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Abstraction of Sulfur Atoms from Carbonyl Sulfide by Atomic Hydrogen

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The reaction of H atoms, produced by the mercury photosensitized decomposition of H₂, with COS was investigated in the temperature range 27-252°. The only primary reaction of importance is $H + COS \rightarrow CO$ + SH (1). The rate coefficient of reaction 1 was determined in competition with the reaction H + $H_2S \rightarrow$ $H_2 + SH$ to have the value $k_1 = (9.1 \pm 1.2) \times 10^{12} \exp((-3900 \pm 370)/RT) \text{ cc mol}^{-1} \text{ sec}^{-1}$.

Introduction

Relatively few studies have been reported on the reaction of hydrogen atoms with sulfur compounds.¹

In a concurrent study at this laboratory² the only detectable reaction of hydrogen atoms with ethylene episulfide was found to be sulfur atom abstraction with a rate coefficient of 5.6 \times 10¹³ exp(-1940/RT) cc mol⁻¹ sec⁻¹. The analogous sulfur atom abstraction from carbonyl sulfide

$$COS + H \longrightarrow CO + SH \qquad \Delta H = -9.8 \text{ kcal mol}^{-1}$$
 (1)

was demonstrated by Oldershaw and Porter³ and by Rommel and Schiff.⁴ The latter authors reported a value for k_1 of 1.3×10^{10} cc mol⁻¹ sec⁻¹ at 298°K.

The main purpose of the present study was to determine the Arrhenius parameters of reaction 1 and to examine its kinetic, mechanistic features.

Experimental Section

The apparatus consisted of a 5×10 cm quartz cell fitted to a circulatory system with total volume of 510 ml. The fan type circulator was constructed of glass and Teflon and was driven by an induction motor. A small side arm containing liquid mercury at room temperature was connected close to the cell. The cell itself was surrounded by an aluminum block furnace which was fitted with pencil heaters;

the temperature was measured by standardized iron-constantan thermocouples.

The light source was a Hanovia low-pressure mercury arc equipped with a 2537-Å interference filter and a collimating quartz lens.

Hydrogen atoms were produced by the mercury photosensitized decomposition of hydrogen. In most experiments the pressure of hydrogen was kept at 500 \pm 20 Torr and the pressure of COS and/or H₂S at less than 10 Torr. At these concentrations the direct photolysis or mercury sensitized decomposition of COS or H_2S was negligible. Thermolysis of COS could also be discounted since the onset of decomposition lies higher than the highest temperature, 252°, employed.5

Carbonyl sulfide (Matheson) was purified as described previously.⁶ H_2 (Matheson, stated purity 99.9%) was used as received. H_2S (Matheson) was purified by bulb-to-bulb distillation at -130° .

After irradiation, the reaction mixture was slowly pumped through two 5-ft long spiral traps at -196° , the second one being packed with molecular sieve. Carbon monoxide and traces of hydrogen were then removed from the second trap at 100°, measured in a gas buret, and transferred to a copper oxide furnace at 380°. The resulting carbon dioxide was then analyzed by gas chromatography on a 5-ft long Porapak Q column at 50°.

				rormation"			
Pressure,	Torr						
H_2S	COS	H_2S/COS	φ(CO)	1/¢(CO)			
27°							
1.01	15.8	0.064	0.581	1.72			
1.01	10.4	0.097	0.450	2.22			
1.02	10.0	0.102	0.395	2.53			
1.02	10.0	0.102	0.391	2.56			
1.03	10.0	0.103	0.441	2.27			
1.04	10.0	0.104	0.420	2.38			
1.05	10.0	0.105	0.422	2.37			
1.01	5.21	0,194	0.251	3,98			
1.02	5.18	0.197	0.269	3.72			
2.08	10.34	0.201	0.273	3,66			
1.04	4.13	0.252	0.214	4.67			
0.998	3.38	0.295	0.187	5.36			
1.02	3.37	0.303	0.181	5.54			
1.02	3.37	0.303	0.160	6.25			
1.03	3.40	0.303	0.169	5.91			
1.02	3.36	0.304	0.168	5.96			
1.03	3.31	0.311	0.183	5.45			
2.06	6.00	0.343	0.156	6.41			
1.02	2.60	0.392	0.140	7.14			
81°							
1.03	9.75	0.103	0.592	1.69			
1.01	10.0	0.101	0.606	1.65			
1.01	5.26	0.192	0.386	2.59			
1.01	3.34	0.302	0.281	3.56			
1.05	3.37	0.312	0.259	3,86			
		121°					
1.04	9.96	0.104	0.754	1.33			
1.05	10.0	0.105	0.679	1.47			
1.01	9.37	0.108	0.734	1.36			
1.00	5.23	0.191	0.512	1.96			
1.01	5.23	0.193	0.529	1.89			
1.01	3.32	0.304	0.370	2.70			
		252°					
1.01	10.6	0.095	1.12	0.893			
1 02	10.0	0.102	1.04	0.961			
1.02	10.0	0.103	0.935	1.07			
1.05	10.0	0.105	0.992	1.01			
1.00	5 23	0.193	0.810	1.23			
1.01	3 32	0.304	0.592	1.69			
- 10 - 200	10.02	0.001	J.00	1100			

 TABLE I: Effect of Temperature and H₂S-COS

 Concentration on the Quantum Yield of CO Formation^a

 $^{a}P_{\mathrm{H}_{2}}=500\pm10$ Torr.

Light intensities were determined by propane actinometry⁷ using $\phi(H_2) = 0.58$ at 27°. The approximate value of the maximal absorbed intensity was 3×10^{-8} einstein min⁻¹.

Results

The $Hg(^{3}P_{1})$ (Hg*) photosensitization of hydrogen and carbonyl sulfide mixtures at room temperature leads to the formation of CO, H₂S, sulfur, and HgS. The latter product is deposited on the cell face in the form of a thin black film, decreasing the window transparency, and attenuating the absorbed light intensity. The attenuation, which rendered quantitative product yield measurements difficult, was more serious at room temperature than at elevated temperatures. In order to correct for the gradual changes in trans-



Figure 1. –Log *I*//₀ as a function of irradiation time for $P_{\rm COS} = 10.0$ Torr, $P_{\rm H_2S} = 0$ (O); $P_{\rm H_2S} = 1.0$ Torr, $P_{\rm COS} = 10.0$ Torr (\bullet); $P_{\rm H_2S} = 1.0$ Torr, $P_{\rm COS} = 3.36$ Torr (\bullet), $P_{\rm H_2} = 500 \pm 20$ Torr in every case.



Figure 2. Corrected ϕ_{CO} as a function of irradiation time. From top to bottom, $P_{H_2S} = 0$, $P_{COS} = 10$ torr ($\phi_{CO} = 1.21$); $P_{H_2S} = 1.0$ Torr, $P_{COS} = 10.0$ torr ($\phi_{CO} = 0.41$); $P_{H_2S} = 1.0$ Torr, $P_{COS} = 3.36$ Torr ($\phi_{CO} = 0.17$); $P_{H_2} = 500 \pm 20$ Torr in every case.



Figure 3. ϕ_{CO} as a function of P_{COS} for $P_{H_2} = 480$ Torr (O) and 1005 Torr (\bullet).

parency, actinometric determinations of light intensities were done before and after photolyses.

The results of a series of experiments in which the photolysis time was varied using $COS-H_2$ and $COS-H_2S-H_2$ mixtures are shown in Figure 1. The plot of log (I/I_0) vs. irradiation time, where I_0 and I are the initial and final intensities, is linear, satisfying the relationship $-\log (I/I_0) = (\beta/2.303)t$. Absorbed light intensities in the quantum yield determinations were then calculated using the integrated form of the above equation

$$I(t) = I_0 (1 - e^{-\beta t}) / \beta$$
 (I)

where $\beta/2.303$ is the slope of the plot in Figure 1. The corrections at a fixed pressure of hydrogen, 500 Torr, were independent of the COS concentrations used or of the presence of added hydrogen sulfide.

The quantum yields of CO formation were determined as a function of COS concentration at a fixed pressure of hydrogen. The measured yields became independent of the exposure time only when they were corrected for light intensity attenuation by eq I, Figure 2. From the plot in Figure 3, it is seen that the limiting value of $\phi(CO)$ is about 1.45 at COS pressures above 30 Torr in 500-1000 Torr of hydrogen.

In order to determine the value of the absolute rate coefficient for reaction 1, competitive experiments were carried out with added hydrogen sulfide. The quantum yields of CO formation were monitored as a function of the $[H_2S]/$ [COS] ratios at four different temperatures. The results are compiled in Table I.

Discussion

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

$$\begin{array}{rcl} Hg^{*} &+ H_{2} \longrightarrow Hg + 2H \\ Hg^{*} &+ H_{2} \longrightarrow HgH + H \end{array}$$

Although the quantum yield of HgH formation is high, 0.67,⁸ the lifetime of HgH with respect to dissociation is short and the overall kinetics would be indistinguishable from that of H atoms. Thus, the system can be treated as a source of H atoms with $\Phi(H) = 2.0.9$

The principal elementary reactions occurring in the $H_2S-COS-H_2$ mixtures are

$$H + COS \longrightarrow CO + HS$$
 (1)

$$H + H_2 S \longrightarrow H_2 + HS$$
 (2)

$$2HS \longrightarrow H_2S + S(^3P)$$
(3)

$$2HS + M \longrightarrow H_2S_2 + M$$
 (4)

 $HS + M \longrightarrow H_2S_2 + M$ $2HS \longrightarrow H_2 + S_2$ (4)
(5)

$$S(^{3}P) + COS \longrightarrow CO + S_{2}$$
 (6)

If scavenging of the H and S atoms by COS were complete at the concentrations involved, this mechanism would predict a quantum yield of CO formation of between two and three. As the experimental value of $\phi(CO)$ is only 1.45, it is evident that the scavenging of neither atoms is complete. Complete scavenging of both atoms was achieved in the analogous system H₂-Hg*-ethylene episulfide; there, the quantum yield of ethylene formation via the abstraction reactions

$$H + C_2H_4S \longrightarrow C_2H_4 + HS$$
(7)
$$S(^{3}P) + C_2H_4S \longrightarrow C_2H_4 + S_2$$

had a value of 2.4, and it was also shown that at room temperature 41% of the HS radicals disappeared via the disproportionation step 3^2 and the remainder via steps 4 and 5 and by combination reactions with the S_2 - S_7 sulfur radicals and S_3 H- S_7 H sulfhydril radicals present as transient intermediates in the system

 TABLE II: Arrhenius Parameters for Sulfur Atom

 Abstraction by Hydrogen Atoms and Methyl Radicals

Reaction	Log A, cc mol ⁻¹ sec ⁻¹	E_{a} , kcal mol ⁻¹	k(300°K), cc mol ⁻¹ sec ⁻¹	Ref
H + COS	12.96	3.9	$1.3 imes10^{10}$	This
				work
			$1.3 imes10^{10}$	4
$H + H_2S$	12.89	1.7	$4.5 imes10^{11}$	10
			$2.3 imes10^{11}$	4
H + S	13.75	1.9	$2.3 imes10^{12}$	2
$CD_3 + COS$	11.58	11.35	$2.0 imes10^3$	11
$CH_3 + S$	11.35	7.4^{a}	$8.9 imes10^5$	11
$CH_3 + S$	11.33	7.5^{a}	$7.3 imes10^5$	b
CH, + S	12.31	6.8 ^a	$2.2 imes 10^7$	b
$S(^{3}P) + COS$	13.7	~5	\sim 1.1 $ imes$ 10 ¹⁰	11
	(assumed)			
$S(^{3}P) + S \qquad \qquad \bigtriangleup$, , ,		$1.7 imes10^{13}$	C

 a Uncorrected for secondary C₂H₄ producing reactions. b M. G. Ahmed, M.Sc. Thesis, University of Alberta, Edmonton, Alberta, 1974. c A. van Roodselaar and O. P. Strausz, to be submitted for publication.

$$HS + S_{(x)} \longrightarrow HS_{(x+1)}$$
(8)

$$HS_{(x+1)} + HS_{(y)} \longrightarrow H_2S_{(x+y+1)}$$
(9)

$$HS_{(x+1)} + HS_{(y)} \longrightarrow H_2S_{(x+y-1)} + S_2, \text{ etc.}$$
(10)

The difference between the CO and C_2H_4 yields from the respective systems is attributable to the difference in the rates of the reactions involved. From the rate constant values compiled in Table II it can be predicted that abstraction of sulfur by H and S atoms will go to completion with C_2H_4S ; however with COS both reactions will be slow and loss of H atoms, S atoms, and HS radicals may occur via the reactions

$$S + Hg + M \longrightarrow HgS + M$$
 (11)

$$S + HS + M \longrightarrow HS_2 + M$$
 (12)

$$S + S_{(x)} \longrightarrow S_{(x+1)}$$
 (13)

$$S + HS_{(x)} \longrightarrow HS_{(x+1)}$$
 (14)

$$H + S_{(x)} \longrightarrow HS_{(x)}$$
(15)

$$H + HS_{(x)} \longrightarrow H_2S_{(x)}$$
(16)

$$H + HS_{(x)} \longrightarrow H_2 + S_{(x)}$$
 (17)

$$H + HgS \longrightarrow Hg + HS, etc.$$
 (18)

Since the amount of HS produced is independent of the ratio $[H_2S]/[COS]$, it may be assumed that the rates of steps 15–18 relative to step 1 are constant, and that step 6 is negligibly slow as compared to other reactions consuming S atoms. On this basis one can derive the following expression for the quantum yield of CO formation:

$$1/\phi(CO) = \frac{1}{2} \left(1 + \alpha + \frac{k_2 [H_2S]}{k_1 [COS]} \right)$$
(II)

where α is the sum of the rates of steps 15-18 relative to that of step 1. Equation II is plotted at four different temperatures, 27, 81, 121, and 252° within the [H₂S/COS] range 0.06-0.4, Figure 4. From the values given in Table III it is seen that the intercept is independent of temperature

TABLE III: Slope and Intercept Values of the Plots in Figure 5

<i>T</i> , °C −	Slope	Intercept	k_{2}/k_{1}
27 81 181 252	$\begin{array}{c} 16.6 \pm 0.4 \\ 9.86 \pm 0.41 \\ 6.80 \pm 0.15 \\ 3.50 \pm 0.02 \end{array}$	$\begin{array}{c} 0.656 \pm 0.081 \\ 0.688 \pm 0.054 \\ 0.624 \pm 0.029 \\ 0.677 \pm 0.041 \end{array}$	$\begin{array}{c} 33.2 \pm 0.8 \\ 19.7 \pm 0.8 \\ 13.6 \pm 0.3 \\ 7.0 \pm 0.04 \end{array}$
00 4 2 0 0 0 0 0	0,1		81 [*] 252 [*]

Figure 4. ϕ_{CO} as a function of H₂S/COS at 27, 81, 121, and 252°.



Figure 5. Log (k_2/k_1) as a function of T^{-1} .

but the slope gradually decreases with increasing temperature. The Arrhenius plot for k_2/k_1 is shown in Figure 5 from which the value of the rate coefficient ratio is $\log k_2/$ $k_1 = -(0.068 \pm 0.015) + (2190 \pm 190)/2.3RT$. Accepting Braun and coworkers¹⁰ value for the Arrhenius parameters of reaction 2 of $A_2 = (7.77 \pm 0.90) \times 10^{12} \text{ cc mol}^{-1} \text{ sec}^{-1}$ and $E_a = 1709 \pm 60$ cal mol⁻¹, the Arrhenius parameters of reaction 1 are computed to be A = (9.1 \pm 1.2) \times 10¹² cc $\rm mol^{-1}~sec^{-1}$ and $E_{\rm a}$ = 3.9 \pm 0.4 kcal mol^{-1}. These lead to a rate constant value of 1.3 \times $10^{10}~{\rm cc}~{\rm mol}^{-1}~{\rm sec}^{-1}$ at room temperature,¹² in excellent agreement with that measured by Rommel and Schiff⁴ in a discharge flow system at room temperature using mass spectrometric detection.

The A factor of the reaction is $9.1 \times 10^{12} \text{ cc mol}^{-1} \text{ sec}^{-1}$ which corresponds to an entropy of activation of -15.0gibbs mol⁻¹. It is interesting to compare this value with an estimate based on a simple procedure adopted by Benson,¹³ where the entropy of the activated complex is calculated by comparison with analogous molecules.

For the estimate of the standard entropy of the $H\cdots$ S \cdots CO activated complex, $S^{0\ddagger}$, we start with the stan-

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dard entropy of the SCO molecule. There is a rotational contribution of 0.6 gibbs mol^{-1} from the increased principal moments of inertia in the activated complex and a spin contribution of $R \ln 2$. Thus

$$S^{0*} = S^0(COS) + 0.6 + 1.4$$

and the entropy of activation at 300°K is $\Delta S_p^{\ddagger} = S^0(COS)$ $+ 2.0 - S^{0}(COS) - S^{0}(H) = -25.4 \text{ gibbs mol}^{-1} \text{ or, convert-}$ ed to the standard state of 1 M, $\Delta S_c^{\ddagger} = \Delta S_p^{\ddagger} - R\Delta n (\Delta n)R \ln (RT) = -25.4 + 8.4 = -17.0$ gibbs mol⁻¹. Agreement with the experimental value can be achieved by assuming a vibrational contribution of 2.0 gibbs mol^{-1} from the $H \cdots S \cdots C$ degenerate bending modes. This is equivalent to a vibrational frequency of 400 cm^{-1} and indicates a rather tight structure for the activated complex.

For the reaction $H + H_2S = HS + H_2$ the experimental A factor is 7.77×10^{12} cc mol⁻¹ sec^{-1 10} and the corresponding entropy of activation is -15.3 gibbs mol⁻¹. The standard entropy of the $H \cdots H \cdots SH$ activated complex can be estimated in a similar manner from the standard entropy of the H₂S molecule. There will be a rotational contribution of 1.0 gibbs mol⁻¹ and spin and loss of symmetry will contribute each an $R \ln 2$ term. Thus

$$S^{0\pm} = S^{0}(H_{2}S) + 1.0 + 2.8$$

and the entropy of activation at 300°K is $\Delta S_p^{\ddagger} = S^0(H_2S)$ $+3.8 - S^{0}(H_{2}S) - S^{0}(H) = -23.6 \text{ gibbs mol}^{-1}$ or, converted to the standard state of 1 M, $\Delta S_c^{\dagger} = \Delta S_p^{\dagger} + 8.4 = -15.2$ gibbs mol^{-1} in agreement with the experimental value.

In this estimate any vibrational contribution from the degenerate bending modes of the $H \cdots H \cdots S$ bonds is neglected. However, a negligibly small vibrational contribution to the entropy requires a vibrational frequency of at least 800 cm⁻¹ at 300°K and this again indicates a tight structure for the activated complex.

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