An Easily Implemented Flash Photolysis Experiment for the Physical Chemistry Laboratory

The Isomerization of 4-Anilino-4′-nitroazobenzene

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Flash photolysis is widely applied to the study of photochemical reactions but is seldom included as an undergraduate laboratory experiment (1). Although an experiment using this technique introduces students to important aspects of photochemistry and kinetics, construction of a flash photolysis apparatus or modification of a spectrometer can be prohibitively expensive or time-consuming for the instructor. The experiment presented here enables students to perform and analyze a complete flash photolysis study without specialized equipment or modification of existing equipment. In this experiment, an inexpensive electronic camera flash initiates the reaction, and a visible spectrometer monitors its progress. Although the complete experiment is most appropriate for an undergraduate physical chemistry course, portions of the experiment could easily be included in a first-year college chemistry laboratory.

4-Anilino-4′-nitroazobenzene is called a "push–pull" azobenzene because it is substituted with an electron donor (anilino-) and an electron acceptor (nitro-) at the p and p' positions of the conjugated aromatic system. This type of substitution results in contribution from a resonance structure containing an N—N single bond, as illustrated in Figure 1. The concomitant weakening of the N=N bond changes the visible absorption spectrum of 4-anilino-4′-nitroazobenzene, in comparison to that of azobenzene. The substituent groups effectively increase the energy of the N=N π bonding orbital and lower the energy of the π^* antibonding orbital, thus lowering the energy of the $\pi^* \leftarrow \pi$ transition. For both cis and trans isomers of 4-anilino-4′-nitroazobenzene the wavelength of the N=N $\pi^* \leftarrow \pi$ chromophore is red shifted compared to unsubstituted azobenzene (2), as shown in Table 1. The visible absorption spectrum of 4-anilino-4′-nitroazobenzene also changes with solvent. In polar solvents, the $\pi^* \leftarrow \pi$ absorption is red shifted slightly for azobenzene and more strongly for 4-anilino-4′-nitroazobenzene (2). Polar solvents would be expected to stablize the zwitterionic form of the molecule, contributing to the observed red shift. In addition, the polarity of the solvent may cause a change in the N–N–C angle and thus the energy of electronic transitions of the N=N bond (2).

The cis → trans isomerization of azobenzenes has been investigated using flash photolysis as well as other techniques (2–7). Due to steric interaction, the trans isomer is the energetically favored configuration in the ground electronic state. Upon irradiation with visible light, the dye is electronically excited. Although the mechanism of electronic energy dissipation is not well understood, the ground state cis isomer is subsequently formed. The cis isomer then returns to the more stable trans form via a rapid thermal
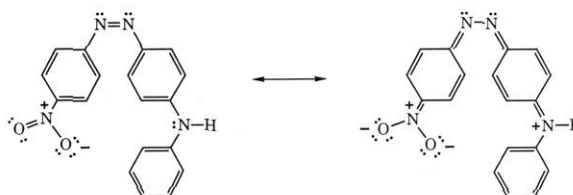
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Figure 1. Resonance structures of 4-anilino-4′-nitroazobenzene, a "push–pull" substituted azobenzene.

Table 1. Absorption Maxima and Molar Absorptivities of Azobenzene and 4-Anilino-4′-nitroazobenzene $\pi^* \leftarrow \pi$ Transitions in Cyclohexane[a]

	Azobenzene	4-Anilino-4′-nitro-azobenzene
cis		
λ_{max} (nm)	247	332
ϵ (M^{-1} cm^{-1})	11500	7900
trans		
λ_{max} (nm)	316	435.5
ϵ (M^{-1} cm^{-1})	22000	16800

[a] Values listed are from ref. 2.

reaction. The mechanism of this thermal azobenzene isomerization has been the subject of several investigations (2–5). The rate of thermal cis → trans isomerization for many azobenzenes is relatively rapid and usually independent of the solvent or the substitution of the azobenzene (3, 4). Since an isomerization mechanism involving rotation about the N=N bond would be expected to show solvent and substituent effects, an in-plane inversion mechanism, with a linear, sp-hybridized transition state was proposed (4). For "push–pull" azobenzenes, substituent and solvent effects are evident, however. This may indicate that a rotational mechanism applies for these molecules (2–5). Alternatively, the change in N–N–C angle caused by solvent polarity for "push–pull" substituted azobenzenes may change the isomerization rate for an inversion mechanism, as well. Recent work on a series of "push–pull" substituted azobenzenes indicates that both inversion and rotational mechanisms occur; the operative mechanism is thought to be determined by the strength of the interaction between the particular dye and solvent (5). The isomerization mechanism of these "push–pull" substituted azobenzenes is not completely understood and remains the subject of study (2).

In this investigation a flash of light initiates the photochemical and subsequent thermal isomerization. A camera flash excites the ground state trans 4-anilino-4′-nitroazobenzene, generating an electronically excited species and then the ground state cis isomer. In the ground electronic state, the cis form then returns to the more stable trans

isomer by a thermal reaction occurring over a period of approximately 30 min. The overall reaction can be written schematically as

$$\text{trans} \xrightarrow{h\nu} \text{[electronically excited species]} \rightarrow \text{cis} \xrightarrow{k} \text{trans} \quad (1)$$

with k representing the rate constant for the thermal isomerization. The reaction monitored in this experiment is the thermal isomerization following the initial photochemical isomerization. This experiment, in which the thermal reaction of a photoproduct is observed, differs from many flash photolysis experiments, where an electronically excited species is monitored.

The rate of the thermal reaction can be written

$$\frac{-d[\text{cis}]}{dt} = \frac{d[\text{trans}]}{dt} = k[\text{cis}] \quad (2)$$

Although theoretically the concentration of either isomer could be monitored to determine the reaction rate, in practice the concentration of the trans isomer is followed over time by observing the change in its absorbance. The concentration of the trans form is more easily monitored because the cis isomer does not contribute to the absorbance at the maximum of the trans isomer $\pi^* \leftarrow \pi$ transition, while the trans isomer does contribute to the absorbance at the wavelength of the cis transition (2).

To integrate eq 2, an expression is needed to relate the concentration of the trans to that of the cis isomer at any time. If isomerization is the only process occurring, the concentration of trans isomer at any time, t, during the reaction ($[\text{trans}]_t$) plus the concentration of cis isomer at that time ($[\text{cis}]_t$) is equal to the concentration of trans isomer after the reaction is completed ($[\text{trans}]_\infty$). This can be written

$$[\text{trans}]_\infty = [\text{cis}]_t + [\text{trans}]_t \quad (3)$$

Note that the concentration of trans isomer after the reaction is completed, $[\text{trans}]_\infty$, will equal the concentration before the flash. Substituting eq 3 into the rate law of eq 2 yields:

$$\frac{d[\text{trans}]_t}{dt} = k\{[\text{trans}]_\infty - [\text{trans}]_t\} \quad (4)$$

This can be integrated to give

$$\ln\{[\text{trans}]_\infty - [\text{trans}]_t\} = -kt + \ln\{[\text{trans}]_\infty - [\text{trans}]_0\} \quad (5)$$

where $[\text{trans}]_0$ is the absorbance of the trans isomer at the start of the thermal reaction, immediately after the flash.

Beer's law can now be used to relate the absorbance to concentration:

$$A = \epsilon l[\text{trans}] \quad (6)$$

where A is the absorbance at a given wavelength, ϵ is the molar absorptivity at that wavelength, and l is the path length of the cell. In using this equation, we assume that the molar absorptivity of the cis isomer is zero at the observed wavelength. For the isomerization of 4-anilino-4'-nitroazobenzene, observed at the peak of the trans isomer $\pi^* \leftarrow \pi$ absorption, this assumption is very good (2). Substituting for concentration in eq 5 and eliminating the molar absorptivity and path length yield a rate equation in terms of absorbance:

$$\ln(A_\infty - A_t) = -kt + \ln(A_\infty - A_0) \quad (7)$$

Thus, the rate constant, k, can be determined from a plot of $\ln(A_\infty - A_t)$ vs. time. The absorbance at infinite time can be determined from either the absorbance prior to the flash or the absorbance at times long after the flash.

The rate constant of this reaction varies with temperature according to the Arrhenius equation:

$$k = \mathcal{A} \exp(-E_a/RT) \quad (8)$$

where E_a is the activation energy and $\mathcal{A}$ is the frequency factor. Equation 8 can be rewritten as

$$\ln k = \ln \mathcal{A} - E_a/RT \quad (9)$$

The activation energy and frequency factor can now be determined from a plot of $\ln k$ vs. $1/T$.

Experimental Procedure

4-Anilino-4'-nitroazobenzene was puchased from Aldrich under the common name Disperse Orange 1. The sample supplied contained approximately 25% dye by weight, with the remaining mass consisting of NaCl and other salts (8). The salts did not dissolve in the organic solvents used, and dye solution was decanted from the undissolved material. HPLC-grade solvents were obtained from Fisher and used without purification. Solution concentrations were approximately 10^{-6} M. Solutions were placed in amber bottles and allowed to equilibrate overnight in the dark prior to performing the experiment. Polyethylene gloves were worn during all sample handling.

All absorbance data presented here were obtained using a Perkin–Elmer Lambda 6 spectrophotometer. The experiment was also performed using Cary 14 and Cary 210 spectrophotometers with similar results. Sample temperature was controlled by a Lauda K-2/R refrigerated recirculating water bath and monitored by a copper–constantan thermocouple (9) with a junction inside the Pyrex sample cuvette. Thermocouple voltage was monitored with either a Keithly 197 or 199 digital multimeter. The uncertainty in the temperature control and measurement was estimated to be ±1 °C. For the data presented here, the photolytic flash was provided by a Sunpak Auto 231 camera flash. The experiment was also performed successfully using the flash in a Kodak Ektralite 10 pocket camera with the yellow plastic filter removed from the front of the flash.

After the sample was placed in the spectrometer and allowed to reach the desired temperature, the absorption spectrum was measured to determine the wavelength at the maximum of the trans isomer $\pi^* \leftarrow \pi$ transition. The spectrometer was then set at this wavelength, and the chart drive was started in order to record the absorbance as a function of time. After a short period of time (1–2 min), the sample was quickly removed from the spectrometer and irradiated with the camera flash. The flash was placed against the window of the cuvette and fired by depressing the test button. The cuvette was immediately replaced in the spectrometer, and the sample compartment was closed. The monitoring continued until the absorbance returned to the level observed before excitation with the camera flash.

Results and Discussion

The results of the flash photolysis study of 4-anilino-4'-nitroazobenzene are summarized in Figures 2–5 and Tables 2 and 3. A typical plot of absorbance vs. time is shown in Figure 2. The absorbance initially remains constant over
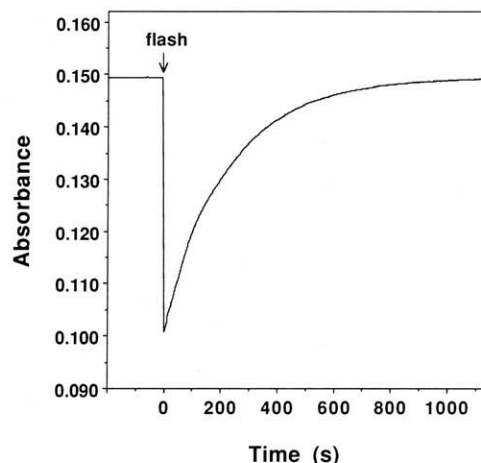

Figure 2. Change in the absorbance of *trans*-4-anilino-4'-nitroazobenzene at 434 nm as a function of time. Reaction was monitored at 40 °C in cyclohexane. The zero of time for the thermal isomerization reaction immediately follows the abrupt change in absorbance caused by the flash.
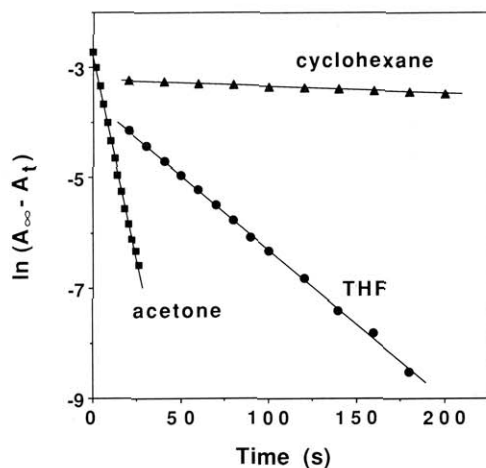
Figure 3. Plot of ln $(A_\infty - A_t)$ vs. time for the isomerization of 4-anilino-4′-nitroazobenzene in different solvents at ambient temperature. As the solvent polarity increases (cyclohexane < THF < acetone) the isomerization rate increases. Rate constants are given in *Table 2*.

Table 2. Wavelength of Maximum Absorbance and Isomerization Rate Constants of 4-Anilino-4′-nitroazobenzene in *Different* Solvents at Ambient Temperature

Solvent	λ (nm)	Rate Constant (s⁻¹)
Acetone	460	0.14
Tetrahydrofuran	465	0.025
Cyclohexane	435	0.0016

time, decreases immediately following irradiation with the camera flash, and returns to its initial value after several minutes. To determine the isomerization rate constant from the recovery of the absorbance, zero time is established immediately after the flash, as shown in Figure 2. The absorbance at infinite time can be determined from the value before the flash or at long times following the flash. If these absorbance values are not equal, the sample did not reach the equilibrium mixture of cis and trans isomers prior to excitation. In this circumstance, the data can be analyzed using the Guggenheim method, which does not require knowledge of A_∞ (10).

Rate constants for the isomerization are obtained from plots of ln $(A_\infty - A_t)$ vs. time, as given by eq 7. Figure 3 illustrates such plots for 4-anilino-4′-nitroazobenzene in three solvents of varying polarity. The wavelengths of maximum absorbance and the rate constants are listed in Table 2. The change in rate constant with solvent polarity may indicate that isomerization occurs by a rotational mechanism for this substituted azobenzene. This does not obviate isomerization by inversion, however, because the polarity of the solvent may change the N–N–C angle and thus the rate of reaction (2). The trend in rate with solvent polarity shown in Figure 3 agrees qualitatively with the results of Kobayashi et al. (2). Since the isomerization monitored in Figure 3 was observed at ambient temperature over a period of several days, quantitative comparison with the rate constants measured at 25 °C by Kobayashi (2) is not appropriate.

The isomerization rate was measured at several temperatures in cyclohexane to determine the activation energy of the reaction. Figure 4 shows plots of ln $(A_\infty - A_t)$ vs. time for five temperatures. The resulting rate constants are given in Table 3. Uncertainties in the rate constants were evaluated by measuring the rate at 40 °C eight times over a period of several days. The uncertainty listed in Table 3 for the rate at
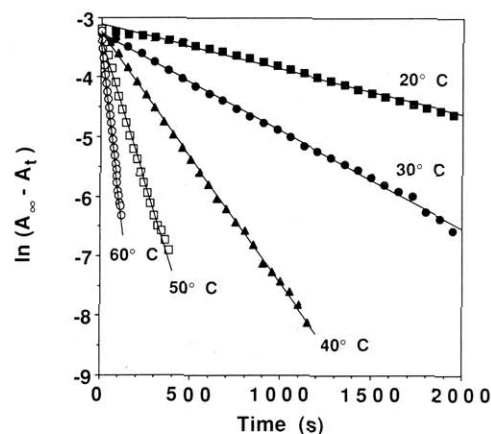

Figure 4. Plot of ln $(A_\infty - A_t)$ vs. time for the isomerization of 4-anilino-4′-nitroazobenzene in cyclohexane at different temperatures. Rate constants determined from linear plots are given in Table 3.

Table 3. Isomerization Rate Constants, Activation Energy, and Frequency Factor for 4-Anilino-4′-nitroazobenzene

Temperature (°C) (±1 °C)	Rate Constant × 10³ (s⁻¹)
20	0.76 ± 0.07
30	1.6 ± 0.2
40	4.2 ± 0.2
50	10 ± 1
60	26 ± 3
Activation Energy	72 ± 9 kJ/mol
ln $\mathcal{A}$	22 ± 3

40 °C is a 95% confidence limit of the mean of the eight values. The uncertainties given for the rate constants at the *remaining* temperatures were estimated assuming the same relative standard deviation and an uncertainty of 2σ.

Figure 5 is a plot of ln k vs. $1/T$ (eq 9). The activation energy determined from the slope is 72 ± 9 kJ/mol, which agrees with the literature to within the experimental uncertainty (2). The intercept of the line yields a value for ln $\mathcal{A}$ of 22 ± 3, corresponding to a frequency factor in the range of 3
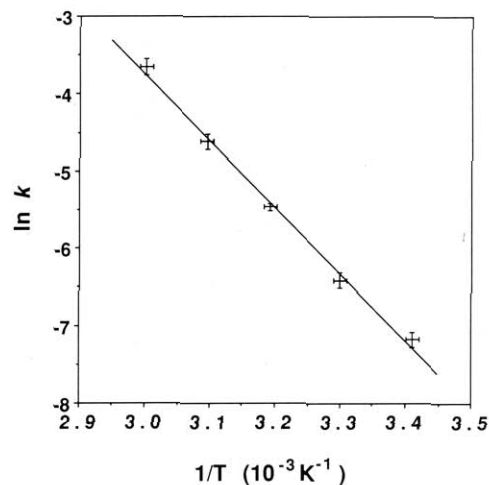

Figure 5. Arrhenius plot for the isomerization of 4-anilino-4′-nitroazobenzene in cyclohexane. The activation energy and frequency factor for the isomerization reaction are given in Table 3.

$\times 10^8$ to 6×10^{10} s^{-1}. The uncertainties quoted are 95% confidence limits obtained from a linear least-squares fit to the data. The vertical error bars shown in Figure 5 represent the uncertainty in the rate constants given in Table 2. The uncertainty in the temperature is shown by the horizontal error bars in Figure 5.

Conclusions

In performing this experiment, students measured the isomerization rate of 4-anilino-4'-nitroazobenzene, observed a change in the rate with solvent, and determined the activation energy of the reaction. There are several ways of organizing the laboratory experiment, depending on the time and equipment available. If sample temperature control is not possible, the reaction rate can be measured at ambient temperature in different solvents. In this form, the experiment could be performed by first-year college chemistry students using a Spectronic 20 and a strip chart recorder. If temperature control is available, the activation energy can be determined by observing the reaction at several temperatures in a single solvent. Depending on the time available, each group of students could measure the rate at several temperatures or several groups could determine the rate at one or two temperatures and share their data to calculate the activation energy.

This investigation introduces important aspects of photochemistry and kinetics methods without requiring elaborate construction or modification of equipment. Although the apparatus used in this flash photolysis experiment was "low tech", the accuracy of student results was generally good and response to the experiment was enthusiastic.

Literature Cited

1. Undergraduate flash photolysis experiments have been described by Matthews, G. P. *Experimental Physical Chemistry*; Clarendon: Oxford, 1985; pp 460–469; Kozubek, H.; Marciniak, B.; Paszyc, S. *J. Chem. Educ.* **1984**, *61*, 835–837.
2. Kobayashi, S.; Yokoyama, H.; Kamei, H. *Chem. Phys. Lett.* **1987**, *138*, 333–338 and references therein.
3. Nishimura, N.; Sueyoshi, T.; Yamanaka, H.; Imai, E.; Yamamoto, S.; Hasegawa, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1381–1387.
4. Wildes, P. D.; Pacifici, J. G.; Irick, G., Jr.; Whitten, D. G. *J. Am. Chem. Soc.* **1971**, *93*, 2004–2008.
5. Shin, D.–M.; Whitten, D. G. *J. Am. Chem. Soc.* **1988**, *110*, 5206–5208.
6. Fischer, E.; Frei, Y. *J. Chem. Phys.* **1957**, *27*, 328–330.
7. Brode, W. R.; Gould, J. H.; Wyman, G. M. *J. Am. Chem. Soc.* **1952**, *74*, 4641–4646.
8. Aldrich Chemical Company, Dye and Stain Division Technical Support, personal communication, 1989.
9. General information about thermocouples can be found in the catalog *Temperature Measurement Handbook and Encyclopedia*; Omega Engineering, Inc.; Stamford, CT, 1985; pp T7–T9.
10. Shoemaker, D. P.; Garland, C. W.; Nibler, J. W. *Experiments in Physical Chemistry*, 5th ed.; McGraw–Hill: New York, 1989; pp 289–290.