

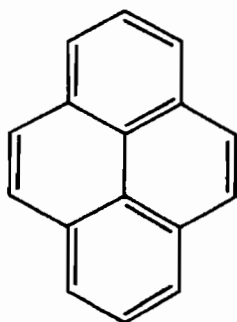
Experiment 36

The Enthalpy and Entropy of Excimer Formation

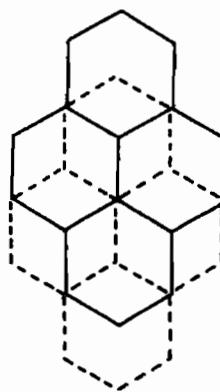
Objective To determine the enthalpy and entropy of formation of the dimer between ground state and electronically excited pyrene molecules in solution.

Introduction We know that the physical and chemical properties of a molecule are dictated by the nature of its electronic structure. It is not surprising, therefore, that such properties as acidity, dipole moment, and chemical reactivity may change considerably upon electronic excitation, in which there may be an abrupt change in the electronic wavefunction. In this experiment, you will investigate the pairwise interaction between pyrene molecules. The characteristics that we consider here relate to the *difference* in the properties of the interaction potential between two *ground state* molecules and also between a ground state and an electronically excited molecule.

Consider, then, the approach of two pyrene molecules along an axis perpendicular to their molecular planes. If both molecules are in the ground electronic state, there will be a very weak van der Waals attraction at moderate distances. At much closer approach, of course, significant intermolecular repulsion occurs. If, however, one of the molecules is in its *electronically excited* state (as a result of light absorption), and it is allowed to approach a ground state species with the appropriate orientation, a *stable dimer* will form. This dimer, whose structure is proposed to have a “sandwich” configuration (see below), is formed reversibly; that is, it can thermally dissociate back into an electronically *excited* pyrene molecule (excited monomer) and a ground state species.¹ This unusual dimeric species is stable *as long as it possesses electronic excitation* but dissociates as soon as this electronic excitation is dissipated and the system returns to the ground state. Such a species is called an *excimer* (from *excited dimer*).



Pyrene



Pyrene crystal dimer

A bound state that arises from the interaction between two dissimilar species when one is electronically excited is sometimes called an *exciplex* (excited complex) or heteroexcimer. Like

an excimer, an exciplex is dissociative in the electronic ground state. Because the excimer forms only when an electronically excited molecule and a ground state molecule come into specific and close contact with each other, excimer fluorescence is often used as a probe of molecular interactions. For example, pyrene-end-capped polymers are used to study the conformational structure and dynamics of linear chains. Excimer (or exciplex) emission is also used as a probe of the intercalation or binding of aromatic molecules into the crevices of certain macromolecules.

Figure 1 illustrates the potential energy diagram for electronic transitions and excimer formation. At large intermolecular separation (which occurs at low concentration), electronic transitions involving the excited monomer (absorption and fluorescence) are shown. The involvement of molecular vibrations in these transitions is also indicated. Although the monomer absorption and fluorescence spectra show vibrational structure (usually involving a skeletal mode), excimer emission is structureless. This is characteristic of electronic transitions (absorption or emission) between bound and unbound states.

The maximum in the excimer emission spectrum corresponds to transitions between the minimum of the excimer potential well (which exists at the equilibrium separation between the excimer components) and the unbound, ground state dimer having the *same* intermolecular separation as the excimer. Hence, excimer formation involves the creation of a bound species subsequent to photon absorption. Conceptually, this is the reverse of *photodissociation*, in which light absorption results in bond breakage. Moreover, photon emission in the excimer (fluorescence) brings about molecular dissociation, since the repulsive ground state pair rapidly dissociates.

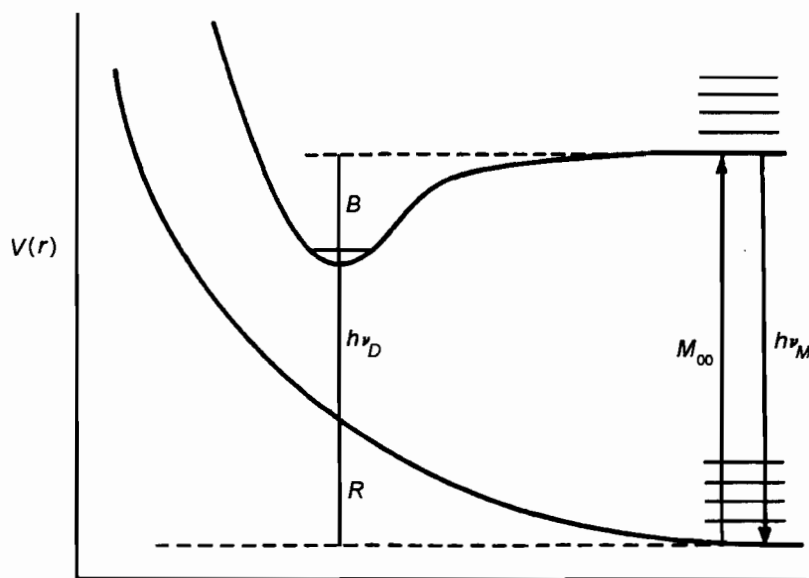


Figure 1. Potential energy of two pyrene molecules as a function of intermolecular separation. The coordinate r describes the approach of the molecules having the equilibrium orientation of the excimer. The right-hand transitions represent the isolated monomer (M).

The potential energy diagram in Figure 1 can also be used to compare the emission energies of monomer and excimer in terms of the excimer binding energy, B , and the ground state repulsion energy, R . Thus,

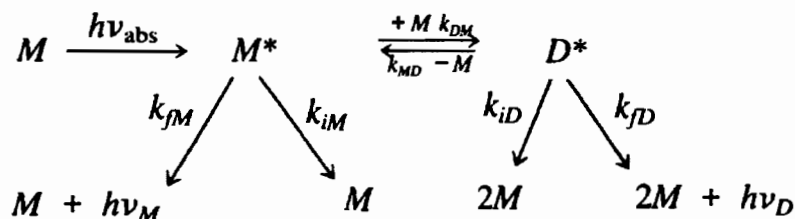
$$h\nu_M = h\nu_D + B + R, \quad (1)$$

where $h\nu_M$ represents the *monomer* fluorescence energy (called the 0-0 energy because the transition takes place between excited and ground state monomers possessing zero quanta of vibrational energy), and $h\nu_D$ is the energy of the *excimer* fluorescence maximum. The binding energy of the excimer is just the negative of its enthalpy of formation, i.e., $B = -\Delta H$ (the system is studied at constant pressure).

Kinetic Scheme

Excimer formation (called photoassociation) and reversible dissociation can be represented by the following set of elementary processes, or mechanism:

Process	Equation	Rate Constant
1. Electronic excitation	$M + h\nu_{\text{abs}} \rightarrow M^*$	(rate = I_{abs})
2. Photoassociation	$M^* + M \rightarrow D^*$	k_{DM}
3. Excimer dissociation	$D^* \rightarrow M + M^*$	k_{MD}
4. Excited monomer decay	$M^* \rightarrow M + h\nu_M$ $M^* \rightarrow M + \dots$	k_{fM} k_{iM}
5. Excimer decay	$D^* \rightarrow (M_2)' + h\nu_D$ $D^* \rightarrow 2M + \dots$	k_{fD} k_{iD}



In the above scheme, I_{abs} is the number of moles of photons (einsteins) absorbed by ground state monomer per cubic decimeter per second. For convenience, k_M and k_D are defined as the total *intrinsic* (i.e., intramolecular) decay rate constants of monomer and excimer, respectively, *independent* of photoassociation or dissociation, i.e.,

$$k_M = k_{fM} + k_{iM} \quad \text{and} \quad k_D = k_{fD} + k_{iD}. \quad (2)$$

k_{DM} is the second-order rate constant for excimer formation from M and M^* (DM denotes "dimer from monomer"), and k_{MD} refers to the first-order rate constant for the dissociation of the excimer into M^* and M (MD denotes "monomer from dimer"). The formation rate of excited monomer (in $\text{mol dm}^{-3} \text{s}^{-1}$) is

$$\frac{d[M^*]}{dt} = I_{\text{abs}} - (k_M + k_{DM}[M])[M^*] + k_{MD}[D^*], \quad (3)$$

while that for the excimer is

$$\frac{d[D^*]}{dt} = k_{DM}[M][M^*] - (k_D + k_{MD})[D^*]. \quad (4)$$

Note that $k_{DM}[M]$ is the pseudo-first-order rate of formation of excimer from excited and ground state monomers. Also, it is implied that $[M^*] \ll [M]$; i.e., a very small fraction of monomer is electronically excited. In experiments using conventional light sources (arc lamps, not focused lasers) this is indeed the case.

Under conditions of steady-state illumination, the rates in both equations (3) and (4) are equal to zero (photostationary conditions). The ratio of $[D^*]$ to $[M^*]$ can be thus obtained

$$\frac{[D^*]}{[M^*]} = \frac{k_{DM}[M]}{k_D + k_{MD}}. \quad (5)$$

It stands to reason that since the objective of this experiment is the determination of thermodynamic quantities, we must determine the temperature dependence of the excimer formation equilibrium constant. Therefore, the first thing we need to do is to obtain the *equilibrium concentrations* of M , M^* , and D^* . First, we will assume that the equilibrium ground state concentration $[M]$ is equal to the bulk pyrene concentration. This is consistent with the inequality $[M^*] \ll [M]$ discussed above. The second crucial, and fundamental, assumption is that the fluor (i.e., fluorescent species) concentration (i.e., $[M^*]$ or $[D^*]$) is proportional to its respective *fluorescence intensity*. This is a basic tenet of spectrofluorimetry and is perhaps analogous to Beer's law in absorption spectrophotometry.

This experiment is based on the fact that it is possible to obtain the ratio of excimer to excited monomer concentrations from the measured fluorescence intensities, each measured at the appropriate wavelength. Both of the fluor concentrations are assumed to be proportional to the respective *integrated fluorescence intensities* (areas under the monomer and excimer fluorescence spectra),

$$I_{fM} = k_{fM}[M^*] \quad \text{and} \quad I_{fD} = k_{fD}[D^*], \quad (6)$$

where the proportionality constants are the *radiative rate constants*. The dimensions of I_f are einsteins $\text{dm}^{-3} \text{s}^{-1}$ (an einstein is 1 mol of photons). Combining equations (5) and (6), we have

$$\frac{I_{fD}}{I_{fM}} = \frac{k_{fD}k_{DM}[M]}{k_{fM}(k_D + k_{MD})}. \quad (7)$$

Equation (7) is central to the application of photostationary techniques to the study of photoassociation. (The distinction between the integrated and “instantaneous” fluorescence intensities will be discussed below.)

Because we seek thermodynamic data, we will examine the temperature dependence of equation (7). First, we make the general observation that both the formation and dissociation rate constants are temperature-dependent and can be expressed in Arrhenius form:

$$k_{DM} = A_{DM} \exp\left(\frac{-E_{DM}}{RT}\right) \quad \text{and} \quad k_{MD} = A_{MD} \exp\left(\frac{-E_{MD}}{RT}\right), \quad (8)$$

where the A 's and E 's are the preexponential factors and activation energies, respectively. Because intermolecular excimer formation is restricted only by molecular transport, or diffusion, the activation energy, E_{DM} , is related to the activation to viscous flow of the solvent medium. E_{MD} , however, reflects the intrinsic strength of the “excimer bond” as well as the energetics of molecular diffusion. This is because E_{MD} represents the activation energy for the *dissociation* of the bound excimer into *separated* and individually solvated excited and ground state constituents.

If we assume that the temperature dependence of k_{MD} , the rate constant for thermally activated excimer dissociation, is much larger than that for k_D , the intrinsic decay rate of excimer (indeed, for many systems, k_D is nearly temperature-independent), we have $k_{MD} \gg k_D$ in the limit of high temperature. Applying this result to equation (7), we have

$$\frac{I_{fD}}{I_{fM}} \approx \frac{k_{fD}k_{DM}[M]}{k_{fM}k_{MD}} \quad (\text{high temperature}). \quad (9)$$

If we furthermore make the general assumption (which has been confirmed by measurements of several monomer/excimer systems) that both radiative rate constants (k_{fM} and k_{fD}) are temperature-independent, an Arrhenius plot of I_{fD}/I_{fM} yields, in the limit of high temperature, a slope

$$\frac{d \ln \left(\frac{I_{fD}}{I_{fM}} \right)}{d \left(\frac{1}{T} \right)} = \frac{-(E_{DM} - E_{MD})}{R} \quad (\text{high temperature}). \quad (10)$$

See equations (7) and (8). Because $E_{MD} > E_{DM}$, the desired binding energy (the negative of the enthalpy of formation) of the excimer can be determined as the slope of such a plot.

At low temperatures, where excimer dissociation is slow compared with its intrinsic decay rate (i.e., $k_{MD} \ll k_D$), we can write equation (7) as

$$\frac{I_{fD}}{I_{fM}} \approx \frac{k_{fD}k_{DM}[M]}{k_f M k_D} \quad (\text{low temperature}). \quad (11)$$

An Arrhenius plot of the left-hand side of (7) will have a slope approaching

$$\frac{d \ln \left(\frac{I_{FD}}{I_{FM}} \right)}{d \left(\frac{1}{T} \right)} = \frac{-E_{DM}}{R} \quad (\text{low temperature}). \quad (12)$$

E_{DM} has been found to be closely related to the activation energy associated with molecular diffusion (hence bulk viscous flow) in the solvent medium. This is one of the reasons that excimer formation is interpreted as a diffusion-controlled process.

An Arrhenius plot of equation (7) illustrates the behavior of the monomer and excimer fluorescence spectra over a wide temperature range (Figure 2). At low temperature, the ratio of excimer to monomer emission is small because excimer formation is impeded by the high viscosity of the solvent; indeed, in a glass or rigid medium, excimer formation does not take place because of the inability of excited monomer and ground state species to diffuse. (It is possible, however, that weak van der Waals dimers may be stable at low temperatures and that emission from these directly photoexcited dimers may be observed. Strictly speaking, this is not excimer emission.) At very high temperature, excimer emission is also suppressed because of the high dissociation rate of the excimer. Thus there is an intermediate temperature at which there is a maximum excimer emission intensity relative to the excited monomer. This temperature depends not only on the nature of the excimer system (its binding energy and entropy of formation) but also on the solvent characteristics such as its viscosity and activation to viscous flow.

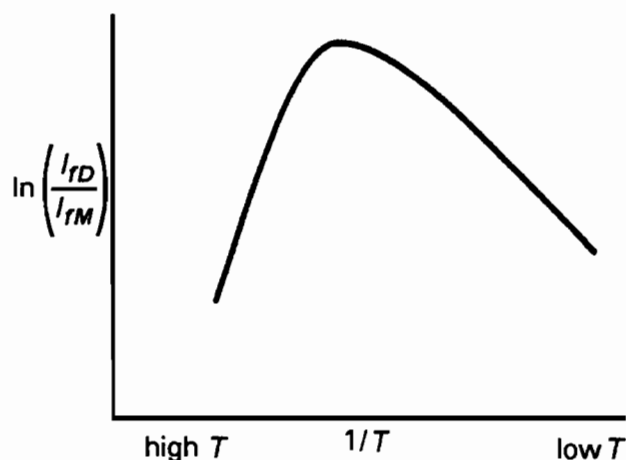


Figure 2. Arrhenius plot of the ratio of excimer to monomer fluorescence intensities. The low-temperature regime (right) reflects the activation energy of excimer formation, whereas the high-temperature regime (left) indicates the “equilibrium” enthalpy of excimer formation.

Another very important condition, which is pertinent to the high-temperature limit and is crucial to this experiment, concerns the fact that if interconversion between photoexcited monomer and excimer is rapid relative to the intrinsic decay rates of M^* and D^* , these species are in *dynamic equilibrium*. Thus with

$$k_{DM}[M] \gg k_M \quad \text{and} \quad k_{MD} \gg k_D,$$

$K_{\text{eq}} = [D^*]_{\text{eq}}/[M^*]_{\text{eq}}[M]_{\text{eq}}$, we can express the true *equilibrium constant* (we assume unit activity coefficients) for photoassociation as the ratio of the formation and dissociation rate constants. Using this result and rearranging equation (9), we have

$$K_{\text{eq}} = \frac{k_{DM}}{k_{DM}} = \frac{k_{fM} I_{fD}}{f_{fD} I_{fM} [M]}. \quad (13)$$

The high-temperature or dynamic equilibrium regime can be depicted by an analogy to two leaky containers connected to each other by two tubes, each containing a pump. Refer to Figure 3. The containers are filled with a liquid. If the leak rate in container A is small compared with the rate of transport of liquid from container A to container B , and, likewise, the leak rate of container B is small relative to the flow rate from B to A , the amounts of liquid present in each container depend only on the $A \rightarrow B$ and $B \rightarrow A$ flow rates. This situation thus represents the dynamic equilibrium state; the volumes of liquid in A and B are intrinsic to the plumbing between them. On the other hand, if one of the leak rates is too large, the volume of liquid in that container will be depleted and will not reflect the "equilibrium" condition.

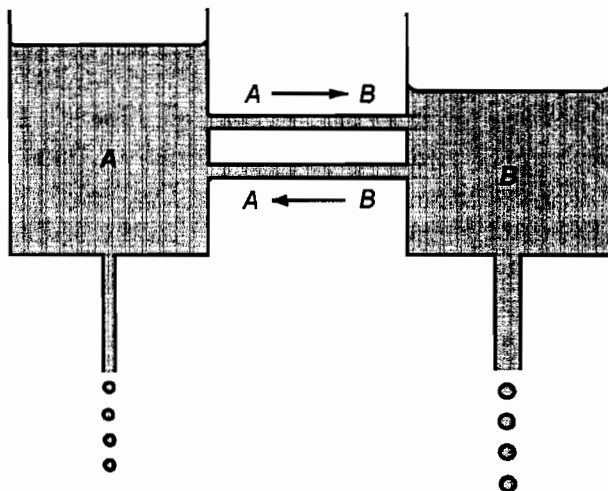


Figure 3. Hydrodynamic model of reversible reactions between two metastable (electronically excited) species.

The link between K_{eq} and the enthalpy and entropy of excimer formation is

$$-RT \ln K_{\text{eq}} = \Delta G^\circ - T \Delta S^\circ, \quad (14)$$

and if we combine the expressions in equations (13) and (14), we can represent the temperature dependence of I_{fD} and I_{fM} as

$$\ln \left(\frac{I_{fD}}{I_{fM}} \right) = -\ln \left(\frac{k_{fM}}{k_{fD} [M]} \right) + \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}. \quad (15)$$

Assuming that k_{fM} and k_{fD} are temperature-independent, a plot of $\ln (I_{fD}/I_{fM})$ vs. $1/T$ should be linear, having a slope equal to $-\Delta H^\circ/R$. The intercept can also provide a value of ΔS° if we know the ratio of the radiative rate constants of the excimer and monomer. While this information can be obtained from fluorescence lifetime and efficiency studies, Stevens and Ban have described a photostationary fluorimetric technique for obtaining ΔS° and ΔH° ;² we will discuss this below.

There is another interesting consequence of high-temperature conditions. Although the *distribution* between D^* and M^* changes with temperature in this regime, the *total* concentration of excited states ($D^* + M^*$) remains constant. In other words, M^* and D^* form a "closed system." Hence,

$$[M^*]_T + [D^*]_T = \text{constant} = [M^*]_0, \quad (16)$$

where the temperature dependence of the excited monomer and excimer concentrations is explicit. The spectrometric significance is that there is a specific wavelength between the maxima of the monomer and excimer emission spectra at which the emission intensity is independent of temperature. This position, called the *isostilbic* (equal brightness) *point*, is analogous to the isosbestic point (equal extinction) seen in absorption spectra when there is linear relationship between the concentrations of two absorbing species.

In order to proceed with the fluorimetric analysis, we must consider the important distinction between the total molecular fluorescence intensity, I_{fM} (area under the spectrum), and the fluorescence intensity at a specific wavelength, f_M . The latter is a function of energy or wavenumbers [$f_M(\bar{\nu})$ represents the monomer emission spectrum], whereas the former is a constant at a given temperature and monomer concentration. This distinction is important, because in this experiment, we measure fluorescence intensities of the monomer and excimer emission spectra at *specific* wavelengths (e.g., the respective maxima) rather than the total areas under the spectra. The relationships between the total intensity and the instantaneous intensity are

$$I_{fM} = C \int f_M(\bar{\nu}) d\bar{\nu} \quad \text{and} \quad I_{fD} = C' \int f_D(\bar{\nu}) d\bar{\nu}. \quad (17)$$

C and C' are instrumental constants that link the integrals of instantaneous intensities with the molecular fluorescence strengths.

One problem with the analysis presented thus far is that we need the ratio of the excimer and monomer radiative rate constants, $k_{D^{\circ}}/k_{M^{\circ}}$ [see equations (7), (9), and (11)]. Although this information can be obtained independently from fluorescence lifetime and (absolute) quantum efficiency measurements, Stevens and Ban have described an approach that gets around this problem. Observe in equation (15) that the value of $k_{D^{\circ}}/k_{M^{\circ}}$ is needed only to determine the *entropy* of photoassociation (i.e., an absolute intercept).

Although the method for obtaining this information from fluorimetric measurements is straightforward, the development of the result is presented in the appendix. The approach is as follows.

Let R_D° and R_M° be the recorded intensities of excimer and monomer at their respective maxima. In the high-temperature regime, a plot of R_D° vs. R_M° (for different temperatures) is expected to be linear with a negative slope ($-a/b$). Thus, as the temperature increases, the excimer intensity decreases with a concomitant increase in the monomer intensity. The relation used to obtain the entropy and enthalpy of excimer formation is

$$\ln \left(\frac{R_D^{\circ}}{R_M^{\circ}} \right) = \ln \left\{ [M] \left(\frac{b}{a} \right) \right\} + \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \quad (18)$$

Safety Precautions

- Safety glasses that block ultraviolet light must be worn during this experiment.
- Wear gloves when handling pyrene.
- Make sure you are instructed in proper pipetting techniques. Never pipet by mouth.
- If solid pyrene or its solutions come in contact with the skin, immediately wash the affected area with soap and water.
- A cylinder containing N_2 at high pressure is used. Be sure it is securely attached to a firm foundation. A reducing valve is used to deliver the N_2 at a pressure slightly above ambient (< 5 psig). Do not change this pressure.
- The fluorimeter may produce ozone. Make sure the ultraviolet source is vented. If you notice a sharp, pungent odor, inform your instructor immediately.
- The experiment must be performed in an open, well-ventilated laboratory.

Procedure

Prepare 25 mL of a 5.0×10^{-3} M solution of pyrene in methylcyclohexane. The pyrene should be of high purity (and should be sublimed or recrystallized before use if necessary). The solvent must have a negligible fluorescence background and preferably should be of spectrometric quality.

Add sufficient solution to a fluorescence cell that is equipped with a gas-tight, PTFE (Teflon) stopper. Deaerate by bubbling a fine stream of pure dry N_2 through the solution for 4 to 6 min. Control the gas flow so that solution is not expelled from the cell. [Deaerating with N_2 is *essential* because it displaces dissolved oxygen, which significantly quenches the pyrene fluorescence. This procedure is an application of Henry's law; the air above the liquid is replaced

by an atmosphere of nitrogen and thus the solubility of oxygen approaches a very low value commensurate with the residual oxygen composition in the nitrogen used. Bubbling of the nitrogen through the liquid hastens gas-liquid equilibrium.]

Immediately after deaerating, firmly stopper the fluorescence cell. Wipe the four windows (cleaning if necessary with ethanol) using lens paper or the equivalent; be sure not to scratch the cell. Place the cell in the fluorimeter cavity.

Your instructor will show you how to obtain emission spectra using the particular fluorimeter and how to vary and measure the temperature of the sample. Use an excitation wavelength of ~370 to 380 nm. When the sample is exposed to the ultraviolet radiation, you should be able to see the bright blue-violet fluorescence. Scan the emission between 370 and about 500 nm. The number of spectra you obtain will depend on the available time, but you should acquire *at least five spectra*, taken between 60 and 100°C. The temperature should remain constant (to within 0.5°C) during a given scan.

If possible, overlap these spectra on a common wavelength axis. Preferably, and if time permits, run spectra over a wider temperature range, e.g., 0 or 20 to 100°C. Note that even if the excitation lamp fluctuates or drifts during the experiment, the data are still valid as long as this change does not occur *during a particular scan*.

Data Analysis

Tabulate in a spreadsheet the recorded fluorescence intensities of the monomer and excimer (R_M^0 and R_D^0) at each temperature; choose convenient wavelengths (e.g., at or near the respective maxima).

Plot R_M^0 vs. R_D^0 and determine b/a from the linear portion (corresponding to the high-temperature regime).

From equation (18) determine ΔS^0 and ΔH^0 for the pyrene excimer formation in methylcyclohexane using the values of b/a and $[M]$.

Determine the binding energy of the pyrene excimer as well as the repulsion energy of the ground state pyrene pair having the excimer geometry [equation (1)].

If you achieved low enough temperatures in the experiment, estimate the activation energy to excimer formation and compare it with the activation energy of viscosity of the solvent (or similar hydrocarbon).

Estimate the errors in ΔS^0 , ΔH^0 , B , and R .

Questions and Further Thoughts

1. What effect would solvent polarity (e.g., acetonitrile vs. cyclohexane) have on the transition energies of the monomer and excimer and the binding energy of the excimer? Consider the same effect(s) on an exciplex, e.g., pyrene (or anthracene) and *N,N*-dimethylaniline.

2. The "excimer" laser is based on transitions between the bound state formed with rare gas and halogen atoms [e.g., (ArF)^{*}, XeCl^{*}] and the dissociative ground state of these species. One of the advantages of an excimer laser is that after emission takes place from the excited complex, the ground state is rapidly removed because it is dissociative. This allows a significant population inversion to be achieved, and this enhances lasing efficiency.

3. Does this statement make sense: The ground state of an excimer is an excited state?
4. The probability that the ends of a linear chain oligomer (or polymer) come into close proximity can be probed by attaching pyrene probes to the ends of the molecule (end-capped polymers). How does such a technique work? What type of experiment is needed to gather information about the end-to-end interactions?
5. The fluorescence of some excimers can readily be observed only at moderately low temperatures (and high concentrations), yet at very low temperatures, where the solvent becomes glassy or crystalline, excimer fluorescence nearly vanishes. How can you explain these observations?
6. Suppose the pyrene excimer were formed in the gas phase, and each ground state pyrene molecule formed as a result of excimer fluorescence had a recoil energy. Estimate the speed of the recoiling molecules. Describe the trajectory.
7. Reducing the dissolved O_2 concentration by bubbling the solution with N_2 (deaeration) is an application of Henry's law. Explain how deaeration works in the context of Henry's law.
8. Suggest some ideas that account for the fluorescence quenching effect by dissolved O_2 .

Notes

1. J. B. Birks, *Photophysics of Aromatic Molecules*, pp. 301–371, Wiley-Interscience (London), 1970.
2. B. Stevens and M. I. Ban, *Trans. Faraday Soc.*, 60:1515 (1964).

Further Readings

- J. B. Birks, D. J. Dyson, and I. H. Munro, *Proc. Roy. Soc. A*, 275:575 (1963).
 B. Stevens, Photoassociation in Aromatic Systems, in *Advances in Photochemistry*, J. N. Pitts, Jr, G. S. Hammond, and W. A. Noyes, Jr., vol. 8, pp. 161–226, Wiley-Interscience (New York), 1971.

Appendix

The fluorescence intensity at the isostilbic point (at wavenumber I) is composed of the separate contributions of monomer and excimer emission

$$f_i = f_{iM} + f_{iD} \quad (19)$$

Each emission is, in turn, proportional to its respective integrated fluorescence spectrum, i.e.,

$$f_{iM} = m \int f_M(\bar{\nu}) d\bar{\nu} \quad \text{and} \quad f_{iD} = d \int f_d(\bar{\nu}) d\bar{\nu} \quad (20)$$

After combining equations (17), (19), and (20), we have for the isostilbic intensity,

$$f_i = \frac{m}{C} I_{JM} + \frac{d}{C} I_{JD} \quad (21)$$

Now, using equation (6), which expresses the absolute fluorescence intensities in terms of radiative rate constants and excited state concentrations, and equation (16), which states the "closed system" constraint of the high-temperature limit, equation (21) becomes

$$f_i = \frac{m}{C} k_{fM} [M^*] + \frac{d}{C} k_{fD} \{ [M^*]_0 - [M^*] \}, \quad (22)$$

which can be factored to give

$$f_i = \frac{d}{C} k_{fD} [M^*]_0 + [M^*] \left(\frac{m}{C} k_{fM} - \frac{d}{C} k_{fD} \right). \quad (23)$$

Because both f_i and the first term of the right-hand side of equation (22) are independent of temperature (in the high-temperature regime), while $[M^*]$ is temperature-dependent, the bracketed term in equation (22) must be zero. Thus, $d/m = k_{fM}/k_{fD}$, and combining this result with equations (20) and (17) furnishes the relation

$$\frac{f_{iD}}{f_{iM}} = \frac{dI_{fD}}{mI_{fM}} = \frac{k_{fM}I_{fD}}{f_{fD}I_{fM}},$$

or

$$\frac{I_{fD}}{I_{fM}} = \left(\frac{k_{fD}}{k_{fM}} \right) \left(\frac{f_{iD}}{f_{iM}} \right). \quad (24)$$

The importance of equation (24) is that we can now express the enthalpy and entropy of photoassociation in terms of the experimentally determined contributions of monomer and excimer fluorescence to the isostilbic intensity. Combining equations (24) and (15), we have

$$\ln \left(\frac{f_{iD}}{f_{iM} [M]} \right) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}. \quad (25)$$

Now, the problem is to find a way of decomposing f_i into f_{iM} and f_{iD} . We again follow the Stevens and Ban procedure. To understand this approach, we must make the distinction between the *absolute* fluorescence intensity (f_{iM} , referred to above) and the *observed instrumental* response, or signal strength (R_{iM}). Because the combination of the analyzing monochromator and photomultiplier tube in the particular fluorimeter used has a unique, nonuniform wavelength dependence, a given emission spectrum will be distorted by an instrumental sensitivity function, $S(\lambda)$, which can be expressed as

$$R(\lambda) = [S(\lambda)][I(\lambda)], \quad (26)$$

where $R(\lambda)$ is the actual wavelength distribution of the instrument response to a radiant source of known wavelength distribution, $I(\lambda)$.

There are various experimental techniques that can be used to determine the sensitivity function $S(\lambda)$. For example, a standard emission source having a known output spectrum [absolute power density as a function of

wavelength, $I(\lambda)$] may be used to calibrate the analyzing system. These sources are often a quartz halogen tungsten lamp—a black-body radiator—for the near-infrared and visible region, and a deuterium lamp for the ultraviolet range. The observed emission profile of the lamp is obtained using the particular fluorimeter, $R(\lambda)$, and the sensitivity function is then obtained by performing a point-by-point division of $R(\lambda)$ by $I(\lambda)$. This can easily be achieved if the R and S data are acquired digitally. Many fluorimeter manufacturers furnish these calibration data with the particular instrument.

At the isostilbic point, the observed emission intensity, R_i , is composed of contributions from excited monomer and excimer at that wavelength:

$$R_i = R_{iD} + R_{iM} \quad (27)$$

Because the sensitivity function, S_i , is the *same* for both species at a common wavelength (e.g., the isostilbic point), the ratio of the response contributions will be equal to that of the absolute intensities:

$$\frac{f_{iD}}{f_{iM}} = \frac{R_{iD}}{R_{iM}} \quad (28)$$

Now, we relate these response values to those at different reference wavelengths at which it is assumed *only* excimer and excited monomer, respectively, emit (these reference wavelengths may be taken to be the maxima of the monomer and excimer emission spectra; see Figure 1). Referring to the observed instrumental responses at these reference wavelengths as R_D° and R_M° , respectively, we can assume the following proportion between R_{iD} and R_D° , etc.:

$$R_{iD} = aR_D^\circ \quad \text{and} \quad R_{iM} = bR_M^\circ \quad (29)$$

where the constants a and b are temperature-independent. Combining equations (28) and (29) gives

$$\frac{f_{iD}}{f_{iM}} = \frac{aR_D^\circ}{bR_M^\circ} \quad (30)$$

The ratio a/b can be obtained from a plot of R_M° vs. R_D° in which the set of $\{R_M^\circ, R_D^\circ\}$ is obtained over the temperature range for which $k_{MD} \gg k_D$ and $k_{DM}[M] \gg k_M$ (i.e., the high-temperature regime). This is justified by using equations (27) and (29):

$$R_i = \text{constant} = aR_D^\circ + bR_M^\circ$$

Differentiation of R_M° with respect to R_D° gives

$$\frac{dR_M^\circ}{dR_D^\circ} = -\frac{a}{b} \quad (\text{high temperature}). \quad (31)$$

Hence, a/b can be obtained by plotting R_M° vs. R_D° in this way, the needed fluorescence intensity ratio can be obtained from the observed instrumental response data. See equation (30).

The final working result in the Stevens-Ban method, obtained by combining equations (25) and (30), is equation (32):

$$\ln \left(\frac{R_D^\circ}{R_M^\circ} \right) = \ln \left\{ [M] \frac{b}{a} \right\} + \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (32)$$