

The Kinetics of a Diffusion-Controlled Reaction

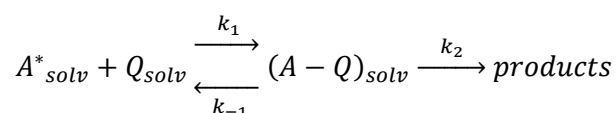
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Introduction and Objective

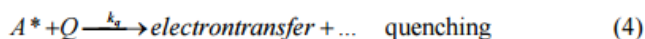
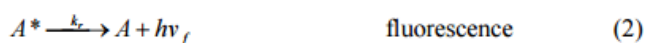
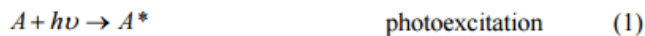
This experiment attempts to model and understand the kinetics of a diffusion-controlled reaction. The “reaction” studied in this lab is the fluorescence quenching that occurs between anthracene (represented as **A**), a polycyclic aromatic hydrocarbon, which fluoresces if excited (at which point it is represented as **A***) and CBr₄ (**Q**), which is capable of quenching this fluorescence. The quenching involves an electron transfer from the excited species A* to Q (which is more electronegative than A* due to the presence of bromine atoms). The reaction, or quenching only takes place once the molecules are within a certain distance of each other, **R**, known as the collision radius. Since the molecules have to pass through the solvent to reach each other, the rate at which they come within a distance R to each other is determined by the rate of their diffusion through the solvent. When the molecules do come near each other to react, they enter a “solvated encounter complex” at which point there are no more solvent molecules separating the two reactants, but rather they are both surrounded by a solvent cage. Once the reactants are in this solvent cage, the quenching reaction proceeds very quickly, as there are no remaining barriers preventing the electron transfer from A* to Q. What this means is that in the reaction scheme below is that $k_2 \gg k_1$ and that the rate of reaction is determined by the rate of diffusion of the reactants into the cage, or the formation of the caged intermediate, therefore, it can be said that the kinetics of this reaction are diffusion-controlled.



This is a slight simplification as the rate of diffusion into the cage and formation of the encounter complex, is determined by the rate of formation of this complex, the rate of dissociation of this complex, and the rate of reaction in the complex to form the products. Since the reaction proceeds so quickly once the encounter complex is formed, it appears that the rate of formation of this complex is 0, this is also known as the steady-state approximation, represented below.

$$\frac{d[A^* - Q]}{dt} = k_1[A^*][Q] - k_{-1}[A^* - Q] - k_2[A^* - Q] = 0$$

The kinetics of this reaction deviates from the diffusion controlled model when the concentration of reactants is high because when this is the case, the distance between the reactants is smaller, by nature of there being more of them in solution, so much so that the rate of reaction no longer depends on the diffusion of the molecules into the solvent cage. Once some of the reactants turn into products and the overall concentration of reactants is low, the rate of reaction can once again be modelled by diffusion-controlled kinetics. This first part of the reaction, when reactant concentrations are high, is reflected in the kinetics model by a “transient term” that disappears once reactant concentrations are low.



The transformations involved in the fluorescence of a molecule are represented to the right. When a quencher is not present in solution, the fluorescent species will naturally decay through fluorescent and nonradiative decay. As the quencher concentration increases in solution

process (4) on the right begins to compete with (2) and (3) and the fluorescence decays at a faster rate. If the fluorescence intensity of a non-quenched species, I_0 , is compared to that of a quenched species, a relationship can be determined between this ratio of non-quenched to quenched fluorescence I_0/I , and the concentration of the quencher. This relationship is summarized in the Stern-Volmer equation

$$\frac{I_0}{I} - 1 = k_1\tau_0[Q]$$

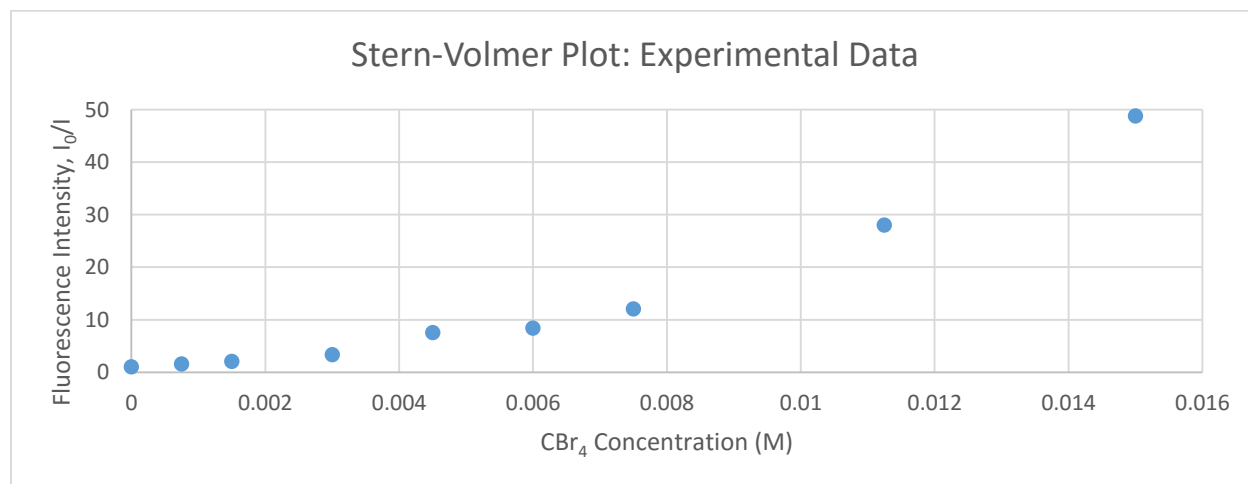
The goal of this experiment is to use the fluorescence intensities of solutions containing varying ratios of A^* to Q to model the kinetics of this reaction using the Stern-Volmer equation and the Stokes-Einstein-Smoluchowski (SES) equation.

Experimental Procedure

First 250 mL of 0.1 mM anthracene was prepared with hexane as the solvent. Then 25 mL of 0.015 M CBr_4 was prepared using the first solution as the solvent. Nine dilutions of the CBr_4 stock solution were made using the anthracene solution as a solvent. Both 0% CBr_4 and 100% CBr_4 solutions were prepared. About 2 mL of each dilution was placed in a quartz fluorescence cell and deaerated with nitrogen gas for two minutes. The cell was stoppered to prevent re-aeration. The fluorescence spectrum was recorded from 300 nm to 650 nm at an excitation wavelength of 283 nm. The excitation slit was set to 2.5 nm. The emission slit was set to 2.5 nm. The PMT voltage was set to 400 V. The fluorescence intensity of each sample at the emission maximum of 398 nm was recorded.

Results and Discussion

The final concentration of CBr_4 , was determined for each dilution. Then the ratio of unquenched fluorescence intensity, I_0 , to quenched fluorescence intensity, I , was determined for each solution. This ratio I_0/I was plotted against $[Q]$, the concentration of the quenching species, as can be seen in Graph 1 below.



Graph 1: The experimental "unquenched fluorescence intensity to quenched fluorescence intensity" ratio, I_0/I plotted against the concentration of the quenching species, CBr_4 , $[Q]$.

Next, the Stokes-Einstein-Smoluchowski equation was used to determine the rate constant of this diffusion-controlled reaction. The equation is shown below, where R is the universal gas constant, T is

the temperature, and η is the viscosity of the solvent (hexane in this instance). $R = 8.314 \times 10^7 \text{ erg mol}^{-1} \text{ K}^{-1}$, $T = 298 \text{ K}$, $\eta = 0.003 \text{ P}$

$$k_1 \cong \frac{8RT}{3000\eta} \quad \text{Equation 1}$$

By this method, k_1 was found to equal $2.202 \times 10^{10} \text{ dm}^3 \text{ s}^{-1} \text{ mol}^{-1}$.

Then by using the following relation, it is possible to determine the collision radius, R .

$$\lim_{t \rightarrow \infty} k_1 = \frac{4\pi R D N_A}{1000} \rightarrow R = \frac{1000 k_1}{4\pi D N_A} \quad \text{Equation 2}$$

In this equation D is the diffusion coefficient $D_{\text{hexane}} = 5.60 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (it was calculated based on the diffusion coefficient of n-heptane, $D_{\text{heptane}} = 4.35 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) and $N_A = 6.022 \times 10^{23}$ is Avogadro's number. The lab manual states that D is proportional to T/η .

$$D = C \frac{T}{\eta} \quad \text{so} \quad D\eta = CT \quad \text{and} \quad D_{\text{heptane}}\eta_{\text{heptane}} = CT = D_{\text{hexane}}\eta_{\text{hexane}}$$

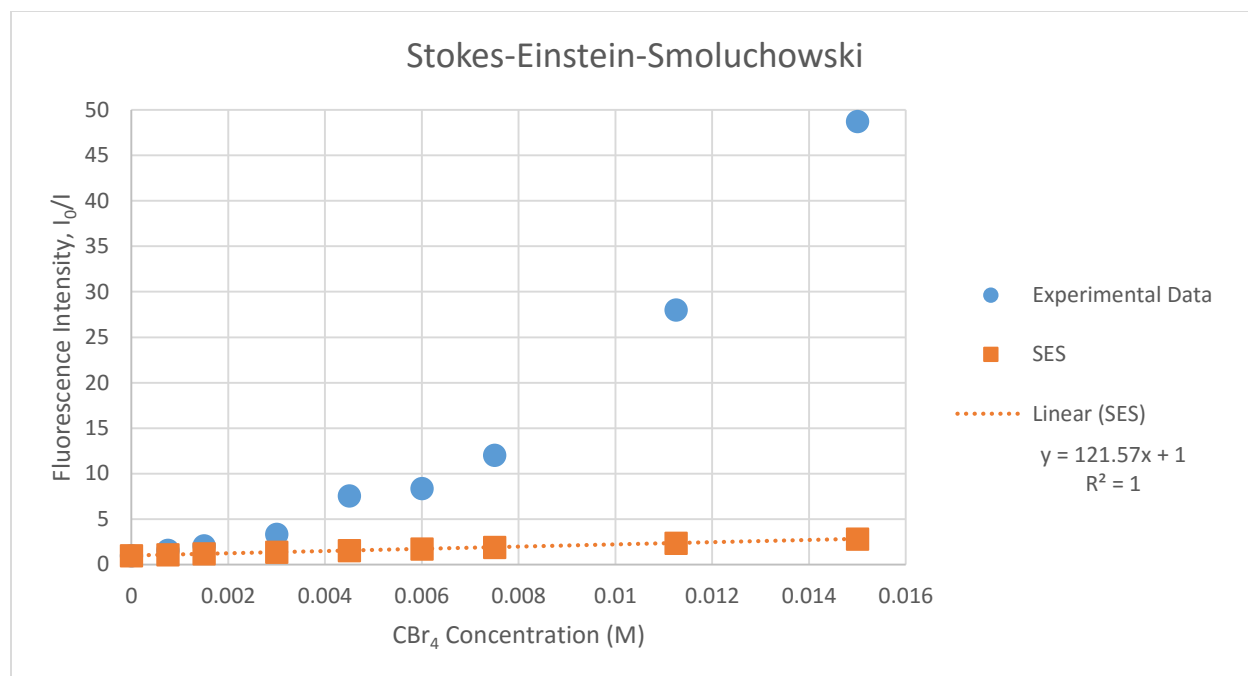
$$D_{\text{hexane}} = \frac{D_{\text{heptane}}\eta_{\text{heptane}}}{\eta_{\text{hexane}}} = \frac{(4.35 \times 10^{-5} \text{ cm}^2/\text{s})(0.00376 \text{ P})}{0.003 \text{ P}} = 5.60 \times 10^{-5} \text{ cm}^2/\text{s}$$

The collision radius was found to equal $5.120 \times 10^{-10} \text{ m}$ or 5.120 \AA .

Using the k_1 value determined from the SES equation, and knowing the fluorescence lifetime, $\tau_0 = 5.52 \times 10^{-9} \text{ s}$, it was possible to plot theoretical I_0/I values using the following relation known as the steady state Stern-Volmer relation.

$$\frac{I_0}{I} - 1 = k_1 \tau_0 [Q] \quad \text{Equation 3}$$

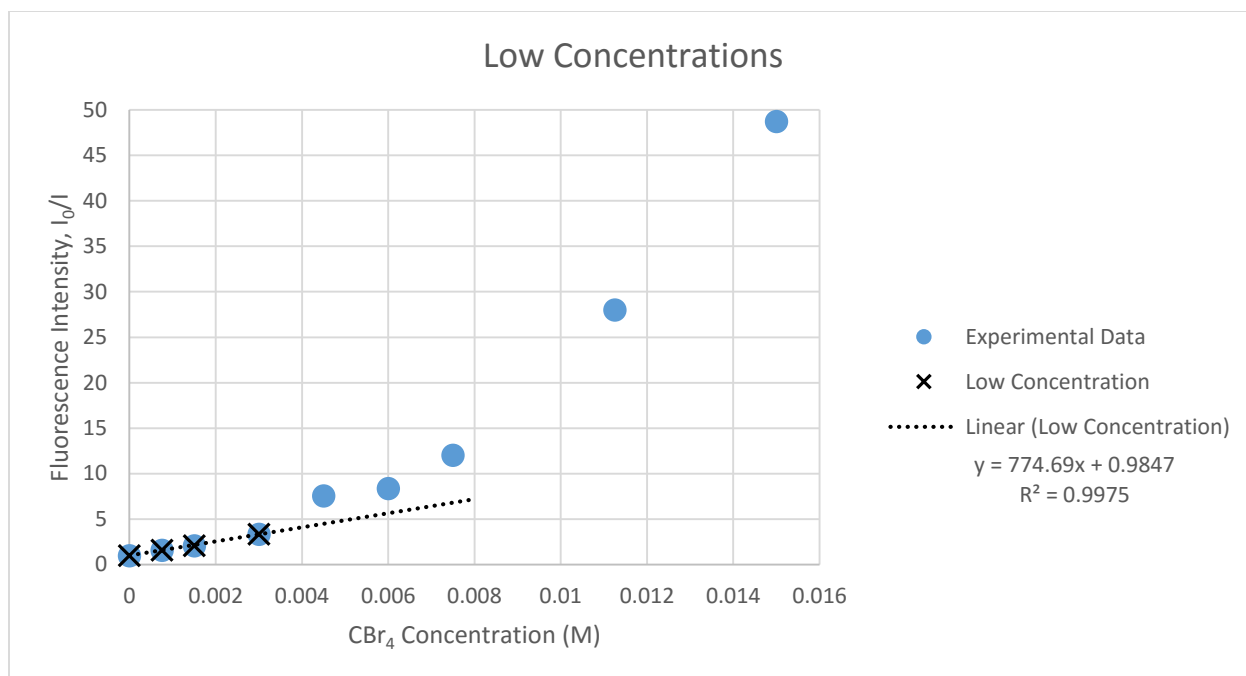
These values of I_0/I were plotted versus their respective values of $[Q]$, creating a curve whose slope is equal to $k_1 \tau_0$ and y-intercept is equal to 1; Graph 2 below shows the resulting plot overlaid with the experimental data collected.



Graph 2: The Stokes-Einstein-Smoluchowski equation, which determines the rate constant of a diffusion-controlled reaction based on the viscosity of the solvent in which the reaction takes place, plotted in relation to the experimental data.

The line determined from the SES equation is calculated based on a k_1 value that is found theoretically based on the solvent's viscosity, indicating that it is a rate constant based on the ability of reactants to diffuse through the reaction medium. Thus, the SES equation models the Stern-Volmer relation in the region where the transient term dies out, or in other words, the region of the plot with low concentrations of reactants. This is clear even from visual inspection, which shows that the SES equation fits the low concentration portion of the experimental data.

Next, the rate constant was determined once again, this time ignoring the transient term in the Stern-Volmer relation. To do this, a line was fit to the experimental data corresponding to low CBr₄ concentrations. The slope of this line was again equal to $k_1\tau_0$, and thus, it was possible to determine another value for the rate constant. From this value of k_1 , another value was determined for the collision radius, R , using the relationship described in Equation 2 above. The described fitting is represented in Graph 3 below.



Graph 3: The low concentration region of the experimental data fit to a linear equation to determine the Stern-Volmer relation ignoring the transient term. $k_1 = 1.403 \times 10^{11} \text{ dm}^3 \text{ s}^{-1} \text{ mol}^{-1}$. $R = 33.13 \text{ \AA}$.

From a slope of 774.69 and $\tau_0 = 5.52 \times 10^{-9} \text{ s}$, k_1 was determined to be equal to $1.403 \times 10^{11} \text{ dm}^3 \text{ s}^{-1} \text{ mol}^{-1}$. The collision radius was found to be $3.313 \times 10^{-9} \text{ m}$ or 33.130 \AA .

Finally, the collision radius was determined by fitting the Stern-Volmer equation (**including the transient term**) to the experimental data. This equation is shown below

$$\frac{I_0}{I} = \frac{\left[1 + 4\pi RD \left(\frac{N_A}{1000} \right) \tau_0 [Q] \right]}{Y} \quad \text{Equation 4}$$

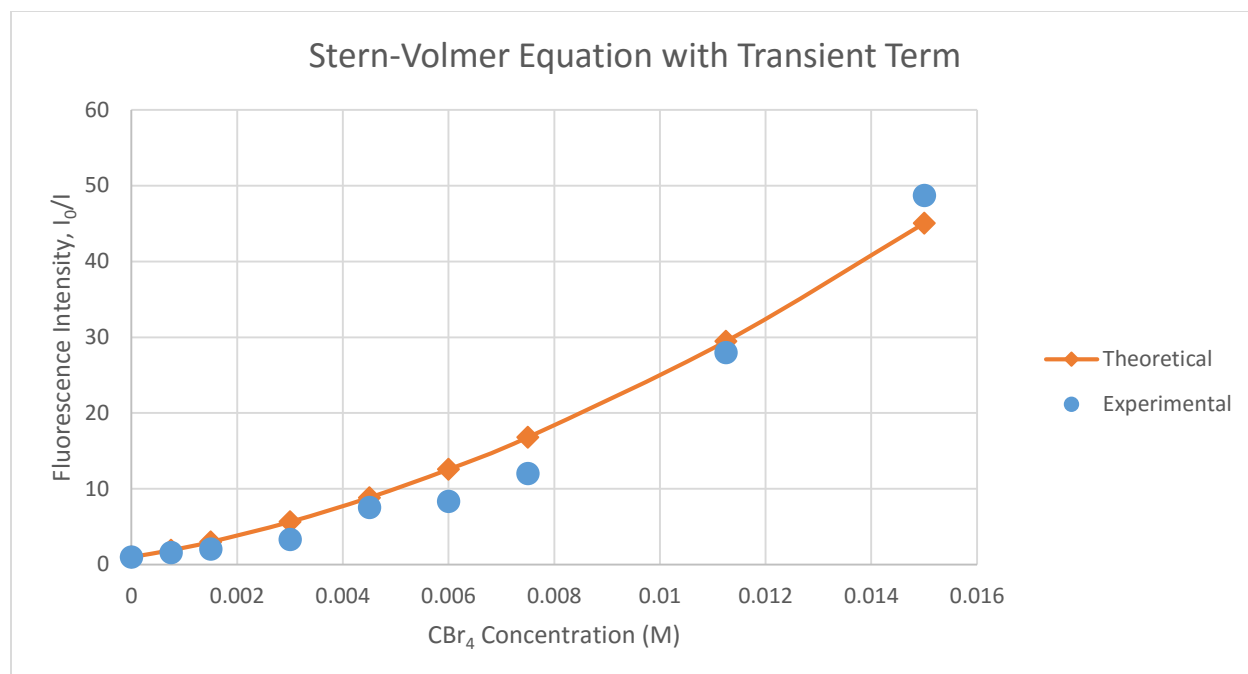
where Y is equal to:

$$Y = 1 - \frac{b\sqrt{\pi}}{\sqrt{a}} \exp\left(\frac{b^2}{a}\right) \text{erfc}\left(\frac{b}{\sqrt{a}}\right) \quad \text{Equation 5}$$

and a and b are given by:

$$a = \frac{1}{\tau_0} + \frac{4\pi RD N_A}{1000} [Q] \quad b = \frac{4R^2 \sqrt{\pi D} N_A}{1000} [Q] \quad \text{Equation 6a and 6b}$$

The I_0/I values obtained from this equation were compared to the experimental values obtained. The square differences of these values for each value of $[Q]$ were determined. Then the sum of these differences was minimized by optimizing the value of R in the cell being referenced by the Stern-Volmer equation represented in Equation 4 above. This nonlinear regression analysis was done using the Solver Application in Excel. The fitted Stern-Volmer fluorescence intensity ratio is shown overlapped with the experimental data in Graph 4 below.



Graph 4: The Stern-Volmer Equation fit to the experimental data via non-linear regression analysis. $R = 30.11 \text{ \AA}$.

The collision radius determined from this regression analysis was equal to $3.011 \times 10^{-9} \text{ m}$ or 30.11 \AA .

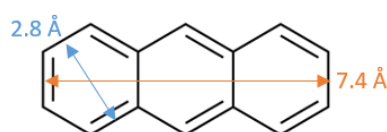
The rate constants and collision radii determined via the various methods are summarized in the table below.

SES Equation	$k_1 (\text{dm}^3/(\text{s} \cdot \text{mol}))$	2.202 e10
	$R (\text{\AA})$	5.120
Steady-State Equation 3 (Graph 3)	$k_1 (\text{dm}^3/(\text{s} \cdot \text{mol}))$	1.403 e11
	$R (\text{\AA})$	33.130
Transient Term Equation 4 (Graph 4)	$R (\text{\AA})$	30.11

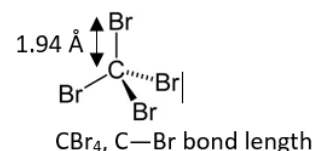
Table 1: The rate constants and collision radii determined in this experiment via several methods are summarized in this table.

Conclusion

The collision diameter between two molecules is approximately equal to the sum of the molecular diameters of the reactants. Assuming the diameter of anthracene can be between the diameter of benzene (2.8 \AA)^[8] (shown in blue) and three times that of benzene 7.4 \AA (in orange) and that the diameter of a CBr_4 molecule is approximately double that of a $\text{C}-\text{Br}$ bond length, 1.94 \AA ^[5], the collision diameter can be approximated to range from 4.74 \AA to 9.34 \AA . The collision radius was determined three different ways in this experiment. The first method used the SES equation to determine a rate constant based on the viscosity of the solvent, and the radius was determined from that value to be 5.120 \AA , making the collision diameter



Anthracene Molecule – Approximated Diameter



10.24 Å, which is reasonably close to the predicted range of values. The other two methods for determining R were to fit the experimental data to either the linear portion involving low concentrations of Q or to the entire set of the data that reflected the presence of a transient term at high concentrations of Q . These methods resulted in R values of 33.13 Å and 30.11 Å respectively, translating to 66.26 Å and 60.22 Å. These values seem to be over estimations of the collision diameter. This error could have resulted from conducting the experiment at a higher temperature than recommended by the lab manual (25 °C rather than 0 or 1 °C) and also prolonging the exposure of the samples to light during the experiment. The effect of the higher temperature would be a faster reaction rate, meaning that the k_1 value was higher than it would have been at 0 °C. The higher k_1 value would lead to a higher R value. The prolonged exposure of light would cause the fluorescent species in the solution to undergo some photobleaching. This would perhaps decrease the number of fluorophores able to fluoresce, decreasing the intensity of the sample's fluorescence. This would mean the I_0/I ratios were greater than if the light exposure was better controlled. These greater values would also skew the results, giving a larger k_1 value and thus a greater R value as well. These errors may explain the discrepancy in the theoretically calculated and experimental values of the collision diameter between the excited state of anthracene and CBr_4 .

Questions and Further Thoughts

- *Why is the anthracene fluorescence quenching diffusion controlled, as opposed to chemical controlled?*

The reaction between an excited anthracene molecule and the quencher CBr_4 has a very small, if any at all, energy barrier to reaction. Activation energy usually reflects the fact that molecules need to be in very specific orientations relative to each other in order to react (pre-exponential factor in E_a) or that they need to collide with a certain velocity for the reaction to be successful (temperature dependence of E_a). With the formation of the encounter complex, the molecules enter the proper distance and orientation (although this reaction seems to be orientation independent) to react. Thus once this complex is formed, there are no more barriers to reaction and the quenching occurs very quickly. So it is the formation of this encounter complex that is the barrier or limiting step in the reaction and this step, which involves the *diffusion* of the molecules into the solvent cage will determine the rate at which the quenching will occur. A chemically controlled reaction would be one in which the actual reaction between the molecules takes longer than it takes for them to approach each other through the solvent, which is not the case between anthracene and CBr_4 .

- *What effect would a polar solvent have on the ground- and excited-state interactions between AN and CBr_4 ?*

A polar solvent would force the nonpolar anthracene and CBr_4 to aggregate as described by the hydrophobic effect that says that when solutes are solvated by water, the solutes aggregate and are surrounded by ordered/structured water "cages." This structured formation, reduces the entropy of the water, which is unfavorable. Thus, rather than solvating each nonpolar molecule separately (huge total surface area of cage structures), the nonpolar substances will be forced to aggregate to reduce the surface area of the structured water cage that surrounds the surface of the nonpolar species in solution, and therefore minimizing the loss of entropy. If this hydrophobic effect is indeed observed in a polar solvent, then the anthracene and CBr_4 will already be in their "encounter complex" intermediate as soon as they are mixed together. When

the solution is exposed to the excitation beam, the quenching will occur much faster, since the reaction will no longer be diffusion controlled, because the two reactants do not have to diffuse toward one another in solution. Instead, the entire reaction will be under chemical control.

- *If you wanted to do a fluorescence quenching experiment that demonstrated the transient effect in diffusional processes, what qualities of solvent viscosity and fluorescence probe lifetime would you seek?*

As described in the previous question/answer, a polar solvent would force the nonpolar reactants together, removing the likelihood of a diffusion-controlled reaction. The kinetics of the reaction that would take place would instead resemble the kinetics of the transient phase of a diffusion-controlled reaction. So, to exemplify the transient effect, the solvent conditions should keep the solutes close together, which could be best accomplished using a cold, viscous, polar solvent.

- *The lowering of dissolved oxygen by bubbling the solution with dry N₂ gas is an application of Henry's law. Explain how deaeration works in this context.*

Henry's law says that the amount of dissolved gas is proportional to its partial pressure in the gas phase. Bubbling nitrogen gas through the solution causes the partial pressure of N₂ to increase relative to the other gases. The amount of N₂ dissolved in solution increases until the solution is saturated with nitrogen and all other gases have been forced out because their partial pressure is so low relative to the nitrogen gas. In addition, by using an excess of N₂, the air above the solution also becomes saturated with nitrogen, ensuring that any gas that is dissolved in solution will be nitrogen, and the amount of nitrogen that is dissolved in solution will remain constant as long as the partial pressure of nitrogen in the air above the solution is constant.

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