

# One-Electron Redox Potential of Thiobenzoic Acid. Kinetic Characteristics of Benzoylthiyl Radical $\beta$ -Fragmentation

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**Abstract:** By means of pulse radiolysis, one-electron oxidation of benzoylthiolate ( $\text{PhCOS}^-$ ) was achieved by the azide radical ( $\text{N}_3^*$ ) in aqueous solution. The spectrum of the resulting benzoylthiyl radical ( $\text{PhCOS}^*$ ) shows a broad absorption in the wavelength region from 350 to 500 nm. With  $\text{N}_3^*/\text{N}_3^-$  as reference couple, the reduction potential  $E^\circ(\text{PhCOS}^*/\text{PhCOS}^-)$  was measured to be 1.21 V vs NHE. Using the  $\text{p}K_a$  of 2.48 for thiobenzoic acid ( $\text{PhCOSH}$ ), we derive the standard reduction potential  $E^\circ(\text{PhCOS}^*, \text{H}^+/\text{PhCOSH})$  to be 1.36 V vs NHE. This reduction potential implies an S–H bond energy of  $\text{PhCOSH}$  of 87 kcal/mol, which is very close to the bond energy of an alkylthiol S–H bond (87.4 kcal/mol). At 22 °C, the  $\text{PhCOS}^*$  radicals decay with a rate constant of  $8.5 \times 10^3 \text{ s}^{-1}$  to form colorless species. This process is presumed to be the  $\beta$ -fragmentation of the  $\text{PhCOS}^*$  radical,  $\text{PhCOS}^* \rightarrow \text{Ph}^* + \text{COS}$ . The kinetics of the  $\beta$ -fragmentation of the  $\text{PhCOS}^*$  radical was found to follow the Arrhenius equation,  $\log(k_2/\text{s}^{-1}) = (12.3 \pm 0.1) - (11.4 \pm 0.2)/\theta$ , where  $\theta = 2.3RT$  kcal/mol. Strong evidence for this process was provided byproduct identification by GC-MS, where the main products of the  $\gamma$ -irradiation-induced  $\text{N}_3^*$  radical oxidation of  $\text{PhCOS}^-$  in 0.1 M  $\text{NaN}_3$  solution were found to be phenyl azide ( $\text{PhN}_3$ ) and aniline ( $\text{PhNH}_2$ ). These products were formed via addition of the  $\text{Ph}^*$  radical to  $\text{N}_3^-$  to form the  $\text{PhN}_3^{*-}$  radical anion, which subsequently disproportionated. In the Discussion, we summarize the reduction potentials and the bond dissociation energies of related thiols and their oxygen counterparts. The  $\beta$ -fragmentation of  $\text{PhCOS}^*$  radicals resembles that of the oxygen counterpart, benzoyloxyl radical ( $\text{PhCOO}^*$ ), and their thermochemical properties are also compared.

## Introduction

Thiols and sulfur-centered reactive intermediates have important roles in both chemistry and biology.<sup>1</sup> The free radical chemistry of thiobenzoic acid ( $\text{PhCOSH}$ ), as an example of acyl thiol ( $\text{RCOSH}$ ), is particularly interesting because it represents the chemistries of both thiols and the sulfur counterpart of carboxylic acids. Radical reactions of alkyl thiols ( $\text{RSH}$ , where R denotes alkyl), especially amino acid thiols have been studied extensively because of their important role in biochemical systems.<sup>1–5</sup> Aryl thiols ( $\text{ArSH}$ ), their reaction kinetics and redox properties, were recently studied and were compared to their oxygen counterparts, phenols.<sup>6,7</sup> However, very little is known about the redox properties and reactivities of acyl thiols ( $\text{RCOSH}$ ) and acylthiyl radicals ( $\text{RCOS}^*$ ). In organic free radical chemistry, carboxylic acids ( $\text{RCOOH}$ ) are an important class of compounds, which have been extensively studied since they play practical roles in many areas.<sup>8,9</sup> In contrast, the acyl

thiol acids, despite their uses in chemistry and polymer synthesis,<sup>10,11</sup> are not well studied.

One characteristic reaction of benzoyloxyl radicals ( $\text{PhCOO}^*$ ) is their  $\beta$ -fragmentation to form phenyl radical ( $\text{Ph}^*$ ) and carbon dioxide (eq 1).  $\text{PhCOO}^*$  can be formed by thermal or



photochemical decomposition of the parent diaryl peroxides.<sup>12,13</sup> Equation 1 has a first-order rate constant of ca.  $2 \times 10^6 \text{ s}^{-1}$  in  $\text{CCl}_4$ .<sup>13</sup> For the benzoylthiyl radical ( $\text{PhCOS}^*$ ), a similar reaction would be expected (eq 2, where COS is carbonyl sulfide).



Related to this topic, there have been some early electrochemical investigations comparing the  $\beta$ -fragmentation of acyloxyl radicals ( $\text{RCOO}^*$ ) with that of acylthiyl radicals

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(RCOS<sup>•</sup>).<sup>14,15</sup> In the electrochemical oxidation of carboxylic acids, also known as the Kolbe reaction, the decarboxylation of RCOO<sup>•</sup> to form alkyl radicals R<sup>•</sup> is widely used to initiate polymerization.<sup>16</sup> However, during electrooxidation of RCOO<sup>•</sup>, the resulting RCOS<sup>•</sup> radicals dimerize into diacyl disulfides without decomposition.<sup>14,16</sup> This suggests that RCOS<sup>•</sup> radicals have a higher stability in comparison to RCOO<sup>•</sup> radicals.

In the present investigation, thiobenzoic acid (PhCOSH) was used to examine the characteristics of the benzoylthiyl radical (PhCOS<sup>•</sup>). The oxidation of benzoylethiolate (PhCOS<sup>-</sup>) was achieved by the azide radical (N<sub>3</sub><sup>•</sup>) or the dibromide radical anion (Br<sub>2</sub><sup>-•</sup>), produced by pulse or  $\gamma$ -radiolysis of aqueous solutions. The spectroscopic, kinetic, and redox characteristics of PhCOS<sup>•</sup> radicals were examined.  $\beta$ -Fragmentation of PhCOS<sup>•</sup> radicals was found to occur as evidenced by both kinetic analysis upon pulse radiolysis and product identification by gas chromatography/mass spectrometry (GC-MS). The thermochemical properties of related thiol species and their  $\beta$ -fragmentation reactions are summarized and compared with those of their oxygen counterparts.

## Experimental Section

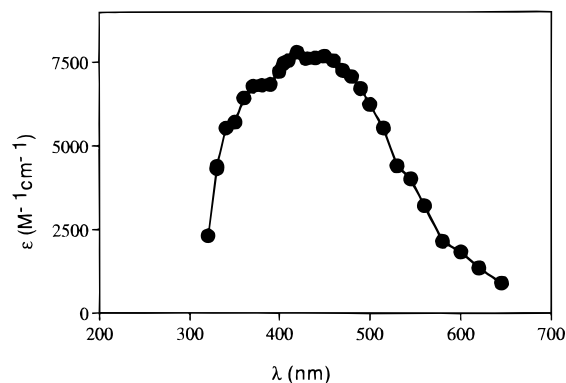
Thiobenzoic acid (PhCOSH) of commercial grade (from Sigma) was purified by vacuum distillation before use. Diammonium 2,2'-azinobis-(3-ethylbenzothiazoline-6-sulfonate) (ABTS), methyl viologen hydrate (MV<sup>2+</sup>), aniline (PhNH<sub>2</sub>), sodium azide (NaN<sub>3</sub>), sodium bromide (NaBr), potassium thiocyanate (KSCN), dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), and sodium hydroxide (NaOH), obtained from Sigma-Aldrich, were of the highest purity commercially available and used as received.

Pulse radiolysis was performed using doses of 10–26 Gy/pulse, corresponding to  $6 \times 10^{-6}$  to  $1.6 \times 10^{-5}$  M radicals. The 3-MeV linear accelerator used has a pulse length of 6 ns. The computerized optical detection system has been described elsewhere.<sup>17</sup> Dosimetry was performed with a N<sub>2</sub>O-saturated  $10^{-2}$  M KSCN solution taking  $G\epsilon = 4.42 \times 10^{-3}$  Gy<sup>-1</sup> cm<sup>-1</sup> at 500 nm.<sup>18</sup> The temperature of the solutions was varied using a jacketed irradiation cell connected to a thermostatically controlled bath. A thermoelement probe was inserted into the outlet of the cell to measure the temperature of the irradiated solutions.

$\gamma$ -Radiolysis was performed in a <sup>60</sup>Co  $\gamma$ -source (AECL Gammacell 220), with a dose rate of 0.13 Gy/s as determined by the Fricke dosimeter.<sup>19</sup>

All experiments were performed in N<sub>2</sub>O-saturated aqueous solutions where the primary radiation chemical yield of OH<sup>•</sup> radicals,  $G_{OH}$ , was set to  $5.6 \times 10^{-7}$  mol J<sup>-1</sup>.<sup>20</sup> In N<sub>2</sub>O-saturated solutions containing high molar concentrations of NaN<sub>3</sub> or NaBr, OH<sup>•</sup> radicals are quantitatively converted into N<sub>3</sub><sup>•</sup> radicals or Br<sub>2</sub><sup>-•</sup> radical anions. Solutions were prepared using Millipore-deionized water. Since PhCOSH is an acid with a pK<sub>a</sub> value of 2.48,<sup>21</sup> the solutions of thiolate ion, PhCOS<sup>-</sup>, were obtained by always adding an equimolar amount of NaOH to the acid solutions.

Products formed on  $\gamma$ -irradiation were extracted by dichloromethane and subsequently concentrated using a rotating vacuum evaporator. A



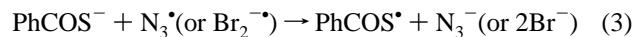
**Figure 1.** The transient absorption spectrum of benzoylthiyl radicals observed 2  $\mu$ s after electron pulse irradiation of a solution containing 5 mM PhCOS<sup>-</sup> and 0.1 M NaN<sub>3</sub>.

solid-phase microextraction (SPME) technique<sup>22</sup> was also used to extract the organic products. The extraction fiber had 65  $\mu$ m carbowax/divinylbenzene coating, selective for polar analytes (from SUPELCO). The extracted samples were subsequently separated and identified using a GC-MS (Finnigan SSQ 7000) connected to a Varian 3400 GC. A 30-m DB-5MS fused silica column (J & W Scientific, i.d. 0.25 mm, film thickness 0.25  $\mu$ m) was used in the GC. The injection temperature was set at 250  $^{\circ}$ C, and the column temperature was programmed to increase from 28 to 200  $^{\circ}$ C, at a rate of 10 deg/min.

All experiments were carried out at room temperature ( $22 \pm 2$   $^{\circ}$ C), except for the Arrhenius plot measurements.

## Results

**1. The Spectrum of PhCOS<sup>•</sup> Radical.** One-electron oxidation of PhCOS<sup>-</sup> by N<sub>3</sub><sup>•</sup> or Br<sub>2</sub><sup>-•</sup> yields the PhCOS<sup>•</sup> radical (eq 3). The transient absorption observed 2  $\mu$ s after electron



pulse irradiation of a solution containing 5 mM PhCOS<sup>-</sup> and 0.1 M NaN<sub>3</sub> is shown in Figure 1.

The spectrum of PhCOS<sup>•</sup> exhibited a broad absorption peak in the region from 300 to 600 nm, with a maximum between 400 and 460 nm. The extinction coefficient at the maximum was measured to be 7900 M<sup>-1</sup> cm<sup>-1</sup> when the dithiocyanate radical anion (SCN)<sub>2</sub><sup>-•</sup> was used as reference.<sup>20</sup> The build-up rate of the PhCOS<sup>•</sup> absorption at 460 nm was titrated versus the PhCOS<sup>-</sup> concentration. The rate constant of eq 3, obtained as the slope of a linear fit of the observed rates vs [PhCOS<sup>-</sup>], was found to be ca.  $3 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> and  $6 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> for Br<sub>2</sub><sup>-•</sup> and N<sub>3</sub><sup>•</sup>, respectively. When measuring the rate constant of eq 3 for N<sub>3</sub><sup>•</sup>, a constant ratio of N<sub>3</sub><sup>-</sup>/PhCOS<sup>-</sup> of 10 was maintained, since the  $E^{\circ}(\text{N}_3^{\bullet}/\text{N}_3^-)$  is rather close to  $E^{\circ}(\text{PhCOS}^{\bullet}/\text{PhCOS}^-)$  (see below).

Alkylthiyl radicals are known to easily form radical anion complexes with thiolate (equilibrium in eq 4). The RSSR<sup>-•</sup>



species usually have absorption in the region of 390–450 nm, which is in the region of the absorption peak shown in Figure 1. It is thus important to investigate whether the absorption is attributable to PhCOS<sup>•</sup> or PhCOSSOCPh<sup>-•</sup>. The following reasons led us to conclude that the equilibrium shown in eq 4 for the PhCOS<sup>•</sup> radical to form PhCOSSOCPh<sup>-•</sup> radical anion is not important. First, the shape of the spectrum and the decay rate did not change in the microsecond time region, when

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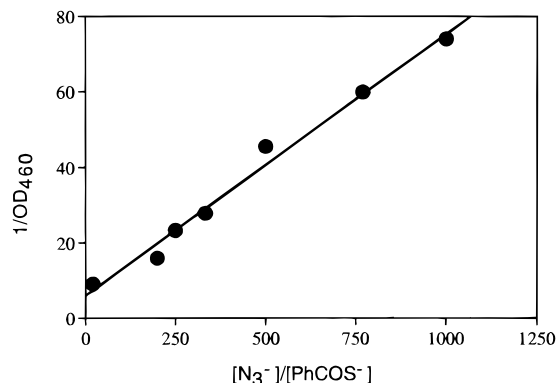
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**Figure 2.** The inverse of optical density of PhCOS<sup>•</sup> radicals at 460 nm as a function of the ratio between N<sub>3</sub><sup>-</sup> and PhCOS<sup>-</sup>. The linear curve fit of the data is in accord with eq 6, and K<sub>3</sub> = 125 can be derived by dividing the intercept with the slope of the line.

different concentrations of the thiolate were used. Second, the 400–460 nm transient was found not to react with MV<sup>2+</sup> to form MV<sup>+</sup>, while RSSR<sup>-•</sup> radicals are known to reduce MV<sup>2+</sup>.<sup>3</sup>

When ABTS was used to capture the oxidative radicals in the above system, full yield of ABTS<sup>•+</sup>, as monitored at 645 nm, was observed. The PhCOS<sup>•</sup> decayed as the ABTS<sup>•+</sup> built up (eq 5). The build-up rate of ABTS<sup>•+</sup> at 645 nm was titrated



versus the ABTS concentration in solutions containing 0.1 M NaN<sub>3</sub> and 5 × 10<sup>-3</sup> M PhCOS<sup>-</sup>. The rate constant of eq 5, obtained as the slope of a linear fit of the observed rates vs [ABTS], was found to be 2 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>.

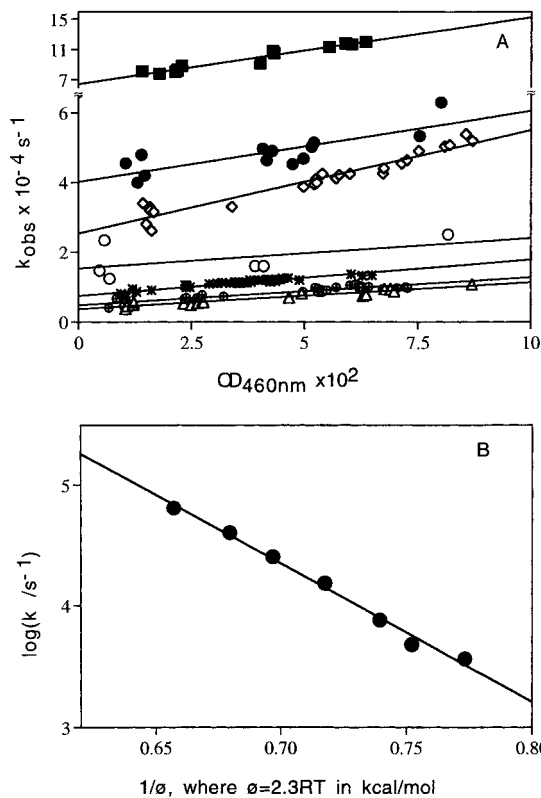
**2. Reduction Potential of PhCOS<sup>-</sup>/PhCOS<sup>•</sup> Couple.** The relatively long lifetime of the PhCOS<sup>•</sup> radical (ca. 100 μs, see below) as compared to PhCOO<sup>•</sup> radical (ca. 1 μs) made the measurement of the reduction potential of the PhCOS<sup>-</sup>/PhCOS<sup>•</sup> couple possible. Using I<sub>2</sub><sup>-•</sup>/2I<sup>-</sup> as reference couple, the approximate value of E°(PhCOS<sup>•</sup>/PhCOS<sup>-</sup>) was found to be 1.2–1.3 V. Since N<sub>3</sub><sup>•</sup>, having a reduction potential of 1.33 V,<sup>23</sup> rapidly oxidizes PhCOS<sup>-</sup>, it was chosen as the reference for more accurate measurements. When the N<sub>3</sub><sup>•</sup> radical oxidizes PhCOS<sup>-</sup>, the following equilibrium is established.



In irradiated N<sub>2</sub>O-saturated solutions containing different concentrations of PhCOS<sup>-</sup> and N<sub>3</sub><sup>-</sup>, with the latter in excess, the following relationship is obtained.

$$\text{OD}_{460}^{\circ}/\text{OD}_{460} = 1 + [\text{N}_3^{-}]/K_3[\text{PhCOS}^{-}] \quad (6)$$

Here, OD<sub>460</sub> is the optical density at 460 nm of PhCOS<sup>•</sup> at equilibrium, K<sub>3</sub> is the equilibrium constant of eq 3, and OD<sub>460</sub><sup>°</sup> is the optical density when the equilibrium in eq 3 is completely shifted to the right. In the experiments, the concentrations of N<sub>3</sub><sup>-</sup> and PhCOS<sup>-</sup> were adjusted so that the equilibrium in eq 3 was reached before significant radical decay occurred. A plot of 1/OD<sub>460</sub> versus [N<sub>3</sub><sup>-</sup>]/[PhCOS<sup>-</sup>] gives a straight line (Figure 2), and K<sub>3</sub> was found to be 125 by dividing the intercept by the slope of the line. The rate constant of eq -3 was deduced to be 4.8 × 10<sup>7</sup> M<sup>-1</sup> s<sup>-1</sup> by dividing k<sub>3</sub> by K<sub>3</sub>. From the equilibrium constant K<sub>3</sub>, we calculated E°(PhCOS<sup>•</sup>/PhCOS<sup>-</sup>) to be 1.21 V vs NHE when E°(N<sub>3</sub><sup>•</sup>/N<sub>3</sub><sup>-</sup>) = 1.33 V was used as reference. The pK<sub>a</sub> of thiobenzoic acid is given as 2.48,<sup>21</sup> lower



**Figure 3.** (A) The experimental decay rate of PhCOS<sup>•</sup> (k<sub>obs</sub>) versus its maximal optical density measured at 460 nm at (Δ) 10, (⊕) 18, (\*) 23, (○) 32, (◇) 41, (●) 49, (■) 60 °C. The intercepts of the linear fits of the data represent the first-order rate constants (k<sub>2</sub>). (B) Arrhenius plot of log(k<sub>2</sub>/s<sup>-1</sup>) versus 1/θ, where θ = 2.3RT kcal/mol. The solutions are N<sub>2</sub>O saturated and contain 0.1 M NaN<sub>3</sub> and 5 × 10<sup>-3</sup> M PhCOS<sup>-</sup>.

than its homologue, benzoic acid (pK<sub>a</sub> ca. 4.2). Thus, E°(PhCOS<sup>•</sup>, H<sup>+</sup>/PhCOSH) is calculated to be 1.36 V vs NHE.

**3. β-Fragmentation of PhCOS<sup>•</sup> Radical.** In the pulse radiolysis experiments, the 460-nm transient decayed by mixed first- and second-order kinetics within the dose range applied. Kinetic traces were obtained by irradiating N<sub>2</sub>O-saturated solutions containing 0.1 M NaN<sub>3</sub> and 5 × 10<sup>-3</sup> M PhCOS<sup>-</sup>. The initial part of the decay was used to calculate a first-order rate constant. In Figure 3A, these values are plotted against its maximal optical density, which should be proportional to the doses applied. By extrapolating the straight line to zero absorption (zero dose), the intercept k<sub>int</sub> should be the first-order component. Since phenyl radicals (Ph<sup>•</sup>) are known to absorb only weakly in the region below 300 nm,<sup>24</sup> along with the evidences from product analysis (see below), k<sub>int</sub> should be k<sub>2</sub>, the β-fragmentation of the PhCOS<sup>•</sup> radical to form Ph<sup>•</sup> and COS. The second-order decay of the transient is due to radical recombination reactions, which always exist as competing reactions. The decay rate was also found to be independent of pH in the pH range of 2–14. The rate constant k<sub>2</sub> was measured over a range of temperatures (10–60 °C, see Figure 3A).

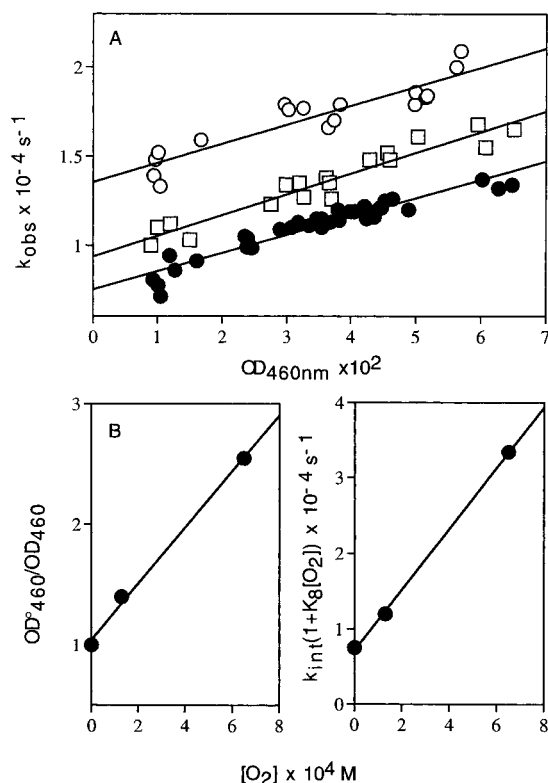
The Arrhenius plot for eq 2 shown in Figure 3B yielded the following temperature dependence

$$\log(k_2/s^{-1}) = (12.3 \pm 0.1) - (11.4 \pm 0.2)/\theta \quad (7)$$

where θ is 2.3RT kcal/mol and the errors correspond to 2σ. Equation 7 gave an activation energy of 11.4 kcal/mol (47.7 kJ/mol) for eq 2. At room temperature, k<sub>2</sub> is ca. 8.5 × 10<sup>3</sup> s<sup>-1</sup>.

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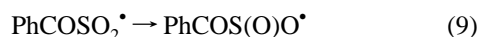


**Figure 4.** (A) The decay rate of PhCOS\* ( $k_{\text{obs}}$ ) versus its maximal optical density measured at 460 nm when the solutions containing 0.1 M NaN<sub>3</sub> and  $5 \times 10^{-3}$  M PhCOS<sup>-</sup> were saturated with (●) N<sub>2</sub>O, (□) N<sub>2</sub>O/O<sub>2</sub> (90:10) and (○) N<sub>2</sub>O/O<sub>2</sub> (50:50). (B) Plot of OD<sub>460</sub><sup>o</sup>/OD<sub>460</sub>, the maximal optical density of PhCOS\* at 460 nm in N<sub>2</sub>O (OD<sub>460</sub><sup>o</sup>) divided by that in N<sub>2</sub>O/O<sub>2</sub> saturated solutions, versus the oxygen concentration. (C) Plot of  $k_{\text{int}}(1 + K_8[\text{O}_2])$  versus the oxygen concentration, where  $k_{\text{int}}$  is the first-order decay rate of PhCOS\* radicals given by the intercept of the linear fit of the data in A and  $K_8$  is the equilibrium constant for eq 8.

**4. Reaction between the PhCOS\* Radical and O<sub>2</sub>.** Normal alkylthiyl radicals are known to react with O<sub>2</sub> to form peroxy radicals.<sup>1,25,26</sup> The formation and the decay of PhCOS\* radicals in the presence of O<sub>2</sub> in solutions were studied. When the solutions containing 0.1 M NaN<sub>3</sub> and  $5 \times 10^{-3}$  M PhCOS<sup>-</sup> were saturated with three different concentrations of oxygen, as shown in Figure 4B, with same the doses applied, the maximal optical densities of PhCOS\* radicals at 460 nm were found to decrease with increasing oxygen concentrations. It appears that benzoylthiyl peroxy radicals are formed in eq 8.



In Figure 4A, the experimental decay rate of PhCOS\* ( $k_{\text{obs}}$ ) is plotted versus its maximal optical density measured at 460 nm. The intercept was found to increase with increasing oxygen concentrations. The PhCOSO<sub>2</sub>\* radicals thus undergo a first-order reaction presumably to form PhCOS(O)O\* radicals.



This is seen to be an exact parallel to the case with alkylthiyl radicals. The rate constants of  $k_8$  and  $k_{-8}$  for alkylthiyls were reported to be  $2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , and  $6 \times 10^5 \text{ s}^{-1}$ .<sup>25,26</sup> For

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2-mercaptoethanol,  $k_9$  was reported to be  $2 \times 10^3 \text{ s}^{-1}$ .<sup>25</sup> If we assume similar rapid equilibrations for PhCOS\* radicals in reaction 8, eq 10 is valid.

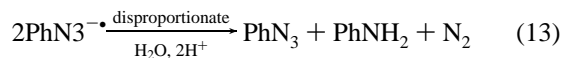
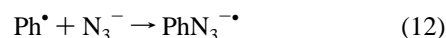
$$\text{OD}_{460}^{\circ}/\text{OD}_{460} = 1 + K_8[\text{O}_2] \quad (10)$$

A plot of OD<sub>460</sub><sup>o</sup>/OD<sub>460</sub> versus oxygen concentrations in Figure 4B gave an estimation of  $K_8$  to be  $2.3 \times 10^3 \text{ M}^{-1}$ . The first-order decay rate of PhCOS\* radicals, as given by the intercept of the linear fit of the data in Figure 4A, follows eq 11.<sup>27</sup>

$$k_{\text{int}}(1 + K_8[\text{O}_2]) = k_2 + k_9K_8[\text{O}_2] \quad (11)$$

In Figure 4C, a plot of  $k_{\text{int}}(1 + K_8[\text{O}_2])$  versus the oxygen concentration gave an estimation of  $k_9$  to be  $1.7 \times 10^4 \text{ s}^{-1}$ .

**5. Product Identification by GC-MS.** Upon  $\gamma$ -radiolysis of N<sub>2</sub>O-saturated aqueous solutions of PhCOSH, products with low water solubility were formed. With dichloromethane as the extraction solvent or with the SPME technique, the same products were detected. In gas chromatograms of samples after steady-state  $\gamma$ -radiolysis of N<sub>2</sub>O-saturated solutions containing 0.1 M NaN<sub>3</sub> and  $5 \times 10^{-3}$  M PhCOS<sup>-</sup>, two main product peaks were observed. The mass spectra of the two peaks were found to resemble those of phenyl azide (PhN<sub>3</sub>) and aniline (PhNH<sub>2</sub>), respectively, when their mass spectra were compared with those found in the Finnigan NS library. In Figure 5, the mass spectra of the radiolytic products PhN<sub>3</sub> and PhNH<sub>2</sub> are presented along with the standard in the Finnigan NS library. These main products are presumably formed through eqs 12 and 13.



Formation of aniline was clearly proved by GC-MS upon comparison with the GC-MS of an authentic sample, while authentic samples of phenyl azide are not available. The disulfide (PhCOSSCOPh) which would be formed from dimerization of the PhCOS\* radicals was not found.

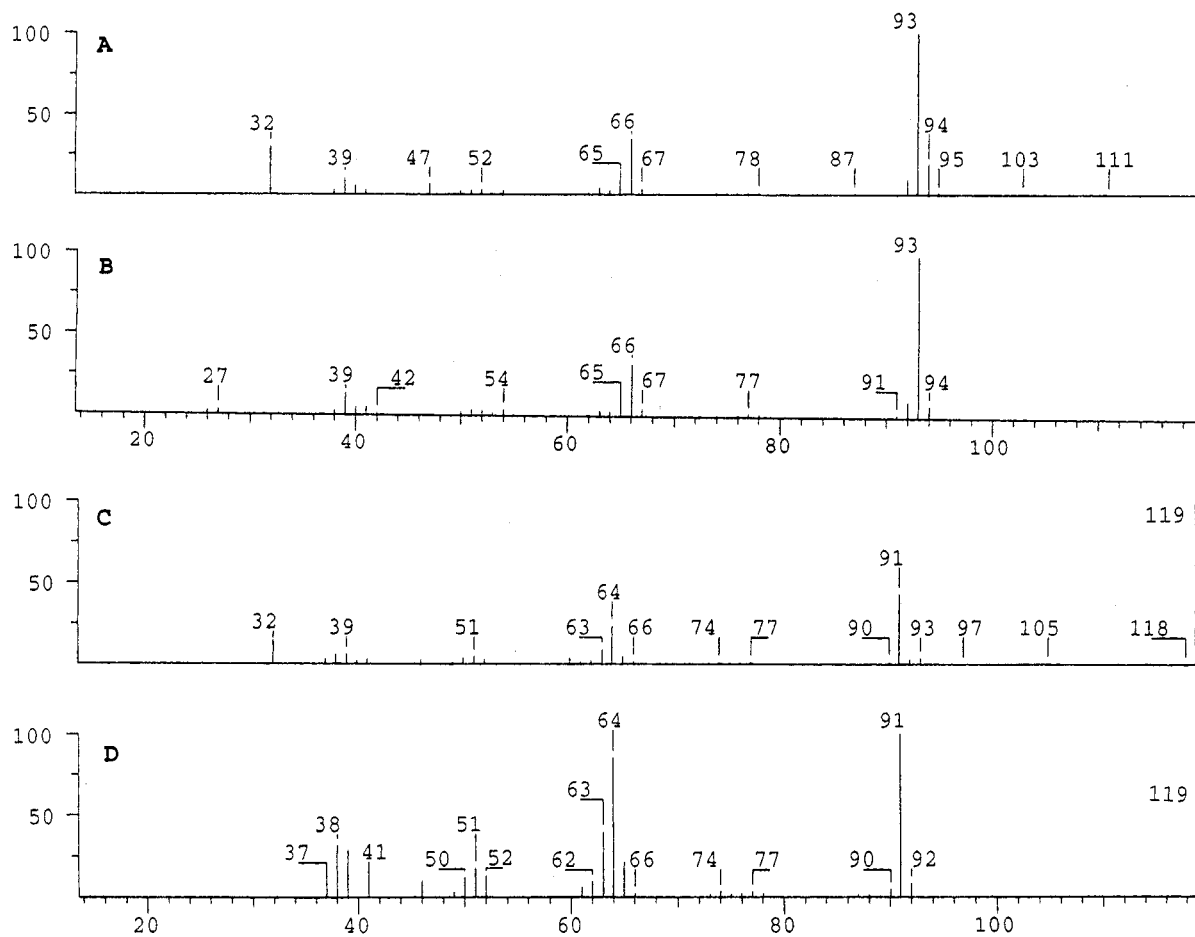
## Discussion

**Structure of PhCOS\* Radical.** Normal alkylthiyl radicals usually have weak absorption in the region from 300 to 330 nm. The PhS\* radicals, due to their resonance stabilization by the phenyl ring, have absorption in the 400–510 nm region with  $\epsilon_{460\text{nm}} = 2590 \text{ M}^{-1} \text{ cm}^{-1}$ .<sup>28</sup> The spectrum of the PhCOS\* radical measured in aqueous solution is rather similar to that of PhS\* radical but covers a broader wavelength interval and has a much higher intensity. The spectrum of PhCOS\* radical is attributed to the resonance stabilization of sulfur radical by the carbonyl group. Since for its oxygen counterpart PhCOO\* radical, the absorption in 500 to 700 or 800 nm was assigned also to a transition that is localized in the COO\* moiety of the radical.<sup>12</sup> A carbonyloxyl radical (e.g., ROCOO\*) has a similar absorption band in the region.<sup>29</sup>

(27) Assuming the fast equilibration in eq 8,  $C = [\text{PhCOS}^*] + [\text{PhCOSO}_2^*]$ ,  $K_8 = [\text{PhCOSO}_2^*]/[\text{PhCOS}^*][\text{O}_2]$ . Thus,  $k_{\text{int}}C = k_2[\text{PhCOS}^*] + k_9[\text{PhCOSO}_2^*] = (k_2 + k_9K_8[\text{O}_2])[\text{PhCOS}^*]$ . Therefore,  $k_{\text{int}}(1 + K_8[\text{O}_2]) = k_2 + k_9K_8[\text{O}_2]$ .

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**Figure 5.** The mass spectra of the radiolytic products, (A) PhNH<sub>2</sub> and (C) PhN<sub>3</sub>, along with the standard in the Finnigan NS library, (B) PhNH<sub>2</sub> and (D) PhN<sub>3</sub>.

Another noteworthy finding is that PhCOS<sup>•</sup> and PhS<sup>•</sup> radicals behave similarly in that, unlike normal alkylthiyl radicals, they do not favor the formation of disulfide radical anions (eq 4).<sup>28</sup> The latter are known to form sulfur-centered three-electron bonds ( $2\sigma/1\sigma^*$ ) in RS<sup>••</sup>SR<sup>-</sup>.<sup>30</sup> The fact that the PhSSPh<sup>••</sup> and the PhCOSSOPh<sup>••</sup> species are not favored in eq 4 also suggests the PhS<sup>•</sup> and PhCOS<sup>•</sup> radicals to be resonance stabilized. Upon the formation of these disulfide radical anions, the three electron S<sup>••</sup>S bonds are too weak to compensate for the destruction of the resonance between the sulfur centered radicals with the phenyl ring or the carbonyl group.

**Reduction Potential and Bond Strength.** In a recent publication, Robert et al.<sup>15</sup> reported the voltammetrically measured one-electron oxidation potential of PhCOS<sup>-</sup> to be 0.72 V vs the reference electrode Ag/AgCl, KCl saturated in DMA/N(Et)<sub>4</sub>ClO<sub>4</sub>, 0.1 M, when *N,N*-dimethylacetamide (DMA) was used as solvent. This value corresponds to  $E^\circ(\text{PhCOS}^\bullet/\text{PhCOS}^-) = 0.94$  V vs NHE in DMA. By comparison, our present value of  $E^\circ(\text{PhCOS}^\bullet/\text{PhCOS}^-) = 1.21$  V vs NHE in aqueous solution is higher by ca. 0.27 V. The higher reduction potential of the PhCOS<sup>•</sup> radical in water can be largely attributed to the higher solvation energy of the PhCOS<sup>-</sup> anion in water as compared to that in DMA. Assuming similar solvation energies for the PhCOS<sup>•</sup> radical in water and DMA, we estimate the solvation of the PhCOS<sup>-</sup> anion to be stronger by ca. 6.2 kcal/mol in water than in DMA.

At this point it is worthwhile and interesting to examine the S–H bond strengths in various related compounds and compare

**Table 1.** Summary of pK<sub>a</sub>, Reduction Potential  $E^\circ$  in V, and BDE in kcal/mol for Thiols and Their Oxygen Counterparts

	pK <sub>a</sub> <sup>a</sup>	$E^\circ(\text{A}^\bullet/\text{A}^-)$	$E^\circ(\text{A}^\bullet, \text{H}^+/\text{A}^-)$	BDE
CH <sub>3</sub> S–H	10	~0.8 <sup>f</sup>	~1.3 <sup>j</sup>	87.4 <sup>h</sup>
RS–H	9.6	0.8 <sup>d</sup>	1.37 <sup>d</sup>	87.4 <sup>h</sup>
PhS–H	6.6	0.69 <sup>e</sup>	1.08 <sup>e</sup>	80 <sup>e</sup>
CH <sub>3</sub> COS–H	3.35 <sup>b</sup>	~1.1 <sup>f</sup>	~1.3 <sup>j</sup>	~87 <sup>f</sup>
PhCOS–H	2.48 <sup>c</sup>	1.21 <sup>f</sup>	1.36 <sup>f</sup>	87 <sup>f</sup>
CH <sub>3</sub> O–H	15.1	~1.16 <sup>f</sup>	~2.05 <sup>j</sup>	104.4 <sup>i</sup>
PhO–H	10.0	0.79 <sup>g</sup>	1.38 <sup>g</sup>	86 <sup>g</sup>
CH <sub>3</sub> COO–H	4.75	~1.9 <sup>f</sup>	~2.2 <sup>j</sup>	106 <sup>f</sup>
PhCOO–H	4.19	~2.0 <sup>f</sup>	~2.2 <sup>j</sup>	~106 <sup>f</sup>

<sup>a</sup> Reference 31. <sup>b</sup> Reference 32. <sup>c</sup> Reference 21. <sup>d</sup> Reference 33. <sup>e</sup> Reference 7. <sup>f</sup> This work. <sup>g</sup> Reference 34. <sup>h</sup> Reference 35. <sup>i</sup> Reference 36. <sup>j</sup> Estimated.

them with the corresponding O–H bonds. A representative selection is found in Table 1, where the pK<sub>a</sub> values, the reduction potentials, and the corresponding standard reduction potentials are compiled.

In the table, the bond dissociation energy (BDE) of CH<sub>3</sub>–COS–H was assumed to be the same as that of PhCOS–H. Similarly, the BDEs of CH<sub>3</sub>COO–H and PhCOO–H are also assumed to be the same. The bond dissociation energy of the corresponding S–H and O–H bonds in the gas phase is related to the standard reduction potential through the equation, BDE (kcal/mol) = 23.1 $E^\circ(\text{A}^\bullet, \text{H}^+/\text{A}^-)$  + 56.7.<sup>37,38</sup> Using this relation,

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the reduction potentials of the species were estimated, whenever literature values were not available. Inspecting the table, we can see that it agrees with the general trend that S–H bonds are weaker than the corresponding O–H bonds. The trends in thiyl radical reduction potentials and S–H bond energies upon going from aryl and to acyl thiols resemble those of the corresponding oxygen counterparts. It is especially noticeable that the S–H bond of thiobenzoic acid is almost identical to that of the S–H bond of an alkyl thiol, while the S–H bond of an aryl thiol is much weaker due to the resonance stabilization of PhS• radical. The fact that PhCOS• is also a resonance stabilized radical indicates the similar extent of stabilization of the PhCOSH molecule itself.<sup>39</sup> In comparison to that of the RSH molecule, the dipole moment of the S–H group in PhCOSH is larger due to the electron-withdrawing carbonyl group which stabilizes the partial negative charge on the sulfur. The same trend is seen for the O–H bond energies in the corresponding oxygen counterparts, i.e., the O–H bond of benzoic acid is rather close to that of the O–H bond of an alcohol, while the O–H bond of a phenol is much weaker.

Finally, the  $K_8$  of  $2.3 \times 10^3 \text{ M}^{-1}$  for PhCOS• radicals equilibrating with PhCOSO<sub>2</sub>• radicals is close to that,  $3.2 \times 10^3 \text{ M}^{-1}$ , for the 2-mercaptoethanol thiyl radicals equilibrating with its peroxy radicals.<sup>25</sup> This suggests the S–O bond strengths in RS–O<sub>2</sub>• and PhCOS–O<sub>2</sub>• radicals are rather close each other.

**$\beta$ -Fragmentation of PhCOS• Radical.** Strong evidence for the PhCOS• radicals to undergo  $\beta$ -fragmentation was provided by both kinetic analysis upon pulse radiolysis and product identification by gas chromatography–mass spectrometry (GC-MS). The first-order rate constant of  $8.5 \times 10^3 \text{ s}^{-1}$  for the  $\beta$ -fragmentation of the PhCOS• radical is seen to be smaller than for its oxygen counterpart, the PhCOO• radical. Equation 7 for the PhCOS• radical  $\beta$ -fragmentation in aqueous solution can be compared with the one obtained by Chateaufort et al.,<sup>12</sup>  $\log(k_1/\text{s}^{-1}) = (12.6 \pm 0.1) - (8.6 \pm 0.3)/\theta$ , for the PhCOO• radical decarboxylation in pure CCl<sub>4</sub>. As can be seen, the preexponential factors are very similar, suggesting simple bond cleavage reactions. Unlike the symmetrical PhCOO• radical, the PhCOS• radical should be more localized on the sulfur site. The asymmetry of the PhCOS• radical could result in higher bending energy for the O–C–S angle to form a linear state in the  $\beta$ -fragmentation process.

As mentioned in the Introduction, electrochemical studies on product formation upon oxidation of carboxylic acids and

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thiocarboxylic acids give different types of final products. While RCOO• radicals decarboxylate, RCOS• radicals dimerize to form the corresponding disulfide. Our product studies show that, in aqueous solutions, the  $\beta$ -fragmentation of PhCOS• radicals is the dominant route. This apparent contradiction can be resolved knowing that the rate of  $\beta$ -fragmentation of PhCOS• radicals is only  $8.5 \times 10^3 \text{ s}^{-1}$  and considering the difference in local radical concentrations between  $\gamma$ -radiolysis and electrolysis. In the steady state  $\gamma$ -radiolysis of benzoyl thiolate solutions, the radical production rate is rather low (ca  $7.8 \times 10^{-8} \text{ M}$  radicals per second), in contrast to the electrolytic processes, in which high radical concentrations are usually localized at the electrode.

The phenyl radical which is formed from the  $\beta$ -fragmentation of PhCOS• radical is known to add to double bonds. The rate constant of eq 12 was measured to be ca.  $10^7 \text{ M}^{-1} \text{ s}^{-1}$ , when Ph• radicals were produced by the one-electron reduction of iodobenzene (PhI) in the presence of N<sub>3</sub><sup>−</sup> (Lind et al., unpublished results). The PhN<sub>3</sub><sup>−</sup> radical anion has a weak absorption at 480 nm ( $\epsilon = \text{ca. } 1000 \text{ M}^{-1} \text{ cm}^{-1}$ ) and is not oxidized by O<sub>2</sub> or Fe(III)(CN)<sub>6</sub><sup>3−</sup>. Only bimolecular decay was observed, presumably to form PhN<sub>3</sub> and PhNH<sub>2</sub> (eq 13).

From the  $\beta$ -fragmentation of PhCOS• radicals in eq 2, carbonyl sulfide, COS, is expected to be one of the main products. Attempts to measure COS failed most probably because it is hydrolyzed to form CO<sub>2</sub> and H<sub>2</sub>S (at 25 °C, the pseudo-first-order rate constant is  $0.0011 \text{ s}^{-1}$ ).<sup>40</sup> The hydrolysis is also known to be catalyzed by Brønsted bases.<sup>40</sup> The products PhN<sub>3</sub> and PhNH<sub>2</sub> formed in the irradiated solution may catalyze the hydrolysis of COS.

## Summary

One-electron oxidation of PhCOS<sup>−</sup> ions form PhCOS• radicals. The reduction potential  $E^\circ(\text{PhCOS}^\bullet/\text{PhCOS}^-)$  and  $E^\circ(\text{PhCOS}^\bullet, \text{H}^+/\text{PhCOSH})$  were measured to be 1.21 and 1.36 V vs NHE, respectively. The PhCOS• radicals subsequently undergo  $\beta$ -fragmentation to form Ph• radical and COS with a rate constant of  $8.5 \times 10^3 \text{ s}^{-1}$  at room temperature. The  $\beta$ -fragmentation of the PhCOS• radical follows the Arrhenius equation,  $\log(k_2/\text{s}^{-1}) = (12.3 \pm 0.1) - (11.4 \pm 0.2)/\theta$ , where  $\theta = 2.3RT \text{ kcal/mol}$ . In 0.1 M NaN<sub>3</sub> solutions, the Ph• radicals add to N<sub>3</sub><sup>−</sup> to form PhN<sub>3</sub><sup>−</sup> radical anion, which subsequently disproportionate to form PhN<sub>3</sub> and PhNH<sub>2</sub> as final products. The experimental data for the kinetic and thermochemical properties of PhCOSH and PhCOS• radicals obtained in this work are compared with those of their oxygen counterpart PhCOOH and PhCOO• radicals.

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