

Flash Photochemical Measurements in the Physical Chemistry Laboratory

Kinetics of Deactivation of Electronically Excited Aromatic Molecules by Oxygen

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As the study of chemical reaction mechanisms has progressed, investigators have asked increasingly detailed questions about the fundamental events that occur as molecules react. In the early years, mechanistic insight was gained through the study of just the reactants and products of reactions. More recently, the development of more sensitive experimental probes with faster response times has permitted us to observe chemical intermediates directly.

Due to their typically high reactivity, intermediates have very short lifetimes. They exist in very low concentrations, which makes their detection and quantitative study difficult. However, during the last four decades several techniques have been developed to permit the direct detection and study of extremely reactive molecules.

Flash Photolysis

One of the oldest of these techniques is flash photolysis (1). In a typical flash photolysis experiment, an intense pulse of light directed at an appropriate precursor molecule generates the desired reactive species. The reaction of this species with other molecules in the system is usually tracked by optical absorption spectroscopy, either in the UV-vis or the infrared.

Although it is a common technique among researchers, flash photolysis has only slowly found its way into the undergraduate physical chemistry laboratory. This is presumably due to the technical demands of doing these experiments. In spite of this, several articles have appeared in *this Journal* (2-7) that describe flash photolysis experiments that have been successfully incorporated into the undergraduate curriculum. This has been achieved by looking at relatively slow molecular events ($\tau_{1/2} > 20$ ms) for which the instrumental requirements are less demanding.

Time Resolution

However, many bimolecular-solution and gas-phase reactions have lifetimes on the order of microseconds and nanoseconds, respectively, while unimolecular gas-phase reactions and energy-transfer processes have been observed to occur in less than a picosecond. Much of the current excitement in the field of chemical reaction dynamics centers on the study of these faster and often more fundamental processes.

Experimental probes are now used that have far greater time resolution than those used in the past. Consequently, we are attempting to upgrade our teaching of kinetics to reflect this. This article describes one such experiment

that involves the study of the kinetics of molecular energy transfer. We currently offer this experiment in our physical chemistry laboratory.

Our Experiment

In this experiment, students examine the kinetics by which molecular oxygen deactivates the electronically excited triplet states of the polycyclic aromatic hydrocarbon phenanthrene in hexane solution (8-11). Triplet state phenanthrene is formed in this experiment by flash photolysis. Its rate of return to the ground state is studied as a function of oxygen concentration. In deoxygenated hexane, triplet phenanthrene has a reported (9) lifetime ($\tau = 1/k$) of 93 μ s. The addition of small amounts of oxygen dramatically shortens this lifetime.

As shown in Figure 1, absorption of a near-UV photon promotes phenanthrene from its ground electronic state (S_0) to its first excited singlet state (S_1). From the S_1 state, it may return to the ground electronic state by one of the three paths described below.

- It may emit a photon in a process called fluorescence.
- It may convert the energy of electronic excitation into other modes of motion, particularly vibrational, within the S_1 state, which are then quenched by collisions with the solvent (internal conversion).
- It may undergo a spin-forbidden transition to the lowest triplet state (T_1). (This process, known as intersystem crossing, is only possible if the resulting change in spin angular momentum can be balanced by changes in the angular momentum elsewhere in the molecule or in neighboring molecules.)

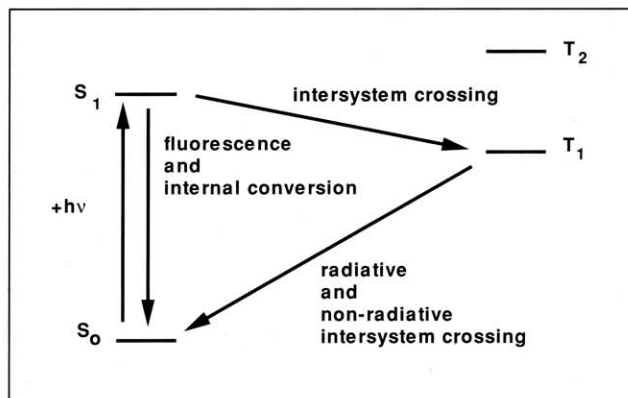


Figure 1. Energy transfer pathways between the low-lying electronic states of phenanthrene.

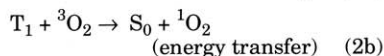
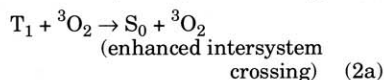
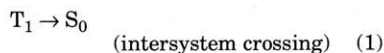
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Although such processes are often slow and unimportant, intersystem crossing is often the preferred path out of the S_1 state with aromatic hydrocarbons.

Molecules in the T_1 state may return to S_0 by either a radiative pathway (phosphorescence) or a nonradiative pathway. In room temperature hydrocarbon solutions, phenanthrene takes the latter path. Nonradiative decay from T_1 occurs either via intersystem crossing to high vibrational states of S_0 or via energy transfer to another molecule (quenching). Molecular oxygen is known to deactivate triplet phenanthrene by both processes. The purpose of this experiment is to use flash photolysis to study the kinetics of deactivation of triplet phenanthrene by oxygen.

Kinetic Analysis

We can write the following kinetic scheme for the nonradiative deactivation of the T_1 state of phenanthrene.



In reaction 2a, oxygen promotes intersystem crossing to high vibrational states of S_0 through formation of a transient charge-transfer complex. This has been shown to be an important step in the deactivation mechanism for triplet phenanthrene (12). The rate equation corresponding to this three-step decay mechanism is

$$-\frac{d[T_1]}{dt} = k_1[T_1] + k_{2a}[T_1][{}^3O_2] + k_{2b}[T_1][{}^3O_2]$$

$$= (k_1 + k_{2a}[{}^3O_2] + k_{2b}[{}^3O_2])[T_1]$$

$$= (k_1 + k_2[{}^3O_2])[T_1]$$

$$k_2 = k_{2a} + k_{2b}$$

where k_2 is the sum of the second-order rate constants for reactions 2a and 2b. Since $[{}^3O_2] \gg [T_1]$ under the conditions of this experiment, the rate equation is pseudo-first-order.

$$-\frac{d[T_1]}{dt} = k_{\text{obs}}[T_1] \quad (3)$$

where

$$k_{\text{obs}} = k_1 + k_2[{}^3O_2] \quad (4)$$

The lifetime is

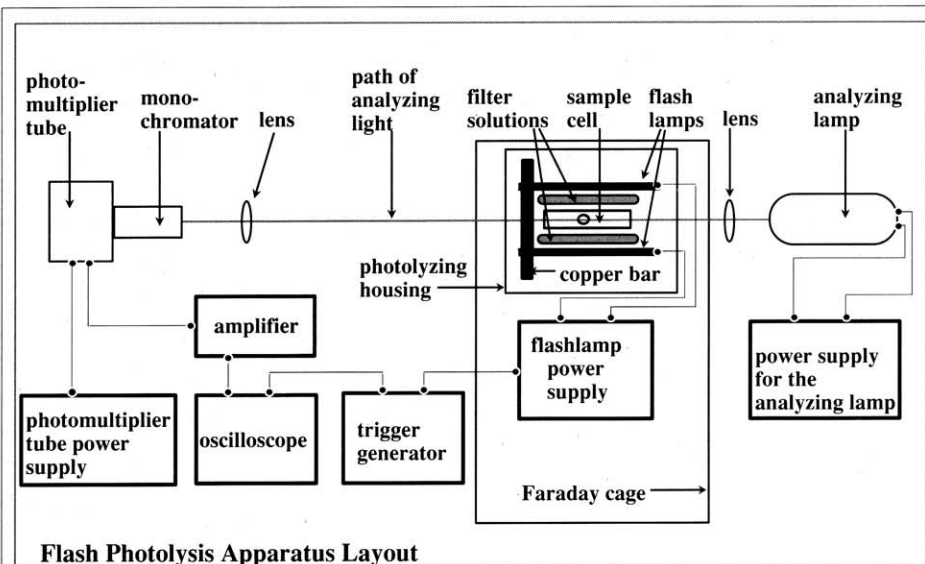
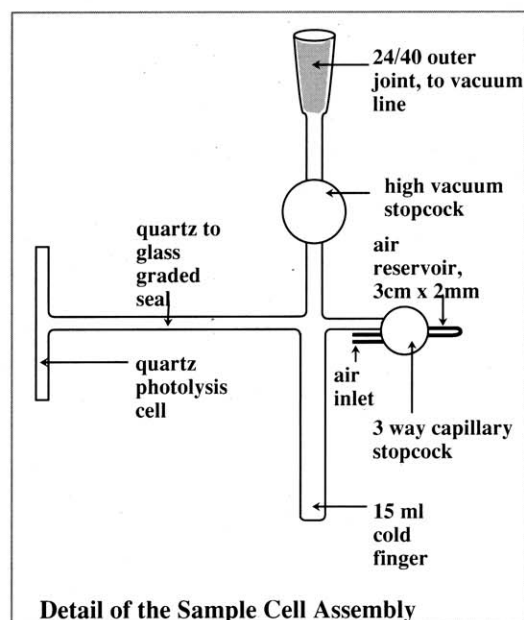


Figure 2. Diagram of the flash photolysis apparatus and sample cell assembly.



$$\tau = \frac{1}{k_{\text{obs}}} \quad (5)$$

Integration of the first-order rate equation (eq 4) and application of the Beer-Lambert Law

$$A = \epsilon l [T_1]$$

to the triplet concentration, yields

$$\ln A = -k_{\text{obs}}t + \ln A_0 \quad (6)$$

where A is the transient absorbance of triplet phenanthrene. A plot of $\ln A$ versus time at any concentration of added oxygen gives k_{obs} from the slope. Furthermore, a plot of k_{obs} versus $[{}^3O_2]$ gives k_2 from the slope (eq 4).

Experimental

Preparation of Sample

A magnetic stirring bar and approximately 0.2 mg of phenanthrene (Aldrich, 98%) are placed in the coldfinger of the sample assembly shown in Figure 2. The assembly is then evacuated to less than 10^{-5} torr, filled with purified argon, and reevacuated. Then *n*-hexane (15 mL, Aldrich

99+%), deoxygenated by three freeze-pump-thaw cycles, is trap-to-trap distilled into the coldfinger. The solution is stirred until the phenanthrene dissolves, giving an approximately 1×10^{-4} M solution. Then it is poured into the quartz cell (1 cm \times 12 cm) by tipping the assembly.

Flash Photolysis

Phenanthrene solutions are flashed in a conventional flash photolysis rig (Xenon Model 457A, modified to deliver 400 J/flash), which is shown in Figure 2. Light from a pair of xenon discharge lamps (Xenon) is used. This activating light is filtered through 10 mm of a filter solution prepared by adding 200 g/dm³ of CoCl₂ · 6H₂O and 100 g/dm³ of NiCl₂ · 6H₂O to aqueous 1 M HCl.

The peak transmittance of this solution is 290 nm, with upper and lower wavelength cutoffs at about 380 and 240 nm, respectively. The filter solutions permit the passage of the short-wavelength light needed to excite phenanthrene to the S₁ state. At the same time, they block longer wavelength (482 nm) light from the flashlamps used to monitor the absorbance of the transient triplet species. If the longer wavelength emissions from the flashlamps were not blocked, they would interfere with the absorbance measurements of the continuous probe light.

Flash energies ranging from 100 to 400 J are used, but lower intensities should also yield good transient absorbances. The flash intensity of our system reaches a maximum approximately 10 μ s after triggering. It decays to 10% of the maximum within 30 μ s and to less than 1% of the maximum in 40 μ s. Readings are taken of percent transmittance at 482 nm (the absorption maximum of the T₁ state of phenanthrene (8)) versus time, starting 40 μ s after initiation of the flash. This transient absorbance is monitored for 500 μ s after flash initiation using light from a 150-W continuous xenon arc lamp (PRA).

The variation in the transmitted intensity of the probe light through the sample cell is measured with a photomultiplier tube (Hamamatsu 1 P28) attached to a 10-cm pathlength monochromator (Instruments SA). The output from the PMT is amplified and fed to a storage oscilloscope (Tektronix Model 5115) for display as percent transmittance versus time. All runs are done at room temperature. No attempt is made to control temperature because reactions as fast as these will have small activation energies. Thus, their rate constants will show little temperature dependence.

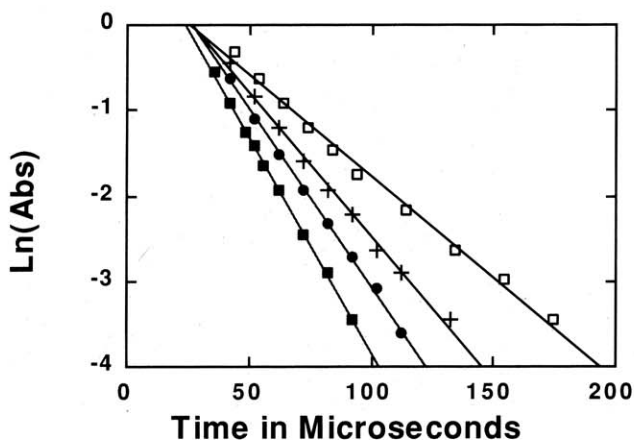


Figure 3. Transient absorbance of triplet state phenanthrene at 482 nm after four successive additions of air. Dioxygen concentrations: $\square = 7.1 \times 10^{-6}$, $+ = 14 \times 10^{-6}$, $\bullet = 21 \times 10^{-6}$, and $\blacksquare = 28 \times 10^{-6}$ M.

Addition of Oxygen

Small volumes of air are added to the sample by rotating the three-way stopcock (2-mm-i.d. capillary sidearms, Lab Glass) shown in Figure 2, pouring the solution back into the coldfinger, and stirring for 10 min. With the stopcock plug in one position, the reservoir in the sealed sidearm is open to the atmosphere. Rotating the plug 180° from this position admits an aliquot of air to the sample assembly. A reasonable volume of air to admit per run is 0.15 cm³. Four such additions will almost completely quench the transient absorbance of the triplet, although this will vary depending upon the concentration of the phenanthrene solution and the volume of the sample assembly.

The molar concentration of O₂ dissolved in hexane can be obtained for each run from Henry's Law (13) using a constant of

$$1.94 \times 10^{-5} \frac{\text{mol O}_2}{\text{L of solution}} \text{ mm Hg of O}_2 \text{ over the solution}$$

In calculating the O₂ pressure over the solution, we corrected for the amount of O₂ that dissolved in the solvent, although this has only a small effect on the plot of k_{obs} versus [O₂]. It may be neglected in all but the most careful work.

Safety Considerations

Safety goggles must be worn at all times when using glassware under vacuum. The electrical components of the flash apparatus should be constructed so that the high-voltage section is isolated and automatically turned off when accessed. In our system, all high-voltage components are in a grounded Faraday cage with an interlock on the door that shuts off the high voltage when the door is opened. The flash housing in our system is totally enclosed to block exposure to the intense light from the flashlamps. Furthermore, firing the flashlamps gradually weakens their walls, ultimately leading to their explosive failure. A totally enclosed flash housing will contain the flying glass.

To protect eyes from the high intensity analyzing light, UV filtering goggles should be worn during the photolysis steps. Also, an instructor is assigned fulltime to this experiment for reasons of safety and procedural complexity.

Results

Figure 3 shows typical results when a hexane solution of phenanthrene is flash-photolyzed with four successive aliquots of oxygen. Our results confirm the expected linearity

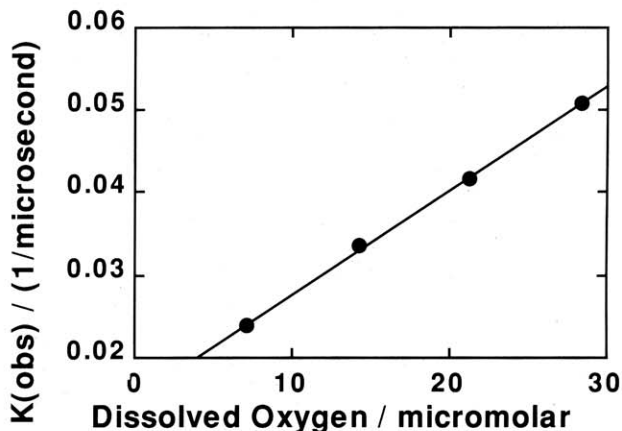


Figure 4. A plot of the pseudo-first-order rate constant for decay of the triplet state of phenanthrene (k_{obs}) versus O₂ concentration in *n*-hexane solvent.

of the plot of $\ln A$ versus time. Figure 4 contains a plot of k_{obs} versus $[\text{O}_2]$ from which the rate constant for deactivation of the triplet state by oxygen can be obtained from the slope.

We obtain a value of $(1.2 \pm 0.4) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ for k_2 in good agreement with Gijzeman, Kaufman, and Porter's (11) value of $1.33 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. The y intercept is equal to k_1 , the rate constant for first-order decay of T_1 . Our value of $(1.2 \pm 0.4) \times 10^4 \text{ s}^{-1}$ compares well with Porter and Wilkinson's (9) value of $1.07 \times 10^4 \text{ s}^{-1}$.

Discussion

Success with this experiment depends on a well-functioning vacuum line that can reach pressures less than 10^{-5} torr. We do this experiment in one 4-h laboratory period. However, the instructor must spend 1/2–1 h before lab attaching the hexane reservoir and sample cell assembly to the vacuum line and placing a weighed sample of phenanthrene in the sample cell.

Students gain experience with instrumentation that can track chemical reactions on a microsecond timescale. They also gain experience in preparing air-sensitive samples on a high-vacuum line. We discuss in some detail the principles of operation of our vacuum line while the students work—first while they degas their hexane solvent by a freeze–pump–thaw procedure, and then while they prepare their solution by trap-to-trap distilling a measured amount of the solvent into the cell containing the phenanthrene crystals.

A recent compilation of spectral parameters associated with triplet–triplet transitions of organic molecules in condensed phases by Carmichael and Hug (14) gives the extinction coefficient for T_1 phenanthrene at 482 nm as about $23,000 \text{ M}^{-1}\text{cm}^{-1}$. Instructors may wish to have their students use this number to calculate the approximate concentration of T_1 phenanthrene as a function of time for each of their runs. Using this number, the students can verify the assumption made in the kinetic analysis that $[\text{O}_2] \gg [T_1]$.

The focus of this experiment is on deactivation of triplet phenanthrene by O_2 . Another mode for deactivating T_1 phenanthrene is via interaction with another triplet phenanthrene in a process known as triplet–triplet annihilation. At least three parallel branches must be considered in the mechanism of triplet–triplet deactivation.



Liu and Faulkner (15) have measured the composite second-order rate constant k_7 for triplet–triplet annihilation for phenanthrene in ethanol solution. They report a value of $4.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. An informative exercise for students is to use this rate constant and their estimated concentration of triplet phenanthrene at an early stage of the deactivation

process (e.g., 40 μs after flash initiation) to calculate the rate of triplet–triplet annihilation (eq 8).

$$-\frac{d[T_1]}{dt} = k_7[T_1]^2 \quad (8)$$

This result can be compared with the rate of first-order deactivation (reactions 1 and 2) calculated from eq 3 for each of the oxygen concentrations used by the students to determine how important triplet–triplet annihilation is relative to reactions 1 and 2 in the deactivation of triplet phenanthrene.

Higher concentrations of phenanthrene solution will produce higher triplet concentrations, making triplet–triplet deactivation competitive with deactivation by first-order processes. Conversely, increasing oxygen pressures will favor the first-order processes. As a result, plots of $\ln A$ versus time, such as that shown in Figure 3, may show some curvature at low oxygen concentrations or high phenanthrene concentrations.

Conclusion

We have described an experiment that is suitable for the undergraduate physical chemistry laboratory. It uses flash photolysis to study the kinetics of oxygen-promoted deactivation of triplet excited states of aromatic hydrocarbons. Solutions of phenanthrene in hexane that contain known amounts of dissolved oxygen are prepared and flash-photolyzed. Measurement of the rate of decay of the transient absorbance due to T_1 phenanthrene as a function of oxygen concentration gives the rate constant for oxygen deactivation of triplet phenanthrene. This experiment introduces students to reactions that are important in the chemistry of excited-state molecules, as well as to techniques for studying fast reactions and preparing samples on a vacuum line.

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