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 of 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 to the right 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 refers to the total electronic spin angular momentum of the molecule, corresponding, respectively, to zero (singlet, spin multiplicity of 1) or two (triplet, spin multiplicity of 3) 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.
When benzophenone \((C_6H_5)_2CO\) absorbs a UV/Visible photon, it is excited to its first electronic state:

\[
k_1 \quad \text{(C}_6\text{H}_5\text{)}_2\text{CO + h\nu} \rightarrow \text{(C}_6\text{H}_5\text{)}_2\text{CO* } (S_1) \quad (1)
\]

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

\[
k_2 \quad \text{(C}_6\text{H}_5\text{)}_2\text{CO* } (S_1) \rightarrow \text{(C}_6\text{H}_5\text{)}_2\text{CO* } (T_1) \quad (2)
\]

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

\[
k_3 \quad \text{(C}_6\text{H}_5\text{)}_2\text{CO* } (T_1) \rightarrow \text{(C}_6\text{H}_5\text{)}_2\text{CO } (S_0) \quad (3)
\]

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

\[
k_4 \quad \text{(C}_6\text{H}_5\text{)}_2\text{CO* } (T_1) + \text{(CH}_3\text{)}_2\text{CHOH} \rightarrow \text{(C}_6\text{H}_5\text{)}_2\text{C^\bullet OH} + \text{(CH}_3\text{)}_2\text{C^\bullet OH} \quad (4)
\]

The \((\text{CH}_3)_2\text{C^\bullet OH}\) radical can interact with the ground state of benzophenone to generate even more protonated ketyl radicals:

\[
k_5 \quad \text{(C}_6\text{H}_5\text{)}_2\text{CO} + \text{(CH}_3\text{)}_2\text{C^\bullet OH} \rightarrow \text{(C}_6\text{H}_5\text{)}_2\text{C^\bullet OH} + \text{(CH}_3\text{)}_2\text{CO} \quad (5)
\]

In the above equation note that abstraction of a hydrogen atom from the \((\text{CH}_3)_2\text{C^\bullet OH}\) radical forms a diradical which rapidly rearranges to acetone. In a basic solution, the protonated ketyl radicals can disassociate:

\[
K_6 \quad \text{(C}_6\text{H}_5\text{)}_2\text{C^\bullet OH} \leftrightarrow \text{(C}_6\text{H}_5\text{)}_2\text{C^\bullet O^-} + \text{H}^+ \quad (6)
\]

Note that the protonated neutral radical and deprotonated radical anion 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:

\[
k_7 \quad \text{(C}_6\text{H}_5\text{)}_2\text{C^\bullet OH} + \text{(C}_6\text{H}_5\text{)}_2\text{C^\bullet O^-} \rightarrow \text{(C}_6\text{H}_5\text{)}_2\text{(OH)C-C(O^-)(C}_6\text{H}_5\text{)}_2 \quad (7)
\]

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:

\[
\frac{\partial [T_1]}{\partial t} = -k_3[T_1] - k_4[T_1][\text{ROH}]
\]

(8)

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

\[
\frac{\partial [T_1]}{\partial t} = -k_3[T_1] - k_4[T_1] = -k'[T_1]
\]

(9)

where \(k' = k_3 + k_4[\text{ROH}]\). The solution to the differential equation given in Eq. (9), the decay of the triplet species as a function of time, is:

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

(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 at the 632.8 nm wavelength of the He-Ne laser and the decay lifetime is much shorter than the ~millisecond response time of the instrument. Therefore we will examine 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 an overall second order process

\[
\frac{\partial \left[ (C_6H_5)_2CO^- \right]}{\partial t} = -k_7 \left[ (C_6H_5)_2CO^- \right] \left[ (C_6H_5)_2C^*O^{-} \right]
\]

(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

\[
[(C_6H_5)_2C^*OH] = [(C_6H_5)_2C^*O^-][H^+] / K_6
\]

(12)

Now substituting equation 12 into equation 11 yields:

\[
\frac{\partial \left[ (C_6H_5)_2CO^- \right]}{\partial t} = -k_{\text{obs}} \left[ (C_6H_5)_2C^*O^- \right]^2
\]

(13)

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

$$\frac{1}{\left[\left(C_6H_5\right)_2C^\bullet O^-\right]_t} = k_{\text{obs}} t + \frac{1}{\left[\left(C_6H_5\right)_2C^\bullet O^-\right]_0}$$

(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 schematic of the experimental apparatus is shown below:

![Experimental Apparatus Schematic](image)

All glassware must be very clean for this experiment to work properly. To clean the sample cell, rinse it thoroughly with distilled 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 do not add the isopropanol until you are ready to use it and be sure to protect the solution from visible light at all times. Therefore, before adding the solvent, wrap the bottle in aluminum foil and turn off the lights in 2013 and 2013 A. Working
under these conditions can be aided by turning on the lamp attached to the flash experiment glass bench top which has a red light bulb in it.

You need to make 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 distilled water and adding the stock solution dropwise until the desired pH is reached.

Prepare three basic benzophenone solutions by 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 measured pH values in your calculations. Make sure the solutions are mixed and then degassed. Now that the NaOH has been mixed with the benzophenone, you must perform the flash experiment immediately.

Use a syringe and inject the first solution into the photolysis cell until the cell is about 2/3 full. Carefully 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 nitrogen to bubble through the benzophenone solution for ~ 15 minutes and make sure that N₂ bubbles throughout the entire volume of the solution. Remember to keep the cell shielded from light during this purging.

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 EXPERIMENTAL PROCEDURE**

**Turning on Power for Experiment**
1. Turn On Power Strip - Laser Power Supply (Blue Box) plugged in
2a. Turn On Lab Station Power Supply – make sure it is plugged in
2b. Turn On Laser - requires ~ 45 minutes to warm up for stable operation
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

**Initializing Software**
6. Launch LOGGER PRO Software - LED on GO! LINK turns from RED to GREEN
7a. Click On: EXPERIMENT - REMOVE INTERFACE - GO! LINK: 1
7b. Click On: EXPERIMENT - CONNECT INTERFACE - GO! LINK USB
8. Click On: EXPERIMENT - SET UP SENSORS - SHOW ALL INTERFACES
9. Under GO! Select Box - Choose Sensor - Instrumentation Amplifier
10. Close Box - Time vs. Potential Graph should appear (0.0 mV should be displayed)
11. EXPERIMENT - Data Collection
12a. In Mode: Time Based - set Length to 20 Seconds
12b. and set Sampling Rate 200 Samples/Second
13. DONE

**Aligning Laser and Photolysis Cell**
14. Focus Laser Beam into wooden Sensor Block onto Face of Photodiode. Keep just enough space between block and laser to accommodate photolysis cell.
15. Adjust Potential (read on Screen) to > 750 mV but < 1000 mV by moving where the laser beam strikes the photodiode.
16. 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 as close to the photodiode as possible. The potential on the screen will drop slightly. Adjust position of cell to maximize the signal. If the solution has turned cloudy, you need to remake it.

**Photolyzing and Collecting Data**
17. Turn On Power Switch of FLASH LAMP and position lamp as close as possible to photolysis cell.
18. Collect Sample - Green Box upper right
19. After 5 Seconds PRESS FLASH BUTTON
20. After FLASH finish the RUN
21. After RUN Save DATA or EXPORT as TEXT

Collect 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 N₂.

SHUT DOWN (Follow complete shut down procedure posted on wall.)
1. Exit LOGGER PRO Program
2. Unplug GO! LINK from USB Cable
3. Turn off Power Switch of Flash Lamp and remove batteries
4. Turn off Laser
5. Turn off Power Strip

Lastly, make sure you properly dispose of your solutions.

Some hints:
1. Keep solutions out of light by wrapping in aluminum foil.
2. Thoroughly purge solutions.
3. Make sure the He-Ne laser is properly aligned and passing through the solution.
4. Keep the flash as close as possible to the photolysis cell.
5. Remember to stop purge before collecting data.
6. Remember to keep lights off.

IV. Lab Report

Your ultimate objective is to calculate the rate constant for the rate of decay of the deprotonated ketyl radical anion, \( k_7 \) in equation 11. Since your data only includes the time dependence of the concentration of this radical anion (through the absorbance which you are measuring at 632.8 nm) and pH, the calculation first entails determining an intermediate rate constant, \( k_{\text{obs}} \) in equation 14. From the \( k_{\text{obs}} \) values you determine at each of the three pH’s the linear relation between \( k_{\text{obs}} \) and the hydrogen ion concentration used to determine \( k_7 \). All data analysis can be easily performed in a spreadsheet (e.g., OpenOffice or Excel). Use the following procedure for each of your three good runs (trials) for each of the three benzophenone solutions (pH=11, 12, and 13).

You must convert the time dependent laser intensity \( I(t) \) to absorbance \( A(t) \) via

\[
A(t) = -\log\left[ \frac{I(t)}{I(0)} \right]
\]  

(15)

where \( I(0) \) is the initial laser intensity before photolysis. 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 on the previous page, that appears to have occurred a little after 4 seconds. You will want to identify this point in your spreadsheet and use the AVERAGE function to find the average of the signal during this time. Once you have this average or \( I(0) \), in another column or on another sheet of the workbook, remove all of these “baseline points” so that your first point starts when the experiment “began”, i.e., at the lowest laser light intensity which is a little greater than 200 mV in the above example. With the points prior to the flash removed, correct the time so that the first data point has \( t = 0 \) by
subtracting from all of the remaining times the time that corresponds to when the experiment “began”. The absorbance can then be calculated via eq. 15.

The absorbance being monitored is directly proportional to the concentration of the deprotonated ketyl radical anion. From equation 14 you can see that a plot of the inverse of the absorbance versus time should be linear with a slope equal to \( k_{\text{obs}} \). You need to determine in another column or on another workbook sheet the inverse of the absorbance. The difficulty here is that you do not want to use all the data because at long times the signal is really poor. Make a plot of the inverse of the absorbance versus time and you will see that at later times the signal becomes noisier. However equation 14 shows that the plot should be linear. You can simply determine the number of data points you need to consider by using the built in functions SLOPE, INTERCEPT, and RSQ (this is for the “goodness of fit” given by \( r^2 \)). You must balance the fact that you need to use as many points as possible but you must also have a positive slope and intercept. Examine how well the line fits the data by using the “goodness” of the fit \( (r^2) \) criterion. Remember that \( r^2 \) is between 0 and 1 and that 1 is a perfect fit. Once you have determined the optimal number of points, do a linear regression on this data and use the slope to calculate \( k_{\text{obs}} \). Since \( A = \varepsilon \cdot c \cdot l \) where the sample cell path length \( l \) is 5 cm and the extinction coefficient \( \varepsilon \) is 5000 M\(^{-1}\) cm\(^{-1}\), the slope of the line you fit is equal to \( k_{\text{obs}} / \varepsilon \cdot l \).

Use the appropriate number of significant figures and report the slope \( m \) and its error \( \sigma_m \), the intercept \( b \) and its error \( \sigma_b \), and the value for \( k_{\text{obs}} \) and its error.

Once you have calculated \( k_{\text{obs}} \) for each pH you need to make a final linear least squares fit to determine \( k_7 \). Since \( k_{\text{obs}} \) is equal to \( k_7[H^+] / K_6 \), a plot of \( k_{\text{obs}} \) versus the hydrogen ion concentration has a slope which is \( k_7 / K_6 \). Knowing that \( K_6 \) is 6×10\(^{-10}\) M, you can now calculate \( k_7 \) from a linear regression on this data. Using the appropriate number of significant figures report the slope \( m \) and its error \( \sigma_m \), the intercept \( b \) and its error \( \sigma_b \), and the value for \( k_7 \) and its error.

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 \( k_{\text{obs}} \) from all nine runs as well as the average from the three runs at each pH.

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