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THE CONSTRUCTION AND TESTING OF A SYSTEM FOR FLASH PHOTOCHEMICAL STUDIES OF ORGANOTRANSITION METAL COMPOUNDS

By

Robin Lynn Miller

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Submitted in partial fulfillment
of the requirements for
Honors in the Department of Chemistry

UNION COLLEGE

June 1989

ABSTRACT

MILLER, ROBIN L.: The Construction and Testing of a System for Flash Photochemical Studies of Organotransition Metal Complexes.

The main objective of my research efforts was to construct a flash photolysis system which would enable one to carry out time-resolved studies of photoinitiated reactions of organometallic hydrides. Such a development involved two major tasks. First, it required establishing a functioning vacuum line. Organometallic complexes are extremely sensitive to oxygen and water. Therefore these contaminants must be removed if one is to have any success in studying their reactions. A vacuum line is the most efficient means for degassing both solvent and solute Second, it involved modifying our flash photolysis apparatus. Changes in the flash rig included upgrading the micropulser from 100 to 400 joules, modifying the design of the flash housing and incorporating an amplifier circuit into the detector system.

Before embarking on original research, we felt it was necessary to test the effectiveness of our newly modified equipment. Therefore, we sought to reproduce the findings of other flash photolysis investigations. Replication of the literature would be a good indication of a properly functioning system.

The systems we studied included; measuring the half life of triplet state phenanthrene; measuring the half life of the transient $CpFe(CO)(n^3\text{-}CH_2C_6H_4\text{-}p\text{-}Me)$ which results upon photolysis of the complex $CpFe(CO)_2(n^1\text{-}CH_2C_6H_4\text{-}p\text{-}Me)$; and monitoring the reaction dynamics of the "tricoordinate" intermediates $MCl(PPh_3)_2$ (M = Rh and Ir) which result upon flash photolysis of the carbonyls $MCl(CO)(PPh_3)_2$.

ACKNOWLEDGEMENTS

I would like to thank Professor David M. Hayes for allowing me the opportunity to work on this project. His knowledge, patience and and support made my first research experience a very positive and productive one. I would also like to thank Professor Hayes for the guidance and direction he showed me when I was selecting a graduate school. His advise was invaluable. Lastly, I wish to thank him for his friendship and concern.

I would also like to express my gratitude towards Professor Susan E. Hayes. She was an important member of our research group. Her innovative ideas and glassblowing skills made much of our research possible.

I wish to acknowledge Ed Lin for his contributions to the project. He was a supportive colleague and made our research environment an enjoyable one.

Finally, I would like to thank my parents for their love and support throughout my four years at Union. Without them, I would not have been able to achieve any of my goals.

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INTRODUCTION

Most investigations of photochemical reactions involve continuous photolysis techniques in which the details of the photoinitiated reactions taking place are inferred from the nature of the products obtained. The technique of flash photolysis, however, allows one to initiate a photochemical reaction in a short period of time (10 microseconds) and then monitor the chemical changes which occur as a function of time. With flash photolysis the formation and depletion of reactive intermediates can be observed as well as the formation of stable products. Thus, greater detail concerning the mechanism of a reaction can be obtained.

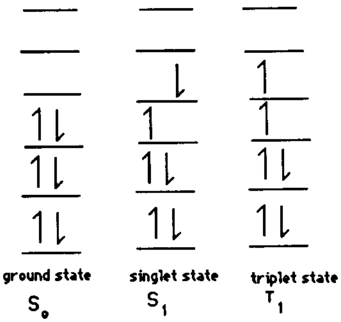
The main objective of my research efforts was to construct a flash photolysis system which would enable one to carry out time-resolved studies of photoinitiated reactions. Such a development involved two major tasks. First, it required upgrading the existing flash rig. Changes in the flash rig included stepping up the micropulser, modifying the design of the flash housing and incorporating an amplifier circuit into the data collection process. Second, it included developing a procedure for sample handling and preparation. Our long range plans involve the study of transition metal hydrides, compounds which are extremely sensitive to oxygen and water. Therefore, it is critical that our procedures for sample preparation allow for sample handling under an inert atmosphere and include additional steps to remove any oxygen and/or water contaminants which might be present initially in either the solvent or solute. To fulfill these stringent sample handling requirements, it was necessary to establish a functioning vacuum line, design a solvent purification system and develop a meticulous step by step procedure for sample preparation.

Once the flash rig was modified and the sample handling procedures developed, it was necessary to test the effectiveness of our new system. To do so, we decided to study systems previously examined in hope of reproducing the observed behavior. Replication of the literature would indicate a properly functioning system.

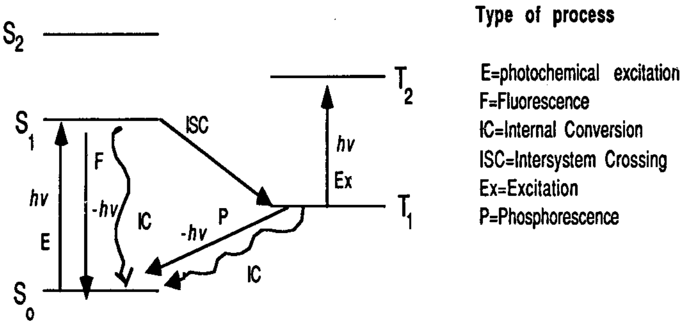
There were four different test systems that we examined. The first one involved measuring the half life of triplet state phenanthrene, an aromatic hydrocarbon. The other three systems we studied were concerned with organotransiton metal complexes. In particular, we were interested in studying the reaction kinetics which occur upon photolysis of $CpFe(CO)_2(n^1\text{-}CH_2C_6H_4\text{-}p\text{-}Me)$, $RhCl(CO)(PPh_3)_2$ and $IrCl(CO)(PPh_3)_2$. When irradiated with UV-vis light, all three species undergo CO photolabilization. The subsequent reaction simply consists of the resulting transient recombining with the dissociated ligand to regenerate the starting material. The bimolecular rate constant for this recombination reaction is known for each complex. It was these values that we wished to reproduce. Each system will be examined in great detail and what we hoped to learn from each discussed. First, consider the phenanthrene case.

Phenanthrene is a system whose excited T_1 state is efficiently quenched by oxygen. Therefore, it serves as a good test for the degree to which the sample handling procedure actually removes oxygen from the system. In order to understand the results of this test and their implications, one needs to know more about the photophysical reaction kinetics of electronically excited phenanthrene.

Phenanthrene is a molecule which absorbs UV light readily in the 220-300 nm range without significant chemical change. When a solution of phenanthrene in hexane is flashed with a short but intense pulse of UV light, the phenanthrene absorbs a photon which causes a paired electron in the highest occupied molecular orbit to be excited to a higher energy unoccupied molecular orbit. The electron configuration in which as many electrons have spin up as have spin down is called the singlet electronic state. When the promoted electron flips its spin so that the two unpaired electrons have parallel spin orientations, the molecule is said to be in the triplet state. (see below)



The triplet state will always be a little lower in energy than the corresponding singlet state. Below is diagramed the low-lying electronic states of phenanthrene.



Here S_0, S_1, and T_1 represent the ground state, first excited singlet state and the first excited triplet state of phenanthrene, respectively.

Despite the fact that T_1 is lower in energy than the first excited singlet state, excitation out of the singlet ground state through absorption of a photon will always result in a singlet excited state, never a triplet.[1] This is the result of a fundamental law of physics which states that angular momentum must always be conserved. When a molecule is excited from the ground state to S_1, it maintains the same electronic spin orientation. In both states, the electrons have opposite spins. However, if the molecule was to assume the T_1 state from the ground state, an electron would have to flip its spin. This change in electronic spin does not conserve spin angular momentum. Such a transition is forbidden.

Once in the first excited singlet state S_1, the phenanthrene molecule may follow one of four pathways. It may fluoresce. In this process, the excited molecule emits a photon and returns to the ground state. It may be quenched by transferring its excitation energy to neighboring molecules via collisions. It may undergo internal conversion to convert the electronic excitation into other modes of motion in the same molecule. Lastly, the S_1 can undergo the forbidden transition to the T_1 state. Such a process is called intersystem crossing and is possible only when the change in spin angular momentum can be balanced by changes in angular momentum elsewhere. In a polycyclic aromatic hydrocarbon such as phenanthrene, intersystem crossing is especially important because more than half the molecules in S_1 decay to S_0 via T_1.[2]

It is the half life of this T_1 state of phenanthrene that we wish to measure. There are three different ways a molecule in the T_1 state can return to the ground state. It can emit a photon, a process known as phosphorescence. However, in the case of phenanthrene this is not a significant deactivation route. It can give up its excitation energy through collisions with other molecules termed quenchers, or it can simply undergo internal conversion. In the case of phenanthrene in both the vapor state and in liquid solutions, T_1 is quenched primarily via internal conversion or through collisions with other molecules. The pathways for the deactivation of triplet state phenanthrene are summarized below.[3]

$$T_1 \xrightarrow{k_1} S_0 \qquad \text{(internal conversion)}$$

$$T_1 + M \xrightarrow{k_2} S_0 + M \qquad \text{(collisional quenching with solvent)}$$

$$T_1 + T_1 \xrightarrow{k_3} S_0 + S_1 \qquad \text{(triplet-triplet annihilation)}$$

$$T_1 + O_2 \xrightarrow{k_4} S_0 + O_2 \qquad \text{(collisional quenching by } O_2\text{)}$$

Assuming all four reactions occur, the rate equation for the deactivation of triplet state phenanthrene is:

$$-d[T_1]/dt = k_1[T_1] + k_2[T_1][M] + k_3[T_1]^2 + k_4[T_1][O_2]$$

Since [M] represents the solvent hexane and is a constant, the rate law can be simplified to:

$$-d[T_1]/dt = k[T_1] + k_3[T_1]^2 + k_4[T_1][O_2] \qquad \text{where } k = k_1 + k_2[M]$$

At phenanthrene concentrations less than 0.01 M, the triplet-triplet annihilation process is reported to be insignificant. We were working at approximately 0.0003 M concentrations and therefore could delete the term $k_3[T_1]^2$. Since our sample was prepared under an inert atmosphere and extensive measures were taken to rigorously remove water and oxygen from the system, the concentration of O_2 should be close to zero. The last term of the rate law could then be dropped leaving the expression:

$$-d[T_1]/dt = k[T_1]$$

According to this equation, the decay of the T_1 state follows first order kinetics. If this is valid, a plot of $\ln[T_1]$ versus time should yield a straight line with the slope equal to the negative of the rate constant for this decay. The T_1 concentration , initially zero, will pass through a maximum as a result of the S_1 to T_1 intersystem crossing and then decay back to zero. This change in the triplet state concentration can be followed by monitoring the T_1 to T_n optical absorption at 482 nm. By Beer's law, absorbance can be plotted against time instead of the actual T_1 concentration.

If our vacuum line and sample handling procedures are effective, little oxygen will be present, and a straight line will be observed for the plot of ln A versus time. The half life for the triplet state of phenanthrene may then be simply calculated as follows:

$$t_{1/2} = .693/k$$

Porter and Wilkinson reported the half life of triplet state phenanthrene to be 64.7 usec.[4] The presence of oxygen in our vacuum line would be indicated by obtaining a much shorter half life for T_1 since oxygen is such an efficient quencher of the triplet state. The outcome of this experiment and its implications will be discussed in the results section.

As another test to prove the efficiency of our newly modified flash photolysis system we sought to reproduce the work done on the organotransition metal complex, $CpFe(CO)_2(n^1\text{-}CH_2C_6H_4\text{-}p\text{-}Me)$. Richard Herrick of Holy Cross College had synthesized and extensively studied this compound. He found that flash photolysis of a hexane solution of $CpFe(CO)_2(n^1\text{-}CH_2C_6H_4\text{-}p\text{-}Me)$ saturated in carbon monoxide produced a transient which decayed exponentially back toward the original baseline but never quite reached it. Similar experiments with excess PPh_3 under a nitrogen atmosphere produced the same transient absorption. However, under these conditions the transient absorption decayed exponentially to a distinctly new baseline of increased absorbance. Solutions containing PPh_3 were also noted as undergoing a color change from yellow to orange following a single flash. An intense band appearing at 1917 cm^{-1} (hexane) indicated the formation of $CpFe(CO)(PPh_3)(n^1\text{-}CH_2C_6H_4\text{-}p\text{-}Me)$.[5]

Herrick concluded that photolyzing $CpFe(CO)_2(n^1\text{-}CH_2C_6H_4\text{-}p\text{-}Me)$ results in the labilization of a CO ligand to form the transient, $CpFe(CO)(n^3\text{-}CH_2C_6H_4\text{-}p\text{-}Me)$.

$$\mathrm{CpFe(CO)_2(n^1\text{-}CH_2C_6H_4\text{-}p\text{-}Me)} \xrightarrow{hv} \qquad (1)$$

$$\mathrm{CpFe(CO)(n^3\text{-}CH_2C_6H_4\text{-}p\text{-}Me)} + \mathrm{CO}$$

"T"

When the complex is photolyzed in the presence of CO only, the resulting transient simply recombines with the dissociated ligand to regenerate the starting complex.

$$\mathrm{CpFe(CO)(n^3\text{-}CH_2C_6H_4\text{-}p\text{-}Me)} + \mathrm{CO} \xrightarrow{k2} \qquad (2)$$

$$\mathrm{CpFe(CO)_2(n^1\text{-}CH_2C_6H_4\text{-}p\text{-}Me)}$$

Note that the transient absorption does not return completely to the original baseline despite the fact that the original complex is being regenerated.

When the organotransition metal complex is photolyzed in the presence of added $\mathrm{PPh_3}$, the complex again undergoes dissociation of a CO ligand (reaction 1). However, the secondary reaction that occurs is different. The $\mathrm{PPh_3}$ combines with the transient to yield the complex, $\mathrm{CpFe(CO)(PPh_3)(n^1\text{-}CH_2C_6H_4\text{-}p\text{-}Me)}$. This new species is evidenced by the absorption at 1917 $\mathrm{cm^{-1}}$.

$$\mathrm{CpFe(CO)(n^3\text{-}CH_2C_6H_4\text{-}p\text{-}Me)} + \mathrm{PPh_3} \xrightarrow{k3} \qquad (3)$$

$$\mathrm{CpFe(CO)(PPh_3)(n^1\text{-}CH_2C_6H_4\text{-}p\text{-}Me)}$$

Reaction 2 is in competition with reaction 3 and is therefore rendered insignificant in this case where the PPh_3 is present in excess.

The bimolecular rate constant for the recombination of the transient and ligand have been determined for both reaction (2) and (3). Recombination with CO and PPh_3 in hexane give bimolecular rate constants of 151 $M^{-1}s^{-1}$ and 1.34×10^3 $M^{-1}s^{-1}$ respectively, yielding a competition ratio of 8.9.[6]

We were only interested in the reaction kinetics associated with the photolysis of $CpFe(CO)_2(\eta^1\text{-}CH_2C_6H_4\text{-}p\text{-}Me)$ in the presence of excess CO. Examining reaction (2), the rate equation for the decay of the transient can be expressed as follows:

$$-d[T]/dt = k_2[T][CO]$$

[T] represents the transient concentration. This is a second order reaction. By carrying out the initial photolysis in the presence of excess CO, the rate equation can be simplified to :

$$-d[T]/dt = k'[T] \qquad \text{where } k' = k_2[CO]$$

The reaction is now pseudo first order. A plot ln [T] versus time should yield a straight line with the slope equal to the negative of the rate constant for this decay:

$$\ln([T]/[T]_0) = -k't$$

By Beer's law, absorbance can be plotted against time instead of the actual transient concentration:

$$[T] = (\varepsilon)(l)(A_t - A_*)$$

$$[T]_0 = (\varepsilon)(l)(A_0 - A_*)$$

$$\ln[(A_t - A_*)/(A_0 - A_*)] = -k't$$

A_* represents the absorption at infinite time. As stated above, the slope of this line gives the value of the rate constant k'. The half life of the transient can be determined using the formula, $t_{1/2} = .693/k'$. Herrick reported the half life of the transient $CpFe(CO)(\eta^3\text{-}CH_2C_6H_4\text{-}p\text{-}Me)$ to be .55 s. The results of our work will be discussed later.

It is important to note that k' is the observed rate constant . To determine the bimolecular rate constant for the recombination of the transient and CO ligand, one could measure the observed rate constant as a function of the added CO and then plot k' versus [CO]. The slope of this plot would yield the desired rate constant for reaction (2). (Note that k_2 could also be calculated if k' was measured at a single known CO concentration. However, this value may not be as accurate as the one obtained from the plot of k' versus [CO].)

We next directed our efforts to a kinetics flash photolysis investigation of the rhodium (I) complex $RhCl(CO)(PPh_3)_2$. Wink and Ford[7] found that when benzene solutions of $RhCl(CO)(PPh_3)_2$ under argon were irradiated with light greater than 315 nm a transient species A was formed. This transient displayed a stronger absorption relative to the starting complex and decayed via second order kinetics over a period of several milliseconds to give absorbances corresponding to the formation of a second species B. This second transient in turn decayed back to the original baseline over several seconds. The observed decay of transient B was determined to be first order.

Flash photolysis of benzene solutions of $RhCl(CO)(PPh_3)_2$ in the presence of excess CO ($0.3 - 1.5 \times 10^{-4}$ M) again resulted in the formation of transient A. However, under these conditions, A decayed at a much faster rate back to the original baseline. There was no evidence for the formation of species B. Plots of ln A versus time were linear, indicating a first order reaction. The observed rate constant was proportional to the CO concentration which implied that the rate law for the decay of A was

$$d[A]/dt = k_5[A][CO]$$

with $k_5 = (6.9 \pm 0.2) \times 10^7\ M^{-1}s^{-1}$.[8]

When benzene solutions of $RhCl(CO)(PPh_3)_2$ were photolyzed in the presence of added PPh_3, A decayed to a new absorption baseline which suggested the formation of another species C. This transient displayed the same spectrum as does $RhCl(PPh_3)_3$,[9] and eventually decayed via second-order kinetics to reform the starting complex $RhCl(CO)(PPh_3)_2$.

Ford and Wink concluded that photolysis of the rhodium (I) complex $RhCl(CO)(PPh_3)_2$ results in the dissociation of the CO ligand to yield the "tricoordinate" intermediate $RhCl(PPh_3)_2$.

$$\underset{}{RhCl(CO)(PPh_3)_2} \xrightarrow{hv} \underset{A}{RhCl(PPh_3)_2} + CO \qquad (4)$$

The secondary reactions which take place depend on the added ligand. A reacts with CO and PPh_3 to give $RhCl(CO)(PPh_3)_2$ and $RhCl(PPh_3)_3$, respectively.

$$RhCl(PPh_3)_2 + CO \xrightarrow{k5} RhCl(CO)(PPh_3)_2 \qquad (5)$$

$$RhCl(PPh_3)_2 + PPh_3 \xrightarrow{k6} \underset{C}{RhCl(PPh_3)_3} \qquad (6)$$

The decay of C back to the original baseline via second order kinetics can be interpreted as follows:

$$RhCl(PPh_3)_3 + CO \xrightarrow{k7} RhCl(CO)(PPh_3)_2 + PPh_3 \qquad (7)$$

The source of the CO ligand is the original rhodium complex. Support for reaction (7) arises from the fact that this reaction is found to be independent of the concentration of added PPh_3. The rate constant for reaction (7) was $k_7 = (2.0 \pm 0.4) \times 10^5\ M^{-1}s^{-1}$.[10]

The nature of transient B (which was detected when benzene solutions of $RhCl(CO)(PPh_3)_2$ were photolyzed in the absence of other added ligands) was the only observation yet to be explained. The spectrum of this longer lived transient is close to that of the known dimer $[RhCl(PPh_3)_2]_2$[11]. Spectral differences were attributed to the fact that the transient spectrum after several milliseconds represents a mixture of the dimer and $RhCl(CO)(PPh_3)_2$. It was concluded that B was formed by the dimerization of $RhCl(PPh_3)_2$, and that this dimerization reaction was in competition with trapping of A by the CO (reaction 5).

$$2\ RhCl(PPh_3)_2 \xrightarrow{k8} [RhCl(PPh_3)_2]_2 \qquad (8)$$

The rate constant for this dimerization was estimated at $k_8 = (2.6 +/- 0.6) \times 10^7\ M^{-1}s^{-1}$.[12] The decay of transient B back to the baseline was explained by the reaction of the dimer with the CO ligand to reform the starting complex.

$$[RhCl(PPh_3)_2]_2 + 2\ CO \xrightarrow{k9} 2\ RhCl(CO)(PPh_3)_2 \qquad (9)$$

It should be fairly obvious that photolyzing a solution of $RhCl(CO)(PPh_3)_2$ in the absence of added ligands will result in a more complicated transient spectrum due to the competition between the dimerization of A (reaction 8) and the recombination of A with the dissociated CO ligand (reaction 5). It was estimated that about

40% of A dimerized to give B in competition with the back reaction with photoliberated CO to give the starting material.[13]

Photolyzing $RhCl(CO)(PPh_3)_2$ under excess CO, however, will render the dimerization reaction insignificant and greatly simplify the reaction kinetics. This is evidenced by Ford and Wink's finding that in the presence of added CO the transient A decayed back to the original baseline without forming the transient B now known to be the dimer $[RhCl(PPh_3)_2]_2$. It was this aspect of their investigation that we sought to reproduce. In particular, we wanted to determine the bimolecular rate constant for the recombination of the "tricoordinate" intermediate $RhCl(PPh_3)_2$ and the CO ligand.

The reaction kinetics of this experiment are very similar to the those of the $CpFe(CO)_2(CH_2C_6H_4\text{-p-Me})$ complex described earlier. Examining reaction (5) it is noted that the decay of transient A should be second order. Photolyzing the rhodium (I) complex in the presence of excess CO however, results in a pseudo first order reaction. A plot of ln A versus time for a specified CO concentration should be linear with the magnitude of the slope equal to the observed pseudo first order rate constant. Carrying out the experiment at various concentrations of CO and plotting k_{obs} as a function of [CO] should also yield a straight line with slope equal to the bimolecular rate constant for reaction 5. We were trying to reproduce the rate constant $k_5 = (6.9 \pm 0.2) \times 10^7 M^{-1}s^{-1}$.

Wink and Ford also conducted a flash photolysis investigation of the iridium complex $IrCl(CO)(PPh_3)_2$. This compound, commonly referred to as Vaska's complex, is the iridium analog of the rhodium (I) compound discussed earlier. When benzene solutions of $IrCl(CO)(PPh_3)_2$ were photolyzed, a transient was observed which decayed via simple second order kinetics to regenerate the original baseline. The second-order kinetics for the decay of this transient suggested that photoexcitation of $IrCl(CO)(PPh_3)_2$ leads to the reversible labilization of one ligand as seen for the rhodium (I) analog.

$$IrCl(CO)(PPh_3)_2 \xrightarrow{hv} IrCl(PPh_3)_2 + CO \quad (10)$$

The observed relaxation process is simply the recombination of the transient $IrCl(PPh_3)_2$ with the CO ligand.

$$Ir\,Cl(PPh_3)_2 + CO \xrightarrow{k11} IrCl(CO)(PPh_3)_2 \quad (11)$$

The transient formed upon photolysis of Vaska's complex does not dimerize. Therefore, the reaction kinetics associated with the flash photolysis of $IrCl(CO)(PPh_3)_2$ are simpler than those associated with its rhodium (I) analog. Photolyzing solutions of $IrCl(CO)(PPh_3)_2$ in the presence of excess CO , will render the reaction pseudo first order as was the case with the $CpFe(CO)_2(n^1\text{-}CH_2C_6H_4\text{-p-Me})$ and

$RhCl(CO)(PPh_3)_2$ complexes described earlier. Plotting the observed rate constant as a function of CO concentration, Ford and Wink determined the value of the bimolecular rate constant for the recombination of $IrCl(PPh_3)_2$ and CO to be (2.7 +/- 0.7) x 10^8 $M^{-1}s^{-1}$.[14] We wished to reproduce this value.

EXPERIMENTAL

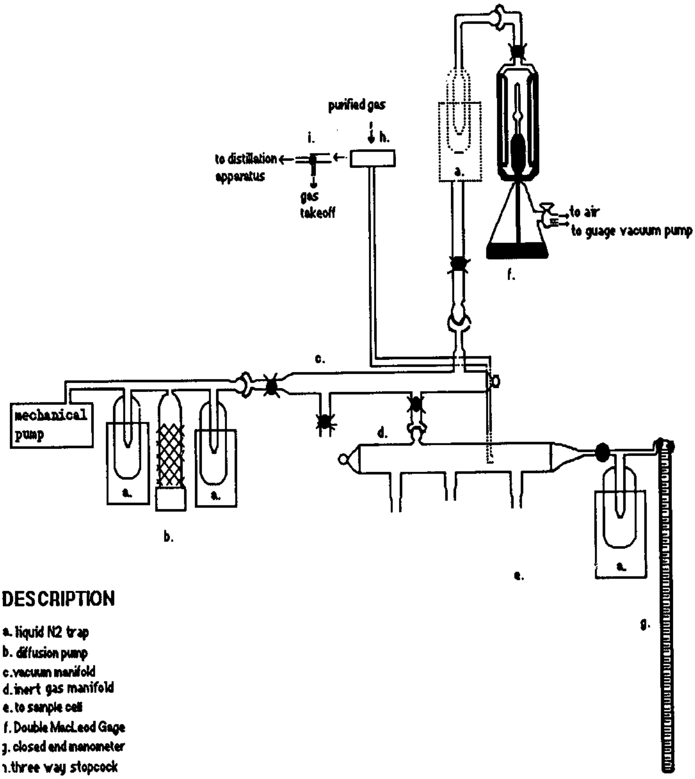
The experimental procedures involved in conducting a flash photolysis investigation are quite rigorous and can be divided into two sections, solution preparation and sample photolysis. In the paragraphs that follow, the design, function and operation of the equipment required for both these aspects will be discussed. First consider the equipment and procedures necessary for sample preparation.

As stated in the introduction, we wanted to construct a system which would allow us to study transition metal hydrides via flash photolysis. Such compounds, however, are extremely sensitive to oxygen and water and must therefore be prepared under an inert atmosphere. To achieve such a condition, we employed a vacuum line (Figure 1). The primary components of this vacuum line include evacuation pumps, a vacuum manifold, an inert gas manifold, a Double McLeod Gauge and a gas purification system. Each component as well as the instructions for operating the vacuum line will now be discussed in detail.

Perhaps the most prominent feature of our vacuum line is the main manifold . This manifold is separated from the pumps by a stopcock. When the stopcock is open, the pumps actively pull a vacuum on the manifold. When closed, the pumps are isolated from the manifold. This design is important for it allows the pumps to be turned off and vented without exposing the manifold to air.

There are two pumps employed to produce the desired vacuum.

FIGURE 1



DESCRIPTION

a. liquid N2 trap
b. diffusion pump
c.vacuum manifold
d.inert gas manifold
e. to sample cell
f. Double MacLeod Gage
g. closed end manometer
h.three way stopcock
i. two way stopcock

VACUUM LINE

The primary pump is a mechanical pump which can evacuate the system to a pressure of 1×10^{-3} torr. The secondary pump is an oil diffusion pump which further reduces the pressure of the system. When both pumps are operating at maximum efficiency, the pressure obtained should be as low as 1×10^{-6} torr. Actively pumping on our line, a pressure of $2\text{-}3\times10^{-6}$ torr is achieved.

The pressure inside the vacuum line is measured using a device known as the Double McLeod Gauge. This sophisticated gauge employs the use of 24 pounds of mercury to measure pressures ranging from 1 torr to 1×10^{-6} torr. As a result of the great quantity of mercury, one must exercise extreme caution when using the Double McLeod Gauge. Detailed instructions for its use are posted on the wall behind the vacuum line.

Another important aspect of the pumping system are the liquid nitrogen traps which are located upstream of both pumps. These traps serve to condense out potentially corrosive vapors before they reach the pumps thereby preventing damage to the pumps and harmful vapors from being pulled into the laboratory. A liquid nitrogen trap is also placed after the Double McLeod Gauge to prevent any mercury vapors from entering the vacuum manifolds.

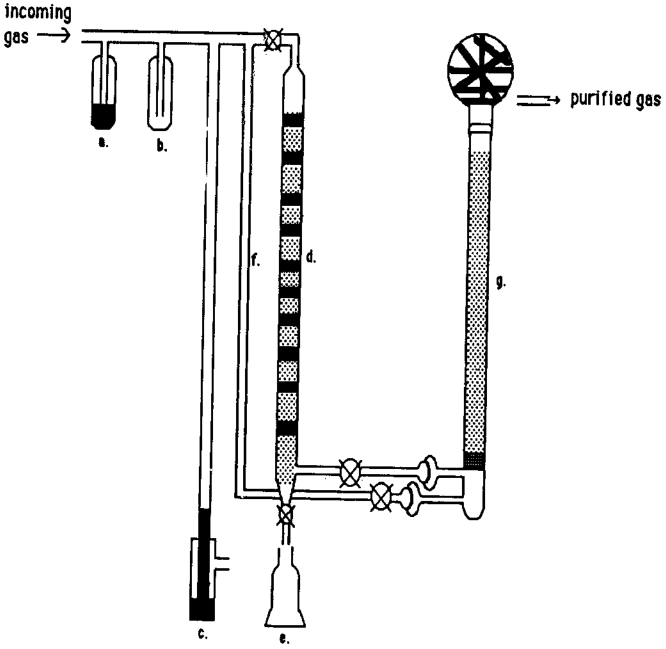
The most interesting aspect of our vacuum line, however, is the secondary manifold (often called the inert gas manifold) for this is where sample preparation takes place. There are three ports located on this manifold where the solvent and sample can be introduced. However, before the caps to these ports can be removed and the Schlenk tube containing the solvent and the T-assembly containing the sample be attached, the evacuated secondary manifold must be pressurized. To do so, a source of inert gas has been incorporated into the design of the vacuum line. This inert gas line is separated from the secondary manifold via a stopcock. By opening this stopcock, one allows inert gas to flow into the secondary manifold thereby pressurizing it and enabling it to be opened to the atmosphere. (Note before opening the stopcock leading to the inert gas line, it is important to first close the stopcock joining the primary and secondary manifolds for it is not necessary to pressurize the entire system.) In our vacuum line, argon is the inert gas used. Argon was selected over other inert gases because it is heavier than air. Thus when opened to the atmosphere, air will not filter back into the manifold and serve as a contaminant provided the flow of argon is sufficiently high. The inert gas manifold therefore provides for a continuously oxygen and water free environment. It should be obvious that the inert gas manifold should only be exposed to the atmosphere when attaching or removing the Schlenk tube and/or T-assembly.

Before the argon enters the inert gas manifold however, it must first pass through a gas purification system (Figure 2). This is such because the high purity gases obtained commercially are not sufficiently pure enough for our stringent requirements. The main purpose of this gas purification system is to remove any oxygen and water present in the argon so that these contaminants are not introduced into the manifold upon pressurizing it.

The main features of this gas purification system are an oil

FIGURE 2

GAS PURIFICATION SYSTEM



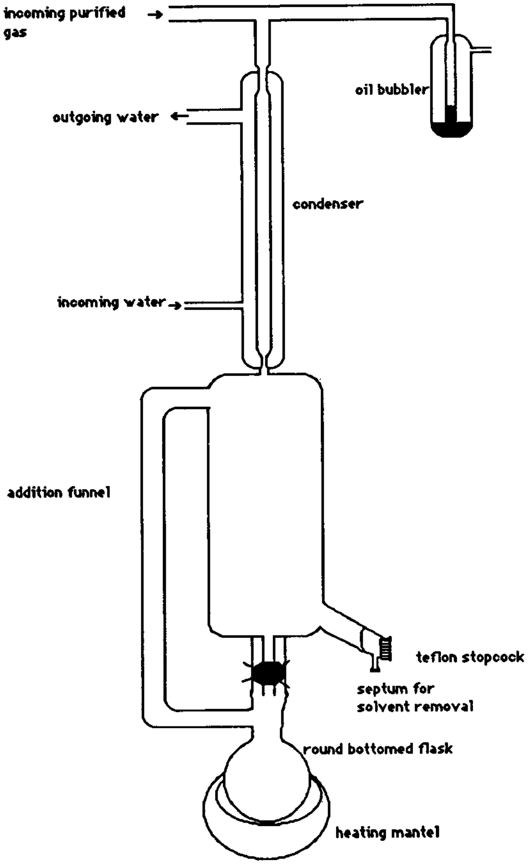
DESCRIPTION
a.oil bubbler
b. empty trap
c. Hg blowout
d.BASF catalyst column wrapped with heating tape
e.BASF water takeoff
f.BASF column bypass
g.P205 column

bubbler, an Hg blowout, a BASF catalyst column and a P_2O_5 column. The oil bubbler is simply used for gas flow regulation. The Hg blowout is a safety feature which will prevent breakage if the system is accidentally overpressurized. The BASF column is used to remove oxygen from the argon. BASF catalyst is an oxygen scavenger and is purchased as a mixture of copper, magnesium, barium, chromium and zinc oxides. Hydrogen gas is passed over this catalyst which reduces the oxides to the reactive metals. When the argon flows through this column, any oxygen in the gas will react with the metals to form the oxides and in the process be removed from the argon. The P_2O_5 column is important because it removes any water present in the argon. P_2O_5 reacts with water to form phosphoric acid.

Above is summarized the major aspects of our vacuum line. There is still one piece of apparatus separate from the vacuum line yet crucial to sample preparation that must be discussed. This is the solvent purification system (Figure 3). Extensive measures are taken to remove oxygen and water from the solvent and solute once they are attached to the vacuum line, and these steps will be discussed later in the section detailing sample preparation. However, in addition to these steps, we felt it was important to prepurify the solvent before it reached the vacuum line.

The design of the solvent purification system is shown in Figure 3. The still is important to sample preparation for it allows the solvent to be refluxed over $LiAlH_4$ and distilled under purified argon.

FIGURE 3



solvent purification system

The $LiAlH_4$ serves to reduce any water present in the solvent, while the the argon displaces the oxygen liberated as the solvent refluxes.

The procedure developed for operating the still is fairly straightforward. When first starting up the still the solvent (approximately 250 ml) and the $LiAlH_4$ (approximately 1-2 teaspoons) are placed in the round bottom flask and refluxed for 48 hours. While refluxing, the teflon stopcock separating the addition funnel and round bottom is open. Thus, the solvent vapors simply condense back into the flask. (It is during this process that any contaminating O_2 molecules are displaced by the argon.) To withdraw some solvent, the stopcock between the funnel and flask is closed and the teflon stopcock leading to the sidearm opened. This allows the solvent to collect in the addition funnel and sidearm. The solvent can then be removed via a gas-tight syringe injected through the septum covering the sidearm. Note that it is necessary to reflux the solvent for 48 hours when the solvent is first introduced into the still. For successive runs, the solvent only has to be refluxed long enough to collect the desired volume of solvent. Note also that Figure 3 only shows one still. Our solvent purification system actually consists of two such stills. Both are identical in design but are used for two different solvents. Presently, one still contains purified benzene and the other hexane. This is a great convenience for we no longer have to continuously clean and restart the still when we want to alternate between experiments using benzene and hexane as solvents.

Thus far the equipment necessary for preparing an oxygen and water free solution has been described in much detail but little has been said concerning the step by step procedure one follows in preparing such a sample. Figure 4 shows the procedural flowchart for doing a run.

FIGURE 4

PROCEDURAL FLOWCHART FOR SAMPLE PREPARATION

1. Measure the pressure using the Double McLeod Gauge. Pressure must be between 2-3x10e^{-6} torr in order to proceed with preparation.

2. Weigh out the desired amount of sample into a glass boat. (Typical quantities for phenanthrene and $RhCl(CO)(PPH_3)_2$ runs are $4x10^{-4}$ and $1\text{-}1.5x10^{-3}$ grams, respectively.) Place the boat and a small magnetic stirring bar in the cold- finger of the T-assembly.

3. Prepare a sodium-potassium alloy by heating 1 part of sodium and 5 parts of potassium under xylene until melted and carefully mixing the molten metals with a stirring rod. The alloy should be one large globule. (Note this step does not have to be repeated for every run. The excess alloy made can be saved and used for future experiments.)

4. Transfer approximately .25 ml of the Na/K alloy via disposable pipet into the schlenk tube. A small magnetic stirring bar

should also be placed in the schlenk tube.

5. Connect both the T-assembly and schlenk tube to the vacuum line. To do so, first close the stopcock between the main manifold and inert gas manifold and then open the stopcock leading to the inert gas source. Argon will flow into the secondary manifold and pressurize it. (Note that the mercury blowout will indicate when the inert gas manifold is pressurized, and the oil bubbler will aid in gas flow regulation.) Remove the caps from the ports, attach the T-assembly and schlenk tube and then close the stopcock to the Argon source.

6. Open the stopcock separating the main and secondary manifold. Pump on the inert gas manifold for 5 minutes.

7. Pump out the bulb of the T-assembly stopcock for 1 minute. Then open the stopcock and pump on the cold-finger for 3 minutes.

8. Close the stopcock separating the main and inert gas manifolds, and fill the secondary manifold, schlenk tube and T-assembly with argon. Once pressurized, open the main stopcock and pull a vacuum on these three sections. Repeat this backfill operation one more time. This ensures the removal of the oxygen present in the schlenk tube and T-assembly when they were first introduced onto the vacuum line.

9. Fill the inert gas manifold and schlenk tube (but not the T-assembly) with argon.

10. Withdraw 20 ml of prepurified solvent from the still using a gas-tight syringe and transfer it into the schlenk tube. The schlenk tube has a sidearm into which the solvent can be injected.

11. Freeze the solvent and pump on the inert gas manifold for 5 minutes to remove the argon previously added. Close the stopcock between the main and secondary manifolds. Thaw the solvent and stir it for five minutes.

12. Carry out 4 freeze-pump-thaw cycles. Each cycle involves freezing the solvent so that it is not evaporated during the pumping process, pulling a vacuum on the schlenk tube for 5 minutes to remove any gases especially oxygen, thawing the solvent and stirring it for 5 minutes to release any gases trapped in it.

13. Open the T-assembly stopcock and distill over 12.5 ml of solvent into the cold-finger. The original cold-finger was calibrated, and the volume of the solvent could be directly read. However, it cracked while performing an experiment and could only be replaced with an uncalibrated one. The formula which relates the height of the liquid's meniscus to the volume is:

$$n \text{ cm} = 1 \text{ cm} + (x \text{ ml} - 0.70 \text{ ml})/(1.08 \text{ ml/cm})$$

where n denotes the height of the liquid's meniscus above the outside bottom of the cold-finger , and x represents the desired volume of solvent.

14. Close the T-assembly stopcock. Thaw the solvent in the cold-finger, and stir the solution for 15 minutes. The sample is now ready to be flashed.

15. Pressurize the inert gas manifold in order to remove the T-assembly and schlenk tube. Cap the ports immediately after removal to minimize the exposure of the manifold to the atmosphere.

Before describing the procedure involved in photolyzing a sample, it is important to mention the purity and sources of the materials that we used in our various experiments. For our phenanthrene work, we used 98+% pure and zone refined,99.5+% pure phenanthrene obtained from Aldrich Chemical Company. Unexpected results led us to believe that both these compounds contained some anthracene contamination. Therefore, the 98+% phenanthrene was purified twice using the procedure outlined in Figure 5 to specifically remove the anthracene. The $CpFe(CO)_2(n^1\text{-}CH_2C_6H_4\text{-p-Me})$ compound was synthesized by and received from Richard Herrick of Holy Cross College. The rhodium (I) complex $RhCl(CO)(PPh_3)_2$ and its iridium analog $IrCl(CO)(PPh_3)_2$ were both purchased from Strem Chemical, Inc. located in Newburyport, MA. All three organotransition metal complexes were used without further purification. Solvents used in our work included spectragrade benzene and hexane both obtained from Aldrich Chemical Company.

FIGURE 5

PROCEDURE FOR THE PURIFICATION OF PHENANTHRENE

1. Dissolve 10.00 g of phenanthrene in 25.00 ml of benzene. Saturate the solution with maleic anhydride. Reflux the mixture for 4 hours. Maleic anhydride reacts selectively with anthracene to form

an addition product.

2. Remove the benzene by roto evaporation.

3. Transfer the remaining solid consisting of phenanthrene, the addition product and unreacted maleic anhydride into a 250 ml beaker. Add just enough 95% EtOH to get the aforementioned compounds into solution. Gentle heating is required to dissolve the solids (use a hot plate). Be careful not to overheat.

4. In a separate beaker, dissolve in a minimum amount of water the quantity of KOH required to convert the addition product and unreacted maleic anhydride into salts. Since maleic anhydride and anthracene react in a 1:1 ratio, the molar amount of KOH required should equal the molar amount of maleic anhydride added. However, in this experiment KOH is added in 6 fold excess. Add this KOH solution to the beaker containing the phenanthrene, addition product and maleic anhydride.

5. Remove the beaker from the hot plate. As the solution cools, the phenanthrene will start to precipitate. Add enough water to the solution to precipitate the rest of the phenanthrene out. Note that the addition product and unreacted maleic anhydride were converted into salts upon addition of KOH and therefore are soluble in water. Phenanthrene however, is insoluble in water.

6. Filter to collect the phenanthrene.

7. Wash the phenanthrene with 100 ml of 1% NaOH solution.

8. Wash the phenanthrene 3 times with water using 50 ml each time.

9. Recrystallize the phenanthrene. Remove the phenanthrene

from the filter paper and place in a 250 ml beaker. While gently heating, dissolve the phenanthrene in the necessary amount of 95% EtOH. Remove the solution from the hot plate and allow it to cool slowly.

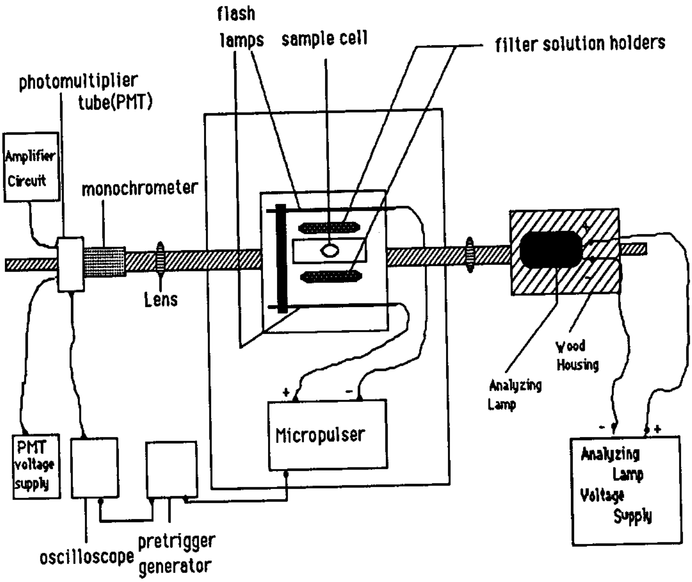
10. Filter the phenanthrene and place it in an oven to dry. The oven should be maintained at 80°C for phenanthrene melts at 101°C.

Preparing the oxygen free sample is only half the battle. Now one has to photochemically excite the sample and watch for the formation of any transients. To photolyze our samples, we used the flash photolysis apparatus shown in Figure 6. The main components of this rig are the micropulser, the flash housing containing the flash lamps and filter solutions, the analyzing lamp, the monochromator, the photomultiplier tube (PMT), the amplifier circuit and the oscilloscope. Before describing each component in detail and the operation of the flash rig, it is important to discuss the changes we made in its design.

The flash photolysis apparatus was modified in three important respects. First, the micropulser was sent to Xenon Corporation to be upgraded from 100 to 400 joules per flash. This change gives us more flexibility in terms of the reactions we could study.

Second, the larger flash lamps necessary at these higher energies required some changes in the design of the flash housing. The basic layout of the housing remained the same. The sample cell was still located between two brass plates, and the plates were still in front of the filter solutions which proceeded the flash lamps. The

FIGURE 6



Flash Photolysis Apparatus

important modification, however, was in the distance between the two brass plates. We decreased the width between these plates from 3.5 cm to 1.5 cm so that the cell was almost flush against the plates. This change was made in order to reduce the amount of scattered light that was previously being observed. Although seemingly trivial, such a task required us to completely reconstruct the housing. Another change we made in the flash housing was to install resistors which would aid in triggering the flash lamps.

The last modification we made in the flash rig was to incorporate an amplifier circuit into the detector system. This circuit was designed and built by Chris Steding who works in the electrical engineering shop on campus. This addition was invaluable for it allows us to study reactions for which the transient absorptions are low. A basic description of the flash rig and how it is used to photolyze a sample will now be discussed.

Once the sample is prepared, it is placed in the flash housing between the two brass plates. The analyzing lamp, flash housing, and monochromator are then aligned so that the beam from the analyzing lamp shines directly through the cell, and the amount of light reaching the monochromator is a maximum. Lenses are used to focus the analyzing light through the sample cell and onto the monochromator. The alignment is facilitated by the fact that all the elements are mounted on an optical rail. Once the alignment is satisfactory, the voltage on the photomultiplier voltage supply is dialed up until the trace on the oscilloscope is deflected 5 boxes. This deflection corresponds to 100% transmittance.

The capacitor in the micropulser is then charged to 10,000 volts. Upon triggering, the flash lamps filled with xenon gas fire, and 400 Joules of energy are released. Before reaching the sample cell, the light from the flash lamps encounters filter solutions which only allow certain wavelengths of light to pass through and absorb the rest. When selecting a filter solution, it is important to remember that filter solutions should transmit the wavelengths required for excitation or photodissociation and absorb the wavelength at which the species of interest is being monitored. Failure of the filter solutions to block the monitoring wavelength will result in the attenuated signal from the analyzing light being "swamped out" by the much brighter flash light. With phenanthrene, the exciting wavelengths are in the range of 220-300 nm while the monitoring wavelength corresponding to the T_1 to T_n transition is 482 nm. A solution of $NiCl_2$ and $CoCl_2$ was selected as the filter because such a solution transmits light between 247 and 332 nm and strongly absorbs light greater than 474 nm. The spectral properties of the $NiCl_2$ and $CoCl_2$ solution were obtained by running a UV-VIS spectrum. For $RhCl(CO)(PPh_3)_2$ and its iridium analog $IrCl(CO)(PPh_3)_2$ the irradiation wavelengths are >315 nm and >260 nm, respectively. For a UV cutoff of 320nm, a 0.1 M solution of $NaNO_3$ was used, while for a UV cutoff of 260 nm, a 0.1 M solution of $Na_2S_2O_3$ was employed.[15] Note that in photolyzing $IrCl(CO)(PPh_3)_2$ the UV absorbance of benzene limited useful excitation to >295 nm.

Light that passes through the filter solutions then enters the sample cell. Provided it is of the correct wavelength, the light will be absorbed by the sample, and a chemical reaction will take place. As a reminder, the photophysical reaction that is taking place in the phenanthrene experiment is the populating of the T_1 state. For the three organotransition metal complexes, photoexcitation results in the labilization of a CO ligand to form a transient. Once we have started the reaction and generated the transient, we need a way to monitor the reaction as a function of time. This is where the analyzing light, monochromator and photomultiplier tube play a role.

In flash photolysis studies, the photoinitiated reactions are examined by monitoring the absorption of a transient as a function of time. In all the systems we have studied, the transient absorption peaks immediately after flashing the sample and then decays over time. By recording the rate of decay a great deal of information concerning the reaction can be ascertained. It is the analyzing lamp that provides the light that the transient absorbs. When the analyzing light passes through the sample cell, the transient generated absorbs a particular wavelength. The analyzing beam after the cell is therefore attenuated with respect to that particular wavelength. This beam then goes to the monochromator. The monochromator is set to pass light of only one wavelength onto the photomultiplier tube. This preferred wavelength corresponds to the wavelength that the transient absorbs at. The PMT then converts this light signal into a proportional current which is then changed into a voltage reading. If desired, this output can be amplified using the amplifier circuit. Finally, the output signal is recorded on an oscilloscope in the form of percent transmittance versus time. Transmittance can be converted into absorption via Beer's law, and absorbance can be plotted as a function of time to see if the decay of the transient follows first order kinetics.

RESULTS AND DISCUSSION

Measurement of the half-life of triplet state phenanthrene.

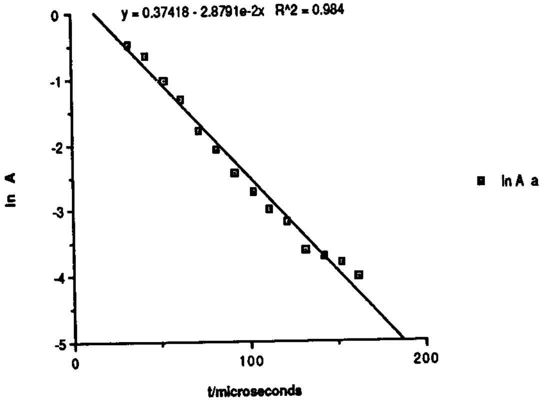
The first system we studied was phenanthrene. As stated in the introduction, phenanthrene is a molecule whose excited T_1 state is efficiently quenched by oxygen. Therefore, it serves as a good test for determining the efficiency of our vacuum line. The presence of oxygen in the vacuum line would be indicated by a much shorter half life for the triplet state of phenanthrene. We performed many phenanthrene experiments, and the results of the more significant runs will now be discussed.

The sample handling procedure outlined in Figure 4 is more involved than the one Porter and Wilkinson followed. Since the T_1 state of phenanthrene is only sensitive to oxygen and not to water like most organotransition metal complexes, they only degassed the solvent . They did not prepurify the solvent or use a Na/K alloy. In trying to duplicate the half life of the T_1 state of phenanthrene, we felt it was necessary to simulate the experimental conditions explicitly as outlined in the literature. Therefore, we only carried out the four freeze-pump-thaw cycles and the trap to trap distillation. No further purification steps were taken. (This type of run in which no further purification steps are made will be referred to as a basic run.) If our vacuum line is functioning properly, the phenanthrene sample will be oxygen free, and the decay of the T_1 state will be first order. A plot of the natural log of absorbance versus time should yield a straight line with a slope equal to the rate constant for the transient decay. Figure 7 shows the results of this first basic phenanthrene run.

FIGURE 7

RUN 062488a

BASIC PHENANTHRENE RUN



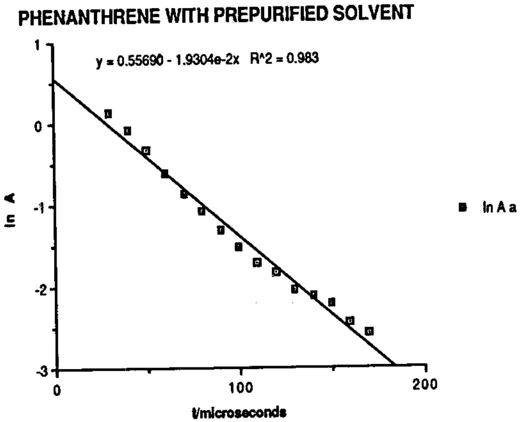
Carefully examining the plot, it is noted that there was some curvature in the fit. Assuming the decay was first order, the half life of the T_1 state was calculated to be 24 usecs. Recall that Porter and Wilkinson reported a half life of 64.7 usecs. Phenanthrene is a well studied system, and there is little doubt that the T_1 decay is first order under the conditions outlined in the introduction. The greatly shortened half life indicated that there was significant oxygen contamination.

In an attempt to reduce the oxygen concentration in the phenanthrene sample, we added a purification step. Instead of using solvent directly from the bottle, prepurified solvent from our still was used (Figure 3). This solvent was refluxed over $LiAlH_4$ and under an argon atmosphere and as such should contain less water and oxygen. However before proceeding with this second run, the pressure inside the vacuum line was measured and discovered to be too high. Apparently there was a leak in the line. By regreasing some suspicious stopcocks and fixing the black wax seals of selected joints, we were able to reduce the pressure to an acceptable level ($2x10^{-6}$ torr) after pumping on the system for an extended period of time. Figure 8 shows the decay of triplet state phenanthrene when prepurified solvent was used. The half life of the T_1 state was found to be 36 usecs. This value is closer to the literature value but still indicated the presence of some oxygen. Also, the plot shows some curvature.

In the next run, a Na/K alloy was added to the Schlenk tube containing solvent that was taken directly from the bottle. Prepurified solvent was not used in order to view the effects of each purification step separately. Before the run was started, a pressure reading was taken. The pressure was at the system's optimum. Figure 9 illustrates the results obtained.

FIGURE 8

RUN 070588a

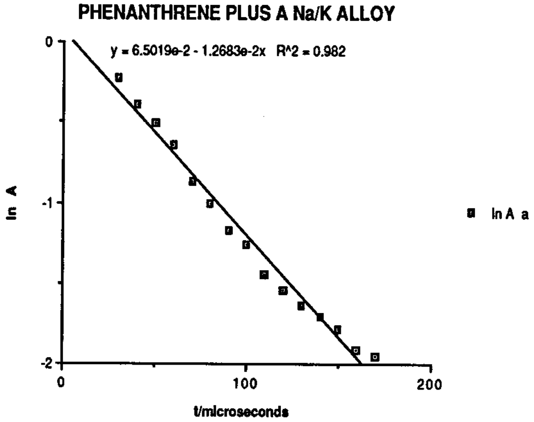


The half life of the T_1 state for the Na/K alloy run was determined to be 54 usecs. This value is much closer to the published half life and was therefore very encouraging. We were making progress as far as increasing the half life of triplet state phenanthrene. However, the question as to why the decay was not linear still remained.

At first glance, it appeared that the additional purification steps were effective. The half life of T_1 improved from 24 usecs to 36 usecs when prepurified solvent was used and increased to 54 usecs when the Na/K alloy was employed. However, these results can be

FIGURE 9

RUN 070788a

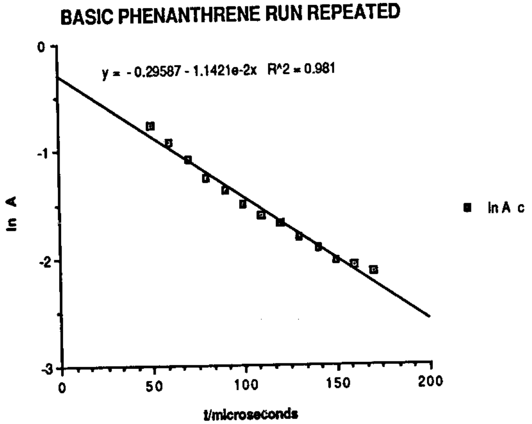


misleading. The improvement observed could and most likely was the result of the vacuum line itself functioning better. In the beginning, the pressure was not being monitored everyday, and the system was being shut down at night. A leak could develop, and we would be unaware of it. It was only on the Na/K run that we were confident and pleased with the pressure. It was then also that we decided to leave the vacuum line pumping all the time and check the pressure before each run.

Skeptical that our system might have been leaking during the early experiments, we decided to step back and repeat the basic phenanthrene run. Figure 10 is the plot we obtained.

FIGURE 10

RUN 070888c



The half life of T_1 for this repeated run was found to be 61 usecs. This is in good agreement with the half life value cited by Porter and Wilkinson. From this run we concluded that the additional purification steps (prepurified solvent and the Na/K alloy) were unnecessary when preparing phenanthrene samples. The fact that the half life of T_1 increased and approached the published value with each additional purification step was most probably due to a better functioning vacuum line. However, we retained the additional purification steps as part of the procedure for phenanthrene preparation for practice. Organometallic compounds are extremely sensitive to water in addition to oxygen. Therefore, prepurified solvent and the Na/K alloy are crucial to the preparation of these complexes for such steps remove the water. Since the additional steps do not require a lot more time and do not have a negative effect on the phenanthrene reaction, we included them in our phenanthrene work in order to establish a routine which could also be used in our organometallic work.

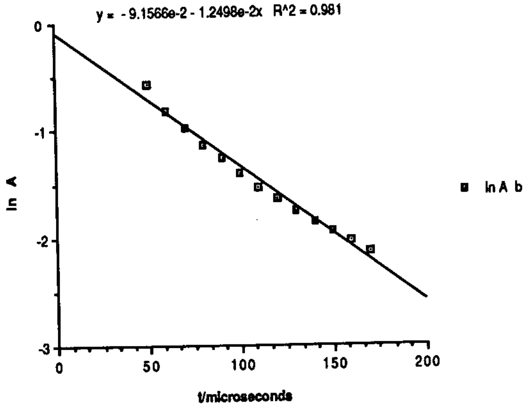
The half life of the T_1 state obtained in the run above is well within the range of experimental error associated with the published value. However, we were troubled by the fact that we were not observing the straight line associated with a first order decay. We hypothesized that the curvature might be the result of "bumping". This means that the solution bubbles when flashed, and this leads to the nonlinear effect. To test this hypothesis, we pressurized the cell with argon before removing the T-assembly from the vacuum line. Pressurizing the cell would prevent the solution from bubbling. Figure 11 shows the results of this experiment. Curvature was still observed in the plot. Therefore, it did not appear that bumping was the explanation. The half life value for triplet state phenanthrene in this run was 55 usecs.

We next hypothesized that perhaps another species was present in our phenanthrene sample which was deactivating the T_1 state. This would explain the nonlinear behavior observed because the first order rate law derived for the decay of T_1 is only valid assuming no quenchers are present. Anthracene was our guess as the most probable contaminant. Anthracene seemed likely because it is a structural isomer of phenanthrene and is therefore very difficult to separate from it. Also, efficient quenching of triplet state phenanthrene by anthracene whereby the latter is raised to the triplet level has been previously cited.[16]

FIGURE 11

RUN 071188b

PHENANTHRENE PLUS ARGON TO PREVENT "BUMPING"



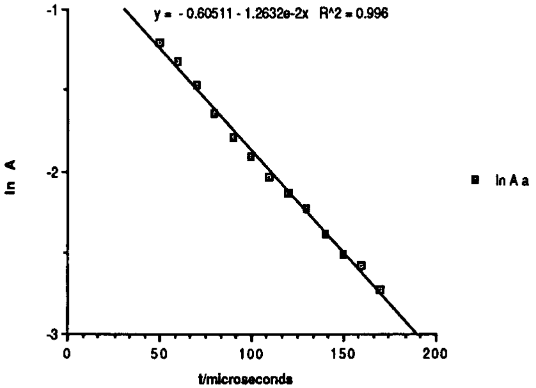
A UV-VIS absorption spectrum of a 1.0×10^{-2} M solution of our phenanthrene sample in cyclohexane was then ran. Absorption peaks at 357 nm, 370 nm and 376 nm were observed. Such absorptions are characteristic of anthracene. To verify that these peaks were in fact due to anthracene, the solution was then spiked with pure anthracene and another spectrum taken. The absorbances at the aforementioned wavelengths increased dramatically. It was therefore concluded that anthracene was present in the phenanthrene sample. Using Beer's Law, it was determined that the phenanthrene sample (which had a nominal purity of 98+%) had approximately 0.1% anthracene contamination.

We therefore obtained from Aldrich Chemical Company the highest purity phenanthrene they had. This sample was rated at 99.5+% pure. A basic run using this higher purity phenanthrene was then performed. The result of this experiment is shown in Figure 12.

FIGURE 12

RUN 071888a

BASIC RUN USING 99.5+% PURE PHENANTHRENE



The plot appears to have much less curvature. One could even venture to say it was a straight line. However, one has to be extremely careful when interpreting this plot. When this sample was flashed, it was noted that the peak transient absorption was only 50% whereas peak absorptions were typically 80-85%. It was also our experience in the past that we only obtained straight lines when the total change in percent transmittance was not large. Therefore, the fact that we obtained a straight line might be due to the fact that we were only plotting a relatively small change in signal. The half life for T_1 in this experiment was 55 usecs.

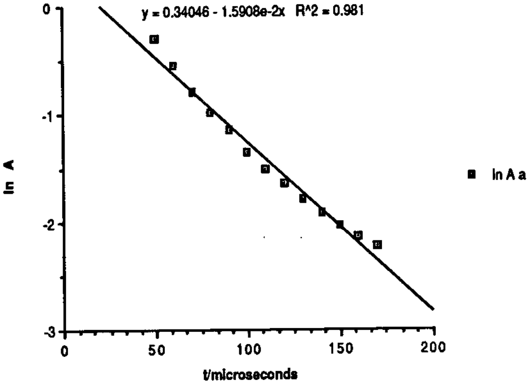
To determine if the reduced curvature was really the result of using a higher purity sample of phenanthrene or due to plotting only a small change in transmittance, we repeated the run making sure to weigh out 0.4 mg of phenanthrene. In the former run, 0.3 mg of phenanthrene was presumably weighed out, but the actual amount might have been even less than this. It is extremely difficult to weigh out such small quantities with accuracy . The amounts we used in our phenanthrene work were almost equal to the drift associated with our balance. Figure 13 shows the plot obtained when a greater quantity of phenanthrene was used.

The total change in transmittance for this run was much greater than for the previous one. The transient absorption peaked at 93% and then decayed to 22% over approximately 200 microseconds. Examining Figure 13, it is obvious that the data points did not fall in a straight line. Therefore, we concluded that our hypothesis (which proposed that the nonlinear behavior observed was the result anthracene quenching triplet state phenanthrene) was incorrect. The half life for this run was 44 usecs.

FIGURE 13

RUN 071988a

REPEATED BASIC RUN USING 99.5% PURE PHENANTHRENE



It then occurred to us that perhaps the 99.5+% pure phenanthrene sample had some anthracene present in it. Therefore, we ran a UV-VIS absorption spectrum of a 1.0×10^{-2} M solution of this phenanthrene sample in cyclohexane. The results were shocking. Not only were there absorbances at 357 nm, 370 nm and 376 nm indicating the presence of anthracene, but they were stronger than the absorbances observed for the 98+% pure sample. Using Beer's Law, the 99.5+% pure phenanthrene sample was estimated to contain 0.85% anthracene. Presumably the process Aldrich employs for purifying phenanthrene is not specific for anthracene removal and only serves to concentrate it. Therefore, our hypothesis might still be true: Anthracene contamination might be the cause of the nonlinear behavior.

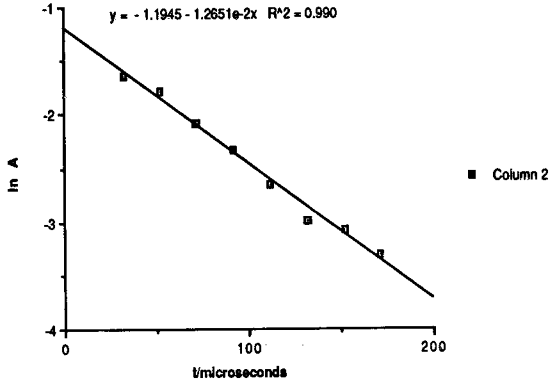
We took it upon ourselves to free the phenanthrene from the anthracene. Carrying out the procedure outlined in Figure 5 twice and then running a UV-VIS spectrum on the purified phenanthrene, it was noted that the absorption peaks characteristic of anthracene were no longer present. This indicated that the anthracene concentration was reduced beyond the limit of detection. A basic run using this purified phenanthrene sample was then performed. Figure 14 is the plot of ln A versus time for this particular experiment. The plot appears to be linear. The half life for T_1 was calculated to be 55 usecs.

We carried out another run using this anthracene free phenanthrene in the hope of reproducing these results. If the results of the aforementioned experiment were reproducible, then we could be confident that anthracene was the cause of the previously observed nonlinear decay. The procedure followed was the same as the one for the run above with one exception. Prepurified solvent from the still was used instead of solvent directly from the bottle. Figure 15 shows the results. The plot is a definite curve. We were now sure that anthracene was not the cause of the nonlinear decay.

FIGURE 14

RUN 110388f

BASIC RUN USING PHENANTHRENE FREED FROM ANTHRACENE

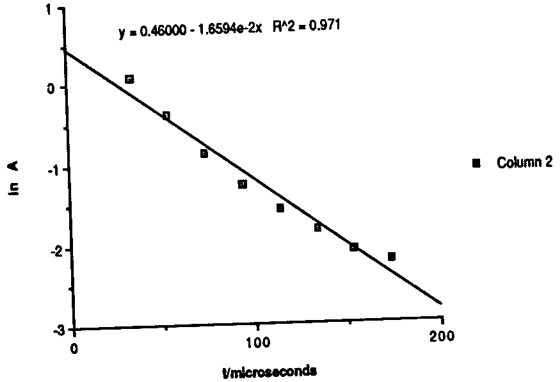


Having eliminated "bumping" and anthracene quenching as the cause of the nonlinear plots, it was thought that perhaps triplet-triplet annihilation was responsible for the deviation from first order kinetics. At phenanthrene concentrations less than 0.01 M, this annihilation process is reported to be insignificant. We were working at concentrations lower than this, but perhaps this assumption is not valid, and triplet-triplet annihilation is an important deactivation pathway for the T_1 state.

FIGURE 15

RUN 111988c

PHENANTHRENE FREED FROM ANTHRACENE PLUS PREPURIFIED SOLVENT



If triplet-triplet annihilation was occurring in the solution, one would expect the process to cease or become negligibly small as the T_1 concentration was reduced. If triplet-triplet annihilation caused the deviation from first order kinetics, one would expect a plot of ln A versus time to yield a straight line once the concentration of the T_1 state was sufficiently low. This was the theory behind our next experiment. We wanted to test if our plots would become linear as we decreased the T_1 concentration.

To control the concentration of the triplet state, we varied the energy of our flash rig. The more energy delivered to the sample cell, the greater the number of excited phenanthrene molecules and the more populated the T_1 state. Normally the capacitor is charged to 10,000 volts which results in 400 Joules of energy being delivered to the flashlamps. In this experiment, however, we stepped down the voltage in approximately 1,000 volt increments. Obtaining linear plots at the lower voltages would support the hypothesis that triplet-triplet annihilation was the cause of the deviation from first order decay. Figures 16 and 17 show the plots obtained when the capacitor is charged to 10,000 volts and 6,000 volts, respectively. For both these runs, the purified phenanthrene was used. No other purification steps were taken.

FIGURE 16

RUN 120688d

FLASHING PURIFIED PHENANTHRENE WITH CAPACITOR CHARGED TO 10,000 volts

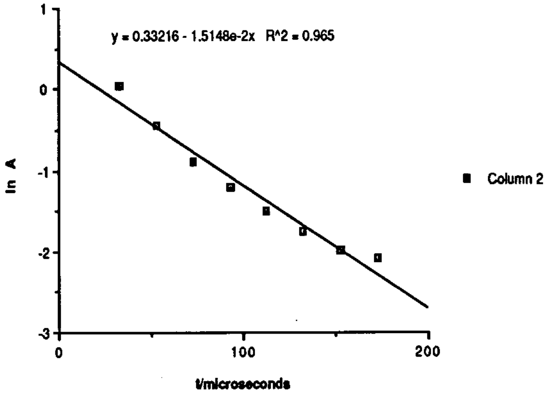
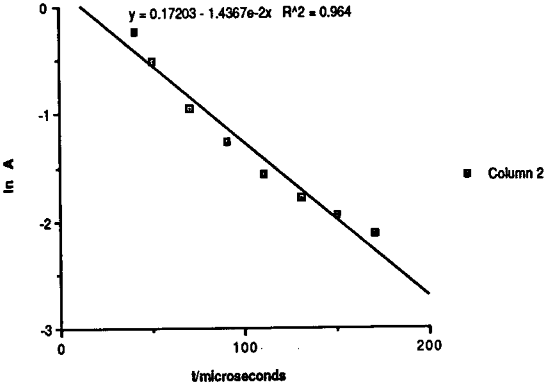


FIGURE 17

RUN 120688r

FLASHING PURIFIED PHENANTHRENE
WITH CAPACITOR CHARGED TO 6,000 volts



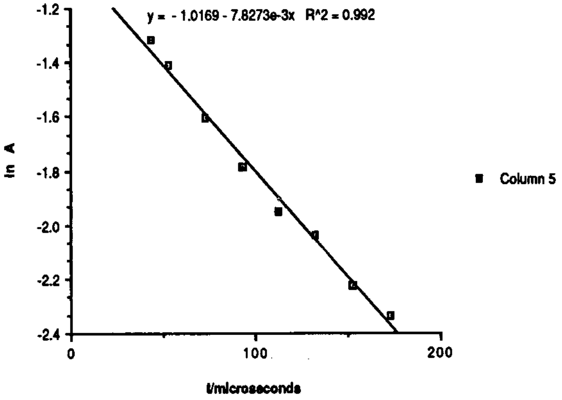
Both of these plots showed curvature. First order kinetics was not observed even at the lower energy. Therefore, it was concluded that triplet-triplet annihilation was probably not the cause of the nonlinearity. The half lives associated with Figures 16 and 17 were 46 usecs and 48 usecs, respectively.

To completely rule out the possibility of triplet-triplet annihilation as the cause of all our grief, we flashed a phenanthrene sample at a substantially lower concentration, 4.6×10^{-6} M. (Note because of the small amount of phenanthrene needed for this run, we decided not to weigh the required crystalline material directly into a glass boat. Instead, we prepared a stock solution of the purified phenanthrene using hexane right from the reagent bottle. We then removed the volume of this stock solution that contained the desired moles of phenanthrene and placed it in a glass boat. The solvent was allowed to evaporate. The boat was then put in the cold-finger of the T-assembly, and the sample prepared as usual. The exact concentration was determined by running a UV-VIS spectrum on the sample after it was flashed.) Because the phenanthrene concentration is significantly lower, the T_1 concentration should also be small. If triplet-triplet annihilation was occurring in the other solutions, it should be dramatically reduced in this less concentrated sample. Figure 18 shows the result of this experiment.

FIGURE 18

RUN 120988a

FLASHING A PHENANTHRENE SOLUTION OF LOW CONCENTRATION TO ELIMINATE TRIPLET-TRIPLET ANNIHILATION



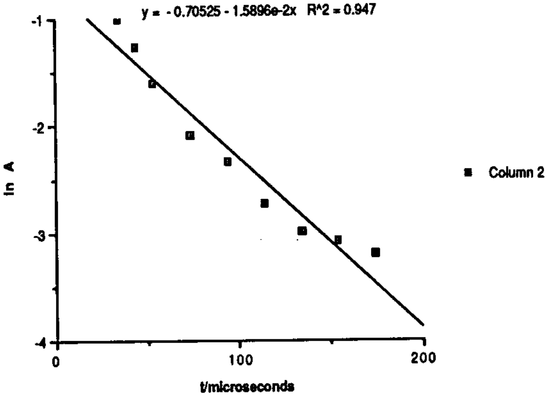
At this low phenanthrene concentration, triplet-triplet annihilation was presumably eliminated. The fact that nonlinearity was still observed implied that some other process was causing it.

The fact that we observed straight lines when the total change in transmittance was small led us to believe that perhaps there was a fault in our detector system. It was possible that our system was not capable of tracking large changes in signal over a short period of time. To test this hypothesis, we decided to decrease the the signal output. Examining Beer's Law, $A = \varepsilon c l$, where A represents absorbance, and ε, c and l represent the extinction coefficient, concentration and path length respectively, it is noted that absorbance can be decreased by using a sample cell with a shorter path length. We only have cells that are 12 cm long, but we could decrease the path length by taping portions of this cell. Taping the cell with black tape prevents light from photolyzing the phenanthrene in that section. Therefore the species of interest, T_1, will not be formed. Recall that it is the path length of the absorbing species that is important and not the physical length of the cell. If the nonlinearity was a result of the detector system not being capable of tracking large changes in signal over a short period of time, one would expect a straight line when the change in signal was relatively small.

Taping 67% of our cell with black tape (4 cm on each end), we were able to decrease the path length of the triplet state phenanthrene enough to reduce the peak absorption to 58%. Figure 19 shows the plot of ln A versus time for this experiment in which the total change in signal was deliberately made small.

FIGURE 19

RUN 120688v
FLASHING PURIFIED PHENANTHRENE WITH
97% OF SAMPLE CELL TAPED



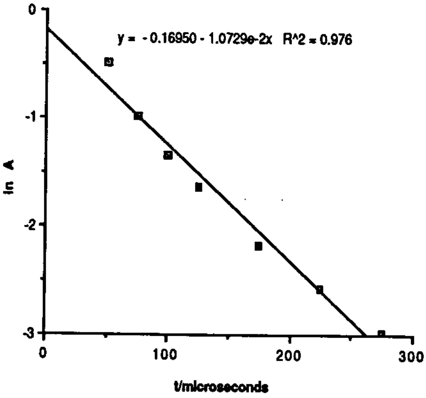
The linearity problem was not solved by decreasing the output signal. From this we concluded that it was probably not a fault in our detector system that was causing the observed curvature.

Our last attempt at solving the phenanthrene caper was to recrystallize the phenanthrene from 95% ethanol again, and then do a basic run. The last step in the phenanthrene purification process required one to place the phenanthrene in a drying oven to remove any solvent. In the process of drying, the phenanthrene melted because the oven was too hot. Instead of being light and fluffy flakes, the phenanthrene fused into one clump. We thought this would have no effect on the phenanthrene and used it for all the experiments above which called for purified phenanthrene. However, we decided to recrystallize the phenanthrene just to make sure that in the process of melting it did not decompose. Figure 20 shows the results.

FIGURE 20

RUN 010989e

BASIC RUN USING PHENANTHRENE RECRYSTALLIZED FROM 95% EtOH



The plot obtained was similar to the previous ones. Therefore we concluded that the phenanthrene did not decompose upon melting. The half life for T_1 in this run was 65 usecs.

We spent a great deal of time investigating the phenanthrene system, yet we were still unable to solve the linearity problem. With no more ideas to try, we decided to leave the phenanthrene system for awhile. It is important to note that our phenanthrene work was not completely fruitless. We were successful in increasing the half life of triplet state phenanthrene. Recall that for our first phenanthrene run we got a T_1 half life of 24 usecs. By improving our vacuum line and sample handling techniques we were able to increase this half life to 65 usec which is in good agreement with the half life Porter and Wilkinson reported.

A flash photolysis investigation of $IrCl(CO)(PPh_3)_2$.

The next system we investigated was the iridium complex, $IrCl(CO)(PPh_3)_2$. Recall from the introduction that this complex undergoes dissociation of the CO ligand to form the "tricoordinate" intermediate $IrCl(PPh_3)_2$ when photolyzed. We were interested in monitoring the decay of this "tricoordinate" transient which results from the species simply recombining with the photolabilized CO. The decay follows simple second order kinetics. Ford and Wink previously studied this system and determined the bimolecular rate constant for the recombination reaction to be (2.7 +/- 0.7) x 10^8 $M^{-1}s^{-1}$. If we could reproduce this work we could be fairly certain that our flash system was working properly.

Unfortunately the experiment did not proceed as planned. When we flashed a 1.0×10^{-4} M solution of $IrCl(CO)(PPh_3)_2$ in benzene, no transient absorption was noted at 460 nm as observed by Ford and Wink. Believing that the crystalline material might have sublimed when we pumped on it to remove the oxygen, we conducted an experiment to determine the rate of sublimation of $IrCl(CO)(PPh_3)_2$ under vacuum with active pumping. It was concluded that little if any sublimation occurs. We then repeated the experiment hoping that the first run was an exception. When the second 1.0×10^{-4} M solution was flashed, no transient absorption was observed again. We then feared the reason we were not getting any transient absorption was because our system was not delivering enough energy to the cell, and as a consequence, the starting material was not being photolyzed. We placed reflective foil in the flash housing in an attempt to direct scattered light into the sample cell, but this had no effect.

If insufficient energy was the reason no transient absorption was observed in the Vaskas' experiment, then we were faced with a major crisis. As stated in the introduction, we wanted to develop a flash system that would permit the study of organometallic hydrides. If there was not enough energy to dissociate the $IrCl(CO)(PPh_3)_2$ complex, then there would probably be insufficient energy to photolyze other organometallic compounds. We would be limited to investigating systems for which 400 joules was enough to cause a reaction. Upgrading our system was not an alternative. We just had our flash rig upgraded from 100 to 400 joules, and it would be too expensive and time consuming to have it modified again. It was at this point that we began studying the complex

$CpFe(CO)_2(n^1\text{-}CH_2C_6H_4\text{-}p\text{-}Me)$.

Flash Photolysis of $CpFe(CO)_2(n^1\text{-}CH_2C_6H_4\text{-}p\text{-}Me)$

Richard Herrick of Holy Cross College synthesized and extensively studied the complex, $CpFe(CO)_2(n^1\text{-}CH_2C_6H_4\text{-}p\text{-}Me)$. He discovered that it underwent labilization of a CO ligand upon photolysis to yield the intermediate $CpFe(CO)(n^3\text{-}CH_2C_6H_4\text{-}p\text{-}Me)$. This intermediate then combined with the dissociated ligand to regenerate the starting material. The decay of the transient followed simple second order kinetics. By carrying out the reaction in the presence of excess CO ligand, however, Herrick was able to determine the pseudo first order rate constant for the decay. Using this observed rate constant, he then calculated the half life of the transient to be .55 second. If we could reproduce this work, we would be able to answer many questions concerning our flash system. First, if we were able to generate a transient, we could be more confident that our system was energetic enough to allow for organometallic studies. Second, if the transient generated had the same half life as the value Herrick determined, we could conclude that our system was functioning properly.

Upon receiving the compound, it was noted that the complex had darkened somewhat. Therefore, before preparing a sample for flashing, we ran an infrared spectrum on the sample to ensure that it had not decomposed. Herrick indicated that the compound should show absorption peaks at approximately 2000 cm^{-1} and 1947 cm^{-1}. The infrared spectrum we ran displayed absorptions at 2000 cm^{-1} and 1955 cm^{-1}. It was thus concluded that the compound was fine. It is also important to note that the infrared spectrum was taken under an argon atmosphere for solutions of $CpFe(CO)_2(n^1\text{-}CH_2C_6H_4\text{-p-Me})$ are not air stable.

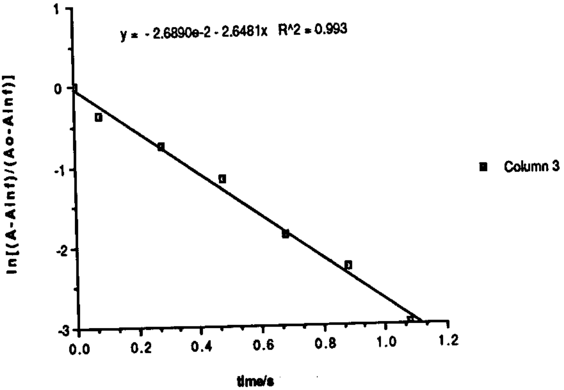
The procedure for preparing the $CpFe(CO)_2(n^1\text{-}CH_2C_6H_4\text{-p-Me})$ sample differed from that outlined in Figure 4. The procedure used was less involved and is as follows. Approximately 1.7 mg of the solid $CpFe(CO)_2(n^1\text{-}CH_2C_6H_4\text{-p-Me})$ was put in the cell. The cell was then flushed with CO through a septum. Next hexane was added using a syringe. Then CO was bubbled through the mixture for 15 minutes. The sample was flashed as usual. Figure 21 shows the results.

This run was significant in two respects. First, a transient absorption was observed. This implied that our system was energetic enough to photolyze an organometallic complex. Second, the plot of ln A versus time was linear. Recall that the reaction was made pseudo first order by carrying out the photolysis in the presence of excess CO. This run would have been perfect if the half life of the transient was .55 seconds. Unfortunately, the half life was almost twice as short. For this run, the half life was calculated to be .26 seconds. Even though we did not duplicate Herrick's half life for the $CpFe(CO)(n^3\text{-}CH_2C_6H_4\text{-p-Me})$ species, we were encouraged by our results.

FIGURE 21

RUN 120188b

PHOTOLYZING A CpFe(CO)2(n1-CH2C6H4-p-Me) SOLUTION PREPARED WITHOUT THE USE OF THE VACUUM LINE

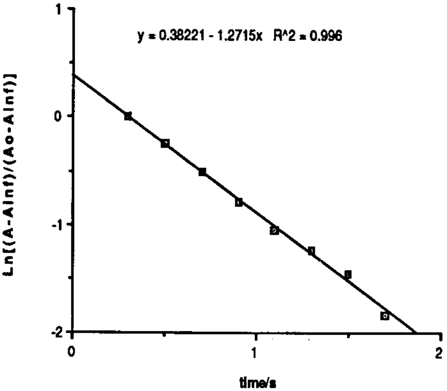


Noting that solutions of CpFe(CO)$_2$(n^1-CH$_2$C$_6$H$_4$-p-Me) are sensitive to air , we thought that the half life of the transient might be increased if we were more efficient in degassing the cell. Therefore we decided to prepare the sample using the vacuum line. The procedure used for sample preparation is as follows. 2.1 mg of CpFe(CO)$_2$(n^1-CH$_2$C$_6$H$_4$-p-Me) was weighed out and transferred to the T-assembly. The T-assembly was then attached to the vacuum line, evacuated and backfilled with argon. (Note that the T-assembly was evacuated and backfilled with argon twice.) The cell was then flushed with CO, and 21 ml of dried and degassed solvent added using a syringe. The sample was flashed as usual. Note when flashing a solution of $CpFe(CO)_2(n^1\text{-}CH_2C_6H_4\text{-p-Me})$, it is important to minimize the sample's exposure to the analyzing light for the sample is slightly photochromic. Figure 22 shows the results of this experiment.

FIGURE 22

RUN 121388a

PHOTOLYZING A CpFe(CO)2(n1-CH2C6H4-p-Me) SOLUTION PREPARED WITH THE USE OF THE VACUUM LINE



Again the plot was linear indicating the transient decay was first order. The half life for the transient was calculated to be .545 seconds. This is what Herrick observed! Preparing the sample on the vacuum line appeared to make the difference.

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This run was very important. In addition to boosting our morale, it indicated that our system was functioning properly. It also led us to believe that the nonlinearity observed in our phenanthrene work was not the result of our equipment, but the consequence of something inherent in the phenanthrene system.

Having a great success with the $CpFe(CO)_2(n^1\text{-}CH_2C_6H_4\text{-}p\text{-}Me)$, I wish we could stop here. However, we were determined to get another test system to work. Therefore, we returned to the $IrCl(CO)(PPh_3)_2$ system.

We prepared and flashed several $IrCl(CO)(PPh_3)_2$ solutions. However, we did not observe a transient in any of the runs. Once a signal was observed. It was so large that it went off screen. We were encouraged, but later discovered this was due to an electrical effect. The circuit was underdamped. We were puzzled by the fact we were not seeing a transient absorption. We then decided to look at the rhodium analog of Vaska's complex.

Recall that the kinetics associated with the flash photolysis of $RhCl(CO)(PPh_3)_2$ are more complicated than those observed for $IrCl(CO)(PPh_3)_2$. This is such because the transient which results upon photolysis of $RhCl(CO)(PPh_3)_2$ can undergo two reactions. It can recombine with the dissociated ligand to generate the starting material, or it can react with another transient to form a dimer. If a solution of $RhCl(CO)(PPh_3)_2$ is flashed in the absence of added ligands, the recombination reaction and the dimerization reaction are in competition with each other. It is therefore very difficult to interpret the decay of the transient. Photolyzing the complex in the presence of excess CO, however, renders the dimerization reaction insignificant, and a pseudo first order decay for the transient is observed. Knowing the observed rate constant for this first order decay at various CO concentrations (or simply one [CO]), the bimolecular rate constant for the recombination reaction can be determined. If we could reproduce the rate constant Ford and Wink determined for this recombination, we would have another positive test indicating the efficiency of our system.

We are currently in the process of modifying our vacuum line to allow for the addition of CO. Therefore, we have not yet flashed a solution $RhCl(CO)(PPh_3)_2$ in the presence of excess CO. This will be our next experiment. However, I will mention that we did flash a basic $RhCl(CO)(PPh_3)_2$ solution for some qualitative information, and a transient absorption was observed. This is very encouraging.

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