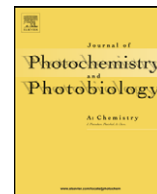




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## Kinetics and mechanism of sensitized photooxidation of tetramethylammonium salt of 2-(phenylthio)acetic acid in solution Steady-state and flash photolysis studies

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### ABSTRACT

The mechanism for the photo-induced oxidation of the tetramethylammonium salt of 2-(phenylthio)acetic acid was elucidated. The photosensitizer was the benzophenone triplet in acetonitrile solutions. Time-resolved absorption spectra and kinetics were used to follow the intermediates which included the triplet of benzophenone, the ketyl radical of benzophenone, and an ion pair consisting of a radical anion of benzophenone and a tetramethylammonium cation. Rate constants for the growth and decay of the transients were determined along with the quantum yields of the transients. The intermediacy of other radicals was inferred by the products observed following steady-state photolysis. Quantum yields were also determined for photoproducts resulting from the steady-state irradiation. The mechanism was proposed that rationalized the quantitative observations. Of particular note was how the nature of the counter ion effected the secondary reactions of the radicals and the radical ions.

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### 1. Introduction

Organic acids are used as co-initiators in the photoinitiation of free-radical polymerizations. Salts of the organic acids are often used to make the organic co-initiators more soluble in the polymerization mixtures. Tetraalkylammonium salts of carboxylic acids are particularly useful, offering a compromise between inorganic cations and the acids themselves [1–3].

The precise nature of the initial photoinitiator/co-initiator reactions is of interest because, ideally, these reactions need to be rapid and efficient in producing the free radicals that ultimately initiate the polymerizations. Electron-transfer processes can be potentially diffusion controlled as opposed to H-atom abstractions that normally have rate constants distinctly below diffusion limit [4–6]. On the other hand, the resulting radicals from H-abstractions tend to be suitable for initiating polymerizations, whereas the radical ions, typically produced from electron-transfer quenching, may or may

not be useful. Fragmentations and deprotonations of the radical ions to produce secondary radicals can, however, lead to free radicals that are more efficient initiator radicals than the ones produced in the photoinitiator/co-initiator reaction [7].

In a recent work [8], tetraalkylammonium salts of 2-(phenylthio)acetic acid were used as co-initiator in just such a study. Four different tetraalkylammonium salts were used (methyl, ethyl, *n*-propyl, and *n*-butyl). Based, in part, on an observed linear correlation of the photopolymerization rates and the square root of the quantum yield for CO<sub>2</sub> formation  $\sqrt{\Phi(\text{CO}_2)}$ , it was concluded that C<sub>6</sub>H<sub>5</sub>SCH<sub>2</sub><sup>•</sup> radicals were responsible for the common initiation step of the polymerizations for all four of the co-initiating tetraalkylammonium salts. This conclusion was drawn in spite of the fact that the three largest alkyl moieties have beta carbons and were found to undergo Hofmann eliminations [8]. No such secondary reaction is possible in the tetramethylammonium ion.

In the current paper, we investigate the quantitative details of the mechanism for the sensitized photo-induced oxidation of the tetramethylammonium salt of 2-(phenylthio)acetic acid. Knowledge of its primary and secondary photochemical mechanisms is then of interest to see how they contrast and compare to the other three tetraalkylammonium salts, previously studied in detail [8]. The question is how can the secondary reactions in the tetramethyl

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case be different from the other three tetraalkylammonium salts and yet all four salts apparently have, ultimately, a common initiator? In particular, even though the tetramethylammonium ion cannot be involved in Hofmann elimination, it is of interest to unravel the details of its secondary photochemical processes to see how the  $C_6H_5SCH_2^*$  radical can still be responsible for the polymerization initiation in the tetramethyl salt as it is in the other three tetraalkyl salts.

## 2. Experimental part

### 2.1. Materials

Benzophenone (BP) and all reactants used for the preparation of the tetramethylammonium salt of 2-(phenylthio)acetic acid (PTAAS),  $C_6H_5-S-CH_2-COO-N^+(CH_3)_4$  were purchased from Aldrich. The PTAAS salt (PTAAS AS) was obtained by treating 2-(phenylthio)acetic acid in boiling water along with a molar equivalent of the tetramethylammonium hydroxide. After the evaporation of water, the clammy residue was dried in a vacuum desiccator, yielding transparent crystals. Carbon dioxide, thioanisole, formaldehyde, trimethyl amine, 1,2-bis(phenylthio)ethane, and acetonitrile (for HPLC) were purchased from Merck, Aldrich, or Alfa Aesar.

### 2.2. Steady-state irradiations

Steady-state experiments were carried out in  $1\text{ cm} \times 1\text{ cm}$  rectangular UV cells on standard optical-bench systems. A high-pressure mercury lamp HBO 200 (Narva) together with a water filter, quartz windows, an interference filter (366 nm), and glass cut-off filters ( $<290\text{ nm}$ ) were used as the excitation source for the 366-nm irradiations ( $I_0 = 1.76 \times 10^{-4}\text{ einstein dm}^{-3}\text{ min}^{-1}$ ). Solutions of photosensitizer and PTAAS in acetonitrile were purged with high-purity argon (30 min) and then irradiated. UV-vis spectra were measured at room temperature using a Cary 300 Bio Varian spectrophotometer.

The progress of sensitized PTAAS was monitored by HPLC using a Waters 600E Multisolvant Delivery System pump previously described [9]. Analytical HPLC analyses were carried out on a Waters XTerra RP<sub>18</sub> reverse phase column. 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-Ultra 1 and Chrompack PorapLOT Q capillary columns. 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.

The intensity of the incident light (366 nm) for the quantum-yield determinations was measured using a benzophenone-benzhydrol actinometer, taking its quantum yield as 0.68 [10]. All quantum yields for sensitizer disappearance and  $CO_2$  formation were extrapolated back to zero-percent conversion of the substrate in order to obtain initial quantum yields.

### 2.3. Laser flash photolysis

Two different nanosecond laser flash photolysis systems were used for the time-resolved experiments. The first apparatus (at the Notre Dame Radiation Laboratory) and its data-acquisition system have previously been described in detail [11]. A nitrogen laser (Lambda-Physics) provided 8 ns, 6 mJ pulses at 337 nm. The second nanosecond laser flash photolysis system used was a LKS 60 Laser Flash Photolysis apparatus (Applied Photophysics). Excitation

at 355 nm was from the third harmonic of a Q-switched Nd:YAG Lambda Physik laser (model LPY 150) operating with a pulse width of 4–5 ns [8]. All experiments were carried out with rectangular quartz optical cells ( $0.5\text{ cm} \times 1\text{ cm}$  or  $1\text{ cm} \times 1\text{ cm}$ , respectively).

A solution of BP (2 mM) in acetonitrile [12] was used as an external relative actinometer. Triplet concentrations (actinometry) were computed by monitoring the triplet-triplet absorptions of BP ( $\epsilon_{520} = 6500\text{ M}^{-1}\text{ cm}^{-1}$ ) [13].

## 3. Results and discussion

The mechanism for the sensitized photooxidation of the tetramethylammonium salt of 2-(phenylthio)acetic acid in acetonitrile was studied using nanosecond laser flash photolysis and steady-state photochemistry irradiations. The photosensitizer employed was benzophenone. The results of this investigation are compared with results of analogous earlier studies on tetraalkylammonium salts where the alkyl groups (R) were *n*-butyl, *n*-propyl, and ethyl [8].

### 3.1. Laser flash photolysis

Benzophenone triplet state was shown to be quenched by  $PhSCH_2COO-N^+(CH_3)_4$  in acetonitrile with a quenching rate constant,  $k_q$ , equal to  $1.1 \times 10^9\text{ M}^{-1}\text{ s}^{-1}$  (Table 1). Similar values of  $k_q$  were obtained for the salts with the other alkyl substituents [8] and were in the same range as the quenching rate constants for organic compounds containing thioether moieties in aqueous solutions [14,15]. These results suggested that the quenching mechanism involved an electron-transfer process from the sulfur atom to the benzophenone triplet as a primary photochemical step.

The transient absorption spectra following triplet quenching of BP by  $PhSCH_2COO-N^+(CH_3)_4$  are presented in Fig. 1. (The concentration of the quencher was chosen to quench more than 90% of the BP triplet.) The results are similar to those obtained for the *n*-butyl, *n*-propyl, and the ethyl derivatives of the tetraalkylammonium salts of 2-(phenylthio)acetic acid [8]. The formation of a long-wavelength absorption band around 700 nm was observed together with the appearance of a transient absorption due to the ketyl radical (550 nm). As presented in Fig. 2A the decay of the BP triplet corresponds to the growth of the 700 nm absorption band. This is similar to the behavior observed in the analogous systems of the other alkyl derivatives. Thus by analogy to the results for tetra-*n*-butyl-, tetra-*n*-propyl-, and tetraethylammonium salts, the 700 nm intermediate for the tetramethyl derivative can be attributed to the ion pair  $[BP^{\bullet-} \cdots N^+(CH_3)_4]$ . There are, however, some differences in the transient absorption spectra for tetramethylammonium deriva-

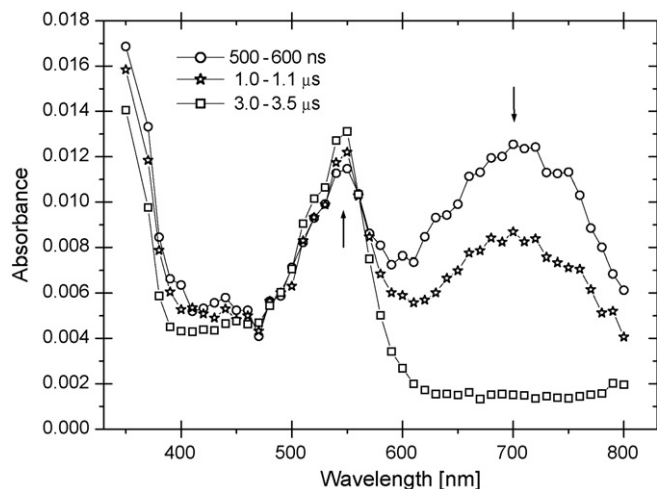
**Table 1**

Rate constants for the quenching of the BP triplet state and the quantum yields obtained from steady-state and laser flash photolysis for the BP-sensitized photooxidation of 2-(phenylthio)acetic tetramethylammonium salt in acetonitrile in comparison with the tetrabutylammonium salt ( $[BP] = 2\text{ mM}$ ,  $[Ph-S-CH_2-COO-N^+(R)_4] \approx 10\text{ mM}$ )

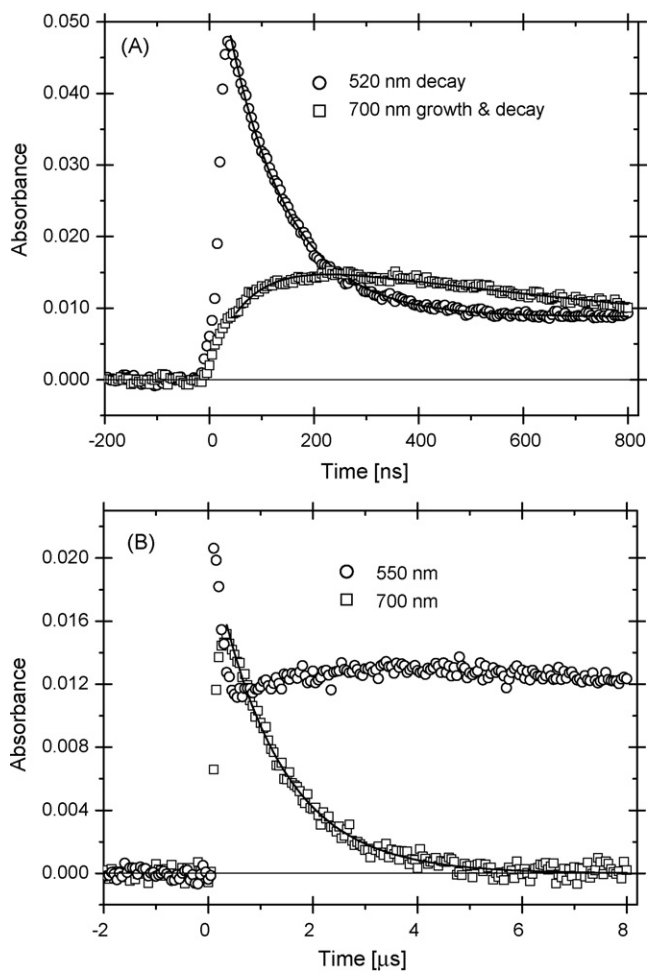
R	-CH <sub>3</sub>	-C <sub>4</sub> H <sub>9</sub> <sup>b</sup>
$k_q$ ( $M^{-1}\text{ s}^{-1}$ )	$1.1 \times 10^9$	$1.1 \times 10^9$
$\Phi_{[BP^{\bullet-} \cdots N^+(R)_4]}$ <sup>a</sup> ( $\pm 10\%$ )	0.11 <sup>a</sup>	0.33
$\Phi_{BP^{\bullet}}$	0.46	0.33
$\Phi_{CO_2}$ ( $\pm 20\%$ )	0.18	0.45
$\Phi_{BP}$ ( $\pm 10\%$ )	0.38	0.42
$\Phi_{salts}$ ( $\pm 10\%$ )	0.52	0.81
$\Phi_{NR_3}$	$\sim 0.09$	0.20
$\Phi_{PhSCH_3}$	0.14	0.43

<sup>a</sup> Taking  $\epsilon_{700} = 18,000\text{ M}^{-1}\text{ cm}^{-1}$  [16].

<sup>b</sup> From previous work [8,16].



**Fig. 1.** Transient absorption spectra following triplet quenching of BP (2 mM) by  $C_6H_5-S-CH_2-COO^-N^+(CH_3)_4$  (10 mM) after various delays after the flash in acetonitrile.



**Fig. 2.** Kinetic traces obtained in the flash photolysis experiments (BP (2 mM),  $C_6H_5-S-CH_2-COO^-N^+(CH_3)_4$  (10 mM) in acetonitrile): (A) at 520 and 700 nm on the hundreds of nanosecond time scale; (B) at 550 and 700 nm on the microsecond time scale.

tive in comparison with tetra-*n*-butylammonium salt. First of all, the 700 nm band is less intense than in the case of the tetra-*n*-butylammonium salt, but, opposite to the *n*-butyl derivative, the 700 nm band of the methyl derivative has similar intensity to the initial spectrum of the ketyl radical (see Fig. 1). (In the *n*-butyl derivative, the ketyl radical is not initially observed [8].) This indicates the existence of an efficient channel of ketyl-radical formation as a primary photochemical step for the tetramethylammonium salt. In addition, the decay of the 700 nm transient is much faster for the tetramethyl derivative ( $\tau = 1.25 \mu s$ , Fig. 2B) than in the case of the tetra-*n*-butylammonium salt ( $\tau = 30 \mu s$ ) [8]. In the tetramethyl derivative, the 700 nm decay is accompanied by the growth of the ketyl-radical absorption at 550 nm ( $\tau = 1.2 \mu s$ ). The phenomena presented in Fig. 2B clearly indicate that a second channel for the ketyl-radical formation was occurring from the ion pair  $[BP^{\bullet-} \cdots N^+(CH_3)_4]$ .

Using a similar procedure to that described in ref [8] and employing the BP triplet-triplet absorption as an external actinometer, the quantum yields of the ion pair  $[BP^{\bullet-} \cdots N^+(CH_3)_4]$  and ketyl radical were measured (Table 1). The  $\Phi_{[BP^{\bullet-} \cdots N^+(CH_3)_4]}$  was determined assuming that the molar absorption coefficient at 700 nm is  $18,000 M^{-1} cm^{-1}$ , by the analogy to the ion pair for the *n*-butyl derivative [8,16]. The value obtained for the  $PhSCH_2COO^-N^+(CH_3)_4$  salt is then 3–4 times lower than for the other alkyl derivatives [8]. Note that for the tetramethylammonium salt, the quantum yield for ketyl-radical formation,  $\Phi_{BP^{\bullet-}} = 0.46$  (Table 1), represents the total quantum yield from two distinct processes, a primary and a secondary one. In the primary process, ketyl radicals were formed ( $\Phi'_{BP^{\bullet-}} = 0.36$ ) after the decay of the BP triplet, whereas in the secondary process, ketyl radicals were formed ( $\Phi''_{BP^{\bullet-}} = 0.10$ ) concomitantly with the decay of the 700 nm intermediate. In contrast, the formation of the ketyl radicals in the analogous primary process was shown to be negligibly small in the cases of the tetraalkylammonium salts where the alkyl groups were *n*-butyl, *n*-propyl, or ethyl [8].

### 3.2. Steady-state irradiation. Stable-products formation

Steady-state irradiation experiments were performed for solutions containing BP (4 mM) and the  $PhSCH_2COO^-N^+(CH_3)_4$  salt (about 10 mM) in acetonitrile in order to identify stable products and subsequently to determine their quantum yields. Using similar analytical techniques and procedures as for the other alkyl derivatives (see [8]), the following stable products were identified: carbon dioxide ( $CO_2$ ), trimethylamine ( $N(CH_3)_3$ ), formaldehyde ( $H_2CO$ ), thioanisole ( $PhSCH_3$ ), 1,2-bis(phenylthio)ethane ( $PhSCH_2CH_2SPh$ ), 1,2-bis(phenylthio)methane ( $PhSCH_2SPh$ ), and thiophenol ( $PhSH$ ), in addition to benzpinacol ( $Ph_2C(OH)C(OH)Ph_2$ ). Thus, the products identified for the tetramethylammonium salt were the same as for the tetra-*n*-butyl, tetra-*n*-propyl, or tetraethyl derivatives with the exception of formaldehyde (identified in the case of the tetramethyl salt), whereas alkenes were identified in the other three cases. The formation quantum yields of the stable products, in addition to the quantum yields of BP and salt disappearances, were determined using an external actinometry method in a manner analogous to that presented in ref. [15]. The results obtained are summarized in Table 1 where the appropriate values for tetra-*n*-butylammonium salt are also included for comparison.

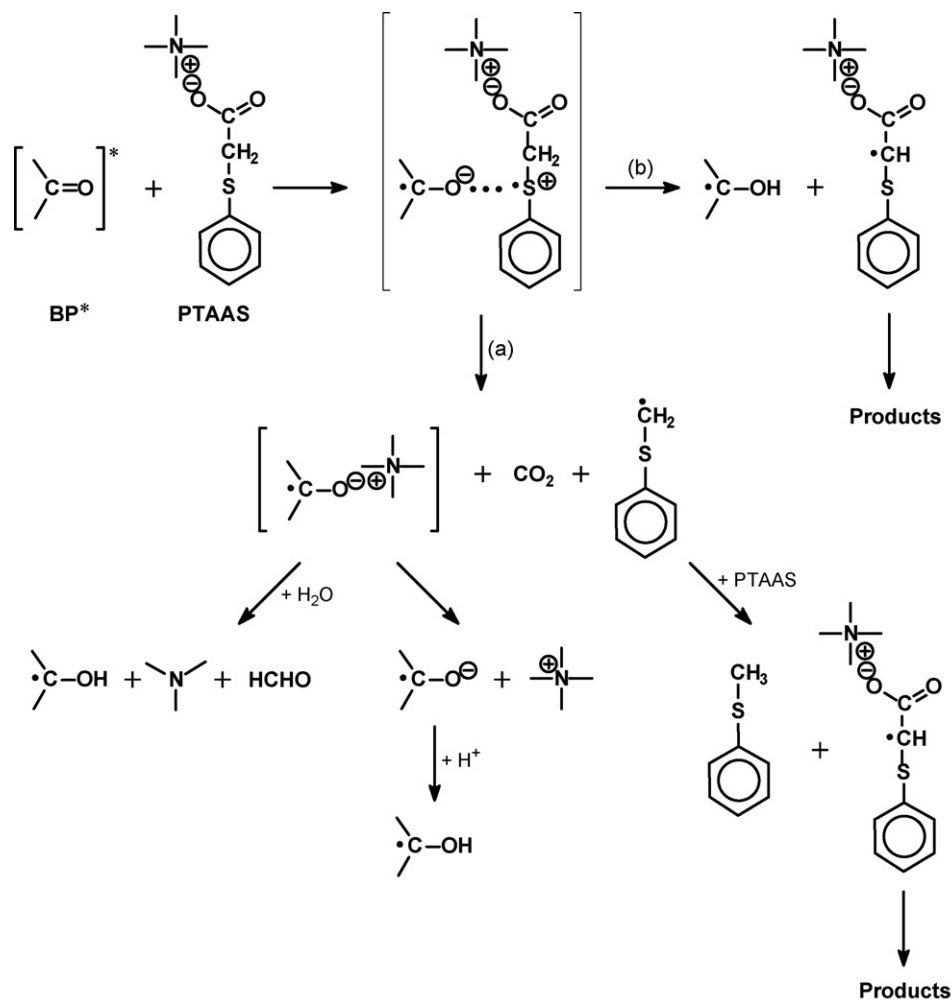
The formation quantum yields,  $\Phi_{CO_2}$  and  $\Phi_{PhSCH_3}$ , and that for salt disappearance,  $\Phi_{salt}$ , were found significantly lower than those for the tetra-*n*-butyl salt. The quantum yield of BP disappearance,  $\Phi_{BP}$ , was determined to be equal, within experimental error, for the methyl and *n*-butyl derivatives. The results of the formation quantum yield of trimethylamine were not determined due to analytical difficulties with the quantitative evaluation of the  $N(CH_3)_3$  concentration.

### 3.3. Mechanism of benzophenone-sensitized photooxidation of tetramethylammonium salt of 2-(phenylthio)acetic acid in acetonitrile

On the basis of laser flash photolysis and steady-state results, a mechanism for the primary and secondary photochemical reactions is proposed (Scheme 1) for the sensitized photooxidation of the tetramethylammonium salt of 2-(phenylthio)acetic acid in acetonitrile. An electron-transfer reaction between the BP triplet state and the  $\text{PhSCH}_2\text{COO}^-\text{N}^+(\text{CH}_3)_4$  salt led to the formation of the radical-ion pair  $[\text{BP}^{\bullet-}\cdots\text{S}^{\bullet+}]$  which was not observed directly in the current nanosecond flash photolysis study. This radical-ion pair can decay in two parallel reactions. Reaction (a), Scheme 1: The first reaction is a decarboxylation leading to the formation of an ion pair  $[\text{BP}^{\bullet-}\cdots\text{N}^+(\text{CH}_3)_4]$ ,  $\text{CO}_2$ , and a  $\text{PhSCH}_2^{\bullet}$  radical. Reaction (b), Scheme 1: The second reaction of the radical-ion pair  $[\text{BP}^{\bullet-}\cdots\text{S}^{\bullet+}]$  is a proton-transfer reaction from the  $\text{CH}_2$  group of the thioether moiety of the salt to the  $\text{BP}^{\bullet-}$  leading to the formation of a ketyl radical,  $\text{BPH}^{\bullet}$ , and an  $\alpha$ -(alkylthio)alkyl radical. The observation of the  $\text{BPH}^{\bullet}$  ketyl radical and the  $[\text{BP}^{\bullet-}\cdots\text{N}^+(\text{CH}_3)_4]$  ion pair (the 700 nm intermediate) following BP triplet decay is direct evidence for reactions (a) and (b). The ion pair  $[\text{BP}^{\bullet-}\cdots\text{N}^+(\text{CH}_3)_4]$  cannot decay via a Hofmann-elimination reaction as was the case with the tetra-*n*-butyl, tetra-*n*-propyl, and tetraethylammonium salts. However, in the presence of traces of water,  $[\text{BP}^{\bullet-}\cdots\text{N}^+(\text{CH}_3)_4]$  can decay to form trimethylamine and formaldehyde (both compounds were experi-

mentally detected). Further reaction of the  $\text{PhSCH}_2^{\bullet}$  radical (from reaction (a)) with the excess  $\text{PhSCH}_2\text{COO}^-\text{N}^+(\text{CH}_3)_4$  salt led to the formation of thioanisole and an  $\alpha$ -(alkylthio)alkyl radical that can fragment to form a phenylthiyl radical (see ref. [8]). The detection of thioanisole ( $\text{PhSCH}_3$ ), 1,2-bis(phenylthio)ethane ( $\text{PhSCH}_2\text{CH}_2\text{SPh}$ ), 1,2-bis(phenylthio)methane ( $\text{PhSCH}_2\text{SPh}$ ), and thiophenol ( $\text{PhSH}$ ) supports the mechanism presented in Scheme 1.

Additional support for the mechanism presented in Scheme 1 can be taken from a comparison of the quantum yields from the time-resolved and stationary-state experiments. Assuming  $18,000\text{ M}^{-1}\text{ cm}^{-1}$  to be  $\epsilon_{700}$  for  $[\text{BP}^{\bullet-}\cdots\text{N}^+(\text{CH}_3)_4]$ , the quantum yield of this ion pair ( $\Phi_{[\text{BP}^{\bullet-}\cdots\text{N}^+(\text{CH}_3)_4]} = 0.11$ ) corresponds, within experimental error, to the values of (i) the  $\text{CO}_2$  quantum yield ( $\Phi_{\text{CO}_2} = 0.18$ ), (ii) the formation quantum yield of thioanisole ( $\Phi_{\text{PhSCH}_3} = 0.14$ ), and (iii) the quantum yield of ketyl-radical formation ( $\Phi_{\text{BPH}^{\bullet}} = 0.10$ ) in the secondary reaction. The approximate agreement of the latter three quantum yields with the former is consistent with the mechanism in Scheme 1. Furthermore, the quantum yield of trimethylamine, estimated to be  $\sim 0.09$  (Table 1), indicates that the formation of  $\text{N}(\text{CH}_3)_3$  is the main reaction of the  $[\text{BP}^{\bullet-}\cdots\text{N}^+(\text{CH}_3)_4]$  ion pair. The total quantum yield of ketyl-radical formation ( $\Phi_{\text{BPH}^{\bullet}} = 0.46$ ), within experimental error, is equal to the value of quantum yield of BP disappearance from the steady-state measurements ( $\Phi_{\text{BP}} = 0.38$ ). The quantum yield of the  $\text{PhSCH}_2\text{COO}^-\text{N}^+(\text{CH}_3)_4$  salt disappearance ( $\Phi_{\text{salt}} = 0.52$ ) corresponds well with the sum of the quantum yield of the ketyl



Scheme 1.

radical ( $\Phi_{\text{BP}^{\bullet}} = 0.46$ ) and the ion pair  $[\text{BP}^{\bullet-} \cdots \text{N}^+(\text{CH}_3)_4]$  formation ( $\Phi_{[\text{BP}^{\bullet-} \cdots \text{N}^+(\text{CH}_3)_4]} = 0.11$ ). In summary, this detailed quantitative evaluation of the stable and short-lived intermediates confirms the mechanism presented in Scheme 1.

A comparison of the mechanism of sensitized photooxidation of the tetramethylammonium salt of 2-(phenylthio)acetic acid (by the triplet state of benzophenone) with the mechanism for tetraalkylammonium salt (where alkyl is *n*-butyl, *n*-propyl, and ethyl) [8] indicates several differences. First of all, in the case of the methyl salt, two competing parallel primary photochemical reactions (a) and (b) were observed (Scheme 1). The reaction (b) – proton transfer within the radical-ion pair  $[\text{BP}^{\bullet-} \cdots \text{S}^{\bullet+}]$  leading to a ketyl radical – is the main reaction channel. On the other hand, in the case of the *n*-butyl (also *n*-propyl and ethyl) salt, the main primary reaction is the formation of the 700-nm intermediate – reaction (a) [8]. This second reaction (a) – decarboxylation leading to the formation of an ion pair  $[\text{BP}^{\bullet-} \cdots \text{N}^+(\text{CH}_3)_4]$  (the 700 nm intermediate) – is 3–4 times less efficient in the case where the alkyl groups are methyl (see  $\Phi_{[\text{BP}^{\bullet-} \cdots \text{N}^+(\text{R})_4]}$  in Table 1).

This difference in behaviour of the methyl substituents compared to the other alkyl substituents can be rationalized by considering how the size of the quaternary ammonium ions effect the reaction dynamics, in particular the competing reactions: (a) decarboxylation and (b) proton transfer (see Scheme 1). One possibility is that the smaller size of the tetramethylammonium ion might affect the steric aspects of the competing reactions. However, the triplet quenching rate constants are almost the same for all the quaternary ammonium salts, indicating little steric effects on the quenching reaction itself. This is also reasonable since the quaternary ammonium ions would likely favor a position near the carboxylate moiety and away from the initially neutral electronic transfer site at the sulfur. In addition, electron-transfer matrix elements have an exponential dependence on the distance of transfer, and, thus, the associated proton transfer (reaction b) will already be near to the electron-transfer site and away from the quaternary ammonium ions. Thus the size of the quaternary ammonium salt will not be expected to effect the proton-transfer reaction (b) in Scheme 1.

However, the small size of the tetramethylammonium ion, residing in the neighborhood of the carboxylate site in the salt, can have an effect on the decarboxylation reaction (a) in Scheme 1. The decarboxylation of the carboxylate [17] moiety of the sulfur radical zwitterion can be thought of, mechanistically, as presented in Scheme 2. This mechanism in Scheme 2 is analogous to that for the photosensitization of carboxylic acids [18].

In Scheme 2, the strong electric field of the small tetramethylammonium cation should affect the strength of the ion-pairing interaction more strongly than those analogous interactions with the larger tetraalkylammonium ions. If so, this would lead to a slowing down of the decarboxylation reaction (a) in Scheme 1. The consequence of this would be an observed favoring of the competing, parallel, proton-transfer reaction (b). Such is the case as measured by the smaller yield of the 700 nm absorption in

the tetramethylammonium salts ( $\Phi_{[\text{BP}^{\bullet-} \cdots \text{N}^+(\text{CH}_3)_4]} = 0.11$  compared to 0.33 for the *n*-butyl derivative, see Table 1). This reduced absorption in the tetramethylammonium salt is a measure of the reduced ability of the decarboxylation route (a) (see Scheme 1) to compete with the proton transfer (b).

A second difference between the photochemistry of the methyl-substituted quaternary ammonium salts and the previously studied alkyl substituents concerns is the nature of reaction for the disappearance of the ion pair  $[\text{BP}^{\bullet-} \cdots \text{N}^+(\text{CH}_3)_4]$ . In the case of the tetraalkylammonium salts (where alkyl is *n*-butyl, *n*-propyl, or ethyl), Hofmann elimination can occur (only for alkyl substituents with beta carbons). For the methyl derivative, this reaction cannot occur because it lacks  $\beta$ -hydrogens. Thus, the ion pair  $[\text{BP}^{\bullet-} \cdots \text{N}^+(\text{CH}_3)_4]$  must decay via a different type of reaction. One plausible reaction is a proton transfer from the methyl group to the benzophenone radical anion followed by the decomposition of the intermediates, yielding trimethylamine and a carbene. It is well known that carbenes are very reactive and, in the presence of water, can yield formaldehyde or can undergo other specific reactions, e.g., an insertion reaction (chain extending or chain branching reaction) [19,20]. Such differences in the nature of the decay reactions of the different  $[\text{BP}^{\bullet-} \cdots \text{N}^+(\text{R})_4]$  for methyl vs. other alkyl substituents could account for the much slower decay of the 700-nm transients for *n*-butyl, *n*-propyl and ethyl salts compared to the decay of the 700-nm transient of the tetramethylammonium derivative. For the tetraalkylammonium salts (*n*-butyl, *n*-propyl and ethyl), the Hofmann-elimination reaction is generally much more favorable than the  $\alpha$ -elimination because alkenes are much more stable than carbenes [19,20].

In our earlier papers on photopolymerization using tetraalkylammonium salts as the co-initiators [15], we have documented that the radicals  $(\text{Ph}-\text{S}-\text{CH}_2^{\bullet})$  obtained from decarboxylation of the zwitterionic radical  $\text{Ph}-\text{CH}_2\text{S}^{\bullet+}\text{COO}^-$  – not the radicals  $(\text{Ph}-\text{S}-\text{CH}^{\bullet}-\text{COO}^-)$  from proton transfer within  $[\text{BP}^{\bullet-} \cdots \text{S}^{\bullet+}]$  – are mainly responsible for the observed efficient polymerization initiation. This was verified by the observed linear correlation between the photoinitiated polymerization rates and  $\sqrt{\Phi(\text{CO}_2)}$ , where  $\Phi(\text{CO}_2)$  represented the quantum yields of  $\text{CO}_2$  which were equal to the quantum yields of the  $\text{Ph}-\text{S}-\text{CH}_2^{\bullet}$  radicals. Thus, a detailed knowledge of the mechanism of the primary and secondary photochemical reactions occurring in these photoinitiating systems allowed us to determine the mechanism of free-radical polymerization initiated by benzophenone/tetraalkylammonium salts of 2-(phenylthio)acetic acid, including tetramethylammonium salt.

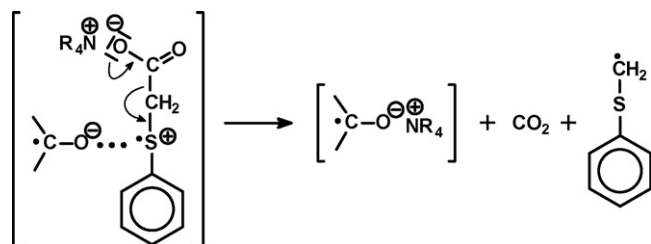
In summary, the use of the laser flash photolysis technique and steady-state irradiation experiments led to a detailed quantitative description of the primary and secondary reactions in the case of sensitized photooxidation of tetramethylammonium salt of 2-(phenylthio)acetic acid in acetonitrile by benzophenone. This mechanism was compared with the mechanism for tetraalkylammonium (*n*-butyl, *n*-propyl, and ethyl) salts, and the differences were contrasted.

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Scheme 2.

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