Benzophenone−Phenylthioacetic Acid Tetraalkylammonium Salts as Effective Initiators of Free-Radical Photopolymerization of Vinyl Monomers, Mechanistic Studies

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Received July 17, 2007; Revised Manuscript Received September 12, 2007

ABSTRACT: The mechanism of the photooxidation of tetraalkylammonium salts of phenylthioacetic acid, $C_6H_5-S-CH_2-COO^-N^+R_4$, was investigated in detail in order to understand why they turned out to be efficient co-initiators of free-radical polymerizations. The photosensitizer was benzophenone (BP), and the alkyl substituents (R) were *n*-butyl, *n*-propyl, or ethyl. The techniques used were steady-state and nanosecond flash photolysis. It was shown that electron transfer from the sulfur atom to the benzophenone triplet state was the primary photochemical step followed by a decarboxylation reaction leading to CO_2, the $C_6H_5-S-CH_2^{\bullet}$ radical, and a $[BP^{\bullet-}\cdots N^+R_4]$ ion pair. The latter underwent a Hofmann elimination (unexpected in these mild experimental conditions) leading to alkene-1 and trialkyl amine. The quantum yields of all the observed transients and the stable products were determined. The mechanism of primary and secondary photochemical reactions was quantitatively described, and it was shown to be similar for all of the alkyl derivatives used. The results of photochemical studies were compared with respect to the polymerization studies where the systems consisting of benzophenone and tetraalkylammonium salts of phenylthioacetic acid (and phenylthioacetic acid for comparison) were used as photoinitiating couples for free-radical polymerizations using 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate as the monomer. A linear correlation was found for the polymerization rates with respect to the square root of the CO_2 quantum yields. This justified the hypothesis that the $C_6H_5SCH_2^{\bullet}$ radical is the initiator of the free-radical polymerizations for the $BP/C_6H_5-S-CH_2-COO^-N^+R_4$ photoredox pairs studied in this work.

Introduction

Excited-state electron transfer often plays a key role in photoinduced free-radical polymerizations.[1−5] Photoinduced electron-transfer processes can lead to the formation of free radicals that are effective initiators of polymerizations. The efficiency of the initiating radical formation depends on two main factors. The first factor is the precise nature of the reacting partners taking part in the electron-transfer process. The second is the efficiency of any subsequent fragmentations yielding secondary radicals and radical ions[6−16] that are often much more effective in initiating polymerizations than the primary radicals. Therefore, a detailed knowledge of such primary and secondary photochemical mechanisms is critical for the design of practical systems of initiating polymerizations.

In the past decade, there have been several extensive studies on the photooxidation of sulfur-containing organic compounds and the subsequent fragmentation reactions of the photon-generated sulfur-centered radical cations.[17−20] These studies are of general interest because of their potential applications in photopolymerization,[21−23] their importance as intermediates in organic synthesis,[24] and their relevance to biological and medical research in the areas of oxidative stress and aging.[25] Although the goal of the basic research into the photochemical mechanisms is to understand the fundamental chemistry, any results are likely to aid these more applied areas by providing a deeper insight into the underlying principles governing their material behavior.

In the area of polymerization, for example, it was recently shown[22] for the series of sulfur-containing carboxylic acids, radicals of what type would be the most effective initiators of polymerizations. This information gives polymer chemists the opportunity to design efficient initiating systems for photoinduced polymerizations. The basic knowledge on the efficient initiating radicals came from a detailed quantitative description of the mechanism of secondary reactions following photoinduced electron transfer. The photoredox pairs in the study consisted of the photoreceptor 4-carboxybenzophenone (CB) and a series of co-initiators. The co-initiators were sulfur-containing aromatic carboxylic acids. The sulfur-centered radical cations formed upon photoinduced electron transfer were found to be susceptible to decarboxylation and deprotonation reactions. These reactions lead to the formation of carbon-centered radicals. The observed correlation between the polymerization rates and the square root of the quantum yields of the appropriate radical formation indicated which radicals were responsible for the initiations.

Preliminary results of photochemical studies for new photosensitizer/co-initiator systems have been recently described by us.[26] The photoredox pairs consisted of benzophenone and tetrabutylammonium salts of phenylthioacetic acid as photoredox couples. The initial motivation for using tetraalkylammonium salts was to enhance the solubility of the photosensitizer and/

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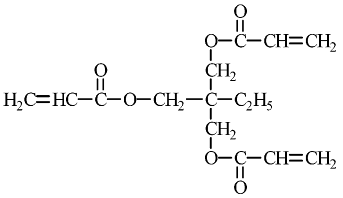
10.1021/ma071581g CCC: $37.00

Chart 1



or the co-initiator in the polymerizing media under consideration. This redox pair could potentially be used as an electron-transfer initiator of free-radical polymerizations. It was shown that an initial electron-transfer process is followed by the efficient decarboxylation reaction leading to an ion pair $[BP^{\bullet-}\cdots N^{+}(C_4H_9)_4]$ and a $C_6H_5{-}S{-}CH_2^{\bullet}$ radical. The $C_6H_5{-}S{-}CH_2^{\bullet}$ radical is potentially an efficient initiator of polymerizations. The ion pair underwent a Hofmann elimination (unexpected in these mild experimental conditions). The observed products were butene-1 and tributyl amine which are typical products for this type of elimination.

In the current work, further detailed mechanistic studies are given using tetraalkylammonium salts of phenylthioacetic acid (PTAAS), $C_6H_5{-}S{-}CH_2{-}COO^{-}N^{+}R_4$, as redox couples with benzophenone as a photosensitizer. In the formula for the salts, R stands for *n*-butyl, *n*-propyl, or ethyl. The photosensitized electron-transfer studies were performed using steady-state and flash-photolysis techniques in acetonitrile. In addition, the results of photochemical studies are compared and discussed with respect to the polymerization studies where systems consisting of benzophenone and tetraalkylammonium salts of phenylthioacetic acid were used as photoinitiating couples for free-radical polymerizations.

Experimental Part

Materials. Phenylthioacetic acid (PTAA), $C_6H_5{-}S{-}CH_2{-}COOH$; benzophenone (BP), and 4-carboxybenzophenone (CB) were the reactants used for the preparation of the tetraalkylammonium salts of phenylthioacetic acid, $C_6H_5{-}S{-}CH_2{-}COO^{-}N^{+}R_4$ (PTAAS), where R = *n*-butyl, *n*-propyl, ethyl, or methyl. 2-Ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA) was used as the monomer (Chart 1) for the polymerization studies. All of the above reagents were purchased from Aldrich. The tetraalkylammonium salts of PTAA were obtained by treating phenylthioacetic acid in boiling water along with a molar equivalent of the corresponding tetraalkylammonium hydroxide. After the evaporation of water, the clammy residue was dried in a vacuum desiccator, yielding transparent crystals. Carbon dioxide, thioanisole, butene-1, propene-1, ethylene, and acetonitrile (for spectroscopy) were purchased from Merck and J. T. Baker or Aldrich.

Steady-State Irradiations. 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 a water filter, quartz windows, an interference filter (366 nm), and glass cutoff filters (<290 nm) were used as the excitation source for the 366-nm irradiations ($I_0 = 1.76 \times 10^{-4}$ einstein dm^{-3} 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 both a diode array spectrophotometer HP 8452A and a Cary 300 Bio Varian spectrophotometer.

The progress of the sensitized photoreaction of PTAAS during irradiation was monitored by HPLC using a Waters 600E multisolvent delivery system pump described previously.[27] 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). 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 (0.32 mm × 25 m) and Chrompack PoraPLOT Q (0.53 mm × 25 m) 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 (30 m).

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 Phenylthioacetic Tetraalkylammonium Salts in Acetonitrile ([BP] = 2 mM and $[Ph{-}S{-}CH_2{-}COO^{-}\ N^{+}(CH_2CH_2\text{-}R')_4] \approx 10$ mM for the Quantum Yield Determinations)

R′	$-C_2H_5$	$-CH_3$	$-H$
k_q (M^{-1} s^{-1})	1.1×10^9	1.3×10^9	1.8×10^9
$\Phi_{[BP^{\cdot-}\cdots N^{+}(C_2H_4-R')_4]}$[a] (±10%)	0.35[b]	0.37	0.36
$\Phi_{BPH^{\cdot}}$	0.28−0.38[b]	0.18−0.48	0.19−0.44
Φ_{CO_2} (±20%)	0.45[b]	0.39	0.42
Φ_{BP} (±10%)	0.42[b]	0.42	0.36
Φ_{salts} (±10%)[c]	0.81	0.75	0.80
$\Phi_{N(C_2H_4-R')_3}$ (±10%)	∼0.20[b]	0.40	0.31
$\Phi_{CH_2=CHR'}$	∼0.26[b]	*d*	*d*
Φ_{PhSCH_3}	0.43	0.40	0.43

[a] Taking $\epsilon_{700} = 18\,000$ M^{-1} cm^{-1} (ref 26). [b] From previous work.[26] [c] Quantum yield of salt disappearance. [d] Not determined quantitatively.

The intensity of the incident light (366 nm) for the quantum-yield determinations were measured using a benzophenone−benzhydrol actinometer, taking its quantum yield as 0.68.[28] 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.

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.[29] A 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.

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 about 4−5 ns (10 mJ/pulse). Transient absorbances at preselected wavelengths were monitored by a detection system consisting of a monochromator, a photomultiplier tube (Hamamatsu R955), and a pulsed xenon lamp (150 W) as the monitoring source. The signal from the photomultiplier was processed by a Hewlett-Packard/Agilent Infiniium 54810A digital storage oscilloscope and an Acorn compatible computer. All experiments were carried out with rectangular quartz optical cells (0.5 cm × 1 cm) or (1 cm × 1 cm).

Two relative actinometers were used. One was a solution of 4-carboxybenzophenone (CB) (2 mM) at neutral pH, and the other was BP (2 mM) in acetonitrile.[30] Triplet concentrations (actinometry) were computed by monitoring the triplet−triplet absorptions of CB ($\epsilon_{535} = 6250$ M^{-1} cm^{-1})[31] or BP ($\epsilon_{520} = 6500$ M^{-1} cm^{-1}).[32]

Kinetics of Polymerization. The kinetics of free-radical polymerization were monitored by determining the rate of the heat evolution during the polymerization of a cured actual sample. The measurements involved recording photopolymerization isotherms using a single-cell calorimeter based on a thick-film heat flux sensor (semiconducting diode) immersed in a polymerizing formulation (0.25 mL). The irradiations of the polymerization mixtures were carried out with an Innova 90-4 argon-ion laser (351 and 361 nm lines). The average incident power of the irradiations (20 mW/0.785 cm^2) was measured with a Coherent model Fieldmaster power meter.

The polymerization formulations were composed of 2 mL of 1-methyl-2-pyrrolidinone (MP), 8 mL of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA), and an appropriate amount of the photoinitiating systems. The photoinitiating systems were (a) benzophenone (0.040 M) alone, (b) benzophenone (0.040 M) in the presence of PTAA (10 mM and 0.1 M), or (c) benzophenone (0.040 M) in the presence of the tetraalkylammonium salts of PTAA (10 mM). This concentration of the salts was found to give the maximum efficiency of photoinitiation. Blank photochemical experiments were also performed on a pure monomeric formulation. In order to avoid the possibility of nonisothermal reaction conditions, only the data for initial times of the polymerizations were used for the calculation of the polymerization rates. The average values for the rates of polymerization were calculated based on at least two measurements.

Results and Discussion

1. Mechanism of the Sensitized Photooxidation of Phenylthioacetic Acid Tetraalkylammonium Salts by Benzophenone in Acetonitrile.

1.1. Quenching Rate Constants of the BP Triplet State by PTAAS. Three tetraalkylammonium salts of phenylthioacetic acid (where the alkyl groups are *n*-butyl, *n*-propyl, and ethyl) were used as quenchers of the BP triplet state in acetonitrile solutions. The quenching rate constants, k_q, were obtained by monitoring the triplet−triplet absorption decay rates (k_{obs}) of BP as a function of quencher concentration, monitoring at the fixed wavelength of 520 nm. The bimolecular rate constants were taken as the slope to the linear-least-squares fits to the Stern−Volmer relation:

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

where τ_T is the lifetime of the BP triplet in the absence of quencher.

The k_q values were in the range of $(1.1-1.8) \times 10^9$ M^{-1} s^{-1} (Table 1) and did not depend significantly on the alkyl substituent. (A similar triplet-quenching rate constant was obtained for the tetramethylammonium salt of PTAA ($k_q = 1.1 \times 10^9$ M^{-1} s^{-1}).[33] These triplet-quenching rate constants were comparable with those for the sulfur-containing carboxylic acids in aqueous solutions,[19,22] but they were an order of magnitude higher than the analogous triplet-quenching rate constants for PTAA in acetonitrile. These relatively high values of k_q are indicative that the triplet-quenching mechanism involved electron transfer. The other reaction that is typical of triplet aromatic ketones, H-atom abstraction, has much lower rate constants which are in the range of 10^5-10^6 M^{-1} s^{-1}.[34] The effect of changing solvent from water to acetonitrile led to a lowering of the BP triplet-quenching rates constants by PTAA. This effect has been discussed previously.[35]

1.2. Nanosecond Laser Flash Photolysis. Transient Absorption Spectra, Kinetics, and Quantum Yields. The acetonitrile solutions of benzophenone and PTAAS used in the flash photolysis and steady-state photolysis experiments were first examined spectroscopically for any evidence of ground-state associations. No evidence for ground-state complexation was found under the experimental conditions used.

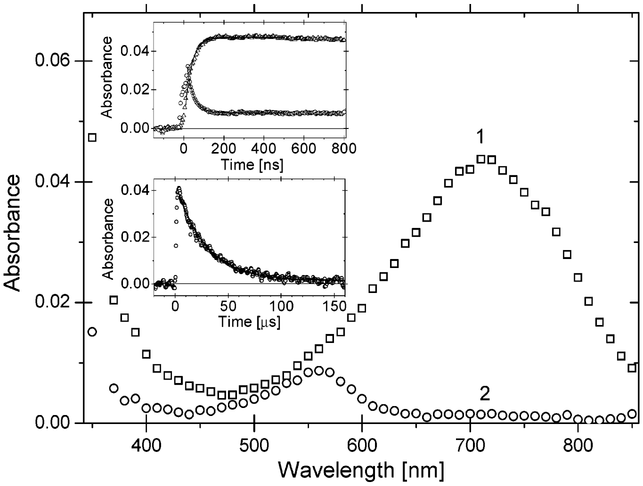


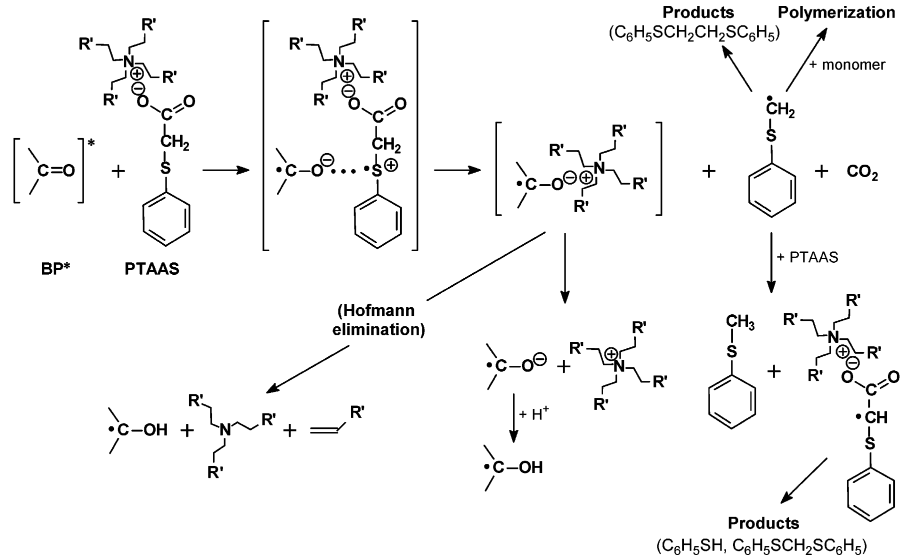
Figure 1. Transient absorption spectra following triplet quenching of BP (2 mM) by $C_6H_5-S-CH_2-COO^-N^+R_4$ (10 mM) after (1) 1 and (2) 150 μs delays after the flash in acetonitrile solution. Upper inset: kinetic traces at 520 and 710 nm on the hundreds of nanosecond time scale. Lower inset: kinetic trace at 710 nm on the hundreds of microsecond time scale.

Deoxygenated solutions of BP (2 mM) and PTAAS (10 mM) in acetonitrile were irradiated with 337 nm (or 355 nm) laser pulses. High concentrations of quenchers were used to rapidly quench more than 95% of the BP triplets. The transient absorption spectra were measured in the region of 370−850 nm at various delay times following the laser pulse. After the laser pulse was incident on the sample, a broad transient absorption grew in at 710 nm. This phenomenon occurred in all the PTAAS salts used. This behavior was similar to that observed in the *n*-butyl derivative previously described.[26] The growth rate of the 710 nm transient was found to be identical to the decay rate of the BP triplet (Figure 1 upper inset). Thus, the 710 nm transient can be considered to be the primary photochemical product formed directly from the BP triplet. The decay of this transient (lower inset) occurred on the microsecond time scale and could be analyzed by a monoexponential decay with a lifetime of 30 μs. Similar results were also obtained for the *n*-propyl and ethyl salts. Analogous to what was found in our previous work,[26] the formation of the 710 nm transients were only observed when the phenylthioacetate anion and the various N^+R_4 cations were present together as a salt. The addition of tetraalkylammonium pechlorate (up to 0.1 M) to the reaction system studied did not change the kinetics of the formation and decay of the 710 nm transient. The 710 nm transient was assigned as the $BP^{\bullet-}$ radical anion present in the form of the $[BP^{\bullet-}\cdots N^+R_4]$ ion pair.[26] A residual spectrum remaining after the decay of the 710-nm transient (Figure 1) was assigned to the long-lived ketyl radical ($BPH^{\bullet}$).[26]

Assuming (as it was done for the butyl derivative)[26] that the decay of the $[BP^{\bullet-}\cdots N^+R_4]$ ion pair leads to the formation of the $BPH^{\bullet}$ radical, the molar absorption coefficient of the ion pair at 710 nm was estimated to be 18 000 M^{-1} cm^{-1}. This value was obtained taking $\epsilon_{550} = 3400$ M^{-1} cm^{-1} as the molar absorption coefficient of the ketyl radical.[36] These values for the molar absorption coefficients of the $[BP^{\bullet-}\cdots N^+R_4]$ ion pairs and the $BPH^{\bullet}$ radicals were used, in conjunction with the relative actinometry (see the experimental part), to compute the quantum yields for the formation of the $[BP^{\bullet-}\cdots N^+R_4]$ ion pair and the ketyl radical (Table 1). Because of overlapping decays and spectra of the two radicals, particularly at the 550 nm maximum of $BPH^{\bullet}$, only a range of $\Phi_{BPH^{\bullet}}$ values could be estimated. For all three salts used, the quantum yields of ion-pair formation, $\Phi_{[BP^{\bullet-}\cdots N^+R_4]}$ are equal within experimental error and are in the range of the quantum yields of ketyl radical formation.

1.3. Steady-State Photolysis. Stable Product Analysis. Deoxygenated solutions of BP (4 mM) and PTAAS (5 mM) in acetonitrile were irradiated with monochromatic light $\lambda = 366$ nm. The progress of the reactions was monitored by GC and HPLC detection. Comparison of the retention times of the photoproducts in the irradiated solutions with those for authentic samples, together with GC−MS analysis, provided information

Scheme 1

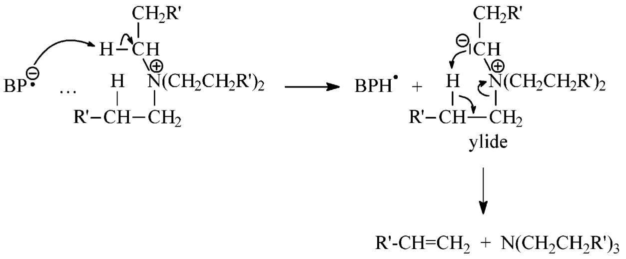


that allowed us to identify the stable products. The stable products observed were carbon dioxide, CO_2, trialkyl amines, $N(C_2H_4R')_3$, (where $R' = C_2H_5$, CH_3, and H), the corresponding alkenes, $CH_2{=}CHR'$, thioanisole, $C_6H_5SCH_3$, and traces of 1,2-bis(phenylthio)ethane, $C_6H_5SCH_2CH_2SC_6H_5$. In addition, benzopinacol, the product of benzophenone reduction, was followed during the reactions using the same techniques. Additional GC and HPLC studies allowed us to detect the following stable products in low concentrations: thiophenol, C_6H_5SH, and bis(phenylthio)methane, $C_6H_5SCH_2SC_6H_5$. These products are indicative that fragmentation reactions occurred in the radical that was initially formed from PTAAS (see below). Since standard samples of all the stable products were commercially available, it was possible to determine the photoproducts' quantum yields by calibrating the appropriate chromatographic analyses. The intensities of absorbed light were determined using an external actinometer (see experimental section). The changes in the concentrations of benzophenone and PTAAS were determined by HPLC analysis. From these measurements, quantum yields were determined for the disappearances of BP and PTAAS. All quantum yields measured at various irradiation times were extrapolated back to zero-percent conversion of the reactants in order to obtain the initial quantum yields. The quantum yields determined by these methods are listed in Table 1.

There are several conclusions that can be drawn based on the results presented in Table 1. (i) The quantum yields of CO_2 correspond to the quantum yields of BP consumption and to the quantum yields of ketyl and $[BP^{\bullet-}\cdots N^+R_4]$ ion-pair formation. (ii) The quantum yields of PTAAS disappearance are about double that of the respective benzophenone disappearances (Φ_{BP}). (iii) The quantum yields of thioanisole formation were equal to the respective disappearances of benzophenone. (iv) The quantum yields of trialkyl amine formation were equal (within experimental error) to the respective quantum yields of $[BP^{\bullet-}\cdots N^+R_4]$ ion-pair formation. In addition, for the butyl salt, the quantum yield of the butene-1 formation ($\Phi_{CH_2=CHR'} \sim 0.26$) is in the range of the quantum yield of the $[BP^{\bullet-}\cdots N^+R_4]$ ion-pair formation. No quantitative analysis was done for the formation of alkenes in the other salts because of analytical problems.

A mechanism (Scheme 1) can be proposed for the primary and secondary photochemical reactions based on the experimental observations above. An electron-transfer process is the main pathway for the quenching of the benzophenone triplet state at high concentrations of sulfur-containing carboxylic acid. The resulting $[BP^{\bullet-}\cdots{>}S^{\bullet+}]$ radical−ion pair undergoes a fast (on the nanosecond time scale)[13,37] decarboxylation leading to the formation of the $[BP^{\bullet-}\cdots N^+R_4]$ ion pair. This species is assigned as the 710 nm absorbing intermediate that is directly observed. In addition, CO_2 and the α-(arylthio)alkyl radical, $C_6H_5SCH_2^\bullet$, are produced from the initially formed $[BP^{\bullet-}\cdots{>}S^{\bullet+}]$ ion pair. The $C_6H_5SCH_2^\bullet$ radical cannot be observed directly in the spectral range used since its absorbance maximum at 330 nm[38] is masked by the ground-state absorption of benzophenone. Thus, its quantum yield could not be determined directly from spectroscopic measurements. The equality between the formation quantum yields of CO_2 and the $[BP^{\bullet-}\cdots N^+R_4]$ ion pair supports the mechanism in Scheme 1. Additional support comes from the quantum yields of thioanisole that are equal to the respective values of Φ_{CO2} (see below).

Scheme 2



The formation of the $[BP^{\bullet-}\cdots N^+R_4]$ ion pair can be rationalized by the stabilization of the radical pair by the electrostatic interaction of the $BP^{\bullet-}$ radical anion and the tetraalkylammonium cation. The decay of the $[BP^{\bullet-}\cdots N^+R_4]$ ion pair was observed on the microsecond time scale. Since the $BP^{\bullet-}$ radical anion can be considered to be a base, the close contact of both ions ($BP^{\bullet-}$ and N^+R_4) may lead to an efficient proton abstraction from the α-carbon adjacent to the nitrogen in N^+R_4, yielding a 1-alkene ($CH_2{=}CHR'$) and a trialkyl amine ($N(C_2H_4R')_3$), see Scheme 2. This type of reaction is known as a Hofmann elimination and is observed in quaternary ammonium ions.[39] In the system studied in this paper, however, the Hofmann elimination occurred under mild conditions without the presence of strong bases. A similar unusual Hofmann elimination under mild conditions was made for polymerizable cationic surfactant systems.[40]

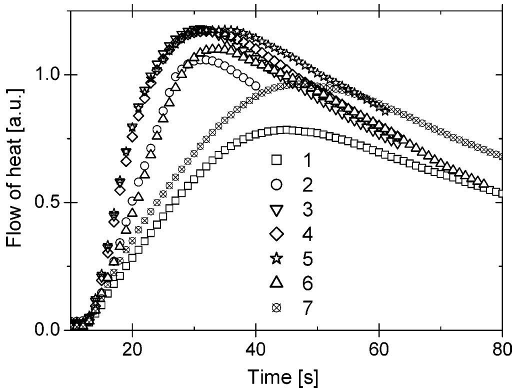


Figure 2. The photopolymerization kinetic traces recorded for the polymerizations of the TMPTA−MP (8:2) mixture initiated by the following photoinitiating systems: 1, BP; 2, (BP + $C_6H_5{-}S{-}CH_2{-}COOH$, [0.1 M]); 3, (BP + $C_6H_5{-}S{-}CH_2{-}COO^-N^+(C_4H_9)_4$, [0.01 M]); 4, (BP + $C_6H_5{-}S{-}CH_2{-}COO^-N^+(C_3H_7)_4$, [0.01 M]); 5, (BP + $C_6H_5{-}S{-}CH_2{-}COO^-N^+(C_2H_5)_4$, [0.01 M]); 6, (BP + $C_6H_5{-}S{-}CH_2{-}COO^-N^+(CH_3)_4$, [0.01 M]); 7, (BP + $C_6H_5{-}S{-}CH_2{-}COOH$, [0.01 M]).

In addition to the reaction mechanism proposed in ref 8 for the BP/tetrabutylammonium salt system, an additional reaction of $C_6H_5SCH_2^\bullet$ with the excess (5−10 mM) of PTAAS is proposed in the present studies (Scheme 1). The mechanism is supported by the observation that the quantum yields of salt disappearance (Φ_{salts}) was twice the respective quantum yields for BP disappearance and formation of thioanisole. Further support for the suggested mechanism comes from the structure of the additional products that are likely formed during fragmentations of the $C_6H_5SCH^\bullet COO^-\ N^+R_4$ radicals. An S−C bond cleavage has been suggested for the fragmentation of the $C_6H_5SCH^\bullet COOH$ radical.[35] Similar fragmentations likely occurred in the $C_6H_5SCH^\bullet COO^-\ N^+R_4$ ion pairs and led to the observed formation of thiophenol and bis(phenylthio)methane (see Scheme 1).

The BP/tetramethylammonium salt of the PTAA system can undergo similar primary photochemical reactions as in the case of butyl, propyl, and ethyl derivatives leading to decarboxylation and formation of CO_2 and the α-(arylthio)alkyl radical, $C_6H_5SCH_2^\bullet$. The secondary reactions in the tetramethylammonium salt, however, were found to be different from the other salts studied due to lack of hydrogens located at the β carbon in the other tetraalkylammonium cations (lack of Hofmann elimination). The mechanism of the reactions for the methyl derivative will be discussed in detail in the following paper.[33]

2. Polymerization. Polymerization experiments were carried out in order to compare the rates and efficiencies of the polymerizations that were initiated by the various photoinitiating systems under consideration in this work. These results were then correlated with the photochemical data, i.e., the quantum yields of radical formation. As described in the experimental part, the kinetics of the free-radical polymerizations were measured based on the heat-evolution rates during the polymerizations. The family of such kinetic traces was recorded for the polymerizations of TMPTA−MP (8:2) mixtures that were initiated by the various photosensitizer/co-initiator systems.

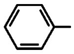
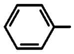
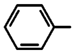
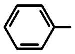
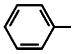
Figure 2 shows typical kinetic traces that are derived from the heat-flow measurements accompanying photopolymerization. From Figure 2, it can be seen that the polymerization kinetic traces are very similar for the photoinitiating systems containing BP and three of the tetraalkylammonium salts (*n*-butyl, *n*-propyl, and ethyl). All three led to practically identical polymerization rates 73.8−76.0 μmol/s (Table 2) as calculated from the time-dependent polymerization curves. The kinetic trace associated with the tetramethylammonium salt in Figure 2 is distinctly different from the first three cases just mentioned. The rate of polymerization using this tetramethylammonium salt was found to be 50.1 μmol/s. From the kinetic traces in Figure 2, the polymerization rates initiated by the BP/PTAA co-initiating pair were determined to be 28.4 and 52.9 μmol/s depending on the concentration of the acid used (0.01 and 0.1 M, respectively). Finally, the rates of polymerization using BP alone as the initiator were found to be much lower, 23.4 μmol/s.

The initial polymerization quantum yields are also included in Table 2. These quantum yields were calculated for an initial time of polymerization, in particular for the time of polymerization where the linear part of the kinetic curves in Figure 2 was observed. Since the slope of the linear part of the kinetic curves describes (after appropriate calibration), the rate of polymerization expressed in micromoles per second, one can obtain the quantum yields of polymerization by dividing this value by the light intensity (expressed in microeinstein per second). The depth of the penetration of light in the polymerization experiments was about 2 mm, so the calculated quantum yields represent effective values as observed by the thermal sensor used in the heat-flow measurements. It was shown[41] that such a quantum yield value may strongly depend on the light intensity for initiation, the type of initiating system, and the structure of monomer. However, since identical conditions (same monomer and BP sensitizer concentrations) were used for all the systems in the current study, the quantum yields of polymerizations can be treated as relative values. Furthermore they should be of the same order of magnitude as those in the previous work[41] that used the same monomer.

The almost identical polymerization results for the three tetraalkylammonium salts PTAAS (R = ethyl, *n*-propyl, *n*-butyl) being used as co-initiators can be rationalized by their similar quantum yields for forming the initiating radicals. This argument can be pursued in a quantitative manner because the quantum yields of decarboxylation can be taken as a measure of the initiating radicals' quantum yields, see Table 1 and Scheme 1. The CO_2 formation quantum yields for the BP/PTAA ($\Phi_{CO_2} = 0.28$)[35] and the BP/PTAAS (R = methyl) ($\Phi_{CO_2} = 0.18$) photoinitiating systems in acetonitrile were determined to be much lower than those for the BP/PTAAS (R = ethyl, *n*-propyl, and *n*-butyl) systems. The latter three values can be seen from Table 1 to be $\Phi_{CO_2} = 0.42$, 0.39, and 0.45, respectively. The differences between values of Φ_{CO_2} can be explained by the presence of additional reactions in the initially formed radical ion pair $[BP^{-\bullet} \cdots {>}S^{+\bullet}]$ in the case of tetramethylammonium salt and the acid, i.e., proton-transfer reactions leading to the formation of ketyl radicals $BPH^\bullet$ and $C_6H_5SCH^\bullet COON^+R(CH_3)_4$ or $C_6H_5SCH^\bullet COOH$ radicals, respectively. This mechanism will be discussed in detail in the following paper.[33]

Before a quantitative correlation is attempted, special consideration needs to be given to PTAA because of its low triplet-quenching rate constant. It quenches the triplet of BP with a rate constant ($k_q = 8.7 \times 10^7\ M^{-1}\ s^{-1}$)[35] that is about 10 times lower than those for the PTAA salts used in this work. Thus, the 10 mM concentration of PTAA used in co-initiated polymerizations was too low to quench all of the benzophenone triplets. Therefore, in the case of the BP/PTAA system, the polymerization rate was determined for a concentration of PTAA that was 10 times higher, i.e., 0.1 M, than the concentrations used in the analogous PTAAS experiments.

Table 2. Rates of Polymerization (R_p), Quantum Yields of Polymerization (Φ_p), and Quantum Yields of CO_2 Formation (Φ_{CO_2})

Photoinitiating system	R_p [μmol/s]	$\sqrt{\Phi_{CO_2}}$	Φ_p
BP alone	23.4	–	400
BP +  $-S-CH_2-COOH$	52.9[a] 28.4[b]	0.53[d]	910[a] 480[b]
BP +  $-S-CH_2-COO^{\ominus}\ \overset{\oplus}{N}(CH_3)_4$	50.1	0.42[c]	850
BP +  $-S-CH_2-COO^{\ominus}\ \overset{\oplus}{N}(C_2H_5)_4$	76.0	0.65	1300
BP +  $-S-CH_2-COO^{\ominus}\ \overset{\oplus}{N}(C_3H_7)_4$	74.5	0.62	1270
BP +  $-S-CH_2-COO^{\ominus}\ \overset{\oplus}{N}(C_4H_9)_4$	73.8	0.67	1260

[a] For concentration of acid 0.1 M. [b] For concentration of acid 0.01 M. [c] From ref 33. [d] From ref 35.

The polymerization rate from the direct initiation by the sensitizer BP is not included in the following correlation. The small polymerization rate observed for BP alone (Table 2) can be explained as the polymerizations being initiated by a relatively unreactive radical formed in an H-atom abstraction from the monomer by the BP triplet. It is not included in the correlation since this initiating radical is bound to be of a different chemical nature from the other experiments where co-initiators were used.

A theoretical expression was derived for the correlation between the polymerization rates and the square root of the quantum yields of the appropriate radical formation.[22] When the unimolecular decomposition rate (k_d) of the initiating radical $R^\bullet$ is much less than the rate of its pseudo-first-order reaction (k_i[M]) with the monomer M, then the polymerization rate, R_p, is given by

$$R_p = k_p[M]\sqrt{\frac{\Phi_{R^\bullet} I_A}{k_t}} \qquad (2)$$

where k_p is the propagation rate constant for the macroradical $RM_n^\bullet$; $\Phi_{R^\bullet}$ is the quantum yield of formation of the initiating radical; and I_A is the incident light flux. In deriving eq 2, the assumption was made that all the rate constants of radical−radical termination (primary and macroradicals) were equal to k_t, the termination rate constant for the macroradicals.[22]

From eq 2, one can compare the polymerization rate with the square root of radical formation for methyl and the other alkyl ammonium salts. Since the decarboxylation reaction of the [$BP^{\bullet-}\cdots{>}S^{\bullet+}$] radical-ion pair led to the formation of CO_2 and $C_6H_5SCH_2^\bullet$ in the ratio of 1:1 (Scheme 1), the quantum yields of CO_2 can be taken as the quantum yields of the initiating radicals in eq 2. Similarly for the BP sensitized photochemistry of PTAA in acetonitrile,[35] the Φ_{CO_2} represents the quantum yield of the $C_6H_5SCH_2^\bullet$ radical formation. The resulting linear correlation of the polymerization rates with the square root of the CO_2 quantum yields is presented in Figure 3. This is additional justification for the conclusion that the α-(arylthio)-alkyl radical, $C_6H_5SCH_2^\bullet$, is the radical that is initiating the free-radical polymerizations (Scheme 1) using the BP/PTAAS photoredox pairs studied in this work.

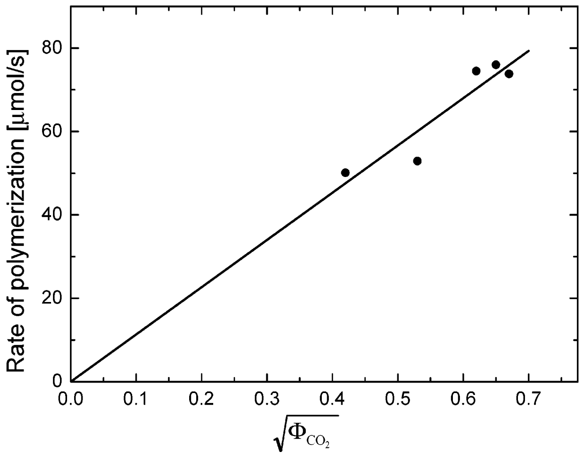


Figure 3. Plot of polymerization rate (R_p) vs square root of the CO_2 quantum yield. Linear least-square fit of relation in eq 2 with $\Phi_{R^\bullet} = \Phi_{CO_2}$.

Conclusions

(1) Benzophenone in combination with tetraalkylammonium salts of phenylthioacetic acid were shown to be effective co-initiators of free-radical photopolymerizations. The largest polymerization rates were found for the photoinitiating systems containing BP and three of the tetraalkylammonium salts (*n*-butyl, *n*-propyl, and ethyl), but the polymerization rates were much lower for the methyl derivative and for the parent acid, itself. A linear correlation was found for the polymerization rates vs the square root of the CO_2 quantum yields, and this indicates that the $C_6H_5SCH_2^\bullet$ radicals are responsible for the initiation step of the polymerizations studied in this work. (2) A detailed quantitative description was presented for the mechanisms of the primary and secondary photoreactions in the BP sensitized photooxidation of phenylthioacetic acid tetraalkylammonium salts in acetonitrile. Through the knowledge gained of these fundamental processes, it was then possible to unravel the mechanism of free-radical photopolymerizations in which BP/PTAAS photoredox pairs were used as photoinitiators. (3) A Hofmann elimination reaction occurred in the [$BP^{\bullet-}\cdots N^+R_4$] ion pairs leading to the formation of alkenes and trialkyl amines for R = *n*-butyl, *n*-propyl, and ethyl.

Acknowledgment. This work described herein was supported by the Ministry of Research and Higher Education Poland (Grant No. 3 T09A 165 28) and by the Office of Basic Energy Sciences of the U.S. Department of Energy. This is Document No. NDRL 4739 from the Notre Dame Radiation Laboratory.

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MA071581G