Photochemistry of Benzophenone in 2-Propanol: An Easy Experiment for Undergraduate Physical Chemistry Courses

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Photochemistry of Benzophenone in 2-Propanol

An Easy Experiment for Undergraduate Physical Chemistry Courses

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In this article we describe a laboratory experiment for undergraduate physical chemistry courses dealing with the photophysics and photochemistry of benzophenone in 2-propanol. This is an easy-to-perform experiment aimed to introduce the basic concepts of photochemistry that may help to achieve a systematic approach to the subject, incorporating related topics of chemical kinetics and molecular spectroscopy (1–3). This experiment makes use of the Stern–Volmer kinetic relationship and provides quantitative data regarding the lifetime of short-lived excited species, without requiring expensive time-resolved techniques (4).

Introduction and Theory

Figure 1 shows a typical energy state diagram for an organic molecule. Absorption of a photon promotes the ground state S_0 to one of the excited vibrational levels of an excited electronic state S_n. According to the selection rules, the spin multiplicity is conserved in this transition. Let us consider that S_1 is the state reached by photoexcitation. In turn, S_1 may deactivate, preserving its chemical identity by photophysical processes. For instance, the nonradiative decay (internal conversion) and the emission of a photon ν_f (fluorescence) relax S_1 to S_0. As expected for allowed transitions, these are relatively fast unimolecular photophysical paths. From the above argument, it follows that singlet excited states are hardly involved in bimolecular events; however, they may undergo intramolecular rearrangements. On the other hand, the population of the excited triplet state T_1 is attained by the nonradiative transition (intersystem crossing) from S_1. Since radiative (phosphorescence) and nonradiative relaxations from T_1 to the ground state S_0 are spin forbidden, T_1 is much more long-lived and usually available for bimolecular physical or chemical processes (1–3).

Let us assume that the irradiation is carried out in the presence of another species, Q, for which the states are denoted by S_0', S_1', and T_1'. Collisional deactivation of the ex-
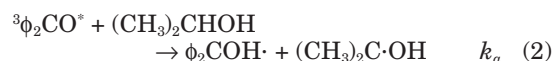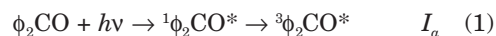
cited molecule may be achieved by electronic energy transfer (quenching). For a quenching process to be effective, the energy levels must be arranged as shown in Figure 1 for benzophenone and naphthalene as the quencher. Notice that the fundamental vibrational energy levels of S_1' and T_1' bracket those of S_1 and T_1: this guarantees that the light is absorbed exclusively by benzophenone and that energy transfer from T_1 to T_1' is not activated. The bimolecular rate constant k_q for the quenching reaction

$$T_1 + S_0' \rightarrow S_0 + T_1' \qquad k_q$$
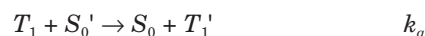
can be estimated from the diffusion-controlled rate coefficient derived by Smoluchowski (5). Thus, a very useful method of determining excited-state lifetimes is provided by the study of the yield of any process originated in this state (emission or chemical reaction) and its competition with the quenching at variable Q concentrations. This treatment leads to the so called *Stern–Volmer kinetic relationship* (6).

The Photoreduction of Benzophenone in 2-Propanol

When a solution of benzophenone in 2-propanol, without oxygen, is exposed to UV light, benzopinacol and acetone are produced (7). Reported quantum efficiencies of benzophenone disappearance—that is, the ratio between the rate of benzophenone photoreduction and the photon absorption—ranged between approximately 1 and 2, depending on its concentration. These facts can be explained by the mechanism proposed by Bäckström and Pitts (8, 9):

$$\phi_2CO + h\nu \rightarrow {}^1\phi_2CO^* \rightarrow {}^3\phi_2CO^* \qquad I_a \quad (1)$$

$$\begin{aligned}{}^3\phi_2CO^* + (CH_3)_2CHOH \\ \rightarrow \phi_2COH\cdot + (CH_3)_2C\cdot OH \qquad k_a \quad (2)\end{aligned}$$

$$\phi_2CO + (CH_3)_2C\cdot OH \rightarrow \phi_2COH\cdot + (CH_3)_2CO \qquad k_t \quad (3)$$

Here I_a is the absorbed light intensity and ${}^3\phi_2CO^*$, ${}^1\phi_2CO^*$, and ϕ_2CO stand for triplet T_1, singlet S_1, and ground state S_0 benzophenone, respectively. ${}^1\phi_2CO^*$ is very short-lived and undergoes rapid intersystem crossing with near unitary efficiency to ${}^3\phi_2CO^*$ (2).

The identity of the excited state reactive towards hydrogen abstraction from 2-propanol can be elucidated by analyzing the quenching of benzophenone triplets by naphthalene. It has been shown that benzophenone phosphorescence at 77 K declines as naphthalene concentration increases, being replaced by naphthalene phosphorescence (2). This is due to a triplet-triplet energy transfer from benzophenone to naphthalene. Similarly to the quenching of phosphorescence, the quantum yield of benzophenone disappearance in 2-propanol reduces in the presence of naphthalene (Q), indicating that the first triplet state is the reactive species. The change of the quantum yield with the concentration of naphthalene is nonlinear and arises from the competition between hydrogen abstraction from the solvent (reaction 2) and energy transfer to naphthalene by triplet benzophenone (reaction 4).

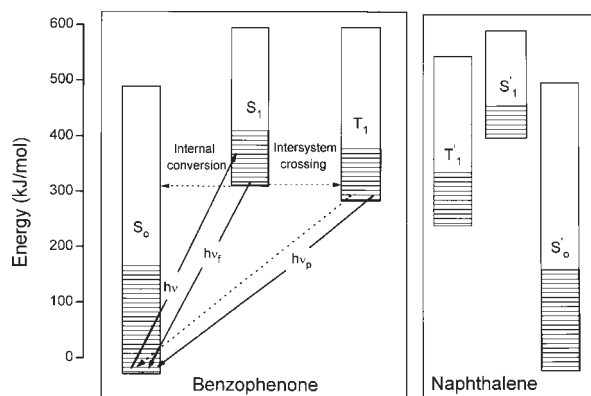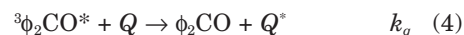$$ {}^3\phi_2CO^* + Q \rightarrow \phi_2CO + Q^* \qquad k_q \quad (4)$$

Figure 1. Energy state diagram for benzophenone and naphthalene. Filled and dotted arrows shown for benzophenone indicate radiative and nonradiative transitions, respectively. Relative energies of the electronic levels were extracted from references *2* and *8*.

All other processes different from steps 2 and 4, which may consume $^3\phi_2CO^*$, are included in reaction 5:

$$^3\phi_2CO^* \rightarrow \phi_2CO \qquad \Sigma k \quad (5)$$

where the sum, Σk, extends over every first-order event such as emission, or nonradiative paths. On the other hand, self-recombination of diphenylketyl radicals, $\phi_2COH\cdot$, not shown for simplicity, renders benzopinacol.

Considering the set of reactions 1 to 5, the quantum yield of benzophenone disappearance, Φ, can be expressed as:

$$\Phi = -\frac{1}{I_a} \cdot \frac{d[\phi_2CO]}{dt} = \frac{\Phi_0 k_a\left[(CH_3)_2CHOH\right]}{k_a\left[(CH_3)_2CHOH\right] + k_q[Q]} \quad (6)$$

where Φ_0 stands for the quantum yield in absence of quencher. This expression can be obtained by using the steady-state approximation for the reactive intermediates. In addition, one can derive the Stern–Volmer linear expression rearranging the above equation (1, 8):

$$\frac{\left(\Phi_0 - \Phi\right)}{\Phi} = \frac{k_q[Q]}{k_a\left[(CH_3)_2CHOH\right]} \quad (7)$$

Measurements of quantum yields at variable Q concentrations, according to eq 7, allow the determination of the ratio k_a/k_q. Since only relative values, Φ_0/Φ, are involved, the measure of the absorbed light intensity is not required as long as one ensures identical optical configuration. If the extent of the reaction does not exceed 20%, (for $[\Phi_2CO] < 10^{-1}$ M), neither acetone nor benzopinacol is expected to absorb noticeably at 333 nm (8). Thus optical density measurements should provide a rapid and easy way to quantify benzophenone conversion. However, oxygen-sensitive intermediates (***Light Absorbing Transients***), formed by coupling reactions between mixed ketyl radicals can seriously interfere the determinations (8, 10, 11):

$$\phi_2COH\cdot + (CH_3)_2C\cdot OH \rightarrow \mathbf{1, 2}$$
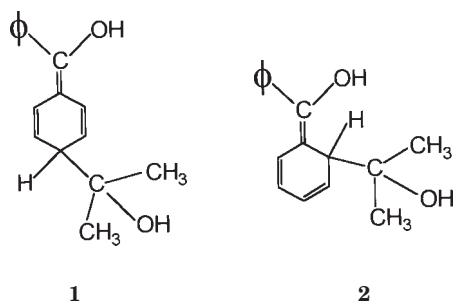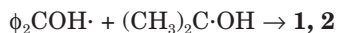

1   **2**

Figure 2 clearly depicts this problem: the spectrum taken immediately after the irradiation in *anaerobic conditions* shows that the absorbance at 333 nm is nearly double the initial value. As shown in this figure, LAT strongly absorb in the range of 300–400 nm and the $\lambda_{max} \sim 333$ nm (curve a) has shifted to shorter wavelengths ~ 328 nm (curve b). When oxygen is admitted to the cell, the absorbance goes down (curve c). It is interesting to point out that the enhancement in the absorbance may be overlooked depending on the time interval elapsed between the admission of oxygen after the photolysis and the registration of the spectrum. Still, it takes nearly a day to achieve a constant absorbance—that is, the complete LAT depletion (curve d). From Figure 2, one can evaluate a conversion of about 24%

for benzophenone. Notice that according to the value of the extinction coefficient of the intermediate, $\varepsilon_{LAT, 333 nm} \sim 5 \times 10^4$ $M^{-1} cm^{-1}$ (11), one can estimate from curve b that the concentration of LAT is less than 1% of the total amount of photoproducts. It should be said that LAT formation is nearly suppressed if the reaction is performed in nonpolar hydrogen-donor solvents such as hexane or cyclohexane. Also, a possible strategy to avoid the complications arising from LAT production is to perform the photoreduction with 2-propanol in an inert solvent such as benzene.

We will describe below in more detail how experiments can be carried out in order to derive the rate constant for H abstraction, k_a. Also, we will suggest a series of additional experiments to bridge the common gap between experimental and theoretical photochemistry. Students interested in the nature of LAT might consult references 8, 10, and 11.

Experimental Procedures

Benzophenone and naphthalene (Merck) were used as received. 2-Propanol (Mallinckrodt) was distilled. Solutions of benzophenone and naphthalene in 2-propanol were placed in a 1-cm quartz cell tightly covered with a rubber septum. Ten minutes bubbling with dry nitrogen into the covered cell displaced oxygen from the solutions. This procedure is essential because oxygen is one of the most efficient quenchers. The nitrogen stream was previously saturated in a trap containing 2-propanol to avoid changes in the concentration. Sample temperature was kept constant at 25 °C during the irradiation.

The illumination system consisted of a 1000-W high-pressure Hg-Xe lamp and a high-intensity monochromator (Kratos–Schoeffel). The output of a standard mercury lamp (250 W Osram-HWL) and optical filters with cutoff at about 310 nm are also suitable to perform the irradiation experiments. Absorption spectra were measured with a UV-vis scanning spectrophotometer (Shimadzu UV-2101PC).

Further analyses of the solutions were carried out in a high-pressure liquid chromatograph (Konik KNK-500-A) with optical detection. The column used was Econosphere C18 5U (250 mm length, 4.6 mm I.D., Alltech). Methanol–water 75:25 at 2 mL/min proved to be an appropriate mobile phase.
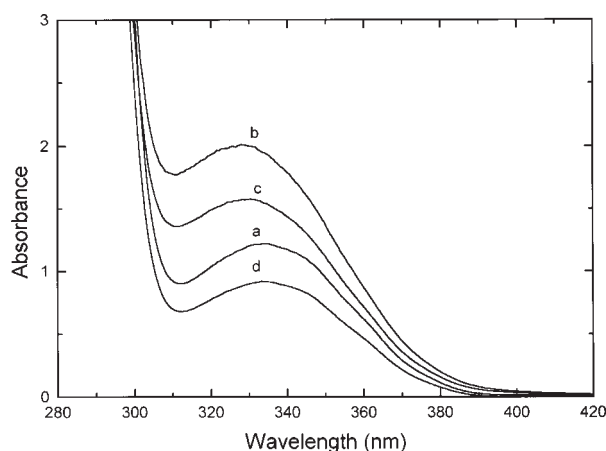

Figure 2. Absorbance spectra for a sample of 7×10^{-3} M benzophenone in 2-propanol irradiated during 7 min at 366 ±10 nm. (a) Before irradiation. (b) Immediately after irradiation, under anaerobic conditions. (c) After irradiation and five minutes in the dark under air-saturated conditions. (d) After irradiation and 30 hours in the dark under air-saturated conditions.

Safety

Considerable caution must be exercised when working with UV light. Never look directly toward the light source.

Some care should be taken when preparing benzophenone solutions and during handling of the solvents. Special precautions against explosive flammability of acetonitrile, cyclohexane, and hexane should be taken. All of these chemicals are moderately toxic. Benzene is carcinogenic.

Procedure

Reaction mixtures from Table 1 are exposed to light of 366 ± 10 nm for an adequate time interval, t, to achieve conversions around 10% (10–15 min under our experimental conditions). Notice that the increase in naphthalene concentration will obviously entail longer times to ensure nearly the same extent of reaction. Since LAT will also act as an *inner filter* (*12*) by absorbing part of the incident light I_0, small conversions should help to minimize this problem. Also, if some effect is yet operative, a constant conversion will provide a systematic deviation in all experiments, (i.e., almost equal amounts of light absorbed by benzophenone).

To achieve a rapid determination of benzophenone depletion, HPLC technique is highly recommended. Under the conditions described above, benzophenone elutes at 5 min, providing a proper separation. Alternatively, the photolyzed solutions can be stored in dark air-saturated flasks until λ_{max} is restored to 333 nm and no further change in the absorbance is observed. At this point, it is assumed that LAT do not interfere, as can be confirmed by chromatographic analyses. At least 24 hours seem to be necessary to guarantee the complete destruction of the LAT.

If A^{∞} denotes the absorbance at 333 nm in the absence of LAT and A^i is the optical density before irradiation, $\Delta A = A^{\infty} - A^i$ can be taken as a measure of the extent of photoreaction. As the quantum yield is proportional to the rate (i.e., to $\Delta A/t$), the first term in eq 7 is converted into

$$\frac{(\Phi_0 - \Phi)}{\Phi} = \frac{\Delta A_0/t_0 - \Delta A/t}{\Delta A/t} \qquad (8)$$

The above expression holds for a fixed optical geometry.

Figure 3 shows a Stern–Volmer plot resulting from the experiments at the various naphthalene concentrations indicated in Table 1. From the slope of this plot the ratio $k_q/k_a[(CH_3)_2CHOH]$ is obtained. The value of k_q can be estimated if one considers that the triplet energy transfer is a diffusion-controlled process. Thus, combining Smoluchowski with the Stokes–Einstein relationships we obtained $k_q = 2.70 \times 10^9$ $M^{-1}s^{-1}$ in 2-propanol at 25 °C (*13*). From the data displayed in Figure 3, the specific rate constant for the hydrogen abstraction process is $k_a = 1.37 \pm 0.10 \times 10^6$ $M^{-1}s^{-1}$.

Suggested Additional Activities

Experiments Varying Benzophenone Concentration

Measurements of the initial rates of photoreduction in 2-propanol as a function of benzophenone concentration will help students to rationalize the expected dependence of the quantum yields according to the proposed mechanism.

Experiments Varying the Solvent

Solvents with different R–H bond energies modify quantum yields for benzophenone photoreduction. Water, hexane, toluene, acetonitrile, and ethanol are suggested. It should be observed that under the same conditions, the extent of photoreaction changes. Students are encouraged to compare the observed trends with bond dissociation energies R–H and ionization potential of ·R (*14*).

Absolute values of the incident light do not need to be measured. However, when benzophenone concentration is varied, corrections must be considered to take into account the differences in benzophenone absorbance, since $I_a = I_0 \times (1 - 10^{-A})$.

Table 1. Reaction Mixtures for Quenching Studies of Photoreduction of Benzophenone in 2-Propanol

Component	Experiment					
	I	II	III	IV	V	VI
	volume (mL)					
2.7×10^{-2} M benzophenone	1.0	1.0	1.0	1.0	1.0	1.0
2.45×10^{-2} M naphthalene	0.0	0.5	1.0	1.5	2.0	2.5
2-propanol	2.5	2.0	1.5	1.0	0.5	0.0

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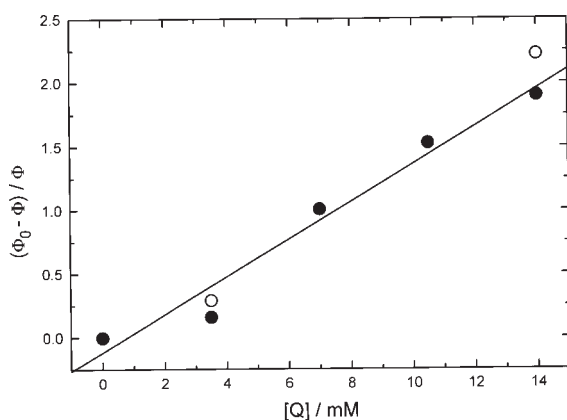14. Naguib, Y. M. A.; Steel, C.; Cohen, S. G.; Young, M. A. *J. Phys. Chem.* **1987,** *91*, 3033–3036.

Figure 3. $\dfrac{(\Phi_0 - \Phi)}{\Phi}$ values vs. naphthalene concentration. Filled circles were calculated using eq 8, from absorbance measurements. Open circles account for data obtained by quantitative HPLC analysis.