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The triplet state photophysics of phenanthrene

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The Triplet State Photophysics
of Phenanthrene

by

Roberta Susnow

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of the requirements for
Honors in the Department of Chemistry

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Abstract

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The first excited triplet state (T1 state) of aromatic hydrocarbons such as phenanthrene acts as an intermediate in many chemical and photochemical reactions. The T1 state is a metastable state and its lifetime can be measured in terms of its decay to the ground state. The duration of this decay is on the order of microseconds. Therefore, techniques for measuring the kinetics of fast reactions must be employed in the determination of the rate of the T1 state decay. One such technique that is utilized in this research is flash photolysis.

The rate of the T1 state decay is greatly enhanced by the presence of oxygen. Therefore, to accurately measure the first order T1 state decay, the phenanthrene solution must be degassed prior to flashing in order to remove dissolved oxygen. A vacuum line is designed for this purpose.

Based on the experimental data, it was determined that scattered flash light must be eliminated from the flash apparatus and that the vacuum line must be redesigned for more efficient degassing.

Acknowledgements

I would like to take this opportunity to acknowledge Professor David Hayes, my thesis advisor, for the guidance and knowledge that he has brought to this research. I would also like to thank him for all that he has taught me during these past three terms.

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Table of Contents

	<u>Page</u>
Abstract	ii
Acknowledgements	iii
Table of Figures	v
Chapter 1: Introduction.....	1
Aromatic Quenchers of the T1 State.....	8
The Exchange Transfer Mechanism	17
Quenching of the Triplet State by Molecular Oxygen	20
Delayed Fluorescence	23
The Scope of the Research Project	24
Chapter 2: Experimental	25
Improvements in Experimental Design	39
The Vacuum Line	42
Chapter 3: Results	44
Chapter 4: Discussion	47
References	49

Table of Figures

<u>Figure</u>	<u>Title</u>	<u>Page</u>
1	Energy diagram for phenanthrene.	2
2	The energy transfer process between phenanthrene and an aromatic quencher.	15
3	An overhead view of the flash apparatus.	27
4	Spectrum of the filter solution.	31
5	A cross section of the sample cell.	33
6	An example of the data obtained from the flash apparatus.	34
7	Flash profile taken at 290nm.	36
8	Flash profile taken at 482nm.	38
9	Improvements in the experimental design.	41
10	The vacuum line and I-assembly.	43
11	Plot of $\ln A$ versus time.	45

Introduction

Triplet states of aromatic hydrocarbons have been detected and studied extensively. Although the first excited triplet state is a transient, it is postulated that this triplet state acts as an intermediate in many chemical and photochemical reactions. The long lifetime of the excited triplet state relative to the excited singlet state is the basis for this postulation.

The triplet state is formed upon photochemical excitation of the aromatic hydrocarbon. The mechanism of the photochemical formation of the triplet state can be understood by evaluating the energy diagram in figure 1. This energy diagram represents the phenanthrene molecule as well as other aromatic hydrocarbons with structures similar to that of phenanthrene.

The ground state (S_0 state) absorbs a wavelength of ultra-violet or visible light from an excitation source and forms the first excited singlet state (S_1 state). The S_1 state can then deactivate to the ground state via a radiative or radiationless process. The radiative process is referred to as fluorescence, while

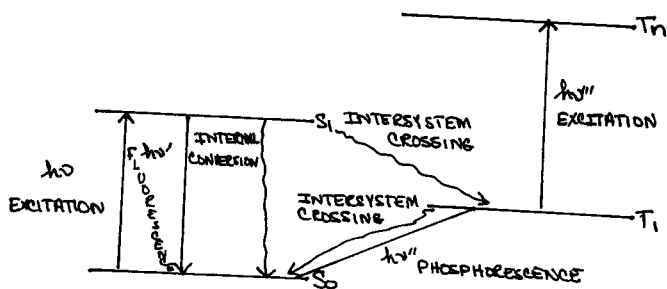


Figure 1: Energy diagram for Phenanthrene.

the radiationless process is called internal conversion. During fluorescence, the excited molecule deactivates to the ground state and releases its excess energy by emitting a wavelength of ultra-violet or visible light. During internal conversion, the molecule also deactivates to the ground state. However, the molecule releases its excess energy by imparting vibrational energy to the surrounding solvent in the system. Presumably, the release of this excess energy is not the rate determining step in either the radiative or the radiationless deactivation process.

The first excited triplet state (T₁ state) is formed via a radiationless intersystem crossing from the S₁ state. The T₁ state can then deactivate to the ground state via a radiative or non-radiative process. These processes are similar to the ones undergone by the S₁ state. However, the radiative T₁ decay is termed phosphorescence. The T₁ state can also undergo further excitation and make a transition to a higher triplet state.

The T₁ state is referred to as the phosphorescent level. It is the lowest excited electronic state. It has a lifetime (even in fluid solvents) of 10^{-4} sec,¹ which is several orders of magnitude greater than that of the excited singlet states.¹ Its chemical behavior

is characteristic of a biradical and it is an intermediate in energy transfer processes and in chemical and biochemical reactions.²

Previously, most work on triplet state chemistry was carried out in rigid media. These studies in rigid media involved the radiative process of deactivation (phosphorescence). With the advent of flash photolysis the triplet state is observed directly by means of its triplet-triplet absorption spectrum.

The flash photolysis apparatus consists of a UV-visible xenon arc lamp (analyzing light), two xenon flash lamps energized by a 10,000V micropulser, a monochromator, a photomultiplier tube, and an oscilloscope. The experimental technique of flash photolysis involves the initial excitation of a sample via the flash lamps. This excitation forms the S₁ electronic state. The T₁ state is then formed through intersystem crossing. The T₁ state absorbs energy from the analyzing light, leading to a reduction in the intensity of light striking the photomultiplier tube, which is connected to the oscilloscope. Based on this attenuation, the T₁ concentration versus time can be monitored on the oscilloscope. This transient absorption spectrum allows for the evaluation of the decay of the T₁ state. A more detailed description of the flash apparatus set-up and functioning is offered

in the experimental section.

The rate law for the decay of the T1 state of phenanthrene and other similar aromatic molecules is given below.

$$-d[T]/dt = k_1[T] + k_2[T]^2 + k_3[T][Q]$$

The first term of this rate law is the first order intramolecular process of internal conversion from the T1 state to the S0 ground state. This first order process is independent of the initial phenanthrene concentration. The second term describes the second order intermolecular triplet-triplet self-quenching, which will be discussed in detail under the context of delayed fluorescence. The third term describes the second order intermolecular quenching of the T1 state by a quencher that is introduced into the phenanthrene system. These three modes of T1 deactivation all involve a change in the spin multiplicity of phenanthrene.

At low concentrations of phenanthrene, the second term involving triplet-triplet self-quenching can be ignored. In the absence of an outside quencher, the third term can be ignored as well. Therefore, the decay

of the T1 state would be dependent solely upon the concentration of T1.³

It might be expected that the transition T1→S0 (described by k1) would have a low probability since total spin momentum is not conserved. However, this radiationless transition is quite favorable. The explanation of this unexpected high favorability is based on the fact that the high probability of the radiationless conversion between electronic states may, in the absence of spin and other restrictions, have a rate constant exceeding 10^{11} sec^{-1} (several orders of magnitude greater than the radiative transition of phosphorescence). If a change of spin multiplicity is involved in the radiationless transition, the rate may be reduced by a factor of 10^4 . This rate will, however, still be great enough to compete with other modes of deactivation of the T1 state (phosphorescence).

In rigid media, the radiationless crossing from S1 to T1 occurs with a rate constant of the order 10^8 sec^{-1} . On the other hand, the similar radiationless crossing T1→S0 is not observed in rigid media (rate less than 10^{-1} sec^{-1}). The triplet decay rate is not rate determined by energy transfer to the solvent. Therefore, the transition T1→S0 is not expected to be viscosity dependent. However, the configuration of the

T₁ state is clamped by viscous or rigid solvents, and this clamping does not allow the triplet state to attain a configuration that is similar to the ground state configuration, which would allow this transition to occur.

In fluid solvents the rate of the radiationless conversion of T₁ → S₀ would be much greater than the phosphorescence rate. This is the reason for the absence of phosphorescence in solutions and gases. However, in rigid solvents the radiationless transition is impeded and the competing radiative transition (phosphorescence) wins. Thus, phosphorescence is observed in rigid or viscous solvents or at very low temperatures (liquid nitrogen temperatures).²

Aromatic Quenchers of the T1 State

In the presence of a quencher, the decay of the triplet state is greatly enhanced. Effective quenchers may be aromatic compounds, paramagnetic species (oxygen, nitric oxide), or transitional and inner transitional metal ions.⁴ With the addition of a quencher, the rate constant for the quenching of the T1 state would no longer be negligible. The rate law for the decay of the T1 state would now be represented as:

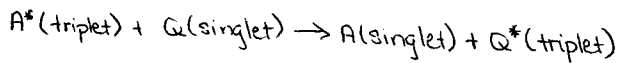
$$-d[T]/dt = k_1[T] + k_q[A][T]$$

The quenching of the T1 state is described in terms of donor-acceptor pairs. The energy transfer from the triplet level of the donor molecule results in the deactivation of the donor molecule and its return to the ground state. The acceptor molecule is elevated from its ground state to an excited state.

In most molecules, such as the aromatic hydrocarbons, the ground state is a singlet state, whereas the lowest excited state is a triplet state. As previously stated, the triplet state has a lifetime that is several orders of magnitude greater than that

of the excited singlet state. Therefore, it is reasonable that the triplet state, rather than the singlet state, is an intermediate in this energy transfer process.

Aromatic quenchers tend to exist in a singlet ground state and then excite to the first triplet state during energy transfer. This process is described below:



It is important to note that overall spin conservation is maintained in this process.

Several aromatic quenchers of phenanthrene have been reviewed in the literature. These donor-acceptor pairs are described in the following pages.

Phenanthrene and Naphthalene

In this system, the donor molecule is phenanthrene and the acceptor is naphthalene. The energy transfer

mechanism has been studied in solvents such as hexane and ethylene glycol. Prior to the addition of naphthalene to the phenanthrene solution, the transient triplet absorption of phenanthrene is observed. However, when naphthalene is added to the phenanthrene solution, the triplet state absorption of phenanthrene is completely suppressed, and is replaced with the transient triplet absorption spectrum of naphthalene.

The disappearance of the phenanthrene transient absorption spectrum and the simultaneous appearance of the naphthalene transient absorption spectrum indicates that energy transfer is taking place. The phenanthrene T1 state is deactivated by the naphthalene singlet ground state. Phenanthrene then returns to the ground state, while naphthalene excites to its first excited triplet state (T1 state). The absorption spectrum that is observed after energy transfer is the triplet-triplet absorption of the newly formed naphthalene T1 state.

The first order rate constant for the decay of triplet naphthalene formed by energy transfer is identical with the rate constant for the decay of triplet naphthalene formed by direct excitation of naphthalene in the presence or absence of phenanthrene. This further indicates that the first excited triplet state of naphthalene is, indeed, formed during energy

transfer with phenanthrene.

To check for the possibility of complex formation between phenanthrene and naphthalene, the absorption spectrum taken of the phenanthrene-naphthalene solution was evaluated. It was determined that no new bands were observed. That is, the absorption spectrum of the mixture was simply a sum of the separate absorption spectra of the two components.

It is also observed that the fluorescence yield of phenanthrene is unaffected by the presence of naphthalene.

Phenanthrene and 1-Bromonaphthalene

This system was studied in hexane and in ethylene glycol. Identical results were obtained with this donor-acceptor pair as in the phenanthrene-naphthalene system. Again the transient triplet absorption spectrum of phenanthrene disappeared upon addition of 1-bromonaphthalene and was replaced with the triplet-triplet absorption spectrum of 1-bromonaphthalene. This confirmed the fact that energy transfer was taking place.

There was no complexation observed between phenanthrene and 1-bromonaphthalene and the fluorescence yield of phenanthrene was unchanged by the presence of 1-bromonaphthalene.

Phenanthrene and 1-Iodonaphthalene

In the case of phenanthrene with naphthalene or 1-bromonaphthalene, the occurrence of energy transfer was confirmed by the disappearance of the triplet-triplet absorption spectrum of phenanthrene and its replacement by the triplet-triplet absorption spectrum of naphthalene or 1-bromonaphthalene. However, 1-iodonaphthalene does not show a triplet-triplet absorption spectrum. Therefore, this type of observation is not possible in the phenanthrene - 1-iodonaphthalene system.

The quenching of phenanthrene by 1-iodonaphthalene was detected by adding various concentrations of 1-iodonaphthalene to phenanthrene and measuring the rate of decay of the triplet state. The rate of decay of the triplet can be described by the equation below:

$$-d[\tau]/dt = \{k_1 + k_2[\alpha]\}[\tau] = k_n[\tau]$$

$$k_n = k_1 + k_2[\alpha]$$

A linear plot of k_R versus $[Q]$ can be used to determine the value of k_Q .

Again, no complexation was observed and the fluorescence yield of phenanthrene was unaffected by the presence of the quencher.

Systems Showing No Quenching of the Triplet State

1) Phenanthrene and Anthracene

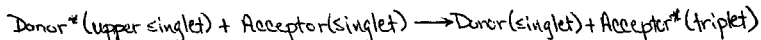
2) Phenanthrene and Ethyl Iodide

Phenanthrene was only slightly quenched by ethyl iodide.

Mechanism of Energy Transfer

The energy transfer process between phenanthrene and an aromatic quencher has been described in terms of a phenanthrene triplet state molecule transferring energy to a singlet ground state acceptor. Phenanthrene returns to its singlet ground state, while the aromatic acceptor excites to its first excited triplet state.

Another energetically possible alternative is that phenanthrene transfers energy from its upper singlet state to a singlet ground state acceptor. Phenanthrene returns to its singlet ground state and the acceptor excites to its first excited triplet state:



This alternative mechanism is improbable since total spin momentum is not conserved. Also, the upper singlet state has an extremely short lifetime, which would not allow ample time for energy transfer to occur. Experimentally this mechanism can be excluded on the grounds that it has been observed that the fluorescence yield of phenanthrene is not affected by the presence of the quencher. This alternative mechanism implies that a portion of the S₁ population is consumed in the energy transfer process. If this were the case, the fluorescence yield of phenanthrene would decrease since there would be a decrease in the number of molecules in the S₁ state available for radiative deactivation.⁴

A diagram explaining the energy transfer process between phenanthrene and an aromatic quencher is given in figure 2.⁵

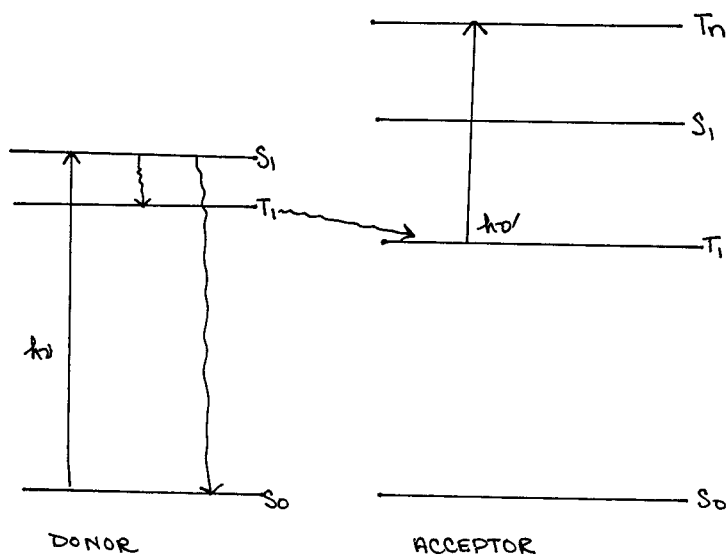


Figure 2: The energy transfer process between phenanthrene and an aromatic quencher.

The Magnitude of the Quenching Rate Constant for Aromatic Quenchers

The rate constants of energy transfer fall into 3 categories.

1) The triplet level of the donor is much higher than that of the acceptor. In this case the quenching rate will be very close to the encounter rate of the donor with the acceptor. This encounter rate can be described by the equation of Debye:

$$k_d = 8RT/3000n \text{ l.mole}^{-1} \text{ .s}^{-1}$$

where k_d is the diffusion controlled rate constant, and n is the solvent viscosity. The effect of solvent viscosity will be discussed in the following pages.

2) The triplet level of the donor and the acceptor lie very close in energy, but the energy of the acceptor is below that of the donor. In this case, the quenching rate is considerably below the encounter. An example of this can be seen in the phenanthrene-naphthalene system.

3) When the triplet level of the donor is below that of the acceptor no quenching is observed.⁶

The Exchange Transfer Mechanism

The energy transfer process occurring between phenanthrene and an aromatic quencher can be explained in terms of the exchange transfer mechanism. The basis of this mechanism is that energy transfer occurs between molecules during encounters at normal collisional distances. During this encounter, overlap of the orbitals of the two molecules occurs and an exchange of electrons may occur, resulting in the trans of energy between phenanthrene and the quencher.

Dexter in 1953 formulated the probability relationships involved in the exchange transfer mechanism. Dexter submits that the probability of energy transfer between two molecules can be described by the formula presented below.

$$P_{DA} = \frac{4\pi^2}{h} z^2 \int f_D(E) f_A(E) dE$$

The integral $\int f_D(E) f_A(E) dE$ is a type of overlap integral between the emission spectrum of the donor and

the absorption of the acceptor.

Z^2 is energy squared and is not directly related to optical experiments. The separation and concentration dependencies of the donor-acceptor pair are described by this parameter. Z^2 varies approximately as:

$$Y (e^4 / K^2 R_0^2) \exp(-2R/L)$$

R_0 is the effective average Bohr radius of the unexcited states of the donor and the acceptor. L is the effective average Bohr radius of the excited states of the donor and the acceptor. K is the dielectric constant of the medium and e is the charge on the electron. R is the distance between the two molecules. Y is a dimensionless quantity ($\ll 1$), which takes into account sign changes in the wavefunctions involved in the probability of exchange transfer.

According to this probability equation, the exchange transfer times can be very short but can increase quite rapidly as molecular separation increases (transfer times increase by a factor of 10^2 when the molecular separation increases by one molecular diameter).

The exchange transfer mechanism is dependent upon the encounter between the donor and the acceptor

molecules. Therefore, it can be concluded that the values of the quenching rate constants cannot exceed those calculated for diffusion controlled encounters between molecules.⁴

Quenching of the Triplet State by Molecular Oxygen

Oxygen is often an impurity in reaction systems. The two low-lying excited states of oxygen ($^1\Sigma$, $^1\Delta$) enable oxygen to be an effective quencher of the triplet state of aromatic hydrocarbons. This quenching leads to an enhancement of the decay rate of the first excited triplet state.⁷

With the introduction of oxygen into the phenanthrene system, the expression for the decay rate of the T1 state includes the quenching term, which is neglected in the absence of a quencher.

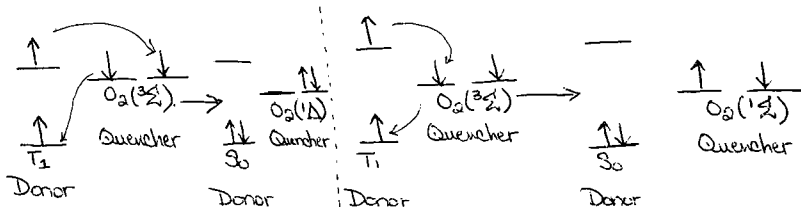
$$-d[T]/dt = k_1[T] + k_q[O_2][T]$$

The concentration of oxygen in the system can be taken to be constant. In this case, the pseudo-first order rate constant can be expressed as:

$$k_A = k_1 + k_q[O_2]; \quad -d[T]/dt = k_A[T]$$

Ground state molecular oxygen exists in the triplet state. Upon quenching of the T1 state, oxygen is promoted to a singlet excited state. A molecular

orbital description of the triplet state quenching is given below:



During this process total spin momentum is conserved.⁸

Experimentally, it has been determined that the quenching of the T_1 state is viscosity dependent. This implies that the quenching rate is controlled by the diffusion of the quencher to the excited triplet molecule. Solvent viscosity is inversely proportional to the diffusion coefficient of the solvent. Therefore, the quenching rate decreases with increasing solvent viscosity, since the number of encounters between a quenching molecule and a T_1 state molecule decreases.

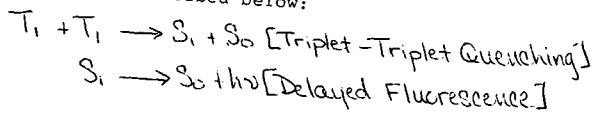
The viscosity dependence of the quenching rate exists for a number of aromatic quenchers as well as for molecular oxygen. However, oxygen diffuses throughout the solvent at a considerably faster rate than most organic molecules, leading to a larger pseudo-first order rate constant. Therefore, oxygen

will be a more effective quencher of the triplet state relative to the aromatic hydrocarbons discussed previously.⁹

Delayed Fluorescence

At high excitation intensities and high triplet concentrations the intermolecular triplet-triplet quenching becomes significant enough to be included in the rate law for the decay of the T1 state. This second order decay process leads to delayed fluorescence.

When two molecules in the first excited triplet state collide, energy transfer occurs, wherein the first excited singlet state (S1) and the ground state (S0) are formed. The mechanism for delayed fluorescence is described below:



Experimentally it has been found that at comparable concentrations, anthracene exhibits a greater intensity of delayed fluorescence relative to phenanthrene.¹⁰

The Scope of The Research Project

The majority of the experimentation involved in this research project is geared to the assessment of the accuracy and the proper functioning of the flash apparatus and the vacuum line. To carry out this assessment, the rate constant for the first order decay of the phenanthrene T1 state (k_1) was evaluated and then compared with the literature values. This procedure will be discussed in detail in the experimental and the results section.

EXPERIMENTAL

Flash photolysis involves the excitation of a ground state molecule via the high intensity emission of UV or visible radiation from flash lamps. This high intensity emission has a duration on the order of microseconds. The high intensity creates a significant T1 population, while the short duration of the lamp pulse insures that the subsequent T1 state absorption of UV or visible light from an analyzing beam can be measured without interference from further excitation of the ground state to the T1 state. These excitation characteristics allow for the attainment of an accurate transient triplet absorption spectrum, which consists of the analyzing beam attenuation versus time.

The flash apparatus consists of a UV-visible Xenon arc lamp (analyzing light) and its power supply with DC rectifier, 2 Xenon electric discharge flash lamps energized by a 10,000V micropulser that is connected to a trigger/pretrigger switch, 2 quartz lenses, a monochromator, a photomultiplier tube and its voltage source, and an oscilloscope. The flash lamps and the micropulser are housed in a Faraday cage so that the oscilloscope will not respond to their electronic output. A diagram describing the flash apparatus is

given in figure 3.

The electric discharge flash lamps consist of quartz tubing that is filled with xenon gas. A four inch spark gap exists across each flash lamp. The flash lamps are hooked up in series with the micropulser. One hundred joules are stored in the electric field of the micropulser capacitor when it is charged to 10,000V ($C = 2\mu\text{F}$). This energy is released upon triggering, which causes the capacitor to discharge, creating a potential across the flash tubes resulting in the ionization of the xenon gas. The ionized xenon gas allows the current to arc across the four inch spark gaps of the flash lamps, leading to the emission of light. This emission is the excitation flash.

The type of gas and the pressure of the gas in the flash tubes will affect the nature of the flash spectrum. If the gas pressure is too high the resistance in the flash tubes will be too high and arcing will not occur. If the pressure is too low, the resistance will be too low and prefiring will occur. The flash tubes in this experiment are filled so that the peak intensities of excitation occur in the region of 300-400nm.

The analyzing light is a xenon lamp, which operates on the same principle as the flash lamps, but the

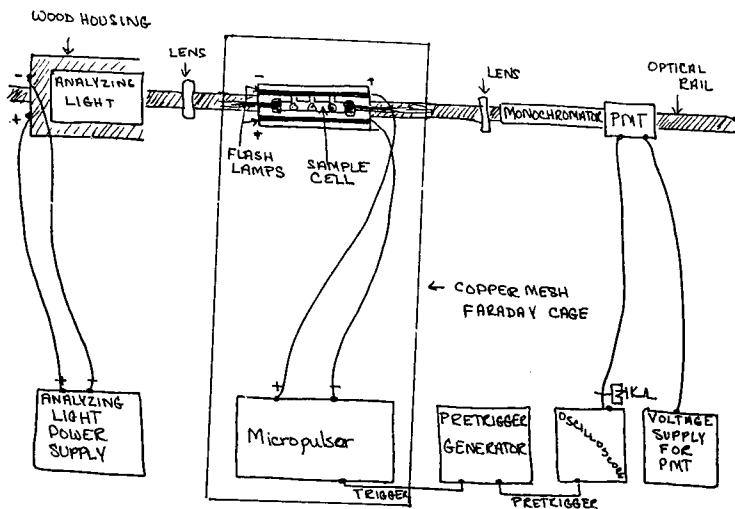


Figure 3: An overhead view of the flash apparatus.

analyzing light is much less intense and operates continuously. The analyzing light is connected to a power supply, which acts as a DC rectifier and provides the necessary voltage to ionize the xenon gas and create arcing. After rectification, the ripple in the voltage at maximum output is 0.1% peak to peak of the DC level. The analyzing light will maintain a constant spectrum and intensity of light as long as the voltage on its supply remains constant after the initial ionization.

The xenon arc lamp that is used in this experiment is operated at 22 DC volts and 7.0 DC amperes. The lamp cannot be operated with the current greater than 7.5 amperes or it will burn out. The arc lamp is ignited by a single pulse of 25 kilovolts. The desired intensity is maintained by maintaining a constant current through the lamp.

The nature of the spectrum emitted by the analyzing light will be affected by the gas pressure and the type of gas, just as in the case of the flash lamps. The output from the analyzing lamp in our system is rich in UV radiation.

The intensity of the analyzing light at a particular wavelength is measured by a photomultiplier tube. A 1P28 photocathode tube with quartz encasing is used in

our system for the measurement of UV-visible light. The basis of the operation of a photomultiplier tube is the photoelectric effect. A photon of light strikes the photomultiplier tube, which leads to the creation of a free electron. A cascading effect amplifies this free electron by a factor of 2.5×10^6 , which results in a current flow. In this experiment, the voltage applied to the PMT is approximately 400-500V.

The current output of the photomultiplier tube is converted to a voltage signal by running the current through a 1K ohm resistor. The voltage drop across this resistor is measured by an oscilloscope with an impedance of 1M ohm, connected in parallel with the resistor.

The time response of the photomultiplier tube is 2.2 ns. This means that a time lapse of 2.2 ns exists between the input to the photomultiplier tube and the actual response of the photomultiplier tube.

The main purpose of flashing a sample on the flash apparatus is to obtain a transient absorption spectrum ($T_1 \rightarrow T_n$), which will then be utilized in order to determine the rate constant for the decay of the T_1 state. A typical run on the flash apparatus involves several steps. During the first step in this procedure, the analyzing light settings are adjusted to

maintain the proper lamp intensity. The lamp is then activated and its intensity at 482nm is monitored by the photomultiplier tube. This initial intensity establishes the intensity prior to flashing the sample. Generally, the photomultiplier tube voltage is set so as to obtain a 100%T baseline on the oscilloscope corresponding to a 50mV full scale deflection (0 voltage corresponding to 0 deflection).

The micropulser is then charged and triggered, which excites phenanthrene from the ground state to the first excited state (S_1 state); phenanthrene has a maximum absorbance in the region of 230nm to 290nm. Subsequently the T_1 state is formed via intersystem crossing. Once the T_1 state has been formed, the analyzing light is attenuated at 482 nm as a result of the T_1 state absorption (the maximum in the $T_1 \rightarrow T_n$ band occurs at 482 nm). This attenuation is monitored on the oscilloscope as a reduction in the original 50mV full scale deflection.

The phenanthrene solution is flashed in a jacketed cell containing filter solution so that 482nm light from the flash lamps does not interfere with the measurement of the analyzing beam attenuation. This filter solution consists of $CuCl_2$ and $NiCl_2$ in a 1M HCl solution. The spectrum of the filter solution is given in figure 4. A drawing of the sample cell is given in

Figure 4: Spectrum of the filter solution.

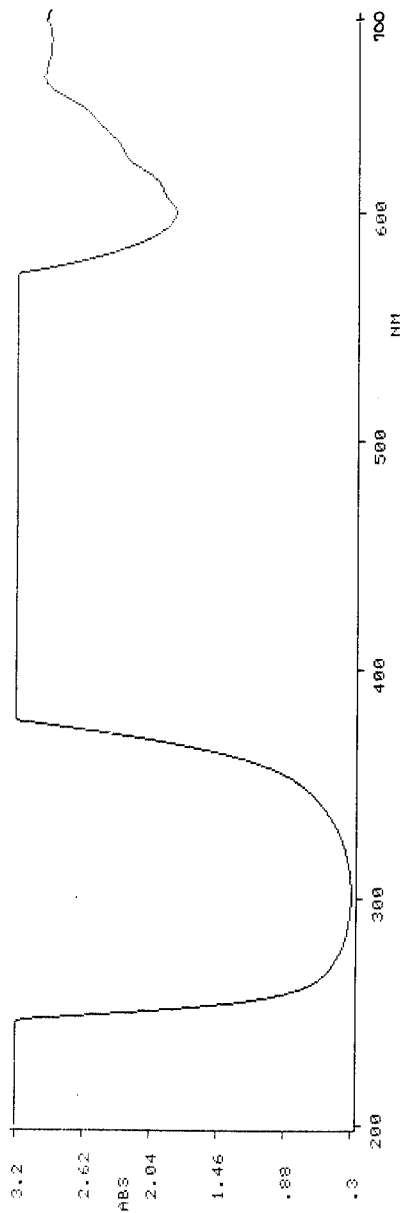


figure 5.

The decay of the T1 state is measured by a decrease in the intensity of transitions to the Tn state and ,hence, a decrease in the attenuation of the analyzing light at 482nm. The extent of analyzing beam attenuation is expressed in terms of percent transmittance.

The baseline for 100% transmittance by the ground state sample corresponds to a 50mV deflection on the oscilloscope. This baseline is marked by the pretrigger switch. A decrease in the %T will occur as the excited sample absorbs energy from the analyzing light. An example of the data obtained from the oscilloscope is illustrated in figure 6.

To accurately interpret the data obtained from the oscilloscope, the pulse characteristics of the flash must be known. It is important to know when the initial excitation of phenanthrene is complete so that the decay of the first excited triplet state can be measured without interference from the simultaneous generation of new T1 states. Also, a measurement of the duration of scattered flash light at 482nm must be made so that triplet decay measurements can be taken without error from superimposed scattered flash light. Flash profiles taken at 290 and at 482nm provide the

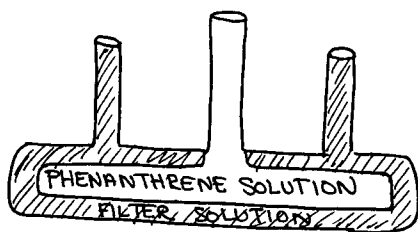


Figure 5: A cross section of the sample cell.

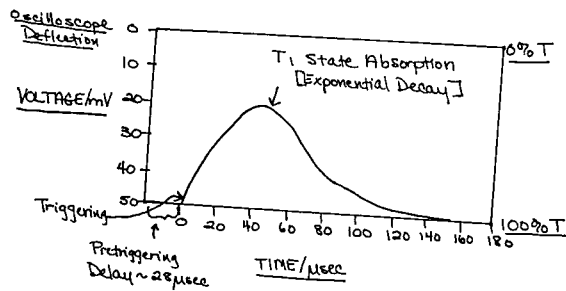


Figure 6: An example of the data obtained from the oscilloscope.

necessary information to guide the proper data interpretation.

The flash profile taken at 290nm is shown in figure 7. The voltage on the photomultiplier tube is set at 450V and the analyzing light is not turned on.

The flash profile is a measure of the flash lamp intensity at 290nm as a function of time. The maximum intensity of the flash occurs at 3 μ sec after triggering and corresponds to a deflection of 2.1V from the baseline. A second smaller maximum occurs at 12 μ sec. At 52 μ sec, the deflection is 0.57% of the first maximum. At 72 μ sec, the deflection is 0.095% of the first maximum, and at 92 μ sec the deflection is approximately 0% of the first maximum.

This flash profile indicates that the flash lamp intensity at 32 μ sec is less than 1% of the first maximum, with even further reduction in the flash intensity occurring with an increase in time. Therefore, the utilization of the portion of the data from the transient triplet absorption spectrum starting with 32 μ sec is reasonable, since T1 state generation is negligible during this time interval. Thus, the decay of the T1 state can be determined with minimal error due to simultaneous T1 state formation.

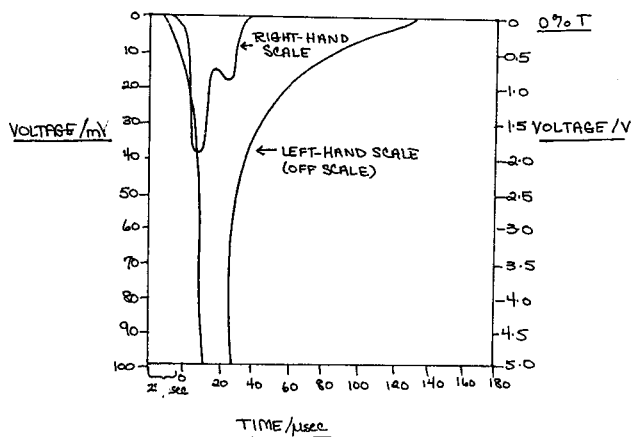


Figure 7: Flash profile taken at 290nm.

The flash profile taken at 482nm is shown in figure 8. This profile is a characteristic of the scattered flash pulse at the wavelength the Tl absorption is being measured. It is taken of a sample consisting of heptane alone. The analyzing light is on and the voltage on the photomultiplier tube is set at 565V to obtain a 50mV full scale deflection as a 100%T baseline.

The maximum at 2 μ sec corresponds to 450%T. The flash intensity then rapidly decreases until at about 32 μ sec the intensity is 106%. Therefore, from the standpoint of scattered light and excitation, it is reasonable to utilize data starting with 32 μ sec, in order to provide an accurate description of the decay of the Tl state.

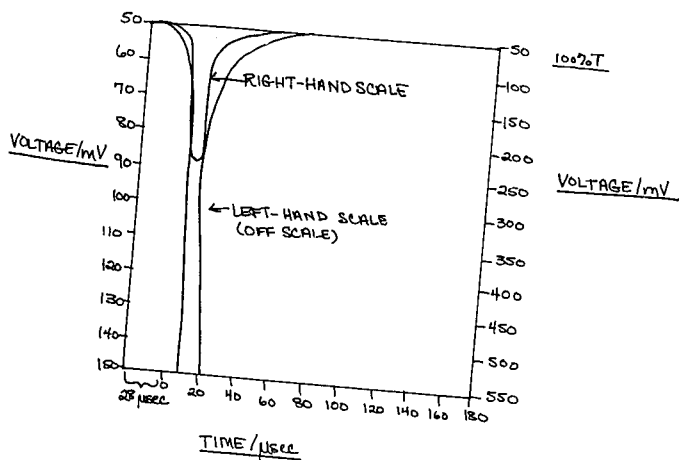


Figure 8: Flash profile taken at 482nm.

Improvements in Experimental Design

A major obstacle encountered during the course of our work is the problem of scattered light from the flash lamps. Presumably, the filter solution contained in the jacketed cell should eliminate any stray 482nm light from the flash lamps by absorbing it. However, this is not the case, and a great deal of time was spent in an attempt to eliminate the scattered light problem.

The first step in rectifying the scattered light problem involves the determination of the pathway of the scattered light to the photomultiplier tube. Initially, it was assumed that the light was coming through the sides of the copper mesh Faraday cage or through the filter solution. Therefore, the Faraday cage was covered with black cloth and the concentration of the filter solution was approximately doubled. This eliminated some of the scattered light, but not all of it. Next, it was assumed that the path from the sample tube needed to be further collimated; copper tubing was then placed at the ends of the sample cell. Again, this eliminated some, but not all of the scattered light.

Finally, it was determined that light was coming in

from the edges of the sample cell. To eliminate the light coming in from this pathway, the edges of the sample tube were taped with black tape and removable copper collars were placed on the ends as well. This procedure eliminated a great deal, but by no means all of the scattered light in the system. A diagram illustrating these experimental improvements can be seen in figure 9.

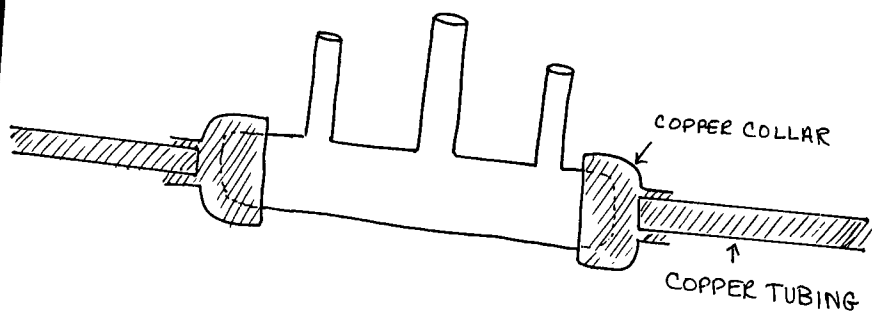


Figure 9: Improvements in the experimental design.

The Vacuum Line

The vacuum line is designed for the purpose of degassing the phenanthrene solution prior to flashing. The vacuum line consists of a mechanical pump, an oil diffusion pump, a mercury manometer (measures pressures > 1 torr), a Double McLeod Gauge (measures pressures from 1 torr to 5×10^{-6} torr), and various stopcocks where equipment can be attached. A T-assembly containing the phenanthrene in heptane solution is attached to the line for degassing. A diagram of the vacuum line and the T-assembly is given in figure 10.

With the use of both the mechanical pump and the oil diffusion pump, the vacuum line should attain a pressure of 10^{-5} to 10^{-6} torr. We are installing a Double McLeod Gauge to check on the actual vacuum achieved. The phenanthrene solution is degassed by a process of about four freeze/thaw cycles. These cycles consist of first allowing the dissolved oxygen to equilibrate with the O_2 partial pressure in the vacuum line and then freezing the solution with a liquid nitrogen dewar so that the air above the frozen solution can be pumped out. With each successive cycle, the amount of oxygen in the phenanthrene solution decreases.

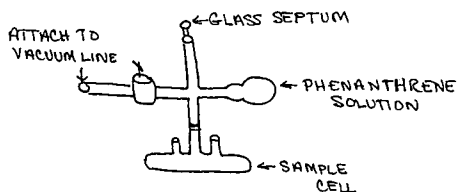
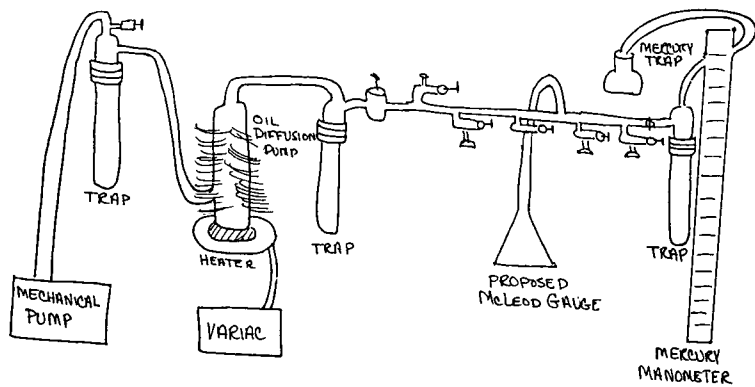


Figure 10: The vacuum line and I-assembly.

Results

A 2×10^{-3} M solution of phenanthrene in heptane was degassed by four freeze/thaw cycles and then flashed. A triplet-triplet absorption spectrum ($T_1 \rightarrow T_n$) was obtained, corresponding to the $\%T$ of the phenanthrene solution versus time. As the T_1 state decays, the $\%T$ of the sample will increase since there is less T_1 population available to attenuate the analyzing beam. Thus, the transient absorption spectrum is a measure of the T_1 decay versus time.

Presumably, the rate of decay that is being measured in our system occurs by a unimolecular process:

$$-d[T_1]/dt = k_1[T_1]$$

When this rate law equation is integrated, the equation below results:

$$\ln[T_1] = -k_1[T_1] + C$$

The T_1 concentration can be described in terms of absorbance, which is obtained by converting the $\%T$ from the transient absorption spectrum to absorbance. Once this has been done, the slope of the $\ln A$ versus time will yield the negative of the rate constant k_1 . This plot is shown in figure 11.

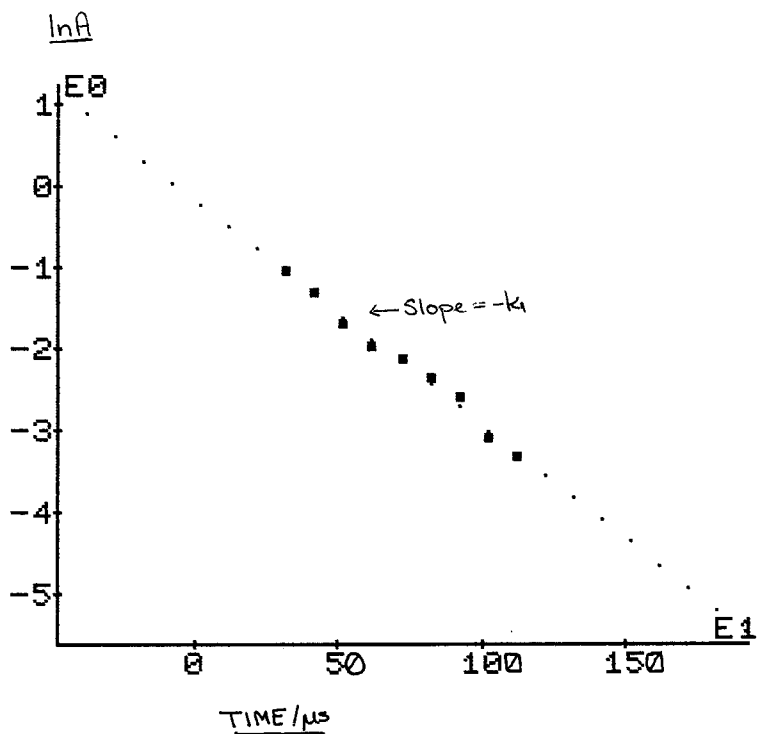


Figure 11: Plot of $\ln A$ versus time.

By least squares analysis, the value of k_1 was determined as $2.43 \times 10^4 \text{ sec}^{-1}$. This value is approximately a factor of two greater than the literature value determined by Parker and Hatchard ($1.07 \times 10^4 \text{ sec}^{-1}$).

Discussion

The fact that the experimental value of k_1 is approximately twice as large as the literature value suggests that the phenanthrene solution was not as thoroughly degassed as in the experiments described in the literature. It is conceivable that leaks in the vacuum line as well as poor gas flow out of the vacuum line have lead to the incomplete degassing of the phenanthrene solution.

As discussed in the experimental section, several improvements in the design of the flash apparatus have been made in order to improve its performance. It appears that design changes in the vacuum line are also needed. One such improvement might be an increase in the bore holes in the stopcock openings. Presently, the bore holes are 2mm in diameter. An increase in these openings would facilitate the removal of oxygen from the phenanthrene solution by allowing the equilibrated oxygen above the solution to be pumped out at a greater efficiency. Also, the vacuum line should again be thoroughly checked for leaks and its pressure measured to 10^{-6} torr with the newly installed Double McLeod Gauge.

The future direction of this project might involve the determination of the oxygen quenching rate constant for the decay of the phenanthrene T1 state. This determination requires that the phenanthrene solution be thoroughly degassed and that a system for adding known quantities of oxygen to the phenanthrene solution be devised. Before embarking on this new level of experimentation, it is quite important that the experimental improvements outlined above be worked out and implemented.

Overall, this project illustrates the power of flash photolysis as a tool for studying the kinetics of very fast reaction systems.

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