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The Construction of an Apparatus to do Fast Transient IR Spectroscopy

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THE CONSTRUCTION OF AN APPARATUS
TO DO FAST TRANSIENT IR SPECTROSCOPY

By

Eugene Jerome Bernard

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

UNION COLLEGE

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ABSTRACT

BERNARD, EUGENE The Construction of an Apparatus to do Fast Transient IR Spectroscopy. Department of Chemistry June 1991.

Photocatalytic reactions of metal carbonyl complexes with organic substrates have been studied extensively over the past decade. The reaction mechanisms proposed for most reactions studied have come from varying the concentrations and conditions on the reactants and examining the effects on the products. The intermediate steps of the reaction mechanism are inferred from these kinds of experiments, but most intermediates are too short lived to be seen directly with conventional IR spectroscopy.

This thesis describes the construction of an apparatus that uses fast transient IR spectroscopy to study the reaction intermediates that are too short lived to be detected by conventional IR spectroscopy. The apparatus uses flash photolysis to start the photocatalysis reaction and a diode laser to provide the IR probe radiation to measure the change in absorbance of the reaction intermediates. These experiments will provide the first direct observation of intermediate steps in reactions that, until this point in time, have been only postulated to exist in reaction mechanisms.

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Chapter I: A Literature Review of Iron Carbonyl Photocatalyzed Olefin Hydrosilation Reactions

The photochemistry of transition metal complexes is receiving an increasing amount of attention lately from physical, inorganic and organic chemists. A particularly interesting and promising aspect of this chemistry is the ability of some metal carbonyls to catalyze a wide variety of organic reactions including insertion reactions, olefin isomerization reactions, and the hydrogenation and hydrosilation of unsaturated hydrocarbons.

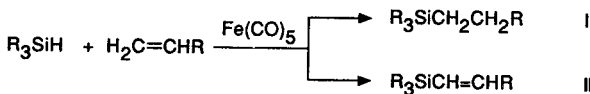
The metal carbonyls can be activated as catalysts either by intense ($>120^{\circ}\text{C}$) thermal conditions or, as later discovered, under much milder conditions (25°C) by irradiation with UV light. The photoactivated transition metal carbonyl complexes have received much attention recently because of the tremendous increase in the efficiency and selectivity of photocatalyzed reactions over the high temperature and pressure conditions necessary for thermal activation of the catalyst.

This report focuses specifically on iron carbonyl complexes that can photocatalyze hydrosilation reactions of terminal olefins in solution. The catalytic properties of these iron carbonyl complexes have been studied over the past three decades by several research groups throughout the world. A literature review of these hydrosilation reactions will provide an understanding of how these reactions work as well as give a historical perspective of how our research will add to this understanding.

The first olefin hydrosilation reactions involving iron carbonyl complexes were reported in 1961 by Nesmeyanov, Freidlina, and Chukovskaya¹. The iron

¹ Nesmeyanov, A.N.; Freidlina, R.Kh.; Chukovskaya, E.C.; Petrova, R.G.; Belyasky, A.B. *Tetrahedron*, 1962, 17, 61-68

pentacarbonyl catalyst ($\text{Fe}(\text{CO})_5$) was thermally activated between 100-140°C to convert the trialkylsilane and olefin substrates into alkylsilane (I) and alkenylsilane (II) products.



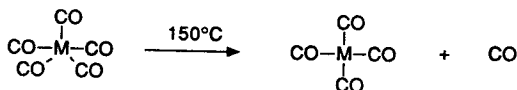
The paper describes experiments to find a relationship between the relative concentrations of the reactants and products. They found, in some cases, that an excess of silicon hydride relative to olefin causes an increase in the saturated alkylsilane product over the unsaturated alkenylsilane. The significance of this paper is that it provides the first reported evidence for olefin hydrosilation with a thermally activated iron carbonyl catalyst. The paper, however, does not attempt to go beyond rough, qualitative relationships between the reactants and products and does not postulate any reaction mechanisms for the process.

The discovery of thermal catalysis for the hydrosilation of olefins with iron carbonyl complexes, along with a growing number of other metal carbonyl complexes, prompted Chalk and Harrod² to look for evidence that might provide clues about a possible mechanism for the reaction. A proposed mechanism for a similar class of reactions, the hydrogenation of olefins with metal carbonyls, had recently been published³. Chalk and Harrod believed the mechanism for each type of reaction should be virtually identical except for the molecular hydrogen in the hydrogenation reaction being substituted by a silane in the hydrosilation reaction. They presented a paper in 1964 that described the

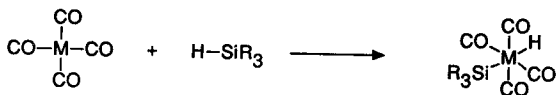
²Chalk, A.J.; Harrod, J.F. *J. Am. Chem. Soc.*, **1965**, *87*, 16-21

³Chalk, A.J.; Harrod, J.F. *J. Am. Chem. Soc.*, **1964**, *86*, 1776

behavior of thermal hydrosilation reactions catalyzed by Pt(II) and Ir(I) carbonyl complexes and compared them to analogous olefin hydrogenation reactions. The evidence seemed to support their assertion that the two mechanisms are similar and they proposed a olefin hydrosilation mechanism based on the one for hydrogenation. The mechanism went in four stages starting with the elimination of a carbonyl ligand under the intense thermal conditions:

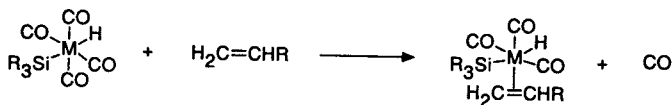


Next comes the oxidative addition of an alkylsilane Si-H bond to the unsaturated metal center of the unsaturated complex:

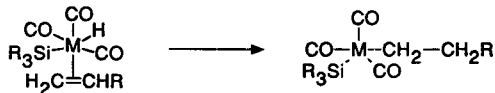


The oxidative addition of the Si-H bond of the silane to the unsaturated metal carbonyl is analogous to the addition of the H-H bond of molecular hydrogen in the hydrogenation reaction.

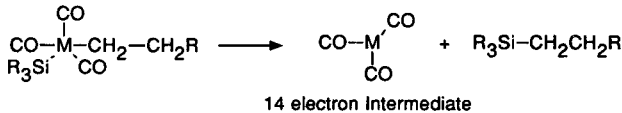
After the oxidative addition of the silane has formed a metal-hydride and metal-silane bond to the carbonyl complex, another CO group will be eliminated and an olefin group will coordinate to the carbonyl complex:



Coordination of the olefin to the carbonyl complex results in a weakening of the C=C bond which then undergoes an insertion reaction into the M-H bond:



The final step of the mechanism involves the reductive elimination of both the silane group and the alkyl group from the carbonyl complex and their combination to form the alkyl silane product:



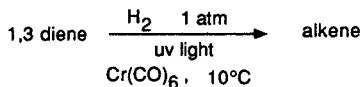
The mechanism explained the formation of alkenylsilane and alkane reaction products, also detected in the reactions, as various recombinations of hydrides, silanes, alkyl and alkenyl groups that could also be eliminated from the carbonyl complex.

While intensive investigations by various groups of thermal catalysis of olefin hydrogenation reactions were continuing, evidence was discovered that light, instead of intense heat, might also produce an activated metal carbonyl catalyst. In a paper by Jetz and Graham⁴ in 1970, the first evidence was announced of an oxidative addition of a silane group to a metal carbonyl using

⁴ Jetz, W.; Graham, W.A.G. *Inorg. Chem.*, 1971, 10, 4-9

light at temperatures below 25°C. The paper reported that mixtures of metal carbonyl complexes, including $\text{Fe}(\text{CO})_5$, and excess trichlorosilane (Cl_3SiH) or triphenylsilane ($(\text{C}_6\text{H}_5)_3\text{SiH}$) in heptane solvent, produced substantial quantities (>70% yield for each silane, of silane product, $(\text{Cl}_3\text{Si})\text{FeH}(\text{CO})_4$ and $(\text{C}_6\text{H}_5)\text{SiFeH}(\text{CO})_4$, respectively. The mixtures were irradiated for approximately a day with UV light from a filtered mercury lamp at temperatures far below (<25°C) the threshold required for thermal addition of silanes to metal carbonyl complexes. While these studies did not focus on hydrosilation reactions of olefins, they showed these metal carbonyl complexes could be manipulated, and perhaps activated into a catalyst, with light.

Wrighton and Schroeder⁵ announced in a communication in 1973 they had found evidence for the hydrogenation of several 1,3-dienes using catalytic amounts of $\text{Cr}(\text{CO})_6$ irradiated with uv light (Reaction 1):



The very mild thermal conditions of the reaction (10°C) made it obvious that light played a role in activating the catalyst. The communication further addressed the question of whether this was a photoassisted reaction or whether a true photocatalyst had been formed in the irradiation of the metal carbonyl. In photoassisted reactions, a photon is required for the completion of each reaction cycle. Since at least one mole of photons must be absorbed for every mole of reaction products produced, the maximum quantum yield of photoassisted reaction is one. Conversely, true photocatalytic reactions involve the photo-generation of a catalyst that enters a thermal catalytic cycle. Once the

⁵Schroeder, M.A.; Wrighton, M. *J. Am. Chem. Soc.*, 1973, 95, 5764-5765

catalytic complex is photoactivated from an inert pre-catalyst, only thermal energy is required to power the reaction cycle. The thermally driven photocatalyst can continue to produce reaction products after the initial irradiation, and quantum yields for true photocatalytic reactions normally exceed one.

Wrighton and Schroeder found a quantum yield greater than one for the hydrogenation reactions of $\text{Cr}(\text{CO})_6$, clearly indicative of the formation of a true photocatalyst. Further evidence for formation of a true photocatalyst is the observation that the reaction will continue for several hours after the reaction vessel is placed in the dark.

Once Wrighton and Schroeder found evidence for a photocatalytic olefin hydrogenation reaction with a metal carbonyl, they tried the same catalyst ($\text{Cr}(\text{CO})_6$) in an olefin hydrosilation reaction. Evidence, first from Chalk and Harrod's paper that postulated similar reaction mechanisms for olefin hydrogenation and hydrosilation reactions with metal carbonyls and later from Jetz and Graham who found evidence that oxidative addition of a silane group to a metal carbonyl could be photoactivated, gave Wrighton and Schroeder good reason to believe the analogous photoactivated hydrosilation reaction may also occur with some metal carbonyls. Later in 1973, Wrighton and Schroeder⁶ announced in another communication they had indeed found evidence for photocatalytic olefin hydrosilation reactions involving $\text{Cr}(\text{CO})_6$.

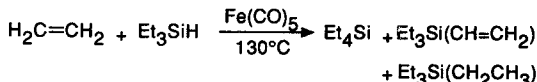
Over the next several years Wrighton and Schroeder studied photocatalytic reactions of metal carbonyls, and in 1977, they published a paper⁷ postulating a mechanism for olefin hydrosilation reactions with

⁶ Schroeder, M.A.; Wrighton, M.S. *J. Am. Chem. Soc.*, **1974**, *96*, 6235-6237

⁷ Schroeder, M.A.; Wrighton, M.S. *J. Organometal. Chem.*, **1977**, *128*, 345-357

photocatalytic iron carbonyl complexes.

The starting materials for these reactions include the substrates, an alkene (C_nH_{2n}) and a trialkylsilane ($HSiR_3$), and an iron carbonyl complex ($Fe(CO)_5$) to act as a precatalyst. Photoactivation of the iron carbonyl complex is not necessary for these hydrosilation reactions to occur. The thermal conditions necessary for the reaction to occur in the absence of light, however, are "significantly more stringent" than when the complex catalyst is photoactivated. For example, the thermal hydrosilation of ethylene with iron pentacarbonyl ($Fe(CO)_5$) proceeds according to the reaction:



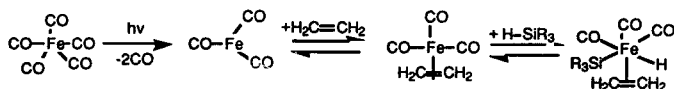
The same reaction, photoactivated, proceeds at room temperature, $25^\circ C$.

It has been suggested that photoactivation of the $Fe(CO)_5$ shifts the rate determining step to a previously "fast" step in the thermally driven part of the mechanism allowing the reaction to proceed under much milder thermal conditions.

The quantum yields measured for the photoactivated hydrosilation reactions typically exceed 7 which indicate that a true photocatalyst is being produced in the course of the reaction. Increasing concentrations of reaction products were measured after the light source was turned off, providing further evidence for the presence of a true photocatalyst.

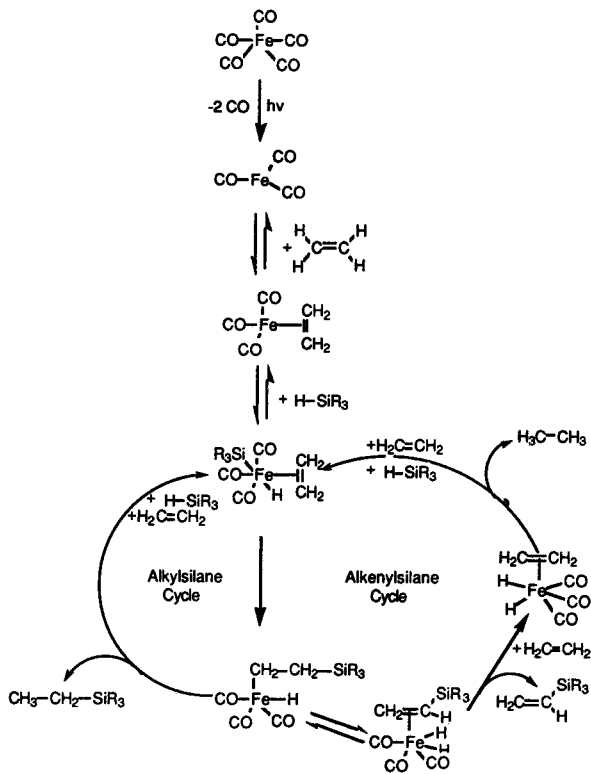
As previously noted, the first step of a photocatalytic hydrosilation reaction involves elimination of one or more of the carbonyl (CO) ligands to produce a coordinatively unsaturated intermediate complex. The elimination of the CO ligands allows the unsaturated iron complex to bind the alkene and

silane ligands:



Wrighton and Schroeder found $\text{Fe}(\text{CO})_4\text{X}$ intermediates to be too stable to act as the photocatalyst for the hydrosilylation reaction. Instead they proposed the photo-elimination of two carbonyl groups, giving a $14e^-$ iron tricarbonyl intermediate as a necessary step in the formation of the catalytically active species.

Once the alkene and silane ligands have been added to the photogenerated iron tricarbonyl, the intermediate enters a thermally driven catalytic cycle. The mechanism of the catalytic cycle was believed to behave similarly to the mechanism for thermal olefin hydrogenation catalysis and the reaction products from each catalysis method were virtually identical. The mechanism for the cycle proposed by Wrighton and Schroeder accounted for alkane, alkylsilane and alkenylsilane reaction products:



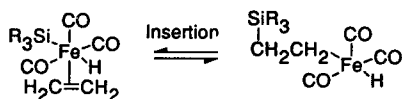
pathways: The leftward pathway shows the reductive elimination of the tetralkylsilane group followed by the oxidative addition of a new trialkylsilane group and coordination of an alkene. The net result of this pathway is the generation of the alkylsilane product and the regeneration of $(R_3Si)(H)Fe(CO)_3(alkene)$ to complete the catalytic cycle. The rightward pathway starts out with the reversible β -elimination of a hydrogen from the alkylsilane group on $HFe(CO)_3(alkylsilane)$ to form $(H)_2Fe(CO)_3(alkenylsilane)$. The $(H)_2Fe(CO)_3(alkenylsilane)$ then undergoes an irreversible reaction to produce the alkenylsilane product and $(H)_2Fe(CO)_3(alkene)$ which further reacts to produce the alkane product and regenerate $(R_3Si)(H)Fe(CO)_3(alkene)$ for completion of the cycle. The linking of the production of alkenylsilane and alkane product in the rightward pathway of the mechanism accounts for the 1:1 ratio of these products commonly found in these iron carbonyl catalyzed olefin hydrosilation reactions.

The most intriguing part of the proposed mechanism is the original formation of $HFe(CO)_3(alkylsilane)$ from $(R_3Si)(H)Fe(CO)_3(alkene)$. At the time this paper was published it was not known whether the alkene group inserted directly into the Fe-Si or into the Fe-H bond. In the first scenario, alkylsilane is produced by subsequent reductive elimination and coupling of the hydride (H-) and silane ($-CH_2CH_2SiR_3$) ligands. In the second, reductive elimination and coupling of the ethyl group ($-CH_2CH_3$) and the silane group ($-SiR_3$) occurs. While the idea of simple alkene insertion into the Si-Fe bond seemed plausible, nobody had yet found evidence for its existence.

In 1986, Randolph and Wrighton⁸ published a paper announcing

⁸ Randolph, C.L.; Wrighton, M.S. *J. Am. Chem. Soc.*, **1986**, *108*, 3366-3374

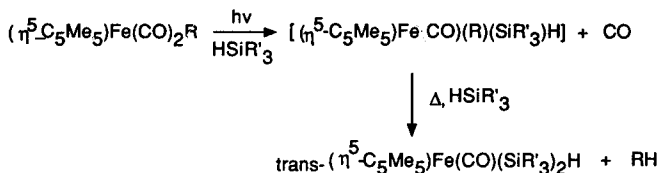
evidence for alkene insertion into the M-Si bond as an intermediate step in some iron carbonyl photocatalyzed olefin hydrosilation reactions. The postulated mechanism has the alkene ligand on the iron carbonyl complex insert into the M-Si bond of the silane ligand to form a new M-C bond with the alkylsilane:



The evidence for the alkene insertion product was found with IR, ^{13}C -NMR and

^1H -NMR spectroscopy. Further evidence came from photoreaction of

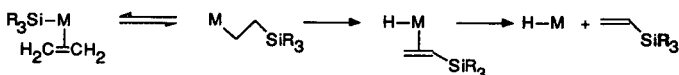
$(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{R}$ with hydrosilane (HSiR'_3) which resulted in an irreversible loss of alkane, but no alkylsilane product:



In the mechanism proposed by Chalk and Harrod, the addition of the second silane group to the complex should result in reductive elimination of silyl and alkyl groups to produce the alkylsilane product. If olefin insertion into the M-Si bond is an important step in the hydrosilation mechanism, the predicted lack of alkylsilane product in this reaction is explained by the absence of olefin: Since no olefin is present during any part of the reaction, no olefin can insert into the

M-Si bond in the complex and, hence, no alkylsilane product can form.

Another important feature of the M-Si insertion mechanism is the relative ease with which the $\text{M-CH}_2\text{CH}_2\text{SiR}_3$ ligand can undergo β -elimination to form a new metal hydride bond and an alkenylsilane group:



The formation of the alkenylsilane ligand is irreversible and this helps to account for

the large amount of alkenylsilane product measured in many of these reactions.

Current understanding of iron carbonyl photocatalysis of olefin hydrosilation reactions has come from studying the relative concentrations of the products of the reaction. A reaction mechanism is then inferred by making a reaction scheme that fits all the empirical data on the reactants and products for the reaction. The mechanisms proposed for photocatalytic olefin hydrosilation reactions with iron carbonyls have not been confirmed by the actual observation of reaction intermediates.

The actual observation and measurement of reaction intermediates will advance the understanding of these reactions tremendously: Observation of the reaction intermediates would provide the most definitive evidence possible to confirm or refute currently proposed reaction mechanisms. Furthermore, measuring the changes in the concentrations of intermediates over time would provide kinetic information about the rates of intermediate reactions.

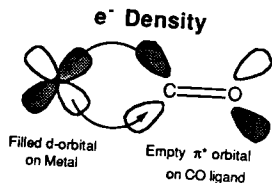
Chapter II: Experimental Requirements for Studying Short Lived Reaction Intermedites:

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Any experimental apparatus that is proposed to detect reaction intermediates during photocatalyzed metal carbonyl olefin hydrosilation reactions must satisfy two requirements: First, the apparatus must be able to measure some property that can distinguish between each reactant, intermediate, and product of the reaction and, second, the apparatus must be able to measure the intermediates during the very short period they exist.

Many photocatalytic intermediates have one or more carbonyl (CO) ligands. These carbonyl groups have characteristic stretching frequencies in the infrared region of the spectrum, typically between $1700-2100\text{ cm}^{-1}$, that can be detected with IR spectroscopy. The stretching frequency of a particular carbonyl group on a particular reaction intermediate is unique and allows each reaction intermediate of a reaction mechanism to be distinguished.

The CO stretching frequencies of metal carbonyl complexes are dependent upon the distribution of electron density between the central metal group and the π^* antibonding orbital on the carbonyl group. This metal to π^* bonding is called pi-backbonding and involves the donation of electron density from a filled d-orbital on the metal to the empty π^* orbital on the carbonyl ligand:



While pi-backbonding acts to strengthen the M-CO bond overall, strong backbonding into the antibonding orbital of the carbonyl group acts to weaken the C=O bond. This causes a decrease in the C=O stretching frequency.

Measuring the C=O stretching frequencies can also give information about the electronegativity of the central metal atom. For example, information about a CO stretching frequency of an iron carbonyl intermediate can indicate whether it's an Fe(0), Fe(I) or Fe(II) complex. The electron density around the central iron atom is considerably greater for Fe(0) than Fe(II) and the Fe(0) atom is able to donate more electron density to the π^* antibonding orbital of the carbonyl group. The result is that the weaker C=O bond in the Fe(0) means a lower CO stretching frequency. This information can be very helpful in determining the formal oxidation state of the central atom and its surrounding ligands in an intermediate complex.

Measuring the carbonyl absorption frequencies of metal carbonyl complexes is commonly done with conventional IR spectroscopy. Conventional IR spectroscopy, however is only applicable to the measurement of absorbing species that are stable over periods of at least several seconds. The transient intermediates of metal carbonyl complexes, acting as photocatalysts in olefin hydrosilylation reactions, have lifetimes ranging from 10^{-5} second to 10^{-2} seconds. These intermediates would form and react much faster than conventional IR spectroscopy can detect their existence.

The metal carbonyl complex intermediates produced throughout the photocatalytic reaction mechanism are also found in very low concentrations. The concentrations of the intermediates can be so low that provisions must be made in an experimental apparatus to compensate for the very weak signal

generated by them. One method commonly used to enhance the signal to noise ratio is to repeat a measurement several times and average the results of all the measurements. The averaging acts to reduce the level of random background noise toward zero while the signal remains at a constant level. The effect of this signal averaging is to increase the intensity of the true signal over the background noise thereby increasing the signal to noise ratio. The larger the number of measurements that are averaged, the greater the enhancement of the signal to noise ratio. Therefore, an apparatus that uses this technique should be able to collect and average several runs on an individual signal in a practical amount of time.

Another way to enhance the signal to noise ratio is to provide an intense IR source that can increase the intensity of the probe light over the stray and scattered light that makes up much of the background noise. This problem of source intensity may be further compounded if reactions are being studied in solution rather than the gas phase. In solution, the solvent molecules themselves can absorb some of the IR radiation of the probe source, further weakening the intensity of probe light. The greater the difference in intensity between the IR probe radiation and the background noise that reaches the detector the better the signal to noise ratio for the absorption measurement.

There are two kinds of IR probe sources that can be used in an apparatus for studying reaction intermediates in metal carbonyl complex reactions. The older source is a globar that generates IR radiation over the entire IR region of the electromagnetic spectrum. The radiation generated by the globar must be filtered by a monochromator so that only the IR frequency of interest will reach the detector. While the globar source has the attractive feature of providing IR radiation over a broad frequency range, the intensity of the source is very weak

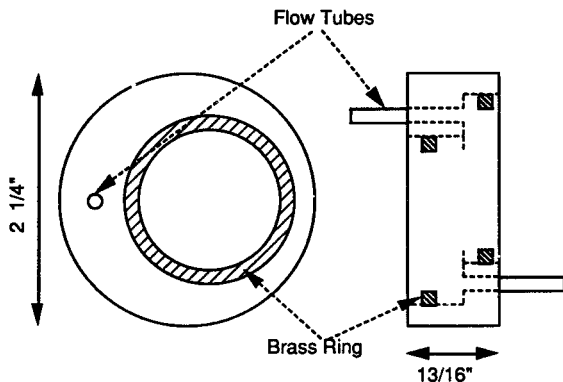
and, therefore, the signal to noise ratio of the measurement is low.

A more recently developed kind of IR source is an IR laser. The IR lasers can provide a very intense beam of probe radiation at a given frequency, however the total frequency range that a given laser can scan is limited. Furthermore, a laser is much more expensive both to purchase and to operate than a globar source. Ultimately, however, the most important requirement of any IR probe source used to study metal carbonyl photocatalysis reactions, especially in solution phase, is to have a high intensity probe beam. Therefore, an IR laser is the outstanding choice for an IR probe source for studying these reactions.

Chapter III: The Apparatus

The experimental apparatus we have built to examine iron carbonyl photocatalyzed olefin hydrosilation reactions employs fast transient IR spectroscopy to measure the short lived reaction intermediates. This type of IR spectroscopy differs from conventional IR spectroscopy in the time required by the apparatus to detect the signal of the absorbing species. The detection time for conventional, rapid scan FT-IR spectroscopy ranges between 1/10 second to 1 second while the detection time for fast transient IR spectroscopy is typically on the order of 1 μ second or even faster. The much faster detection times of the fast transient technique allows the measurement of short lived (10 μ sec to 10 mililsec) iron carbonyl complex intermediates that would be impossible to detect with conventional IR spectroscopy.

We plan to study iron carbonyl photocatalyzed olefin hydrosilation reactions in the solution phase and we have designed a sample cell for the solution phase work. The cell is a stainless steel cylinder 13/16" long and 2-1/4" in diameter that sandwiches the sample solution between two CaF_2 plates that are recessed in the cylinder.



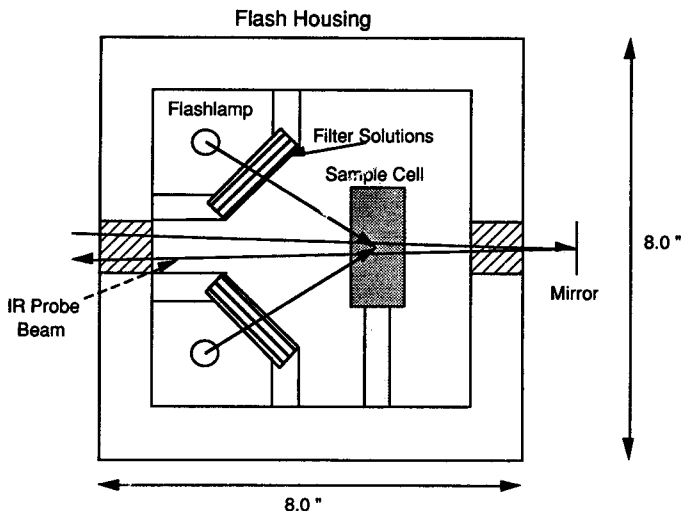
The two CaF_2 plates are held tightly in place on each side of the cell by brass rings that can screw into the holes and press the plates down onto rubber o-rings that seal the solution between the plates. The solution can constantly flow into and out of the sample cell by being pumped through two 'ports' at opposite sides of the inner chamber. The solution flow through the sample cell can be powered either by a peristaltic pump or compressed inert gas.

The photocatalytic reaction is initiated with UV radiation striking the iron carbonyl complexes in the solution flowing through the sample cell. The UV radiation is supplied by xenon flashlamps that have a power output of $\sim 400\text{J}/\text{flash}$ and a FWHM of $17\text{ }\mu\text{sec}$. The total irradiation time for the lamps is approximately $30\text{ }\mu\text{sec}$ which may interfere with the measurements of the shorted lived metal carbonyl intermediates in the $10\text{ }\mu\text{sec}$ to $30\text{ }\mu\text{sec}$ range.

A problem found in earlier flash photolysis systems is that the electrical discharge from the flashlamps creates an electromagnetic pulse which

interferes with the oscilloscope used to record the transient spectra of the intermediates. In order to prevent this electrical interference that could distort the signal collected by the oscilloscope, we enclosed all the high voltage components in a Faraday cage consisting of a wood frame covered with a double layer of copper screening.

The sample cell and the flashlamps are contained in the flash housing:



The housing serves to shield the sample cell from stray and scattered background light from the room as well as keep the relative position between the flashlamps and sample cell constant. Glass IR filters are placed between the flashlamps and the sample cell to prevent any IR radiation generated by the

flashlamps from interfering with the IR probe absorption signal of the carbonyl complex intermediates.

A mirror is placed behind the sample cell just outside the flash housing to reflect the IR probe beam through the sample solution for a second time. Double passing of the IR probe beam through the sample is a relatively easy way to enhance the intensity of the carbonyl absorption signal over the background noise to improve the signal to noise ratio of the measurement.

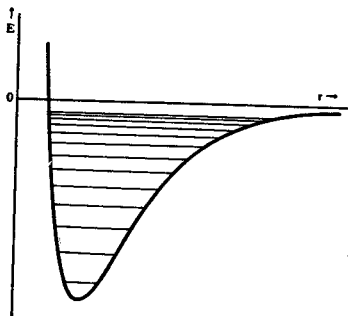
The most important, as well as the most costly, decision to make about the construction of a fast transient IR apparatus is the type of IR probe source to choose⁹. The discussion at the end of the previous section states that the high intensity IR laser source is superior to a global source. The next step is to decide what type of IR laser source will best fit the requirements, and our budget, for studies on metal carbonyl photocatalysis.

There are two types of lasers that fit our requirements as an IR probe source for the experimental apparatus and both have many benefits as well as drawbacks. The first type of laser we considered was a continuous wave CO laser. The continuous wave CO laser operates by lasing at a frequency corresponding to a particular vibrational-rotational transition in the CO molecule. The vibrational-rotational transition lines for the CO laser are spaced approximately 4 cm^{-1} apart and this limits the resolution of spectra taken with a CO laser to the same 4 cm^{-1} value. This, however was not a concern because it would take too long to plot spectra with better than 4 cm^{-1} resolution regardless of the resolution of the IR probe source.

⁹ For an excellent review of IR probe sources see:

Poliakoff, M.; Weitz, E. *Adv. in Organometallic Chem.*, 1986, 25, 277-313

The laser line is tuned by rotating a diffraction grating at one end of the laser cavity to change the laser transition line which changes the output frequency of the laser. The CO laser can be tuned over a relatively wide range of the IR region (1600 cm^{-1} to 2060 cm^{-1}) that covers most of the C=O stretching frequencies that will be studied. The higher the frequency of output from the laser, the lower the level of the vibrational transitions. This is based upon the effect of the shape of the potential energy well of a vibrating diatomic molecule has on the spacing of the quantum mechanical vibrational energy levels:



This potential energy well, called the Morse potential, is shaped such that the energy gap between vibrational energy levels increases as the levels of the transition decreases. Therefore, the highest energy, and therefore the highest frequency, output from a CO laser is due to the $V=1 \rightarrow V=0$ vibrational transition corresponding to a 2170 cm^{-1} output. Achieving these high output frequencies becomes more and more difficult because the CO gas in the laser must

be cooled to very low temperatures in order to increase the population of CO molecules at the lower vibrational levels. Obtaining output frequencies between 1900 cm^{-1} and 2000 cm^{-1} requires a closed cycle cooling apparatus that can cool the laser down to 153K. Output higher than 2020 cm^{-1} requires even more expensive cryogenic cooling of the CO laser down to liquid nitrogen temperatures (77K). Because many of the carbonyl stretching frequencies of the iron carbonyl intermediates have absorptions between 2000 cm^{-1} and 2100 cm^{-1} , we must figure the cost of buying and operating expensive cooling apparatus into the price of the CO laser.

The intensity of the CO laser output is excellent. The output power is on the order of tens of milliwatts (~50 milliwatts) which is more than enough light to keep the probe signal well above the background level.

The lasing lines for the CO laser, however, are known to be somewhat unstable, and fluctuations in the intensity of the probe beam can occur on the same timescale as the absorption measurements of the iron carbonyl reaction intermediates. These fast intensity fluctuations could be a problem for measuring the CO stretching frequencies of reaction intermediates because it would not be known if the fluctuations were due to a change in the concentration of the measured intermediate or a change in the intensity of the CO laser output.

The CO laser is a large piece of equipment with the pyrex laser tube that contains the CO gas measuring approximately 162 cm (~5.33 ft) in length. If floor vibrations are strong enough for the apparatus to require expensive, vibrationally damped optical benches to keep the system stable, the large CO

laser will require a large, expensive, optical bench.

Furthermore, the CO laser operates at 20,000 Volts which presents a serious safety hazard.

The other type of laser which is a viable option for an IR probe source for our system is a solid state, diode laser. The diode laser operates by applying a potential difference across a special piece of doped semiconductor material that is cooled to near liquid nitrogen temperatures (77K). The potential difference across the diode material acts to create a population inversion across the p-n junctions in the diode that release photons upon returning to the ground state. The diode materials can be doped with various combinations and concentrations of materials to give the diode laser an incredibly wide range of output frequencies (350 cm^{-1} to 3100 cm^{-1}). The drawback, however, is that any particular diode, which costs about \$2600 each, spans a tuning frequency range of only 200 cm^{-1} . Thus to cover the frequency range required to probe metal carbonyl intermediates (1700 cm^{-1} to 2100 cm^{-1}) it would be necessary to buy at least two diodes, and probably a third since there is some frequency range overlap between the diodes.

The diode laser has a much weaker intensity (~ 1 milliwatt) than the CO laser (~ 50 milliwatts) and may be weak enough to cause some concern about the strength of the IR probe signal relative to the background noise. After talking with other groups that use diode lasers for spectroscopy, we felt that the diode laser could fulfill our power requirements for an IR probe source in a fast transient IR spectroscopy apparatus.

The intensity of the lasing lines in the diode laser are stable for periods of several minutes. This eliminates any concerns about fluctuations in the line

intensity on the time scale of the reaction intermediates (10 μ sec to 10 millisec) that could distort the spectra of the C=O stretching frequencies of the reaction intermediates.

The diode laser, with dimensions of 13" x 15", is much less bulky than the CO laser. The diode laser can easily fit on the end of a single optical bench that holds all the vibrationally sensitive parts of the apparatus unlike the CO laser that requires its own optical bench. Furthermore, the diode laser operates at standard line voltage

(110 Volts) making it much safer than the CO laser with a 20,000 Volt potential difference across the laser tube.

The IR probe signal, generated by the C=O stretching absorptions of the iron carbonyl intermediates, goes to a detector that converts the light signal into an electrical current signal. The electrical current signal is then converted by an amplifier into a voltage signal that can be read and stored in a digital oscilloscope for later use. Thus the function of the detector is to translate the light signal of the IR probe source into the voltage signal that can be used by the oscilloscope and computer to store and manipulate the information from the signal.

The detector used in our apparatus is a Judson model J10D-M204-R01M-30-Si InSb detector with a model PA-7 detector amplifier. Indium Antimonide, InSb, is one of two possible materials that can be used to detect C=O stretching frequencies in the 1700 cm^{-1} to 2100 cm^{-1} range. The other material, Mercury-Cadmium-Telluride (HgCdTe), has a much wider frequency range (500 cm^{-1} to 5000 cm^{-1}) than the InSb (1900 cm^{-1} to 5000 cm^{-1}). The InSb however has a greater sensitivity to light in the frequency region from 1850 cm^{-1} to 2100 cm^{-1} than HgCdTe, and therefore will give a

better signal to noise ratio for detected light in this region. The importance of a good signal to noise ratio for measurements of the C=O stretching absorptions led us to choose the InSb material over the HgCdTe.

Additional features of our detector include using silicon, rather than the more conventional sapphire, as the window material to cover the detector. Sapphire is transparent to light ranging from frequencies in the UV, through the visible, and into the IR, while silicon is opaque to UV - visible frequencies and transparent only to light in the IR region of the spectrum. Using a silicon window will filter out the stray and scattered light in the UV-visible spectral region that gets generated from the Hg flashlamps when they photoactivate the metal carbonyl complexes. The decrease in the background light from the flashlamps will improve the signal to noise ratio of the C=O stretching frequency.

Stray and scattered background light can be reduced even further by narrowing the cone angle of the light that the detector can detect. The light coming from the IR probe source will be perpendicular to the surface of the detector, while stray and scattered background light will hit the detector from every possible direction. Restricting the angle of the light that can reach the detector as close as possible to the narrow angle of the IR probe beam will reduce the level of background light and improve the signal to noise ratio. The angle of detection for light coming into our detector is 30° which is half of the standard 60° cone angle for InSb detectors.

The response time of the detector is about 80 nsec which is much shorter than the shortest lived intermediates ($\sim 10 \mu\text{sec}$) we plan to study. The risetime of the detector amplifier to convert the current signal into a voltage signal is also important in figuring the overall response time of the detector. The model PA-7 amplifier has three gain settings for current to voltage signal conversion and the

smallest gain setting, which has the fastest response time, has a risetime of 90 kHz corresponding to an approximately 3.5 μ sec response time.

After the conversion of the IR probe signal into a voltage signal by the detector amplifier, the signal is read by the digital oscilloscope. The oscilloscope used in our apparatus is a LeCroy model 9410, 150 MHz digital oscilloscope. The oscilloscope displays the probe signals, generated by the metal carbonyl species in solution, as plots of the percent change in transmittance, $\Delta\%T$, of a particular IR frequency vs. time. The plots made by the oscilloscope are finally sent to a computer that can tie all the waveforms together into a single fast transient IR spectrum.

Chapter IV: Making and Interpreting a Fast Transient IR Spectrum:

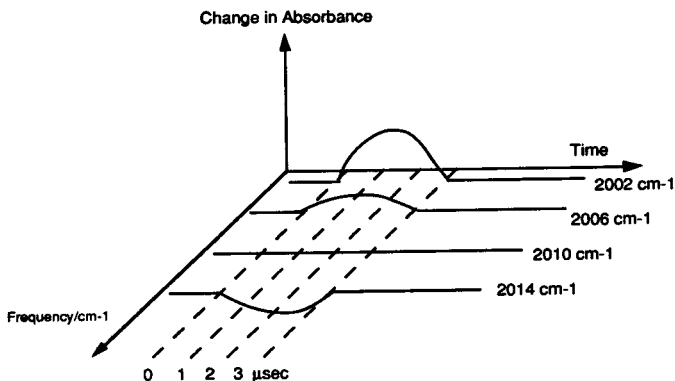
This final chapter describes how data is collected on the metal carbonyl intermediates of photocatalytic carbonyl complex reactions and processed into a fast transient IR spectrum. The spectrum shows how the reactants, intermediates, and products of the reaction form and react and can provide an experimental basis for postulating a reaction mechanism.

The process of making a fast transient IR spectrum starts with the oscilloscope collecting carbonyl stretching frequency data from the carbonyl intermediates and plotting a waveform of the percent transmittance, $\Delta\%T$, vs. time for each IR probe frequency used. An example of such a waveform is shown in Fig.1 for the photoreaction of gaseous iron pentacarbonyl ($\text{Fe}(\text{CO})_5$) and ethylene ($\text{H}_2\text{C}=\text{CH}_2$) in argon. This reaction starts with one 351 nm photon knocking two carbonyl groups off an $\text{Fe}(\text{CO})_5$ molecule to form an unsaturated, 14 electron $\text{Fe}(\text{CO})_3$ intermediate. The reaction continues with the coordination of ligands from the surrounding gas mixture to the unsaturated $\text{Fe}(\text{CO})_3$ to make $\text{Fe}(\text{CO})_3\text{XY}$ where X and Y are C_2H_4 and/or H_2 .

The reaction in Fig.1 shows a sudden increase in the $\Delta\%T$ at 1959 cm^{-1} immediately following irradiation by the UV flashlamps which suggests the new carbonyl complex is formed in the primary photochemical reaction. The most likely candidate for the new complex is the $\text{Fe}(\text{CO})_3$ which is the only intermediate formed as a direct result of the UV irradiation. Fig.1 also shows the $\Delta\%T$ signal decay back to background levels after an approximately 5 μsec time interval. The decay of the $\text{Fe}(\text{CO})_3\text{CO}$ is due to reaction with C_2H_4 to form $(\text{C}_2\text{H}_4)\text{Fe}(\text{CO})_3$ which does not absorb at 1959 cm^{-1} .

Each waveform generated at a particular IR frequency for a metal carbonyl photocatalytic reaction can be grouped together in a three dimensional plot of

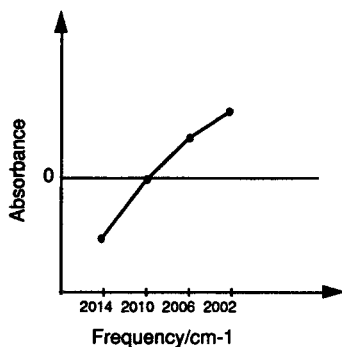
Δ Absorbance vs. Frequency vs. time:



This plot shows four waveforms taken between 2002 cm^{-1} and 2014 cm^{-1} at 4 cm^{-1} intervals over a period of $3\text{ }\mu\text{sec}$ after the flash ($t=0$). The plot illustrates the changes that can occur in the CO absorption spectra over a range of IR frequencies and a range of times.

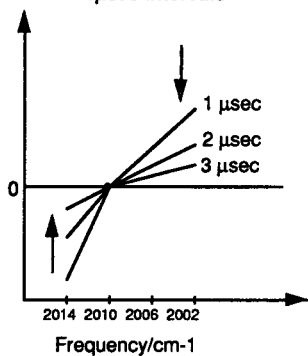
The waveforms of the Frequency vs Absorbance vs time are next transferred to a two dimensional coordinate axis of Δ Absorbance vs frequency at a given delay relative to the flash. Using the data from the three dimensional plot above, a plot of Δ Absorbance vs frequency at $t = 1\text{ }\mu\text{sec}$ would look like:

**Spectrum 1.0 μsec
after Photolysis Shot**



These plots of Δ Absorbance vs Frequency are made for selected time intervals and superimposed on a single plot of Δ Absorbance vs Frequency:

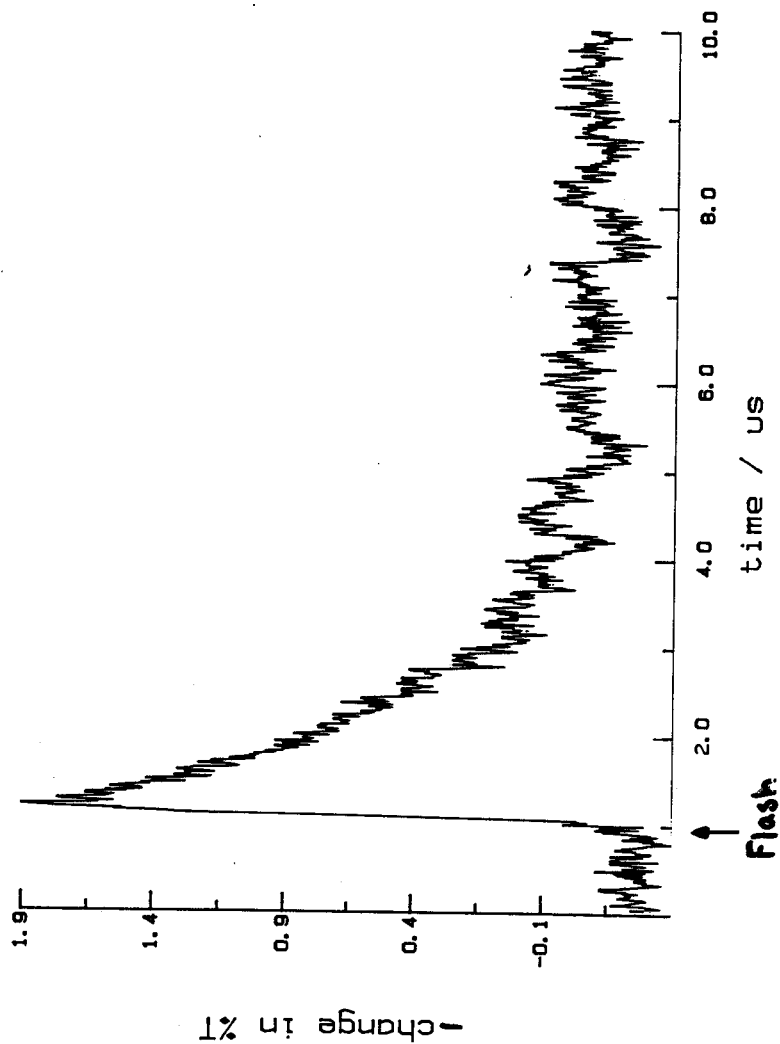
**Time-Resolved Spectrum
1 μsec Intervals**



The superposition of the plots at various time intervals shows an increase in the absorption at 2014 cm^{-1} , after an initial decrease in absorbance due to the consumption of parent metal carbonyl in the primary photochemical event, with a simultaneous decrease in absorption at 2002 cm^{-1} . The constant absorbance point at 2010 cm^{-1} , called an isobestic point, clearly indicates that a carbonyl complex with a CO stretching absorbance at 2002 cm^{-1} is reacting to form another carbonyl complex with a CO stretching absorbance at 2014 cm^{-1} .

Putting together all the Δ Absorbance vs Frequency spectra over appropriate time intervals gives a time-resolved IR spectrum of the intermediates involved in the metal carbonyl photoreaction. Fig. 2 shows an example of a complete sample spectrum for the gas phase photoreaction of $\text{Fe}(\text{CO})_5$ and ethylene in argon buffer gas. The five labeled peaks on the spectrum in Fig.2 illustrate how reactants, reaction intermediates and products can be represented spectroscopically: The first peak is formed during the photolysis flash and shows a steady decrease in absorbance over the time interval of the reaction. The steady decrease in absorbance intensity, corresponding to a decrease in the concentration of the species, indicates that peak 1 is due to a species formed during the primary photolysis reaction which is subsequently undergoing reaction. Peak two represents a species that starts out increasing in concentration and later decreases. This is behavior characteristic of a reaction intermediate which can be formed by a reactant and consumed in the formation of a product to give concentration levels that can go both up and down over the course of the reaction. Finally, peaks 3, 4, and 5 show absorption intensities that consistently increase during the reaction. These peaks represent one or more carbonyl complexes that are the final reaction products for this reaction.

Fe(CO)5 + C2H4 + Ar, 1959 cm⁻¹, 07139001



-change in %T

Figure 1

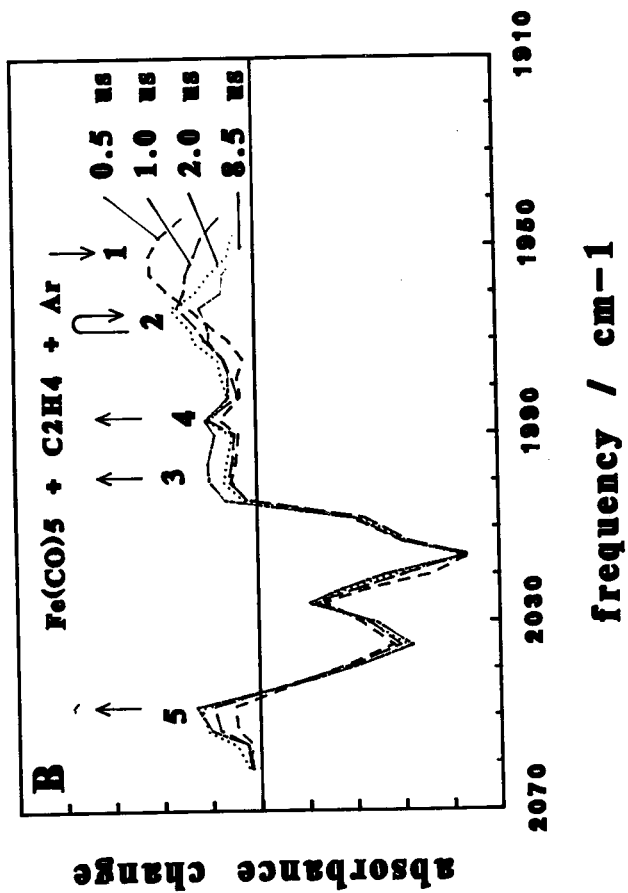


Figure 2