Flash Photolysis of Benzophenone  
(developed by Luke Hanley)

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 concentration of the photolytically formed deprotonated ketyl radical by monitoring its optical absorption of He-Ne laser radiation.

Before you begin these experiments, read the section on kinetics in your physical chemistry textbook [1].

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 molecular then must relax by means of radiative (photon emitting) or nonradiative pathways. The diagram above 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 ($S_1$). From $S_1$ it can fluoresce back down to $S_0$, emitting a photon in the process. From $S_1$ it may also nonradiatively jump back to $S_0$ via internal conversion or intersystem cross over to the triplet state, $T_1$. The notation 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 permanent chemical change in a molecule, like photodissociation. A more detailed description of the fate of electronic excited
states can be found in your text book [2]. The present laboratory will focus on the photolysis of benzophenone. The fate of benzophenone following electronic absorption can be described by a number of elementary mechanistic steps. When benzophenone ((C₆H₅)₂CO or Ph₂CO) absorbs a UV/visible photon, it is excited to its first electronic state:

\[
\text{Ph}_2\text{CO} (S_0) + \text{hv} \rightarrow \text{Ph}_2\text{CO}^* (S_1) \quad (1)
\]

Excited Ph₂CO (denoted Ph₂CO*) can then undergo intersystem crossing to the triplet state:

\[
\text{Ph}_2\text{CO}^* (S_1) \rightarrow \text{Ph}_2\text{CO}^* (T_1) \quad (2)
\]

The triplet state can slowly phosphoresce back down to the ground state:

\[
\text{Ph}_2\text{CO}^* (T_1) \rightarrow \text{Ph}_2\text{CO} (S_0) \quad (3)
\]

In the presence of isopropanol, a much faster relaxation process occurs in which a proton is abstracted from the alcohol to form a protonated ketyl radical:

\[
\text{Ph}_2\text{CO}^* (T_1) + \text{ROH} \rightarrow \text{Ph}_2\text{COH} + \text{R'OH} \quad (4)
\]

The alcohol radical which remains can react with ground state Ph₂CO to form yet more ketyl radicals:

\[
\text{Ph}_2\text{CO} + \text{R'OH} \rightarrow \text{Ph}_2\text{COH} + \text{R'O} \quad (5)
\]

In basic solution, the protonated ketyl radicals can then deprotonate:
Finally, the protonated and deprotonated forms of the ketyl radical can dimerize, forming benzopinacol:

\[
\begin{align*}
\bullet & \quad K_6 \quad \bullet \\
\text{Ph}_2\text{COH} & \quad \text{ <-> } \quad \text{Ph}_2\text{CO}^- + \text{H}^+ \\
\end{align*}
\]

(Notice that \( K_6 \) is an equilibrium constant)

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

\[
d[T_1]/dt = -k_3[T_1] - k_4[T_1][\text{ROH}] \\
\]

The rate equation can be reduced to a pseudo first order expression since the excess of alcohol effectively prevents [ROH] from changing during the reaction:

\[
d[T_1]/dt = -k'[T_1] \\
\]

where \( k' = k_3 + k_4[\text{ROH}] \). By solution of the differential equation 9, the triplet decay rate law as a function of time \( t \) is then

\[
[T_1]_t = [T_1]_0 \exp(-k't) \\
\]

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 near the 632.8 nm He-Ne laser line and the decay lifetime is much shorter than the response time of the instrument (the SCI Interface has a millisecond response time). For these reasons, we instead will look at a different step in the benzophenone photolysis.

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

\[
d[\text{Ph}_2\text{CO}^-]/dt = -k_7[\text{Ph}_2\text{COH}][\text{Ph}_2\text{CO}^-] \\
\]
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

$$[\text{Ph}_2\text{COH}] = \frac{[\text{Ph}_2\text{CO}^\cdot][H^+]}{K_6}$$

(12)

Substituting equation 12 into equation 11, we get

$$d[\text{Ph}_2\text{CO}^\cdot]/dt = -k_{\text{obs}} [\text{Ph}_2\text{CO}^\cdot]^2$$

(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 $[H^+]$. Solving the differential equation 13 yields a rate law of

$$[\text{Ph}_2\text{CO}^\cdot]_t^{-1} = k_{\text{obs}} t + [\text{Ph}_2\text{CO}^\cdot]_0^{-1}$$

(14)

Equation 14 is the rate law which you monitor in this experiment: it has a lifetime in the range of milliseconds and the deprotonated ketyl radical absorbs at 630 nm, allowing its concentration to be monitored by absorption of the He-Ne laser beam.

**III. Experimental Protocol**

This experiment uses an electronic flash unit to induce the photodissociation of benzophenone. The concentration of ketyl radical with respect to time is monitored with a photodiode by absorption of 632.8 nm radiation from a He-Ne laser. Both the flash unit and photodiode are controlled with the computer through the SCI Technologies Interface box. A schematic diagram of the experimental apparatus is shown below.
All glassware must be very clean in order for this experiment to work. To clean the sample cell rinse it thoroughly with water followed by isopropanol. Do not soap. Drying is not necessary. Discard the washing in the proper waste container.

Prepare a 250 ml stock solution of $5 \times 10^{-3}$ M benzophenone using isopropanol as a solvent. Pour equal amounts of this solution into each of three brown storage bottles and label them with your names, your TA’s name, and number them from #1 to #3. Protect the solution from light by wrapping the bottles with aluminum foil.

Prepare ~100 ml of a solution of 0.1 M NaOH solution from the solid NaOH provided (you do not need to standardize this solution).

**Calibration of the pH meter:** Rinse the pH meter with distilled water and gently shake the excess water off. Immerse the probe in a beaker with pH 10 buffer. Make sure that there is enough solution in the beaker to cover the glass bulb at the tip of the probe. Calibrate the pH meter with the buffer solution. Keep the pH probe in its own solution or in pH 7 standardizing buffer when you do not use it. Do not allow the probe to dry.

**Adjustment of the pH of the benzophenone solution:** Transfer the solution #1 in a beaker wrapped in aluminum foil and place it on a stirring plate in the dark. Rinse the pH probe with distilled water, shake the excess off. Rinse the probe thoroughly with isopropanol (do not forget the glass bulb) and immerse it in the benzophenone solution. Place the magnetic stirrer in the solution and adjust the stirrer speed to avoid splattering. (DO NOT USE THE pH PROBE TO STIRR THE SOLUTION!). If a magnetic stirrer is not available simply shake the beaker. Be careful not to damage the pH probe. Add NaOH solution in small portions until the pH reaches the desired value. Allow the pH to equilibrate before each reading. The equilibrium time would be very long if you did not rinse the probe thoroughly with isopropanol. The pH of the solution should be close to 11, 12 or 13 respectively.

*Having added the NaOH to this solution, you must immediately proceed to run the experiment.*
Inject benzophenone solution #1 using a syringe into the photolyis cell until the cell is about 2/3 full. Turn on the nitrogen gas tank regulator so that you get a slow flow from the 1/8” white plastic 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. Make sure that N\textsubscript{2} bubbles through the whole volume of solution. Rotation of the cell with respect to the N\textsubscript{2} tube might help. During the purge, the photolysis cell should be shielded from room light with the cover provided.

While the solution is being purged, proceed with the alignment of the laser and the diode. Place the laser and the diode in straight line, leaving only enough space between them to accommodate the cell. Turn on the laser. Plug the three banana plugs for the photodiode into the DAC2 banana receptacles on the SCI interface, matching the colors of the plugs. To access the flash photolysis software, open the Lab Works program. Load the FLASH4.EXP experiment. Choose “TEXT” for the screen mode and choose “INTERFACE” for the source data. Give a different filename for each run. Two numbers will appear on the screen: the first is time and the second is photodiode signal intensity: use the latter to align the photodiode and laser. The alignment is critical to success of the experiment and is indicated by a large negative. The reading could be as large as –20. You might need to allow a few minutes for the intensity of the laser beam to stabilize. Once the laser diode is aligned, cover the whole set up with a black cover.

Caution: DO NOT LOOK DIRECTLY INTO THE LASER BEAM

Once the solution is purged, seal the inlets of the cell with parafilm and place the cell between the laser and the diode as close to the diode as possible. Adjust the position of the cell to regain as much of the signal intensity as possible. (The maximum intensity will be a few units smaller then in the absence of the cell). Cloudiness of the solution might occasionally interfere with the reading. In this case you will need to prepare a new solution of the given pH. Position the flash lamp as shown in the picture of the experimental set-up, bringing it as close to the cell as possible. Once the set-up is aligned you are ready to start the measurements. Avoid exposure of the sample to visible light as much as possible during the experiment.

Press "S" to clear the screen, plug the two banana plugs for the Flash unit into SIDE 1 of the OUTPUTS section of the SCI interface, again matching the colors of the plugs and then follow the screen instructions. When the “W” button on the SCI interface lights up, press it. This starts the data acquisition. The flash unit should flash after ~2 seconds. The data will be automatically saved in a spreadsheet. When the acquisition is over, press any key to go back to the main menu.

The FLASH4 program does not plot your data on the screen. You can check your data either from QuattroPro or from DOS using EDIT command. In order to access QuattroPro you need to go back to the Windows. For the second choice, choose DOS SHELL from the main menu and type “edit Name.dat”. Use the arrows to move
up and down in the file. Exit the editor and type “exit” to return to the LABWORKS. A good set of data can be recognized from the jump towards zero of the intensity values occurring around 2000 or 4000 ms, depending on the program used. The longer the jump the better the data set. The jump is followed by a slow come back toward the original value $I_0$.

Run the FLASH4 program again until you collect three good runs. If the three runs cannot be collected in about 5-7 min from the purging of the solution, purging for about 2 min between runs can be used to improve the quality of the data. Make sure that the Laser, the cell and the diode are properly aligned for each run.

Repeat the procedure for solution #2 and #3 after you adjust the pH to 12 and 13, respectively. Adjust the pH of each solution just prior to using it. Save all data on your diskette.

Dispose of the benzophenone solution in the marked beaker located in the fumehood.

Some Experimental Hints:
1) Keep solutions wrapped in Aluminum foil
2) Purge solutions thoroughly
3) Make sure the He-Ne laser beam is aligned and going through the solution
4) Keep the flash unit as close to cell as possible
5) Stop the purging before you begin to acquire the data
6) Remove batteries from flash unit after experiments have been completed
7) The lights in the sections of the lab where the experiment occurs should be turned off during the experiment

IV. Lab Report

For all of your data, you must convert the He-Ne laser intensity at time $t$, $I_t$, to absorbance, $A_t$

$$A_t = -\log \left( \frac{I_t}{I_0} \right)$$  \hspace{1cm} (15)

where $I_0$ is the laser intensity without photolysis (from your runs without the flash unit). Note that higher signal from the photodiode means a higher light intensity.

Calculate $A_t$ at a number of different times using equation 15. To determine $k_{obs}$, plot $1/A_t$ versus $t$ as indicated by equation 14, then do a linear least squares fit to get the best line. Since $A = e c L$, the slope of this line is equal to $k_{obs}/e L$ where $L$, the sample cell path length is 5 cm, and $e$, the extinction coefficient, is 5000 M$^{-1}$cm$^{-1}$. Compute $k_{obs}$ for each pH. Now plot $k_{obs}$ versus $[H^+]$ and do a linear least squares fit again. Since $k_{obs} = k_7[H^+]/K_6$, the slope is equal to $k_7/K_6$. Use $K_6 = 6 \times 10^{-10}$ M to compute $k_7$. 
In addition to the usual information you are expected to put into a lab report, include the following:
1) All of the above calculations and graphs, along with $k_{obs}$ and $k_7$.
2) A few characteristic graphs of your data: there is no need to display graphs of all of your raw data. However, you should tabulate the results of calculations on all your data.

Also, answer these questions in your lab 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 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 of 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.

**References**


Instructor References

Chemicals (per group only)- benzophenone, 0.45 g for 3 samples, lifetime supply in lab
   - isopropyl alcohol, 500 ml for 3 samples, from Chemistry stockroom
   - pH solution to standardize pH meter, 100 ml, from Chemistry stockroom

Equipment and Supplies Required
   - one computer
   - SCI Technologies interface
   - SCI photodiode
   - 632.8 nm interference filter, 1/2" x 1" (Edmund Scientific #J30,701)
   - ground glass slide and interference filter are embedded in wooden spectrophotometer blocks which come from SCI (photodiode inserts into block)
   - SCI pH meter and pH paper for the basic range
   - flashlamp specially designed for experiment (remove cover from bulb)
   - 3 AA batteries for flashlamp
   - Uniphase He-Ne laser (0.5 mW, 632.8 nm, Edmund Scientific #J34,891)
   - custom built pyrex photolysis cell
   - rubber septums to seal photolysis during purge
   - tank of N2 gas with regulator and 1/8" tubing to purge cell
   - syringe to introduce benzophenone into photolysis cell
   - three brown storage bottles, ~200 ml

Extra Instructions for TAs
   - The program FLASH3 displays time in milliseconds.

Potential Experimental Errors
   - Benzophenone/isopropanol solution exposed to light too long prior to photolysis.
   - Solution is not purged long enough to remove oxygen, which causes quenching.
   - Laser-photolysis cell-photodiode are not aligned or beam does not pass through solution.
   - Flash unit positioned too far away from photolysis cell.
   - Purge still running while experiment is running: splashing scatters laser beam.
   - pH has not been adjusted properly