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Electron Transfer Processes in the Photochemistry of β-(Dimethylamino)propiophenone

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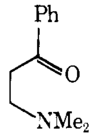
Abstract: The photochemistry of β-(dimethylamino)propiophenone has been examined in aqueous solvents using laser flash photolysis techniques. The triplet state decays via charge-transfer interactions which lead to intramolecular electron transfer and a product which is best described as a biradical zwitterion; the yield of biradical generation is 0.18 in aqueous methanol (1:4). The triplet decay is strongly pH dependent and is suggested to be preceded by deprotonation at pH values below pK_a. The lifetime of the nonprotonated triplet is short enough to prevent the complete establishment of the acid-base equilibria in the excited state. The triplet lifetimes are concentration dependent as a result of self-quenching. The biradical zwitterions produced in the triplet decay process can be trapped by a variety of electron acceptors, including 1,1′-dimethyl-4,4′-bipyridylium dications. From a study of the pH dependence of the trapping reaction we have determined the pK_a value of the biradical as 10.0. The biradical lifetimes are in the neighborhood of 1–2 μs, considerably longer than those derived from simple phenyl alkyl ketones.

Hydrogen abstraction and charge transfer interactions are common processes in the photochemistry of carbonyl compounds.[2] Both types of behavior can be observed in inter- and intramolecular reactions. In the limiting case charge transfer interactions lead to full electron transfer, and the transient products of reaction have occasionally been characterized.[3,4] In the case of intramolecular processes involving charge transfer, there is no conclusive evidence for a full electron transfer in the literature, although Padwa et al.[5] and Wagner et al.[6] have obtained clear evidence showing that charge transfer interactions are important in the photochemistry of aromatic amino ketones. We have examined the photochemistry of β-(dimethylamino)propiophenone (**1**) and its protonated form (**2**), with the aim of understanding the types of interactions involved.



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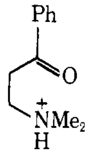

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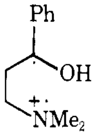
We found that electron transfer processes play an important role in the photochemistry of **1** and **2** in aqueous solvents. In turn the biradical zwitterions (**3** and **4**) produced in the triplet decay process can also undergo electron transfer reactions, to yield radical ions whose final fate is frequently controlled by electron transfer processes.



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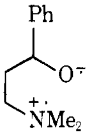

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We have chosen **1** for our study because it has no γ hydrogens and therefore intramolecular hydrogen abstraction is relatively unimportant. While the unimportance of permanent chemical change obviously eliminates an interesting dimension of the problem, it also facilitates the study of transient phenomena.

This paper reports a study of the photochemistry of **1** in aqueous solvents at room temperature. The behavior of the excited triplet state was found to be strongly dependent upon the characteristics of the media, particularly pH and ketone concentration. We have also examined the lifetime, trapping, and acid-base properties of **3** and **4** and compared them with those of simpler type II biradicals. From a study of the pH dependence of trapping reactions we have been able to measure the pK_a of **3**.

Results

UV irradiation of the hydrochloride of **1** in ice at 77 K leads to a strong phosphorescence with a lifetime of 72 ms. The lifetimes are strongly dependent upon the pH of the starting solution, as indicated in Table I. When the neutral form of **1** is irradiated under similar conditions in organic solvents the triplet lifetimes are considerably shorter, e.g., 1 ms in benzene. The long triplet lifetime observed in acid media is indicative of a π,π^* low-lying triplet, while the short lifetime in nonpolar solvents, e.g., benzene, can be due to either a low-lying $^3n,\pi^*$ state or intramolecular quenching by the amino group.[7]

Flash spectroscopic experiments show no evidence for photoreduction of **1** when it is irradiated in the presence of diphenylmethanol in methanol-water mixtures (8:2 mixture, monitoring at 535 nm and using **1**·HCl as a solute).[8] The absence of diphenylhydroxymethyl radicals is also consistent with the presence of a considerable degree of π,π^* character in the triplet state.

Most of the experiments described in this section have been carried out using the pulses (337.1 nm, ~3 mJ, 8 ns) from a nitrogen laser for excitation, and monitoring transient absorptions using a system with nanosecond response (see Experimental Section). The triplet state of the title compound can be easily observed in acid media (i.e., **2***) and led to a rather featureless spectrum shown in the insert in Figure 1.

The behavior of **1** is strongly dependent on acidity of the media and ketone concentration. These effects are illustrated in Figure 1 for three different values of pH, adjusted with 0.1 M phosphate buffers. We have observed that the triplet lifetimes show a small dependence with the buffer concentration. This difference is also present in the limit of very low ketone concentrations; unfortunately, under these conditions the measurements become very difficult owing to the weak signals involved. For example, when the concentration of the buffer consisting of equal parts of $H_2PO_4^-$:HPO_4^{2-} is changed from 0.22 to 0.024 M the rate of triplet decay decreases by 22% for a concentration of **1** of 0.005 M (pH 5.8).

From the slope in Figure 1, we obtain the rate of self-quenching as $k_{sq} = 2.6 \times 10^7$ M^{-1} s^{-1} in water at pH 2.8, the value being only slightly dependent on the pH in the range of 2.0–7.2; see Table II. For comparison, under similar conditions the rate of quenching by triethylamine (Et_3N^+H) is $k_q \leq 4 \times 10^6$ M^{-1} s^{-1}.

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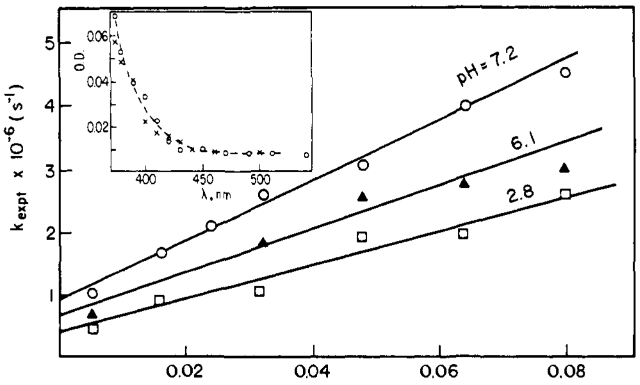


Figure 1. Dependence of the rate of triplet decay upon pH and ketone concentration. Insert: transient spectra observed by irradiation of β-(dimethylamino)propiophenone, (○) pH 2.3, (x) pH 8.0.

Table I. Phosphorescence Data for **1** at 77 K[a]

solvent	pH[b]	τ_p, ms
water	2.0	340
water	6.3	72
water	11.5	37
methanol-water (4:1)		149
methanol-water (4:1)	NaOH (0.1 M)	128
acetonitrile-water (4:1)		106
benzene[c]		1.0
$CHCl_3$[c]		7.0

[a] The phosphorescence spectra are usually very well resolved (C=O stretching and overtones) in basic solution or in organic solvents. Under these conditions the 0,0 band can be characterized; for example, in chloroform $\lambda(0,0) = 402.2$ nm, which gives $E_T = 71.1$ kcal/mol. In acid solution we observe a red shift, and, in the case of **1**·HCl in water, if we assume a similar C=O stretching (the band is not well resolved), we estimate $E_T \simeq 67$ kcal/mol. [b] Initial pH, at room temperature, usually using phosphate buffers. [c] Neutral form of **1**.

Experiments in D_2O showed no isotope effect on k_{sq} or the triplet lifetime extrapolated to zero ketone concentration. The hydrochloride of **1** was used in all the experiments; in order to establish which fraction of the quenching could be attributed to chloride ions, we carried out a series of experiments with NaCl as a quencher. We found that for chloride ions $k_q = 7 \times 10^5$ M^{-1} s^{-1}.

The pK_a of **1**–**2** was measured from the titration curve as 9.3. The value is reasonable in view of those reported for other tertiary amines.[9]

The triplet decay traces obtained in the flash experiments follow clean first-order kinetics, and can be quenched by typical triplet quenchers, e.g., *cis*-1,3-pentadiene. Unfortunately, these experiments cannot be carried out in pure water because of the insolubility of the diene and had to be carried out in methanol-water mixtures. The triplet lifetimes are essentially identical in both solvents. Figure 2 shows a plot of $\tau^{-1} - \tau_0^{-1}$ vs. the concentration of diene, where τ and τ_0 are the triplet lifetimes in the presence and absence of quencher. The insert in Figure 2 shows a typical triplet decay trace.[10] From the plot in Figure 2 we obtain a rate constant for quenching of 8.2×10^9 M^{-1} s^{-1}, which is close to the diffusion-controlled limit, and supports the assignment of the species observed (see Figure 1) as the triplet state. Similarly, in wet acetonitrile we obtain $k_q = 10.5 \times 10^9$ M^{-1} s^{-1}. Further confirmation for this assignment was obtained in experiments in which the cis–trans isomerization of 1,3-pentadiene was sensitized by **1**. From plots of Φ_{isom}^{-1} vs. $[\text{diene}]^{-1}$ we obtain values of $k_q\tau$ in agreement with those measured in the flash experiments.

We have also observed that 2,5-dinitrobenzoic acid is a very efficient triplet quencher. Flash experiments similar to those with *cis*-1,3-pentadiene led to the value of k_q given in Table II. 2,5-Dinitrobenzoic acid is fairly soluble in water, a property which could make it a useful quencher in aqueous media.

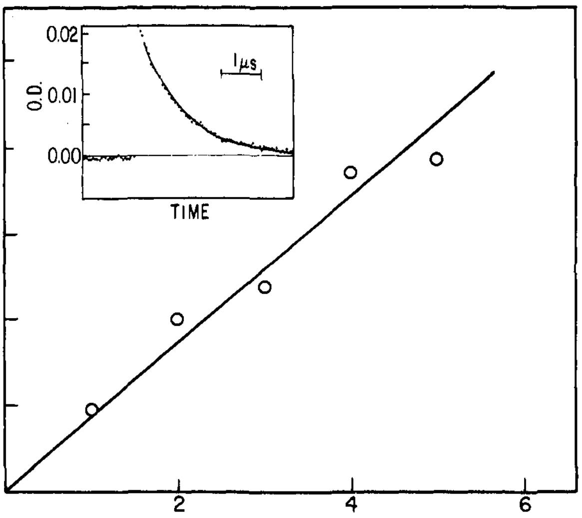


Figure 2. Triplet quenching by *cis*-1,3-pentadiene. Insert: typical triplet decay trace.

Table II. Kinetic Data for the Quenching of the Triplet State

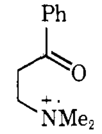
substrate	solvent	pH	$k_q \times 10^{-7}$/ M^{-1} s^{-1}
2	water	7.2	4.7
2	water	6.1	3.4
2	water	4.5	2.7
2	water	2.8	2.6
2	water	2.2	3.2
2,5-dinitrobenzoic acid	water	7.2	330
triethylamine	water	4.5	≤0.4
cis-1,3-pentadiene	acetonitrile–water (4:1)	(HOAc[a] 0.1 M)	1050
cis-1,3-pentadiene	methanol–water (4:1)		820
chloride	water	4.5	0.07

[a] Acetic acid.

We have examined the quantum yield of intersystem crossing of **1** in methanol-water mixtures (4:1) containing sodium hydroxide (0.1 M) or acetic acid (0.1 M) by comparing the yield of sensitization of the cis–trans isomerization of 1,3-pentadiene by **1** and by acetophenone under conditions of total quenching.[11] Both values are within experimental error one.

The decay of **1*** leads to the generation of **4** with moderate yields (vide infra). At pH values below the pK_a of the biradical, **4** will protonate significantly to give **3**.

Our results on the behavior and lifetimes of **3** and **4** have been obtained from the study of electron transfer processes using nanosecond flash photolysis techniques. In this approach the biradical B transfers an electron to an acceptor A to give $A^{-\cdot}$ and the oxidized form of B, **5**, according to reaction 1. The



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$$B + A \xrightarrow{k_1} A^{-\cdot} + \mathbf{5} + (H^+) \qquad (1)$$

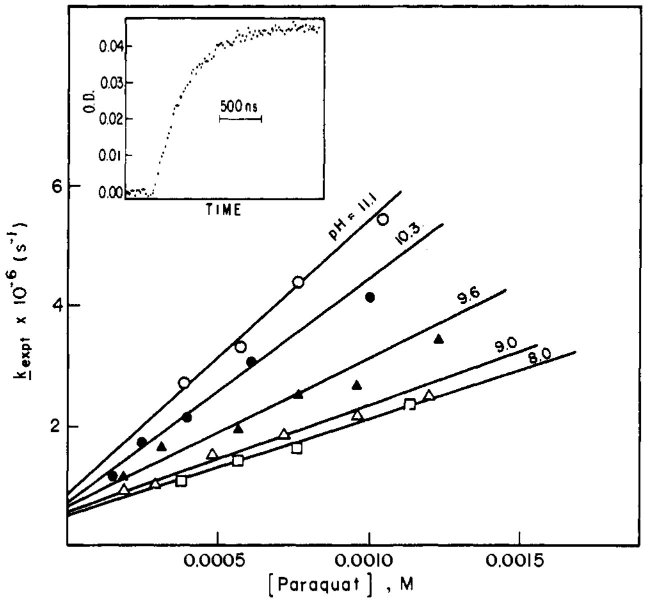


Figure 3. Biradical trapping by paraquat dication in water at various pH values. Insert: absorbance vs. time profile for $[PQ^{2+}] = 0.0012$ M at pH 9.0.

proton will be a product of reaction only when **3** is the precursor.

In this type of study the critical assumption is made that the formation of B is a fast process compared with its decay.[12] Several conditions have to be fulfilled in order for this assumption to be valid; those which are related to the laser photolysis system have been discussed elsewhere[12] and only those related to the chemical system involved are discussed here. The essential condition is that the triplet lifetime has to be short compared with the biradical lifetime. Since the triplet state can be detected directly in solution, it becomes straightforward to determine whether this criteria is met. Such is the case at pH ≥7.5. In a few experiments at lower pH values it was necessary to shorten the triplet lifetime using suitable triplet quenchers, in particular *cis*-1,3-pentadiene when aqueous methanol is used as the solvent.[13] Typical diene concentrations were in the neighborhood of 2×10^{-3} M, which lead to formal triplet lifetimes of less than 60 ns. While this technique leads to convenient triplet lifetimes, it also causes the quantum yield of biradical formation to decrease accordingly.[14] As a result of this decrease in yield (and therefore in signal), it was necessary to use computer averaging techniques in those experiments.

The insert in Figure 3 shows a typical trace corresponding to the formation of the paraquat radical cation ($PQ^{+}\cdot$) from paraquat dication (1,1′-dimethyl-4,4′-bipyridylium, PQ^{2+}). Kinetic analysis of these traces using eq 2 leads to k_{expt}, the pseudo-first-order rate constant. A_∞ and A are the optical densities in the "plateau" region and at time τ, respectively.[12]

$$\ln \frac{A_\infty}{A_\infty - A} = k_{expt}t \qquad (2)$$

The biradical lifetime, τ_B, and k_1 can be evaluated from the values of k_{expt} according to eq 3 and Figure 3.[14]

$$k_{expt} = \tau_B{}^{-1} + k_1[A] \qquad (3)$$

τ_B is only slightly dependent on the pH (note the intercepts in Figure 3), but a rather marked effect is observed in the case of k_1. The change in k_1 presumably reflects the acid-base equilibria between the two biradical forms, **3** and **4**. Figure 4 shows a plot of k_1 vs. the pH, from which a pK_a value of 10.0 can be derived for the biradical. The lifetime of **3** in water is 2.0 μs, and that of **4** 1.2 μs, and both are independent of buffer concentration.

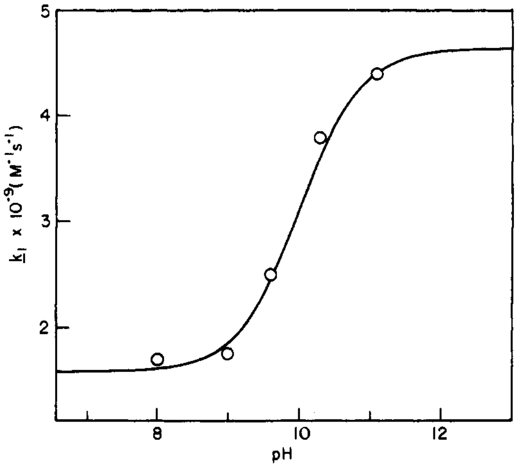


Figure 4. pH dependence of k_1 for paraquat dications in water. The computer fit shown corresponds to pK_a = 10.0 and limiting rate values of 1.58×10^9 (acid) and 4.6×10^9 M^{-1} s^{-1} (base).

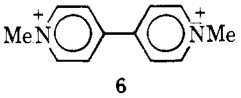
The biradical lifetimes were also measured in aqueous methanol containing acids or bases. These results and the values of k_1 are summarized in Table III.

The quantum yield of biradical production can be derived from a comparison of the plateau absorbances (see insert in Figure 3) in matched samples containing a constant concentration of paraquat radical ions and β-(dimethylamino)propiophenone or γ-methylvalerophenone; the latter is known to give a quantum yield of biradical production of 1.0.[15] The plateau absorbances and the corresponding quantum yields of biradical formation, ϕ_B, are related by

$$\frac{A_\infty}{A_\infty{}^s} = \frac{\phi_B}{\phi_B{}^s}\,\frac{k_1}{k_1{}^s}\,\frac{(\tau_B{}^s)^{-1} + k_1{}^s[PQ^{2+}]}{\tau_B{}^{-1} + k_1[PQ^{2+}]} \qquad (4)$$

The superscript "s" in eq 4 refers to a standard reference for which ϕ_B, τ_B, and k_1 are known, γ-methylvalerophenone being used for this purpose.[12] When the concentration of paraquat dications is large enough to trap the majority of the biradicals the rate expressions on the right-hand side term of eq 4 (after the term $\phi_B/\phi_B{}^s$) approach unity and minimize the effect of errors in the values of τ_B and k_1. From a study of this type we obtain $\phi_B = 0.18$ in water-methanol (1:4) containing 0.1 M sodium acetate. The number could be subject to up to 30% error, since the measurement of absolute yields of transients is always a difficult problem.

In addition to paraquat dications (**6**) a number of other substrates, **7–10**, are also efficient scavengers of **3** and **4**.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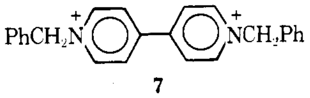
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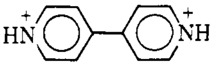
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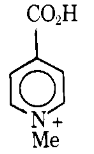
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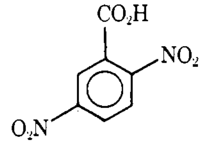
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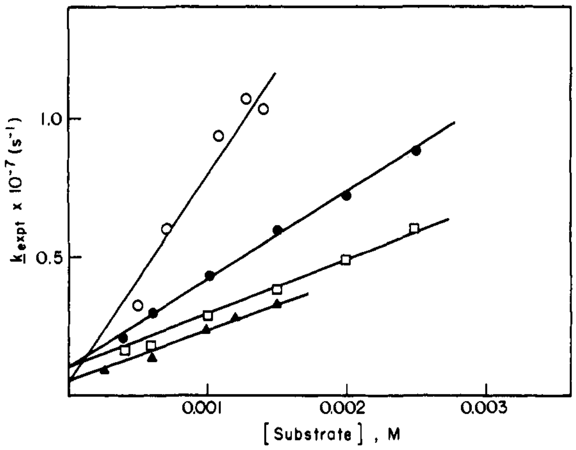


Figure 5. Plot for k_{expt} vs. the concentration of substrate for (○) **8** in methanol-water (4:1) containing 0.1 M acetic acid; (●) **10** in methanol-water (4:1) containing 0.1 M sodium hydroxide; (□) **9**, same solvent; (▲) **7** in methanol-water (4:1) containing 0.1 M sodium acetate.

Table III. Biradical Lifetimes and Kinetics of the Trapping by Paraquat

solvent	pH	τ_B, μs	$k_t \times 10^{-9}$, $M^{-1} s^{-1}$
water	11.1	1.2	4.7
water	10.3	1.4	3.8
water	9.6	1.5	2.5
water	9.0	1.8	1.8
water	8.0	2.0	1.7
methanol-water (4:1)	HOAc (0.1 M)[a]	2.6	0.9
methanol-water (4:1)		2.3	0.96
methanol-water (4:1)	NaOAc (0.1 M)[b]	2.1	2.0

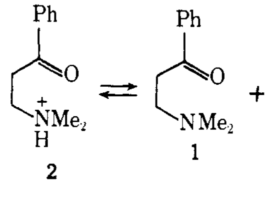
[a] Acetic acid. [b] Sodium acetate.

A few other examples of plots of k_{expt} vs. [acceptor] are shown in Figure 5, and Table IV gives a summary of kinetic results. These experiments were carried out under conditions where the triplet lifetime can be neglected in comparison with the biradical lifetime. Comparable lifetimes tend to introduce errors in the kinetics analysis, while long-lived triplets can participate in other reactions with the substrates.[16]

β-(Dimethylamino)propiophenone is essentially photostable in acid solutions in the absence of biradical traps. In the presence of bases some chemical change occurs, as indicated by the slow consumption of the parent ketone and the yellowish coloration of the solutions. The quantum yield of consumption of **1** is less than 0.03. This aspect of the problem was not pursued any further, though it is clear that permanent chemical change is a minor process under our experimental conditions and need not be considered as important in the interpretation of transient phenomena. Even in the presence of biradical traps (i.e., electron acceptors), the main reaction path is frequently the disproportionation of the radicals and radical ions to yield the starting materials.

Discussion

Most of the experiments discussed in this paper have been carried out under conditions where the acid-base equilibrium of reaction 5 is largely displaced toward the protonated form, **2**.



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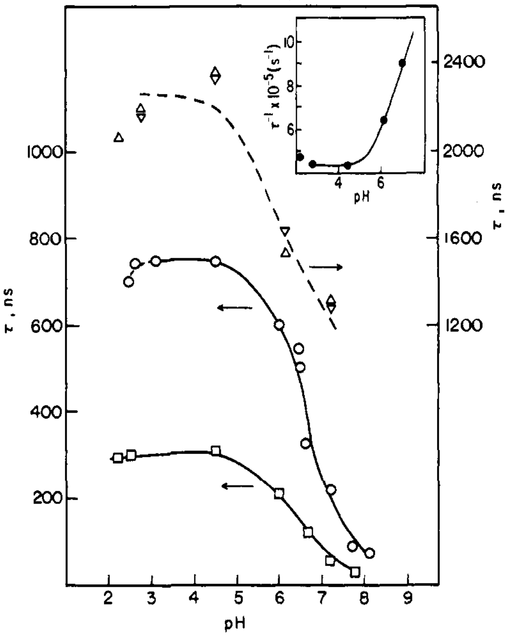


Figure 6. Dependence of the triplet lifetimes on the pH: (□) 0.1 M; (○) 0.025 M; (▽) 0.005 M; (△) extrapolated to zero concentration. Insert: rates of triplet decay extrapolated to zero concentration.

Table IV. Summary of Kinetic Results for Biradical Trapping Processes

substrate	solvent	pH	τ_B, μs	$k_t \times 10^{-9}$, $M^{-1} s^{-1}$
7	water	11.1	1.2	3.6
7	water	8.0	2.0	1.4
7	methanol-water (4:1)	NaOAc[a] (0.1 M)	2.1	2.0
8	methanol-water (4:1)	HOAc[b] (0.1 M)	2.6	7.5
9	methanol-water (4:1)	NaOH (0.1 M)	1.0	1.9
10	methanol-water (4:1)	NaOH (0.1 M)	1.0	3.2
10	water	11.1	1.2	3.6

[a] Sodium acetate. [b] Acetic acid.

Luminescence spectra recorded at 77 K (Table I) are indicative of a low-lying π,π* triplet under our experimental conditions. Further support for this conclusion comes from the absence of photoreduction in the presence of diphenylmethanol; by contrast, Wagner[6] has proposed that γ-(dimethylamino)butyrophenone undergoes considerable photoreduction in methanol suggesting that in pure organic solvents amino ketones can have low-lying n,π* states. The short phosphorescence lifetimes observed (see also ref 5) are consistent with this suggestion.

The trapping of **3** and **4** by electron acceptors unequivocally shows that the decay of the triplet state involves the reduction of the keto group to either a ketyl radical or a keto radical anion moiety. The efficiency of full electron transfer is considerably less than unity, 0.18 in the system examined. This inefficiency suggests that the initial charge-transfer interactions can either proceed to products or result in energy wasting. Similar mechanisms are common in intermolecular processes.[2]

An interesting question is whether the triplet state can abstract an electron from the protonated amino group, and if this is the mechanism of triplet decay. Apparently the reaction does not take place intermolecularly with measurable efficiency (see, for example, the case of triethylamine in Table II).[18] We believe that triplet decay leading to **3** and **4** must occur by an alternative mechanism. The possibility of a decay involving a simple abstraction of the hydrogen on the nitrogen atom would lead to a significant deuterium isotope effect; as pointed out above this is not the case. Therefore, we conclude that triplet decay does not involve hydrogen abstraction as an important reaction path. The absence of photoreduction in the presence of diphenylmethanol is also consistent with this conclusion.

Another possibility would be to explain both the intramolecular decay and the intermolecular self-quenching as arising from the nonprotonated amine in equilibrium with the protonated form. This type of mechanism would be expected to lead to an almost constant triplet lifetime from the very acid limit to around 1 or 2 pH units below the pK_a of the amino ketone. Figure 6, calculated from Figure 1 and similar experiments, clearly shows that this is not the case. If we assume that the amino groups in the ground and triplet state have similar pK_a values, then significant changes occur around 4 pH units below pK_a. In addition, if self-quenching took place by this mechanism the slopes in Figure 1 would be inversely proportional to the hydrogen ion concentration. Further, buffer concentration has been shown to have an effect on the triplet lifetimes, an effect which cannot be predicted by an equilibrium model. Examination of the insert in Figure 6 shows that the triplet lifetime of the nonprotonated amino ketone must be extremely short. Similar conclusions have also been reported by Wagner[6] and Padwa[5] in the case of other amino ketones. We propose that the short triplet lifetime of **1** prevents the establishment of an acid-base equilibrium between **1*** and **2***. The decay of **2*** is then controlled mainly by the rate of deprotonation (k_d), i.e.:

$$\begin{tikzcd}
\mathbf{2}^* \arrow[r, shift left, "k_d"] \arrow[d, "?"'] & \mathbf{1}^* \arrow[l, shift left, "k_p"] \arrow[d, "k_r"] \\
\mathbf{3} \arrow[r, shift left, "pK_a"] & \mathbf{4} \arrow[l, shift left]
\end{tikzcd}$$

The acid-base equilibrium between **1*** and **2*** will usually be approached by protonation and deprotonation reactions which can involve a variety of ions present in the system. The value of k_d will be largely determined by the concentration of potential proton acceptors (Z^-) in the system, i.e.

$$\mathbf{2}^* + Z^- \xrightarrow{k_Z} \mathbf{1}^* + ZH \tag{6}$$

$$k_d = \sum_i (k_Z)_i[Z^-]_i \tag{7}$$

All the anions present in the system can potentially serve as Z^-, with OH^- and the various phosphate ions as the most important ones. This is probably the reason for the small dependence of the triplet lifetimes on buffer concentration. A similarly complex expression is also expected for the protonation reaction.

The mechanism suggested above resembles in many ways that proposed by Wagner and Chen[20] for the photoenolization of *o*-methylacetophenone, where the disappearance of a long-lived triplet state is controlled by bond rotations which lead to the reactive triplet. While the nature of the changes involved in our system is different, the basic idea is the same: the decay of a long-lived triplet being mainly controlled by the rate of its interconversion into the reactive species.

We turn now to the lifetime and properties of the biradicals **3** and **4**. Attempts to detect these transients directly have so far been unsuccessful. We attribute this to the combination of several factors. (1) The yield of biradical generation is substantially lower than one. In the example measured, only one out of every six triplets gives biradicals. (2) In order to avoid triplet self-quenching the concentration of ketone was kept rather low, resulting in only partial absorption of the excitation beam. (3) Under some of our experimental conditions we had to add quenchers in order to shorten the triplet lifetime (acid media), while, in the presence of strong base, **4** rather than **3** is the predominant form of the biradical. The keto anion chromophore might have weaker absorption bands than the ketyl radical.

The lifetimes measured are only slightly sensitive to the acid-base properties of the media (Table IV). In general the lifetime decreases as the pH increases, suggesting that the internal disproportionation of **4** is somewhat faster than that of **3**. The values of τ_B are surprisingly longer than those measured for simpler ketones, e.g., γ-methylvalerophenone. In recent publications, we have reported evidence supporting the fact that the values of τ_B for biradicals derived from phenyl alkyl ketones are controlled by intersystem crossing.[12] While it is conceivable that the same ideas apply here, it is also clear that their applicability should not be taken for granted. Whether the lifetimes are controlled by spin inversion or by chemical factors is not clear, but it is noteworthy that biradical decay is surprisingly slow.

The value of 10.0 for the pK_a (Figure 4) represents the first measurement of a pK_a value for a biradical; it is quite similar to those for ketyl radicals, e.g. $CH_3\dot{C}(OH)Ph$,[21] suggesting that the interaction between biradical ends is weak enough to make the acid-base properties of the ketyl group indifferent to the presence of a second radical site in the molecule. Similar conclusions have been reached in an earlier study of the absorption characteristics of the ketyl chromophore in the biradical from γ-methylvalerophenone.[22]

The intermolecular reactivity shown by the biradicals from β-(dimethylamino)propiophenone is somewhat different than that shown by the biradical from γ-methylvalerophenone (**11**).[12,23] For example, **11** reacts faster than **3** with paraquat dication (**6**), while in the cases of **8**, **9**, and **10** the reactions of the biradicals examined in this paper are faster. It seems apparent that, as the positive charge on the electron acceptor decreases, or even becomes negative, the reactivity favors the biradicals from β-(dimethylamino)propiophenone. We note that **8** can deprotonate partially or totally under basic conditions.

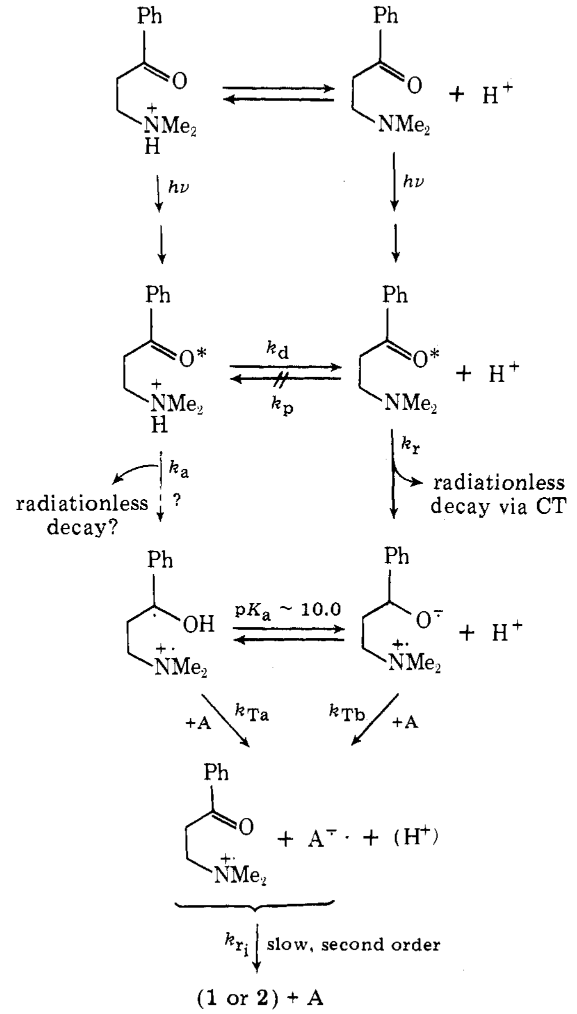
Scheme I shows the processes which we propose are involved in the photochemistry of β-(dimethylamino)propiophenone in aqueous solvents. Only the process of self-quenching has been omitted; unfortunately, the molecular interactions involved in this reaction are not clear yet. The rate constants k_{Tb} and k_{Ta} refer to the trapping of the basic and acid biradical species. The radical ions produced in the trapping step frequently disproportionate (k_{ri}) to give the starting materials. The reaction is slow only in the sense that the decay of $A^-\cdot$ is an unimportant process in the time scale of its formation (flat plateaus are observed in studies of the buildup of $A^-\cdot$). Typical rates of disproportionation (with bipyridilium derivatives) are in the 10^8-10^9 M^{-1} s^{-1} range.

Finally, we thought that it could be possible to trap the amino radical cation site in **3** and **4** using electron donors. For example, diphenylamine could be expected to be a good donor and lead to the easily detectable[24] $Ph_2NH^+\cdot$ (**12**). While our experiments always gave small yields of **12**, we were unable to eliminate contributions resulting from electron abstraction by the excited triplet, and any conclusion would be highly speculative.

Conclusion

The triplet state of β-(dimethylamino)propiophenone decays via charge transfer interactions which lead to full electron transfer with moderate yields. The decay of the nonprotonated triplet (**1***) is extremely rapid, probably in the subnanosecond time scale. The protonated triplet, **2***, usually decays by deprotonation leading to **1***. The triplet state has substantial π,π^*

Scheme I



character in hydroxylic solvents; its decay is strongly pH and concentration dependent; the latter is the result of efficient self-quenching. The biradical intermediates have a pK_a of 10.0 and are very efficient electron donors. The rates of electron transfer are pH dependent, reflecting the different donor abilities of the acid and basic forms of the ketyl chromophore. The radical ions produced in the trapping reaction can decay via disproportionation (and frequently do) which generates the starting materials. As a result, the abundant transient phenomena which occur in the photochemistry in the presence of electron acceptors lead to systems which are frequently quite photostable.

The relative importance of full electron transfer is likely to decrease as the solvent becomes less polar and is probably unimportant in nonhydroxylic organic solvents.

Experimental Section

Materials. β-(Dimethylamino)propiophenone hydrochloride (Aldrich) was treated with aqueous sodium hydroxide, extracted with benzene, and reprecipitated by bubbling hydrogen chloride. Repetition of this procedure did not affect the triplet lifetimes.

2,5-Dinitrobenzoic acid (K&K), paraquat dichloride (K&K), 4,4′-bipyridyl dihydrochloride (Aldrich), benzyl viologen (K&K), and 4-carboxymethylpyridinium chloride (Aldrich) were all recrystallized prior to use.

Methanol and acetonitrile were Aldrich Gold Label products. *cis*-1,3-Pentadiene was from K&K. Water was either triple distilled or taken from a Milli-RO15 Millipore filtering system. The different phosphates used for buffer preparation were all Baker Certified products. Triethylamine (Eastman) was distilled prior to use and diphenylmethanol (Aldrich) was sublimed twice.

Laser Photolysis. The system used was the same one described previously.[12,23] The last experiments were carried out using computer averaging techniques and employing a Tektronix R7912 transient digitizer for data acquisition. Full details on the computerized laser photolysis facility will be reported elsewhere.[25]

The reduced forms of all the electron acceptors used show absorption maxima in the 380–600-nm region, and in each case a convenient band was chosen in order to monitor transient absorptions; however, a detailed spectroscopic study was also carried out and showed that the spectra of the different $A^{-}\cdot$ were in good agreement with those previously reported.[26]

Spectroscopy. Luminescence spectra were obtained in an Aminco-Bowman spectrofluorimeter. UV-vis spectra were recorded in a Cary 14 spectrophotometer. NMR spectra were recorded in a Varian A-60A or XL-100 instrument; examination of fresh and irradiated samples in D_2O did not show evidence for consumption.

Phosphorescence Lifetimes. These were measured using a right-angle arrangement of flash lamp, a suitable filter, the sample, a Bausch and Lomb high-intensity monochromator, and a 1P28 photomultiplier tube terminated into 2000 Ω. A cutoff filter (λ <360 nm) was used in front of the excitation source.

Quantum Yields. Experiments where the consumption of the parent ketone was monitored were carried out in a merry-go-round fitted in a Rayonet reactor equipped with 16 RPR-3500 lamps. In all cases the samples were contained in matched tubes made of precision bore tubing (i.d. 0.2500 ± 0.0002 in., made of Corning 7740 glass, Laboratory Crest Scientific) and were degassed by three freeze-pump-thaw cycles to a residual pressure of ca. 10^{-5} Torr. Gas chromatography (Beckman GC-5 with f.i. detector) did not show evidence for significant yields of new products. The yields of cis-trans isomerization of 1,3-pentadiene were monitored by gas chromatography using a column of β,β′-oxydipropionitrile on Chromosorb G and using acetophenone (matched absorbance) as a standard with $\phi_{ISC} = 1$. These experiments were carried out at 313 nm using as light source a Bausch and Lomb 200-W high-pressure mercury lamp and a high-intensity monochromator. A merry-go-round was used to ensure that all the samples received the same radiation dose.

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Photopolymerization in Chiral Crystals. 3.[1] Toward an "Absolute" Asymmetric Synthesis of Optically Active Dimers and Polymers with Quantitative Enantiomeric Yield

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Abstract: An "absolute" asymmetric synthesis of chiral dimers and polymers of variable optical yield and an asymmetric synthesis with quantitative enantiomeric yield starting from a monomer of low optical purity are described. Irradiation of polycrystalline ethyl 2-cyano-3-(*p*-*sec*-butyl-3′-(*E*)-propenoate)phenyl(*E*)-propenoate (**1**) of 60% optical purity or above leads to the formation of chiral dimers and oligomers with quantitative enantiomeric yield. Carefully crystallized samples of **1** of 22–60% optical purity lead to enantiomeric excesses of 90% or above. Racemic **1** crystallizes from the melt either in the form of a stable eutectic mixture or in the form of an isomorphous, chiral, metastable phase of different microcomposition. A method for the characterization of the two phases, based on photodimerization and NMR analysis of the diastereomeric dimers, is described. Irradiation of samples of the chiral metastable phase with one enantiomorphous crystal form in excess leads to an "absolute" asymmetric synthesis with variable optical yield, of both signs. Possible routes to the achievement of an "absolute" asymmetric synthesis with quantitative enantiomeric yield, in systems related to **1**, are discussed.

Introduction

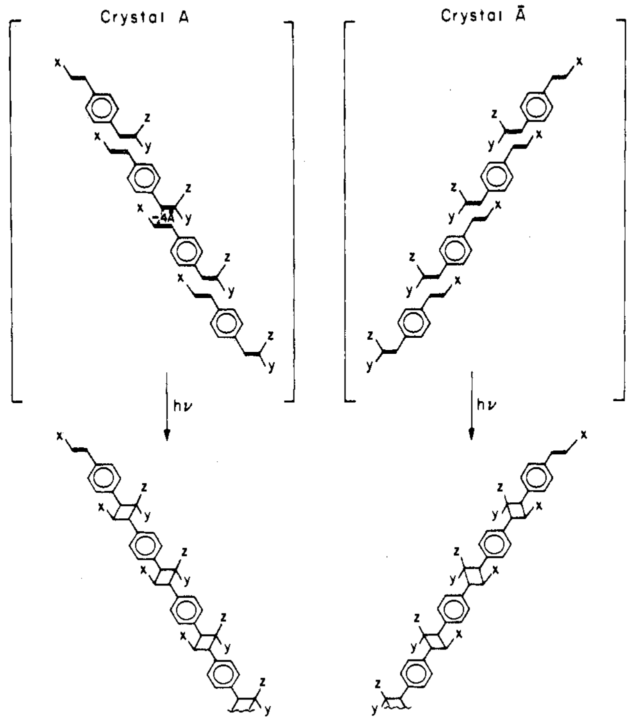
The achievement of asymmetric synthesis starting from racemic or achiral reagents and in the absence of any external chiral agent has long been an intriguing challenge to chemists.

A number of such asymmetric syntheses have been recently described, which exploit the method of spontaneous asymmetric crystallization of achiral compounds coupled with topochemical transformations.[2-10]

In the present series of studies we are testing this approach by "engineering" crystals of appropriate monomers which upon photopolymerization can yield polymers with quantitative enantiomeric yield.

Recently we have described the planning and successful execution of an asymmetric synthesis of dimers and polymers with quantitative diastereomeric yield, starting from optically pure monomer ethyl 2-cyano-3-(*p*-*sec*-butyl-3′-(*E*)-propenoate)phenyl-(*E*)-propenoate (**1**), by a process involving crystallization of the monomer in a chiral crystal ($a = 13.17$ Å, $b = 6.94$ Å, $c = 5.25$ Å, $\alpha = 103.1°$, $\beta = 95.5°$, $\gamma = 90.1°$, $P1$, $Z = 1$), followed by a $[2\pi + 2\pi]$ topochemical photocycloaddition.[11,12] The reaction is schematically represented in Scheme I.

Scheme I



Resolved 1 : x = COOsec But (R) or (S) y = COOEt z = CN
Racemic 1 : x = " (R) and (S) randomly distributed

We have demonstrated that the optical yield in this reaction is quantitative both in the initiation and in the propagation steps and we presented experimental evidence which strongly suggested that the chiral induction in the various stages of the polymerization is entirely due to the asymmetric crystalline environment and not to the chiral handle itself. Racemic **1** is isostructural with the crystal of the pure enantiomer ($a = 13.35$ Å, $b = 7.03$ Å, $c = 5.41$ Å, $\alpha = 104°$, $\beta = 93°$, $\gamma = 92°$, $P1$, $Z = 1$), as can be seen from the identity in space group and from the similarity in crystallographic constants and X-ray diffraction intensities.[13] Therefore the chiral crystals of the racemate consist of a disordered solid–solution of the two enantiomers; while in the enantiomeric crystal all *sec*-butyl

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