

6-1992

Construction Of An Instrument For Doing Fast Time-Resolved Infrared Spectroscopy

Susan R. Richter

Union College - Schenectady, NY

Follow this and additional works at: <https://digitalworks.union.edu/theses>

 Part of the [Chemistry Commons](#)

Recommended Citation

Richter, Susan R., "Construction Of An Instrument For Doing Fast Time-Resolved Infrared Spectroscopy" (1992). *Honors Theses*. 2036.

<https://digitalworks.union.edu/theses/2036>

This Open Access is brought to you for free and open access by the Student Work at Union | Digital Works. It has been accepted for inclusion in Honors Theses by an authorized administrator of Union | Digital Works. For more information, please contact digitalworks@union.edu.

UN X2
K5516
1992

**Construction Of An Instrument For Doing
Fast Time-Resolved Infrared Spectroscopy**

By

Susan R. Richter

• • • • •

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

Union College

June, 1992

ABSTRACT

ii

RICHTER, SUSAN Construction of an Instrument for Doing Fast Time-Resolved Infrared Spectroscopy. Department of Chemistry, June 1992.

We have designed and assembled a system for doing flash photochemical studies of organotransition metal carbonyl complexes with fast time-resolved infrared detection. Photolysis is with conventional xenon flashlamps (400J/flash) and time resolved infrared absorption spectra are measured with a diode laser (Laser Photonics, Inc.) and indium antimonide detector operating in the range 1700 - 2100 cm^{-1} . Signals are collected and averaged on a digital oscilloscope (LeCroy 9410) for subsequent computer storage and analysis. The waveform is downloaded to the computer where calculations of percent transmittance and absorbance vs time are calculated. The information is then transferred to a spreadsheet where further calculations can be done and the information can be plotted. The spectral range of the probe laser corresponds to the CO stretching region in transition metal carbonyl complexes thus making it suitable for detailed time resolved studies of the kinetics and mechanisms of these species.

Table of Contents

III

Section I: Introduction.....	1
Section II: Flow System.....	4
Section III: Flash System.....	7
Section IV: IR Probe System.....	10
Section V: Data Collection and Analysis.....	12
Section VI: Test Reaction with $Mn_2(CO)_{10}$	14

Table of Figures

iv

Figure I: System Schematic.....	3
Figure II: Flow System.....	5
Figure III: Flash Housing.....	7
Figure IV: Sample Cell.....	8
Figure V: Absorbance vs time for Mn(CO) ₅ at 827 nm.....	22
Figure VI: 1/Absorbance vs time for Mn(CO) ₅ at 827 nm.....	23
Figure VII: Absorbance vs time for Mn ₂ (CO) ₉ at 500 nm.....	24
Figure VIII: 1/Absorbance vs time for Mn ₂ (CO) ₉ at 500 nm.....	25

We are interested in the photochemical kinetics and mechanisms of organotransition metal carbonyl complexes. We wish to use flash photolysis to initiate these reactions and both UV/Vis and IR absorption spectroscopy to track the formation/depletion of reactants, intermediates, and products. The duration of these reactions ranges from a few microseconds to several seconds. The focus of my research, which is described here, was to construct an instrument that will track the progress of these very fast reactions using fast IR detection.

Four goals were set at the beginning of this project. The first was to design a system to do fast time-resolved infrared spectroscopy. Many critical decisions and judgments had to be made here. For example, the type of IR source, detector, amplifier, and monochromator to use. Furthermore, the design of the flow system and solution cell were determined. The second goal was to build the system. The third goal was to create computer software for data collection and analysis. The final goal set for this project was to test the instrument by replicating the published work on $\text{Mn}_2(\text{CO})_{10}$. The first three goals have been accomplished and the fourth is in progress.

The instrument is divided into four components for discussion. The four components are the flow system, the flash system, the IR probe system, and the data acquisition and analysis system. As shown in Figure 1, the solution flows into the sample cell from the flow system (not shown), where it is flash photolyzed. The flashlamps are activated by the flashlamp power supply. Changes in the absorbance of the solution are monitored by the continuous beam from a tunable IR laser. As shown in Figure 1, this beam passes through the monochromator, double passes through the sample cell and goes to the detector. The transient signal is amplified, sent to the oscilloscope, where it is

digitized and displayed, and finally transferred to a computer where the information is saved for subsequent analysis.

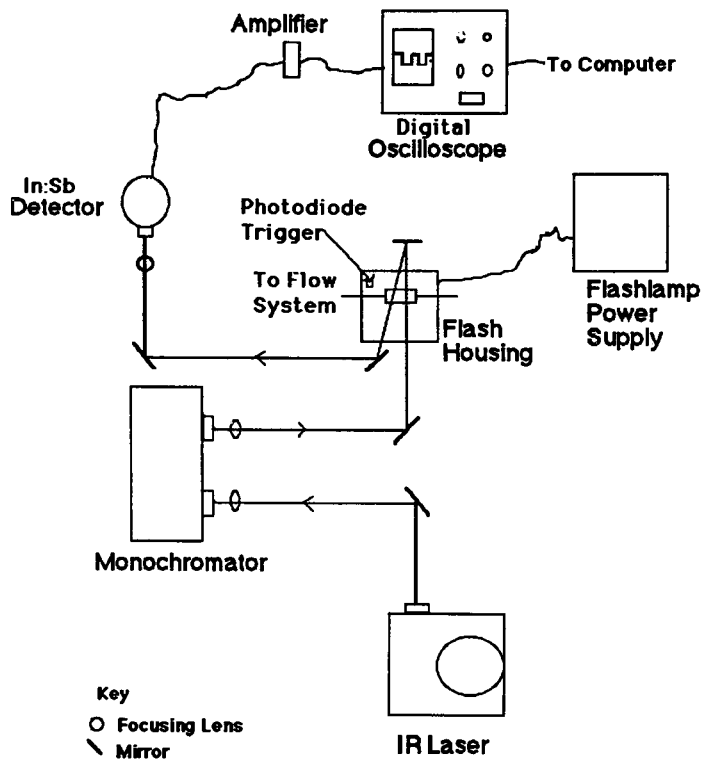


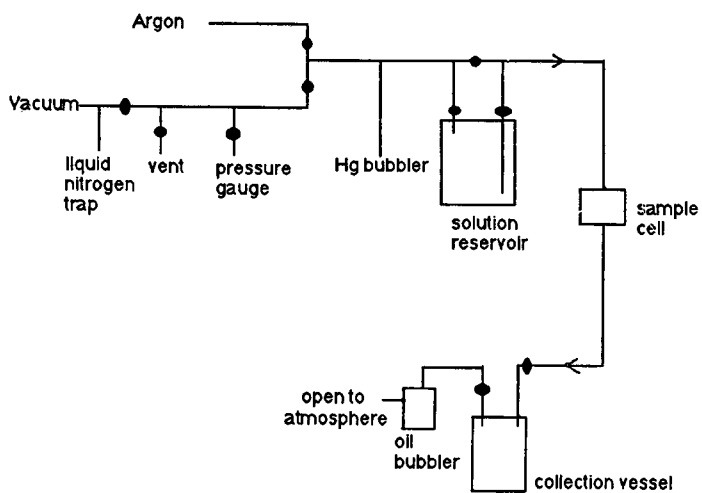
Figure 1: SYSTEM SCHEMATIC

FLOW SYSTEM

The purpose of using a flow cell rather than a conventional static cell, is to be able to perform multiple runs without demounting the cell after each run to replace the reactants. The flow system allows the solutions to continuously flow from the solution reservoir through the sample cell as runs are performed. This design is important in our system because we want to discard the products formed after each run. Using the flow cell allows us to flush the products out of the cell as new solution flows in. The transition metal carbonyl complexes that will be studied are air-sensitive, so the flow system must be able to flow the solution from the solution reservoir through the sample cell without exposure to air.

The solution also has to be prepared unexposed to air. This is achieved by preparing the solution in a glove bag. The glove bag is flushed with nitrogen gas several times to purge it of air. The bag is then filled with nitrogen gas and the solution is prepared in the reservoir in the glove bag. The reservoir is then attached to a high-vacuum line where a series of freeze-pump-thaws are performed to remove the nitrogen gas and remaining air. The reservoir is then attached to the flow system with the valves from it to the flow system closed.

The first thing that must be done in preparing the flow system for use is to pump out the air present in the system. As shown in Figure 11, this is done by pulling a vacuum on the system to remove the air. A gauge is used to measure and monitor the pressure in the flow system. When the appropriate pressure is reached (~2 mtorr), and the system is holding that pressure (no leaks in the system), the system is repressurized with argon gas. This is done by closing the



KEY

● Vacuum Valves

Figure II: FLOW SYSTEM

vacuum pump valve and opening the argon valve. A mercury bubbler is used to prevent an overpressure of argon in our flow system. An oil bubbler is used as an outlet for the argon gas. When the mercury begins to bubble, we know our system is slightly above 1 atm. pressure with argon gas. The argon valve is closed and the vacuum valve is opened again. This procedure is done three times to purge the system of air. When the system is flushed out, the argon gas is allowed to flow continuously through the system.

The system is now ready to be used. The valves to the solution reservoir are opened. An overpressure of argon pushes the solution out of the reservoir, through the sample cell, and into the collection vessel. When one is finished performing runs, the valves to the solution reservoir are closed. The collection vessel is detached and the waste solution is distilled in order to recycle the solvent.

FLASH SYSTEM

The flash system is composed of the sample cell, the flash housing, the Faraday cages, the filter solutions, and the flashlamps.

As shown in Figure III, the flash housing is a wood frame box which contains the flashlamps, filter solutions and the sample cell. The housing separates the cell from the flashlamps by filter solutions. This permits us to control the wavelength of light from the flashlamps used to photolyze our solutions. The flash housing has openings on two sides to allow the IR probe beam to pass through the cell.

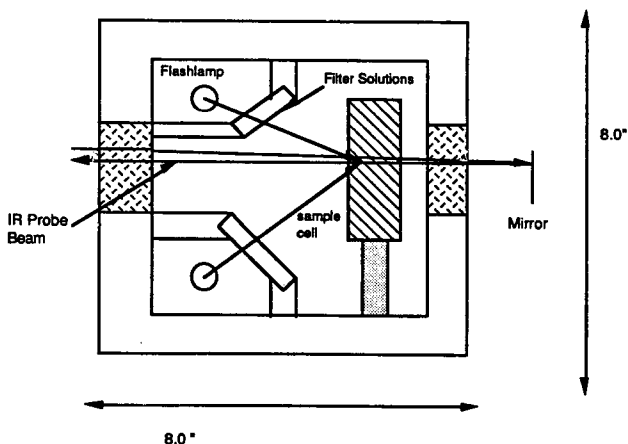


Figure III: FLASH HOUSING

As shown in Figure IV, the cell is a stainless steel cylinder with entrance and exit holes for the solution to flow through. The solution passes between two CaF_2 windows where the solution is flash photolyzed. The windows are held in place by two threaded brass rings. An o-ring is placed on both sides of the windows to make an airtight seal.

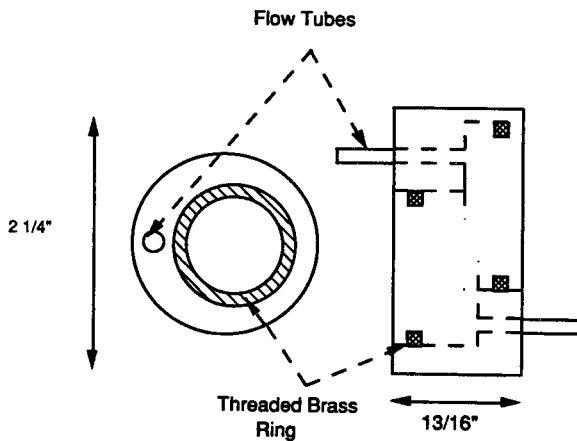


Figure IV: SAMPLE CELL

Two xenon flashlamps which are operated at 400 J/pulse (FWHM = 17 μ sec) are used to initiate the photochemistry in the sample cell. The flashlamps are activated by the flashlamp power supply. The flashlamps are positioned in front of slits which angle to the sample cell to maximize the amount of light hitting the cell. Filter solutions are placed between the cell and flashlamps to control the wavelength of light hitting the sample and to keep unwanted IR light from the flashlamps from hitting the detector.

The discharging flashlamps produce a high intensity electromagnetic pulse which may interfere with the detector, amplifier, and oscilloscope. Therefore, we have constructed a Faraday cage around the flash housing and the flashlamp power supply to block this interference. The Faraday cage is a wood frame with copper mesh placed around it. It has openings on two sides to allow the IR beam to pass through. There is also a safety interlock attached which turns off the high voltage power supply when the housing is accessed.

IR PROBE SYSTEM

The IR probe system consists of an IR laser, monochromator, In:Sb detector, amplifier, oscilloscope, and photodiode trigger. As shown in Figure 1, the IR beam goes through the monochromator, double passes through the sample cell, goes to the detector, to the amplifier, and then to the oscilloscope.

The IR laser is a Laser Analytics Inc., liquid nitrogen cooled diode laser. This laser was chosen for use over an alternative CO laser for reasons discussed by Eugene Bernard (1). The laser is tunable throughout the carbonyl stretching range, 1700 - 2100 cm^{-1} . Additional diodes are needed to probe at lower or higher frequencies. This frequency range is of interest because the transition metal carbonyl intermediates generated in the flash photolysis absorb in this frequency range.

The laser beam first goes to the monochromator which operates as a filter to select the desired wavelength from the laser beam. The light produced from the laser is not purely monochromatic, so the monochromator is needed to select the desired wavelength. The dial on the monochromator is numbered arbitrarily so a calibration between the monochromator readings and the actual frequency of light passing through it had to be determined. This was done by Steven Kinne (2).

After the desired wavelength of light comes out of the monochromator it double passes through the cell. Double passing the beam through the cell enhances the signal to noise ratio. The IR beam, whose transmitted intensity may have been changed by the formation of intermediates or products or by the consumption of reactants as it passed through the solution, goes to the detector where it is converted to a proportional electrical signal. The detector used is an

EG&G Judson model J10D-M204-R01M-30-WB In:Sb detector which has maximum sensitivity in the range of $1900 - 5000 \text{ cm}^{-1}$. The response time of the detector is 80 nsec. This is appropriate because we are unable to look at intermediates that last under $30 \mu\text{sec}$ because of the limitations from the flashlamps which have a lifetime of $\sim 20 \mu\text{sec}$.

The signal from the detector is amplified by an EG&G Judson model PA-7-70 amplifier and sent to a LeCroy model 9410 digital oscilloscope. The signal is digitized and stored. Signal averaging can also be done to enhance the signal to noise ratio. The oscilloscope is triggered to start collecting the signal by a photodiode located next to the sample cell inside the flash housing. We also have the alternate option of triggering both the flashlamps and oscilloscope directly from a dual output trigger generator. The disadvantage of this method is that flashlamp ignition is delayed somewhat relative to oscilloscope triggering due to a small ($\sim 25 \mu\text{sec}$) delay in the circuit which fires the flashlamps. Using the photodiode trigger eliminates this uncertainty. The oscilloscope is triggered at the same time the solution is flashed which gives a true zero time.

DATA COLLECTION AND ANALYSIS

The information from the oscilloscope is downloaded to the computer using two different programs. The first program, 94Rem transfers the information in binary form to the computer. The second program, 94Tran converts the binary file to an ASCII file. This file contains a list of voltages from the oscilloscope which corresponds to the captured waveform.

This file is read into a Fortran program written by myself which converts this list of voltages to percent transmittance and absorbance. Our program first prompts the user to enter the file name in which the voltages are saved. Either 8000 or 10,000 voltages are transferred to the computer from the oscilloscope depending on the setting of the sweep rate. This is too many to work with so the computer program prompts the user to enter the number of voltages they wish to keep. For example, if 10,000 voltages are read in and the user wishes to keep 500 of them, then the program will keep every twentieth voltage to give a total of 500 voltages.

The program then calculates a time to coincide with each voltage. This requires that the user enter the oscilloscope sweep rate in response to a prompt. The voltages are then converted into percent transmittance and absorbance. The computer then prompts the user to enter a file name which will contain the calculated time, percent transmittance, and absorbance of each point. This file can be transferred to a Macintosh SE using the Apple File Exchange utility. At this time we choose to use the programs we already have on the Macintosh SE for further analysis of the data. In the future we may switch to one of the several available commercial programs which are discussed by Steven Kinne (2).

Further processing of the data is currently done with the Excel spreadsheet program. For example, tables of $\ln(\text{Abs})$ and $1/\text{Abs}$ can be created. On the spreadsheet one is also able to manipulate the information to choose the desired range of data to be plotted. The spreadsheet information can be transferred to Cricket Graphics for plotting and curve fitting.

TEST REACTION WITH $Mn_2(CO)_{10}$

Our intention is to look at the photochemistry of $Mn_2(CO)_{10}$ using fast time-resolved infrared spectroscopy. This reaction has previously been studied (1-5); nonetheless, we wish to look at this reaction in order to test our system. Before we look at this reaction using fast time-resolved infrared spectroscopy (new system), we will look at the reaction using flash photolysis with time resolved UV/Visible absorption spectroscopy (old system) to test our solution preparation techniques and our data analysis programs.

The techniques for solution preparation are very tedious. Since the concentration of the chemicals being used is very low, small impurities in the solvent can cause problems. The first solvent we tried was hexane but we were unable to obtain good agreement with published work. We believe this is due to olefin impurities. Yesaka et al. (1) and Church et al. (2) report work on the photochemistry of $Mn_2(CO)_{10}$ in cyclohexane solvent. Unlike hexane, cyclohexane does not need to be purified of olefin contaminants; hence the work reported here was done in cyclohexane. We dried it by refluxing over $LiAlH_4$ under flowing argon for at least twenty hours. Our $Mn_2(CO)_{10}$ was purchased from Strem, sublimed under vacuum at $50^\circ C$, and stored refrigerated under argon. Solutions of $Mn_2(CO)_{10}$ in cyclohexane are prepared in a glove bag filled with nitrogen gas at a concentration of about 1×10^{-4} M. They are then transferred to the reaction cell. The reaction cell is attached to the vacuum line where six freeze-pump-thaws are performed to remove both nitrogen gas and residual air.

Various papers on the products of the photolysis of $Mn_2(CO)_{10}$ have

been reported. There are different opinions about the photoproducts.

Hughey et al. in 1976 (3) reported that the photolysis of $\text{Mn}_2(\text{CO})_{10}$ gives $\text{Mn}(\text{CO})_5$ and a second photoproduct. They use a concentration of $\text{Mn}_2(\text{CO})_{10}$ around 1.4×10^{-5} M and cyclohexane as the solvent. They perform at least six freeze-pump-thaws to degas the solutions. They observe two transient spectral changes followed by regeneration of $\text{Mn}_2(\text{CO})_{10}$ by both a fast second-order reaction and a slower first-order process. They also saw that both of these changes are independent of added CO. They assign the second-order process to the reaction:



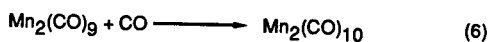
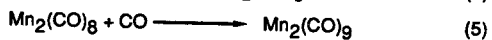
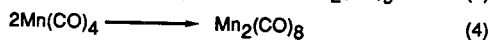
They determine that the second intermediate formed is also a primary photoproduct of $\text{Mn}_2(\text{CO})_{10}$. Because the thermal reaction of $\text{Mn}(\text{CO})_5$ shown above follows near perfect second-order kinetics it is unlikely that this arises from $\text{Mn}(\text{CO})_5$.

Wegman et al. 1980 (4) also reported that the photolysis of $\text{Mn}_2(\text{CO})_{10}$ gives $\text{Mn}(\text{CO})_5$ which follows second-order recombination. They also observe another slower recombination following second order kinetics. Addition of CO has no effect on either species. When using cyclohexane as a solvent they determined that $k_1 = 3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The concentration of $\text{Mn}_2(\text{CO})_{10}$ ranged from 1×10^{-5} to 2×10^{-5} M. The solution was degassed using five freeze-pump thaws. When CO is added and hexane is used as a solvent, the results observed are similar to Hughey et al. except that the minor long-lived photoproduct they report was not seen. They obtain a $k_1 = 9.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.

When the solution had no CO added, different results were obtained. The time for the intermediate(s) to return to $\text{Mn}_2(\text{CO})_{10}$ were longer. Furthermore, a new photoproduct is produced. Since this new species is not observed when CO is present, it is concluded that the species is due to coordinatively unsaturated carbonyl complexes. Also since it takes longer for this species to form, it is not part of the primary photochemical step. They suggest that this species forms by loss of CO from $\text{Mn}(\text{CO})_5$ (equation 2) and competes with the recombination reaction 1.

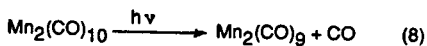
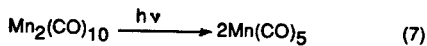


When CO is present the reverse reaction is accelerated increasing the concentration of $\text{Mn}(\text{CO})_5$, so the only observable thermal process is reaction 1. When CO is not present, this reaction proceeds more to the right producing $\text{Mn}(\text{CO})_4$. The authors suggest the following thermal reactions also occur:



A computer simulation was done to determine the rate constants for these equations. They concluded from these results that the loss of CO from $\text{Mn}(\text{CO})_5$ occurs slowly. If the concentration of CO is at least 0.01 M then this process is not observed. Overall they determine that two photoproducts are observed when no CO is added, but only one of these is a primary photoproduct.

Rothberg et al. 1982 (5) use picosecond flash photolysis to look at the photochemistry of $\text{Mn}_2(\text{CO})_{10}$. Their work provides the first evidence for two primary pathways when $\text{Mn}_2(\text{CO})_{10}$ is photolyzed.

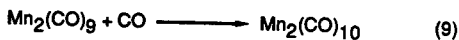


The concentration of $\text{Mn}_2(\text{CO})_{10}$ used was 0.05 M and ethanol was the solvent. The excitation pulse was 25 ps long.

Two absorption maxima are obtained at 780 and 480 nm. $\text{Mn}(\text{CO})_5$ is assigned to 780 nm. This is the first time that $\text{Mn}(\text{CO})_5$ is directly observed in solution flash photolysis. Since the second photoproduct is formed in 25 ps, it is unlikely to be a secondary photoproduct, and is assigned to be a second primary photoproduct. The second species could be from a loss of CO or it may be due to a carbonyl bridged species.

Herrick and Brown 1984 (6) also show that both loss of CO from $\text{Mn}_2(\text{CO})_{10}$ and breaking of the Mn-Mn bond occurs as primary processes when it is photolyzed. The concentration of $\text{Mn}_2(\text{CO})_{10}$ ranged from 1×10^{-4} to 1×10^{-5} M and solutions were degassed with four freeze-pump-thaws.

When hexane is used as a solvent, they observe a $\lambda_{\text{max}} = 510$ nm, which is attributed to $\text{Mn}_2(\text{CO})_9$. The absorbance decays by second-order kinetics and is consistent with the following process.



When CO was added the decay was faster and followed first-order kinetics. They estimate that 70% of the primary photochemical product is $\text{Mn}(\text{CO})_5$ and 30% is $\text{Mn}_2(\text{CO})_9$.

Yesaka et al. in 1984 (1) also reported two primary photoproducts in the flash photolysis of $\text{Mn}_2(\text{CO})_{10}$. Cyclohexane was used as the solvent and six

freeze-pump thaws were performed.

They observe two peaks, one at 827 nm and the other at 500 nm which they assign to two primary photoproducts. The 827 nm band decays after 30 μ sec while the 500 nm peak decays in a longer time frame. They assign $\text{Mn}(\text{CO})_5$ to the 827 nm peak which decays following second-order kinetics. The rate constant is estimated to be $8.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. The 500 nm peak is assigned to the loss of CO from $\text{Mn}_2(\text{CO})_{10}$. This absorbance also decays following second order kinetics. The rate constant is estimated to be $1.2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$.

Church et al. in 1984 (2) report the first results of flash photolysis of $\text{Mn}_2(\text{CO})_{10}$ using infrared detection. The concentration of $\text{Mn}_2(\text{CO})_{10}$ used is $8 \times 10^{-4} \text{ M}$ and both cyclohexane and n-heptane are used as the solvents. Two intermediates are observed, $\text{Mn}(\text{CO})_5$ and $\text{Mn}_2(\text{CO})_9$. The $\text{Mn}(\text{CO})_5$ absorbs at 1988 cm^{-1} , $k_1 = 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, and the $\text{Mn}_2(\text{CO})_9$ absorbs at 2058, 2022, 2088, 1996, 1968, and 1760 cm^{-1} , $k_9 = 2.7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ when n-heptane is the solvent. The $\text{Mn}_2(\text{CO})_9$ decay rate is affected by addition of CO and the $\text{Mn}(\text{CO})_5$ is not. The solvent used also affected the decay rate of $\text{Mn}_2(\text{CO})_9$. It disappeared faster in n-heptane than in cyclohexane.

They also did this work using uv-visible detection. Both these methods show that $\text{Mn}_2(\text{CO})_9$ is an important photoproduct. The $\text{Mn}(\text{CO})_5$ absorbs at 820 nm, $k_1 = 7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and the $\text{Mn}_2(\text{CO})_9$ absorbs at 480 nm, $k_9 = 5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ when cyclohexane is used as solvent.

As can be seen, over the years various results have been reported for the photolysis of $\text{Mn}_2(\text{CO})_{10}$. Originally it was thought that two photoproducts were formed although only one could be identified. Subsequently, they determined what these two photoproducts were but they thought that only the $\text{Mn}(\text{CO})_5$ was a primary photoproduct and the $\text{Mn}_2(\text{CO})_9$ was not. The most recent work shows that two primary photoproducts are formed, $\text{Mn}(\text{CO})_5$ and $\text{Mn}_2(\text{CO})_9$ which absorb in the visible at 827 nm and 500 nm, respectively. It is also shown that both decay following second-order kinetics and the decay time for $\text{Mn}(\text{CO})_5$ is faster.

The results from our flash photolysis with time resolved UV/Vis absorption spectroscopy of $\text{Mn}_2(\text{CO})_9$ are presented in Figures V - VIII. These results are from our old flash system but using the LeCroy digital oscilloscope and the new computer programs.

Figure V is absorbance vs time for $\text{Mn}(\text{CO})_5$ at 827 nm. Initially, the absorbance is zero. The solution is flashed and the absorbance quickly rises as $\text{Mn}(\text{CO})_5$ is formed. The absorbance decreases as the $\text{Mn}(\text{CO})_5$ is converted back into $\text{Mn}_2(\text{CO})_{10}$. It decays back to $\text{Mn}_2(\text{CO})_{10}$ in about 200 μsec . Figure VI is 1/absorbance vs time for $\text{Mn}(\text{CO})_5$ at 827 nm. The plot is fairly straight showing second-order decay kinetics with $k/c = 1.4 \times 10^6 \text{ cm s}^{-1}$.

Figure VII is absorbance vs time for $\text{Mn}_2(\text{CO})_9$ at 500 nm. The plot shows that it decays back to $\text{Mn}_2(\text{CO})_{10}$ in about one second. Figure VIII is 1/absorbance vs time for $\text{Mn}_2(\text{CO})_9$ at 500 nm. The plot is a straight line showing second-order decay kinetics with $k/c = 392 \text{ cm s}^{-1}$.

These results agree with the results from the published work which are

summarized in Table I. Therefore it is safe to say that our solution preparation techniques are correct and our computer programs are working correctly.

K/ε for Mn₂(CO)₉ at 500 nm

Experimental / cm s⁻¹	Literature / cm s⁻¹
392	1.2 x 10 ² (3) 5 x 10 ² (4)

K/ε for Mn(CO)₅ at 827 nm

Experimental / cm s⁻¹	Literature / cm s⁻¹
1.4 x 10 ⁶	1.1 x 10 ⁶ (3) 1 x 10 ⁵ (4) 8.8 x 10 ⁵ (4)

Table I: Experimental and Literature Values for the Flash Photolysis of Mn₂(CO)₁₀. References are indicated in parentheses.

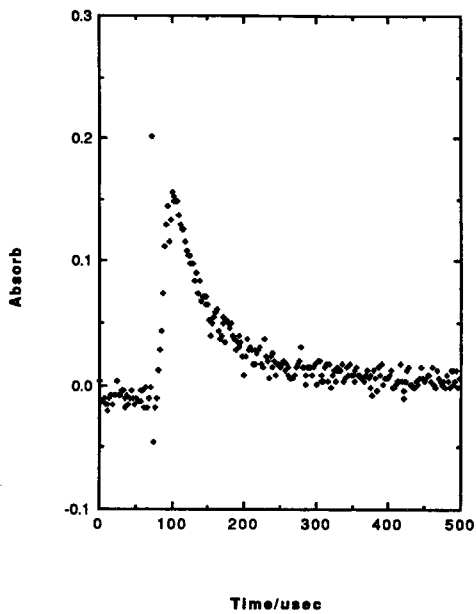


Figure V: Abs vs time for $\text{Mn}(\text{CO})_5$ at 827 nm

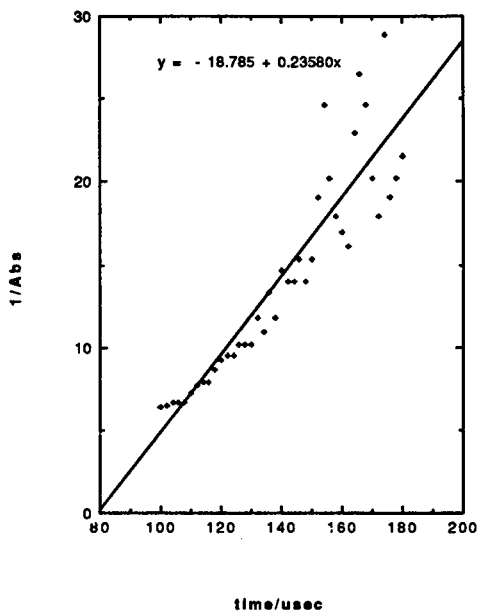


Figure VI: 1/Abs vs time for $\text{Mn}(\text{CO})_5$ at 827 nm

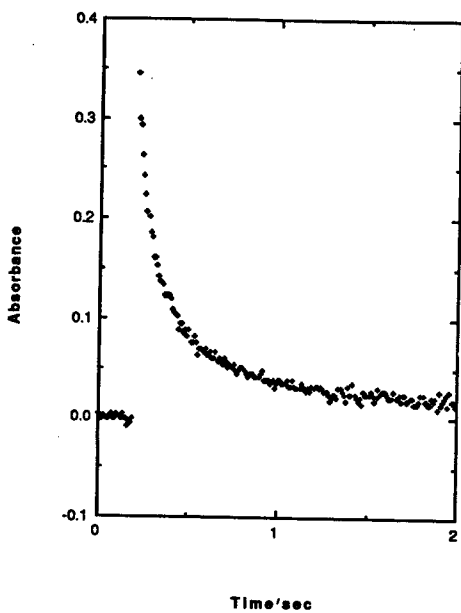


Figure VII: Abs vs time for $\text{Mn}_2(\text{CO})_9$ at 500 nm

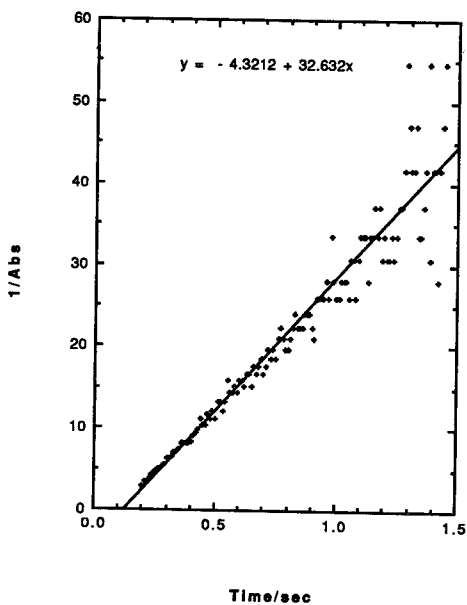


Figure VII: 1/Abs vs time for $\text{Mn}_2(\text{CO})_9$ at 500 nm

References

- (1) Bernard, E.J.; "The Construction of an Apparatus to Do Fast Transient IR Spectroscopy"; Thesis Union College, 1991.
- (2) Kinne, S.W.; "The Theory and Operation of the Fast Time-Resolved Infrared Flash Photolysis Apparatus"; Internal Paper Union College, 1991.
- (3) Yesaka, H.; Kobayashi, T.; Yasufuku, K.; Nagakura, S. *J. Am. Chem. Soc.* **1983**, *105*, 6249-6252.
- (4) Church, S.P.; Hermann, H.; Grevels, F.W.; Schaffner, K. *J. Chem. Soc., Chem. Commun.* **1984**, 785-786.
- (5) Hughey, J.L., IV; Anderson, G.P.; Meyer, T.J. *Journal of Organometallic Chemistry* **1977**, C49-C52.
- (6) Wegman, R.W.; Olsen, R.J.; Gard, D.R.; Faulkner, L.R.; Brown, T.L. *J. Am. Chem. Soc.* **1981**, *103*, 6089-6092.
- (7) Rothberg, L.J.; Cooper, N.J.; Peters, K.S.; Vaida, V. *J. Am. Chem. Soc.* **1982**, *104*, 3536-3537.
- (8) Herrick, R.S.; Brown, T.L. *Inorg. Chem.* **1984**, *23*, 4550-4553.