Rates of chemical reactions are usually determined by mixing the reagents and measuring how rapidly a product is formed or how rapidly a reagent is consumed. But if the reaction is sufficiently rapid, the time required to mix the reagents can be too long in comparison to the reaction time and time "zero" can't be defined. For example, the neutralization of an acid with a base proceeds as rapidly as the two are mixed. In order to overcome the time ambiguity imposed by mixing, one frequently starts with a system already mixed and creates a new species throughout the system with a sudden burst of light. If the light pulse is fast enough, this results in a uniformly mixed system created at a well-defined time.

Flash photolysis, the subject of this experiment, is an example of a perturbation technique\(^1\). Briefly, all perturbation techniques start with a system already at equilibrium. A sudden change, or perturbation, is applied, such as high pressure, high electric field, high temperature, etc., and the rate at which the system returns to the new equilibrium position is measured. For example, the rate of reaction between OH\(^-\) and H\(^+\) has been measured this way. In flash photolysis, a short flash of light (microsecond duration) can produce a new species, and the rate of reaction of this already mixed species can be followed spectrophotometrically.

I. Preparation

a) Read this writeup and Ch 1, Introduction to Computer Data Acquisition. Review the kinetics section in your freshman text. The data acquisition and analysis in this experiment will be performed using Matlab.

b) Work out the exercise in the Data Analysis section before you come to lab. This will require several hours of preparation. You need to have used DSCOPE and the file handling routines, WFLASH and RFLASH and to have performed the exercise. You do not need to perform the error analysis for the exercise.

II. Photopinacolization of Benzophenone: Introduction

Benzophenone (1) absorbs light in the UV to form an excited triplet state molecule which is highly reactive:

\[
\text{1} \quad \text{hv} \quad \phi_2\text{CO}^* \text{ (triplet state)} \quad (1)
\]

In isopropanol, the triplet state abstracts a hydrogen atom to form the ketyl radical (denoted as A):

\[\phi_2\text{CO} \rightarrow \phi_2\text{CO}^* \text{ (triplet state)} \quad (1)\]

---

\[ \phi_2 \text{CO}^* + \text{Me}_2\text{CHOH} \longrightarrow \phi_2^*\text{COH} + \text{Me}_2\text{COH} \]  

(2)

The ketyl radical is too stable to react further with isopropanol, but as soon as two radicals diffuse together they couple to form benzopinacol (2):

\[
\begin{array}{c}
\phi_2^*\text{COH} \\
\text{A}
\end{array}
\xrightarrow{k_3}
\begin{array}{c}
\phi_2 \text{C}--\text{C}\phi_2 \\
\text{2}
\end{array}
\]

(3)

Reaction (2) occurs as soon as the reagents diffuse together, and reaction (3) occurs with rate constant \( k_3 = 5.9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1} \), which means that the reaction would be half over in \( t_{1/2} = [A]^{-1} k_3^{-1} = 170 \mu \text{s} \) for \([A] = 10^{-4} \text{ M}\), which is near the limit of the capability of our apparatus.

The system can be modified by studying the process occurring in basic solution. Here the ketyl radical anion \([B^-]\) is easily formed:

\[
\begin{array}{c}
\phi_2^*\text{COH} \\
\text{A}
\end{array}
\xrightarrow{\text{[B]}^-}
\begin{array}{c}
\phi_2 \text{CO}^- + \text{H}^+ \text{,} \\
\text{B}^-
\end{array}
\]

(4)

and the anion reacts to form the benzopinacol anion:

\[
\begin{array}{c}
\phi_2^*\text{CO}^- + \phi_2^*\text{COH} \\
\text{B}^- \text{ and } \text{A}
\end{array}
\xrightarrow{k_5}
\begin{array}{c}
\phi_2 \text{C}--\text{C}\phi_2 \\
\text{2}
\end{array}
\]

(5)

The rate of reaction (5) is sufficiently slow to be measured in our apparatus and the radical anion \([B^-]\) absorbs light in the visible so that we can measure its concentration spectrophotometrically. The rate of reaction (5) is given by the expression

\[
- \frac{d[B^-]}{dt} = k_5 [A] [B^-] \]

(6)

where \([B^-]\), \([A]\) are the concentrations of \( B^- \) and \( A \), \( k_5 \) is the rate constant, and \(-d[B^-]/dt\) is the rate of disappearance of \( B^- \). The concentrations of \( A \) and \( B^- \) are related through the acid dissociation constant,

\[
\frac{[H^+] [B^-]}{[A]} = K_A, \quad \text{or} \quad [A] = \frac{[H^+] [B^-]}{K_A} \]

(7)

Substituting Eq. 7 in Eq. 6, we have

\[
- \frac{d[B^-]}{dt} = k_5 \frac{[H^+] [B^-]^2}{K_A} = k_{OBS} [B^-]^2 \]

(8)

Eq. 8 can be integrated to give

\[
\frac{1}{[B^-]} = \frac{1}{[B^-]_0} + k_{OBS} t \]

(9)

A plot of \( 1/[B^-] \) versus \( t \) is linear with slope \( k_{OBS} \), where \( k_{OBS} \) depends on pH and is given by
\[ k_{\text{OBS}} = \frac{k_5 [H^+]}{K_A} \]  

(10)

The hydrogen ion concentration can in turn be obtained from

\[ [H^+] [OH^-] = K_W, \]  

(11)

yielding

\[ k_{\text{OBS}} = \frac{k_5 K_W}{[OH^-] K_A} \]  

(12)

A series of determinations of \( k_{\text{OBS}} \) at different \([OH^-]\) concentrations will be used to obtain \( k_5 \). It is difficult to measure pHs in nonaqueous solutions, since the activity of \( H^+ \) ions relative to that in a glass electrode, for example, depends on the solvent. The ratio \( K_A/K_W \) has been measured to be \( 6.3 \times 10^4 \text{ M}^{-1} \) in 50-50 isopropanol-water mixtures, and suffices for this experiment.

### III. Procedure

#### A. Apparatus

A schematic diagram of the apparatus is shown below:

![Schematic Diagram of Apparatus](image)

A solution of benzophenone is irradiated by light from the flash gun. The probe light beam passes through the cell and through the filter monochromator and is detected at the photomultiplier (PMT). If a species in the cell absorbs at the wavelength passed by the monochromator (630 nm), less light is incident on the PMT and a smaller voltage is produced by the PMT. The output voltage of the PMT is thus a monitor of the concentration of absorbing species.

The flash produces the triplet state of benzophenone as in Rxn (1). The triplet abstracts an H atom from isopropanol in Rxn (2) to form the ketyl radical \( \phi_2\text{COH}^• \) and in basic solution (rxn 4) the ketyl proton is stripped off to give the ketyl radical anion, \( \phi_2\text{CO}^- \). \( B^- = \phi_2\text{CO}^- \). \( B^- \) is readily observable since it absorbs light in the red at 630 nm, and light from the probe beam lamp is used to monitor the time varying concentration of \( B^- \). Since \( B^- \text{ absorbs} \) light at 630 nm, a solution containing \( B^- \) reduces the amount of 630 nm light passing through. Less light is transmitted through the filter monochromator (set to transmit 630 nm light), less light is incident upon the photomultiplier, and a smaller voltage is produced by the photomultiplier. The concentration of \( B^- \) is reduced by reaction (5), and the light reaching the PMT at 630 nm increases with time. The concentration, \( c \), of \( B^- \) is related to the absorbance, \( A \), by Beer’s law,
where $\varepsilon$ is the molar absorptivity, $c$ is the concentration of absorber, and $l$ is the path length. Absorbance vs time measurements can thus be converted into concentration vs time from which the rate of reaction may be calculated. The time varying signal will be viewed and stored by using MATLAB to transfer the signal to the computer via the MIO analog-to-digital converter board.

**B. Solutions**

From the NaOH solution supplied, aqueous solutions of NaOH of 0.002M, 0.01M, 0.02M, 0.03M, 0.06M should be made.

Pipet 25 ml of a NaOH solution into a 100 ml graduated cylinder. Add an equal volume of 0.005N benzophenone in isopropanol solution. The solution must now be bubbled with (hopefully) isopropanol-saturated nitrogen for about 15 minutes to displace oxygen dissolved in the solution. This step is necessary because O$_2$ quenches (destroys) the triplet state formed in Reaction (1). During the bubbling some of the alcohol may evaporate, so you must record the final volume in order to calculate [OH$^-$]. Close the valves on the N$_2$ cylinder when you are finished.

Wash the cell three times with the solution and then fill the cell completely and cap it. Dry the outside of the cell and carefully wipe off any fingerprints on the windows. Mount the cell in front of the flash unit. Loosen only the top mounting screw in order to mount the cell without disturbing the alignment.

**BE CAREFUL.** ONLY LIGHT PRESSURE is required to hold the cell in place. Check to see that the reference light passes completely through the cell and is centered on the PMT. Ideally, the reference light should be focused in the center of the cell.

**NOTES**

1. Once the cell is aligned, remove the cell only by loosening the single mounting screw. Do not move anything else for the rest of the experiments.
2. The pressure on the cell must be firm enough to prevent it from falling out.
3. Do not allow a filled cell to sit in the probe light for an extended period of time because the solution will absorb light and warm up, resulting in your data being obtained at different temperatures and making your efforts meaningless.

**C. Apparatus Set-up: (See Fig 1.)**

1. Check to see that the oscilloscope, lamp, flash and PMT power supply are all plugged in, and that the power strips are turned on.
2. Triggering of the data acquisition routine will be initiated by the computer. The flash is detected by a photodiode which can be connected to the external trigger of the oscilloscope. The PMT signal will be detected on the oscilloscope as well as by the computer, so the PMT should be connected both to Channel A (or B) of the oscilloscope and to a channel of your choice on the interface box to the data acquisition board. (This channel must be input to the computer as a parameter in scopet.)
3. Turn on all except the high voltage power supply for the PMT.
4. **WARNING:** The photomultiplier operates at LETHAL voltages! Be sure both voltage controls on the high voltage supply are initially turned to the lowest levels [full
left (CCW) position]. The PMT signal is greater at higher voltages and will be adjusted later. Turn the PMT power supply on and then turn up the voltage; a good voltage for now is 600 V.

![Flash Photolysis Schematic Wiring Diagram](image)

Fig 1. Schematic wiring diagram. MHV and BNC cables connected to the PMT are similar but different. Do not force an MHV cable onto a BNC jack or vice versa.

D. Experimentation

You are now ready to take data using the Matlab routine `scopet.mex`. Refer to the help file for `scopet` (or `dscopet`). You will have to experiment with your combination of Points and Dwell, although for starters you might try 1000 points and 100 µs dwell. Channel needs to be set to whatever channel you are using for the PMT and is labelled on the interface box as 0-3. When using the `.mex` files it is necessary to set the matlab directory and the flash needs to be initially disarmed. Matlab files `disarm.m` and `fire.m` will set the directory, call `scopet` and then plot the results. Disarm should be called when Matlab is first started, and `fire` can be copied to another file with your choice of name and edited to use whatever number of points, dwell time, and channel you wish. When you call `fire`, it will call `scopet` which fires the flashgun, collects the data, and plots the data. But it will not save the data unless you use `wflash`. Wflash stores your date in the file `flashdata` located in the partition `users`. If you do not save the date it will be overwritten the next time you call `scopet`.

Fire the flashgun. You should see a trace sweeping across the oscilloscope and the computer should indicate that data has been acquired. Increase the gain on the PMT so that the minimum signal in the trace is below -5 V, but DO NOT EXCEED 600 V ON THE POWER SUPPLY. Make sure that the PMT filter is set to 630 nm.

The rising and then slowly falling trace, denoted $V(t)$, corresponds to a decreasing, then increasing amount of light transmitted by the sample. This reflects an increase of absorbing species in solution due to formation by the flash, followed by a slower decrease caused by reaction of the absorbing species. The signal is negative because the PMT outputs a negative current which is converted to a negative voltage when sent through the input impedance of the oscilloscope and data acquisition board. Depending on the nature of your trigger, you may also see an initial rapid fall and then rise of the signal due to reflected light from the flash, which is what initiates the sweep.
When gain, points and dwell time have been optimized, save a trace in a data file to see if the data acquisition routines are in order. To check that the waveform was saved correctly, run WFLASH to store the waveform and RFLASH to retrieve it.

After these preliminary adjustments, you need to determine the offset, if any, when no light is present, \( V_{\text{dark}} \). Block the transmission of light to the PMT in front of the sample cell (but not in front of the photodiode). Flash the sample to start the data acquisition and store the waveform. This is the 100% absorbance or "light off" position.

Now you are ready to take the kinetics data. Proceed as follows:

1. Check to see that the sample cell is in position and filled and the light to the PMT unblocked. Adjust the dwell time so that the entire decay trace is digitized. You wish to measure the concentration of \( B^- \) and according to eq 13, you need the ratio \( I/I_0 \) as a function of time. It is important that the trace decays essentially entirely, since you will obtain \( I_0 \), the intensity of transmitted light when no absorbing species is present, from the points at the end of the trace.

2. When the dwell time has been satisfactorily set, digitize and store a waveform. Record the dwell time, room temperature, and solution concentration. NOTE: you will need the dwell time (\( \Delta t \)) to analyze your waveforms later.

3. Digitize and store two additional waveforms from the same solution. To be sure that the data was saved correctly, you may want to run RFLASH.

4. Repeat the measurements using the other solutions.

IV. DATA ANALYSIS

![Graph](image)

Fig 1 An example of a flash photolysis waveform.

You will obtain waveforms similar to that shown in fig 1. The data shown in fig 1 is the photomultiplier output obtained after photolysis of a solution of benzophenone in isopropanol as discussed above. The photomultiplier puts out electrons and greater output corresponds to a more negative signal; zero volts corresponds to no light. There is an initial very fast negative spike corresponding to light (more light = more negative) from the flash. The flash produces the ketyl radical anion \( B^- \) which absorbs light leading to a less negative
signal. As B\textsuperscript{−} reacts, its concentration decreases, more light is transmitted by the solution, and the signal decays to a baseline characteristic of the solution before it was flashed.

Your objective is to determine \( k_{\text{obs}} \) defined in eq (9), by plotting \( 1/[\text{B}^-] \) vs \( t \). Keep in mind that you want to measure the concentration of the radical anion as a function of time. Fig 1 qualitatively describes how \([\text{B}^-]\) varies with \( t \), but it is necessary to extract \([\text{B}^-]\) vs \( t \) before proceeding. It is important to be aware of exactly what is measured: in this case it is the PMT voltage. The PMT voltage is linearly dependent on the light intensity, \( V = a + bI \), where \( a \) is due to the dark current of the PMT. (In selected and very expensive tubes this can amount to a few counts/sec \( \Rightarrow a \approx 10^{-18} \text{ A} \); thousands of counts/sec, \( \approx 10^{-16} \text{ A} \) may be more typical.) Since we are shining a light directly into the PMT, \( I \) is very large and probably swamps the signal due to the small dark current: \( a = 0 \) and \( V = bI \).

The concentration of absorber \([\text{B}^-]\) is given by Beer's law,

\[
\log_{10} \left( \frac{I_0}{I} \right) = \varepsilon c l = A = \text{Absorbance} \tag{13}
\]

where \( I_0 \) is the transmitted light intensity with no absorbing species present, \( I \) is the light intensity transmitted by the absorbing sample, \( l \) is the path length (5.0 cm), \( c \) is the concentration of radical, \([\text{B}^-]\), and \( \varepsilon \) is the molar extinction coefficient, \( \varepsilon = 5.0 \times 10^3 \text{ cm}^{-1} \text{ M}^{-1} \). Since the dark current is probably negligible here, the output voltage of the PMT (vertical scale on the oscilloscope) is directly proportional to the intensity of light incident on the phototube and the proportionality constant cancels out. Beer's law can thus be written

\[
\varepsilon c l = A = \log_{10} \left( \frac{V_0 - V_{\text{dark}}}{V - V_{\text{dark}}} \right) = \log_{10} \left( \frac{V_0}{V} \right) \tag{14}
\]

and

\[
[\text{B}^-] = c = \frac{1}{\varepsilon l} \log_{10} \left( \frac{V_0}{V} \right). 
\]

You should have checked to see if \( V_{\text{dark}} \) can be neglected in the experimental section by blocking the phototube from the interrogating light.

You need to determine \( V_0 \), which is the voltage corresponding to no absorption. This occurs before the flash, or at very long times after the flash, \( t \to \infty \). In order to determine \( V_0 \) you must thus take data for quite a long time after the flash, or you must somehow extrapolate the data to large time. (The latter can be done by plotting \( V \) vs \( 1/t \) and extrapolating \( 1/t \) to 0.) After you have determined \( V_0 \), you can use eq (14) to calculate \( c \), provided that Beer's law is valid. It is not valid during the flash (because the signal is due to light directly from the flash) so you have to exclude those points.

After calculating \( c(t) \), you need to plot \( 1/c(t) \) vs \( t \) to determine the rate constant. This will be a straight line provided that reaction(5) is solely responsible for the time variation of the signal. It's not, of course. At small times the production of the radical anion is convoluted in with its disappearance, so this analysis is limited to the decay, well after all the radicals are generated. At very long times, noise can cause \( V_0 \) to fluctuate wildly from point to point and this measurement ultimately becomes useless. You will thus have to limit your analysis to points beyond the flash, but not so far away that the signal is swamped by noise.
Summary of the analysis:
1. Determine $V_{\text{dark}}$.
2. Extrapolate the data to obtain $V_0$, the signal with no absorber.
3. Calculate $c(t)$ from Beer's law.
4. Plot $1/c(t)$ vs $t$; evaluate the rate constant from the slope.

**Exercise.** Write a MATLAB routine to analyze the data of fig 1, extracting the effective rate constant, $k_{\text{OBS}}$. Using RFLASH, read the data for fig 1 (stored in TAflash.183549) and determine the baseline, $V_0$. Once $V_0$ is determined, calculate $[B^-]$ using eq 14. Then plot $1/[B^-]$ vs $t$ to get a linear fit. Note that a straight line will not fit all of the values of $B$ vs $t$ because in some instances there are major systematic errors. The fast negative spike represents not the concentration of $B^-$ but mostly the amount of scattered light. Likewise, the rising portion of the waveform is due also to the production of $B^-$ and this rate in not included in eq 1. Thus eq 1 applies only after $B^-$ is generated. You must thus tailor your analysis to include only those points which satisfy the assumptions made in deriving eq (1). Turn in your Matlab program, your fit to $[B^-]$ vs $t$, and your value for $k_{\text{OBS}}$.

For analysis of your experimental data you need to revise the MATLAB routine you submitted for the exercise to include the weighting described below. Extract the effective rate constant, $k_{\text{OBS}}$, and its standard uncertainty (i.e., the standard deviation of the slope). Analyze each trace for each of the different samples at $[\text{OH}^-]$ concentrations between 0.001 and 0.03 that you prepared, and report the results in a table.

**Weighting the Fit**

Some values of $[B^-]$ are known more accurately than others and you should weight those points more heavily in your analysis.

First, let's examine the situation qualitatively. If you see a initial large negative spike as in Fig 1, it arises because a lot of light is detected from the flash. We do not know how the flash depends on time, and our analysis doesn't include any contribution from the flash. Consequently, any points taken while the flash is on can't be analyzed and must be discarded.

At very large times nothing is happening, and $V = V_0$. Noise fluctuations can cause $V$ to be larger or smaller than $V_0$ and $c(t)$ can fluctuate wildly. So points at "large" values of $t$ should not be included. As $t$ becomes "large" our values become less certain and should be weighted less as time goes on. The following is a prescription for how to do the weighting. Be sure your final result agrees with this qualitative assessment!

From Eq (14), the uncertainty in $[B^-]$ will depend on $\sigma_V$, the uncertainty in $V$, and we proceed as follows to determine $\sigma_V$: If we were to count photons to determine the light intensity, Poisson statistics would apply, and $\sigma_I = \sqrt{I}$. In this experiment $I \sim V$, and we approximate $\sigma_V \sim \sqrt{V}$. We don't know the proportionality constant, but we can empirically determine $\sigma_V(0)$ from the asymptotic long-time signal used to calculate $V_0$. The uncertainty $\sigma_V(t)$ is then given by

\[
\sigma^2_V(t) = \sigma^2_V(0) \left[ \frac{V(t)}{V(0)} \right] 
\]

(15)

Proceed now as follows:
1. Read in the data using RFLASH.
2. Calculate $\Delta V(t) = V_{\text{dark}} - V(t)$. This is a positive quantity and it is this quantity which is proportional to $I$ and which should be used in subsequent calculations. $V_{\text{dark}}$ is small and constant and its uncertainty can be neglected.

3. Calculate $V_0$ and $\sigma_V(0)$ using the long-time behavior of $\Delta V(t)$. Do not weight the points; determine $\sigma_V(0)$ from the spread of these points.

4. Calculate $\sigma_V(t)$ from eq (15).

5. Calculate $c(t)$ and $1/c(t)$. Using $\sigma_V(t)$ propagate the random errors (Eq 2-20) and calculate $\sigma_C(t)$ and $\sigma_{1/C}(t)$.

6. Fit the data using experlsq.m to plot $1/c(t)$ vs $t$, weighting each point using $w = \frac{1}{\sigma^{2}_{1/C}}$.

   Note that you weight each point separately, and thus while the Poisson distribution was used initially to obtain $\sigma_V(t)$, the Poisson mode is not used in experlsq.m. You must exercise control over which points are used. You can't take logs of negative numbers, for instance, and if $t$ is too short the radical ion is being formed as well as reacting. Report $k_{\text{obs}}$ and $\sigma_{k_{\text{obs}}}$. 

7. Plot both the data and the fit according to Ea (9). Use your head......

8. Summarize your results. At each $[\text{OH}^-]$ give the mean value of $k_{\text{OBS}}$ and its standard error (standard deviation of the mean).

   Do the uncertainties in $k_{\text{OBS}}$ at a given $[\text{OH}^-]$ determined by propagating errors (i.e., calculating $\sigma_{1/C}$, inputting it to EXPERLSQ.m, and taking $\sigma_{\text{slope}}$) seem reasonable? If not, you will need to estimate the uncertainties by some other means. Use equation 12 to calculate $k_5$ values and report the mean value for $k_5$ plus the uncertainty appropriate for a 95% confidence level. The literature value for $k_5$ is $1.07 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

   In your discussion, you should indicate the main sources of systematic and random error in this experiment. Is the agreement with the literature value satisfactory? Can any discrepancy be accounted for?

   Your report should include sample calculations and plots representative of each different kind of calculation. In addition, you should include an analysis of the data in TAflash.183549 to test your Matlab programs. You should include a summary of what the analysis routine calculates, as well as a hard copy of the routine.