Radical Recombination Kinetics

Objective

The objective of this experiment is to synthesize a dimer, which upon irradiation, undergoes dissociation to a radical. The order and rate constant of the subsequent recombination reaction will be determined using UV-visible spectroscopy and the presence of the radical will be verified by EPR spectroscopy.

Introduction

Chemical kinetics, or the study of reaction rates or speeds, has long been investigated as a means to provide clues to the ways in which reactants are transformed into products in a chemical reaction. A reaction mechanism, a detailed description of the way a reaction occurs based on the behavior of atoms, molecules, and ions, can be proposed based upon kinetic studies. However these studies are not always straightforward. The rates of chemical reactions can depend upon a number of factors, including pressure, temperature, and the presence of a catalyst. Therefore it is necessary, when studying a reaction, to know and control as many of these parameters as possible so you can accurately determine the rates.

Reaction rates usually depend upon the concentrations of one or all of the reacting substances. For each chemical reaction there is an associated mathematical expression relating the concentrations and rate known as the rate equation or rate law. The rate law takes the general form:

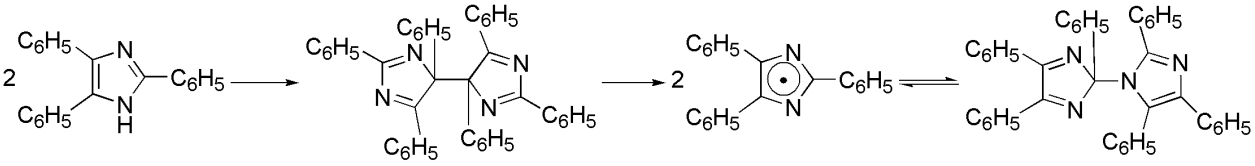
$$rate = k[A]^x[B]^y\ldots$$

where A and B are reactants (this can be expanded or reduced as needed for the number of reactants participating in the reaction), *k* is the rate constant, and x and y are the orders with respect to that reactant. The overall order of the reaction is given by the sum of the exponents in the rate equation (x + y + …). While frequently the values of x and y are whole numbers, reactions of fractional order and zero order are known. The form of the rate equation and the value of *k* must be determined experimentally and as such, it is valid only for the range of conditions (concentration, temperature, nature of reaction medium, etc.) for which it has been tested.

One method for determining the rate law is to monitor the consumption of a reactant over time. By plotting the concentration of one reactant over time (while carefully controlling all other factors in the experiment) it is possible to determine the initial reaction rate from the [A] vs. time plot by calculating the tangent to the curve at the beginning of the reaction. Additionally, inspection of the data can be used to determine the order with respect to that particular reactant. For example, for a reaction that is first order, a plot of log[A] vs. time will yield a straight line, for which the slope is equal to the rate constant with respect to that reactant. For a second order reaction, a plot of 1/[A] vs. time will yield a straight line, again with the slope being equal to *k*. For a zero order reaction, a plot of [A] vs. time will yield a straight line. While this can be a relatively simple method of determining the rate of a reaction, there is one problem—you have to

be able to know the concentration of the reactant you are interested in throughout the course of the reaction.

A common solution to this problem is the use of spectroscopic techniques to monitor the concentration of a reactant throughout the reaction. If the species you are interested in monitoring has a spectroscopic feature that is unique to it only (as compared to the other reactants and products in the reaction) you can monitor the concentration with relative ease. Frequently this is accomplished by UV-visible spectroscopy. The Beer-Lambert law allows you to directly relate the concentration of a species to the absorption at a particular wavelength.



triphenylimidazole dimer I radical dimer II

The reaction of interest in today's experiment involves the formation of a free radical and its subsequent recombination to form dimer II, shown above. Through the use of UV-visible spectroscopy and the techniques described above we will determine the rate of the recombination reaction and use EPR spectroscopy to verify the presence of the radical.

Safety

WEAR SAFETY GOGGLES AT ALL TIMES WHEN IN THE LABORATORY

Ethyl alcohol is a flammable, toxic solvent; keep away from open flame or other sources of ignition. Potassium hydroxide solutions are corrosive and will cause skin irritation. In case of contact, immediately wash with water and soap and rinse thoroughly for several minutes under running water.

Materials

2,4,5-Triphenylimidazole, potassium hydroxide, ethanol, sodium hypochlorite and toluene.

Procedures

Be sure to record all scientific observations during each step of the procedure.

Preparation of the dimer

1. Prepare a solution of alcoholic KOH by combining approximately 3 g KOH with 35 mL ethanol in a 400 mL beaker.
2. Accurately weigh 1 g of 2,4,5-triphenylimidazole into a plastic weigh boat. Add this to the alcoholic KOH solution and stir until completely dissolved. It may be necessary to

gently warm the solution (do not heat above 45 ˚C) in order to completely dissolve the solid.
3. Once the solution is completely dissolved, place in an ice bath and cool the solution to 5-10 ˚C with stirring.
4. In a separate beaker, prepare a mixture of 10 mL of 5.25% sodium hypochlorite solution with 140 mL H_2O.
5. Slowly pour the hypochlorite solution into the cold triphenylimidazole solution (5-10 mL/min) with constant stirring and cooling.
6. Collect the solid by vacuum filtration and wash with a small amount of cold water. Spread the collected solid out on a watch glass and set aside to dry.

Measurement of rate of recombination

1. In a small beaker, dissolve 30-50 mg of the prepared dimer in 20 mL of dry toluene. It is not necessary that the sample be completely dissolved. Note any observations in your laboratory notebook.
2. Filter a small amount of the dimer solution through a filter pipette and place in a cuvette. Do not discard the remainder of the solution. Set aside for later use.
3. Measure the absorbance of the solution at 560 nm. If the absorbance is above 0.8, allow the solution to stand for a few minutes until the absorbance decreases.
4. Once the absorbance has reached an appropriate level, continue measuring the absorbance of the solution once every minute until the absorbance is approximately half the initial concentration. Between readings, remove the cuvette from the spectrometer and keep the cuvette in the dark and place in a water bath to maintain a constant temperature. Water baths may be made from a Styrofoam cup with a lid filled with water.
5. Based on your data, determine the order of the radical recombination reaction.

Measurement of EPR spectrum

1. From the toluene solution prepared above (Step 1), filter a small amount of the solution through a filter pipette and place into a 4 mm EPR tube. Loosely affix the cap.
2. Record the EPR spectrum of the free radical. Determine the *g*-factor for your compound and explain the origin of any fine structure observed.
3. Wait 10-15 minutes and record the EPR spectrum again. How does this spectrum differ from the first? What does this tell you about the species responsible for the EPR signal?

Additional Information

For additional reading about chemical kinetics see:

Atkins, P., Chapter 25: The Rates of Chemical Reactions. In *Physical Chemistry*, 6th ed.; W. H. Freeman and Company: New York, 1998; pp 761-792.

For additional reading about EPR spectroscopy see:

Atkins, P., Chapter 18: Spectroscopy 3: Magnetic Resonance. In *Physical Chemistry*, Sixth ed.; W. H. Freeman and Company: New York, 1998; pp 527-566.

Ebsworth, E. V. A.; Rankin, D. W. H.; Cradock, S., Chapter 3: Electron Spin and Nuclear Quadrupole Resonance Spectroscopy. In *Structural Methods in Inorganic Chemistry*, Second ed.; CRC Press: Boca Raton, 1991; pp 115-141.

For a more in-depth review:

Weil, J.; Bolton, J. R., *Electron Paramagnetic Resonance: Elementary Theory and Pratical Applications*. Second ed.; John Wiley & Sons, Inc.: Hoboken, 2007; p 664.

Atherton, N. M., *Principles of Electron Spin Resonance*. Ellis Horwood PTR Prentice Hall: New York, 1993; p 585.