# Functionalization of [60]Fullerene using Organometallic Complexes and Amines 

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#### Abstract

The organometallic functionalization of $\mathrm{C}_{60}$ 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 $\mathrm{C}_{60}$ is critical for their chemical manipulations and technological applications.

The reactions of $\mathrm{C}_{60}$ 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 $\mathrm{C}_{60}\left([\mathrm{pip}] \gg\left[\mathrm{C}_{60}\right]\right)$. Plots of absorbance versus time were biexponential, indicative of 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. Also, we are reporting the mechanisms of $\mathrm{C}_{60}$ dissociation from $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$. 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 $\mathrm{C}_{60}$ 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 $\mathrm{C}_{60}$ concentration.


## Resumen

La funcionalización organometálica de $\mathrm{C}_{60}$ 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 $\mathrm{C}_{60}$ para manipulaciones químicas y aplicaciones tecnológicas.

Las reacciones de $\mathrm{C}_{60}$ con aminas primarias y secundarias ${ }^{[2-4]}$ producen aductos que pueden ser precursores de catalíticos. Reaccionan formando aductos de $\mathrm{C}_{60}-(\mathrm{pip})_{4}(\mathrm{O})$ (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 $\mathrm{C}_{60}$ ([pip] $\gg\left[\mathrm{C}_{60}\right]$ ). 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 $\mathrm{C}_{60}-(\text { pip })_{4}(\mathrm{O})$. Además, se reportan los mecanismos de la disociación de $\mathrm{C}_{60}$ del complejo $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$. 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 $\mathrm{C}_{60}$. Estos dos ejemplos para la funcionalización de $\mathrm{C}_{60}$ muestran como las propiedades de $\mathrm{C}_{60}$ 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 $\mathrm{C}_{60}$ ) 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 $\mathrm{C}_{60}$ 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 $\mathrm{C}_{60} . \mathrm{C}_{60}$ solubility at room temperature ranges from $0.001 \mathrm{mg} / \mathrm{mL}$ in ethanol up to $51 \mathrm{mg} / \mathrm{mL}$ in 1-chloronaphthalene. ${ }^{[6]}$

These molecules are stable, but not unreactive. The $\mathrm{sp}^{2}$-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 $\mathrm{sp}^{2}$-hybridized carbons into $\mathrm{sp}^{3}$-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 $\mathrm{C}_{60}$ 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 $\pi$-back bonding with transition metals. ${ }^{[8]}$ There exist a variety of organometallic complexes functionalized with $\mathrm{C}_{60}$. Among these complexes are fac- $\left(\eta^{2}\right.$-dppe $)\left(\eta^{2}-\mathrm{C}_{60}\right) \mathrm{Cr}(\mathrm{CO})_{3}{ }^{[9]}$ (see figure 1.1), fac- $\left(\eta^{2}\right.$-phen $)\left(\eta^{2}-\right.$ $\left.\mathrm{C}_{60}\right) \mathrm{W}(\mathrm{CO})_{3}{ }^{[10]}$, fac- $\left(\eta^{2}\right.$-phen $)\left(\eta^{2}-\mathrm{C}_{60}\right) \mathrm{Mo}(\mathrm{CO})_{3}{ }^{[11]}$ (dppe $=1,2$ bis(diphenylphosphino)ethane and phen $=1,10$-phenanthroline). The functionalization of $\mathrm{C}_{60}$ 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 $\operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ 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 $\mathrm{C}_{60}{ }^{[12]}$ The preparation of $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ was reported in the literature. ${ }^{[13]}$ The dissociation of $\mathrm{C}_{60}$ from $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ is presented in this work. Here will be presented the reactions of $\mathrm{C}_{60}$ with secondary amines producing aminofullerene epoxides.

The amines react to form $\mathrm{C}_{60}-(\text { amine })_{\mathrm{n}}$ adducts. These adducts can be used to study the chemical properties of $\mathrm{C}_{60}$.

This thesis reports the kinetics and mechanistic studies of the chemical modification of $\mathrm{C}_{60}$ with organometallic complexes and secondary amines.


Figure 1.1: Representation of the complex fac- $\left(\eta^{2}-\mathrm{dppe}\right)\left(\eta^{2}-\mathrm{C}_{60}\right) \mathrm{Cr}(\mathrm{CO})_{3}$, where dppe $=$ 1,2 bis(diphenylphosphino)-ethane. ${ }^{[9]}$

### 1.1 Objectives

The purpose of this is research project is to functionalize $\mathrm{C}_{60}$ using organometallic complexes and secondary amines. It is well known that $\mathrm{C}_{60}$ 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 $\mathrm{C}_{60}$ 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 $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ complex.
- Study the dissociation of $\mathrm{C}_{60}$ from $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$.
- Perform kinetics experiments of the reactions of $\mathrm{C}_{60}$ with piperidine and pyrrole.
- Estimate the thermodynamic parameters: activation enthalpy $\left(\Delta \mathrm{H}_{\text {obs }}^{\ddagger}\right)$ and activation entropy ( $\Delta \mathrm{S}^{\ddagger}$ obs ) for the $\mathrm{C}_{60}$ dissociation from $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ and for the reactions of $\mathrm{C}_{60}$ with piperidine.


## Chapter II

## Previous Works

In the past decades numerous studies of $\mathrm{C}_{60}$ 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 $\mathrm{C}_{60}$ with organometallic complexes occurs in a dihapto mode $\left(\eta^{2}\right)$ as reported previously. ${ }^{[8]}$ One of the most important properties of $\mathrm{C}_{60}$ is it capacity to participate in $\pi$-back bonding with transition metals. ${ }^{[8]}$ The extent at which $\mathrm{C}_{60}$ participate in $\pi$-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 $\left(\operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}\right)$ has a characteristic vco absorption band in the stretching region at $1953 \mathrm{~cm}^{-1}$ for the solid disperse in a fluorolube mull. ${ }^{[13]}$ After the reaction of $\operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ with $\mathrm{C}_{60}$ the vco band appears at $2014 \mathrm{~cm}^{-1}$ due to $\pi$-back bonding. ${ }^{[13]}$ The reaction of $\operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ with $\mathrm{C}_{60}$ to produce $\left(\eta^{2}-\mathrm{C}_{60}\right) \mathrm{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ was reported in 1991 by Raston et. al. X-ray diffraction studies of the product of this reaction suggests that $\mathrm{C}_{60}$ is attached to Ir in a dihapto mode $\left(\eta^{2}\right)$ through a 6-6 ring fusion with a bond lengths of $2.19 \AA$ 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 $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ from data collected by X-ray diffraction. ${ }^{[13]}$

The infrared spectrum of $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ in dichloromethane shows a vco band at $1965 \mathrm{~cm}^{-1}$ due to the presence of $\operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ and no absorption is present in the $2100-2000 \mathrm{~cm}^{-1}$ region. ${ }^{[13]}$ The ${ }^{31} \mathrm{P}$ NMR spectrum in chloroform shows a resonance at 24.5 ppm , which is the same as the observed for $\operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl} .{ }^{[13]}$ These results suggest that the formation of $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ 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 $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ in solution (results from our laboratory). This infrared spectrum was performed in a [ $\mathrm{C}_{60}$ ] saturated solution in benzene. Three bands appear in the spectra. The band at $1818 \mathrm{~cm}^{-1}$ was assigned to the $\mathrm{v}_{\mathrm{C}=\mathrm{C}}$ stretching of $\mathrm{C}_{60}$ and the band at $1965 \mathrm{~cm}^{-1}$ was assigned to the vco stretching of $\operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$, by comparison with spectrums of pure samples. The band at $2017 \mathrm{~cm}^{-1}$ was ascribed to the vco stretching of $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$.


Figure 2.2: Infrared spectrum in benzene of: A. $\operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ and B. $\left(\eta^{2}-\right.$ $\left.\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ in a $\mathrm{C}_{60}$-saturated solution.

The reactions of $\mathrm{C}_{60}$ 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 $\mathrm{C}_{60}$ under photochemical conditions in an aerobic environment to produce tetra(amino)fullerene epoxide. ${ }^{[3]}$ Multiple addition of a nucleophile to $\mathrm{C}_{60}$ it is possible due to the high electron affinity of $\mathrm{C}_{60} .{ }^{[12,20-24]}$ Near-infrared analysis of a mixture of $\mathrm{C}_{60}$ and
piperidine in a deaerated dimethyl sulfoxide ( DMSO )/chlorobenzene $(\mathrm{PhCl})$ mixture indicated equilibrium formation of [60]fullerene radical anion $\left(\mathrm{C}_{60}{ }^{\circ}\right)$ but react immediately with $\mathrm{O}_{2}$ producing tetra(amino)-fullerene epoxides, as presented in figure 2.3. ${ }^{[2]}$ A Benesi-Hildebrand analysis indicated that a $\left[\mathrm{C}_{60}{ }^{--}\right.$piperidine $\left.{ }^{-+}\right]$radical ion pair is formed at room temperature as a result of amine to $\mathrm{C}_{60}$ single electron transfer. ${ }^{[2]}$


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

Interestingly the displacement reactions of $\mathrm{C}_{60}$ from $\left(\eta^{2}-\mathrm{C}_{60}\right) \mathrm{Cr}(\mathrm{CO})_{5}$ by piperidine (pip) producing $\left(\eta^{1}-\mathrm{pip}\right) \mathrm{Cr}(\mathrm{CO})_{5}$ 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 $\mathrm{C}_{60}$ from the parent complex, whereas the second and third increasing segments were assigned to step-wise additions of piperidine to uncoordinated $\mathrm{C}_{60}$. In view of the reported fullerene amino epoxide formations, it was necessary a reinvestigation of the reactions of $\mathrm{C}_{60}$ 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 ( 407 nm ) versus time for the displacement of $\mathrm{C}_{60}$ from $\left(\eta^{2}-\mathrm{C}_{60}\right) \mathrm{Cr}(\mathrm{CO})_{5}$ by piperidine in chlorobenzene to form $\left(\eta^{1}-\mathrm{pip}\right) \mathrm{Cr}(\mathrm{CO})_{5}$ at 328.2 K under flooding conditions where $[\mathrm{pip}] \gg\left[\left(\eta^{2}-\mathrm{C}_{60}\right) \mathrm{Cr}(\mathrm{CO})_{5}\right] .{ }^{[25]}$

## Chapter III

## $\mathrm{C}_{60}$ dissociation from $\left(\boldsymbol{\eta}^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathbf{C O})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$

### 3.1 Materials and Methodology

### 3.1.1 General

The reagents used to prepare the complex $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ were $\mathrm{C}_{60}$ and Vaska's complex $\left(\operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}\right)$. 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 $\left(\boldsymbol{\eta}^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathbf{C O})\left(\mathrm{PPh}_{3}\right)_{2} \mathbf{C l}$

The complex $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ was prepared from $\operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ and $\mathrm{C}_{60}$ following a reported method. ${ }^{[13]}$ In a 15 mL round bottom flask equipped with a magnetic stirrer and a nitrogen inlet, $20.28 \mathrm{mg}(25.99 \mu \mathrm{~mol})$ of $\operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ and $18.60 \mathrm{mg}(25.83 \mu \mathrm{~mol})$ 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 $\mathrm{C}_{60}$ to a yellow solution of $\operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ 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 $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ showed a characteristic ${ }^{[13]} v_{\mathrm{CO}}$ band at $2012 \mathrm{~cm}^{-1}$, as shown in figure 3.2.


Figure 3.1: Schematic representation of the equipment used for the preparation of the complex $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$.


Figure 3.2: Infrared spectrum in the stretching carbonyl region of $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ in KBr pellet.

### 3.2 Kinetic Studies of $\mathrm{C}_{60}$ dissociation from $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$

### 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 $0.1^{\circ} \mathrm{C}$ using a Julabo $\mathrm{F}-12$ constant temperature bath. An EC model heating and refrigerating circulator and a $\mathrm{K} / \mathrm{J}$ 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 $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ 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 $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$

The dissociation of $\mathrm{C}_{60}$ from $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ 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 $289.5 \mathrm{~K}, 291.3 \mathrm{~K}, 293.1$ $\mathrm{K}, 295.3 \mathrm{~K}, 298.3 \mathrm{~K}, 300.4 \mathrm{~K}$ 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 $\mathrm{C}_{60}$ 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:

$$
\begin{equation*}
\mathrm{Y}=\left(\mathrm{A}_{1}\right) \mathrm{e}^{-\mathrm{x} / t 1}+\mathrm{Y}_{0} \tag{3.1}
\end{equation*}
$$

where Y is the dependant variable at time $\mathrm{t} ; \mathrm{Y}_{0}$ is the value of Y at time 0 or initial value; $A_{1}$ 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:

$$
\begin{equation*}
\mathrm{A}_{\mathrm{t}}=\left(\mathrm{A}_{0}-\mathrm{A}_{\infty}\right) \mathrm{e}^{-\mathrm{k}^{*} \mathrm{t}}+\mathrm{A}_{\infty} \tag{3.2}
\end{equation*}
$$

where the correspondence is: $A_{t}=Y,\left(A_{0}-A_{\infty}\right)=A_{1}, k=1 / t_{1}, t=x$ and $A_{\infty}=Y_{0}$. Where $A_{t}$ represents the value of the absorbance at a given time, $\mathrm{A}_{0}$ represents the absorbance at time zero, $\mathrm{A}_{\infty}$ 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 $\mathrm{C}_{60}$ with $\operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ (Vaska's Complex $=\mathrm{V}$ ) in benzene produced $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}^{[13]}$. The infrared spectrum for the carbonyl stretching region for $\left(\eta^{2}-\mathrm{C}_{60}\right) \mathrm{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ are shows two bands, one at $2012 \mathrm{~cm}^{-1}(\mathrm{~s})$ and the other one at $1963 \mathrm{~cm}^{-1}(\mathrm{~s})$ is shown in figure 3.2. The band at $2012 \mathrm{~cm}^{-1}$ was attributed to the complex $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ by comparison with the literature. ${ }^{[13]}$ The band at $1963 \mathrm{~cm}^{-1}$ was unequivocally assigned to $\operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ 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:

$$
\begin{equation*}
-\frac{d\left[\mathrm{VC}_{60}\right]}{d t}=k_{o b s d}\left[\mathrm{VC}_{60}\right] \tag{3.4}
\end{equation*}
$$

where $\mathrm{k}_{\text {obsd }}$ is the experimental rate constant. Based on the equilibrium reaction, the rate law becomes:

$$
\begin{equation*}
-\frac{d\left[\mathrm{VC}_{60}\right]}{d t}=\left(k_{1}+k_{-1}\left[C_{60}\right]\right)\left[\mathrm{VC}_{60}\right] \tag{3.5}
\end{equation*}
$$

where $\mathrm{k}_{\mathrm{obsd}}=k_{1}+k_{-1}\left[\mathrm{C}_{60}\right]$.
The reactions were studied under conditions where the concentration of $\mathrm{C}_{60}$ was negligible. The only source of $\mathrm{C}_{60}$ comes from the dissociation reaction. In addition, the reactions were performed at different concentrations of $\mathrm{C}_{60}$ in benzene. The results kinetic experiments suggest that the rate constant values ( $k_{\text {obsd }}$ ) were independent of the concentration of $\mathrm{C}_{60}$, 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 $\mathrm{C}_{60}$ 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 $\mathrm{C}_{60}$ 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 $\mathrm{C}_{60}$ dissociation from $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ 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 $\mathrm{A}_{\mathrm{t}}=\left(\mathrm{A}_{0}-\mathrm{A}_{\infty}\right) \mathrm{e}^{-\mathrm{kobsd}^{*} \mathrm{t}}+\mathrm{A}_{\infty}$ where $\left(\mathrm{A}_{0}-\mathrm{A}_{\infty}\right)=0.61166, \mathrm{k}_{\text {obsd }}=$ $1.28 \times 10^{-2} \mathrm{~s}^{-1}$ and $\mathrm{A}_{\infty}=0.08087$.


Figure 3.4: Plot of absorbance versus time at 550 nm for $\mathrm{C}_{60}$ dissociation from $\left(\eta^{2}-\right.$ $\left.\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ in benzene at 295.2 K in a $\left[\mathrm{C}_{60}\right]$ saturate solution. The continuous trace is for absorbance values obtained from the equation that best describes the relation between absorbance versus time. Equation $\mathrm{A}_{\mathrm{t}}=\left(\mathrm{A}_{0}-\mathrm{A}_{\infty}\right) \mathrm{e}^{- \text {-kobsd*t}}+\mathrm{A}_{\infty}$ where $\left(\mathrm{A}_{0}-\mathrm{A}_{\infty}\right)$ $=0.14414, \mathrm{k}_{\mathrm{obsd}}=1.25 \times 10^{-2} \mathrm{~s}^{-1}$ and $\mathrm{A}_{\infty}=0.15706$.


Figure 3.5: Plot of absorbance versus time at 550 nm for $\mathrm{C}_{60}$ dissociation from $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ 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 $\mathrm{A}_{\mathrm{t}}=\left(\mathrm{A}_{0}-\mathrm{A}_{\infty}\right) \mathrm{e}^{- \text {kobsd*t }}+\mathrm{A}_{\infty}$ where $\left(\mathrm{A}_{0}-\mathrm{A}_{\infty}\right)=$ $0.07284, \mathrm{k}_{\text {obsd }}=2.27 \times 10^{-2} \mathrm{~s}^{-1}$ and $\mathrm{A}_{\infty}=0.26946$.

Table 3.1: Values of $\mathrm{k}_{\text {obsd }}$ for the dissociation of $\mathrm{C}_{60}$ from $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ in benzene at various temperatures.

| Temperature (K) <br> $( \pm \mathbf{0 . 1 ~ K )}$ | $\mathbf{k}_{\text {obsd }} \mathbf{1 0}^{-\mathbf{- 2}}$ <br> $\left.\mathbf{s}^{\mathbf{- 1}}\right)$ |
| :---: | :--- |
| 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 | $1.951(4)$ |
|  | $1.47(1)$ |
| 300.4 | $1.567(3)$ |
|  | $3.45(5)$ |
|  | $2.71(5)$ |
|  | $3.49(6)$ |
|  | $3.14(3)$ |
|  | $2.55(3)$ |
| 303.2 | $6.52(2)$ |
|  | $11.23(6)$ |
|  | $9.23(8)$ |

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

Table 3.2: Values of $\mathrm{k}_{\text {obsd }}$ for the dissociation of $\mathrm{C}_{60}$ from $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ in dichloromethane at various temperatures.

| Temperature (K) <br> $( \pm \mathbf{0 . 1 ~ K})$ | $\mathbf{k}_{\text {obsd }} \mathbf{1 0}^{-2}$ <br> $\left(\mathbf{s}^{-1}\right)$ |
| :---: | :---: |
| 295.2 | $1.52(7)$ |
|  | $2.28(6)$ |
| 299.1 | $2.9(2)$ |
|  | $2.74(7)$ |
| 303.1 | $3.6(2)$ |
|  | $5.7(5)$ |

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

Table 3.3: Values of $\mathrm{k}_{\text {obsd }}$ for the dissociation of $\mathrm{C}_{60}$ from $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ in benzene solutions for different [ $\mathrm{C}_{60}$ ] at 295.2 K .

| Concentration <br> $(\mathbf{m M})$ | $\mathbf{k}_{\text {obsd }} \mathbf{1 0}^{-\mathbf{2}}$ <br> $\left(\mathbf{s}^{-1}\right)$ |
| :---: | :---: |
| 0.5 | $1.184(5)$ |
| 0.8 | $1.139(5)$ |
|  | $1.147(4)$ |
| 1.0 | $1.210(9)$ |
| $2.36^{*}$ | $1.245(3)$ |
|  | $1.585(9)$ |

*Concentration for a saturated solution of $\mathrm{C}_{60}$ in benzene.
The values given in parenthesis are the uncertainties for the last digit reported of the rate constant values.

Table 3.4: Values of activation parameters for $\mathrm{C}_{60}$ dissociation from $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ in benzene and dichloromethane.

| Solvent | $\Delta \mathrm{H}_{\text {obsd }}$ <br> $(\mathrm{kJ} / \mathrm{mol})$ | $\Delta \mathrm{S}^{\ddagger}{ }_{\text {obsd }}$ <br> $(\mathrm{J} / \mathrm{K} \mathrm{mol})$ |
| :---: | :---: | :---: |
| Benzene | $166(10)$ | $279(30)$ |
| Dichloromethane | $81(6)$ | $-4(2)$ |

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

Table 3.5: $\mathrm{k}_{\text {obsd }}$ average values and $\mathrm{k}_{1}$ and $\mathrm{k}_{2}$ estimated values for the dissociation of $\mathrm{C}_{60}$ from $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ for mixed solvents kinetics experiments at 295.2 K .

| Temperature (K) $( \pm 0.1)$ | Token ligand | [Token ligand] (M) | Average k $\left(10^{-2}, \mathrm{~s}^{-1}\right)^{\text {bbd }}$ | $\begin{gathered} * \mathrm{k}_{1} \\ \left(10^{-2}, \mathrm{~s}^{-1}\right) \end{gathered}$ | $\begin{gathered} * * \mathrm{k}_{2} \\ \left(10^{-2}, \mathrm{~s}^{-1}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 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 $\mathrm{k}_{\mathrm{obs}}$ 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 $\ln (\mathrm{k} / \mathrm{T})$ versus $1 / \mathrm{T}$ is expected to be linear for small temperature ranges.

$$
\begin{equation*}
\ln \frac{k}{T}=-\frac{\Delta H^{\mp}}{R}\left(\frac{1}{T}\right)+\ln \frac{k_{B}}{h}+\frac{\Delta S^{\mp}}{R} \tag{3.6}
\end{equation*}
$$

Values for $\Delta \mathrm{H}^{\ddagger}{ }_{\text {obsd }}$ can be calculated from the slope of this line $(=-\mathrm{m} \cdot \mathrm{R})$ and values for $\Delta \mathrm{S}_{\text {obsd }}^{\ddagger}$ can be calculated from the intercept of the line $\left(=\mathrm{R}\left\{\mathrm{b}-\ln \left(\mathrm{k}_{\mathrm{B}} / \mathrm{h}\right)\right\}\right)$, were $\mathrm{k}_{\mathrm{B}}=$ Boltzmann's constant $\left[1.381 \times 10^{-23} \mathrm{~J} \cdot \mathrm{~K}^{-1}\right], \mathrm{T}=$ absolute temperature in Kelvin $(\mathrm{K})$, and $h$ $=$ Plank's constant $\left[6.626 \times 10^{-34} \mathrm{~J} \cdot \mathrm{~s}\right]$. 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 $\mathrm{C}_{60}$ dissociation from $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ in benzene.


Figure 3.7: Eyring plot for $\mathrm{C}_{60}$ dissociation from $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ in dichloromethane.

The $k_{\text {obsd }}$ values for $\mathrm{C}_{60}$ dissociation from $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ are independent of the concentration of $\mathrm{C}_{60}$ 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 $k_{\mathrm{obs}}$ (equation 3.7 and 3.9) were based on the proposed mechanism shown in figure 3.8.


Figure 3.8: Proposed mechanisms for $\mathrm{C}_{60}$ dissociation from $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$. Path-I describes solvent-assisted dissociation whereas Path-II describes a non solventassisted dissociation. TS are transitions state.

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

$$
\begin{equation*}
k_{\text {obsd }}=\left(k_{1}[\text { solvent }]+k_{-1}\left[C_{60}\right]\right) \tag{3.7}
\end{equation*}
$$

Since $k_{\text {obsd }}$ is independent of the concentration of $\mathrm{C}_{60}$, equation 3.7 becomes:

$$
\begin{equation*}
k_{\text {obsd }} \approx k_{1}[\text { solvent }] \tag{3.8}
\end{equation*}
$$

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

$$
\begin{equation*}
k_{\text {obsd }}=\frac{k_{2} k_{3}[\text { solvent }]^{n}}{k_{-2}\left[\mathrm{C}_{60}\right]+k_{3}[\text { solvent }]^{n}} \tag{3.9}
\end{equation*}
$$

Likewise, since $k_{\text {obsd }}$ is independent of the concentration of $\mathrm{C}_{60}$, equation 3.9 becomes:

$$
\begin{equation*}
k_{o b s d} \approx k_{2} \tag{3.10}
\end{equation*}
$$

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 $] \gg\left[\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}\right]$ 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] $\gg\left[\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}\right]$. Thus the equation for $k_{\text {obsd }}$ is:

$$
\begin{equation*}
k_{\text {obsd }}=k_{1}[\text { token ligand }]+k_{2}[\text { benzene }] \tag{3.11}
\end{equation*}
$$

Plots of $k_{\text {obsd }}$ versus [token ligand] were lineal (figure 3.9). This plot suggests that $k_{\text {obsd }}$ 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:

$$
\begin{equation*}
k_{\text {obsd }}=k_{1}[\text { token ligand }]+k_{2} \tag{3.12}
\end{equation*}
$$

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 $\mathrm{k}_{\text {obsd }}$ versus [Token ligand] for $\mathrm{C}_{60}$ dissociation from ( $\eta^{2}$ $\left.\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ for mixed solvents kinetics experiments at 295.2 K . In which dichloromethane $(\triangle)$ 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 $0.1^{\circ} \mathrm{C}$ using a Julabo F-12 constant temperature bath. An EC model heating and refrigerating circulator and a $\mathrm{K} / \mathrm{J}$ 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 $\mathrm{C}_{60}$ 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 $\mathrm{C}_{60}$ with piperidine were studied observing the increase in absorbance at a wavelength of 407 nm . The reactions were performed in cyclohexane at temperatures of: $318.2 \mathrm{~K}, 328.2 \mathrm{~K}$ 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:

$$
\begin{equation*}
Y=\left(A_{1}\right) e^{-x / t 1}+\left(A_{2}\right) e^{-x / t 2}+Y_{0} \tag{4.1}
\end{equation*}
$$

where Y is the dependant variable at time t ; $\mathrm{Y}_{0}$ is the value of Y at time 0 or initial value; $\mathrm{A}_{1}$ and $\mathrm{A}_{2}$ 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:

$$
\begin{equation*}
A_{t}=\alpha e^{-\operatorname{kobsd1}^{*} t}+\beta e^{- \text {kobsd2 }^{*} t}+A_{\infty} \tag{4.2}
\end{equation*}
$$

where the correspondence is: $A_{t}=Y ; \alpha=A_{1} ; \beta=A_{2} ; k_{n}=1 / t_{n}$ (where $n=1$ or 2 ); $t=x$ and $A_{\infty}=Y_{0}$. In which $A_{t}$ is the value of the absorbance at a given time; $A_{0}$ represents the absorbance at time zero; $\mathrm{A}_{\infty}$ represents the absorbance at time infinite, $\alpha$ and $\beta$ 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 $\mathrm{C}_{60}$ 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 $\mathrm{C}_{60}$. 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 ( $\mathrm{k}_{\mathrm{obsd1}}$ and $\mathrm{k}_{\mathrm{obsd} 2}$ ) 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 $\mathrm{C}_{60}$ 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 $\% \mathrm{C}=86.87$ and $87.21 ; \% \mathrm{~N}=5.12$ and 5.20 ; and $\% \mathrm{H}=4.28$ and 4.16 for the duplicated analysis. The composition calculated for $\mathrm{C}_{80} \mathrm{~N}_{4} \mathrm{H}_{40} \mathrm{O}$ is $\% \mathrm{C}=89.55 ; \% \mathrm{~N}$ $=5.22$; and $\% \mathrm{H}=3.73$.

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 $\mathrm{C}_{60}$. The rate constants values were obtained from these plots.


Figure 4.2: Plot of absorbance versus time at 407 nm for the reaction of $\mathrm{C}_{60}$ with piperidine to produce tetra(pip)-fullerene epoxide. The reaction was performed in cyclohexane at 328.2 K , [pip] $=0.950 \mathrm{M}$, under flooding conditions where the concentration of [piperidine] $\gg$ [fullerene]. The continuous trace is for absorbance values obtained from the equation that best describes the relation between absorbance versus time. Equation $\mathrm{A}_{\mathrm{t}}=\alpha \mathrm{e}^{-\mathrm{kobsd} 1^{* t}}+\beta \mathrm{e}^{-\mathrm{kobsd2}{ }^{* t}}+\mathrm{A}_{\infty}$ where $\alpha=0.09678$, $\beta=0.10183, \mathrm{k}_{\text {obsd1 }}=2.67 \times 10^{-3} \mathrm{~s}^{-1}, \mathrm{k}_{\text {obsd2 }}=3.59 \times 10^{-4} \mathrm{~s}^{-1}$ and $\mathrm{A}_{\infty}=0.31887$.

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.

$$
\begin{gathered}
\mathrm{C}_{60}+2 \text { pip }+\mathrm{O}_{2} \xrightarrow{\mathrm{k}_{\text {obsd1 }}} \mathrm{C}_{60^{-}}(\text {pip })_{2}+\mathrm{H}_{2} \mathrm{O}_{2} \\
\mathrm{C}_{60^{-}}(\text {pip })_{2}+2 \text { pip }+\mathrm{O}_{2} \xrightarrow{\mathrm{k}_{\text {obsd2 }}} \mathrm{C}_{60^{-}}(\text {pip })_{4}(\mathrm{O})+\mathrm{H}_{2} \mathrm{O}
\end{gathered}
$$

Figure 4.3: The chemical reaction of $\mathrm{C}_{60}$ 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:

$$
\begin{gather*}
-\frac{d\left[\mathrm{C}_{60}\right]}{d t}=k_{\text {obsd } 1}\left[\mathrm{C}_{60}\right]  \tag{4.3}\\
-\frac{d\left[\mathrm{C}_{60}-(\mathrm{pip})_{2}\right]}{d t}=k_{\text {obsd } 2}\left[\mathrm{C}_{60}-(\mathrm{pip})_{2}\right] \tag{4.4}
\end{gather*}
$$

where $k_{\text {obsd1 }}$ is the rate constant for the first segment and $k_{\mathrm{obsd} 2}$ is the rate constant for the second segment of the plot of absorbance versus time.

Table 4.1: Values of $\mathrm{k}_{\mathrm{obsd} 1}$ for the reaction of $\mathrm{C}_{60}$ 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] $\gg$ [fullerene].

| Temperature (K) <br> $\mathbf{( \mathbf { 0 . 1 } \mathbf { ) }}$ | $[$ Piperidine <br> $\mathbf{( M )}$ | $\mathbf{k}_{\text {obsd1 }}$ <br> $\left(\mathbf{1 0}^{-4}, \mathbf{s}^{-1}\right)$ |
| :---: | :---: | :---: |
| 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 | $39(1)$ |
|  |  |  |
|  | 0.0152 | $1.59(2)$ |
|  | 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 | $30(7)$ |
|  |  |  |
|  | 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 | $66(2)$ |

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

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

| Temperature (K) <br> $\mathbf{( \pm \mathbf { 0 . 1 } )}$ | $[$ Piperidine $]$ <br> $\mathbf{( M )}$ | $\mathbf{K}_{\text {obsd }} \mathbf{2}$ <br> $\left(\mathbf{1 0}^{-4}, \mathbf{s}^{-1}\right)$ |
| :---: | :---: | :---: |
| 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 | $7.32(7)$ |
|  |  |  |
|  | 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 $k_{\text {obsd1 }}$ values for the reaction of $\mathrm{C}_{60}$ with piperidine to produce tetra(pip)-fullerene epoxide are dependent of the concentration of piperidine. The mathematical behavior of the relation between $k_{\mathrm{obsd} 1}$ 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 $k_{\mathrm{obsd} 1}$, based on the proposed mechanism, using the steady-state approximation for the intermediates species is given by equation 4.5.

$$
\begin{equation*}
k_{\text {obsd } 1}=\frac{k_{1} k_{2}[p i p]\left[O_{2}\right]}{k_{-1}+k_{2}\left[O_{2}\right]} \tag{4.5}
\end{equation*}
$$

Assuming that the intermediates species are in steady state concentration and that $k_{2}\left[O_{2}\right] \gg k_{-1}$, equation 4.5 becomes:

$$
\begin{equation*}
k_{\mathrm{obsd} 1}=k_{1}[p i p] \tag{4.6}
\end{equation*}
$$

equation 4.6 (mechanism-based) is mathematically equivalent to equation 4.3. (experimentally-based). Plots of $k_{\text {obsdı }}$ 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 $k_{\text {obsd }}$ 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 $k_{\text {obsd1 }}$. Figure 4.5 describes the mechanism for the second segment, designed by $k_{\text {obsd2 }}$.










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






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


Figure 4.6: Plot of $\mathrm{k}_{\text {obsd } 1}$ versus [piperidine] for the reaction of $\mathrm{C}_{60}$ with piperidine to produce tetra(pip)-fullerene epoxide. The reaction was performed at different piperidine concentrations in cyclohexane at various temperatures ( $\vee$ ) 318.2 K , ( $\bullet$ ) 328.2 K , and ( $■$ ) 338.2 K.

The rate constant values determined from the second segment of the biphasic plot are designed by $k_{\mathrm{obsd} 2}$. The $k_{\mathrm{obsd} 2}$ values are dependent of the concentration of piperidine. The mathematical behavior of the relation between $k_{\text {obsd } 2}$ 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 $k_{\mathrm{obsd} 2}$, based on the proposed mechanism, using the steady-state approximation for the intermediates species is given by equation 4.7

$$
\begin{equation*}
k_{\mathrm{obsd} 1}=\frac{k_{4} k_{5}[p i p]\left[O_{2}\right]}{k_{-4}+k_{5}\left[O_{2}\right]} \tag{4.7}
\end{equation*}
$$

Assuming that the intermediates species are in steady- state concentration and that $k_{5}\left[\mathrm{O}_{2}\right] \gg k_{-4}$, equation 4.7 becomes:

$$
\begin{equation*}
k_{o b s d 2}=k_{4}[p i p] \tag{4.8}
\end{equation*}
$$

equation 4.8 (mechanism-based) is mathematically equivalent to equation 4.4 (experimentally-based). Plots of $k_{\text {obsd } 2}$ 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 $k_{\text {obsd2 }}$ versus [pip]. Those values are presented in table 4.4.


Figure 4.7: Plot of $\mathrm{k}_{\text {obsd2 }}$ versus [piperidine] for the reaction of $\mathrm{C}_{60}$ 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 $\mathrm{k}_{\mathrm{obsd} 2}$ versus [piperidine] for the reaction of $\mathrm{C}_{60}$ 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 $\ln (\mathrm{k} / \mathrm{T})$ versus $1 / \mathrm{T}$ is expected to be linear for small temperature ranges.

$$
\begin{equation*}
\ln \frac{k}{T}=-\frac{\Delta H^{\mp}}{R}\left(\frac{1}{T}\right)+\ln \frac{k_{B}}{h}+\frac{\Delta S^{\mp}}{R} \tag{4.8}
\end{equation*}
$$

Values for $\Delta \mathrm{H}^{\ddagger}$ obsd can be calculated from the slope of this line $(=-\mathrm{m} \cdot \mathrm{R})$ and values for $\Delta \mathrm{S}_{\text {obsd }}$ can be calculated from the intercept of the line $\left(=\mathrm{R}\left\{\mathrm{b}-\ln \left(\mathrm{k}_{\mathrm{B}} / \mathrm{h}\right)\right\}\right)$, were $\mathrm{k}_{\mathrm{B}}=$ Boltzmann's constant $\left[1.381 \times 10^{-23} \mathrm{~J} \cdot \mathrm{~K}^{-1}\right], \mathrm{T}=$ absolute temperature in Kelvin (K), and $h$ $=$ Plank's constant $\left[6.626 \times 10^{-34} \mathrm{~J} \cdot \mathrm{~s}\right]$. 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 $\mathrm{k}_{\text {obds1 }}$ for the reaction of $\mathrm{C}_{60}$ with piperidine in cyclohexane.

As shown in table 4.3 and 4.4, the highly negative values of activation entropy $\left(\Delta \mathrm{S}^{\ddagger}{ }_{\text {obsd1 }}=-232 \mathrm{~J} / \mathrm{K} \mathrm{mol}\right.$ and $\left.\Delta \mathrm{S}_{\text {obsd2 }}^{\ddagger}=-237 \mathrm{~J} / \mathrm{K} \mathrm{mol}\right)$ suggest an associative process that is consistent with the mechanistic description. The observed activation enthalpy $\left(\Delta \mathrm{H}_{\text {obsd1 }}^{\ddagger}\right)$ is actually the activation enthalpy of the step governed by $\mathrm{k}_{1}$. Since its value involves the $\mathrm{N}-\mathrm{C}$ bond forming ( $305 \mathrm{~kJ} / \mathrm{mol}$ ), C-C bond forming ( $347 \mathrm{~kJ} / \mathrm{mol}$ ), and $\mathrm{C}=\mathrm{C}$ bond breaking ( $611 \mathrm{~kJ} / \mathrm{mol}$ ), thus the difference between bond forming and bond breaking is estimated $\Delta \mathrm{H}^{\ddagger} \xlongequal[1]{ } \cong 41 \mathrm{~kJ} / \mathrm{mol}$. In contrast the observed activation enthalpy $\Delta \mathrm{H}_{\text {obsd1 }}^{\ddagger}=21$ $\mathrm{kJ} / \mathrm{mol}$, 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 $\mathrm{sp}^{2}$-hybridized carbon atoms of $\mathrm{C}_{60}$ 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 $\mathrm{C}_{60}$ reduces angle strain by changing $\mathrm{sp}^{2}$-hybridized carbons into $\mathrm{sp}^{3}$-hybridized ones. The change in hybridized orbitals, due to the addition, causes the bond angles to decrease from around $120^{\circ}$ in the $\mathrm{sp}^{2}$ orbitals to around $109.5^{\circ}$ in the $\mathrm{sp}^{3}$ 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 $\left(\Delta \mathrm{H}^{\ddagger} \cong 41 \mathrm{~kJ} / \mathrm{mol}\right)$ due to the angle strain that $\mathrm{C}_{60}$ 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 $\mathrm{C}_{60}$.

Table 4.3: Values of rate constant $\left(k_{1}\right)$ and activation parameters of $\mathrm{k}_{\text {obsd1 }}$ for the reaction of $\mathrm{C}_{60}$ 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] $\gg$ [fullerene].

| Temperature <br> (K) ( $\pm 0.1$ ) | ${ }^{*} \mathrm{k}_{1}\left(10^{-3}, \mathrm{~s}^{-1}\right)$ | $\underset{(\mathrm{kJ} / \mathrm{mol})}{\Delta \mathbf{H}^{\ddagger} \text { obs }}$ | $\stackrel{\Delta S^{\ddagger} \text { gos }}{\left(\mathrm{J} / \mathrm{K}_{\mathrm{mol}} \mathrm{~mol}\right)}$ |
| :---: | :---: | :---: | :---: |
| 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 $\mathrm{k}_{\text {obsd1 }}$ vs. [pip].
The values given in parenthesis are the uncertainties for the value reported.

Table 4.4: Values of rate constant ( $\mathrm{k}_{4}$ ) and activation parameters of $\mathrm{k}_{\mathrm{obsd} 2}$ for the reaction of $\mathrm{C}_{60}$ 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] $\gg$ [fullerene].

| Temperature <br> (K) ( $\pm 0.1$ ) | ${ }^{*} \mathbf{k}_{4}\left(10^{-4}, \mathrm{~s}^{-1}\right)$ | $\begin{aligned} & { }^{* *} \Delta H^{\ddagger}{ }_{\text {obs }} \\ & \text { (kJ/ mol) } \end{aligned}$ | $\begin{gathered} { }^{* *} \Delta S^{\ddagger} \text { obs } \\ (\mathrm{J} / \mathrm{K} \mathbf{~ m o l}) \end{gathered}$ |
| :---: | :---: | :---: | :---: |
| 328.2 | 2.3(2) | 26(2) | -237(31) |
| 338.2 | 3.2(4) |  |  |

${ }_{* * *}^{*}$ Estimated values from the slope for the plot of $\mathrm{k}_{\text {obsd2 }}$ 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 10 mm path length. The temperature was set to be constant within approximately $0.1^{\circ} \mathrm{C}$ using a Julabo F-12 constant temperature bath. An EC model heating and refrigerating circulator and a $\mathrm{K} / \mathrm{J}$ 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 $\mathrm{C}_{60}$ 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 $\mathrm{C}_{60}$ with pyrrole were studied observing the increase in absorbance at a wavelength of 350 nm . The reactions were performed in cyclohexane at temperatures of: $318.2 \mathrm{~K}, 328.2 \mathrm{~K}$ 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:

$$
\begin{equation*}
Y=\left(A_{1}\right) e^{-x / t 1}+\left(A_{2}\right) e^{-x / t 2}+Y_{0} \tag{5.1}
\end{equation*}
$$

where Y is the dependant variable at time t ; $\mathrm{Y}_{0}$ is the value of Y at time 0 or initial value; $\mathrm{A}_{1}$ and $\mathrm{A}_{2}$ is the amplitude of the exponential it precede; 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 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:

$$
\begin{equation*}
A_{t}=\alpha e^{- \text {kobsd1 }^{* t}}+\beta e^{- \text {kobsd2*t }}+A_{\infty} \tag{5.2}
\end{equation*}
$$

where the correspondence is: $\mathrm{A}_{\mathrm{t}}=\mathrm{Y} ; \alpha=\mathrm{A}_{1} ; \beta=\mathrm{A}_{2} ; \mathrm{k}_{\mathrm{n}}=1 / \mathrm{t}_{\mathrm{n}}$ (where $\mathrm{n}=1$ or 2 ) $; \mathrm{t}=\mathrm{x}$ and $A_{\infty}=Y_{0}$. In which $A_{t}$ is the value of the absorbance at a given time; $A_{0}$ represents the absorbance at time zero; $\mathrm{A}_{\infty}$ represents the absorbance at time infinite; $\alpha$ and $\beta$ 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 $\mathrm{C}_{60}$. 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: $k_{\mathrm{obsd}}$ and $k_{\text {obsd2 }}$. 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 ( $k_{\mathrm{obsd} 1}$ and $k_{\mathrm{obsd} 2}$ ) 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 $\mathrm{C}_{60}$ and pyrrole in cyclohexane produced $\mathrm{C}_{60}$-(pyrrole) $\mathrm{n}_{\mathrm{n}}$ adduct.


Figure 5.1: Plot of absorbance versus time at 350 nm for the reaction of $\mathrm{C}_{60}$ with pyrrole. The reaction was performed in cyclohexane at $328.2 \mathrm{~K},[$ pyrrole $]=0.3813 \mathrm{M}$, 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 $A_{t}=\alpha e^{- \text {kobsd1*t }}+\beta \mathrm{e}^{-\mathrm{kobsd2}{ }^{* t}}+$ $\mathrm{A}_{\infty}$ where $\alpha=0.16842, \beta=0.68122, \mathrm{k}_{\mathrm{obsd} 1}=5.6 \times 10^{-3} \mathrm{~s}^{-1}, \mathrm{k}_{\text {obsd } 2}=3.14 \times 10^{-4} \mathrm{~s}^{-1}$ and $\mathrm{A}_{\infty}=$ 1.26704.


Figure 5.2: Plot of $\mathrm{k}_{\text {obsd } 1}$ versus [pyrrole] for the reaction of $\mathrm{C}_{60}$ with pyrrole. The reaction was performed in different pyrrole concentrations in cyclohexane at 318.2 K .


Figure 5.3: Plot of $\mathrm{k}_{\text {obsd } 1}$ versus [pyrrole] for the reaction of $\mathrm{C}_{60}$ with pyrrole. The reaction was performed in different pyrrole concentrations in cyclohexane at 328.2 K .


Figure 5.4: Plot of $\mathrm{k}_{\text {obsd } 1}$ versus [pyrrole] for the reaction of $\mathrm{C}_{60}$ with pyrrole. The reaction was performed in different pyrrole concentrations in cyclohexane at 338.2 K .


Figure 5.5: Plot of $\mathrm{k}_{\mathrm{obsd} 2}$ versus [pyrrole] for the reaction of $\mathrm{C}_{60}$ with pyrrole. The reaction was performed in different pyrrole concentrations in cyclohexane at 318.2 K .


Figure 5.6: Plot of $\mathrm{k}_{\text {obsd } 2}$ versus [pyrrole] for the reaction of $\mathrm{C}_{60}$ with pyrrole. The reaction was performed in different pyrrole concentrations in cyclohexane at 328.2 K .


Figure 5.7: Plot of $\mathrm{k}_{\text {obsd2 }}$ versus [pyrrole] for the reaction of $\mathrm{C}_{60}$ with pyrrole. The reaction was performed in different pyrrole concentrations in cyclohexane at 338.2 K .

Table 5.1: Values of $\mathrm{k}_{\text {obsd1 }}$ for the reaction of $\mathrm{C}_{60}$ with pyrrole. The reaction was performed in cyclohexane at various temperatures under flooding conditions where the concentration of [pyrrole] $\gg$ [fullerene].

| Temperature (K) <br> $\mathbf{( 0 \mathbf { 0 . 1 } )}$ | $[$ Pyrrole $]$ <br> $\mathbf{( M )}$ | $\mathbf{K}_{\text {obsd } 11}$ <br> $\left(\mathbf{1 0}^{-3} \mathbf{s}^{-1}\right)$ |
| :---: | :---: | :---: |
| 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 | $10.4(8)$ |
|  |  |  |
|  | 0.0147 | $3.69(5)$ |
| 328.2 | 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 | $15(1)$ |
|  |  |  |
|  | 0.0380 | $3.92(8)$ |
|  | 0.0936 | $10.9(6)$ |
|  | 0.2838 | $3.28(6)$ |
|  | 0.3898 | $6.3(2)$ |
|  | 0.4693 | $2.9(1)$ |

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

Table 5.2: Values of $\mathrm{k}_{\text {obsd } 2}$ for the reaction of $\mathrm{C}_{60}$ with pyrrole. The reaction was performed in cyclohexane at various temperatures under flooding conditions where the concentration of [pyrrole] $\gg$ [fullerene].

| Temperature (K) <br> $\mathbf{( \mathbf { 0 } . 1 )}$ | $[$ Pyrrole $]$ <br> $\mathbf{( M )}$ | $\mathbf{K}_{\text {obsd }} \mathbf{2}$ <br> $\left(\mathbf{1 0}^{-4}, \mathbf{s}^{-1}\right)$ |
| :---: | :---: | :---: |
| 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 | $14.9(4)$ |
|  |  |  |
|  | 0.0380 | $2.96(2)$ |
|  | 0.0936 | $5.66(2)$ |
|  | 0.2838 | $2.11(2)$ |
|  | 0.3898 | $3.93(4)$ |
|  | 0.4693 | $1.85(2)$ |
|  |  |  |

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 $\mathrm{C}_{60}$. 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 $\mathrm{C}_{60}$ from $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ shows plots of absorbance versus time that were decreasing exponential. The $k_{\text {obsd }}$ values are independent of [ $\mathrm{C}_{60}$ ]. Since $k_{\text {obsd }}$ values vary depend on the nature of the solvent; $\mathrm{C}_{60}$ 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 $\left(\Delta S^{\ddagger}{ }_{\text {obsd }}=+279(30) \mathrm{J} / \mathrm{K} \mathrm{mol}\right)$ suggest that in benzene the dissociation reaction is not solvent- assisted. In this case the value of activation enthalpy $\left(\Delta \mathrm{H}_{\text {obsd }}^{\ddagger}=166(10) \mathrm{kJ} / \mathrm{mol}\right)$ should be close to the actual thermodynamic $\mathrm{Ir}-\mathrm{C}_{60}$ 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 ( $k_{\mathrm{obsd} 1}$ and $k_{\mathrm{obsd} 2}$ ) 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 $\left(\eta^{2}\right)$ 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 $\mathrm{C}_{60}$ 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 $\mathrm{C}_{60}$ 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.

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## APPENDICES

## Appendices A

## Appendix A. 1

Plot of absorbance versus time for $\mathrm{C}_{60}$ dissociation from $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ in benzene at various temperature.


Figure A.1.1: Plot of absorbance versus time for $C_{60}$ dissociation from ( $\eta^{2}$ $\left.\mathrm{C}_{60}\right) \mathrm{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ in benzene at 289.5 K .

```
Data: Datal_B
Model: ExpDec1
Equation: y = A1 *exp(-x/t1) + y0
Weighting:
y No weighting
Chi^2/DoF = 0.00007
R^2 = 0.99772
y0 0.12 0.00042
A1 0.71697 0.00081
tl 462.1524 1.20973
```



Figure A.1.2: Plot of absorbance versus time for $\mathrm{C}_{60}$ dissociation from ( $\eta^{2}$ $\left.\mathrm{C}_{60}\right) \mathrm{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ in benzene at 295.5 K .

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



Figure A.1.3: Plot of absorbance versus time for $\mathrm{C}_{60}$ dissociation from ( $\eta^{2}$ $\left.\mathrm{C}_{60}\right) \mathrm{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ in benzene at 303.2 K .

Data: Data1_B
Model: ExpDec1
Equation: $y=A 1 * \exp (-x / t 1)+y 0$
Weighting:
y No weighting
Chi^2/DoF $=2.754 \mathrm{E}-6$
$\mathrm{R}^{\wedge} 2=0.99759$

| y0 | 0.06981 | 0.00018 |
| :--- | :--- | :--- |
| A1 | 0.16993 | 0.00092 |
| t1 | 10.83004 | 0.09749 |

## Appendix A. 2

Plot of absorbance versus time for $\mathrm{C}_{60}$ dissociation from $\left(\eta^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathbf{C l}$ in dichloromethane at various temperature.


Figure A.2.1: Plot of absorbance versus time for $C_{60}$ dissociation from ( $\eta^{2}$ $\left.\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ in dichloromethane at 295.2 K .

Data: Datal_B
Model: ExpDec1
Equation: $y=A 1 * \exp (-x / t 1)+y 0$
Weighting:
y No weighting
$\mathrm{Chi}^{\wedge} 2 / \mathrm{DoF}=5.1781 \mathrm{E}-6$
$\mathrm{R}^{\wedge} 2=0.98601$
$\begin{array}{lll}\mathrm{y} 0 & 0.26946 & 0.00055\end{array}$
A1 $0.07284 \quad 0.00071$
t1 $43.94887 \quad 1.20278$


Figure A.2.2: Plot of absorbance versus time for $\mathrm{C}_{60}$ dissociation from ( $\eta^{2}$ $\left.\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ in dichloromethane at 299.1 K .

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



Figure A.2.3: Plot of absorbance versus time for $C_{60}$ dissociation from ( $\eta^{2}$ $\left.\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ in dichloromethane at 303.1 K .

Data: Data1_B
Model: $\operatorname{Exp} \bar{D} e c 1$
Equation: $y=A 1 * \exp (-x / t 1)+y 0$
Weighting:
y No weighting
Chi^2/DoF $=5.5362 \mathrm{E}-6$
$\mathrm{R}^{\wedge} 2=0.97875$

| y 0 | 0.23151 | 0.00153 |
| :--- | :--- | :--- |
| A1 | 0.06099 | 0.00133 |
| t1 | 27.74053 | 1.8615 |

## Appendix A. 3

Plot of absorbance versus time for $\mathbf{C}_{60}$ dissociation from ( $\left.\boldsymbol{\eta}^{\mathbf{2}}-\mathbf{C}_{60}\right) \operatorname{Ir}(\mathbf{C O})\left(\mathbf{P P h}_{3}\right)_{2} \mathbf{C l}$ in benzene solutions for different $\left[\mathrm{C}_{60}\right]$ at $\mathbf{2 9 5 . 2} \mathbf{K}$.


Figure A.3.1: Plot of absorbance versus time for $\mathrm{C}_{60}$ dissociation from ( $\eta^{2}$ $\left.\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ in benzene at 295.2 K in $\left[\mathrm{C}_{60}\right]=0.5 \mathrm{M}$.

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



Figure A.3.2: Plot of absorbance versus time for $\mathrm{C}_{60}$ dissociation from ( $\eta^{2}$ $\left.\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ in benzene at 295.2 K in $\left[\mathrm{C}_{60}\right]=1.0 \mathrm{M}$.

## Data: Datal B <br> Model: ExpDec1

Equation: $y=A 1 * \exp (-x / t 1)+y 0$ Weighting:
y No weighting
Chi^2/DoF $=6.552 \mathrm{E}-7$
$\mathrm{R}^{\wedge} 2=0.99825$
$\begin{array}{lll}\mathrm{y} 0 & 0.05286 & 0.00005\end{array}$
A1 $0.08678 \quad 0.00017$
$\begin{array}{lll}\text { t1 } 87.15212 & 0.30507\end{array}$


Figure A.3.3: Plot of absorbance versus time for $\mathrm{C}_{60}$ dissociation from ( $\eta^{2}$ $\left.\mathrm{C}_{60}\right) \mathrm{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ in benzene at 295.2 K in $\mathrm{C}_{60}$ saturate solution.

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


## Appendix $\mathbf{A .} 4$

Plot of absorbance versus time for $\mathrm{C}_{60}$ dissociation from $\left(\boldsymbol{\eta}^{2}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathbf{C O})\left(\mathbf{P P h}_{3}\right)_{2} \mathbf{C l}$ 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 ( $\eta^{2}$ $\left.\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ for mixed solvents kinetics experiments at 295.2 K . Where dichloromethane $(0.247 \mathrm{M})$ was the token ligand and benzene was the solvent.

Data: Datal_B
Model: ExpDec1
Equation: $y=A 1 * \exp (-x / t 1)+y 0$
Weighting:
y No weighting
$\mathrm{Chi}^{\wedge} 2 / \mathrm{DoF}=2.2288 \mathrm{E}-6$
$\mathrm{R}^{\wedge} 2=0.96874$
$\begin{array}{lll}\mathrm{y} 0 & 0.10293 & 0.00016\end{array}$
A1 $0.03679 \quad 0.00057$
t1 $25.0895 \quad 0.69832$


Figure A.4.2: Plot of absorbance versus time for $C_{60}$ dissociation from ( $\eta^{2}$ $\left.\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ for mixed solvents kinetics experiments at 295.2 K . Where dichloromethane $(1.2027 \mathrm{M})$ was the token ligand and benzene was the solvent.

```
Data: Datal_B
Model: ExpDec1
Equation: \(y=A 1 * \exp (-x / t 1)+y 0\)
Weighting:
y No weighting
Chi^2/DoF \(=5.9629 \mathrm{E}-7\)
R^2 \(=0.99955\)
\(\begin{array}{lll}\mathrm{y} 0 & 0.06297 & 0.00009\end{array}\)
A1 \(0.16167 \quad 0.00035\)
t1 17.817450 .06756
```



Figure A.4.3: Plot of absorbance versus time for $C_{60}$ dissociation from ( $\eta^{2}$ $\left.\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ for mixed solvents kinetics experiments at 295.2 K . Where dichloromethane $(3.2055 \mathrm{M})$ was the token ligand and benzene was the solvent.

Data: Data1_B
Model: ExpDec1
Chi^2/DoF $=3.4166 \mathrm{E}-6$
$\mathrm{R}^{\wedge} 2=0.98119$

| y0 | 0.15119 | $\backslash(177) 0.00015$ |
| :--- | :--- | :--- |
| A1 | 0.0791 | $\backslash(177) 0.00101$ |
| t1 | 11.15551 | $\backslash(177) 0.22697$ |

## Appendix $\mathbf{A . 5}$

Plot of absorbance versus time for $\mathrm{C}_{60}$ dissociation from $\left(\boldsymbol{\eta}^{\mathbf{2}}-\mathrm{C}_{60}\right) \operatorname{Ir}(\mathbf{C O})\left(\mathrm{PPh}_{3}\right)_{2} \mathbf{C l}$ for mixed solvents kinetics experiments at $\mathbf{2 9 5 . 2} \mathbf{K}$. Where toluene was the token ligand and benzene was the solvent.


Figure A.5.1: Plot of absorbance versus time for $\mathrm{C}_{60}$ dissociation from ( $\eta^{2}$ $\left.\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ for mixed solvents kinetics experiments at 295.2 K . Where toluene $(0.1028 \mathrm{M})$ was the token ligand and benzene was the solvent.

Data: Data1_B
Model: ExpDec1
$\mathrm{Chi}^{\wedge} 2 / \mathrm{DoF}=1.5833 \mathrm{E}-6$
$\mathrm{R}^{\wedge} 2=0.98151$
y0 $0.14196 \quad \backslash(177) 0.00009$
A1 $0.0421 \quad \backslash(177) 0.00035$
t1 $49.79616 \quad \backslash(177) 0.71623$


Figure A.5.2: Plot of absorbance versus time for $C_{60}$ dissociation from ( $\eta^{2}$ $\left.\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ for mixed solvents kinetics experiments at 295.2 K . Where toluene $(0.4382 \mathrm{M})$ was the token ligand and benzene was the solvent.

Data: Datal_B
Model: $\operatorname{Exp} \bar{D} e c 1$
Equation: $y=A 1 * \exp (-x / t 1)+y 0$
Weighting:
y No weighting
$\mathrm{Chi}^{\wedge} 2 / \mathrm{DoF} \quad=1.1606 \mathrm{E}-6$
$\mathrm{R}^{\wedge} 2=0.96324$
y0 0.07670 .00009
A1 $0.02662 \quad 0.0004$
t1 $27.20095 \quad 0.6810312$


Figure A.5.3: Plot of absorbance versus time for $C_{60}$ dissociation from ( $\eta^{2}$ $\left.\mathrm{C}_{60}\right) \operatorname{Ir}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}$ for mixed solvents kinetics experiments at 295.2 K . Where toluene $(1.1136 \mathrm{M})$ was the token ligand and benzene was the solvent.

Data: Datal_B
Model: ExpDec1
Equation: $y=A 1 * \exp (-x / t 1)+y 0$
Weighting:
y No weighting
$\mathrm{Chi}^{\wedge} 2 / \mathrm{DoF} \quad=9.4613 \mathrm{E}-7$
$\mathrm{R}^{\wedge} 2=0.94891$

| y0 | 0.06296 | 0.00011 |
| :--- | :--- | :--- |
| A1 | 0.01889 | 0.00046 |
| t1 | 16.16018 | 0.68368 |

Appendices B

## Appendix B. 1

Plot of absorbance versus time for the reaction of $\mathrm{C}_{60}$ 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 $\mathrm{C}_{60}$ with piperidine to produce tetra(pip)-fullerene epoxide in cyclohexane.

```
[pip] = 0.0991 M
Temperature = 318.2 K
Data: Datal_C
Model: ExpDec1
Equation: \(y=A 1 * \exp (-x / t 1)+y 0\)
Weighting:
y No weighting
Chi^2/DoF \(=6.4641 \mathrm{E}-6\)
\(\mathrm{R}^{\wedge} 2=0.99791\)
\(\begin{array}{lll}\mathrm{y} 0 & -1.43378 & 0.1714\end{array}\)
A1 \(1.34918 \quad 0.17107\)
t1 \(47204.61139 \quad 6467.17293\)
```



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

```
[pip] = 0.1161 M
Temperature = 318.2 K
```

Data: Datal_C
Model: $\operatorname{Exp} \bar{D} e c 1$
Equation: $y=A 1 * \exp (-x / t 1)+y 0$
Weighting:
y No weighting
Chi^2/DoF $=6.3773 \mathrm{E}-7$
$\mathrm{R}^{\wedge} 2=0.99877$
$\begin{array}{lll}\mathrm{y} 0 & -0.19726 & 0.00306\end{array}$
A1 $0.16539 \quad 0.00296$
t1 11199.52351 281.72977


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

```
[pip] = 0.1545 M
Temperature = 318.2 K
```

Data: Datal_C
Model: ExpDec1
Equation: $y=A 1 * \exp (-x / t 1)+y 0$
Weighting:
y No weighting
$\mathrm{Chi}^{\wedge} 2 / \mathrm{DoF} \quad=5.2319 \mathrm{E}-6$
$\mathrm{R}^{\wedge} 2=0.99877$
$\begin{array}{lll}\mathrm{y} 0 & -0.5227 & 0.00559\end{array}$
A1 $0.407 \quad 0.00531$
t1 8922.05022 179.54515


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

```
\([\mathrm{pip}]=0.2173 \mathrm{M}\)
Temperature \(=318.2 \mathrm{~K}\)
```

Data: Data1_C
Model: ExpDec1
Equation: $y=A 1 * \exp (-x / t 1)+y 0$
Weighting:
y No weighting
Chi^2/DoF $=3.105 \mathrm{E}-7$
$\mathrm{R}^{\wedge} 2=0.99981$
$\begin{array}{lll}\mathrm{y} 0 & -0.22392 & 0.00034\end{array}$
A1 $0.17499 \quad 0.00029$
tl $4363.80124 \quad 17.76596$


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

```
[pip] = 0.3350 M
Temperature = 318.2 K
Data: Datal_C
Model: ExpDec2
Equation: y = A1* exp(-x/t1) + A2* exp(-x/t2) + y0
Weighting:
y No weighting
Chi^2/DoF = 6.91E-8
R^2 = 0.99986
y0 -0.13838 0.00738
A1 0.06763 0.00368
t1 1585.15312 48.75576
A2 0.0352 0.00376
t2 9482.91587 4152.28905
```



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

```
\([\mathrm{pip}]=0.4987 \mathrm{M}\)
Temperature \(=318.2 \mathrm{~K}\)
```

Data: Data1_C
Model: ExpDec2
Equation: $\mathrm{y}=\mathrm{A} 1 * \exp (-\mathrm{x} / \mathrm{t} 1)+\mathrm{A} 2 * \exp (-\mathrm{x} / \mathrm{t} 2)+\mathrm{y} 0$
Weighting:
y No weighting
Chi^2/DoF $=2.2949 \mathrm{E}-7$
$\mathrm{R}^{\wedge} 2=0.99987$
$\begin{array}{lll}\mathrm{y} 0 & -0.22651 & 0.0004\end{array}$
A1 $0.04716 \quad 0.00135$
t1 $\quad 653.84195 \quad 17.33842$
A2 $0.13374 \quad 0.00108$
$\begin{array}{lll}\mathrm{t} 2 & 3009.48168 \quad 42.77307\end{array}$


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

```
[pip] = 0.9858 M
Temperature = 318.2 K
```

Data: Datal_C
Model: ExpDec2
Equation: $\mathrm{y}=\mathrm{A} 1 * \exp (-\mathrm{x} / \mathrm{t} 1)+\mathrm{A} 2 * \exp (-\mathrm{x} / \mathrm{t} 2)+\mathrm{y} 0$
Weighting:
y No weighting
Chi^2/DoF $=6.1516 \mathrm{E}-7$
$\mathrm{R}^{\wedge} 2=0.99934$
$\begin{array}{lll}\mathrm{y} 0 & -0.24233 & 0.00038\end{array}$
$\begin{array}{lll}\mathrm{A} 1 & 0.06018 \quad 0.00081\end{array}$
$\begin{array}{lll}\text { t1 } 383.18819 & 8.46139\end{array}$
A2 0.089210 .00058
t2 $2841.00342 \quad 49.16202$


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

```
[pip] = 1.4660 M
Temperature = 318.2 K
```

Data: Datal_C
Model: ExpDec2
Equation: $\mathrm{y}=\mathrm{A} 1 * \exp (-\mathrm{x} / \mathrm{t} 1)+\mathrm{A} 2 * \exp (-\mathrm{x} / \mathrm{t} 2)+\mathrm{y} 0$
Weighting:
y No weighting
Chi^2/DoF $=1.137 \mathrm{E}-6$
$\mathrm{R}^{\wedge} 2=0.99971$
y0 -0.46157 0.00033
A1 $0.22352 \quad 0.00039$
$\begin{array}{lll}\mathrm{t} 1 & 187.3802 & 4.32145\end{array}$
A2 $0.06897 \quad 0.00078$
t2 $2594.668 \quad 14.3752$

## Appendix B. 2

Plot of absorbance versus time for the reaction of $\mathrm{C}_{60}$ 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 $\mathrm{C}_{60}$ with piperidine to produce tetra(pip)-fullerene epoxide in cyclohexane.
$[\mathrm{pip}]=0.0152 \mathrm{M}$
Temperature $=328.2 \mathrm{~K}$

Data: Datal_C
Model: $\operatorname{Exp} \bar{D} e c 1$
Equation: $y=A 1 * \exp (-x / t 1)+y 0$
Weighting:
y No weighting
Chi^2/DoF $=2.8685 \mathrm{E}-7$
$\mathrm{R}^{\wedge} 2=0.99888$
y0 -0.14765 0.00069
$\begin{array}{lll}\mathrm{A} 1 & 0.08397 & 0.00062\end{array}$
t1 $6307.07551 \quad 89.23356$


Figure B.2.2: Plot of absorbance versus time for the reaction of $\mathrm{C}_{60}$ with piperidine to produce tetra(pip)-fullerene epoxide in cyclohexane.
$[\mathrm{pip}]=0.0936 \mathrm{M}$
Temperature $=328.2 \mathrm{~K}$

Data: Datal_C
Model: ExpDec1
Equation: $y=A 1 * \exp (-x / t 1)+y 0$
Weighting:
y No weighting
$\mathrm{Chi}^{\wedge} 2 / \mathrm{DoF}=1.0063 \mathrm{E}-6$
$\mathrm{R}^{\wedge} 2=0.99962$
$\begin{array}{lll}\mathrm{y} 0 & -0.43136 & 0.00327\end{array}$
$\begin{array}{lll}\mathrm{A} 1 & 0.35232 & 0.00315\end{array}$
t1 $10326.13418 \quad 133.706$


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

```
[pip] = 0.2388 M
Temperature = 328.2 K
```

Data: Datal_C
Model: ExpDec1
Equation: $y=A 1 * \exp (-x / t 1)+y 0$
Weighting:
y No weighting
$\mathrm{Chi}^{\wedge} 2 / \mathrm{DoF}=1.6012 \mathrm{E}-6$
$\mathrm{R}^{\wedge} 2=0.99984$
y0 $\quad-0.54848 \quad 0.00061$
A1 $0.41876 \quad 0.0005$
t1 3827.0069912 .65733


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

```
[pip] = 0.3505 M
Temperature = 328.2 K
Data: Data1_C
Model: ExpDec2
Equation: y = A1* exp(-x/t1) + A2* exp(-x/t2) + y0
Weighting:
y No weighting
Chi^2/DoF = 1.2267E-7
R^2 = 0.99984
y0 -0.17169 0.02323
A1 0.08896 0.00318
t1 1495.75623 35.08299
A2 0.05095 0.02004
t2 15346.6193 10820.89323
```



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

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



Figure B.2.6: Plot of absorbance versus time for the reaction of $\mathrm{C}_{60}$ with piperidine to produce tetra(pip)-fullerene epoxide in cyclohexane.
$[\mathrm{pip}]=1.4665 \mathrm{M}$
Temperature $=328.2 \mathrm{~K}$

Data: Datal_C
Model: ExpDec2
Equation: $y=A 1 * \exp (-x / t 1)+A 2 * \exp (-x / t 2)+y 0$
Weighting:
y No weighting
Chi^2/DoF $=8.3848 \mathrm{E}-7$
$\mathrm{R}^{\wedge} 2=0.99926$
$\begin{array}{lll}\mathrm{y} 0 & -0.25603 & 0.00039\end{array}$
$\begin{array}{lll}\mathrm{A} 1 & 0.10218 & 0.00059\end{array}$
t1 $2743.90904 \quad 42.32495$
A2 $0.06349 \quad 0.00083$
$\begin{array}{lll}\mathrm{t} 2 & 336.24948 & 7.85824\end{array}$


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

```
[pip] = 2.9311 M
Temperature = 328.2 K
```

Data: Datal_C
Model: ExpDec2
Equation: $\mathrm{y}=\mathrm{A} 1 * \exp (-\mathrm{x} / \mathrm{t} 1)+\mathrm{A} 2 * \exp (-\mathrm{x} / \mathrm{t} 2)+\mathrm{y} 0$
Weighting:
y No weighting
Chi^2/DoF $=2.8327 \mathrm{E}-6$
$\mathrm{R} \wedge 2=0.9988$
y0 $\quad-0.4883 \quad 0.00021$
A1 $0.08845 \quad 0.00151$
tl $152.21287 \quad 5.15844$
A2 $0.16948 \quad 0.00117$
$\begin{array}{lll}\mathrm{t} 2 & 1366.00858 & 12.58322\end{array}$

## Appendix B. 3

Plot of absorbance versus time for the reaction of $\mathrm{C}_{60}$ 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 $\mathrm{C}_{60}$ with piperidine to produce tetra(pip)-fullerene epoxide in cyclohexane.

```
[pip] = 0.0778 M
Temperature = 338.2 K
```

Data: Datal_C
Model: ExpDec1
Equation: $y=A 1 * \exp (-x / t 1)+y 0$
Weighting:
y No weighting
$\mathrm{Chi}^{\wedge} 2 / \mathrm{DoF} \quad=2.2639 \mathrm{E}-7$
$\mathrm{R}^{\wedge} 2=0.99983$
y0 -0.41713 0.00453
A1 $0.35788 \quad 0.00446$
t1 $12369.0813 \quad 193.36277$


Figure B.3.2: Plot of absorbance versus time for the reaction of $\mathrm{C}_{60}$ with piperidine to produce tetra(pip)-fullerene epoxide in cyclohexane.
$[p i p]=0.1293 \mathrm{M}$
Temperature $=338.2 \mathrm{~K}$

Data: Datal_C
Model: ExpDec1
Equation: $y=A 1 * \exp (-x / t 1)+y 0$
Weighting:
y No weighting

```
Chi^2/DoF = 1.4707E-7
R^2 = 0.99991
y0 -0.27919 0.00064
A1 0.20929 0.00059
t1 5130.52684 25.64457
```



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

```
[pip] = 0.3250 M
Temperature = 338.2 K
Data: Datal_C
Model: ExpDec2
Equation: y = A1* exp(-x/t1) + A2* exp(-x/t2) + y0
Weighting:
y No weighting
Chi^2/DoF = 1.61E-7
R^2 = 0.99995
y0 -0.29851 0.00406
A1 0.09863 0.00816
tl 3937.24587 643.84819
A2 0.1344 0.01203
t2 1197.4601 47.67521
```



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

$$
\begin{aligned}
& {[\text { pip }]=0.9502 \mathrm{M}} \\
& \text { Temperature }=338.2 \mathrm{~K}
\end{aligned}
$$

```
Data: Datal_C
Model: ExpDec2
Equation: \(\mathrm{y}=\mathrm{A} 1 * \exp (-\mathrm{x} / \mathrm{t} 1)+\mathrm{A} 2 * \exp (-\mathrm{x} / \mathrm{t} 2)+\mathrm{y} 0\)
Weighting:
y No weighting
Chi^2/DoF \(=1.603 \mathrm{E}-7\)
\(\mathrm{R}^{\wedge} 2=0.9998\)
\(\begin{array}{lll}\mathrm{y} 0 & -0.19837 & 0.00021\end{array}\)
A1 \(0.07505 \quad 0.00063\)
t1 \(1983.73918 \quad 30.26673\)
A2 \(0.06594 \quad 0.00051\)
\(\begin{array}{lll}\mathrm{t} 2 & 328.1089 & 3.78441\end{array}\)
```



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

```
\([\mathrm{pip}]=2.3951 \mathrm{M}\)
Temperature \(=338.2 \mathrm{~K}\)
Data: Datal_C
Model: ExpDec2
Equation: \(\mathrm{y}=\mathrm{A} 1 * \exp (-\mathrm{x} / \mathrm{t} 1)+\mathrm{A} 2 * \exp (-\mathrm{x} / \mathrm{t} 2)+\mathrm{y} 0\)
Weighting:
y No weighting
Chi^2/DoF \(=3.8709 \mathrm{E}-6\)
\(\mathrm{R}^{\wedge} 2=0.99828\)
\(\begin{array}{lll}\mathrm{y} 0 & -0.46019 & 0.00024\end{array}\)
A1 0.156960 .0018
t1 \(1130.84409 \quad 14.91461\)
A2 \(0.11051 \quad 0.00204\)
\(\begin{array}{lll}\mathrm{t} 2 & 151.93838 & 5.29633\end{array}\)
```


## Appendices C

## Appendix C. 1

Plot of absorbance versus time for the reaction of $\mathrm{C}_{60}$ 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 $\mathrm{C}_{60}$ with pyrrole in cyclohexane.

```
[pyrrole] = 0.0262 M
Temperature = 318.2 K
Data: Datal_C
Model: ExpDec2
Equation: \(y=A 1 * \exp (-x / t 1)+A 2 * \exp (-x / t 2)+y 0\)
Weighting:
y No weighting
\(\mathrm{Chi}^{\wedge} 2 / \mathrm{DoF} \quad=9.5164 \mathrm{E}-7\)
\(\mathrm{R}^{\wedge} 2=0.99995\)
y0 \(\quad-0.82409 \quad 0.00193\)
A1 \(0.11707 \quad 0.00149\)
\(\begin{array}{ll}\mathrm{t} 1 \mathrm{6} 3.12847 & 9.96182\end{array}\)
A2 \(0.52557 \quad 0.00073\)
\(\begin{array}{lll}\mathrm{t} 2 & 4921.18714 & 46.93974\end{array}\)
```



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

```
[pyrrole] = 0.1082 M
Temperature = 318.2 K
Data: Datal_C
Model: ExpDec2
Equation: \(y=A 1 * \exp (-x / t 1)+A 2 * \exp (-x / t 2)+y 0\)
Weighting:
y No weighting
Chi^2/DoF \(=8.7991 \mathrm{E}-7\)
\(\mathrm{R}^{\wedge} 2=0.99994\)
\(\begin{array}{lll}\mathrm{y} 0 & -0.74231 & 0.00067\end{array}\)
A1 \(0.06085 \quad 0.00064\)
\(\begin{array}{lll}\mathrm{t} 1 & 203.74624 & 4.34753\end{array}\)
A2 0.50280 .00043
t2 \(4050.73941 \quad 13.26354\)
```



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

```
[pyrrole] = 0.3011 M
Temperature = 318.2 K
Data: Datal_C
Model: ExpDec2
Equation: \(y=A 1 * \exp (-x / t 1)+A 2 * \exp (-x / t 2)+y 0\)
Weighting:
y No weighting
Chi^2/DoF \(=1.8578 \mathrm{E}-7\)
\(\mathrm{R} \wedge 2=0.9999\)
y0 \(\quad-0.29145 \quad 0.00011\)
A1 \(0.15364 \quad 0.00018\)
t1 \(177.31011 \quad 3.90157\)
A2 \(0.0301 \quad 0.00033\)
\(\begin{array}{lll}\mathrm{t} 2 & 2265.19413 & 6.70319\end{array}\)
```



Figure C.1.4: Plot of absorbance versus time for the reaction of $\mathrm{C}_{60}$ with pyrrole in cyclohexane.
[pyrrole] $=0.3903 \mathrm{M}$
Temperature $=318.2 \mathrm{~K}$

Data: Datal_C
Model: ExpDec2
Equation: $y=A 1 * \exp (-x / t 1)+A 2 * \exp (-x / t 2)+y 0$
Weighting:
y No weighting
Chi^2/DoF $=4.0084 \mathrm{E}-6$
$\mathrm{R}^{\wedge} 2=0.99903$
$\begin{array}{lll}\mathrm{y} 0 & -0.53181 & 0.00063\end{array}$
A1 $0.09069 \quad 0.00152$
t1 $141.86054 \quad 4.71053$
A2 $0.22814 \quad 0.00061$
t2 $2685.49368 \quad 25.13831$


Figure C.1.5: Plot of absorbance versus time for the reaction of $\mathrm{C}_{60}$ with pyrrole in cyclohexane.
[pyrrole] $=0.4987 \mathrm{M}$
Temperature $=318.2 \mathrm{~K}$

Data: Datal_C
Model: ExpDec2
Equation: $y=A 1 * \exp (-x / t 1)+A 2 * \exp (-x / t 2)+y 0$
Weighting:
y No weighting
$\mathrm{Chi}^{\wedge} 2 / \mathrm{DoF} \quad=1.7382 \mathrm{E}-6$
$\mathrm{R}^{\wedge} 2=0.99933$
y0 -0.62409 0.00025
A1 $0.10979 \quad 0.00105$
t1 $173.17411 \quad 3.35477$
A2 $0.16343 \quad 0.00069$
$\begin{array}{lll}\mathrm{t} 2 & 1876.64763 & 14.87381\end{array}$

## Appendix C. 2

Plot of absorbance versus time for the reaction of $\mathbf{C}_{60}$ 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 $\mathrm{C}_{60}$ with pyrrole in cyclohexane.
[pyrrole] $=0.1940 \mathrm{M}$
Temperature $=328.2 \mathrm{~K}$

| Data: Data1 C <br> Model: ExpDec2 |  |  |
| :---: | :---: | :---: |
|  |  |  |
| Equation: y = A1 |  | (-x/t1) + A |
| Weighting: |  |  |
| y | No weighting |  |
| Chi^2/DoF $=4.1415 \mathrm{E}-7$ |  |  |
|  | $=0.99986$ |  |
| 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 $\mathrm{C}_{60}$ with pyrrole in cyclohexane.
[pyrrole] $=0.3111 \mathrm{M}$
Temperature $=328.2 \mathrm{~K}$

Data: Datal_C
Model: ExpDec2
Equation: $y=A 1 * \exp (-x / t 1)+A 2 * \exp (-x / t 2)+y 0$
Weighting:
y No weighting
$\mathrm{Chi}^{\wedge} 2 / \mathrm{DoF} \quad=6.9272 \mathrm{E}-7$
$\mathrm{R}^{\wedge} 2=0.99979$
$\begin{array}{lll}\mathrm{y} 0 & -0.41354 & 0.00024\end{array}$
A1 $0.21208 \quad 0.00024$
t1 $118.20346 \quad 3.61615$
A2 $0.04207 \quad 0.00066$
t2 $2589.69509 \quad 10.00863$


Figure C.2.3: Plot of absorbance versus time for the reaction of $\mathrm{C}_{60}$ with pyrrole in cyclohexane.
[pyrrole] $=0.3813 \mathrm{M}$
Temperature $=328.2 \mathrm{~K}$

Data: Datal_C
Model: ExpDec2
Equation: $y=A 1 * \exp (-x / t 1)+A 2 * \exp (-x / t 2)+y 0$
Weighting:
y No weighting
Chi^2/DoF $=6.7399 \mathrm{E}-6$
$\mathrm{R} \wedge 2=0.9998$
$\begin{array}{lll}\mathrm{y} 0 & -1.26704 & 0.00115\end{array}$
A1 0.681220 .00083
t1 179.774623 .98866
A2 0.168420 .00186
t2 $3183.20491 \quad 16.06652$


Figure C.2.4: Plot of absorbance versus time for the reaction of $\mathrm{C}_{60}$ with pyrrole in cyclohexane.
[pyrrole] $=0.4886 \mathrm{M}$
Temperature $=328.2 \mathrm{~K}$

Data: Datal_C
Model: ExpDec2
Equation: $y=A 1 * \exp (-x / t 1)+A 2 * \exp (-x / t 2)+y 0$
Weighting:
y No weighting
Chi^2/DoF $=7.582 \mathrm{E}-7$
$\mathrm{R}^{\wedge} 2=0.99928$
y0 -0.3876 0.00011
A1 $0.04616 \quad 0.0008$
$\begin{array}{lll}\mathrm{t} 1 & 94.98157 & 3.35184\end{array}$
A2 0.11980 .00049
$\begin{array}{lll}\mathrm{t} 2 & 1196.82123 & 7.55063\end{array}$


Figure C.2.5: Plot of absorbance versus time for the reaction of $\mathrm{C}_{60}$ with pyrrole in cyclohexane.
[pyrrole] $=0.9662 \mathrm{M}$
Temperature $=328.2 \mathrm{~K}$

Data: Datal_C
Model: ExpDec2
Equation: $y=A 1 * \exp (-x / t 1)+A 2 * \exp (-x / t 2)+y 0$
Weighting:
y No weighting
$\mathrm{Chi}^{\wedge} 2 / \mathrm{DoF}=2.1944 \mathrm{E}-6$
$\mathrm{R}^{\wedge} 2=0.9955$
y0 -0.39282 0.00022
A1 $0.05014 \quad 0.00197$
$\begin{array}{lll}\text { t1 } 91.27779 & 6.57424\end{array}$
A2 $0.07178 \quad 0.00176$
$\begin{array}{lll}\mathrm{t} 2 & 671.21236 & 18.70141\end{array}$

## 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 $\mathrm{C}_{60}$ with pyrrole to in cyclohexane.
$[$ pyrrole $]=0.0380 \mathrm{M}$
Temperature $=338.2 \mathrm{~K}$

Data: Datal_C
Model: ExpDec2
Equation: $\mathrm{y}=\mathrm{A} 1 * \exp (-\mathrm{x} / \mathrm{t} 1)+\mathrm{A} 2 * \exp (-\mathrm{x} / \mathrm{t} 2)+\mathrm{y} 0$
Weighting:
y No weighting
$\mathrm{Chi}^{\wedge} 2 / \mathrm{DoF}=2.0282 \mathrm{E}-6$
$\mathrm{R}^{\wedge} 2=0.99985$
$\begin{array}{lll}\mathrm{y} 0 & -0.64841 & 0.00078\end{array}$
A1 $0.09536 \quad 0.00101$
tl $254.81569 \quad 5.46842$
A2 0.431920 .00052
t2 $3373.95036 \quad 18.28165$


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

```
[pyrrole] \(=0.0936 \mathrm{M}\)
Temperature \(=338.2 \mathrm{~K}\)
```


## Data: Datal_C

Model: ExpDec2
Equation: $\mathrm{y}=\mathrm{A} 1 * \exp (-\mathrm{x} / \mathrm{t} 1)+\mathrm{A} 2 * \exp (-\mathrm{x} / \mathrm{t} 2)+\mathrm{y} 0$ Weighting:
y No weighting
Chi^2/DoF $=5.469 \mathrm{E}-7$
$\mathrm{R}^{\wedge} 2=0.99971$
$\begin{array}{lll}\mathrm{y} 0 & -0.27047 & 0.00012\end{array}$
A1 $0.16573 \quad 0.00027$
t1 $91.79274 \quad 5.0381$
A2 $0.02289 \quad 0.00064$
t2 1767.12537 6.09249


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

```
[pyrrole] = 0.2838 M
Temperature \(=338.2 \mathrm{~K}\)
```


## Data: Datal_C

Model: ExpDec2
Equation: $\mathrm{y}=\mathrm{A} 1 * \exp (-\mathrm{x} / \mathrm{t} 1)+\mathrm{A} 2 * \exp (-\mathrm{x} / \mathrm{t} 2)+\mathrm{y} 0$
Weighting:
y No weighting
$\mathrm{Chi}^{\wedge} 2 / \mathrm{DoF} \quad=7.5564 \mathrm{E}-6$
$\mathrm{R}^{\wedge} 2=0.99987$
y0 -1.60486 0.00305
A1 $0.97405 \quad 0.00187$
t1 $304.96418 \quad 5.47877$
A2 $0.21206 \quad 0.00187$
t2 $4721.48945 \quad 34.11164$


Figure C.3.4: Plot of absorbance versus time for the reaction of $\mathrm{C}_{60}$ with pyrrole to in cyclohexane.
[pyrrole] $=0.3898 \mathrm{M}$
Temperature $=338.2 \mathrm{~K}$

Data: Data1_C
Model: ExpDec2
Equation: $y=A 1 * \exp (-x / t 1)+A 2 * \exp (-x / t 2)+y 0$
Weighting:
y No weighting
Chi^2/DoF $=4.9398 \mathrm{E}-6$
$\mathrm{R}^{\wedge} 2=0.99891$
$\begin{array}{lll}\mathrm{y} 0 & -0.53864 & 0.00065\end{array}$
A1 $0.23695 \quad 0.00076$
t1 $159.44553 \quad 5.94355$
A2 $0.08965 \quad 0.00166$
t2 $2545.34367 \quad 25.63347$


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

```
[pyrrole] = 0.4693 M
Temperature = 338.2 K
Data: Datal_C
Model: ExpDec2
Equation: \(\mathrm{y}=\mathrm{A} 1 * \exp (-\mathrm{x} / \mathrm{t} 1)+\mathrm{A} 2 * \exp (-\mathrm{x} / \mathrm{t} 2)+\mathrm{y} 0\)
Weighting:
y No weighting
Chi^2/DoF \(=3.7751 \mathrm{E}-6\)
\(\mathrm{R}^{\wedge} 2=0.99985\)
\(\begin{array}{lll}\mathrm{y} 0 & -1.0215 & 0.00299\end{array}\)
A1 \(0.72375 \quad 0.00199\)
t1 \(345.9139 \quad 13.38431\)
A2 \(0.06986 \quad 0.00135\)
t2 \(5415.64191 \quad 47.59956\)
```

