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The $S_2 \rightarrow S_1$ Internal Conversion of Benzophenone and *p*-Iodobenzophenone[1]

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Two modes of excitation ($S_0 \rightarrow S_2$ and $S_0 \rightarrow S_1$) of benzophenone (BP) and *p*-iodobenzophenone (*p*-IBP) in acetonitrile have been examined by ultrafast pump−probe experiments. The S_1 states ($\lambda_{max} \sim 575-580$ nm) of BP and *p*-IBP were observed to be generated with lifetimes of 0.53 and 0.59 ps, respectively, following excitation at 267 nm, and this has been attributed to the $S_2 \rightarrow S_1$ internal conversion. The rates of the $S_1 \rightarrow T_1$ ISC have been observed to be similar following either 267 or 335 nm excitation for both BP ($\sim 1 \times 10^{11}$ s^{-1}) and *p*-IBP ($\sim 2.3 \times 10^{11}$ s^{-1}).

Introduction

Although a wide variety of excited reaction intermediates have been characterized spectroscopically, the same cannot be said of upper excited states of stable organic molecules.[2] It is generally believed that the lifetimes of upper excited states are too short to allow direct detection, even with modern spectroscopic techniques. The short lifetime of upper excited states may be due to intramolecular chemical processes that take place as a consequence of the high energies possessed by these states, as well as ultrafast radiationless deactivation processes such as internal conversion that result from large Franck−Condon factors.

Since Hammond and co-workers elucidated the mechanism of the photoreduction of benzophenone (BP), its photophysical and photochemical properties have become familiar to photochemists.[3] The molecular photophysics and photochemistry of benzophenone and its derivatives in fluid organic solvents represent a keystone in the development and history of mechanistic organic photochemistry.[4] Photoexcitation of BP to the S_1 state is followed by rapid intersystem crossing (ISC) with unit quantum yield to the triplet state.[4,5] Formation of the triplet state absorption ($\lambda_{max} = 530$ nm) can be observed spectroscopically. Several transient spectroscopic studies have revealed that the growth of the triplet state takes places in a range of 6 to 30 ps depending on the solvent.[6,7]

Although there is an abundance of data available on the triplet state of BPs,[6−8] there are limited reports on the spectroscopic observation of the S_1 state.[7,9] The S_1 state of BP absorbs with a λ_{max} of 575 nm,[7] at a higher wavelength than that at which the triplet state absorbs. This is also true for substituted benzophenones such as *tert*-butyl 4-(4′-methylbenzoyl)perbenzoate and *tert*-butyl 4-(4′-bromomethylbenzoyl)perbenzoate, in which cases the kinetics of the decay of the S_1 state have been clearly shown to be within the experimental error of the growth of the triplet state.[10]

In fact, BP undergoes the $\pi \rightarrow \pi^*$ ($S_0 \rightarrow S_2$) and $n \rightarrow \pi^*$ ($S_0 \rightarrow S_1$) electronic transitions upon excitation at 230−310 and 310−400 nm, respectively. Irrespective of the excitation wavelength, it has always been the population of the triplet state that has been observed and recognized spectroscopically. The $\pi \rightarrow \pi^*$ transition produces the S_2 state, which can then undergo internal conversion to populate the S_1 state. It may also be possible that the S_2 state directly intersystem crosses into the triplet state.[6a] However, the effects of excitation wavelengths on the initial population of either the S_2 or S_1 state have not been addressed so far.

This investigation details the relaxation kinetics of BP and *p*-iodobenzophenone (*p*-IBP) obtained by ultrafast pump−probe experiments (instrument response function ~150 fs). Excitation of BP and *p*-IBP at 267 and 335 nm in acetonitrile yielded different results in terms of the population of the S_1 state of these compounds. Experimental data on the rate of the $S_2 \rightarrow S_1$ internal conversion are presented. The effects of the excitation wavelengths on the $S_1 \rightarrow T_1$ ISC are discussed.

Results and Discussion

The transient spectra obtained from BP in acetonitrile at room temperature following excitation at 267 and 335 nm are shown in Figures 1 and 2, respectively. The spectra are similar in that a broad early absorption ($\lambda_{max} = 570$ nm) was observed during either 267 or 335 nm excitation and can be assigned to the $S_1 \rightarrow S_n$ transition.[7,9] The initial changes in the spectra are attributed to the $S_1 \rightarrow T_1$ ISC, resulting at longer delay times in the well-known absorption corresponding to the $T_1 \rightarrow T_n$ transition ($\lambda_{max} = 530$ nm). The absorption of the triplet state persisted up to the maximum delay of 1.6 ns.

The spectra of the primary transients were similar at both excitation wavelengths, but formation of the S_1 state was observed to be instantaneous after 335 nm excitation, whereas it was not so after 267 nm excitation (vide infra). Similar spectra corresponding to the $S_1 \rightarrow S_n$ transition ($\lambda_{max} \sim 580$ nm) and the $T_1 \rightarrow T_n$ transition ($\lambda_{max} \sim 540$ nm) were recorded of *p*-IBP under similar experimental conditions (not shown). It is clear from Figures 1 and 2 that the absorption spectrum of the S_1 state overlaps with that of the triplet state. The time profiles pictured in Figure 3 show interesting dynamic differences. The early rise times observed during 335 nm excitation were within or close to the instrument response function (IRF ~0.15 ps) for both BP and *p*-IBP and are listed in Table 1 as IRF.

The shorter rise times obtained from 267 nm excitation ($S_0 \rightarrow S_2$ transition) experiments are, however, considerably longer than the IRF for both compounds, indicating that formation of the S_1 state is not instantaneous. Thus, the rise times ~0.53

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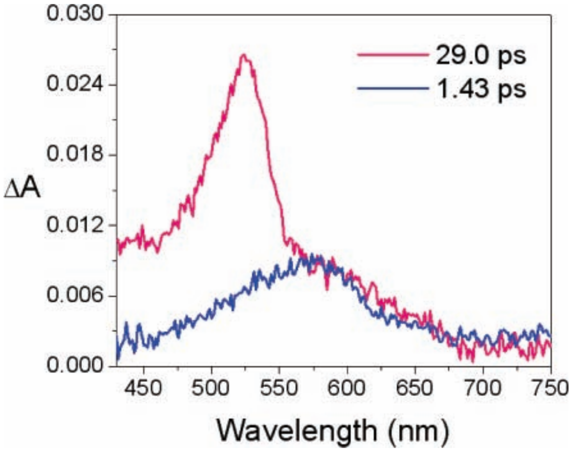

Figure 1. Transient absorption spectra obtained from ultrafast pump−probe experiments of BP (6.12×10^{-4} M) in acetonitrile, recorded 1.43 ps (blue) and 29.0 ps (pink) after the laser pulse (excitation at 267 nm).

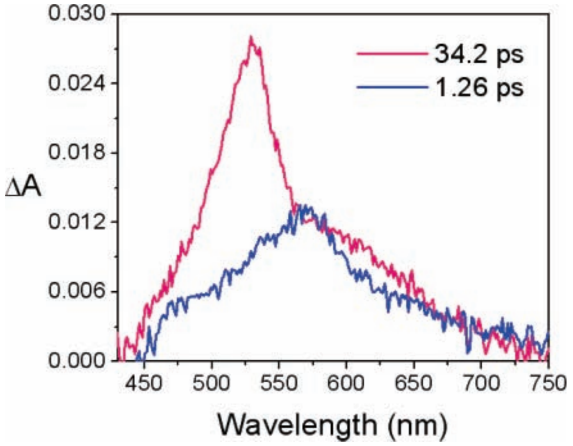

Figure 2. Transient absorption spectra obtained from ultrafast pump−probe experiments of BP (5.52×10^{-2} M) in acetonitrile, recorded 1.26 ps (blue) and 34.2 ps (pink) after the laser pulse (excitation at 335 nm).

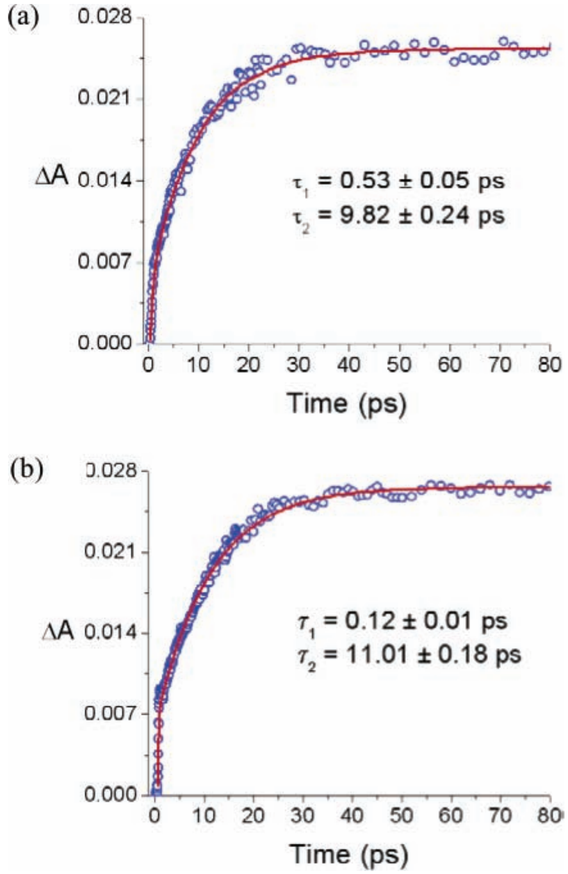

Figure 3. Time profiles monitored at 530 nm following ultrafast pump−probe experiments of BP (a) 1.53×10^{-4} M in acetonitrile, excitation at 267 nm and (b) 1.38×10^{-2} M in acetonitrile, excitation at 335 nm.

TABLE 1: Lifetimes of the S_2 (τ_{S2}) and S_1 (τ_{S1}) States of BP and *p*-IBP in Acetonitrile

excitation wavelength (nm)	BP τ_{S2} (ps)	BP τ_{S1} (ps)	*p*-IBP τ_{S2} (ps)	*p*-IBP τ_{S1} (ps)
267	0.53 ± 0.05	9.82 ± 0.24	0.59 ± 0.07	4.29 ± 1.81
335	0.12[a]	11.01 ± 0.18	0.07	4.38 ± 0.10

[a] Within instrument response function (IRF).

and ~0.59 ps observed for BP and *p*-IBP, respectively, could represent internal conversion of $S_2 \rightarrow S_1$ type or vibrational relaxation on the S_1 surface.[11] Nevertheless, it has been proposed that relaxation within the vibronic levels of the S_1 state is a slow process in benzophenones (~4×10^{11} s^{-1}).[12] Vibrational relaxation would also cause spectral changes. Because the spectra of the S_1 state was independent of wavelength and remained the same at different delay times (see Supporting Information, Figure S2), it is concluded that these measured rise times are the lifetimes of the precursor of the S_1 state, viz. the S_2 states. The observed rate of the $S_2 \rightarrow S_1$ internal conversion of BP ($k_{S_2 \rightarrow S_1} = 1.9 \times 10^{12}$ s^{-1}) and *p*-IBP ($k_{S_2 \rightarrow S_1} = 1.7 \times 10^{12}$ s^{-1}) is close to the quoted value of the $S_2 \rightarrow S_1$ internal conversion of BP ($k_{IC} \sim 1 \times 10^{12}$ s^{-1}).[4,13]

There have been reports of formation of a ground-state oxygen−BP complex[14] and a triplet−triplet dimer excited state of BP.[15] It has been suggested that the doubly excited dimer state relaxes efficiently to the lowest excited singlet dimer state, which is expected to dissociate into an excited singlet monomer (S_1) and a ground-state monomer.[15] Interference of the triplet−triplet dimeric state, if formed, can be ruled out in our kinetic measurements on the basis of the observed time of formation of the S_1 state. The oxygen−BP complex has been reported to not affect the 530 nm absorption of the triplet state.[14] Moreover, the effects of these complexes would have been similar to the results obtained by both 267 and 335 nm excitation. Contribution of the triplet growth is little if not negligible at 580 nm during the initial delay times (<10 ps). The kinetics monitored at this wavelength for BP, which represents the growth of only the S_1 state, was monoexponential (Figure 4). The lifetime obtained (0.51 ps) was within the experimental error of the shorter rise time observed at 530 nm, which assured us that this rise time is indeed the lifetime of the S_2 state.

The rate of the $S_1 \rightarrow T_1$ ISC of BP observed in acetonitrile is similar to previously reported values in the same solvent.[9,16] There is a decrease in the time of the $S_1 \rightarrow T_1$ ISC from BP (~10 ps) to *p*-IBP (~4.29 ps). This can be attributed to the heavy atom induced rate of ISC.[17] It is also noted that changing the excitation wavelength does not significantly affect the lifetime of the S_1 state (τ_{S_1}) of either BP or *p*-IBP; the τ_{S_1} values obtained using either 335 or 267 nm excitation are similar for each compound (Table 1). This is consistent with the previous reports in which no effect of excitation wavelengths on the rate of the $S_1 \rightarrow T_1$ ISC of BP has been observed.[6c,9] Even when BP is excited at the onset of its absorption spectrum (400 nm), the time of the $S_1 \rightarrow T_1$ ISC has been observed to be ~10−11

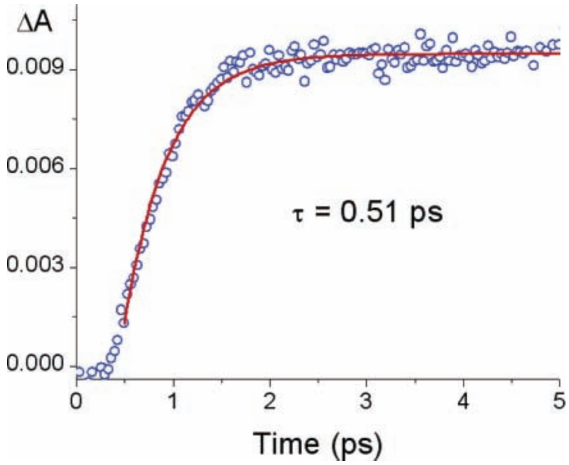

Figure 4. Time profile monitored at 580 nm during ultrafast pump−probe experiments of BP (6.12×10^{-4} M) in acetonitrile (excitation at 267 nm).

ps in benzene and methanol, most probably indicating that this time represents the $S_1 \rightarrow T_1$ ISC from the vibrationally relaxed S_1 ($\upsilon = 0$) state.[6c] Observation of the similar rates of the $S_1 \rightarrow T_1$ ISC during our experiments may also indicate that population of the triplet state exclusively takes place from the S_1 surface, irrespective of whether the molecules are initially excited to the S_2 or S_1 state. The direct $S_2 \rightarrow T_1$ relaxation does not seem to be involved in the photophysical pathway of BP and *p*-IBP in solution.

Experimental Section

Materials. BP (Aldrich) and *p*-IBP (Trans World Chemicals) were twice recrystallized from methanol before use. Twice distilled acetonitrile was used as the solvent.

Ultrafast Spectrometry. The system for the ultrafast transient absorption spectrometric experiments consisted of a Ti:sapphire laser (Spectra-Physics, Hurricane), the output of which was typically 1 mJ/pulse (fwhm ~150 fs) at a repetition rate of 1 kHz. The Hurricane output was steered into a third harmonic generator (CSK Super Tripler) to obtain the 267 nm excitation wavelength. An optical parametric amplifier (OPA-800C, Spectra-Physics) was used to obtain the 335 nm excitation wavelength. A total of 92% of the fundamental laser output was used to generate the required excitation wavelength whereas 8% of the output was used for white light generation. A 3 mm thick sapphire plate (Crystal Systems, Inc., HEML UX grade) was used for continuum generation.

Prior to generating the probe continuum, the amplified fundamental was passed to a delay line (Newport) that provided an experimental time window of 1.6 ns. The energy of the probe pulses was <1 μJ/cm^2 at the sample. The pump beam was typically arranged to be 5 μJ/pulse with spot size of 1−2 mm diameter at the sample. The angle between the pump and probe beam was 5−7°. The sample flow-through cell had an optical path of 2 mm and was connected to a solution reservoir and flow system. Both beams were coupled into 200 μm fiberoptic cables after the sample cell and thereafter input into a CCD spectrograph (Ocean Optics, S2000 UV−vis) for time-resolved spectral information (425−800 nm). Typically, 5000 excitation pulses were averaged to obtain the transient spectrum at a particular delay time. The CCD spectrograph, the delay line, and the shutters were driven by a computer-controlled system.

In-house LabVIEW (National Instruments) software allowed automatic spectral acquisition over a series of delay line settings. Kinetic traces at appropriate wavelengths were assembled from the accumulated spectral data. Sample solutions were prepared to have an absorbance of 0.8−1.1 at the excitation wavelength in the 2 mm flow cell and were used without deaeration. All measurements were conducted at room temperature, 22 ± 2 °C.

Conclusions

In ultrafast pump−probe experiments photoexcitation of BP and *p*-IBP at 267 nm ($S_0 \rightarrow S_2$) and 335 nm ($S_0 \rightarrow S_1$) in acetonitrile yielded different results in terms of the population of the S_1 state. Following the growth of the absorption of the S_1 state during 267 nm excitation, the rates of the $S_2 \rightarrow S_1$ internal conversion of these compounds have been obtained ($k_{S_2 \rightarrow S_1} \sim 1.7-1.9 \times 10^{12}$ s^{-1}). The rates of the $S_1 \rightarrow T_1$ ISC have been observed to be similar following either 267 or 335 nm excitation for both BP ($k_{ISC} \sim 1 \times 10^{11}$ s^{-1}) and *p*-IBP ($k_{ISC} \sim 2.3 \times 10^{11}$ s^{-1}). The observed data indicate that a direct $S_2 \rightarrow T_1$ type of relaxation pathway may not be available for BP or *p*-IBP in solution.

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Supporting Information Available: Transient spectra of *p*-IBP and lifetime curve fittings. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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