may not be represented reliably by the Gaussian approximation for chains of so few bonds, and this may contribute in some smaller degree to the disparity between the calculated and observed values for K_4.

The results of Brown and Slusarczuk[2] describe a shallow minimum near $x = 12$. Those of Hartung and Camiolo[6] and of Carmichael and Winger[7] corroborate the rapid decrease in K_x with x between 4 and 10, and thus tend to confirm an impending minimum for $x > 10$. Superficially similar minima are observed for cyclization of organic compounds, *e.g.*, for homologous cyclic esters and cyclic ketones in the range of 9 to 13 skeletal bonds (in contrast to *ca.* 22 bonds at the minimum for the cyclic siloxanes). These minima have been attributed to crowding of hydrogen atoms within rings of the specified size.[10] The same explanation cannot be supported for the macrocyclic siloxanes. Examination of models for macrocyclic dimethylsiloxanes with $x = 10$ to 14 reveals no indication of crowding of substituents or of other steric interactions which might account for the indicated minimum. No alternative explanation for the minimum is apparent. A detailed examination of various conformations which fulfill condition i above with the object of assessing the conditional probability of meeting condition ii might be instructive in this connection. The task would be formidable, however.

Deviations from the calculations for comparatively small rings, whatever may be their causes, are overshadowed by the excellent agreement at large x. Here the manifest limitations of statistical theory vanish. The sole remaining premise resides in the assumption of unperturbed random-coil configurations for PDMS chains in the bulk state and in concentrated solutions. The comparison of theory and experiment bears ample testimony to the validity of this assumption, which is already supported by a considerable body of evidence.[11] A previous suggestion that PDMS chains occur in the form of more or less regularly coiled helices,[12] for example, is refuted unequivocally by the observations presented here.

Acknowledgment. This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research Contract No. AF49(638)-1341.

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(10) E. W. Spanagel and W. H. Carothers, *J. Am. Chem. Soc.*, **57**, 929 (1935).

(11) See, for example, P. J. Flory, A. Ciferri, and R. Chiang, *ibid.*, **83**, 1023 (1961); J. E. Mark and P. J. Flory, *ibid.*, **87**, 1423 (1965); C. A. J. Hoeve and M. K. O'Brien, *J. Polymer Sci.*, **A1**, 1947 (1963); and P. J. Flory, "Lectures in Materials Science," P. Leurgens, Ed., W. A. Benjamin, Inc., New York, N. Y., 1963, pp 37–42.

(12) A. J. Barry and H. N. Beck, "Inorganic Polymers," F. G. A. Stone and W. A. G. Graham, Ed., New York, N. Y., 1962, p 266 ff.

The Reaction of Hydrogen Sulfide and Atomic Oxygen[1]

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Abstract: A study of the mechanism for H_2S + O atoms showed that the initial reaction was $H_2S + O \rightarrow HS + OH$ (5), followed by the chain reactions $HS + O \rightarrow SO + H$ (6) and $H + H_2S \rightarrow H_2 + HS$ (3). Since a mixture of D_2S and H_2S + O atoms produced equilibrated HD, the reaction $H_2S + O \rightarrow H_2 + SO$ (4) has to be disregarded. The reaction rate for the initial reaction, k_5, was found to be $4 \pm 2 \times 10^{-14}$ cm^3 molecule^{-1} sec^{-1}.

This investigation involves the study of the reaction of H_2S + O atoms using a time-of-flight mass spectrometer to detect the species formed and to measure the over-all rate constant of the reaction. The reaction of O atoms with H_2S occurs readily producing a blue luminescence[2a] with yields of SO_2, SO_3, H_2O, H_2SO_4,[2b] H_2, S_2O, and S_2O_2 both at room temperature[3] and at low temperature.[4] However, the rate of the H_2S + O atom reaction, and the mechanism of the over-all process for the oxidation and the formation of final products, has not been established.

The thermal oxidation of H_2S in the 100-mm range has been studied by several investigators (see ref 5 for an account of the previous literature). Marsden[5] studied the H_2S combustion using a mass spectrometer and identified the intermediates: H_2S_2, H_2SO_2, S_2, and SO and S_2O. Norrish and Zeelenberg,[6] studying the flash photolysis of $H_2S + O_2$, identified the species (HS, OH, SO, and S_2O_2 and SO_2) whose concentration strongly depended upon reaction time and initial composition of the H_2S–O_2 mixture. Recently, MacDonald and Goll[7,8] obtained the electronic paramagnetic resonance spectra of radicals such as HS and SO by passing water vapor through a microwave discharge and permitting the products to react with H_2S (total pressure less than 1 mm).

The over-all mechanism of the oxidation depends strongly upon conditions. From the literature it appears that in the oxidation of H_2S, HS is primarily

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(1) This research was supported by the U. S. Atomic Energy Commission under Contract AT(30-3)-321.

(2) (a) P. Harteck and U. Kopsch, *Z. Physik. Chem.*, **B12**, 327 (1931); (b) *Z. Elektrochem.*, **26**, 714, (1930).

(3) G. Liuti, S. Dondes, and P. Harteck, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept 1963, Abstract 40T.

(4) P. N. Schenk and H. Jablowowski, *Z. Elektrochem.*, **95**, 650 (1939).

(5) D. G. H. Marsden, *Can. J. Chem.*, 41, 2607 (1963).

(6) R. G. W. Norrish and A. D. Zeelenberg, *Proc. Roy. Soc.* (London), **A240**, 293 (1957).

(7) C. C. MacDonald, *J. Chem. Phys.*, **39**, 2587 (1963).

(8) C. C. MacDonald and R. Z. Goll, *J. Phys. Chem.*, **69**, 293 (1965).

formed, and this HS partakes in a series of chain propagation reactions, as

$$HS + O_2 \longrightarrow SO + OH \tag{1}$$

$$OH + H_2S \longrightarrow H_2O + HS \tag{2}$$

This chain mechanism plays a key role in the thermal oxidation of H_2S. If H atoms are present, they will react fast, according to

$$H + H_2S \longrightarrow H_2 + HS \tag{3}$$

In this investigation, the reaction of the H_2S molecule with O atoms has been studied at low pressure (~0.5 mm). A time-of-flight mass spectrometer was used to determine the products of the reaction. In addition, D_2S–H_2S mixtures replacing pure H_2S were used to determine the initial step in the reaction between H_2S and O atoms.

Experimental Section

The reaction of H_2S + O atoms has been studied in a fast flow reactor, similar to that described by Phillips and Schiff.[9]

Tank O_2 or a mixture of 90% Ar–10% O_2, obtained from the Matheson Co., was passed through a trap immersed in liquid oxygen and then into a dc-discharge tube to produce oxygen atoms. The gas stream containing O atoms was then mixed with an H_2S and Ar mixture through a multihole jet inlet to produce good mixing action. The reacting gases were sampled with a Bendix time-of-flight mass spectrometer, Model 12, through an aluminum mass spectrometer leak (100-μ diameter) placed within the reaction region. The leak was located 0.3 mm from the ionizing region of the mass spectrometer. The position of the jet could be varied continuously to permit a change in the reaction time.

In order to determine the role played by molecular oxygen, a series of experiments as conducted in which O atoms were produced from the reaction $N + NO \rightarrow N_2 + O$, without normal molecular oxygen being present. In this system, tank nitrogen, argon, and oxygen (The Matheson Co.) were passed through a trap immersed in liquid oxygen prior to entering the system. Nitric oxide was passed through a trap immersed in Dry Ice. Tank H_2S (Matheson purified grade) was further purified by condensing in a trap immersed in Dry Ice and permitting the more volatile compounds such as carbon dioxide to be pumped away. The purified gas was then injected into the system. D_2S, obtained from the Nuclear Equipment Chemical Corp., was subjected to a mass spectrometric analysis and isotopic evaluation and used directly. The D_2S was found to be 98% isotopically pure.

The Bendix time-of-flight mass spectrometer was calibrated for the various gases used as follows. A known flow rate of the gas mixture was permitted to pass into the reaction chamber and through the mass spectrometer leak. Once the flow rate reached a stationary level, the gas pressure was measured with an MKS baratron gauge and a mass spectrometer recording taken. The sensitivity of the mass spectrometer to molecular oxygen, O atoms, and H_2S was measured after every run. The sensitivity of the mass spectrometer to H_2 and SO_2 was measured daily. The O-atom concentration was determined with the mass spectrometer by observing the decrease of the signal of m/e[10] 32. The O-atom concentration was also determined by the NO_2 titration method.[12]

The two methods gave results in good agreement.

The fast flow existing in this system (about 13 m/sec) made back diffusion practically negligible. A total pressure of the gas mixtures, between 0.38 and 0.53 mm, was used in these experiments.

To avoid any isotopic exchange between D_2S and H_2S occurring before the gases entered the reaction zone, a new reactor chamber was constructed (Figure 1). The moveable inlet was replaced by four jets. These were located at two different regions of the reaction tube, *i.e.*, 18 and 10 cm from the mass spectrometer leak.

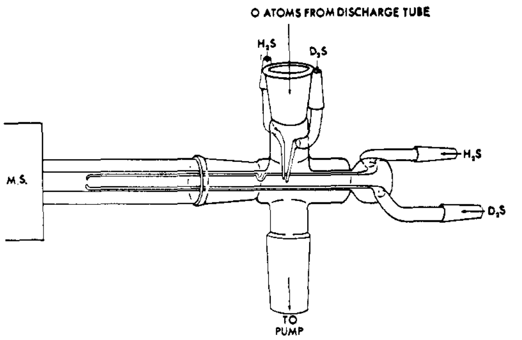

Figure 1. Schematic diagram of the reaction area for H_2S–D_2S mixture and O atoms.

Under these conditions the isotopic exchange, measured by the rise of the signal at m/e 35 upon mixing of the two gases, was found to be less than 5% for the inlet at 18 cm from the mass spectrometer leak.

There was no change in the remainder of the apparatus.

Results

In the reaction of H_2S + O atoms, the following occurred: a blue luminescence at the point of mixing of the two gas streams; a decrease in the mass spectrometric signals corresponding to m/e 34 (H_2S) and m/e 16 (O); and the appearance of m/e signals at 2 (H_2), 18 (H_2O), 48 (^{32}SO), 50 (^{34}SO), 64 ($^{32}SO_2$), 66 ($^{34}SO_2$), 80 ($^{32}S^{32}SO$), and 82 ($^{34}S^{32}SO$).

Table I shows the data of a typical series of experiments. In the last column of this table, the rate constant was calculated using the following integrated second-order equation

$$k = \frac{1}{(A_0 - B_0)t} \ln \frac{B_0\,(A_0 - X)}{A_0\,(B_0 - X)} \tag{I}$$

Here A_0, B_0, and X are the initial concentration of O atoms, the initial concentration of H_2S, and the amount of H_2S remaining, respectively. The use of eq I in this form to calculate the rate constant implies a 1:1 ratio for the disappearance of H_2S and O atoms. Experimentally the ratio was found to vary between O/H_2S = 1.25:1 and 1.1:1. This difference can be readily accounted for by the over-all mechanism. However, it was indeed surprising how well eq I described our findings.

Figures 2–5 show the consumption of H_2S and the formation of H_2, SO_2, SO, and S_2O *vs.* time with different mixtures. In determining the concentration of SO and S_2O, the mass spectrometric sensitivity to these species had to be estimated. The signal at m/e 80 was attributed entirely to S_2O and not SO_3 because the associated isotopic peak at m/e 82 ($^{32}S^{34}S^{16}O$) was about 9% of m/e 80 (natural abundance of ^{34}S is 4.2%); there was also a weak signal at m/e 84 ($^{34}S^{34}S^{16}O$).

From Figures 2 and 3, it can be seen that for each molecule of H_2S consumed about 0.8 molecule of H_2 is formed. The remainder (0.2) may have gone into the formation of water, which, in a system containing sulfur, cannot be measured readily. The sulfur was almost all found as SO and SO_2. In addition, in the case of low O-atom concentrations, S_2O and traces of elementary sulfur were observed.

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[9] L. F. Phillips and H. I. Schiff, *J. Chem. Phys.*, **36**, 1509 (1962).

[10] When the discharge was activated. The decrease divided by the O_2 sensitivity at m/e 32 and multiplied by 2 gives the partial pressure of O atoms.[11]

[11] J. O. Sullivan and P. Warneck, *Ber. Bunsenges. Physik. Chem.*, **69**, 7 (1965).

[12] P. Harteck, R. R. Reeves, Jr., and G. Mannella, *J. Chem. Phys.*, **29**, 608 (1958).

Table I. Reactants Consumption and Rate Constant for H_2S + O Atoms Reaction

Run	Total pressure, mm × 10^3	Time, msec	Initial partial pressure, mm × 10^3		Partial pressure, mm × 10^3		Rate constant $k \times 10^{13}$
			H_2S	O atoms	H_2S reacted	O reacted	
1	380	0.0	19.8	14.8			
		4.85			5.9	6.8	1.99
		6.8			7.2		1.96
		9.8			8.3	10.7	1.73
		12.75			9.6		1.80
		15.7			10.7	13.4	1.95
18	420	0.0	17.0	30.0		...[a]	
		5.1			9.5		2.00
		6.4			10.8		2.02
		8.1			12.0		1.95
		10.2			12.9		1.93
		11.7			13.3		1.86
		13.5			14.0		1.93
		15.5			14.5		1.88
15	455	0.0	19.7	11.8		...[a]	
		5.15			5.6		2.20
		8.1			6.8		2.08
		10.1			7.9		2.28
		11.75			8.3		2.16
		13.5			8.9		2.27
		15.35			9.2		2.20
14	495	0.0	17.7	42		...[a]	
		5.65			13.5		2.32
		8.0			14.8		1.89
		10.2			15.5		1.99
		11.6			15.8		1.87
		13.3			16.1		1.80
		15.1			16.5		1.79
7	530	0.0	20.0	38.0			
		4.3			12.4	14.5	2.18
		6.25			14.15	16.7	1.90
		7.0			14.6	17.3	1.97
		10.45			16.7	19.5	1.96
		13.2			17.7	20.4	1.95
		14.7			18.15		1.98

Average = 2.01 ± 0.17 × 10^{-13} cm^3 molecule^{-1} sec^{-1}

[a] O atoms not measured.

Discussion

A major result, derived from the reaction of the D_2S–H_2S mixture with O atoms and the subsequent formation of equilibrated HD (see Table II), was that the occurrence of the reaction

$$H_2S + O \longrightarrow H_2 + SO \tag{4}$$

has to be disregarded. The HD must have been formed by an attack of an H atom on a D-containing compound, very likely D_2S, or a D atom attacking H_2S. Using pure H_2S, H_2 must be formed by an attack of H atoms on H_2S.

Table II. Isotope Distribution in the H_2S–D_2S + O Atoms Reaction

Total pressure, mm × 10^3	Initial partial pressure, mm × 10^3			Partial pressure of products, mm × 10^3			Distance from the leak, cm
	D_2S	O atoms	H_2S	D_2	HD	H_2	
450	16.0	~70	...	10.9	~0	...	18
	16.0	~70	14.3	5.8	~11.3	4.8	18
	16.0	~70	...	6.2	~0	...	10
	16.0	~70	14.3	3.4	~6.6	2.7	10

Another consideration is that one dominant step in the mechanism must be the formation of SO. Since the consumption of O atoms is 10 to 20% greater than the consumption of H_2S, we are led to assume a mechanism where O atoms initiate the reaction and later on react predominantly to produce SO. The OH formed in the initial reaction (5) does not appear to play an important role. The following mechanism fulfills these conditions.

$$H_2S + O \longrightarrow HS + OH \tag{5}$$

$$HS + O \longrightarrow SO + H \tag{6}$$

$$H + H_2S \longrightarrow H_2 + HS \tag{3}$$

Reactions 3 and 6 form the chain mechanism for the major products, H_2 and SO observed. However, from the second-order relationship (*i.e.*, reactant consumption proportional to H_2S and O atoms), the chain carriers must be consumed on the walls of the reaction vessel and not in the gas phase. The recombination rate of the radicals in the gas phase should be negligible. Under our conditions, the HS radicals can readily reach the walls of the reaction vessel and be consumed. The H atoms may also be consumed on the walls by reaction with any deposits. We had noticed upon the completion of a run and the addition of O atoms into the reaction vessel, the appearance of a faint blue luminescence and signals at m/e 48, 64, and 80, indicating that the walls were covered with a thin layer of a sulfur-containing compound, but most probably elemental sulfur.

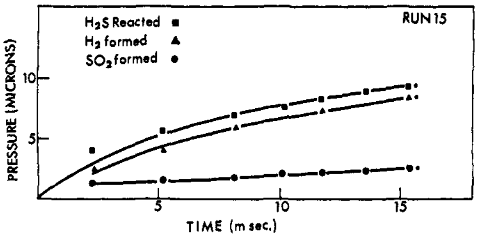

Figure 2.

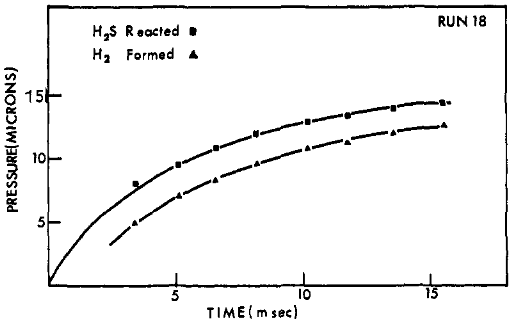

Figure 3.

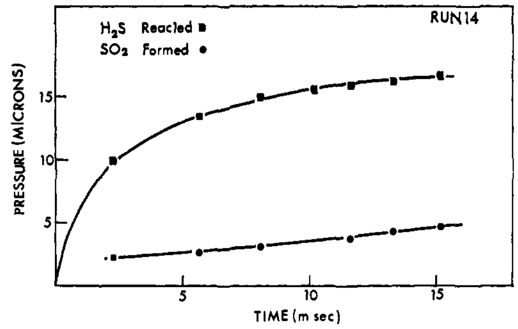

Figure 4.

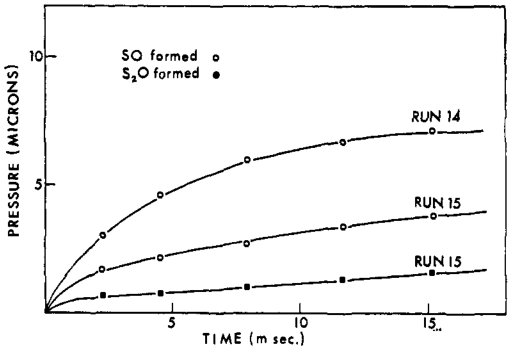

Figure 5.

The question arises as to the fate of the OH radical from the initial reaction 5. The OH radical may react as follows

$$OH + H_2S \longrightarrow H_2O + HS \qquad (2)$$

or[13]

$$OH + O \longrightarrow O_2 + H \qquad (7)$$

The rate of reaction 7 is known to be 4 × 10^{-11} cm^3 $molecule^{-1}$ sec^{-1}, therefore very fast, whereas the rate of reaction 2 is unknown but may be fast also. If reaction 5 were a predominant factor, then for each molecule of H_2S consumed, more than the 1.1–1.25 of O atoms would be required to be consumed. From the small amounts of water formed, from reaction 2 (even though the water could not be accurately measured owing to the water being removed from the walls of the discharge tube when the discharge was on), we can only conclude that the OH radical plays no major role.

This study provides for the determination of the reaction rate for the initial reaction, k_5. From the measurements in Table I, the over-all consumption of H_2S and O atoms occurs with a reaction rate of 2 × 10^{-13} cm^3 $molecule^{-1}$ sec^{-1}. However, as shown earlier, a chain mechanism is operative. Therefore the consumption of H_2S must be divided by the chain length for the computation of k_5. (By chain length, we mean the number of H_2S molecules consumed before the HS radicals or H atoms go to the walls.) From the ratio of the H_2S consumed to the H_2 formed and from the ratio of the H_2S consumed to the O atoms consumed, it can be estimated that the chain length is not smaller than 4 or larger than 7 (see Figures 2 and 3). With an average chain length of 5 ± 1.5, the measured experimental reaction rate must be divided by this factor. Unfortunately, this makes our experimental reaction rate, which could be reproduced within 10%, uncertain by 50%. The rate constant k_5, for the initiating reaction, therefore becomes $4 \pm 2 \times 10^{-14}$ cm^3 $molecule^{-1}$ sec^{-1} at room temperature.

The reactions of SO were not specifically investigated in this study. However, it is known that SO can react as

$$SO + SO \longrightarrow SO_2 + S \qquad (8a)$$

$$S \longrightarrow S_{(walls)} \qquad (8b)$$

$$SO + S_{(walls)} \longrightarrow S_2O \qquad (9)$$

In our experiments where the O atoms had a higher concentration than the H_2S, only SO and S_2O were found. With H_2S in surplus, S_2O was found together with a slight deposit of sulfur. The series of reactions of SO did not interfere in our general mechanism and is in agreement with literature data.[11] From the kinetics of the formation of SO and SO_2, K_8 can be estimated as $10^{-12 \pm 1}$ which is in good agreement with the results of Sullivan and Warneck,[11] who found 4 × 10^{-12} for reaction 8a.

Acknowledgment. We thank Mr. Ralph Haskell for his assistance in the performance of these experiments.

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(13) The reaction $OH + OH \rightarrow H_2O + O$ can be disregarded.