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EXPERIMENT 23

Kinetics of the Decomposition of Benzenediazonium Ion

In an acidic aqueous solution, benzenediazonium ion ($C_6H_5N_2^+$) will decompose[1] to form nitrogen and phenol:

$$C_6H_5N_2^+ + H_2O \longrightarrow C_6H_5OH + N_2(g) + H^+ \tag{1}$$

In this experiment you will follow the course of the above reaction by a spectrophotometric measurement of the unreacted diazonium ion.[2] The reaction order with respect to $C_6H_5N_2^+$, the rate constant k, and the activation energy for the reaction will be determined.

THEORY

The rate of reaction (1), $-d(C_6H_5N_2^+)/dt$, can be written in terms of the concentrations of the reacting species as

$$-\frac{d(C_6H_5N_2^+)}{dt} = k'(C_6H_5N_2^+)^n(H_2O)^m \tag{2}$$

As written here, the reaction is nth-order with respect to $C_6H_5N_2^+$, mth-order with respect to water, and has an overall order of $n + m$. The reaction is not acid catalyzed, although very high acid concentrations (say, 12 M HCl) seem to increase the rate slightly.[1] Thus the effect of changes in the H^+ concentration due to reaction (1) can be completely neglected. Since the present experiment will be performed in a dilute aqueous solution, the concentration of water (H_2O) will be very nearly constant throughout the reaction. Thus the factor $(H_2O)^m$ can be absorbed into the rate constant and Eq. (2) can be written as

$$-\frac{dc}{dt} = kc^n \tag{3}$$

where c represents the instantaneous concentration ($C_6H_5N_2^+$).

Equation (3) can readily be integrated to give

$$c = c_0e^{-kt} \qquad \text{for } n = 1 \tag{4a}$$

$$c^{1-n} - c_0^{1-n} = (n-1)kt \qquad \text{for } n \neq 1 \tag{4b}$$

where c_0 is the concentration at $t = 0$. In other words, if the reaction is first order, a plot of $\log c$ versus t should give a straight line of slope $-k/2.303$ and intercept $\log c_0$. If the reaction is nth order where n (which need not be an integer) is not equal to unity, a plot of c^{1-n} versus t should give a straight line of slope $(n-1)k$ and intercept c_0^{1-n}. By making such plots for various trial values of n and determining which gives the best straight-line dependence over a wide range of concentration, one can obtain the order n of the reaction and then determine the appropriate rate constant k_n.

If the value of a rate constant is measured at several different temperatures, it is almost always found that the temperature dependence can be represented by

$$k = \mathcal{A}e^{-E_a/RT} \tag{5}$$

where the factor $\mathcal{A}$ is independent of temperature. The Arrhenius activation energy E_a can be easily determined by plotting log k versus $1/T$. This should give a straight line of slope $-E_a/2.303R$.

METHOD

Any physical variable giving an accurate measure of the extent to which a reaction has gone toward completion can be used to obtain rate data. In this experiment we shall monitor the concentration of unreacted diazonium ion by measuring the absorption of ultraviolet light by the solution.

According to the Beer–Lambert law,[3] the intensity of light I transmitted by an absorbing medium is given by

$$I = I_0 e^{-c\varepsilon' d} \tag{6}$$

where c is the concentration of absorbing molecules, d is the path length, I_0 is the intensity of incident light, and ε' is an "extinction coefficient." The *absorbance* A, defined as $\log(I_0/I)$, thus gives a direct measure of the concentration:

$$A \equiv \log\frac{I_0}{I} = \frac{c\varepsilon' d}{2.303} = c\varepsilon d \tag{7}$$

where ε is called the *molar absorption coefficient* when the concentration is expressed in mol L^{-1} units. When the sample is a solute in solution, I is the intensity of light transmitted by a cell filled with the solution and I_0 is the intensity transmitted by the cell filled with pure solvent.

For first-order reactions, the quantity εd will cancel out of Eq. (4*a*) and k can be obtained directly from a plot of log A versus t. However, for orders different from first order, εd does not cancel out of Eq. (4*b*). In such cases εd must be evaluated by measuring the absorbance of a solution of known concentration in order to permit k to be calculated in concentration units.

A description of spectrophotometers and their use in determining the absorbance is given in Chapter XIX.

EXPERIMENTAL

Kinetic runs are to be made at 25, 30, and 40°C. Well-regulated thermostat baths operating at about these temperatures will be required. The actual temperatures of each of these baths should be measured with a good thermometer and recorded.

The concentration of benzenediazonium ion can be determined by the absorbance at wavelengths between 295 and 325 nm. Below 295 nm, products of the reaction produce interfering absorption; and above 325 nm, the molar absorption coefficient is too small to permit effective measurement of changes in the benzenediazonium ion concentration.[4] The absorbance will be measured using a suitable spectrophotometer such as a Beckman model DU-20 UV; detailed instructions for operating the instrument will be provided in the laboratory. A wavelength of 305 nm should be used, with a slit width of 0.3 mm. Make two absorbance readings on each sample.

The diazonium salt that should be used in this experiment is benzenediazonium fluoborate ($C_6H_5N_2BF_4$, $M = 191.9$). The great majority of diazonium salts are notoriously unstable solids and can decompose with explosive violence. The fluoborates are by far the safest to use and are not known to explode; however, reasonable caution should be used in preparing the compound. Since even benzenediazonium fluoborate will decompose slowly, it should not be prepared too far in advance, and it must be stored in a refrigerator. A simple high-yield procedure for its preparation has been given by Dunker, Starkey, and Jenkins.[5] Recrystallization of the product from 5 percent fluoboric acid yields white needlelike crystals, which can be dried by vacuum pumping at 1 Torr for several hours.†

The diazonium salt should be available at the beginning of the experiment. Remove a *small* quantity from the refrigerator and warm it rapidly to room temperature. Prepare approximately 10^{-3} M solutions by placing an accurately weighed 15- to 20-mg sample of the salt into each of three 100-mL volumetric flasks, and then make up to the mark with a 0.2 M HCl solution. Label the flasks and be sure to record the exact weight of salt placed in each flask. Return the unused diazonium salt to the refrigerator at once. Be careful not to waste it.

Using a hypodermic syringe, withdraw a sample of about 5 mL of each solution *as soon as possible* after it is made up. Chill these samples by placing them in test tubes set in crushed ice, then put them aside for absorbance measurements (to be made as soon as conveniently possible). These measurements will provide a value for εd in case it is needed later on.

Suspend one of the volumetric flasks in each of the three constant-temperature baths, and record the time. Allow about 20 min for the solutions to achieve thermal equilibrium. After thermal equilibrium has been attained, you may begin taking samples for spectrophotometric analysis.

When you take a sample, use the following procedure. Withdraw about 1 mL of the solution with the hypodermic syringe and use this to rinse out the syringe. Then quickly withdraw a 5-mL sample and place it in a labeled test tube set in crushed ice for chilling. Record the time of discharge into the test tube. After the sample is chilled (3 to 5 min), use about 1 mL of it to rinse out the spectrophotometer cell. Fill the cell with the remaining sample and measure its absorbance, using the 0.2 M HCl solution as a blank. These cells are fragile and expensive; handle them with care.

The reason for chilling the sample is to slow down the reaction rate so that a negligible amount of reactant will decompose between the time you chill the sample and the time you make the absorbance measurement. Since it is impossible to eliminate completely errors due to reaction after withdrawal and cooling, it is important to try to perform the sample removal and chilling procedure in as reproducible a fashion as possible. This will lead to a partial cancellation of such errors.‡

†After storage at 0°C in a vacuum desiccator for several weeks, these crystals tend to stick together. After six months there is clear evidence of decomposition; fortunately, the main impurity is phenol (2 to 3 percent), which does not interfere much with rate studies in aqueous solution. By a very careful purification, it is possible to obtain a benzenediazonium fluoborate sample that can be stored at 0°C for several months without any signs of decomposition. The sample is dissolved in acetone, and then chloroform is added until a few crystals are formed. When the solution is then chilled to −20°C for 30 min, the compound will crystallize out in the form of tiny white needles. After three such recrystallizations, the sample can again be dried by pumping and can be stored in a vacuum desiccator.

‡If a spectrophotometer with a cell compartment that can be temperature controlled is available, the procedure can be greatly improved and simplified. Adjust the bath temperature to 30°C, turn on the circulating pump, and wait until the cell compartment (with cell holder in place) has become stable. Then prepare a solution as described above and fill two spectrophotometer cells as soon as possible. (A third cell should already have been filled with 0.2 M HCl solution, for use as a blank.) Place the cells in the cell holder, and record the time at which the cell holder is returned to the cell compartment. Obtain absorbance readings on both samples as soon as possible; these initial readings will provide values of εd. Allow about 20 min for the solutions to achieve thermal equilibrium, and then begin measuring the absorbance every 15 min. Since the runs are made sequentially rather than simultaneously, it is advisable to replace the slow run at 25°C with a run at 45°C (use 5-min intervals). Fresh solutions are needed for each temperature studied.

Take as many measurements as you reasonably can without rushing. Since the runs at the higher temperatures will proceed more rapidly, it will be necessary to take samples from them at more frequent intervals. A suggested interval might be once every 25 min for the 25°C bath, every 15 min for the 30°C bath, and every 10 min for the 40°C bath.

At the end of the experiment, wash the cells thoroughly with distilled water and dry them very carefully. Store them in a safe place.

CALCULATIONS

Using all the data points from any single run, prepare plots of the following: (1) $A^{1/2}$ versus t (order $\frac{1}{2}$), (2) $\log A$ versus t (order 1), (3) A^{-1} versus t (order 2), and (4) any additional plots you feel to be necessary in order to establish the order of the reaction.

Having determined the order of the reaction, make the appropriate plot for each of the runs and determine the value of k (in concentration units) for each temperature. It is convenient to make these plots using A values rather than c values. The value of the slope can then be corrected, if necessary, to obtain k in concentration units by utilizing the value of εd. You should also carry out a least-squares analysis of your data using the appropriate form of Eq. (4). Report both sets of k values, together with the standard deviations for the least-squares values. Finally, plot $\log k$ versus $1/T$ and determine E_a.

Report your result for the order of the reaction and list the best values obtained for $k(T_1)$, $k(T_2)$, and $k(T_3)$. Report also the activation energy E_a. Give the correct units for each quantity, using s as the unit of time, mol L^{-1} for concentration, and kJ for energy.

DISCUSSION

From your results, calculate the extent of reaction that would occur in a sample of the initial solution after 30 min at 0°C. Does this indicate that varying lengths of time between the chilling of a sample and its absorbance measurement would introduce serious or negligible errors in your data?

SAFETY ISSUES

None.

APPARATUS

Spectrophotometer, such as one of the Beckman model DU series; two or more quartz sample cells; constant-temperature baths set at 25, 30, and 40°C; lens tissue; three 100-mL volumetric flasks; clock, stopwatch, or other timer; hypodermic syringe; about 20 test tubes; plastic pail or large battery jar; beaker.

Benzenediazonium fluoborate (75 mg), stored in a refrigerator; 0.2 *M* hydrochloric acid (400 mL); crushed ice.

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EXPERIMENTS IN PHYSICAL CHEMISTRY, EIGHTH EDITION

Published by McGraw-Hill, a business unit of The McGraw-Hill Companies, Inc., 1221 Avenue of the Americas, New York, NY 10020.

1 2 3 4 5 6 7 8 9 0 QPD/QPD 0 9 8

ISBN 978–0–07–282842–9
MHID 0–07–282842–0

Publisher: *Thomas Timp*
Senior Sponsoring Editor: *Tamara L. Hodge*
Director of Development: *Kristine Tibbetts*
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Associate Design Coordinator: *Brenda A. Rolwes*
Cover Designer: *Studio Montage, St. Louis, Missouri*
Compositor: *Laserwords Private Limited*
Typeface: *10/12 Times Roman*
Printer: *Quebecor World Dubuque, IA*

Cover description: The figure depicts the absorption and emission spectra of CdSe nanocrystals, whose color is a sensitive function of size. The figure is based on spectral data provided by NN-Labs. The authors thank both NN-Labs and Evident Technologies for CdSe samples used in the development of the quantum dot experiment.

Library of Congress Cataloging-in-Publication Data

Garland, Carl W.
Experiments in physical chemistry.—8th ed. / Carl W. Garland, Joseph W. Nibler, David P. Shoemaker.
p. cm.
Includes index.
ISBN 978–0–07–282842–9—ISBN 0–07–282842–0 (hard copy : acid-free paper)
1. Chemistry, Physical and theoretical—Laboratory manuals. I. Nibler, Joseph W.
II. Shoemaker, David P. III. Title.
QD457 .S56 2009
541.078—dc22

2007043492

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