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ARTICLES

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

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Formation and reactions of the $\cdot SH/\cdot S^-$ and $HSSH\cdot^-/HSS\cdot^{2-}$ radicals in aqueous solutions have been studied by excimer laser flash photolysis and by pulse radiolysis. Acidic H_2S solutions can be photolyzed with 193 nm laser pulses and produce a transient species with λ_{max} at 240 nm, ascribed to the $\cdot SH/\cdot S^-$ radical. Solutions of SH^- can be photolyzed also with 248 nm laser pulses to produce the $\cdot SH/\cdot S^-$ radical. The same radical is formed by oxidation of SH^- ions with $SO_4\cdot^-$ and $CO_3\cdot^-$ radicals. At pH > 5, $\cdot SH/\cdot S^-$ reacts with SH^- ($k_f = 4 \times 10^9$ L mol^{-1} s^{-1}, $k_r = 5 \times 10^5$ s^{-1}) to form $HSSH\cdot^-/HSS\cdot^{2-}$, with λ_{max} at 380 nm. Both $\cdot SH/\cdot S^-$ and $HSSH\cdot^-/HSS\cdot^{2-}$ react rapidly with O_2; the former produces $SO_2\cdot^-$ ($k = 5 \times 10^9$ L mol^{-1} s^{-1}), and the latter produces $O_2\cdot^-$ ($k = 4 \times 10^8$ L mol^{-1} s^{-1}). Both radicals react with olefinic compounds. The monomeric radical oxidizes $Fe(CN)_6^{4-}$, SO_3^{2-}, 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 pH 7 was determined from one-electron transfer equilibria with $Mo(CN)_8^{3-}$ and with the 4-methoxyaniline radical cation and found to be 0.69 V vs NHE. From the equilibrium constant $K = [HSS\cdot^{2-}]/[SH^-][\cdot S^-] = 8 \times 10^3$ L mol^{-1}, the reduction potential for $(\cdot S^-,H^+/SH^-)$ 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.[1,2] The major products and intermediates include S_8, SO_3^{2-}, $S_2O_3^{2-}$, and SO_4^{2-}, with a distribution dependent on the presence of a catalyst, pH, and the oxygen concentration. H_2S, 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 H_2S in aqueous solution include autoxidation, both catalytic[1−4] and without added catalyst,[2,5−7] oxidation under ultrasonic irradiation,[8] photooxidation,[9,10] oxidation induced by γ-radiolysis,[11] and reaction with oxidants such as hydrogen peroxide, Fe^{III}(EDTA),[12] ferric oxides,[13] I_3^-,[14] and Fe(VI).[15] The use of the oxidation of H_2S to induce the oxidation of saturated hydrocarbons to ketones and alcohols has been reported recently.[16,17] In many of these studies, the formation of the sulfhydryl radical, $\cdot$SH, by hydrogen abstraction or electron transfer, has been suggested as the initiation step, for example,

$$\cdot OH + H_2S \rightarrow H_2O + \cdot SH \qquad (1)$$

which has a rate constant of 1.5×10^{10} L mol^{-1} s^{-1} in the aqueous phase[18] and 2.7×10^9 L mol^{-1} s^{-1} in the gas phase.[19]

Studies in aqueous solutions have revealed that the $\cdot$SH radical reacts with SH^- to form a dimeric species, $HSSH\cdot^-$.[18]

$$\cdot SH + SH^- \rightleftarrows HSSH\cdot^- \qquad (2)$$

The dimeric radical, $HSSH\cdot^-$, 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 ($k_f = 5.4 \times 10^9$ L mol^{-1} s^{-1}, $k_r = 5.3 \times 10^5$ s^{-1})[20] and the rate constants for the reactions of $\cdot$SH and HSSH$\cdot^-$ with O_2. ESR studies also identified the $\cdot$SH radical in irradiated glassy solutions of sulfides and determined that its reaction with O_2 leads to formation of $SO_2\cdot^-$ (OSO$\cdot^-$ not $^-$SOO$\cdot$).[21] Both the pulse radiolysis and the ESR studies also indicated that the $\cdot$SH radical is present as such in acidic solutions but exists mostly as $\cdot S^-$ in neutral solutions.

$$\cdot SH \rightleftarrows \cdot S^- + H^+ \qquad (3)$$

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

$$HSSH\cdot^- \rightleftarrows HSS\cdot^{2-} + H^+ \qquad (4)$$

Because of overlapping equilibria and because of further bonding to form polysulfide species, it has not been possible to determine the pK_a values for reactions 3 and 4. Since the pK_a for the $\cdot$OH radical is almost 4 units lower than that for H_2O, it may be expected that the pK_a for the $\cdot$SH radical also will be about 4 units lower than that for H_2S, i.e., between 3 and 4.

Beyond this basic set of reactions, there is little information in the literature on the chemical behavior of $\cdot$SH and HSSH$\cdot^-$.[22] In contrast to this situation, the reactivity of $\cdot$SH has been investigated extensively in the gas phase.[23] The $\cdot$SH radical reacts rapidly with NO_2, NO, N_2O, O_3, HO_2, Cl_2, and HBr but does not react with 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 H_2S/SH^- system, to characterize the monomeric and dimeric radical species. We confirm the earlier results and extend the studies to reactions of $\cdot SH/\cdot S^-$ and HSS$\cdot^{2-}$ with several inorganic and organic compounds. Furthermore, pulse radiolysis experiments were performed to determine the rate constants for oxidation of SH^- by various inorganic radicals ($SO_4\cdot^-$, $CO_3\cdot^-$, and $I_2\cdot^-$) and the reduction potentials of $\cdot S^-$ and HSS$\cdot^{2-}$ radicals from one-electron transfer equilibria.

Experimental Section[24]

Sodium sulfide ($Na_2S\cdot 9H_2O$) was obtained from Aldrich and H_2S 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 H_2S 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 KOH or $HClO_4$. To minimize the escape of H_2S 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 H_2S solution) was added, and the bubbling was stopped.

The laser flash photolysis system was based on a Questek model 2320 excimer laser, using Ar/F for 193 nm and Kr/F for 248 nm, with a pulse duration of 25 ns.[25] Pulse radiolysis experiments were carried out using either the Febetron[26] or the linear accelerator[27] 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 ± 2 °C, and all rate constants are given with their estimated overall standard uncertainties.

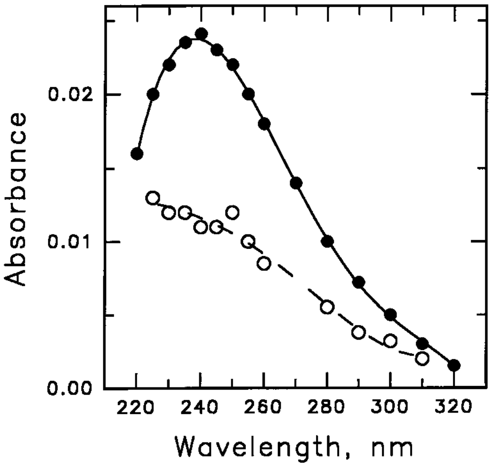

Figure 1. Absorption spectra of the $\cdot SH/\cdot S^-$ radical (●) and its decay product (○). Monitored by 193 nm laser flash photolysis of a deoxygenated aqueous solution containing 5×10^{-4} mol L^{-1} H_2S at pH 3.5, 2 (●) and 40 (○) μs after the pulse.

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

reaction	pH	k, L mol^{-1} s^{-1}
$H_2S + e_{aq}^-$	4.7	$(9.2 \pm 1.4) \times 10^9$
$H_2S + H\cdot \rightarrow H_2 + \cdot SH$	3.0	$\approx 1 \times 10^{10}$
$H_2S/SH^- + SO_4\cdot^- \rightarrow \cdot SH + SO_4^{2-}$	7.0	$(3.0 \pm 0.5) \times 10^9$
$H_2S/SH^- + CO_3\cdot^- \rightarrow \cdot SH + CO_3^{2-}$	7.0	$(2.0 \pm 0.3) \times 10^8$
$H_2S/SH^- + I_2\cdot^-$	7.0	$(4.6 \pm 0.6) \times 10^8$
$H_2S/SH^- + C_6H_5NH_2\cdot^+$	6.2	$(7.0 \pm 1.0) \times 10^8$
$\cdot SH + \cdot SH \rightarrow H_2S_2$	3.2	$(9 \pm 2) \times 10^9$
$\cdot S^- + SH^- \rightarrow HSS\cdot^{2-}$	7.0	$(4.0 \pm 0.6) \times 10^9$
$HSS\cdot^{2-} \rightarrow \cdot S^- + SH^-$	7.5	$(5.1 \pm 0.7) \times 10^5$
$\cdot SH + O_2 \rightarrow SO_2\cdot^- + H^+$	3.2	$(5.0 \pm 0.7) \times 10^9$
$HSS\cdot^{2-} + O_2 \rightarrow HSS^- + O_2\cdot^-$	7.0	$(4.0 \pm 0.6) \times 10^8$

Results and Discussion

Photochemical Generation of $\cdot$SH and Its Reaction with O_2. To study the $\cdot$SH radical, it is advantageous to work in the absence of SH^- ions in order to prevent the rapid formation of the dimeric species (see below). Therefore, we investigated the photolysis of acidic solutions of H_2S. These solutions do not absorb light at 248 nm and had to be photolyzed with 193 nm laser pulses. Photolysis of H_2S solutions at pH 3.5 resulted in the formation of a transient species with λ_{max} at 240 nm (Figure 1). This spectrum can be ascribed to the $\cdot$SH radical formed by the following reactions: The absorption was formed partly during

$$H_2S + h\nu \rightarrow H\cdot + \cdot SH \qquad (5)$$

$$H\cdot + H_2S \rightarrow H_2 + \cdot SH \qquad (6)$$

the laser pulse and partly within ~1 μs after the pulse. The rate of this increase in absorption at 240 nm after the pulse increased with increasing [H_2S] and was attributed to reaction 6. We were unable to derive a precise value for the rate constant, but estimated $k_6 \approx 1 \times 10^{10}$ L mol^{-1} s^{-1} at pH 3.0. This value is an order of magnitude higher than that estimated previously.[18] It is also higher than the rate constant in the gas phase,[23] in line with previous findings that reactions of H atoms take place more rapidly in aqueous solutions than in the gas phase.[28]

The photolysis of H_2S 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 $\cdot$SH with SH^- to form the dimer radical (see below). The

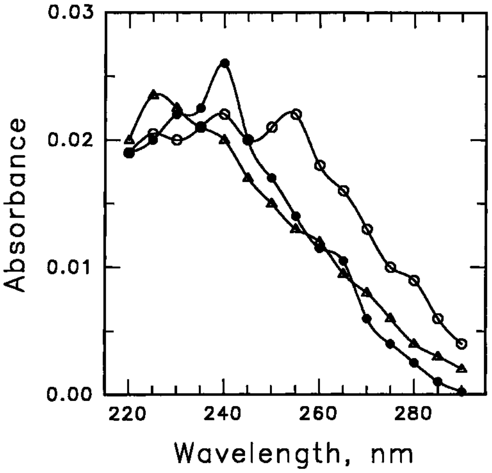

Figure 2. Absorption spectra monitored following 193 nm laser flash photolysis of an aqueous solution containing 5 × 10^{-4} mol L^{-1} H_2S and 1.8 × 10^{-5} mol L^{-1} O_2 at pH 3.2, 2 (●), 10 (○), and 30 μs (△) after the pulse.

decrease at lower pH values is probably due to protonation and dimerization to form a species absorbing at higher wavelengths.[29]

The self-decay of ·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 ·SH was accelerated in the presence of O_2, and the kinetics became first order. From the dependence of k_{obs} on the concentration of O_2 at pH 3.2, we derived a rate constant of 5 × 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 ·SH, with $\lambda_{max} = 240$ nm, is found to shift within ~10 μs to an absorption at 255 nm and after ~30 μs to 225 nm. The magnitude and time of these changes were dependent on the relative concentrations of H_2S and O_2. These changes in the spectrum can be rationalized by a reaction of ·SH with O_2 to form $SO_2{\cdot}^-$ ($\lambda_{max} = 255$ nm)[25] and then $HO_2{\cdot}$ ($\lambda_{max} = 225$ nm)[30] according to the following reactions:

$$H{\cdot} + O_2 \rightarrow HO_2{\cdot} \qquad (7)$$

$$\cdot SH + O_2 \rightarrow SO_2{\cdot}^- + H^+ \qquad (8)$$

$$SO_2{\cdot}^- + O_2 + H^+ \rightarrow SO_2 + HO_2{\cdot} \qquad (9)$$

Reaction 7 is in competition with reaction 6, and its contribution depends on the relative concentrations of H_2S and O_2. The spectrum shown in Figure 2 was recorded with low [O_2] so that reaction 7 is unimportant. The conversion of ·SH into $SO_2{\cdot}^-$ takes place within ~10 μs, with no indication of an intermediate species (such as HSOO·). 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[21] which demonstrated that ·SH reacts with O_2 to form $SO_2{\cdot}^-$ and $O_2{\cdot}^-$. The molar absorption coefficient of ·SH was determined by comparing the absorbance of ·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 $\epsilon_{260}(HO_2{\cdot}) = 1400$ L mol^{-1} cm^{-1},[30] the molar absorption coefficient of ·SH was calculated to be (1.8 ± 0.3) × 10^3 L mol^{-1} cm^{-1}.

Photochemical Generation of $HSS{\cdot}^{2-}$ and Its Reaction with O_2. Flash photolysis of H_2S/SH^- ($pK_a = 6.97$) solutions 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_{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.[18] The photolytic process probably involves photoionization of SH^- ions to yield e_{aq}^- and ·SH radicals, which react rapidly with SH^- to form the dimer. In the presence

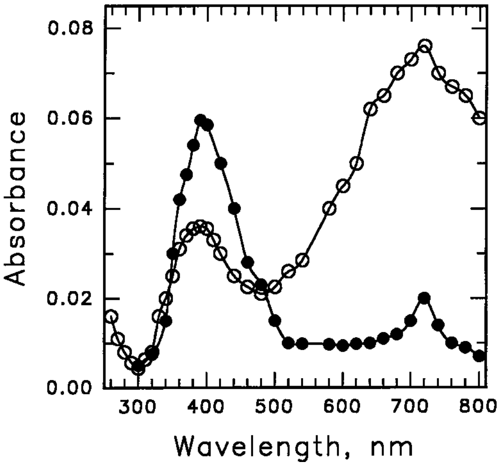

Figure 3. Absorption spectra monitored following 248 nm laser flash photolysis of an aqueous solution containing 5 × 10^{-4} mol L^{-1} H_2S/SH^- at pH 7.0 under N_2 (○) and under N_2O (●).

$$SH^- + h\nu \rightarrow \cdot SH + e_{aq}^- \qquad (10)$$

$$\cdot SH \rightleftarrows \cdot S^- + H^+ \qquad (3)$$

$$\cdot S^- + SH^- \rightleftarrows HSS{\cdot}^{2-} \qquad (11)$$

of N_2O, 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_{aq}^- into ·OH by the N_2O and the subsequent reaction of ·OH with SH^- ($k = 9 \times 10^9$ L mol^{-1} s^{-1}).[31] In the absence of N_2O, the rate of decay of e_{aq}^- was dependent on the concentration of H_2S/SH^-. It has been reported before that e_{aq}^- reacts rapidly with H_2S (to form H·) but not with SH^- ions.[18] To determine the rate constant for the reaction of e_{aq}^- with H_2S, we carried out the photolysis at pH 6 and pH 4.7 and followed the decay at 720 nm as a function of H_2S concentration. We derived a rate constant of (9.2 ± 1.4) × 10^9 L mol^{-1} s^{-1}, in agreement with the earlier value.[18] Since this rate constant is much higher than those for proton transfer to e_{aq}^- from other weak acids,[31] it may be concluded that the reaction of e_{aq}^- with H_2S involves addition followed by elimination of HS^-, similar to the mechanism of reaction of e_{aq}^- with organic thiols.

Photolysis of H_2S/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 $k_f = 4.0 \times 10^9$ L mol^{-1} s^{-1}, close to the value reported before,[20] and $k_r = 5.1 \times 10^5$ 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_{aq}^-. By taking $\epsilon_{720}(e_{aq}^-) = 19\,000$ L mol^{-1} cm^{-1},[31] we calculated $\epsilon_{380}(HSS{\cdot}^{2-}) = (7.5 \pm 1.1) \times 10^3$ L mol^{-1} cm^{-1}, in agreement with that determined by pulse radiolysis.[18] The 380 nm absorbance was highest at pH 7 to pH 8 but much lower at pH ≤ 6 due to the lack of SH^- ions necessary for the formation of

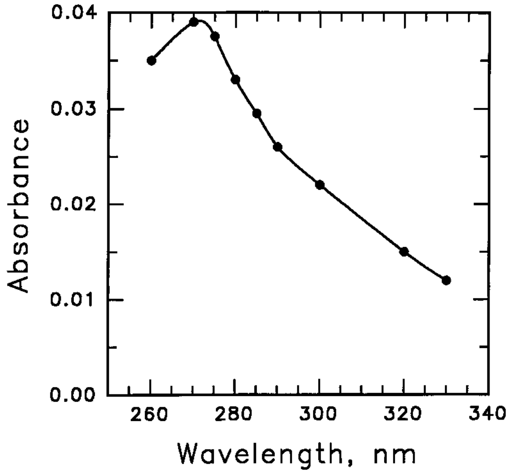

Figure 4. Absorption spectrum of the product formed upon decay of the dimeric radical in deoxygenated solutions (conditions as in Figure 3).

the dimer. At pH ≥ 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 $\lambda_{\max} \approx$ 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.[32] Addition of 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 $\cdot SH/\cdot S^-$ with O_2, discussed above, which competes with the dimer formation process. Acceleration of the decay is due to reaction of the dimer radical with O_2. In O_2-saturated solutions, the absorbance at 380 nm is greatly decreased and a new species is observed at 260 nm, most probably the $O_2\cdot^-$ radical.

$$HSS\cdot^{2-} + O_2 \rightarrow HSS^- + O_2\cdot^- \qquad (12)$$

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 O_2, we determined the second-order rate constant for reaction 12 at pH 7−8. A similar determination was carried out by pulse radiolysis at pH 7. The average value was found to be $k_{12} = (4.0 \pm 0.6) \times 10^8$ L mol^{-1} s^{-1}, in good agreement with the earlier measurement.[20]

Other Reactions of $\cdot SH/\cdot S^-$ and $HSS\cdot^{2-}$. The reactions of $\cdot SH/\cdot S^-$ and $HSS\cdot^{2-}$ radicals with various organic and inorganic compounds were studied at pH 7. The rate constants for the reactions of $\cdot SH/\cdot S^-$ 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 $\cdot S^-$ radical reacts with unsaturated compounds with rate constants of the order of 10^9 L mol^{-1} s^{-1}, faster than the reaction of $\cdot SH$ with olefins in the gas phase. The dimeric $HSS\cdot^{2-}$ 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,[33] we conclude that both of these radicals add to the double bond to form SH or S^- adducts.

$$\cdot SH + R_2C{=}CR_2 \rightarrow HSCR_2{-}CR_2\cdot \qquad (13)$$

TABLE 2. Rate Constants for Reactions of the Sulfhydryl Radicals

reaction	pH	k, L mol^{-1} s^{-1}
$\cdot SH/\cdot S^- +$ chlorpromazine	4.5	$(9.4 \pm 1.2) \times 10^9$
$\cdot SH/\cdot S^- +$ chlorpromazine	2.9	$(8.0 \pm 1.1) \times 10^9$
$\cdot SH + HFe(CN)_6^{3-} \rightarrow H_2S + Fe(CN)_6^{3-}$	2.5	$(2.6 \pm 0.4) \times 10^9$
$\cdot S^- + Fe(CN)_6^{4-} + H^+ \rightarrow SH^- + Fe(CN)_6^{3-}$	7.0	$(8.0 \pm 1.2) \times 10^8$
$\cdot S^- + HSO_3^-/SO_3^{2-}$[a]	7.0	$(4.1 \pm 0.6) \times 10^8$
$\cdot S^- + ClO_2^-$	7.0	$(1.3 \pm 0.2) \times 10^9$
$\cdot S^- +$ acrylamide	7.0	$(1.6 \pm 0.3) \times 10^9$
$\cdot S^- +$ acrylonitrile	7.0	$(2.2 \pm 0.3) \times 10^9$
$\cdot S^- +$ crotonaldehyde	7.0	$(1.2 \pm 0.2) \times 10^9$
$\cdot S^- +$ crotonate ion	7.0	$(2.0 \pm 0.3) \times 10^9$
$\cdot S^- +$ 3-methyl-3-buten-1-ol	7.0	$(8.1 \pm 1.2) \times 10^8$
$HSS\cdot^{2-} + Fe(CN)_6^{4-}$	7.0	$(5.5 \pm 0.7) \times 10^7$
$HSS\cdot^{2-} +$ *N*-methylpyridinium-4-aldehyde	7.0	$(1.7 \pm 0.3) \times 10^8$
$HSS\cdot^{2-} +$ 2,2′-bipyridyl	7.0	$\approx 3 \times 10^5$
$HSS\cdot^{2-} +$ acrylamide	7.0	$(1.4 \pm 0.2) \times 10^8$
$HSS\cdot^{2-} +$ acrylonitrile	7.0	$(3.5 \pm 0.6) \times 10^8$
$HSS\cdot^{2-} +$ crotonaldehyde	7.0	$(2.1 \pm 0.3) \times 10^8$
$HSS\cdot^{2-} +$ crotonate ion	7.0	$(1.0 \pm 0.2) \times 10^7$
$HSS\cdot^{2-} +$ 2-cyclohexen-1-ol	7.0	$(3.7 \pm 0.6) \times 10^7$
$HSS\cdot^{2-} +$ 3-methyl-3-buten-1-ol	7.0	$(3.8 \pm 0.6) \times 10^7$

The $\cdot S^-$ radical oxidizes $Fe(CN)_6^{4-}$, SO_3^{2-}, and ClO_2^- relatively rapidly. On the other hand, the $HSS\cdot^{2-}$ 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 $\cdot SH/\cdot S^-$ and the $\cdot OH/\cdot O^-$ radicals. In the oxygen pair, $\cdot OH$ adds rapidly to double bonds but does not react with O_2, whereas $\cdot O^-$ does not add to double bonds but reacts very rapidly with O_2.[31] In contrast, in the sulfur pair, $\cdot S^-$ reacts rapidly with O_2 as well as with olefins. Although the exact pK_a of the $\cdot SH$ radical is unknown, it appears that $\cdot SH$ also reacts with O_2 in a process that may be concerted with deprotonation.

Reduction Potential of the Sulfhydryl Radical. Stanbury[34] reviewed the various estimations of the reduction potential for the $\cdot SH/SH^-$ 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 $\cdot SH/\cdot S^-$ with excess sulfide (reactions 2 or 11). Our findings that $\cdot S^-$ reacts with ClO_2^- ($E° = 0.934$ V) rapidly (Table 2) and that $I_2\cdot^-$ ($E° = 1.03$ V) reacts with 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 pH 7. Experimental measurements with $HSS\cdot^{2-}$ are more accessible due to the longer lifetime and higher absorbance of this species as compared with $\cdot S^-$. At pH 7, the monomeric and dimeric radicals exist predominantly in the form of $\cdot S^-$ and $HSS\cdot^{2-}$ but the parent sulfide is an equilibrium mixture of H_2S (p$K_a = 6.97$) and SH^-. We avoided going to a higher pH to convert all the sulfide into the 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 $HSS\cdot^{2-}$ at 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

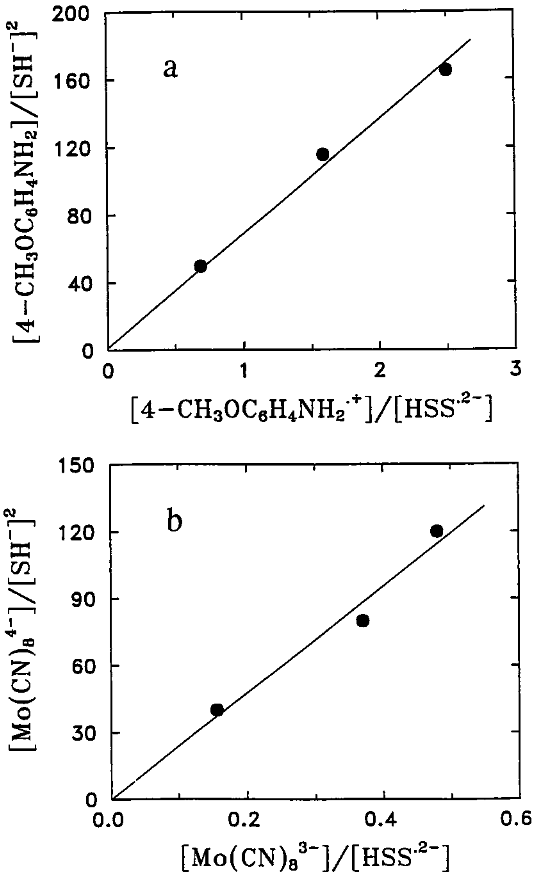

Figure 5. Determination of the equilibrium constants for reactions 14 and 15 by pulse radiolysis. (a) The solutions contained 5.5 × 10^{-3} mol L^{-1} sodium sulfide, (1.5−5.0) × 10^{-3} mol L^{-1} 4-methoxyaniline, and 6 × 10^{-2} mol L^{-1} phosphate buffer at pH 7.0 and were saturated with N_2O; the 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 × 10^{-3} mol L^{-1} sodium sulfide, (1.0−3.0) × 10^{-3} mol L^{-1} octacyanomolybdate, and 5 × 10^{-2} mol L^{-1} phosphate buffer at pH 7.0 and were saturated with N_2O; the dose per pulse was 4.7 Gy, and the absorbance at equilibrium was measured at 400 nm.

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

$$4\text{-}CH_3OC_6H_4NH_2^{\bullet +} + 2SH^- \rightleftarrows 4\text{-}CH_3OC_6H_4NH_2 + HSS^{\bullet 2-} + H^+ \quad (14)$$

These experiments were carried out at pH 7.0, where the 4-methoxyaniline radical cation is not deprotonated ($pK_a = 9.6$)[35] and 4-methoxyaniline is mostly in the neutral form ($pK_a = 5.36$). Other conditions are specified in Figure 5a, which shows a linear plot of $[4\text{-}CH_3OC_6H_4NH_2]/[SH^-]^2$ vs $[4\text{-}CH_3OC_6H_4NH_2^{\bullet +}]/[HSS^{\bullet 2-}]$. In this calculation, the concentration of H^+ formed in reaction 14 is not taken into account, due to the presence of excess buffer, and the total sulfide concentration is included in $[SH^-]$ despite the fact that about half of it is in the form of H_2S. Sufficient SH^- is present to achieve equilibrium 14 rapidly (within <1 μs), but the protonation equilibrium between SH^- and H_2S is established much more rapidly. The plot in Figure 5a gives an equilibrium constant $K_{14} = 68 \pm 10$ L mol^{-1}. Thus, the difference in reduction potentials between the two redox pairs is 0.11 ± 0.01 V, and from the reduction potential of 4-methoxyaniline 0.79 ± 0.02 V,[35] we calculate the reduction potential for the $HSS^{\bullet 2-},H^+/2SH^-$ couple as 0.68 ± 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

$$Mo(CN)_8^{3-} + 2SH^- \rightleftarrows Mo(CN)_8^{4-} + HSS^{\bullet 2-} + H^+ \quad (15)$$

equilibrium was determined are given in Figure 5b, and the results lead to $K_{15} = 240 \pm 30$ L mol^{-1}. By using $E(Mo(CN)_8^{3-}/Mo(CN)_8^{4-}) = 0.84$ V,[36] we calculate $E(HSS^{\bullet 2-},H^+/2SH^-) = 0.70 \pm 0.02$ V. Both of the above measurements were carried out at the optimal SH^- concentration, near 5 mmol L^{-1}, 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 $E(HSS^{\bullet 2-},H^+/2SH^-) = 0.69 \pm 0.03$ V vs NHE at pH 7.

The equilibrium constant for reaction 11 has been determined in this study to be 8 × 10^3 L mol^{-1} and in a previous study[20] to be 1 × 10^4 L mol^{-1}. By taking the average of these two values, we calculate the reduction potential for the $^{\bullet}S^-,H^+/SH^-$ couple to be 0.92 ± 0.03 V vs NHE at pH 7. The potential for the $^{\bullet}SH/H_2S$ couple in acidic solutions may be calculated from the above value if the pK_a of $^{\bullet}SH$ is determined. Our attempts to determine this pK_a value failed however. Changes in UV absorbance between $^{\bullet}SH$ and $^{\bullet}S^-$ 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 $^{\bullet}SH$ and $^{\bullet}S^-$ will be different and that has no pK_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 pK_a value for $^{\bullet}SH$ is <3 or the reactivities of $^{\bullet}SH$ and $^{\bullet}S^-$ with chlorpromazine are very similar. Therefore, determination of the pK_a of the $^{\bullet}SH$ radical and of the reduction potential for the $^{\bullet}SH/H_2S$ couple must await future experiments.

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