1. Photoreduction of Benzophenone in 2-Propanol

Topic: photochemistry, photophysics, kinetics, physical-organic chemistry
Level: undergraduate physical chemistry
Time: 2 x 2 hours (separated by ~24 hours)
Equipment: volumetric flasks, quartz cells, rubber septa, degassing needles, nitrogen or argon tank, UV/Vis spectrometer
Chemicals: benzophenone, 2-propanol, naphthalene

Abstract

This experiment is a kinetic study of the photoreduction of benzophenone in 2-propanol. Hydrogen abstraction by photoexcited benzophenone from 2-propanol yields benzopinacol and acetone as stable products. In the presence of naphthalene, energy transfer from photoexcited benzophenone to naphthalene competes with hydrogen abstraction. The rate constant for the hydrogen abstraction reaction can be determined by varying the naphthalene concentration and making use of the Stern-Volmer kinetic relationship.

Introduction

This experiment is a kinetic study of the photoreduction of benzophenone in 2-propanol which has been adapted from experiments described by P.Natarajan\(^1\) as well as M.S. Churio and M. A. Grela.\(^2\) Hydrogen abstraction by photoexcited benzophenone from 2-propanol yields benzopinacol and acetone as stable products. As the reaction proceeds, benzophenone is depleted; its disappearance can be monitored with a UV/Vis spectrometer. In the presence of naphthalene, the rate of benzophenone depletion is reduced because energy transfer to naphthalene competes with hydrogen abstraction from 2-propanol (Figure 1). The rate constant for the hydrogen abstraction reaction can be determined using the Stern-Volmer kinetic relationship.

![Figure 1. The competition between hydrogen abstraction from 2-propanol and energy transfer to naphthalene.](image-url)
Background and Theory

Absorption of a photon by a molecule excites it from its ground state ($S_0$) to an electronically excited singlet state. This transition is the result of an electron jump from a low energy orbital into a higher energy orbital with conservation of electron spin angular momentum. The singlet excited state ($S_n$) which is initially populated is not necessarily the lowest singlet excited state ($S_1$). $S_1$ is populated after vibrational relaxation (VR) and internal conversion (IC) of the first-formed $S_n$. The processes which lead to the formation of the lowest vibrational level of $S_1$ occur with unity efficiency for most molecules. Possible deactivation pathways from $S_1$ are chemical reaction, fluorescence, IC back to $S_0$ and intersystem crossing (ISC) to a triplet excited state ($T_n$), which may be the lowest triplet excited state ($T_1$). ISC is an isoelectronic transition between states of differing multiplicities which involves flipping an electron's spin. Possible deactivation pathways from $T_1$ are chemical reaction, phosphorescence and ISC back to $S_0$. These processes are represented schematically in a Jablonski diagram (Figure 2).

Figure 2. A Jablonski diagram.

A quantum yield, $\Phi$, is a measure of the efficiency of a photochemical process, and is defined as the number of times that a process occurs per photon absorbed. Upon photoexcitation of benzophenone, ISC to its triplet state occurs with a rate constant of $\sim 10^{11}$ s$^{-1}$ and a $\Phi = 1$. Therefore, every time that a molecule of benzophenone absorbs a photon it reaches its $T_1$. The $T_1$ of benzophenone has an electronic structure which corresponds to an electron being promoted from a non-bonding $n$ orbital on oxygen to a $\pi^*$ orbital. This configuration is referred to as an $n,\pi^*$ triplet state. It is this species that is
responsible for the intermolecular hydrogen abstraction reaction of photoexcited benzophenone from 2-propanol. The \( n,\pi^* \) triplet state of carbonyl compounds is diradicaloid in nature, with their reactivity modeled by alkoxy radicals; hence, their tendency to participate in hydrogen abstraction reactions.\(^3\) Any hydrogen abstraction process from \( T_1 \) which occurs must do so in competition with other modes of triplet decay which, in the case of benzophenone in 2-propanol, occur with a rate constant of \(~1 \times 10^5\) s\(^{-1}\).\(^4\)

While hydrogen abstraction reactions are relatively specific to the photochemistry of carbonyl containing compounds, a much more general process in photochemistry is that of energy transfer. In the presence of certain molecules (quenchers), which have an excited state energy lower than that of a molecule which has absorbed a photon (the sensitizer), energy transfer may occur to form an excited state of the quencher molecule, as shown in Figure 3.

\[
\text{Sensitizer} + \text{Quencher} \xrightarrow{\text{hv}} \text{Sensitizer}^* + \text{Quencher} \quad \xrightarrow{k_{ET}} \text{Sensitizer} + \text{Quencher}^*
\]

Figure 3. Energy transfer between a sensitizer and quencher.

In this experiment, benzophenone acts as a sensitizer for the naphthalene triplet excited state; a corollary to this is that naphthalene acts as a quencher of the benzophenone triplet excited state. Under conditions in which energy transfer is very exothermic (>5 kcal/mol), as is the case for benzophenone and naphthalene which have triplet energies of 69 and 61 kcal/mol,\(^5\) respectively, the rate constant for energy transfer occurs as quickly as diffusion of the two species in the solvent will allow. In 2-propanol, the rate constant for a diffusion-controlled process is \(2.7 \times 10^9\) M\(^{-1}\)s\(^{-1}\).\(^2\)

The reactions involved in the photoreduction of benzophenone to benzopinacol in the presence of a quencher appear in Figure 4.\(^6,7\) A consideration of the competition between naphthalene quenching and hydrogen abstraction from 2-propanol by triplet benzophenone in deaerated solutions via the Stern-Volmer kinetic analysis allows for the determination of the rate constant for hydrogen abstraction from the following expression, the derivation of which appears in the appendix:

\[
\frac{\Phi_o}{\Phi} = 1 + \frac{k_q[Q]}{k_h[(CH_3)_2CHOH]}
\]

This is a very powerful technique as it allows for determination of kinetic parameters for processes which occur on the microsecond timescale without the benefit of time resolved techniques.
Figure 4. Reactions involved in the photoreduction of benzophenone to benzopinacol in the presence of a quencher. $\phi_2\text{CO}$, $^1\phi_2\text{CO}^*$ and $^3\phi_2\text{CO}^*$ represent the benzophenone $S_0$, $S_1$ and $T_1$ states, respectively.

Cross-coupling reactions between the diphenyl ketyl radical and the dimethyl ketyl radical to yield the products in Figure 5 also occur to a very small extent. These products are often referred to as light absorbing transients because their extended conjugation makes them efficient absorbers of light and they are eventually removed from the reaction mixture via reaction with oxygen. The presence of these species interferes with any attempts to measure the progress of the photoreduction of benzophenone by UV/Vis spectrometry.

Figure 5. The light absorbing transients formed via cross-coupling radical reactions.

**Equipment and Chemicals**

volumetric flasks, quartz cells, rubber septa, degassing needles, nitrogen or argon tank, UV/Vis spectrometer, benzophenone, 2-propanol, naphthalene
Procedure

1. Prepare separate solutions of 25 mL of 25 mM benzophenone and 25 mM naphthalene in 2-propanol. Prepare 6 solutions for irradiation in cells which can be sealed with a septum by combining the aforementioned benzophenone and naphthalene solutions with 2-propanol in the amounts designated below:

<table>
<thead>
<tr>
<th>Component</th>
<th>Volume (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzophenone</td>
<td>1.0 1.0 1.0 1.0 1.0 1.0</td>
</tr>
<tr>
<td>naphthalene</td>
<td>0.0 0.5 1.0 1.5 2.0 2.5</td>
</tr>
<tr>
<td>2-propanol</td>
<td>2.5 2.0 1.5 1.0 0.5 0.0</td>
</tr>
</tbody>
</table>

2. Remove oxygen from the samples by inserting a long needle through the septum to deliver the inert gas into the bottom of the solution and adding a short needle to allow for escape of the gas. Bubble gently with the inert gas for 10 minutes.

3. Place the solutions in the carousel of a Luzchem photo reactor equipped with three lamps on the wall.

4. Irradiate the solutions for a length of time adequate to achieve approximately 10% conversion. Longer irradiation times are required for those solutions containing high naphthalene concentrations. (Consult your instructor for the appropriate irradiation times)

5. Depletion of the benzophenone can be measured using a UV/Vis spectrometer and recording the change in absorbance at 333 nm. This measurement cannot be performed immediately after the irradiation due to absorbance of the light absorbing transients. Measurements must be made no less than 24 hours after the irradiations have been completed, during which time the samples must be stored in the dark and exposed to air.

Data Analysis

In order to make use of the Stern-Volmer kinetic relationship described earlier, it must be converted to include experimentally measurable quantities for the quantum yield values. After disappearance of the light absorbing transients, the change in absorbance at 333 nm, ΔA, obtained by measurements before and after irradiation can serve as a measure of the extent of the photoreaction because the only species which contributes to the absorbance at this wavelength is benzophenone. Therefore, the value ΔA/t is proportional to the rate of benzophenone disappearance. Since the quantum yield for the reaction is proportional to its rate, you obtain the expression:

\[ \Phi = \frac{\Delta A}{\Delta t} \]

These values can be plotted vs. the naphthalene concentration to give a straight line with the equation:
\[
\frac{\Delta A_s}{t_o} = 1 + \frac{k_s}{k_h[(CH_3)_2CHOH]}
\]

Based on the information given and assuming a constant concentration of 2-propanol, solve for \(k_h\).

**Questions**

1. What would you expect to happen if solvents other than 2-propanol were used, such as water, methanol, hexane or toluene?
2. The quantum yield for intersystem crossing for benzophenone is 1.0. Explain the meaning of this, and the reason why this value is so high for benzophenone.
3. Why is it necessary to degass the solution by bubbling with nitrogen or argon?
4. Where does the factor of 2 come from in the expression for the quantum yield of benzophenone photoreduction?
5. Based on the value for \(k_h\) you obtained, was it a valid approximation to neglect \(k_d\) in the kinetic treatment of the data?

**Appendix**

The quantum yield for benzophenone photoreduction in the absence of quencher is given by the expression:

\[
\Phi_o = 2 \frac{k_h \int \phi_2CO^* (CH_3)_2CHOH}{k_{abs} \int \phi_2CO \int \nu}
\]

An expression for the concentration of benzophenone triplet excited states can be obtained by first applying the Steady-State approximation to the benzophenone singlet excited state to obtain an expression for its concentration:

\[
\frac{d[\phi_2CO^*]}{dt} = 0 = k_d[\phi_2CO^*] + k_{isc}[\phi_2CO^*] - k_{abs}[\phi_2CO \int \nu]
\]

Substituting this expression into the one obtained by applying the Steady-State approximation to the benzophenone triplet excited state yields an expression for the concentration of benzophenone triplet excited states:
\[
\frac{-d[3\phi_2\text{CO}^-]}{dt} = 0 = -k_{\text{isc}} \frac{k_{\text{abs}}[\phi_2\text{CO}]hv}{k_d + k_{\text{isc}}} + k_d[3\phi_2\text{CO}^-] + k_h[3\phi_2\text{CO}^-] + k_q[3\phi_2\text{CO}^-]O_2
\]

\[
[3\phi_2\text{CO}^-] = \frac{k_{\text{isc}}k_{\text{abs}}[\phi_2\text{CO}]hv}{(k_d + k_{\text{isc}})(k_d + k_h[CH_3)_2\text{CHOH} + k_q[O_2])}
\]

Substituting into the expression for the quantum yield for benzophenone photoreduction in the absence of quencher yields:

\[
\Phi = \frac{2}{k_{\text{isc}}(CH_3)_2\text{CHOH} + k_h[CH_3)_2\text{CHOH} + k_q[O_2])}
\]

Since the quantum yield for intersystem crossing in benzophenone is 1, this expression simplifies to:

\[
\Phi = 2 \left( \frac{k_h[CH_3)_2\text{CHOH} + k_q[O_2])}{k_d + k_h[CH_3)_2\text{CHOH} + k_q[O_2])} \right)
\]

It follows that the quantum yield for benzophenone photoreduction in the presence of naphthalene is given by:

\[
\Phi = 2 \left( \frac{k_h[CH_3)_2\text{CHOH} + k_q[\text{naphthalene})}{k_d + k_h[CH_3)_2\text{CHOH} + k_q[\text{naphthalene})} \right)
\]

A useful equation which does not require the actual determination of quantum yields is obtained by combining the previous two equations:

\[
\frac{\Phi}{\Phi_o} = 1 + \left( \frac{k_q[\text{naphthalene})}{k_d + k_h[CH_3)_2\text{CHOH} + k_q[\text{naphthalene})} \right)
\]

This equation can be further simplified by noting that \(k_d'\) should be very small relative to the other terms and can be neglected without introducing more than 0.5% error.

References