

Experiment V¹

Spectroscopy and Kinetics of An Inorganic Photochromic Compound

This experiment involves a kinetic study of a photochromic metal compound. The compound is mercury dithizonate, $\text{Hg}(\text{Dz})_2$. (dithizonate is diphenyl-thiocarbazonate). In this compound, a $\text{Hg}(\text{II})$ center is coordinated to nitrogen and sulfur donors in a distorted tetrahedral environment. The $\text{Hg}(\text{Dz})_2$ complex is orange and can be converted to a blue isomer, Compound B, by exposure to sun light. The color change is thought due to the monomolecular photo-isomerization process shown in Figure 1. The N-H----S hydrogen bond in the yellow isomer is broken and anti-syn isomerization about the C=N bond being followed by electronic rearrangement and a N to N proton transfer that establishes a new weaker hydrogen bond. The resulting activated blue structure represents a dramatically altered chromophore containing a thiocarbonyl group. The color of both isomers is due to ligand centered transitions with little (if any) metal-to-ligand or ligand-to-metal charge transfer character.

Interestingly, the blue isomer converts back to the orange starting complex in the dark by a first-order process. The kinetics can be monitored by time resolved visible spectroscopy and the rate constant can be abstracted from analysis of this temporal spectroscopic data.

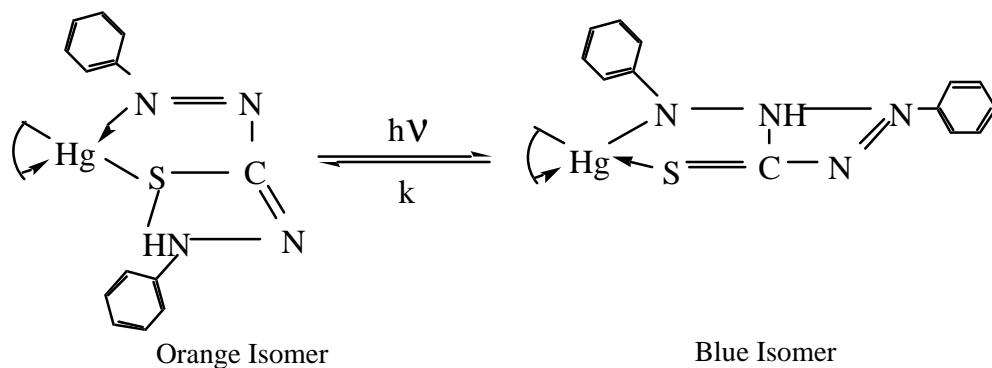


Figure 1.

Hazards

Xylene is a flammable mobile liquid with a flash point at 29 C. It can be narcotic at high concentrations. The toxicity is not well defined but, it is less toxic than benzene.

Mercury Dithizonate. No toxicity data is currently available. It is a poisonous solid and skin contact should be avoided.

Experimental Procedure.

Prepare a 10 mL solution of approximately 10^{-5} M mercury (II) dithiozate in xylene. This is most easily done by: 1) dissolving a minimal amount of the complex in xylene; 2) recording its absorption spectrum from 350 to 750 nanometers; 3) using Beer's Law to calculate the concentration; and 4) adjusting the concentration with additional xylene or $\text{Hg}(\text{Dz})_2$. The extinction coefficient of $\text{Hg}(\text{Dz})_2$ is $7 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 490 nanometers. Record the absorption spectrum of the final solution from 350 to 750 nm.

Place the solution in bright sunlight or, if it is a cloudy day, a separate white light source. Watch the solution turn a uniform blue color. This should take about five minutes. Quickly place the cuvette in the diode array and record the full absorption spectrum from 350 to 750 nm every 45 seconds for five minutes. Observe and mark the isosbestic points.

Place the solution back in the light until the intense blue color reappears. Record the absorption intensity at the wavelength where the blue isomer absorbs most strongly every 20 s for five minutes. This is the data from which you will abstract the rate constant.

Data Analysis

A. First-Order Reactions.

Suppose that the reaction $\text{B} \rightarrow \text{O}$ is first-order, that is the rate depends only on the concentration of B. The rate law is:

$$r = -\frac{d[\text{B}]}{dt} = k[\text{B}] \quad \text{I}$$

To solve this differential equation, we rearrange terms and integrate with respect to time:

$$\ln \frac{[\text{B}]}{[\text{B}]_0} = -kt \quad \text{or} \quad [\text{B}] = [\text{B}]_0 e^{-kt} \quad \text{II}$$

where $[\text{B}]_0$ is the molar concentration at $t = 0$. Thus for a first-order reaction, *the concentration of B decreases exponentially with time.*

B. Graphical Methods of Analysis.

Many analysis methods exist for abstracting rate constants from time-resolved experimental data.³ While most techniques require linear regression, the procedure outlined below will allow you to graphically obtain the rate constant from your data.

All studies of first-order reactions are based on the following relationship:

$$A_t = (A_0 - A_\infty) \exp(-kt) + A_\infty \quad \text{III}$$

where A_t , A_0 , and A_∞ are the magnitudes of the signal at times t , 0, and infinity and k is the first-order rate constant. Differentiating with respect to time, we obtain the rate expressions

$$\text{at } t \quad \left(\frac{dA}{dT} \right)_t = (A_0 - A_\infty)(-k) \exp(-kt) = R(t) \quad \text{IV}$$

$$\text{at } t + \Delta \quad \left(\frac{dA}{dT} \right)_{t+\Delta} = (A_0 - A_\infty)(-k) \exp(-kt) \cdot \exp(k\Delta) = R(t + \Delta). \quad \text{V}$$

The ratio of equations IV/V gives

$$\frac{R(t)}{R(t + \Delta)} = \exp(k\Delta) = r. \quad \text{VI}$$

It can be seen that this ratio, equation VI, is constant for all values of t . It can thus be calculated at different times throughout the course of the reaction, and a mean value can be obtained. The rate constant k is obtained from this mean r_m :

$$k = (\ln r_m)/\Delta \quad \text{VII}$$

A simple procedure for analyzing your results is the following.

- Chose a time interval Δ to obtain around six equidistant points over the whole reaction curve, $A(t)$.
- Draw the tangents to the curve at each of these points.
- Calculate the slope R_i in arbitrary units.
- Calculate the five ratios R_i/R_{i+1} for the six slopes.
- Take the mean and use equation VII to obtain k .

As an optional exercise, you are encouraged to use the computer tools in the MacLab (Remsen 312) to perform a numerical analysis of the rate law. Computer programs, such as Kaleidagraph, are available to undergraduates enrolled in this course.

Current Research Efforts

Research in photochromism is an active area in both industry and academia. The mercury dithiozate/xylene system explored above is in fact very general. Photochromism is observed in most solvents and when different metals are coordinated to diphenylthiocarbazone.^{2,6} Organic, inorganic and solid state materials are actively being explored for applications as displays, optical switches, glasses for eye protection, photography, actinometry, radiometry, memory storage, recording media, and temperature indicators. A recent review of work in this field is available in the library⁴ and an article with potential switching applications by Dr. Cowan and coworkers has recently appeared.⁵

References

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