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Laser Flash Photolysis Studies on the Monohydroxy Derivatives of Benzophenone

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Time-resolved studies in the pico- and nanosecond time domain have been performed to characterize the triplet states of monohydroxy-substituted benzophenones, namely, *para-* (*p-*), *meta-* (*m-*), and *ortho-* (*o-*) hydroxybenzophenones (HOBP). Due to a very fast intersystem crossing (ISC) process, only the triplet states have been detected in the subnanosecond time domain. Spectral characteristics and lifetimes of the triplet states of HOBP have been seen to be extremely sensitive to the position of the OH group in the phenyl ring as well as the solvent characteristics. In case of *m*-HOBP and *p*-HOBP, the excited triplet state in non-hydrogen-bond-forming solvents has an $n\pi^*$ configuration and is capable of abstracting a hydrogen atom from another unexcited molecule to form ketyl and phenoxy type radicals. But in hydrogen-bond-forming solvents, the triplet state, which is strongly associated with the solvent molecules as a hydrogen-bonded complex, is very short-lived due to fast nonradiative relaxation via hydrogen-stretching vibrations in intermolecular hydrogen bonds with the solvents and is capable of abstracting a hydrogen atom neither from the solvent molecule nor from another unexcited HOBP molecule. In the case of *o*-HOBP, due to strong intramolecular hydrogen bonding, the internal conversion in the excited singlet state is very efficient and hence the yield of the triplet state is low ($<15\%$) and also the triplet state is very short-lived. However, in methanol and DMSO, due to disruption of the intramolecular hydrogen bond, the triplet yield is higher and also the generation of the phenolate ion via excited-state proton transfer is a significant process. Deprotonation reactions probably taking place from both the excited singlet state as well as the triplet state of the other two derivatives also have been found to be significant in polar solvents.

1. Introduction

One of the widely studied and the most important photochemical reactions undergone by aromatic carbonyl compounds is photoreduction in the presence of hydrogen atom donors.[1−5] The process occurs by a variety of mechanisms depending on the identity of the hydrogen atom donor, ranging from pure alkoxy radicallike abstraction[6,7] to one initiated by charge or electron transfer to the excited carbonyl compound from the hydrogen atom donor followed by hydrogen atom transfer[3,8−11] or by a mechanism involving the intermediate hydrogen-bonded triplet exciplex.[12,13] The nature of the lowest excited triplet state and hence the electron distribution in this state of the carbonyl compound is of decisive importance in the process of hydrogen atom transfer.[14]

The reactivity of the aromatic carbonyl compounds toward hydrogen atom abstraction reaction has long been associated with the fundamental difference between the two kinds of triplets, namely, either $n\pi^*$ or $\pi\pi^*$, and this in turn is governed by the nature and position of the substituent in the aromatic ring and also the solvent polarity.[11,14−17] It is well established that the ketones with the $\pi\pi^*$ lowest triplet state undergo aliphatic or benzylic hydrogen atom abstraction with reduced observed rate constants and reduced efficiency.[14] However, it has also been established that aromatic ketones with either $\pi\pi^*$ or $n\pi^*$ lowest triplet states can abstract phenolic hydrogen atoms at rates much faster than those for aliphatic or benzylic hydrogen atoms; e.g., abstraction of phenolic hydrogen atom by benzophenone occurs with rates 2−3 orders of magnitude faster than those for benzylic hydrogen atom abstraction and also significantly faster in nonpolar solvents than in polar solvents.[12,13]

Detailed investigations have been carried out by different groups to explain the mechanisms involved in different hydrogen abstraction reactions. It is well-known that $n\pi^*$ excitation of the carbonyl compounds produces an alkoxy radicallike excited state, in which the electron deficiency at the oxygen induces typical radical reactivity in the molecule.[6,14c,19] However, the fact that the rate constants of benzylic hydrogen atom abstraction from alkylbenzenes by the triplets of aromatic ketones are much larger than expected for simple aliphatic hydrogen abstraction via an alkoxy radical type mechanism indicates that the ketone triplets react by a different mechanism. Since the rate constants, isotope effects, and product selectivity all show good correlation with the reduction potentials of the triplet ketones, it is clear that both the $n\pi^*$ and $\pi\pi^*$ triplets react predominantly via the formation of an intermediate charge-transfer type of exciplex.[11a] Both the formation and reactions of these intermediates are sensitive to the degree of electron transfer involved in the complexation. Inspite of the fact that both the triplets share

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the same gross mechanism, product selectivity reflects different orientations for complex formation and hence different degrees of partial electron transfer within the exciplexes. The two types of triplets show similar reactivity for the more easily reduced triplets. But for the ketones harder to reduce, $\pi\pi^*$ reactivity drops to one-tenth of that of $n\pi^*$ of comparable triplet reduction potential and the overall reaction by the latter resembles more nearly the simple hydrogen abstraction by the alkoxy radical type mechanism. Hence, the fact that triplet-state reactivity of ketones with $\pi\pi^*$ lowest triplets decreases as the energy gap ΔE_T between the $\pi\pi^*$ and $n\pi^*$ triplet increases, which effect is shown by aromatic ketones with more electron donating substituents in more polar solvents, suggests that these ketones react primarily from the low equilibrium concentration of the upper $n\pi^*$ triplets, populated thermally from the lower $\pi\pi^*$ state.[15]

Leigh et al. have investigated the mechanism of phenolic hydrogen abstraction reaction by substituted benzophenone derivatives in detail.[13] They identified the hydrogen abstraction mechanism for electron acceptor substituted benzophenones as the normal mechanism for quenching of $n\pi^*$ ketone triplets by phenols in that it exhibits similar characteristics of abstraction from alkylbenzenes. However, for the donor-substituted benzophenones, a different mechanism is operative. The most likely mechanism is one in which hydrogen abstraction is initiated by partial transfer of the phenolic proton followed by electron transfer to yield the radical pair, phenoxy and ketyl, probably via the involvement of a hydrogen-bonded exciplex between the ketone triplet and phenol. This mechanism, which should be strongly dependent on the acid−base properties of the ketone triplet and phenol and the thermodynamics of electron transfer within the hydrogen bonded complex, is the dominant one for phenolic hydrogen abstraction by the lowest $\pi\pi^*$ triplet state of the ketones. In the benzophenones, it requires the involvement of the higher energy $\pi\pi^*$ triplet and, hence, it will become more important as the triplet $n\pi^*-\pi\pi^*$ energy gap is reduced by increasingly strong donor substitution and the abstraction by the normal mechanism becomes less favorable.

The lowest excited triplet state of benzophenone (BP) has been seen to have the $n\pi^*$ configuration in nonpolar, moderately polar, or not very strong hydrogen-bond-forming solvents.[20,21] However, on substitution of electron-donating groups such as $-OR$ or $-NR_2$ ($R = H$, alkyl group) onto the aromatic rings of benzophenone, the relative positions of the $n\pi^*$ and $\pi\pi^*$ states in the singlet as well as the triplet manifold are largely affected by the solvent polarity, the latter having a strong ring to carbonyl charge transfer (CT) component.[11a,14,15] In alcoholic solvents, the benzophenone triplet can abstract a hydrogen atom from the solvent molecule with a quantum yield of unity but its amino derivative, 4-aminobenzophenone, does not.[10,22] Such a difference in photoreactivity has been found to be related to the nature of the lowest triplet excited state of 4-aminobenzophenone, which is $n\pi^*$ in nonpolar solvents but $\pi\pi^*$ or CT (which has been described as a special $\pi\pi^*$ state exhibiting equivalent symmetry but differs distinctly by the electrical charge at the carbonyl group) in polar media.[10] In the CT state of 4-aminobenzophenone, a charge of about 0.8 e is transferred from the aniline moiety to the carbonyl π^* orbital, which essentially prevents any interaction with the electron cloud around an approaching hydrogen atom.[10,14a] In polar protic solvents, such as ethanol, the triplet yield has also been found to be very low for 4-aminobenzophenone as a result of quenching of the CT singlet excited state by proton transfer.[10,22]

Several attempts have been made to study the spectroscopic and photochemical properties of the *ortho*- and *para*-hydroxy derivatives of benzophenone.[14,23−27] However, little information is available on the photochemical properties of *m*-HOBP. The reported results on the photophysical properties of *para*-substituted hydroxy and methoxy derivatives have been discussed in detail in section 3 and are compared with that obtained in the present studies. Singlet states of BP itself and both the *ortho*- and *para*-hydroxy derivatives have been found to be very short-lived and undergo intersystem crossing (ISC) to the triplet manifold within a few picoseconds.[24,28] Except for the picosecond laser flash photolysis studies on *o*-HOBP by Merritt *et al.*[24a] and Hou et al.,[24b] the transient absorption studies have been made in low-temperature matrixes to make the lifetimes of the triplet state sufficiently long to study using nanosecond techniques.[23,25] To our knowledge, no other report is available regarding the detailed photophysical properties of the triplet state of these hydroxy derivatives, particularly the spectral characteristics in different kinds of media and also the true information about the quantum yield of the triplet state and lifetime. In the present work, an effort has been made to characterize the properties of the triplet state of the three monohydroxy derivatives of benzophenone in different organic solvents using pico- and nanosecond laser flash photolysis techniques.

2. Experimental Section

Hydroxy-substituted benzophenones (about 98% pure) were obtained from Aldrich (Milwaukee, WI). The *para* and *meta* derivatives were purified by recrystallization from aqueous ethanol and the ortho derivative by vacuum sublimation. All the solvents used were of spectroscopic grade. Whenever required the solvents were dried and distilled by standard methods. Iolar grade N_2 (Indian Oxygen, purity >99.9%) was used to deaerate the samples. All the experiments were carried out at room temperature (298 ± 1 K) unless specified otherwise. Steady-state absorption spectra were recorded on a Shimadzu model UV-160A spectrophotometer. Steady-state phosphorescence spectra were recorded and lifetimes were determined in ethanol and methylcyclohexane (MCH) glasses at 77 K using a Hitachi model F4010 fluorescence spectrometer equipped with a phosphorescence accessory. The picosecond laser flash photolysis set up has been described in detail elsewhere.[29] Briefly, the third (355 nm, 3 mJ) or fourth (266 nm, 1.5 mJ) harmonic output pulses (35 ps) from an active-passive mode locked Nd:YAG laser (Continuum, model 501-C-10) were used for excitation and the continuum (400−900 nm) probe pulses were generated by focusing the residual fundamental in H_2O/D_2O mixture. The probe pulses were delayed with respect to pump using 1 m long linear translational stage, and the transient absorption at different probe delays (up to 6 ns) were recorded by an optical multichannel analyzer (Spectroscopic Instruments, Munich, Germany) interfaced to an IBM-PC. The zero delay position has been assigned to that when the probe light reaches the sample just after the end of the pump pulse. Transient absorption signals above 100 ns were studied by monitoring the optical absorption using the same picosecond Nd:YAG laser for excitation and a cw tungsten lamp in combination with a Bausch & Lomb monochromator (350−800 nm), Hamamtsu R928 PMT, and 500 MHz digital oscilloscope (Tektronix, TDS-540A) connected to a PC. Pulse radiolysis experiments were carried out using 7 MeV electrons from a linear accelerator using a kinetic spectrophotometric detection system, details of which are given in ref 30.

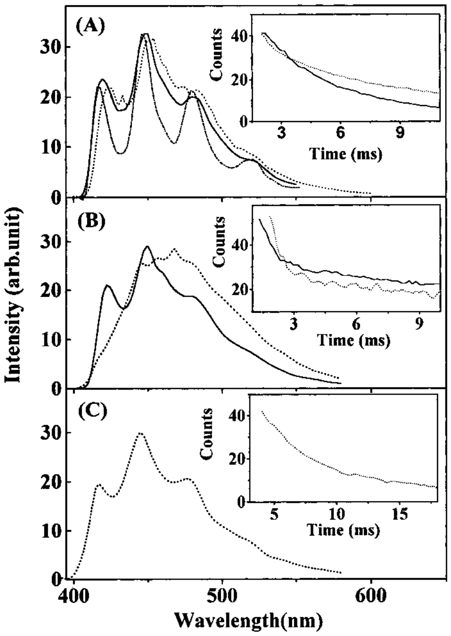


Figure 1. (A) Phosphorescence spectra of *p*-HOBP in MCH (—) and ethanol glass (···) at 77 K with the phosphorescence spectrum of BP in ethanol glass at 77 K (— .. —). Inset: Phosphorescence decay traces recorded for *p*-HOBP in MCH (—) and ethanol (···). (B) Phosphorescence spectra of *m*-HOBP in MCH (—) and ethanol glass (···). Inset: Phosphorescence decay traces recorded in MCH (—) and ethanol glass (···). (C) Phosphorescence spectrum of *o*-HOBP in ethanol glass (···) at 77 K. Inset: Phosphorescence decay trace recorded in ethanol glass (···).

3. Results and Discussion

A. Phosphorescence Study. Phosphorescence emission spectra of the three hydroxy-substituted benzophenones in methylcyclohexane (MCH) and ethanol glass at 77 K have been presented in Figure 1. Phosphorescence spectra of *m*-HOBP and *p*-HOBP in MCH and *o*-HOBP in ethanol glass are very similar to that of BP (Figure 1A) including the fine structures characteristic of the nπ* triplets, although very poorly resolved, but that of *m*-HOBP in ethanol glass is significantly different. Phosphorescence emission is too weak to allow the recording of the spectrum for *o*-HOBP in MCH glass. The spectrum of *m*-HOBP in ethanol glass is seen to be appreciably broadened to a single band so that no sharp vibrational progression characteristic of C=O stretching frequencies is evident and also the maximum is significantly red shifted (~33 nm) as compared to those of BP and the other two derivatives. A few more important features in the phosphorescence spectra of the hydroxybenzophenones can be compared with that of BP. In case of *p*-HOBP, all the peaks in the vibrational progression have been red shifted by about 4 and 8 nm in MCH and ethanol, respectively, as compared to those of BP for which they are similar in both the solvents. Also, for *p*-HOBP in ethanol, the phosphorescence emission spectrum shows two small and new emission peaks at ~433 and 475 nm at either side of the main peak at 450 nm. In the case of *m*-HOBP in ethanol the 0−0 band is considerably weakened and blue shifted as compared to that of BP. Similar types of changes in phosphorescence spectrum of BP have also been observed in ethanol−water and trifluoroethanol (TFE)−water mixtures as we observed for *p*-HOBP and *m*-HOBP, respectively, in ethanol glass.[31] The triplet energies estimated from the positions of the highest energy peak or shoulder and the phosphorescence lifetimes are given in Table 1.

TABLE 1.

compd	solvent	E_T (kcal mol^{-1})	τ_p (ms)
BP	MCH	68.4 ± 0.3	4.5 ± 0.5
	ethanol	68.9 ± 0.3	6.2 ± 0.5
o-HOBP	MCH		
	ethanol	68.9 ± 0.3	3.4 ± 0.5, 20.0 ± 1.0
m-HOBP	MCH	67.6 ± 0.3	0.6 ± 0.3, 5.7 ± 0.5
	ethanol	68.1 ± 0.5	1.7 ± 0.3, 30.0 ± 1.0
p-HOBP	MCH	67.9 ± 0.3	3.7 ± 0.5
	ethanol	67.4 ± 0.3	1.0 ± 0.2, 11.0 ± 1.0

The triplet energy level of *o*-HOBP in ethanol glass is nearly the same as that of BP in MCH or ethanol glass. But for *p*- and *m*-HOBP's, the triplet energy levels are lowered by about 1 kcal mol^{-1} in both the glasses. However, the E_T value of *m*-HOBP in ethanol glass from the energy of the highest energy shoulder is less accurate than the other values. It is now known that the nπ* triplet excitation energies of ketones are about 2 kcal mol^{-1} lower in solutions than in the rigid media.[32] However, the reactivity of the ketone triplet is not dependent on the triplet energy, E_T.

It is well established that for the nπ* lowest triplet state the phosphorescence spectrum generally exhibits a prominent vibrational progression characteristic of the C=O stretching frequency (1600−1800 cm^{-1}) and is short-lived (typically a few milliseconds).[33] On the other hand, $\pi\pi$* emission is weaker, the phosphorescence spectrum is broad or the vibrational structure is much different from that observed for a nπ* triplet state, and also the lifetimes are usually considerably longer (on the order of seconds in some cases).[34] Applying this criteria to the phosphorescence spectra, it becomes evident that the lowest triplet states of *o*- and *p*-HOBP in both MCH and ethanol glass and that of *m*-HOBP in MCH glass are mainly the nπ* type, but the lowest triplet state of *m*-HOBP in ethanol glass has $\pi\pi$* character. Table 1 shows that the phosphorescence of hydroxy derivatives in both the glasses, except that of *p*-HOBP in MCH glass, display nonexponential decay which can be analyzed as the sum of two exponential decays. The lifetimes of the shorter lived component of the two and also the monoexponential decay of *p*-HOBP in MCH glass are smaller than that of benzophenone, and the longer lived component has a longer lifetime than that of BP. All these facts indicate that although for BP in both media the lowest triplet state is nπ* and far below the next higher $\pi\pi$* state, in hydroxy-substituted benzophenones the $\pi\pi$* state comes down closer to the lowest nπ* state in polar media and in the case of *m*-HOBP, in polar media, the $\pi\pi$* state becomes the lowest triplet state. Dual components in the phosphorescence decay indicate that the two states are close and equilibrate thermally before emitting. Li and Lim suggested that the intermediate lifetimes and anomalous phosphorescence properties arise due to strong mixing of nπ* and $\pi\pi$* triplets.[35] Hamanoue and co-workers[31] also observed the dual exponentiality of the phosphorescence decay of BP in TFE−water and ethanol−water mixtures and attribute that the shorter component (3.7 ms) to the lowest triplet state of free benzophenone with normal nπ* character and the long-lived component to the lowest triplet state of a complex BP−H_2O−TFE with mixed nπ*−$\pi\pi$* character. In a similar argument, the longer component in the phosphorescence decay of the HOBP's observed in the present work can be attributed to the $\pi\pi$* triplet state which lies closer to the nπ* state.

Hence, the nature of the phosphorescence spectra and lifetimes of the hydroxy derivatives studied here clearly indicate that the lowest triplet states (T_1) of *p*- and *m*-HOBP in MCH glass and *o*- and *p*-HOBP in ethanol glass can be assigned to the nπ* configuration but that of *m*-HOBP in ethanol has the

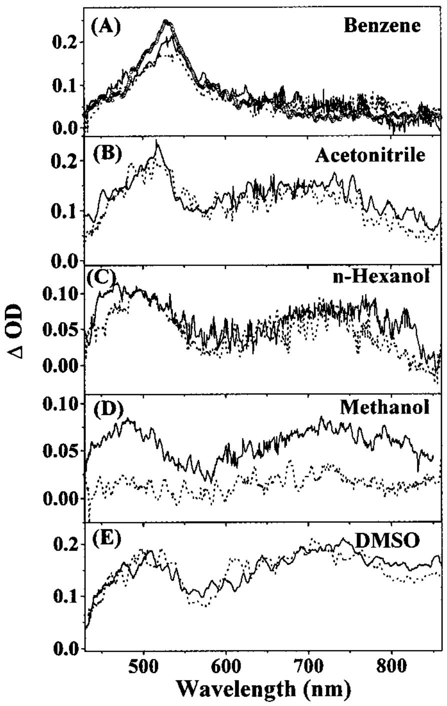


Figure 2. Transient absorption spectra of *p*-HOBP recorded immediately (—) and 5 ns (···) after the 35 ps laser pulses of 355 nm in benzene, acetonitrile, *n*-hexanol, methanol, and DMSO. The curve shown with open circles (○) in (A) represents the T−T absorption spectrum of benzophenone in benzene obtained on 355 nm excitation.

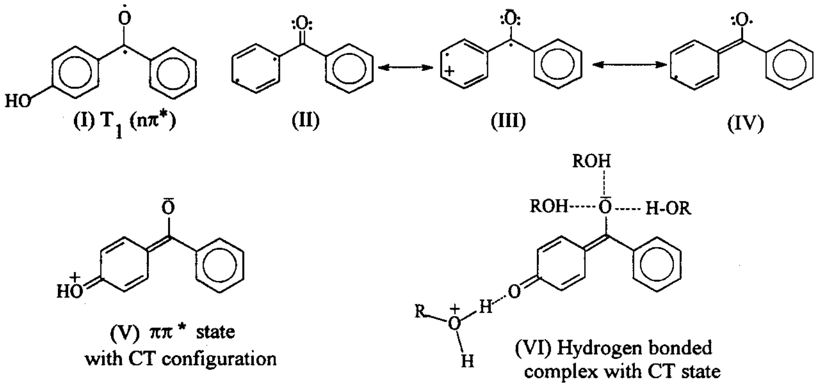
pure $\pi\pi^*$ configuration. However, in all these cases, the $n\pi^*$ and $\pi\pi^*$ states are more close to each other as compared to those in BP in similar types of media.

B. Flash Photolysis Study. *(i) p-HOBP.* Transient absorption spectra of *p*-HOBP at two delay times following excitation at 355 nm in five different solvents are shown in Figure 2. Considering a fast ISC process which occurs during the pulse, the spectra obtained immediately after the 35 ps laser pulse, i.e., at 0 ps delay, in the above solvents can be attributed to the triplet−triplet (T−T) absorption spectra of *p*-HOBP at room temperature (298 K). The triplet absorption spectrum in benzene, a nonpolar and non-hydrogen-bonding solvent, shows the only band (A) with maximum at 525 nm and shoulders at 450 and 570 nm and is very similar to that of BP in any type of solvent (for comparison the T−T absorption spectrum of BP in benzene is included in Figure 2A). However, the T−T absorption spectra of *p*-HOBP in polar and/or hydrogen-bond-forming solvents show another broad absorption band (B) in the near-IR region, centered at ca. 700 nm apart from the one (A) at ca. 500 nm. Both the bands show extreme sensitivity toward the nature of the solvent. For the spectrum recorded at 0 ps delay, the ratio of the band intensities (i.e., B to A) increases gradually as the polarity and hydrogen-bonding ability of the solvents are increased. Also the position of the peak in the case of band A shifts toward blue in more polar solvents or solvents having hydrogen-bonding abilities. The peak of the band A is at 530 nm in benzene, 520 nm in acetonitrile, 500 nm in *n*-hexanol, 475 nm in methanol, and 510 nm in dimethyl sulfoxide (DMSO). A large shift of the triplet absorption peak at 475 nm in methanol can be rationalized due to solvation of the triplet state via formation of intermolecular hydrogen bond due to both the hydrogen-bond-donating and -accepting ability of methanol. This is supported by the time-resolved study in the picosecond time domain, which shows that while the triplet state in benzene, acetonitrile, *n*-hexanol, and DMSO does not decay appreciably within 6 ns, the lifetime of the triplet state is only about 2 ns in methanol. Moreover, the triplet yield in methanol has been found to be much lower as compared to other solvents (see later). It is well-known that the $n\pi^*$ triplet states of aromatic carbonyl compounds abstract H atoms from C−H bonds of alcoholic solvents to give ketyl radicals. However, it may be noted that following the triplet decay in methanol, no spectral change that could be assigned to the formation of ketyl radical has been observed up to 6 ns delay (Figure 2C), in spite of the fact that phosphorescence study has shown that the lowest triplet state of *p*-HOBP in ethanol glass is $n\pi^*$.

Hoshino has carried out laser flash photolysis of *p*-HOBP in ethanol solutions in the temperature range 77−300 K.[23] He observed that the T−T absorption spectrum has maxima at ca. 510 and 720 nm at 77 K. The spectrum recorded at 120 K showed peaks at ca. 480 and 740 nm, but at higher temperatures the near-IR band (B) disappears and the near-UV band (A) is further blue shifted. The spectrum reported by him at 77 K resembles very well that obtained by us in acetonitrile, and the spectrum obtained at 120 K, that in methanol obtained immediately after the laser pulse. According to Hoshino, the 740 nm band in the triplet absorption spectrum of *p*-HOBP in ethanol results from a red shift of the absorption shoulder at 570 nm, present in the spectrum of *p*-HOBP and BP in benzene, by the electron-donating ability of the substituent group of OH as well as the hydrogen bonding with the solvent molecules. However, Leigh et al. have also observed the presence of the band (B) in the T−T absorption spectra of 4-alkoxybenzophenone derivatives in acetonitrile.[13] The presence of the band B in the triplet absorption spectrum of *p*-HOBP in acetonitrile solution too, indicates that the band (B) is definitely characteristic of the benzophenones substituted with electron-donating groups, such as −OH or −OR shown in polar solvents, not necessarily to be due to formation of the hydrogen-bonded complex in hydrogen-bond-forming solvents as predicted by Hoshino.[23]

It is already mentioned that the lowest triplet state (T_1) of BP normally is $n\pi^*$, but in HOBP's the energy spacing between the $T_1(n\pi^*)$ (structure I of Chart 1) and the next higher triplet state T_2 ($\pi\pi^*$) is reduced and they come closer to each other. Among the two, which one should be the lower depends on the nature of the solvent. However, Wagner et al. observed that the natures of the $^3\pi\pi^*$ states of benzophenone and substituted benzophenones are not altogether clear.[15a] They explained the reduced reactivity of the $\pi\pi^*$ triplets on the basis of the orbital correlation diagram that mainly the three resonance forms which have the valence bond representations as shown in Chart 1 (structures II−IV) contribute to the $^3\pi\pi^*$ state. Among them, the resonance forms II and III are predominant in unsubstituted benzophenones, but a para substitution with an electron-donating group (such as NR_2 or OR) can stabilize the charge-transfer (CT) form (III), attesting to its predominance.[15a] It is this kind of charge-transfer state which was probably suggested by Porter and Suppan[14] as the lowest triplet state (T_1) in the case of *p*-aminobenzophenone in alcoholic solvents. They predicted about 0.8 e charge transferred from the substituent to the carbonyl group although no quantitative evidence has been presented.[14a] However, although OH is not a strong enough donor compared to NH_2, an unsymmetrical charge distribution in the $\pi\pi^*$ state is very much expected so as to have a major contribution of the CT form III, which can be represented by structure V for *p*-HOBP. This kind of triplet state is expected to be further stabilized in polar and hydrogen-bond-forming solvents due to solvation and/or formation of a hydrogen-bonded complex (structure VI).[23] Hence, it is possible that, in aceto-

CHART 1



nitrile, the near-IR band (B) arises due to the existence of the CT state in equilibrium with the $T_1(n\pi^*)$ state, which is still the lowest triplet state. This CT state may be further stabilized in hydrogen-bond-forming solvents, e.g., methanol and DMSO, by the formation of a hydrogen-bonded complex so that it now becomes the lowest energy triplet state going below the $n\pi^*$ state. The spectral shift observed at higher temperatures in the transient absorption studies has been interpreted by Hoshino due to reorientation of the solvent molecules attached to the hydroxy group of *p*-HOBP in the excited triplet state of the hydrogen-bonded complex. The distance and mutual orientation between the OH group in *p*-HOBP and the solvent molecules are different between the ground and excited triplet state of the hydrogen-bonded complex. However, we have not observed any spectral changes at different delay times in polar and protic solvents used, which could be correlated with the change over from $n\pi^*$ configuration to $\pi\pi^*$ or CT configuration due to orientation of solvent molecules as was suggested by Hoshino.[23]

At room temperature, the reorientation time of the solvent molecules being very fast (probably a few picoseconds for methanol),[36] we observe the $\pi\pi^*$ state with CT configuration, which is already resolvated or with reoriented hydrogen-bonded solvent molecules in equilibrium with $n\pi^*$ state which is energetically very close to the former, immediately after the 35 ps laser pulse. Reorientation of the solvent molecules being very slow in rigid medium, we observed the $n\pi^*$ state as the lowest triplet in the phosphorescence study. Following these arguments, we assign the triplet states observed by us in benzene purely to a $n\pi^*$ configuration and in acetonitrile an equilibrium concentration of $n\pi^*$ and $\pi\pi^*$ triplets. In these solvents, the $n\pi^*$ triplet is relatively longer lived, retaining its character and reactivity toward hydrogen abstraction reaction which has been studied in the nanosecond time domain (discussed later). However, in methanol, having both hydrogen-bond-donating and -accepting ability, the triplet lifetime is very short, about 2 ns. In hexanol, having lower hydrogen-bond-donating ability than that of methanol, and in DMSO, a hydrogen bond acceptor, the triplet lifetimes are a few tens of nanoseconds, which we could not determine accurately due to limitations of our spectrometer. In hydrogen-bond-forming solvents the lowest triplet state (T_1) is probably of $\pi\pi^*$ origin with a major contribution from the CT configuration (structure VI), and the short lifetimes of the triplet in these solvents can be understood in terms of very fast nonradiative relaxation processes via intermolecular hydrogen-bond-stretching vibrations.[37]

Figure 3 shows the transient absorption spectra of *p*-HOBP (8×10^{-4} mol dm^{-3}) obtained on excitation at 355 nm in N_2-saturated acetonitrile solution in 350−750 nm spectral region in the nano- and microsecond time domain. The transient absorption spectrum recorded at 500 ns (curve A in Figure 3), having the bands at 525 nm and ca. 680 nm, could be assigned to the T−T absorption spectrum of *p*-HOBP due to its close resemblance with that obtained in the picosecond time domain (see Figure 2B). However it is important to note that the ratio of the absorbance at 520 nm to that at 680 nm recorded at 500 ns has been seen to be higher than that seen in the spectrum recorded immediately after the picosecond laser pulse (Figure 2B). This may be due to the presence of ketyl radical of *p*-HOBP (*p*-HOBPH$^\bullet$) which has already been formed and has absorbance maxima at 560 nm with a shoulder at 520 nm. However, the spectrum recorded at 9 μs shows the presence of the ketyl radical only which could be identified owing to its close similarity to the spectrum reported by Shida[38] in low-temperature glasses and also to the one obtained by us in a pulse radiolysis study.[39a] The decay kinetics of the transient species have been carefully analyzed at three different wavelengths, ca. 680, 560, and 410 nm. The decay of the transient absorbance monitored at 680 nm, where only the triplet state absorbs, fits to a clean single-exponential decay. However, the rate of decay of the triplet is seen to be dependent on the concentration of *p*-HOBP in solution. The inset of Figure 3 shows the dependence of the decay rate of the triplet as a function of the concentration of *p*-HOBP varying in the range 5×10^{-4} to 3×10^{-3} mol dm^{-3}. The transient spectra obtained at 500 ns at the highest *p*-HOBP concentration of 6×10^{-3} mol dm^{-3}

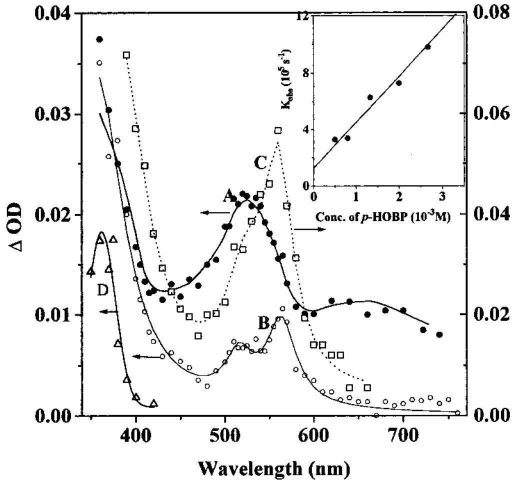
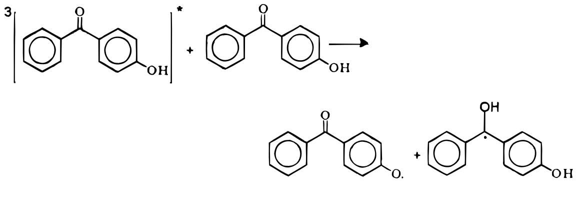


Figure 3. Time-resolved transient absorption spectra of *p*-HOBP (8×10^{-4} mol dm^{-3}) obtained in deaerated acetonitrile solution on excitation at 355 nm, at 0.5 μs (A) and 9 μs (B). (C) represents the transient spectrum recorded at 0.5 μs in a deaerated acetonitrile solution of 6×10^{-3} mol dm^{-3} *p*-HOBP. (D) is the transient absorption spectrum of *p*-HOBP obtained in deaerated methanol solution. Inset: Plot of decay rate of the triplet (k_{obs}) vs [*p*-HOBP] obtained at 680 nm.

indicates the presence of the ketyl radical only (curve C in Figure 3). It is well-known that acetonitrile is a poor hydrogen atom donor and the rate constant for the hydrogen atom abstraction reaction of benzophenone triplet with this solvent molecule is of the order of 130 dm^3 mol^{-1} s^{-1}.[40] Hence, the possibility of abstraction of a hydrogen atom from solvent acetonitrile by the triplet *p*-HOBP can be excluded at the time scale of observation. So, it is concluded that the ketyl radical is formed due to an intermolecular hydrogen atom abstraction reaction between the excited triplet and a ground state *p*-HOBP molecule (reaction 1). Das et al. and Leigh et al. have already reported the abstraction of phenolic hydrogen atoms by the triplet states, both nπ* and $\pi\pi$* types, of the ketones.[12,13] Hence it is not surprising to observe that the triplet state of *p*-HOBP can abstract a hydrogen atom from the OH group of another *p*-HOBP molecule in the ground state.



(1)

·OBP HOBPH·

Such an intermolecular hydrogen atom transfer reaction might be favored by excitation of the intermolecularly hydrogen-bonded complex as formed in the ground state. Dimeric or higher aggregated forms of HOBP could arise by intermolecular bonding between the carbonyl group of one molecule and the phenolic group of another molecule. However, the ground-state absorption spectra obtained at different concentrations up to 4 × 10^{-3} mol dm^{-3} do not show any spectral change which could be attributed to the hydrogen-bonded complex. Merill too has found from NMR measurements that in CCl_4, a non-hydrogen-bonding solvent, there is no intermolecular hydrogen bonding in *p*-HOBP up to the concentration of 10^{-2} mol dm^{-3}.[41] This fact has been corroborated by Beckett and Porter by the molecular weight determination and verification of Beer's law.[22a] Hence, it is reasonable to accept the mechanism for phenolic hydrogen atom abstraction as suggested by Leigh et al. involving the intermediate hydrogen-bonded triplet exciplex, which yields the corresponding radicals by sequential electron and proton transfer.[13]

As stated above, the decay traces obtained at 680 nm were found to follow good first-order kinetics which depend on the concentration of *p*-HOBP. The inset of Figure 3 shows the plot of k_{obs} vs concentration of *p*-HOBP. From the slope of the least-squares fit, the second-order rate constant for hydrogen atom abstraction reaction by the triplet of *p*-HOBP has been evaluated to be 3 × 10^8 dm^3 mol^{-1} s^{-1}, which is much slower than the diffusion-controlled rate in this solvent. This rate constant for phenolic hydrogen atom abstraction by *p*-HOBP is about 1 order of magnitude slower than those reported by Das *et al.*[12] and Leigh *et al.*,[13] who measured the same for benzophenone, methoxybenzophenone, and also other various substituted ketones and phenols.

The intrinsic lifetime of the triplet state which should be independent of the concentration of *p*-HOBP is also calculated by extrapolation of the least-squares fit line to the zero concentration of *p*-HOBP and was evaluated to be 8 μs. To corroborate these facts we have also carried out the flash photolysis of *p*-HOBP in acetonitrile using 266 nm excitation for which it was possible to use a very low concentration of *p*-HOBP because of higher extinction coefficient (1.3 × 10^4 dm^3 mol^{-1} cm^{-1}) of the ground-state absorption at 266 nm compared to that at 355 nm (2 × 10^2 dm^3 mol^{-1} cm^{-1}), thus reducing the possibility of interaction of the triplet state with another unexcited parent molecule. Figure 4 shows the time-resolved absorption spectra obtained in a N_2-saturated acetonitrile solution of *p*-HOBP (3 × 10^{-5} mol dm^{-3}) at 1 and 30 μs after the excitation pulse, which clearly show the triplet state as the only transient, and formation of the ketyl radical was not observed at a later time. The decay of the triplet state recorded at 525 nm is seen to follow a clean first-order kinetics (inset of Figure 4) with a rate constant of 1.2 × 10^5 s^{-1} (τ = 8.3 μs), which is in excellent agreement with the value obtained by extrapolation to zero concentration in flash photolysis experiments using 355 nm excitation. This lifetime of 8 μs in acetonitrile can be compared only with the reported value of 12 μs in deaerated benzene solution reported by Favaro.[42] This value is shorter than that of BP (14 μs in acetonitrile[43]) but much higher than that of *p*-methoxybenzophenone in cyclopentane.[7b]

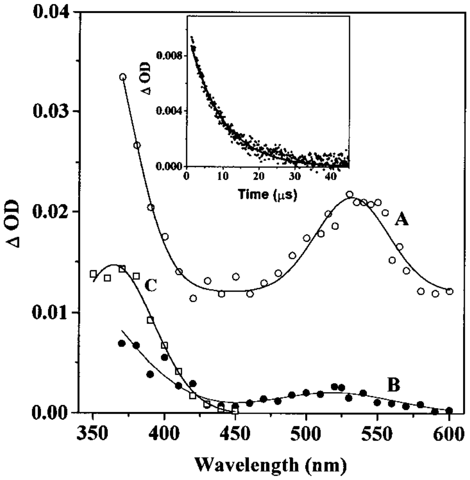


Figure 4. Time-resolved absorption spectrum of *p*-HOBP (3 × 10^{-5} mol dm^{-3}) obtained in deaerated acetonitrile solution on 266 nm excitation, at 1 μs (A) and 30 μs (B). (C) is the transient spectrum of *p*-HOBP obtained on excitation at 266 nm in deaerated methanol solution. Inset: Plot of Δ(OD) vs time recorded in the above acetonitrile solution at 525 nm.

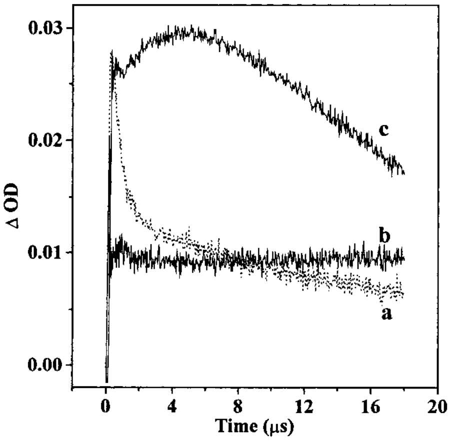


Figure 5. Kinetic traces recorded in deaerated acetonitrile solution of *p*-HOBP on excitation at 355 nm (a) at 530 nm ([*p*-HOBP] = 4 × 10^{-3} mol dm^{-3}) and (b, c) at 410 nm, with [*p*-HOBP] = 8 × 10^{-4} and 4 × 10^{-3} mol dm^{-3}, respectively.

The decay trace at 530 nm (Figure 5a) shows the presence of two components—the faster component, which follows first-

TABLE 2.

compd	solvent (E_T^N)	triplet lifetime τ	ϕ_T[a]	ϕ_D(deprotonation)[a] [β]	$k_{(OBP^- + H^+)}$ (dm^3 mol^{-1} s^{-1})	$2k_{HOBPH}$ (dm^3 mol^{-1} s^{-1})[h]
p-HOBP	benzene (0.111)	*b*	0.71	0.0 [0.10]		$(5.5 \pm 0.3) \times 10^9$
	acetonitrile (0.46)	8 ± 0.05 μs	0.59	0.10 [0.31]	*e*	$(3.8 \pm 0.2) \times 10^9$
	hexanol (0.559)	*c*	0.46	0.04	*e*	*f*
	methanol (0.762)	2 ± 0.2 ns	0.20	0.30 [0.62]	$(1.0 \pm 0.1) \times 10^9$	*f*
	DMSO (0.444)	*c*	0.40	0.30 [0.76]	$(7.3 \pm 0.5) \times 10^8$	*f*
m-HOBP	benzene	*b*	0.67	0.0		$(2.6 \pm 0.2) \times 10^9$
	acetonitrile	*b*	0.54	0.20	$(9.5 \pm 0.9) \times 10^8$	$(7.84 \pm 0.4) \times 10^9$
	hexanol	2.3 ± 0.2 ns[d]	0.45	0.05	*e*	*f*
	methanol	3.1 ± 0.2 ns[d]	0.30	0.20	$(9.2 \pm 0.8) \times 10^8$	*f*
	DMSO	2.0 ± 0.5 ns, 4 ± 0.05 μs	0.55	0.35	$(2.5 \pm 0.2) \times 10^8$	*f*
o-HOBP	benzene	0.5 ± 0.15 ns	0.12	0.0		*f*
	hexane (0.009)	0.2 ± 0.1 ns	0.10	0.0 [0.0]		*f*
	acetonitrile	0.5 ± 0.2 ns	0.05	0.0		*f*
	methanol	1.5 ± 0.2 ns	0.07	0.12	*e*	*f*
	DMSO	2.5 ± 0.2 ns	0.15	0.30	$(3.4 \pm 0.3) \times 10^8$	*f*

[a] Error limits in the determination of numerical values are about 10−15%. However, in polar and hydrogen-bond-forming solvents, due to the presence of more than one kind of triplet species, the value can be taken as the lower limit of its real value. [b] Lifetimes could not be determined due to overlapping absorptions of the triplet and the ketyl radical. [c] Lifetimes are a few tens of a nanosecond which we could not determine due to the limitations of our spectrometer. [d] There were two components of the decay. Due to weak absorption of the longer lived species, its lifetime could not be determined. [e] The value could not be estimated due to a weak signal level. [f] Ketyl radicals were not observed in these solvents. [h] Calculated by using the extinction coefficient values of ketyl radicals obtained from pulse radiolysis work in aqueous solution.[39]

order kinetics, could be attributed to the triplet decay, whereas the slower one, which follows the second-order kinetics, is assigned to the decay of ketyl radical. The $2k/\epsilon_{R^\cdot}$ value (where $2k$ is the second-order decay rate constant and $\epsilon_{R^\cdot}$ the extinction coefficient for ketyl radical at 530 nm) has been determined to be 1.1×10^6 cm s^{-1}. To determine the value of $\epsilon_{R^\cdot}$, ketyl radicals were generated in pulse radiolysis of aqueous solution of HOBP through electron reaction and subsequent protonation of the anion produced (reaction 2).[39b] In a solution buffered at

$$\mathrm{HOBP} + e_{aq}^{-} \rightarrow \mathrm{HOBP}^{\bullet-} \xrightarrow{H^+} \mathrm{HOBPH}^{\bullet-} \qquad (2)$$

pH = 5, the formation of ketyl radical is quantitative, and from the known value of dose per pulse, the $\epsilon_{R^\bullet}$ value for the ketyl radical was evaluated to be 3.4×10^3 dm^3 mol^{-1} cm^{-1}. This value is in good comparison with that reported for benzophenone ketyl radicals.[44] Assuming these values do not change appreciably in other solvents, the decay rate constants ($2k$) for the ketyl radical could be calculated and are given in Table 2.

If the optical density at the λ_{max} of the spectral absorption of the triplet produced in solutions of the hydroxy derivatives are compared with that of BP in acetonitrile (for which the triplet quantum yield $\phi^s{}_T = 1$ and extinction coefficient for the triplet $\epsilon^s{}_T = 6800 \pm 500$ dm^3 mol^{-1} cm^{-1} at 525 nm[12,43]) recorded immediately after the 355 nm excitation pulse, the $\phi_T\epsilon_T$ (ϕ_T, the quantum yield value of the triplet formation for the hydroxy derivatives; ϵ_T, the extinction coefficient for T−T absorption) values were determined according to eq I.[43]

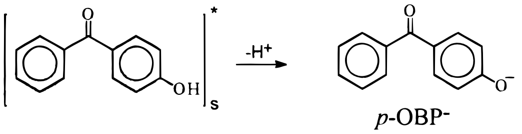
$$\frac{\phi_T}{\phi^S{}_T} = \frac{C_T}{C^S{}_T} = \frac{OD_T/\epsilon_T}{OD^S{}_T/\epsilon^S{}_T} \qquad (I)$$

$$\phi_T = \left(\frac{OD_T}{OD^S{}_T}\right)(\phi^S{}_T\epsilon^S{}_T)/\epsilon_T$$

For quantitative estimation of ϕ_T, we need to determine the value of ϵ_T for the triplet absorption at λ_{max}. But due to strong reactivity of the triplet toward its own ground-state molecules and unavailability of any suitable triplet energy acceptor/donor for them, it has not been possible to evaluate the ϵ_T values up to a satisfactory accuracy (using either the flash photolysis or the pulse radiolysis technique). In the absence of these data, we assumed that ϵ_T values in different solvents are same as, i.e., 6800 ± 500 dm^3 mol^{-1} cm^{-1}, at the λ_{max} of the band (A) of the corresponding T−T absorption spectra. ϕ_T values thus evaluated are given in Table 2. However, this assumption is much too approximate because the nature of the triplet state differs in different solvents with respect to electron distribution and the solvation state of it and, hence, it is expected that the error limits in our reported values of triplet quantum yields are rather high (10−15%). In polar and hydrogen-bonding solvents, the ϕ_T values can be taken only as the lower limit of the real values. Porter and Suppan[14b] have predicted a very high quantum yield of *p*-HOBP in cyclohexane as inferred from its quantum yield (0.9), and Favaro[42] reported the ϕ_T value of ~0.87 from sensitized phosphorescence measurements in benzene at 77 K. Our value of 0.71 is much lower than both the reported values. However, with the yield of ketyl radicals ($\phi_{R^\bullet}$) on flash photolysis of these compounds in benzene and acetonitrile being dependent on the concentration of the *p*-HOBP and also on laser intensity (i.e. concentration of the triplet initially produced), no meaningful quantitative values for these could be provided.

The transient decays monitored at 410 nm for different concentrations of *p*-HOBP have been found to follow a complicated kinetics. At low concentration of *p*-HOBP, the transient absorption attains an equilibrium value which does not decay up to several milliseconds. But at higher concentration of *p*-HOBP, the transient absorption shows a initial decay component followed by a growth up to 9 μs. Beyond 9 μs the transient is seen to follow mixed-order kinetics. Such complicated kinetics arises due to the presence of three different species, namely, the triplet, ketyl radical (HOBPH$^\bullet$) and phenoxy radical ($^\bullet$OBP) (reaction 1), all of which absorb in this spectral region.[45] In the absence of further information it is difficult to extract quantitative information about the decay behavior of the transient species at this wavelength. We hope to have better understanding from time-resolved ESR experiments planned by us.

Although our picosecond laser flash photolysis study on *p*-HOBP in methanol reveals that no transient species absorbing in the spectral region 400−900 nm survives beyond 6 ns, the detection technique in the nanosecond time domain detects a transient species absorbing in the region 350−400 nm region having a peak at 365 nm on excitation at both 355 and 266 nm (Figures 3D and 4C). Hoshino et al. have attributed this transient absorption band observed in ethanol solution due to the anion of *p*-HOBP (*p*-OBP$^-$), resulting from the photoinduced deprotonation of *p*-HOBP from the excited singlet state (reaction 3).[14b,27] Study of the pK_a of reaction 3 in the excited singlet



(3)

and triplet states showed that deprotonation must occur very efficiently in the CT states and pK_a's of the excited singlet and triplet states are < -2.[14b,46] Porter et al. predicted that although the CT singlet state lies at much higher energy than the nπ^* singlet state in nonpolar solvents, the CT singlet gets stabilized in polar solvent over the nπ^* singlet states to come closer to the latter and facilitates the deprotonation reaction for the singlet state. The deprotonation reaction should be feasible from the triplet state too. But it is not possible to indicate quantitatively the extent of deprotonation reaction taking place from each of the two states because reaction 3 should be faster than any diffusion-controlled reactions.[36] However, it should be appreciated that predominance of the deprotonation reaction in hydrogen-bond-forming solvents is responsible for the short lifetime and lack of reactivity of the triplet state of *p*-HOBP.

The molar extinction coefficient values of OBP$^-$, which is a stable species in alkaline solutions of the polar nonaqueous solvents, were determined spectrophotometrically from the known concentration of *p*-HOBP in solutions. Using these extinction coefficient values of OBP$^-$, the excited-state deprotonation yields were obtained by comparing the optical densities with that of benzophenone triplet as given in eq I and presented in Table 2. The decay of OBP$^-$ was found to follow pseudo-first-order rates which were dependent on the concentration of acid added to the solutions. The dependence of the decay rate of OBP$^-$ on acid concentration indicates that the decay of OBP$^-$ is due to back-protonation reaction generating back the HOBP. The bimolecular rate constants for back-protonation reaction determined from the slope of the linear plots of the pseudo-first-order rate constants vs the concentration of the acid have been presented in Table 2.

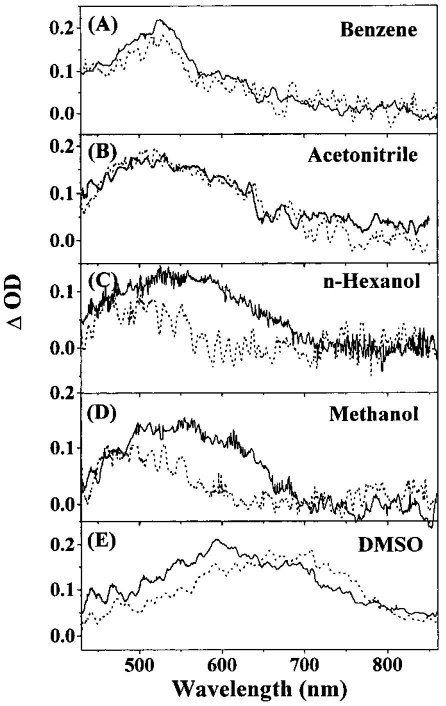


Figure 6. Transient absorption spectra of *m*-HOBP recorded immediately (—) and 5 ns (···) after the 35 ps laser pulses of 355 nm in benzene, acetonitrile, *n*-hexanol, methanol, and DMSO.

(ii) m-HOBP. Figure 6 shows the transient absorption spectra of *m*-hydroxybenzophenone (*m*-HOBP) in different organic solvents at two delay times following excitation at 355 nm. Following the arguments presented above, the spectra obtained at 0 ps can be attributed to the T−T absorption of *m*-HOBP in these solvents. The triplet absorption spectrum of *m*-HOBP in benzene can be compared to that of BP and *p*-HOBP (shown in Figure 2A); the spectrum shows a peak at 525 nm, but shoulders at 500 and 600 nm are more prominent. In other solvents the spectral characteristics are seen to be quite different from those of both BP and *p*-HOBP in many respects. First, the intensity of the 600 nm shoulder, shown in the spectrum in benzene, increases gradually from acetonitrile to methanol and DMSO. In DMSO the absorption spectrum becomes very broad spreading the wavelength region of 500−700 nm with the disappearance of the peak at 525 nm. Except in DMSO, the broad absorption band in the 550−850 nm wavelength region as seen in the case of *p*-HOBP in polar solvents (Figure 2) is not present in the case of *m*-HOBP. Also the lifetimes of the triplet are seen to be differently affected by the nature of the solvent. While the triplet of *m*-HOBP in benzene or acetonitrile does not decay at all within 6 ns, the triplet spectra in *n*-hexanol, methanol, and DMSO show different kinetics at different wavelength regions on the same time scale. In *n*-hexanol and methanol the absorbance at 600 nm shoulder shows a faster decay with a net effect of shifting the absorption peak to 480 nm at 6 ns after the laser pulse. Whereas in DMSO, the absorbance at 500 nm decays faster than that at 600 nm and, hence, the absorption spectrum develops a new peak at 700 nm at 6 ns after the laser pulse. Due to very low optical densities of the transients produced in *n*-hexanol and methanol, only approximate estimates of the lifetimes of the shorter lived species have been made by monitoring the decay of the transient absorption at 600 nm, and the values are given in Table 2. In DMSO the lifetime of the shorter lived transient could be estimated to be about 2 ns by monitoring the absorbance decay in the 550 nm region. Whereas for the longer lived transient having peak maxima at ca. 700 nm, the lifetime was determined to be 4 μs. In spite of the longer lifetime of the triplet in DMSO, the formation of the ketyl radical has not been observed. The quantum yields of the triplet state of *m*-HOBP in different solvents have been determined by following the same method as adopted for *p*-HOBP and are given in Table 2.

The absence of the near-IR band (B) in *m*-HOBP can probably be understood from the fact that the CT configurations which could not be presented in this case in terms of molecular orbital description of valence bond structures similar to those of *p*- and *o*-HOBP's (structure II) do not contribute to the electron distribution of the $\pi\pi^*$ state. Although due to the very low quantum yields of the triplet it has not been possible to identify the different transient species produced on flash photolysis of *m*-HOBP, different spectroscopic and dynamical characteristics of the triplet species in hydrogen-bond-donating and -accepting solvents indicate that, in hydrogen-bond-forming solvents, probably, more than one type of triplet state which differ in hydrogen-bonded structures with the solvents exist in solution. However, in the present contribution we have not been able to provide the details of these species.

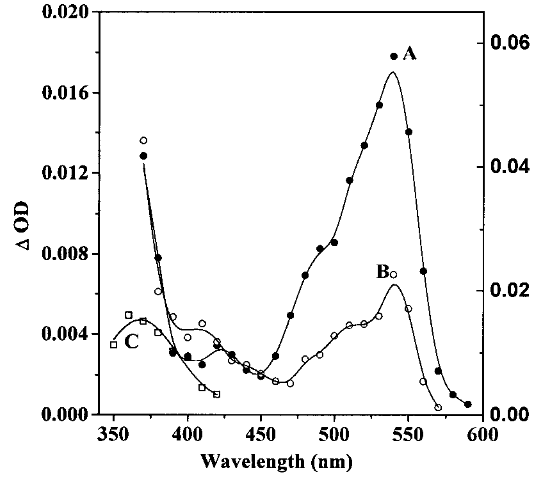


Figure 7. Time-resolved transient absorption spectra of *m*-HOBP (1.7 × 10^{-3} mol dm^{-3}) obtained in deaerated acetonitrile solution on 355 nm excitation at 1 μs (A) and 20 μs (B) after the laser pulse. (C) is the transient spectrum of *m*-HOBP obtained on excitation at 355 nm in deaerated methanol solution

The transient absorption spectra obtained in deaerated acetonitrile solution of *m*-HOBP (1.7 × 10^{-3} mol dm^{-3}) on 355 nm excitation at 1 and 20 μs after the laser pulse are shown in the Figure 7. The spectrum obtained at 1 μs is different from the T−T absorption spectrum of *m*-HOBP (Figure 6B) and displays a broad absorption band with a peak at ca. 540 nm (Figure 7A). This spectrum can be assigned to the ketyl radical of *m*-HOBP due to its similarities to the spectrum obtained in our pulse radiolysis experiments.[39] The decay of the species was also found to follow a clean second-order kinetics, and the decay rate is given in Table 2. Similar observation was made in benzene solution too. Both in benzene and acetonitrile, it has not been possible to distinguish the triplet absorption from that of ketyl radical even by best optimization of the experimental conditions, e.g. using minimum possible ground-state concentration of *m*-HOBP, excitation energy, and also either of the excitation wavelengths, i.e., 266 and 355 nm, due to strong reactivity of the triplet toward its ground state via the hydrogen atom abstraction process. Hence, no meaningful values of the triplet lifetimes could be given and also the rate of hydrogen abstraction reaction could not be estimated. In the other three solvents, no ketyl radical absorption was observed. However, in all the polar solvents, the transient species showed an absorbption band below 400 nm (Figure 7C) and could be attributed to the anion spectrum of *m*-HOBP (*m*-OBP$^-$) resulting from excited-state deprotonation. The deprotonation yields were determined in all the solvents studied here and are given in Table 2.

(iii) o-HOBP. Figure 8 represents the transient absorption spectra obtained on laser flash photolysis of *o*-HOBP in different solvents. The spectrum obtained immediately after the 35 ps laser pulse definitely could be assigned to the triplet state of *o*-HOBP since the lifetime of the singlet state has been reported to be less than 10 ps in non-hydrogen-bond-forming solvent such as hexane[24a] and around 30 ps in ethanol.[24b] In benzene, hexane, and acetonitrile the triplet absorption band is very narrow and has a maximum at ca. 490 nm with a very weak shoulder at ca. 550 nm. The transient absorption spectrum in methanol, obtained immediately after the laser pulse, has one intense band with a maximum at 470 nm and a very low intensity band in the near-IR wavelength region, 600−850 nm. In DMSO, the low-intensity band in this wavelength region has been more prominent, almost equivalent to that in the near-UV, which too has been red shifted to 520 nm. This near-IR band can be compared to that observed in *p*-HOBP and assigned to the CT state. However, apparently the near-IR band decays faster than the one in the near-UV, and a new transient spectrum which has maximum at ca. 475 nm is evident at 6 ns after the laser pulse. In other polar solvents too, a very weakly absorbing species with absorption maxima at ca. 450 nm was observed. This species was assigned to the phenolate ion of *o*-HOBP generated via excited-state proton transfer.[24c]

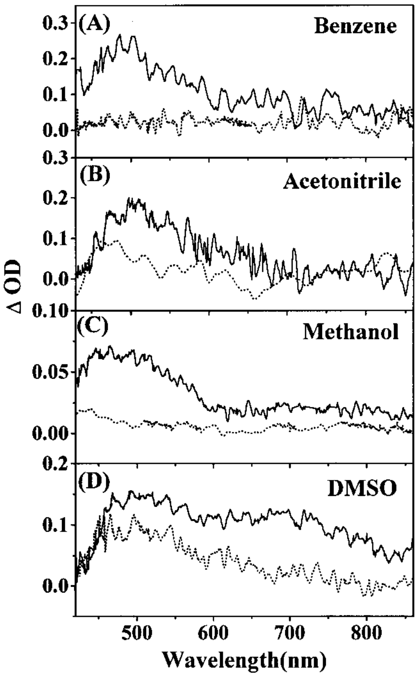


Figure 8. Transient absorption spectra of *o*-HOBP recorded on excitation at 355 nm in various solvents: benzene, 0 ps (—) and 1.5 ns (···); acetonitrile, 0 ps (—) and 0.9 ns (···); methanol, 0 ps (—) and 3.5 ns (···); DMSO, 0 ps (—) and 5 ns (···) after the laser pulse.

The quantum yield values of the triplet state have been determined using the assumptions described earlier and have been presented in Table 2. The quantum yield values have been seen to be low as compared to those of the other two derivatives. The lower quantum yields in nonpolar and non-hydrogen-bond-forming solvents can be rationalized due to very efficient nonradiative relaxation (by internal conversion) process from the excited singlet state (S_1) via hydrogen-stretching vibrations in strong intramolecular hydrogen bonding.[24,37] In hydrogen-bond-forming solvents, methanol and DMSO, due to the possibilities of formation of intermolecular hydrogen bonds between *o*-HOBP and the solvents, which act either as a hydrogen-bond acceptor (e.g. DMSO) or as both a donor and an acceptor (e.g. methanol), the strength of the intramolecular hydrogen bond is weakened or disrupted and the efficiency of the nonradiative relaxation process in the S_1 state is expected to be reduced.[47,48] Hence, the higher triplet yield is expected in these solvents. But the strong association of the solvent molecules with the CT state via the formation of a hydrogen-bonded complex also provides another efficient channel for radiationless deactivation process. Our ϕ_T value (0.07) in methanol is lower than that (0.15) reported by Lamola and Sharp.[24d] But our estimated ϕ_T values in benzene and hexane (0.12 and 0.10, respectively) are higher than the one reported by them. Apparently, it is very surprising to observe the triplet absorption spectra in benzene and hexane, in spite of the fact that phosphorescence emission was very weak in MCH glass. To confirm that the transient absorption has not arisen due to the presence of some hydrogen-bonding species as impurities in the solvent, solvents were carefully dried and distilled. Even then the absorption was observed due to the triplet species. Hou et al.[24b] did not observe any transient absorption in hexane using 532 nm as the monitoring wavelength, probably because the λ_{max} of the triplet absorption of *o*-HOBP is blue shifted to 490 nm. On the other hand, Merritt et al.[24a] observed very weak transient absorption spectrum similar to those presented by us in Figure 8. But the delay at which they recorded the spectrum is too long for the survival of the triplet with a lifetime of less than 0.5 ns. Also Lamola and Sharp estimated the ϕ_T value of ~0.03 in cyclohexane using the method of sensitized dimmerization of isoprene, which is limited by the diffusion-controlled rate competing with the very fast relaxation of *o*-HOBP in hexane ($\tau = 0.2$ ns). Hence the reported values of ϕ_T and spectral information about *o*-HOBP in nonpolar solvents should be more reliable because they have been observed and measured in real time. The ϕ_T values reported for other similar intramolecularly hydrogen-bonded molecules, e.g., 1,4-dihydroxyanthraquinone and 1-hydroxy- and 1,4-dihydroxynaphthoquinone, for which no phosphorescence emissions have been detected, are comparable or higher.[49] Hence, it is not surprising to observe the ϕ_T value of ~0.1 in nonpolar non-hydrogen-bonding solvents in spite of strong intramolecular hydrogen bonding.

The triplet lifetimes determined by us have also been reported in Table 2. However, due to low quantum yields of the triplet, the errors involved in this parameter are relatively higher. The lifetime of 1.5 ns in methanol determined by us agrees well with the value reported by Hou et al.[24b] in ethanol. The deprotonation channel has been observed in methanol and DMSO solvents, and the deprotonation yields determined are given in Table 2.

In conclusion, the photophysical properties of the triplet states of the hydroxy-substituted benzophenones have been seen to be markedly different from that of benzophenone and similiarly substituted methoxybenzophenone and also very sensitive to solvent characteristics. Unlike the latter, the intersystem crossing efficiencies for these hydroxy-substituted derivatives are less than unity in all the solvents studied. Table 2 shows that ϕ_T values have good correlation with the solvent parameter E_T^N, which is indicative of the dipolarity or polarizability and the hydrogen-bonding ability of the solvents.[50] The ϕ_T values show a decreasing trend in the solvents having higher E_TN values. In polar and hydrogen-bond-forming solvents, the triplet yields are very low due to the presence of the deprotonation reaction taking place from the singlet CT state, which, for these hydroxy derivatives, is stabilized in these solvents in both the singlet and triplet manifolds of states. Deprotonation is possible from the triplet CT state too. Table 2 shows that deprotonation yield, ϕ_D, can be correlated with the solvent parameter, β, which indicates the hydrogen-bond-accepting ability of the solvents. In the hydrogen-bond-forming solvents the triplet states are very short-lived due to their strong association with the solvents via the formation of hydrogen-bonded complex and very unreactive toward alkylic hydrogen abstraction reactions from the solvents or phenolic hydrogen abstraction from another unexcited parent molecule. However, in nonpolar and non-hydrogen-bond-forming solvents, the triplet is longer lived and capable of abstracting the phenolic hydrogen from another parent molecule.

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