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Photochemistry of Benzophenone–Cyclodextrin Inclusion Complexes[†]

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The photochemistry of benzophenone aqueous solutions in the presence of cyclodextrins (CDx) has been studied by stationary and pulsed techniques. Quenching of the phosphorescence is the consequence of hydrogen abstraction following the inclusion in the cyclodextrin cavity of the triplet benzophenone. The H-abstraction process has close analogies with the same reaction in micelles. Radical pair decay is controlled by the dimensions of the CDx cavity: intersystem crossing prevails in the presence of β-CDx, radical exit in the presence of α- and γ-CDx. The fate of the escaped radical also depends on the cavity dimensions, as revealed by the photoreduction quantum yields.

Introduction

The photochemistry of benzophenone (BP) and its derivatives in homogeneous media has been for decades the subject of an enormous number of investigations[1] and is still now a topic actively studied. Most recently, the behavior of benzophenone in micelles has attracted the attention of several research groups.[2-11] By use of the laser flash photolysis technique it has been shown that the dynamic behavior of both the triplet benzophenone and of the radical pair formed by hydrogen abstraction of the excited carbonyl group from the micelle is very sensitive to the microenvironment.

Cyclodextrins (CDx) are water-soluble, torus-shaped, cyclic oligosaccharides characterized by an external wall that is relatively hydrophilic and an internal cavity that is relatively hydrophobic.[12,13] The most important property of Cdx's is the ability to accommodate guest molecules of the appropriate size in their cavity. A relatively large number of papers describe the changes induced by CDx's complexation in the photophysical properties of the guest molecules.[14] Some papers have examined the effect of CDx's complexation on the photoreactivity of the guest molecules.[15-20] In the reactions described in these papers, the CDx's have an essentially physical role, i.e., the dimensions of the cavity affect the radical fragments recombination of the photo-Fries rearrangement of esters[16,17] and amides,[18] enhance the efficiency of the photodimerization of anthracene derivatives by favoring the mutual orientation of the reagents,[19] slow the ions recombination in photoinduced electron-transfer reactions,[20] and hinder some molecular degree of freedom of the electronically excited azobenzene thus changing the efficiency of the S_1 and S_2 deactivation paths.[15]

In this work we investigate the hydrogen abstraction by the benzophenone triplet from the CDx molecules: in this case, CDx acts either as a chemical partner of the excited benzophenone or as a physical boundary that influences the photoreactivity of the included chromophore by affecting, according to the dimensions of the cavity, the cage processes following the H abstraction. For the sake of comparison, the interaction of triplet benzophenone (^{3}BP) with noncyclic model oligosaccharides was also studied.

Experimental Section

Materials. Benzophenone (Baker) was recrystallized three times from ethanol. Glucose, saccharose (Merck), and cyclodextrins (Aldrich or Fluka) were used as received. Water was purified by passage through a Millipore Milli-Q system.

Steady-State Measurements. UV absorption spectra were measured by a Perkin-Elmer 320 spectrometer. Induced circular dichroism spectra (icd) were obtained by a JASCO J500 dichrograph. Phosphorescence spectra were obtained by a Perkin-Elmer MPF 44 spectrofluorimeter equipped with an accessory for spectral correction. Benzophenone disappearance quantum yields were determined by UV spectrophotometry of irradiated 5.5×10^{-5} M BP solutions. The light source was a low-pressure mercury arc coupled with a narrow-band interference filter (Ealing) peaked at 254 nm. The intensity of the incident light was determined by ferrioxalate actinometry.[21] The solutions were deaerated by bubbling for 10 min with pure nitrogen.

Irradiations were carried out up to a 7% maximum of conversion. The quantum yield in pure water was found to be 6.65×10^{-3}, in our experimental conditions.

Time-Resolved Measurements. All the solutions were degassed to 10^{-5} Torr by repeated freeze–pump–thaw cycles. BP concentration ranged between 4×10^{-5} and 2×10^{-4} M depending on the experiment.

Emission lifetimes were measured by exciting the samples with a pulsed N_2 laser (Lambda Physik M100A, 3,5-ns fwhm, λ_{exc} = 337 nm, maximum energy 2 mJ). Phosphorescence decays were detected at 450 nm with right-angle geometry, by a 1P28 photomultiplier with a 9 dynode chain configuration, a Bausch-Lomb grating monochromator (0.2 m, *f*/2.8), and a Tektronix R-7912 transient digitizer. The signals were processed by a Cromenco C-System One microcomputer, and standard iterative nonlinear procedures were used to analyze the decay curves.

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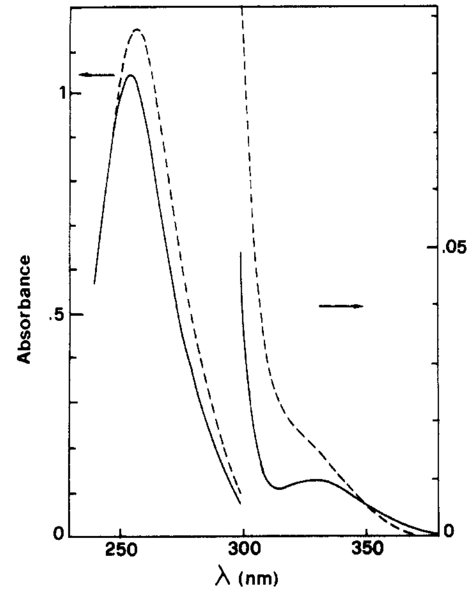

Figure 1. Absorption spectra of 5.65×10^{-5} M BP: dashed line, in pure water; continuous line, in 10^{-2} M β-CDx (cell, 10 mm).

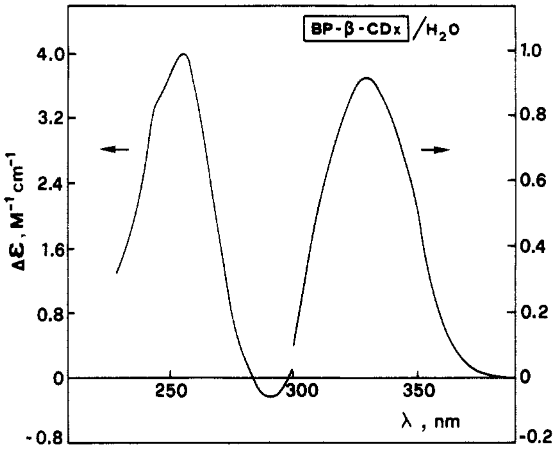

Figure 2. Induced circular dichroism spectrum of the BP–β-CDx inclusion complex in water.

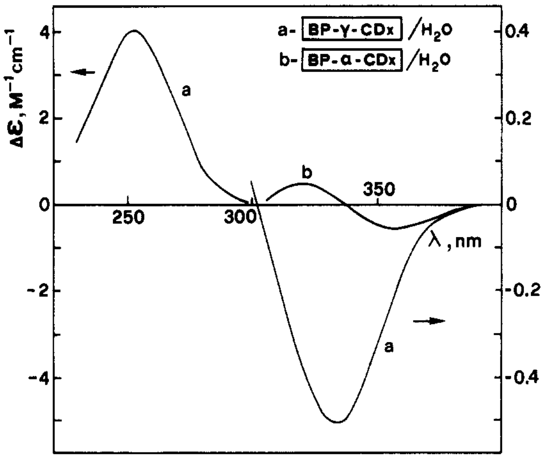

Figure 3. Induced circular dichroism spectra of the BP–CDx inclusion complexes in water: curve a, BP–γ-CDx; curve b, BP–α-CDx.

Laser flash photolysis was performed by using a pulsed frequency quadrupled Nd:YAG laser (J. K. Lasers HY750, 15-ns fwhm, maximum energy 750 mJ at 1.06 μm). The energy of a single 266-nm pulse was monitored by using a beam splitter and a pyroelectric energy meter (Laser Precision Corp.). Laser-induced transient transmission changes were monitored, perpendicularly to the laser beam, by using a Xe arc lamp (ILC UV 300P). The analyzing light passed through a 2-mm-wide section of the excited sample and was then focused at the entrance slit of a 0.25-m, double-grating monochromator (PTI $f/4$, spectral resolution 3 nm). A photomultiplier (Hamamatsu R955) and a digital storage oscilloscope (Tektronix Model 468) or a Tektronix R-7912 transient digitizer, interfaced to a PDP 11/23 microcomputer (Digital) were used to acquire and process the signals. The sequence generators, lamp pulsing unit, and back-off system were homemade.

The magnetic field of 700 G was provided by a permanent magnet.

Ketyl Radical Quantum Yield Determination. The ketyl quantum yields were determined by using ^{3}BP in water as a standard. Aqueous solutions (4×10^{-5} M BP) were excited with a laser pulse whose energy was low enough to avoid light saturation effects (incident energy at 266 nm less than 1.6 mJ/cm^2; less than 12% BP ground state converted to the triplet). In these conditions the decay of the triplet state is pseudo-first-order ($\tau_T = 100$ μs) and is not complicated by the T–T annihilation process. The triplet yield was estimated by measuring the optical density (OD) at 520 nm, the maximum of benzophenone T–T absorption, by assuming $\epsilon_{520} = 5750$ M^{-1} cm^{-1}.[22] In the absence of quenchers, the OD at 540 nm, the maximum of the ketyl free radical absorption in water, is negligible after the triplet absorption has decayed, probably due to the very low efficiency of the H-abstraction process from water.[23]

In the presence of quencher concentrations such that over 90% of the triplet is quenched, the yield of the ketyl radical was obtained from the OD at 540 nm by assuming $\epsilon_{540} = 3220$ M^{-1} cm^{-1} for the ketyl radical.[24] The decay of the neutral radical being much slower than that of the triplet, the "maximum" OD$_{540}$ was obtained by a short extrapolation of the initial portion of the radical decay curve back to zero time. To convert yield values to quantum yields, we used the value of $\phi_{ISC} = 1$ for BP in water.[22] The concentration of BP–CDx ground-state inclusion complex (see Discussion) in these experiments was kept at <12%.

Results and Discussion

Absorption Spectra. In Figure 1 are reported the absorption spectra of aqueous solutions of BP and BP + 10^{-2} M β-CDx. With respect to the spectrum in pure water, the spectrum of BP + 10^{-2} M β-CDx shows a blue shift of the π,π^* absorption band (λ_{max} shifts from 257.5 nm in water to 254.5 nm in 10^{-2} M β-CDx) and a better resolution of the n,π^* band, which, in water, appears as a shoulder of the much more intense π,π^* band. A red shift of the n,π^* band in the presence of β-CDx is also observable. The addition of 10^{-2} M α- and γ-CDx to a water solution of BP does not affect the absorption spectrum of the ketone itself. The spectral variations in the presence of 10^{-2} M β-CDx point to a quite apolar microenvironment for the carbonyl group and can be explained with the formation of an inclusion compound between β-CDx and BP, as already suggested on the basis of icd measurements.[25] This indicates a tight contact between the carbonyl group and the rather apolar interior of the cavity (internal diameter 7 Å[12,13]) arising from a full occupancy of the cavity itself by the guest ketone.

α- and γ-CDx also form inclusion compounds with BP, as shown by icd studies (see later). The absence of spectral variations in the absorption spectra of BP in the presence of α- and γ-CDx can be accounted for either by the lower complexing ability of these CDx's or by a different mode of inclusion of the ketone in the cavity. In the presence of γ-CDx this could be ascribed to the larger dimensions of its cavity (8.5 Å) in which BP and water molecules can be accommodated simultaneously. Last, for the

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TABLE I: Quenching of ^{3}BP Phosphorescence by CDx's and Glucose and Saccharose as Model Compounds

	k_q,[a] mol^{-1} s^{-1}	k_q,[b] mol^{-1} s^{-1}
α-CDx	5.1×10^7	5.0×10^7
β-CDx	7.5×10^8	8.3×10^8
γ-CDx	4.5×10^8	4.6×10^8
glucose	1.3×10^6	1.4×10^6
saccharose	2.3×10^6	2.5×10^6

[a] Values obtained from plots of τ_0/τ versus [quencher]. [b] Values obtained from plots of I_0/I versus [quencher].

BP–α-CDx complex, a prevailing inclusion of the phenyl ring in the cavity (4.5 Å) can be hypothesized in agreement, also, with icd spectra.

Circular Dichroism Spectra. BP in water, in the presence of CDx's, exhibits icd signals arising from both the π,π* and n,π* transitions (Figures 2 and 3). The formation of inclusion complexes with 1:1 stoichiometry is the origin of the Cotton effects. By application of the Benesi–Hildebrand[26] treatment to the icd signals, the equilibrium constants for complex formation at 293 K were obtained: K_{eq} = 50 M^{-1} for α-, 1500 M^{-1} for β-, and 170 M^{-1} for γ-CDx–BP, respectively. The equilibrium constant found for the β-CDx–BP complex is in a fairly good agreement with the values reported for β-CDx–BP derivatives[25] and other aromatic ketones.[27]

β-CDx possesses the best complexing ability: accordingly, the BP–β-CDx complex shows the most intense icd signals characterized by a positive sign in both the π,π* (λ_{max} = 255 nm) and n,π* (λ_{max} = 330 nm) absorption band (Figure 2). Strong Cotton effects with the same λ_{max} are observed in the presence of γ-CDx (Figure 3, curve a). However, the sign change in the n,π* transition indicates a different orientation of the BP molecule in the γ-CDx cavity. Induced circular dichroism effects in the presence of α-CDx are very weak, pointing out a scarce penetration of the BP molecules in the small cavity. A signal is detectable only in the n,π* region and appears split into two bands of opposite sign (Figure 3, curve b).

Quenching of ^{3}BP Phosphorescence Emission. The intensity of the phosphorescence emission of ^{3}BP is quenched in the presence of CDx's. Over 90% quenching is observed in ranges of concentration well below those in which ground-state complexation appreciably takes place, [α-CDx] < 2×10^{-3} M, [β-CDx] < 10^{-4} M, and [γ-CDx] < 5×10^{-5} M, as can be calculated by the K_{eq}'s reported above. The bimolecular rate constants k_q listed in Table I together with those for glucose and saccharose, inserted for the sake of comparison, were determined from the Stern–Volmer plots of both lifetime and emission intensity quenching, by using the same BP concentration in the two sets of experiments. In fact, self-quenching phenomena have been observed for ^{3}BP in water: the rate constant for the process was found 1.3×10^8 M^{-1} s^{-1}, in agreement with a previous determination.[23] The coincidence of the k_q values obtained by the two methods confirms the absence of ground-state interactions in the experimental conditions used.

All the quenching rate constants are below the diffusion limit, but the CDx's have a quenching ability higher than that of the model compounds, even if a correction factor for the number of glucose units per molecule is introduced. This fact indicates that the interaction between ^{3}BP and CDx's is related to the specific geometry of these macrocycles. We suggest that the quenching occurs with inclusion of ^{3}BP in the cavity of the CDx's. Association constants larger for ^{3}BP than for ground-state BP can be accounted for by the more planar geometry and the smaller dipole moment of the triplet state with respect to the ground state.[28]

Transient Phenomena after Laser Excitation. Transient optical density changes were detected after laser excitation of 4×10^{-5} M BP aqueous solutions containing CDx's in concentrations such that the amount of BP included in the ground state is <12%. In these conditions the species absorbing the light is largely the free BP. Accordingly, the difference spectrum, observed immediately after the pulse, with maxima at 330 and 520 nm is consistent with the formation of ^{3}BP in water.[22] During the following tens of microseconds, the transient absorbance increase in the UV and decreases in the visible, and λ_{max} shifts toward 540 nm. These features are in agreement with the formation of the benzophenone ketyl radical (BP·) as the consequence of the H abstraction from a glucose unit.[22]

TABLE II: BP Disappearance Quantum Yield at 10^{-2} M Saccharides and Limit Quantum Yields of the Ketyl Radical Production

	ϕ_{-BP}	$\phi_{BP\cdot}$
α-CDx	0.05 ± 0.004	0.70 ± 0.12
β-CDx	0.12_5 ± 0.007	0.16 ± 0.04
γ-CDx	0.13 ± 0.009	0.62 ± 0.10
glucose	0.07_5 ± 0.005	0.91 ± 0.16
saccharose	0.05_6 ± 0.004	0.75 ± 0.12

The decay of BP· was found to follow second-order kinetics. By assumption of the occurrence of a reaction between like partners, a rate constant $2k = 1.7 \times 10^9$ M^{-1} s^{-1} was determined, in fairly good agreement with previous determinations.[23,29] As an alternative, a reaction with the equimolar counterradical, not absorbing in the visible region, can be hypothesized.

The quantum yields of ketyl radical production for total triplet quenching, determined as reported in the Experimental Section, are shown in Table II. The reaction is quantitative with glucose as quencher, while lower yields are found with the other quenchers, in particular with β-CDx. These results can be explained if fast decay processes occur in the "solvent" cage so that we are actually observing only the fraction of escaping ketyl radicals. The second-order character of their disappearance kinetics is consistent with this interpretation.

The diffusive quenching of ^{3}BP must be prevented from being the rate-determining process to gain more insight in the mechanism of the cage reactions. This can be achieved by choosing a β-CDx concentration such that most of the ground-state BP molecules are included in the cavity. In Figure 4 are reported the difference spectra obtained by excitation of an aqueous solution containing 4×10^{-5} M BP and 5.7×10^{-3} M β-CDx at 0 ns (a), 750 ns (b), and 7 μs (c) after the laser pulse. With the above concentrations about 90% of BP molecules are complexed before the laser excitation. Spectrum a, characterized by two bands with maxima at 332 and 530 nm, is attributed to the benzophenone triplet included in the cavity: this agrees with the literature spectra of ^{3}BP in apolar media.[24,30] Spectrum b exhibits the same maxima but corresponds to the evolution of the triplet into a different species with extinction coefficients higher in the UV region: the evidence for the formation of this new species comes mainly from the kinetics. In the inset of Figure 4 the initial change in the optical density at 337 nm is followed by a phase of further increase; then ΔOD decreases until a plateau is reached which corresponds to spectrum c. Kinetic analysis shows that, in the whole wavelength range, ΔOD(t) can be fitted by a biexponential law consistent with the occurrence of two consecutive first-order reactions:

$$\Delta\mathrm{OD}(t) = a_1 \exp(-k_1 t) + a_2 \exp(-k_2 t) + a_3$$

with $k_1 = 2.86 \times 10^6$ s^{-1} and $k_2 = 6.25 \times 10^5$ s^{-1}, wavelength- and laser-intensity-independent parameters. We attribute the shorter lifetime to the benzophenone triplet included in the CDx cavity and the longer to the triplet geminate radical pair ensuing from H abstraction. The very short triplet lifetime is justified by the close proximity of the excited carbonyl group to a tertiary hydrogen of the interior cavity (as indicated, also, by the ground-state absorption spectrum), which should greatly favor the H abstraction. The observed lifetime, ≃350 ns, is in agreement with the values reported for benzophenone in micelles[5,8,11] where the H abstraction was proved to be the rate-determining process of the triplet decay.

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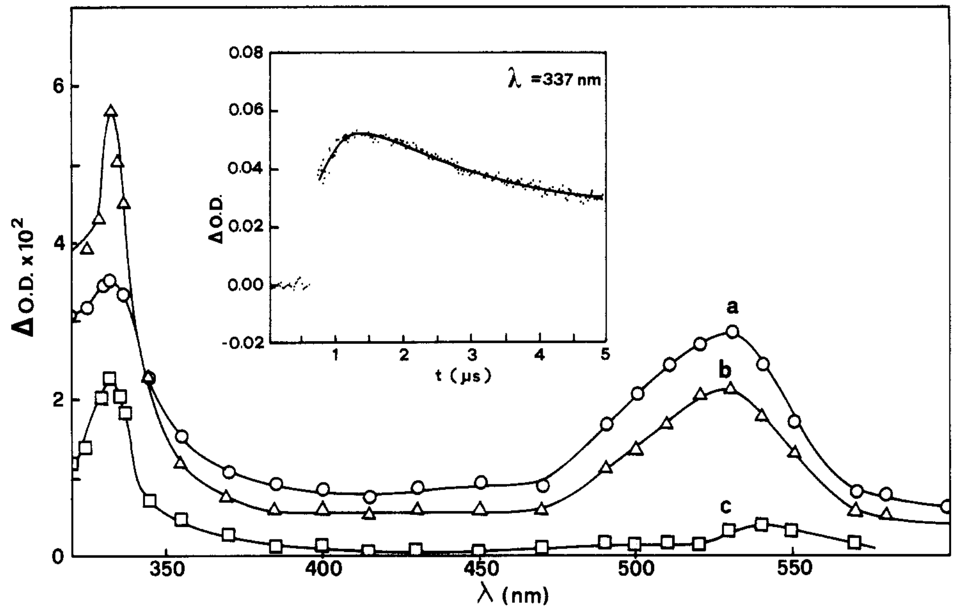

Figure 4. Transient OD changes observed in a 4.0 × 10^{-5} M BP aqueous solution containing 5.7 × 10^{-3} M β-CDx: (a) 0 ns; (b) 750 ns; (c) 7 μs after a 2.4 mJ/cm² laser pulse.

By consideration of the inclusion complex as a single molecular species, the radical pair formed by H abstraction can be regarded as a biradical with an electronic configuration similar to that of the triplet precursor: this explains the close similarity of the electronic spectra of the two transients. With the assumption that the extinction coefficients at 530 nm of the ^{3}BP–β-CDx inclusion complex and the triplet geminate radical pair are similar, the quantum yield for the H-abstraction process from the cavity appears to be nearly quantitative. The first-order decay kinetics of the triplet radical pair (τ = 1.6 μs) is proposed to correspond to the sum of intersystem crossing (ISC) and escape processes by analogy with the findings in micelles.[5,8]

Spectrum c, characterized by a band at 330 nm and a weak visible band with maximum at 540 nm, is attributed to the fraction of ketyl radicals escaped from the cavity. The quantum yield of the escaped radical is 0.14, in good agreement with the value given in Table II. On the basis of the k_2 value reported above, the rate constants for ISC and escape processes for the triplet radical pair are $k_{ISC} = 5.3 \times 10^5$ s^{-1} and $k_{esc} = 0.9 \times 10^5$ s^{-1}. These rates are significantly lower than the corresponding rates observed in micellar media;[5,8] this implies that the β-CDx cage is more efficient than the micellar boundary in preventing the diffusive separation of the two radical partners. The triplet phase relationship is thus preserved for a time longer than in micelles, and the irreversible escape is inhibited.[31] In fact, contrary to what is observed in micelles,[5,8] no changes in the yield of escape and in the decay rate of the radical pair were observed by applying a magnetic field of 700 G. The lack of effect indicates that the hyperfine coupling mechanism[31] to induce ISC in the radical pair is not operating in the present case. The possible explanation is the close proximity of the radical centers, which makes the triplet and singlet levels of the two electrons not degenerate. In fact, recent work on cyclohexanone-derived biradicals clearly demonstrate that relatively weak external magnetic fields affect k_{ISC} only if the distance between the radical centers is large enough to leave T and S levels almost degenerate and coupled via the hyperfine interactions.[32,33]

With α- and γ-CDx, due to the presence of an appreciable amount of free BP even in the presence of 10^{-2} M CDx, we were not able to disentangle the processes occurring in the cavity from the diffusive quenching. However, with 60–65% BP included in the cavity of γ-CDx, the quantum yield of the free ketyl radical was found to coincide with that reported in Table II. In this case again, no magnetic field effects were detected.

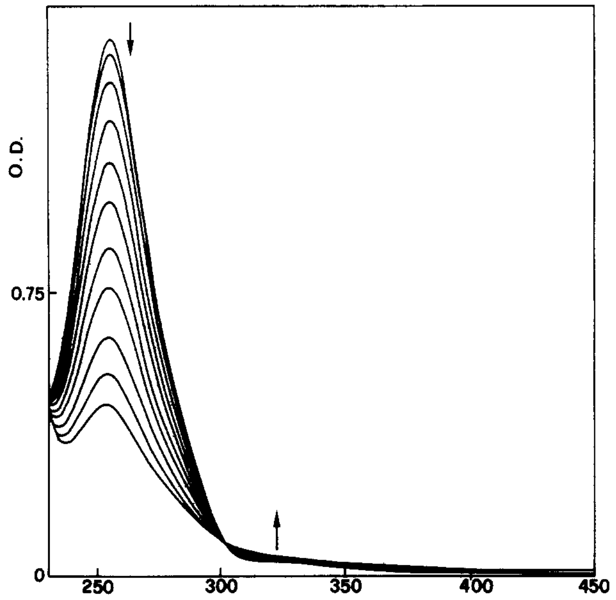

Figure 5. Spectral variations of 5.0 × 10^{-5} M BP aqueous solution containing 10^{-2} M β-CDx after irradiation at 254 nm.

Steady-State Irradiations. The spectral modifications due to the irradiation of a degassed 5 × 10^{-5} M BP aqueous solution containing 10^{-2} M β-CDx are shown in Figure 5. The π,π^* band strongly decreases in intensity, while the red tail of the spectrum, above 310 nm, slightly increases. Similar behavior is shown by solutions of BP in 10^{-2} M γ-CDx. The increase of absorption at $\lambda > 310$ nm might be attributed to the formation of "light absorbing transients" (LATs), which, in homogeneous solution, accounts for about 1% of the photoreduction products.[34,35]

However, on the basis of the spectral variations observed, the amount of LATs formed by irradiation of BP in 10^{-2} M CDx's is much lower than that formed in cyclohexane or in sodium dodecyl sulfate micelles.[5] Solutions of BP plus 10^{-2} M glucose,

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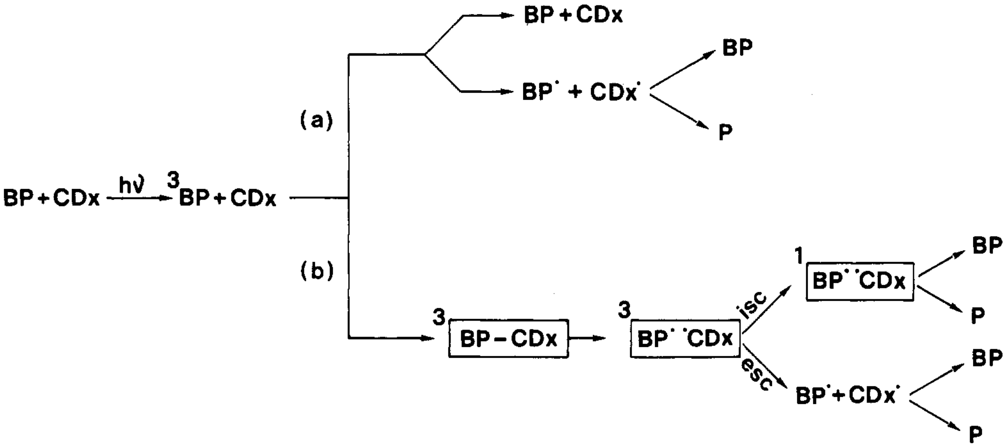
SCHEME I



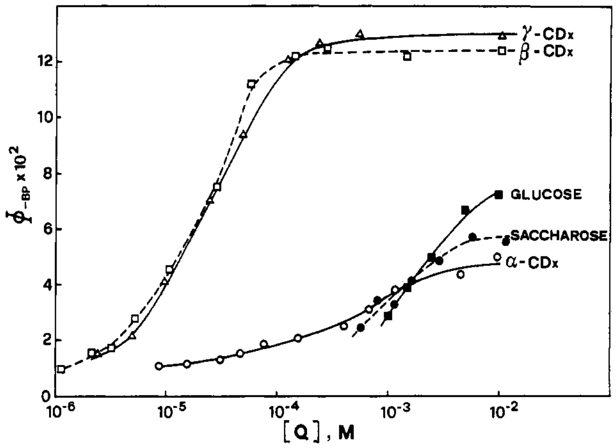


Figure 6. Semilogarithmic plot of BP disappearance quantum yield as a function of saccharide concentration.

saccharose, or α-CDx behave, under irradiation, like solutions of BP in water: the decrease in the π,π^* is accompanied by an important increase of the absorption above 310 nm. When the disappearance of BP is more than ~8%, the formation of a finely disperse precipitate is easily observable. This precipitate is, probably, the main cause of the absorption increase above 310 nm, but the formation of a small amount of LATs cannot be excluded. It is likely that the lack of formation of a precipitate in the presence of β- and γ-CDx is due to the fact that the benzophenone photoreduction products also form inclusion complexes with these dextrins that hinder their precipitation.

Figure 6 shows a semilogarithmic plot of the BP disappearance quantum yield as a function of the CDx's and model compounds concentration. The plot shows that the disappearance yield increases with increasing oligosaccharide concentration up to values of about 0.125 for β- and γ-CDx and about 0.05 for α-CDx and the model saccharides. The yield at 10^{-2} M does not correspond, for glucose and saccharose, to a true limiting yield (~60% of ^{3}BP is quenched by 10^{-2} M glucose, on the basis of the k_q value reported in Table I) while, for 10^{-2} M α-CDx, the yield can be considered a limiting value, being ^{3}BP quenched to an extent higher than 95% in these conditions.

Comparison of BP disappearance and BP• production quantum yields, reported in Table II, indicates that, in general, following the decay of ketyl radicals BP is regenerated to a high extent. This reversibility, already proven in homogeneous media by CIDNP experiments,[22,36,37] can be explained by the accessibility of the reaction site for BP• when the quenchers are α-CDx and model saccharides. With β-CDx the values of BP disappearance and BP• production coincide, which could indicate that BP disappearance occurs exclusively via the free ketyl radical coupling. However, since the second-order kinetics of the free ketyl radical disappearance is the same in the presence of CDx's and the model compounds, we believe that the coincidence is accidental and that the BP• decay channels are common to all the saccharides. In the case of the β-CDx and γ-CDx, a partial reentry of the escaped radical in the cavity of the dextrins, to a different extent according to their dimensions, might be hypothesized. The relative contribution of ketyl–ketyl and ketyl–counterradical reactions cannot be quantified with our techniques. However, as demonstrated by the behavior of the geminate radical pair in the BP–β-CDx inclusion complex (see above), regeneration of BP is an efficient process among the reactions occurring in the cavity.

Conclusions

The interaction between ^{3}BP and CDx's can be described by Scheme I. Path 1 represents the interaction of ^{3}BP with the external wall of the CDx's: on the basis of the results obtained with the model saccharides, this channel can be considered of minor importance. Path 2 represents the inclusion of the excited molecule in the cavity: this process is highly efficient as demonstrated by the fact that the same yield of ketyl radical is obtained by exciting directly the BP–CDx inclusion compound or a solution of BP and CDx in which only ~10% of BP is complexed in the ground state. For some aspects the inclusion complex ^{3}BP–CDx behaves like ^{3}BP in micelles: included ^{3}BP quantitatively abstracts H from the interior wall of CDx that leads to the formation of a triplet radical pair whose absorption spectrum is very similar to that of the triplet precursor but different from that of the ketyl free radical. The fate of triplet radical pair depends on the dimension of the cavity: escape processes dominate in α- and γ-CDx; intersystem crossing prevails in β-CDx. On the other hand, the formation of LATs, a process that occurs more readily in micelles than in homogeneous solution, remains a largely minor process for benzophenone in cyclodextrins.

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Registry No. BP, 119-61-9; BP•, 16592-08-8; glucose, 50-99-7; saccharose, 57-50-1.

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