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Homolytic Displacement at Sulfur by the Hydrogen Atom. Formation of Hydrogen Sulfide in the Liquid-Phase Photolysis of Thiols

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Abstract: The photochemistry of several thiols in the liquid phase has been investigated, and the products are reported. In all cases, products are obtained that can be rationalized as arising from the primary photoscission of the carbon–sulfur bond. Possible mechanisms for the formation of these products are discussed, and evidence is presented for a mechanism involving a free-radical displacement reaction on the sulfur atom by hydrogen atoms, eq 8. This reaction appears to have an activation energy only some 3.8 kcal/mol higher than the activation energy for abstraction of the sulfhydryl hydrogen, eq 2. It is also suggested that in the presence of certain solvents (e.g., tetrahydrofuran), interactions between excited thiol and the solvent may alter the course of the photochemical decomposition of the thiol. This may be involved in the discrepancies in the literature on the photo- and radiation chemistry of alcohols when thiols are used as the H-atom source.

Introduction

Thiols and thiyl radicals have long been recognized as species which play important roles in many biochemical systems.[1] The discovery that certain thiols protect living cells from radiation damage has led to considerable interest in the radiochemistry and radiation biology of thiols and other sulfur-containing molecules of biological importance.[2]

Surprisingly, however, very little is known about the fundamental photochemistry of thiols in solution. We have made extensive use of thiol photolysis as a source of hydrogen atoms in solution,[3] and thiol photolysis has been studied by numerous workers in the gas phase[4] and in solid matrices at low temperatures.[5] However, there is only one report of a detailed study of the photochemistry of thiols in solution.[6]

In the single reported study of the photolysis of neat liquid ethanethiol, Carlson and Knight reported that the only observable products are hydrogen and diethyl disulfide. To account for these products, they proposed a simple three-reaction sequence involving thiyl radicals and hydrogen atoms as the only radical intermediates.

$$RSH \xrightarrow{h\nu} RS\cdot + H\cdot$$

$$H\cdot + RSH \rightarrow RS\cdot + H_2$$

$$2\ RS\cdot \rightarrow RSSR$$
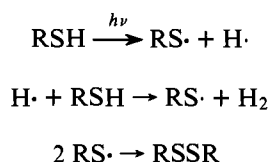
Their conclusions, if general for the photolysis of thiols, are quite surprising in view of the reported reaction of hydrogen atoms with thiols to form hydrogen sulfide when the hydrogen atoms are generated by radiochemical means[7,8] or by electrical discharge.[9,10]

$$H\cdot + RSH \rightarrow R\cdot + H_2S$$
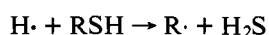
Since the photochemistry of thiols, thiyl radical chemistry, and the use of thiol photolysis as a source of hydrogen atoms are

of interest to us, we undertook a detailed study of the solution photochemistry of thiols.

Experimental Section

Hydrogen Analysis. The irradiation cell containing the sample to be analyzed was attached to a Toepler pump, and the sample was frozen in a liquid nitrogen bath. Hydrogen was transferred from the irradiation cell to a manifold of known volume where its pressure was determined, and the number of moles present was calculated assuming ideal gas behavior. Several freeze–thaw cycles were employed to ensure the complete removal of hydrogen from the sample. The manifold was calibrated with known amounts of hydrogen gas.

Hydrogen Sulfide Analysis. A modification of the methylene blue procedure of Jacobs, Braverman, and Hochheiser[11] was followed. The following solutions were prepared.

Trapping Reagent. To a rapidly stirred solution of 4.30 g of cadmium sulfate ($3CdSO_4 \cdot 8H_2O$, Merck reagent) in 800 mL of H_2O in a 1-L volumetric flask was added a solution of 0.32 g of NaOH in 100 mL of H_2O (precipitate forms). The suspension was diluted to 1 L total volume, and was stirred rapidly as aliquots were withdrawn for use.

Diamine Stock Solution. In a mixture of 50 mL of concentrated H_2SO_4 and 30 mL of water was dissolved 16.32 g of N,N-dimethyl-p-phenylenediamine sulfate (Eastman, recrystallized from water-acetone). The stock solution was placed in a dark bottle and stored in the refrigerator.

Diamine Working Solution. To a 250-mL volumetric flask was added 12.5 mL of diamine stock solution, and the flask was filled to volume with 50% (v/v) H_2SO_4 solution and stored in the refrigerator.

Ferric Chloride Solution. A solution of 100 g of $FeCl_3$ in 50 mL of H_2O was diluted to 100.0 mL for use.

Hydrogen Sulfide Trapping Methods. The following three methods were used to separate H_2S from the reaction mixture and trap it as CdS.

Method A. The irradiation cell was attached to an evacuated double-trap manifold; the cell was opened, and the reaction mixture was allowed to distill into the first trap, precooled to −131 °C in a pentane slush bath. Hydrogen sulfide passed into the second trap, where it was condensed at liquid nitrogen temperature. The second trap was then
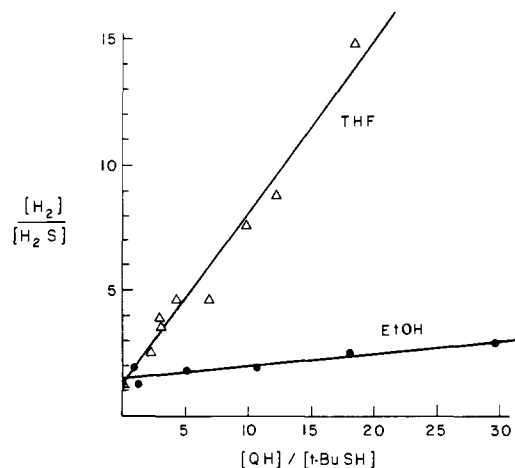
Figure 1. Effect of added hydrogen donor (QH) on hydrogen/hydrogen sulfide yield in the photolysis of *tert*-butyl mercaptan (*t*-BuSH). For THF, the least-squares parameters are slope, 0.68 ± 0.03; intercept, 1.3 ± 0.2. For EtOH: slope, 0.05 ± 0.01; intercept, 1.5 ± 0.1.
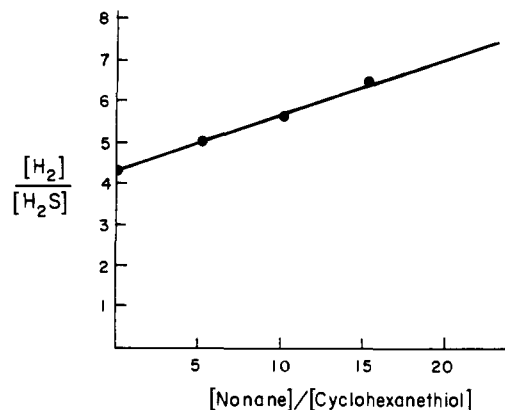

Figure 2. Effect of added nonane on the hydrogen/hydrogen sulfide yield in the photolysis of cyclohexanethiol. The least-squares parameters are slope, 0.136 ± 0.003; intercept, 4.32 ± 0.03.

Table I. Relative Efficiencies of Product Formation in the Photolysis of Thiols

Reactant RSH	Product ratios (relative to hydrogen)					Relative efficiency of conversion[a]
	H_2	H_2S	RH	RSR	RSSR	
tert-Butyl mercaptan	(1)	0.69	ND[b]	0.47	1.72	1.00
Cyclohexanethiol	(1)	0.23	0.16	0.12	1.08	0.99
Thiophenol	(1)	0.17	0.12	0.00	1.30	0.32

[a] Sum of the relative quantum yields (in arbitrary units) for the formation of H_2 and H_2S. This is a measure of the efficiency of the primary photolytic process(es) of each thiol. [b] Not determined quantitatively, but shown to be present qualitatively by VPC analysis.

sealed, and the reaction mixture was retransferred from trap 1 to the irradiation cell; this cycle was repeated twice. The H_2S was then swept at room temperature from the second trap into 50 mL of trapping reagent by means of a current of nitrogen or argon.

Method B. Hydrogen sulfide was distilled as in method A into a modified two-trap manifold. The modification allowed the direct addition of 50 mL of trapping reagent to trap 2. Subsequent color development was also carried out in trap 2 itself.

Method C. A stream of nitrogen was bubbled into the reaction mixture in the irradiation cell. The effluent from the cell was bubbled into 50 mL of trapping reagent. The N_2 sweep was continued for 1 h to remove all of the H_2S from the reaction mixture.

Color Development. The trapping solution from the above procedures was cooled for 15 min in an ice water bath; 2.5 mL of diamine working solution and 0.5 mL of $FeCl_3$ solution were added. The mixture was shaken vigorously and allowed to warm to room temperature as the methylene blue color developed. After 15 min the solution was transferred to a 250-mL volumetric flask and diluted to volume. Color development was allowed to continue for a total of 30 min. A blank, prepared from 50 mL of fresh trapping solution, was handled in parallel fashion. The spectrum of the sample solution vs. the blank was recorded on a Cary 14 or Beckman 24 spectrometer, and the amount of H_2S originally present was determined from the absorbance at 665 nm according to a calibration curve prepared from known samples of H_2S. A new calibration curve was prepared each time a new diamine working solution was prepared or a new trapping method was employed.

Gas Chromatographic Analysis for Other Products. After removal of hydrogen sulfide from the irradiation mixture, a predetermined amount of a suitable internal standard was added to the solution, and the remaining products were determined by analytical gas chromatography. Peak areas were measured by a Spectra Physics Autolab System I integrator, and were converted to the amount of compound present in the original sample by means of detector response factors calculated from mixtures of authentic samples of the photoproducts and an internal standard. Averages of several injections were computed by the integrator.

General Procedure for the Irradiation of Neat Thiols at 254 nm, Room Temperature. Freshly distilled thiol was vacuum transferred into an irradiation cell consisting of a cylindrical Pyrex chamber for freeze-thaw operations and a quartz side arm of square cross section for irradiation. The thiol sample (2–3 mL) was thoroughly degassed and irradiated at 254 nm with three Rayonet RPR-2537-A lamps. During irradiation, the cell was masked so that only the liquid phase was illuminated. The solution was stirred by a magnetic stir bar placed within the cell. Analyses for hydrogen, hydrogen sulfide, and other products were performed as described above. Results are summarized in Table I.

Irradiation of *tert*-Butyl Mercaptan in the Presence of Hydrogen Donors. Ethanol was dried over CaH_2, distilled, placed in a graduated cylindrical cell, and degassed thoroughly. Tetrahydrofuran (THF)

was dried over sodium, distilled, and degassed in a graduated cell. Freshly distilled *tert*-butyl mercaptan was similarly degassed and stored.

For each run, the approximate volume of *tert*-butyl mercaptan and hydrogen donor (ethanol or THF) necessary to make 3 mL of a solution of the approximate composition desired was transferred into a tared irradiation cell. The weight of each component of the solution was determined, and the precise ratio of reactants ([QH]/[RSH]) was calculated. The solution was degassed and irradiated (254 nm). Hydrogen and hydrogen sulfide yields were determined and the H_2/H_2S ratio was calculated. The results for the *tert*-butyl mercaptan/ethanol and *tert*-butyl mercaptan/THF mixtures are presented in Figure 1.

Irradiation of Cyclohexanethiol in the Presence of Nonane. Normal nonane (Phillips) was stirred with concentrated H_2SO_4, dried, and distilled. Analysis by UV showed the distillate to be essentially transparent at 254 nm. Three solutions of freshly distilled cyclohexanethiol in nonane were prepared in 10-mL volumetric flasks, in which the final [QH]/[RSH] ratios were respectively 5.02, 10.13, and 15.28. For each run, 2.5 mL of the appropriate solution was transferred by syringe into the irradiation cell, thoroughly degassed, and irradiated (254 nm, room temperature). Analysis of hydrogen and hydrogen sulfide, using trapping method C, was performed as described above. The results are presented in Figure 2. The value for [QH]/[RSH] = 0 is the average of several runs with neat thiol. The value for [QH]/[RSH] = 5.02 is the average of duplicate runs on the same solution.

Irradiation of *tert*-Butyl Mercaptan at 300 nm, 29 °C. A sample of neat, degassed *tert*-butyl mercaptan contained in a Pyrex vessel was irradiated at 29 °C with light from ten RPR-3000-A lamps for 18 h. The vessel was masked so only the liquid phase was exposed to light. Hydrogen and H_2S were distilled together from the reaction mixture at -131 °C and transferred to a gas sample cell. The ratio

of H_2 to H_2S was determined on a CEC-21 mass spectrometer by measurement of the intensity of the m/e 2 and 34 peaks, with reference to standard mixtures of the gases. The observed ratio of H_2 to H_2S was found to be 1.29.

Irradiation of *tert*-Butyl Peroxyformate (BUP) in *tert*-Butyl Mercaptan. *tert*-Butyl peroxyformate (BUP) was synthesized by the method of Ruchardt and Hecht[12] and purified by repeated washing of a pentane solution of BUP with water. The pentane solution was dried (MgSO₄) and concentrated (rotary evaporator). Analysis of the residue by NMR showed the composition to be 82% BUP, the remainder being *tert*-butyl alcohol. No formic acid was present.

Two Pyrex irradiation cells, each containing 4.0 mL of a 0.75 M solution of BUP in *tert*-butyl mercaptan, were thoroughly degassed. One cell was masked with aluminum foil so as to expose only the liquid; the other cell was completely masked with foil. The two cells were irradiated in parallel at 350 nm, at a temperature of 46 °C. Each cell was then analyzed for H_2 and H_2S. In the "dark" cell, neither H_2 nor H_2S was detected. The irradiated cell contained both H_2 and H_2S in a mole ratio of 1.04.

The experiment was repeated, using as a control a 4-mL sample of neat thiol irradiated in parallel with a cell containing 4 mL of a 0.54 M solution of BUP in thiol at 41 °C. The cell containing neat thiol produced no detectable amount of H_2 or H_2S; the BUP solution produced both H_2 and H_2S in the ratio of 0.99:1.

In another experiment, a solution of BUP in *tert*-butyl mercaptan (0.81 M) was irradiated in a water-jacketed irradiation cell, in which the temperature was maintained at 25.0 ± 0.05 °C. Other conditions of the irradiation were identical with those above. The ratio of H_2 to H_2S produced in this experiment was 1.41.

Results and Discussion

The products formed during the irradiation of several thiols are shown in Table I. In addition to the relative product yields for each thiol system, Table I lists the relative quantum yields (in arbitrary units) for the sum of H_2 and H_2S for each system. This quantity indicates the efficiency of the primary photochemical process(es) (cf. discussion below), and allows a comparison of the relative efficiencies of reaction. The reduced efficiency for thiophenol is to be expected, since the benzene ring itself may dissipate some of the excitation energy and also may act as a hydrogen scavenger.[13a]

In gas-phase studies,[4a] the wavelength of irradiation has been shown to affect the amount of H_2S produced. Therefore, neat liquid *tert*-butyl mercaptan was irradiated at 300 nm at 29 °C, and the relative amounts of H_2 and H_2S were determined. In contrast to the gas-phase study in which longer wavelengths produced less H_2S, the H_2S/H_2 ratio for neat liquid thiol was found to be somewhat greater using 300-nm light than the corresponding ratio for 254-nm irradiation (vide infra).

The detection of substantial yields of H_2S and hydrocarbon (RH) in all three thiols clearly requires that the simple reaction scheme of Carlson and Knight[6] be expanded to include the additional products. Hydrogen sulfide has been observed in the gas-phase photolysis of methanethiol[4c] and ethanethiol,[4a,b] and two mechanisms have been proposed to account for its formation. The first involves "sensitized" cleavage of the thiol carbon–sulfur bond by a vibrationally excited molecule, M*, followed by abstraction of a hydrogen atom from a thiol by the sulfhydryl radical.

$$RSH + M^* \rightarrow M + R\cdot + HS\cdot$$

$$HS\cdot + RSH \rightarrow RS\cdot + H_2S$$
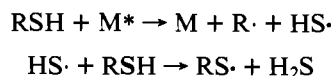
The second mechanism involves the direct photochemical cleavage of the thiol carbon–sulfur bond to generate the sulfhydryl radical. Hydrogen abstraction then gives rise to H_2S.
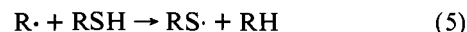
$$RSH \xrightarrow{h\nu} R\cdot + HS\cdot$$
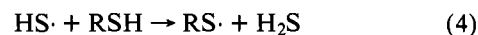
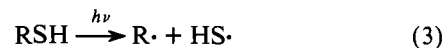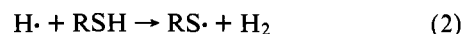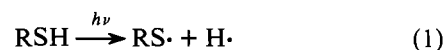$$HS\cdot + RSH \rightarrow RS\cdot + H_2S$$
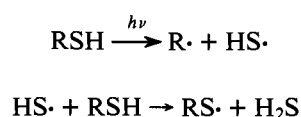
Although involvement of the vibrationally excited species of the "sensitized decomposition" mechanism is unlikely in the present condensed-phase reaction, the C–S photolysis mechanism cannot be eliminated a priori, especially since the C–S bond is weaker than the S–H bond by some 17–23 kcal/mol.[13b]

Finally, an additional mechanism, which amounts to a free-radical displacement by hydrogen on sulfur, must be considered. Although this mechanism has been ignored in the photochemical literature, it has been proposed for other thiol plus hydrogen atom systems,[7,9] and is analogous to a legion of "S_H2-type" displacements[14] on divalent sulfur by other radicals.[15]
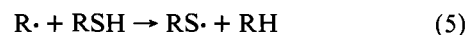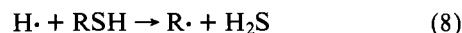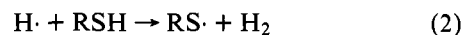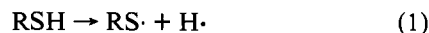
Thus, two mechanisms may be reasonably considered as accounting for the products observed in the present experiments. Scheme I contains two primary photochemical processes: S–H (eq 1) and C–S bond cleavage (eq 3). Hydrogen abstraction and radical–radical recombination then give rise to the observed products.

Scheme I

$$RSH \xrightarrow{h\nu} RS\cdot + H\cdot \tag{1}$$

$$H\cdot + RSH \rightarrow RS\cdot + H_2 \tag{2}$$

$$RSH \xrightarrow{h\nu} R\cdot + HS\cdot \tag{3}$$

$$HS\cdot + RSH \rightarrow RS\cdot + H_2S \tag{4}$$

$$R\cdot + RSH \rightarrow RS\cdot + RH \tag{5}$$

$$R\cdot + RS\cdot \rightarrow RSR \tag{6}$$

$$2RS\cdot \rightarrow RSSR \tag{7}$$

The alternative mechanism (Scheme II) contains only one primary photochemical process, S–H bond cleavage (eq 1). The hydrogen atom generated in eq 1 may then either abstract hydrogen (eq 2) or displace the R group from thiol (eq 8).

Scheme II

$$RSH \rightarrow RS\cdot + H\cdot \tag{1}$$

$$H\cdot + RSH \rightarrow RS\cdot + H_2 \tag{2}$$

$$H\cdot + RSH \rightarrow R\cdot + H_2S \tag{8}$$

$$R\cdot + RSH \rightarrow RS\cdot + RH \tag{5}$$

$$R\cdot + RS\cdot \rightarrow RSR \tag{6}$$

$$2RS\cdot \rightarrow RSSR \tag{7}$$

Solvent Dependence of the H_2/H_2S Ratio. In order to differentiate between these two mechanisms, thiols were irradiated in the presence of photochemically inert hydrogen donors (QH) which could compete with thiol in "trapping" the radical intermediates formed in the primary photolytic step:

$$H\cdot + QH \rightarrow Q\cdot + H_2 \tag{2a}$$

$$HS\cdot + QH \rightarrow Q\cdot + H_2S \tag{4a}$$
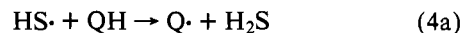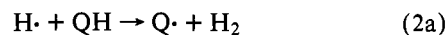
When these reactions are included in Scheme I the ratio of the rates of formation of H_2 and H_2S can be shown to be independent of the amount of added QH, provided that the efficiencies of the primary photolytic reactions (1 and 3) are unaffected by the addition of QH (vide infra). On the other hand, if eq 2a is added to Scheme II, addition of QH should divert the H atom from a hydrogen sulfide forming path (eq 8) to a hydrogen-forming path (eq 2a). Thus, in Scheme II the ratio of H_2 to H_2S formed in a given time is a linear function of the [QH]/[RSH] ratio:

$$\frac{[H_2]}{[H_2S]} = \frac{k_2}{k_8} + \frac{k_{2a}}{k_8}\frac{[QH]}{[RSH]} \tag{9}$$

Three thiol/QH systems were investigated: *tert*-butyl mercaptan/ethanol, *tert*-butyl mercaptan/THF, and cyclohexanethiol/*n*-nonane. For each system, mixtures of thiol and hydrogen donor were prepared and irradiated to low conversion (254 nm, room temperature), and the ratio of H_2 to H_2S was determined. Results of these experiments are presented in Figures 1 and 2. Clearly, the H_2/H_2S ratio does depend on the QH/RSH ratio as predicted by eq 9, implying the correctness of Scheme II.

The ability to distinguish between Schemes I and II by the use of added H atom trapping solvents depends on the assumption that the relative efficiencies of the two primary processes in Scheme I (eq 1 and 3) are unchanged by the added hydrogen donor, QH. The ultraviolet absorption spectra of thiols above 180 nm are generally characterized by two maxima centered around 200 and 230–240 nm. The former, relatively intense band ($\epsilon \simeq 1–2 \times 10^3$) has been identified as a $\sigma\sigma^*$ charge-transfer band consisting of an electronic transition from a bonding C–S orbital to an antibonding S–H orbital; the lower energy, less intense ($\epsilon \simeq 200$) band has been characterized as an $n\sigma^*$ transition, a transfer of an electron from a nonbonding orbital on sulfur to one of the antibonding molecular orbitals.[16]

On the basis of these spectral assignments and the dependence upon excitation wavelength of the H_2/H_2S product ratio in the photolysis of ethanethiol in the gas phase,[4a] as well as the observation of HS· as a transient in the gas-phase photolysis of methanethiol at 195 nm,[17] Knight has suggested[18] that the $n\sigma^*$ excited state associated with the 230-nm band leads to S–H bond cleavage (eq 1), while the $\sigma\sigma^*$ excited state associated with the 200-nm band leads to C–S cleavage (eq 3). In our studies of *tert*-butyl mercaptan and cyclohexanethiol we have observed a pronounced blue shift of the lower energy $n\sigma^*$ band when the solvent is changed from nonpolar (cyclohexane) to polar (ethanol). One might argue, therefore, that in a polar environment the energies of the two states are more nearly equal, and irradiation at 254 nm could lead to population of both excited states, so that both reactions 1 and 3 would be observed. (A similar argument has been advanced to explain the effect of solvent polarity on the reactivity of certain β,γ-unsaturated ketones.[19])

However, our results indicate that the H_2/H_2S ratio increases upon addition of both nonpolar and polar solvents, whereas polar solvents should produce a decrease in the H_2/H_2S ratio. Moreover, our observation that irradiation at 300 nm gives a lower H_2/H_2S ratio than does irradiation at 254 nm is contrary to the wavelength effect demanded by the preceding rationalization. (This observation can be easily explained when the temperatures of the two experiments are taken into account; see below.)

Relative Reactivities of Hydrogen Donors toward the H Atom. If Scheme II is indeed correct and eq 9 is valid, then the relative rates of reactions 2 and 2a, hydrogen abstraction from thiol and from QH, respectively, may be obtained from the slope and intercept of the plots of eq 9 in Figures 1 and 2. Comparison of the present results with those of other studies is hampered by a lack of uniformity among data obtained by different methods and in different laboratories, and some caution must be used. For example, the rate constant for reaction 2 (in aqueous solution) for cystein is reported by Navon and Stein[10] to be 7.4×10^8 M^{-1} s^{-1}, whereas that for 2-mercaptoethanol is given by Jayson et al.[20] as 1.7×10^9 M^{-1} s^{-1}.

Relative rate studies in these laboratories,[3d] in nonaqueous systems very similar to those used here, may be combined with absolute rate data compiled by Anbar and Netta[21] (taking into account a kinetic isotope effect of 1.60 at 25 °C[22]) to obtain a range of values of k_2 for *tert*-butyl mercaptan of 0.46 to 6.6 $\times 10^8$ M^{-1} s^{-1}, the average of four values being 3.2×10^8 M^{-1}

Table II. A Comparison of the Relative Rate Constants k_2 as Determined by Several Methods

Hydrogen donor (QH)	This work	Pryor and Stanley[a]	Aqueous radiolysis[b]
Nonane	(1)	(1)	(1)[c]
Ethanol	1.1 ± 0.3	0.5	1.3
Tetrahydrofuran	17 ± 4	4.2	2.4

[a] Reference 3d. [b] Compiled in ref 3d from the data of ref 21. [c] Nonane was not studied; this relative rate was estimated from the rate reported for 2,3-dimethylbutane, together with relative rate data reported in ref 3d.

s^{-1}. This range of values reflects the uncertainty in comparing aqueous and nonaqueous systems, where relative rates of reaction are not always parallel. It is noteworthy, however, that our rate constants for *tert*-butyl mercaptan (and for thiophenol as well[3d]) are all consistently lower than the rate constants found for aqueous systems.

Taking the average value of 3.2×10^8 M^{-1} s^{-1} for k_2, and the slopes and intercepts of the plots of Figures 1 and 2, the following rate constants for hydrogen abstraction are obtained: nonane, $1.0 \pm 0.03 \times 10^7$ M^{-1} s^{-1}; ethanol, $1.1 \pm 0.3 \times 10^7$; and THF, $1.7 \pm 0.5 \times 10^8$.

The value for nonane is in good agreement with that derived from an earlier determination under similar reaction conditions (1.1×10^7).[3d] The value for ethanol is somewhat higher than the value obtained in our previous study (0.6×10^7) but this is in line with our opinion that the earlier value appeared to be low on the basis of comparison with similar compounds.[3d] The rate for THF, however, appears to be substantially higher than that obtained from our earlier study (0.5×10^8) as well as that of the radiochemical literature (0.3×10^8).[21]

When the results are expressed on a relative basis,[23] to avoid the necessity of transferring absolute rate constant obtained in aqueous systems to organic solvents, the same trends are found. The rate constants for reaction 2a, relative to nonane, are presented in Table II along with comparable published determinations.

The relative reactivity of ethanol is within the agreement expected for data of this type, but THF appears to be abnormally reactive in our system. Anomalously high reactivity of THF toward hydrogen atoms, as well as toward other free radicals, has been noted before,[3d,21,24,25] although no satisfying explanation has been advanced. Comparison of the results obtained in these[24] and other laboratories[21] demonstrates that the observed rate of abstraction of hydrogen from THF by hydrogen atoms strongly depends on the source of the hydrogen atoms, the reaction medium, and other facets of the experimental design. This suggests that, at least in some systems, other processes besides those of Scheme II are important. In the present case, for example, one could envision a charge-transfer interaction between the $n\sigma^*$ excited thiol, with its electron-deficient sulfur atom, and THF. Subsequent proton transfer to the thiol radical anion (by analogy with the reaction of its ground-state counterpart[20]) from THF could then yield H_2 by a pathway not involving free H atoms at all. Alternatively, a concerted electron-transfer–proton-transfer reaction might be invoked, by analogy with reactions proposed for other systems involving THF and an electron acceptor.[25]

Whatever the details, it is clear that the occurrence of any process which produces H_2 without involving free H atoms will invalidate eq 9, and the value of k_{2a} calculated from it will be higher than the true rate constant for eq 2a. (In this context, it is noteworthy that a significantly lower value of k_{2a} for THF was obtained by a method in which thiol was not present.[24])

Reaction of *tert*-Butyl Mercaptan with Independently Generated Hydrogen Atoms. Direct and unambiguous evidence

for Scheme II was obtained from studies of the photochemical decomposition of *tert*-butyl peroxyformate (BUP) in the presence of *tert*-butyl mercaptan. The thermal[26] and photochemical[27,28] decompositions of BUP have been studied, and it has been shown that free hydrogen atoms are produced in the latter, but not the former, decomposition. Studies of hydrogen atom reactions in these laboratories[27,28] using the photolysis of BUP as a source of hydrogen atoms have given results quite comparable to those in which other methods of H-atom generation have been used.

Irradiation of a 0.75 M solution of BUP in *tert*-butyl mercaptan at 350 nm and a temperature of 41 °C produced both hydrogen and hydrogen sulfide in a mole ratio of 1:1 (± 0.05). When a similar solution was irradiated at 25.0 °C, the observed H_2/H_2S ratio was 1.41 ± 0.05.

Control experiments demonstrated that *tert*-butyl mercaptan was inert to irradiation at 350 nm. It was also shown that, although some thermal decomposition of BUP occurred at the temperature of the reaction (CO_2 was observed[26]), neither H_2 nor H_2S was produced in the dark reaction.

The observation of a larger proportion of H_2S in the BUP photolysis at 41 °C than was observed in the BUP photolysis at 25 °C continues the trend of temperature effects observed in the 254-nm (25 °C) and 300-nm (29 °C) direct thiol irradiations. The variation of the H_2/H_2S ratio (equal to the k_2/k_8 ratio, cf. eq 9) with temperature may be plotted according to the Arrhenius equation to obtain an estimate of the difference in activation energies of reactions 2 and 8, $\Delta E_a = E_8^\ddagger - E_2^\ddagger$, of 3.8 ± 0.3 kcal/mol. This result may be compared with a similar result obtainable from the radiolysis data of Armstrong et al.[7] for cysteine (at two temperatures only), where $\Delta E_a \simeq 6.6$ kcal/mol. Although the error in the ΔE_a estimate for cysteine cannot be determined for a two-point plot, the fact that ΔE_a for cysteine is higher than ΔE_a for *tert*-butyl mercaptan is qualitatively in agreement with our observation (cf. Table I) that k_8 decreases, relative to k_2, on going from a tertiary to a secondary thiol.[23] Thus cysteine, as a primary thiol, would be expected to have a still lower k_8/k_2 ratio. Given similar preexponential factors for corresponding reactions of all three thiols, this requires a larger ΔE_a for cysteine than for *tert*-butyl mercaptan.

Conclusion

The present study has demonstrated that the production of hydrogen sulfide is a general feature of the photolysis of thiols in the liquid phase. This finding contrasts with a previous report of the photolysis of ethanethiol in the liquid phase,[6] but it is consistent with the observation of hydrogen sulfide as a product in gas-phase photolysis[4] and of radiolysis of thiols in aqueous systems.[7,8]

Of the several mechanisms proposed to account for the cleavage of the C–S bond, our results clearly point to eq 8 in Scheme II, in which the C–S bond is cleaved by the attack of hydrogen atom on sulfur, as the major if not sole mechanism. Although analogous displacements on divalent sulfur in sulfides and disulfides are known to occur,[15] the present reaction is the only one, to our knowledge, in which such a displacement has been shown to be competitive with abstraction of the labile sulfhydryl hydrogen.

The present results also indicate the presence of other, as yet unidentified reactions between the photoexcited thiol and tetrahydrofuran. An unusual reactivity of THF has been noted by us[3d] as well as by Ahlgren.[25] Perhaps these thiol–THF photoreactions are responsible for the discrepancies involving THF reactivities.

References and Notes

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