

□ Experiment 20

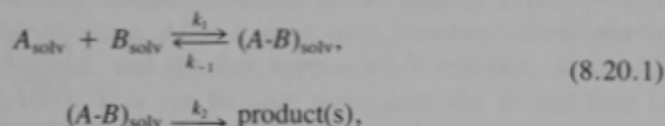
Kinetics of a Diffusion-Controlled Reaction

Objective

To determine the rate constant and collision diameter of a diffusion-controlled reaction (photoexcited anthracene and carbon tetrabromide) using the technique of fluorescence quenching.

Introduction

This experiment examines a very fast bimolecular reaction between two different species in solution. We will assume that the reactants, A and B , which are electrically neutral, undergo independent, random motion. There is a certain probability that A and B will encounter each other at some close distance, R , where R is approximately equal to the sum of the molecular radii. This arrangement is called an *encounter complex*. Because there is a tendency for the solutes A and B to maintain constant random motion, it is inevitable that, once loosely held in this complex, they will subsequently separate from each other unless a chemical reaction (or other definitive process) first links them together. Since this random motion takes place in a "bath" of solvent molecules (assumed to be unreactive with respect to A and B), the separation of the A - B encounter complex will be impeded by the neighboring solvent molecules. This artificial holding together of the two molecules is called the "cage effect." The important point is that there is a kinetic competition between a net (thus measurable) reaction between A and B via the collision complex, and the release of A and B from the solvent cage back into the solvent medium where no reaction occurs. These processes can be represented by the following kinetic scheme:



where A_{solv} , e.g., represents the solvated A molecule, and $(A-B)_{\text{solv}}$ is the encounter complex. The rate constants for these elementary steps are denoted as k_1 , for the bimolecular formation of the encounter complex, or diffusion into the solvent cage; k_{-1} , for the unimolecular dissociation of the complex, or diffusion out of the solvent cage; and k_2 for the "unimolecular" reaction between A and B in the complex.

Since the encounter complex is present in very small concentration, it is amenable to the steady-state approximation, according to which the net formation rate of $(A-B)_{\text{solv}}$ is equal to zero. Thus,

$$\frac{d[A-B]}{dt} = k_1[A][B] - (k_{-1} + k_2)[A-B] = 0,$$

and the reaction rate can be expressed as

$$\text{Rate} = k_2[A-B] = \frac{k_1 k_2}{k_{-1} + k_2} [A][B].$$

For convenience, we define the second-order rate coefficient, k_{obs} , as

$$k_{\text{obs}} = \frac{k_1 k_2}{k_{-1} + k_2}. \quad (8.20.2)$$

This analysis leads to two limiting cases with respect to k_{obs} : one in which reaction between A and B is very slow compared with their departure (or separation) from the solvent cage, i.e., $k_{-1} \gg k_2$, and the other in which A - B reaction is much faster than their separation, or $k_2 \gg k_{-1}$. The first case describes a reaction that is under *chemical control*, with $k_{\text{obs}} \sim k_1 k_2 / k_{-1}$, and the second pertains to a *diffusion-controlled* reaction for which $k_{\text{obs}} \sim k_1$. It is the latter situation that is considered in this experiment. More details of the reaction, which involves fluorescence quenching, will be described after a discussion of the necessary theory.

Diffusional Mass Transport

The basic issue in a diffusion-controlled reaction concerns the dynamics of mass transport in the condensed phase. The fundamental equations describing mass transport are embodied by Fick's laws of diffusion. These laws are encountered and discussed in Experiments 17 and 18. Fick's first law says that the number of molecules (dn) diffusing through a unit area, A , per unit time (dt) in the x direction (i.e., the flux, J_x) is proportional to the concentration gradient at that point, i.e.,

$$J_x = \frac{1}{A} \frac{dn}{dt} = -D \frac{dC}{dx}, \quad (8.20.3)$$

where D , the proportionality constant, is called the *diffusion coefficient*. The cgs units of D are $\text{cm}^2 \text{s}^{-1}$. The minus sign in equation (8.20.3) indicates that transport goes *against* the concentration gradient (i.e., from high to low concentration values).

Fick's second law states that the change in the concentration of molecules, dC , diffusing across an infinitesimally thin plane per unit time, dt , is proportional to gradient of the flux:

$$\left(\frac{dC}{dt} \right)_x = - \left(\frac{dJ_x}{dx} \right)_t. \quad (8.20.4)$$

Again, the minus sign ensures that concentration increases in time in response to a flux that decreases with increasing x . If D is assumed to be independent of x , the expression for J_x from Fick's first law may be substituted into the second to give

$$\left(\frac{dC}{dt} \right)_x = D \left(\frac{d^2 C}{dx^2} \right)_t. \quad (8.20.5)$$

Since we are concerned with a three-dimensional and isotropic space, i.e., equal forces in all directions, Fick's second law can be written in more general form as

$$\left(\frac{dC}{dt} \right)_{x,y,z} = D(\nabla^2 C)_t, \quad (8.20.6)$$

where ∇^2 is the Laplacian operator, $\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$.

The solution of Fick's second law is an equation that expresses concentration as a function of *space*, i.e., distance (r), and *time* (t). We are interested in solving equation (8.20.6) with the boundary conditions

$$C(r,0) = C_0,$$

$$C(\infty,t) = C_0,$$

$$C(r = R,t) = 0,$$

where $r = [x^2 + y^2 + z^2]^{1/2}$ and C_0 denotes the bulk concentration.

The first boundary condition states that initially, the bulk concentration prevails throughout the system; the second says that even after the reaction starts ($t > 0$) the concentration very far away from the reactant is constant (C_0); and the third indicates that the reactant concentration is zero at a distance equal to the sum of the reactant collision radii. It should be realized that the diffusion coefficient, D , contained in equations (8.20.3), (8.20.5), and (8.20.6) is the *sum* of the individual diffusion coefficients of the reactants, $D_A + D_B$. This essentially allows the motion of one of the reactants to be considered *relative* to the other.

The solution of Fick's second law for this set of boundary conditions (first rendered by Smoluchowski in 1917) yields, for the space-time dependence of C ,

$$C(r,t) = C_0 \left[1 - \left(\frac{R}{r} \right) \right] \operatorname{erfc} \left[\frac{r - R}{2(Dt)^{1/2}} \right], \quad (8.20.7)$$

in which erfc is the *co-error function*,

$$\operatorname{erfc}(x) = 1 - \frac{2}{\sqrt{\pi}} \int_0^x \exp(-y^2) dy.$$

The time dependence of reactant at the reaction boundary $r = R$ becomes expressible in terms of the flux of reactant, J_R , or its rate of transport across a hypothetical spherical surface with radius R . Thus

$$J_R = \frac{4\pi R D N_A C_0}{1000} \left[1 + \frac{R}{(\pi D t)^{1/2}} \right] \quad (\text{molecules s}^{-1})_1 \quad (8.20.8)$$

where N_A is Avogadro's number. Equation (8.20.8) indicates that the flux is actually time-dependent. This time dependence comes from $R/(\pi D t)^{1/2}$, which is sometimes referred to as the *transient term*. Physically, the transient term accounts for the fact that initially nearby reactant molecules do not have to diffuse through the bulk medium in order to react. After a short time, however, these nearby reactant molecules are depleted, and the flux approaches a constant, or steady-state, value, $4\pi R D N_A C_0/1000$. This can be seen mathematically in that time is represented in equation (8.20.8) as $t^{-1/2}$.

Because J_R represents the rate of passage of one of the reactants (having a bulk concentration C_0 in moles dm^{-3}) through a spherical reaction surface with the other reactant at the center, the rate of the reaction represented by equation (8.20.1) is merely J_R itself. Hence the bimolecular, diffusion-controlled rate constant k_1 is J_R/C_0 ,

$$k_1 = \frac{4\pi R D N_A}{1000} \left[1 + \frac{R}{(\pi D t)^{1/2}} \right] \quad (\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}). \quad (8.20.9)$$

This rate constant is not a true *constant*, however, because of the transient term. As t becomes large enough,

$$k_1 \rightarrow \frac{4\pi R D N_A}{1000} \quad (\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}), \quad (8.20.10)$$

and equation (8.20.10) can be used to determine the diffusion-controlled rate constant if the mutual diffusion constant ($D_A + D_B$) and collision radii ($R_A + R_B$)

are known. It should be emphasized that the units of k_1 presented above are $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$, if R and D are expressed in cm and $\text{cm}^2 \text{s}^{-1}$, respectively.

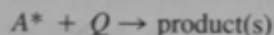
Often, however, R and D are not known, and an indirect method is used to estimate k_1 . This approach, developed by Einstein using Stokes's law (see Experiment 19), allows the diffusion coefficient to be expressed in terms of a bulk property, the solvent viscosity, η . Thus

$$k_1 \sim \frac{8RT}{3000\eta} \quad (\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}), \quad (8.20.11)$$

in which R is the gas constant. Equation (8.20.11), which is often referred to as the Stokes-Einstein-Smoluchowski (SES) equation, holds when the reactants A and B are different and their sizes are larger than that of the solvent molecules.

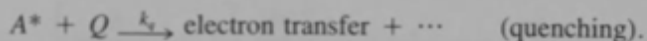
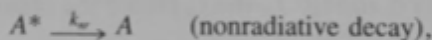
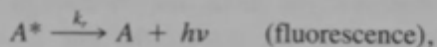
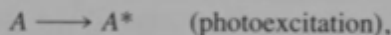
Fluorescence Quenching

The reaction studied in this experiment takes place between an *electronically excited* molecule and a *quencher*, a species that removes the electronic excitation. The advantages of using an electronically excited molecule as one of the reactants are: (1) the reaction begins only when the system is exposed to light; (2) the concentration of electronically excited molecules can be readily followed fluorometrically (via fluorescence detection); and (3) the reaction itself is intrinsically *fast*: it has no activation energy per se. Experiment 24 also utilizes fluorescence quenching as a "kinetic" technique. The overall reaction of fluorescence quenching can be represented as



where A^* represents the electronically excited (fluorescent) state of a molecule (e.g., anthracene), Q denotes the quencher (e.g., CBr_4) that extinguishes the A^* fluorescence, and "product(s)" indicate the species into which the fluorescent molecule is eventually transformed. This deexcitation process may occur through a charge-transfer intermediate ($A^+ - Q^-$). For the system encountered in this experiment, electron transfer from A^* to the quencher occurs very rapidly. In general, it is possible that the consequence of fluorescence quenching is the return of A to its electronic ground state, i.e., $A + Q$.

The bimolecular quenching reaction above competes with intrinsic, first-order, fluorescence decay of A^* . A more complete scheme is



If a solution containing A and Q is irradiated with a *steady-state* light source (at a wavelength at which A absorbs), a very small time-independent concentration of A^* is produced. The probability that A^* will fluoresce, P_f , is the ratio of the fluorescence (or radiative) rate constant to the *sum* of *all* the rate constants that deplete A^* , namely,

$$P_f = \frac{k_r}{k_r + k_{nr} + k_q[Q]}, \quad (8.20.12)$$

where k_r , k_{nr} , and $k_q[Q]$ are, respectively, the radiative, nonradiative, and pseudo-

first-order quenching rate constants. Since $[Q] \gg [A^*]$, the diffusion-controlled, bimolecular quenching step becomes pseudo-first-order. If the amount of light absorbed by A is constant (i.e., independent of $[Q]$), the fluorescence intensity, I , measured by the detector (i.e., the response) is proportional to P_f . In the absence of quencher, $I = I_0 = k_r/(k_r + k_{nr})$, and the ratio of fluorescence intensities of unquenched to quenched samples of A becomes

$$\frac{I_0}{I} = 1 + \frac{k_q[Q]}{k_r + k_{nr}}. \quad (8.20.13.)$$

Identifying $1/(k_r + k_{nr})$ as the reciprocal of the fluorescence lifetime of A^* in the absence of quencher (τ_0), equation (8.20.13) can be written as

$$\frac{I_0}{I} - 1 = k_q \tau_0 [Q]. \quad (8.20.14)$$

This is known as the steady-state *Stern-Volmer* (S-V) relation as applied to fluorescence quenching. It predicts that a plot of $(I_0/I - 1)$ vs. $[Q]$ should be linear, having an intercept of zero and a slope equal to $k_q \tau_0$. (See also Experiment 24.) The latter is called the Stern-Volmer constant, K_{SV} (units of $\text{dm}^3 \text{mol}^{-1}$). If fluorescence quenching is diffusion-controlled (which is the case in the anthracene/ CBr_4 system), k_q can be identified with k_1 [see equations (8.20.1), (8.20.2), and (8.20.9) to (8.20.11)].

In the absence of the transient effect, which is a type of "static" quenching in that some A^* molecules are quenched by nearby Q molecules that do not have to fully undergo transport through the solvent medium in order to approach A^* within a distance R , the S-V plot should be linear, and knowledge of τ_0 allows the determination of k_q . Alternatively, if the process is known to be diffusion-controlled, and if k_1 is determined from the SES (or some other) equation [e.g., Equation (8.20.10)], the fluorescence lifetime of A^* can be estimated from the measured K_{SV} . This is a case in which a dynamic property (a rate constant) can be obtained from a static experiment (I_0/I measurements).

The S-V relation can be expressed in terms of the diffusion-controlled rate constant that contains the transient term, e.g., equation (8.20.9). The time dependence was treated by Ware and Novros, who applied equation (8.20.9) to the condition pertinent to this experiment, namely, that the system is considered to be suddenly exposed to a steady-state excitation source, called a step function (see Figure 8.20.1).

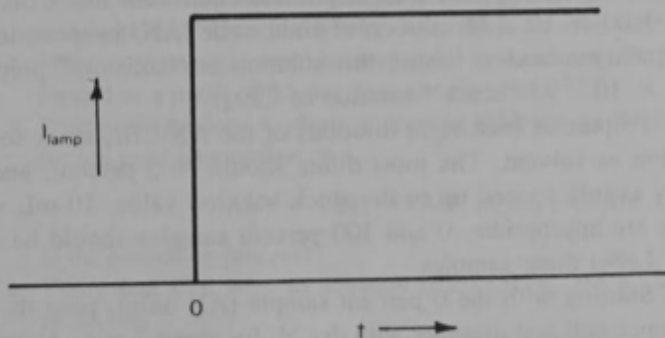


FIGURE 8.20.1 Step function excitation. At time = 0, absorbing radiation is suddenly "switched on."

In this case, the S-V equation becomes more complicated:

$$\frac{I^0}{I} = \frac{1 + 4\pi RDN_A/1000[Q]\tau_0}{Y},$$

where

$$Y = 1 - \frac{b}{a^{1/2}\pi^{1/2}} \exp\left(-\frac{b^2}{a}\right) \operatorname{erfc}\left(\frac{b}{a^{1/2}}\right), \quad (8.20.15)$$

in which

$$a = \frac{1}{\tau_0} + \frac{4\pi RDN_A}{1000[Q]},$$

$$b = \frac{4R^2(\pi D)^{1/2}N_A}{1000[Q]}.$$

If $Y = 1$, equation (8.20.15) reduces to equation (8.20.14) in which $k_q = k_1$ from (8.20.10). (Verify this!)

The Stern-Volmer plot based on equation (8.20.15) will be curved upward. If the mutual diffusion coefficient of the reacting pair is known, the S-V plot of experimental data can be fit using equation (8.20.15) with R used as a "fitting" parameter. For a satisfactory match between experiment and theory, however, the value of R that provides a good fit of the data must be physically reasonable. That is, R should be approximately equal to the sum of the molecular diameters of A (actually A^*) and Q .

Safety Precautions

- ☐ Always wear safety glasses or goggles; these glasses should block ultraviolet light. Ordinary plastic safety goggles or glasses may not be effective in absorbing all the ultraviolet radiation. Check with your instructor.
- ☐ Do not allow solid anthracene to come in contact with the skin. Wear gloves when handling anthracene and CBr_4 .
- ☐ Ozone is sometimes produced by ultraviolet light sources. If you detect this gas, which has a sharp, slightly acrid odor, notify your instructor and immediately shut off the source. Increase ventilation, and leave the room immediately.
- ☐ The compressed-gas cylinder used in deaerating should be securely strapped to a firm support. The delivery pressure should never exceed a few (e.g., 5) psig.
- ☐ The experiment should be performed in an open, well-ventilated laboratory.

Procedure

1. Using freshly sublimed or purified anthracene and CBr_4 , prepare 250 mL of a ca. $1.00 \times 10^{-4} M$ solution of anthracene (AN) in spectrometric (or fluorometric) quality n -hexane. Using this solution as "solvent," prepare 25 mL of a ca. $1.50 \times 10^{-2} M$ "stock" solution of CBr_4 .

2. Prepare at least eight dilutions of the AN/ CBr_4 stock solution using the AN solution as solvent. The most dilute should be 5 percent, and the rest should be nearly evenly spaced up to the stock solution value. 10-mL volumes of each solution are appropriate. 0 and 100 percent samples should be included for uniformity. Label these samples.

3. Starting with the 0 percent sample (AN only), pour the solution into a fluorescence cell and deaerate with dry N_2 for about 2 min. Avoid using an excessive flow rate that will cause the solution to splatter from the cell or to otherwise result in undue solvent evaporation. Promptly stopper the cell.

4. Record the full fluorescence spectrum using the instrumental conditions previously outlined by the instructor. Label the spectrum while it is recorded.

5. Using exactly the same excitation wavelength as above, measure the fluorescence intensity of the most dilute and subsequently more concentrated AN/CBr₄ solutions. Each sample must be deaerated in a consistent procedure (i.e., identical bubbling time). Instead, however, of obtaining the entire fluorescence spectrum, only the AN maximum need be monitored (near 398 nm). Make sure you are at the maximum by first scanning that region slowly. If you have any doubt as to the steadiness of the exciting source, switch back to the AN sample and compare its maximum intensity with that of the first sample run.

6. As increasingly more concentrated samples are examined, the fluorescence intensity will diminish to the point that the instrument gain should be increased to ensure maximal reading sensitivity. The background, or "dark check," should be established when the instrument sensitivity is changed.

7. The following procedural points should be borne in mind: (a) the temperature of the sample should be held constant to 0.5 to 1°C; (b) the exposure times of all the samples (especially those rich in CBr₄) to the excitation source (and even room light) should be minimized; and (c) samples should be stored in the dark until they are used.

Data Analysis

1. Tabulate the data as I_f (AN fluorescence intensity), and $[Q]$ (CBr₄ concentration).

2. Make a Stern-Volmer plot of the data.

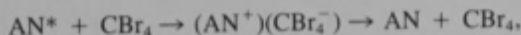
3. Superimpose on this plot the straight line expected if the transient term is ignored. The following information can be used: Ware and Novros reported a value of $D = 4.35 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ in *n*-heptane at 25°C. To obtain D for *n*-hexane at some other temperature, assume that D is proportional to T/η . They also reported a value of $\tau_0 = 1.81 \times 10^8 \text{ s}^{-1}$. You can assume this to be temperature-independent.

4. Also indicate the straight line expected on the basis of the SES equation. Tabulate the two calculated k_1 values and their error limits.

5. Using equation (8.20.15), calculate several points for the S-V plot using a fixed value of R . If you are not using a computer to generate these points, choose them judiciously so you can discern the general shape of the calculated plot. Start with a value of 6 Å and increase R in steps of 0.5 Å until satisfactory agreement with the data is obtained.

Questions and Further Thoughts

1. Why is the anthracene fluorescence quenching diffusion-controlled, as opposed to chemical-controlled? Thus justify why the reaction between AN* and CBr₄ is very fast.
2. What experiment(s) could be performed to determine whether a stable photoproduct is formed as a result of the fluorescence quenching?
3. What could be done to obtain supporting evidence for the existence of a charge-transfer (or ion pair) intermediate, e.g.,



in the quenching process?

4. Verify that if $Y = 1$ in equation (8.20.15), $k_q \Rightarrow k_1$; see equations (8.20.14) and (8.20.10).
5. One of the undesirable complications associated with this type of experiment is the presence of *ground-state* complexes that might exist between AN and CBr₄. If such a complex competes for light absorption with uncomplexed, free anthracene, it could

cause a decrease in fluorescence intensity without there having to be a diffusion between AN^* and CBr_4 . This is sometimes called static quenching. For this reason, it is desirable to work with quencher concentrations as low as possible. What experiment could be done to obtain evidence of a ground-state complex? How could the equilibrium constant of such a complex be determined?

6. What effect would a *polar* solvent, e.g., acetonitrile (CH_3CN), have on the ground- and excited-state interactions between AN and CBr_4 ?
7. If one wanted to do a fluorescence quenching experiment that demonstrated (and thus maximized) the "transient effect" in diffusional processes, what qualities of solvent viscosity and fluorescence probe lifetime would be sought (i.e., high or low viscosity; long or short fluorescence lifetime)?

Further Readings

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