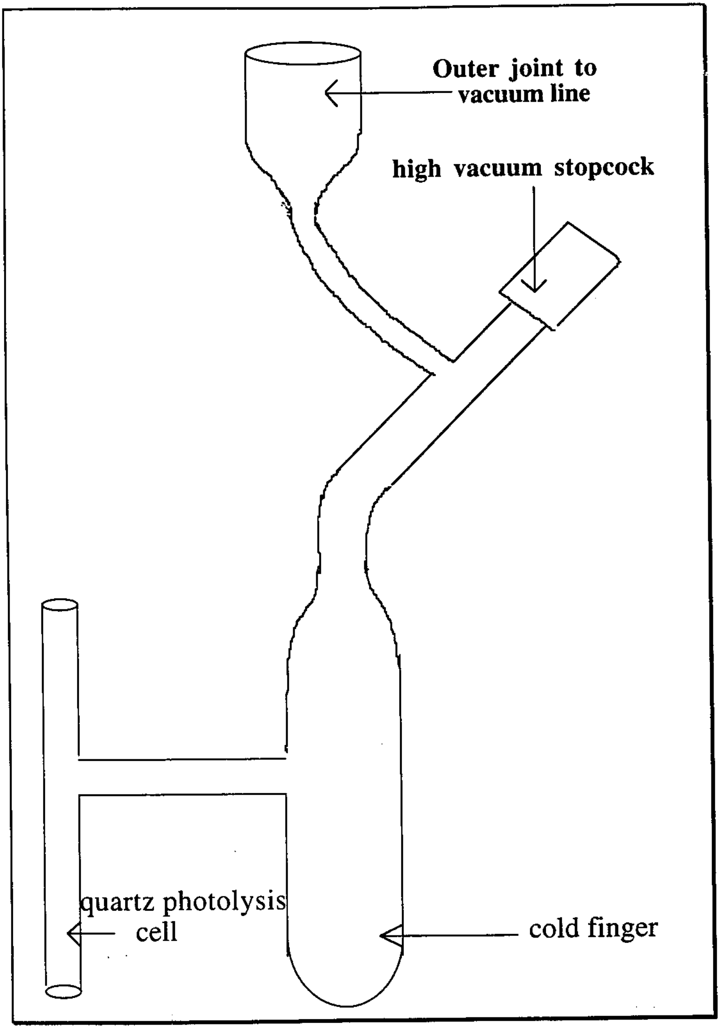
A 99+% pure, HPLC grade cyclohexane solvent purchased from Aldrich was used for all of the experiments. The solvent was dried by refluxing over CaH_2 for 12 hours under flowing purified argon and then distilled into a round bottom flask. A second distillation was then performed in a fractionating column filled with glass beads in order to remove traces of CaH_2 which was found to transfer during the first distillation by mechanical action. In order to minimize the amount of impurities collected, the first ~10 ml of the distillate were discarded by drawing it out with a gas tight syringe. When the necessary amount of cyclohexane was collected, 20 ml was drawn into the gas tight syringe for solution preparation.

Solution Preparation

The solution was prepared inside a photolysis cell (Figure 1). The cell, glassblown by Bill Jones at the General Electric Research and Development Center in Niskayuna, NY, was attached to the vacuum line and exposed to high vacuum (about 10^{-5} torr) for approximately fifteen minutes in order to remove adsorbed water or atmospheric gases. It was then filled with purified argon and the greaseless stopcock to the atmosphere was removed allowing argon to flow out of the cell.

The $Cr(CO)_6$ (Strem chemicals, 99%) was stored under 1 atmosphere of air with no additional purification before use. When it was time to prepare the solution, 1.0 mg of $Cr(CO)_6$ was weighed out and transferred to the cell via weighing paper. It was then washed down into the cold finger of the cell with 20 ml of purified cyclohexane to give a solution of concentration $2x10^{-4}$ M. After a magnetic stirring bar was dropped into the cold finger, the stopcock was replaced. The solution was then stirred with a magnetic stirrer for

Figure 1: Sample cell assembly



approximately five minutes to ensure that all of the chromium hexacarbonyl was dissolved. The solution was then degassed by being subjected to:

1) 2 successive pump, freeze, pump, thaw cycles followed by
2) 4 successive freeze, pump, thaw cycles

During the first procedure, the cell stopcock was very slowly opened, exposing the liquid solution to vacuum while it was being stirred, until it was possible to see the formation of convection currents in the solution. After one minute of pumping on the liquid, the solution was cut off from the vacuum by closing the stopcock. The solution was then slowly frozen by submerging the cold finger portion of the cell into a dewar filled with liquid nitrogen. After the solution was frozen solid, it was exposed to high vacuum for ten minutes. It was then 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 ten minutes and the procedure repeated one more time. The procedure for the last four freeze-pump-thaw cycles was the same as above, except the liquid solution was never exposed to the vacuum. When all the freeze-pump-thaw cycles were completed, the vacuum line was flooded with purified argon and the cell was transferred to the flash photolysis apparatus.

CO additions

Carbon monoxide gas was purified by passing it through two copper columns packed with activated charcoal. The first column was maintained at 180 °C with a heating tape in order to decompose and trap $Fe(CO)_5$

contaminants in the CO gas stream. The second column was U-shaped and partially submerged in a dry ice-ethanol bath at -79 °C. This column was used to remove condensable impurities.

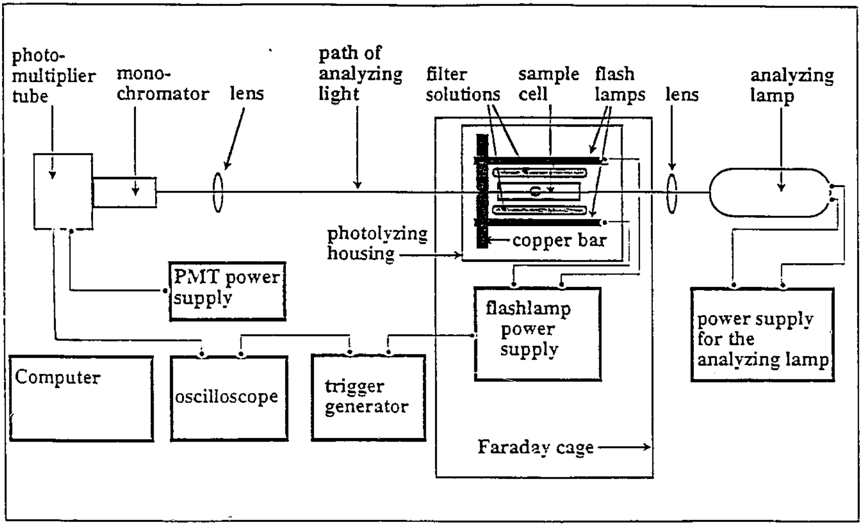
When addition of carbon monoxide to the $Cr(CO)_6$ solutions was necessary, the solutions were frozen in an acetone-dry ice bath (-67°C) in order to prevent freezing of CO, which would have taken place if liquid nitrogen (-270 °C) was used. Before the CO gas was added to the solution, the gas line and the secondary manifold were purged with purified CO. The purging procedure was done by first opening the main valve on the CO tank so that the gauge read the pressure in the tank. The main valve was then closed and the second, diaphragm, valve opened until the second stage gauge read 10 psi. The amount of CO added was controlled by a third valve ,with the pressure being displayed on a Baratron pressure gauge (MKS instruments, type 122) attached to the secondary manifold. The manifold was twice filled with 20 torr of CO and evacuated. Afterwards, the secondary manifold was pressurized to the desired CO pressure and the photolysis cell stopcock opened until the pressure inside the cell equilibrated. The pressure of the CO inside the cell was recorded and after the solution was thawed, the vacuum line was pressurized with argon gas and the cell was removed. The solution was shaken for five minutes to ensure its complete saturation with CO and then transferred to the flash photolysis apparatus.

Flash Experiment and Data Collection

A schematic drawing of the flash photolysis apparatus is presented in Figure 2. Before the photolysis cell was placed inside the apparatus, several steps were followed:

1. The xenon analyzing lamp and the lamp water supply were turned on for approximately forty minutes before flashing in order to allow the beam to stabilize.
2. The LeCroy 9410 Dual Beam 150 MHz digital oscilloscope was turned on, and the gain was set to .2 V/div. The input signal was then set to ground and the trace was aligned with the first box from the top of the screen.
3. The wavelength on the ISA Instruments monochromator was set at 503 nm.
4. $CuSO_4$ + $CoCl_2$ filter solutions for the xenon flash lamps are used so that the lamps photolyzed into the low energy (low wavelength) band of the $Cr(CO)_6$ spectrum - between 340 and 500 nm. The photolysis cell is made of Pyrex, which also doesn't allow transmission of light below 300 nm. This will block excitation of shorter wavelength bands of $Cr(CO)_6$, which would initiate additional photochemical reactions.
5. Both the trigger generator and the computer were turned on.

Figure 2: Flash Photolysis Apparatus Layout



When all of the steps were performed, the photolysis cell was tilted so that the solution filled the side arm of the cell. It was important to make sure that there were no gas bubbles trapped in the side arm, as they would affect the measured absorbance of the solution. The cell was then placed inside the Faraday cage 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 the voltage on the PMT was increased until a 1 V (5 box) difference existed between the DC signal and the ground on the oscilloscope. The optimum voltage on the PMT, in order to prevent a lot of noise, is around 500 V, 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 slits of the monochromator. After the desired cell orientation was achieved, the back of the Faraday cage was closed and the flashlamp power supply turned on. After the capacitor was charged, the voltage on the flashlamp power supply was set to 9000 V and the front door of the Faraday cage was closed.

For the $Cr(CO)_6$ experiments without CO additions, the oscilloscope sweep rate is set to about 20-50 ms/div; for runs with added CO additions, the sweep rate varied between 10-0.1 ms/div. The sweep rate was often adjusted after the initial flash in order to maximize the amount of data collected. Once the sweep rate was optimized, the collection mode on the oscilloscope was changed from auto sweep to single sweep, the signal was reset to 1 V by adjusting the PMT power supply, and then the lamps were triggered. The trace was displayed on the screen and then transferred to the computer by entering the 94rem directory on the C: drive and running the 94g program. Once in the program, 'S' was entered to store the trace, channel 1 was the selected input from the oscilloscope, and the trace on the oscilloscope was given a file name. The file name consisted of the date of the experiment 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 typing a '.bin' at the end. A sample filename for the second run on May 12, 1997 should look like this:

051297b.bin

The data was then ready for the data analysis.

Section 6: Data Analysis

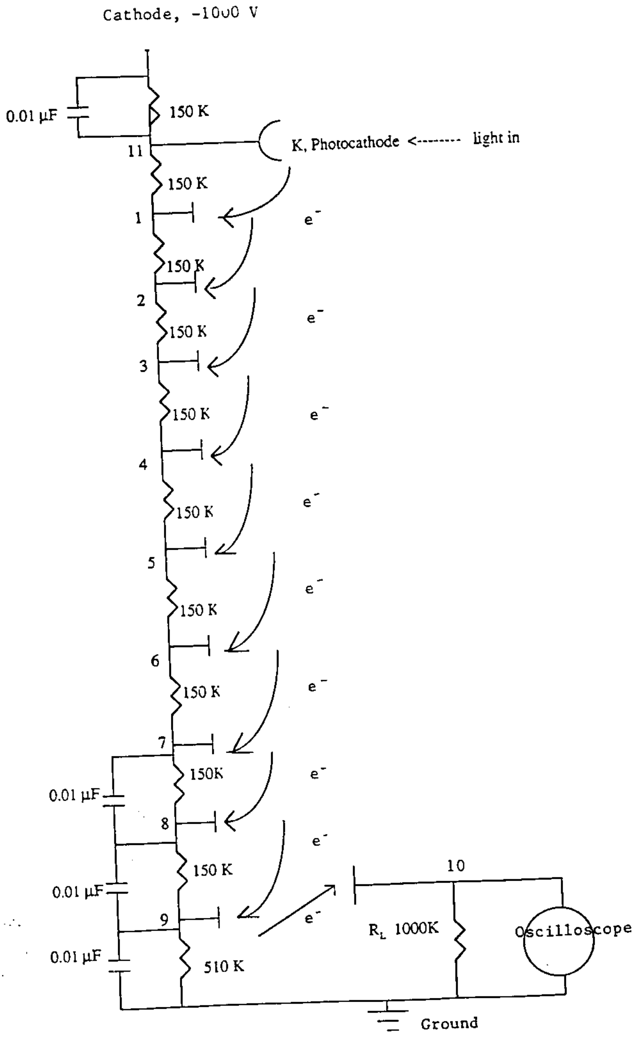
In order to analyze the data it was necessary to convert it from binary form to absorbance values. The first step involved using the 94tran program provided with the oscilloscope to convert the data from binary to ASCII format. The data was then converted from voltage values to percent transmittance and finally absorbance values by using the Voltages program written in FORTRAN by Susan Richter and Professor David Hayes. The file was then imported into the data analysis program Axum written by Trimetrix Systems. In Axum, plots of Absorbance vs. Time, Ln Absorbance vs. Time, and Inverse Absorbance vs. Time were constructed. In order to see the detailed description of the procedures necessary for the data analysis, please refer to Appendix A: Computerized Data Analysis.

Results

Photomultiplier tube problem

Data obtained by the previous student on this project was inconsistent with similar studies on chromium hexacarbonyl solutions reported in the literature. In an attempt to trace the source of the problem, we decided to examine all of the possible factors that could have an effect on the $Cr(CO)_6$ system. One source of the problem might be with the photomultiplier tube (PMT), which measures the transmitted light intensity of the analyzing light after the flash and converts it to a proportional current and voltage. If the PMT is not operating linearly, then the second-order kinetic behavior of the chromium hexacarbonyl system might not be observed. As a result, before performing any experiments on $Cr(CO)_6$ we checked whether the photomultiplier tube was operating linearly. When the PMT is operating linearly, the output current and voltage is linearly proportional to the incident light intensity. A schematic drawing of the PMT is shown in Figure 3. The principle of its operation is as follows: when light hits the photocathode, electrons are knocked off and directed to the first dynode. Because each dynode is made more positive than the preceding one by an external power supply, electrons accelerate through the chain with a gain factor characteristic of the tube and the voltage drop. As electrons reach the anode, a voltage drop is created across a load resistor which is then displayed on the oscilloscope. To check the linearity of the PMT we used several NIST calibrated neutral density filters, where each filter is of a particular transmittance (from 10% - 79%).

Figure 3: Schematic drawing of PMT



If the PMT is operating linearly, the percent transmittance displayed on the oscilloscope, after the analyzing light passes through a particular filter, should correspond to the actual calibrated transmittance of that filter, which we checked and confirmed with a diode array spectrophotometer. We found that when a filter calibrated to have 79% transmittance was placed in the beam of light just in front of the PMT, a 72% transmittance signal was observed on the oscilloscope; when a 50% transmittance filter was used -- 40% transmittance was observed, and so on. It became apparent that the PMT was not functioning linearly. We found out from the manufacturer (Hamamatsu, Inc.) that this PMT operates linearly if it draws no more than 10-15 μA from the anode. The actual current drawn by our PMT was calculated to be 50 μA, indicating that the reason for the nonlinearity was too much light reaching the PMT. The problem was corrected by placing a 10% transmittance neutral density filter in the beam of our analyzing light. This course of action, however, led to a decrease in output voltage measured across the load resistor at the oscilloscope. In order to correct for this effect, the gain on the PMT was increased. The major side effect of increasing the voltage on the PMT, however, is an increase in the noise of a signal. One way to decrease the noise is to increase the load resistance (R_L). In order to make sure that an increase in R_L would not significantly affect the RC time constant of the circuit, we brought the PMT and the oscilloscope to the Physics department and used their diode laser, powered by a square wave generator, to track PMT output vs. signal input as R_L was increased. We determined that changing the load resistor from 1 kΩ to 24 kΩ caused a big increase in the signal to noise ratio while not measurably affecting the response time of the PMT. Signals with rise/decay times of $\geq$ 100 ns were faithfully tracked by the detector. Finally, the linearity of the PMT was reconfirmed.

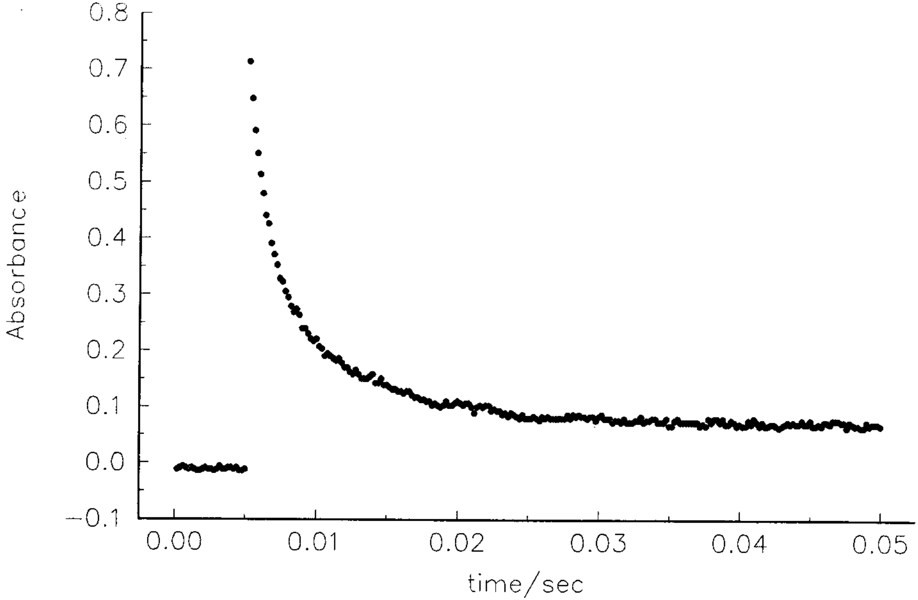
Solvent purification

When it was time to perform experiments, we started out by doing a basic run where $Cr(CO)_6$ was the only species present in solution (Figure 4). The reaction should have followed second order kinetics in which case the Inverse Absorbance vs. Time plot would be straight while the first order Ln Absorbance vs Time plot would be curved. As seen in Figures 5 & 6, however, the second as well as the first order kinetic plots turned out to be curved. We attributed this kinetic behavior to reactions of $Cr(CO)_5$ with impurities present in the solvent. After consulting the literature, a number of solvent purification procedures were performed:

Treatment with $LiAlH_4$ and fractionation

$LiAlH_4$ is known to be a more vigorous drying agent than CaH_2, which was used as the drying agent in the basic run. The solvent was purified by refluxing cyclohexane over $LiAlH_4$ for 24 hours. As with CaH_2, gray precipitate was observed on the walls of the collection flask of the $LiAlH_4$ still, indicating that $LiAlH_4$ was coming over by mechanical action. In order to remove $LiAlH_4$ from the solvent, a second distillation was performed in a fractionating column.

Figure 4: Cr(CO)5 followed at 500 nm
run 020196b



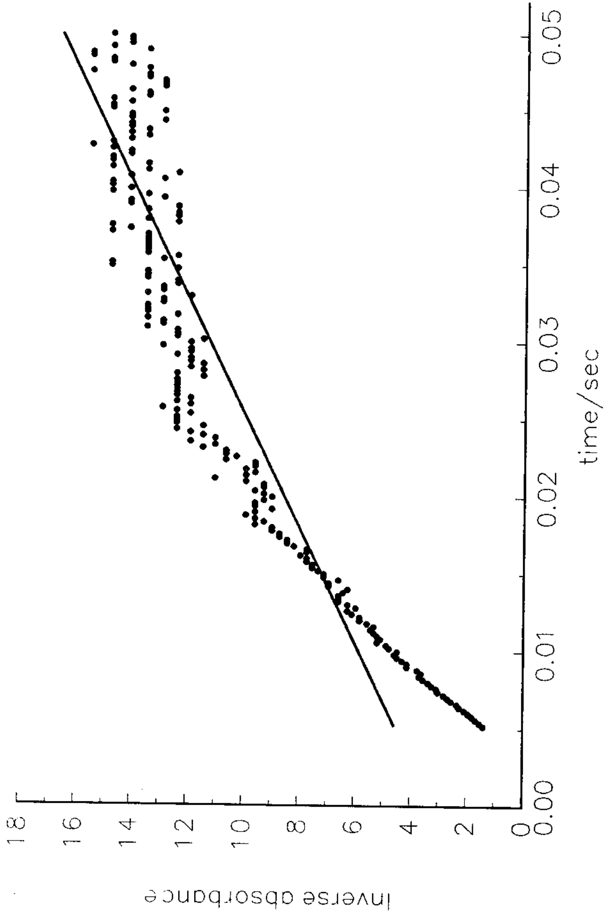
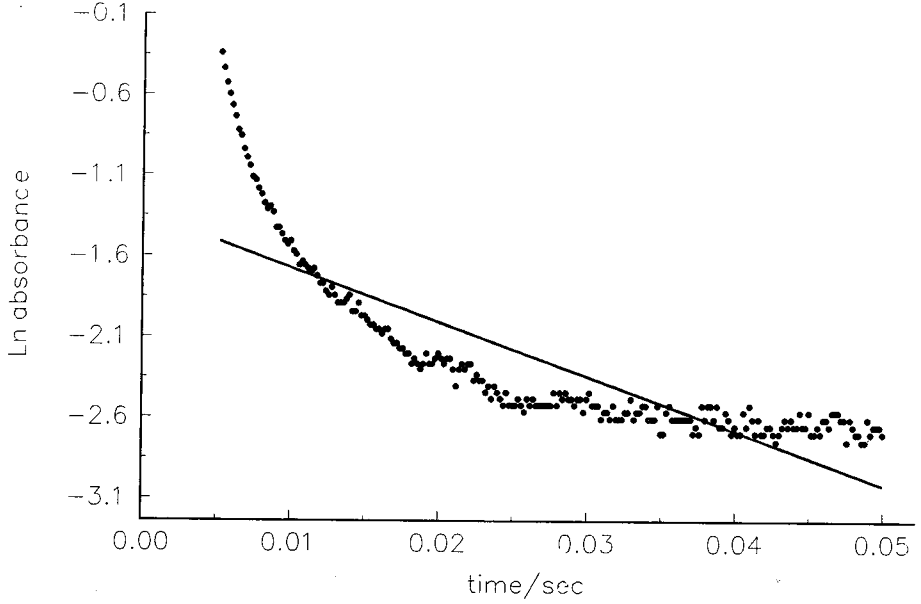


Figure 5: Cr(CO)5 followed at 500 nm
run 020196b

Figure 6: Cr(CO)5 followed at 500 nm
run 020196b



The rest of the experiment proceeded as described in the Experimental section. Neither first nor second order kinetic reactions were observed.

Treatment with H_2SO_4 and CaH_2

In order to remove any potential alkene impurities, the cyclohexane solvent was treated with sulfuric acid wash as described in the literature: 30 ml of concentrated H_2SO_4 and 300 ml of cyclohexane were added to a 500 ml round bottom flask containing a magnetic stirring bar and then stirred for 24 hours in order to sulfonate any alkenes present. The cyclohexane phase was then separated with a separatory funnel and washed three times with 100 ml of water. 100 ml of saturated $NaHCO_3$ was then added to the flask with cyclohexane, and was stirred for another 24 hours in order to neutralize any excess H_2SO_4. The cyclohexane phase was again separated and was washed three more times with 100 ml of water. One tablespoon of $CaCl_2$ was then 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 section. Neither first nor second order kinetic reactions were observed.

Treatment with H_2SO_4, $LiAlH_4$, and fractionation

In order to see if the sulfuric acid treatment was more effective with $LiAlH_4$ than with CaH_2, the solvent was washed with the sulfuric acid, 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 section. Neither first nor second order kinetic reactions were observed.

Treatment with Na metal

Sodium metal reacts vigorously with water and oxygen to form NaOH and Na_2O, and thus is a very effective drying and degassing agent. As a result, cyclohexane solvent was refluxed over Na metal for 24 hours. Before addition to the cyclohexane, sodium metal was washed with isopropyl alcohol (IPA) and untreated cyclohexane in order to remove any oxides. The rest of the experiment proceeded as described in the Experimental section. Neither first nor second order kinetic reactions were observed.

Treatment with Sodium Benzophenone Ketyl

Sodium benzophenone ketyl is known to be a more efficient drying and degassing agent than just Na metal by itself. Thus, cyclohexane solvent was refluxed over sodium benzophenone ketyl for 24 hours. Sodium metal was prewashed and added to the solvent as previously described, and several teaspoons of benzophenone were then added to the flask. The solution was 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 section. Neither first nor second order kinetic reactions were observed

CO additions

It appeared that none of the solvent purification techniques succeeded in sufficiently reducing impurities in our solvent. Thus, to make the reaction of $Cr(CO)_5$ with impurities unimportant, we decided to push the reaction into a pseudo-first order regime by saturating the solution with increasing pressures of CO gas. Since there is an excess amount of CO in solution, $Cr(CO)_5$ will likely react more with CO than with impurities, with the order of the reaction depending only on $Cr(CO)_5$ concentration. When the data from CO additions was analyzed, however, we obtained results that were inconsistent with a first-order reaction. Instead of getting straight Ln Absorbance vs. Time plots, which are indicative of first-order kinetics, we saw plots that were sometimes straight, sometimes partially straight and often curved (Figures 7, 8, 9). We consulted the literature, and it suggested that CO might react with Fe present in the walls of the steel container where it is stored, and can then be carried over as $Fe(CO)_5$ complex. Since $Fe(CO)_5$ is easily photolyzed, with products absorbing in the same region as $Cr(CO)_5$, our inconsistent results could be due to the interference from this contaminant. We followed a suggested purification scheme in which CO gas is passed through a heated activated charcoal copper tube, where $Fe(CO)_5$ would be decomposed and absorbed, followed by passage through a cooled (-79 °C) activated charcoal packed U-shaped copper tube, where condensable materials are trapped. After the gas was purified, the CO addition

Figure 7: Cr(CO)5 followed at 500 nm(80.7torr CO)
run 091296d

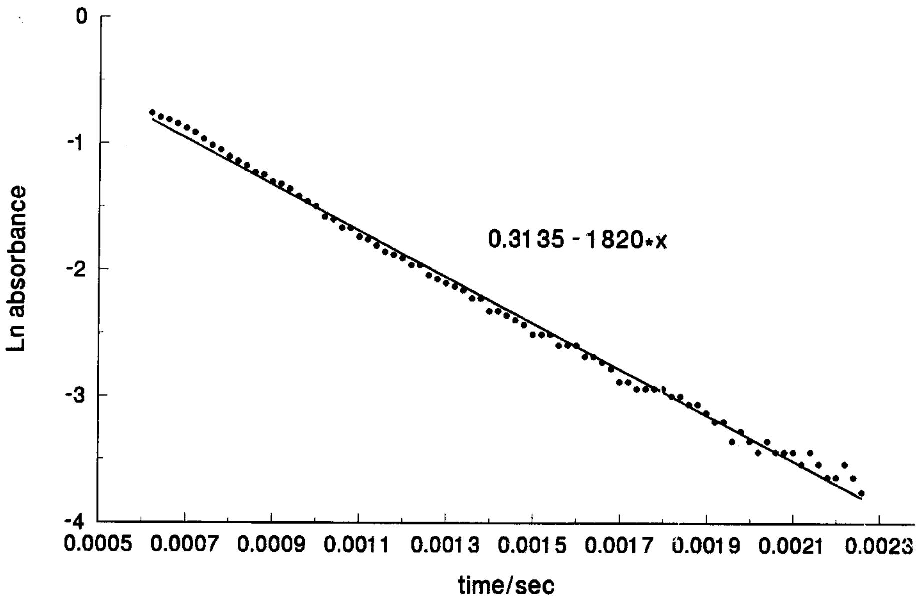


Figure 8: Cr(CO)5 followed at 500 nm(1 00.0 torr CO)
run 091 296e

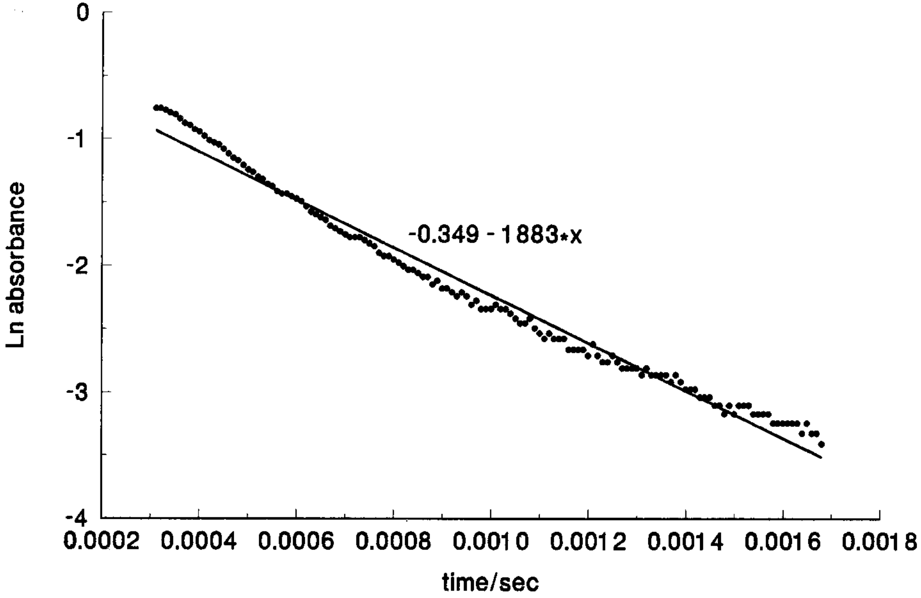
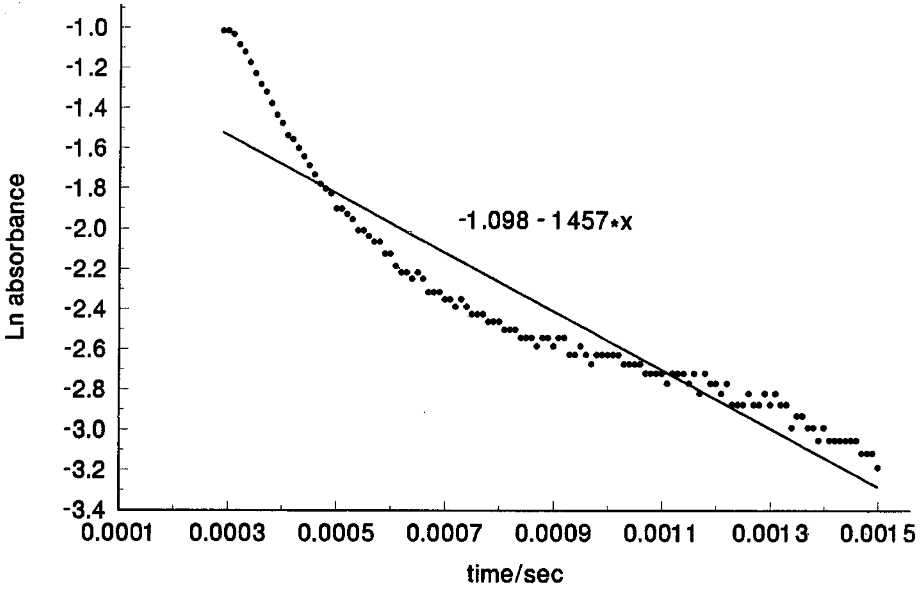


Figure 9: Cr(CO)5 followed at 500 nm (200.8 torr CO)
run 091696b



experiments were repeated and first-order kinetic behavior was observed (Figures 10, 11).

In order to compare our results with those in the literature, the second order rate constant for recombination of $Cr(CO)_5$ with CO had to be found. As mentioned previously, when our solution is saturated with CO, the reaction of $Cr(CO)_5$ with CO is induced to follow pseudo-first order kinetics, where k_{obs} is the observed first order rate constant. Since $k_{obs} = k[CO]$, the actual second order rate constant, k, can be found by plotting k_{obs} vs. [CO], where k is the slope. When such a plot was obtained (Figure 12), the second order rate constant (1.1×10^5 $M^{-1}s^{-1}$) turned out to be almost 30 times slower than the literature value of 3.0×10^6 $M^{-1}s^{-1}$ found by Kelly and Gustorf.[3] This suggested that $Cr(CO)_5$ continued reacting with impurities and we are observing the decay kinetics of $Cr(CO)_5X$, which we have shown has an overlapping absorption with $Cr(CO)_5$ at 500 nm.

Argon problem and Final results

We tried to figure out what else could bring over contaminants. It occurred to us that many solution preparation steps are performed under flowing argon which was further purified by flowing over Cu catalyst (BASF, Inc.) to remove O_2 and then P_4O_{10} granules to remove H_2O. We thought that this purification scheme may not be effective in removing impurities. To test our hypothesis, we performed a run where chromium hexacarbonyl solution was saturated with Ar gas for a period of 30 min. Even before the data was analyzed,

Figure 10: Cr(CO)6 followed at 500 nm(200.1 torr CO)
run 101696a

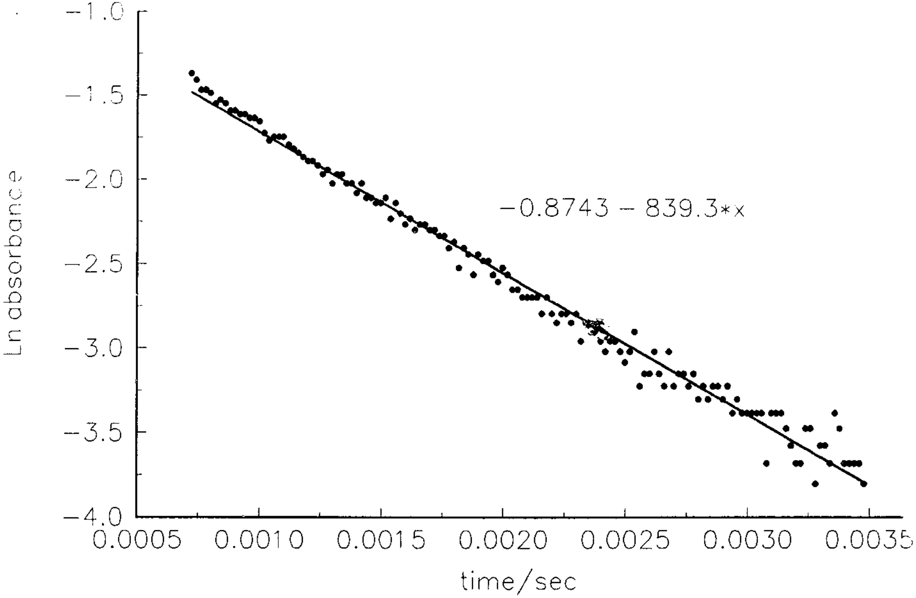


Figure 11: Cr(CO)5 followed at 500 nm(400.1 torr CO)
run 101696c

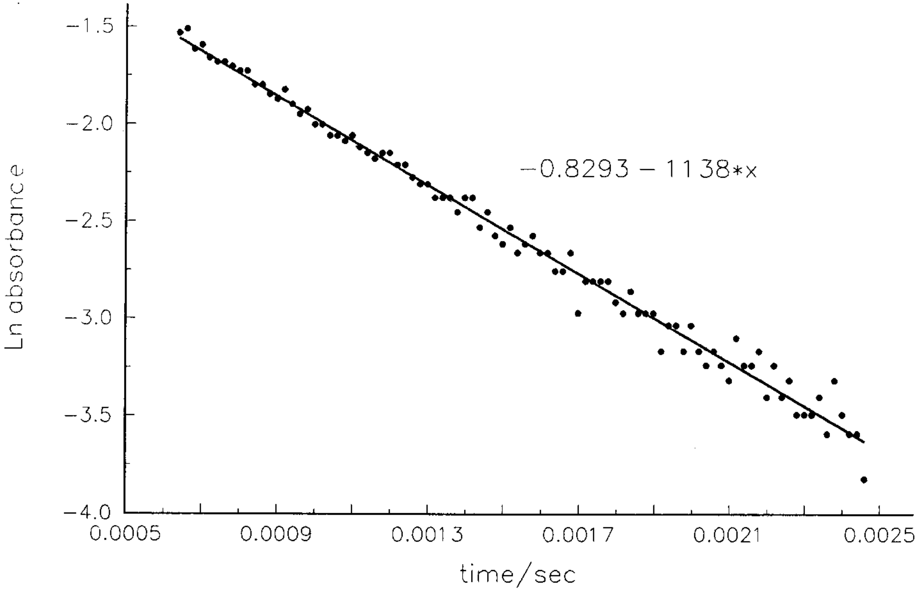
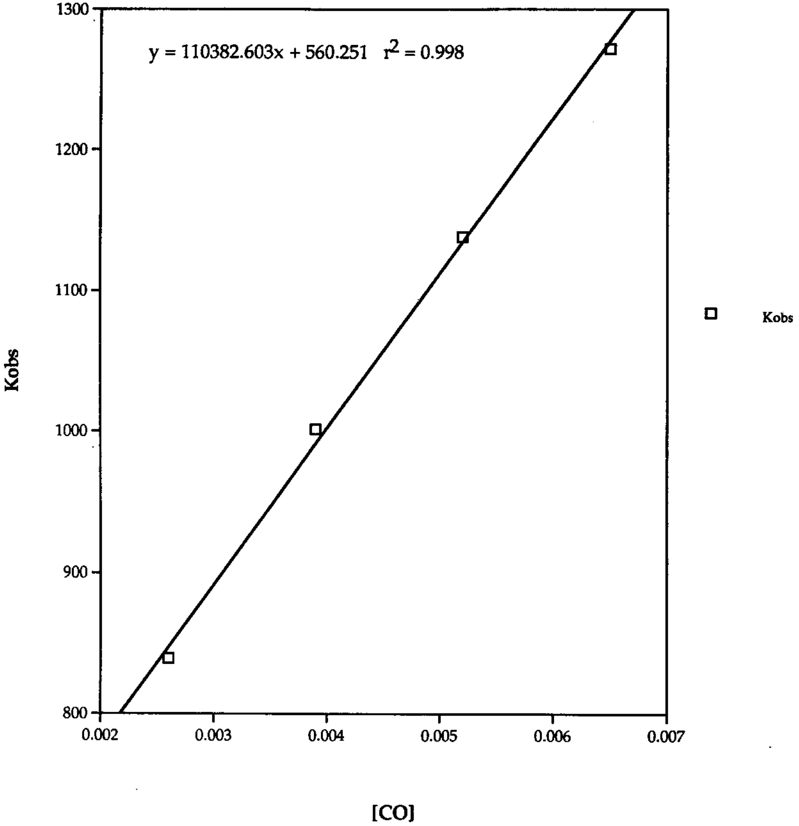


Figure 12: Kobs vs. [CO]

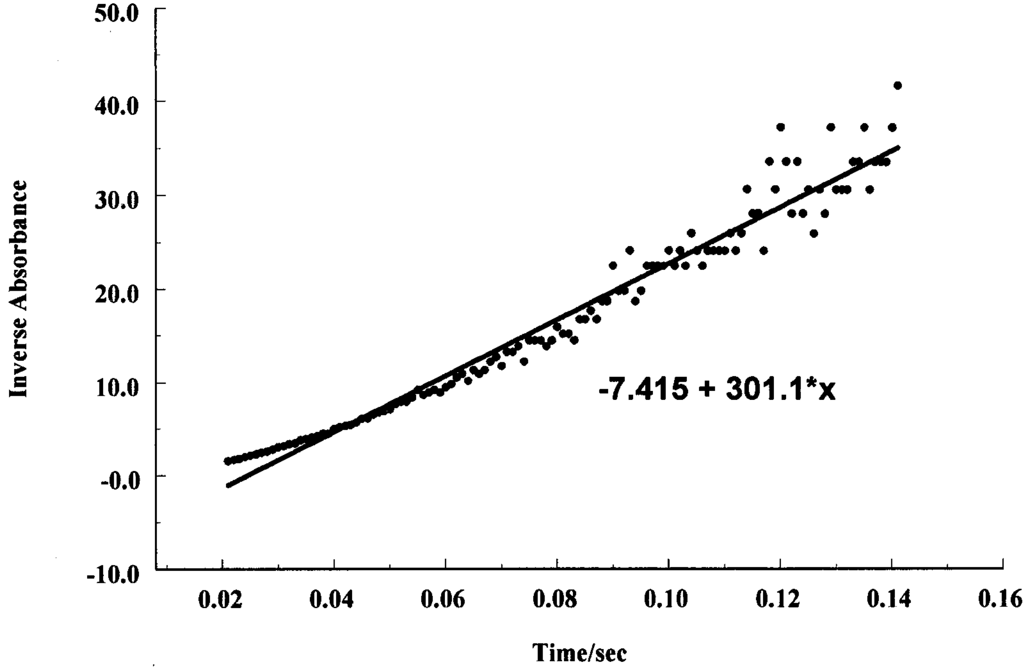


it became apparent that the reaction kinetics changed significantly. The oscilloscope sweep rate for the experiment before Ar addition was 20 ms/div. The sweep rate after chromium hexacarbonyl solution was saturated with Ar, changed to 50 ms/div. The analysis of the data only confirmed the suspicion that Ar was bringing over contaminants. Figures 13 and 14 show the change in reaction kinetics as solution was saturated with argon gas. It thus became apparent that we needed to change the method of argon purification. There are two ways to purify gases: one way is to make purification columns yourself, as was done previously with Ar and CO; and the other way is to purchase ready made gas purification columns. We decided on the latter. After consulting the Aldrich catalog, we purchased two 13x molecular sieves columns, which are suppose to remove water, oil, and other organic materials from inert carrier gases, and two oxygen traps; each of the columns and O_2 traps were installed into the gas line carrying Ar to the vacuum line and stills.

After all the purification columns were in place, we repeated the basic experiment, where $Cr(CO)_6$ is the only species present in solution, and achieved much better agreement with published results. The Ln Absorbance vs. Time plot was curved and Inverse Absorbance vs. Time plot was linear, indicating that reaction followed second-order kinetics as expected (Figures 15 & 16). We then proceeded to perform CO additions to the chromium hexacarbonyl solution with CO being added at regular pressure intervals. All of the runs followed first-order kinetics (Figures 17-22). The second order rate constant, k (1.7×10^6 $M^{-1}s^{-1}$), obtained from the slope of k_{obs} vs. [CO] plot (Figure 23), was still almost

Figure 13: Cr(CO)5 followed at 500 nm (no Ar added)

101096a



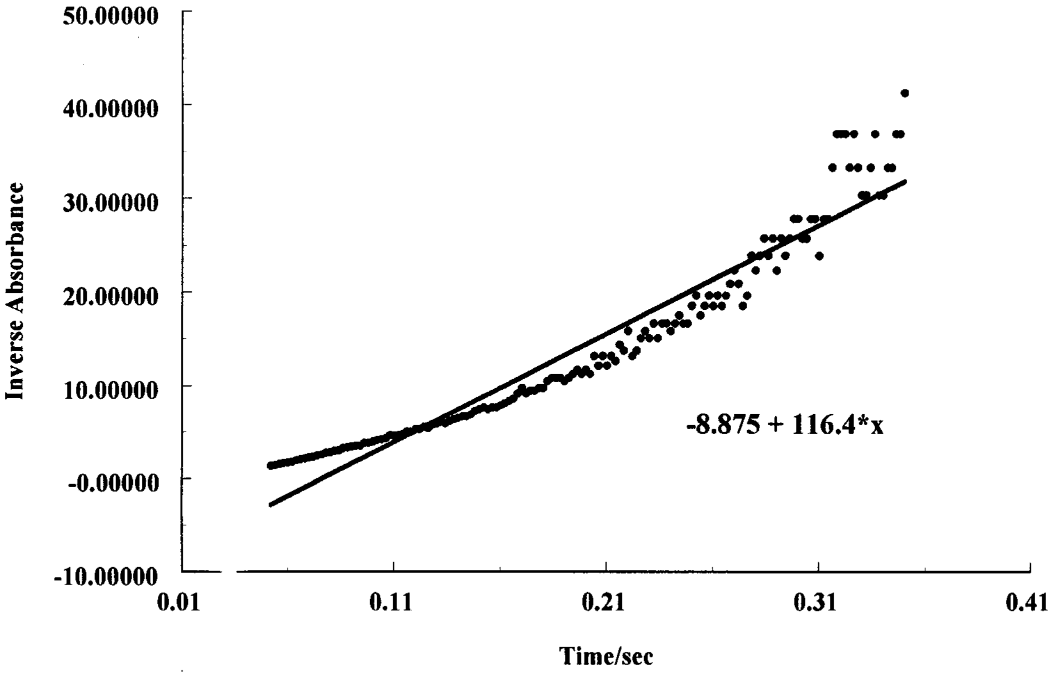


Figure 14: Cr(CO)5 followed at 500 nm (saturated with Ar)

101096b

Figure 15: $Cr(CO)5$ followed at 500 nm (purified Ar)

040397a

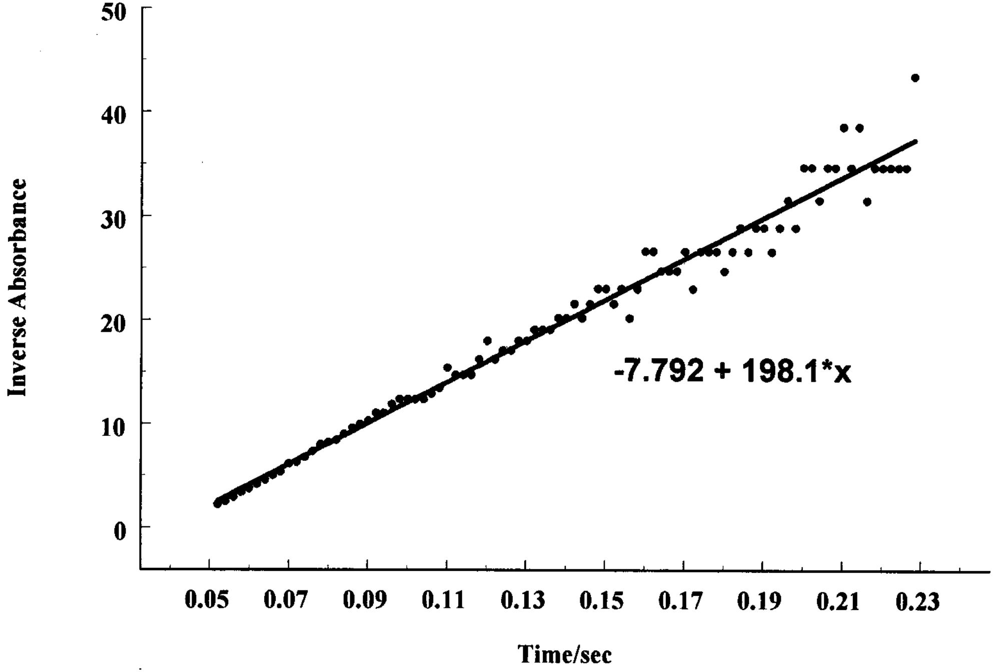


Figure 16: Cr(CO)5 followed at 500 nm (purified Ar)

040397a

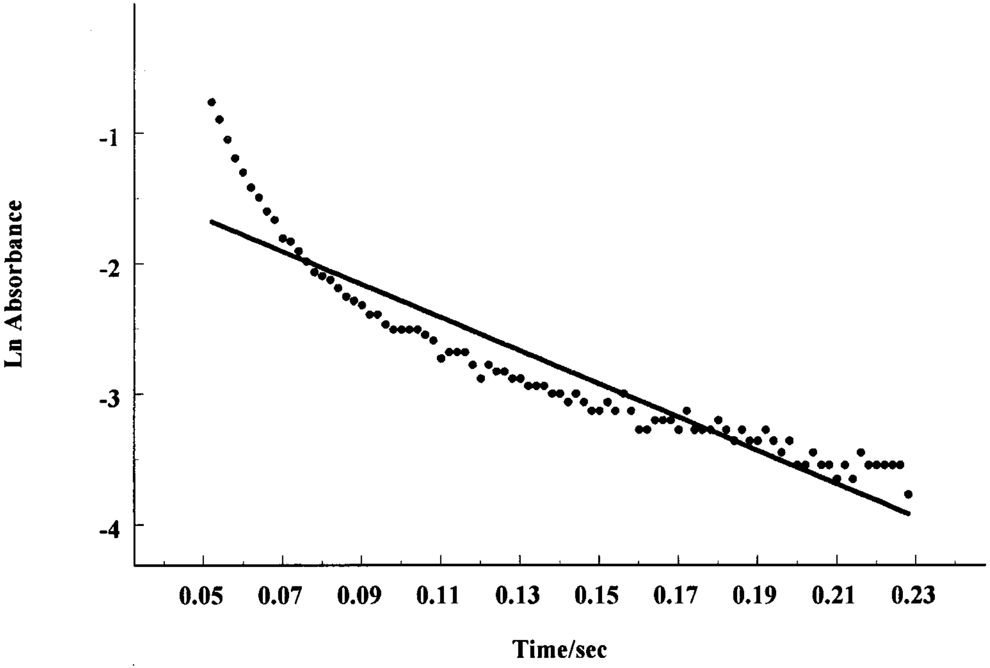


Figure 17: Cr(CO)5 followed at 500 nm (23.5 torr CO)

040797b

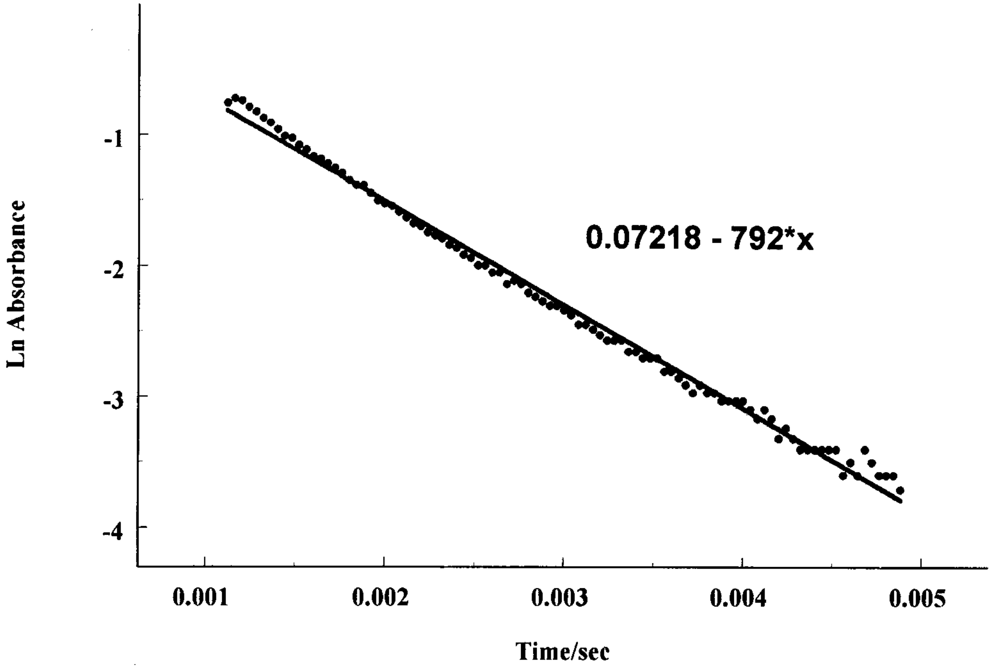


Figure 18: Cr(CO)5 followed at 500 nm (69.5 torr CO)

040797d

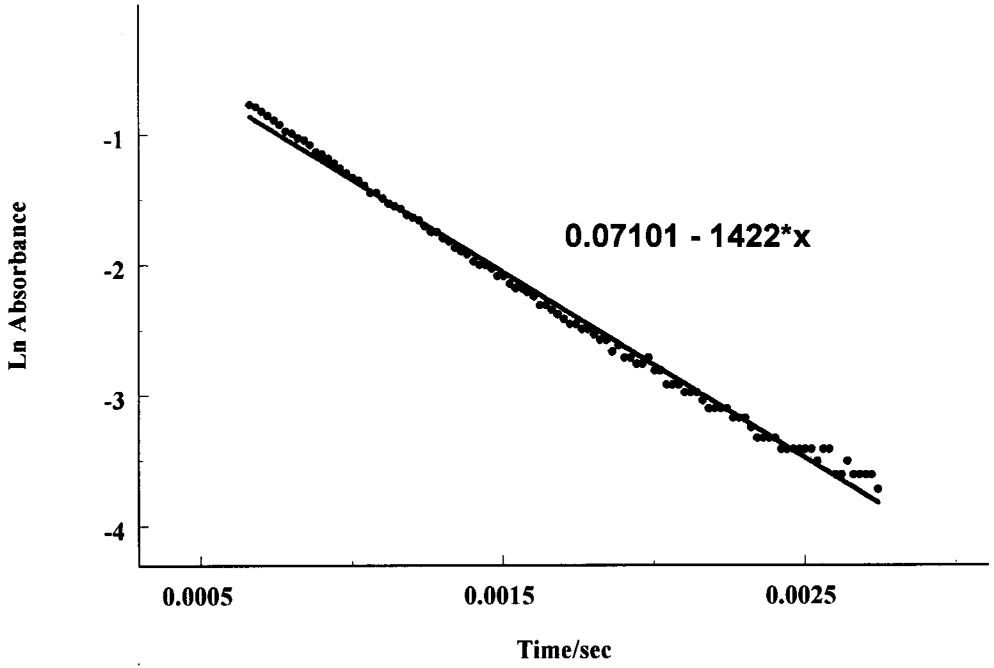


Figure 19: Cr(CO)5 followed at 500 nm(102.8 torr CO)

040797e

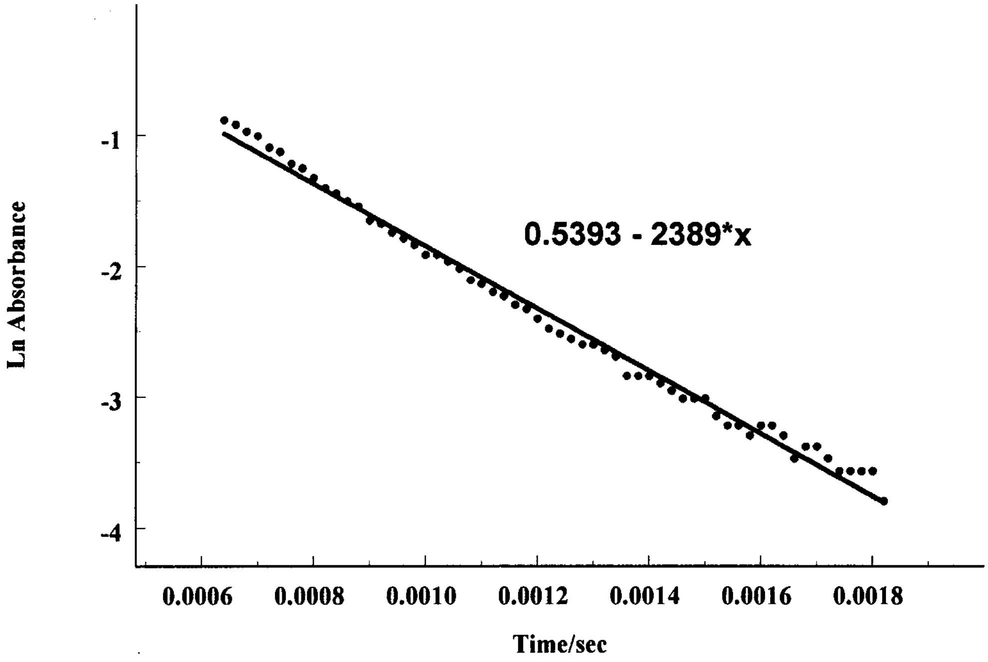


Figure 20: Cr(CO)5 followed at 500 nm (196.3 torr CO)

040397c

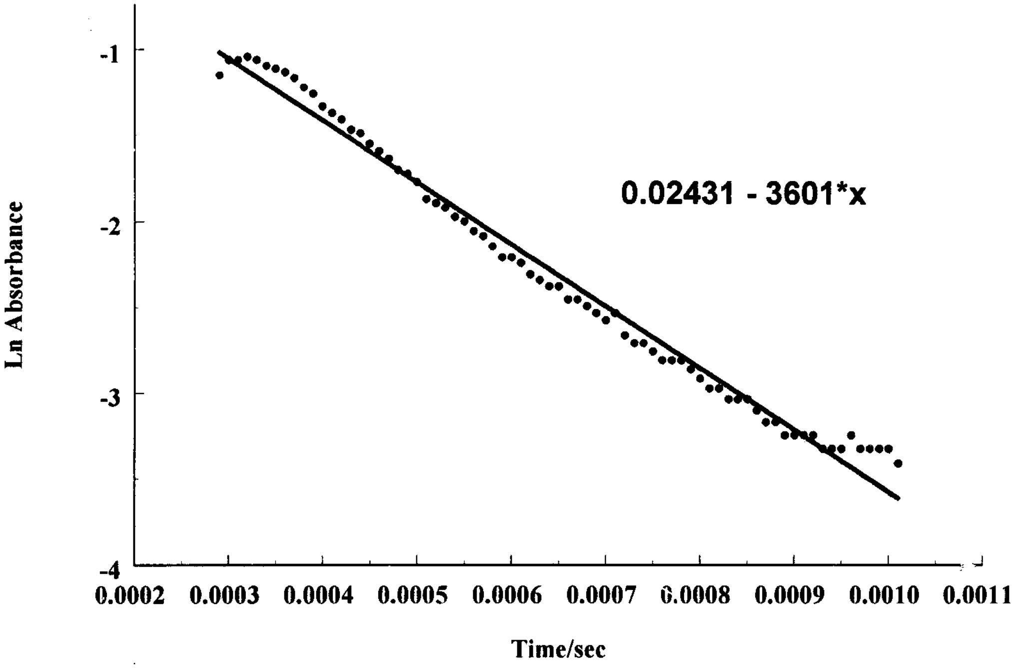


Figure 21: Cr(CO)5 followed at 500 nm(291.5 torr CO)

040397d

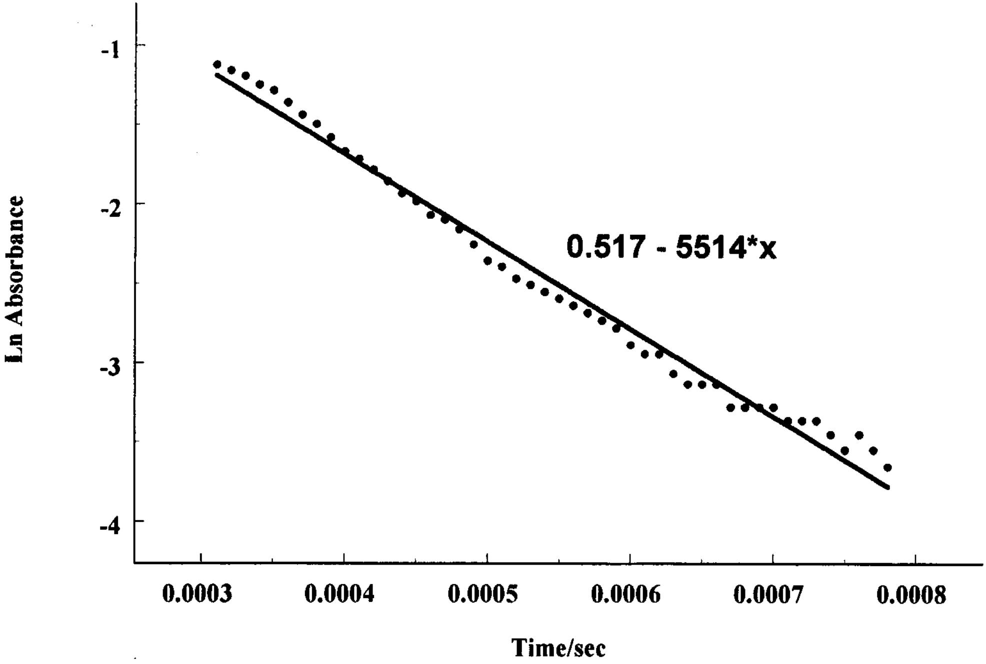


Figure 22: Cr(CO)5 followed at 500 nm (391.6 torr CO)

040397e

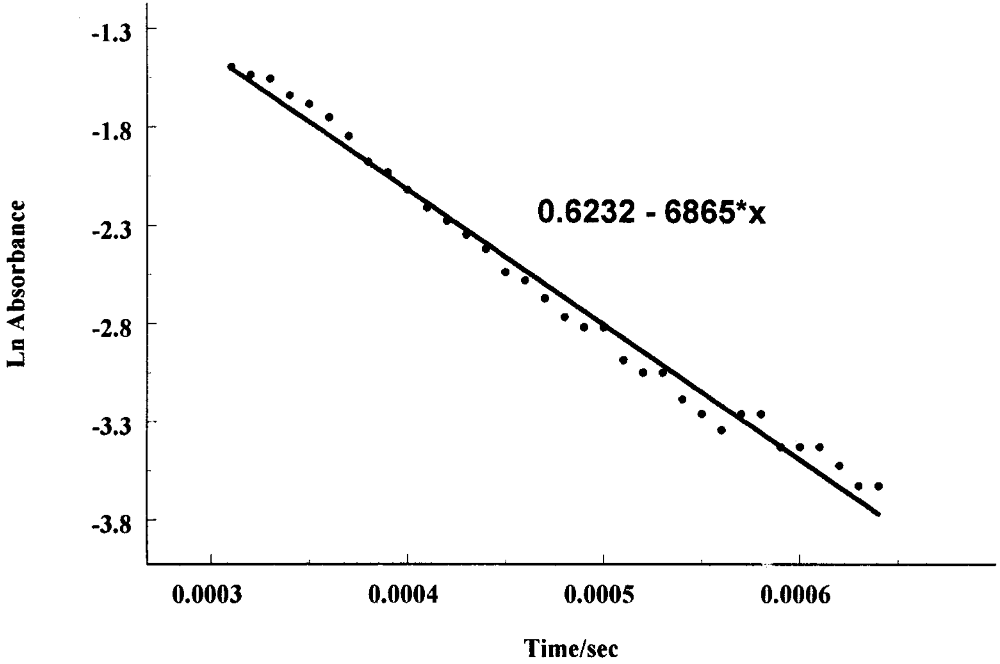
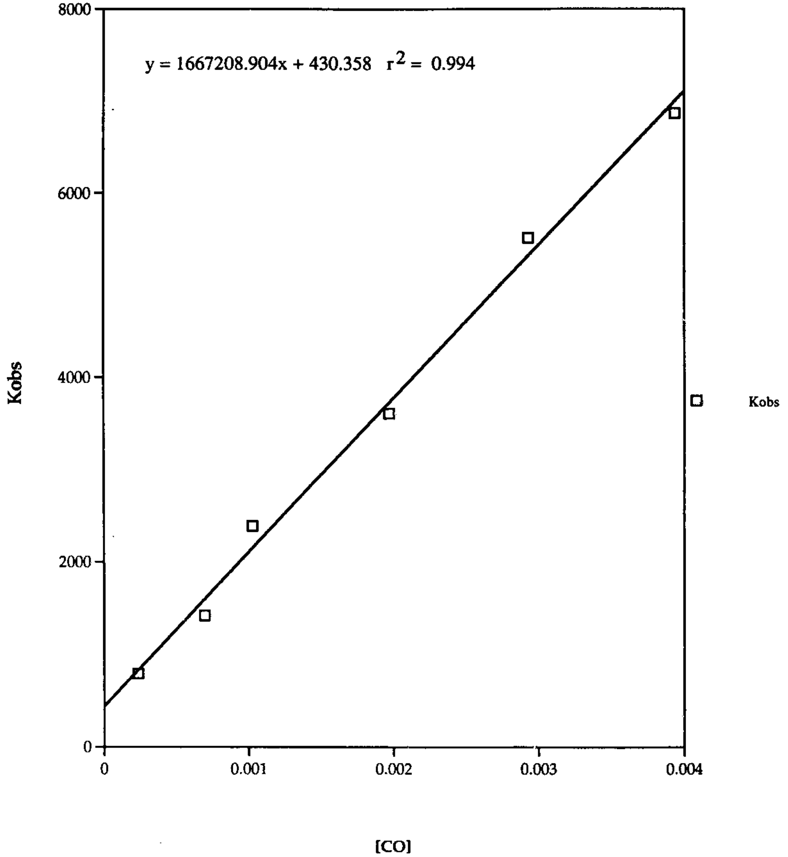


Figure 23: Kobs vs. [CO]



two times slower than the literature value of 3.0×10^{6} $M^{-1}s^{-1}$. One explanation for the difference in second-rate order constants may be our failure to recalibrate the Baratron pressure gauge used to measure the added CO pressures. The pressure gauge read 960 torr at atmospheric pressure, which indicated that the actual CO pressure added to the solution was less than what was read on the pressure gauge. This would cause our measured rate constants to be too low. In order to confirm our suspicions, we are planning to repeat the CO addition experiments after the pressure gauge is calibrated.

Discussion

Our study of the chromium hexacarbonyl system has been successful. We have managed to identify the source of the impurities which were interfering with our studies. It turned out to be argon gas, and after purifying it, we achieved satisfactory results. Flash photolysis of chromium hexacarbonyl solution, without added CO, followed second order kinetics, as expected, while saturating the solutions with increasing pressures of purified carbon monoxide gas induced the reaction to follow pseudo-first order kinetics. That the obtained second order rate constant was almost two times slower than the literature value may be due to the uncalibrated baratron pressure gauge used to measure added CO. We will be recalibrating this gauge shortly.

Now, that we have succeeded in removing impurities and driving the $Cr(CO)_5$ reaction pseudo-first order with respect with CO, we want to study other reactions involving chromium carbonyls. One set of experiments may involve studying the reaction kinetics of $Cr(CO)_5$ with alkenes. Previous studies have looked at reactions with simple alkenes, such as C_2H_4. We, on the other hand, would like to look at reactions of $Cr(CO)_5$ with longer chain as well as substituted alkenes in order to see what factors determine metal-olefin complex stability: steric or electronic effects.

Another set of experiments that would be interesting to look at is the flash photolysis of $Cr(CO)_4$(diene) complexes. One example which is readily available and which shows photocatalytic activity with respect to hydrogenation is $Cr(CO)_4$(NBD), where NBD stands for norbornadiene. The reaction could follow several pathways: one, where a single CO ligand is photolytically removed and then recombines with $Cr(CO)_3(NBD)$ via second-order kinetics; second, where flash photolysis causes a complete dissociation of NBD from the metal; and, finally, where only one ene-Cr bond is broken. One way to determine what happens after the solution is photolyzed would be to saturate the solution with CO gas. If a single CO ligand is removed, then, saturating the solution with CO would induce it to follow pseudo-first-order kinetics and the rate of reformation of $Cr(CO)_4(NBD)$ would increase with increasing CO pressure. If, on the other hand, complete dissociation of NBD from the metal takes place, then saturating the solution with CO will generate $Cr(CO)_6$. The production of $Cr(CO)_6$ and consumption of $Cr(CO)_4(NBD)$ can be observed in a time-resolved UV/Vis spectrum. Finally, in the case of partial dissociation, saturating the solution with CO may generate the $Cr(CO)_5(NBD)$ complex, where the diene is coordinated to the metal center via only one double bond, or may have no effect on the reaction. In the first case, the reaction would follow second-order kinetics, show a CO dependent rate, and produce a new chromium complex, $Cr(CO)_5(NBD)$. In the second case, the kinetics will be first order, will not show a CO dependent rate, and will lead only to reformation of $Cr(CO)_4(NBD)$.

Although chromium carbonyl systems have been studied for many years, as a model for transition metal carbonyl complexes which can act as photocatalysts, there are still many unanswered questions about the mechanistic and kinetic details of $Cr(CO)_6$ catalyzed reactions. For these reasons, researchers continue to probe deeper into the kinetics and mechanism of this system.

Appendix A: Computerized Data Analysis

UN82 ZAYDMAN, MARINA KINETICS AND MECHANISM OF, ETC.
Z39k/1997 CHEMISTRY HRS. 6/97 2-2

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

- Click on the Start, go to Programs and then choose MS-DOS prompt.
- Type cd\ (this will get you out of Windows).
- When the trace is on the screen, type 94REM; press Enter and then 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, but the .BIN is standard procedure.
- Enter 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 C: directory type \FORTRAN\SOURCE\SAMPLES\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. 1.0 V
    e. FILENAME.ABS

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

- In the C: directory type WIN (this will get 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 FILE and click on IMPORT DATA.
- next to 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 precision to 6.

5. Using Axum for Data Analysis: Calculating Ln Abs and 1/Abs

- Label column 4 as Time2 (change precision to 6)
- Label column 5 as Absorb2
- Label column 6 as LnAbsorb
- Label column 7 as InvAbsorb
- Scan the data looking for the row **just after** the firing of the flashlamps (will see a sudden drop in PercentT)
- Highlight only the Time and Absorbance column from just after the lamps were fired until Abs = 0.02.
- Copy each column and paste the Time column under Time2 and Absorb column under Absorb2.
- Click on Transform option (it is a capital X on the top tool bar).
- in the provided window type:

```
\6=Ln(\5);
\7=1/(\5);
```

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

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

- Save the Data sheet.

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

- Holding down the Ctrl key, click on column Time and Absorb. This will highlight both columns.
- Click on the 2-D plot option (it is located on the top tool bar next to the transform option).
- From the appeared graph menu, click on the Scatter option (top left)

- You will see a graph of your data. Before plotting it, however, your need to add a title and label the axis.

Adding a Title:

- Go to Insert menu and click on Titles
- Choose Main and type in a 1-line title (I have it set up that it will always give me the same title. If you need to change it, just type over it).
- If you need a second line to your title, choose Sub from the Titles menu (usually, it is the name of the run, eg. 101096a).

Labeling the Axis:

- I have the axis names, thickness and font saved as default (they will appear the same all the time).
- If you need to change them, click on the label and type the desired name.
- Click on Font to change the size and font.
- The size of the data point has also been set as default (I found this size to be optimum). If you want to change it, double click on the data point.
- Go to symbol and change Height to the desired number.
- Save the graph.

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

- Holding down Ctrl. key, highlight Time2 and LnAbsorb or InvAbsorb columns.
- Click on 2-D plot
- Click on the Linear fit option (has scatter points with a line going through them).
- To name the graph and label the axis follow the same directions as in Section #6.
- To display the equation of the line do the following:
    - go to Insert
    - click on Curve fit equation
    - use the mouse to drag the equation to the desired location
    - to change the font or size, double-click on the equation and do the desired changes.
- Save the graph.

8. Opening the 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

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