activation energy for hydrogen atom transfer from SiH₄ and GeH₄ to H by 3.2 and 3.1 kcal/mol, respectively, for Si-H and Ge-H bond energies of 98.3 and 90.2 kcal/mol, respectively. The generality of this new potential function remains however to be established.)

- (26) That hydrogen atoms may add to silane giving SiH_5 was suggested to P.P.G. by the late Professor Richard Wolfgang in 1970.
- (27) The relative rate of hydrogen abstraction from silane by deuterium atoms compared with the rate of addition of deuterium atoms to perdeuterioethylene obtained by Obi et al.^{3a} has been combined with our absolute value for addition of hydrogen atoms to ethylene for the purpose of comparing the absolute rate of hydrogen abstraction deduced by Obi et al. with our own.

Reaction of Hydrogen Atoms with Thiirane

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Hydrogen atoms, produced from the mercury photosensitization of H_2 , react with thiirane to yield ethylene and hydrogen sulfide as the only retrievable products with quantum yields of 2.46 and 0.40, respectively, at room temperature. The sole primary reaction occurring is sulfur atom abstraction, $H + C_2H_4S \rightarrow HS +$ C_2H_4 (1). The rate coefficient of reaction 1 was determined in competition with the reaction $H + H_2S \rightarrow$ $H_2 + HS$ to have the value $k_1 = (5.7 \pm 0.7) \times 10^{13} \exp((-1944 \pm 175)/RT) \text{ cm}^3 \text{ mol}^{-1} \sec^{-1}$. It is shown that at room temperature 41% of the HS radicals undergo disproportionation, $2HS \rightarrow H_2S + S(^{3}P)$, while the rest are scavenged by mercury atoms, $Hg + SH + M \rightarrow \frac{1}{2}(HgSH)_2 + M$, and perhaps the S_{2-7} and HS_{3-7} radicals present in the system. The relative importance of disproportionation decreases with increasing temperature.

The desulfurization of thiiranes in the liquid phase by nucleophilic reagents such as tertiary phosphines,² tertiary phosphites,³ alkyl lithium, and aryl lithium⁴ has been reported. More recently studies on radical reactions in the gas phase with thiiranes also appeared. Desulfurization has been shown to occur upon attack by $S(^{3}P)$, $S(^{1}D_{2})^{5}$, carbon atoms,⁶ and excited triplet state thiiranes.⁷ In the case of the *tert*-butoxy radical + methylthiirane system,⁸ hydrogen abstraction was the only observable reaction.

The reactions of methyl radicals with thiirane, methylthiirane, and dimethylthiirane have been reported in recent studies from this laboratory.⁹ In all three cases there are two primary steps which occur parallel and in competition: hydrogen abstraction and sulfur abstraction. The latter is unique in that it is the first known example of a reaction wherein a divalent atom in a bridgehead position is abstracted by a monovalent radical. All desulfurization reactions feature a high degree of stereospecificity and probably occur in a single step, concerted process.

In order to ascertain whether the desulfurization reaction is common to other monovalent radicals the reaction of hydrogen atoms with thiirane was examined. The results are presented in this article.

Experimental Section

The apparatus, general vacuum, and analytical techniques were similar to those employed in previous studies. 9,10

Hydrogen atoms were produced by the mercury photosensitization of H₂. The light source was a low-pressure Hg resonance lamp equipped with a 253.7-nm interference filter and a collimating quartz lens. The cylindrical quartz reaction cell (5 \times 10 cm) was enclosed in an aluminum

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block furnace and connected to a circulatory system having a total volume of 510 cm^3 . Circulation was effected by a fan type, magnetically driven pump.

Pressures of thiirane and hydrogen sulfide were always very much smaller than that of hydrogen in order to avoid direct or Hg sensitized decomposition.

Light intensities, as in the previous study of the H + COS reaction,¹⁰ were determined by propane and nitrous oxide actinometry. The mean value of the absorbed intensity was about 0.03 μ einstein min⁻¹.

The reaction mixtures consisting of $H_2 + C_2H_4S$ or $H_2 + H_2S + C_2H_4S$ were equilibrated by circulation for 20 min prior to irradiation. After each experiment the cell window was thoroughly baked. At the conclusion of irradiation the excess hydrogen was pumped off through traps cooled with liquid nitrogen and solid nitrogen. Ethylene and hydrogen sulfide were distilled from the reaction mixture at -130° . In the runs with added hydrogen sulfide, ethylene was distilled at -161° . The yields of C_2H_4 and H_2S were determined by gas chromatography on a 6-ft silica gel column at 90° using He as carrier.

The upper limit of the reaction temperature, 150°, was determined by the thermal decomposition of thiirane.

Materials in general were the best grades available commercially. Hydrogen (Matheson, 99.999%) was used without purification. Hydrogen sulfide (Matheson) was purified by distillation at -130° and degassing at -196° . Thiirane (Aldrich, 99%) was distilled at -78° and degassed at -130° . It was stored in the dark at -78° .

Results and Discussion

The $Hg(^{3}P_{1})(Hg^{*})$ photosensitization of hydrogen and thiirane mixtures leads to the formation of $C_{2}H_{4}$, $H_{2}S$, and

TABLE I: Quantum Yields for H_2S and C_2H_4 Formation as a Function of Exposure Time^a

Time, min	$I_a \times 10^8$ Einstein/min	$\phi(C_2H_4)$	$\phi(H_2S)$		
15	3.19	2.49	0.39		
30	3.15	2.47	0.39		
45	3.11	2.46	0.40		
60	3,07	2.44	0.41		
90	2.98	2.42	0.42		
a D(II) = c		rm m 059			

 $^{a}P(H_{2}) = 500 \text{ Torr}, P(C_{2}H_{4}S) = 5 \text{ Torr}, T = 27^{\circ}.$

TABLE II: Rates of Formation of C_2H_4 and H_2S as a Function of Thiirane Pressure^a

	Rates, $\times 10^8$ mole/min			
$P(C_2H_4S),$ Torr	C_2H_4	H ₂ S		
1.00	7.05	1.22		
2.15	8.13	1.38		
2.01	7.28	1.27		
3.03	7.47	1.34		
5.20	7.65	1.01		
5.09	7.13	1.19		
4.81	8.03			
5.32	7.60	1.30		
7.22	7.82	1.27		

 $^{a}P(H_{2}) = 490 \pm 10$ Torr, $T = 27^{\circ}$, exposure time = 60 min.

elemental sulfur which forms a solid deposit on the cell window. Ethanethiol, a possible product, was demonstrably absent.

First the quantum yields of C_2H_4 and H_2S were determined as a function of exposure time. In order to correct for the change in window transparency due to sulfur deposition during photolysis, light intensities were measured before and after each irradiation and the mean values were used to compute the quantum yields. The data compiled in Table I show that within experimental error, approximately $\pm 3\%$, the quantum yields determined this way are independent of the time of irradiation.

The effect of thiirane pressure on product yields was examined in a series of experiments by varying the pressure of thiirane between 1 and 7 Torr at a fixed hydrogen pressure of 490 Torr. The results are presented in Table II. Even at 1 Torr pressure the scavenging of hydrogen atoms appears to be complete and within the error limits of the experiments an increase in the pressure of thiirane has no significant effect on product yields.

The quantum yield data obtained at 96 and 152° are tabulated in Table III and the mean values for the three temperatures are given in Table IV.

Under the experimental conditions of the present study the excited mercury atoms are totally quenched by hydrogen

$$Hg^* + H_2 \rightarrow Hg + 2H$$

 $Hg^* + H_2 \rightarrow HgH + H$

The quantum yield of HgH formation has been reported to be high,¹¹ 0.67, but the lifetime of HgH with respect to dissociation is short and overall kinetics would be indistinguishable from those of H atoms. Thus the system can be treated as a source of H atoms with $\phi(H) = 2.0.^{12}$

TABLE III: Quantum Yields for	C_2H_4 and
H ₂ S Formation at 96 and 152° ^a	

T, °C	$\begin{array}{c} P(\mathbf{C}_{2}\mathbf{H}_{4}\mathbf{S}),\\ \mathbf{Torr} \end{array}$	$\phi(C_2H_4)$	$\phi(H_2S)$
96	5.4	2.38	0.39
96	5.4	2.29	0.38
96	5.0	2.33	0.36
96	4.9	2.38	0.41
96	5.0	2.55	0.39
152	5.5	2.25	0.16
152	5.2	2.22	0.16
152	5.1	2.27	0.21
152	5.1	2.19	0.22

^a Exposure time 60 min.

TABLE	IV: Mean	Values of	Quantum	Yields for
C ₂ H₄ and	d H ₂ S For	mation as	a Function	n of Temperature

Temp, °C	$\phi^0(C_2H_4)$	$\phi^0(\mathrm{H_2S})$	$ \begin{array}{c} \phi^{0}(C_{2}H_{4}) - \\ \phi^{0}(H_{2}S) \end{array} $
27	2.46 ± 0.03	0.40 ± 0.01	2.06
96	$\textbf{2.39} \pm \textbf{0.07}$	$0.39~\pm~0.01$	2.00
152	$\textbf{2.23} \pm \textbf{0.03}$	0.19 ± 0.03	2.04
$a D(\mathbf{H}) =$	400 • 10 Tom P(C)	$\mathbf{U} = \mathbf{E} 0 + 0 \mathbf{T}_{0}$	m +0'a damata

^a $P(H_2) = 490 min 10$ Torr, $P(C_2H_4S) = 5.2 \pm 0.2$ Torr. ϕ^{0} 's denote ϕ 's from H₂-C₂H₄S system.

The nature and yields of the observed products can be accounted for in terms of the following sequence of elementary steps:

 $H + C_2 H_4 S \rightarrow HS + C_2 H_4 \tag{1}$

$$2HS \rightarrow H_2S + S(^3P) \tag{2}$$

$$S(^{3}P) + C_{2}H_{4}S \rightarrow S_{2} + C_{2}H_{4}$$
(3)

$$S_2 + S_2 + M \rightarrow S_4 + M \tag{4}$$

$$S_2 + S_4 + M \rightarrow S_6 + M \tag{5}$$

$$S_2 + S_4 \rightarrow 2S_3 \tag{6}$$

$$S_2 + S_3 + M \rightarrow S_5 + M \tag{7}$$

$$S_3 + S_4 + M \rightarrow S_7 + M \tag{8}$$

$$HS + S_2 + M \rightarrow HS_3 + M \tag{9}$$

$$HS + S_{3-7} \to HS_2 + S_{2-6}$$
(10)

$$HS_3 + S_3 \rightarrow HS_2 + S_4 \tag{11}$$

 $HS_2 + HS \rightarrow H_2S + S_2(^{3}\Sigma_g^{-}, {}^{1}\Delta_g {}^{1}\Sigma), \text{ etc.}$ (12)

$$HS + Hg + M \rightarrow HgSH + M$$
 (13)

$$2HgSH + M \rightarrow (HgSH)_2 + M$$
(14)

$$HgSH + SH + M \rightarrow Hg(SH)_2 + M$$
 (15)

Scavenging of the H and S atoms by thiirane at the concentrations involved is complete. Consequently the yield of C_2H_4 from step 3 is equal to that of H_2S , and $\phi(C_2H_4)$ from reaction 1 should be equal to $\phi(C_2H_4) - \phi(H_2S)$. The values for this quantity, given in the last column of Table IV, are equal to two, within experimental error, at the three temperatures studied and we are forced to conclude that the only primary mode of interaction between H atoms and thiirane is sulfur atom abstraction, step 1.

<i>T</i> , [∞] C	$P(H_2)$, Torr	$P(C_2H_4S),$ Torr	P(H ₂ S), Torr	$P(H_2S)/P(C_2H_4S)$	$R_{C_2H_1}$, 10 ⁻⁸ mol/min	$\phi(\mathbf{C}_{2}\mathbf{H}_{1})$) '
27	485	4.33	1.05	0.242	7.25	2.36	0.513
	474	3.02	1.02	0.300	7.37	2.40	0.503
	502	4.89	4.89	1.00	6.77	2.21	0.556
	487	3.00	3.02	1.00	6.42	2.09	0.595
	505	2.89	5.63	1.95	5.72	1.87	0.685
	490	3.05	5.97	1.96	5,82	1.90	0.671
96	488	3.07	0.998	0.325	7.23	2.36	0.508
	496	2.97	2.89	0.973	6.30	2.05	0.602
	458	3.02	3.07	1.02	6.67	2.17	0,562
	424	3.00	3.10	1.03	6.43	2.10	0.585
	486	3.00	5.97	1.99	5.68	1.85	0.685
	441	2.77	5.91	2.13	5.77	1.88	0.671
152	496	3.10	0.95	0.306	6.63	2.16	0.508
	498	2.94	0.97	0.330	6.38	2.08	0.529
	503	2.41	0.88	0.365	6.58	2.14	0.513
	497	3.43	3.00	0.875	6.20	2.02	0.546
	476	3.02	3.00	0,993	5.69	1.85	0.602
	499	3.00	3.20	1.07	5,98	1.95	0.568
	505	3.05	5.86	1.92	5.22	1.70	0.662
	504	3.02	5.99	1.98	5,28	1.72	0.654
	499	2.89	5.89	2.04	5.13	1.67	0.676

TABLE V: Rate of C_2H_4 Formation as a Function of $P(H_2S)/P(C_2H_4S)^a$

^a Exposure time, 60 min.

With regard to reaction 2, a recent study of the photolysis of hydrogen sulfide established a quantum yield value of unity for hydrogen production¹³ suggesting that the only important mode of interaction between two sulfhydril radicals is disproportionation into $S + H_2S$ and that hydrogen or H_2S_2 are not produced in significant yields. The present results shed additional light on the fate of the HS radical the two plausible scavengers of which are the sulfur or sulfhydril radicals and mercury atoms according to the scheme indicated by reactions 9-15. Mercurous sulfhydride is a poorly characterized compound the synthesis of which has been reported^{14,15} in 1928 from the reaction of solid mercurous chloride with liquid hydrogen sulfide. In the interpretation of the present results cognizance must be taken of the data obtained in recent studies on the photolysis of hydrogen sulfide¹³ in the presence and absence of mercury. The mercury free photolysis gave a quantum yield value of unity for both hydrogen formation and hydrogen sulfide disappearance the latter determined from the yield of solid, elemental sulfur. In the presence of mercury vapor, however, while the yield of hydrogen remained unaffected, the yield of sulfur in the solid film which coated the cell wall increased by 19-29%. This yield increase in the sulfur content of the solid is attributed to the formation of $(HgSH)_2$ and perhaps $Hg(SH)_2$ via reactions 13-15. Therefore, we conclude that the principal scavengers of the sulfhydril radical in the present system are the mercury atoms. If scavenging by the sulfur or sulfhydril radicals occurs at all it must be via complexing with thiirane, C₂H₄S. SH, $C_2H_4S \cdot S_x$, $C_2H_4S \cdot S_xH$, since the pure hydrogen sulfide system where S_x radicals are also present, scavenging is inefficient. The presence of small concentrations of the HS_2 radical in flash photolyzed hydrogen sulfide and the production of $S_2({}^1\Delta_g)$ in the self-disproportionation reactions of HS_2

$$2\mathrm{HS}_2 \to \mathrm{H}_2\mathrm{S}_2 + \mathrm{S}_2(^1\Delta_\mathrm{g}) \tag{16}$$

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and its cross disproportionation, step 12, have been demonstrated in previous flash spectroscopic studies.¹⁶ Also, the presence of small concentrations of H_2S_2 in flashed H_2S was detected earlier by kinetic mass spectrometric techniques.¹⁷ The detection of small concentrations of H_2S_2 and presumably of all higher polysulfides by conventional analytical techniques is exceedingly difficult and unreliable owing to their well-known tendency to undergo surface decomposition to yield H_2S and elemental sulfur.

It is interesting to note that the relative rates of scavenging and disproportionation of the HS radical are temperature dependent and scavenging becomes more important with increasing temperature. This may be due to a slight increase in the mercury vapor concentration at elevated temperatures.

Reaction 3 is very rapid, its rate coefficient being 1.7–2.7 $\times 10^{13}$ cm³ mol⁻¹ sec⁻¹.^{5,18}

In order to determine the rate coefficient of reaction 1, competitive studies were carried out with added H_2S , in which the ratio of H_2S to thiirane pressure was varied between 0.2 and 2 at a constant hydrogen pressure of 500 Torr. The ethylene yields obtained at 27, 96, and 152° are given in Table V.

Steady-state treatment of the competing reactions 1 and

$$H + H_2 S \rightarrow H_2 + HS \tag{17}$$

leads to the following kinetic expression:

$$\gamma = [\phi(C_2H_4) - \phi^0(H_2S)]^{-1} = 0.50 + \frac{k_{17}}{2k_1} \frac{P(H_2S)}{P(C_2H_4S)}$$
(I)

As the yield of HS per hydrogen atom produced is unaffected by the H_2S to C_2H_4S ratios, the value of γ can be obtained from the measured yield of C_2H_4 and the H_2S yields $\phi^0(H_2S)$, from the $H_2-C_2H_4S$ system.

From the plots of γ vs. $P(H_2S)/P(C_2H_4S)$, shown in Figure 1, it can be seen that eq I is obeyed and the slope and

intercept values obtained by least mean square treatment of the data are given in Table VI. Plotting the logarithm of k_1/k_{17} values against 1/T, Figure 2, the activation energy difference and A factor ratio of reactions 17 and 1 are found to have the values: $E_1 - E_{17} = 235 \pm 115$ cal mol⁻¹ and 7.3 \pm 1.2, respectively. If Braun and coworkers'¹⁹ values of $E_{17} = 1709$ cal mol⁻¹ and $A_{17} = 7.78 \times 10^{12}$ cm³ mol⁻¹ sec⁻¹ are accepted,²⁰ then for the Arrhenius parameters of reaction 1 we obtain

$$k_1 = (5.7 \pm 0.7) \times 10^{13} \exp((-1944 \pm 175)/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$$

These values appear to be reasonable when compared to those of other, similar reactions, which are compiled in Table VII. The entropies of activation given in Table VII were obtained by the method of Benson.²¹ To calculate the entropy of the H…SJ activated complex we start with the



Figure 1. $\gamma = (\phi_{C_2H_4} - \phi_{H_2S}^0)^{-1}$ plot against $P_{[H_2S]}/P_{[C_2H_4S]}$.

TABLE VI: Slopes and Intercepts from γ vs. $P(H_2S)/P(C_2H_4S)$ Plots

<i>T</i> , °C	Slope, $k_{17}/2k_1$	Intercept		
27	0.101 ± 0.006	0.478 ± 0.008		
96	0.0942 ± 0.0082	0.485 • 0.011		
152	0.0899 ± 0.0051	0.485 ± 0.007		

S1 molecule. If the $C_{2\nu}$ symmetry is retained there will be a contribution of $R \ln 2$ from spin only, because the increase in the moments of inertia is negligible:

$$S^{\circ \ddagger} = S^{\circ}(S^{\triangleleft}) + 1.4 \text{ eu}$$

and the entropy of activation

$$\Delta S_{p}^{\ddagger} = S^{\circ}(S^{\ddagger}) + 1.4 - S^{\circ}(S^{\ddagger}) - S^{\circ}(H) = 1.4 - 27.4 = -26.0 \text{ eu}$$

or, by transformation to the standard state of 1 M

$$\Delta S_{c}^{\dagger} = \Delta S_{p}^{\dagger} - R\Delta n - (\Delta n)R \ln (RT) = -17.6 \text{ eu}$$

This value differs from the experimentally obtained entropy of activation by 6.3 eu. The difference can be assigned to the contribution from the degenerate bending modes of the new H...S bond corresponding to a vibrational frequency of 125 cm^{-1} which seems to indicate a rather loose structure for the activated complex.

If the C_{2v} symmetry is lost in the activated complex, as is probably the case,⁹ another $R \ln 2$ term must be added to estimate the absolute $S^{\circ \ddagger} = S^{\circ}(S \triangleleft) + 2.8$ eu, and the entropy of activation $\Delta S_p^{\ddagger} = 2.8 - 27.4 = -24.6$ eu or $\Delta S_c^{\ddagger} = -16.2$ eu. The difference from the experimental entropy of activation is now only 4.9 eu indicating somewhat stiffer H-...S bending modes with frequencies of about 200 cm⁻¹.



Figure 2. Arrhenius plot for S abstraction from ethylene episulfide by H atoms.

Reaction	$A_{t}, \operatorname{cm}^{3}$ mol ⁻¹ sec ⁻¹	E _f , kcal mol ⁻¹	$S_{\mathbf{f}}^{\dagger}$, eu	Ref	$A_{\rm r}, {\rm cm}^3$ mol ⁻¹ sec ⁻¹	E_r , kcal mol ⁻¹	ΔS_r^{\dagger} , eu
$CH_3 + S \xleftarrow{t}{CH_3S} + CH_3S + C_2H_4$	7.08×10^{10}	6.7	-24.6 (C _{2v})	10	8.65×10^{9}	18.5	-28.8
$CH_3 + COS \stackrel{f}{\leftarrow r} CH_3S$	3.80×10^{11}	11.35	-21.3	10	3.34×10^{10}	9.65	-26.1
$CH_3 + H_2S \stackrel{f}{\longleftarrow} CH_4 + HS$	$\textbf{5.00}\times \textbf{10}^{10}$	2.9	-25.3	25	3.94×10^{11}	16.0	-21.2
$\overline{}$							
$H + S \xrightarrow{f} HS + C_2H_1$	5.66×10^{13}	1.9	$-11.3 (C_{2v})$	This	$2.78 imes 10^{11}$	26.8	-21.9
$H + COS \stackrel{f}{\longleftarrow} HS +$	9.10×10^{12}	3.9	-15.0	11 NOTK	3.17×10^{10}	15.3	-26.2
$H + H_2 S \xleftarrow{f}{r} HS + H_2$	7.77×10^{12}	1.7	-15.3	18	4.0×10^{12}	15.0	-16.6

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The Arrhenius parameters and activation entropies for the reverse of the reactions listed in Table VII were also calculated and are presented in the last three columns of Table VII

As was noted before, all the known desulfurization reactions of thiiranes feature a high degree of stereospecificity from which it has been inferred that they proceed via single step, concerted reactions. The CH₃ and H reactions with thiiranes are further characterized by the complete absence of the addition products, the thio ether and thiol radicals, $CH_3SCH_2CH_2$ and $HSCH_2CH_2$, respectively. It is likely that in the $H + C_2H_4S$ system the initial interaction involves the nonbonding 3p orbital of the S atom



leading to a symmetrical transition state. The potential energy of activation for a symmetrical pull of the sulfur using a modified form of the bond energy-bond order method,^{9,22} was found to be 4 kcal/mol if the sulfur atom is assumed to be transferred in its lowest lying (¹D₂) state or zero if the transfer is in the $({}^{3}P_{2})$ ground state. In agreement with the earlier results on the $CH_3 + COS$ and $CH_3 + S rates systems^9$ the experimental value lies close to the arithmetic mean of the computed limits.

In conclusion it should be noted that the analogous deoxygenation reactions with oxirane have not been observed; hydrogen atoms,²³ CH₃,²⁴ and CF₃²⁵ radicals react with oxirane by hydrogen abstraction although energetically, oxygen abstraction would be more favorable. This difference between the chemical behavior of oxiranes and thiiranes has been interpreted⁹ as being due to the higher value of the activation energy for the deoxygenation of oxiranes as compared to desulfurization of thiiranes. The higher activation energy in turn is a consequence of the somewhat lower exothermicity, more stringent obeyance of spin conservation in the reaction, and the higher value of the excitation energy of the ${}^{1}D_{2}$ state of the oxygen than sulfur atom.

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