Laser photolysis investigation of induced quenching in photoreduction of benzophenone by alkylbenzenes and anisoles[†]

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Downloaded on 05 June 2012 Published on 01 January 1998 on http://pubs.rsc.org | doi:10.1039/A707900A a mixture of acetonitrile (ACN) and water (4:1 v/v) have been studied on the basis of rate constants and efficiencies determined by nanosecond laser flash photolysis at 355 nm at 295 K. It was found that (1) the deactivation of ³BP* by ADs in ACN-H₂O (4:1 v/v) was governed by electron transfer (ET) to produce the benzophenone anion (BP⁻⁻) and corresponding cation (AD⁺⁺) radicals with efficiencies, $\alpha_{ET} < 1$ whereas no chemical species were formed in Bz; and (2) photoreduction of ³BP* by ABs resulted in benzophenone ketyl radical (BPK) formation by benzylic hydrogen abstraction (HA) with efficiencies $\alpha_{HA} < 1$ in Bz and ACN-H₂O (4:1 v/v). The residual efficiency (α_{IQ} : 1 - α_{ET} or 1 - α_{HA}) was attributed to a bimolecular process with no photochemical product, which was named 'induced-quenching (IQ)'. The quenching rate constants (k_{α}) of ³BP* by ADs and ABs were less than the diffusion limits of both Bz and ACN-H₂O (4:1 v/v). The net bimolecular rate constants for the ET, HA and IQ processes were estimated from the k_{a} values and efficiencies. The rate constants (k_{ET} and k_{IO}) of ET and IQ with AD versus the oxidation potential (E_{ox}) of AD followed Rehm–Weller behaviour while logarithmic rate constants (k_{HA} and k_{IO}) of HA and IQ by ABs increased linearly with a decrease in the E_{ox} of AB. It was suggested, for the deactivation mechanism of ³BP* by ABs and ADs (RH), that (1) the IQ process was intersystem crossing (ISC) enhanced by the partial charge-transfer (CT) character of the triplet exciplexes, ${}^{3}(BP^{\delta-}\cdots RH^{\delta+})^{*}_{cage}$; (2) radical ion formation by ET might be accomplished in a polar solvent by further CT interaction in the exciplex; (3) the process of BPK formation was inferred to be H-atom transfer in the exciplex, where the more protic H-atom was readily mobile, rather than ET followed by proton transfer and (4) the loss of efficiencies of photochemicalproduct formation was derived not from back ET but from the IQ process, inherent to photoreactions, via triplet exciplexes. The deactivation processes of ³BP* by RH are illustrated in Scheme 1.

The quenching processes of triplet benzophenone $({}^{3}BP^{*})$ by alkylbenzenes (AB) and anisole derivatives (AD) in benzene (Bz) and



Photoreduction of triplet ketones by alkanes, alcohols, amines, *etc.* has been studied experimentally and theoretically since it is preceded by elemental chemical reactions, H-atom and electron transfer (HT and ET).^{1–14} The mechanism of the primary photoreduction of benzophenone (BP) has been extensively studied by means of product analysis and laser photolysis techniques.^{15–45} The development of pico-, and femto-second laser instruments has enabled it to be shown^{36–42} that photoreduction of triplet BP (³BP*) by amines (AH) proceeds *via* ET followed by proton transfer (PT) in the ion pair or exciplex with strong CT character, resulting in the production of the benzophenone ketyl radical (BPK) (the ETPT mechanism):^{2,11,17,33b,36–42}

$$^{3}BP^{*} + AH \xrightarrow{ET} ^{3}(BP^{-}\cdots AH^{+}) \xrightarrow{PT} BPK + A$$

where A' represents an amine radical. The quantum yields of BPK formation by some amines were found to be less than

unity.^{34,39} The loss in product yield was considered to be due to back ET in the ion pair or CT complex prior to PT leading to BPK formation.^{11,17,37,39} In the formation of BPK from ³BP* by amines, a strong CT exciplex or ion pair plays an important role in the primary step of photoreduction.

When the quenching of the excited molecules is governed by CT interaction, the quenching rate constant depends on the redox potentials of the reactants.⁴⁶ Plots of the quenching rate constant of ³BP* versus the ionization (or oxidation) potentials of quenchers, not only amines but also alkylbenzenes, have well documented CT interaction.43,44 Wagner et al. showed by the product-analysis method that triplet acetophenone derivatives were reduced in a CT process, even by alkylbenzenes.²⁸ Such processes may involve triplet exciplexes with weak CT interaction, while no formation of the BP anion radical nor CT exciplex was reported for reduction of ³BP* by alcohols.²³ There have been many reports of rate constants for HA of ³BP* by alkylbenzenes to produce BPK.^{1a,4,28b} However, the rate constant of BPK formation has been regarded to be equal to that of the quenching process. In other words, the efficiency of BPK formation has been assumed to be unity. In order to understand the HA mechanism by alkylbenzenes where exciplex formation may be

[†] A preliminary discussion of their work was given at the 54th Okazaki Conference: Dynamic Studies on Hydrogen Atom Transfer Reactions, January, 1996, Okazaki, Japan and it was presented at the XVIth IUPAC Symposium on Photochemistry, July, 1996, Helsinki, Finland.

involved, the efficiency and net rate constant for BPK formation should be determined precisely.

In our previous work on photoreduction of BP by toluene derivatives substituted with halogen atom(s) (XPhCH₃), the deactivation pathways of ³BP* were investigated in terms of heavy atom effects by nanosecond laser flash photolysis techniques.⁴⁵ It was found that the efficiency of BPK formation from ³BP* was less than unity. The residual efficiency implied another deactivation pathway of ³BP* as well as HA; this was called 'induced quenching (IQ)'.



where XPhCH₂ stands for the corresponding benzyl-type radicals. In the XPhCH₃ case, the rate constant of HA of ³BP* from XPhCH₃ was almost independent of the spin-orbit coupling constants (ξ) of XPhCH₃, whereas those of IQ increased with an increase in the ξ^2 value. These results implied that IQ would have an intersystem crossing pathway.⁴⁵ However, the total mechanism of deactivation, including the IQ process, has not yet been made clear.

In the present study, nanosecond laser photolysis was used to investigate the photoreduction of BP by alkylbenzenes with various oxidation potentials. For comparison, anisole derivatives were employed, as they had no benzylic H-atom to be abstracted and lower oxidation potentials than alkylbenzenes. The deactivation mechanism of ³BP* by benzene derivatives was discussed in terms of triplet exciplexes with CT character originating ET, HA and IQ processes.

Experimental

BP was purified by recrystallization from ethanol. Anisole, 4methoxytoluene (4MeOTol), mesitylene (135MeB), 1,2,4-trimethoxybenzene (124MeOB), *p*-xylene (14MeB), *m*-xylene (13MeB), 1,2,4-trimethylbenzene (124MeB) and 1,2,3,4-tetramethybenzene (1234MeB) were distilled *in vacuo*. 1,3,5-Trimethoxybenzene (135MeOB), 1,2,3-trimethoxybenzene (123MeOB), 1,4-dimethoxybenzene (14MeOB), pentamethylbenzene (PMeB), hexamethylbenzene (HMeB) and durene (1245MeB) were purified by vacuum sublimation. These materials were commercially available. Toluene (Tol, Infinity Pure from Wako) was used as supplied. 1,2,4,5-Tetramethoxybenzene (1245MeOB) was synthesized according to the literature.⁴⁷

The oxidation potentials (E_{ox}) of AB and AD were obtained from the literatures^{48,49} or determined from the CT absorption band with tetracyanoethylene in acetonitrile (ACN) at 295 K.⁵⁰ Benzene (Bz, Dojin Spectrosol) was used as supplied. ACN and deionized water were distilled. Bz and a mixture of ACN and H₂O (4:1 v/v) were used as solvents.

The concentration of BP was 6.7×10^{-3} mol dm⁻³ throughout this work. All samples, in a quartz cell of a 10 mm path length, were thoroughly degassed by freeze-pump-thaw cycles on a high vacuum line.

Laser flash photolysis was carried out at 295 K by using the third harmonics (355 nm) of an Nd³⁺ : YAG laser from J. K. Lasers (HY-500). The pulse duration, energy and diameter of the laser beam were 8 ns, 40 mJ pulse⁻¹, and 12 mm, respectively. The detection system for transient absorption spectra has been reported elsewhere.⁵¹

Results

Quenching of ³BP* by ABs

It is well known that toluene behaves as an H-donor for

³BP*.^{1a,4,28b} Fig. 1(a) shows the time-resolved transient absorption spectra obtained by laser flash photolysis at 355 nm in the BP–Tol (2.8 mol dm⁻³) system in Bz. The absorption band at 530 nm observed at 300 ns is ascribed to the triplet-triplet (T–T) absorption of BP in a non-polar solvent.⁵² With time, the T–T absorption of BP decreases in intensity with a first-order decay rate (k_{obsd}) to give the absorption spectrum of the BPK radical having a peak at 545 nm⁵³ at 4.0 µs. Thus, Fig. 1(a) demonstrates that the deactivation of ³BP* in the presence of Tol involves HA from Tol to give BPK and the benzyl radical which has no absorption in the wavelength range used 380–650 nm.⁵⁴ The experimentally obtained k_{obsd} value increased linearly with increase in [Tol]. Thus, the k_{obsd} value may be expressed by:

$$k_{\text{obsd}} = k_0 + k_{\mathfrak{q}}[\text{Tol}] \tag{1}$$

where k_q and k_0 represent the rate constants for the quenching of ³BP* by Tol and the decay of ³BP* in the absence of Tol, respectively. From eqn. (1), k_q (3.1 × 10⁵ dm³ mol⁻¹ s⁻¹) and k_0 (3.3 × 10⁵ s⁻¹) values in the BP-Tol system in Bz were obtained.

The efficiency (α_{HA}) for HA of ³BP* from Tol was determined on the basis of the quantum yield (Φ_{BPK}) for the formation of BPK. The Φ_{BPK} value was determined from the net absorbance (ΔA_{545}) at 545 nm due to formation of BPK after depletion of ³BP* [see *e.g.* Fig. 1(b)] by:

$$\Phi_{\rm BPK} = \Delta A_{545} \, \varepsilon_{545}^{\rm BPK-1} I_{\rm abs}^{-1} N_{\rm A} \tag{2}$$

where ε_{545}^{BPK} , I_{abs} and N_A are the molar absorption coefficient of BPK at 545 nm (3700 dm³ mol⁻¹ cm⁻¹),⁵³ the absorbed photon flux of an incident laser pulse and Avogadro's number, respectively. I_{abs} was evaluated by using the T–T absorption of BP in ACN as an actinometer. After laser pulsing in an ACN solution of BP in a 10 mm path length cell, the initial absorbance change (ΔA_{520}) due to ³BP* at 520 nm is related to I_{abs} by:

$$\Delta A_{520} = \Phi_{\rm ISC}^{\rm BP} \varepsilon_{520}^{\rm BP} I_{\rm abs} N_{\rm A}^{-1} \tag{3}$$

where $\Phi_{\rm ISC}^{\rm BP}$ and $\varepsilon_{520}^{\rm BP}$ represent the triplet yield of BP (1.0)⁵⁵ and the molar absorption coefficient of ³BP* in ACN at 520 nm (6500 dm³ mol⁻¹ cm⁻¹),⁵⁶ respectively. The plots of $\Phi_{\rm BPK}$, obtained experimentally in the BP–Tol system, in Bz, as a function of [Tol] are shown in Fig. 2.

With an increase in [Tol], the $\Phi_{\rm BPK}$ value increases, showing a negative curve. On the other hand, the $\Phi_{\rm BPK}$ value



Fig. 1 (a) Transient absorption spectra at 300 ns (\bigcirc) and 4.0 µs (\bigcirc) obtained by 355 nm laser flash photolysis in the BP–Tol (2.8 mol dm⁻³) system in Bz. (b) The time profile of the transient absorbance at 545 nm for the corresponding system.



Fig. 2 $\Phi_{\rm BPK}$ vs. [Tol] for the BP–Tol system in Bz. The solid curve was calculated by eqn. (4). See text for details.

can be formulated by:

$$\Phi_{\rm BPK} = \frac{k_{\rm q} \,\alpha_{\rm HA}[\rm Tol]}{k_0 + k_{\rm q}[\rm Tol]} \,\Phi_{\rm ISC}^{\rm BP} \tag{4}$$

Using a best-fit technique, the α_{HA} value was found to be 0.77 \pm 0.04. The solid curve in Fig. 2 was simulated with the best-fit parameters. The residual efficiency ($\alpha_{IQ} = 1 - \alpha_{HA}$) was considered to be attributed to IQ of ³BP* by Tol, since no reaction except for HA occurred during the decay of ³BP*, as seen from the transient absorption spectral changes. Hence, the α_{IQ} value was determined to be 0.23 \pm 0.04 for the BP–Tol system in Bz.

The rate constants $(k_{\text{HA}} \text{ and } k_{\text{IQ}})$ for HA and IQ are given by:

$$k_{\rm HA} = \alpha_{\rm HA} \, k_{\rm q} \tag{5}$$

$$k_{\rm IQ} = \alpha_{\rm IQ} \, k_{\rm q} \tag{6}$$

where $k_q = k_{HA} + k_{IQ}$. The k_{HA} and k_{IQ} values were 2.4 × 10⁵ and 7.1 × 10⁴ dm³ mol⁻¹ s⁻¹, respectively, for the BP–Tol system in Bz.

Since formation of BPK was observed in other BP–AB systems in Bz as well as in $ACN-H_2O$ (4:1 v/v), the AB used seemed to behave as an H-atom donor. The efficiencies and rate constants for other BP–AB systems were determined by the same procedures as for Tol, and are listed in Table 1.

Quenching of ³BP* by anisole derivatives

Upon 355 nm laser excitation in the BP–AD systems in Bz, the T–T absorption of BP decreased according to first-order kinetics, giving no residual absorption spectrum. Hence, the deactivation processes of ³BP* by ADs in Bz were due completely to IQ, *i.e.* $\alpha_{IQ} = 1.0$. The k_q [= k_{IQ} , see eqn. (6)] values were obtained by the same procedure as for the BP–AB system.

On changing the solvent from Bz to ACN-H₂O (4:1 v/v), a surprising change was observed in the quenching profile of



Fig. 3 (a) Transient absorption spectra observed at (1) 100, (2) 180, (3) 300 and (4) 800 ns after 355 nm laser pulsing for BP-1245MeOB $(6.0 \times 10^{-4} \text{ mol dm}^{-3})$ in ACN-H₂O (4 : 1 v/v). (b) Reference absorption spectra for BP⁻ (----) and 1245MeOB⁺⁺ (---).

³BP* by AD. Fig. 3(a) shows the time-resolved transient absorption spectra obtained by laser flash photolysis at 355 nm in the BP-1245MeOB (6.0×10^{-4} mol dm⁻³) system in ACN-H₂O (4:1 v/v). The transient absorption spectrum at 520 nm observed at 100 ns may be ascribed to ³BP* in a polar solvent.⁵² With time, the T-T absorption of BP decreases in intensity according to first-order kinetics to give residual absorption bands with peaks at 630 and 450 nm at 800 ns with isosbestic points at 555 and 465 nm. This residual absorption spectrum was reproduced by superposing those of the benzophenone anion (BP⁻⁻)⁵⁷ and 1245MeOB cation (1245MeB⁺⁺)⁵⁸ radicals [see Fig. 3(b)] in a 1:1 concentration ratio. Hence, the spectral changes in Fig. 3(a) demonstrate ET from 1245MeOB to ³BP* to produce BP⁻⁻ and 1245MeOB⁺⁺.

The quantum yield (Φ_{ani}) for formation of BP⁻⁻ was obtained from:

$$\Phi_{\rm ani} = \Delta A_{630} \,\varepsilon_{630}^{\rm ani-1} I_{\rm abs}^{-1} \tag{7}$$

where ΔA_{630} and ε_{630}^{ani} represent the net absorbance at 630 nm due to formation of BP⁻⁻ and the molar absorption coefficient of BP⁻⁻ at 630 nm (5700 dm³ mol⁻¹ cm⁻¹)[†] respectively.§

On the other hand, the Φ_{ani} value may be calculated from eqn. (8) with the use of the efficiency (α_{ET}) of ET between ³BP* and 1245MeOB.

[‡] By taking the ε value of BPK as 3700 dm³ mol⁻¹ cm⁻¹ at 545 nm,⁵³ ε for BP⁻⁻ was re-estimated to be 5700 dm³ mol⁻¹ cm⁻¹ at 630 nm by the method given in ref. 57(*a*).

§ The AD cation radicals, except for 135MeOB^{•-}, produced in this work had no absorption at 630 nm. The ϵ_{630}^{135} value of 135MeOB^{•+} at 630 nm was 500 dm³ mol⁻¹ cm⁻¹ in ACN-H₂O (4 : 1 v/v). In analysis for the 135MeOB case, ϵ_{630}^{ani} in eqn. (7) was replaced by $\epsilon_{630}^{ani} + \epsilon_{630}^{135}$.

Table 1 E_{ox} of AB and efficiencies and rate constants obtained for the BP–AB system in Bz and ACN–H₂O (4:1 v/v)^a

			Bz					ACN- H_2O (4 : 1 v/v)				
AB	$E_{\mathrm{ox}}^{\ \ b}/\mathrm{V}$	k_{q}^{c}	$\alpha_{\rm HA}^{\ \ d}$	α_{IO}^{e}	$k_{\rm HA}{}^f$	k _{IO} ^g	k_{q}^{c}	$\alpha_{\rm HA}^{\ \ d}$	α_{IO}^{e}	$k_{\rm HA}{}^f$	k _{IO} g	
Tol	2.25	3.1×10^{5}	0.77	0.23	2.4×10^{5}	7.1×10^{4}	n.d. ^h	n.d. ^h	n.d. ^h	n.d. ^h	n.d. ^h	
13MeB	2.11	1.5×10^{6}	0.50	0.50	7.5×10^{5}	7.5×10^{5}	n.d. <i>"</i>	n.d. <i>"</i>	n.d."	n.d. <i>"</i>	n.d. <i>"</i>	
14MeB	2.06^{i}	1.7×10^{6}	0.73	0.27	1.2×10^{6}	4.6×10^{5}	n.d. ^{<i>h</i>}	n.d. ^{<i>h</i>}	n.d. ^{<i>h</i>}	n.d. ^{<i>h</i>}	n.d. ^h	
135MeB	2.02	9.9×10^{6}	0.21	0.79	2.1×10^{6}	7.8×10^{6}	4.7×10^{7}	0.11	0.89	5.2×10^{6}	4.2×10^{7}	
124MeB	1.89 ⁱ	7.2×10^{6}	0.44	0.56	3.2×10^{6}	4.0×10^{6}	3.5×10^{7}	0.25	0.75	8.8×10^{6}	2.6×10^{7}	
1245MeB	1.79	3.2×10^{7}	0.36	0.64	1.2×10^{7}	2.0×10^{7}	1.7×10^{8}	0.27	0.73	4.6×10^{7}	1.2×10^{8}	
1234MeB	1.76	3.1×10^{7}	0.31	0.69	9.6×10^{6}	2.1×10^{7}	1.7×10^{8}	0.21	0.79	3.6×10^{7}	1.3×10^{8}	
PMeB	1.71	1.8×10^{8}	0.16	0.84	2.9×10^{7}	1.5×10^{8}	8.7×10^{8}	0.25	0.75	2.2×10^{8}	6.5×10^{8}	
HMeB	1.58	1.1×10^{9}	0.08	0.92	8.8×10^{7}	1.0×10^{9}	4.2×10^{9}	0.24	0.76	1.0×10^{9}	3.2×10^{9}	
4MeOTol ^j	1.58 ^k	2.4×10^{7}	0.17	0.83	4.1×10^{6}	2.0×10^{7}	1.9×10^{8}	0.26	0.58	4.9×10^{7}	1.1×10^8	

^{*a*} Errors within 5% for rate constants and efficiencies. ^{*b*} vs. SCE in ACN. Data from ref. 48. ^{*c*} Quenching rate constant of ³BP* by AB in dm³ mol⁻¹ s⁻¹. ^{*d*} Efficiencies for BPK formation. ^{*e*} Efficiencies for IQ of ³BP* by AB. ^{*f*} Rate constants for HA of ³BP* from AB in dm³ mol⁻¹ s⁻¹. ^{*b*} Rate constants for IQ of ³BP* by AB in dm³ mol⁻¹ s⁻¹. ^{*b*} Not determined due to low solubility. ^{*i*} vs. SCE in trifluoroacetic acid. ^{*j*} See text for details. ^{*k*} Obtained by the CT method. See text.

$$\Phi_{\rm ani} = \frac{\alpha_{\rm ET} k_{\rm q} [1245 \text{MeOB}]}{k_{\rm 0} + k_{\rm a} [1245 \text{MeOB}]} \Phi_{\rm ISC}^{\rm BP}$$
(8)

Using a best-fit technique for the experimental Φ_{ani} values and the k_q (7.6 × 10⁹ dm³ mol⁻¹ s⁻¹) and k_0 (1.5 × 10⁵ s⁻¹) values for the BP-1245MeOB system in ACN-H₂O (4 : 1 v/v), as for Tol, the α_{ET} value was found to be 0.96 ± 0.05. The residual efficiency due to IQ ($\alpha_{IQ} = 1 - \alpha_{ET}$) of ³BP* by 1245MeOB was found to be 0.04 ± 0.05.

The rate constants ($k_{\rm ET}$ and $k_{\rm IQ}$) for the BP-1245MeOB system in ACN-H₂O (4:1 v/v) were determined to be 7.3 × 10⁹ and 3.0 × 10⁸ dm³ mol⁻¹ s⁻¹, using eqn. (9) and (6), respectively.

$$k_{\rm ET} = \alpha_{\rm ET} k_{\rm q} \tag{9}$$

The formation of radicals was observed in other BP-AD systems in ACN-H₂O (4:1 v/v), except for the anisole case, where the deactivation of ³BP* involved only IQ. The rate constants and efficiencies for ADs are summarized in Table 2.

Quenching of ³BP* by 4MeOTol

In Bz, 4MeOTol quenched ³BP* efficiently to yield BPK as well as other ABs. The same procedures for determination of the rate constants and efficiencies as used for ABs were employed. In ACN-H₂O (4 : 1 v/v) however, simultaneous formation of both BPK and BP⁻⁻ was found. The $\Phi_{\rm BPK}$ and $\Phi_{\rm ani}$ values were evaluated from the transient absorbances at 545 and 630 nm by eqn. (10) and (7), respectively, since BPK had no absorption at 630 nm.

$$\Phi_{\rm BPK} = (\Delta A_{545} - \Delta A_{630} \,\varepsilon_{545}^{\rm ani} \,\varepsilon_{630}^{\rm ani-1}) \varepsilon_{545}^{\rm BPK-1} I_{\rm abs}^{-1} N_{\rm A} \tag{10}$$

where ε_{545}^{ani} is the molar absorption coefficient of BP⁻⁻ at 545 nm (2850 dm³ mol⁻¹ cm⁻¹).⁵⁷ The efficiency of IQ in ACN-H₂O (4 : 1 v/v) was calculated from eqn. (11).

$$\alpha_{\rm IQ} = 1 - \alpha_{\rm HA} - \alpha_{\rm ET} \tag{11}$$

Discussion

The bimolecular rate constants of quenching (k_q) were found to be less than the diffusion limits of Bz $(1.1 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})^{55}$ and ACN-H₂O (4:1 v/v) $(1.4 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$. This indicates that the deactivation of ³BP* by AB and AD proceeds *via* collision processes. It is reasonable to assume formation of collision complexes immediately after encounter of ³BP* with AB or AD. In ACN-H₂O (4:1 v/v), ET between ³BP* and AD was observed with bimolecular rate constants (k_{ET}) . Such outer-sphere ET in the triplet state is often explained by the Rehm-Weller mechanism.⁴⁶ Fig. 4 shows the plots of k_{ET} for the BP-AD systems as well as k_{IQ} as





Fig. 4 Logarithmic plots of $k_{\rm ET}$ (\bullet) and $k_{\rm IQ}$ (\bigcirc) in ACN-H₂O (4:1 v/v) and $k_{\rm IQ}$ (\triangle) in Bz for the BP-AD systems, as a function of the $E_{\rm ox}$ of AD. The solid curve was calculated for $k_{\rm ET}$ by eqn. (12). See text for details.

a function of the oxidation potential (E_{ox}) of AD. With a decrease in the E_{ox} value of AD, the k_{ET} value increases and then levels off. The k_{ET} value can be expressed by an Arrhenius-type expression:⁴⁶

$$k_{\rm ET} = A \, \exp(-\Delta G_{\rm ET}^{\ddagger}/RT) \tag{12}$$

where $\Delta G_{\rm ET}^{\ddagger}$ is the activation energy which is correlated by the Rehm–Weller equation with the Gibbs energy change ($\Delta G_{\rm ET}$) of ET.⁴⁶

$$\Delta G_{\rm ET}^{\ddagger} = \Delta G_{\rm ET}/2 + \left[(\Delta G_{\rm ET}/2)^2 + (\Delta G_{\rm ET}^{\ddagger}(0))^2 \right]^{1/2}$$
(13)

where $\Delta G_{\rm ET}^{\dagger}(0) \ (= 2.4 \ {\rm kcal \ mol}^{-1})^{59}$ denotes the Gibbs energy of activation at $\Delta G_{\rm ET} = 0$. The $\Delta G_{\rm ET}$ value was evaluated from:⁴⁶

$$\Delta G_{\rm ET} = 23.06(E_{\rm ox} - E_{\rm red}) - E_{\rm T} - \delta$$
 (in kcal mol⁻¹) (14)

where $E_{\rm red}$, $E_{\rm T}$ and δ represent the reduction potential of BP (-1.83 V vs. SCE in ACN),⁵⁵ the triplet energy of BP (68.1 kcal mol⁻¹ at 295 K)⁴⁵ and the calibrating term, respectively. The solid curve in Fig. 4 was calculated using eqn. (12) with the best-fit parameters, $A = 1.4 \times 10^{10}$ dm³ mol⁻¹ s⁻¹ and $\delta = 8.0$ kcal mol⁻¹. Hence, the ET in the BP-AD system may be interpreted by the Rehm-Weller relation. The radical formation process via ET can be analysed into two steps as follows: according to the conservation rule of spin-multiplicity, a triplet radical pair, ${}^{3}(\text{BP}^{-} + \text{AD}^{+})_{\text{cage}}$ is produced in a solvent cage after ET in a collision complex (${}^{3}\text{BP}^{*} + \text{AD})_{\text{col}}$ formed between ${}^{3}\text{BP}^{*}$ and AD.

$$({}^{3}\mathrm{BP}^{*} + \mathrm{AD})_{\mathrm{col}} \xrightarrow{\mathrm{ET}} {}^{3}(\mathrm{BP}^{*-} + \mathrm{AD}^{*+})_{\mathrm{cage}}$$
 (I)

The rate of ISC of the triplet radical pair would be less than that of escaping from the solvent cage, owing to its relatively long triplet lifetime. That is, the triplet radical pair can escape readily from the solvent cage before ISC to the singlet state where back ET becomes possible.

$$^{3}(BP^{\cdot -} + AD^{\cdot +})_{cage} \xrightarrow{escape} BP^{\cdot -} + AD^{\cdot +}$$
 (II)

Table 2 E_{ox} of AD and efficiencies and rate constants and rate constants obtained in the BP-AD systems in Bz and ACN-H₂O (4:1 v/v)^a

			D-7				
AD	$E_{\mathrm{ox}}^{\ \ b}/\mathrm{V}$	k_q^c	$\alpha_{\rm ET}^{\ \ d}$	α_{IO}^{e}	$k_{\rm ET}{}^f$	k10 ^g	k_{IO}^{g}
Anisole	1.76	1.2×10^{7}	0	1.0	0	1.2×10^{7}	2.1×10^{6}
4MeOTol	1.58 ^h	1.9×10^{8}	0.16	0.58	3.0×10^{7}	1.1×10^{8}	2.0×10^{7}
135MeOB	1.49	5.1×10^{8}	0.27	0.73	1.4×10^{8}	3.7×10^{8}	9.1×10^{7}
123MeOB	1.42	6.6×10^{8}	0.41	0.59	2.7×10^{8}	3.9×10^{8}	1.3×10^{8}
14MeOB	1.34	3.8×10^{9}	0.96	0.04	3.6×10^{9}	1.5×10^{8}	5.1×10^{8}
124MeOB	1.12	5.9×10^{9}	0.92	0.08	5.4×10^{9}	4.7×10^{8}	2.0×10^{9}
1245MeOB	0.81	7.6×10^{9}	0.96	0.04	7.3×10^{9}	3.0×10^{8}	4.5×10^{9}

^{*a*} Errors within 5% for rate constants and efficiencies. ^{*b*} vs. SCE in ACN. Data from ref. 49. ^{*c*} Quenching rate constants of ³BP* by AD in dm³ mol⁻¹ s⁻¹. ^{*d*} Efficiency for the formation of BP⁻. ^{*e*} Efficiency for IQ of ³BP* by AD. ^{*f*} Rate constant of ET of ³BP* from AD in dm³ mol⁻¹ s⁻¹. ^{*g*} Rate constant of IQ of ³BP* by AD in dm³ mol⁻¹ s⁻¹. ^{*h*} Obtained by the CT method. See text.

Hence, back ET is no longer the major process for reduction in the efficiency of radical formation. The precursor of the IQ process should be effective before formation of the triplet radical pair in the solvent cage. Considering the k_{IQ} values in both Bz and ACN-H₂O (4:1 v/v), they follow Rehm-Weller behaviour versus the E_{ox} . These results imply that the intermediate for the ET process would be common with that for IQ. In order to describe the mechanism including both ET and IQ, we propose a triplet exciplex with CT character, ³(BP^{δ^-}···AD^{δ^+})^{*}_{cage} as a common precursor.

$$({}^{3}\mathrm{BP}^{*} + \mathrm{AD})_{\mathrm{col}} \rightarrow {}^{3}(\mathrm{BP}^{\delta^{-}} \cdots \mathrm{AD}^{\delta^{+}})_{\mathrm{cage}}^{*}$$
 (III)

After collisions between ³BP* and AD, electronic interaction starts to form a partial CT exciplex [eqn. (III)]. Since little change in the absorption spectrum of ³BP* was observed throughout the present study, CT interaction must be weak. It has been reported that partial CT enhances ISC from the excited singlet to the triplet state.^{60–62} Similarly, it may enhance crossing from the triplet to the ground state [eqn. (IV)].

$$^{3}(\mathrm{BP}^{\delta^{-}}\cdots\mathrm{AD}^{\delta^{+}})^{*}_{\mathrm{cage}} \xrightarrow{\mathrm{ISC}} \mathrm{BP} + \mathrm{AD}$$
 (IV)

Considering the change in spin-multiplicity for IQ, the corresponding process is ISC. We have shown that IQ undergoes the heavy atom effect, which is characteristic of ISC.⁴⁵ Thus, we tentatively conclude that IQ is enhanced by the CT character of the triplet exciplexes. In the present work, no radical formation was observed in Bz whose relative permittivity $\varepsilon = 2.3.^{55}$ In the CT exciplex in Bz, the rate of radical-ion formation may be less than that of ISC induced by the CT character. On the other hand, in the more polar solvent, the partial CT readily proceeds to full charge separation, *i.e.* ET, since the radical ions produced are then stabilized by solvent molecules.

$${}^{3}(BP^{\delta-}\cdots AD^{\delta+})^{*}_{cage} \xrightarrow{ET} {}^{3}(BP^{*-} + AD^{*+})_{cage}$$
(V)

Owing to the large polarity of ACN-H₂O (4:1 v/v) (κ = 44.5),** the rate of charge separation may increase sufficiently to compete with ISC.

When AD was replaced by AB as a quencher, HA occurred in both Bz and ACN-H₂O (4:1 v/v) to yield BPK together with the corresponding benzyl radicals (BzyR). Considering the formation process of these radicals step by step, a triplet radical pair might be produced *via* the collision complex, according to the spin-conservation rule.

$$({}^{3}BP^{*} + AB)_{col} \xrightarrow{HA} {}^{3}(BPK + BzyR)_{cage}$$
 (VI)

Fig. 5 shows plots of k_{HA} and k_{IQ} for the BP-AB systems in both Bz and ACN-H₂O (4 :1 v/v). Both logarithmic rate constants show a linear correlation with the E_{ox} of AB. These linear plots imply CT interaction of precursors for HA and IQ. By analogy with the BP-AD system, even in the BP-AB system, we assume a CT exciplex, ${}^{3}(\text{BP}^{\delta} \cdots \text{AB}^{\delta+})_{\text{cage}}^{*}$ to induce ISC as a common precursor with HA.

$$({}^{3}BP^{*} + AB)_{col} \xrightarrow{3} (BP^{\delta} - \cdots AB^{\delta})_{cage}^{*}$$
 (VII)

$${}^{3}(BP^{\delta^{-}}\cdots AB^{\delta^{+}})^{*}_{cage} \longrightarrow BP + AB \qquad (VIII)$$

$${}^{3}(BP^{\delta^{-}}\cdots AB^{\delta^{+}})^{*}_{cage} \xrightarrow{HA} {}^{3}(BPK + BzyR)_{cage}$$
(IX)

As mentioned for the IQ mechanism in the BP-AD system, ISC may be enhanced by the CT character of the triplet exciplex [eqn. (VIII)]. As for HA in the CT exciplex [eqn. (IX)], it can be safely said that the mechanism for BPK formation is



Fig. 5 Logarithmic plots of k_{IQ} in Bz (\odot) and ACN-H₂O (4:1 v/v) (\blacktriangle), and of k_{HA} in Bz (\bigcirc) and ACN-H₂O (4:1 v/v) (\triangle) for the BP-AB systems, as a function of E_{ox} of AB

not the ETPT process, considering the pK_a values of ABs (e.g. 42 for toluene),⁶³ but HT. We have reported on HT in triplet exciplexes of benzophenone, that the more protic H-atom is the more reactive in HT.^{64,65} In the present case, the E_{ox} can be a measure of the degree of CT interaction. As E_{ox} decreases, the degree of partial CT may increase. In other words, AB with the smaller E_{ox} has the more protic H-atom(s) to be transferred to the electron-sufficient carbonyl site in the CT exciplex.

From the viewpoint of bimolecular quenching processes of ³BP* by ABs and ADs (RH), IQ was an inherent deactivation pathway originating from the CT character in the exciplexes involved in a diffusion process. 4MeOTol employed in the present study, anticipated as a hybrid molecule for electron and H-atom donors, showed both reactions in ACN-H₂O (4:1 v/v). Photochemical reactions (ET and HA) concomitant with IQ depended on the E_{ox} value of RH, the solvent polarity and the presence of an H-atom to be abstracted by ³BP*. Consequently, the total deactivation scheme of ³BP* by RH can be illustrated in Scheme 1.

It was revealed in the present study that IQ competing with ET and HA was ISC-enhanced by the CT character of the triplet exciplexes. One should realize that the efficiencies of photoreactions of triplet ketones are not always unity because of the inherent IQ process.

Concluding remarks

Laser flash photolysis studies on IQ in the photoreduction of BP by ABs and ADs were carried out in both benzene and a mixture of acetonitrile (ACN) and water (4:1 v/v) at 295 K. We may conclude that (1) the IQ process of ³BP* by AB and AD was ISC-enhanced by the partial CT character of the triplet exciplexes, ${}^{3}(BP^{\delta-}\cdots RH^{\delta+})^{*}_{cage}$. (2) Radical ion formation by ET might be accomplished in a polar solvent by strong CT interaction in the exciplex. (3) Radical formation was inferred to be HT in the exciplex, where the more protic H-atom was readily mobile, rather than ET followed by PT. (4) The loss in efficiency of photochemical product formation arose not from back ET, but from the IQ process inherent to photoreactions *via* the triplet exciplexes.

The deactivation processes of ${}^{3}\text{BP*}$ by AB and AD (RH) are illustrated in Scheme 1.

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^{**} The ε value of ACN-H₂O (4:1 v/v) was estimated to be proportional to the molar fraction of those of ACN (37.5)⁵⁵ and H₂O (80.2).⁵⁵

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