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Absolute rate of the reaction of $O(^{3}P)$ with hydrogen sulfide over the temperature range 263 to 495 K

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The technique of flash photolysis coupled with time resolved detection of O via resonance fluorescence has been used to obtain rate constants for the reaction of $O({}^{3}P)$ with $H_{2}S$ at temperatures from 263 to 495 K and at pressures in the range 10-400 torr. Under conditions where secondary reactions are avoided, the measured rate constants for the primary step obey the Arrhenius equation $k = (7.24 \pm 1.07) \times 10^{-12} \exp(-3300 \pm 100/1.987 T)$ cm³molecule⁻¹sec⁻¹. The results are discussed and comparisons are made with previous work and theoretical predictions. Experiments with $D_{2}S$ show that the reaction exhibits a primary isotope effect, in support of a hydrogen abstraction mechanism.

INTRODUCTION

The rate constant for the reaction of $O({}^{3}P)$ with $H_{2}S$ has been the subject of considerable interest during the past ten years.¹⁻⁷ This interest arises in part from the possible importance of this reaction in the chemistry of combustion processes, in polluted terrestrial atmospheres and in the atmosphere of Venus.

The mechanistic studies of Liuti, Dondes, and Harteck² showed that molecular elimination of H_2 , with concurrent formation of SO, was not an important process. They explained their results on the basis of the three step mechanism:

$$O + H_2 S \rightarrow OH + SH$$
, (1)

 $O + SH \rightarrow SO + H$, (2)

$$H + H_2 S - H_2 + SH .$$
(3)

Subsequently other workers, $^{4-6}$ in particular Cupitt and Glass, expanded this mechanism to include other possible secondary reactions and showed that the chain process, Reactions (2) and (3), was fast and would contribute to the overall O atom consumption.

Previous investigations all employed the dischargeflow technique. The mass spectrometric method of detection was used in three of the previous studies. 2,3,7 Two studies used chemiluminescence from

$$SO + O \rightarrow SO_2 + h\nu$$
 (4)

as the O atom detection method^{1,5} and ESR detection of both O atom and radical products was employed in the other two studies.^{4,6} The room temperature rate constants vary by more than a factor of three. The results from the two variable temperature studies^{6,7} also do not agree. Slagle, Baiocchi, and Gutman obtained $k_1=3.3\times10^{-11} \exp(-4000/1.987 T) \text{ cm}^3$ molecule⁻¹ · sec⁻¹ between 250 and 500 K, whereas Hollinden, Kurylo, and Timmons reported $k_1=2.9\times10^{-13} \exp(-1500/1.987 T) \text{ cm}^3$ molecule⁻¹ · sec⁻¹ from 205 to 300 K. The disagreements probably result from inaccurate assessment of the overall reaction stoichiometry. Although attempts⁴⁻⁶ have been made to assess the stoichiometric corrections, including a computer simulation⁴ of the expanded reaction scheme, this correction will vary with $[H_2S]/[O]$ ratio for any given apparatus. Furthermore, the correction will be temperature dependent since the temperature dependence of the various rate constants in the mechanism will differ.

The disagreements noted above have motivated the present study using the flash photolysis-resonance fluorescence technique for the temporal measurement of [O]. This technique allows very low atom concentrations to be used ($< 10^{11}$ cm⁻³) and affords experimental conditions where the first step in a reaction scheme may be isolated. Thus, uncertain stoichiometric corrections do not complicate the analysis even in reactions like the present where fast secondary reactions can contribute to O atom removal.

EXPERIMENTAL

The method employed in this kinetic study was that of flash photolysis coupled with time resolved detection of $O({}^{3}P)$ by resonance fluorescence. The apparatus and techniques have been described in detail previously.⁸⁻¹⁰ In the present study, three-component mixtures of H₂S, O₂ and argon diluent were flash photolyzed at wavelengths above 136 nm to produce atomic oxygen (~ $\leq 10^{11}$ cm⁻³) in an excess of both H₂S and the source compound, O₂. The reaction mixture flowed through the cell at a rate sufficient to replenish the mixture every 1–2 flashes. A BaF₂ window was used on the photoflash to preclude formation of the O(¹S) excited state¹¹ and a CaF₂ window on the microwave discharge resonance lamp prevented transmission of the 121.6 nm Lyman- α line.

The pseudo-first-order rate constants, obtained from the exponential decay of the resonance fluorescence of $O({}^{3}P)$, were composite since, in addition to reaction with H₂S, O atoms were lost by reaction with O₂

$$O + O_2 + M \rightarrow O_3 + M \tag{5}$$

and by diffusional loss out of the reaction viewing zone. The correction term K^* for the latter two loss pro-

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FIG. 1. Plot of k_{bi} vs log of the initial relative O atom concentration. O: for the conditions 298 K, 500 mtorr O_2 , 100 mtorr H_2S and $P_{Ar} = 20$ torr; Δ : 345 K, 2 torr O_2 , 300 mtorr H_2S and $P_{Ar} = 200$ torr; \Box : 495 K, 1 torr O_2 , 100 mtorr H_2S and $P_{Ar} = 100$ torr. Equation (7) and (8) were always used to obtain k_{bi} irrespective of bending in the ln[O] vs t plots at high flash energies.

cesses,⁸

$$K^* = k_3[O_2][M] + k_d$$
, (6)

was determined independently by flash photolyzing mixtures of O_2 and argon at the various experimental temperatures and pressures employed in this study. K^* was typically of the order of 15% of the total observed first-order rate constant. The delay between the photoflash and accumulation of kinetic decay data for [O] was $\geq 300 \ \mu s$.

The argon and oxygen used in this study were from Matheson and had minimum purities of 99.9995% and 99.99%, respectively. Both were used without further purification. The only detectable impurity in the H_2S (Matheson, C. P. Grade) was a few percent of CO_2 which was reduced to <0.4% by extensive bulb-to-bulb distillation at 113 K. D_2S (Merck, Sharpe and Dohme) was degassed and used without further purification. Mass spectrometric analysis indicated an isotopic purity of 96%.

RESULTS

Under the pseudo-first-order conditions employed here, with $[H_2S] \gg [O]$, the decay of O atoms may be expressed experimentally as

$$\ln[\mathbf{O}] = -k_{\text{observed}} t + \ln[\mathbf{O}]_0, \qquad (7)$$

where the observed pseudo-first-order rate constant is given by

$$k_{\text{observed}} = k_{\text{bi}} [H_2 S] + K^* .$$
(8)

 K^* is the correction term defined by Eq. (6) and k_{bi} is the bimolecular rate constant which is equal to k_1 in the limit of unit stoichiometry.

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A major concern in this work was to avoid contributions to O atom removal from species formed either in the photolysis flash or from the reaction, which would result in $k_{\rm bi}$ containing a stoichiometry factor other than unity. The relatively slow rate of the primary step and the evidence of previous work that secondary reactions are important at low $[H_2S]/[O]$ ratios suggested that the observed rate constant in the present experiments would exhibit flash intensity dependence. Preliminary experiments at room temperature showed that over a range of flash energies, and hence a range of $[O]^8$, Eq. (7) was strictly followed with plots of ln[O] vs t exhibiting good linearity over at least 2 decay lifetimes. At higher flash energies $k_{observed}$ and hence k_{bi} was observed to increase and at the upper limit of flash energy clear bending in the $\ln[O]$ vs t plots was apparent.

The increase in k_{bi} at high flash energies is direct evidence of the onset of secondary reactions contributing to the O atom decays. This is seen more clearly in Fig. 1, where k_{bi} is plotted as a function of the initial relative O atom concentration. Whichever reactions cause the rate constant k_{bi} to increase, the low intensity limiting k_{bi} is obtained under conditions which are unaffected by competing secondary reactions of O atoms and corresponds to k_1 . Values of k_1 were obtained from series of experiments, such as the three series shown in Fig. 1, over a wide range of experimental conditions. The results are shown in Table I, where the quoted k_1 is the mean value obtained from the intensity-independent values for k_{bi} for each series of experiments. There is clearly no pressure dependence of k_1 in the range 10-400 torr.

Figure 2 shows an Arrhenius plot of the mean k_1 at each of the six temperatures studied. A linear least squares treatment provides the equation $k_1 = (7.24 \pm 1.07) \times 10^{-12} \exp(-3300 \pm 100/1.987 T) \text{ cm}^3$ molecule $\cdot \sec^{-1}$.

Several series of experiments were performed using D_2S in place of H_2S , under comparable conditions to those used for the H_2S experiments. Values of k_{1D}

$$O + D_2 S \rightarrow OD + SD$$
 (1_D)

were obtained by procedures similar to those described for k_1 and are listed in Table II. The uncertainty in k_{1D} is larger than for k_1 because the slower rate of Reaction (1_D) made the experiments more difficult to perform. A linear least squares treatment for the four temperatures studied yields the equation

$$k_{1D} = (1.05 \pm 0.57) \times 10^{-11} \exp(-4260 \pm 310/1.987 T)$$

 $\times \text{ cm}^3 \text{ molecule}^{-1} \cdot \text{sec}^{-1}$

DISCUSSION

The constancy of k_{bi} over a wide range of flash intensity for each set of experimental conditions (Fig. 1 and Table I) confirms that potential complications due to secondary reactions involving O atoms were absent

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TABLE I. Rate data for the reaction $O + H_2S$.

т (К)	P _{total} (Torr)	P _{O2} (mTorr)	^Г н _г е (mTorr)	Flash energy (J)	Number of experiments	k_1^{b} (10 ⁻¹⁴ cm ³ molecule ⁻¹ · sec ⁻¹)
495	100	1000	100	5 1-110	16	28.9+2.3
495	100	1000	50	4 4-56	9	25 1 . 2 2
495	200	2000	100	23-144	8	27 2 2 0
100		2000		50 111		$\frac{27.4 \pm 2.7}{27.4 \pm 2.7}$ a
450	10	1000	100	20-101	6	16.1 + 0.9
450	20	2000	200	31 - 68	3	17, 2 + 1, 0
450	200	500	50	14 - 36	3	18,9+2,5
						17.1 ± 1.8 ^a
400	10	1000	100	9.0-81	6	10.6+1.0
400	20	2000	200	9.0-56	5	11.7 ± 0.8
400	50	500	75	9.0-36	4	12.0 ± 0.6
400	100	1000	150	9.0-20	3	11.9 ± 0.7
400	200	2000	300	14 - 36	3	11.5 ± 0.7
400	200	667	100	9.0-56	4	11.4 ± 1.1
400	300	1000	150	9.0-20	2	11.5 ± 1.1
400	400	1000	100	8,1-81	7	$\frac{11.3 \cdot 1.2}{11.4 \cdot 1.0}$
0.15		500	100		~	5.50 0.50
345	20	500	100	9.0-36	5	5.52 ± 0.52
345	100	1000	150	1.1-5.1	6	3.35 ± 0.40
345	200	2000	300	1.8-9.0	7	$\frac{5,40+0,30}{5,42+0,30}$
298	20	200	100	5,0-20	4	2.98 ± 0.27
298	20	500	100	2.3-9.0	5	2.99 ± 0.15
298	40	400	200	14 - 56	4	3.07 ± 0.12
298	100	333	50	6.5 - 20	5	$3,07 \pm 0,14$
298	100	1000	150	7.3-14	4	2,92+0,26
298	200	2000	300	7.3-36	4	2.87 ± 0.29
298	200	667	100	5,1-14	6	$2,82 \pm 0,27$
298	300	1000	150	13.20	2	3, 23 : 0, 32
298	400	1333	200	14	1	2,92
						2.97 0.23 ^a
263	10	1000	300	7.3-18	4	1.34 ± 0.27
263	15	750	225	9.0,11	2	1.25 .0.04
263	20	1000	300	2,3-9.0	7	1.16 ± 0.15
263	25	1250	375	5.1-16	7	1.15 ± 0.04
263	50	500	150	5.1,8.1	2	1.49 ± 0.06
263	50	500	75	5.8-9.9	4	1.61 ± 0.25
263	100	1000	300	3.8-7.3	5	1.34 ± 0.07
263	100	1000	150	3.2-7.3	5	1.44:0.09
						1.31 ± 0.21 a

^aMean value of k_1 at that temperature.

^bError limit in k_1 is the standard deviation.

under these conditions. The increase in k_{bi} at higher flash energies under all conditions indicates the onset of secondary reactions. The fact that an increase in k_{bi} of a factor of five above the low energy limit could be observed under certain conditions (low temperature and high flash energy) is direct confirmation of previous suggestions^{2,4} that a chain mechanism can become operative in this system. Figure 1 shows that the increase in k_{bi} above its limiting value moves to higher flash energies as the temperature increases. This means that the onset of stoichiometric complications is temperature dependent and indicates that higher $[H_2S]/[O]$ ratios are required to isolate the primary step at low temperatures than at high temperatures. It also indi-



FIG. 2. Arrhenius plot of the bimolecular rate constant (k_1) for the reaction O+H₂S.

cates strongly that previous assumptions⁶ of a constant stoichiometry over a range of temperature, under conditions where secondary reactions were operative, were probably in error.

A comparison of the present k_1 values with those obtained previously is presented in Fig. 3. The value of k_1 obtained in this study at room temperature is lower than all but two of the previous determinations. It is in excellent agreement with that obtained by Timmons and co-workers⁶ but is almost a factor of 2 higher than that of Cupitt and Glass.⁴ The latter workers obtained this low value for k_1 by computer simulation of reaction profiles; however, in order to explain their results, they had to invoke a k_3 value which is much higher than the accepted literature value.^{12,13} It now appears that "hot" H atoms may have been an added complication in their system¹⁴ and this may provide an explanation for the low k_1 and the high k_3 which they obtained.

The temperature dependence of k_1 found here is different from that of previous workers. The lower A factor and activation energy obtained by Timmons and co-workers⁶ probably reflect an underestimate of the stoichiometry of the reaction at the two lowest tem-

ГΑ	BLE	п.	Rate	data	for	the	reaction	0+1	$D_2S.$
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Т (К)	P _{total} (Torr)	P _{O2} (mTorr)	P _{D2} s (mTorr)	Flash energy (J)	Number of experiments	k_{1u}^{a} (10 ⁻¹⁴ cm ³ molecule ⁻¹ · sec ⁻¹)
450	10-20	1000-2000	100-200	13-81	13	9.23 ± 1.49
400	20-100	500-2000	100-200	11-46	21	5.20 ± 1.12
345	100-200	500-2000	100 - 200	7.3-23	22	1.80 ± 0.46
2 9 8	20-100	500-2000	100-200	2.7-20	37	0.859 ± 0.192

^aError limit in k_{1D} is the standard deviation.

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FIG. 3. Comparison of k_1 values: \Box , Ref. 3; Δ , Ref. 2; \times , Ref. 5, O, Ref. 6; \bullet , Ref. 4; dotted line, Ref. 7; solid line, this work.

peratures they employed, although part of the discrepancy may be associated with temperature dependence of the A factor since their temperature range was very different from that used here. The very recent study of Gutman and co-workers, ⁷ over a temperature range almost identical to that employed here, gives a higher k_1 at every temperature. The discrepancy is probably within the experimental error at 263 K but increases with temperature to a factor of greater than two at 495 K; presumably stoichiometric complications are again the root cause of the differences.

The mechanism of the reaction has been regarded, until recently, as a straightforward hydrogen abstraction reaction. Recent work on the reaction of O atoms with alkylated analogs of H_2S , ^{7,10} where the reactions appear to involve an addition process, suggests that addition cannot be ruled out for $O + H_2S$. Although we observed no pressure effect on k_1 , this could simply mean that the adduct has a very short lifetime. The experiments with D_2S , where a primary isotope effect was observed, are evidence for a hydrogen abstraction mechanism. The observed ratios of k_1/k_{1D} of ~3 at 298 K and ~ 2 at 450 K are exactly as predicted on the basis of the simple equation $k_1/k_{1D} = \exp(\Delta E_0/RT)$ where ΔE_0 is the difference in zero point energies for the stretching frequencies of the S-H and S-D bonds. The isotope effect seems good evidence for an abstraction mechanism, although a contribution from addition may not be ruled out.

model, with no adjustable parameters, predicts a very "loose" complex that is close to reactants, in agreement with the transition state theory calculation of Timmons and co-workers.⁶ The BEBO model predicts an activation energy of 2. 2 kcal mol⁻¹ and an A factor of 3. 0 $\times 10^{-11}$ cm³ molecule⁻¹ · sec⁻¹. Although these values are not in close agreement with experiment, the disagreements are not unexpected in view of the approximate nature of the theory.^{15,16} Thus the calculation is not inconsistent with an abstraction mechanism, but dynamical experiments probably will be needed to identify the mechanism with certainty.

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Finally, it is felt that use of the sensitive resonance fluorescence technique has avoided the stoichiometric complications inherent in previous work and the present k_1 value is recommended for the modeling of earth and other planetary atmospheres, e.g., Venus.

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A complete BEBO calculation based on an abstraction

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