FLASH PHOTOLYSIS :
THE TECHNIQUE AND ITS APPLICATION

by

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ABSTRACT

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The application of flash photolysis in photochemistry offers an effective means to directly investigate reactive intermediates. This powerful technique rapidly converts a high percentage of molecules in their ground electronic state to upper excited states. This enables the disappearance of the excited species to be observed and kinetic information concerning the rate law and rate constants to be measured.

The purpose of our work is to investigate the kinetics of the rate of decay of triplet anthracene in dilute solutions and to obtain rate constants for this reaction. The reduced expression for the decay of triplet anthracene is written: $-\frac{d[T]}{dt} = k_1[T] + k_{O_2}[O_2][T]$. The radiationless decay constant, k_1, is obtained by thoroughly degassing solutions of 5.5×10^{-4} M anthracene in heptane using a vacuum line. These solutions are flashed and the resulting trace of the decay of triplet anthracene, monitored at 424 nm, is measured from an oscilloscope. Values of %T are converted to absorbance and plots for ln A_t vs time are constructed. Results show that these plots are linear; thus, the reaction follows first-order kinetics. The lowest value of k_1 obtained is 4490 sec^{-1} which is an order of magnitude greater than the literature value,

630 sec^{-1}. This indicates that quenching by residual oxygen is occurring and is incorporated in k_1 giving $k_{obs.} = k_1 + k_{o_2}[O_2]$.

The quenching rate constant is obtained by adding known aliquots of oxygen to degassed solutions and plotting values of $k_{obs.}$ vs. $[O_2]$. The slope of these plots is k_{o_2}.

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I. Introduction

The application of flash photolysis in photochemistry offers an effective means to directly investigate reactive intermediates produced by electronic excitation. There are two distinguishable features associated with this technique which gives flash photolysis more advantages over steady photolysis techniques. The first is that it generates a high concentration of reactive intermediates. This is important because it enables the absorption spectrum of the intermediate to be recorded. Prior to flash photolysis, no free radical or intermediate could be detected by its absorption spectrum because its concentration was too low. Using the new method, one could identify the short-lived intermediates formed in the primary photochemical process through their characteristic absorbance in the ultraviolet or visible region of the spectrum. This helped to determine the mechanism by which their photochemical reaction occurred.

The second distinguishable feature associated with flash photolysis is that it rapidly converts a high percentage of molecules in their ground electronic state to upper excited states. This enables the disappearance of the species in the excited state to be observed and kinetic information concerning the rate law and rate constants to be measured. Methods using steady photolysis create an equilibrium between molecules in the ground electronic state and upper excited states according to the Boltzman distribution. Quantitative analyses using the flash photolysis technique

in kinetic spectrophotometric experiments have been applied to determining extinction coefficients [1,3,4,5] and quantum yields [23] for the reactive intermediates produced. These and other similar experiments conducted attest to the strength and versatility of the flash photolysis technique.

The purpose of our work is to investigate the rate and mechanism of the decay of electronically excited anthracene in dilute solutions and to obtain rate constants for this reaction. Anthracene is one of the many aromatic hydrocarbons which photoluminesce. This indicates that the primary transient species produced upon electronic excitation is an energetically metastable triplet state, T_1, whose energy lies between the singlet ground state, S_0, and the first excited state, S_1, of the molecule. (See fig.1)

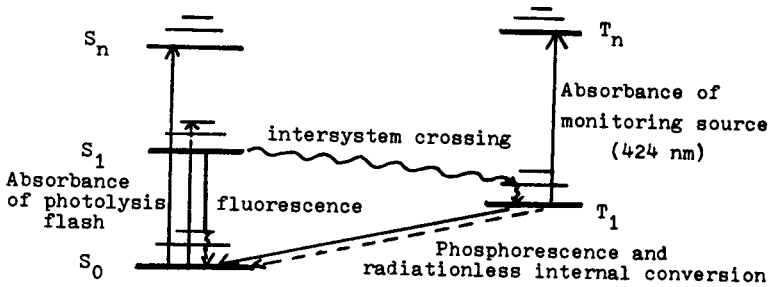


Figure 1.
Modified Jablonski Diagram for transitions involved in the flash photolysis study of the triplet state of anthracene.

The triplet state is formed as a result of intersystem crossing from the first excited singlet state, $S_1 \rightsquigarrow T_1$. Intersystem crossing is a process in which the spin of an excited electron is reversed and the change in spin multiplicity results. A molecule in the excited triplet state is then deactivated either by phosphorescence or internal conversion, $T_1 \rightsquigarrow S_0$. The preferred path to the ground state is that which minimizes the lifetime of the excited state. For anthracene in dilute solution, phosphorescence is not observed. This indicates that a molecule formed in the triplet state is deactivated by spontaneous unimolecular decay with great efficiency before it can radiate.[1] Through our study of electronically excited anthracene, we hope to account for the factors which determine the lifetimes of triplet states in fluid media.

Also of significant importance is the competing deactivation process involving the interaction and energy transfer between a triplet molecule and another species. Molecular oxygen is one such efficient quencher which is significant even at concentrations on the order of 10^{-6} Molar. Thus, it is also our goal to quantitatively investigate the effect of oxygen on the decay of triplet anthracene and measure rate constants corresponding to unquenched (deoxygenated) and quenched reactions.

II. A Theoretical Approach to the Study of the Triplet State in Fluid Solvents

A. Historical Prelude:

The technique of flash photolysis was developed in 1949 by Sir George Porter and R. Norrish.[2] Immediately after its development, the technique was applied to experiments to study the triplet state of various aromatic molecules. The triplet state was postulated as being the principle intermediate in chemical reactions according to previous phosphorescence and fluorescence studies in the 1940's on polynuclear aromatic compounds in rigid media at very low temperatures. Phosphorescence and fluorescence are radiative processes occuring by different mechanisms. (See I.Fig.1.) They can be distinguished experimentally by observing the lifetime of the excited state. Fluorescence is usually characterized by an emission lifetime of less than 10^{-6} seconds while phosphorescence usually occurs over a longer period, sometimes up to several seconds.

A great deal of experimental work has been done during the last thirty years which is directed toward understanding the nature of these radiative processes. For example, only at low temperatures and in rigid media could phosphorescence, attributed to the triplet state, be observed. When illuminated, aromatic molecules dissolved in fluid solvents did not phosphoresce. These molecules were only observed to fluoresce and had a lifetime on the

order of 10^{-8} seconds. This suggests that aromatic molecules are deactivated with great efficiency via non-radiative pathways. Thus, the lifetime of the triplet is much less than the lifetime of the radiative process, but no direct measurements of this lifetime had been made until the 1950's. One might expect that the lifetime of the triplet should be longer than the radiative lifetime of the singlet state (10^{-8} seconds). This is now known because the $S_1 \rightarrow S_0$ transition conserves spin angular momentum whereby the $T_1 \rightarrow S_0$ transition is forbidden by the electronic selection rule which prohibits intercombination between states of different spin multiplicities. Since the flash photolysis technique allows one to follow the course of the reaction occuring on the order of a few microseconds, it was feasible for Porter and his colleagues to study triplet lifetimes which were on the order of a few milliseconds.

Since 1950, a good deal of work has been done on the study of anthracene triplet decay in the gaseous and solution states. Photochemical reactions in solution are of particular interest because the lifetime of the triplet state is much greater than that in the gas phase. Therefore by establishing the rate law for the decay of the triplet state and investigating factors which contribute to this decay, one can postulate mechanisms for the processes involved in the photochemical reactions of anthracene in fluid solvents. This theoretical review

of some of the important areas of research on the decay of triplet anthracene over the past thirty years will address the effect of oxygen and other quenching species, solvent viscosity, and temperature in an effort to determine the nature of the radiationless conversion process to the ground state.

B. Kinetics of the Decay of the Triplet State

The rate law for the decay of the triplet state can be written: [12]

$$\frac{-d[T]}{dt} = k_0[T] + k_1[T] + k_2[T]^2 + k_3[T][G] + \sum_Q K_Q[T][Q] \quad \text{eqn.1.}$$

where k_0 = radiative decay constant for $T_1 \rightarrow S_0$

k_1 = radiationless decay constant for $T_1 \rightarrow S_0$

k_2 = bimolecular rate constant for triplet-triplet annihilation

k_3 = quenching rate constant of a triplet molecule by a molecule in the ground state, G.

K_Q = quenching rate constant of the triplet by all other species, Q.

When the decay of the triplet state of anthracene in fluid solvents was first investigated in the 1950's, it was found to follow first-order kinetics.[1,4] The second-order process, $k_2[T]^2$, representing the bimolecular encounter of two triplet molecules, was dropped from the

rate expression because its contribution was considered negligible.

First-order plots of $\log_{10}\epsilon cl$ (proportional to the triplet concentration) versus time for degassed 10^{-5} M anthracene in hexane were linear "within the accuracy of the experiment". The term $k_3[T][G]$ was also dropped because it was shown that the half-life of the triplet state is independent of the concentration range 2×10^{-6} to 5×10^{-3} M. [1,5] The term $k_0[T]$ representing the radiative process was also considered as contributing insignificantly to the rate of decay because $k_0[T] \ll k_1[T]$ in fluid media. Therefore, the new rate expression became:

$$-\frac{d[T]}{dt} = k_1[T] + k_q[T][Q] \qquad \text{eqn.2.}$$

The first term in the rate law represents the non-radiative unimolecular decay and the second term represents quenching by adventitious or added quenchers.

Standard experimental procedure at this point required that solvents be further purified and solutions of anthracene be degassed prior to photolysis runs. Investigations were concerned with oxygen as the principle quenching species, especially since it had a marked effect at extremely low concentration (10^{-7} M). Kinetic data was analyzed with the following rate expression:

$$-\frac{d[T]}{dt} = k_1[T] + k_{o_2}[O_2][T] \qquad \text{eqn.3.}$$

Early in the 1960's, the validity of the earlier published values of the first-order radiationless decay constant, k_1 , was challenged. The experiments conducted in the previous decade relied upon inadequate experimental methods for removing dissolved oxygen, reflected in values of k_1 which were two orders of magnitude greater than more recently published values.[5,6,7,8,12] This meant that k_1 was never directly determined; rather, through rearrangement of equation 3, incorporated with k_1 was a pseudo-first-order process giving $k_{obs} = (k_1 + k_{o_2}[O_2])$ where the quenching by residual oxygen dominated the observed first-order decay.

Studies in the 1960's also determined that the second-order process of $k_2[T]^2$ which had been previously neglected did contribute significantly to the rate expression.[5,6,7,8,11] Specifically, this bimolecular term is predominant at high concentrations of triplet and high exciting light intensities. The rate of decay therefore conforms to:

$$-\frac{d[T]}{dt} = k_1[T] + k_2[T]^2 + k_q[Q] \qquad \text{eqn.4.}$$

In conclusion, the summary of knowledge concerning the decay of the triplet state of anthracene in solution to date is expressed by the rate law in equation 4. The first term represents the radiationless decay constant, k_1 , because measurements in anthracene show $k_0 < 0.25$ seconds^{-1} and $k_0 + k_1 \leq 110$ sec^{-1} which indicates that k_0 is negligible.[12]

The second term, $k_2[T]^2$, is a bimolecular interaction between two triplet molecules. Quantitatively its contribution to the rate law can be determined by looking at its dependence on solvent visosity.[16] The third term to consider is that of quenching (predominantly by O_2), to be explored in further depth.

1. Effect of Dissolved Oxygen

The efficiency of oxygen in expediting the rate of decay of triplet anthracene in solution was first measured by Porter and Windsor.[1] They noted that as one increased the concentration of oxygen, the triplet concentration decreased until it was no longer detected. Further studies noted that this depletion was also a function of the number of times a solution was flashed and the interval of time between flashes.[1,4] For example, when a typical solution containing 1.48×10^{-5} M oxygen was flashed ten times repetitively, the rate approached a limiting value independent of the initial concentration of oxygen. This limiting value approached the value for k_1 measured in the absence of oxygen. It was suggested that oxygen was removed through flashing, although more recently it has been attributed to photo-oxidation of the compound or sensitized auto-oxidation of the solvent which scavenges the dissolved oxygen.[18] As for the time lapse between flashes, the rate constant k_1 increases slightly as oxygen further dissolved from the gas phase into solution. The lifetime of the triplet state is

extremely sensitive to the smallest amount of oxygen present (10^{-7} M) which necessitates that solutions which have been exposed to the atmosphere be thoroughly deoxygenated.

Investigations also sought to determine if oxygen is specific in its quenching effect. Solutions were degassed and aliquots of nitrogen gas were added. The resulting effect was less that 1/1000 that of oxygen. However, when a paramagnetic gas was added (NO) it behaved very similary to oxygen, giving a similar k_0 of 4×10^9 1/mole-sec.[4] The mechanism of this quenching process will be discussed in a later section.

2. The Effect of Solvent Viscosity

The rate of decay of triplet anthracene as a function of solvent viscosity has been thorcughly studied to determine how viscosity can affect the rate of the unimolecular radiationless process expressed as k_1 [T] . When investigations were first conducted by Porter and Windsor in the 1950's, they erroneously believed that they were measuring the "true" radiationless decay constant k_1 (i.e. in total lack of O_2) over a range of solvents which varied in viscosity. They had actually observed a rate constant, k', which incorporated k_1 within the pseudo first-order oxygen quenching term, $k' = (k_1 + k_q[O_2])$. This was further supported by results from later experiments giving lower values of k' as techniques for purifying and degassing improved. Porter and Windsor showed that k_1 decreased as solvent vis-

cosity increased as $k_1 \propto \frac{1}{\eta}$.[1,4] This relationship attests to the decay process as being a diffusion controlled reaction between a triplet molecule and another species, but this empirical result is not a simple inverse proportionality such as appears in the Stokes-Einstein equation for bimolecular reactions (also called the Debye equation):[25]

$$k_{diff} \sim \frac{8\ R\ T}{3000\eta}$$

1/mole-sec

η = coefficient of viscosity (newton-sec/m^2)
R = 8.3 J/K-mole

The undesired presence of oxygen and other impurities which were able to quench at rates limited only by their diffusion through the solvent[26] became uniformly accepted as contributing principally to the decay of the triplet molecule.[5,6] Then in 1954, Porter and Wright acknowledged that the second-order process $k_2[T]^2$ contributed significantly to the rate law for the triplet decay. As a result of this second-order contribution the previous first-order rate constants in earlier work were higher.[6] (Values of k_1 are obtained from slopes of first-order plots.) Porter and Wright stated that the occurrence of a second order process immediately suggested a possible explanation for the previously published dependence of k_1 on solvent viscosity and that it was necessary to study the effect of viscosity on first- and second-order rates separately.[6] With the advent of Porter and Wright's work came numerous investigations in the early 1960's led by several research teams. The uni-

molecular decay constant k_1 was determined to be relatively independent of solvent viscosity in the low region (.3-500 centipoise) but increasingly more dependent as solvents increased in viscosity.[7,8] However, this was quickly recognized as being a function of residual impurities, especially since the more viscous solvents were more difficult to degas efficiently. In an attempt to diminish the interfering pseudo first-order process, Linschitz, Steel and Bell arrived at a value of k_1 of about 150 sec^{-1} and showed that the anomalously large viscosity dependence of this rate constant is assigned to the pseudo first-order process rather than to an intrinsic effect. Then, in 1964 Hilper, Porter, and Stief determined that k_1 is only slightly if at all dependent upon viscosity.[14] They conducted flash photolysis investigations over the temperature range 25° to -196° C to connect studies of phosphorescence (radiative decay of triplet anthracene at low temperatures in rigid media) with the present studies of triplet decay in fluid media at room temperatures. Ten years later, in 1974, Watkins conducted a carefully controlled quantitative study of the decay of triplet anthracene, concentrating mainly on the quantum yield as a function of flash intensity.[23] He confirmed that k_1 is independent of solvent composition and small deviations are most likely due to adventitious quenchers.

Investigations were also concerned with the dependence of diffusion-controlled bimolecular reactions on solvent viscosity. This has particular relevance to the decay of

triplet anthracene since the process of radiative decay (phosphorescence) is observed in rigid media which eliminates collisional deactivation and not in fluid solvents. The two bimolecular reactions investigated are triplet-triplet annihilation and quenching by oxygen. One would expect that the second-order rate constant, k_2, and quenching rate constant k_q be inversely proportional to η (the coefficient of viscosity) as predicted by equation 5. Recent studies show that plots of k_2 vs. $1/\eta$ depart slightly from linearity at regions of high viscosity. It has therefore been suggested that the Stokes-Einstein equation is invalid in relating diffusion coefficient and viscosity.[23] Livingston also states that this equation "seriously underestimates" the diffusionally- limited rates of reactions quenched by oxygen, especially in regions of high viscosity.[18]

3. The Effect of Temperature

The effect of temperature was also investigated as a rate-determing variable on the decay of the triplet state. Early studies by Livingston and Tanner found that the half-life of the triplet state decreased as temperature increased.[5] However, their measured values of k_1 incorporated the term $k_q[O_2]$ due to the presence of adventitious oxygen, so that they had established a dependence of $k_{obs.} = (k_1 + k_q [O_2])$ on temperature. Porter, Hilpern and Stief measured values for the rate constants as a function of temperature and constructed Arrhenius plots of log k_1 vs. $1/T$ (K). They stated

that their plots would be linear if the first-order decay of the triplet state is diffusionally controlled or controlled by the rate of activation.[14] Their data showed that k_1 was independent of temperature. Later studies by Jackson and Livingston were conducted over the temperature range 30° to -70° C. They plotted their experimental values of k_1 vs. k_2 and extrapolated to obtain a y-intercept. This indirect method was devised as a means to obtain the true value of k_1 without the presence of oxygen. Their results showed that k_1 has a unique temperature independent value for a given hydrocarbon and solvent. For example, anthracene in hexane has a $k_1 = 160\ sec^{-1}$ with a 30% uncertainty. Linschitz et al [11] obtained values for anthracene in hexane by extrapolation of their measured k_1's and obtained a value on the order of 150 sec^{-1}.

C. Mechanism for the Decay of the Triplet State

In view of the rate expression for the decay of triplet anthracene in pure solutions:

$$-\frac{d[T]}{dt} = k_1[T] + k_2[T]^2 + k_q[O_2][T]$$

a mechanistic approach is one that is concerned with the photophysical processes of how, on the molecular level, deactivation of the excited moleucle occurs. Empirical studies discussed in the literature have addressed the following important features with various qualitative statements and speculations:

1) Intramolecular energy transfer

   i. intersystem crossing and internal conversion associated with the radiationless process $k_1[T]$

   ii. role of the solvent in these above processes

2) Intermolecular energy transfer

   i. triplet-triplet annihilation

   ii. paramagnetic quenching

Intramolecular energy transfer pertains to the exchange of electronic energy spontaneously between states of different multiplicities in an excited molecule. Intersystem crossing $S_1 \rightsquigarrow T_1$ occurs when the potential energy surfaces of these two electronic states intersect.[27] A molecule may cross from one state to another, without radiating, when the nuclear configurations, potential, and kinetic energies of these two states are equivalent. To arrive at this point requires that a molecule, which has initially been excited to an upper vibrational level of S_n, cascade downward until it reaches a vibrational level located at the point of crossing of the potential energy curves for the two states. This is accomplished when a molecule thermally transfers its excess vibrational energy to the surroundings.

Similarly, internal conversion, $T_1 \rightsquigarrow S_o$, appears to occur efficiently when two electronic energy levels are close enough for good overlap in their vibrational levels [28]. Internal conversion describes the process $T_1 \rightsquigarrow S_o$ which is a genuine unimolecular decay process that can occur spon-

taneously in an isolated molecule (29).

Porter and Windsor's [1,6] early flash photolysis work was primarily concerned with the factors which affect the rates of the processes $S_1 \rightsquigarrow T_1$ called c_1 and $T_1 \rightsquigarrow S_o$ called c_2. They determined that the efficiency of c_1 was not affected by the nature of the solvent. They had considerably more difficulty determing the rate of the process c_2 because of the presence of residual oxygen. They postulated, however, that the role of the solvent was to inhibit the crossing of the potential energy surfaces between these two states by restricting the nuclear motion and reducing the probability that the molecule would assume the necessary configuration. Linschitz, Steel, and Bell[11] continued to study other possible factors which might cause the large difference in viscosity dependence between c_1 and c_2. They showed that this dependence was an artifact because of oxygen quenching interfering with the rate of $T_1 \rightsquigarrow S_o$. They suggested that the $T_1 \rightsquigarrow S_o$ transition was intrinsically slower becuase of the Franck-Condon principle. principle states that electronic transitions occur with little immediate change in molecular geometry or kinetic energy. That is to say, relaxation of the molecular geometry is slow relative to transition times. Thus, a line depicting a transition on a potential energy diagram must be drawn vertically; 30

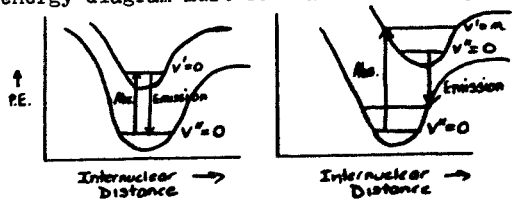


Figure 2. Franck-Condon Principle

Thus, viscosity was believed to make it difficult for a molecule to distort properly to assume the necessary geometric configuration for a large Franck-Condon overlap. However, the unimolecular decay constant, k_1, has been shown to be independent of solvent viscosity in the complete absence of oxygen. The mechanism of internal conversion, $T_1 \rightsquigarrow S_o$, is still not well understood and the role of the solvent is not yet completely defined.

Intermolecular energy transfer processes require that another molecule be present to accept the electronic energy from the excited species. The bimolecular encounter of two triplet molecules is one such example. Their combined energy is sufficient to excite one of them into the fluorescent state, S_1, which then decays to the ground state, S_o, emitting a photon of light. This emission process is called "delayed fluorescence" and the mechanism for this process is written:[13, 14]

$$T_1 + T_1 \rightarrow S_o + S_1$$
$$S_1 \rightarrow S_o + h\nu$$

Delayed fluorescence has the same spectrum as normal fluorescence, but its lifetime is much slower and on the order of the rate of triplet decay. Studies of this phenomena have been conducted by means of the flash photolytic technique. It has been determined that the intensity of delayed fluorescence is proportional to the square of the standing triplet concentration. At low flash intensities, on the order of 50 Joules, triplet molecules decay principally by first-

order kinetics and delayed fluorescence is not observed.

Another intermolecular energy transfer process is that of quenching by molecular oxygen. Oxygen is a paramagnetic molecule (i.e. triplet ground state) which is believed to temporarily associate with the triplet anthracene molecule and remove the spin restriction so that the process $T_1 \rightarrow S_o$ is expedited.[10] Investigations led by Porter in 1972 postulated that intermolecular enhancement of a spin forbidden excited state decay by paramagnetic species is thought to be due to electronic interaction with T_1 and the quenching species within a collision complex.[21] This complex, $(^3M\ ^3O_2)$ will give back anthracene in its ground state and molecular oxygen.

III. Experimental

A. Flash Photolysis Apparatus

The essential componants of a flash photolysis apparatus can be classified into three categories:

1. a high-intensity photolysis of short duration
2. a sample cell
3. a monitoring device suitable for proper detection and recording

Our apparatus is specific for kinetic spectrophotometry because it is designed to monitor the disappearance of the excited species at one wavelength over a period of time. The photoelectric devices which offer the necessary degree of resolution associated with this process include a monochrometer, a photomultiplier tube, and an oscilloscope. The analogue to kinetic spectrophotometry is flash spectroscopy which records the absorption spectrum of the excited species over a range of wavelengths at one time.

The design for our apparatus is shown by the block diagram in figure 3.

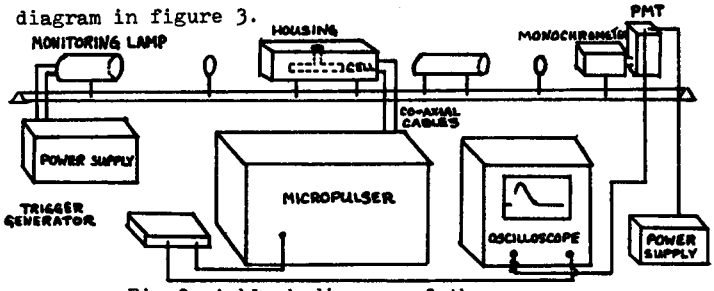


Fig.3. A block diagram of the flash photolysis apparatus

The micropulser is a high voltage source which powers two flashtubes. Attached to the micropulser is a dual-output trigger generator. This generator triggers the micropulser which dissipates its stored energy to the flashtubes creating a photolysis flash. The intense flash irradiates the solution in the cell generating electronically excited species. The cell is positioned between the flashtubes along an optical bench so that the incident light from the photolysis flash is perpendicular to the analyzing light generating by a monitoring lamp. Two lenses and a collimator are also positioned along the optical bench to focus and collimate the analyzing light through the sample cell and onto the slit of the monochrometer. These componants aid in increasing the signal to noise ration of the detection system. The monochromatic light hits the photocathode of the photomultiplier tube which in turn generates a signal proportional to the intensity of this incident light. The signal leaves the anode and is fed into an oscilloscope which writes and stores the trace on its screen. The specific characteristics and function of each of these principal components in the flash photolysis apparatus will be discussed further.

Dual-Output Trigger Generator

The dual-output trigger generator was manufactured by PRA (Photochemical Research Associates, Inc.). This component is useful in flash photolysis because it produces two essential output signals. The first, or Pretrigger,

creates a signal which triggers the oscilloscope to form a horizontal baseline on the oscilloscope screen of variable and predetermined duration. This initial trace acts as the origin from which the progress of the ensuing reaction can be measured. The second, or Trigger, originates from, but is delayed with respect to, the Pretrigger. The Trigger can be set in the continuous mode at a desired rate to perform repetitive flashes.

Micropulser

The Micropulser (Xenon, Model 457) is a simple high-voltage power supply and energy storage and discharge circuit designed to power flashtubes. The Micropulser and flashtubes together, when reduced to simple circuitry terms, constitute an LCR circuit:

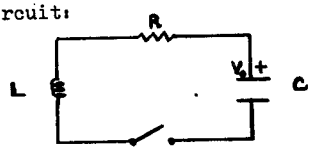


Fig. 4. An equivalent flash lamp discharge circuit (31.)

whereby the capacitor and the flashtubes contribute to the circuit inductance, L, and the flashtubes to the circuit resistance, R, and the capacitance, C, is a constant 2.0 μF.

It is desirable to have a high-powered flash (i.e. high energy output per flash) with minimal duration. The duration of the flash for a half-period is proportional to $\sqrt{LC}$ and the expression for the average power dissipation or peak

power as proportional to the ratio of the capacitor volrage, V_0 , to the circuit impedance:[32]

$$V_0^2 / \sqrt{LC}$$

Therefore, V_0 should be large relative to the circuit impedance. The energy stored in a capacitor is calculated by:

$$E = \tfrac{1}{2} C (V_0)^2$$

For our system, the maximum suggested operating voltage is 10,000 volts. Thus, the energy stored in the capacitor is 100 Joules. Because the capacitance is constant, the power dissipated to the flashtubes increases and flash duration decreases as the circuit inductance is reduced. The Xenon Micropulser conforms to these theoretical relationships in that it has a low inductance associated with its storage capacitor. The unit is designed to supply a maximum average power of 300 watts to the flashtube load which restricts the number of repetitive flashes using the auto-trigger (or continuous mode on the dual-output trigger generator) to a maximum of three pulses per second.

An important componant of the Micropulser is the thyratron tube. It ensures that the flashtubes fire reproducibly when manually triggered and not while the capacitor is charging. It accomplishes this by becoming a low resistance circuit when V_0 reaches a certain critical value.[33] When the capacitor is discharged to the flashtubes, the current is channeled through co-axial cables. Although these cables are well shielded, it is often required that the oscilloscope also be shielded to prevent it from picking up interfering magnetic perturbrations.[34]

Flashtubes

The Xenon flashtubes are constructed so that their performance and lifetime are maximized enabling them to produce a high energy output in the shortest time possible. First, they are made of quartz which permits ultraviolet radiation as well as visible light to be emitted. A graph of their spectral distribution shows that their peak emission occurs between 200-500 nm and then tails out above 500 nm. If one were to use pyrex, the cell walls would filter out energy in the ultraviolet region.

Second, these flashtubes are filled with xenon gas. The greater the gas pressure, the more the spectral output distribution is pushed toward the ultraviolet range. Pressure also gives the flashtubes a specific resistance. It is essential that the resistance, R , be great enough to give a critically damped circuit expressed as : (35)

$$R = 2\sqrt{L/C}$$

and introducing k as the damping coefficient,

$$R = 2k\sqrt{L/C}$$

When k is less than one, corresponding to low resistance, the circuit is underdamped and will oscillate resulting in extended "ringing". This interferes with the flash duration and resolution of kinetic measurements. For k greater than one, the circuit is overdamped causing the circuit profile to have a long tail.

The Xenon flashtubes are constructed to specific dimensions and placed in series to give them a value of

R corresponding to a critically damped circuit. This is demonstrated by the following relationship:

$$\text{lamp } R \propto l/D$$

l = discharge path length
D = diameter of lamp

Certain parameters require that D be small. Therefore, proper resistance is achieved with the two flashtubes in series. (A parallel arrangement will reduce the circuit R below the critically damped value.) Short co-axial cables also aid in minimizing the value of l.

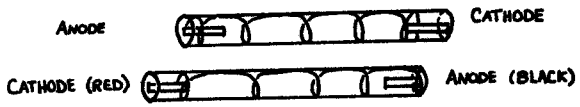


Fig.5. Xenon flashtubes with trigger wire

Our experimental work has shown a typical flash duration to be on the order of 40 microseconds. (See Fig.6.) This duration is sufficiently short to give versatility in studying reactions with short lifetimes ie. complete in 60 microseconds or greater.

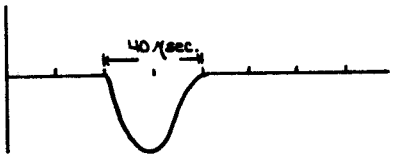


Fig.6. Flash with analyzing light on.

Although not all energy dissipated from the capacitor is transformed into light, it is still worthwhile to note that the instantaneous power per flash equals 100 Joules per 40 microseconds or 2.5 million watts!

Analyzing Light

The analyzing light is an Osram Model 150 W/S Xenon arc-lamp enclosed in a PRA Model ALH-215 housing. It is connected to a PRA M303X power supply which is a constant current device. The power supply stablizes the intensity of the light generated by the arc-lamp. This is essential because the analyzing light is used to monitor changes in intensity of the absorbing transient over a period of time. The power supply is listed as having low ripple; fluctuations of this nature in any lamp should not exceed 0.1%. However, fluctuations in intensity can also occur from hot air currents generated by the hot lamp envelope. The lamp anode is water cooled to reduce the heat, but experimentally it has been determined that the water flowing through the lamp causes it to vibrate.[18] This effect results in large variations in intensity reaching the photomultiplier tube which can be alleviated by firmly clamping the lamp.

When conducting spectrophotometric investigations, it is always necessary to maximize the signal to noise ratio. This ratio is proportional to $\sqrt{I}$, where I is the intensity of the monitoring beam. Therefore, it is desirable to use as intense a monitoring lamp as possible and a monochrometer

of high efficiency. Low light intensities result in very broad or noisy oscilloscope traces. Our horizontally mounted lamp has an elliptical reflector positioned behind it to focus the emitting light. At the focal point of the lamp, a dark spot, due to the shadow cast by the xenon lamp, is present. Care must be taken in aligning the lamp that this dark spot not fall on the sample cell. Maximum light intensity at the sample cell is achieved by directing the focal point of the arc-lamp slightly to one side of the cell.

Sample Cell

The sample cell is ten centimeters long and is cylindrical with plane, parallel ends. The cell is made of quartz which, unlike pyrex, permits light in the far ultra-violet region to pass through. This offers versatility in choosing to follow molecular species which absorb either in the ultra-violet or visible region.

The flash light which is scattered by the solution and sample cell is called "scattered light" and interferes with the signal hitting the photomultiplier tube. Restricting the flash light to certain wavelengths using filters is an effective means to eliminate problems associated with scattered light. For example, cellophane sheets are inexpensive filters which are commercially available and can be wrapped around the sample cell. The disadvantage to

using these is that they must be replaced after a few flashes because they are photolabile.[18]

We have purchased solid rectangular filters to reduce the effect of scattered light in our detection system. These filters transmit in the region where anthracene in its ground electronic singlet state absorbs to upper excited singlet states ($\lambda_{max.}$ = 380 nm). These filters also cut off light of wavelengths greater than 400 nm where we are monitoring anthracene's triplet-triplet absorption ($\lambda_{max.}$ = 424 nm).

The effects of scattered light have also been minimized by two other means. First, the cell housing has built-in cylindrical covers which shield the cell windows from the photolysis flash and block the light scattered by the cell window walls. Second, the path length between the cell and the photomultiplier tube has been maximized to reduce the ratio of stray to collimated light.

The sample cell is part of a larger apparatus designed by C.W.J. Scaife and D. Sprague. This sample cell apparatus was constructed so that it can be attached to a vacuum line, also designed and constructed by this research group, is used to degas solutions. After the sample cell apparatus has been degassed, it has a very small internal pressure. The energy from the photolysis flash and monitoring light causes the solution to be heated and boil. The subsequent bubbles interfere with the signal reaching the photomultiplier tube. By introducing inert nitrogen gas to the

sample cell via the vacuum line, the boiling effect can be eliminated.

Temperature control is also desirable when performing kinetic spectrophotometry. A jacketed water-cooled sample cell can maintain a solution at a desired temperature by circulating water through it. One need not be concerned with an instantaneous change in solution temperature with each flash because the absorbing molecules rapidly transfer the energy from the flash to the solvent which acts as a heat sink, thus maintaining isothermal conditions.

Monochrometer

The monochrometer (Instruments SA Model 1200) receives a collimated beam from the analyzing light at the entrance slit and renders this light monochromatic. This light leaves the exit slit and enters the attached photomultiplier tube. The light striking the photocathode can be controlled by adjusting the slit widths of the monochrometer. These slits are metal plates which can be mechanically replaced. In general, the signal generated by the photomultiplier tube is less noisy for larger monochrometer slit widths. However, if the entrance slit width is too great, the light leaving the exit slit is only roughly monochromatic. This could potentially cause deviations from Beer's Law; however, there is no problem if the monitoring wavelength chosen lies on the peak of a fairly broad curve of a substance's

spectrum. Care must also be taken when choosing the wavelength for the experiment so that fluorescence emissions do not occur at the monitoring wavelength.

Photomultiplier Tube

The photomultiplier tube is by far the best photodetector and amplifier for fast transient applications. It has a high gain ie. 10^3 to 10^9, a short response to rapidly changing intensities, and is capable of producing an electrical signal proportional to the intensity of light striking it. It is important that a suitable photomultiplier tube be chosen whose characteristics are compatible with the requirements of the application, or poor performance may result. For example, the PMT used in our present experimental work is a Hammamatsu IP28. It has a quartz window which transmits 90% of the incident light to the photocathode down to 200 nm. The correct choice of the photocathode type was made by studying spectral response curves which show quantum efficiency (%) versus wavelength where quantum efficiency is related to absolute sensitivity by:

$$Q.E.\% = \frac{124}{nm} \times \frac{mA}{W}$$

In addition to the photocathode, there are two other essential componants of the PMT: the dynode chain and the anode. The dynode chain is comprised of ten dynodes which accelerate electrons forming a photocurrent, I_c . The

voltage drop between each dynode is equivalent although increasingly more positive than the dynode before it. This is accomplished by introducing a negative voltage source, $-V_0$, from a power supply at the beginning of the chain and grounding the other end. When a photon of light hits the photocathode, an electron is emitted and travels to the first dynode since it is of more positive potential than the cathode. Upon striking it, the electron causes the emission of several additional electrons. These electrons are accelerated toward the second dynode and the process continues for all ten dynodes giving a gain at the last stage which varies depending on the dynode voltage. These electrons are collected at the anode forming an anodic current, I_a . (See fig.7)

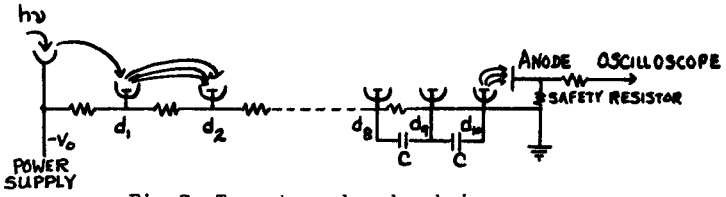


Fig.7. Ten stage dynode chain

The stability and lifetime of a PMT is reduced if continuous high output currents are drawn from it. The suggested maximum mean anodic current is 1 milliamp. We are drawing 50 microamps. Linearity of a PMT response is essential for a good detection system. Non-linearity arises

if the induced dynode currents are on the same order of magnitude as the dynode chain current.[36] It is therefore necessary that the dynode chain current be at least ten times the continuous anode current. Our original dynode chain had ten 1 megaohm resistors and was operated at 500 volts. According to:

$$V = IR$$

$$R = (10 \text{ dynodes})(10^6 \Omega/\text{ dynode}) = 1 \times 10^7 \Omega$$

$$V = 500 \text{ volts}$$

$$I_d = \frac{V}{R} = 50 \text{ microamps}$$

This meant that 50 microamps were being drawn as the anodic current and 50 microamps were being produced by the power supply operating the dynode chain. Dr. Robert L. Strong at RPI pointed out that no gain could be achieved under these conditions. To establish linearity, I_d was chosen so that $\bar{I}_a < 10\ I_d$ and the resistors in the circuit were changed to 100K. Therefore, $I_d = \frac{500}{10^6} = 500$ microamps which is now 10 times I_d. The linearity of the PMT response was experimentally checked using Melles Griot Calibrated Neutral Density Filters. For optimal response, the voltage shoud be on the plateau region of the curve of gain versus voltage. (See fig.8.) This corresponds to peak collection efficiency at the anode and hence to an electrical signal directly proportional to the intensity of the light reaching the photocathode.

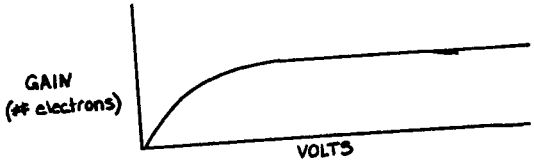


Fig.8. Gain Linearity:
The dependence of output current
on input stimulus

In the normal operating mode, the PMT power supply is increased until a 50 millivolt deflection occurs on the oscilloscope corresponding to I_a of 50 microamps. A neutral density filter of 0.2 will allow 50.0% transmittance of light at 424 nm. When the filter was placed in front of the monochrometer, the signal decreased to a 25 millivolt deflection which was expected. This signifies that the PMT responds linearly under the conditions we are operating at.

Oscilloscope

The Tektronix Oscilloscope has several features suitable for application to fast photochemical reactions. It can be operated in a single sweep mode and storage mode which records an experimental run with accurate sensitivity and response. The sweep time and vertical displacement can be adjusted to give a full screen deflection. A graticule on the screen can be used to measure vertical and horizontal displacement.

B. Procedure

From the wide realm of topics for investigation using the technique of flash photolysis, we have chosen to focus on the triplet state of an aromatic hydrocarbon in solution: anthracene in heptane. Many studies have been done on this system which permit us to test the new flash photolysis apparatus, adjust it to work perfectly, and to run a check on our experimental procedure. Anthracene is a desirable substance because its electronic transition from the ground state to the excited state occurs readily upon excitation. This in turn generates a large signal at the oscilloscope in terms of percent transmittance corresponding to the triplet-triplet absorption at 424 nm.

From our work with anthracene in heptane, we will develope an experiment for the Physical Chemistry course. This experiment is significant in that it will provide students with an experiment in fast chemical kinetics combining the use of the vacuum line with the use of the flash photolysis apparatus. The objective of the experiment is to obtain an unquenched rate constant, k_1, and quenching rate constant, k_{0_2}, for the triplet decay process.

1. Solution Preparation

The suggested concentration range for anthracene in solution is 10^{-3} to 10^{-5} M. We have chosen to work at 10^{-4} M. Original work we did at 10^{-5} M gave a small percent

transmittance. Solutions were made of spectroscopic grade heptane and crystalline anthracene, neither of which were further purified.

2. Utilizing the Vacuum Line

The vacuum line can be used for two purposes:

a. To carry out gas expansions and reduce the partial pressure of oxygen in a sample gas bulb to a desired value. From this bulb, aliquots of oxygen can be introduced to the sample cell apparatus.

b. To degas the sample cell apparatus using a freeze-thaw cycle method.

a.

i. Determine how much oxygen should be dissolved in the solution when an aliquot is introduced to the sample apparatus to produce a noticeable quenching effect:

$$k_{obs.} = k_1 + k_{O_2}[O_2]$$

$$[O_2] = \frac{k_{obs.} - k_1}{k_{O_2}}$$

One experimental run with a "degassed" solution gave $k_{obs.} = 10{,}000\ sec^{-1}$. Oxygen is assumed to be present since much lowere literature values have been determined.

$$[O_2] = \frac{10{,}000\ sec^{-1} - 630\ sec^{-1}}{3.95 \times 10^9\ 1/\ mole\text{-}sec} \qquad (7.)$$

$$[O_2] = 2.37 \times 10^{-6}\ \underline{M}$$

ii. From the solubility of oxygen in heptane, determine $[O_2]$ in terms of partial pressure (atm.) from the atmosphere.

$[O_2]$ = 0.330 Bunsen absorption coefficient at 25° C.[24]

In 1 liter of heptane, there is 0.330 l O_2 dissolved at STP.

$$n = \frac{P\,V}{R\,T} = \frac{(1\ \text{atm})(0.330\ \text{l})}{(0.8206\ \text{l-atm/mol-K})(273.15\ \text{K})}$$

$$n = 1.47 \times 10^{-2}\ \text{moles}$$

Therefore, $[O_2] = 1.47 \times 10^{-2}$ moles/ 1 liter of solution

Henry's Law states: $\chi = \frac{P}{K_H}$, where χ = mole fraction
P = partial pressure
K_H = constant

$$P_{O_2} = K_{O_2} \times [O_2]$$

$$P_{O_2} = (68.03\ \text{l-atm/mole})(2.37 \times 10^{-6}\ \underline{M})$$

$P_{O_2} = 1.61 \times 10^{-4}$ atm above the solution in the sample apparatus

iii. Determine relative volumes before performing expansion work. (See fig.9) First, measure relative volumes of sample gas bulb , vacuum line manifold and ballast bulb.

Let $V_1 = V_{bulb}$

$V_2 = V_{bulb} + V_{manifold}$

$V_3 = V_{bulb} + V_{manifold} + V_{ballast\ bulb}$

$$P_1V_1 = P_2V_2 = P_3V_3$$

$\frac{V_1}{V_2} = \frac{P_2}{P_1}$ = the reduction in pressure for one expansion cycle.

Barometric pressure: 767.0 torr

Manometer : 764 torr

Therefore, $P_1 = 764$

$P_2 = 764 - (683-210) = 291$ torr
with the ballast bulb out of line

$P_3 = 764 - (811-80) = 33$ torr

$$\frac{V_1}{V_2} = \frac{P_2}{P_1} = \frac{291}{764} = 0.381 \text{ or } \underline{1 : 2.62} \text{ volume ratio}$$

$$\frac{V_1}{V_3} = \frac{P_3}{P_1} = \frac{33}{764} = 0.0432 \text{ or } \underline{\underline{1 : 23.1}} \text{ volume ratio}$$

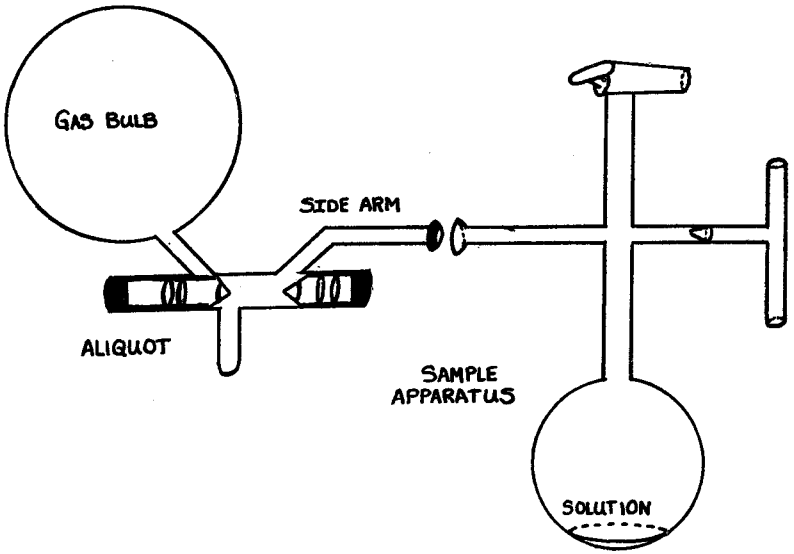


Fig.9.

Diagram of apparatus

and Important Relative Volumes

Absolute Volumes *

V_{bulb} = 269.0 ml (with stopcock closed)

$V_{aliquot}$ = 5.0 ml (with one stopcock closed and one open.)

$V_{side\ arm}$ = 5.9 ml (with stopcock closed)

$V_{sample\ apparatus}$ = 142 ml

$V_{solution}$ = 20.0 ml

* All volumes were measured in terms of the volume of water that each componant held.

Important Relative Volumes:

Expanding gas bulb into the aliquot bulb -

$V_{bulb} + V_{ali.} = 274$ ml

Expanding aliquot bulb into sample apparatus -

$V_{sample\ app.} - V_{solution} + V_{ali.} + V_{sidearm} = 132.9$ ml

iv. Obtain the desired partial pressure of oxygen in the sample gas bulb to give the partial pressure in the aliquot which was determined in section ii.

First, as determined in section ii, the partial pressure of oxygen in the sample apparatus over the solution should be 1.61×10^{-4} atm. Working backward:

$P_1V_1 = P_2V_2$, $P_1 = ?$ = the pressure in the aliquot bulb before expansion into the sample apparatus.

$V_1 = V_{ali.\ bulb}$ (ie. an initial volume)

$P_2 = 1.61 \times 10^{-4}$ atm

V_2 = volume after expanding the aliquot bulb into the sample apparatus

$$P_1 = \frac{P_2V_2}{V_1} = \frac{(1.61 \times 10^{-4})(132.9\ ml)}{(5.0\ ml)} = \underline{4.3 \times 10^{-3}\ atm}$$

Second, calculate the pressure desired in the sample gas bulb which, when allowed to expand into the aliquot bulb, will give a final pressure of 4.3×10^{-3} atm. of O_2 .

$P_1V_1 = P_2V_2$,

P_1 = ? = pressure in the gas bulb

$V_1 = V_{bulb}$

P_2 = final pressure in the gas bulb and aliquot bulb

$V_2 = V_{bulb} + V_{ali.\ bulb}$

$$P_1 = \frac{P_2 V_2}{V_1} = \frac{(4.3 \times 10^{-3})(274)}{269} = \underline{4.4 \times 10^{-3} \text{atm } O_2}$$

Third, determine the number of expansions which will give 4.4×10^{-3} atm of O_2 using the vacuum line:

$$P_1V_1 = P_2V_2 = P_3V_3$$

$\frac{V_1}{V_2} = \frac{P_2}{P_1}$ = the reduction in pressure for one expansion cycle without the ballast bulb

$\frac{V_1}{V_3} = \frac{P_3}{P_1}$ = the reduction in pressure for one expansion cycle with the ballast bulb in line

$$P_3 = \frac{P_1V_1}{V_3} = (0.21 \text{ atm}^*)\left(\frac{33}{764}\right) = 9.1 \times 10^{-3} \text{atm}$$

$$P_2 = \frac{P_1V_1}{V_2} = (9.1 \times 10^{-3} \text{ atm})\left(\frac{291}{764}\right) = \underline{3.5 \times 10^{-3} \text{ atm } O_2}$$

* Given that the partial pressure of oxygen in the atmosphere is 0.21 atm.

Therefore, one must carry out two successive expansions to achieve the desired partial pressure of oxygen in the sample gas bulb.

b. The freeze-thaw cycle is a method which is used to thoroughly deoxygenate a solution. This method uses liquid nitrogen to freeze the solution leaving oxygen in the air above it which is then vacuumed off. The purpose of thawing and agitating the solution at the end of each cycle is to liberate dissolved oxygen into the vacuum above the solution. Each cycle takes approximately 30 minutes.

steps

i. introduce solution to the sample apparatus
ii. freeze and wait five minutes
iii. pump with roughing pump for 15 minutes
iv. pump with roughing pump and oil-diffusion pump for 10 minutes.
v. close off vacuum line and warm solution to room temp.
vi. agitate and vibrate the solution
vii. repeat from step ii. five times.

3. Preparing the flash photolysis apparatus

The sample cell must be placed in the cell housing and aligned so that the beam from the analyzing light passes directly through it. The monochrometer is set

to 424 nm to monitor anthracene's triplet-triplet absorption. With the PMT shutter closed, the oscilloscope baseline is established corresponding to zero % transmittance. The oscilloscope must also be set on external mode and auto trigger. After opening the shutter, the PMT power supply is increased until a 50 millivolt vertical displacement occurs. At this point, the oscilloscope settings can be changed to read: storage mode, single sweep, and reset.

With the conclusion of this preliminary procedure, the micropulser can then be charged to 10,000 volts. After the flashtubes are fired, the trace of the disappearance of triplet anthracene will be recorded and stored.

4. Kinetic Analysis of Data

The kinetic analysis is a relatively simple procedure if only one short-lived species is produced. We are interested in determining the rate constants k_1 and k_{O_2} for the first-order decay of triplet anthracene:

$$-\frac{d[T]}{dt} = k_1[T] + k_{O_2}[T][O_2] \qquad (1)$$

In the absence of oxygen:

$$-\frac{d[T]}{dt} = k_1[T] \qquad (2)$$

Separating variables and integrating:

$$\int_{T_0}^{T_t} \frac{-d[T]}{[T]} = k_1 \int_0^t dt \qquad (3)$$

$$\ln [T]_t - \ln [T]_0 = -k_1 t \qquad (4)$$

$$\ln \frac{[T]_t}{[T]_0} = -k_1 t \qquad (5)$$

Applying Beer's Law: $A = \epsilon c l$

$$\text{or } c = A/\epsilon l \qquad (6)$$

$$[T]_t = \frac{(A_t - A_\infty)}{(A_0 - A_\infty)} [T]_0 \qquad (7)$$

Rearranging:

$$\frac{[T]_t}{[T]_0} = \frac{(A_t - A_\infty)}{(A_0 - A_\infty)} \qquad (8)$$

Substituting into equation (5):

$$\ln \frac{(A_t - A_\infty)}{(A_0 - A_\infty)} = -kt \qquad (9)$$

$$\ln (A_t - A_\infty) = -kt + \ln (A_0 - A_\infty) \qquad (10)$$

Since $A_\infty = 0$,

$$\underline{\underline{\ln A_t = -kt + A_0}} \qquad (11)$$

Therefore, to determine k_1, plot ln A_t vs. t. The slope of this plot gives $-k_1$. To obtain k_{O_2}, go back to equation (1):

$$-\frac{d[T]}{dt} = k_1[T] + k_{O_2}[T][O_2]$$

$$= (k_1 + k_{O_2}[O_2])\,[T]$$

let $k_{obs.} = k_1 + k_{O_2}[O_2]$

$$\underline{\underline{-\frac{d[T]}{dt} = k_{obs.}[T]}}$$

By plotting $k_{obs.}$ vs. O_2, you will get a line with slope k_{O_2}.

IV. Results and Discussion

Traces of the decay of triplet anthracene in heptane were measured from the oscilloscope giving percent transmittance versus time. Values of % T were converted to absorbance and plots for ln A_t vs. time were constructed. Table 1 gives values of A_t with corresponding times for one of our kinetic runs with 5.5×10^{-4} M anthracene in heptane. A plot of ln A_t vs. time for this run is linear and gives a k_1 of 4490 sec^{-1}. Since the first three points of the graph lay on the peak of the absorbance curve, they have been neglected. The line generated from the remaining points indicates that the rate law follows first-order kinetics and that second-order effects from triplet-triplet annihilation may not contribute to the rate expression. However, we may be seeing such effects when the trace of the decay of triplet anthracene falls below the pre-trigger baseline on the oscilloscope.

The value of k_1 reported above is the lowest we have obtained thus far. This is due to improvement in our degassing technique. Magnetic stirring bars were placed in the sample bulb to agitate the solution and free dissolved oxygen. Linschitz, Steel, and Bell used this procedure and obtained the lowest value of k_1 by far. (See Table 2)

Table 1

Obtaining k_1 for the unquenched reaction of anthracene in heptane

time axis (# div)	time (s)	% T (# div)	% T	Abs.	ln A_t
0.9	90	3.7	26	0.585	-0.536
1.3	130	3.2	36	0.444	-0.813
1.45	145	3.0	40	0.398	-0.921
1.7	170	2.7	46	0.337	-1.09
2.1	210	2.3	54	0.268	-1.32
2.5	250	2.0	60	0.222	-1.51
2.7	270	1.85	63	0.201	-1.61
3.7	370	1.3	74	0.131	-2.03
4.3	430	1.0	80	0.0969	-2.33
4.7	470	0.9	82	0.0862	-2.45
5.7	570	0.6	88	0.0555	-2.89
6.7	670	0.4	92	0.0362	-3.32
7.7	770	0.25	95	0.0223	-3.80
8.7	870	0.15	97	0.0132	-4.33

Calculation of % T: (5 - (%T # div)) 20

Abs: $\log_{10}(100/\%T)$

Experimental parameters:

Without sample cell in housing: PMT at 238 volts
Oscilloscope at 2 mv/div
20 μs/div

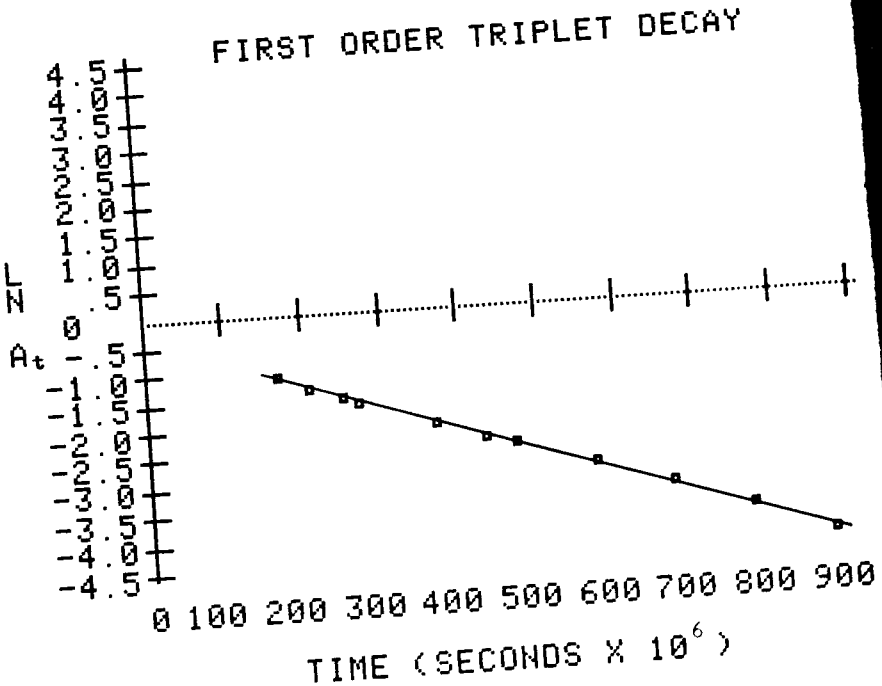
Flash duration: 32 μsec

With sample cell in path: PMT at 275 volts
Oscilloscope at 2 mv/div
.1 ms/div

Graph of Results for Table 1

Degassed Anthracene in Heptane

5.5×10^{-4} M



Calculated Fit of the Points on the Line:

slope = m = -4.49×10^{-3} $(\text{microseconds})^{-1}$

therefore, $k_1 = 4490$ $(\text{seconds})^{-1}$

r = 0.9994 ; the correlation coefficient

Table 2

Chronological List of Reported Values for rate constants k_1 and k_{0_2} for anthracene in hexane

k_1 (sec-1)	k_{0_2} (l/mol-sec)	degassing technique	reference
13,000 ± 3000	3×10^9	Twice; evaporate off solvent, refill to mark	1.
17,500 ± 1000	3.8×10^9	Twice; anthracene de-degassed separately in side arm cell	4.
1300	4×10^9	Freeze-thaw until pressure = .001 (above solution)	6.
1100 ± 100	---	trap to trap distillation	9.
160	3×10^4	degas 4-8 x	8.
56 + 76	---	stirring bar/agitation	11.

Table 3

Rate Constants for Anthracene in Heptane

k_1 (sec^{-1})	k_{0_2} (l/ mole-sec)	reference
630	3.95×10^9	7.
4490	---	Our results

The table and results for this run (Table 2) were obtained prior to changes in our photomultiplier circuitry which renders them as suspect. Recall from section III. that the anodic current I_a equalled 50 microamps and the dynode chain current I_d also equalled 50 microamps. This meant that investigations were conducted in the non-linear region of the photomultiplier response.

Further work attempted to discern whether repetitive flashing depleted the oxygen content in solution as was noted in the literature. Although these experiments were done without knowledge that our detection was not functioning properly, the results from Tables 4 through 7 and corresponding graphs are interesting to note. The rate constant , k_1 , increases as the number of flashes increase. A plausible explanation is that a leak may be present. This warns us that proper care must be taken in handling the sample cell and making sure that all stop-cocks are properly sealed.

Investigations regarding the effects of degassing, flash repetition, and time lapse between flashing were continued for unquenched reactions. Unfortunately, spectral curves became distorted giving graphs that "tailed-out" significantly. Work was discontinued on the experimental runs and focused on eliminating bugs in our detector.

TABLE 4

Results for Anthracene Triplet Decay in Heptane (5.5×10^{-4} M) after 5 repetitive flashes

time axis # div	time (μs)	% T axis # div	% T	Abs.	ln A_t *
0.9	90	3.6	28	0.553	-0.593
1.1	110	3.3	34	0.469	-0.758
1.4	140	3.0	40	0.398	-0.921
1.7	170	2.65	47	0.328	-1.16
2.35	235	2.0	60	0.222	-1.51
2.7	270	1.7	66	0.180	-1.17
3.3	330	1.3	74	0.131	-2.03
3.7	370	1.1	78	0.108	-2.23
3.95	395	1.0	80	0.0969	-2.33
4.7	470	0.70	84	0.0757	-2.58
5.7	570	0.50	90	0.0458	-3.08
6.7	670	0.30	94	0.0269	-3.62
7.7	770	0.15	97	0.0132	-4.33

Oscilloscope settings: y = 2 mv/division
x = 100 μsec/division

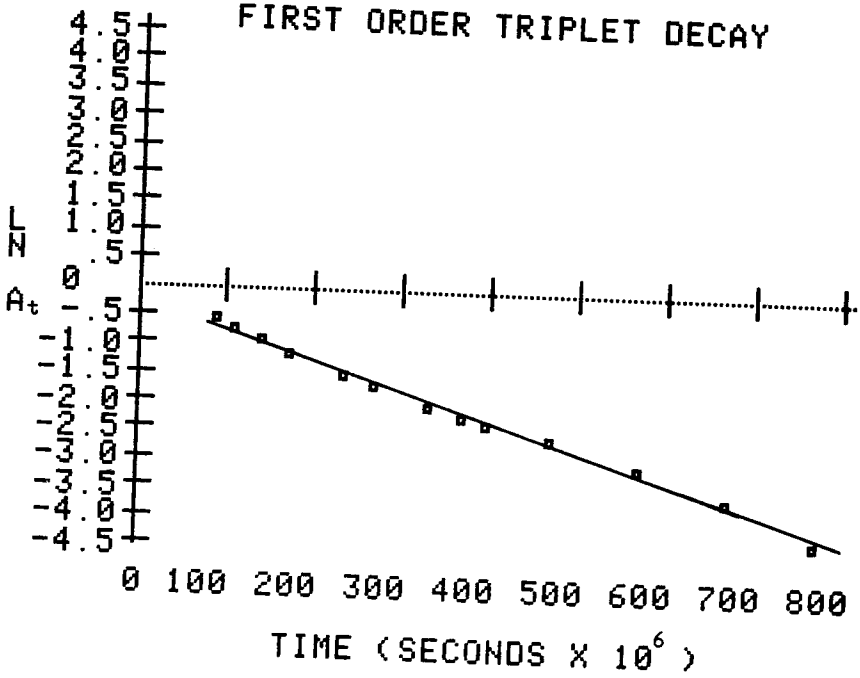
* Note: For results in tables 4 through 7, $A_\infty = 0$. The same solution was used and was degassed five times.

Graph of Results for Table 4

Degassed Anthracene in Heptane

5.5×10^{-4} M

after 5 repetitive flashes



Calculated Fit of the Points on the Line:

slope = m = -5.20×10^{-3} (microseconds)$^{-1}$

therefore, k_1 = 5200 (seconds)$^{-1}$

r = 0.9974 ; the correlation coefficient

TABLE 5

Results for Anthracene Triplet Decay in Heptane after 10 repetitive flashes

time axis # div	time (μs)	% T axis # div	% T	Abs.	ln A_t
0.9	90	3.70	26	0.585	-0.536
1.3	130	3.15	37	0.432	-0.840
1.4	140	3.05	39	0.409	-0.894
1.7	170	2.65	47	0.328	-1.16
2.25	225	2.05	59	0.229	-1.47
2.70	270	1.65	67	0.174	-1.75
3.20	320	1.35	73	0.137	-1.99
3.70	370	1.05	79	0.102	-2.28
4.70	470	0.65	87	0.0605	-2.81

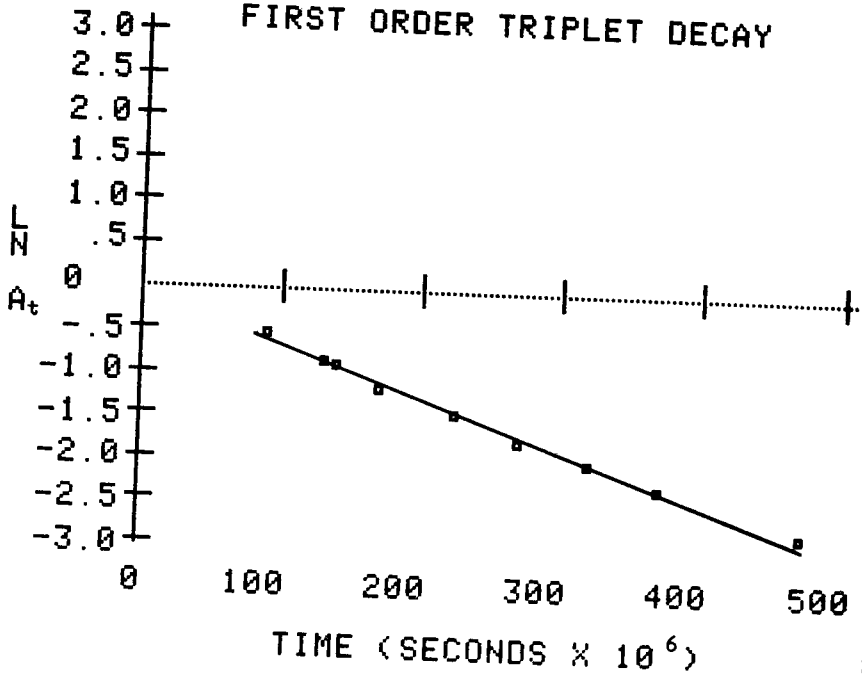
Oscilloscope settings: y = 2 mv/division
x = 100 μsec/division

Graph of Results for Table 5

Degassed Anthracene in Heptane

5.5×10^{-4} M

after 10 repetitive flashes



Calculated Fit of the Points on the Line:

slope = m = -5.92×10^{-3} (microseconds)$^{-1}$

therefore, $k_1 = 5920$ (seconds)$^{-1}$

r = 0.9975 ; the correlation coefficient

TABLE 6

Results for Anthracene Triplet Decay in Heptane after 20 repetitive flashes

time axis # div.	time (μs)	% T axis # div.	% T	Abs.	ln A_t
1.2	120	2.95	41	0.387	-0.949
1.7	170	2.25	55	0.260	-1.35
2.0	200	1.95	61	0.215	-1.54
2.3	230	1.65	67	0.174	-1.75
2.7	270	1.35	73	0.137	-1.99
3.4	340	0.95	81	0.0915	-2.39
3.7	370	0.80	84	0.0757	-2.58
4.7	470	0.50	90	0.0458	-3.08

Oscilloscope settings: y = 2 mv/division

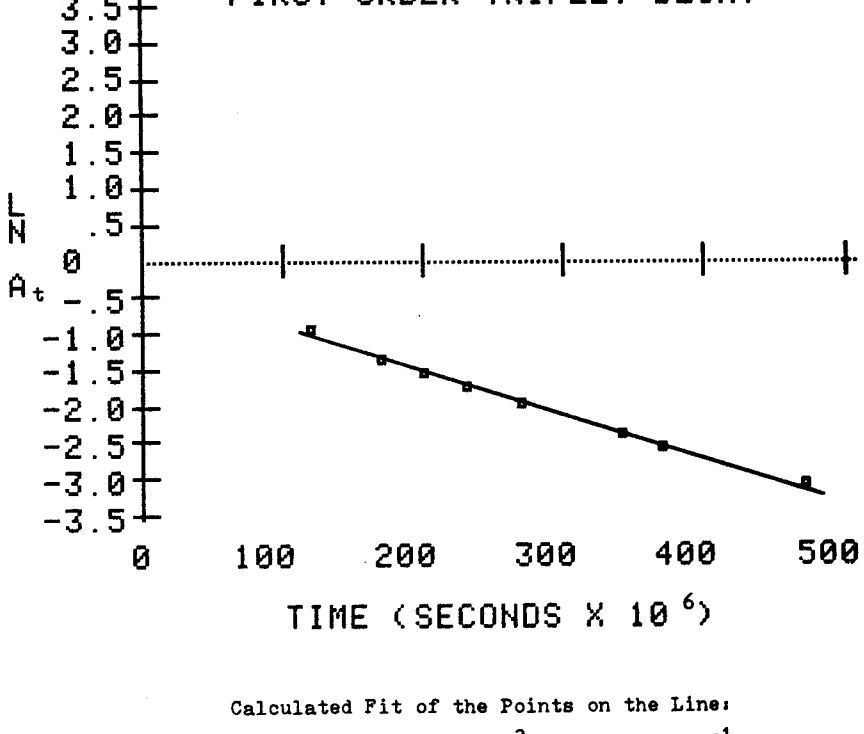
x = 100 μsec/division

Graph of Results for Table 6

Degassed Anthracene in Heptane

5.5×10^{-4} M

after 20 repetitive flashes



Calculated Fit of the Points on the Line:

m = slope = -6.04×10^{-3} (microseconds)$^{-1}$

therefore, $k_1 = 6040$ (seconds)$^{-1}$

r = 0.9972 ; the correlation coefficient

TABLE 7

Results for Anthracene Triplet Decay in Heptane after 30 repetitive flashes

time axis # div.	time (μs)	% T axis # div.	% T	Abs.	ln A_t
0.90	90	3.2	36	0.444	-0.813
0.95	95	3.0	40	0.398	-0.921
1.3	130	2.5	50	0.301	-1.20
1.6	160	2.0	60	0.222	-1.51
1.7	170	1.9	62	0.208	-1.57
2.2	220	1.3	74	0.131	-2.03
2.7	270	1.0	80	0.0969	-2.33
3.1	310	0.75	85	0.0706	-2.65
3.7	370	0.50	90	0.0458	-3.08
4.7	470	0.25	95	0.0223	-3.80

Oscilloscope settings: y = 2 mv/division

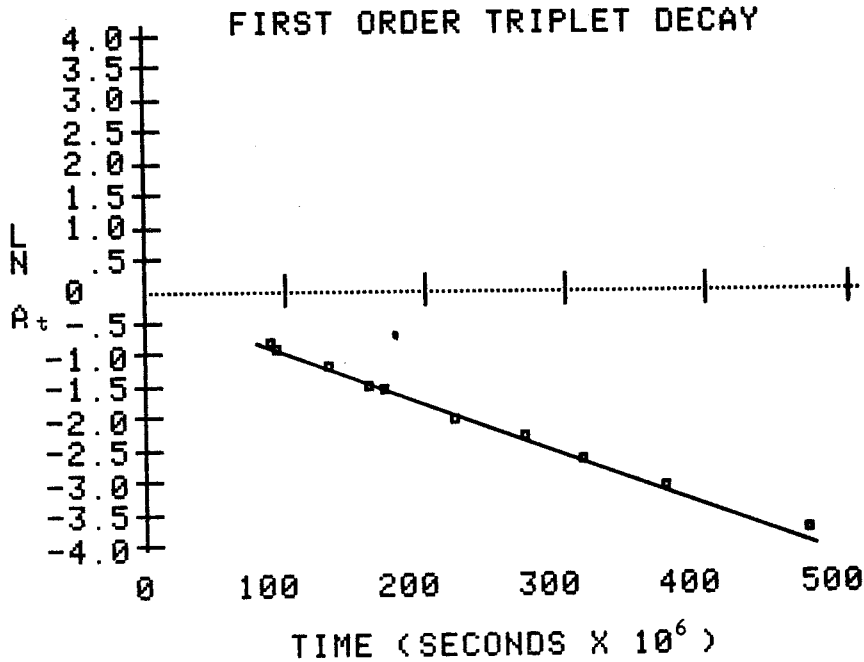
x = 100 μsec/division

Graph of Results for Table 7

Degassed Anthracene in Heptane

5.5×10^{-4} M

after 30 repetitive flashes



Calculated Fit of the Points on the line:

slope = m = -7.77×10^{-3} (microseconds)$^{-1}$

therefore, k_1 = 7770 seconds^{-1}

r = 0.9981 ; the correlation coefficient

After the dynode resistors were replaced in the photomultiplier tube, an experimental run was performed. With a large decrease in the gain of the oscilloscope, extraordinary curves were seen. These curves were on the order of 500 microseconds in duration and of 0.5 volt deflection. (See fig.10). The cause of these large signals is not known, but it is believed to be due to one of the following possibilities: scattered light, fluorescence, or malfunctioning detector. The latter could be the result of the electromagnetic flux from the discharging capacitors or flash lamps.

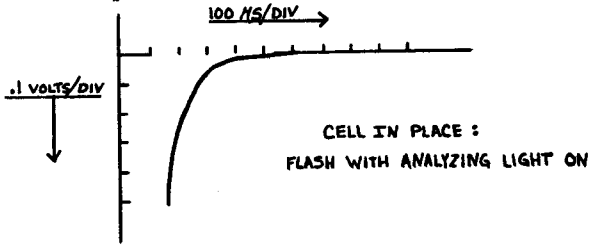


Figure 10.
Large Unexplained Signals

More recently, we are experiencing a phenomena of "resetting" whereby the oscilloscope only registers the signal from the pre-trigger. This effect could also be due to magnetic perturbrations from the high powered discharge originating from the micropulser. We will try shielding the oscilloscope or removing it from the vicinity of the micropulser to stop resetting from occuring.

This describes the present status of the flash photolysis apparatus. It is anticipated that all problems will be solved and work on obtaining the rate constants, k_1 and k_{0_2}, for the decay of triplet anthracene will continue.

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ADDENDUM TO THESIS

Spring, 1982

The purpose of our work for this term is twofold: First, to get the flash photolysis apparatus to work properly. This entails resolving the cause of large anomalous signals on the oscilloscope and frequent failure of the oscilloscope to complete its trace. Once this is accomplished, the project which began one year ago to assemble the flash photolysis apparatus and render it operable will be complete. Second, to resume work on obtaining a low value of the first-order rate constant, $k_{obs.}$, for the decay of triplet anthracene. This will give a direct measure of the efficiency of our degassing technique which we would like to perfect.

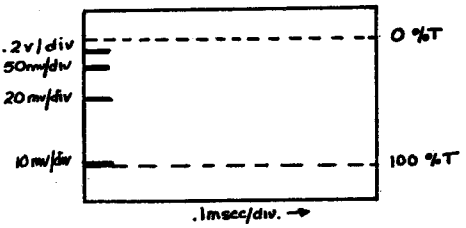
Through systematic investigation and consultation with people with experience in electronics, we have accomplished these goals. This addendum recounts how we isolated and corrected the problems associated with the detection system and includes results for our continued work with the decay of triplet anthracene.

I. Recurring Problems in the Detection System

A. "Resetting"

The term "resetting" describes the failure of the oscilloscope to complete its trace when the flashtubes are fired. Since the only signal which is recorded is the short horizontal sweep from the pre-trigger, the phenomena of "resetting" prevents any experimental runs from being performed. This effect could be due to scattered light, fluorescence, or interfering electromagnetic radiation. The first two sources would cause the photocathode in the PMT to be exposed to too much light, making it incapable of responding quickly enough, if at all, to the sudden change in intensity with a proportional signal at the anode. The third source, electromagnetic or R-F (radio-frequency) radiation from the discharging capacitor in the micropulser, would interfere with any signals within the oscilloscope, the PMT, or the cables attached to these components.

To determine whether scattered light or fluorescence is responsible for overexposing the photocathode with light and therefore causing the oscilloscope trace to cut-off, the gain was decreased on the oscilloscope. This, in effect, expanded the screen enabling one to pick up a trace which may have previously been off-scale. When this was done, no trace was seen.



A.

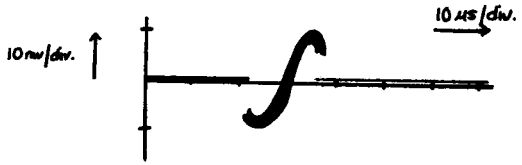
PMT attached to the oscilloscope and open or closed

The second test performed was to flash the flashtubes without the sample cell in the path of the monitoring light. This would reduce scattered light from arising from the change in refractive index as the monitoring light passes through the cell filled with solvent. It would also eliminate the possibility of fluorescence from impurities in the solvent. The results for this test also showed that "resetting" occurred reproducibly.

The conclusive test which showed that scattered light and fluorescence were not causing the failure of the oscilloscope to complete its trace was suggested to us by D. Peak, Assistant Professor of Physics. This test required that the flashtubes be fired with the PMT shutter closed. This would prevent the photocathode from receiving outside stimulus and therefore a completed trace initiated by the pre-trigger should occur across the oscilloscope

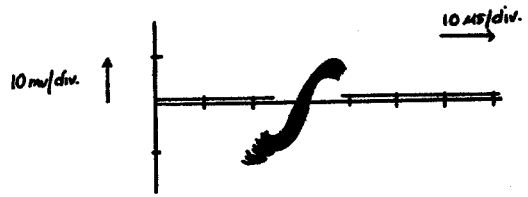
screen. Then, if the trace were completed, changing the monitoring wavelength would differentiate between scattered light and fluorescence. This test resulted in an incomplete trace, indicating that R-F is interfering with the detection system.

With the problem now isolated, the next step was to determine which components of detection system were being affected by R-F, and in addition to investigate how prevailing conditions contribute to the "resetting" phenomena. D. Peak suggested that the system be flashed with the PMT disconnected from the oscilloscope at the PMT end. This would demonstrate whether or not the oscilloscope was picking up the electromagnetic radiation. The result showed that this was indeed the case.



B.
PMT disconnected

The sine wave produced from the flux in the current when the capacitor is discharged is depicted above. If the PMT were disconnected from the oscilloscope at the oscilloscope end, the same curve is generated with a slight increase in noise in the signal.

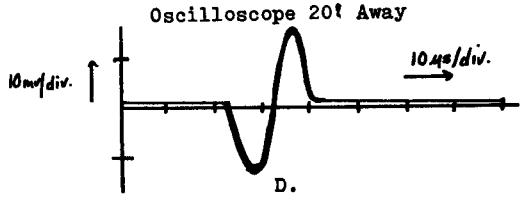


C.

PMT disconnected

E. J. Craig, Professor of Electrical Engineering, suggested that it is probably due to the T-bar which is attached to the oscilloscope acting as an antenna.

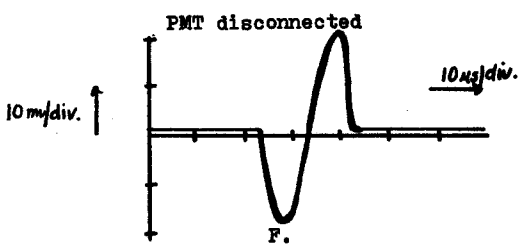
Since the oscilloscope and PMT are both in proximity of the micropulser, moving the oscilloscope twenty feet away would be a test to see whether it is the component picking up the R-F. Two long cables were attached to the oscilloscope, allowing greater separation from the PMT and the pretrigger.



D.

PMT attached and closed

E.



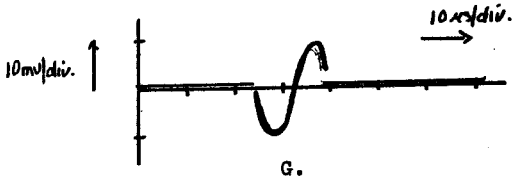
F.

PMT attached and open

Digrams D, E, and F demonstrate the signals which appeared when the oscilloscope was twenty feet away. Resetting occurred in case A, when the oscilloscope was one foot from the micropulser. This effect was eliminated in cases D and F, which involved greater separation of the components. The diminished effect of the R-F as a function of distance is seen in E, where the sine wave is flattened as compared to B.

After determining the effect of distance between components on the signal, the PMT was shielded to see if this would also reduce the magnitude of the sine wave. Copper sheets were wrapped around the PMT to intercept interfering radiation. The shielding was effective and the resulting

curve was twice as small.



G.

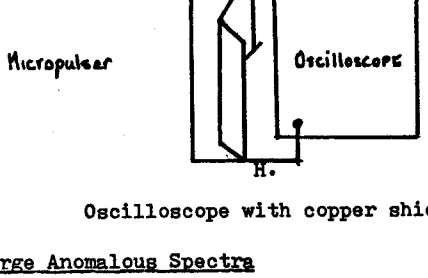
The effect of shielding

The oscilliscope was then brought within five feet of the micropulser and the PMT and coaxial cables were further shielded. This was done to establish a convenient location for the oscilloscope and to eliminate the possibility of "resetting". Then, the copper sheets were slowly unwrapped and the system was checked until the components were fully uncovered. Repeatedly, the osilloscope completed its trace. If a five foot separation would prevent the oscilloscope from resetting, then one would believe that an arrangement could be made which would allow the oscilloscope to be next to the micropulser once again. This arrangement was worked out, and requires that the following criteria be met:

1. The cover of the oscilloscope must be further grounded.
2. A copper metal barricade which is placed between the micropulser and oscilloscope must also be grounded.

3. At least one of the two long cables is left attached to the oscilloscope from either the pretrigger or the PMT.

(The first two suggestions were offered by E. J. Craig.)



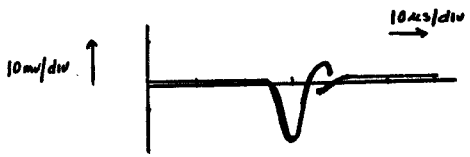
Oscilloscope with copper shield

B. Large Anomalous Spectra

Frequently, distorted spectra for triplet decay in heptane have been noted. These curves are on the order of 500 microseconds in duration and 0.5 volt deflection. The cause of these large signals was believed to be scattered light or fluorescence. To isolate the cause of this effect, successive spectra were recorded without the sample cell, with the empty sample cell, with the sample cell containing water, and finally with the sample cell containing heptane only. With the first three conditions, a similar sine wave was seen, ruling out the possible contribution of scattered light to the anomalous curves. However, the test with heptane alone gave a curve of 0.2 v deflection and 50 microseconds duration. Other solvents were checked and only

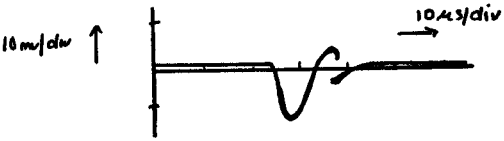
heptane gave unconventional results.

Solvent-only Spectra



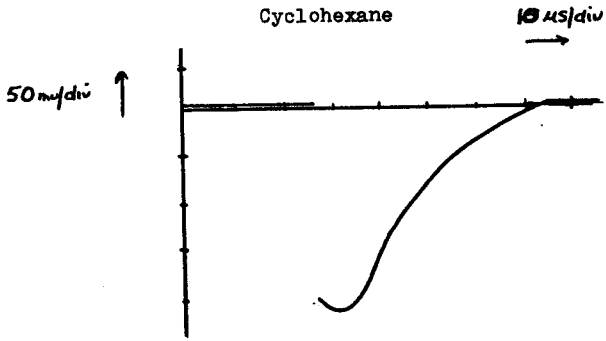
I.

Hexane



J.

Cyclohexane



K.

Heptane

It is possible that a small, unavoidable impurity content in the heptane causes fluorescence. Due to the observed phenomenon with heptane as a solvent, either cyclohexane or hexane will be used in future studies of the decay of triplet anthracene.

II. Results for the Decay of Triplet Anthracene in Cyclohexane

A Quantitative Study of the Effectiveness of Numerous Freeze-Thaw Cycles

Experiments from November of 1981 involving anthracene in cyclohexane gave a typical rate constant, $k_{obs.}$, of 37,000 sec^{-1}. These solutions underwent five freeze-thaw cycles, including no more than fifteen minutes pumping per cycle. Results from recent studies with 5.5×10^{-5} M anthracene in cyclohexane are recorded in Table 1. A first-order plot of this data gives a $k_{obs.}$ of 2520 sec^{-1}. This run was with a solution which had been degassed four times. Comparing the two values of $k_{obs.}$, the more recent value attests to the increased efficiency of the present degassing technique.

Two improvements in the degassing technique contributed to the tremendous reduction in the value of $k_{obs.}$. Magnetic stirring bars were used to agitate the thawed solution and free dissolved oxygen. In addition, the pumping period was extended from 15 to 90 minutes in the preliminary and final degassing cycles.

Table 2 and the corresponding plot of ln $(A_t - A_\infty)$ vs. time are the result of 20 repetitive flashes on the same solution. The rate constant obtained from the slope of this plot is 2540 sec^{-1}. Since this does not vary significantly from the rate constant obtained from the first plot, repetitive flashing does not appear to reduce the amount of

oxygen in solution. This indicates that with the low concentration of residual oxygen achieved by thorough degassing, very little O_2 scavenging occurs with repetitive flashing.

A final study investigated the extreme effect of eight freeze-thaw cycles. Table 3 and the corresponding plot illustrate the effect of increased removal of oxygen. The rate constant obtained for this run is 490 sec^{-1}, which approaches values currently reported in the literature. The first-order plot exhibits some scattering of experimental points around the best-fit line. This effect may arise from the gain setting on the oscilloscope, which was decreased from that of previous runs. As a result, the portion of the curve which has experimental interest, that is, the segment with the greatest slope, was more condensed than before. This adversely affected data collection. The possibility of second-order decay was ruled out by a plot of $1/A_t$ vs. time, which did not result in a straight line.

Table 1

Obtaining $k_{obs.}$ for degassed Anthracene in Cyclohexane

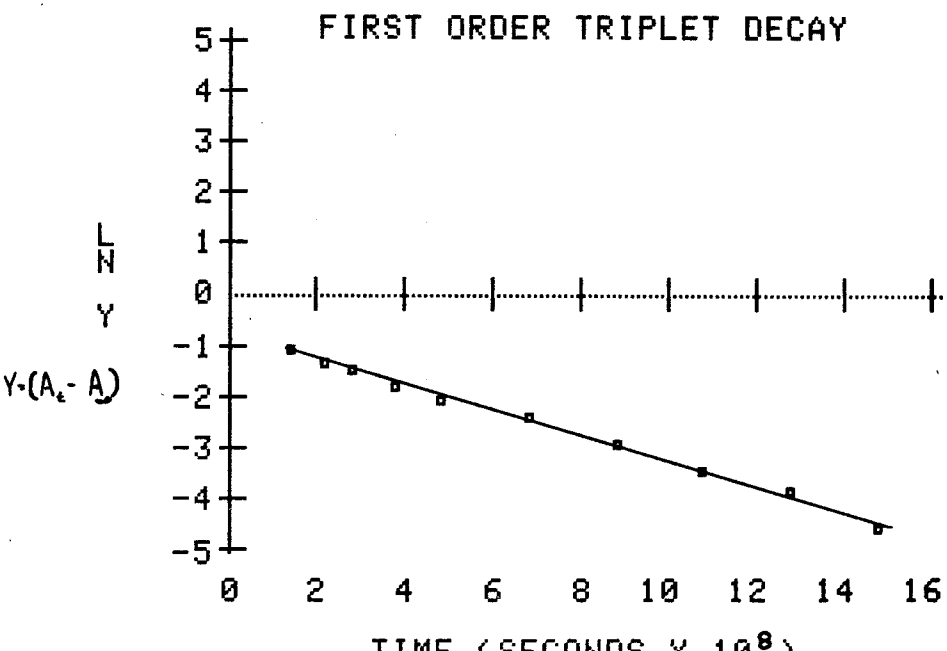
time x 10^8 sec	ln $(A_t - A_\infty)$
1.40	-1.07
2.20	-1.33
2.80	-1.51
3.80	-1.79
4.80	-2.08
6.80	-2.44
8.80	-2.95
10.80	-3.48
12.80	-3.90
14.80	-4.61

Graph of Results for Table 1

Degassed Anthracene in Cyclohexane

5.5×10^{-5} M

After 3 repetitive flashes



Calculated Fit of the Points on the Line:

slope = m = -2.52×10^{-3} μsec^{-1}

k = 2520 sec^{-1}

r = .9983

Table 2

Obtaining $k_{obs.}$ for Degassed Anthracene in Cyclohexane

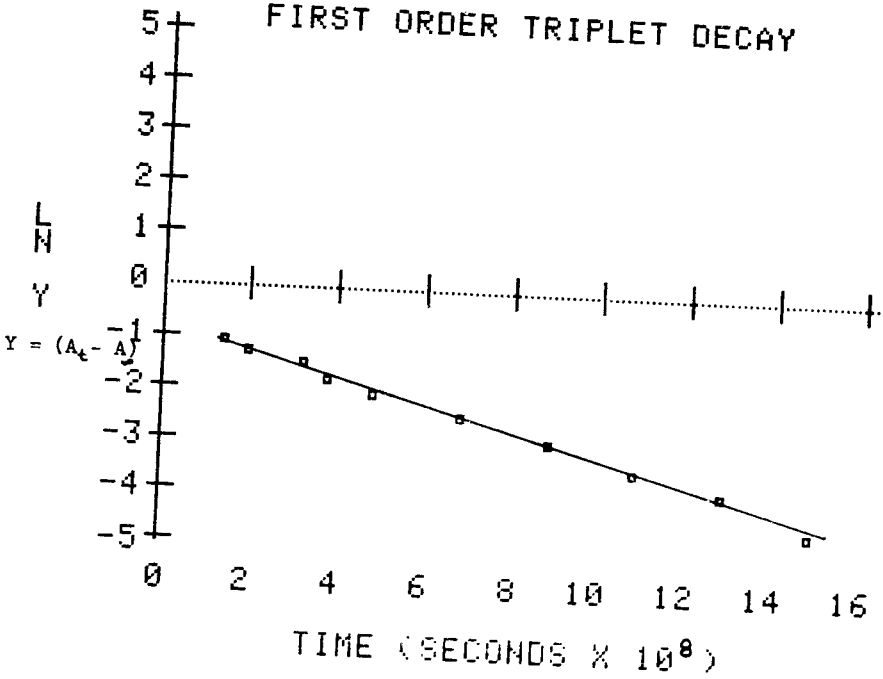
time x 10^8 sec	ln $(A_t - A_\infty)$
1.40	-1.07
2.00	-1.27
3.20	-1.51
3.80	-1.79
4.80	-2.08
6.80	-2.51
8.80	-2.95
10.80	-3.48
12.80	-3.90
14.80	-4.61

Graph of Results for Table 2

Degassed Anthracene in Cyclohexane

5.5×10^{-5} M

After 20 repetitive flashes



Calculated fit of the Points on the Line:

slope = m = -2.54×10^{-3} sec^{-1}

k = 2540 sec^{-1}

r = .9983

Table 3

Obtaining $k_{obs.}$ for Degassed Anthracene in Cyclohexane For Eight Freeze-Thaw Cycles

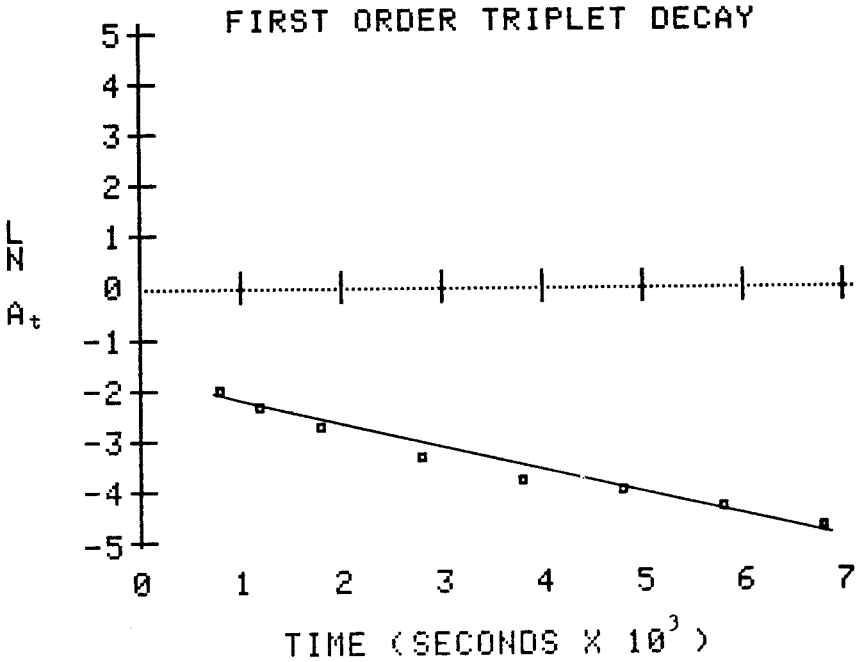
time x 10^3 sec	ln A_t
0.8	-1.99
1.2	-2.33
1.8	-2.73
2.8	-3.32
3.8	-3.80
4.8	-4.03
5.8	-4.33
6.8	-4.74

Graph of Results for Table 3

Degassed Anthracene in Cyclohexane

5.5×10^{-5} M

Eight Freeze-Thaw Cycles



Calculated Fit of the Points on the Line:

slope = m = -0.440 $msec^{-1}$

k = 440 sec^{-1}

r = .9860