COULOMBIC EFFECTS ON PHOTOINDUCED ELECTRON-TRANSFER REACTIONS BETWEEN BENZOPHENONE DERIVATIVES AND LEUCO CRYSTAL VIOLET

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Summary

Photo-oxidation of leuco crystal violet (DH) to crystal violet dye (D^+) was studied in the benzophenone (BP) derivatives–DH–acetonitrile systems. The BP derivatives with a tetraalkylammonium substituent (R_3N^+; I, II and III) exhibited much higher photo-oxidizing efficiencies than BP itself. Under deaerated conditions, nearly quantitative photo-oxidation of DH by the absorbed photons was attained by I whereas BP itself showed a poor ability to photo-oxidize DH. Addition of tetraalkylammonium salts (R_4NX), such as cetyltrimethylammonium chloride or tetra-*n*-butylammonium chloride to the BP–DH system also enhanced the quantum yield by a factor of about 10. The enhancement of quantum yield by the use of I, II or III, or by the addition of R_4NX to BP was interpreted as due to stabilization of the BP anion radical or the DH cation radical by ion pairing with the tetraalkylammonium substituent on BP or with the added R_4NX. In the case of I, II and III, the electrostatic repulsion between the DH cation radical and the R_3N^+ substituent on BP, which enhanced the charge separation efficiency, was the main cause of the high photo-oxidation yields.

1. Introduction

Molecular aggregated systems such as micelles, vesicles and polymers have received special attention in connection with their characteristic photochemical and photophysical properties as well as in view of their application to highly efficient chemical conversion of photoenergy [1]. With regard to molecular aggregation effects on photoinduced electron-transfer reactions, we demonstrated that the photo-oxidation yield of leuco crystal violet was improved by the use of polymeric or micellar photosensitizers with an anthryl group, in comparison with the yield for the relevant non-aggregated homogeneous systems. This was interpreted as a result of light harvesting by

energy migration among the aggregated chromophores [2]. A number of similar results have been reported which confirmed our results [3].

Another aspect of molecular aggregation is related to coulombic effects. It has been reported that the ion recombination between the pyrene (Py) anion radical and the N,N-dimethylaniline (DMA) cation radical produced by photoinduced electron transfer is suppressed in cationic micelles but not in anionic or non-ionic micelles [4]. Such micellar effects originate from coulombic repulsion between the cationic micellar surface and the DMA cation radicals and consequently the cation radicals were pushed out into the bulk water phase to achieve effective charge separation.

Micelles [5] or polyelectrolytes [6] also provide unique effects on the dynamics of electron-transfer processes. In the case of oxidative quenching of the excited tris(2,2'-bipyridine)ruthenium(II) complex by a cationic quencher such as methylviologen or Cu^{2+}, the presence of anionic micelles or polyanions strongly influences the quenching dynamics since the electrostatic association of methylviologen or Cu^{2+} in the anionic micelle or the polyanion periphery changes luminophore—quencher distributions. Such coulombic effects are not confined to molecular aggregated systems. In the course of studying surfactant analogues of benzophenone (BP) derivatives, we found that non-aggregating BP derivatives with a tetraalkylammonium substituent exhibited very much enhanced photo-oxidizing efficiencies towards leuco crystal violet (DH) as compared with BP itself [7].

From the point of view of investigating the coulombic effects as well as using the effects on photoinduced electron-transfer reactions, non-aggregated systems are more advantageous than micellar or polymeric systems. In this paper, we report the effects of cationic BP substituents and added tetraalkylammonium salts on the photo-oxidation of DH to crystal violet dye (D^+). The present study will provide a clearer understanding of photoredox processes in more complicated molecular aggregated systems.

2. Experimental details

2.1. Materials

The structures and abbreviations for the BP derivatives used in this study are shown in Fig. 1. The preparation and purification methods of the BP derivatives are described elsewhere [8]. Leuco crystal violet (DH) was recrystallized several times from ethanol. Tetra-n-butylammonium chloride (Bu_4NCl) or the perchlorate (Bu_4NClO_4), cetyltrimethylammonium chloride (CTAC) or the bromide (CTAB) and cetylpyridinium chloride (CPC) were recrystallized from ethanol—acetone or ethanol—ether. Acetonitrile was refluxed over CaH_2 for several hours and fractionally distilled before use. Spectroscopic grade methanol and ethanol were used as supplied.
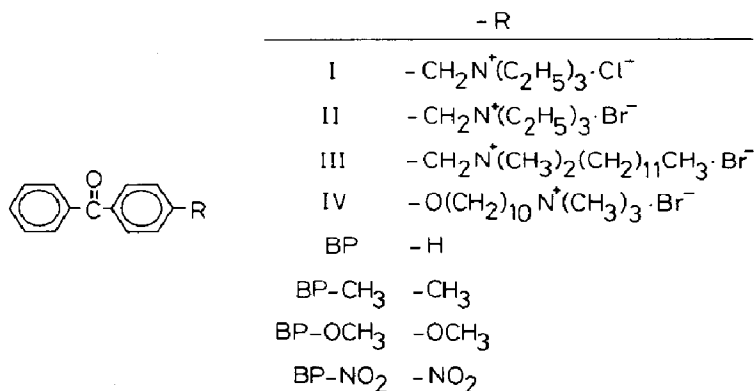
Fig. 1. Structures and abbreviations for the benzophenone derivatives.

2.2. Procedures

Photoreactions were done in a quartz cell with monochromatic irradiation by a JASCO Spectroirradiator CRM-FA. The incident light intensity was determined by Hatchard–Parker actinometry [9]. Absorption and emission spectroscopy measurements were made with a Shimadzu UV-200S spectrophotometer and a Hitachi MPF-4 spectrofluorometer. Emission lifetime measurements and emission quenching experiments were conducted with a combination of an Nd:YAG laser (Quanta Ray, DCR-1), a transient memory (Kawasaki Electronika M50E) and a phototube (Hamamatsu R928). Every emission decay obeyed a single exponential function at any concentration of quencher. Deaerated samples were prepared by nitrogen-gas purging for 30 min.

3. Results

Photo-oxidation from DH to D^+ was studied in the BP or BP derivatives $(1 \times 10^{-3} \text{ M})$–DH $(3 \times 10^{-4} \text{ M})$ systems in acetonitrile under both aerated and deaerated conditions. The BP derivatives were selectively irradiated at 365 nm and D^+ formation was monitored at the absorption maximum around 590 nm ($\epsilon = 1.1 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) [10]. Figure 2 shows the time-conversion profile of D^+ formation using various BP derivatives in the absence (Fig. 2(a)) and presence (Fig. 2(b)) of tetraalkylammonium salts (R_4NX) as additives. From the initial slope of the time-conversion profile, the quantum yields of D^+ formation were estimated (Table 1). Important results derived from Fig. 2 and Table 1 are as follows.

(i) The BP derivatives having a tetraalkylammonium substituent such as I, II or III show higher photo-oxidizing efficiencies than BP itself. Furthermore, the quantum yields depend largely on the structure of the substituent. The photo-oxidizing yield in the I–DH–O_2 system is 11 times as large as that in the BP–DH–O_2 system, whereas the yields with II, III and IV are lower than that in the I–DH–O_2 system. The lower photo-oxidizing yield with II,
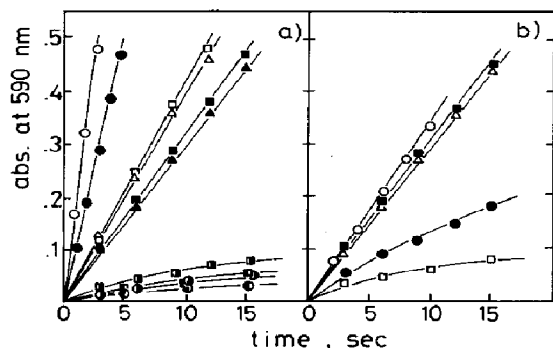
Fig. 2. Time-conversion profile of D^+ formation (under aerated conditions unless otherwise noted): (a) with BP derivatives $I-N_2$ (○), I (●), $II-N_2$ (⊔), II (■), $III-N_2$ (△), III (▲), IV (□), BP (◐), BP-CH$_3$ (◉), BP-OCH$_3$ (▣); (b) effects of added salt in the BP–DH system, additives Bu$_4$NCl (△), Bu$_4$NClO$_4$ (□), CTAC (○), CTAB (●), CPC (■). [BP] = 1×10^{-3} M, [DH] = 3×10^{-4} M, [R$_4$NX] = 1×10^{-3} M.

TABLE 1

Quantum yields of D^+ formation

Run	Sensitizing system	Φ_{O_2}[a]	Φ_{N_2}[b]
1	BP	0.026	0
2	BP-CH$_3$	0.011	0
3	BP-OCH$_3$	0.016	0
4	BP-NO$_2$	≈ 0	0
5	I	0.286	0.420
6	II	0.092	0.111
7	III	0.083	0.097
8	IV	0.030	≈ 0
9	BP–Bu$_4$NClO$_4$	0.032	0
10	BP–Bu$_4$NCl	0.107	0
11	BP–CTAC	0.106	0
12	BP–CTAB	0.061	0
13	BP–CPC	0.120	0

[a] Determined under air-saturated conditions.
[b] Determined under deaerated conditions. [BP derivatives] = 1×10^{-3} M, [DH] = 3×10^{-4} M, [R$_4$NX] = 1×10^{-3} M in acetonitrile.

as compared with that with I, can be attributed to the heavy-atom effect of Br⁻ which exists in the periphery as a counter-ion. The excited triplet lifetime of II thus decreases. The decreasing sequence of the reactivity from II to III or IV is attributed to structural differences between these BP derivatives, as discussed in the following section.

   (ii) Both electron-withdrawing and electron-donating substituents on BP have almost no effect on the quantum yield. Since the reduction potentials of the BP derivatives are estimated to be -2.02 V $vs.$ the saturated calomel electrode (SCE) (BP-CH$_3$ and BP-OCH$_3$, in 0.1 M tetraethylam-

monium perchlorate–acetonitrile), −1.48 V(SCE) (I and III) and −1.02 V (BP-NO$_2$), the sequence of electron-accepting ability does not coincide with the photo-oxidizing efficiency of the BP derivatives. The high photo-oxidizing efficiency of I, II or III cannot be explained by the substituent effects on the reduction potential of BP.

(iii) In the BP–DH–O$_2$ system, the quantum yield is enhanced by adding some R$_4$NX, such as Bu$_4$NCl, CTAC, or CPC, by a factor of 4 - 5, while the addition of Bu$_4$NClO$_4$ or CTAB brings about only minor changes in the quantum yield. The quantum yield depends upon the nature of the counter-anion of the added R$_4$NX but not on the structure of the quaternary ammonium group. The quantum yield decreased in the order Cl$^-$ > Br$^-$ > ClO$_4^-$ with the variation of the counter-anion.

(iv) Under deaerated conditions, the effects of the tetraalkylammonium substituent on BP on the quantum yield are very striking. Photo-oxidation of DH is inhibited in the BP–DH system under deaerated conditions both in the presence and in the absence of R$_4$NX. However, the quantum yields by I, II, and III are larger for deaerated than for aerated systems. The maximum efficiency of the DH photo-oxidation to D$^+$ was attained in the I–DH–N$_2$ system (Φ = 0.42). Since the theoretical quantum yield of the DH photo-oxidation to D$^+$ is 0.5 (discussed in the following section) [10], the results indicate that nearly quantitative photo-oxidation of DH is achieved in this system.

From these results, it is concluded that the tetraalkylammonium substituent on BP and the addition of R$_4$NX, where X is Cl$^-$, to the BP–DH system enhance the quantum yield enormously. In the following sections, the mechanistic origin of these phenomena will be elucidated on the basis of spectroscopic and kinetic studies.

4. Discussion

4.1. Absorption and phosphorescence spectra of the BP derivatives

Absorption spectra of the BP derivatives used in this study have been reported [8]. The n–π^* and π–π^* transitions of BP, I, II and III lie around 330 nm and 250 nm respectively and are unaffected by structural differences in the substituent on BP. However, the n–π^* and π–π^* transitions of IV shift to higher and lower energy regions respectively relative to those of other BP derivatives. Such shifts in the transitions of IV, by the introduction of an electron-donating alkoxy group, are well documented in the literature [11].

Figure 3 shows phosphorescence spectra of BP, I, and IV in ethanol–methanol (4:1, volume ratio). All the BP derivatives showed similar phosphorescence spectra at room temperature, as well as at 77 K. The spectrum is not affected by the addition of R$_4$NX. Although emission bands of I at 77 K shift slightly to lower energies as compared with those of BP and IV, we could not observe any appreciable change in the excited triplet state
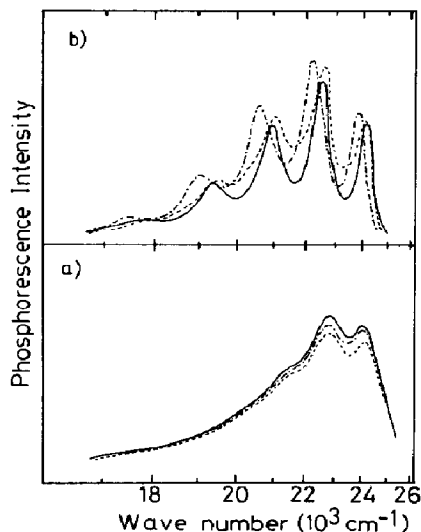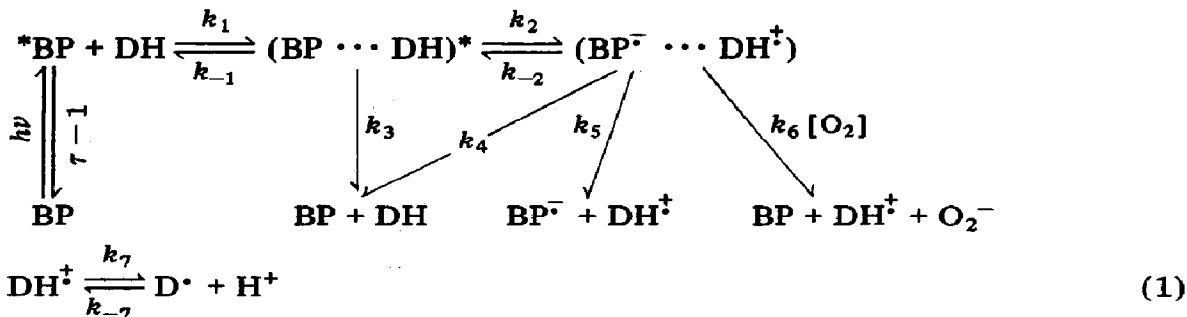
Fig. 3. Phosphorescence spectra of BP (———), I (— · —), and IV (- - - -) at (a) room temperature and (b) 77 K.

energies. Furthermore, the vibrational progression between the 0–0 and 0–1 phosphorescence bands are 1650 cm^{-1} for I and 1630 cm^{-1} for BP, in good agreement with the frequency of the IR carbonyl stretching absorption of BP (1630 cm^{-1}).

4.2. Kinetics

A kinetic analysis was attempted to explain the high quantum yields of the photo-oxidation of DH in the I–DH and BP–DH–R$_4$NX systems. The elementary processes involving an encounter complex (BP$\cdots$DH)* and an ion radical pair (BP$^-\cdots$DH$^+$) are described below.

$$*\text{BP} + \text{DH} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (\text{BP}\cdots\text{DH})^* \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (\text{BP}^-\cdots\text{DH}^+)$$

$$\text{DH}^+ \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} \text{D}^\cdot + \text{H}^+ \tag{1}$$

$$\text{DH}^+ + \text{D}^\cdot \xrightarrow{k_8} \text{D}^+ + \text{DH} \tag{2}$$

In acetonitrile, electron transfer has been known to occur between the excited triplet state of BP (*BP) and N,N-dimethylaniline [12]. Furthermore,

the electron transfer from DH to *BP (excited triplet state energy, 69.3 kcal mol^{-1} [13]) calculated from their redox potentials ($E_{1/2}$(BP/BP$^-$) = −1.72 V(SCE) [14] and $E_{1/2}$(DH‡/DH) = +0.74 V(SCE) [15] in CH$_3$CN) is highly exothermic (−13.9 kcal mol^{-1}), so that the photoinduced electron-transfer mechanism described above is a reasonable assumption. The dye formation mechanism is expressed in eqns. (1) and (2) as reported previously [10]. The dye is produced by disproportionation reaction between the DH cation radical and the D radical and thus the theoretical quantum yield of D$^+$ formation is 0.5.

Under aerated conditions, an additional reaction leading to superoxide anion (O$_2^-$) formation, k_6, is expected since the free energy change of the electron transfer from the BP anion radical to oxygen ($E_{1/2}$(O$_2$/O$_2^-$) = −0.57 V(SCE) [16]) is calculated to be −26.5 kcal mol^{-1}. The inhibition of photo-oxidation of DH in the BP–DH–N$_2$ system (Table 1) indicates the participation of oxygen in D$^+$ formation. If the BP anion radicals are not scavenged by oxygen, no net reaction will be observed, owing to immediate recombination of the BP anion radicals with the DH cation radicals. Such an assumption is supported by CCl$_4$ effects on the photo-oxidation of DH. Since CCl$_4$ is known as an anion radical scavenger, photo-oxidation of DH is expected to occur in the BP–DH–CCl$_4$ system even under deaerated conditions. Indeed, D$^+$ is produced efficiently in the presence of CCl$_4$ as shown in Fig. 4. Under aerated conditions, where k_6[O$_2$] $\gg$ ($k_{-2} + k_4 + k_5$) holds, succesive electron transfer from BP anion radical to oxygen plays an important role for D$^+$ formation.

Assuming stationary state concentrations for all intermediates in the scheme, the inverse of the quantum yield can be derived as eqn. (3) (see Appendix A).

$$\Phi^{-1} = \frac{2}{k_2(k_5 + k_6[O_2])}\left\{(k_1 k_e - k_2 k_{-2})\left(1 + \frac{1}{k_1 \tau[DH]}\right) - k_1 k_{-1}\right\} \qquad (3)$$
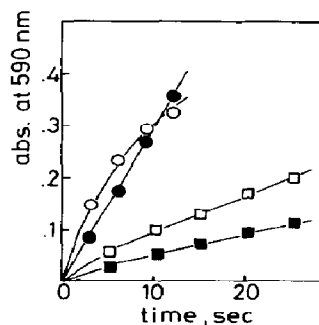

Fig. 4. Effects of carbon tetrachloride on D$^+$ formation: BP–O$_2$ (■), BP–N$_2$ (□), BP–CTAC–O$_2$ (●), BP–CTAC–N$_2$ (○). [BP] = 1 × 10^{-3} M, [DH] = 3 × 10^{-4} M, [CCl$_4$] = 1 × 10^{-3} M.

where k_i and k_e are the sum of the deactivation processes from the ion radical pair $(k_i = k_{-2} + k_4 + k_5 + k_6[O_2])$ and from the encounter complex $(k_e = k_{-1} + k_2 + k_3)$ respectively. Measuring the quantum yields, Φ, at various DH concentrations, we obtained linear Stern–Volmer plots as shown in Fig. 5. Since we know the excited triplet lifetime τ of BP, the k_1^{SV} value defined by eqn. (4) can be calculated from the intercept i and slope s values of the plots.

$$k_1^{SV} = \frac{i}{s\tau} = \frac{k_1\{k_i(k_2 + k_3) - k_2 k_{-2}\}}{k_i(k_2 + k_3 + k_{-1}) - k_2 k_{-2}} \tag{4}$$

The results of lifetime measurements and phosphorescence quenching are summarized in Table 2. Important results are as follows.

(i) The limiting quantum yields of D^+ formation (the inverse of the intercept in Fig. 5) are 0.45 for the I–DH–O_2 (run 2) and 0.48 for the I–DH–N_2 (run 3) systems while that of the BP–DH–O_2 system (run 1) is only 0.10. Since the theoretical limit of Φ is 0.5, nearly 100% utilization of absorbed photons to photo-oxidize DH to D^+ is attained in these systems under an infinite DH concentration.

(ii) The phosphorescence quenching rate constants (k_q) approach close to the diffusion limit in acetonitrile $(2 \times 10^{10} \text{ s}^{-1})$ and therefore $k_q = k_1$, while k_1^{SV} varied from 1×10^8 to 2×10^{10} M^{-1} s^{-1} with the reaction systems. Under the conditions $k_2 \gg k_{-1}$ and $(k_4 + k_5 + k_6[O_2]) \gg k_{-2}$, eqn. (4) is simplified as $k_1^{SV} = k_1$ and consequently $k_1^{SV} = k_q$. When backward rate constants, k_{-1} and k_{-2}, are negligibly small compared with the other processes, k_1^{SV} should agree with k_q. Indeed, k_1^{SV} is in fair agreement with k_q in both the BP–DH–R_4NX and the I–DH–O_2 systems with the rate constant of $(1 \cdot 2) \times 10^{10}$ M^{-1} s^{-1}, indicating that k_{-1} and k_{-2} are negligible in these systems. However, k_1^{SV} is much smaller than k_q in the BP–DH–O_2 system. These results, together with the low quantum yield, indicate that k_{-1} and k_{-2} have meaningful values. The effects of added R_4NX (X $\equiv$ Cl$^-$) on D^+ formation in the BP–DH–R_4NX systems are thus attributable to the suppression
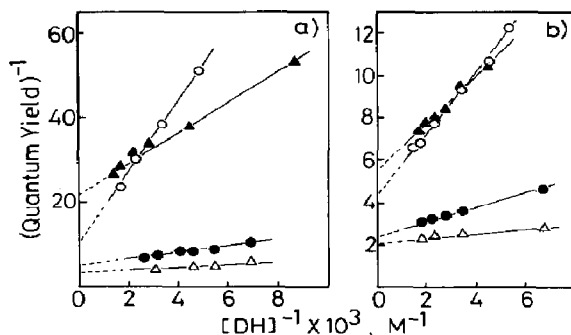

Fig. 5. Stern–Volmer plots for D^+ formation (under aerated conditions unless otherwise noted): (a) BP (○), BP–Bu$_4$NClO$_4$ (▲); (b) I–N$_2$ (△), I (●), BP–Bu$_4$NCl (○), BP–CTAC (▲). [BP] = 1 × 10^{-3} M, [R$_4$NX] = 1 × 10^{-3} M.

TABLE 2

Stern–Volmer plots of D^+ formation and phosphorescence quenching of BP and I by DH in acetonitrile

Run	System[a]	Intercept[b] (Φ_{lim})	Slope[b] (10^3 M^{-1})	Lifetime[c] (μs) (N_2)	K_1^{SV} (10^9 M^{-1} s^{-1})	k_q[d] (10^9 M^{-1} s^{-1})
1	BP	10.0(0.10)	8.95	0.27(15.6)	4.10	15.6
2	I	2.2(0.45)	0.38	0.27(18.7)	21.2	14.3
3	I–N$_2$[e]	2.1(0.48)	0.07	0.27(18.7)	1.56	14.3
4	BP–Bu$_4$NClO$_4$	22.4(0.04)	3.71	0.27(14.8)	22.2	16.8
5	BP–Bu$_4$NCl	4.5(0.22)	1.40	0.27(16.2)	11.7	17.4
6	BP–CTAC	5.6(0.18)	1.10	0.27(16.2)	18.5	18.5

[a] Under aerated conditions except for run 3.
[b] The intercept and slope values in Fig. 5.
[c] Excited triplet lifetime of BP under aerated (τ_{O_2}) (deaerated, τ_{N_2}) conditions. τ_{O_2} was determined by $\tau_{O_2} = \tau_{N_2} + k'[O_2]$. k' is the bimolecular (energy transfer) quenching rate constant of *BP by oxygen, 1×10^9 M^{-1} s^{-1} [17]. [O$_2$] has been reported to be 1.4×10^{-3} M in acetonitrile [18].
[d] Phosphorescence quenching rate constant of BP or I determined under N$_2$ atmosphere.
[e] Under deaerated conditions.

of the backward processes of k_{-1} and k_{-2}. Further discussion on the effects of R$_4$NX will be presented in the next section.

   (iii) In the I–DH–N$_2$ system, however, k_1^{SV} having a smaller value than k_q cannot be explained in the same way since the high quantum yield in this system is inconsistent with the assumption of non-negligible k_{-1} and k_{-2} values. Under deaerated conditions, D^+ formation is observed only in the I, II or III systems, while it is inhibited in the BP–DH–R$_4$NX systems, indicating an extremely strong effect of the tetraalkylammonium substituent on BP. In the BP–N,N-dimethylaniline–NaClO$_4$ or 4-[(p-dimethylamino)-benzyl]benzophenone–NaClO$_4$ system in acetonitrile, Simon and Peters recently reported that the rate constant for counter-cation exchange of the BP anion radical from the N,N-dimethylaniline cation radical to Na$^+$ was 7×10^8 M^{-1} s^{-1} as demonstrated by picosecond laser photolysis [19]. In the present case, the initially formed BP anion radical–DH cation radical pair will easily exchange its counter-cation to the BP anion radical–R$_3$N$^+$ group pair as schematized in Fig. 6. This stabilizes the BP anion radical and the DH cation radical, and also suppresses the back electron transfer to the encounter complex. The concept of ion pairing between the BP anion radical and the tetraalkylammonium substituent on BP is supported by the fact that the remotely located R$_3$N$^+$ group does not influence the efficiency as demonstrated for IV. Furthermore, coulombic repulsion between the DH cation radical and the R$_3$N$^+$ group will certainly promote efficient charge separation.

   (iv) In the I–DH–N$_2$ system, the BP anion radical is supposed to be stabilized by ion pairing with the R$_3$N$^+$ group on BP; however, there was no indication of accumulation of the BP anion radical during photoirradiation.
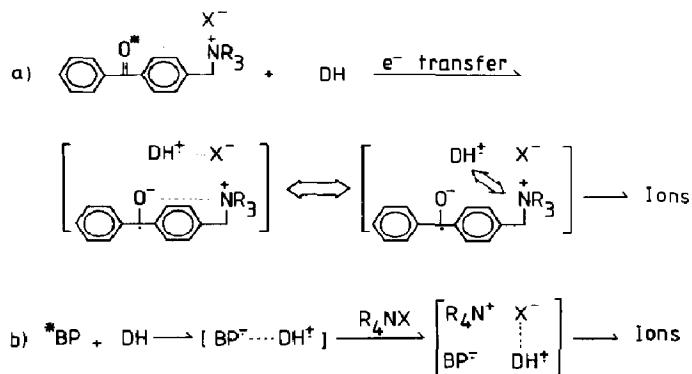
Fig. 6. Schematic representation of the effects of (a) a tetraalkylammonium substituent on BP and (b) added R_4NX on unsubstituted BP.

Although we have not carried out a product analysis, we suppose that the BP anion radical will react with H^+ (eqn. (1)) or with a small amount of water as an impurity in the solvent to give a BP radical. Transient absorption spectroscopy will provide further information on the fate of the BP anion radical.

For the photoinduced electron-transfer reaction between porphyrin derivatives, with cationic or anionic substituents, and methylviologen, it has been reported that the electrostatic interaction between charged porphyrin and methylviologen influences both encounter and charge separation processes [20]. In the present systems, where the reactions are between neutral and charged species, the encounter process is free from any coulombic effect and the ionic substituent attached to BP becomes effective only after primary electron transfer.

4.3. Effects of tetraalkylammonium salts on the photo-oxidation of DH

The concentration dependence of R_4NX on the quantum yield of D^+ formation was examined in detail for the $BP-DH-R_4NX$ system. The quantum yield increases considerably with the concentration of R_4NX as shown in Fig. 7. The addition of 1×10^{-3} M of CTAB or CTAC to the $BP-DH$ system enhances the yield by a factor of two or four relative to that in the absence of R_4NX. The rate constant of an ionic reaction between a and b in the presence of electrolyte is given by eqn. (5) [21].

$$\log k = \log k' + \frac{Z_a Z_b A \mu^{1/2}}{1 + B \mu^{1/2}} \tag{5}$$

where k and k' are the rate constants in the presence and absence of electrolyte. Z_a and Z_b are the number of charges of the reactants and μ is the ionic strength of the medium. A and B are constant at a given temperature and in a given solvent. Apparently, the present salt effects, specific to the type of salt, cannot be explained in terms of the general salt effect on the activity coefficient of the ions. Micelle formation is also unlikely under the present conditions in acetonitrile. Furthermore, the phosphorescence
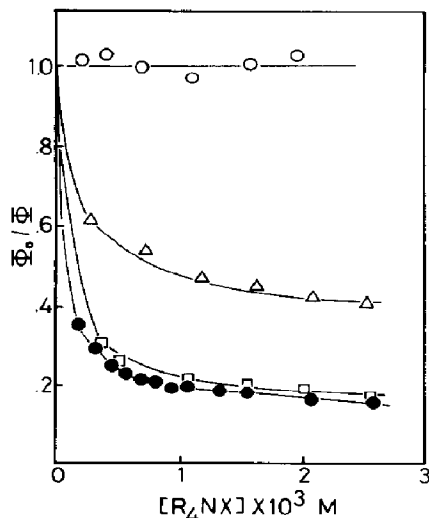
Fig. 7. Effects of tetraalkylammonium salts (R_4NX) on D^+ formation in the BP–DH system in acetonitrile. $R_4NX \equiv Bu_4NClO_4$ (○), Bu_4NCl (□), CTAC (●), CTAB (△).

quenching rate constant k_q in Table 2, of *BP, is not influenced by added salts so the successive processes after primary electron transfer from DH to *BP are considered to be subject to salt effects.

In organic solvents, electrolytes do not dissociate to free ions but rather form ion pairs [22]; so it is likely that the ion pairing between the BP anion radical and R_4N^+ or between the DH cation radical and X^- produced by counter-ion exchange reaction [19] enhances charge separation efficiencies (Fig. 6). Since the quantum yields depend on the nature of X^- but not on the structure of R_4N^+, the enhancement of the yield is mainly ascribed to ion pair formation between the DH cation radical and X^-.

The structure dependence of R_4NX on the DH photo-oxidation may be explained as follows. Solvation around cations or anions is facilitated in a solvent having a high donor number (DN) or a high acceptor number (AN) respectively [23]. Acetonitrile, having a high AN (19.3) as well as a high DN (14.1), solvates both cations and anions strongly. For R_4N^+, however, cationic charge localizes on a nitrogen atom so that the degree of solvation around R_4N^+ will not depend on the structure of the alkyl group unless steric hindrance is important. However, solvation around uninegative anions will depend strongly on their size. The sequence of catalytic activity of R_4NX for a given R decreases with increasing size of X^-: $Cl^- > Br^- > ClO_4^-$ (Fig. 7). However, the effect of R on Φ is almost negligible for a given X^- (Table 1, runs 10, 11, and 13, and Table 2, runs 5 and 6), indicating that the nature of the ion pair between the DH cation radical and X^- is the key to separating the DH cation radical from the BP anion radical. Recently, we reported that the exciplex emission from pyrene–1,4-dicyanobenzene or pyrene–N,N-dimethylaniline was quenched by various compounds R_4NX in chloroform [24]. It was concluded that the electrostatic interaction or ion pairing between R_4NX and the dipolar exciplexes promoted the dissocia-

tion process leading to exciplex quenching. Similarly, the action of R_4NX in the present experiments is interpreted as a result of reduced interaction between ion radicals.

5. Conclusions

The photo-oxidation efficiency of DH was highly improved using BP derivatives with tetraalkylammonium substituents (*i.e.* I, II and III) as well as by the addition of tetraalkylammonium salts to the BP–DH system. The high photo-oxidizing efficiencies of I, II and III could be attributed to the stabilization of the BP anion radical by ion pairing with the R_3N^+ substituent on BP as well as to the electrostatic repulsion between the DH cation radical and the R_3N^+ group of BP (Fig. 6). Furthermore, in the BP–DH–R_4NX system, ion pair formation between the DH cation radical and X^- enormously enhanced the charge separation efficiencies, thus giving high quantum yields.

Such effects on electron-transfer reactions by the ionic substituent on an electron-transfer sensitizer or by added electrolyte are general phenomena. Analogous coulombic effects have been demonstrated on the photoinduced electron-transfer reactions between phenothiazine derivatives, with cationic, anionic or neutral substituents, and methylviologen or propylviologen sulphonate [25]. The photoreduction yields of methylviologen were also improved by the addition of an electrolyte in the *N*-methylphenothiazine–methylviologen–aqueous acetonitrile system [26]. The present results indicate that the use of coulombic effects can provide an effective approach for the improvement of quantum yields for various electron-transfer reactions.

References

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Appendix A

Applying the steady state approximation to all intermediates (*i.e.* *BP, the encounter complex $\equiv$ X, the ion radical pair $\equiv$ Y, DH^{+} and $D^{\cdot}$), we derived eqn. (3) as follows.

The steady state concentrations of *BP, X and Y are expressed as eqns. (A1), (A2) and (A3) respectively, where I represents absorbed photons.

$$[*BP] = \frac{I + k_{-1}[X]}{\tau^{-1} + k_1[DH]} \tag{A1}$$

$$[X] = \frac{Ik_1[DH] + k_{-2}[Y](\tau^{-1} + k_1[DH])}{k_e(\tau^{-1} + k_1[DH]) - k_1 k_{-1}[DH]} \tag{A2}$$

$$[Y] = \frac{Ik_1 k_2[DH]}{(k_1 k_e - k_2 k_{-2})(\tau^{-1} + k_1[DH]) - k_1 k_{-1} k_1[DH]} \tag{A3}$$

The equilibrium constant for eqn. (1) is written as

$$K = \frac{k_{-7}}{k_7} = \frac{[D^{\cdot}][H^+]}{[DH^{+}]} \tag{A4}$$

On the assumption that $k_7[D^{\circ}][H^+] \gg k_8[DH^{+}][D^{\cdot}]$, eqns. (A5) and (A6) are obtained.

$$[DH^{\dagger}] = \frac{(k_5 + k_6[O_2])[Y]}{k_7 + k_8[D^{\cdot}] - k_{-7}K} \tag{A5}$$

$$[D^{\cdot}] = \frac{k_7 - k_{-7}K}{k_8} \tag{A6}$$

The quantum yield of D^+ formation, Φ, is expressed in eqn. (A7),

$$\Phi = \frac{k_8[DH^{\dagger}][D^{\cdot}]}{I} \tag{A7}$$

so that Φ can be rewritten as in eqn. (A8) using eqns. (A3), (A5) and (A6).

$$\Phi = \frac{k_1 k_2[DH](k_5 + k_6[O_2])}{2(k_1 k_e - k_2 k_{-2})(\tau^{-1} + k_1[DH]) - k_1 k_{-1}k_1[DH]} \tag{A8}$$

The inverse of eqn. (A8) corresponds to eqn. (3) in the main text.