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SUBSTITUENT EFFECTS IN THE QUENCHING OF ACETOPHENONE AND BENZOPHENONE TRIPLETS BY OXYGEN AND THE DI-*tert*-BUTYLNITROXY RADICAL, AND THE EFFICIENCY OF SINGLET OXYGEN PHOTOGENERATION

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Summary

The behavior of the triplets of a number of *p*-substituted acetophenones and benzophenones with respect to quenching by oxygen and the di-*tert*-butylnitroxy radical (DTBN) has been examined in benzene and acetonitrile using 337.1 nm laser flash photolysis. In several cases the efficiency ϕ_Δ of singlet oxygen (${}^1O_2{}^*$) generation in the course of triplet quenching by oxygen has been determined using 1,3-diphenylisobenzofuran as the trapping agent for ${}^1O_2{}^*$. The variation of the rate constants for triplet quenching with respect to the substituent nature suggests that the aromatic carbonyl triplets act as donors and acceptors in the quenching interaction with oxygen and DTBN respectively. Relative to the rate constant for quenching by oxygen, the substituent effect on ϕ_Δ is less pronounced, particularly in the case of benzophenones; the ϕ_Δ are limited to the range 0.3 - 0.7 in the two solvents. Fast equilibration among the various spin configurations of the encounter complex responsible for the nearly substituent-independent ϕ_Δ for benzophenones and back electron transfer in charge-transfer-derived ion pairs leading to ${}^1O_2{}^*$ formation are suggested.

1. Introduction

Because of the small magnitude of the energy (22.5 kcal mol^{-1}) needed for excitation, singlet oxygen (${}^1O_2{}^*$) is generally formed in a facile manner in the course of the quenching of electronically excited states by oxygen and plays an important role as an activated oxidizing species [1] in photooxidation reactions. A great deal of controversy appears to exist in the results concerning the efficiency ϕ_Δ of ${}^1O_2{}^*$ generation as a result of triplet

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quenching by oxygen [2 - 10]. The benzophenone triplet constitutes a specific example for which ϕ_Δ values have been reported to be significantly less than unity (0.4 - 0.6) in some studies [2 - 4, 9], while in measurements by other workers [5] a ϕ_Δ value close to one has been claimed for the same system. A charge transfer (CT) mechanism [2, 10] and, more recently, favorable intersystem crossing from singlet to triplet configurations in the encounter complex of the triplet with oxygen [4], both accounting for inefficient $^1O_2{}^*$ production, have been implicated in the oxygen quenching of the benzophenone triplet and related systems.

In the work to be described here we have examined the effect of *p*-substituents on the interaction of acetophenone and benzophenone triplets with oxygen and the di-*tert*-butylnitroxy (DTBN) radical as manifested in the quenching rate constants k_{q,O_2}^T and $k_{q,DTBN}^T$ as well as in the efficiency ϕ_Δ of $^1O_2{}^*$ generation. Nanosecond laser flash photolysis based on 337.1 nm excitation has been used. The aim has been to shed light on the importance of the CT interaction by varying the donor/acceptor capability of the carbonyl triplets, *i.e.* by introducing electron-releasing and electron-withdrawing groups. Specifically, we have found that the substituents affect k_{q,O_2}^T and $k_{q,DTBN}^T$ in opposite ways and that ϕ_Δ is a less sensitive function of the substituents than is k_{q,O_2}^T.

2. Experimental details

The aromatic ketones were purchased from Aldrich, except the following for which the commercial sources are given in parentheses: *p*-methylacetophenone (Eastman), *p*-trifluoromethylacetophenone (Pfaltz and Bauer) and *p*-trifluoromethylbenzophenone (Pfaltz and Bauer). The liquids were vacuum distilled and the solids were recrystallized from benzene or ethanol (except for Michler's ketone (MK) and *p*-methoxyacetophenone which were sublimed under vacuum). Benzene and acetonitrile were of spectral grades (Aldrich Gold Label); these solvents and DTBN (Eastman) were used as received. 1-Methylnaphthalene (1MN) and 1,3-diphenylisobenzofuran (DPBF), both from Aldrich, were purified by vacuum distillation and recrystallization from ethanol respectively.

The laser flash photolysis set-up including the kinetic spectrophotometer and computer-controlled data collection system has been described in previous papers [9, 11, 12] from this laboratory. Nitrogen laser pulses (337.1 nm; 8 ns; 2 - 3 mJ) from a Molectron UV-400 system were used in all the experiments. The aromatic ketone concentrations were in the range (5×10^{-4}) - 10^{-1} M and the path lengths of the rectangular quartz cells for photolysis were 2 or 3 mm along the direction of the monitoring light. In experiments for measuring ϕ_Δ via the consumption of DPBF, an interference filter (Oriel 5429) was placed in the path of the analyzing light to minimize the consumption of DPBF by $^1O_2{}^*$ produced by the action of this light.

Deoxygenation of solutions was effected by bubbling oxygen-free argon (10 - 15 min). For quenching experiments at varying oxygen concentrations, the solutions were saturated with O_2–N_2 mixtures of known compositions (Linde). The oxygen concentrations were calculated using 1.9 mM as the solubility of oxygen in both air-saturated benzene [13] and air-saturated acetonitrile [14].

3. Results

3.1. Kinetic data for quenching by oxygen and the di-tert-butylnitroxy radical

Except for MK in acetonitrile, the aromatic ketones under examination produce triplets with quantitative yields ϕ_T upon direct excitation (337.1 nm) in both benzene and acetonitrile; the ϕ_T were found to be within ±10% of unity. They were measured with respect to benzophenone in benzene (or acetonitrile) by comparing the absorbance changes ΔOD_{1MN} at 420 - 425 nm due to the 1MN triplet produced at a maximum 99% quenching of the ketone triplets in optically matched solutions containing high concentrations (0.10 - 0.15 M) of 1MN. In these experiments the fractional absorption of 337.1 nm laser photons by 1MN was less than 3% of the absorption by the ketones. The ϕ_T of MK in acetonitrile was found to be low (0.47 ± 0.07). However, this result is in agreement with the pronounced drop in ϕ_T previously noted [15] for this ketone on going from cyclohexane to alcohols and attributed [15] to a reversal in the relative location of the lowest-lying ^{1}CT and $^3(n, \pi^*)$ states upon increasing solvent polarity.

The kinetics of the decay of the carbonyl triplets, which was monitored by spectral absorption at 350 - 410 nm for acetophenones [16] and at 520 - 540 nm for benzophenones [17], were measured in the presence of varying concentrations of oxygen (0 - 4 mM) and DTBN (0 - 15 mM). Unless observed at low laser intensities (0.2 - 0.5 mJ pulse^{-1}), the carbonyl triplet decay in the absence of a quencher was complicated by the contribution from a second-order component (triplet–triplet annihilation) in most cases. However, in the presence of oxygen or DTBN at a minimum concentration of 0.5 mM the decay of triplet absorption could be fitted very well to first-order kinetics characterized by pseudo-first-order rate constants k^T_{obs}. The slopes of the linear plots of k^T_{obs} against quencher concentrations gave the bimolecular rate constants k^T_q for quenching. Several such plots are shown in Fig. 1. The k^T_q data are presented in Table 1.

Almost no residual absorption attributable to ketyl radicals was observed on DTBN quenching of the aromatic ketone triplets in benzene and acetonitrile. The DTBN quenching of the triplets of benzophenone and its *p*-methoxy and *p*-trifluoromethyl derivatives was also studied in 2:3 (by volume) acetonitrile–water. The k^T_q which are given in parentheses in Table 1, fifth column, were slightly smaller in the aqueous acetonitrile (relative to acetonitrile); again, no ketyl radical formation was noted in the aqueous solutions.

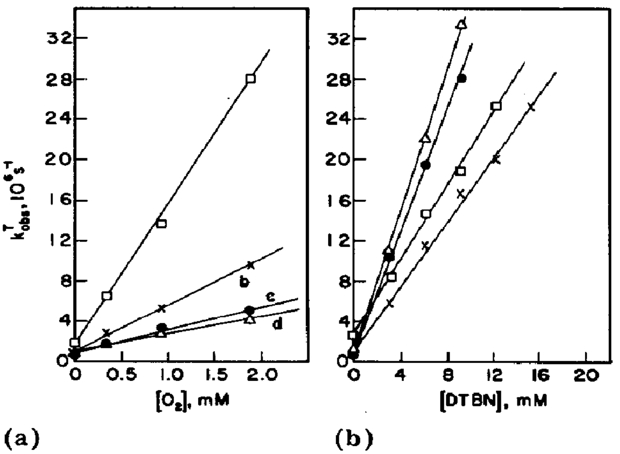


Fig. 1. Representative plots for the observed pseudo-first-order rate constants k^T_{obs} for triplet decay in benzene *vs.* (a) oxygen and (b) DTBN concentrations: □, Michler's ketone; ×, *p,p'*-dimethoxybenzophenone; ●, benzophenone; △, *p*-trifluoromethylbenzophenone.

TABLE 1

Bimolecular rate constants k^T_q for the quenching of aromatic ketone triplets by oxygen and di-*tert*-butylnitroxide

Substituent	$k^T{}_q{}^a$ ($\times 10^9$ M^{-1} s^{-1})			
	O₂–Bz	*O₂–MeCN*	*DTBN–Bz*	*DTBN–MeCN*
Acetophenones				
None (1)	4.5	3.7	3.7	4.9
p-Amino (2)	9.4	10.7	3.0	1.7
p-Methoxy (3)	6.0	6.7	1.3	1.9
p-Methyl (4)	4.0	3.7	2.3	2.4
p-Fluoro (5)	3.8	3.4	3.6	3.8
p-Chloro (6)	2.3	2.4	3.3	3.8
p-Trifluoromethyl (7)	2.5	3.2	4.6	5.1
p-Cyano (8)	0.52	0.66	5.6	5.5
Benzophenones				
None (9)	2.3	2.3	2.9	4.6 (4.1)[b]
p,p'-Bis-(*N,N*-dimethylamino) (10)	12.6	11.4	1.8	1.1
p,p'-Dimethoxy (11)	4.6	5.6	1.6	2.6
p-Methoxy (12)	3.7	4.7	2.7	3.2 (2.7)[b]
p-Methyl (13)	2.3	2.9	2.8	4.3
p-Fluoro (14)	2.1	2.3	3.3	4.2
p-Chloro (15)	1.9	1.9	3.1	3.6
p,p'-Dichloro (16)	1.6	1.4	3.5	4.8
p-Trifluoromethyl (17)	1.5	1.6	3.7	5.1 (4.5)[b]

Bz, benzophenone; MeCN, acetonitrile.

[a] ±15%.

[b] The data in parentheses were obtained in 2:3 (by volume) MeCN–H_2O.

3.2. *Efficiency of singlet oxygen generation*

With several of the aromatic ketones under study, the fraction ϕ_Δ of triplets quenched by oxygen that led to ${}^1O_2{}^*$ production was determined under oxygen saturation using DPBF as the monitor for ${}^1O_2{}^*$. For benzophenone in acetonitrile, ϕ_Δ was first measured in the manner described for this ketone in benzene in an earlier paper [9]. A 0.05 M solution of benzophenone in oxygen-saturated acetonitrile containing 0.05 mM DPBF was flash photolyzed by 337.1 nm laser pulses and the negative absorbance change $\Delta OD^\infty{}_{DPBF}$ due to the depletion of DPBF was monitored at 420 nm following the completion of the bleaching process (over about 80 µs). The laser flash photolysis of an identical solution under deoxygenated conditions gave the end-of-pulse absorbance change $\Delta OD^\circ{}_T$ due to the benzophenone triplet monitored at 520 nm. Figure 2 shows a kinetic trace for DPBF depletion and the first-order fit of the absorbance-change data. ϕ_Δ was calculated using the equation

$$\phi_\Delta = \frac{\Delta OD^\infty{}_{DPBF}}{\Delta OD^\circ_T} \, \frac{\epsilon^T}{\epsilon_{DPBF}} \, \frac{k_d + k_r[DPBF]}{k_r[DPBF]} \, \frac{\tau_T{}^{-1} + k^T_{q,O_2}[O_2]}{k^T_{q,O_2}[O_2]} \qquad (1)$$

where ϵ^T and ϵ_{DPBF} are the extinction coefficients of benzophenone triplet absorption at 520 nm (6.5×10^3 M^{-1} cm^{-1} [18]) and DPBF ground state absorption at 420 nm (2.1×10^4 M^{-1} cm^{-1}) respectively. k_d and k_r are the rate constants for the processes represented by the equations

$$ {}^1O_2{}^* \xrightarrow{k_d} {}^3O_2 \qquad (2)$$

$$ {}^1O_2{}^* + DPBF \xrightarrow{k_r} \text{peroxide} \qquad (3)$$

respectively. The values of k_d and k_r in acetonitrile, which were determined in earlier work [19], are 2.5×10^4 s^{-1} and 1.0×10^9 M^{-1} s^{-1} respectively. Regarding the experiments for measuring ϕ_Δ, the following should be noted.

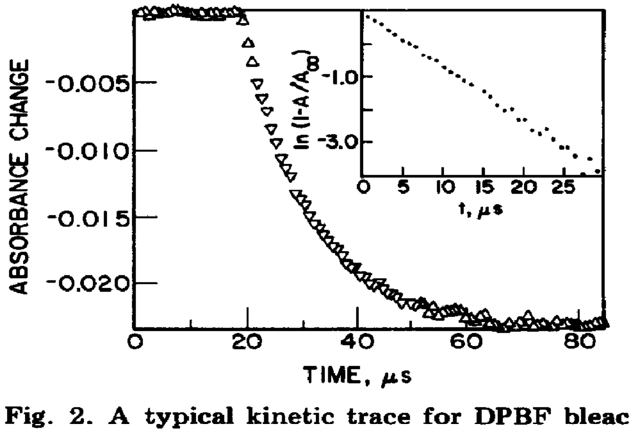


Fig. 2. A typical kinetic trace for DPBF bleaching observed at 420 nm upon 337.1 nm laser flash photolysis of 0.1 M benzophenone in oxygen-saturated acetonitrile containing 0.054 mM DPBF. The inset shows the fitting of the absorbance change data in first-order kinetics.

(i) In oxygen-saturated solution the ketone triplet decayed by at least 95% by interaction with oxygen (*i.e.* $\tau_T^{-1} \ll k^T_q[O_2]$).

(ii) The quenching of ${}^1O_2{}^*$ by the ketones (ground state) was unimportant relative to the processes described by eqns. (2) and (3) (except for MK as discussed later).

(iii) At the low concentrations (0.03 - 0.06 mM) of DPBF used, the fraction of the 337.1 nm laser photons absorbed by it was insignificant (less than 5%) relative to that absorbed by the ketones. Also, the ketone triplet quenching by DPBF was negligible (less than 5%) relative to that by oxygen.

(iv) The laser intensity was attenuated to 30% - 40% of the original level in order to ensure that the consumption of DPBF as a result of the reaction with ${}^1O_2{}^*$ (eqn. (3)) was 10% or less of the concentration of DPBF used.

The amount of ${}^1O_2{}^*$ produced by the quenching of singlet and triplet DPBF resulting from direct laser absorption by it was estimated by blank experiments using solutions containing DPBF alone and was used to correct the observed $\Delta OD^{\infty}{}_{DPBF}$.

By the method described above, ϕ_Δ for benzophenone in acetonitrile was measured to be 0.37 ± 0.07, *i.e.* essentially the same as that in benzene (0.39) [9]. For other ketones in benzene and acetonitrile, solutions containing 10^{-3} - 5×10^{-2} M ketones and 0.05 mM DPBF, optically matched at 337.1 nm, were flash photolyzed at 337.1 nm under (i) oxygen saturation (to measure $\Delta OD^{\infty}{}_{DPBF}$) and (ii) argon saturation in the presence of 0.10 - 0.15 M 1MN (to measure the absorbance change $\Delta OD^{\circ}_{T,\,1MN}$ due to the 1MN triplet formed by quenching of at least 99% of the ketone triplets by 1MN). The ϕ_Δ were calculated relative to benzophenone in benzene or acetonitrile according to the equation

$$\phi_\Delta{}^K = \phi_\Delta{}^{BP} \frac{\Delta OD^{\infty,\,K}_{DPBF}}{\Delta OD^{\infty,\,BP}_{DPBF}} \frac{\Delta OD^{\circ,\,BP}_{T,\,1MN}}{\Delta OD^{\circ,\,K}_{T,\,1MN}} \qquad (4)$$

where the superscripts K and BP signify ketone substrates and benzophenone (reference) respectively. As noted earlier, except for MK, no significant reaction of ${}^1O_2{}^*$ with the ketone ground states was evident from the observed rate constants k_{DPBF} for DPBF bleaching, *i.e.* they were given by $k_d + k_r[DPBF]$ at the ketone concentrations used. With MK at high concentrations, a slight enhancement in k_{DPBF} was noted owing to the quenching of ${}^1O_2{}^*$ by the ketone, and this was taken into consideration by multiplying $\Delta OD^{\infty,\,MK}_{DPBF}$ by $k^{MK}_{DPBF}/k^{BP}_{DPBF}$. The ϕ_Δ data for several aromatic ketones are presented in Table 2.

The benzophenone and acetophenone singlets are characterized by very short lifetimes (0.1 ns or less) [20]. Their quenching by oxygen and the resultant ${}^1O_2{}^*$ production under the conditions of our experiments were insignificant. Among the substituted ketones, MK is known to fluoresce moderately strongly at 77 K [21, 22]. Assuming that among the substituted ketones under consideration in Table 2, the singlet of MK has the longest lifetime and hence is the most susceptible to oxygen quenching leading to ${}^1O_2{}^*$ production as well as assisted intersystem crossing (particularly in the

TABLE 2

Efficiency ϕ_Δ of singlet oxygen production from the quenching of aromatic ketone triplets by oxygen

Substituent	ϕ_Δ [a]	
	Bz	*MeCN*
Acetophenones		
None (1)	0.35	0.52
p-Methoxy (3)	0.27	0.42
p-Cyano (8)	0.49	0.76
Benzophenones		
None (9)	0.39[b]	0.37
p,p'-Bis(*N,N*-dimethylamino) (10)	0.41	0.35
p,p'-Dimethoxy (11)	0.34	0.40
p-Fluoro (12)	0.43	0.44
p-Trifluoromethyl (17)	0.42	0.54

Bz, benzophenone; MeCN, acetonitrile.

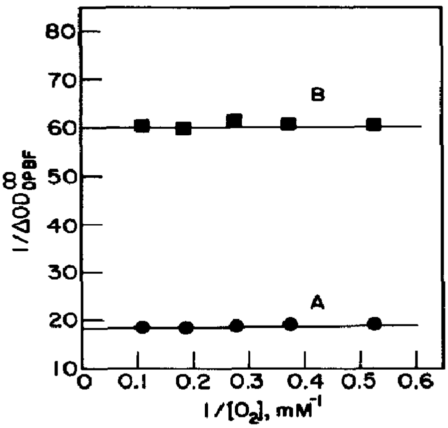
[a] ±20%.

[b] From ref. 9.

polar solvent acetonitrile in which ϕ_T is small), we have measured $\Delta OD^\infty{}_{DPBF}$ as a function of $[O_2]$ for BP and MK in acetonitrile (optically matched at 337.1 nm). The results are shown in Fig. 3. As expected for the triplet quenching ($k^T_{q,O_2}\tau_T \geqslant 10^4$), the slopes of the plots of $1/\Delta OD^\infty{}_{DPBF}$ against $1/[O_2]$ are almost zero. Direct as well as cumulative ${}^1O_2{}^*$ sensitization from the singlet quenching pathway is apparently negligible because this would lead to high positive slopes as well as curvature in the plots.

4. Discussion

An examination of the kinetic data in Table 1 suggests that the substituent effect on $k^T{}_q$ manifests itself in opposite ways in quenching by oxygen and DTBN. The Hammett plots shown in Fig. 4 using the data for acetophenone triplets illustrate these opposing trends. Thus, if CT interaction is important in the quenching processes, the aromatic carbonyl triplets will behave as acceptors and donors with respect to DTBN and oxygen respectively. We can argue against the use of the ground state parameter σ^+ for describing the donor/acceptor behavior of the triplet excited states. However, we note that on going from the ground to the triplet state the redox potential is augmented by the magnitude of the triplet energy E_T, and the substituents in the *p*-position(s) do not have large effects on the E_T of aromatic ketones [13]. The changes in E_T upon *p*-substitution in acetophenones and benzophenones are 2 kcal mol^{-1} or less, except for the cyano and amino groups [13].



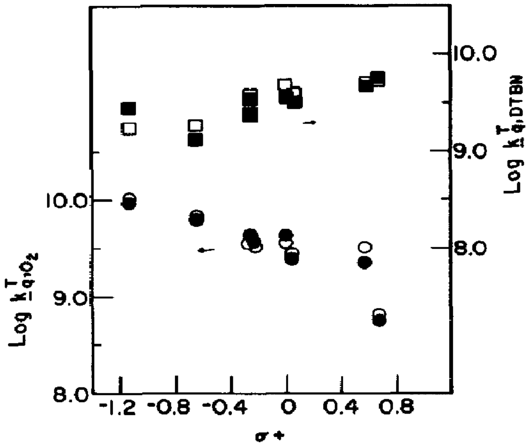


Fig. 3. Double-reciprocal plots of the absorbance change $\Delta OD^{\infty}_{DPBF}$ due to DPBF bleaching against the oxygen concentration in acetonitrile ([DPBF] = 0.054 mM): curve A, in benzophenone (about 0.1 M); curve B, in MK (about 0.5 mM).

Fig. 4. Hammett plots for the rate constants for the quenching of *p*-substituted acetophenone triplets by oxygen in benzene (●) and acetonitrile (○) and by DTBN in benzene (■) and acetonitrile (□). The σ^+ values were taken from ref. 13.

Among the carbonyl compounds under examination, MK appears to have the lowest triplet energy E_T (about 62 kcal mol^{-1} [13]). Energy transfer from them to oxygen [2 - 10, 23] as well as to a nitroxy radical is highly exothermic. The dominance of energy transfer in the quenching of triplets with $E_T > 52$ kcal mol^{-1} by nitroxy radicals has been established in studies of aromatic hydrocarbons and other systems [24 - 27]:

$$^3S^* + {}^3O_2 \xrightleftharpoons{1/9k_{\rm diff}} {}^1(S^*...O_2) \longrightarrow {}^1S + {}^1O_2^* \tag{5a}$$

$$\xrightleftharpoons{1/3k_{\rm diff}} {}^3(S^*...O_2) \longrightarrow {}^1S + {}^3O_2 \tag{5b}$$

$$\xrightleftharpoons{5/9k_{\rm diff}} {}^5(S^*...O_2) \tag{5c}$$

$$^3S^* + {}^2R \xrightleftharpoons{1/3k_{\rm diff}} {}^2(S^*...R) \longrightarrow {}^1S + {}^2R^* \text{ (or } {}^2R) \tag{6a}$$

$$\xrightleftharpoons{2/3k_{\rm diff}} {}^4(S^*...R) \longrightarrow {}^1S + {}^4R^* \tag{6b}$$

As shown in eqns. (5a) and (6a) with oxygen and the nitroxy radical (R·) as triplet quenchers, spin-statistical restrictions are imposed on k^T_q on the basis of the facts that one-ninth and one-third of the encounter complexes should be in singlet and doublet configurations respectively, leading to energy transfer in the two cases. Whereas the observed k^T_q for both oxygen and DTBN in the two solvents (Table 1) are below the limit of diffusion control (*i.e.* $5/9k_{\rm diff}$ or less), in many cases they exceed the limits imposed by the spin-statistical consideration.

The substituent effects constitute about a tenfold change in k^T_{q,O_2} and about a fivefold change in $k^T_{q,DTBN}$ (Table 1); these can be explained by the CT interaction (*i.e.* involvement of low-lying CT states in the collision complex) invoked in earlier studies [2, 10, 27]. An alternative explanation in terms of increasing n,π* character of the triplets with increasing electron-withdrawing capability of the substituents appears attractive for DTBN quenching, because in the triplet excited state the carbonyl oxygen carries less negative charge with increasing n,π* character [28] and this should result in increased dipole–dipole interaction with DTBN. Except in a few cases, $k_{q,DTBN}$ either remains almost unchanged or increases slightly on going from benzene to acetonitrile (Table 1). This behavior is evidence against the dominance of the CT interaction. $k_{q,DTBN}$ for *p*-aminoacetophenone and MK decreases conspicuously on going from benzene to acetonitrile. The lowest-lying triplet state in MK, and by analogy in *p*-aminoacetophenone, is of CT character [15]. Since the CT character becomes enhanced in a polar solvent, the observed solvent effect on $k^T_{q,DTBN}$ as well as the fact that this is small for the amino and methoxy-substituted ketones suggests that the triplets with CT character are less susceptible to quenching by nitroxy radicals (possibly because of less favorable orientation in the collision complex with the negatively charged oxygen centers of the interacting partners aligned towards each other).

In comparison with the magnitude of the substituent effect on k^T_{q,O_2}, that on ϕ_Δ (Table 2) is less pronounced. With benzophenones as triplet photosensitizers ϕ_Δ is almost independent of the substituent nature and there is no significant change in ϕ_Δ on going from benzene to acetonitrile (Table 2). With acetophenones, a gradual increase in ϕ_Δ is noted on changing the *p*-substituent from an electron-releasing species (methoxy group) to an electron-withdrawing species (cyano group); this is particularly true for acetonitrile. This trend may be related to the diminishing importance of the CT interaction in the quenching. However, the importance of the CT interaction in oxygen quenching leading to non-production of $^1O_2$* is apparently not realized in the solvent effect on ϕ_Δ of the acetophenones; in fact, an increase in ϕ_Δ is observed for acetophenones on going from benzene to acetonitrile. It appears that equilibration by way of fast intersystem crossing among the various spin configurations of the encounter complexes occurs prior to their dissociation, and this is reflected in the near constancy of ϕ_Δ. k^T_{q,O_2}, however, bears the direct effect of CT interaction induced by electron-rich substituents.

In view of the fact that the reduction potential of oxygen ($E_{1/2}$ = —0.57 V *versus* a saturated calomel electrode in water [29]) is comparable with that of the paraquat dication (PQ^{2+}) ($E_{1/2}$ = —0.44 V *versus* a normal hydrogen electrode in water [30]), it is of interest to compare the quenching behavior of carbonyl triplets toward these two species in the light of the importance of the CT interaction. In recent studies [17, 31] we have shown that aromatic carbonyl triplets are efficiently quenched by PQ^{2+} and that both the quenching rate constant $k^T_{q,PQ}$ and the efficiency η of the net electron transfer leading to the paraquat radical ion (PQ$^{+\bullet}$) correlate with the electron-releasing character of the substituents. The rate constants for triplet quenching by oxygen and PQ^{2+} show analogous substituent dependence; however, a similarity between the trends of η and $1 - \phi_\Delta$ is not observed, particularly in the case of benzophenones. It is important to point out that back electron transfer in a photogenerated ion pair (triplet) with $O_2^{-\bullet}$ as a partner would be more efficient compared with that with PQ$^{+\bullet}$ because of the coulombic attraction in the former case (bringing the partners closer) and may be responsible for the production of $^3O_2$ (physical quenching) as well as $^1O_2^*$ (CT-mediated energy transfer). The latter process may explain why ϕ_Δ is quite significant (about 0.4) in the oxygen quenching of the MK triplet although the extraordinarily high k^{T}_{q,O_2} (about 1×10^{10} M^{-1} s^{-1}) suggests an extensive involvement of CT interaction in the oxygen quenching of this system.

Acknowledgments

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