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### Reduction Potential of the Sulfhydryl Radical: Pulse Radiolysis and Laser Flash Photolysis Studies of the Formation and Reactions of $\cdot\text{SH}$ and $\text{HSSH}^{\cdot-}$ in Aqueous Solutions

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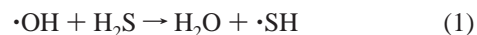
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Formation and reactions of the  $\cdot\text{SH}/\text{S}^{\cdot-}$  and  $\text{HSSH}^{\cdot-}/\text{HSS}^{\cdot 2-}$  radicals in aqueous solutions have been studied by excimer laser flash photolysis and by pulse radiolysis. Acidic  $\text{H}_2\text{S}$  solutions can be photolyzed with 193 nm laser pulses and produce a transient species with  $\lambda_{\text{max}}$  at 240 nm, ascribed to the  $\cdot\text{SH}/\text{S}^{\cdot-}$  radical. Solutions of  $\text{SH}^-$  can be photolyzed also with 248 nm laser pulses to produce the  $\cdot\text{SH}/\text{S}^{\cdot-}$  radical. The same radical is formed by oxidation of  $\text{SH}^-$  ions with  $\text{SO}_4^{\cdot-}$  and  $\text{CO}_3^{\cdot-}$  radicals. At  $\text{pH} > 5$ ,  $\cdot\text{SH}/\text{S}^{\cdot-}$  reacts with  $\text{SH}^-$  ( $k_f = 4 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ ,  $k_r = 5 \times 10^5 \text{ s}^{-1}$ ) to form  $\text{HSSH}^{\cdot-}/\text{HSS}^{\cdot 2-}$ , with  $\lambda_{\text{max}}$  at 380 nm. Both  $\cdot\text{SH}/\text{S}^{\cdot-}$  and  $\text{HSSH}^{\cdot-}/\text{HSS}^{\cdot 2-}$  react rapidly with  $\text{O}_2$ ; the former produces  $\text{SO}_2^{\cdot-}$  ( $k = 5 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ ), and the latter produces  $\text{O}_2^{\cdot-}$  ( $k = 4 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ ). Both radicals react with olefinic compounds. The monomeric radical oxidizes  $\text{Fe}(\text{CN})_6^{4-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{ClO}_2^-$ , and chlorpromazine. The dimeric radical is a weaker oxidant toward ferrocyanide but reduces *N*-methylpyridinium compounds. The reduction potential for the dimeric radical at  $\text{pH} 7$  was determined from one-electron transfer equilibria with  $\text{Mo}(\text{CN})_8^{3-}$  and with the 4-methoxyaniline radical cation and found to be 0.69 V vs NHE. From the equilibrium constant  $K = [\text{HSS}^{\cdot 2-}]/[\text{SH}^-][\text{S}^{\cdot-}] = 8 \times 10^3 \text{ L mol}^{-1}$ , the reduction potential for  $(\text{S}^{\cdot-}, \text{H}^+/\text{SH}^-)$  is calculated to be 0.92 V.

#### Introduction

The oxidation of hydrogen sulfide by dioxygen is a complex process leading to a wide array of products.<sup>1,2</sup> The major products and intermediates include  $\text{S}_8$ ,  $\text{SO}_3^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ , and  $\text{SO}_4^{2-}$ , with a distribution dependent on the presence of a catalyst,  $\text{pH}$ , and the oxygen concentration.  $\text{H}_2\text{S}$ , which is a very toxic gas, has a large number of natural and anthropogenic sources, and the safe removal of this substance has been a matter of ongoing industrial concern. Recent studies of the oxidation of  $\text{H}_2\text{S}$  in aqueous solution include autooxidation, both catalytic<sup>1-4</sup> and without added catalyst,<sup>2,5-7</sup> oxidation under ultrasonic irradiation,<sup>8</sup> photooxidation,<sup>9,10</sup> oxidation induced by  $\gamma$ -radiolysis,<sup>11</sup> and reaction with oxidants such as hydrogen peroxide,

$\text{Fe}^{\text{III}}(\text{EDTA})$ ,<sup>12</sup> ferric oxides,<sup>13</sup>  $\text{I}_3^-$ ,<sup>14</sup> and  $\text{Fe}(\text{VI})$ .<sup>15</sup> The use of the oxidation of  $\text{H}_2\text{S}$  to induce the oxidation of saturated hydrocarbons to ketones and alcohols has been reported recently.<sup>16,17</sup> In many of these studies, the formation of the sulfhydryl radical,  $\cdot\text{SH}$ , by hydrogen abstraction or electron transfer, has been suggested as the initiation step, for example,



which has a rate constant of  $1.5 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$  in the aqueous phase<sup>18</sup> and  $2.7 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$  in the gas phase.<sup>19</sup>

Studies in aqueous solutions have revealed that the  $\cdot\text{SH}$  radical reacts with  $\text{SH}^-$  to form a dimeric species,  $\text{HSSH}^{\cdot-}$ .<sup>18</sup>



The dimeric radical,  $\text{HSSH}^{\cdot-}$ , exhibits intense optical absorption

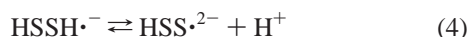
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at 380 nm, and pulse radiolysis studies have provided forward and reverse rate constants for reaction 2 ( $k_f = 5.4 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ ,  $k_r = 5.3 \times 10^5 \text{ s}^{-1}$ )<sup>20</sup> and the rate constants for the reactions of  $\cdot\text{SH}$  and  $\text{HSSH}\cdot^-$  with  $\text{O}_2$ . ESR studies also identified the  $\cdot\text{SH}$  radical in irradiated glassy solutions of sulfides and determined that its reaction with  $\text{O}_2$  leads to formation of  $\text{SO}_2\cdot^-$  ( $\text{OSO}\cdot^-$  not  $-\text{SOO}\cdot$ ).<sup>21</sup> Both the pulse radiolysis and the ESR studies also indicated that the  $\cdot\text{SH}$  radical is present as such in acidic solutions but exists mostly as  $\cdot\text{S}^-$  in neutral solutions.



The ESR studies also indicated that the dimeric species is deprotonated into  $\text{HSS}\cdot^{2-}$  in neutral and alkaline solutions.



Because of overlapping equilibria and because of further bonding to form polysulfide species, it has not been possible to determine the  $\text{p}K_a$  values for reactions 3 and 4. Since the  $\text{p}K_a$  for the  $\cdot\text{OH}$  radical is almost 4 units lower than that for  $\text{H}_2\text{O}$ , it may be expected that the  $\text{p}K_a$  for the  $\cdot\text{SH}$  radical also will be about 4 units lower than that for  $\text{H}_2\text{S}$ , i.e., between 3 and 4.

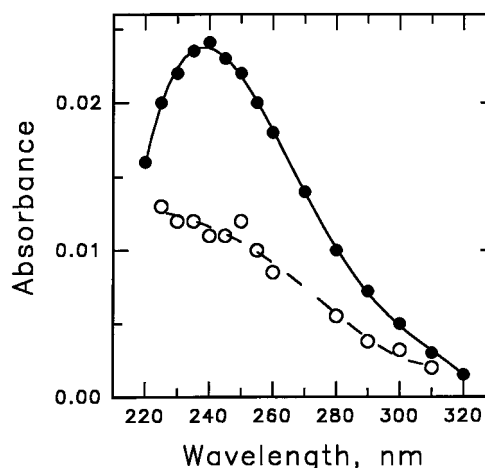
Beyond this basic set of reactions, there is little information in the literature on the chemical behavior of  $\cdot\text{SH}$  and  $\text{HSSH}\cdot^-$ .<sup>22</sup> In contrast to this situation, the reactivity of  $\cdot\text{SH}$  has been investigated extensively in the gas phase.<sup>23</sup> The  $\cdot\text{SH}$  radical reacts rapidly with  $\text{NO}_2$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}$ ,  $\text{O}_3$ ,  $\text{HO}_2$ ,  $\text{Cl}_2$ , and  $\text{HBr}$  but does not react with  $\text{O}_2$  in the gas phase. It also reacts rapidly with butadiene and cyclohexadiene, more slowly with other olefins, and very slowly with ethylene, acetylene, and benzene.

In the present study, we report results from the laser flash photolysis of the  $\text{H}_2\text{S}/\text{SH}^-$  system, to characterize the monomeric and dimeric radical species. We confirm the earlier results and extend the studies to reactions of  $\cdot\text{SH}/\cdot\text{S}^-$  and  $\text{HSS}\cdot^{2-}$  with several inorganic and organic compounds. Furthermore, pulse radiolysis experiments were performed to determine the rate constants for oxidation of  $\text{SH}^-$  by various inorganic radicals ( $\text{SO}_4\cdot^-$ ,  $\text{CO}_3\cdot^-$ , and  $\text{I}_2\cdot^-$ ) and the reduction potentials of  $\cdot\text{S}^-$  and  $\text{HSS}\cdot^{2-}$  radicals from one-electron transfer equilibria.

## Experimental Section<sup>24</sup>

Sodium sulfide ( $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ ) was obtained from Aldrich and  $\text{H}_2\text{S}$  from Matheson. The other inorganic compounds were analytical grade reagents from Mallinckrodt, and the organic compounds were of the highest purity from Aldrich. Water was purified with a Millipore Super-Q system. To prevent oxidation of the  $\text{H}_2\text{S}$  and sulfide, fresh solutions were prepared several minutes prior to irradiation, using previously deoxygenated water. The pH was adjusted with phosphate or borate buffers or with  $\text{KOH}$  or  $\text{HClO}_4$ . To minimize the escape of  $\text{H}_2\text{S}$  gas upon bubbling, the solution was first prepared with all the other components and was thoroughly purged with the desired gas, then the sulfide (or saturated  $\text{H}_2\text{S}$  solution) was added, and the bubbling was stopped.

The laser flash photolysis system was based on a Questek model 2320 excimer laser, using  $\text{Ar}/\text{F}$  for 193 nm and  $\text{Kr}/\text{F}$  for 248 nm, with a pulse duration of 25 ns.<sup>25</sup> Pulse radiolysis experiments were carried out using either the Febetron<sup>26</sup> or the linear accelerator<sup>27</sup> pulse radiolysis facilities. Spectrophotometric detection was used to follow the kinetics and to record transient absorption spectra. All measurements were carried out at room temperature,  $20 \pm 2^\circ\text{C}$ , and all rate constants are given with their estimated overall standard uncertainties.



**Figure 1.** Absorption spectra of the  $\cdot\text{SH}/\cdot\text{S}^-$  radical (●) and its decay product (○). Monitored by 193 nm laser flash photolysis of a deoxygenated aqueous solution containing  $5 \times 10^{-4} \text{ mol L}^{-1} \text{ H}_2\text{S}$  at pH 3.5, 2 (●) and 40 (○)  $\mu\text{s}$  after the pulse.

**TABLE 1. Rate Constants for Formation and Decay of the Sulfhydryl Radicals**

reaction	pH	$k$ , $\text{L mol}^{-1} \text{ s}^{-1}$
$\text{H}_2\text{S} + e_{\text{aq}}^-$	4.7	$(9.2 \pm 1.4) \times 10^9$
$\text{H}_2\text{S} + \text{H}\cdot \rightarrow \text{H}_2 + \cdot\text{SH}$	3.0	$\approx 1 \times 10^{10}$
$\text{H}_2\text{S}/\text{SH}^- + \text{SO}_4\cdot^- \rightarrow \cdot\text{SH} + \text{SO}_4^{2-}$	7.0	$(3.0 \pm 0.5) \times 10^9$
$\text{H}_2\text{S}/\text{SH}^- + \text{CO}_3\cdot^- \rightarrow \cdot\text{SH} + \text{CO}_3^{2-}$	7.0	$(2.0 \pm 0.3) \times 10^8$
$\text{H}_2\text{S}/\text{SH}^- + \text{I}_2\cdot^-$	7.0	$(4.6 \pm 0.6) \times 10^8$
$\text{H}_2\text{S}/\text{SH}^- + \text{C}_6\text{H}_5\text{NH}_2\cdot^+$	6.2	$(7.0 \pm 1.0) \times 10^8$
$\cdot\text{SH} + \cdot\text{SH} \rightarrow \text{H}_2\text{S}_2$	3.2	$(9 \pm 2) \times 10^9$
$\cdot\text{S}^- + \text{SH}^- \rightarrow \text{HSS}\cdot^{2-}$	7.0	$(4.0 \pm 0.6) \times 10^9$
$\text{HSS}\cdot^{2-} \rightarrow \cdot\text{S}^- + \text{SH}^-$	7.5	$(5.1 \pm 0.7) \times 10^5$
$\cdot\text{SH} + \text{O}_2 \rightarrow \text{SO}_2\cdot^- + \text{H}^+$	3.2	$(5.0 \pm 0.7) \times 10^9$
$\text{HSS}\cdot^{2-} + \text{O}_2 \rightarrow \text{HSS}^- + \text{O}_2\cdot^-$	7.0	$(4.0 \pm 0.6) \times 10^8$

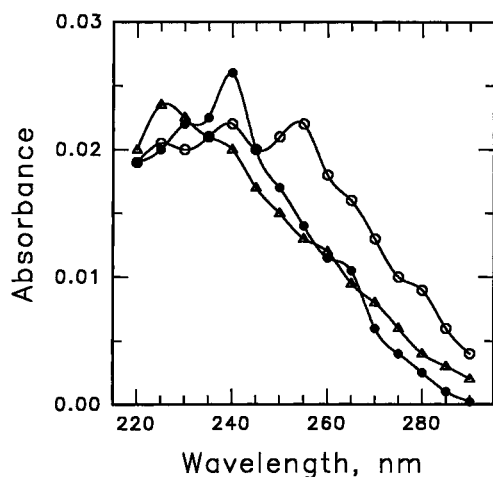
## Results and Discussion

**Photochemical Generation of  $\cdot\text{SH}$  and Its Reaction with  $\text{O}_2$ .** To study the  $\cdot\text{SH}$  radical, it is advantageous to work in the absence of  $\text{SH}^-$  ions in order to prevent the rapid formation of the dimeric species (see below). Therefore, we investigated the photolysis of acidic solutions of  $\text{H}_2\text{S}$ . These solutions do not absorb light at 248 nm and had to be photolyzed with 193 nm laser pulses. Photolysis of  $\text{H}_2\text{S}$  solutions at pH 3.5 resulted in the formation of a transient species with  $\lambda_{\text{max}}$  at 240 nm (Figure 1). This spectrum can be ascribed to the  $\cdot\text{SH}$  radical formed by the following reactions: The absorption was formed partly during



the laser pulse and partly within  $\sim 1 \mu\text{s}$  after the pulse. The rate of this increase in absorption at 240 nm after the pulse increased with increasing  $[\text{H}_2\text{S}]$  and was attributed to reaction 6. We were unable to derive a precise value for the rate constant, but estimated  $k_6 \approx 1 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$  at pH 3.0. This value is an order of magnitude higher than that estimated previously.<sup>18</sup> It is also higher than the rate constant in the gas phase,<sup>23</sup> in line with previous findings that reactions of H atoms take place more rapidly in aqueous solutions than in the gas phase.<sup>28</sup>

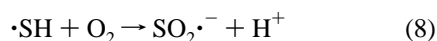
The photolysis of  $\text{H}_2\text{S}$  was carried out at different pH values. The absorbance at 240 nm was found to be the same between pH 3 and pH 4, but it decreased at higher and lower pH values. The decrease at higher pH values is due to the rapid reaction of  $\cdot\text{SH}$  with  $\text{SH}^-$  to form the dimer radical (see below). The



**Figure 2.** Absorption spectra monitored following 193 nm laser flash photolysis of an aqueous solution containing  $5 \times 10^{-4}$  mol L $^{-1}$  H $_2$ S and  $1.8 \times 10^{-5}$  mol L $^{-1}$  O $_2$  at pH 3.2, 2 (●), 10 (○), and 30 μs (Δ) after the pulse.

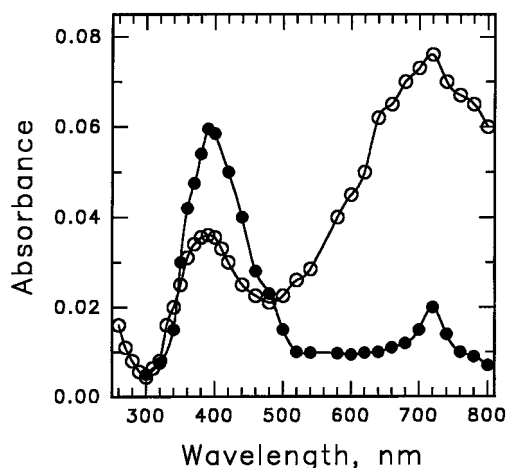
decrease at lower pH values is probably due to protonation and dimerization to form a species absorbing at higher wavelengths.<sup>29</sup>

The self-decay of  $\cdot$ SH followed second-order kinetics with a rate constant of  $2k = 9 \times 10^9$  L mol $^{-1}$  s $^{-1}$  at pH 3.2. The decay of  $\cdot$ SH was accelerated in the presence of O $_2$ , and the kinetics became first order. From the dependence of  $k_{\text{obs}}$  on the concentration of O $_2$  at pH 3.2, we derived a rate constant of  $5 \times 10^9$  L mol $^{-1}$  s $^{-1}$  (Table 1). To characterize the transient species resulting from this reaction, the absorbance was measured at various times after the pulse (Figure 2). The initial absorption of  $\cdot$ SH, with  $\lambda_{\text{max}} = 240$  nm, is found to shift within  $\sim 10$  μs to an absorption at 255 nm and after  $\sim 30$  μs to 225 nm. The magnitude and time of these changes were dependent on the relative concentrations of H $_2$ S and O $_2$ . These changes in the spectrum can be rationalized by a reaction of  $\cdot$ SH with O $_2$  to form SO $_2\cdot^-$  ( $\lambda_{\text{max}} = 255$  nm)<sup>25</sup> and then HO $_2\cdot$  ( $\lambda_{\text{max}} = 225$  nm)<sup>30</sup> according to the following reactions:



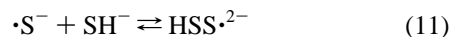
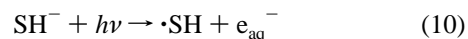
Reaction 7 is in competition with reaction 6, and its contribution depends on the relative concentrations of H $_2$ S and O $_2$ . The spectrum shown in Figure 2 was recorded with low [O $_2$ ] so that reaction 7 is unimportant. The conversion of  $\cdot$ SH into SO $_2\cdot^-$  takes place within  $\sim 10$  μs, with no indication of an intermediate species (such as HSOO $\cdot$ ). Finally, electron transfer from SO $_2\cdot^-$  to O $_2$  leads to production of O $_2\cdot^-$ , which immediately protonates at this pH to form HO $_2\cdot$  (reaction 9). These results are in agreement with the ESR results<sup>21</sup> which demonstrated that  $\cdot$ SH reacts with O $_2$  to form SO $_2\cdot^-$  and O $_2\cdot^-$ . The molar absorption coefficient of  $\cdot$ SH was determined by comparing the absorbance of  $\cdot$ SH at 240 nm with that of the HO $_2\cdot$  produced from its reaction with O $_2$ . By taking into account that each photon absorbed in reaction 5 leads to production of two HO $_2\cdot$  radicals, irrespective of the relative contributions of reactions 6 and 7, and taking  $\epsilon_{260}(\text{HO}_2\cdot) = 1400$  L mol $^{-1}$  cm $^{-1}$ ,<sup>30</sup> the molar absorption coefficient of  $\cdot$ SH was calculated to be  $(1.8 \pm 0.3) \times 10^3$  L mol $^{-1}$  cm $^{-1}$ .

**Photochemical Generation of HSS $\cdot^{2-}$  and Its Reaction with O $_2$ .** Flash photolysis of H $_2$ S/SH $^-$  ( $\text{p}K_{\text{a}} = 6.97$ ) solutions



**Figure 3.** Absorption spectra monitored following 248 nm laser flash photolysis of an aqueous solution containing  $5 \times 10^{-4}$  mol L $^{-1}$  H $_2$ S/SH $^-$  at pH 7.0 under N $_2$  (○) and under N $_2$ O (●).

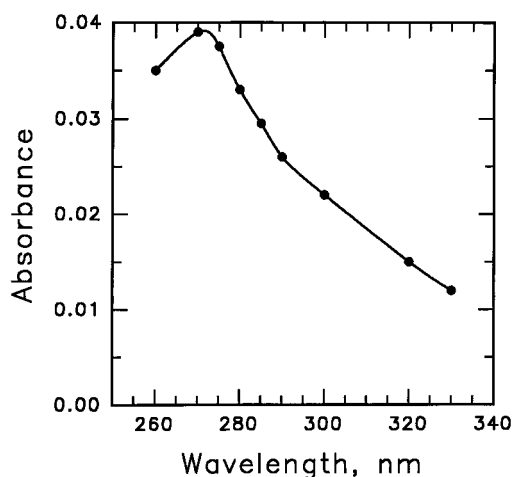
at pH 7 with 193 or 248 nm laser pulses led to the production of transient species with a composite absorption spectrum (Figure 3). The broad peak at 720 nm indicates the formation of e $_{\text{aq}}^-$ ; the peak at 380 nm is ascribed to HSS $\cdot^{2-}$  on the basis of its similarity to the spectrum found for this dimeric radical by pulse radiolysis.<sup>18</sup> The photolytic process probably involves photoionization of SH $^-$  ions to yield e $_{\text{aq}}^-$  and  $\cdot$ SH radicals, which react rapidly with SH $^-$  to form the dimer. In the presence



of N $_2$ O, the 720 nm peak practically disappears and the 380 nm peak is doubled in intensity (Figure 3). This is due to the conversion of e $_{\text{aq}}^-$  into  $\cdot$ OH by the N $_2$ O and the subsequent reaction of  $\cdot$ OH with SH $^-$  ( $k = 9 \times 10^9$  L mol $^{-1}$  s $^{-1}$ ).<sup>31</sup> In the absence of N $_2$ O, the rate of decay of e $_{\text{aq}}^-$  was dependent on the concentration of H $_2$ S/SH $^-$ . It has been reported before that e $_{\text{aq}}^-$  reacts rapidly with H $_2$ S (to form H $\cdot$ ) but not with SH $^-$  ions.<sup>18</sup> To determine the rate constant for the reaction of e $_{\text{aq}}^-$  with H $_2$ S, we carried out the photolysis at pH 6 and pH 4.7 and followed the decay at 720 nm as a function of H $_2$ S concentration. We derived a rate constant of  $(9.2 \pm 1.4) \times 10^9$  L mol $^{-1}$  s $^{-1}$ , in agreement with the earlier value.<sup>18</sup> Since this rate constant is much higher than those for proton transfer to e $_{\text{aq}}^-$  from other weak acids,<sup>31</sup> it may be concluded that the reaction of e $_{\text{aq}}^-$  with H $_2$ S involves addition followed by elimination of HS $^-$ , similar to the mechanism of reaction of e $_{\text{aq}}^-$  with organic thiols.

Photolysis of H $_2$ S/SH $^-$  solutions (248 nm) led to formation of the 380 nm absorption of the HSS $\cdot^{2-}$  radical. The rate of formation was dependent on the concentration of SH $^-$  ions. By following the buildup as a function of [SH $^-$ ], we calculated the rate constant for reaction 11 to be  $k_{\text{f}} = 4.0 \times 10^9$  L mol $^{-1}$  s $^{-1}$ , close to the value reported before,<sup>20</sup> and  $k_{\text{r}} = 5.1 \times 10^5$  s $^{-1}$ .

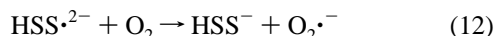
The molar absorption coefficient of the HSS $\cdot^{2-}$  radical at pH 7 was determined by comparing its absorbance with that of e $_{\text{aq}}^-$ . By taking  $\epsilon_{720}(\text{e}_{\text{aq}}^-) = 19\,000$  L mol $^{-1}$  cm $^{-1}$ ,<sup>31</sup> we calculated  $\epsilon_{380}(\text{HSS}\cdot^{2-}) = (7.5 \pm 1.1) \times 10^3$  L mol $^{-1}$  cm $^{-1}$ , in agreement with that determined by pulse radiolysis.<sup>18</sup> The 380 nm absorbance was highest at pH 7 to pH 8 but much lower at pH  $\leq 6$  due to the lack of SH $^-$  ions necessary for the formation of



**Figure 4.** Absorption spectrum of the product formed upon decay of the dimeric radical in deoxygenated solutions (conditions as in Figure 3).

the dimer. At  $\text{pH} \geq 8$ , the absorbance also decreased, slightly for 248 nm excitation and more strongly for 193 nm excitation.

In deoxygenated solutions, the absorption at 380 nm decayed via a mostly second-order process to a product with  $\lambda_{\text{max}} \approx 270$  nm (Figure 4), which persists for a long time. This differential spectrum is ascribed to the formation of a stable product, as is evident from comparison of the spectra of sulfide solutions before and after photolysis.<sup>32</sup> Addition of  $\text{O}_2$  to the system accelerates the buildup as well as the decay at 380 nm. Acceleration of the buildup process is due to the reaction of  $\cdot\text{SH}/\cdot\text{S}^-$  with  $\text{O}_2$ , discussed above, which competes with the dimer formation process. Acceleration of the decay is due to reaction of the dimer radical with  $\text{O}_2$ . In  $\text{O}_2$ -saturated solutions, the absorbance at 380 nm is greatly decreased and a new species is observed at 260 nm, most probably the  $\text{O}_2\cdot^-$  radical.



In this case, the formation of an intermediate species was not observed. By following the decay of the dimer radical at 380 nm at various concentrations of  $\text{O}_2$ , we determined the second-order rate constant for reaction 12 at  $\text{pH}$  7–8. A similar determination was carried out by pulse radiolysis at  $\text{pH}$  7. The average value was found to be  $k_{12} = (4.0 \pm 0.6) \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ , in good agreement with the earlier measurement.<sup>20</sup>

**Other Reactions of  $\cdot\text{SH}/\cdot\text{S}^-$  and  $\text{HSS}\cdot^{2-}$ .** The reactions of  $\cdot\text{SH}/\cdot\text{S}^-$  and  $\text{HSS}\cdot^{2-}$  radicals with various organic and inorganic compounds were studied at  $\text{pH}$  7. The rate constants for the reactions of  $\cdot\text{SH}/\cdot\text{S}^-$  were determined by using the buildup of the dimer radical absorption at 380 nm as a probe and measuring its rate as a function of substrate concentration. The rate constants for the reactions of the dimer radical were determined by following its decay at 380 nm. The measured rate constants are summarized in Table 2.

The  $\cdot\text{S}^-$  radical reacts with unsaturated compounds with rate constants of the order of  $10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ , faster than the reaction of  $\cdot\text{SH}$  with olefins in the gas phase. The dimeric  $\text{HSS}\cdot^{2-}$  radical also reacts with the same compounds, but its rate constants are lower by about an order of magnitude. On the basis of earlier ESR results,<sup>33</sup> we conclude that both of these radicals add to the double bond to form SH or  $\text{S}^-$  adducts.



The  $\cdot\text{S}^-$  radical oxidizes  $\text{Fe}(\text{CN})_6^{4-}$ ,  $\text{SO}_3^{2-}$ , and  $\text{ClO}_2^-$  relatively

**TABLE 2.** Rate Constants for Reactions of the Sulfhydryl Radicals

reaction	pH	k, $\text{L mol}^{-1} \text{ s}^{-1}$
$\cdot\text{SH}/\cdot\text{S}^- + \text{chlorpromazine}$	4.5	$(9.4 \pm 1.2) \times 10^9$
$\cdot\text{SH}/\cdot\text{S}^- + \text{chlorpromazine}$	2.9	$(8.0 \pm 1.1) \times 10^9$
$\cdot\text{SH} + \text{HFe}(\text{CN})_6^{3-} \rightarrow \text{H}_2\text{S} + \text{Fe}(\text{CN})_6^{3-}$	2.5	$(2.6 \pm 0.4) \times 10^9$
$\cdot\text{S}^- + \text{Fe}(\text{CN})_6^{4-} + \text{H}^+ \rightarrow \text{SH}^- + \text{Fe}(\text{CN})_6^{3-}$	7.0	$(8.0 \pm 1.2) \times 10^8$
$\cdot\text{S}^- + \text{HSO}_3^-/\text{SO}_3^{2-a}$	7.0	$(4.1 \pm 0.6) \times 10^8$
$\cdot\text{S}^- + \text{ClO}_2^-$	7.0	$(1.3 \pm 0.2) \times 10^9$
$\cdot\text{S}^- + \text{acrylamide}$	7.0	$(1.6 \pm 0.3) \times 10^9$
$\cdot\text{S}^- + \text{acrylonitrile}$	7.0	$(2.2 \pm 0.3) \times 10^9$
$\cdot\text{S}^- + \text{crotonaldehyde}$	7.0	$(1.2 \pm 0.2) \times 10^9$
$\cdot\text{S}^- + \text{crotonate ion}$	7.0	$(2.0 \pm 0.3) \times 10^9$
$\cdot\text{S}^- + 3\text{-methyl-3-buten-1-ol}$	7.0	$(8.1 \pm 1.2) \times 10^8$
$\text{HSS}\cdot^{2-} + \text{Fe}(\text{CN})_6^{4-}$	7.0	$(5.5 \pm 0.7) \times 10^7$
$\text{HSS}\cdot^{2-} + N\text{-methylpyridinium-4-aldehyde}$	7.0	$(1.7 \pm 0.3) \times 10^8$
$\text{HSS}\cdot^{2-} + 2,2'\text{-bipyridyl}$	7.0	$\approx 3 \times 10^5$
$\text{HSS}\cdot^{2-} + \text{acrylamide}$	7.0	$(1.4 \pm 0.2) \times 10^8$
$\text{HSS}\cdot^{2-} + \text{acrylonitrile}$	7.0	$(3.5 \pm 0.6) \times 10^8$
$\text{HSS}\cdot^{2-} + \text{crotonaldehyde}$	7.0	$(2.1 \pm 0.3) \times 10^8$
$\text{HSS}\cdot^{2-} + \text{crotonate ion}$	7.0	$(1.0 \pm 0.2) \times 10^7$
$\text{HSS}\cdot^{2-} + 2\text{-cyclohexen-1-ol}$	7.0	$(3.7 \pm 0.6) \times 10^7$
$\text{HSS}\cdot^{2-} + 3\text{-methyl-3-buten-1-ol}$	7.0	$(3.8 \pm 0.6) \times 10^7$

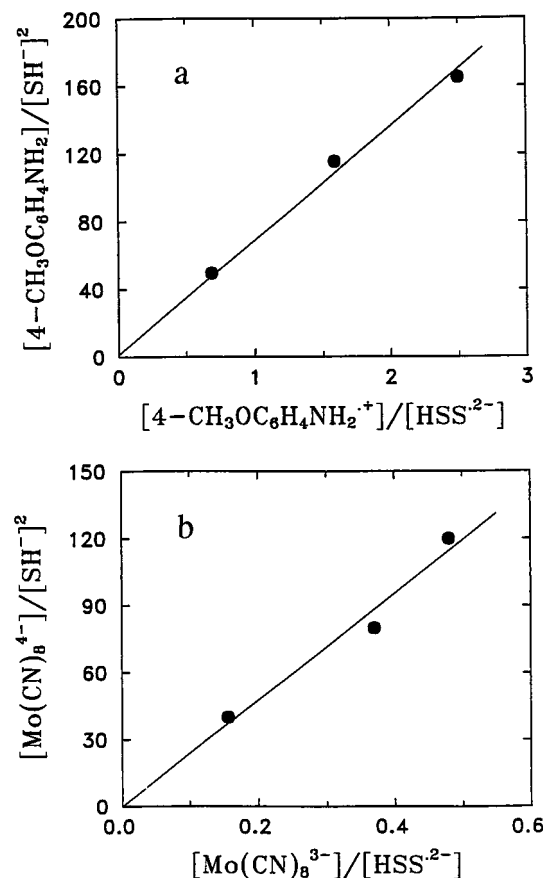
rapidly. On the other hand, the  $\text{HSS}\cdot^{2-}$  radical is less reactive as an oxidant but acts as a reductant toward pyridinium compounds (Table 2).

It is worth noting the difference between the  $\cdot\text{SH}/\cdot\text{S}^-$  and the  $\cdot\text{OH}/\cdot\text{O}^-$  radicals. In the oxygen pair,  $\cdot\text{OH}$  adds rapidly to double bonds but does not react with  $\text{O}_2$ , whereas  $\cdot\text{O}^-$  does not add to double bonds but reacts very rapidly with  $\text{O}_2$ .<sup>31</sup> In contrast, in the sulfur pair,  $\cdot\text{S}^-$  reacts rapidly with  $\text{O}_2$  as well as with olefins. Although the exact  $\text{pK}_a$  of the  $\cdot\text{SH}$  radical is unknown, it appears that  $\cdot\text{SH}$  also reacts with  $\text{O}_2$  in a process that may be concerted with deprotonation.

**Reduction Potential of the Sulfhydryl Radical.** Stanbury<sup>34</sup> reviewed the various estimations of the reduction potential for the  $\cdot\text{SH}/\text{SH}^-$  couple and concluded that the value is approximately 1.1 V vs NHE. We attempted to measure this value by establishing an equilibrium with a reference redox pair, but the experiments were hampered by the short lifetime of this species under most experimental conditions, due to self-decay or to rapid reaction of  $\cdot\text{SH}/\cdot\text{S}^-$  with excess sulfide (reactions 2 or 11). Our findings that  $\cdot\text{S}^-$  reacts with  $\text{ClO}_2^-$  ( $E^\circ = 0.934$  V) rapidly (Table 2) and that  $\text{I}_2\cdot^-$  ( $E^\circ = 1.03$  V) reacts with  $\text{SH}^-$  rapidly (Table 1) may not be significant for estimating the reduction potential, since the reactions may involve atom transfer rather than electron transfer.

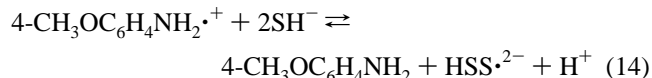
Since the equilibrium constant for reaction 11 is known, we decided to determine the reduction potential of the sulfhydryl radical by measuring the value for its dimeric species at  $\text{pH}$  7. Experimental measurements with  $\text{HSS}\cdot^{2-}$  are more accessible due to the longer lifetime and higher absorbance of this species as compared with  $\cdot\text{S}^-$ . At  $\text{pH}$  7, the monomeric and dimeric radicals exist predominantly in the form of  $\cdot\text{S}^-$  and  $\text{HSS}\cdot^{2-}$  but the parent sulfide is an equilibrium mixture of  $\text{H}_2\text{S}$  ( $\text{pK}_a = 6.97$ ) and  $\text{SH}^-$ . We avoided going to a higher  $\text{pH}$  to convert all the sulfide into the  $\text{SH}^-$  form because that will result in higher complexes of the radical (polysulfide radicals). We searched for suitable redox reference compounds that are not likely to form complexes with sulfide or its radical. Ascorbate was found to be fully oxidized by  $\text{HSS}\cdot^{2-}$  at  $\text{pH}$  7, with no evidence of an equilibrium. Experiments with phenols failed because the electron transfer reaction in neutral solution was too slow to reach equilibrium before significant decay of the radicals took place. (Further, the reaction could not be accelerated by use of higher concentrations of both solutes, since at high sulfide





**Figure 5.** Determination of the equilibrium constants for reactions 14 and 15 by pulse radiolysis. (a) The solutions contained  $5.5 \times 10^{-3}$  mol L<sup>-1</sup> sodium sulfide,  $(1.5\text{--}5.0) \times 10^{-3}$  mol L<sup>-1</sup> 4-methoxyaniline, and  $6 \times 10^{-2}$  mol L<sup>-1</sup> phosphate buffer at pH 7.0 and were saturated with N<sub>2</sub>O; the dose per pulse was 3.3 Gy, and the absorbance at equilibrium was measured at 380 nm, where the difference between the absorbances of the two radicals in equilibrium is the largest. (b) The solutions contained  $5.0 \times 10^{-3}$  mol L<sup>-1</sup> sodium sulfide,  $(1.0\text{--}3.0) \times 10^{-3}$  mol L<sup>-1</sup> octacyanomolybdate, and  $5 \times 10^{-2}$  mol L<sup>-1</sup> phosphate buffer at pH 7.0 and were saturated with N<sub>2</sub>O; the dose per pulse was 4.7 Gy, and the absorbance at equilibrium was measured at 400 nm.

concentrations the HSS<sup>•2-</sup> radical forms polysulfide radicals). The aniline radical cation at pH 6.2 ( $E = 1.02$  V)<sup>35</sup> was found to oxidize sulfide ( $k = 7 \times 10^8$  L mol<sup>-1</sup> s<sup>-1</sup>) completely, but the 4-methoxyaniline radical cation ( $E = 0.79$  V)<sup>36</sup> reacted to reach equilibrium.



These experiments were carried out at pH 7.0, where the 4-methoxyaniline radical cation is not deprotonated ( $\text{p}K_a = 9.6$ )<sup>35</sup> and 4-methoxyaniline is mostly in the neutral form ( $\text{p}K_a = 5.36$ ). Other conditions are specified in Figure 5a, which shows a linear plot of  $[4\text{-CH}_3\text{OC}_6\text{H}_4\text{NH}_2]/[\text{SH}^-]^2$  vs  $[4\text{-CH}_3\text{OC}_6\text{H}_4\text{NH}_2^+]/[\text{HSS}^{2-}]$ . In this calculation, the concentration of H<sup>+</sup> formed in reaction 14 is not taken into account, due to the presence of excess buffer, and the total sulfide concentration is included in  $[\text{SH}^-]$  despite the fact that about half of it is in the form of H<sub>2</sub>S. Sufficient SH<sup>-</sup> is present to achieve equilibrium 14 rapidly (within  $<1$  μs), but the protonation equilibrium between SH<sup>-</sup> and H<sub>2</sub>S is established much more rapidly. The plot in Figure 5a gives an equilibrium constant  $K_{14} = 68 \pm 10$  L mol<sup>-1</sup>. Thus, the difference in reduction potentials between

the two redox pairs is  $0.11 \pm 0.01$  V, and from the reduction potential of 4-methoxyaniline  $0.79 \pm 0.02$  V,<sup>35</sup> we calculate the reduction potential for the HSS<sup>•2-</sup>, H<sup>+</sup>/2SH<sup>-</sup> couple as  $0.68 \pm 0.03$  V vs NHE at pH 7.

The octacyanomolybdate ion was found to be another suitable reference for this purpose. The conditions under which this



equilibrium was determined are given in Figure 5b, and the results lead to  $K_{15} = 240 \pm 30$  L mol<sup>-1</sup>. By using  $E(\text{Mo}(\text{CN})_8^{3-}/\text{Mo}(\text{CN})_8^{4-}) = 0.84$  V,<sup>36</sup> we calculate  $E(\text{HSS}^{\bullet 2-}, \text{H}^+/2\text{SH}^-) = 0.70 \pm 0.02$  V. Both of the above measurements were carried out at the optimal SH<sup>-</sup> concentration, near 5 mmol L<sup>-1</sup>, so that practically all the sulfide radicals are present in the dimeric form and yet formation of polysulfide complexes is negligible. Therefore, the results can be taken to represent the true reduction potential of the dimeric species, and the average value is  $E(\text{HSS}^{\bullet 2-}, \text{H}^+/2\text{SH}^-) = 0.69 \pm 0.03$  V vs NHE at pH 7.

The equilibrium constant for reaction 11 has been determined in this study to be  $8 \times 10^3$  L mol<sup>-1</sup> and in a previous study<sup>20</sup> to be  $1 \times 10^4$  L mol<sup>-1</sup>. By taking the average of these two values, we calculate the reduction potential for the  $\text{S}^{\bullet-}, \text{H}^+/\text{SH}^-$  couple to be  $0.92 \pm 0.03$  V vs NHE at pH 7. The potential for the  $\text{SH}/\text{H}_2\text{S}$  couple in acidic solutions may be calculated from the above value if the  $\text{p}K_a$  of  $\text{SH}$  is determined. Our attempts to determine this  $\text{p}K_a$  value failed however. Changes in UV absorbance between  $\text{SH}$  and  $\text{S}^{\bullet-}$  are not useful for this purpose because an increase in pH leads to formation of the dimeric radical which has more intense absorption. We sought a compound whose rate of oxidation by  $\text{SH}$  and  $\text{S}^{\bullet-}$  will be different and that has no  $\text{p}K_a$  values between pH 2 and 6. Chlorpromazine was tried for this purpose, but its rate constants at pH 4.5 and 2.9 were found to be similar (Table 2). This result indicates that either the  $\text{p}K_a$  value for  $\text{SH}$  is  $<3$  or the reactivities of  $\text{SH}$  and  $\text{S}^{\bullet-}$  with chlorpromazine are very similar. Therefore, determination of the  $\text{p}K_a$  of the  $\text{SH}$  radical and of the reduction potential for the  $\text{SH}/\text{H}_2\text{S}$  couple must await future experiments.

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