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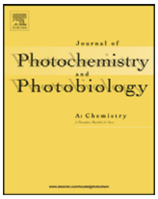

Kinetics and mechanism of sensitized photooxidation of tetramethylammonium salt of 2-(phenylthio)acetic acid in solution Steady-state and flash photolysis studies

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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.

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_2 formation $\sqrt{\Phi(CO_2)}$, it was concluded that $C_6H_5SCH_2^{\bullet}$ 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 $C_6H_5SCH_2^{\bullet}$ 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 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 cut-off 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 a Cary 300 Bio Varian spectrophotometer.

The progress of sensitized PTAAS was monitored by HPLC using a Waters 600E Multisolvent Delivery System pump previously described [9]. Analytical HPLC analyses were carried out on a Waters XTerra RP_{18} 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 cm × 1 cm or 1 cm × 1 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 ($\varepsilon_{520} = 6500\ M^{-1}\ cm^{-1}$) [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 $1.1 \times 10^9\ M^{-1}\ s^{-1}$ (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 mM, $[Ph\text{–}S\text{–}CH_2\text{–}COO^-N^+(R)_4] \approx 10$ mM)

R	$-CH_3$	$-C_4H_9$ [b]
k_q ($M^{-1}\ s^{-1}$)	1.1×10^9	1.1×10^9
$\Phi_{[BP^{\bullet-}\cdots N^+R_4]}$ [a] (±10%)	0.11[a]	0.33
$\Phi_{BPH^{\bullet}}$	0.46	0.33
Φ_{CO_2} (±20%)	0.18	0.45
Φ_{BP} (±10%)	0.38	0.42
Φ_{salts} (±10%)	0.52	0.81
Φ_{NR_3}	~0.09	0.20
Φ_{PhSCH_3}	0.14	0.43

[a] Taking $\varepsilon_{700} = 18{,}000\ M^{-1}\ cm^{-1}$ [16].

[b] From previous work [8,16].