Flash Photolysis of Benzophenone

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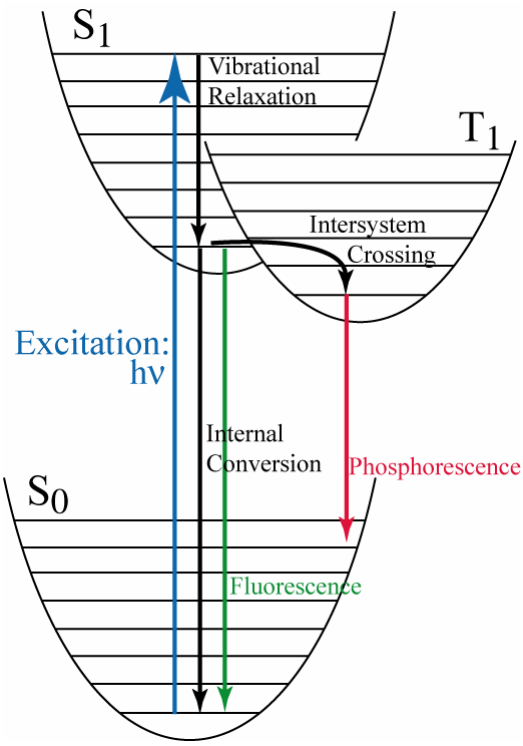
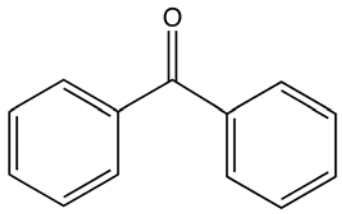
I. Introduction

The study of chemical kinetics is central to many areas of chemistry and biochemistry. One of the most powerful methods in studying the kinetic behavior of chemical reactions is flash photolysis. In this experiment, you will study the flash photolysis of benzophenone using a very simple experimental apparatus. You will monitor the decay in the concentration of the photochemically formed deprotonated ketyl radical by monitoring its optical absorption of He-Ne (helium-neon) laser radiation. Before you begin, read the section on chemical kinetics in your textbook.

II. Theory

Optical absorption of UV/Visible or higher energy photons by a molecule typically leads to electronic excitation (or promotion of an electron to an unoccupied molecular orbital). Once electronically excited, the molecule then must relax by means of radiative (photon emitting) or non-radiative pathways. The diagram below shows some of these pathways, whereby a molecule in its ground, singlet electronic state (S_0) undergoes optical absorption to its first excited, singlet state (S_1). After vibrational relaxation in the S_1 state it can fluoresce back down to S_0, emitting a photon in the process. From S_1 it may also non-radiatively return to S_0 via internal conversion. The excited molecule may also undergo intersystem crossover to the triplet state T_1. The notation of singlet and triplet refer to the total electronic spin of the molecule, corresponding respectively to zero or two unpaired electrons. Overall, these excitation and relaxation processes often lead to a permanent chemical change in the molecule, like photodissociation. A more detailed description of the fate of electronic excited states can be found in your text. The present laboratory will focus on the photolysis of benzophenone. The fate of benzophenone following electronic excitation via absorption can be described by a number of elementary mechanistic steps.





Benzophenone

When benzophenone $(C_6H_5)_2CO$ absorbs a UV/Visible photon, it is excited to its first electronic state:

$$(C_6H_5)_2CO + h\nu \xrightarrow{k_1} (C_6H_5)_2CO^* (S_1) \quad (1)$$

The excited benzophenone (noted as $(C_6H_5)_2CO^*$) can then undergo intersystem crossing to the triplet state:

$$(C_6H_5)_2CO^* (S_1) \xrightarrow{k_2} (C_6H_5)_2CO^* (T_1) \quad (2)$$

The triplet state can either 1) slowly phosphoresce back down to the ground state

$$(C_6H_5)_2CO^* (T_1) \xrightarrow{k_3} (C_6H_5)_2CO (S_0) \quad (3)$$

or, in the presence of isopropanol, 2) undergo a much faster relaxation process in which a proton is abstracted from the alcohol to form a protonated ketyl radical:

$$(C_6H_5)_2CO^* (T_1) + ROH \xrightarrow{k_4} (C_6H_5)_2COH^\bullet + ROH^\bullet \quad (4)$$

Note that there is one OH on the left hand side and two on the right! Where did the extra H come from (specifically why do I have $ROH^\bullet$ vs $RO^\bullet$)? The H in the $ROH^\bullet$ is abstracted from the alcohol molecule itself, like so: $CH_3\text{-}\overset{O^\bullet}{\overset{|}{C}}H\text{-}CH_3 \rightarrow CH_3\text{-}\overset{OH}{\overset{|}{C}}{}^\bullet\text{-}CH_3$. The $ROH^\bullet$ radical can interact with the ground state of benzophenone to generate even more protonated ketyl radicals:

$$(C_6H_5)_2CO + ROH^\bullet \xrightarrow{k_5} (C_6H_5)_2COH^\bullet + RO^\bullet \quad (5)$$

In a basic solution, the protonated ketyl radicals can disassociate:

$$(C_6H_5)_2COH^\bullet \overset{K_6}{\leftrightarrow} (C_6H_5)_2CO^{\bullet-} + H^+ \quad (6)$$

Note that the protonated neutral radical and deprotonated anion radical are in equilibrium and K_6 is an equilibrium constant.

Finally, the protonated and deprotonated forms of the ketyl radicals can dimerize, forming the benzopinacol anion:

$$(C_6H_5)_2COH^\bullet + (C_6H_5)_2CO^{\bullet-} \xrightarrow{k_7} (C_6H_5)_2(OH)C\text{-}C(O^-)(C_6H_5)_2 \quad (7)$$

where a new bond is formed between the carbon atoms.

The rate of benzophenone photolysis is determined by the triplet decay steps, described above in reactions 3 and 4:

$$\frac{\partial[T_1]}{\partial t} = -k_3 \cdot [T_1] - k_4 \cdot [T_1] \cdot [ROH] \qquad (8)$$

where $[T_1]$ is the time dependent concentration of $(C_6H_5)_2CO^*$ (T_1). The rate equation can be reduced to a pseudo-first order expression since the excess of alcohol prevents the concentration of alcohol from ever effectively changing during the reaction:

$$\frac{\partial[T_1]}{\partial t} = -k_3 \cdot [T_1] - k_4 \cdot [T_1] = -k' [T_1] \qquad (9)$$

where k' is $k_3 + k_4[ROH]$.

The solution to the differential (9) the decay of the triplet species as a function of time is:

$$[T_1](t) = [T_1](0) \times \exp(-k't) \qquad (10)$$

where $[T_1](0)$ is the initial concentration of the triplet species.

The instrument used in this apparatus cannot measure the triplet decay rate of equation 10 for two reasons: the triplet absorbs at 525 nm instead of 632.8 nm of the He-Ne laser and the decay lifetime is much shorter than the ~millisecond response time of the instrument. Therefore we will be probing a different step in the benzophenone photolysis.

The rate of decay of the deprotonated ketyl radical anion can be deduced from equation 7 to be overall a second order process:

$$\frac{\partial\left[(C_6H_5)_2CO^{\bullet -}\right]}{\partial t} = -k_7 \cdot \left[(C_6H_5)_2CO^{\bullet -}\right] \cdot \left[(C_6H_5)_2COH^{\bullet}\right] \qquad (11)$$

If we assume that equation 6 rapidly reaches equilibrium with an equilibrium constant of K_6, then its equilibrium relationship can be rearranged to yield

$$[(C_6H_5)_2COH^{\bullet}] = [(C_6H_5)_2CO^{\bullet -}][H^+] / K_6 \qquad (12)$$

Now substituting equation 12 into equation 11 yields:

$$\frac{\partial\left[(C_6H_5)_2CO^{\bullet -}\right]}{\partial t} = -k_{obs} \cdot \left[(C_6H_5)_2CO^{\bullet -}\right]^2 \qquad (13)$$

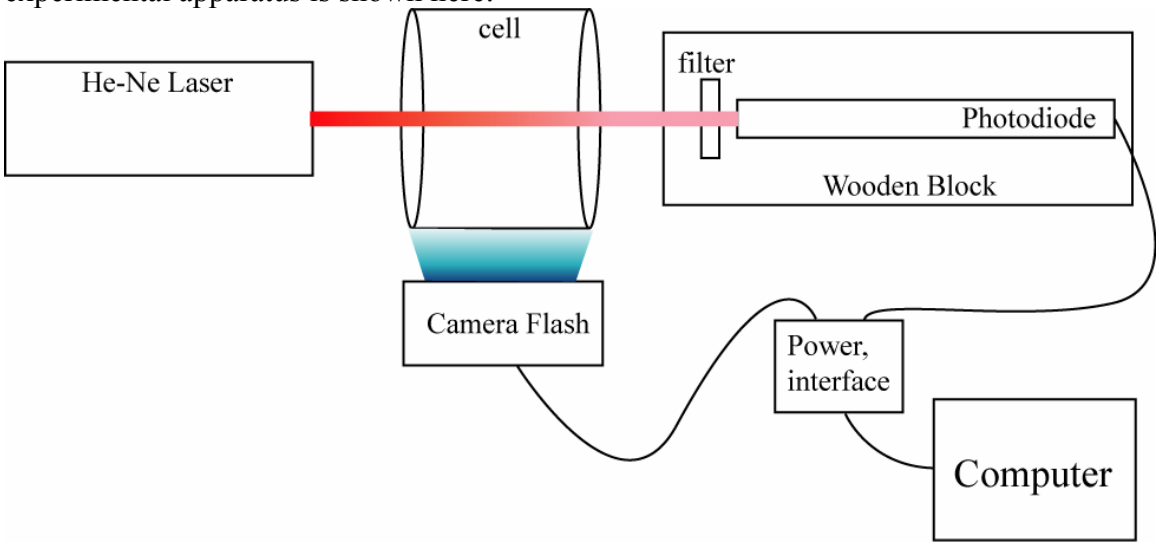
where $k_{obs} = k_7[H^+]/K_6$. The reaction thus appears to be second order with an observed rate constant of Kobs that is directly proportional to $[H^+]$. Solving the differential equation 13 yields a rate law of the form:

$$\frac{1}{\left[(C_6H_5)_2CO^{\bullet -}\right]_t} = k_{obs} \cdot t + \frac{1}{\left[(C_6H_5)_2CO^{\bullet -}\right]_0} \qquad (14)$$

In this experiment you will monitor the concentration of the deprotonated ketyl radical anion appearing in equation 14. Its decay rate has a lifetime of milliseconds. The deprotonated ketyl radical absorbs at 630 nm, allowing its concentration to be monitored by the absorption of the He-Ne laser.

III. Experimental Protocol

This experiment uses an electronic flash unit to induce the photodissociation of benzophenone. The concentration of the ketyl radical with respect to time is monitored with a photodiode which records the absorption of light at 632.8 nm. A scheme of the experimental apparatus is shown here:



All the glassware must be very clean prior to this experiment. To clean the sample cell, rinse it thoroughly with water followed by isopropanol. Do not use soap. Drying is not necessary and discard the washings in the waste container.

Prepare 175 mL of a stock 0.010 M solution of benzophenone in isopropanol in a brown bottle. You will need to use a top loading balance due to the weight of the bottle. Make sure you don't add the isopropanol until your ready to use it and be sure to protect the solution from visible light at all times. Therefore, before adding the solvent, wrap up the bottle in aluminum foil and turn off the lights in 2013 and 2013 A.

You need three solutions of NaOH with pH values of 11, 12, and 13. This can be accomplished by preparing a 100 mL stock solution of 0.10 M NaOH (pH = 13). The

lower pH solutions can be made by taking 50 mL of water and adding the stock solution drop wise until the desired pH is reached.

Prepare three basic benzophenone solutions my mixing equal volumes (50 mL) of the benzophenone stock solution with the NaOH solutions you just prepared. Determine and record the pH, which should remain very close to 11, 12 and 13. Use these measurements in your calculations. Make sure the solutions are mixed and degassed. Now that the NaOH has been mixed with the benzophenone, you must perform the flash experiment immediately.

Inject the first solution into the photolysis cell until it is about 2/3 full. Turn on the nitrogen gas tank regulator so that you get a slow flow from the 1/8" tubing. Attach this tube to the photolysis cell and slide the tube down into the solution so that it is bubbling mildly. Allow the solution to bubble for ~15 minutes and make sure that the N2 bubbles throughout the whole volume of the solution. Also remember to keep the cell shielded from light during this time.

Now you need to turn on the software and align the laser. The following procedure was written by the inventor to collect the data with the computer attached to the photodiode:

FLASH DATA COLLECTION

1.Turn On Power Strip (Laser Power Supply (Blue Box) plugged in)
2a.Turn On Lab Station Power Supply)Plugged in)

2b.Turn On Laser to Warm-up (about 45 Min)

3.Plug in GO-LINK to USB Extension Cable
4.Make Sure Instrumentation Amplifier is Plugged into GO-LINK
5.Set Instrumentation Amplifier to 0-1V Scale

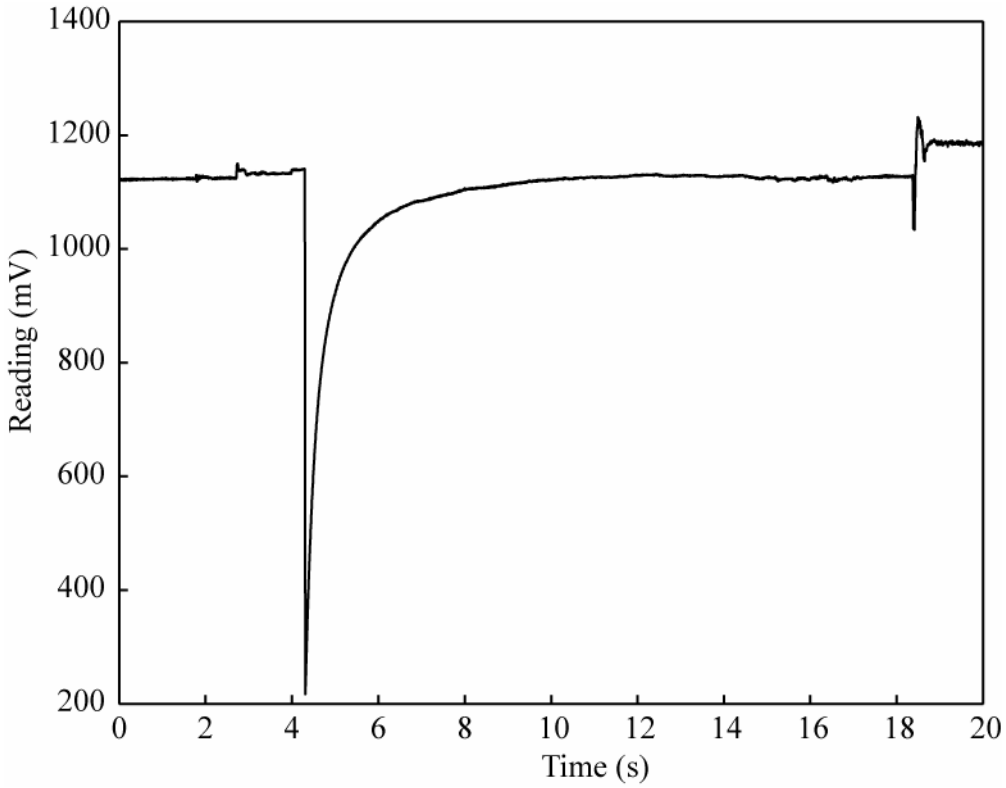
6. Launch LOGGER PRO Software (LED turns RED to GREEN)
7. Go-to EXPERIMENT-REMOVE INTERFACES-GO! LINK
7a. Go-to EXPERIMENT-CONNECT INTEFACES- GO!LINK USB
8. Go-to EXPERIMENT- SETUP SENSORS-SHOW ALL INTERFACES
9.Under GO!_ Select Box-Choose Sensor- Instrumentation Amplifier
10. Close Box- Time vs. Potential Graph Should Appear (0 mV Should be Displayed)

11.EXPERIMENT-Data Collection
12.Time Based-Set Length to 20 Seconds
13. Sampling Rate 200 Samples\Second
14.DONE
15.Adjust Laser Beam into Center Of Sensor Block onto Face of Phototransistor
16.Adjust Potential (Read on Screen) to >750mV but <1000 mV by steering the laser beam into the photodiode.

17. Once the solution is purged, seal the inlets of the cell with a septum or parafilm and place the cell between the laser and the photodiode (and as close to the photodiode as possible). The potential on the screen will drop slightly. Adjust the position of the cell to minimize the loss of signal. If the solution has turned cloudy, you need to remake it.

18.Turn On Power Switch of FLASH LAMP. Place the flash lamp as close as possible to the sample cell.
19. Collect Sample (Green Box Upper Right)
20. After 5 Seconds PRESS FLASH BUTTON
21. After FLASH finish the RUN
22. After RUN Save DATA or EXPORT as TEXT

Try to collect at least three good sets of data from each sample which should look something like this:



If too much time passes from aligning the sample to collecting data you may need to repurge the sample with N_2.

SHUT DOWN
1.EXIT Program
2.Unplug GO-LINK from USB Cable
3.Turn Off Power Switch of FLASH LAMP
4.TURN-OFF Laser
5.Turn Off POWER STRIP

Last, make sure you properly dispose of your solutions.
Some hints:
1. Keep the solution out of light by wrapping it in foil.
2. Thoroughly purge the solutions.
3. Make sure the He-Ne laser is properly aligned and going through the solution.
4. Keep the flash as close as possible to the cell.
5. Remember to stop the purge before you collect the data.
6. Remember to keep the lights off.

IV. Lab Report

For your three good runs for the three benzophenone solutions (pH=11, 12, and 13), you must convert the time dependent laser intensity I(t) to absorbance A(t) via

$$A(t) = -\log[\, I(t) / I(0) \,] \qquad (15)$$

where I(0) is the initial laser intensity before photolysis. An Excel workbook has been prepared for you where all these calculations are done and is posed on the class web site. First, to get I(0) you want to know where the experiment "began" i.e. when you hit go on the flash lamp. In the example above, that appears to have occurred a little after 4 seconds (that's the 863 data point). In the Excel workbook, I(0) is thus the average of the signal during this time which comes out to be 1127.668 mV. On the second sheet of the workbook, all points prior to the flash have been removed, the time is corrected such that the first data point has t=0, and the absorbance is calculated via eq. 15.

To determine k_{obs}, we need to examine the inverse of the absorbance, which is calculated on the third sheet of the Excel workbook. The difficulty here is that you don't want to use all the data because at long times the signal is really poor. In the example workbook, you can see how considering the first 330 data points, 150 data points or first 100 data points after the flash affects the results. You must balance the fact that you need to use as many points as possible but you know you must have positive slopes and intercepts. Also, examine how the line fits the data and the "goodness" of the fit (r^2). In the example, the first 100 points were sufficient to get a good fit but including more points than 100 resulted in a poor fit. This is shown in detail on sheet 4 in the spreadsheet. Once you have determined what the optimal data set to use is, you can use the slope to calculate k_{obs}. Since $A = \varepsilon \cdot c \cdot l$ where l is 5 cm and ε is 5000 $M^{-1}cm^{-1}$, the slope of the line you fit with Excel is equal to $k_{obs}/\varepsilon \cdot l$. Now you can calculate k_{obs} for each pH and make another linear least squares fit to that data. Since k_{obs} is equal to $k_7[H^+]/K_6$, the slope of this line is k_7/K_6. Knowing that K_6 is 6×10^{-10}M, you can now calculate k_7.

As for error analysis, the error of the fit in the intercept and slope from a linear least squares method is a well known formula. Unfortunately, it is not built into Excel, so sheet 5 of the Excel workbook has all those formulas there for you to use. You should show at least one example of the kinetic A(t) trace and the linearization (i.e. 1/A(t)) over the data range you think is best to work with. You should tabulate the k_{obs} from all nine runs as well as the average from the three runs at each pH. Next, you will calculate k_7

from the slope, and assuming no error in the pH or in K_6, use the spreadsheet to calculate k_7 and its error from the linear least squares fit.

Finally, answer the following questions in your report:

1) Why do you position the He-Ne laser as close to the flashlamp as possible? What would happen to the signal if the laser beam were to pass through the sample close to the side of the sample cell opposite to that of the flash unit?

2) Why must the benzophenone solution be purged with nitrogen prior to the flash photolysis scan?

3) What is the overall rate law for the photolytic formation for benzopinacol from benzophenone in basic solution?

4) Do you think that the overall rate law will be the same in acidic solution? Explain your answer.