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Modification of photochemical pathways of sensitized oxidation of phenylthioacetic acid
Effects of solvent and tetrabutylammonium salt

Piotr Filipiak [a], Jarogniew Bartoszewicz [a], Gordon L. Hug [a,b,1,2], Halina Kozubek [a], Jerzy Paczkowski [c], Bronislaw Marciniak [a,*]

[a] Faculty of Chemistry, A. Mickiewicz University, 60-780 Poznan, Poland
[b] Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556, USA
[c] Faculty of Chemical Technology and Engineering, University of Technology and Agriculture, Bydgoszcz, Poland

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Abstract

The mechanisms of triplet-sensitized electron transfer from thioether-containing aromatic carboxylic acids were investigated using steady state and laser flash photolysis in acetonitrile and aqueous solutions. Benzophenone (BP) and 4-carboxybenzophenone were used as the triplet sensitizers, and phenylthioacetic acid and its tetrabutylammonium salt were used as the electron-donating quenchers. In aqueous solution, ($BP^{\bullet -}\cdots{>}S^{\bullet +}$) radical pairs (formed in the electron-transfer quenching of the triplet state of BP) decayed mainly via a charge-separation reaction leading to the formation of ketyl radical anions ($BP^{\bullet -}$) and sulfur-centered radical zwitterions (${>}S^{\bullet +}$). The later transients underwent fast decarboxylation leading to the formation of alkyl-type radicals. In acetonitrile solutions, however, proton transfer between the radical ions was observed with the formation of ketyl radicals ($BPH^{\bullet}$). It was shown that the carboxylic and methylene groups in the phenylthioacetic acid moiety within the radical-ion pair are responsible for the proton-transfer reactions. The presence of counter cations from the tetrabutylammonium salt of phenylthioacetic acid can significantly modify the decay pathways of the photochemically produced radical-ion pairs in acetonitrile. In this case, the reaction leads to the formation of $[BP^{\bullet -}\cdots N^{+}(C_4H_9)_4]$ transients that can undergo Hofmann elimination leading to the formation of an alkene and tributylamine. These results indicate that the photochemical pathways (primary and secondary reactions) for the sensitized oxidation of phenylthioacetic acid depend on its state of ionization (that can be modified by the solvent used), properties of solvent, and the presence of associated counter cations from the tetrabutylammonium salt of phenylthioacetic acid.

Keywords: Sensitized photooxidation; Phenylthioacetic acid; Quenching; Laser flash photolysis; Quantum yields; Thioether group; Electron transfer; Solvent effect

1. Introduction

Photosensitized oxidation reactions of sulfur-containing organic compounds have been investigated for many years [1,2] due to their importance in chemistry (e.g. photopolymerization [3] or specialized organic synthesis [4–6]) and also in diverse areas of biology and medicine (oxidative stress [7], aging [8], or Alzheimer's disease [9]). In early papers, the mechanisms of such reactions (using the triplet states of aromatic carbonyl compounds, e.g. benzophenone (BP) and 4-carboxybenzophenone (CB) as sensitizers) were investigated using simple model systems as triplet quenchers, e.g. thioethers, carboxylic acids, amino acids, and small peptides containing the thioether group [10]. The reactions were found to involve an electron transfer from a sulfur atom to the carbonyl group of the aromatic ketone in its triplet state ($^3BP^*$), producing a sulfur-centered radical cationic site (${>}S^{\bullet +}$) and a carbonyl-centered radical anion ($BP^{\bullet -}$ in the case of benzophenone) [10]. As shown in [10a], the COO^- moiety in the quencher is not responsible for the efficient reduction of the carbonyl triplets.

The overall mechanism is presented in Scheme 1. After an initial formation of a radical-ion pair, there are three main channels

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[*] Corresponding author. Tel.: +48 61 829 1327; fax: +48 61 865 8008.
E-mail address: marcinia@amu.edu.pl (B. Marciniak).
[1] Permanent address: Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556, USA.
[2] Fulbright Scholar at AMU, Poland.

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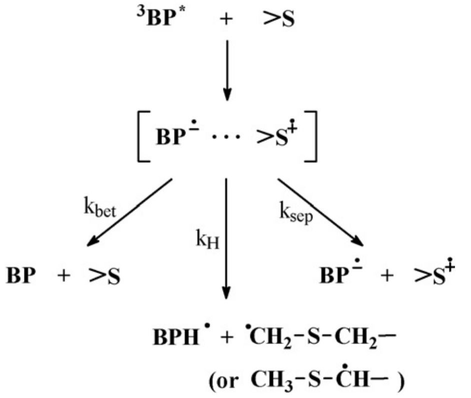


Scheme 1.

of its decay [10]. First is back electron transfer (k_{bet}), to form the reagents in their ground states. Second is proton transfer (k_H), within the radical-ion pair. This involved the deprotonation from a carbon adjacent to the sulfur-centered radical cation $>S^{\bullet+}$ and protonation of the anion radical $BP^{\bullet-}$. Overall this produces an α-alkyl thioalkyl radical and the ketyl radical ($BPH^{\bullet}$). The third pathway for the decay of the radical-ion pair is a separation of radical ions (k_{sep}) to form the free sulfur-centered radical cation $>S^{\bullet+}$ and the anion radical $BP^{\bullet-}$. Further reactions of those intermediates depend on the structure of sulfur(II) containing reactants [10].

Solvent effects on the primary photochemical processes in the photoreduction of benzophenone by amines were the subject of many investigations [11–15]. The presence of $[BP^{\bullet-}\cdots NR_3^{\bullet+}]$ contact radical-ion pairs and solvent-separated, radical-ion pairs were discovered and investigated. The studies of these intermediates involved the interconversion between contact-pairs versus solvent-separated pairs of radical ions. The studies also looked at the effects of hydrogen-bonding with the solvents.

In the current work, mechanisms for the sensitized photooxidation of phenylthioacetic acid (PTAA) in two different solvents (acetonitrile and water) are described. The change of solvent from acetonitrile to water led to a change in the ionic form of the acid, from its protonated –COOH form in acetonitrile to its anionic $-COO^-$ form in aqueous solutions. Steady-state-photolysis and flash-photolysis results on these electron donors (phenylthioacetic acid and its anion) are compared to analogous experiments on the tetrabutylammonium salt of PTAA in acetonitrile. In the latter case, the anionic form of the acid exists as an ion pair with tetrabutylammonium as its counter cation. It is shown how the solvent and the presence of associated counter cations (for tetrabutylammonium salt of PTAA) can modify the photochemical pathways of the primary and secondary photochemical reactions.

2. Experimental section

2.1. Materials

Phenylthioacetic acid (PTAA), C_6H_5–S–CH_2–COOH; 4-carboxybenzophenone (CB), benzophenone (BP), and the reference compounds (thiophenol, C_6H_5–SH; diphenyl disulfide, C_6H_5–S–S–C_6H_5; 1,2-diphenylthioethane, C_6H_5–S–CH_2–CH_2–S–C_6H_5; phenyl-methyl sulfide, C_6H_5–S–CH_3; di (phenylthio) methane, C_6H_5–S–CH_2–S–C_6H_5) were purchased from Aldrich. The deionized water for laser flash photolysis was purified in a reverse osmosis/deionization water system from Serv-A-Pure Co. The deionized water for the steady-state analysis came from a water-purification system provided by a Millipore (Simplicity^{TM}) Co. Carbon dioxide and acetonitrile (for spectroscopy) were purchased both from Merck and J.T. Baker.

2.2. Steady-state photolysis (analysis of stable products and determination of quantum yields)

Steady-state experiments were carried out in 1 cm × 1 cm rectangular UV cells on standard optical-bench systems. A high-pressure mercury lamp HBO 200 (Narva) together with water filter, quartz windows, interference filter (313 nm), and cut-off glass filters (<290 nm) were used as the excitation source for 313-nm irradiations. Solutions of sensitizer and PTAA in acetonitrile and in water (pH 7 adjusted by adding NaOH) were purged with high-purity argon (30 min) and then irradiated.

UV–vis spectra were measured at room temperature using both a diode array spectrophotometer HP 8452A and a Cary 300 Bio Varian spectrophotometer.

The sensitized photooxidation of PTAA and its tetrabutylammonium salt (PTATBA) were monitored by HPLC using a Waters 600E multisolvent delivery system pump described previously [16]. The detection system consisted of a Waters 996 photodiode array UV–vis detector. Analytical HPLC analyses were carried out on a Waters XTerra RP_{18} reverse phase column (4.6 mm × 250 mm, 5 μm particle size). HPLC–MS analyses were performed on this same system using a ZQ (electrospray) mass detector (Waters & Micromass).

Gas chromatographic (GC) analyses were performed on a Hewlett-Packard 5890 II series instrument equipped both with FID and TCD detectors in order to quantify CO_2 and also to identify stable products formed during steady-state photolysis. Analyses were done with both HP-HFAP and ULTRA 1 capillary columns (0.32 mm × 25 m). GC–MS analyses were performed on a Varian Saturn 2100T instrument equipped with an ion trap. Analyses were done with a DB-5 capillary column (30 m).

The intensity of the incident light (313 nm) for the quantum yield determinations were measured using a solution of hexanone-2 in cyclohexane as the actinometer, taking its quantum yield as 0.22 [17]. All quantum yields for sensitizer disappearance and CO_2 formation were extrapolated back to zero percent conversion of substrate in order to get initial quantum yields.

2.3. Laser flash photolysis

The nanosecond laser flash photolysis system at the Notre Dame Radiation Laboratory was used for the time-resolved experiments. This apparatus and its data-acquisition system have previously been described in detail [18,19]. The nitrogen laser (Lambda-Physics) provided 8 ns, 6 mJ pulses at 337 nm. The transients were monitored with a pulsed 1 kW xenon lamp, having the monitoring beam perpendicular to the laser beam. A 500 MHz LeCroy 7200 precision digital oscilloscope (7242 B) was used for collecting the data. All experiments were carried out with a gravity-driven flow system and a rectangular quartz optical cell (0.5 cm × 1 cm). The monitoring light pathlength, *l*, was 0.5 cm. A solution of CB (2 mM) at neutral pH was used as a relative actinometer [20] by monitoring its triplet–triplet absorption ($\varepsilon_{535} = 6250\,\mathrm{M^{-1}\,cm^{-1}}$) [21].

2.4. Spectral resolutions of transient absorption spectra

The spectral-resolution procedure has been previously described in detail [22]. The reference spectra of the various transients were obtained in additional experiments, e.g. in pulse radiolysis (see below). After the transient spectra were taken, these spectra was decomposed into the component spectra associated with the various transient species present [22] via a multiple linear regression method based on the form:

$$\Delta A(\lambda_i) = \sum_j \varepsilon_j(\lambda_i) a_j \qquad (1)$$

where ε_j is the extinction coefficient of the *j*th species and the regression parameters, a_j, are equal to the concentration of the *j*th species times the optical pathlength of the monitoring light. The sum in Eq. (1) is over all species present. For any particular time delay of an experiment, the regression analysis included equations such as Eq. (1) for each λ_i under consideration. The results of this procedure could then be used to produce concentration profiles of the transients with time.

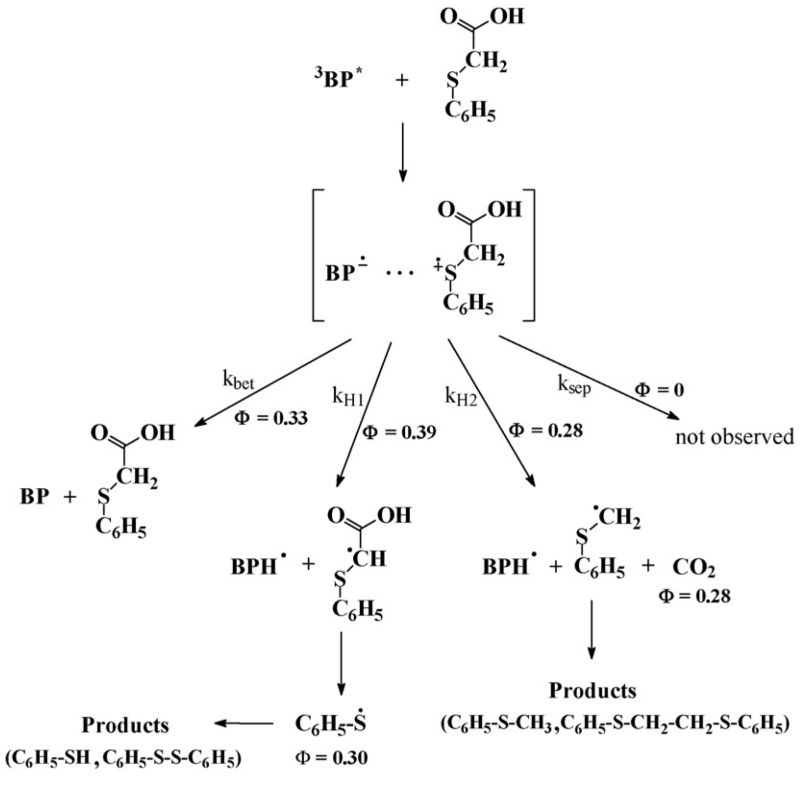
3. Results and discussion

3.1. Sensitized oxidation of PTAA by BP in acetonitrile

3.1.1. Steady-state experiments

The solutions of BP (4 mM) and PTAA (0.05 M) were irradiated with 313-nm light in deoxygenated acetonitrile solutions. The concentration of PTAA was chosen to be high enough to quench more than 94% of the BP triplets. The photooxidation reaction was monitored by absorption spectroscopy, HPLC, and GC analysis. GC–MS chromatography was used for the identification of stable products. The products identified were 1,2-diphenylthioethane, C_6H_5–S–CH_2–CH_2–S–C_6H_5; phenyl-methyl sulfide, C_6H_5–S–CH_3; diphenyl disulfide, C_6H_5–S–S–C_6H_5; thiophenol, C_6H_5–SH; carbon dioxide, CO_2; benzpinacol (BPH-BPH) (see Scheme 2).

The changes, Δc, in the concentrations of BP and CO_2 with irradiation time were determined both by GC and HPLC analyses using samples of authentic compounds as concentration standards. Based on these results and the known values of the intensities of absorbed excitation light, the quantum yields of BP disappearance and CO_2 formation were determined. All quantum yields (see Table 1) were extrapolated back to zero percent conversion of the substrate in order to get initial quantum yields.



Scheme 2.

Table 1
Rate constants (k_q) for quenching of the BP (CB) triplet by PTAA, quantum yields for the decomposition of BP (or CB) and formation of intermediates and carbon dioxide

Solvent	Flash photolysis[a]					Steady state[b]	
	k_q ($M^{-1}\,s^{-1}$)	$\Phi_{BPH^\bullet}$	$\Phi_{BP^{\bullet-}}$	$\Phi_{C_6H_5-S^\bullet}$	$\Phi_{C_6H_5-S-{}^\bullet CH_2}$	Φ_{BP}	Φ_{CO_2}
CH_3CN	8.7×10^7	0.67	0	0.30	~0.28	0.68	0.28
H_2O[c]	1.9×10^9	≤0.10	0.97	0	0.93	0.97	0.92
CH_3CN[d]	1.1×10^9	×	0.35[e]	×	×	0.42	0.45

×, not determined.

[a] Extrapolated to the end of the flash; estimated error ±15%.

[b] Extrapolated to zero percent conversion of substrate; estimated error ±10% for Φ_{BP} and ±20% for Φ_{CO_2}.

[c] Results for 4-carboxybenzophenone (CB) [30].

[d] Results for tetrabutylammonium salt [28].

[e] Quantum yield for the formation of ionic pair $[BP^{\bullet-}\cdots N^+(C_4H_9)_4]$ [28].

3.1.2. Laser flash photolysis

The rate constant for the quenching of $^3BP^*$ by C_6H_5–S–CH_2–CO_2–H was measured by varying the concentration of quencher and fitting the decay of the triplet–triplet absorption of $^3BP^*$ at 520 nm which was fitted to single-exponential decays. The equation describing the pseudo-first-order decays versus concentrations of quencher is presented below:

$$k_{obs} = \tau_0^{-1} + k_q[Q] \qquad (2)$$

where k_{obs} is the reciprocal of the observed triplet lifetime in the presence of quencher with concentration $[Q]$, coming from single-exponential fits to the 520-nm kinetic traces, τ_0 is the triplet lifetime of BP in the absence of quencher, and k_q is the second-order rate constant for the quenching of the triplet by the quencher, Q. The resulting rate constant of $8.7 \times 10^7\ M^{-1}\,s^{-1}$ (Fig. 1) is quite large which is suggestive of triplet-state quenching via electron transfer [10].

Knowing this quenching rate constant, we were able to select suitable concentrations of BP (2 mM) and PTAA (0.02 M) to quench more than 90% of the BP triplet state. Exemplary transient absorption spectra, following the triplet quenching of BP by PTAA, are shown in Fig. 2. Those spectra were generated after a few different delay times (between 50 ns and 160 µs) following the laser pulse.

For electron-transfer quenching, it might be expected that radical ions or their decomposition products would be present in the transient spectra following laser pulses. The species expected (Scheme 1), in this case, would be the benzophenone triplet state ($^3BP^*$), radical anions of BP ($BP^{\bullet-}$), their protonated form, the ketyl radical ($BPH^\bullet$), C-centered radicals derived from the quencher: C_6H_5–S–$^\bullet CH_2$ radical and phenylthiyl radical (C_6H_5–$S^\bullet$), formed from the decomposition of the sulfur-centered radical cation (not shown in Scheme 1). The absorption spectra (see Fig. 3) of the benzophenone triplet state ($^3BP^*$) and the ketyl radical have been previously well characterized with extinction coefficients, $\varepsilon_{520} = 6500\ M^{-1}\,cm^{-1}$ for $^3BP^*$ and $\varepsilon_{545} = 3400\ M^{-1}\,cm^{-1}$ for $BPH^\bullet$ [23]. The reference spectrum of the C-centered radicals derived from the quencher (α-alkylthiophenyl radicals—C_6H_5–S–$^\bullet CH_2$) was presented in Refs. [24–26] and determined to have an extinction coefficient $\varepsilon_{330} = 3800\ M^{-1}\,cm^{-1}$ in water. The reference absorption spectrum of the phenylthiyl radical (C_6H_5–$S^\bullet$) was measured and determined to have $\varepsilon_{490} = 1800\ M^{-1}\,cm^{-1}$ in water [26].

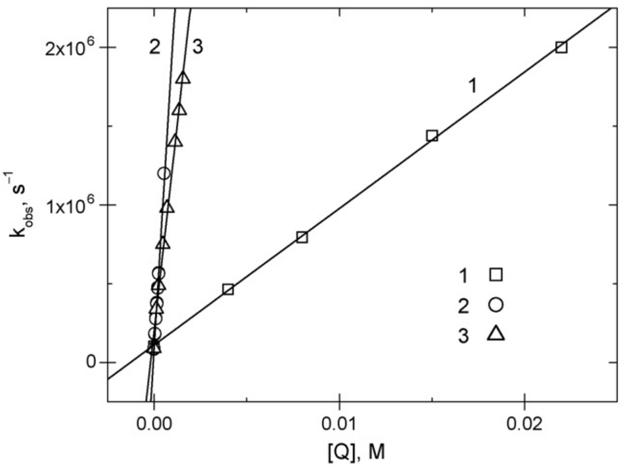


Fig. 1. Pseudo-first-order plot for quenching of the BP and CB triplet state by phenylthioacetic acid (PTAA) and its tetrabutylammonium salt in various experimental conditions: 1, in acetonitrile ([BP] = 2 mM; [PTAA] = 4–22 mM); 2, in aqueous solution at pH 6.7 ([CB] = 2 mM; [PTAA] = 0.05–0.5 mM); 3, in acetonitrile ([BP] = 2 mM; [PTATBA] = 0.1–1.5 mM).

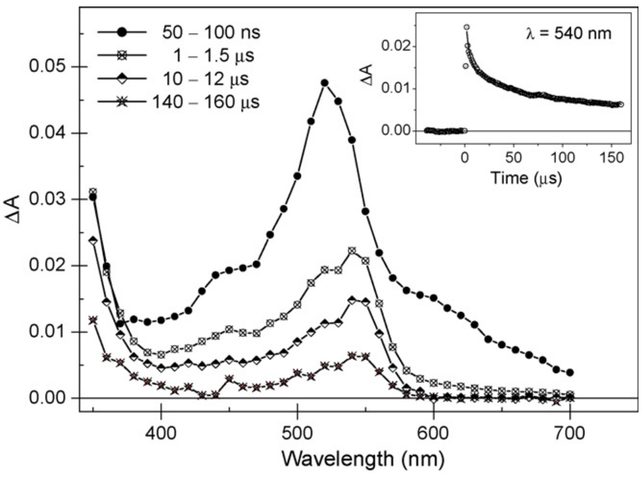


Fig. 2. Transient absorption spectra following triplet quenching of BP by C_6H_5–S–CH_2–CO_2–H (20 mM) in acetonitrile solution. Inset shows kinetic trace at 540 nm.

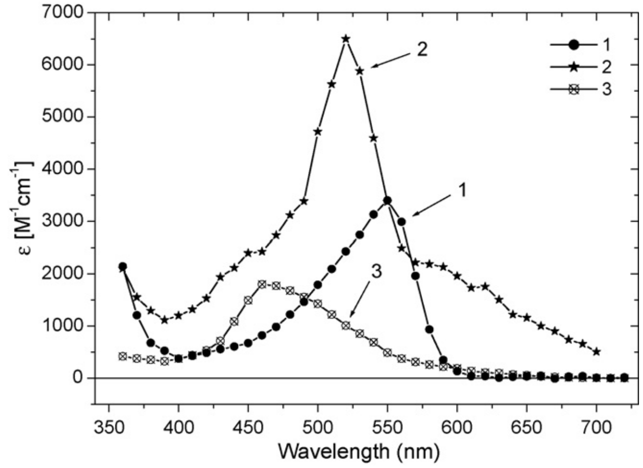


Fig. 3. Reference spectra of intermediates generated during a laser flash photolysis experiments: (i) ketyl radical ($BPH^{\bullet}$) in acetonitrile with 2-propanol; (ii) benzophenone triplet state ($^{3}BP^{*}$) in acetonitrile; (iii) phenylthiyl radical ($C_6H_5{-}S^{\bullet}$) in water, generated during pulse radiolysis experiments [26].

Using the reference spectra and the spectral-resolution procedure presented in Section 2, it was possible to analyze the transient-absorption spectra following the quenching of $^{3}BP^{*}$ by $C_6H_5{-}S{-}CH_2{-}CO_2{-}H$ in acetonitrile. As a result of spectral decomposition, it was found that three intermediates are formed during the quenching reaction following triplet decay. The three transients were the ketyl radical, the phenylthiyl radical, and the α-alkylthioalkyl radical ($C_6H_5{-}S{-}^{\bullet}CH_2$). The radical anion $BP^{\bullet -}$ was not observed. The results of the spectral-resolution procedure could be used to produce concentration profiles of all three of intermediates as a function of delay times following the laser pulse. Using the external actinometer to get the intensity of the laser beam (see Section 2), the formation quantum yields of the intermediates were determined. These formation quantum yields of the intermediates were extrapolated to the end of the laser pulse and are listed in Table 1.

We were also able to calculate rate constants (k) for ketyl radical recombination reactions. The inset in Fig. 2 shows the kinetic trace taken at 540 nm, which corresponds to the decay of the ketyl radical. Using the results given by second-order decay fits to the 540 nm kinetic data and Eq. (3), rate constants (k) for ketyl radical recombination were calculated:

$$k = \frac{a \times \varepsilon \times l}{2} \tag{3}$$

In Eq (3), k (in $M^{-1}\,s^{-1}$) is a rate constant for the ketyl radical recombination reaction, a (in s^{-1}) the fitting parameter obtained from second-order decay fits, ε the extinction coefficient for $\lambda = 540$ nm and is equal to $3400\,M^{-1}\,cm^{-1}$ [23], and l is the optical pathlength equal to 0.5 cm. From this analysis, the rate constant for ketyl-radical recombination reaction was determined to be $2k = 9.4 \times 10^{7}\,M^{-1}\,s^{-1}$, compared to $2k = 2.0 \times 10^{9}\,M^{-1}\,s^{-1}$ in water [27].

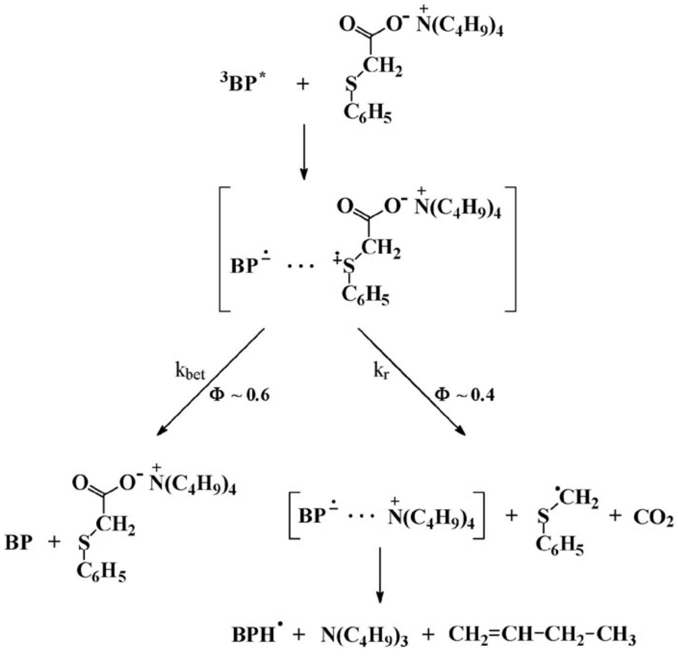
Based on all these results, a mechanism for the quenching of $^{3}BP^{*}$ by $C_6H_5{-}S{-}CH_2{-}CO_2{-}H$ in acetonitrile is proposed in Scheme 2. Of particular note in Scheme 2 is the lack of an efficient pathway for the formation of separated radical ions as a route to the decay of the ($BP^{\bullet -}\cdots{>}S^{\bullet +}$) ion pairs.

3.2. Sensitized oxidation of PTATBA by BP in acetonitrile

The mechanism of photoinduced electron transfer in the benzophenone-phenylthioacetic tetrabutylammonium salt in acetonitrile solutions has been recently studied by us using steady state and nanosecond laser flash photolysis [28]. The results clearly indicated a drastic change in the mechanism of the primary and secondary photochemical steps by exchanging the proton of the carboxylic group by a tetrabutylammonium cation. The resulting overall mechanism is summarized in Scheme 3.

The rate constants for quenching of the BP triplet state by PTATBA in acetonitrile was determined from Eq. (2) to be $k_q = 1.1 \times 10^{9}\,M^{-1}\,s^{-1}$ as measured by the method described in the previous section (see Fig. 1 and Table 1). Using a high concentration of PTATBA, the BP triplet could be quenched efficiently on the nanosecond time scale, and the formation of a new transient, absorbing at 710 nm, could be observed forming on the same time scale as the decay of the triplet state. This was illustrated in Fig. 1 of Ref. [30], where the new transient absorption, at about 710 nm, was assigned as arising from the $BP^{\bullet -}$ present in the $[BP^{\bullet -}\cdots N^{+}(C_4H_9)_4]$ ion pair (see Scheme 3). It is important to note that this transient was not observed if the benzophenone triplet was quenched by PTAA in the presence of an access of tetrabutylammonium chlorate ($N^{+}(C_4H_9)_4Cl^{-}$) in acetonitrile. Thus, the formation of the $[BP^{\bullet -}\cdots N^{+}(C_4H_9)_4]$ ion pair required the presence of the tetrabutylammonium salt of PTAA as the quencher in order to observe the 710-nm transient.

As presented in Scheme 3, there are two main reaction channels of the initially formed $[BP^{\bullet -}\cdots(C_6H_5)S^{\bullet +}CH_2COO^{-}N^{+}(C_4H_9)_4]$ radical-ion pair, e.g. back elec-



Scheme 3.

tron transfer (k_{bet}) and formation of a new intermediate $[BP^{\bullet -}\cdots N^{+}(C_4H_9)_4]$. The latter reaction may be explained by an efficient fragmentation of the sulfur-centered radical cation in the ion pair leading to the formation the stable radical $C_6H_5–S–CH_2^{\bullet}$ and CO_2, in addition to the 710-nm intermediate [28]. A further reaction of $[BP^{\bullet -}\cdots N^{+}(C_4H_9)_4]$ occurred by a Hofmann elimination to form a ketyl radical and two stable products, i.e. tributylamine and butene-1 [28]. Thus in this case, proton transfer (k_H) from the sulfur-centered radical cation $>S^{\bullet +}$ to the anion radical $BP^{\bullet -}$, within the radical-ion pair, was not observed. In particular, no α-alkyl thioalkyl radicals or ketyl radicals ($BPH^{\bullet}$) (Scheme 1) were seen that might have resulted from such a proton transfer within the radical-ion pairs. All quantum yields obtained in the steady state and time-resolved photolysis for the sensitized oxidation of PTATBA by triplet BP in acetonitrile [28] are summarized in Table 1.

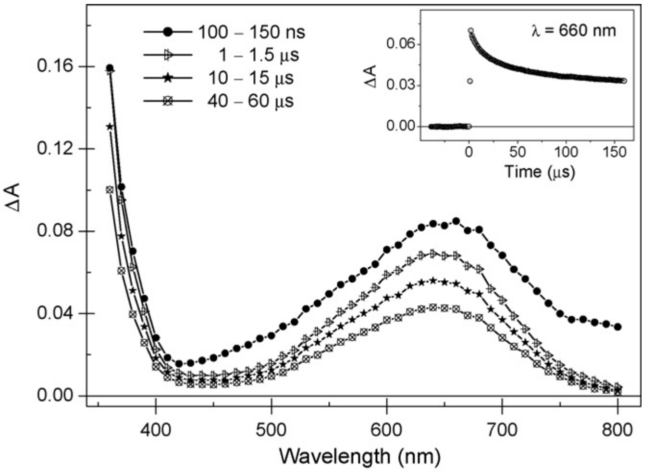


Fig. 4. Transient absorption spectra following triplet quenching of CB by $C_6H_5–S–CH_2–CO_2^-$ (20 mM) + CB (2 mM) in aqueous solution, pH 7.5. Inset show kinetic trace at 660 nm.

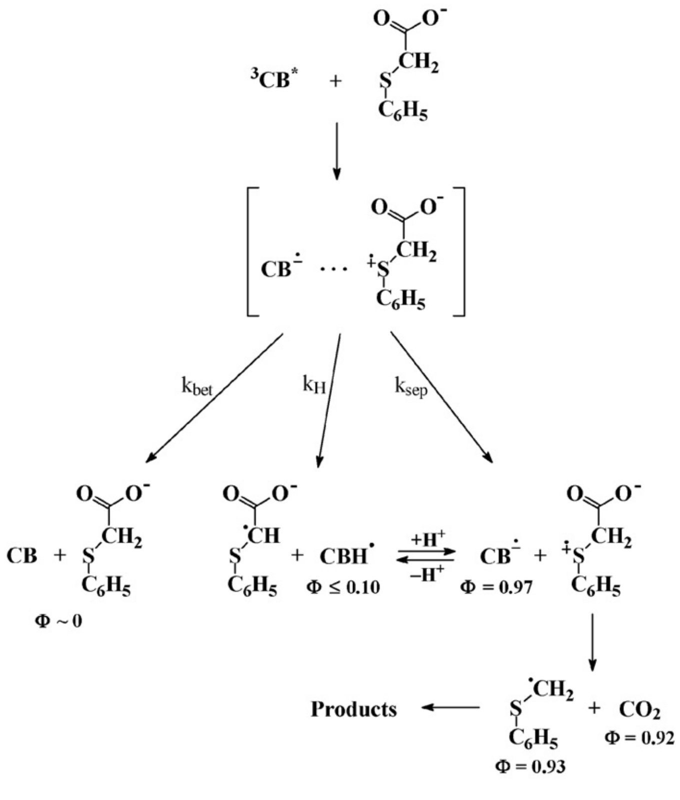
3.3. Sensitized oxidation of PTAA by CB in aqueous solution

Changing the solvent from acetonitrile to water leads to drastic changes in the mechanism for the primary and secondary photochemical reactions of the benzophenone/phenylthioacetic acid system. In this case, 4-carboxybenzophene (CB) was used instead of BP due to water-solubility problems with benzophenone itself. Substitution of the carboxylic group into the benzophenone chromophore does not change the photophysical and photochemical properties, i.e. the intersystem crossing quantum yields of BP and CB are equal to unity in both cases [29]. The mechanisms of the chemical reactions, following the quenching of the CB triplet state by PTAA in neutral aqueous solutions (pH adjusted by adding NaOH) were recently reported by us [30]. In that paper, we determined the rate constant k_q and the quantum yields of product formation, under steady-state photolysis and in nanosecond flash photolysis (Table 1). The changes in the transient absorption spectra during flash photolysis of the CB-PTAA system in aqueous solution are presented in Fig. 4. These results show an intense absorption band around 650 nm which is indicative of the formation of the radical anion $CB^{\bullet -}$. This charge-separation reaction was the main deactivation channel for the radical-ion pair $[CB^{\bullet -}\cdots >S^{\bullet +}]$, see below. The observed transient spectra were resolved into their component spectra, and the initial formation quantum yields for the corresponding chemical intermediates were determined [30]. A mechanism is presented in Scheme 4 that accounts for the primary and secondary photochemical steps of the sensitized oxidation of PTAA by CB in aqueous solution.

3.4. Effect of solvent and tetrabutylammonium salt: comparative studies

It can be seen (Schemes 2–4) that the primary photochemical processes are distinctly different in the two solvents (acetonitrile and water) even though the fundamental process is electron-transfer quenching of the triplet state of an aromatic carbonyl by sulfur-containing organic compounds. Thus, the solvent can modify the photochemical pathways (general Scheme 1) of the sensitized oxidation of phenylthioacetic acid.

In the case of reactions occurring in water (Scheme 4), it was suggested that after electron-transfer (quenching of the CB triplet state) a radical pair was formed [30]. This radical pair could be seen to decay mainly by a charge-separation reaction. Scheme 4, along with the results in Table 1, provide a quantitative description of the reaction mechanism in aqueous solution. The main primary reaction is charge separation ($\Phi_{CB^{\bullet -}} = 0.97$) followed by an efficient decarboxylation leading to $C_6H_5–S–CH_2^{\bullet}$



Scheme 4.

($\Phi = 0.93$) and CO_2 ($\Phi = 0.92$):

$$C_6H_5\text{–}S^{\bullet+}\text{–}CH_2\text{–}CO_2^- \rightarrow {}^{\bullet}CH_2\text{–}S\text{–}C_6H_5 + CO_2 \qquad (4)$$

The decay of the long-lived (hundreds of microseconds) radical anion $CB^{\bullet-}$ is presented in the inset of Fig. 4. Two other primary photochemical reactions (Scheme 1), e.g. the back-electron-transfer and proton-transfer within the radical pair $[CB^{\bullet-}\cdots{>}S^{\bullet+}]$ can be neglected in the case of aqueous solutions. It is important to note that phenylthioacetic acid exists in its anionic form ($C_6H_5\text{–}S\text{–}CH_2\text{–}COO^-$) in neutral aqueous solutions. This was additionally confirmed by observing very efficient CO_2 formation attributed to decarboxylation of the sulfur-centered radical zwitterions, reaction (4).

In the case of acetonitrile solutions, however, the PTAA species exists as neutral molecules which should, in turn, affect the reaction mechanism. The detailed mechanism for primary and secondary photochemical processes for this case is presented in Scheme 2. Results presented in Scheme 2 together with results in Table 1 indicate that, in acetonitrile solution, there are three pathways for the decay of $(BP^{\bullet-}\cdots{>}S^{\bullet+})$: (i) back electron transfer (k_{bet}) ($\Phi = 0.33$), (ii) proton transfer (k_{H1}) from the methylene group (–CH_2–) to the BP radical anion ($\Phi = 0.39$), and (iii) proton transfer (k_{H2}) from the carboxylic group leading to carbon dioxide formation ($\Phi = 0.28$). The existence of two proton-transfer pathways is due to there being two distinct proton donors in the PTAA radical cation, i.e. proton donors at the sites –COOH and $\text{–}S^{\bullet+}CH_2\text{–}$. The ketyl radical ($\Phi = 0.67$) is the main reaction product formed in these two pathways ((k_{H1}) and (k_{H2}) in Scheme 2). The resulting $C_6H_5\text{–}S\text{–}{}^{\bullet}CH\text{–}COOH$ radical, from k_{H1}, may undergo C–S bond cleavage, leading to the formation of the phenylthiyl radical, $C_6H_5\text{–}S^{\bullet}$ ($\Phi = 0.30$). The C–C bond cleavage, from the (k_{H2}) pathway, appears to lead to two different intermediates: the $BPH^{\bullet}$ radical ($\Phi = 0.29$) and the α-alkylthioalkyl radical ($C_6H_5\text{–}S\text{–}{}^{\bullet}CH_2$). The $\Phi(C_6H_5\text{–}S\text{–}{}^{\bullet}CH_2)$ was estimated as ~0.28 taking its molar absorption coefficient at 330 nm as $3800\,M^{-1}\,cm^{-1}$ [26]. The expected complementary (to $C_6H_5\text{–}S\text{–}{}^{\bullet}CH_2$) stable product (carbon dioxide) was also detected, and its quantum yield of formation was determined to be equal to 0.28. All these intermediates are consistent with the steady-state products that were detected and are shown in Scheme 2.

As mentioned in the section describing the sensitized oxidation of PTAA by BP in acetonitrile, the formation of separated radical ions as a route to the decay of the $(BP^{\bullet-}\cdots{>}S^{\bullet+})$ ion pairs can be neglected in this case. The absence of this pathway is likely due to insufficient dielectric screening (by the acetonitrile medium) of the mutually attractive Coulombic force between the radical ions within the ion pair of the collision complex. The macroscopic dielectric constant, ε, of the acetonitrile medium is 36 compared to $\varepsilon = 80$ for water in which the separation of ions was much more efficient.

As shown in the section describing the sensitized oxidation of PTATBA by BP in acetonitrile, there was a dramatic change in the mechanism of the primary and secondary photochemical reactions by exchanging the proton of the carboxylic group (in PTAA) by a tetrabutylammonium cation (in PTATBA) (Scheme 3). The radical-ion pair $[BP^{\bullet-}\cdots S^{\bullet+}(C_6H_5)SCH_2COO^-N^+(C_4H_9)_4]$ appears to be decaying via two pathways. The first is back electron transfer (k_{bet}) ($\Phi \sim 0.6$), which in this case is the main reaction channel. The second channel is decarboxylation (k_r) ($\Phi \sim 0.4$). This leads to the formation of a $[BP^{\bullet-}\cdots N^+(C_4H_9)_4]$ ion pair, an α-alkylthioalkyl radical ($C_6H_5\text{–}S\text{–}{}^{\bullet}CH_2$), and carbon dioxide. The $[BP^{\bullet-}\cdots N^+(C_4H_9)_4]$ ion pair decomposes via Hofmann elimination [28], with the formation of ketyl radicals and the steady-state products shown in Scheme 3.

Thus, an exchange of the proton in the carboxylic group of PTAA for a tetrabutylammonium cation leads to a drastic change in the primary photochemical reactions, in acetonitrile as the solvent. The formation of the $BP^{\bullet-}$ radical anion (observed as the $[BP^{\bullet-}\cdots N^+(C_4H_9)_4]$ ion pair) indicates that even in acetonitrile a charge-like separation reaction similar to that observed in aqueous solution may occur. However, in order to get this charge separation in acetonitrile requires the use of the salt (PTATBA) instead of the acidic form (PTAA). However, the formation quantum yield of the benzophenone radical anion for the sensitized photolysis of the PTATBA salt in acetonitrile solution ($\Phi_{[BP^{\bullet-}\cdots N^+(C_4H_9)_4]} \sim 0.4$), is less than half that observed in aqueous solution ($\Phi_{CB^{\bullet-}} \sim 1.0$).

There is a distinct difference in the BP triplet ($^3BP^*$) quenching rate constant by PTAA in acetonitrile and the analogous rate constant for the quenching of the CB triplet ($^3CB^*$) by the PTAA anion in water, see the first column in Table 1. Since the reactants are so similar and since the quenching appears to be via electron transfer in both cases, the question arises as to what are the sources of the 22-fold difference in these two quenching rate constants. One possibility is that there is a difference in the thermodynamics [31]:

$$\Delta G_{el} = E_{ox} - E_{red} - E^* + C \qquad (5)$$

which is the overall free-energy change (ΔG_{el}) of the electron transfer. In this equation, E_{ox} is the reduction potential of the oxidized radical, E_{red} the reduction potential of the electron acceptor, E^* the triplet state of BP or CB, and C is the overall change in the Coulombic energy of the products compared to the reactants. The other possibility is that the frequency factor ($\nu = k_B T/h$) or the transmission coefficient (κ) in the semi-classical version [32]:

$$k_{el} = \kappa\nu\,\exp\left(\frac{-E^{\neq}}{k_B T}\right) \qquad (6)$$

for the electron-transfer rate constant. In theories of electron transfer, the exponential factor is usually strongly dependent on the overall free-energy change of the electron-transfer reaction, hence the relevance of thermodynamics via the Rehm–Weller expression [31]. In excited-state quenching experiments, it is common to check such correlations by forming plots of $\log k_q$ versus ΔG_{el}. Normally what is observed in fluid solutions is a rise in $\log k_q$ with increasingly negative ΔG_{el}. Furthermore, a plateau is normally reached in $\log k_q$ at large negative ΔG_{el} [31].

The thermodynamics can show up either in the E_{ox} of PTAA versus its anion or in E_{ox} or E_{red} as a function of solvent. As for E_{ox} of PTAA changing with deprotonation, the Hammett σ's are not very different for acid anions as compared to the acids themselves [17]. Hence, the electron-donating ability of the relatively distant sulfur atoms is not expected to change much on deprotonation of PTAA. The changes in $E_{\mathrm{ox}} - E_{\mathrm{red}}$ with solvent have been computed as [33]

$$(E_{\mathrm{ox}} - E_{\mathrm{red}})_{\mathrm{water}} - (E_{\mathrm{ox}} - E_{\mathrm{red}})_{\mathrm{MeCN}} = \frac{e^2}{2}\left(\frac{1}{r_{\mathrm{A}}} + \frac{1}{r_{\mathrm{B}}}\right)\left(\frac{1}{\varepsilon_{\mathrm{water}}} - \frac{1}{\varepsilon_{\mathrm{MeCN}}}\right) \quad (7)$$

Taking the reaction radii (r_{A} and r_{B}) of the donor and acceptor to be 3.5 Å and the dielectric constants to be $\varepsilon_{\mathrm{water}} = 80$ and $\varepsilon_{\mathrm{MeCN}} = 36$ [17], the difference $E_{\mathrm{ox}} - E_{\mathrm{red}}$ is slightly more negative (−6 kJ/mol) for water than for acetonitrile. Thus ΔG_{el} would be expected to be similar for the systems in water and acetonitrile, and k_{q} would be expected to be similar in water in acetonitrile which is contrary to what was determined, see Table 1. A similar condition holds for the Coulombic term in the Rehm–Weller equation:

$$C = w_{\mathrm{p}} - w_{\mathrm{r}} \quad (8)$$

where for CB in water $C = -2$ kJ/mol and for BP in acetonitrile $C = -5.5$ kJ/mol. These Coulombic terms are small, and their relative magnitudes are contrary to expectations from the Rehm–Weller equation and the observed k_{q} values in Table 1. Both of these results (C and $E_{\mathrm{ox}} - E_{\mathrm{rad}}$) point away from the solvent as being the source of the difference between the k_{q}'s for water and acetonitrile.

Although the difference in k_{q} between ^{3}BP* quenched by PTAA in acetonitrile and ^{3}CB* quenched by the PTAA anion in water does not appear to be related to ΔG_{el}, it is possible to get further information by assuming that the rate constants, k_{q}, are on the plateau of the $\log k_{\mathrm{q}}$ versus ΔG_{el} plots for large negative ΔG_{el}. With this assumption and the assumption that the activation free energy for electron transfer follows an asymptotic relationship (e.g. the Agmon–Levine free-energy relationship [34]), it was shown in [22] that the plateau value of $k_{\mathrm{q}}^{\max}$ is given by

$$k_{\mathrm{q}}^{\max} = \frac{\kappa\nu k_{\mathrm{d}}}{\kappa\nu + k_{-\mathrm{d}}} \quad (9)$$

where k_{d} is the diffusion-limited rate constant to form an encounter complex in the solvent and $k_{-\mathrm{d}}$ is the dissociation rate constant of the encounter complex of the triplet state and the quencher (see Scheme I of [22]). Assuming that the quenching rate constants in Table 1 represent values on the plateau of the Weller plots, $k_{\mathrm{q}}^{\max} = 8.7 \times 10^7\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ for ^{3}BP* quenched by the PTAA in acetonitrile, and $k_{\mathrm{q}}^{\max} = 1.9 \times 10^9\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ for ^{3}CB* quenched by the PTAA anion in water. From the Eigen equation [35] for uncharged species in acetonitrile $k_{-\mathrm{d}} = 2.2 \times 10^{10}\,\mathrm{s}^{-1}$ and for the charged ^{3}CB* and the PTAA anion in water [30,36]:

$$k_{-\mathrm{d}} = \frac{3(D_{\mathrm{A}} + D_{\mathrm{B}})}{R^3}\,\frac{z_{\mathrm{A}}z_{\mathrm{B}}r_0}{1 - \exp(-z_{\mathrm{A}}z_{\mathrm{B}}r_0/R)} = 2.4 \times 10^{10}\,\mathrm{s}^{-1} \quad (10)$$

From the Debye equation ($k_{\mathrm{d}} = 8RT/3000\eta$; η is viscosity) [37] $k_{\mathrm{d}} = 1.9 \times 10^{10}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ for acetonitrile, and

$$k_{\mathrm{d}} = \frac{4\pi(D_{\mathrm{A}} + D_{\mathrm{B}})}{1000}\,\frac{-z_{\mathrm{A}}z_{\mathrm{B}}r_0}{1 - \exp(z_{\mathrm{A}}z_{\mathrm{B}}r_0/R)} = 1.0 \times 10^{10}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1} \quad (11)$$

for the charged particles in water [36]. In the last two equations, $r_0 = 7$ Å, $R = 10$ Å (taking the sum of the van der Waals radii of the A and B ions in addition to solvent shells of 1.4 Å for both ions [36]), and $(D_{\mathrm{A}} + D_{\mathrm{B}}) = 2 \times 10^{-9}\,\mathrm{m}^2\,\mathrm{s}^{-1}$ [36].

With these values for the rate constants in eq (9), $\kappa\nu = 5.6 \times 10^9\,\mathrm{s}^{-1}$ for ^{3}CB* quenching by the PTAA anion in water, and $\kappa\nu = 1.0 \times 10^8\,\mathrm{s}^{-1}$ for ^{3}BP* quenching by the PTAA molecule in acetonitrile. Thus the pre-exponential factor $\kappa\nu$ is a factor of 56 larger in water that in acetonitrile. This is qualitatively consistent with the 22-fold increase in the corresponding overall quenching rate constants, k_{q}.

These calculations indicate that it is the frequency factor and the transmission coefficient that are responsible for the differential quenching of ^{3}CB* by the PTAA anion in water compared to the ^{3}BP* quenching by PTAA in acetonitrile. The possible chemical/physical reason for this may be the perchance for hydrogen bonding of PTAA in its acid form in acetonitrile. The geometry of hydrogen bonds is linear which would keep the sulfur site on the PTAA remote from the ^{3}BP* electron-acceptor site, thus accounting for the reduced $\kappa\nu$ in acetonitrile.

4. Conclusions

In summary, it was shown that solvents can significantly modify primary and secondary reactions following the photosensitized oxidation of phenylthioacetic acid (PTAA). Changing the solvent from acetonitrile to water led to a dramatic change in the primary photochemical pathways. In acetonitrile solutions, where the carboxylic group of PTAA is protonated, the main primary photochemical reaction was shown to be proton transfer (resulting from deprotonation of the PTAA carboxylic and methylene groups) within the radical-ion pairs ($\mathrm{BP}^{\bullet-}\cdots{>}\mathrm{S}^{\bullet+}$). This led to the formation of ketyl radicals $\mathrm{BPH}^{\bullet}$. In contrast, a charge-separation reaction of the radical pair ($\mathrm{CB}^{\bullet-}\cdots{>}\mathrm{S}^{\bullet+}$) was the only primary reaction observed in aqueous solutions. When counter cations were present in the form of tetrabutylammonium cations from the associated salt of PTAA, another behavior was seen in acetonitrile. Under these conditions, the proton-transfer reaction within ($\mathrm{BP}^{\bullet-}\cdots{>}\mathrm{S}^{\bullet+}$) was no longer observed, but now the formation of radical ions $\mathrm{BP}^{\bullet-}$ was observed in the form of ion pairs $[\mathrm{BP}^{\bullet-}\cdots\mathrm{N}^{+}(\mathrm{C}_4\mathrm{H}_9)_4]$. Thus, even in acetonitrile solution, a type of charge separation can occur which leads to the formation of ketyl radical anions. The combined use of steady-state and flash-photolysis techniques allowed us to describe quantitatively the mechanism of BP sensitized photooxidation of PTAA under various experimental conditions.

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