therefore, that a peroxyl radical located on an alkyl chain of a molecule forming part of an assembly such as a micelle or bilayer in water will attract that portion of the molecule to the aqueous interface. As suggested by Barclay and Ingold,[2] such behavior would significantly affect chain reactions involving the peroxyl group.

*Acknowledgment.* The authors thank K. U. Ingold for drawing their attention to the importance of this measurement and for his help and interest during preparation of the manuscript.

**Registry No.** $PhCH_2O_2\cdot$, 4399-88-6; benzene, 71-43-2; cyclohexane, 110-82-7; decane, 124-18-5.

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# Intramolecular Quenching of Carbonyl Triplets by β-Phenyl Rings

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The presence of a phenyl ring in a position β to the carbonyl of a phenyl alkyl ketone results in greatly reduced ketone triplet lifetimes. For example, in deaerated benzene solutions, triplet lifetimes were 2700 and 0.89 ns for propiophenone (P) and β-phenylpropiophenone (PP) and 3500 and 50 ns for 4′-methoxypropiophenone (MeOP) and β-phenyl-4′-methoxypropiophenone, respectively. Triplet energy transfer from the ketones to 1-methylnaphthalene (MeN) proceeded at nearly diffusion-controlled rates. The rate of electron transfer from the triplet carbonyls to methylviologen was also found to be very efficient, occurring with rate constants of $8.8 \times 10^9$ and $8.3 \times 10^9$ $M^{-1}$ $s^{-1}$ for MeOP and PMeOP, respectively. From the triplet decays and the shapes of the triplet–triplet absorbance spectra, a quenching mechanism involving intramolecular hydrogen abstraction was ruled out. A process involving an exciplex intermediate, characterized by a degree of charge transfer (CT), was proposed as the likely mechanism for the intramolecular quenching of triplet lifetimes in PP and PMeOP.

## Introduction

The photoprocesses of phenyl alkyl ketones have undergone intensive investigation. Much of this interest derives from the discovery[1] that the triplet manifold in these compounds is generally characterized by two energetically proximate, lowest-lying states of differing electronic configuration. Variations in solvent polarity[1] and phenyl ring substitution[2] allow the modulation of their relative spacing and, in some cases, even invert their ordering.

The energetic proximity of these triplets has been used to formulate quite different rationales[3,4] for the observation[5] of multiple phosphorescences from these compounds in 77 K rigid matrices. In dilute fluid solutions, typical carbonyl photoprocesses such as the Norrish type II reaction are markedly affected by their relative spacing and ordering.[6]

Intermolecular quenching of the excited triplets has also been extensively studied. Quenching mechanisms range from electron-exchange interactions with aromatic hydrocarbons such as naphthalene[7] to less well understood processes involving charge-transfer complexes as intermediates. Typical of the latter are quenching by olefins[8] and amines[9] in which the excited carbonyls act as electron acceptors. An interesting example of quenching by the reverse process has been reported by Das,[10] who used a variety of aromatic ketones to photoreduce paraquat dications.

A particularly remarkable example of intramolecular quenching of excited-state ketones has been reported by several authors.[11-13] Formally nonconjugated phenyl rings, located β to the carbonyl unit along an alkyl chain, drastically affect the photoprocesses typical of the latter chromophore. For example, Wagner et al.[12] have measured a type II quantum yield and a triplet lifetime of 0.025 and 1 ns, respectively, for β-phenylbutyrophenone. Comparable values for butyrophenone were 0.36 and 125 ns. Stermitz et al.[13] reported that, contrary to the situation with acetophenone, benzylacetophenone is inert to photoreduction in methanol and ethanol and is only slightly reactive in 2-propanol. That this situation is not unique to phenyl ketones was demonstrated by Whitten and Punch[11] in their studies of the type II process in the aliphatic ketones 4-methyl-4-phenyl-2-pentanone and 1-phenyl-3-hexanone.

No clear consensus as to the quenching mechanism was arrived at in the above studies. It was felt then that, in contrast to the steady-state methods previously utilized,[11-13] time-dependent measurements might yield additional information. Accordingly, propiophenone (P) and β-phenylpropiophenone (PP) have been examined by using laser flash photolysis techniques. Since the previously published studies[11-13] examined only ketones possessing lowest singlet and triplet n,$\pi^*$ states, it was of interest to see if phenyl alkyl ketones having lowest $^3\pi,\pi^*$ states exhibited the same behavior. Therefore, 4′-methoxypropiophenone (MeOP) and β-phenyl-4′-methoxypropiophenone (PMeOP) have also been studied. This submission is the first comprehensive outline of this work, preliminary results of which have appeared elsewhere.[14]

## Experimental Section

All solvents used were spectrophotometric grade. Benzene (Fisher) was further purified by refluxing over $P_2O_5$ followed by distillation. Acetonitrile (Aldrich Gold Label) was used as re-

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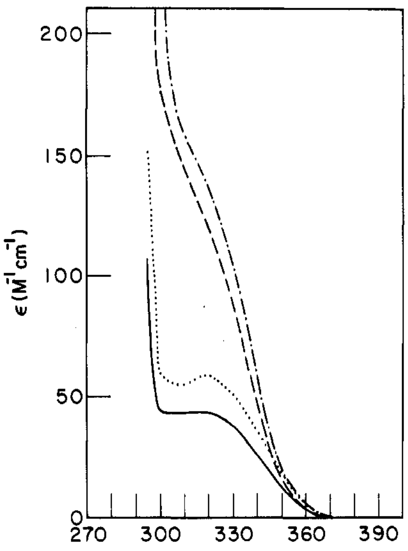

**Figure 1.** UV absorbance spectra of ketones in benzene solutions: (—) P; (···) PP; (---) MeOP; (-·-) PMeOP.

ceived. 2-Propanol (Fisher) was distilled prior to use.

Methylviologen ($MV^{2+}$) (1,1′-dimethyl-4,4′-dipyridinium dichloride), also referred to as paraquat, was obtained from Aldrich. It was further purified by recrystallization from warm ethanol and then dried at 70 °C.

Propiophenone (P) and 4′-methoxypropiophenone (MeOP) were Aldrich materials and were purified by distillation under reduced pressure, retaining only a small center cut. β-Phenylpropiophenone (PP) was synthesized according to literature[15] procedures. The intermediate chalcone was hydrogenated in ethyl acetate solution by using $PtO_2$ as catalyst. β-Phenyl-4′-methoxypropiophenone (PMeOP) was synthesized in the same way, the only difference being that methanol was found to be a better solvent for recrystallizing the chalcone. The final products were purified by multiple recrystallizations from warm methanol solutions. Structures were confirmed by UV, IR, and $^1H$ NMR spectra.

The purity of the four ketones was checked by HPLC using a reverse-phase μ Bondapak $C_{18}$ column (Waters Assoc.) with a mobile phase of 70% methanol and 30% triply distilled water. The flow rate was 1.0 mL $min^{-1}$ at an operating pressure of 1000 psi. The detector was a Vari-Chrom UV–vis variable-wavelength detector (Varian Instruments) set at either 290 or 320 nm, depending on the sample absorbance. No evidence for secondary products was seen in the chromatographs recorded for all four purified ketones.

UV absorbance spectra were obtained with a Cary 219 spectrophotometer.

Triplet lifetimes and transient absorbance spectra were measured by using the pulsed output of a Molectron UV-400 nitrogen laser (337.1 nm, 8 ns, 3 mJ) as the excitation source. Details of this apparatus have been previously described.[16] Solutions for these studies were contained in 3 mm path length, rectangular Suprasil quartz cells and, unless otherwise specified, were thoroughly purged with oxygen-free argon.

## Results

Absorption of the 337.1-nm light from a nitrogen laser by ground-state phenyl alkyl ketones results in the population of their $^1n,\pi^*$ states. Figure 1 shows the UV absorbance, in the region of interest, of the ketones in dilute benzene solutions. Molar decadic extinction coefficients at 320 nm are 43 and 121 for P and MeOP, respectively. For the analogous β-phenyl-substituted ketones PP and PMeOP, these increase slightly to 58 and 138, respectively. A similar effect for aliphatic ketones was reported by Whitten and Punch.[11] A blue shift of the maximum to 318 nm in the more polar solvent 2-propanol, is further evidence for an n–π* transition.

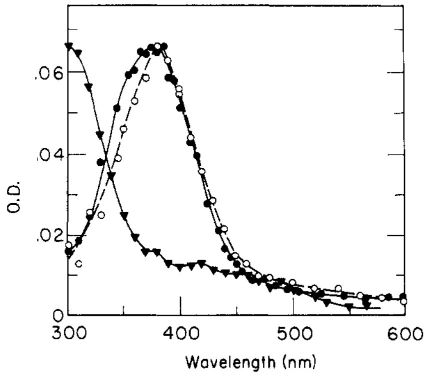

**Figure 2.** Transient absorbance spectra of ketones ($10^{-3}$ M) in deaerated benzene solutions: (▼) P; (●) MeOP; (○) PMeOP.

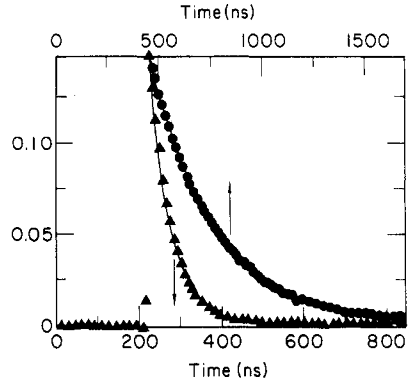

**Figure 3.** Decays of PMeOP triplets in deaerated solutions (note that arrows indicate appropriate time scale): (▲) in benzene; (●) in 2-propanol.

Laser excitation of PP in either benzene or 2-propanol solutions yielded no evidence for a sufficiently long-lived transient species (15–20 ns or longer) that could be observed via its absorbance in the 300–700-nm spectral range. Higher viscosity and/or hydrogen-bonding solvents such as Decalin and glycerol–2-propanol (1:1) were tried in an attempt to decrease the rate of internal rotation of PP to quenching configurations. Again, no transients were observed.

The other three ketones, P, MeOP, and PMeOP formed detectable transients. The spectra measured in dilute ($10^{-3}$ M) benzene solutions are shown in Figure 2. Exact reproducibility in the overlap between exciting and monitoring beams as well as in the laser pulse power was not possible on a day-to-day basis. The spectra, therefore, cannot be compared on the basis of their relative intensities and are shown in Figure 2 as being normalized to the peak height of P.

Lutz et al.[17] have reported the spectral differences in the triplet–triplet absorbances of phenyl alkyl ketones possessing either lowest $^3n,\pi^*$ or $^3\pi,\pi^*$ states. The former are characterized by a strong absorbance band having a maximum somewhere below 330 nm and by the presence of weaker bands at about 410 and 450 nm. Carbonyls having lowest $^3\pi,\pi^*$ states display a structureless spectrum with an intense maximum at around 350 nm. On this basis, the spectra in Figure 2 indicate that, in benzene solution, the lowest triplet of P is $^3n,\pi^*$ while MeOP and PMeOP have lowest $^3\pi,\pi^*$ states.

When the solvent was changed to either 2-propanol or $CH_3CN-H_2O$ (9:1), the transient spectra for P, recorded immediately after the laser flash, were red shifted from that shown in Figure 2. In these solvents a maximum was observed at 325 nm. Lutz

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TABLE I: Lifetimes and Quenching Constants[a] for $^3n,\pi^*$ Carbonyls

| solvent | $10^{-9}k_4$,[b] $M^{-1}\ s^{-1}$ | $k_4'\tau_3$,[c] $M^{-1}$ | $\tau_3$, ns | $10^{-9}k_4'$, $M^{-1}\ s^{-1}$ |
|---|---|---|---|---|
| Propiophenone (P) | | | | |
| benzene | 13.6 | 9840 | 2700[d] | 3.6 |
| $CH_3CN-H_2O$ | 20.1 | 5229 | 2500[d] | 2.1 |
| 2-propanol | | 1428 | 128[d] | 11.2 |
| β-Phenylpropiophenone (PP) | | | | |
| benzene | | 3.2 | 0.89[e] | |
| $CH_3CN-H_2O$ | | 3.5 | 1.67[e] | |
| 2-propanol | | 15.3 | 1.36[e] | |

[a] Using MeN as quencher. [b] Measured by using eq 7. [c] Measured by using eq 9. [d] Measured directly from decay of triplet absorbance in deaerated solutions. [e] Determined by using $k_4'$ values measured for P.

et al.[17] noted similar behavior for triplet acetophenone and ascribed it to an increase[1] in the $^3\pi,\pi^*$ character of the lowest triplet as solvent polarity increases. In 2-propanol, the spectrum for P measured 20 μs after the laser flash (a time much longer than the triplet lifetime, see below) was identical with that of the ketyl radical,[17] formed by hydrogen abstraction from solvent.

For both MeOP and PMeOP, a similar slight red shift of their transient absorbance spectra was observed on changing the solvent from benzene to 2-propanol or $CH_3CN-H_2O$ (9:1). Spectra measured in all three solvents at increasingly longer times following the laser pulse changed only in absolute intensity from those taken immediately after the flash and not in their shapes. No new absorbance band in any solvent or at any time interval following the laser flash was seen in PMeOP as compared to MeOP.

The decays of the transient in PMeOP, in deaerated benzene, and in 2-propanol solutions are shown in Figure 3. Traces obtained for P in benzene and $CH_3CN-H_2O$ (9:1) were similar except for the presence of a very small amount of a long-lived absorbance, due to a species which only slowly disappears on the time scale of the experiment. Its presence was independent of the intensity of the laser pulse. It has been previously ascribed[18] to a small amount of ketyl radical formed by hydrogen abstraction from solvent. In 2-propanol, which possesses a relatively easily abstractable hydrogen atom, this long-lived absorbance dominated the decay trace. Its lifetime was measured to be approximately 14 μs and from its absorbance spectrum (above) is clearly due to ketyl radical.

The transients for PMeOP in Figure 3 follow cleanly single exponential decays. Similar behavior was shown by MeOP. No evidence for a long-lived species was observed in the decays of either MeOP or PMeOP in the solvents benzene, 2-propanol, or $CH_3CN-H_2O$ (9:1). Since both ketones have lowest $^3\pi,\pi^*$ states (Figure 2) which are generally unreactive towards hydrogen abstraction reactions, this supports the above contention that the long-lived absorbance in the decay of the $^3n,\pi^*$ state of P is due to ketyl radical.

Assuming that the triplet states in deaerated solutions are depleted by two major processes, intersystem crossing back to the ground state and hydrogen abstraction (in the case of $n^3,\pi^*$ states) to form a long-lived ketyl radical, it is easily shown that the decay curves can be analyzed according to

$$\ln\left[(OD_t - OD_\infty)/(OD_0 - OD_\infty)\right] = -k_{\text{exptl}}t \qquad (1)$$

where $OD_0$, $OD_\infty$, and $OD_t$ refer to the optical densities of the solutions immediately after, at times long in comparison to the experimental time scale, and at some time $t$ following the laser pulse, respectively. The pseudo-first-order rate constant $k_{\text{exptl}}$ contains the relative contributions of both major depletion processes. Triplet lifetimes, $\tau_3$, obtained as the inverse of $k_{\text{exptl}}$ are listed in Table I for P and in Table II for MeOP and PMeOP.

Quenching of the carbonyl triplets was studied by using 1-methylnaphthalene (MeN). MeN is not directly excited by the 337.1-nm output of the laser. Its triplet state is much longer lived than are the carbonyl triplets and exhibits a strong absorbance at 425 nm. Since the relatively weak absorbance of the carbonyl triplets becomes rapidly overwhelmed by the $^3$MeN absorbance, quenching constants were determined by the rate of sensitization of the latter state.

TABLE II: Lifetimes and Quenching Constants[a] for $^3\pi,\pi^*$ Carbonyls

| solvent | $\tau_3$,[b] ns | $10^{-9}k_4$,[c] $M^{-1}\ s^{-1}$ |
|---|---|---|
| MeOP | | |
| benzene | 3500 | 20.0 |
| $CH_3CN-H_2O$ | 3400 | 6.1 |
| 2-propanol | 6500 | 5.5 |
| PMeOP | | |
| benzene | 50 | 10.8 |
| $CH_3CN-H_2O$ | 76 | 9.6 |
| 2-propanol | 290 | 2.8 |

[a] Using MeN as quencher. [b] Measured directly from decay of triplet absorbance in deaerated solutions. [c] Measured by using eq 10.

The sensitization of $^3$MeN by energy transfer from excited phenyl alkyl ketones in dilute fluid solution can be described by the following scheme, where K refers to ketone:

$$K + h\nu \rightarrow {}^1K \rightarrow {}^3K \qquad (2)$$

$$^3K \xrightarrow{k_3} K \qquad (3)$$

$$^3K + \text{MeN} \xrightarrow{k_4} K + {}^3\text{MeN} \qquad (4)$$

Equation 2 represents excitation into the first singlet state of K followed by rapid intersystem crossing to the lowest triplet state. Equation 3 is a composite of all reaction pathways depleting $^3$K in the absence of MeN and is given by the sum of $k_p$ (phosphorescence), $k_{isc}$ (intersystem crossing back to K), $k_q[O_2]$ (quenching by residual oxygen), and $k_s[S]$ (hydrogen abstraction from the solvent, S).

From the above scheme, it is easily shown that the concentration of $^3$MeN at any time $t$ following the laser pulse is given by

$$[^3\text{MeN}]_t = -(k_4[\text{MeN}]/(k_3 + k_4[\text{MeN}]))(\exp(-(k_3 + k_4[\text{MeN}])t) - 1) \qquad (5)$$

The ratio of rate constants in eq 5 is identified, by letting $t \rightarrow \infty$, as the maximum concentration, $[^3\text{MeN}]_\infty$, of triplet naphthalene that is formed. Since the optical density of the solution at any time $t$, $OD_t$, is directly proportional to $[^3\text{MeN}]_t$, eq 5 can be rewritten as

$$-\ln\left((OD_\infty - OD_t)/OD_\infty\right) = (k_3 + k_4[\text{MeN}])t \qquad (6)$$

Plots of the growth of $^3$MeN absorbance according to eq 6 yield straight lines with slopes $k_{\text{exptl}}$ given by

$$k_{\text{exptl}} = k_3 + k_4[\text{MeN}] \qquad (7)$$

Measurements of $k_{\text{exptl}}$ as a function of [MeN] then yield values for $k_4$, the rate constant for triplet carbonyl quenching by MeN.

Figure 4 shows the results for P in nondeaerated benzene and $CH_3CN-H_2O$ (9:1) solutions, plotted according to eq 7. Values of $k_4$, obtained from the slopes, are listed in Table I. The intercepts yield triplet lifetimes, in the absence of MeN, of 436 and 186 ns in benzene and $CH_3CN-H_2O$ (9:1), respectively. These are much reduced from the lifetimes measured directly in deaerated solutions (Table I) as a result of an enhanced $k_q[O_2]$ contribution in eq 3.

For PP, the growth of $^3$MeN absorbance to its $OD_\infty$ value was too fast to allow the application of eq 7. In this case, eq 5 reduces to

$$[^3\text{MeN}]_\infty^{-1} = 1 + (k_4'\tau_3[\text{MeN}])^{-1} \qquad (8)$$

where $\tau_3$ is the ketone lifetime in the absence of MeN and the

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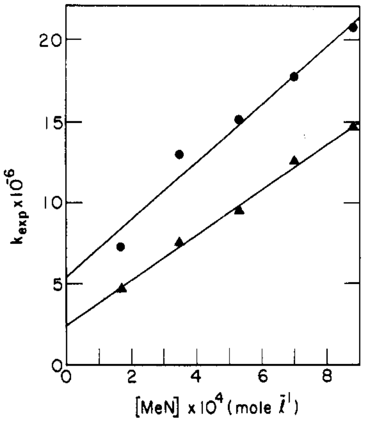

**Figure 4.** Quenching of triplet P by MeN according to eq 7: (●) in $CH_3CN-H_2O$ (9:1); (▲) in benzene.

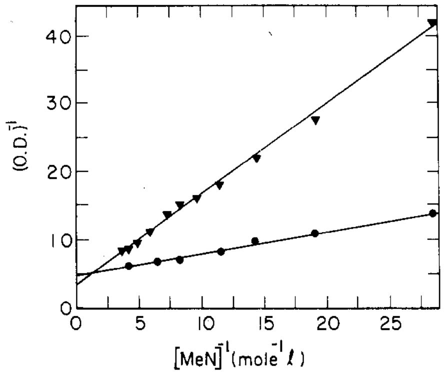

**Figure 5.** Quenching of triplet PP in deaerated solutions by MeN according to eq 9: (▼) in benzene; (●) in 2-propanol.

prime in $k_4'$ is used to distinguish this quenching constant from those determined by using eq 7. Again converting to optical densities

$$OD_\infty^{-1} = a + a(k_4'\tau_3[MeN])^{-1} \qquad (9)$$

where $a$ is a constant. The magnitude of $a$ does not need to be explicitly determined as $k_4'\tau_3$ is obtained from the intercept-to-slope ratio of plots of the maximum $^3$MeN absorbance following the laser flash vs. [MeN]. Eq 9 has been used by Bays et al.[19] to determine very short carbonyl lifetimes. Results for PP in benzene and in 2-propanol plotted according to eq 9 are shown in Figure 5.

Values of $k_4'\tau_3$ for PP are listed in Table I. In order to obtain estimates of $\tau_3$ for PP, values of $k_4'$ in the various solvents are required. These can, to a first approximation, be taken as equal to those determined for P in the same solvents, assuming the addition of a $\beta$-phenyl ring does not significantly alter the rates of material diffusion. Values of $k_4'$ for P determined by using eq 9 and the directly measured triplet lifetimes are also listed in Table I.

From Table I it can be seen that a considerable difference exists between $k_4$ and $k_4'$ measured in a given solvent. The magnitude of $k_4$, 13.6 × $10^9$ $M^{-1}$ $s^{-1}$, for P in benzene is close to the value of 11.1 × $10^9$ $M^{-1}$ $s^{-1}$ for a similarly sized molecule, valerophenone, quenched by MeN as determined by Faure et al.[20] using picosecond laser spectroscopy. Alternatively, the value of $k_4'$, 3.6 × $10^9$ $M^{-1}$ $s^{-1}$, is closer to the quenching constant of 5 × $10^9$ $M^{-1}$ $s^{-1}$ assumed by Wagner et al.,[12] based on early flash photolysis experiments.[21]

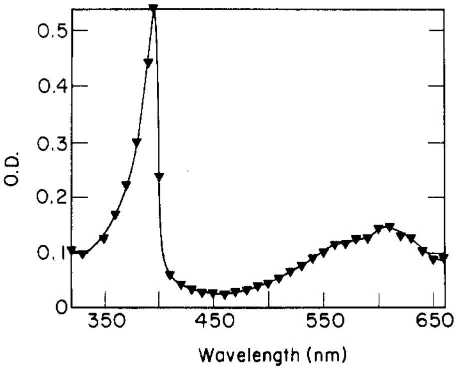

**Figure 6.** Transient absorbance spectrum for a solution of P (3.2 × $10^{-2}$ M) and $MV^{2+}$ (1.7 × $10^{-3}$ M) in deaerated $CH_3CN-H_2O$ (9:1), measured 250 ns after the laser flash.

While the primary source of error in the determination of quenching constants from both eq 7 and 9 lies in the absolute value of $OD_\infty$, eq 9 suffers from the added uncertainty of requiring an extrapolation back to zero quencher concentration to obtain the intercept value. This is particularly true when low ($10^{-3}$–$10^{-4}$ M) quencher concentrations are used, as is the case with long-lived donors. Therefore, it would seem likely that the $k_4$ values for P that are listed in Table I would more closely represent the true quenching constants. However, for the sake of experimental consistency, the values of $k_4'$ for P were used to estimate the triplet lifetimes, $\tau_3$, shown in Table I for PP. Regardless, the effect is minimal. The estimated triplet lifetime of PP in benzene decreases to 0.24 ns from 0.89 ns when $k_4$ is used instead of $k_4'$, still drastically reduced from the 2700-ns lifetime of P in benzene.

Table II contains the directly measured lifetimes of the $^3\pi,\pi^*$ states for the 4′-methoxy-substituted ketones MeOP and PMeOP, in deaerated solutions. Also listed are the rate constants, $k_4$, for the quenching of the triplets by MeN. These were determined by using $k_{exptl}$ measured from the triplet carbonyl decays as shown in eq 1 as

$$k_{exptl} = k_d + k_4[MeN] \qquad (10)$$

where $k_d$ is the inverse of the carbonyl triplet lifetime in the absence of MeN.

The above has concentrated on triplet energy transfer from the carbonyl donors to an acceptor, MeN. Das[10] has shown that electron transfer can also occur in the same direction if methylviologen ($MV^{2+}$) is used as the acceptor. It was thought to be of interest to examine what effect, if any, the $\beta$-phenyl ring has on this.

Figure 6 illustrates the transient absorbance spectrum for a solution of P (3.2 × $10^{-2}$ M) and $MV^{2+}$ (1.7 × $10^{-3}$ M) in $CH_3CN-H_2O$ (9:1). The spectrum was measured 250 ns after the laser flash and is identical with the known[22] spectrum of $MV^{+}\cdot$. Quenching constants were determined from the growth of $MV^{+}\cdot$ absorbance at 605 nm by using eq 6 and 7, where [$MV^{2+}$] replaces [MeN]. Direct measurements of the triplet decays in the presence of $MV^{2+}$ could not be carried out due to the very strong 395-nm absorbance band of $MV^{+}\cdot$.

Rate constants for the quenching of the triplet states of P, MeOP, and PMeOP by $MV^{2+}$ in $CH_3CN-H_2O$ (9:1) solutions were measured to be 5.5 × $10^9$, 8.8 × $10^9$, and 8.3 × $10^9$ $M^{-1}$ $s^{-1}$, respectively. A rate constant for PP as donor could not be measured as the extremely short triplet lifetime necessitated such high $MV^{2+}$ concentrations that solubility of the latter became a significant problem.

The rate of formation of $MV^{+}\cdot$ demonstrates that the triplet carbonyls are highly efficient as electron donors. The higher rate of quenching of MeOP and PMeOP as compared to P is a reflection[10] of the electron-releasing character of the 4′-methoxy groups. Equally important, it is seen that the $\beta$-phenyl ring has

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no effect on the ability of the triplet carbonyl to act as an electron donor, the rate constants for MeOP and PMeOP being identical within experimental error.

## Discussion

From Tables I and II, it can be seen that the presence of a β-phenyl ring has the effect of greatly reducing the carbonyl triplet lifetimes, regardless of their electronic configuration. For example, in benzene solutions, P and MeOP have $\tau_3$ values of 2700 and 3500 ns, respectively, and are reduced to 0.89 and 50 ns for PP and PMeOP, respectively.

The UV spectra shown in Figure 1 suggest that this effect is only significant for the carbonyl triplets, the ground to excited singlet state transitions being relatively unperturbed. In simple carbonyls such as formaldehyde, the symmetry-forbidden transition from the ground to the $^1$n,π* state becomes partially allowed due to coupling of the excited singlet state to a higher vibronic state possessing an assymetric $b_2$ vibration.[23] The latter represents a rocking vibration of the O atom out of the $CH_2$ plane. However, in nonsymmetric phenyl alkyl ketones, Shimada and Goodman[24] have proposed that an a″ vibration (in $C_s$ symmetry), consisting of torsional oscillations of the alkyl group, becomes the important contributor to the intensity-stealing mechanism. The slight increase in extinction coefficients with β-phenyl substitution as shown in Figure 1, is then probably due to an enhancement of the efficiency of this coupling with increasing bulkiness of the alkyl group.

There are a limited number of obvious candidates for the mechanism of triplet carbonyl quenching due to the β-phenyl ring. Of these, the possibility of intramolecular hydrogen abstraction can be most easily eliminated. First, the ketyl radical is distinguishable,[17] both in the spectral distribution of its absorbance spectrum and in its lifetime, from that of the $^3$π,π* state of phenyl alkyl ketones. Figure 2 shows no evidence for ketyl radical absorbance in PMeOP, the spectrum being identical with that of MeOP within experimental error. Similarly, the decays of MeOP and PMeOP in Figure 3 do not indicate the presence of a long-lived species, the disappearance of the triplet absorbance with time being cleanly single exponential. Second, Wagner et al.[25] have shown that the greatly favored transition state preceding intramolecular hydrogen abstraction is a six-membered ring in a torsional strain-free chair configuration. The only reasonable candidates for abstraction in PP and PMeOP are the β-hydrogens of the alkyl chain or the ortho hydrogens of the β-phenyl ring. This would necessitate the formation of much less favored[25] five- and seven-membered-ring intermediates, respectively, with a concomitant reduction in quenching efficiency. Third, while some ketones possessing lowest $^3$π,π* states are not necessarily totally unreactive toward hydrogen abstraction,[6] in general this process is less important[26] in $^3$π,π* than in $^3$n,π* carbonyls by factors of $10^{-4}$–$10^{-6}$. A small amount of reactivity is shown by the lowest $^3$π,π* states of 4′-methoxyphenyl alkyl ketones,[6] arising from either vibronic mixing or thermal population of the higher but energetically proximate $^3$n,π* state. However, this small amount of reactivity, particularly taken in conjunction with the necessity of five- or seven-membered-ring formation, cannot possibly account for the reduction (Table II) of triplet lifetimes from 3500 to 50 ns for MeOP and PMeOP in benzene solution, respectively. This is particularly true in the highly polar 2-propanol and $CH_3CN$–$H_2O$ (9:1) solutions, where the energy gap between the two triplets is expected to be 2100 cm$^{-1}$ or more.[27] Here, the vibronic interactions with or thermal population of the higher $^3$n,π* state is negligible.

A second candidate for the quenching mechanism involves the formation of a charge-transfer (CT) complex between the triplet carbonyl and the β-phenyl ring. CT complexes have become increasingly recognized[26] as intermediates in the interactions of ketone excited states with a variety of substrates. Since the proposal by Saltiel et al.[28] that the relatively short lifetime of benzophenone in benzene is due to quenching by solvent, this rationale has been extended[29,30] to carbonyl–aromatic hydrocarbon interactions in general. Recently, Wilson and Halpern have provided direct evidence for reversible exciplex formation between triplet acetone and benzene[31] and between triplet cyclohexanone and xylene.[32] Wagner et al.[12] have proposed that exciplex formation might well be the cause of the β-phenyl effect.

The CT concept received some early support from the report by Favaro[33] that, for a series of substituted benzophenones, electron-withdrawing substituents enhanced the rate of quenching by benzene. Conversely, electron-donating substituents decreased the rate. The carbonyl triplet lifetimes in Tables I and II indicate similar behavior.

In benzene solution, the ratio of the triplet lifetime (Table I) of P to PP is 3 × 10$^3$ while for MeOP and PMeOP (Table II) it is only 7 × 10$^1$. The triplet lifetimes of the simple ketones, P and MeOP, are given by

$$\tau_3 = (k_p + k_{isc} + k_q[O_2] + k_s[S])^{-1} \qquad (11)$$

where the rate constants are as defined for eq 3. For the ketones PP and PMeOP an additional term, $k_{int}$, must be included to account for the internal quenching:

$$\tau_3 = (k_p + k_{isc} + k_q[O_2] + k_s[S] + k_{int})^{-1} \qquad (12)$$

If the reasonable assumption is made that the β-phenyl ring does not alter the magnitudes of the rate constants common to eq 11 and 12, then $k_{int}$ can be determined by using both equations and the triplet lifetimes listed in Tables I and II. Values of $k_{int}$ for PP and PMeOP in benzene are found to be 1.1 × 10$^9$ and 2 × 10$^7$ s$^{-1}$, respectively. Thus, the internal quenching of the ketone triplet lifetime is considerably reduced when the carbonyl phenyl ring is substituted by an electron-donating methoxy group.

Despite the fact that the two phenyl rings in PP and PMeOP are separated by three carbons, thus ostensibly following the Hirayama rule[34] for efficient intramolecular excimer formation, the bond angles of 120° at the carbonyl carbon and tetrahedral angles of 109.5° at the β-carbon preclude configurations in which they form parallel sandwich structures. Simple molecular models show that, in mutual overlap configurations, the two phenyl rings are tilted in toward each other, resulting in considerable steric interactions at the para positions. Further, such configurations inevitably require loss of planarity (hence resonance stability) in the $COC_6H_5$ moiety. Therefore, the quenching interactions in PP and PMeOP must involve orbitals localized primarily on the carbonyl group with the system of the β-phenyl ring.

Wolf et al.[30] have proposed the formation of two possible exciplexes to rationalize the rate constants for the quenching of excited benzophenones by a variety of substituted benzenes. If the quencher is electron rich, the structure of the exciplex is such that its aromatic ring is perpendicular to the plane of the excited ketone and overlaps the half-vacant n orbital. This configuration was called exciplex **1**. The direction of charge-transfer is to form a $[K^{-}\cdots Q^{+}]^*$ complex. If the quencher is electron deficient, exciplex **2** was proposed, in which the benzene ring of the quencher lies parallel to and above the plane of the carbonyl, overlapping the half-filled π* state of $T_1$. In this case, the direction of charge transfer is to form a $[K^{+}\cdots Q^{-}]^*$ complex. These geometries parallel the rather elegant earlier results of Turro et al.,[35,36] who

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reported on the fluorescence quenching of alkanones by electron-rich and electron-deficient olefins.

Again, simple molecular models show that for PP and PMeOP, significant interactions between the carbonyl and the $\beta$-phenyl ring arise only from configurations corresponding to exciplex **1** and that these are easily arrived at. Further, the $\beta$-phenyl ring can be regarded as a mono-alkyl-substituted benzene, thus falling into the electron-donating class of quenchers acting preferentially[30] through an n-type exciplex **1** intermediate. This provides a basis for an understanding of the large (2 orders of magnitude) difference in internal quenching rate constants, $k_{int}$, between PP and PMeOP.

In PP, the lowest triplet is undoubtedly $^3n,\pi^*$. Quenching via the formation of a $[K^{-}\cdots Q^{+}]^*$ exciplex **1** intermediate is facilitated by the excellent overlap between the half-vacant, electrophilic n orbital on the carbonyl oxygen and the $\pi$ system of the $\beta$-phenyl ring. In PMeOP, however, the lowest triplet is $^3\pi,\pi^*$. In this case, the electronic transition from the ground state results in a net increase in the electron density about the carbonyl oxygen,[26] rendering it more nucleophilic than electrophilic. The likelihood of charge-transfer to it from the electron-rich $\beta$-phenyl ring would be decreased. Further, since internal bond angles reduce the significance of intramolecular configurations of the exciplex **2** type, only "edge-on" overlap, via the exciplex **1** conformer, occurs between the $\pi$ system of the $\beta$-phenyl ring and the half-vacant carbonyl $\pi^*$ orbital. This reduction in orbital overlap could quite easily account for the decrease in the rate of internal quenching, $k_{int}$, for PMeOP as compared to PP.

The formation of the triplet exciplex possessing a degree of charge transfer can be described as follows, where K and P refer to ketone and phenyl ring:

$$^3K-(CH_2)_2-P \underset{k_{-int}}{\overset{k_{int}}{\rightleftarrows}} {}^3[K^{-}-(CH_2)_2-P^{+}] \xrightarrow{k_r} K-(CH_2)_2-P \quad (13)$$

Since this is an intramolecular process, $k_{int}$ reflects rates of rotation about C–C bonds rather than material diffusion. For such a scheme, the time dependence of the triplet absorbance $A_K(t)$ can be described by

$$A_K(t) = C_1[\exp(-\lambda_1 t) + C_2 \exp(-\lambda_2 t)] \quad (14)$$

where $C_1$, $C_2$, $\lambda_1$, and $\lambda_2$ are constants.[37,38]

Equation 14 predicts that the triplet decays for PP and PMeOP should not be simple exponential. With PMeOP, Figure 3 shows that this is not the case within experimental accuracy. Also, donor decays following eq 14 would lead to nonlinear plots in the $^3$MeN sensitization studies, again contrary to observation. These contradictions are resolvable by assuming irreversible exciplex formation and that the exciplex is much shorter lived than the triplet.[30] While this has been demonstrated to be untrue for the quenching of some aliphatic ketone triplets,[31,32] there is no clear evidence to the contrary for aromatic ketones.

Wolf et al.[30] have shown that this leads to the condition that $\lambda_2 \gg \lambda_1$, resulting in the collapse of eq 14 to a single exponential expression containing a single time constant, $\lambda_1$, which can be approximately viewed as the triplet carbonyl lifetime. The single exponential decays of PMeOP and the linear sensitization plots do not necessarily, then, mitigate against an exciplex intermediate.

Such a mechanism, however, is not totally compatible with the results of this study. If the intramolecular quenching process involves an intermediate characterized by a degree of charge transfer, the rate of internal quenching, $k_{int}$, should increase with increasing solvent polarity. Values of $k_{int}$, calculated as above, are $0.6 \times 10^9$ and $1.3 \times 10^7$ s$^{-1}$ for PP and PMeOP, respectively, in $CH_3CN-H_2O$ (9:1) solution and are less than the values of $1.12 \times 10^9$ and $2 \times 10^7$ s$^{-1}$ determined for the less polar solvent, benzene. The much longer lifetime of 290 ns for PMeOP in 2-propanol is probably attributable to hydrogen bonding of the carbonyl with solvent, thereby reducing the ease of internal rotation to quenching configurations. A more extensive study, utilizing a variety of ring substituents, is required to resolve this seeming discrepancy. In the absence of any clear-cut evidence for alternative mechanisms, intramolecular exciplex (CT complex) formation remains the most probable candidate.

Finally, it is of interest to note that Wilson and Halpern[32] have demonstrated that energy transfer from triplet alkanone–alkylbenzene exciplexes can be as efficient as that from the uncomplexed ketone itself. There is no clear evidence that the systems studied in this report behave in a similar fashion. Unless the sensitization of $^3$MeN by the triplet ketones and their exciplex intermediates occurs with roughly identical Stern–Volmer constants, these studies should have yielded nonlinear plots, contrary to observation. Similarly, there is no evidence that the exciplex intermediates functions as electron donors in the reduction of $MV^{2+}$. The ionization potential of the exciplex should be greater than that of the free triplet ketone by an amount equal to the binding energy of the complex. This increase should then be reflected in a reduced rate of $MV^{+\cdot}$ formation with the exciplex as electron donor. Yet the rate constants for the reduction of $MV^{2+}$ were almost identical, being $8.8 \times 10^9$ and $8.3 \times 10^9$ M$^{-1}$ s$^{-1}$ for MeOP and PMeOP, respectively. In conjunction with the observed linearity of the $MV^{+\cdot}$ sensitization plots, this mitigates strongly against the likelihood of efficient electron transfer from the exciplex intermediate.

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**Registry No.** Propiophenone, 93-55-0; $\beta$-phenylpropiophenone, 1083-30-3; 4′-methoxypropiophenone, 121-97-1; $\beta$-phenyl-4′-methoxypropiophenone, 5739-38-8; 1-methylnaphthalene, 90-12-0; methylviologen, 1910-42-5.

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