

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.

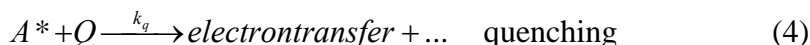
Related Readings

1. Halpern, A. M. "Experimental Physical Chemistry: A Laboratory Textbook." 3rd Ed. Prentice Hall: Upper Saddle River, NJ. [Available on Moodle; Exp 21]
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

See posted assignment

Procedure

This is a general outline of the lab procedure. We have a brand new fluorimeter that hasn't been used yet – by anyone! – and I need to learn how to use it before I can give you specifics. So... the instrument details and specific data collection may change. You will get an additional handout/information in lab with the updates. The lab book by

Halpern (available on Moodle), also gives some guidance on a general procedure. (Note: we will not deaerate the solutions and you do not need to sublime or purify the anthracene.)

The overall goal of the lab is to determine the rate constant, k_q , by recording fluorescence emission spectra at multiple quencher concentrations, $[Q]$. By using equation (5) above and plotting the normalized fluorescence intensity, $I/I_0 - 1$, versus $[Q]$, the rate constant can be determined. You will do these measurements for two cases: anthracene quenched by CBr₄ and Ru(bpy)₃²⁺ quenched by FeNH₄(SO₄).

For each case you need to measure the fluorescence intensity of the non-quenched anthracene or Ru(bpy)₃²⁺ and then the intensity for quenched samples. Therefore, you need to prepare a series of solutions for each case.

- a. For anthracene/CBr₄ case: A stock solution of $\sim 1.0 \times 10^{-3}$ M (check the flask for a more accurate number – true for all stock solutions) anthracene in n-hexane and a stock solution of 1.8×10^{-2} M CBr₄ in n-hexane are available. The solutions you take to the fluorimeter should have $\sim 1.0 \times 10^{-4}$ anthracene and a range of CBr₄ from 0 M to 1.6×10^{-2} . There should be at least 8 total solutions. You'll want 10 mL of each solution.
- b. For the Ru(bpy)₃²⁺/Fe case: Stock solutions of both ([Ru(bpy)₃²⁺] $\sim 9 \times 10^{-5}$ M and [FeNH₄(SO₄)₂] = 1.89 mM) are available in lab; the solvent in this case is DI water. Your solutions should have $\sim 10^{-6}$ M Ru(bpy)₃²⁺ and the following [FeNH₄(SO₄)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.

You will then take these solutions to the fluorimeter to determine the excitation and emission wavelengths needed for each system. At the appropriate conditions, you will measure and record the intensity of each solution. More information on this part of the lab will be available during the lab. With this data, you will then determine the rate constants for the quenching reaction and complete the analysis outlined below.

Safety Precautions

1. Always wear safety goggles and never look into the UV light source.
2. Wear gloves when handling anthracene, Ru(bpy)₃²⁺, and CBr₄.
3. Dispose of your waste in the appropriate waste disposal containers.

Apparatus

All measurements will be taken on the new FluoroMax Fluorescence Spectrometer (fluorimeter). Directions for using this instrument will be available in lab. Be sure to follow all instructions carefully and ALWAYS turn on the instrument before the computer.

Report/Analysis

Follow the guidelines for writing a communication. 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) – *if collected*, 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. Exp # 22." 2nd Ed. Prentice Hall: Upper Saddle River, NJ. Pg 367 [In Nobel 106B or o Moodle]
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.