

Kinetics of a Diffusion Controlled Reaction as Measured by Fluorescence Spectroscopy

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Abstract

The kinetics of a diffusion controlled reaction between an excited anthracene molecules and a ground state quencher molecule is examined via fluorescence spectroscopy. A Stern-Volmer plot is used to determine the rate constant (from the experimental data). A variation of the Stokes-Einstein equation is used to determine the diffusion controlled rate constant, and the two rate constants are compared.

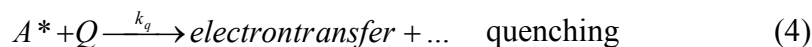
Related Readings

1. Halpern, A. M. "Experimental Physical Chemistry: A Laboratory Textbook." 2nd Ed. Prentice Hall: Upper Saddle River, NJ. [Available in Nobel 107]
2. McQuarrie, D.A., Simon, J.D., "Physical Chemistry: A Molecular Approach." University Science Books: Sausalito, CA. Chs. 15 (sections 15-1 to 15-3) & 28.

Background

We will study the kinetics of a reaction between an electronically excited anthracene molecule and a ground state quencher molecule (CBr₄, Pyrene, or other appropriate molecule). The kinetics of this reaction can be followed by fluorescence spectroscopy because upon excitation, anthracene makes a transition to an excited electronic state (S₀ → S₁). Anthracene decays from this state back to the ground electronic state by emitting a photon. This emission is called fluorescence emission and can easily be monitored within an instrument called a fluorimeter. The quencher molecule (quenchers) can collide with excited anthracene and quench the fluorescence emission through a bimolecular reaction. This quenching shows itself as diminished fluorescence emission as a function of quencher concentration. We will also contrast the fluorescence and quenching of anthracene to the fluorescence of Ru(bpy)₃²⁺ and quenching of this fluorescence with FeNH₄(SO₄)₂.

Important Transformations Involved in Fluorescence and Their Kinetics



In the absence of quencher only the first three processes are important (1-3). As quencher concentration increases process 4 begins to compete with fluorescence leading to a diminished level of fluorescence. If we take I₀ as the fluorescence emission intensity

in the absence of quencher and I as the intensity in the presence of a given concentration of quencher, $[Q]$, the following equation, known as the Stern-Volmer equation, becomes useful for determination of k_q if we have a fluorescence lifetime, τ_0 .

$$\frac{I_0}{I} - 1 = k_q \tau_0 [Q] \quad (5)$$

In order for quenching to compete with the radiative process quencher concentrations ranging from those of anthracene to 10-100 times the concentration may need to be explored. The fluorescence lifetime of anthracene was determined by Ware and Novros³ to be $\tau_0 = 5.52 \times 10^{-9}$ sec. The fluorescence lifetime of $\text{Ru}(\text{bpy})_3^{2+}$ was determined by Rusak et al.⁴ to be $\tau_0 = 0.562 \times 10^{-6}$ sec.

The fluorescence quenching examined here is diffusion-controlled, and, therefore, diffusion theory can be used to determine a theoretical rate constant. This is discussed in detail by Halpern.¹ To summarize, the diffusion controlled rate constant is given by:

$$k_d = \frac{8RT}{3\eta} \quad (6)$$

where R is the gas constant, T is the temperature and η is the viscosity. If R is used in units of $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, T in K, and η in P (poise, $1 \text{ P} = 0.1 \text{ kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$), k_d will have units of $\text{m}^3\cdot\text{mol}^{-1}\cdot\text{sec}^{-1}$ (you may want to convert these to $\text{L}\cdot\text{mol}^{-1}\cdot\text{sec}^{-1}$ for comparison). Table 1 below gives the viscosities of some representative compounds. Note: If the fluorescence quenching is diffusion-controlled for the reaction of interest, $k_q = k_d$.

Table 1. Representative viscosities

Compound	Viscosity, η [cP, $1 \text{ cP} = 10^{-3} \text{ kg/m sec}$] at 298 K
Water	0.891
Methanol	0.553
Benzene	0.601
Hexane	0.326
CCl_4	0.880

Most diffusion-controlled reactions have rate constants on the order of $\times 10^{10} \text{ L}\cdot\text{mol}^{-1}\cdot\text{sec}^{-1}$. For example, the diffusion rate constant for a reaction at 298 K in hexane would be $\sim 2.0 \times 10^{10} \text{ L}\cdot\text{mol}^{-1}\cdot\text{sec}^{-1}$.

Pre-Lab Exercises

1. Read McQuarrie and Simon section 15.1 through 15.3 on fluorescence and other radiative and non-radiative transitions. Prepare a diagram of the excitation and emission processes we will probe for anthracene.
2. Outline a procedure for measuring a rate constant, k_q , by recording fluorescence emission spectra at multiple quencher concentrations, $[Q]$. The lab book by Halpern (available in Nobel 107), will give some guidance for a procedure. (Note: we will not deaerate the solutions and you do not need to sublime or purify the

anthracene.) To help you, some comments on the instrument can be found below in the Apparatus section. **Get this procedure approved prior to starting lab – I'll need to explain the sensitivity of the fluorimeter to you as well.** Your procedure should include:

- Directions for preparing solutions of anthracene and quencher, CBr_4 , in hexane. An anthracene stock solution of 1.07×10^{-4} is available in lab. (Halpern et al.¹ will aid you in determining the appropriate quencher concentrations and dilutions.) You'll want 10 mL of each solution (and ~6-7 solutions in total).
- Directions for preparing solutions of $\text{Ru}(\text{bpy})_3^{2+}$ and quencher, $\text{FeNH}_4(\text{SO}_4)_2$, in DI water. Stock solutions of both ($[\text{Ru}(\text{bpy})_3^{2+}] = 9.83 \times 10^{-5} \text{ M}$; $[\text{FeNH}_4(\text{SO}_4)_2] = 1.89 \text{ mM}$) are available in lab. Your solutions should have $\sim 10^{-6} \text{ M}$ $\text{Ru}(\text{bpy})_3^{2+}$ and the following $[\text{FeNH}_4(\text{SO}_4)_2]$: 0.0 mM, 0.2 mM, 0.4 mM, 0.8 mM, 1.2 mM, 1.6 mM, and 1.8 mM. You'll want 10 mL of each.
- Excitation and emission wavelengths for each system. See Halpern et al.¹ for details on the anthracene system. For the $\text{Ru}(\text{bpy})_3^{2+}$, λ_{max} for excitation is $\sim 460 \text{ nm}$ and λ for emission is $\sim 590 \text{ nm}$. Make adjustments as needed; for example, an Ocean Optics UV-Vis spectrometer can be used to verify the excitation wavelengths.
- Directions for obtaining intensity vs. quencher concentration data. (Be sure to note how you'll clean the cuvette between runs.)
- Detail on how to calculate rate constants.

Safety Precautions

- Always wear safety goggles and never look into the UV light source.
- Wear gloves when handling anthracene, $\text{Ru}(\text{bpy})_3^{2+}$, and CBr_4 .
- Dispose of your waste in the appropriate waste disposal containers.

Apparatus

All measurements will be taken on the Perkin-Elmer 204 Fluorescence Spectrometer (fluorimeter). This fluorimeter uses a Xe lamp for a UV source. Both the lamp and the fluorimeter must be turned on. Let the lamp power supply warm up for ~5-10 minutes before starting it (with the white "start lamp" button) and let the lamp warm up for ~20-30 minutes after starting.

There is a shutter on the monochromator that protects the light source (the excitation shutter) and protects the detector from stray light (the emission shutter). The shutters **MUST BE CLOSED** whenever you open the sample compartment to change the sample. If you see light when you open the compartment, you are not closing the shutters.

Always put your cuvettes in the same position. The easiest way to accomplish this in our fluorimeter is to set the position with the knob in front (1, 2, 3, or 4) and then turn the merry-go-round (by hand) inside to the farthest position. (This method is better than simply trusting the knob controlling the merry-go-round.)

There are a couple of sensitivity controls on the fluorimeter. Due to the differences in systems, these may need to be adjusted when moving between the systems.

Please do this only with the supervision of the lab instructor!

Report/Analysis

Follow the general lab report guidelines. In the experimental section, add a discussion on any deviations from your planned procedure. Your results section should, at a minimum, include the UV-Vis absorption spectra used to determine the excitation wavelength (with an arrow indicating the wavelength used), the Stern-Volmer plot, and a table with the rate constants. In the discussion, be sure to address the following (in addition to your own discussion points):

- Compare and contrast the two different reactions (discuss in terms of rate constants, sensitivity, concentrations used, solvents used, etc).
- Are these reactions diffusion-controlled? Justify. Why might or might not these reaction be diffusion controlled?
- What would happen to the rate constants if you used a more viscous solvent? A higher temperature?
- What are the sources of error in the experiment and how might they be eliminated or reduced?

References

1. Halpern, A. M. "Experimental Physical Chemistry: A Laboratory Textbook." 2nd Ed. Prentice Hall: Upper Saddle River, NJ. [Available in Nobel 107]
2. McQuarrie, D.A., Simon, J.D., "Physical Chemistry: A Molecular Approach." University Science Books: Sausalito, CA. Chapter 15 and 28.
3. Ware, W. R.; Novros, J. S. *Journal of Physical Chemistry* **1966**, *70*, 3246.
4. Rusak, D. A., James, W.H., Ferzola, M.J., Stefanski, M.J. "Investigation of Fluorescence Lifetime Quenching of Ru(bpy)₃²⁺ by Oxygen Using a Pulsed LED." *J. Chem. Ed.* **2006**, *83*(12), 1857-1859.