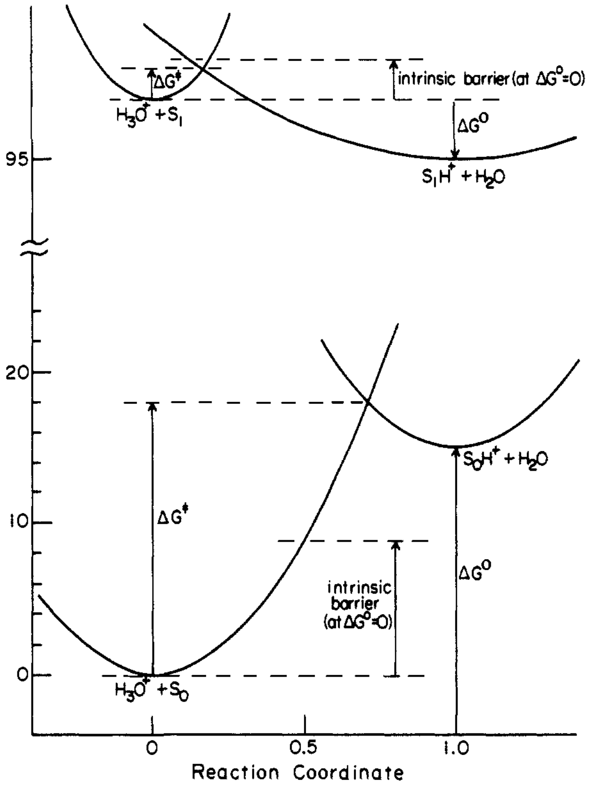

Figure 5. Schematic comparison of energy profiles for thermal (lower curve) and photochemical (upper curve) proton transfers to *p*-methylstyrene.

evident from Figure 5 by comparing the change in α as $\Delta G° = 0$ is approached in each case, this will not be true in general. However, for thermal and photochemical processes of comparable rates and exothermicities, $d\Delta G^\ddagger/d\Delta G°$ will always be smaller for the photochemical process,[20] using any reasonable value of ϵ or ϵ'. The general consequences of introducing asymmetry into the Marcus equations for photochemical proton transfers will therefore be lower intrinsic barriers, lower values of α or earlier transition states, and different curvature in Brønsted plots.

Conclusions

Although obviously much further investigation and testing with additional experimental data needs to be done, it is clear from this exploratory investigation that the Marcus equations can profitably be applied to photochemical reactions, if they are modified empirically to include transition-state asymmetry via an eccentricity parameter ϵ or ϵ'. Therefore, it should be possible to use Marcus theory to interpret the rates of proton transfers involving excited states in a similar way[24] to the extensive applications of this theory to ground-state proton-transfer reactions.

For the types of photoprotonation involved in the photohydration reactions of styrenes and phenylacetylenes, only a value of the eccentricity parameter in the neighborhood 0.3 gives reasonable estimates of the "intrinsic" barrier and reasonable or probable $\Delta G°$ ranges for such reactions. For proton transfers to excited states, which actually have an overall $\Delta G°$ close to zero, typical values of the intrinsic barrier are calculated to be in the 1–3-kcal range.[25] From an examination of the parabolic energy curves represented in Figure 2a,b, and their relationship to the Marcus equations, it seems clear that the Brønsted α values in photochemical reactions should be significantly less than 0.5, even for isoenergetic proton transfers, and for downhill proton transfers should give very low values of this parameter. It may be that values of $\epsilon' \approx 0.3$ are typical of photochemical reactions in general, particularly those involving proton transfer in the primary step, but this conclusion is tentative and must await further experimental work. Finally, it will be very interesting to see whether these ideas can also be applied to base-catalyzed photochemical reactions. The first examples of general base catalysis in photochemical reactions were recently reported by Wubbels.[26] However, as yet no Brønsted relationships have been established for this type of reaction, and hence their extent of curvature is unknown. It is predicted that these reactions also will show different Brønsted curvature from that found for typical base-catalyzed thermal reactions, and that their overall Brønsted β values will be significantly *greater* than 0.5, if proton transfer is rate determining.

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[24] Because of the often wide range of rate constants and catalysts experimentally accessible in photochemical reactions, via Stern–Volmer plots, it may be easier to measure curvature in Brønsted plots over a wider range than in analogous thermal reactions. Therefore it should be easier in most cases to test Marcus theory by using photochemical proton-transfer reactions.

[25] However, any uncertainty in the numerical values obtained for the Brønsted curvature due to the use of nonuniform catalyst types[10] would result in a corresponding uncertainty in the derived values of any Marcus-type parameters, such as the intrinsic barriers.

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The Ground-State Oxygen–Benzophenone Complex

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Abstract: In studies of the photoproduction of triplet excited benzophenone in cyclohexane by picosecond absorption spectroscopy (266-nm pump), it is shown that the presence of dissolved oxygen at 1 atm of pressure decreases the triplet–triplet 347-nm transition by 50% in less than 25 ps, indicating the presence of a stable ground-state oxygen–benzophenone complex. This work suggests that there may be a need to reevaluate any triplet risetime and quantum yield experiments performed on aromatic/carbonyl compounds in nondeoxygenated solutions.

When a solution to be used in a spectroscopic experiment is prepared in the presence of air, it often contains enough dissolved oxygen to affect the photophysics of the solute under investigation. In such cases one is concerned with molecular reactions which usually involve the production of transient species that are extremely sensitive to the presence of such dissolved oxygen. For example, if one were to generate by flash photolysis a population of triplet molecules in solution, the high mobility of molecular oxygen, combined with its ability to efficiently quench excited triplets, would lead to the rapid relaxation of the triplets to the ground state, usually within a few nanoseconds. Such phenomena are well documented to the effect that the study of photophysics at times longer than a nanosecond requires the removal of all dissolved oxygen from the solution.

Experimental studies in the picosecond or femtosecond time regimes are at a distinct advantage in this respect over experiments performed at longer times. Due to the diffusion limited nature of oxygen quenching, photoreactions in the ultrafast time regime ($<10^{-9}$ s) are not sufficiently affected by oxygen migration. For this reason, many picosecond solution studies are performed in the presence of air without regard to dissolved oxygen and its quenching effects.

This disregard of the presence of oxygen may, however, prove to be unwise. We report here the results of a study on the effects of dissolved oxygen on the picosecond photolysis of benzophenone in solution.

Experimental Section

Samples were prepared by dissolving benzophenone (Aldrich Gold Label 99%) in cyclohexane (EM Science Co. Omnisolve). The concentration was adjusted to an optical density of 1.0 at 266 nm for a 2 mm optical path cell (~0.5 mM). The samples were then bubbled for 30 min with cyclohexane-saturated deoxygenated argon. Subsequently these deoxygenated samples were bubbled gently with argon throughout the course of the experiment to maintain an oxygen-free atmosphere and to mix the sample between laser shots. To obtain samples saturated with oxygen, the previously deoxygenated samples were bubbled for 30 min with cyclohexane-saturated oxygen and then gently bubbled with O_2 during the laser experiments. No appreciable change in the UV–vis static absorption spectrum of the sample was detectable upon oxygenation.

To verify that the above procedure was satifactory for the removal and maintenance of oxygen free samples, a second set of samples was prepared on a vacuum apparatus. The deoxygenated samples were prepared in cyclohexane that had been vacuum distilled from 4A molecular sieves. The solutions were then freeze–pump–thawed six times to ensure complete removal of dissolved gases. The oxygenated samples were prepared by introduction of 1 atm of O_2 to the previously degassed samples. Both methods of preparation produced the same results which are presented and discussed below.

The time resolved spectra of benzophenone after excitation to the first allowed electronic state were obtained with a pump–probe absorption spectrometer.[1] A single ~25 ps 1.064 μm laser pulse was extracted from the active/passive mode locked pulse train of a Nd^{3+}/YAG laser with an avalanche Pockels cell pulse selector. The samples were excited with the fourth harmonic (266 nm) of the YAG fundamental and interrrogated with a broad-band UV continuum pulse generated by focussing the second harmonic (532 nm into a 60:40 mixture of H_2O/D_2O, or a visible broad band continuum pulse generated with the fundamental (1064 nm) pulse in the same medium. The probe pulses were dispersed by a monochromator and focused on an EG&G PAR 2D ISIT Vidicon and analyzed with a Data General Eclipse computer. Each experiment required two laser shots, with and without excitation, and the change in optical density was calculated by $\Delta OD = [\log (I_0/I)$ without excitation $- \log (I_0/I)$ with excitation]. Each spectrum consists of at least 150 pairs of laser shots. The specifics of the laser apparatus are described elsewhere.[2] Timing of the pump–probe pulses in the near-UV was obtained by examinng the temporal evolution of the 4,4′-dibromobiphenyl (Br_2Ph_2) triplet–triplet absorption in cyclohexane at 405 nm which is known to have a risetime shorter than our pulse duration. As the triplet–triplet absorption decays insignificantly by 1 ns, Br_2Ph_2 was used as a standard allowing compensation for variation in pump energy and pump–probe pulse overlap at the sample. Timing in the visible was accomplished with the prompt triplet–triplet rise of *trans*-stilbene.

Results and Data

Transient spectra between 340 and 420 nm of freeze–pump–thawed deoxygenated benzophenone obtained at 50 ps after excitation (Figure 1a), using a 266-nm pump to excite the $\pi^* \leftarrow \pi$ intramolecular charge transfer transition,[3] showed a previously unreported picosecond transient absorption band with a maximum at approximately 347 nm. This experiment was repeated after the sample was oxygenated with 1 atm of O_2. The transient absorption observed (Figure 1b) at 50 ps after excitation for the oxygenated sample showed a ΔA decrease of more than 50%; however, no change in shape or wavelength was evident. It is important to note that the sample was degassed again and the absorption of the transient was found to recover completely (Figure 1c).

Transient near-UV spectra in the same wavelength range were also obtained at 25-ps intervals from −50 to +50 ps after excitation for deoxygenated and oxygenated samples with the bubbling technique. No change in the spectra was apparent nor were additional transients observed compared to the freeze–pump–thawed counterparts. This change in intensity was found to occur for the 347-nm band; however, it did not hold true for the 525-nm transition.

Although it is possible to obtain kinetics from the rise and decay of a transient spectrum, it is more efficient and more dependable to obtain single-wavelength time-resolved decay traces after it has been determined that only a single transient absorbs at the interrogation wavelength. With this in mind, we examined the risetimes of the induced absorption at 530 nm following 355-nm pump for the deoxygenated (Figure 2a) and oxygenated (Figure 2b) samples and found them to be identical. The decay trace of this transient for the oxygenated (Figure 2c) sample over a period of 10 ns indicates that the oxygenated sample decays by diffusion limited kinetics. Assuming an oxygen concentration of 1×10^{-2} M, a second-order decay rate of -4.9×10^9 M^{-1} s^{-1} was obtained for bimolecular oxygen quenching, in satifactory agreement with the rate of -1.0×10^9 M^{-1} $s^{-}1$ found in CCl_4[4] solvent.

As a test of the resolution of the streak camera apparatus in these experiments, we also obtained the risetime for the 525-nm absorption of benzophenone dissolved in benzene, prepared without consideration of the effects of atmospheric oxygen (Figure 3). The risetime is noticeably longer in benzene than in cyclohexane, yielding an optimum fit with a risetime of 31 ps in excellent agreement with Hochstrasser's result of 30 ps.[5]

Discussion

There are in general two possible mechanisms, static and dynamic, by which the dissolved oxygen can quench the excited state benzophenone transition.[6] Dynamic quenching can occur in the picosecond regime only when the quencher is present in sufficiently high concentration to be considered a solvent, whereby the probability of having a quencher molecule in the primary solvation shell of the excited solute molecule is quite large. In our case the concentration of the oxygen is only $\sim 10^{-2}$ M; therefore dynamic quenching would be diffusion controlled, occurring in a period of nanoseconds or longer, as discussed in the introduction, and having no observable effect in the picosecond range. Static quenching on the other hand would involve the formation of a ground-state complex between the benzophenone and the oxygen.

The degree to which oxygen binds to benzophenone may be estimated approximately by calculating of the equilibrium constant using the relative intensities of the observed transients. In each of the experimental spectra, it is assumed that only that fraction of the benzophenone molecules that do not have an oxygen molecule bound to them contributes to the transient 347-nm absorption. Also, as only the oxygen concentration is varied, the total benzophenone concentration ($[\mathrm{BZP}]_{\mathrm{total}}$) is identical for both the oxygenated and deoxygenated samples. The subscripts "O_2" and "deox" mean "in the oxygenated sample" and "in the deoxygenated sample", respectively. For the reversible reaction

$$\mathrm{BZP} + \mathrm{O_2} \rightleftarrows \mathrm{BZP{\cdot}O_2}$$

$$K_{\mathrm{eq}} = [\mathrm{BZP{\cdot}O_2}]/[\mathrm{BZP}][\mathrm{O_2}]$$

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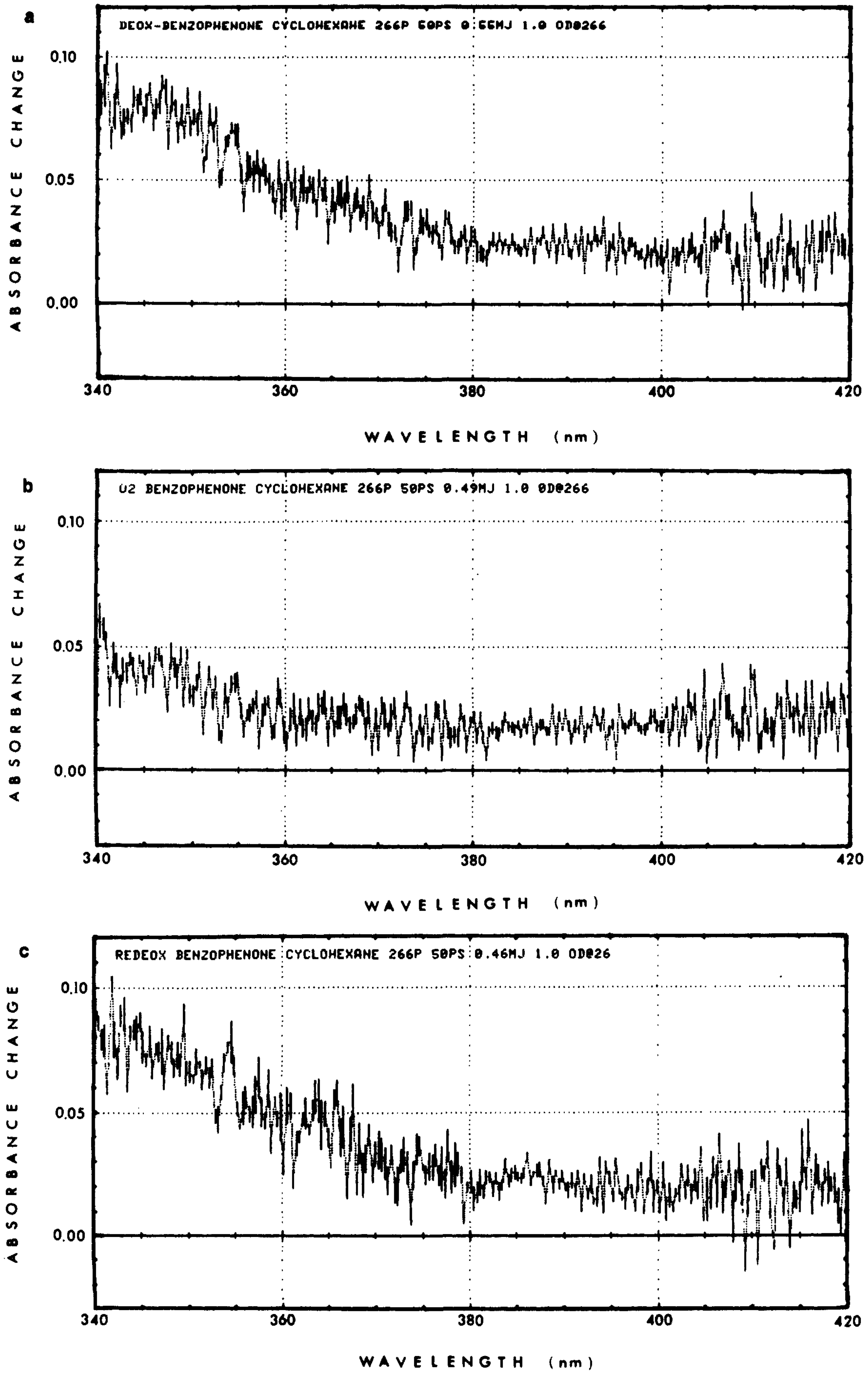

Figure 1. (a) Transient absorption spectrum of deoxygenated benzophenone in cyclohexane, $\lambda_{\text{pump}} = 266$ nm, 50-ps delay, ~0.5 mM. (b) Transient absorption spectrum of oxygenated (~1 atm of pressure) benzophenone in cyclohexane, $\lambda_{\text{pump}} = 266$ nm, 50-ps delay, ~0.5 mM (same sample as in part a). (c) Transient absorption spectrum of benzophenone in cyclohexane after removal of oxygen by freeze–pump–thaw degassing, showing complete recovery of the transient, $\lambda_{\text{pump}} = 266$ nm, 50-ps delay, ~0.5 mM (same sample as in parts a and b).

In the oxygenated sample

$$[\mathrm{BZP}]_{\mathrm{total}} = [\mathrm{BZP}]_{\mathrm{O_2}} + [\mathrm{BZP{\cdot}O_2}]_{\mathrm{O_2}}$$

and as the oxygenated portion does not contribute to the ΔA

$$\Delta A_{347\mathrm{nm}}(\mathrm{O_2}) = [\epsilon_{\mathrm{BZP,347}} - \epsilon_{\mathrm{BAP,347nm}}][\mathrm{BZP}]_{\mathrm{O_2}}L$$

where "L" is the sample optical path length. As $^{\epsilon}$BZP,347 nm is ~100 (a forbidden transition) while $^{\epsilon}$BZP*347 nm is approximately 10^4 (an allowed triplet–triplet transition), the ground-state absorption can be neglected.

In the deoxygenated sample

$$[\mathrm{BZP})_{\mathrm{deox}} = [\mathrm{BZP}]_{\mathrm{total}} = [\mathrm{BZP}]_{\mathrm{O_2}} + [\mathrm{BZP{\cdot}O_2}]_{\mathrm{O_2}}$$

and

$$\Delta A_{347\mathrm{nm}}\ (\mathrm{deox}) = \epsilon_{\mathrm{BZP,347nm}}\{[\mathrm{BZP}]_{\mathrm{O_2}} + [\mathrm{BZP{\cdot}O_2}]_{\mathrm{O_2}}L\}$$

This gives

$$[\mathrm{BZP}]_{\mathrm{O_2}} = (\Delta A_{347\mathrm{nm(O_2)}}/^{\epsilon}{}_{\mathrm{BZP,347nm}})L$$

and

$$[\mathrm{BZP{\cdot}O_2})_{\mathrm{O_2}} = \frac{\Delta A_{347\mathrm{nm(deox)}} - \Delta A_{347(\mathrm{O_2})}}{\epsilon_{\mathrm{BZP,347nm}}L}$$

Therfore

$$K_{\mathrm{eq}} = \frac{(\Delta A_{347\mathrm{nm(deox)}} - \Delta A_{347\mathrm{nm(O_2)}})}{(\Delta A_{347\mathrm{nm(O_2)}})(10^{-2}\ \mathrm{M})}$$

As $\Delta A_{347\mathrm{nm(deox)}} \simeq 0.08$ and $\Delta A_{347\mathrm{nm(02)}} \simeq 0.04$

$$K_{\mathrm{eq}} = \frac{[0.04]}{[0.04][0.01]} \cong 10^2$$

This indicates that oxygen does bind quite well to benzophenone. In the presence at atmospheric oxygen, this would mean that, assuming a 1:1 complex, approximately 16% of the benzophenone molecules would be bound with oxygen.

There is a second type of static quenching that must be considered, one involving some form of long-range interaction. If no complex is formed, the average distance between the benzophenone and the oxygen molecules would be on the order of 14 Å. Although there is some evidence for long-range interactions between paramagnetic transition-metal ions over distances of many angstroms, to our knowledge no similar long-range quenching mechanism has been observed with $\mathrm{O_2}$, and so this possibility is unlikely.

To better understand the molecular events involved, it is important to have an assignment for the transitions involved. Since there is no change in spin pairing energy, the difference in energy between T_2 and T_3 states is the difference in energy between the n and π^* orbitals (Figure 4). Similarly, the difference in energy between the S_2 and S_3 states is the difference in energy between the π and n orbitals. We assume the energy gaps between the π and n orbitals and between the n and π^* orbitals should be approximately equal. Disregarding possible vibrational contributions, a measure of the π,n energy gap is the difference in energy between the n → π^* transition and the $\pi \rightarrow \pi^*$ transition in the ground-state absorption spectrum, which should be the same as the difference in energy between the n → π^* and the n,$\pi \rightarrow \pi^*,\pi^*$ transitions in the excited triplet spectrum. The energy difference between the absorption maxima of the ground-state spectrum at 337 and 252 nm is 10000 cm^{-1}, and the energy difference between the two observed transitions for the triplet transient at 525 and 347 nm is 9770 cm^{-1}. This is strong evidence for the assignment of the 347-nm band as the n,$\pi \rightarrow \pi^*,\pi^*$ triplet–triplet transition.

Photophysics of the Adduct Complexes

Molecular oxygen is known to promote singlet–triplet intersystem crossing and triplet quenching. The oxygen can bind either at the phenyl rings or at the carbonyl. When several facts are taken into consideration they lend evidence for our proposal that the $\mathrm{O_2}$ binds preferentially but not exclusively at the phenyl ring.

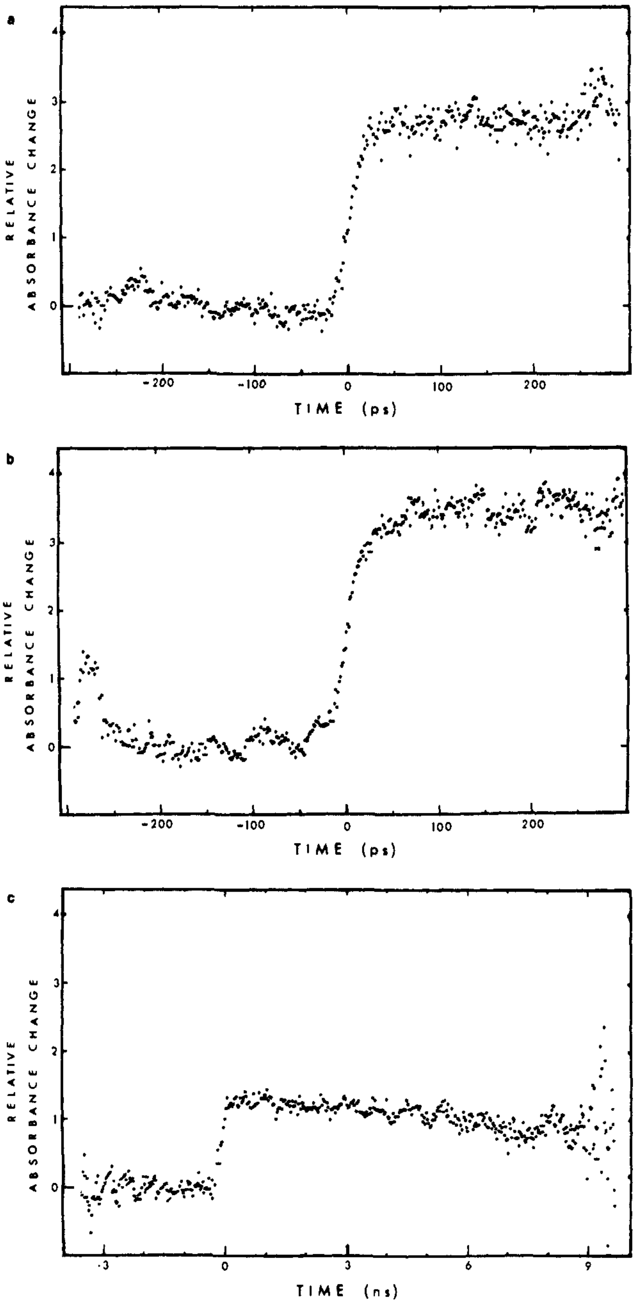

Figure 2. (a) Streak camera absorption trace of benzophenone in Argon saturated deoxygenated cyclohexane, showing rise of triplet. Deconvolution gives $\tau_{\mathrm{rise}} = 15 \pm 10$ ps, which is at the limit of resolution of the apparatus. $\lambda_{\mathrm{pump}} = 355$ nm, $\lambda_{\mathrm{probe}} = 530$ nm, ~30 mM. (b) Streak camera absorption trace of benzophenone under 1 atm of $\mathrm{O_2}$ in cyclohexane, showing triplet rise $\tau_{\mathrm{rise}} = 15 \pm 10$ ps, resolution limited. $\lambda_{\mathrm{pump}} = 355$ nm, $\lambda_{\mathrm{probe}} = 530$ nm, ~30 mM. (c) Streak camera absorption trace of benzophenone under 1 atm of $\mathrm{O_2}$ in cyclohexane, showing diffusion limited triplet quenching. $\tau_{\mathrm{quench}} = -4.9 \times 10^9\ 19^{-1}\ \mathrm{s^{-1}}$ $\lambda_{\mathrm{pump}} = 355$ nm, $\lambda_{\mathrm{probe}} = 530$ nm, ~30 mM.

These include the following: the free energy of binding based on our data is quite small (~2.5 kcal/mol) ($\Delta G = RT \ln K_{\mathrm{eq}}$); and the complex may dissociate when the binding sight is excited. If the $\mathrm{O_2}$ is bound to the phenyl ring, the π,π^* intramolecular charge transfer singlet first created when the benzophenone is pumped (3) would have an enhanced intersystem crossing rate, producing the π,π^* triplet. The π,π^* triplet would then rapidly relax to the n,π^* triplet, and there would be no decrease in the n,$\pi^* \rightarrow \pi,\pi^*$ triplet intensity as the oxygen is not located at the carbonyl. If the $\mathrm{O_2}$ had dissociated during this process, some of the dissociated pairs could geminately recombine and quench the π,π^* triplet, but a short-lived spike should be apparent in the streak record of the oxygenated sample, which, in our experiments, was not

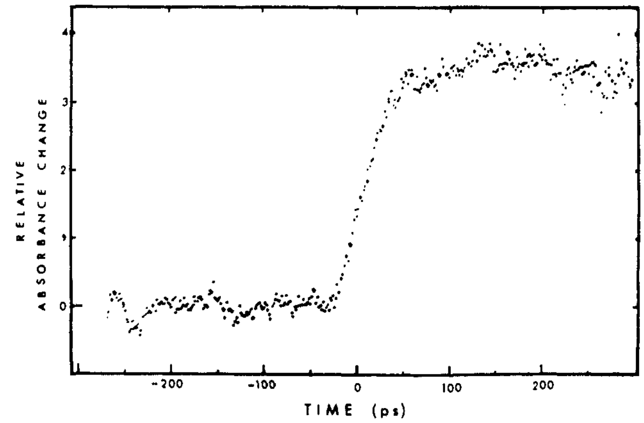

Figure 3. Streak camera absorption trace of benzophenone in benzene under air, showing triplet rise. $\tau_{\text{rise}} = 31 \pm 4$ ps, $\lambda_{\text{pump}} = 355$ nm, $\lambda_{\text{probe}} = 530$ nm, 30 mM.

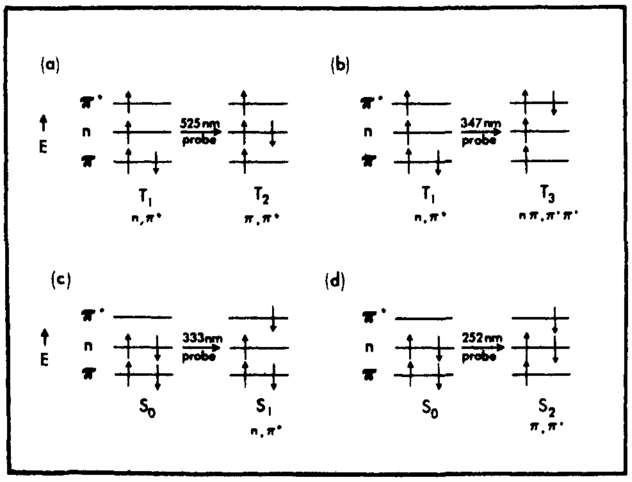

Figure 4. Diagram of the proposed orbital occupancies of the observed benzophenone transitions: (a) the triplet–triplet transition at 525 nm; (b) the triplet–triplet transition at 347 nm; (c) the singlet–singlet transition at 333 nm; (d) the singlet–singlet transition at 252 nm. The upper most π state in each case may be composed of π^* orbitals on both the carbonyl and the aromatic rings.

observed. If the O_2 does not dissociate but remains bound to the phenyl ring upon excitation, there is a possibility of photooxidation whereby the O_2 would add irreversibly to the phenyl ring.[7] As no irreversible changes were observed in the absorption spectrum of the oxygenated samples subsequent to photolysis, this possibility is unlikely.

The alternate conclusion is that the oxygen binds directly to the carbonyl. Having been excited into the π,π^* state, the complex relaxes and intersystem crosses into the n,π^* state and then the oxygen would quench the 525-nm triplet transition. As this transition is not quenched in the oxygenated sample, this lends evidence to the assumption that the O_2 is bound to the phenyl ring. An intriguing possibility is that, if the oxygen photodissociates, it may be produced in the singlet ($^1\Delta$) state. We are at present preparing experiments aimed at revealing possible photodissociation and recombination dynamics and detecting the presence of singlet oxygen on the picosecond time scale. That the complex undergoes photodissociation is supported by the fact that high power pump pulses produce the 347-nm transient, possibly due to absorption of a second pump photon by electronically relaxed dissociated BZP molecules. This nonlinearity should be taken as a caveat for investigators wishing to study this photoreaction.

Conclusion

The photophysics of the excited states of benzophenone has enjoyed a rich history of investigation, ranging from McClure's pioneering work on the solid state[8] and Rentzepis' gas phase work[9] to Hochstrasser's studies of the triplet risetime[10] and experiments on triplet intermolecular energy transfer.[11] It is only with this considerable foundation that a complete and accurate picture of the excited states of aromatic molecules can be constructed. Until these experiments, to our knowledge, it had never been determined whether the O_2 quenching mechanism for benzophenone is entirely diffusion controlled and "contact" in nature or whether an actual complex was formed.[12] It is thus extremely important that future experimenters take care to prepare these samples so as to eliminate any impurities that may influence the desired measurements. In this instance, studies in the picosecond regime show a decrease in the triplet–triplet 347 transient due to the presence of dissolved oxygen, although the subsequent triplet decay is explained by bimolecular quenching kinetics. When benzophenone or other aromatic molecules are examined at successively shorter times, a rapid quenching may well be observed, as will any enhancement of the triplet production by intersystem crossing. This makes it increasingly important to prepare samples anaerobically, in order to assure that the observed molecular kinetics are not due to subtle preparation errors.

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Registry No. Benzophenone, 119-61-9.

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