Functionalization of [60]Fullerene using Organometallic Complexes and Amines

By

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Abstract

The organometallic functionalization of C_{60} can produce novel materials with potential applications in fields such as material science, electronics, and catalysis.^[1] Understanding the structure-dependent electronic and mechanical properties of C_{60} is critical for their chemical manipulations and technological applications.

The reactions of C_{60} with primary and secondary amines^[2-4] produce adducts that can be precursors of active catalysts. They react to form tetra(amino)-fullerene epoxide (amino = piperidine). The progress of adduct formation was followed by monitoring the increase of the absorbance values at 407 nm under flooding conditions where the piperidine concentration is greater than the concentration of C_{60} ([pip] >> [C_{60}]). Plots of absorbance versus time were biexponential, indicative of consecutive first order The first segment of the biphasic plot was ascribed to two consecutive reactions. piperidine additions. The second segment of the biphasic plot was ascribed to another two consecutive piperidine additions. The reaction corresponding to the second segment was followed by a hydrogen peroxide epoxidation producing a tetra(amino)-fullerene epoxide. Also, we are reporting the mechanisms of C_{60} dissociation from $(\eta^2 - C_{60})Ir(CO)(PPh_3)_2CI$. The dissociation was followed observing the decrease of the absorbance values at 550 nm. Plots of absorbance *versus* time were exponential. Two mechanisms of reaction are being proposed. One of the proposed mechanisms may involve solvent-assisted C_{60} dissociation. The order with respect to non-coordinating solvents and to coordinating solvent is zero and first order, respectively. The rate constant values for the dissociation are independent of the C_{60} concentration.

Resumen

La funcionalización organometálica de C_{60} pueden producir materiales noveles con aplicaciones potenciales en los campos de ciencia de materiales, electrónica y catálisis.^[1] Es importante el entender la dependencia estructural en las propiedades electrónicas y mecánicas de C_{60} para manipulaciones químicas y aplicaciones tecnológicas.

Las reacciones de C_{60} con aminas primarias y secundarias^[2-4] producen aductos que pueden ser precursores de catalíticos. Reaccionan formando aductos de C_{60} -(pip)₄(O) (pip = piperidina). El progreso de la formación de los aductos es monitoreando siguiendo el aumento en absorbancia a 407 nm, bajo condiciones "flooding" donde la concentración de piperidina es mayor que la concentración de C_{60} ([pip] >> [C_{60}]). Las graficas de absorbancia versus tiempo muestran un comportamiento biexponencial, indicativo de reacciones consecutivas. El primer segmento de la grafica bifásica se atribuye a la adición consecutiva de dos moléculas de piperidina mediante adiciones. El segundo segmento se atribuye a la adición consecutiva de otras dos moléculas de piperidina mediante adiciones, seguida de una reacción de epoxidación con peróxido de hidrogeno para dar el producto C_{60} -(pip)₄(O). Además, se reportan los mecanismos de la disociación de C_{60} del complejo (n²-C₆₀)Ir(CO)(PPh₃)₂Cl. La disociación se monitoreo observando la disminución en absorbancia a 550 nm. Las graficas de absorbancia versus tiempo son decaimientos exponenciales. Se proponen dos mecanismos de reacción. Los mecanismos propuestos para dicha disociación podrían ser asistidos por el disolvente. El orden con respecto a disolventes no coordinados es de cero orden, mientras que para los disolventes coordinados es de primer orden. Los valores de la constante de rapidez para dicha

disociación son independientes de la concentración de C_{60} . Estos dos ejemplos para la funcionalización de C_{60} muestran como las propiedades de C_{60} participan en la modificación de catalíticos.

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to Esther Capella-Lopéz

"El valor de las cosas no está en el tiempo que duran, sino en la intensidad con que suceden. Por eso existen momentos inolvidables, cosas inexplicables y personas incomparables" Anónimo

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Chapter I

Introduction

Before 1985 there were two known of carbon allotropes (diamond and graphite), then researchers from Rice University and Sussex University discovered other allotropes later collectively called fullerenes. Fullerenes are similar in structure to graphite which is composed of a sheet carbons linked in hexagonal rings. In contrast fullerenes contain pentagonal (or heptagonal) carbons rings that prevent the sheet from being planar.^[5] They are molecules composed entirely of carbon, in the form of a hollow sphere, ellipsoid, or tube. Cylindrical fullerenes are called carbon nanotubes while spherical fullerenes are sometimes called buckyballs. [60]Fullerene (or C₆₀) is the most spherical and symmetrical of the known allotropes. It has a sphericity of 94%.^[5] Due to the large size of the internal volume it is estimated that any atom of the periodic table can fit comfortably inside C₆₀ to form inclusion compounds known as endohedral fullerenes.

The fullerenes are slightly soluble in many solvents. [60]Fullerene is the only known allotrope of carbon that can be dissolved in common solvents at room temperature.^[6] Toluene, benzene and carbon disulfide are the most common solvents used for the C₆₀. C₆₀ solubility at room temperature ranges from 0.001 mg / mL in ethanol up to 51 mg / mL in 1-chloronaphthalene.^[6]

These molecules are stable, but not unreactive. The sp^2 -hybridized carbon atoms must be bent to form the closed sphere, which produces angle strain. The characteristic reaction of fullerenes is electrophilic addition at the 6,6-double bonds, which reduces angle strain by changing sp^2 -hybridized carbons into sp^3 -hybridized ones.^[5]

Fullerenes were under study for potential medicinal use such as binding specific antibiotics to its structure and even target certain cancer cells.^[7] Also, studies of fullerenes as light-activated antimicrobial agents have been reported.^[5] Some of its properties reported include high cohesive force, high hydrophobicity, high compressibility, hardness, heat resistance and superconductivity. Due to these properties C_{60} is extensively studied in the field of nanotechnology.^[5]

[60]Fullerene can be coordinated to organometallic complexes because it has a high electron affinity^[8] and can participate in π -back bonding with transition metals.^[8] There exist a variety of organometallic complexes functionalized with C₆₀. Among these complexes are $fac-(\eta^2-dppe)(\eta^2-C_{60})Cr(CO)_3^{[9]}$ (see figure 1.1), $fac-(\eta^2-phen)(\eta^2 C_{60}$)W(CO)₃^[10], fac-(η^2 -phen)(η^2 -C₆₀)Mo(CO)₃^[11] (dppe = 1,2 bis(diphenylphosphino)ethane and phen = 1,10-phenanthroline). The functionalization of C_{60} is of interest in organometallic catalysis. [60]Fullerene has the potential to modify and enhance the catalytic capacity of existing organometallic catalysts because it can labilize cocoordinated ligands bonds and stabilize electron rich transition states or intermediate species involved in the complexes' ligand exchange reactions.^[10-11] For example, Vaska's complex or Ir(CO)(PPh₃)₂Cl is considered unsaturated and can thus bind to one twoelectron or two one-electron ligands to become electronically saturated with 18 valence electrons. Therefore the electron deficient iridium complexes are capable of reacting with C_{60} .^[12] The preparation of $(\eta^2 - C_{60})$ Ir(CO)(PPh₃)₂Cl was reported in the literature.^[13] The dissociation of C_{60} from $(\eta^2 - C_{60})Ir(CO)(PPh_3)_2Cl$ is presented in this work. Here will be presented the reactions of C₆₀ with secondary amines producing aminofullerene epoxides.

The amines react to form C_{60} -(amine)_n adducts. These adducts can be used to study the chemical properties of C_{60} .

This thesis reports the kinetics and mechanistic studies of the chemical modification of C_{60} with organometallic complexes and secondary amines.



Figure 1.1: Representation of the complex fac- $(\eta^2$ -dppe) $(\eta^2$ -C₆₀)Cr(CO)₃, where dppe = 1,2 bis(diphenylphosphino)-ethane.^[9]

1.1 Objectives

The purpose of this is research project is to functionalize C_{60} using organometallic complexes and secondary amines. It is well known that C_{60} reacts with transition metal carbonyl complexes^[9-11] and also reacts with primary and secondary amines.^[2-4] In order to establish the reactivity properties of C_{60} towards secondary amines such as piperidine and pyrrole, and organometallic complexes (Vaska's complex) it is necessary to perform kinetic experiments. These kinetics experiments will help in the establishment of the reaction mechanism(s) and also in the determination of the activation parameters that can be used to test those mechanisms.

Specific objectives

- Prepare and characterize $(\eta^2 C_{60})$ Ir(CO)(PPh₃)₂Cl complex.
- Study the dissociation of C_{60} from $(\eta^2 C_{60})Ir(CO)(PPh_3)_2Cl$.
- Perform kinetics experiments of the reactions of C₆₀ with piperidine and pyrrole.
- Estimate the thermodynamic parameters: activation enthalpy $(\Delta H^{\ddagger}_{obs})$ and activation entropy $(\Delta S^{\ddagger}_{obs})$ for the C₆₀ dissociation from $(\eta^2-C_{60})Ir(CO)(PPh_3)_2Cl$ and for the reactions of C₆₀ with piperidine.

Chapter II

Previous Works

In the past decades numerous studies of C_{60} have been reported.^[1] [60]Fullerene are molecules that possess the capacity to react with transition metal carbonyl complexes^[9-11] and with primary and secondary amines.^[2-4] The coordination of C_{60} with organometallic complexes occurs in a dihapto mode (η^2) as reported previously.^[8] One of the most important properties of C_{60} is it capacity to participate in π -back bonding with transition metals.^[8] The extent at which C_{60} participate in π -back bonding can be measured by infrared spectroscopy, because the reaction induces a characteristic shift in the stretching frequencies of the coordinated carbon monoxide of the metal.^[14]

For example, the Vaska's Complex (Ir(CO)(PPh₃)₂Cl) has a characteristic vco absorption band in the stretching region at 1953 cm⁻¹ for the solid disperse in a fluorolube mull.^[13] After the reaction of Ir(CO)(PPh₃)₂Cl with C₆₀ the vco band appears at 2014 cm⁻¹ due to π -back bonding.^[13] The reaction of Ir(CO)(PPh₃)₂Cl with C₆₀ to produce (η^2 -C₆₀)Ir(CO)(PPh₃)₂Cl was reported in 1991 by Raston et. al. X-ray diffraction studies of the product of this reaction suggests that C₆₀ is attached to Ir in a dihapto mode (η^2) through a 6-6 ring fusion with a bond lengths of 2.19 Å for both Ir-C bonds.^[13] In addition, shows that the two triphenylphosfine fold back into a nearly *cis* geometry in contrast to their original *trans* position in Vaska's Complex. The carbonyl and chloride ligand retain their *trans* position, as presented in figure 2.1.



Figure 2.1: Perspective view of $(\eta^2 - C_{60})$ Ir(CO)(PPh₃)₂Cl from data collected by X-ray diffraction.^[13]

The infrared spectrum of $(\eta^2-C_{60})Ir(CO)(PPh_3)_2Cl$ in dichloromethane shows a uco band at 1965 cm⁻¹ due to the presence of Ir(CO)(PPh_3)_2Cl and no absorption is present in the 2100-2000 cm⁻¹ region.^[13] The ³¹P NMR spectrum in chloroform shows a resonance at 24.5 ppm, which is the same as the observed for Ir(CO)(PPh_3)_2Cl.^[13] These results suggest that the formation of $(\eta^2-C_{60})Ir(CO)(PPh_3)_2Cl$ is reversible. However no studies have been reported to date concerning the presence of this product in solution. Figure 2.2 presents the first evidence of the existence of $(\eta^2-C_{60})Ir(CO)(PPh_3)_2Cl$ in solution (results from our laboratory). This infrared spectrum was performed in a [C₆₀] saturated solution in benzene. Three bands appear in the spectra. The band at 1818 cm⁻¹ was assigned to the $v_{C=C}$ stretching of C₆₀ and the band at 1965 cm⁻¹ was assigned to the uco stretching of Ir(CO)(PPh_3)_2Cl.



Figure 2.2: Infrared spectrum in benzene of: **A**. $Ir(CO)(PPh_3)_2Cl$ and **B**. $(\eta^2 - C_{60})Ir(CO)(PPh_3)_2Cl$ in a C_{60} -saturated solution.

The reactions of C_{60} with amines^[2-4] and other molecules such as substituted toluenes, anisoles, organocopper reagent and hydrazones among others^[15-18] are well studied due to their importance in functionalizing fullerene. Polyfunctionalized fullerenes have various applications in life and material sciences.^[19] Previous investigations have demonstrated that a secondary amine undergoes multiple addition to C_{60} under photochemical conditions in an aerobic environment to produce tetra(amino)fullerene epoxide.^[3] Multiple addition of a nucleophile to C_{60} it is possible due to the high electron affinity of C_{60} .^[12, 20-24] Near-infrared analysis of a mixture of C_{60} and piperidine in a deaerated dimethyl sulfoxide (DMSO)/chlorobenzene(PhCl) mixture indicated equilibrium formation of [60]fullerene radical anion (C_{60}^{\bullet}) but react immediately with O₂ producing tetra(amino)-fullerene epoxides, as presented in figure 2.3.^[2] A Benesi-Hildebrand analysis indicated that a [$C_{60}^{\bullet-}$ piperidine⁺⁺] radical ion pair is formed at room temperature as a result of amine to C_{60} single electron transfer.^[2]



Figure 2.3: Representation of the reaction of C_{60} with secondary amines in DMSO/PhCl forming: (1) $[C_{60}^{\bullet^{-}}$ piperidine^{*+}] radical ion pair and (2) tetra(amino)-fullerene epoxide.^[2]

Interestingly the displacement reactions of C_{60} from $(\eta^2-C_{60})Cr(CO)_5$ by piperidine (pip) producing $(\eta^1-pip)Cr(CO)_5$ are triphasic. Plots of absorbance versus time^[25], as presented in figure 2.4, consist of three segments. The first decreasing segment of the plot was ascribed to displacement of C_{60} from the parent complex, whereas the second and third increasing segments were assigned to step-wise additions of piperidine to uncoordinated C_{60} . In view of the reported fullerene amino epoxide formations, it was necessary a reinvestigation of the reactions of C_{60} with secondary amines. Therefore, we undertook further characterization and kinetic studies to propose a mechanistic description of adduct formation.



Figure 2.4: Plot of absorbance (407nm) versus time for the displacement of C₆₀ from $(\eta^2-C_{60})Cr(CO)_5$ by piperidine in chlorobenzene to form $(\eta^1-pip)Cr(CO)_5$ at 328.2 K under flooding conditions where $[pip] >> [(\eta^2-C_{60})Cr(CO)_5]$.^[25]

Chapter III

C₆₀ dissociation from (η²-C₆₀)Ir(CO)(PPh₃)₂Cl

3.1 Materials and Methodology

3.1.1 General

The reagents used to prepare the complex $(\eta^2-C_{60})Ir(CO)(PPh_3)_2CI$ were C_{60} and Vaska's complex $(Ir(CO)(PPh_3)_2CI)$. Both were purchased from Aldrich. Benzene (Aldrich), toluene (Fisher) and dichloromethane (Aldrich) were fractionally distilled under phosphorous pentoxide. Infrared spectra, in the CO-stretching region, were obtained on a Bruker Vector 22 Fourier transform infrared spectrophotometer in KBr pellet.

3.1.2 Preparation of the complex $(\eta^2-C_{60})Ir(CO)(PPh_3)_2Cl$

The complex $(\eta^2 - C_{60})Ir(CO)(PPh_3)_2CI$ was prepared from $Ir(CO)(PPh_3)_2CI$ and C_{60} following a reported method.^[13] In a 15 mL round bottom flask equipped with a magnetic stirrer and a nitrogen inlet, 20.28 mg (25.99 µmol) of $Ir(CO)(PPh_3)_2CI$ and 18.60 mg (25.83 µmol) of fullerene were dissolved in 10 mL of benzene. After, the reacting mixture was purged with nitrogen and put under a slow flow of nitrogen for approximately 1.5 hours, as shown in figure 3.1. The addition of a equimolar amount of a purple solution of C_{60} to a yellow solution of $Ir(CO)(PPh_3)_2CI$ in benzene, immediately formed a dark brown solution. After a few minutes, the solution turned into a dark green color. The solvent of the reaction was evaporating with a slow flow of nitrogen. The product was an olive green solid. The complex $(\eta^2-C_{60})Ir(CO)(PPh_3)_2CI$ showed a characteristic^[13] v_{CO} band at 2012 cm⁻¹, as shown in figure 3.2.



Figure 3.1: Schematic representation of the equipment used for the preparation of the complex $(\eta^2-C_{60})Ir(CO)(PPh_3)_2Cl$.



Figure 3.2: Infrared spectrum in the stretching carbonyl region of $(\eta^2-C_{60})Ir(CO)(PPh_3)_2Cl$ in KBr pellet.

3.2 Kinetic Studies of C₆₀ dissociation from (η²-C₆₀)Ir(CO)(PPh₃)₂Cl

3.2.1 General

Kinetics experiments were carried out on a Perkin Elmer Lambda 25 UV-Vis Spectrometer under a nitrogen atmosphere, using a quartz cell of 10 mm path length. The temperature was set to be constant within approximately 0.1°C using a Julabo F-12 constant temperature bath. An EC model heating and refrigerating circulator and a K/J Fluke digital thermometer equipped with a bead thermocouple were used as temperature control devices.

In order to determine the wavelength where the reaction was to be monitored, a UV-Vis scan was performed to a solution of $(\eta^2-C_{60})Ir(CO)(PPh_3)_2Cl$ in benzene. The chosen wavelength was the one at which a significant change in absorbance due to reaction was observed. The reaction monitoring was performed at the chosen wavelength of 550 nm.

The rate constant values were determined from the plots of absorbance versus time using a non-linear regression computer program (OriginPro 7.5). The error limits of the rate constant values are given in parenthesis as the uncertainties of the last digit of the reported value.

3.2.2 Kinetics of the complex $(\eta^2-C_{60})Ir(CO)(PPh_3)_2Cl$

The dissociation of C_{60} from $(\eta^2-C_{60})Ir(CO)(PPh_3)_2CI$ were studied observing the decrease in absorbance at 550 nm. The reactions were performed in various solvents and temperatures. For example, for benzene the temperatures were 289.5 K, 291.3 K, 293.1 K, 295.3 K, 298.3 K, 300.4 K and 303.2 K. In dichloromethane the temperatures were 295.2 K, 299.1 K, and 303.1 K. Also, the reactions were performed at different

concentrations of C_{60} in benzene solutions at 295.2 K. In addition, the reactions were performed in mixtures of solvents. In these mixtures one is used as the solvent and the other is used as ligand (token ligand). Different concentrations of token ligand at 295.2 K were studied. Dichloromethane and toluene are the token ligand and benzene was the solvent.

3.2.3 Data Analysis

Kinetics data was analyzed using OriginPro 7.5, a non-linear least-squares computer program. The plots of absorbance versus time, for the dissociation reaction, were exponential decays. The fit for the plots that best described the experimental data were first order. The functions, for those fits, given by the computer program are described by the following equation:

$$Y = (A_1) e^{-x/t1} + Y_0$$
(3.1)

where Y is the dependant variable at time t; Y_0 is the value of Y at time 0 or initial value; A₁ is the amplitude; x is the independent variable and $1/t_1$ is the rate constant. The family of equations obtained from the computer program is mathematically equivalent to a first order rate equation (equation 3.2) that represents the monitored change of absorbance. The value of absorbance (A), is proportional to the concentration of the species involved in the reaction. The equation for a first order reaction is given by:

$$A_t = (A_0 - A_\infty) e^{-k^* t} + A_\infty$$
 (3.2)

where the correspondence is: $A_t = Y$, $(A_0 - A_\infty) = A_1$, $k = 1/t_1$, t = x and $A_\infty = Y_0$. Where A_t represents the value of the absorbance at a given time, A_0 represents the absorbance at time zero, A_∞ represents the absorbance at time infinite, k is the observed rate constant and t is the time. The rate constant values were determined and are presented in table 3.1, table 3.2 and table 3.3.

3.3 Results

The reaction of C₆₀ with Ir(CO)(PPh₃)₂Cl (Vaska's Complex = V) in benzene produced (η^2 -C₆₀)Ir(CO)(PPh₃)₂Cl^[13]. The infrared spectrum for the carbonyl stretching region for (η^2 -C₆₀)Ir(CO)(PPh₃)₂Cl are shows two bands, one at 2012 cm⁻¹(s) and the other one at 1963 cm⁻¹(s) is shown in figure 3.2. The band at 2012 cm⁻¹ was attributed to the complex (η^2 -C₆₀)Ir(CO)(PPh₃)₂Cl by comparison with the literature.^[13] The band at 1963cm⁻¹ was unequivocally assigned to Ir(CO)(PPh₃)₂Cl by comparison with the spectrum of a solid sample. These results showed that the equilibrium reaction favors the dissociated species (equation 3.3).



The experimental rate law for the dissociation reaction is given by:

$$-\frac{d[\mathrm{VC}_{60}]}{dt} = k_{obsd}[\mathrm{VC}_{60}] \tag{3.4}$$

where k_{obsd} is the experimental rate constant. Based on the equilibrium reaction, the rate law becomes:

$$-\frac{d[VC_{60}]}{dt} = (k_1 + k_{-1}[C_{60}])[VC_{60}]$$
(3.5)

where $k_{obsd} = k_1 + k_{-1} [C_{60}]$.

The reactions were studied under conditions where the concentration of C_{60} was negligible. The only source of C_{60} comes from the dissociation reaction. In addition, the reactions were performed at different concentrations of C_{60} in benzene. The results kinetic experiments suggest that the rate constant values (k_{obsd}) were independent of the concentration of C_{60} , as presented in table 3.3.

Unsuccessful attempts were made to study the dissociation reaction in toluene and chlorobenzene since the reaction was too fast to be monitored. In dichloromethane, the reactions were slow enough to be monitored (figure 3.5). The rate constant values determined for benzene and dichloromethane at various temperatures are presented in table 3.1 and table 3.2 respectively. The rate constant values determined for the reactions in solution of benzene for several concentrations of C_{60} are presented in table 3.3. The activation parameters were determined from the Eyring plots^[26] are presented in table 3.4.

The rate constant values suggest that dissociation of C_{60} may be solvent-assisted depending on the chemical nature of the solvent. Thus, mixed solvents kinetics experiments were performed to test this expectation. The rate constant values determined for mixed solvents kinetics experiments at 295.2 K are presented in table 3.5.



Figure 3.3: Plot of absorbance versus time at 550 nm for C₆₀ dissociation from $(\eta^2 - C_{60})$ Ir(CO)(PPh₃)₂Cl in benzene at 295.3 K. The continuous trace is for absorbance values obtained from the equation that best describes the relation between absorbance versus time. Equation $A_t = (A_0 - A_\infty) e^{-kobsd^*t} + A_\infty$ where $(A_0 - A_\infty) = 0.61166$, $k_{obsd} = 1.28 \times 10^{-2} \text{ s}^{-1}$ and $A_\infty = 0.08087$.



Figure 3.4: Plot of absorbance versus time at 550 nm for C_{60} dissociation from $(\eta^2 - C_{60})$ Ir(CO)(PPh₃)₂Cl in benzene at 295.2 K in a [C₆₀] saturate solution. The continuous trace is for absorbance values obtained from the equation that best describes the relation between absorbance versus time. Equation $A_t = (A_0 - A_\infty) e^{-kobsd^*t} + A_\infty$ where $(A_0 - A_\infty) = 0.14414$, $k_{obsd} = 1.25 \times 10^{-2} s^{-1}$ and $A_\infty = 0.15706$.



Figure 3.5: Plot of absorbance versus time at 550 nm for C₆₀ dissociation from $(\eta^2-C_{60})Ir(CO)(PPh_3)_2Cl$ in dichloromethane at 295.2 K. The continuous trace is for absorbance values obtained from the equation that best describes the relation between absorbance versus time. Equation $A_t = (A_0 - A_\infty) e^{-kobsd^*t} + A_\infty$ where $(A_0 - A_\infty) = 0.07284$, $k_{obsd} = 2.27 \times 10^{-2} s^{-1}$ and $A_\infty = 0.26946$.

Temperature (K) (±0.1 K)	$k_{obsd} 10^{-2}$ (s ⁻¹)
289.5	0.2163 (6)
291.3	0.479 (1)
	0.535 (1)
293.1	0.872 (3)
	0.772 (5)
295.3	1.001 (1)
	1.116 (2)
	1.287 (3)
298.3	1.951 (4)
	1.47(1)
	1.567 (3)
300.4	3.45 (5)
	2.71 (5)
	3.49 (6)
	3.14 (3)
	2.55 (3)
303.2	6.52 (2)
	11.23 (6)
	9.23 (8)

Table 3.1: Values of k_{obsd} for the dissociation of C_{60} from $(\eta^2 - C_{60})Ir(CO)(PPh_3)_2Cl$ in benzene at various temperatures.

The values given in parenthesis are the uncertainties for the last digit reported of the rate constant values.

Temperature (K) (±0.1 K)	k _{obsd} 10 ⁻² (s ⁻¹)		
295.2	1.52 (7) 2.28 (6)		
299.1	2.9 (2) 2.74 (7)		
303.1	3.6 (2) 5.7 (5)		

Table 3.2: Values of k_{obsd} for the dissociation of C_{60} from $(\eta^2 - C_{60})Ir(CO)(PPh_3)_2Cl$ in dichloromethane at various temperatures.

The values given in parenthesis are the uncertainties for the last digit reported of the rate constant values.

Table 3.3: Values of k_{obsd} for the dissociation of C_{60} from $(\eta^2 - C_{60})Ir(CO)(PPh_3)_2Cl$ in benzene solutions for different [C_{60}] at 295.2 K.

Concentration (mM)	$k_{obsd} 10^{-2}$ (s ⁻¹)
0.5	1.184 (5)
0.8	1.139 (5)
1.0	1.147 (4)
2.36*	1.210 (9) 1.245 (3) 1.585 (9)

*Concentration for a saturated solution of C_{60} in benzene.

The values given in parenthesis are the uncertainties for the last digit reported of the rate constant values.

Solvent	$\Delta H^{\ddagger}_{obsd}$ (kJ/mol)	ΔS [‡] _{obsd} (J/K mol)	
Benzene	166(10)	279(30)	
Dichloromethane	81(6)	-4(2)	

Table 3.4: Values of activation parameters for C_{60} dissociation from $(\eta^2-C_{60})Ir(CO)(PPh_3)_2Cl$ in benzene and dichloromethane.

The values given in parenthesis are the uncertainties for the value reported.

Table 3.5: k_{obsd} average values and k_1 and k_2 estimated values for the dissociation of C₆₀ from $(\eta^2-C_{60})Ir(CO)(PPh_3)_2Cl$ for mixed solvents kinetics experiments at 295.2 K.

Temperature (K) (±0.1)	Token ligand	[Token ligand] (M)	Average k $(10^{-2}, s^{-1})$	$(10^{-2}, s^{-1})$	**k ₂ (10 ⁻² , s ⁻¹)
295.2	Dichloromethane	0.0000	1.14	2.1(3)	1.1(6)
		0.2474	2.70		
		0.5240	3.04		
		1.0000	2.67		
		1.2027	4.78		
		1.5000	4.3		
		2.0820	4.4		
		2.3768	5.4		
		3.2055	9.5		
	Toluene	0.0000	1.14	4.4(5)	1.2(3)
		0.1028	1.70		
		0.1944	2.64		
		0.4382	3.64		
		0.6472	3.37		
		1.1136	6.19		

The values given in parenthesis are the uncertainties for the value reported. Estimated values from the *slope and the **intercept of the plot of k_{obsd} versus [Token ligand].

3.4 Discussion

Eyring plots were constructed to estimate the activation parameters. The Eyring equation (equation 3.6) is a theoretical construct, based on the transition state model A plot of $\ln(k/T)$ versus 1/T is expected to be linear for small temperature ranges.

$$\ln\frac{k}{T} = -\frac{\Delta H^{\mp}}{R} \left(\frac{1}{T}\right) + \ln\frac{k_B}{h} + \frac{\Delta S^{\mp}}{R}$$
(3.6)

Values for $\Delta H^{\dagger}_{obsd}$ can be calculated from the slope of this line (= - m·R) and values for $\Delta S^{\dagger}_{obsd}$ can be calculated from the intercept of the line (= R {b -ln (k_B/h)}), were k_B = Boltzmann's constant [1.381x10⁻²³ J · K⁻¹], T = absolute temperature in Kelvin (K), and *h* = Plank's constant [6.626x10⁻³⁴ J · s]. The Eyring plots constructed with experimental data from this work are shown in figure 3.6 and figure 3.7. The values of the activation parameters calculated from these plots are presented in table 3.4.



Figure 3.6: Eyring plot for C_{60} dissociation from $(\eta^2 - C_{60})Ir(CO)(PPh_3)_2Cl$ in benzene.


Figure 3.7: Eyring plot for C_{60} dissociation from $(\eta^2 - C_{60})Ir(CO)(PPh_3)_2Cl$ in dichloromethane.

The k_{obsd} values for C₆₀ dissociation from $(\eta^2-C_{60})Ir(CO)(PPh_3)_2Cl$ are independent of the concentration of C₆₀ but, depends on the nature of the solvent used. The mixed solvents kinetics experiments support this observation as presented in table 3.5. The order with respect to non-coordinating solvents and to coordinating solvent is zero and first order, respectively (figure 3.9). These observations suggest two different mechanistic pathways. One in which the dissociation reaction was not solvent-assisted and other in which the dissociation was solvent-assisted as presented in figure 3.8. The mechanism based-rate law is also given by equation 3.4 where the expressions for k_{obsd} (equation 3.7 and 3.9) were based on the proposed mechanism shown in figure 3.8.



Figure 3.8: Proposed mechanisms for C_{60} dissociation from $(\eta^2 - C_{60})Ir(CO)(PPh_3)_2Cl$. Path-I describes solvent-assisted dissociation whereas Path-II describes a non solvent-assisted dissociation. TS are transitions state.

Assuming that the concentration of the intermediated species is in steady-state concentration, the equation for k_{obsd} for Path-I is:

$$k_{obsd} = (k_1[solvent] + k_{-1}[C_{60}])$$
(3.7)

Since k_{obsd} is independent of the concentration of C₆₀, equation 3.7 becomes:

$$k_{obsd} \approx k_1[solvent] \tag{3.8}$$

The equation for k_{obsd} for Path-II is:

$$k_{obsd} = \frac{k_2 k_3 [solvent]^n}{k_{-2} [C_{60}] + k_3 [solvent]^n}$$
(3.9)

Likewise, since k_{obsd} is independent of the concentration of C₆₀, equation 3.9 becomes:

$$k_{obsd} \approx k_2 \tag{3.10}$$

Path-I describes the solvent-assisted mechanism and Path-II describes the dissociation reaction that is not solvent-assisted. Both paths predict mathematically equivalent rate laws, since the [solvent] >> $[(\eta^2-C_{60})Ir(CO)(PPh_3)_2CI]$ the solvent concentration become constant; satisfying equation 3.4.

In order to prove this proposed mechanism, mixed solvent kinetics experiment were performed for the dissociation reaction. These experiments were done under flooding conditions where [Token ligand] >> [(η^2 -C₆₀)Ir(CO)(PPh_3)_2Cl]. Thus the equation for k_{obsd} is:

$$k_{obsd} = k_1 [token \ ligand] + k_2 [benzene]$$
(3.11)

Plots of k_{obsd} versus [token ligand] were lineal (figure 3.9). This plot suggests that k_{obsd} depends on the concentration of token ligand. Additionally, the activation parameters suggest that the transition state was stabilized by dichloromethane but not by benzene as presented in table 3.4. Thus equation 3.11 becomes:

$$k_{obsd} = k_1 [token \ ligand] + k_2 \tag{3.12}$$

The activation parameters (table 3.4) suggested: (i) that Path-I may be a better description for the dissociation reaction in dichloromethane and (ii) Path-II may be a better description for the dissociation reaction in benzene.



Figure 3.9: Plot of k_{obsd} versus [Token ligand] for C_{60} dissociation from $(\eta^2 - C_{60})Ir(CO)(PPh_3)_2Cl$ for mixed solvents kinetics experiments at 295.2 K. In which dichloromethane (\blacktriangle) and toluene (\bullet) are the token ligand; and benzene was the solvent.

Chapter IV

Kinetics for the reaction of [60]Fullerene with piperidine

4.1 Materials and Methodology

4.1.1 General

The reagents used for the reaction were: [60]fullerene, piperidine and cyclohexane as a solvent. [60]Fullerene was purchased from Aldrich. Cyclohexane and piperidine were purchased from Aldrich and fractionally distilled under phosphorous pentoxide.

4.2 Kinetic Studies of the reaction of [60]Fullerene with piperidine

4.2.1 General

Kinetics experiments were carried out on a Perkin Elmer Lambda 25 UV-Vis Spectrometer under a nitrogen atmosphere, using a quartz cell of 10 mm path length. The temperature was set to be constant within approximately 0.1°C using a Julabo F-12 constant temperature bath. An EC model heating and refrigerating circulator and a K/J Fluke digital thermometer equipped with a bead thermocouple were used as temperature control devices.

In order to determine the wavelength where the reaction was to be monitored, a UV-Vis scan was performed to a solution of piperidine with C_{60} in cyclohexane. The chosen wavelength was the one at which a significant change in absorbance due to reaction was observed. The reaction monitoring was performed at the chosen wavelength of 407 nm.

The rate constant values were determined from the plots of absorbance versus time using a non-linear regression computer program (OriginPro 7.5). The error limits of

the rate constant values are given in parenthesis as the uncertainties of the last digit of the reported value.

4.2.2 Kinetics of the reaction of [60]Fullerene with piperidine

The reactions of C_{60} with piperidine were studied observing the increase in absorbance at a wavelength of 407 nm. The reactions were performed in cyclohexane at temperatures of: 318.2 K, 328.2 K and 338.2 K. The reactions were studied in several concentrations, under flooding conditions where the concentration of [piperidine] >> [fullerene].

4.2.3 Data Analysis

Kinetics data was analyzed using OriginPro 7.5, a non-linear least-squares computer program. The plots of absorbance versus time for the reaction were monophasic and biphasic, dependent on the concentration of piperidine. For concentration under 0.3 M the plots were monophasic, while for higher concentrations the plots were biphasic The functions, for those fits, given by the computer program are described by the following equation:

$$Y = (A_1) e^{-x/t1} + (A_2) e^{-x/t2} + Y_0$$
(4.1)

where Y is the dependant variable at time t; Y_0 is the value of Y at time 0 or initial value; A₁ and A₂ is the amplitude of the exponential it precedes; x is the independent variable and $1/t_1$ and $1/t_2$ are the rate constants. The family of equations obtained from the computer program is mathematically equivalent to a consecutive first order reaction equation (equation 4.2) that represents the monitored change of absorbance. The value of absorbance (A), is proportional to the concentration of the species involved in the reaction. The equation for consecutive first order reactions is given by:

$$A_t = \alpha e^{-kobsd1^*t} + \beta e^{-kobsd2^*t} + A_{\infty}$$
(4.2)

where the correspondence is: $A_t = Y$; $\alpha = A_1$; $\beta = A_2$; $k_n = 1/t_n$ (where n = 1 or 2); t = xand $A_{\infty} = Y_0$. In which A_t is the value of the absorbance at a given time; A_0 represents the absorbance at time zero; A_{∞} represents the absorbance at time infinite, α and β are preexponential constants, k is the observed rate constant and t is the time. The determined rate constant values are shown in table 4.1 and table 4.2.

4.3 Results

The reaction of C_{60} and piperidine (pip) in cyclohexane produced tetra(pip)fullerene epoxide adduct, presented in figure 4.1. The rate of the adduct appearance was monitored by observing an increase in absorbance at 407 nm. The reactions were studied under flooding conditions where the concentrations of piperidine were at least 10^5 times greater than the concentration of C_{60} . The pseudo-first order rate constant values were determined from the plots of absorbance versus time using a non linear least-squares computer program. The rate constant values determined for different concentrations of piperidine at various temperatures are presented in table 4.1 and table 4.2. The rate constants values (k_{obsd1} and k_{obsd2}) were dependent of the concentration of piperidine. The order with respect to piperidine is first order. The activation parameters, were determined from the Eyring plots,^[26] are presented in table 4.3 and table 4.4.



Figure 4.1: Proposed adduct for the reaction of C_{60} with piperidine to produce tetra(pip)-fullerene epoxide.

The reaction product was characterized in duplicate by elemental analysis. The analysis was performed in Midwest Microlab, Indianapolis, IN. The results found a composition of %C = 86.87 and 87.21; %N = 5.12 and 5.20; and %H = 4.28 and 4.16 for the duplicated analysis. The composition calculated for $C_{80}N_4H_{40}O$ is % C = 89.55; %N = 5.22; and %H = 3.73.

Plots of absorbance versus time for the reaction were monophasic and biphasic, depending on the piperidine concentration. The plots were monophasic for concentration under 0.3 M, while for higher concentrations the plots were biphasic. The biphasic plots (showing two segments) are indicative of consecutive reactions. A characteristic plot of absorbance versus time is presented in figure 4.2. Non linear fitting demonstrated that both reactions were first order respect to C_{60} . The rate constants values were obtained from these plots.



Figure 4.2: Plot of absorbance versus time at 407 nm for the reaction of C₆₀ with piperidine to produce tetra(pip)-fullerene epoxide. The reaction was performed in cyclohexane at 328.2 K, [pip] = 0.950 M, under flooding conditions where the concentration of [piperidine] >> [fullerene]. The continuous trace is for absorbance values obtained from the equation that best describes the relation between absorbance versus time. Equation $A_t = \alpha e^{-kobsd1*t} + \beta e^{-kobsd2*t} + A_{\infty}$ where $\alpha = 0.09678$, $\beta = 0.10183$, $k_{obsd1} = 2.67 \times 10^{-3} \text{s}^{-1}$, $k_{obsd2} = 3.59 \times 10^{-4} \text{s}^{-1}$ and $A_{\infty} = 0.31887$.

The first segment of the biphasic plot was ascribed to two consecutive piperidine additions. The second segment of the biphasic plot was ascribed to another two consecutive piperidine additions. The reaction corresponding to the second segment was followed by a hydrogen peroxide epoxidation producing a tetra(amino)-fullerene epoxide.

$$C_{60} + 2 \operatorname{pip} + O_2 \xrightarrow{\mathbf{k_{obsd1}}} C_{60} - (\operatorname{pip})_2 + H_2O_2$$
$$C_{60} - (\operatorname{pip})_2 + 2 \operatorname{pip} + O_2 \xrightarrow{\mathbf{k_{obsd2}}} C_{60} - (\operatorname{pip})_4(O) + H_2O_2$$

Figure 4.3: The chemical reaction of C_{60} with piperidine to produce tetra(pip)-fullerene epoxide.

The experimental rate laws for the reaction are equation 4.3 and 4.4 for the first and second segments, respectively:

$$-\frac{d[C_{60}]}{dt} = k_{obsd1}[C_{60}]$$
(4.3)

$$-\frac{d[C_{60} - (pip)_2]}{dt} = k_{obsd\,2} [C_{60} - (pip)_2]$$
(4.4)

where k_{obsd1} is the rate constant for the first segment and k_{obsd2} is the rate constant for the second segment of the plot of absorbance versus time.

Temperature (K)	[Piperidine]	Kobsd1
(±0.1)	(M)	$(10^{-4}, s^{-1})$
318.2	0.0340	0.12(2)
	0.0991	0.21(3)
	0.1161	0.89(2)
	0.1545	1.12(6)
	0.2173	2.291(9)
	0.3350	6.3(2)
	0.3446	6.5(4)
	2.4478	39(1)
	0.04 .50	
328.2	0.0152	1.59(2)
	0.0519	0.70(1)
	0.0936	0.97(1)
	0.2008	2.596(7)
	0.3408	5.2(3)
	0.4678	6.5(1)
	0.4953	10.4(2)
	1.4665	30(7)
220.2	0.0120	
338.2	0.0139	0.72(5)
	0.0778	0.81(1)
	0.1293	1.95(1)
	0.2049	2.852(8)
	0.3250	8.4(3)
	0.4773	12.5(2)
	0.9502	30.5(4)
	1.4515	36.8(9)
	2.3951	66(2)

Table 4.1: Values of k_{obsd1} for the reaction of C_{60} with piperidine to produce tetra(pip)-fullerene epoxide. The reactions were conducted in cyclohexane at various temperatures under flooding conditions where the concentration of [piperidine] >> [fullerene].

The values given in parenthesis are the uncertainties for the last digit reported of the rate constant values.

Table 4.2: Values of k_{obsd2} for the reaction of C_{60} with piperidine to produce C_{60} tetra(pip)-fullerene epoxide. The reactions were conducted in cyclohexane at various temperatures under flooding conditions where the concentration of [piperidine] >> [fullerene].

Temperature (K)	[Piperidine]	K _{obsd 2}
(±0.1)	(M)	$(10^{-4}, s^{-1})$
318.2	0.3350	1.1(7)
	0.3446	1.3(1)
	0.4987	3.32(5)
	0.9858	3.52(6)
	1.4660	3.85(2)
328.2	0.3408	1.5(2)
	0.3505	0.7(5)
	0.4678	1.0(2)
	0.4953	2.4(9)
	0.9490	3.6(7)
	1.4665	3.64(7)
	1.9377	5.06(9)
	2.9311	7.32(7)
338.2	0.3250	2.5(4)
	0.4773	2.0(2)
	0.9502	5.04(8)
	1.4515	5.13(9)
	1.9195	7.4(2)
	2.3951	8.8(1)

The values given in parenthesis are the uncertainties for the last digit reported of the rate constant values.

4.4 Discussion

The k_{obsd1} values for the reaction of C₆₀ with piperidine to produce tetra(pip)-fullerene epoxide are dependent of the concentration of piperidine. The mathematical behavior of the relation between k_{obsd1} and [pip] is consistent with the proposed mechanism, presented in figure 4.4. The mechanism based-rate law is also given by equation 4.3. Where the expressions for k_{obsd1} , based on the proposed mechanism, using the steady-state approximation for the intermediates species is given by equation 4.5.

$$k_{\text{obsd1}} = \frac{k_1 k_2 [pip] [O_2]}{k_{-1} + k_2 [O_2]}$$
(4.5)

Assuming that the intermediates species are in steady state concentration and that $k_2[O_2] >> k_{-1}$, equation 4.5 becomes:

$$k_{\text{obsd1}} = k_1 [pip] \tag{4.6}$$

equation 4.6 (mechanism-based) is mathematically equivalent to equation 4.3. (experimentally-based). Plots of k_{obsd1} versus [pip] were linear with zero intercepts within experimental error as presented in figure 4.6. The values of rate constant k_1 at various temperatures can be estimated as the slope of the linear plots of k_{obsd1} versus [pip]. Those values are presented in table 4.3.

Plot of absorbance versus time consists of two segments. Figure 4.4 describes the mechanism for the first segment, designed by k_{obsd1} . Figure 4.5 describes the mechanism for the second segment, designed by k_{obsd2} .



Figure 4.4: Proposed mechanism for the reaction of C_{60} with piperidine to produce C_{60} -(pip)₂ non steady-state intermediate adduct.



Figure 4.5: Proposed mechanism for the reaction of C_{60} -(pip)₂ with piperidine to produce C_{60} -(pip)₄, followed by a hydrogen peroxide epoxidation producing tetra(pip)-fullerene epoxide.



Figure 4.6: Plot of k_{obsd1} versus [piperidine] for the reaction of C_{60} with piperidine to produce tetra(pip)-fullerene epoxide. The reaction was performed at different piperidine concentrations in cyclohexane at various temperatures (\checkmark) 318.2 K, (\bullet) 328.2 K, and (\blacksquare) 338.2 K.

The rate constant values determined from the second segment of the biphasic plot are designed by k_{obsd2} . The k_{obsd2} values are dependent of the concentration of piperidine. The mathematical behavior of the relation between k_{obsd2} and [pip] is consistent with the proposed mechanism, presented in figure 4.5. The mechanism-based rate law is also given by equation 4.4. Where the expressions for k_{obsd2} , based on the proposed mechanism, using the steady-state approximation for the intermediates species is given by equation 4.7

$$k_{\text{obsd1}} = \frac{k_4 k_5 [pip] [O_2]}{k_{-4} + k_5 [O_2]}$$
(4.7)

Assuming that the intermediates species are in steady- state concentration and that $k_5[O_2] >> k_{-4}$, equation 4.7 becomes:

$$k_{obsd\,2} = k_4 [\,pip\,] \tag{4.8}$$

equation 4.8 (mechanism-based) is mathematically equivalent to equation 4.4 (experimentally-based). Plots of k_{obsd2} versus [pip] were linear with zero intercepts within experimental error as presented in figures 4.7 and 4.8. The values of rate constant k_4 at various temperatures can be estimated as the slope of the linear plots of k_{obsd2} versus [pip]. Those values are presented in table 4.4.



Figure 4.7: Plot of k_{obsd2} versus [piperidine] for the reaction of C_{60} with piperidine to produce tetra(pip)-fullerene epoxide. The reaction was performed in different piperidine concentrations in cyclohexane at 328.2 K.



Figure 4.8: Plot of k_{obsd2} versus [piperidine] for the reaction of C_{60} with piperidine to produce tetra(pip)-fullerene epoxide. The reaction was performed in different piperidine concentrations in cyclohexane at 338.2 K.

Eyring plots were constructed to estimate the activation parameters. The Eyring equation (equation 4.8) is a theoretical construct, based on the transition state model A plot of $\ln(k/T)$ versus 1/T is expected to be linear for small temperature ranges.

$$\ln\frac{k}{T} = -\frac{\Delta H^{\mp}}{R} \left(\frac{1}{T}\right) + \ln\frac{k_B}{h} + \frac{\Delta S^{\mp}}{R}$$
(4.8)

Values for $\Delta H^{\ddagger}_{obsd}$ can be calculated from the slope of this line(= - m·R) and values for $\Delta S^{\ddagger}_{obsd}$ can be calculated from the intercept of the line (= R {b -ln (k_B/h)}), were k_B = Boltzmann's constant [1.381x10⁻²³ J · K⁻¹], T = absolute temperature in Kelvin (K), and *h* = Plank's constant [6.626x10⁻³⁴ J · s]. The Eyring plots constructed with experimental data from this work are shown in figure 4.9. The values of the activation parameters calculate from these plots are presented in table 4.3 and table 4.4.



Figure 4.9: Eyring plot of k_{obds1} for the reaction of C_{60} with piperidine in cyclohexane.

As shown in table 4.3 and 4.4, the highly negative values of activation entropy $(\Delta S^{\dagger}_{obsd1} = -232 \text{ J/K} \text{ mol and } \Delta S^{\dagger}_{obsd2} = -237 \text{ J/K} \text{ mol})$ suggest an associative process that is consistent with the mechanistic description. The observed activation enthalpy $(\Delta H^{\dagger}_{obsd1})$ is actually the activation enthalpy of the step governed by k₁. Since its value involves the N-C bond forming (305 kJ/mol), C-C bond forming (347 kJ/mol), and C=C bond breaking (611 kJ/mol), thus the difference between bond forming and bond breaking is estimated $\Delta H^{\dagger}_{1} \cong 41 \text{ kJ/mol}$. In contrast the observed activation enthalpy $\Delta H^{\dagger}_{obsd1} = 21 \text{ kJ/mol}$, as shown in table 4.3. [60]Fullerene has a great deal of strain due to its spherical shape. A more detailed examination of this interpretation suggests that the sp²-hybridized carbon atoms of C₆₀ must be bent to form the closed sphere, which produces angle strain. Release of that strain upon change in hybridization by the addition of piperidine may be account for the difference of about a 50% of is activation enthalpy. According to the

mechanism addition of piperidine to C_{60} reduces angle strain by changing sp²-hybridized carbons into sp³-hybridized ones. The change in hybridized orbitals, due to the addition, causes the bond angles to decrease from around 120° in the sp² orbitals to around 109.5° in the sp³ orbitals. This decrease in bond angles provokes less bond bending, making a more stable molecule. It is reasonable to consider that the activation enthalpy for the process governed by k_1 is less than the expected ($\Delta H^{\ddagger}_1 \cong 41$ kJ/mol) due to the angle strain that C_{60} possesses. The same interpretation should be proper for the second segment of the biphasic plot governed by k_4 . But in this case the difference in activation enthalpy was less than 50% due to the previous stabilization gain by the addition of the two piperidine molecules to C_{60} .

Table 4.3: Values of rate constant (k_1) and activation parameters of k_{obsd1} for the reaction of C_{60} with piperidine to produce tetra(pip)-fullerene epoxide. The reaction was performed in cyclohexane at various temperatures under flooding conditions where the concentration of [piperidine] >> [fullerene].

Temperature (K) (±0.1)	*k ₁ (10 ⁻³ , s ⁻¹)	∆H [‡] _{obs} (kJ/mol)	∆S‡ _{obs} (J/K mol)
318.2	1.6(5)	21(3)	-232(28)
328.2	2.1(1)		
338.2	2.8(1)		

*Estimated values from the slope for the plot of k_{obsd1} vs. [pip].

The values given in parenthesis are the uncertainties for the value reported.

Table 4.4: Values of rate constant (k_4) and activation parameters of k_{obsd2} for the reaction of C₆₀ with piperidine to produce tetra(pip)-fullerene epoxide. The reaction was performed in cyclohexane at various temperatures under flooding conditions where the concentration of [piperidine] >> [fullerene].

Temperature (K) (±0.1)	*k ₄ (10 ⁻⁴ , s ⁻¹)	^{**} ∆H [‡] _{obs} (kJ/mol)	^{**} ∆S [‡] _{obs} (J/K mol)
328.2	2.3(2)	26(2)	-237(31)
338.2	3.2(4)		

*Estimated values from the slope for the plot of k_{obsd2} vs. [pip].

**Estimated values using the experimental data from the kinetic experiments performed at 328.2 K and 338.2 K.

The values given in parenthesis are the uncertainties for the value reported.

Chapter V

Kinetics for the reaction of [60]Fullerene with pyrrole

5.1 Materials and Methodology

5.1.1 General

The reagents used for the reaction were: [60]Fullerene, pyrrole and cyclohexane as a solvent. [60]Fullerene was purchased from Aldrich. Cyclohexane (Fisher) was fractionally distilled under phosphorous pentoxide and pyrrole (Aldrich) was fractionally distilled under potassium hydroxide.

5.2 Kinetic Studies of the reaction of [60]Fullerene with pyrrole

5.2.1 General

Kinetics experiments were carried out on a Perkin Elmer Lambda 25 UV-Vis Spectrometer under a nitrogen atmosphere, using a quartz cell of 10mm path length. The temperature was set to be constant within approximately 0.1°C using a Julabo F-12 constant temperature bath. An EC model heating and refrigerating circulator and a K/J Fluke digital thermometer equipped with a bead thermocouple were used as temperature control devices.

In order to determine the wavelength where the reaction was to be monitored, a UV-vis scan was performed to a solution of pyrrole with C_{60} in cyclohexane. The chosen wavelength was the one at which a significant change in absorbance due to reaction was observed. The reaction monitoring was performed at the chosen wavelength of 350 nm.

The rate constant values were determined from the plots of absorbance versus time using a non-linear regression computer program (OriginPro 7.5). The error limits of

the rate constant values are given in parenthesis as the uncertainties of the last digit of the reported value.

5.2.2 Kinetics of the reaction of [60]Fullerene with pyrrole

The reactions of C_{60} with pyrrole were studied observing the increase in absorbance at a wavelength of 350 nm. The reactions were performed in cyclohexane at temperatures of: 318.2 K, 328.2 K and 338.2 K. The reactions were studied in several concentrations, under flooding conditions where the concentration of [pyrrole] >> [fullerene].

5.2.3 Data Analysis

Kinetics data was analyzed using OriginPro 7.5, a non-linear least-squares computer program. The plots of absorbance versus time for the reaction were biphasic. The functions, for those fits, given by the computer program are described by the following equation:

$$Y = (A_1) e^{-x/t1} + (A_2) e^{-x/t2} + Y_0$$
(5.1)

where Y is the dependant variable at time t; Y_0 is the value of Y at time 0 or initial value; A₁ and A₂ is the amplitude of the exponential it precede; x is the independent variable and 1/t₁ and 1/t₂ are the rate constants. The family of equations obtained from the computer program is mathematically equivalent to a consecutive first order reaction equation (equation 5.2) that represents the monitored change of absorbance. The value of absorbance (A), is proportional to the concentration of the species involved in the reaction. The equation for consecutive first order reactions is given by:

$$A_t = \alpha e^{-kobsd1^*t} + \beta e^{-kobsd2^*t} + A_{\infty}$$
(5.2)

(= **^**)

where the correspondence is: $A_t = Y$; $\alpha = A_1$; $\beta = A_2$; $k_n = 1/t_n$ (where n = 1 or 2); t = xand $A_{\infty} = Y_0$. In which A_t is the value of the absorbance at a given time; A_0 represents the absorbance at time zero; A_{∞} represents the absorbance at time infinite; α and β are preexponential constants; k is the observed rate constant and t is the time. The determined rate constant values are shown in table 5.1 and table 5.2.

5.3 Results

The rate of the reaction was monitored by observing an increase in absorbance at 350 nm. The reactions were studied under flooding conditions where the concentrations of pyrrole were at least 10^5 times greater than the concentration of C₆₀. Plots of absorbance versus time for the reaction were biphasic. The biphasic plots (showing two segments) are indicative of consecutive first order reactions. Plot of absorbance versus time is presented in figure 5.1. Two rate constants were obtained from this plot: k_{obsd1} and k_{obsd2} . The pseudo-first order rate constant values were determined from the plots of absorbance versus time using a non linear least-squares computer program. The rate constant values determined for different concentrations of pyrrole at various temperatures are presented in table 5.1 and table 5.2. These results suggest that the rate constant values $(k_{obsd1} \text{ and } k_{obsd2})$ were dependent of the concentration of pyrrole for the reactions performed at 318.2 K and 328.2 K as shown in figures 5.2, 5.3, 5.5 and 5.6. In contrast, the rate constant values seem independent of the concentration of pyrrole for the reaction at 338.2 K as shown in figures 5.4 and 5.7. This unpredicted observation requires more study in order to establish a mechanistic interpretation. Also, characterization by elemental analysis, Infrared Spectroscopy and NMR was necessary in order to elucidate the composition of the product. While the detailed mechanism remains unclear, we speculate that the reaction of C_{60} and pyrrole in cyclohexane produced C_{60} -(pyrrole)_n adduct.



Figure 5.1: Plot of absorbance versus time at 350 nm for the reaction of C₆₀ with pyrrole. The reaction was performed in cyclohexane at 328.2 K, [pyrrole] = 0.3813 M, under flooding conditions where the concentration of [pyrrole] >> [fullerene]. The continuous trace is for absorbance values obtained from the equation that best describes the relation between absorbance versus time. Equation $A_t = \alpha e^{-kobsd1*t} + \beta e^{-kobsd2*t} + A_{\infty}$ where $\alpha = 0.16842$, $\beta = 0.68122$, $k_{obsd1} = 5.6x10^{-3}s^{-1}$, $k_{obsd2} = 3.14x10^{-4}s^{-1}$ and $A_{\infty} = 1.26704$.



Figure 5.2: Plot of k_{obsd1} versus [pyrrole] for the reaction of C_{60} with pyrrole. The reaction was performed in different pyrrole concentrations in cyclohexane at 318.2 K.



Figure 5.3: Plot of k_{obsd1} versus [pyrrole] for the reaction of C_{60} with pyrrole. The reaction was performed in different pyrrole concentrations in cyclohexane at 328.2 K.



Figure 5.4: Plot of k_{obsd1} versus [pyrrole] for the reaction of C_{60} with pyrrole. The reaction was performed in different pyrrole concentrations in cyclohexane at 338.2 K.



Figure 5.5: Plot of k_{obsd2} versus [pyrrole] for the reaction of C_{60} with pyrrole. The reaction was performed in different pyrrole concentrations in cyclohexane at 318.2 K.



Figure 5.6: Plot of k_{obsd2} versus [pyrrole] for the reaction of C_{60} with pyrrole. The reaction was performed in different pyrrole concentrations in cyclohexane at 328.2 K.



Figure 5.7: Plot of k_{obsd2} versus [pyrrole] for the reaction of C_{60} with pyrrole. The reaction was performed in different pyrrole concentrations in cyclohexane at 338.2 K.

Temperature (K)	[Pvrrole]	Kabed 1
(±0.1)	(M)	(10^{-3} s^{-1})
318.2	0.0262	1.63(3)
	0.1082	4.9(1)
	0.3011	5.6(1)
	0.3903	7.0(2)
	0.4987	5.8(1)
	0.9639	10.4(8)
328.2	0.0147	3.69(5)
	0.1940	1.82(4)
	0.3111	8.5(3)
	0.3813	5.6(1)
	0.4886	10.5(4)
	0.9662	11.0(8)
	1.4623	15(1)
338.2	0.0380	3.92(8)
	0.0936	10.9(6)
	0.2838	3.28(6)
	0.3898	6.3(2)
	0.4693	2.9(1)

Table 5.1: Values of k_{obsd1} for the reaction of C_{60} with pyrrole. The reaction was performed in cyclohexane at various temperatures under flooding conditions where the concentration of [pyrrole] >> [fullerene].

The values given in parenthesis are the uncertainties for the last digit reported of the rate constant values.

Temperature (K) (±0.1)	[Pyrrole] (M)	$K_{obsd 2}$ (10 ⁻⁴ , s ⁻¹)
318.2	0.0262	2.03(2)
	0.1082	2.469(8)
	0.3011	4.41(1)
	0.3903	3.72(3)
	0.4987	5.33(4)
328.2	0.0147	3.88(2)
	0.1940	3.83(4)
	0.3111	3.86(1)
	0.3813	3.14(2)
	0.4886	8.36(5)
	0.9662	14.9(4)
338.2	0.0380	2.96(2)
	0.0936	5.66(2)
	0.2838	2.11(2)
	0.3898	3.93(4)
	0.4693	1.85(2)

Table 5.2: Values of k_{obsd2} for the reaction of C_{60} with pyrrole. The reaction was performed in cyclohexane at various temperatures under flooding conditions where the concentration of [pyrrole] >> [fullerene].

The values given in parenthesis are the uncertainties for the last digit reported of the rate constant values.

Chapter VI

Conclusion

The experimental data presented in this research project helps to understand the chemical properties of functionalized C_{60} . The functionalization was performed using organometallic complex and secondary amines. Kinetic experiments were performed to elucidate the reactivity properties of fullerene.

Kinetic experiments, for the dissociation of C₆₀ from $(\eta^2 - C_{60})Ir(CO)(PPh_3)_2Cl$ shows plots of absorbance *versus* time that were decreasing exponential. The k_{obsd} values are independent of [C₆₀]. Since k_{obsd} values vary depend on the nature of the solvent; C₆₀ dissociation may be solvent-assisted. The order with respect to non-coordinating solvents and to coordinating solvent is zero and first order, respectively. The highly positive value of activation entropy ($\Delta S^{\ddagger}_{obsd} = +279(30)$ J/K mol) suggest that in benzene the dissociation reaction is not solvent- assisted. In this case the value of activation enthalpy ($\Delta H^{\ddagger}_{obsd} = 166(10)$ kJ/mol) should be close to the actual thermodynamic Ir-C₆₀ bond enthalpy.

Fullerene reacts with piperidine to form tetra(amino)-fullerene epoxide. Kinetic experiments were biphasic suggesting that the reaction goes via consecutive first order reactions. The first segment of the biphasic plot was ascribed to two consecutive piperidine additions. The second segment of the biphasic plot was ascribed to another two consecutive piperidine additions. The reaction corresponding to the second segment was followed by a hydrogen peroxide epoxidation producing a tetra(amino)-fullerene epoxide. The results suggest that the rate constant values (k_{obsd1} and k_{obsd2}) were dependent of the concentration of piperidine. In addition, the negative values of activation entropies

support an associative process. In contrast to the dihapto mode (η^2) of reaction of fullerene with metal-carbonyl complexes as reported previously,^[8-11] this work presented the functionalization of fullerene with piperidine producing tetra(amino)-fullerene epoxide.

Plots of absorbance versus time for the reaction of C_{60} with pyrrole were biphasic suggesting that the reaction goes via consecutive first order reactions. Although a mechanistic interpretation is difficult to propose, the kinetics experiments indicate that C_{60} undergoes a reaction with pyrrole. This reaction is dependent of pyrrole concentration in a temperature range of 318.2 to 328.2 K. In contrast the reaction seems to be independent of pyrrole concentration at 338.2 K. A more detailed study of this reaction is necessary.

References

- Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K; Huffman, D. R. *Nature* 1990, 347, 354. Bürgi, H. B.; Blanc, E.; Schwarzenbach, D.; Liu, S.; Lu, Y.; Kappes, M. M.; Ibers, *J. Angew. Chem., Int. Ed. Engl.* 1992, 31, 640. Satpathy, S. *Chem. Phys. Lett.* 1986, 130, 545. Hawkins, J. M; Meyer, A.; Lewis, T. A.; Loren, S.; Hollander, F. J., *Science* 1991, 252, 313.
- Isobe, H.; Tanaka, T.; Nakanishi, W.; Lemiègre, L.; Nakamura, E. J. Org. Chem., 2005, 70, 4826–4832.
- 3. Isobe, H.; Tomita, N.; Nakamura, E. Org. Lett., 2000, 2, 3663-3665.
- 4. Modin, J.; Johansson, H. Grennberg, H. Org. Lett., 2005, 7, 3977 3979.
- 5. Kroto, H. W., Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature*, **1985**, 318, 162 163.
- 6. Ruoff, R.S.; Tse, D. S.; Malhotra, R.; Lorents, D.C. J. Phys. Chem., 1993, 91, 3379-3383.
- 7. Tegos, G.; Demidova, T.; Arcila-Lopez, D.; Lee, H.; Wharton, T.; Gali, H.; Hamblin, M. *Chemistry & Biology*, **2005**, 12, 1127-1135.
- 8. Rivera, L.; Colón-Padilla, F.; Del Toro-Novalés, A.; Cortés-Figueroa, J. E. J. Coord. Chem., 2001, 54, 143.
- 9. Igartúa-Nieves, E.; Ocasio-Delgado, Y.; Cortés-Figueroa, J. E. J. Coordination Chem., 2007, 60, 449-456.
- Rivera-Rivera, L. A.; Crespo-Román, G.; Acevedo-Acevedo, D.; Ocasio-Delgado, Y.; Cortés-Figueroa, J. E. *Inorganica Chimica Acta*, 2004, 357, 881-887.
- 11. Ocasio-Delgado, Y., De Jesus-Segarra, J.; Cortes-Figueroa, J. E. J. Organomet. *Chem.* 2005, 690, 3366–3372.
- 12. Qigshan,X.; Pérez-Cordero, E.; Echegoyen, L. Journal of American Chemical Society. 1992, 114, 3978.
- 13. Balch, A. L.; Catalano, B. J.; Lee, J. W. Journal of Inorganic Chemistry, 1991, 30, 3980-3981.

- 14. Vaska, L.; DiLuzio, J.W. Journal of American Chemical Society, **1962**, 84, 679 680.
- 15. Nakae, T.; Matsuo, Y.; Nakamura, E. Org. Lett., 2008,10, 621-623.
- Sawamura, M.; Iikura, H.; Ohama, T.; Hackler, U. E.; Nakamura, E. Journal of Organometallic Chemistry, 2000, 599, 32–36.
- 17. Sawamura, M.; Iikura, H.; Nakamura, E. J. Am. Chem. Soc., 1996, 118, 12850-12851.
- 18. Tzirakis, M. D.; Orfanopoulos, M. Org. Lett., 2008, 10, 873-876.
- (a) Hirsch, A.; Brettreich, M. Fullerenes: Chemistry and Reactions; Wiley-VCH: Weinheim 2005. (b) Kadish, K. M.; Ruoff, R. S. Fullerenes: Chemistry, Physics, and Technology; John Wiley & Sons: New York, 2000. (c) Hirsch, A. The Chemistry of Fullerenes; Theme: Stuttgart, 1994. (d) The Chemistry of Fullerenes; Taylor, R., Ed.; World Scientific: River Edge, NJ, 1995.
- 20. Dubois, D.; Kadish, K. M.; Flanagan, S.; Haufiler, R. E.; Chibante, L. P. F.; Wilson, L. J. J. Am. Chem. Soc,. 1991, 113, 4364.
- 21. Dubois, D.; Jones, M. T.; Kadish, K. M. J. Am. Chem. Soc., 1992, 114, 6446.
- 22. Ohsawa, Y.; Saji, T. J. Chem. Soc. Chem. Commun. 1992, 781.
- 23. Zhou, F.; Jehoulet, C.; Bard, A. J.. J. Am. Chem. Soc., 1992, 114, 11004.
- 24. Haddon, R. C.; Brus, L. E.; Raghavachari, K. Chem Phys. Lett., 1986, 125, 249.
- Igartúa-Nieves, E.; Ocasio-Delgado, Y.; Torres-Castillo, María D. L. A.; Rivera-Betancourt, O.; Rivera-Pagán, J. A.; Ridriguez, D.; López, G. E.; Cortés-Figueroa, J. E. *Dalton Trans.* 2007, 1293-1299.
- 26. Laidler, K.J.; King, M.C. J. Phys. Chem. 1983, 87, 2657-2664.
- 27. Nunzi, F.; Sgamellotti, A.; N. Re, Floriani, C. Dalton Trans. 1999, 19, 3487.
- Vaska, L.; DiLuzio, J.W. Journal of American Chemical Society, 1961, 83, 2784-2785.
- 29. Vaska, L.; Catone, D.L. Journal of American Chemical Society, 1966, 88, 5325-5327.
- 30. Aizenberg, M.; Milstein, D.; Tulip, T. H. Organometallics, 1996, 15, 4093-4095.

- 31. Mooney, K. E.; Bengali, A. A. J. Chem. Education, 2003, 80, 1044-1047.
- 32. Igartúa-Nieves, E.; M.S. Thesis, University of Puerto Rico at Mayagüez, Jul. 2006.
- 33. Hammond, G.S. J. Am. Chem. Soc. 1955, 77, 334.
- 34. Lide, D. R. *CRC Handbook of Chemistry and Physics*, 88^{ht} edition; Taylor & Francis Group: Florida, **2007-08**.
- 35. Kadish, K. M.; Ruoff, R. S. *Fullerenes: Chemistry, Physics and Technology*, 1st edition; Wiley-Interscience: New Yokk, **2000**.
APPENDICES

Appendices A

Appendix A.1

Plot of absorbance versus time for C_{60} dissociation from $(\eta^2-C_{60})Ir(CO)(PPh_3)_2Cl$ in benzene at various temperature.



Figure A.1.1: Plot of absorbance versus time for C_{60} dissociation from $(\eta^2 - C_{60})Ir(CO)(PPh_3)_2Cl$ in benzene at 289.5 K.

Data: Data1 B Model: ExpDec1 Equation: $y = A1 \exp(-x/t1) + y0$ Weighting: No weighting у = 0.00007Chi^2/DoF R^2 = 0.99772y0 0.12 0.00042 0.71697 0.00081 A1 t1 462.1524 1.20973



Figure A.1.2: Plot of absorbance versus time for C_{60} dissociation from $(\eta^2 - C_{60})Ir(CO)(PPh_3)_2Cl$ in benzene at 295.5 K.

Data: Data1_B Model: ExpDec1 Equation: $y = A1 \exp(-x/t1) + y0$ Weighting: No weighting у Chi^2/DoF = 0.00002R^2 = 0.99916 y0 0.00024 0.08087 0.61166 0.00089 A1 t1 77.68744 0.19959



Figure A.1.3: Plot of absorbance versus time for C_{60} dissociation from $(\eta^2 - C_{60})Ir(CO)(PPh_3)_2CI$ in benzene at 303.2 K.

Data: Data1 B Model: ExpDec1 Equation: $y = A1 \exp(-x/t1) + y0$ Weighting: No weighting y Chi^2/DoF = 2.754E-6 R^2 = 0.99759 y0 0.06981 0.00018 A1 0.16993 0.00092 t1 10.83004 0.09749

Appendix A.2

Plot of absorbance versus time for C_{60} dissociation from $(\eta^2 - C_{60})Ir(CO)(PPh_3)_2Cl$ in dichloromethane at various temperature.



Figure A.2.1: Plot of absorbance versus time for C_{60} dissociation from $(\eta^2 - C_{60})Ir(CO)(PPh_3)_2CI$ in dichloromethane at 295.2 K.

Data: Data1 B Model: ExpDec1 Equation: $y = A1 \exp(-x/t1) + y0$ Weighting: No weighting у = 5.1781E-6 Chi^2/DoF R^2 = 0.98601 y0 0.26946 0.00055 0.00071 A1 0.07284 43.94887 1.20278 t1



Figure A.2.2: Plot of absorbance versus time for C_{60} dissociation from $(\eta^2 - C_{60})Ir(CO)(PPh_3)_2CI$ in dichloromethane at 299.1 K.

Data: Data1_B Model: ExpDec1 Equation: $y = A1 \exp(-x/t1) + y0$ Weighting: No weighting у Chi^2/DoF = 9.1782E-7 R^2 = 0.98732y0 0.14036 0.00021 0.03232 0.00032 A1 t1 36.47232 0.9403



Figure A.2.3: Plot of absorbance versus time for C_{60} dissociation from $(\eta^2 - C_{60})Ir(CO)(PPh_3)_2CI$ in dichloromethane at 303.1 K.

Data: Data1 B Model: ExpDec1 Equation: $y = A1 \exp(-x/t1) + y0$ Weighting: No weighting y Chi^2/DoF = 5.5362E-6 R^2 = 0.97875y0 0.23151 0.00153 A1 0.06099 0.00133 t1 1.8615 27.74053

Appendix A.3

Plot of absorbance versus time for C_{60} dissociation from $(\eta^2-C_{60})Ir(CO)(PPh_3)_2Cl$ in benzene solutions for different $[C_{60}]$ at 295.2 K.



Figure A.3.1: Plot of absorbance versus time for C_{60} dissociation from $(\eta^2 - C_{60})Ir(CO)(PPh_3)_2Cl$ in benzene at 295.2 K in $[C_{60}] = 0.5$ M.

Data: Data1 B Model: ExpDec1 Equation: $y = A1 \exp(-x/t1) + y0$ Weighting: No weighting у Chi^2/DoF = 1.3242E-6 R^2 = 0.99805y0 0.0399 0.00008 A1 0.00025 0.11156 84.42926 0.35308 t1



Figure A.3.2: Plot of absorbance versus time for C_{60} dissociation from $(\eta^2 - C_{60})$ Ir(CO)(PPh₃)₂Cl in benzene at 295.2 K in [C₆₀] = 1.0 M.

Data: Data1 B Model: ExpDec1 Equation: $y = A1 \exp(-x/t1) + y0$ Weighting: No weighting у Chi^2/DoF = 6.552E-7 R^2 = 0.998250.00005 y0 0.05286 A1 0.00017 0.08678 87.15212 0.30507 t1



Figure A.3.3: Plot of absorbance versus time for C_{60} dissociation from $(\eta^2 - C_{60})Ir(CO)(PPh_3)_2Cl$ in benzene at 295.2 K in C_{60} saturate solution.

Data: Data1 B Model: ExpDec1 Equation: $y = A1 \exp(-x/t1) + y0$ Weighting: No weighting у Chi^2/DoF = 9.3927E-7 R^2 = 0.99916 y0 0.15706 0.00007A1 0.00021 0.14414 0.22094 t1 80.30187

Appendix A.4

Plot of absorbance versus time for C_{60} dissociation from $(\eta^2-C_{60})Ir(CO)(PPh_3)_2Cl$ for mixed solvents kinetics experiments at 295.2 K. Where dichloromethane was the token ligand and benzene was the solvent.



Figure A.4.1: Plot of absorbance versus time for C_{60} dissociation from $(\eta^2 - C_{60})Ir(CO)(PPh_3)_2Cl$ for mixed solvents kinetics experiments at 295.2 K. Where dichloromethane (0.247 M) was the token ligand and benzene was the solvent.

Data: Data1_B Model: ExpDec1 Equation: $y = A1 \exp(-x/t1) + y0$ Weighting: No weighting у Chi^2/DoF = 2.2288E-6 R^2 = 0.96874y0 0.10293 0.00016 A1 0.03679 0.00057 t1 25.0895 0.69832



Figure A.4.2: Plot of absorbance versus time for C_{60} dissociation from $(\eta^2 - C_{60})Ir(CO)(PPh_3)_2Cl$ for mixed solvents kinetics experiments at 295.2 K. Where dichloromethane (1.2027 M) was the token ligand and benzene was the solvent.

Data: Data1 B Model: ExpDec1 Equation: $y = A1 \exp(-x/t1) + y0$ Weighting: No weighting у Chi^2/DoF = 5.9629E-7 R^2 = 0.99955 y0 0.06297 0.00009 A1 0.16167 0.00035 17.81745 0.06756 t1



Figure A.4.3: Plot of absorbance versus time for C_{60} dissociation from $(\eta^2 - C_{60})Ir(CO)(PPh_3)_2Cl$ for mixed solvents kinetics experiments at 295.2 K. Where dichloromethane (3.2055 M) was the token ligand and benzene was the solvent.

Data: Data1_B Model: ExpDec1

Appendix A.5

Plot of absorbance versus time for C_{60} dissociation from $(\eta^2-C_{60})Ir(CO)(PPh_3)_2Cl$ for mixed solvents kinetics experiments at 295.2 K. Where toluene was the token ligand and benzene was the solvent.



Figure A.5.1: Plot of absorbance versus time for C_{60} dissociation from $(\eta^2 - C_{60})Ir(CO)(PPh_3)_2Cl$ for mixed solvents kinetics experiments at 295.2 K. Where toluene (0.1028 M) was the token ligand and benzene was the solvent.

Data: Data1_B Model: ExpDec1



Figure A.5.2: Plot of absorbance versus time for C_{60} dissociation from $(\eta^2 - C_{60})Ir(CO)(PPh_3)_2Cl$ for mixed solvents kinetics experiments at 295.2 K. Where toluene (0.4382 M) was the token ligand and benzene was the solvent.

Data: Data1_B Model: ExpDec1 Equation: $y = A1 \exp(-x/t1) + y0$ Weighting: No weighting у Chi^2/DoF = 1.1606E-6 R^2 = 0.96324y0 0.0767 0.00009 A1 0.02662 0.0004 t1 27.20095 0.6810312



Figure A.5.3: Plot of absorbance versus time for C_{60} dissociation from $(\eta^2 - C_{60})Ir(CO)(PPh_3)_2Cl$ for mixed solvents kinetics experiments at 295.2 K. Where toluene (1.1136 M) was the token ligand and benzene was the solvent.

Data: Data1_B Model: ExpDec1 Equation: $y = A1 \exp(-x/t1) + y0$ Weighting: No weighting у Chi^2/DoF = 9.4613E-7 R^2 = 0.948910.00011 y0 0.06296 A1 0.01889 0.00046 t1 16.16018 0.68368

Appendices **B**

Appendix B.1

Plot of absorbance versus time for the reaction of C_{60} with piperidine to produce tetra(pip)-fullerene epoxide. The reaction was performed in cyclohexane at 318.2 K.



Figure B.1.1: Plot of absorbance versus time for the reaction of C_{60} with piperidine to produce tetra(pip)-fullerene epoxide in cyclohexane.

[pip] = 0.0991 MTemperature = 318.2 KData: Data1 C Model: ExpDec1 Equation: $y = A1 \exp(-x/t1) + y0$ Weighting: No weighting у Chi^2/DoF = 6.4641E-6 R^2 = 0.99791y0 -1.43378 0.1714 A1 1.34918 0.17107 47204.61139 6467.17293 t1



Figure B.1.2: Plot of absorbance versus time for the reaction of C_{60} with piperidine to produce tetra(pip)-fullerene epoxide in cyclohexane.

[pip] = 0.1161 M Temperature = 318.2 K

Data: Data1_C Model: ExpDec1 Equation: $y = A1 \exp(-x/t1) + y0$ Weighting: No weighting у Chi^2/DoF = 6.3773E-7 R^2 = 0.99877y0 -0.19726 0.00306 0.16539 A1 0.00296 t1 11199.52351 281.72977



Figure B.1.3: Plot of absorbance versus time for the reaction of C_{60} with piperidine to produce tetra(pip)-fullerene epoxide in cyclohexane.

[pip] = 0.1545 M Temperature = 318.2 KData: Data1 C Model: ExpDec1 Equation: $y = A1 \exp(-x/t1) + y0$ Weighting: No weighting у Chi^2/DoF = 5.2319E-6 R^2 = 0.99877y0 -0.5227 0.00559 A1 0.407 0.00531 8922.05022 179.54515 t1



Figure B.1.4: Plot of absorbance versus time for the reaction of C_{60} with piperidine to produce tetra(pip)-fullerene epoxide in cyclohexane.

[pip] = 0.2173 M Temperature = 318.2 K Data: Data1 C Model: ExpDec1 Equation: $y = A1 \exp(-x/t1) + y0$ Weighting: No weighting у Chi^2/DoF = 3.105E-7 R^2 = 0.99981 y0 -0.22392 0.00034 A1 0.17499 0.00029 t1 4363.80124 17.76596



Figure B.1.5: Plot of absorbance versus time for the reaction of C_{60} with piperidine to produce tetra(pip)-fullerene epoxide in cyclohexane.

Temperature = 318.2 KData: Data1 C Model: ExpDec2 Equation: $y = A1 \exp(-x/t1) + A2 \exp(-x/t2) + y0$ Weighting: No weighting у Chi^2/DoF = 6.91E-8 R^2 = 0.99986y0 -0.13838 0.00738 A1 0.06763 0.00368 1585.15312 t1 48.75576 A2 0.0352 0.00376 t2 9482.91587 4152.28905

[pip] = 0.3350 M



Figure B.1.6: Plot of absorbance versus time for the reaction of C_{60} with piperidine to produce tetra(pip)-fullerene epoxide in cyclohexane.

[pip] = 0.4987 M Temperature = 318.2 KData: Data1 C Model: ExpDec2 Equation: $y = A1 \exp(-x/t1) + A2 \exp(-x/t2) + y0$ Weighting: No weighting У Chi^2/DoF = 2.2949E-7 R^2 = 0.99987 y0 -0.22651 0.0004 A1 0.04716 0.00135 t1 653.84195 17.33842 A2 0.13374 0.00108 t2 3009.48168 42.77307



Figure B.1.7: Plot of absorbance versus time for the reaction of C_{60} with piperidine to produce tetra(pip)-fullerene epoxide in cyclohexane.

[pip] = 0.9858 MTemperature = 318.2 KData: Data1 C Model: ExpDec2 Equation: $y = A1 \exp(-x/t1) + A2 \exp(-x/t2) + y0$ Weighting: No weighting у Chi^2/DoF = 6.1516E-7 R^2 = 0.99934y0 -0.24233 0.00038 A1 0.06018 0.00081 383.18819 8.46139 t1 A2 0.08921 0.00058 t2 2841.00342 49.16202



Figure B.1.8: Plot of absorbance versus time for the reaction of C_{60} with piperidine to produce tetra(pip)-fullerene epoxide in cyclohexane.

Temperature = 318.2 KData: Data1 C Model: ExpDec2 Equation: $y = A1 \exp(-x/t1) + A2 \exp(-x/t2) + y0$ Weighting: No weighting у Chi^2/DoF = 1.137E-6 R^2 = 0.99971y0 0.00033 -0.46157 A1 0.22352 0.00039 187.3802 4.32145 t1 A2 0.06897 0.00078 t2 2594.668 14.3752

[pip] = 1.4660 M

Appendix B.2

Plot of absorbance versus time for the reaction of C_{60} with piperidine to produce tetra(pip)-fullerene epoxide. The reaction was performed in cyclohexane at 328.2 K.



Figure B.2.1: Plot of absorbance versus time for the reaction of C_{60} with piperidine to produce tetra(pip)-fullerene epoxide in cyclohexane.

[pip] = 0.0152 M Temperature = 328.2 K

Data: Data1_C Model: ExpDec1 Equation: $y = A1 \exp(-x/t1) + y0$ Weighting: No weighting у Chi^2/DoF = 2.8685E-7 R^2 = 0.99888y0 0.00069 -0.14765 0.08397 A1 0.00062 t1 6307.07551 89.23356



Figure B.2.2: Plot of absorbance versus time for the reaction of C_{60} with piperidine to produce tetra(pip)-fullerene epoxide in cyclohexane.

[pip] = 0.0936 M Temperature = 328.2 K

Data: Data1 C Model: ExpDec1 Equation: $y = A1 \exp(-x/t1) + y0$ Weighting: No weighting y Chi^2/DoF = 1.0063E-6 R^2 = 0.99962y0 -0.43136 0.00327 A1 0.35232 0.00315 t1 10326.13418 133.706



Figure B.2.3: Plot of absorbance versus time for the reaction of C_{60} with piperidine to produce tetra(pip)-fullerene epoxide in cyclohexane.

[pip] = 0.2388 MTemperature = 328.2 KData: Data1 C Model: ExpDec1 Equation: $y = A1 \exp(-x/t1) + y0$ Weighting: No weighting у Chi^2/DoF = 1.6012E-6 R^2 = 0.99984y0 -0.54848 0.00061 A1 0.41876 0.0005 3827.00699 12.65733 t1


Figure B.2.4: Plot of absorbance versus time for the reaction of C_{60} with piperidine to produce tetra(pip)-fullerene epoxide in cyclohexane.

[pip] = 0.3505 M Temperature = 328.2 KData: Data1 C Model: ExpDec2 Equation: $y = A1 \exp(-x/t1) + A2 \exp(-x/t2) + y0$ Weighting: No weighting У Chi^2/DoF = 1.2267E-7 R^2 = 0.99984y0 -0.17169 0.02323 A1 0.08896 0.00318 t1 1495.75623 35.08299 A2 0.05095 0.02004 15346.6193 t2 10820.89323



Figure B.2.5: Plot of absorbance versus time for the reaction of C_{60} with piperidine to produce tetra(pip)-fullerene epoxide in cyclohexane.

[pip] = 0.4953 M Temperature = 328.2 KData: Data1 C Model: ExpDec2 Equation: $y = A1 \exp(-x/t1) + A2 \exp(-x/t2) + y0$ Weighting: No weighting У Chi^2/DoF = 3.0853E-7 R^2 = 0.99991y0 -0.35583 0.00132 A1 0.14482 0.00205 4091.21612 t1 144.1424 A2 0.1215 0.00317 954.86468 17.24588 t2



Figure B.2.6: Plot of absorbance versus time for the reaction of C_{60} with piperidine to produce tetra(pip)-fullerene epoxide in cyclohexane.

[pip] = 1.4665 M Temperature = 328.2 K

Data: Data1 C Model: ExpDec2 Equation: $y = A1 \exp(-x/t1) + A2 \exp(-x/t2) + y0$ Weighting: No weighting у Chi^2/DoF = 8.3848E-7 R^2 = 0.99926y0 -0.25603 0.00039 A1 0.10218 0.00059 t1 2743.90904 42.32495 A2 0.06349 0.00083 t2 336.24948 7.85824



Figure B.2.7: Plot of absorbance versus time for the reaction of C_{60} with piperidine to produce tetra(pip)-fullerene epoxide in cyclohexane.

[pip] = 2.9311 MTemperature = 328.2 KData: Data1 C Model: ExpDec2 Equation: $y = A1 \exp(-x/t1) + A2 \exp(-x/t2) + y0$ Weighting: No weighting у Chi^2/DoF = 2.8327E-6 R^2 = 0.9988y0 -0.4883 0.00021 A1 0.08845 0.00151 152.21287 5.15844 t1 A2 0.16948 0.00117 t2 1366.00858 12.58322

Appendix B.3

Plot of absorbance versus time for the reaction of C_{60} with piperidine to produce tetra(pip)-fullerene epoxide. The reaction was performed in cyclohexane at 338.2 K.



Figure B.3.1: Plot of absorbance versus time for the reaction of C_{60} with piperidine to produce tetra(pip)-fullerene epoxide in cyclohexane.

[pip] = 0.0778 M Temperature = 338.2 K Data: Data1_C Model: ExpDec1 Equation: y = A1*exp(-x/t1) + y0 Weighting: y No weighting

Chi²/DoF = 2.2639E-7R² = 0.99983

y0	-0.41713	0.00453
A1	0.35788	0.00446
t1	12369.0813	193.36277



Figure B.3.2: Plot of absorbance versus time for the reaction of C_{60} with piperidine to produce tetra(pip)-fullerene epoxide in cyclohexane.

[pip] = 0.1293 M Temperature = 338.2 K

Data: Data1 C Model: ExpDec1 Equation: $y = A1 \exp(-x/t1) + y0$ Weighting: No weighting y Chi^2/DoF = 1.4707E-7 R^2 = 0.99991 y0 -0.27919 0.00064 0.00059 A1 0.20929 5130.52684 t1 25.64457



Figure B.3.3: Plot of absorbance versus time for the reaction of C_{60} with piperidine to produce tetra(pip)-fullerene epoxide in cyclohexane.

Temperature = 338.2 KData: Data1 C Model: ExpDec2 Equation: $y = A1 \exp(-x/t1) + A2 \exp(-x/t2) + y0$ Weighting: No weighting у Chi^2/DoF = 1.61E-7 R^2 = 0.99995y0 -0.29851 0.00406 A1 0.09863 0.00816 3937.24587 643.84819 t1 A2 0.1344 0.01203 t2 1197.4601 47.67521

[pip] = 0.3250 M



Figure B.3.4: Plot of absorbance versus time for the reaction of C_{60} with piperidine to produce tetra(pip)-fullerene epoxide in cyclohexane.

[pip] = 0.9502 M Temperature = 338.2 KData: Data1 C Model: ExpDec2 Equation: $y = A1 \exp(-x/t1) + A2 \exp(-x/t2) + y0$ Weighting: No weighting у Chi^2/DoF = 1.603E-7 R^2 = 0.9998y0 -0.19837 0.00021 A1 0.07505 0.00063 t1 1983.73918 30.26673 A2 0.06594 0.00051 328.1089 t2 3.78441



Figure B.3.5: Plot of absorbance versus time for the reaction of C_{60} with piperidine to produce tetra(pip)-fullerene epoxide in cyclohexane.

[pip] = 2.3951 MTemperature = 338.2 K Data: Data1 C Model: ExpDec2 Equation: $y = A1 \exp(-x/t1) + A2 \exp(-x/t2) + y0$ Weighting: No weighting У Chi^2/DoF = 3.8709E-6 R^2 = 0.99828y0 -0.46019 0.00024 A1 0.15696 0.0018 t1 1130.84409 14.91461 A2 0.11051 0.00204 t2 151.93838 5.29633

Appendices C

Appendix C.1

Plot of absorbance versus time for the reaction of C_{60} with pyrrole. The reaction was performed in cyclohexane at 318.2 K.



Figure C.1.1: Plot of absorbance versus time for the reaction of C_{60} with pyrrole in cyclohexane.

[pyrrole] = 0.0262 M Temperature = 318.2 KData: Data1_C Model: ExpDec2 Equation: $y = A1 \exp(-x/t1) + A2 \exp(-x/t2) + y0$ Weighting: No weighting у Chi^2/DoF = 9.5164E-7 R^2 = 0.99995y0 -0.82409 0.00193 A1 0.11707 0.00149 t1 613.12847 9.96182 A2 0.52557 0.00073 t2 4921.18714 46.93974



Figure C.1.2: Plot of absorbance versus time for the reaction of C_{60} with pyrrole in cyclohexane.

[pyrrole] = 0.1082 M Temperature = 318.2 KData: Data1_C Model: ExpDec2 Equation: $y = A1 \exp(-x/t1) + A2 \exp(-x/t2) + y0$ Weighting: No weighting у Chi^2/DoF = 8.7991E-7 R^2 = 0.99994y0 -0.74231 0.00067 0.00064 A1 0.06085 t1 203.74624 4.34753 A2 0.5028 0.00043 t2 4050.73941 13.26354



Figure C.1.3: Plot of absorbance versus time for the reaction of C_{60} with pyrrole in cyclohexane.

[pyrrole] = 0.3011 M Temperature = 318.2 KData: Data1_C Model: ExpDec2 Equation: $y = A1 \exp(-x/t1) + A2 \exp(-x/t2) + y0$ Weighting: No weighting у Chi^2/DoF = 1.8578E-7 R^2 = 0.9999y0 -0.29145 0.00011 A1 0.15364 0.00018 t1 177.31011 3.90157 A2 0.0301 0.00033 t2 2265.19413 6.70319



Figure C.1.4: Plot of absorbance versus time for the reaction of C_{60} with pyrrole in cyclohexane.

[pyrrole] = 0.3903 M Temperature = 318.2 K Data: Data1_C Model: ExpDec2 Equation: y = A1*exp(-x/t1) + A2*exp(-x/t2) + y0 Weighting:

y No weighting

Chi^2/DoF = 4.0084E-6 R^2 = 0.99903 y0 -0.53181 0.00063

A10.090690.00152t1141.860544.71053A20.228140.00061t22685.4936825.13831



Figure C.1.5: Plot of absorbance versus time for the reaction of C_{60} with pyrrole in cyclohexane.

[pyrrole] = 0.4987 M Temperature = 318.2 K

Data: Data1 C Model: ExpDec2 Equation: $y = A1 \exp(-x/t1) + A2 \exp(-x/t2) + y0$ Weighting: No weighting у = 1.7382E-6 Chi^2/DoF R^2 = 0.99933 y0 -0.62409 0.00025 A1 0.10979 0.00105 t1 173.17411 3.35477 A2 0.16343 0.00069 t2 1876.64763 14.87381

Appendix C.2

Plot of absorbance versus time for the reaction of C_{60} with pyrrole. The reaction was performed in cyclohexane at 328.2 K.



Figure C.2.1: Plot of absorbance versus time for the reaction of C_{60} with pyrrole in cyclohexane.

[pyrrole] = 0.1940 M Temperature = 328.2 K

Data: Data1 C Model: ExpDec2 Equation: $y = A1 \exp(-x/t1) + A2 \exp(-x/t2) + y0$ Weighting: No weighting у = 4.1415E-7 Chi^2/DoF R^2 = 0.99986 y0 -0.3508 0.00035 A1 0.07635 0.00141 t1 548.28927 10.70531 A2 0.16038 0.00121 t2 2612.16124 30.44089



Figure C.2.2: Plot of absorbance versus time for the reaction of C_{60} with pyrrole in cyclohexane.

[pyrrole] = 0.3111 MTemperature = 328.2 K

Data: Data1 C Model: ExpDec2 Equation: $y = A1 \exp(-x/t1) + A2 \exp(-x/t2) + y0$ Weighting: No weighting у Chi^2/DoF = 6.9272E-7 = 0.99979R^2 y0 -0.41354 0.00024 A1 0.21208 0.00024 t1 118.20346 3.61615 A2 0.04207 0.00066 2589.69509 t2 10.00863



Figure C.2.3: Plot of absorbance versus time for the reaction of C_{60} with pyrrole in cyclohexane.

[pyrrole] = 0.3813 MTemperature = 328.2 K

Data: Data1 C Model: ExpDec2 Equation: $y = A1 \exp(-x/t1) + A2 \exp(-x/t2) + y0$ Weighting: No weighting у Chi^2/DoF = 6.7399E-6 R^2 = 0.9998y0 -1.26704 0.00115 A1 0.68122 0.00083 3.98866 t1 179.77462 A2 0.16842 0.00186 3183.20491 t2 16.06652



Figure C.2.4: Plot of absorbance versus time for the reaction of C_{60} with pyrrole in cyclohexane.

[pyrrole] = 0.4886 M Temperature = 328.2 KData: Data1 C Model: ExpDec2 Equation: $y = A1 \exp(-x/t1) + A2 \exp(-x/t2) + y0$ Weighting: No weighting у Chi^2/DoF = 7.582E-7 R^2 = 0.99928 y0 -0.3876 0.00011 A1 0.04616 0.0008 t1 94.98157 3.35184 A2 0.1198 0.00049 t2 1196.82123 7.55063



Figure C.2.5: Plot of absorbance versus time for the reaction of C_{60} with pyrrole in cyclohexane.

[pyrrole] = 0.9662 M Temperature = 328.2 KData: Data1 C Model: ExpDec2 Equation: $y = A1 \exp(-x/t1) + A2 \exp(-x/t2) + y0$ Weighting: No weighting у Chi^2/DoF = 2.1944E-6 R^2 = 0.9955 y0 -0.39282 0.00022 A1 0.05014 0.00197 t1 91.27779 6.57424 A2 0.07178 0.00176 t2 671.21236 18.70141

Appendix C.3

Plot of absorbance versus time for the reaction of C_{60} with pyrrole. The reaction was performed in cyclohexane at 338.2 K.



Figure C.3.1: Plot of absorbance versus time for the reaction of C_{60} with pyrrole to in cyclohexane.

[pyrrole] = 0.0380 M Temperature = 338.2 K

Data: Data1 C Model: ExpDec2 Equation: $y = A1 \exp(-x/t1) + A2 \exp(-x/t2) + y0$ Weighting: No weighting у Chi^2/DoF = 2.0282E-6 R^2 = 0.99985 y0 -0.64841 0.00078 A1 0.09536 0.00101 t1 254.81569 5.46842 A2 0.43192 0.00052 t2 3373.95036 18.28165



Figure C.3.2: Plot of absorbance versus time for the reaction of C_{60} with pyrrole to in cyclohexane.

[pyrrole] = 0.0936 M Temperature = 338.2 K

Data: Data1 C Model: ExpDec2 Equation: $y = A1 \exp(-x/t1) + A2 \exp(-x/t2) + y0$ Weighting: No weighting у Chi^2/DoF = 5.469E-7 R^2 = 0.99971y0 -0.27047 0.00012 A1 0.16573 0.00027 91.79274 t1 5.0381 A2 0.02289 0.00064 t2 1767.12537 6.09249



Figure C.3.3: Plot of absorbance versus time for the reaction of C_{60} with pyrrole to in cyclohexane.

[pyrrole] = 0.2838 M Temperature = 338.2 K

Data: Data1 C Model: ExpDec2 Equation: $y = A1 \exp(-x/t1) + A2 \exp(-x/t2) + y0$ Weighting: No weighting у Chi^2/DoF = 7.5564E-6 R^2 = 0.99987y0 -1.60486 0.00305 A1 0.97405 0.00187 t1 304.96418 5.47877 A2 0.21206 0.00187 t2 4721.48945 34.11164



Figure C.3.4: Plot of absorbance versus time for the reaction of C_{60} with pyrrole to in cyclohexane.

[pyrrole] = 0.3898 MTemperature = 338.2 K Data: Data1_C Model: ExpDec2 Equation: y = A1*exp(-x/t1) + A2*exp(-x/t2) + y0 Weighting: y No weighting Chi^2/DoF = 4.9398E-6 R^2 = 0.99891

y0-0.538640.00065A10.236950.00076t1159.445535.94355A20.089650.00166t22545.3436725.63347



Figure C.3.5: Plot of absorbance versus time for the reaction of C_{60} with pyrrole to in cyclohexane.

[pyrrole] = 0.4693 M Temperature = 338.2 KData: Data1_C Model: ExpDec2 Equation: $y = A1 \exp(-x/t1) + A2 \exp(-x/t2) + y0$ Weighting: No weighting у Chi^2/DoF = 3.7751E-6 R^2 = 0.99985y0 0.00299 -1.0215 0.72375 A1 0.00199 t1 345.9139 13.38431 A2 0.06986 0.00135 t2 5415.64191 47.59956