# Reaction between Ozone and Hydrogen Sulfide<sup>1</sup>

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The reaction between  $O_3$  and  $H_2S$  was studied from 25 to 70° over a pressure range of 0.005-0.1 Torr of  $O_3$ and 0.2-5 Torr of  $H_2S$ . Previous work on this reaction employed ozonized oxygen and the stoichiometry was reported as  $O_3 + H_2S \rightarrow SO_2 + H_2O$ . We found that  $O_2$  is the most important product of the reaction and that the  $(O_2 \text{ formed})/(O_3 \text{ used})$  ratio approached 1.5. We also found that the  $H_2O/SO_2$  ratio varied considerably from unity.  $SO_2$ ,  $H_2O$ , and  $H_2S$  in the products were determined and good H, O, and S mass balances were obtained. Runs carried out in the presence of added  $O_2$  or  $CO_2$  showed no change in rate, measured as  $-d[O_3]/dt$ . The rate law found was zero order in  $H_2S$  and  $(1.75 \pm 0.25)$  order in  $O_3$ . Taking the rate constant as  $\frac{4}{2}$  order we find log  $(k/M^{-1/2} \sec^{-1}) = 5.0 \pm 0.5 - (5000 \pm 700)/2.30RT$ . A free-radical mechanism is proposed which accounts for the observed kinetics and which gives qualitative agreement with the observed product ratios.

## Introduction

Ozone and hydrogen sulfide are two important atmospheric pollutants. They react rapidly at room temperature and the reaction is of considerable kinetic interest. Nevertheless, there are surprisingly few reported studies of the kinetics. Gregor and Martin<sup>2</sup> found that sulfur dioxide and water were formed in equal amounts and postulated the stoichiometry as  $O_3 + H_2S \rightarrow H_2O + SO_2$ . Cadle and Ledford (CL) studied the reaction in a flow system<sup>3</sup> and found the rate of  $O_3$  disappearance was  $\frac{3}{2}$  order in  $O_3$  and zero order in H<sub>2</sub>S. They stated that the reaction was in part heterogeneous. A study by Hales, Wilkes, and York (HWY)<sup>4</sup> was also carried out in a flow system and led to the rate law  $d[SO_2]/dt = k[O_3]^{3/2}[H_2S]^{1/2}$ . They disputed the heterogeneity reported by CL but accepted the simple stoichiometry of the reaction. All of these studies used ozonized oxygen or air as the reactant gas.

There are several puzzling aspects of these results. A concerted molecular rearrangement is clearly most unlikely and would not give rise to the observed rate laws. It is not clear whether or not the rate law reported by CL is consistent with that reported by HWY and in any case no explanation has been put forward for these rate laws. In the study reported here we investigated the reaction between  $O_3$  and  $H_2S$  in the absence of molecular oxygen and we find that the most important product is  $O_2$ . We also find that the  $H_2O/SO_2$  product ratio is far from unity. Our results show that the reaction  $H_2S + O_3 \rightarrow H_2O + SO_2$  has neither kinetic nor stoichiometric significance and we offer an alternative explanation for this reaction.

## **Experimental Section**

A conventional high vacuum system was used with traps cooled with Dry Ice to exclude mercury vapor from the quartz reaction vessel. The cylindrical reaction vessel, which was of 21.9 cm length and 460 cm<sup>3</sup> volume, was connected to the reactant inlet and rest of the system by Tef-Ion high vacuum stopcocks. An inlet tube consisting of a "cold finger" of approximately 5 cm<sup>3</sup> volume was attached via a stopcock to the reaction cell. The desired amount of  $H_2S$  was frozen into this inlet tube and allowed to warm before reacting.

The reaction vessel was mounted horizontally in a thermostatted oven  $(\pm 0.8^\circ)$  with quartz windows at each end.

The ozone concentration was monitored by absorption of 254-nm radiation obtained from an Osram low-pressure mercury lamp and two interference filters. The absorption coefficient of ozone was taken<sup>5</sup> as 134 cm<sup>-1</sup> (1 atm at  $273^{\circ}$ K)<sup>-1</sup> (base 10) and Beer plots were linear up to about 0.85 Torr of ozone. Ozone pressures were kept below 1 Torr for reasons of safety and also because the reaction rate became too fast to measure with our system. The transmitted light beam was measured with a 1P28 photomultiplier connected to a Keithley 610A electrometer and a recorder.

Products from runs were trapped with liquid nitrogen and the noncondensible gas measured on a gas buret. For several runs this gas was then exposed to pyrophoric lead<sup>6</sup> and was completely absorbed, showing it to be pure oxygen.

Products other than  $O_2$  were analyzed on a Beckman GC4 chromatograph using a 10-ft Poropak Q column at 100°. Erratic results were sometimes obtained in the GC determination of small amounts of  $H_2O$ , presumably because of loss of  $H_2O$  by absorption. A procedure was therefore developed in which, after the more volatile products had been removed, the  $H_2O$  was allowed to evaporate at room temperature and the pressure measured in a calibrated volume on a thermocouple gage which had been calibrated for  $H_2O$  vapor. This was found to give consistent results.

Ozone was generated by passing oxygen (Matheson Ultrapure grade) through a tesla coil. The ozone was condensed at  $-196^{\circ}$  and the O<sub>2</sub> pumped away. Hydrogen sulfide (Matheson CP grade) was distilled several times before use, rejecting head and tail fractions.

#### Results

Runs were carried out at approximately 25, 50, and 70° and blanks with pure  $O_3$  showed the reaction to be negligibly slow in the absence of  $H_2S$ . The pressure range for the  $O_3$  was 0.005–0.1 Torr and for  $H_2S$  it was 0.2–5 Torr.

*Products.* Apart from excess  $H_2S$ , products measured in decreasing order of abundance were  $O_2$ ,  $H_2O$ , and  $SO_2$ . In addition, traces of sulfur were deposited as a faint white powder which turned yellow on heating. These deposits were found in tubing cooled to  $-196^\circ$  which was connected to the reaction cell, and the GC sample bulbs.

Product data are given in Table I and plotted as a function of initial ozone in Figure 1. Mass balances for sulfur,

Reactants	, $\mu$ mol		Products	, $\mu$ mol	
O <sub>3</sub>	$H_2S$	<b>O</b> <sub>2</sub>	$H_2O$	$SO_2$	$H_2S$
 2.88	16.9	2.99	2,70	1.70	9.47
4.78	17.0	5.57	4.27	2.57	13.0
10.3	83.8	13.2	7.56	3.13	83.2
6.66	84.2	6.99	7.73	1.18	67.1
13.0	83.8	15.3	10.6	3.62	72.5
3.91	81.8	4.54	3,63	1.64	75.5
2.17	81.5	3.11	1.32		
15.5	83.9	18.8	10.2		68.4
8.76	79.2	8.74	11.2		
3.81	82.2	4.19	3.10		
17.9	81.2	22.7	9.40	1.27	71.8
6.42	82.2	7.34	6.26	3.36	80.8
14.8	81.8	18.8	7.91	4.93	78.0
8.84	83.1		6.53		71.4
8.00	80.3	7.51	10.5		66,5
14.5	81.0	19.5	6.92	4.79	69.7
2.66	81.7	3.47	2.13	0.05	69.0
3.53	83.2	4.17	2.62	1.07	68.3
4.73	80.9	6.05	5.06	0.40	

TABLE I: Products of Reaction between Ozone andHydrogen Sulfide at 25°



Figure 1. Effect of amount of initial O<sub>3</sub> on product formation at 25° with initial H<sub>2</sub>S = 80  $\mu$ mol.

hydrogen, and oxygen are shown in Figure 2 as a function of amount of initial ozone. The average mass balances were 86.6% for S, 95.2% for H, and 113% for O. The stoichiometry of (O<sub>2</sub> formed)/(O<sub>3</sub> used) was measured as a function of initial O<sub>3</sub> for a fixed value of initial H<sub>2</sub>S and the results are shown in Figure 3.

Kinetics.<sup>7</sup> The reaction was rapid with a typical half-life



Figure 2. Mass balance for sulfur, hydrogen, and oxygen as a function of amount of initial  ${\sf O}_3.$ 



Figure 3. Ratio of (O\_2 formed)/(O\_3 used) as a function of initial O\_3 at 25° with initial H\_2S = 80  $\mu mol.$ 

of  $\sim 2$  sec under the conditions studied. Assuming a rate law of the form  $-d[O_3]/dt = k[O_3]^m[H_2S]^n$  we studied the kinetics in the presence of excess H<sub>2</sub>S. Log-log plots gave slopes between 1.5 and 2. We therefore used the integrated equations and made plots corresponding to orders of 1, 1.5, 2, and 2.5. The first- and 2.5-order plots were distinctly curved but the 1.5- and second-order plots were both straight with statistical correlation factors of >0.99 in most cases. The 1.5- and second-order rate constants at 25° were measured over a 20-fold range of initial O<sub>3</sub> and the results are shown in Figure 4. Within the estimated errors of the data, both 1.5- and second-order constants fit the results equally well over approximately 90% of the reaction. The effect of initial H<sub>2</sub>S on the rate constant was studied over a 20-fold range of  $[H_2S]$  and no dependence was found, as seen in Table II. On the other hand, plots of rate constants of order of 0.5 or higher in  $H_2S$  against  $[H_2S]$  showed a

TABLE II: Effect of Initial H<sub>2</sub>S on Three-Halves Order Rate Constant at 20°

Initial O $_3$ , $\mu mol$	Initial H <sub>2</sub> S, $\mu mol$	$k, M^{-1/2} \operatorname{sec}^{-1}$	
0.76 0.75 0.90 0.82 0.72 0.68 0.75	$\begin{array}{r} 4.3\\ 18.8\\ 34.7\\ 41.7\\ 59.4\\ 68.6\\ 85.6\end{array}$	$\begin{array}{r} 49.0 \\ 53.5 \\ 63.7 \\ 62.7 \\ 56.2 \\ 45.5 \\ 46.0 \end{array}$	
$s_{2} = 10^{-4}$ , $M^{-1} s^{-1}$	°°° °°°°	0 0 0 0	
0 75 50 50 2/z 25	0000 0000	°°°°	
0	.5 (.0	1.5 2.0 2.5	]
	INTIAL $O_{3,\mu}$ N	IULES	

Figure 4. Plot of three-halves- and second-order rate constants at 25° as a function of initial O3.

clear dependence. We conclude that the rate law is zero order in  $H_2S$  and is given by

$$-d[O_3]/dt = k[O_3]^{1.75\pm0.25}$$
(1)

Experiments were also carried out in the presence of added  $O_2$  and added  $CO_2$ . The presence of more than a 50fold excess of added gas over O3 had no effect.

Rate constants were measured at 25, 50, and 70° and the rate constants were plotted as an Arrhenius plot which gave log  $(k/M^{-1} \sec^{-1}) = 9.2 \pm 0.8 (5200 \pm 1200)/2.3RT$  for the second-order constant and log  $(k/M^{-1/2} \text{ sec}^{-1}) = 5.0 \pm$  $0.5 - (5000 \pm 700)/2.3RT$  for the 1.5-order constant.

# Discussion

As Figure 1 shows, the most abundant product of the reaction between  $O_3$  and  $H_2S$  is  $O_2$ , a fact overlooked by previous investigators. The stoichiometry of  $(O_2 \text{ formed})/$  $(O_3 \text{ used})$  is close to 1.5 as seen in Figure 3, which implies a catalytic decomposition of O3 with little concomitant consumption of the H<sub>2</sub>S. Similarly a plot of H<sub>2</sub>S used vs. initial O<sub>3</sub>, although extremely scattered because of the large excesses of  $\tilde{H}_2S$  employed shows that as  $[O_3]_0$  increases the  $H_2S$  used remains constant.

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The mass balance average of 95.2% for H probably accounts for all H-containing products within the experimental error. However, the mass balance average of 87.6% for S is slightly low. Sulfur was not deposited in the reaction cell and so was not a direct product of the reaction but a product was formed which later decomposed to give sulfur. The high average mass balance for oxygen of 113% is probably due to systematic errors. It should be noted the  $O_2$  was measured on a thermocouple or McLeod gauge, O3 was measured by optical absorbance, SO<sub>2</sub> was measured by GC, and H<sub>2</sub>O was measured by pressure with a calibrated thermocouple gauge. Overall, the mass balances show satisfactory product recovery.

We thus have to explain the various product ratios and account for the observed rate law. We therefore postulate mechanism A. Taking steady states in [HO], [HO<sub>2</sub>], [HS], Mechanism A

[SO], and [HSO] and putting  $M = H_2S$  leads to

$$-d[O_3]/dt = (3 + K)k_1[H_2S][O_3] + (2 + K)k_1^{1/2}k_4k_5^{-1/2}[O_3]^{3/2}$$
(2)

$$-d[H_2S]/dt = (2 + K)k_1[H_2S][O_3] + Kk_1^{1/2}k_4k_5^{-1/2}[O_3]^{3/2}$$
(3)

$$d[H_2O]/dt = (1 + K)k_1[H_2S][O_3] + Kk_1^{1/2}k_4k_5^{-1/2}[O_3]^{3/2}$$
(4)

$$d[SO_2]/dt = Kk_1[H_2S][O_3] + Kk_1^{1/2}k_4k_5^{-1/2}[O_3]^{3/2}$$
(5)

where  $K = k_{6a}/(k_6 + k_{6a})$ . Equations 4 and 5 give

$$\frac{[\mathrm{H}_{2}\mathrm{O}]}{[\mathrm{SO}_{2}]} = \frac{1 + K + k_{1}^{-1/2}k_{4}k_{5}^{-1/2}K[\mathrm{O}_{3}]^{1/2}[\mathrm{H}_{2}\mathrm{S}]^{-1}}{K + k_{1}^{-1/2}k_{4}k_{5}^{-1/2}K[\mathrm{O}_{3}]^{1/2}[\mathrm{H}_{2}\mathrm{S}]^{-1}}$$

A plot of  $[H_2O]/[SO_2]$  should vary from  $2 + k_6/k_{6a}$  to unity as  $[O_3]_0$  increases from zero. Our results are shown in Figure 5 and although there is considerable scatter, the results are in agreement with expectation.

Equation 3 and 5 give

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$$\frac{[\text{H}_2\text{S used}]}{[\text{H}_2\text{O formed}]} = \frac{2 + K + k_1^{-1/2}k_4k_5^{-1/2}K[\text{O}_3]^{1/2}[\text{H}_2\text{S}]^{-1}}{1 + K + k_1^{-1/2}k_4k_5^{-1/2}K[\text{O}_3]^{1/2}[\text{H}_2\text{S}]^{-1}}$$

This function should vary from (2 + K)/(1 + K), which is a number between 1 and 2, to unity as  $[O_3]_0$  increases from zero. Our results are shown in Figure 6 and, with the exception of two apparently low points, are in good agreement with expectations.

Steps 1 and 2 in the mechanism can be replaced by a sequence involving HSO<sub>2</sub> rather than HO<sub>2</sub>. In addition,  $HSO_2$  may also be formed by the reaction between HSO



Figure 5. Ratio of [H<sub>2</sub>O]/[SO<sub>2</sub>] products as a function of initial reactant ratio.



Figure 6. Ratio of (H<sub>2</sub>S used)/(H<sub>2</sub>O formed) as a function of amount of initial Oa.

and O<sub>3</sub>. We postulate, as an alternative possibility, mechanism B together with steps 3, 4, 5, 6, 6a, and 7 of mechanism A.

Mechanism B

This gives the same rate law for ozone disappearance and identical expressions for product ratios as does mechanism A. Thus, our data will not distinguish between the two mechanisms.

At the higher values of initial O<sub>3</sub> used a catalytic destruction of  $O_3$  occurred. This requires a chain component of the mechanism. A likely possibility is step 2 along with

$$HO + O_3 \xrightarrow{*} HO_2 + O_2$$

Evidence for the chain decomposition of O<sub>3</sub> resulting from steps 2 and 9 has recently been obtained by DeMore and Tschuikow-Roux.<sup>8</sup> However, other chain sequences are possible, such as steps 6b and 8.

We did not detect  $H_2S_2$  in our GC analyses, but Gunning et al.9 have reported that this substance readily decomposes:  $H_2S_2 \rightarrow H_2S + S$ . This would account for the sulfur we found deposited and the slightly low mass balance for S. According to Rommel and Schiff,<sup>10</sup> at very low pressures the likely fate for HS radicals is  $2HS \rightarrow H_2S + S$ . However, in the higher pressures of our system step 5 is the most likely reaction.

Neither added CO<sub>2</sub> nor O<sub>2</sub> had any effect on the measured rate constant. The lack of inhibition by  $O_2$  implies that the radical intermediates in the mechanism do not react rapidly with O2. This contrasts with what has been found for the reaction of O3 and unsaturated hydrocarbons.<sup>11</sup>

If the second term on the right in eq 2 predominates over the first then a <sup>3</sup>/<sub>2</sub> order rate law results for the rate of disappearance of ozone. Our observed rate constant is then equal to  $k_1^{1/2}k_4k_5^{-1/2}(2 + K)$ . We compare our rate constant of log  $(k/M^{-1/2} \sec^{-1}) = 5.0 \pm 0.5 - (5000 \pm 700)/$ 2.30RT and our value of  $k(25^{\circ}) = 52 \pm 8 M^{-1/2} \text{ sec}^{-1}$  with that of CL who reported<sup>3</sup> log  $(k/M^{-1/2} \text{ sec}^{-1}) = 6.9$  -8300/2.30RT and  $k(25^{\circ}) = 8.5 \pm 2 M^{-1/2} \text{ sec}^{-1}$ . They used a flow system and found some heterogeneity, and in view of the large differences in experimental methods used, the agreement is encouraging. HWY<sup>4</sup> found  $d[SO_2]/dt =$  $k[H_2S]^{1/2}[O_3]^{3/2}$ . However they studied the system with an air carrier gas. According to our mechanism eq 5 would then become  $d[SO_2]/dt = k[H_2S]^{1/2}[O_3]^{3/2}/[air]^{1/2}$  and at constant total pressure the rate law found by HWY is then compatible with that found by CL and with the one reported here.

There is no direct evidence for the occurrence of steps 1 or 1a but they presumably take place via a five-membered ozonide ring:

$$0_{3} + H_{2}S \rightarrow \begin{bmatrix} 0 & & H \\ 0 & & H \end{bmatrix} \rightarrow HO_{2} + HSO_{2}$$

The overall reaction between O<sub>3</sub> and H<sub>2</sub>S is chemiluminescent and Pitts et al.<sup>12</sup> have attributed the emission to  $SO_2^*$ . This is consistent with the high exothermicity (106 kcal) of step 7. A more detailed study<sup>13</sup> of the chemiluminescence found additional bands which were tentatively identified as HSO\* or  $HSO_2*$  in accord with our mechanisms.

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Supplementary Material Available. Additional kinetic data (Tables III and IV and two additional figures) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche  $(105 \times 148)$ mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.50 for microfiche, referring to code number JPC-75-779.

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