

2010

Mapping the Reactivity Surface of Metal-Olefin Reactions

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Davis, Joshua and Matchett, Stephen A., "Mapping the Reactivity Surface of Metal-Olefin Reactions" (2010). *Student Summer Scholars*. 48.

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Student Summer Scholars 2010

Mapping the Reactivity Surface of Metal-Olefin Reactions

Joshua Davis

Mentor: Stephen A. Matchett

Abstract:

Our overall goal of our project was to map susceptibility for nucleophilic attack on a series of metal-olefin compounds as a function of their geometry. The scope of this paper, however, is directed toward stabilizing our reactants in solution and the developing methods to test the reaction. In order to measure the susceptibility on the series we must know three things: the initial concentration of the nucleophile and the metal-olefin as well as a way measure the rate of reaction. In order to take these measurements, the solvent used must not interact with either reactant, must not interfere with the GC measurement of the nucleophile, and must not interfere with the UV/Vis absorption used to measure the metal-olefin concentration and the rate of reaction.

The nucleophile and metal-olefin used in our stabilization study was triethylamine (TEA) and $\{[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]\text{CH}_2\text{CHNHC}_6\text{H}_4\text{Cl}\}^+ \text{BF}_4^-$. The four solvents used in our study were nitromethane, N-methylpyrrolidone (NMP), tetrahydrofuran, and dichloroethane. Nitromethane showed to react with TEA so it was abandoned as a suitable solvent for our project. In the UV/Vis absorption of the metal-olefin in NMP, the solvent and metal-olefin had overlapping absorption. In THF, the TEA could not be fully separated from THF in GC while the metal-olefin showed to react in THF as well. In DCE we obtained a good calibration curve for the nucleophile, TEA. We observed a slow decomposition of the metal olefin complex in this solvent and ran an initial kinetic analysis to search for the nature of this decomposition. Once the source of the decay is determined proper kinetics measurements should ensure.

Introduction

The production of many plastics and medications rely on a multitude of reactions. Although medicine and plastics have entirely different uses, their synthetic routes can involve the same type of reactions. One of these reactions involves the nucleophilic attack on a metal-olefin. Although common, there is limited knowledge on the mechanism of this reaction. The overall goal of the study is to understand the reaction's mechanism and to map the reactivity as a function of the geometry of the reactants. Our study listed here is to supplement on-going efforts to reach this goal.

In 1981, Myron Rosenblum produced a study on three metal-olefin complexes. In this study, he and his associates examined the effect of geometrical differences on the reactivity of each compound. From the paper, it shows that as the olefin has a symmetrical structure, the metal to olefin bond is also symmetrical. As an electron donating substituent is added to one of the carbon atoms, the metal to olefin bond becomes less symmetrical, with the iron atom moving away from the substituted carbon¹. The structures of the complexes are shown below in Figure 1.

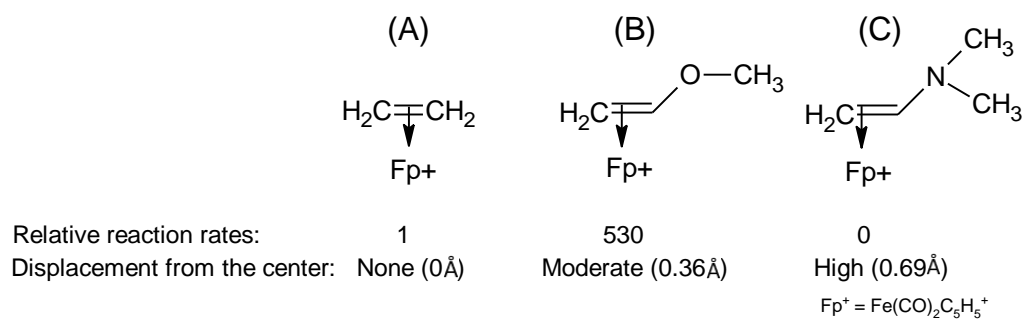


Figure 1: Rosenblum's studied complexes

The first structure (A) shows the metal piece stationed in the center of the olefin as the two carbons are the same. The vinyl ether compound (B) shows the metal slightly displaced from the center while the vinyl amine compound (C) is greatly displaced. Their study suggests that as the metal is displaced from the center the rate of nucleophilic attack at the substituted carbon increases when comparing A and B. Too much displacement, however, halts the reaction completely when comparing B

to C. We speculated that there is an optimized displaced position that allows for the maximum reactivity. The suggested displacement correlation is shown in Figure 2.

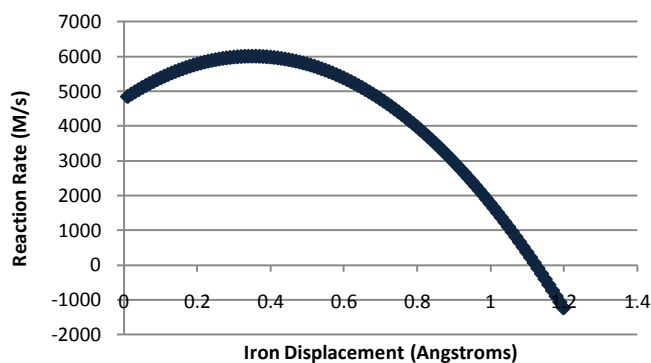


Figure 2: Suggested influence of metal displacement on reactivity

The iron piece is displaced due to overlap of the heteroatom's molecular orbital with the anti-bonding orbital of the olefin. This interaction fundamentally disrupts the bonding between the anti-bonding orbital of the olefin and the d-orbitals of the metal piece. Because of the disruption, the orbital of the olefin reshapes the anti-bonding orbital requiring the metal piece to readjust and move to one carbon². How this electronic structure can affect metal position is shown by the resonance structures in Figure 3. The electrons of the nitrogen atom form a bond with the olefinic carbon moving the metal over.

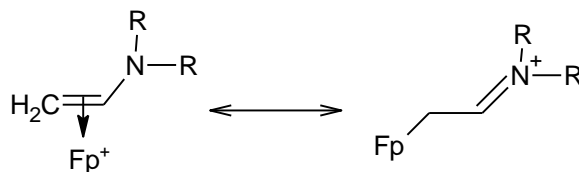


Figure 3: Resonance structures of an iron vinyl amine compound

While this study suggests a relation of reactivity to position of the metal, it only looked at three complexes. To complete this study, we must synthesize a series of metal-olefin compounds that vary the displacement of iron complex and then test the kinetics of a nucleophilic attack on each complex created. A majority of the synthetic routes for each of the compounds is well established³ and our goal

is to develop a reproducible method of measuring the kinetics of the reaction. In order to measure the kinetics of the nucleophilic attack, our method requires us to know three things: the initial concentrations of both reactants and a reliable way to measure the rate of reaction.

Matchett & Bouwman developed a currently unpublished experiment where the rate of reaction was measured by $^1\text{H-NMR}$. The rate was measured by changes in product to reactant NMR peak ratios. This experiment confirmed the relation between geometry and reaction rate, but the error bars were too large to clearly distinguish between each complex. The temperature fluctuations during the loading of the samples into the instruments made it difficult to measure the rates reproducibly. The nucleophile used (*para*-methoxyaniline) involved a three step reaction which further complicated the measurement of just the rate of nucleophilic attack⁴.

Our current project enveloped the use of the Photophysics RX.2000 Stop-Flow injector with the Shimadzu UV/Vis-2450 spectrometer in order to make our kinetics measurements. The RX.2000 injector encased two separate syringes in a temperature controlled water bath allowing for the two reactants to come to a preset temperature before being injected almost instantaneously into the temperature controlled cuvet. This solves the temperature problem of the $^1\text{H-NMR}$ experiment. We also used triethylamine (TEA) as our nucleophile making the mechanism a one step process rather than a three step process as it was in the NMR study.

To measure the initial concentrations of TEA and the metal-olefin, we planned to make a standard curve using gas chromatography for TEA and a standard curve of the metal-olefin in the UV/Vis spectrometer. To measure the rate of reaction, we must measure the wavelength that will show the largest change in absorption as the reaction progresses. This is usually apparent in the metal-olefin spectrum as a shoulder forms as shown in Figure 4.

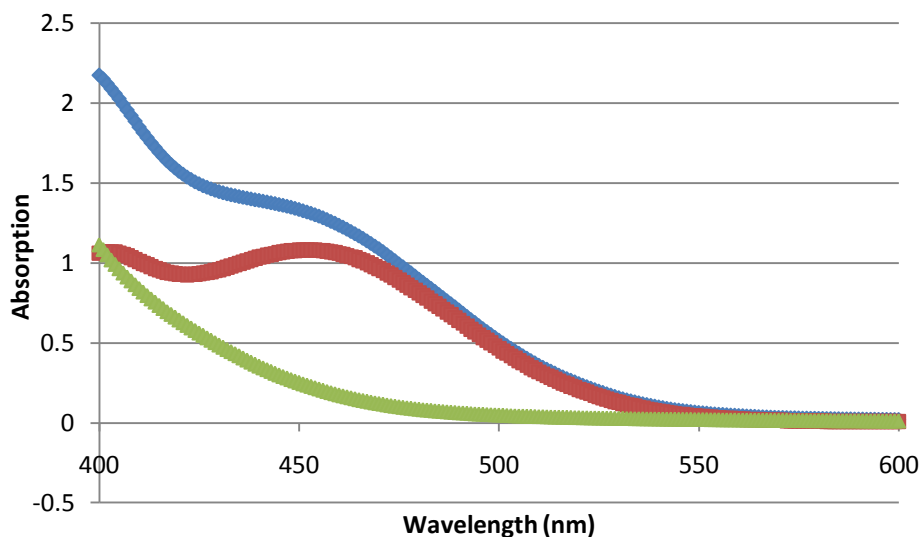


Figure 4: Normal metal-olefin absorption spectrum (blue), metal-olefin spectrum quenched with TEA (green), difference spectra between the two (red).

The blue curve in Figure 3 shows the proper absorption of the metal-olefin; the shoulder is at 452 nm. The red curve is the difference of the blue curve and the green curve which is the absorption of the metal-olefin after it has been quenched with the nucleophile. The red curve shows what wavelength will give the largest change in absorption as the reaction progresses as shown by the maximum at 452 nm. By measuring the absorbance value in the region of the greatest change one gets the most accurate way to monitor the rate of the reaction. Our method should eliminate any temperature variance and time discrepancies that showed up in the NMR study. With these new instruments a reproducible method of measuring kinetics will be eventually developed so the reactivity to metal displacement relationship can be mapped.

Experimental

General:

Distillation of triethylamine, aniline, and diisopropylethylamine was done on a small scale using calcium hydride as the drying agent. Diisopropylethylamine (DIPEA) and TEA were both distilled under nitrogen while the aniline was distilled under vacuum. The purity of the TEA and aniline were tested by

Gas Chromatography (Thermo Scientific Focus GC). The purity of the DIPEA was tested by $^1\text{H-NMR}$. All $^1\text{H-NMR}$ measurements were made on a JEOL Eclipse 300 MHz FTNMR. UV/visible measurements were made on a Shimadzu UV/Vis-2450 Spectrometer using an Applied PhotoPhysics Rapid Injection System.

Dichloroethane, nitromethane, n-methylpyrrolidone (the solvents used for our study) were distilled from 500 ml round bottom flask on calcium hydride. The solvents were distilled over 24/40 9 inch condenser using a heating mantle for 2 to 3 hours for each distillation. Dichloroethane and nitromethane were distilled under nitrogen. The distillation of N-methylpyrrolidone (NMP) was done in the same manner as dichloroethane and N-methylpyrrolidone, but was done at reduced pressure.

N-methylpyrrolidone was fractionally distilled as it was heated from a 500 ml round bottom by heating mantle. Then the NMP was distilled through dry condenser $\frac{3}{4}$ filled with glass helices and over a normal 24/40, 9 in condenser to a collection flask. The distillation was performed at 10 mmHg at 79°C.

Where air sensitivity was present all reactions/preparations were carried out under nitrogen using standard Schlenk techniques.

Synthesis of $\{[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]\text{CH}_2\text{CHNHC}_6\text{H}_4\text{Cl}\}^+\text{BF}_4^-$ (metal-olefin complex for our study)

Under air-free conditions, 1.1 equivalence of *para*-chloroaniline was dissolved in 10 ml of CH_2Cl_2 in a 50 ml Schlenk flask with. This solution was then transferred by cannula to pressurized addition funnel that was attached to a 100ml Schlenk flask containing 1.0 equivalent of $\{[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]\text{CH}_2\text{CHOCH}_2\text{CH}_3\}^+\text{BF}_4^-$ previously dissolved in 20 ml of CH_2Cl_2 . The *para*-chloroaniline solution was added drop-wise to the iron compound over several minutes. A third of the solvent, CH_2Cl_2 , was then removed by vacuum. Enough dry diethyl ether was then added drop-wise (10-20 ml) to precipitate the product out of the solution. The product was isolated by filtration dried under vacuum. The product was stored under refrigeration.

Recrystallization of $\{[C_5H_5Fe(CO)_2]CH_2CHNHC_6H_4Cl\}^+ BF_4^-$

Under air-free conditions, 0.500 grams of $\{[C_5H_5Fe(CO)_2]CH_2CHNHC_6H_4Cl\}^+ BF_4^-$ were dissolved in 40 ml of methylene chloride. The solution was then filtered through a frit to remove any impurities. About 30 ml of dry diethyl ether was then added drop-wise to precipitate the metal-olefin complex from the solution. The suspension was then filtered to collect the purified product, which was dried under vacuum, removed from air-free conditioned and stored under refrigeration.

Standard Curve of Triethylamine in Nitromethane

Stock solutions of TEA and aniline were first both prepared. With a volumetric pipette, 1.00 ml of TEA was dissolved in a 50.00 ml volumetric flask of solvent to make a 0.143 M stock solution. Secondly, 1.00 ml of aniline was dissolved in 50.00 ml volumetric flask of distilled nitromethane to make a 0.220 M stock solution of aniline.

With both stock solutions, a set of five standard solutions were formulated. To five 10.00 ml volumetric flasks, 2.00 ml of the aniline stock solution was added to each flask by volumetric pipette. Sequentially, the varying volumes of the stock TEA solution added are shown in Table 1. Each flask was diluted to 10.00ml with distilled nitromethane. Each of the standards was made to be 0.0439 M aniline (as an internal standard).

Table 1: Concentrations and Volumes of Stock in Each Standard

Standard Number	Volume of the Stock Solution diluted (ml)	Concentration of the Standard Solution (M)
1	7.00	0.100
2	5.00	0.0718
3	3.00	0.0431
4	1.00	0.0143
5	0.500	0.00718

Each of the five standards was analyzed three times by the Gas Chromatography under the profile listed below.

Profile 1:

Start at 50°C, hold 3 min

Ramp: 7°C/min to 200°C, hold 2 min

Split 60:1

The ratio of the integrated peak area of TEA to the integrated peak area of aniline was calculated for each separation. Each standard was injected three times, and the ratios were averaged. A linear fit of the peak ratios as function of TEA concentration was constructed with the standard deviations of the triplicate measurements used as weights⁵.

Standard Curve of Triethylamine in Dichloroethane and N-methylpyrrolidone

Stock solutions of TEA and DIPEA were first both prepared. With a volumetric pipette, 1.00 ml of TEA was dissolved in a 50.00 ml volumetric flask of solvent to make a 0.143 M stock solution. Secondly, 1.00 ml of DIPEA (Diisopropylethylamine) was dissolved in 25.00 ml volumetric flask of solvent to make a 0.23 M stock solution of DIPEA, for use as the internal standard.

With both stock solutions, a set of five standard solutions were formulated. To five 10.00 ml volumetric flasks, 1.00 ml of the DIPEA stock solution was added to each flask by volumetric pipette. Sequentially, varying volumes of the TEA solution, shown in Table 1, were added to each. The same aliquot of TEA used in the preparation of the standards used in nitromethane were used for standards in dichloroethane and NMP. Each flask was diluted to 10.00 ml with distilled solvent. Each of the standards was made to be 0.023 M DIPEA (internal standard).

For dichloroethane, each of the five standards was analyzed three times by the GC under profile 2 listed below.

Profile 2:

Start at 40°C, hold 4.5 min

Ramp 1: 3°C/min to 70°C, hold 1 min

Ramp 2: 15°C/min to 225°C, hold 2 min

Split 60:1

For N-methylpyrrolidone, each the five standards were analyzed three times by GC under Profile 3 listed below.

Profile 3:

Start at 50°C, hold 2 min

Ramp 1: 7°C/min to 170°C, hold 1 min

Ramp 2: 10°C/min to 225°C, hold 2 min

Split 60:1

The ratio of the integrated peak area of TEA to the integrated peak area of the internal standard was calculated for each separation. Each standard was injected three times and the ratios were averaged. A linear fit of the peak ratios as function of TEA concentration was constructed with the standard deviations of the triplicate measurements used as weights⁵.

Metal-Olefin Standard Solutions in N-methylpyrrolidone (these solutions must be kept air-free)

To a 25.00 ml volumetric flask, 0.7426 grams of the metal-olefin were added and measured by difference. The flask was capped with a septum and then degassed three times to replace the air with nitrogen. The flask was then diluted with fractionally distilled NMP under nitrogen to make a stock solution of 0.07117M. The solution was transferred to a 25 ml reaction vial.

From the stock, two standards were made by degassing two 5.00 ml volumetric flasks and adding 0.50 ml of the stock to one and 0.25 ml of the stock to the other. These were diluted to the mark with fractionally distilled NMP. They were labeled standard 1 and standard 2. From standard 2, standard 3 was made by diluting 0.30 ml in a 5.00 ml degassed volumetric flask with distilled NMP. A fourth standard was made by diluting 0.10 ml of the stock in a 10.00 ml degassed volumetric flask. The concentrations of each respected solution were 7.1 mM, 3.6 mM, 0.21 mM, and 0.71 mM. Each solution was scanned by the Shimadzu 2450 UV/Vis Spectrometer at least twice in an Aldrich air-free cuvet.

Metal-Olefin Standard Solutions in THF

Stock solutions were made across a range of concentrations as we explored the best range for kinetics. Solid metal-olefin was weighed in a volumetric flask, degassed and diluted to the line with dry

air-free THF. From each stock, several standards were made. The standards were made by taking an aliquot of the stock by syringe and diluting it in a degassed volumetric flask. The stocks are shown in Table 2 and the standards are shown in Table 3.

Table 2: Stock Preparations in THF

Stock Number	Metal-Olefin Mass	Size of Volumetric Flask	Concentration
1	0.0212 g	10.00 ml	5.08 mM
2	0.0356 g	10.00 ml	8.53 mM
3	0.0157 g	10.00 ml	3.76 mM
4	0.0150 g	25.00 ml	1.44 mM

Table 3: Standard Preparations in THF

Made from stock number	Standard number	Size of aliquant in size of volumetric flask	Concentration
1	1	1.00 ml in 10.00 ml	0.508 mM
2	2	1.00 ml in 10.00 ml	0.853 mM
2	3	1.00 ml in 10.00 ml	0.853 mM
2	4	0.50 ml in 5.00 ml	0.85 mM
2	5	1.00 ml in 10.00 ml	0.853 mM
2	6	1.00 ml in 10.00 ml	0.853 mM
4	7	9.00 ml in 25.00 ml	0.518 mM

The stocks and standards were transferred to a degassed Aldrich UV/Vis cuvet with septum to be measured by the Shimadzu 2450 UV/Vis Spectrometer.

Metal-Olefin Standard Solutions in dichloroethane

A set of stock solutions and a set of standard solutions were made using reaction vials instead of volumetric flasks to improve the air-free conditions. The weights were determined by difference. The solid metal-olefin complexes were loaded into a preweighed reaction vial then diluted with a volume of purified dichloroethane. The volume of dichloroethane added was then determined by weight difference using its density. Stock specifics are shown in Table 4. We assume the volume of dichloroethane should be the volume of the solution as we assume the volume of the metal-olefin is negligible at these weights.

Table 4: Stock Preparations in Dichloroethane

Stock Number	Metal-Olefin Mass	Volume of DCE	Dichloroethane purity methods	Concentration
1	0.0216 g	24.35 ml	Distillation	2.13 mM
2	0.0202 g	24.96 ml	Distillation, freeze-pump-thaw	1.98 mM
3	0.0176 g	25.27 ml	Distillation, freeze-pump-thaw	1.67 mM
4	0.0238 g	25.00 ml	Distillation, freeze-pump-thaw	2.28 mM
5	0.0202 g	25.56 ml	Distillation, freeze-pump-thaw	1.89 mM

From each stock several standards were made. From a stock, an aliquot of the stock was taken by syringe and deposited in a new degassed reaction vial and diluted to 10 ml with purified dichloroethane. The actual volume of the solution was found by weight difference of an empty to a filled reaction vial as described above. Solution preparations are shown Table 5.

Table 5: Standard Preparations in Dichloroethane

From Stock Number	Standard Number	Amount from Stock	Total Volume of Solution	Concentration
1	1	0.50 ml	9.33 ml	0.114 mM
1	2	2.00 ml	10.14 ml	0.419 mM
1	3	3.00 ml	10.10 ml	0.631 mM
1	4	0.50 ml	9.94 ml	0.107 mM
1	5	4.00 ml	10.08 ml	0.843 mM
1	6	3.50 ml	10.07 ml	0.738 mM
2	7	1.00 ml	10.14 ml	0.191 mM
2	8	2.50 ml	10.16 ml	0.476 mM
2	9	3.50 ml	10.16 ml	0.572 mM
3	10	4.00 ml	10.06 ml	0.332 mM
3	11	3.00 ml	10.06 ml	0.248 mM
5	12	4.00 ml	10.36 ml	0.731 mM

Each of the stocks and standards were analyzed by the Shimadzu 2450 UV/Vis Spectrometer in different ways. Standard numbers 1 to 9 were transferred to an air-free Aldrich cuvet in a nitrogen bag and scanned from 400nm-700nm in the Shimadzu 2450 UV/Vis Spectrometer. Stock numbers 3 to 5

glove bag and standard numbers 10 to 12 were injected into the spectrometer with the Photophysics RX. 2000 Stop Flow Injector. The solutions were moved to the injector by syringe. The injector was flushed with the solvent before being exposed to the solutions. As the injector contains two syringes, one syringe was filled with purified solvent making the injection have half the concentration as the standard.

Results & Discussion

The metal-olefin used in this study is $\{[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]\text{CH}_2\text{CHNHC}_6\text{H}_4\text{Cl}\}^+ \text{BF}_4^-$, shown in Figure 5. The substance is crystalline, air stable, and solid at room temperature with a brick red color. Once in solution the solid becomes air sensitive.

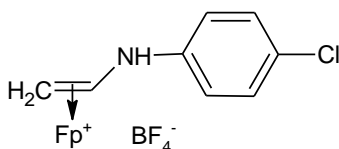


Figure 5: Structure of metal-olefin used (Fp⁺ = C₅H₅Fe(CO)₂⁺)

Unfortunately, finding a suitable solvent to develop our kinetic methodology was difficult. Our idea solvent must not react with either reactant, not interfere with use of gas chromatography to find the concentration of the nucleophile, and have a compatible UV/Vis absorption with our metal-olefin.

As the amount of solution can vary with every GC injection, an internal standard was used for our GC analysis. For our solvent to not interfere with our GC separation, clear peaks for our analyte, internal standard, and solvent must be identifiable for each injection. The GC integration values of the TEA (nucleophile in the study) to internal standard peak ratio must be reproducible with each injection as our standard curve for TEA was made by fitting line to the ratio as a function of TEA concentration.

Nitromethane

In our first solvent, nitromethane, the results were inconsistent, eventually suggesting that the TEA was reacting with the solvent. Our standard curve for TEA in nitromethane using aniline as the

internal standard gave a poor fit to our data. The fit line had a R^2 of 0.6868. While each of the components separated well, repeated injections varied widely. The fit is shown in Figure 6; the large error bars are a testament to how irreproducible the injections were. The average ratio of Standard 1 from Table 1 had a value of 4 ± 2 showing a 50% error.

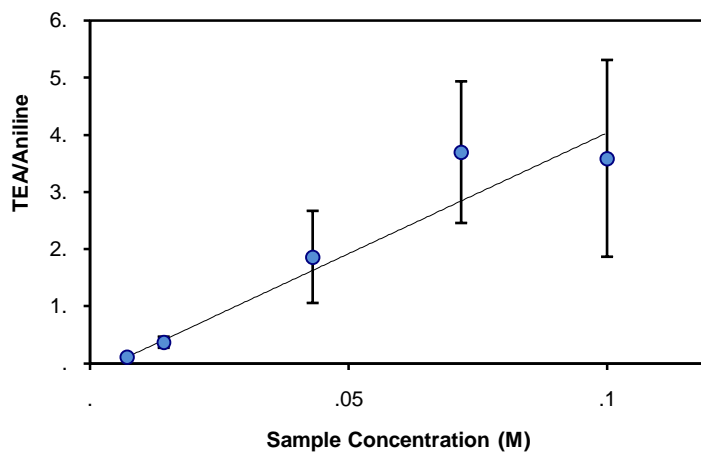


Figure 6: Standard curve of TEA in nitromethane, $y = 42x - 0.20$

Because a stable calibration curve was not able to be made with the internal standard aniline, we sought a new internal standard. We chose alkyl amines as possible candidates because of their similarity to the analyte. A solution that was 1.08 M TEA solution and 1.06 M diisopropylamine solution was analyzed by GC under several profiles, but none gave useable separation. Use of diisopropylamine as an internal standard was abandoned.

We next tried dibutylamine. Profile 4 (below) gave three decent separations of a 5.02 mM TEA and 5.00 mM dibutylamine solution as the peaks were easily identifiable, but again the measurements were not reproducible.

Profile 4:

Start 50°C, hold 2 min

Ramp: 7°C/min to 200°C, hold 2 min

Split 60:1

The retention times for TEA and dibutylamine were around 3.8 min and 10 min while nitromethane had retention time of 2.8 min. The average of the three ratios was 1.5 ± 0.2 making a 15% error, which is still unacceptable.

Because of high variation in the ratios with both dibutylamine and aniline, we hypothesized that the TEA was reacting with the nitromethane. The TEA and nitromethane reaction made it impossible to find the concentration of the TEA so this nucleophile/solvent combination was dismissed. Literature research supported our hypothesis, noting an acid-base reaction as TEA was used as a catalyst to react nitromethane with dimethyl benzoylphosphonate⁶. If the solvent was truly reacting with the TEA then this would explain the lack of observed reproducibility.

N-methylpyrrolidone

The next solvent tried was N-methylpyrrolidone (NMP). A good standard curve of TEA (using DIPEA as the internal standard) was generated with the GC, but a usable standard curve for the metal-olefin complex could not be produced.

Separations using diisobutylamine and diisopropylethylamine (DIPEA) as the internal standard were attempted. Both showed clean useable separations, but DIPEA was decided over diisobutylamine due to the similarity in structure between DIPEA and TEA. Both were analyzed by Profile 5 shown below.

Profile 5:

Start at 50°C, hold 2 min

Ramp 1: 7°C/min to 170°C, hold 1 min

Ramp 2: 10°C/min to 225°C, hold 2 min

Split 60:1

A 0.011 M TEA and 0.0092 M diisobutylamine solution was analyzed three times using the GC. The TEA, diisobutylamine, and NMP retention times were around 3.6 min, 6.8 min, and 10 min. The average of the three ratios was averaged to a value of 0.79 ± 0.02 giving an acceptable percent error of around 2.0%.

A DIPEA and TEA solution was made with the same preparations as the diisobutylamine and TEA

solution to make a 0.011 M TEA and 0.0092 M DIPEA solution. This solution was then run through the same profile three times. Retention times for TEA and DIPEA were around 3.6 min and 5.7 min. The averaged ratios gave a value of 0.94 ± 0.02 giving a percent error of 2.2%. With DIPEA as the internal standard the standard curve of TEA in N-methylpyrrolidone was constructed.

When the UV/Vis absorbance spectrum was taken of the metal-olefin in N-methylpyrrolidone, the absorbance for the solvent overlapped the absorbance of the metal-olefin complex. As mentioned before, our method involves looking for the UV/Vis absorption that will show the largest change as the reaction occurs. Standards 1 and 2 were too concentrated to give proper spectra. Standards 3 and 4 would not show any hint of the shoulder we were searching for. When we would quench our solutions with 200 μ l of TEA the absorbance spectrum of each solution would change minimally. This suggests the absorption spectra of the N-methylpyrrolidone overlapped with the metal-olefin absorption making the rate of reaction impossible to measure. The proper metal-olefin absorption and the absorption in N-methylpyrrolidone are shown in Figure 7.

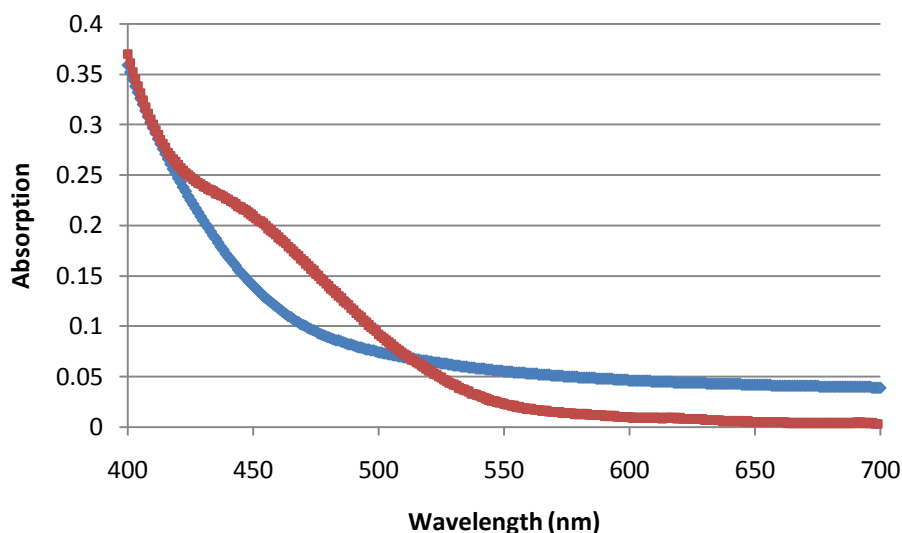


Figure 7: Solutions 0.210mM in N-methylpyrrolidone (red) and 0.835mM in tetrahydrofuran (blue)

With no shoulder, it makes it difficult to find a wavelength that would show any difference as the nucleophilic attack occurs, making this solvent unsuitable.

Tetrahydrofuran

The third solvent to be used was tetrahydrofuran (THF). The solvent proved to be unsuitable for both the metal-olefin and the nucleophile TEA. A proper separation of TEA from THF could never properly be accomplished in using gas chromatography. DIPEA was kept as the internal standard. The trailing peaks of the THF crossed into the path of the peak of the TEA. The attempted GC profiles and retention times of the THF, TEA and the internal standard, DIPEA are shown in Table 6.

Table 6: GC Profiles in Tetrahydrofuran

GC Profile (All Split 60:1)	Tetrahydrofuran Retention Time	Triethylamine Retention Time	DIPEA Retention Time
Profile 6: Start at 50°C, hold 2 min Ramp 1: 7°C/min to 170°C, hold 1 min Ramp 2: 10°C/min to 225°C, hold 2 min	3.36 min	3.88 min	6.37 min
Profile 7: Start at 50°C, hold 4 min Ramp 1: 7°C/min to 170°C, hold 1 min Ramp 2: 10°C/min to 225°C, hold 2 min	3.40 min	4.04 min	7.16 min
Profile 8: Start at 50°C, hold 4 min Ramp 1: 5°C/min to 170°C, hold 1 min Ramp 2: 10°C/min to 225°C, hold 2 min	3.40 min	4.04 min	7.40 min
Profile 9: Start at 50°C, hold 5 min Ramp 1: 5°C/min to 170°C, hold 1 min Ramp 2: 10°C/min to 225°C, hold 2 min	3.41 min	4.06 min	7.83 min
Profile 10: Start at 50°C, hold 1 min Ramp 1: 3°C/min to 70°C, hold 1 min Ramp 2: 15°C/min to 225°C, hold 2 min	3.26 min	3.79 min	6.79 min
Profile 11: Start at 45°C, hold 4 min Ramp 1: 3°C/min to 70°C, hold 1 min Ramp 2: 15°C/min to 225°C, hold 2 min	3.64 min	4.40 min	8.50 min
Profile 11: Start 45°C, hold 4.5 min Ramp 1: 3°C/min to 70°C, hold 1 min Ramp 2: 15°C/min to 225°C, hold 2 min	3.70 min	4.49 min	8.95 min

In addition, the metal-olefin showed stability issues in THF. The UV/Vis spectra showed standards 2-6 (see Table 3) were each the same concentration, but no two spectra gave the same absorbance. The decomposition did not show any measurable time dependence. It was not clear from our trials why the results varied so much, but our inability to get reproducible results forced us to try another solvent.

Dichloroethane

Our fourth and final solution was dichloroethane. A GC standard curve for triethylamine was easily prepared as there was a very successful separation among triethylamine, dichloroethane and the internal standard, diisopropylamine. The retention times were around 5.3 min, 4.5 min, and 9.76 min respectively. The standard curve can be shown in Figure 8.

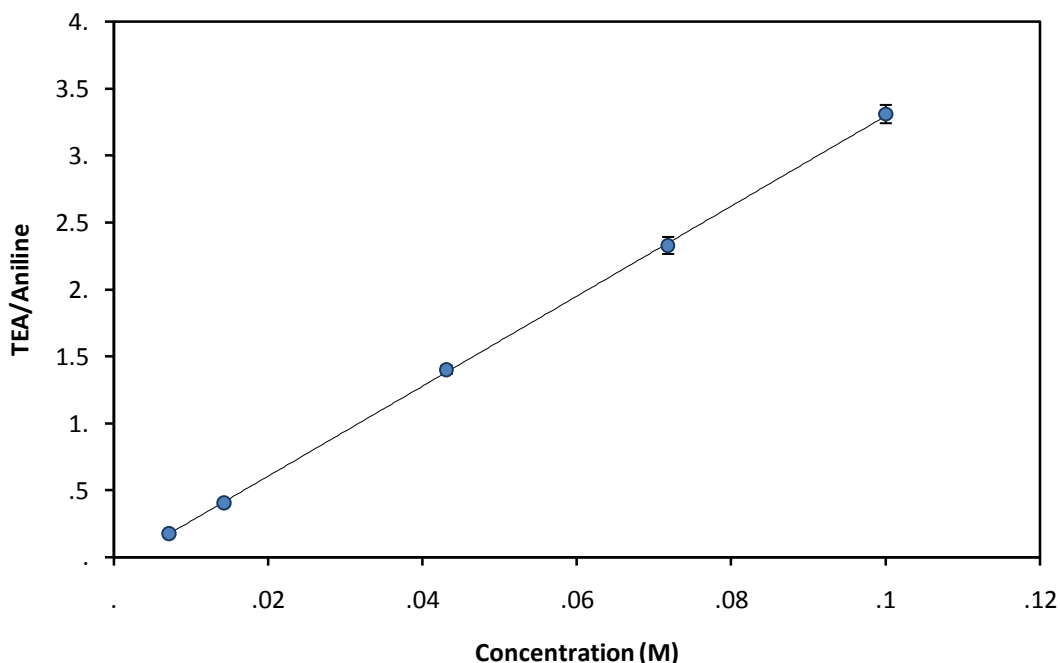


Figure 8: Standard curve of triethylamine in dichloroethane with diisopropylamine as the internal standard. Fit line: $y=33.6x-6.7 \cdot 10^{-2}$, $R^2=0.9999$

The fitted line has very reproducible ratios making the line a very good fit and reliable to predict concentration values in our future experiments. The ratio of the highest concentrated solution had a value of 3.31 ± 0.07 showing a 2.07% error which is an acceptable separation.

The absorption values of metal-olefin standards 1 through 9 at 452 nm were used to make a standard curve, but the fit was poor. This curve was abandoned as we began to observe that stock 3 was decaying over time so our calculated concentrations were not valid.

A loose time dependant study was made on the half dilution of Stock 4 (in Table 4). The time dependent decay was studied by measuring the standard as a function of time (Figure 9 and 10). The absorption of the solution was measured over a course of about 92 hours. As Figure 9 shows the actual changes in the spectra whole, Figure 10 shows how the absorbance at 452 nm changes as a function of time.

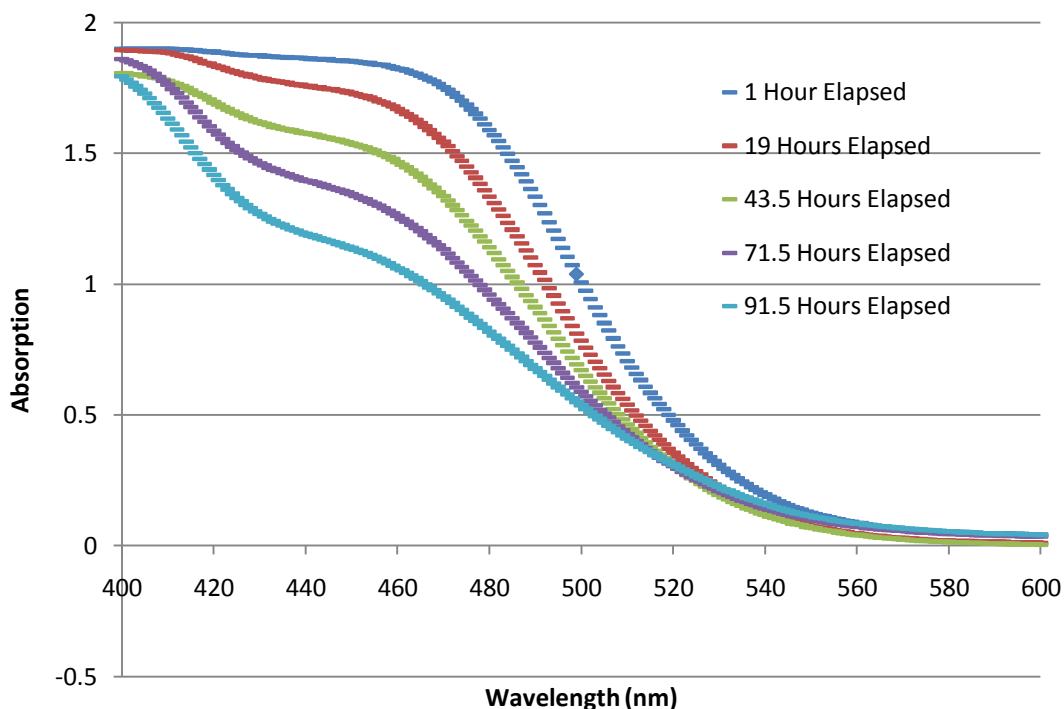


Figure 9: Absorption of 2.28 mM as a function of time (1st scan of each time)

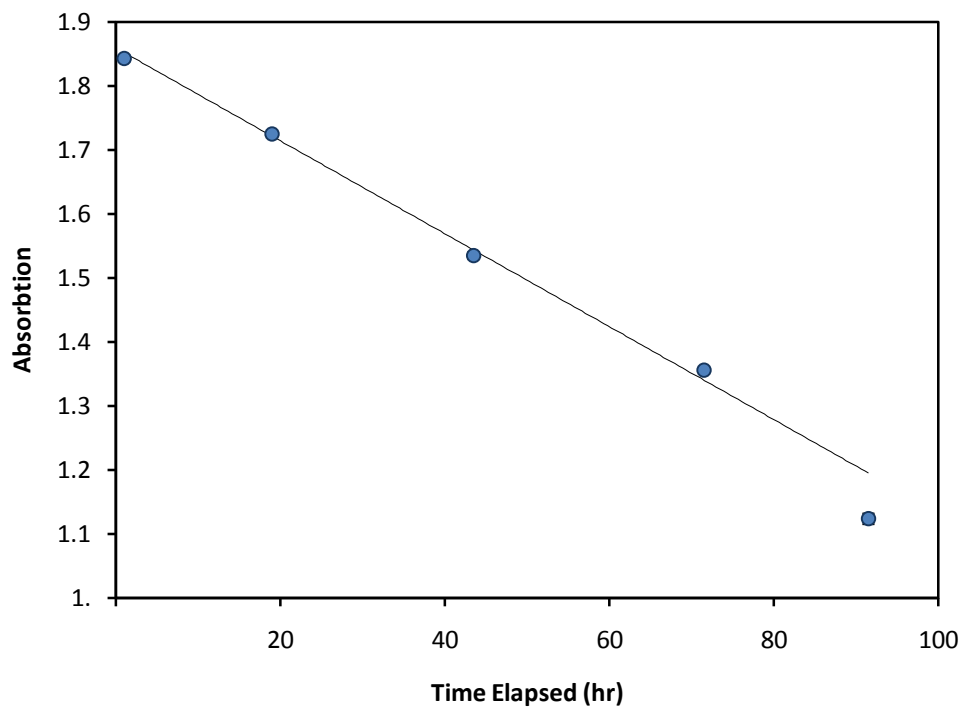


Figure 10: Absorption as a function of time at 452 nm, Fit Line: $y = -7.26 \times 10^{-3}x + 1.860$ $R^2 = 0.9898$

Each measurement repeated at least three times, showing very good reproducibility making the error bars of each measurement very small. The data points are averages of the absorption values at each time; the standard deviations were used as weights

Because the decomposition of the metal-olefin fits so well to a linear decay (as shown in Figure 11), the decomposition appears zero order, suggesting that the metal-olefin may undergo a catalytic decay. Under conditions where the solution is colder, the reaction was slowed. We are unsure whether it is the solvent or an unknown contaminant in the iron salt deposited during its preparation.

Conclusion/Dissemination

No solvent we have explored this summer has met the three criteria needed to allow us to make the reproducible kinetics measurements. We explored a wide range of methodology on how to make our metal-olefin solutions and how to measure them. We went from making our solutions in degassed volumetric flasks topped with septums to making our solutions in reaction vials. The volumetric flasks

were difficult to evacuate and to keep oxygen free as the glassware was not entirely made for air-free synthesis. Our use of the reaction vials for the solutions was chosen to minimize any air contamination as the reaction vials are designed for air-free synthesis. We concluded to using the Photophysics RX.2000 injector to dilute the stock solution was the best way to measure concentration as it helps minimize air contamination. The nucleophile solution can be kept quite stable in our most recent solvent (Dichloroethane), but our metal-olefin solutions have been decaying over time. We postulate that there may be catalytic decay due to contaminants in the metal-olefin or in the solvent. Work for the immediate future will be to understand why the metal-olefin reacts with the current solvent and to locate the source of contamination. Once both reactants can exist in a stable fashion, kinetics methodology can be finalized so we can measure the rates of nucleophilic attack on a whole series of, metal-olefin complexes.

Our plans for dissemination involve presenting our research at Student Summers Scholars Day. If we can solve our contamination issue, we may be able measure enough kinetics data allowing us to fully map reactivity as a function of geometry for our metal-olefins. With that kind of data we would have enough results to present at the national American Chemical Society convention.

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