

lution was stirred for 1 h at 25 °C, an aliquot was withdrawn. The solvent from the sample was evaporated under vacuum. The isolated material exhibits new IR bands at 990, 1265, 1530, and 1690 cm^{-1} . A deoxygenated mixture of benzyl alcohol (0.53 mL, 5.1 mmol) and biphenyl (0.440 g, 0.29 mmol) was added under argon to the remaining solution. The resulting mixture was immersed into a bath heated to 60 °C. At different time intervals, samples were removed by a gas-tight syringe and analyzed by GC. Only 30% of the expected amount of benzaldehyde was formed.

Oxidation of Co(TPP)NO by O_2 in the Presence of Lewis Acids. Under argon, first Co(TPP)NO (0.139 g, 0.20 mmol) was added to deoxygenated 1,2-dichloroethane, followed by benzyl alcohol (0.53 mL, 5.1 mmol) and then $\text{BF}_3\cdot\text{Et}_2\text{O}$ (0.125 mL, 1.02 mmol). Then a slow stream of O_2 was passed through the solution at room temperature. After 1 h, the solvent was evaporated under vacuum, and the residue was treated with a 1:1 mixture (20 mL) of dichloromethane and *n*-heptane under argon. The resulting precipitate was filtered off, washed with 4 portions of dichloromethane-*n*-heptane mixture (20 mL), and dried under vacuum. The IR spectrum of this material shows no Co-NO band. Instead, new bands are observed at 1208, 1313, and 1490 cm^{-1} as well as a broad band at 950-1100 cm^{-1} ascribed to BF_3 and benzyl alcohol.

Oxidation Procedures and Product Analysis. Stoichiometric Oxidation of Alcohols by Cobalt-Nitro Complexes. All stoichiometric alcohol oxidations were carried out in the same manner. Oxidation of benzyl alcohol is chosen as an example. The internal standard, biphenyl (0.760 g, 0.49 mmol), and pyCo(TPP)NO₂ (0.320 g, 0.40 mmol) were placed in a flask and deaerated with argon. A deaerated solution of benzyl alcohol (1.05 mL, 10.1 mmol) in 1,2-dichloroethane (10 mL) was added under an argon flow. The reaction mixture was placed in an argon-filled glovebag where $\text{BF}_3\cdot\text{Et}_2\text{O}$ (0.25 mL, 2.03 mmol) was added. The reac-

tion solution was capped with a serum stopper and immersed in a 60 °C oil bath. Samples for GC analysis were removed at $t = 0, 5, 10, 15, 30, 45,$ and 60 min with a gas-tight syringe. Prior to injection on a GC column, $\text{BF}_3\cdot\text{Et}_2\text{O}$ was neutralized to avoid decomposition of the column packings. This was accomplished by adding 1 drop of pyridine and 1 mL of hexane to a 0.5-mL reaction solution aliquot, followed by filtration to remove the precipitated BF_3 -pyridine complex. GC analysis was performed on either a Hewlett-Packard 5830A equipped with a flame ionization detector or on a Hewlett-Packard 5710A equipped with a thermal conductivity detector. Analysis of the products of cyclohexanol, cycloheptanol, and cyclopentanol oxidations was carried out with a 1.83-m (6 ft) column containing 10% Carbowax on 80/100 Supelcoport. The benzyl alcohol oxidation mixtures were analyzed on a 1.22-m (4 ft) column containing 5% Silar 5 CP supported on 80/100 Gas-Chrom Q. Concentrations of the solution components were determined by computer integration employing biphenyl as the internal standard. Product identities were determined by coinjection with authentic materials and by GC/MS analyses. Complexes from a reaction solution were isolated by removing the solvent under vacuum from a reaction mixture aliquot. The resulting oils were triturated with petroleum ether, yielding a solid which was filtered and dried under argon.

Oxidation of Alcohols by O_2 Catalyzed by Cobalt-Nitro or -Nitrosyl Complexes. An oxygen-saturated solution of the substrate (~10 mmol), biphenyl (internal standard, ~0.5 mmol), and the appropriate cobalt-nitro or -nitrosyl complex (~0.4 mmol) in oxygen-saturated 1,2-dichloroethane (10 mL) was placed into a Fisher-Porter bottle equipped with a Teflon-coated stirring bar. At this time, the reactor was closed, pressurized with O_2 to the required pressure, and immersed into a controlled-temperature bath. Samples were withdrawn through a septum with a glass-tight syringe. The analysis of the samples is described above.

Gas-Phase Reactions of $\text{O}(^3\text{P})$ Atoms with Methanethiol, Ethanethiol, Methyl Sulfide, and Dimethyl Disulfide. 1. Rate Constants and Arrhenius Parameters¹

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Abstract: Absolute values of rate constants have been determined for the reaction of ground-state oxygen atoms, $\text{O}(^3\text{P})$, with CH_3SH , $\text{C}_2\text{H}_5\text{SH}$, CH_3SCH_3 , and CH_3SSCH_3 by using a phase shift technique in which oxygen atoms are generated by mercury-photosensitized decomposition of N_2O and monitored by the chemiluminescence from their reaction with NO. Between 298 and ~560 K, the rate constants are represented by the following equations: $k_{\text{CH}_3\text{SH}} = (1.52 \pm 0.17) \times 10^{-12} + (64 \pm 40) \times 10^{-12} \exp[(-1673 \pm 322)/T]$; $k_{\text{C}_2\text{H}_5\text{SH}} = (2.28 \pm 0.11) \times 10^{-12} + (145 \pm 74) \times 10^{-12} \exp[(-2075 \pm 268)/T]$; $k_{\text{CH}_3\text{SCH}_3} = (1.11 \pm 0.12) \times 10^{-11} \exp[(460 \pm 41)/T]$; $k_{\text{CH}_3\text{SSCH}_3} = (4.35 \pm 0.70) \times 10^{-11} \exp[(251 \pm 61)/T]$ in units of $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$.

Introduction

The detailed role of organic sulfides in the atmospheric portion of the global sulfur cycle is not well understood,³ and even the rate of emission of biogenic organic sulfides, relative to that of H_2S , is in question.⁴⁻⁶ The concentration of dimethyl sulfide has been determined in the atmosphere on the eastern coast of the United States⁷ and has been shown to be released, along with other organic sulfur compounds (CH_3SH , CH_3SSCH_3), from various biogenic sources (algae, bacteria, plants)^{3,8} and from anthropogenic

sources (wood pulp mills, petroleum refineries, sewage treatment plants).⁸ The homogeneous gas-phase reactions of the organic sulfides in the atmosphere probably involve oxidation by hydroxyl radicals and oxygen atoms.⁸⁻¹⁰ Although the rates of the reactions $\text{O} + \text{H}_2\text{S}$ ¹¹ and $\text{O} + \text{CH}_3\text{SH}$ ¹² are too slow to compete significantly with the corresponding hydroxyl radical reactions^{13,14} for the average ambient concentrations of O and OH, the reactions $\text{O} + \text{CH}_3\text{SCH}_3$ ^{12,15,16} and perhaps $\text{O} + \text{CH}_3\text{SSCH}_3$ may be sig-

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nificant. Reliable kinetic and mechanistic information is therefore required for these reactions.

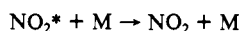
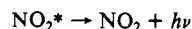
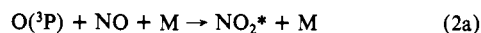
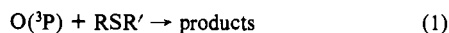
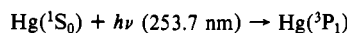
The reported rate constants for the reaction of oxygen atoms with CH₃SH, C₂H₅SH, and CH₃SCH₃ appear to display unusual temperature dependences. The Arrhenius plots for the mercaptans have been reported to be strongly curved,¹² although another study indicates linear behavior,¹⁷ and the rate constants for CH₃SCH₃ have a negative temperature dependence.^{12,15,16} Also, the results of crossed-beam studies with photoionization mass spectrometry have been discussed in terms of an addition mechanism for O + mercaptans and O + methyl sulfide,¹⁸ similar to that for O + olefins,¹⁹ although the extent of abstraction could not be determined.

In the present study, a phase-shift technique was used to determine rate constants for the reaction of oxygen atoms with CH₃SH, C₂H₅SH, CH₃SCH₃, and CH₃SSCH₃. For the first three, measurements were extended to higher temperatures (570 K) to confirm the unusual Arrhenius behavior. Mechanistic information for these reactions was also obtained in separate experiments described in the accompanying paper.²⁰

Experimental Section

The apparatus for the phase-shift measurements has been described in detail elsewhere^{21,22} and will be described only briefly. Ground-state oxygen atoms were produced by mercury-photosensitized decomposition of nitrous oxide with a sinusoidally modulated mercury lamp. The relative concentration of O(³P) was monitored by the NO₂* chemiluminescence obtained when NO was introduced into the reaction mixture. A Corning 3-70 sharp-cut filter (40% transmission at 500 nm) was placed in front of the chemiluminescence detector to eliminate any potential interference from the O + SO afterglow.

The reaction sequence is as follows, where R is CH₃ or C₂H₅ and R' is



is H, CH₃, or SCH₃. The phase shift, ϕ , between the incident 253.7 nm light and the NO₂* chemiluminescence was measured with photomultipliers and a lock-in amplifier. The phase shift is related to the rate constants as shown in eq I, where ν is the modulation frequency

$$2\pi\nu/\tan\phi = k_1[\text{RSR}'] + k_2[\text{NO}][\text{M}] \quad (I)$$

(1600–5970 Hz in these experiments). For constant [NO] and [M], a plot of $2\pi\nu/\tan\phi$ vs. [RSR'] gives a straight line with slope equal to k_1 .

Flow rates were determined by calibrated capillary flowmeters. Because of its low vapor pressure and high reactivity, CH₃SSCH₃ was introduced as a CH₃SSCH₃/N₂O mixture. Ethanethiol (Aldrich, 99.8%), dimethyl sulfide (Matheson Coleman and Bell, 98.8%), and dimethyl disulfide (Eastman Organic, 98.4%) were degassed and fractionally distilled, with the middle third retained for experiments. Methanethiol (Matheson, 99.5%) and nitrous oxide (Matheson, 99.0%)

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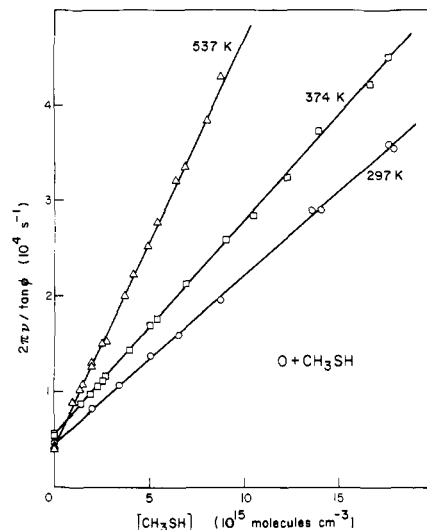


Figure 1. Plots of $2\pi\nu/\tan\phi$ vs. $[\text{CH}_3\text{SH}]$ for the reaction $\text{O}(^3\text{P}) + \text{CH}_3\text{SH}$ at three temperatures.

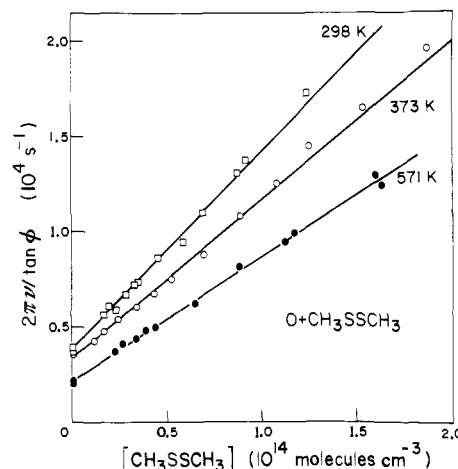
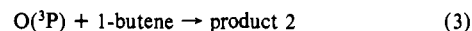
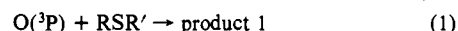


Figure 2. Plots of $2\pi\nu/\tan\phi$ vs. $[\text{CH}_3\text{SSCH}_3]$ for the reaction $\text{O}(^3\text{P}) + \text{CH}_3\text{SSCH}_3$ at three temperatures.

were used without further purification. Nitric oxide (Matheson, 99.0%) was purified by passing the gas through a molecular sieve trap. The indicated purities of the sulfur compounds were obtained by gas chromatography.

Some competitive kinetic measurements were done by analyzing reaction products using the technique described in the accompanying paper.²⁰ The O(³P) + 1-butene reaction was used as a standard, and the products, α -butene oxide and *n*-butanal, were used to monitor the extent of this reaction¹⁹ for various amounts of added sulfur compound. The competing reactions are eq 1 and 3, and the relative rate constant, k_1/k_3 ,



is given by eq II, where $r_{\text{N}_2^*}$ and $r_{\text{product-2}}^*$ denote the rate of formation

$$k_1/k_3 = \left(\frac{r_{\text{N}_2^*}}{r_{\text{N}_2^*}} \frac{r_{\text{product-2}}^*}{r_{\text{product-2}}^*} - 1 \right) \frac{[1\text{-butene}]}{[\text{RSR}']} \quad (II)$$

of N₂ and product 2 in the absence of sulfide. This method was used to measure $k_{\text{O}+\text{CH}_3\text{SCH}_3}$ and $k_{\text{O}+\text{CH}_3\text{SSCH}_3}$ at 300 K. The same technique could not be used to determine rate constants for the reactions O + CH₃SH and O + C₂H₅SH because of interference from the very rapid secondary reactions with the products formed,²⁰ i.e., O + CH₃SSCH₃ and O + C₂H₅SSC₂H₅.

Results

Absolute Rate Constants. Values of k_1 were obtained from the slopes of weighted,²³ linear, least-squares plots of $2\pi\nu/\tan\phi$ vs.

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Table I. Rate Constants for Reactions of O(³P) with CH₃SH, C₂H₅SH, CH₃SCH₃, and CH₃SSCH₃

reactant	temp, K	no. of points	10 ¹⁷ [N ₂ O], molec cm ⁻³	10 ¹⁶ [NO], molec cm ⁻³	10 ⁻¹² k ₁ ^a cm ³ molec ⁻¹ s ⁻¹	10 ⁻³¹ k ₂ ^a cm ⁶ molec ⁻² s ⁻¹	
CH ₃ SH	297	10	7.02	3.37	1.77 ± 0.06	1.80 ± 0.12	
	298	10	8.18	6.66	1.77 ± 0.05	1.67 ± 0.04	
	299	17	19.8	3.60	1.77 ± 0.05	1.34 ± 0.20	
	299 ^b	17	7.29	4.34	1.73 ± 0.05	1.82 ± 0.06	
	335	17	7.10	6.20	2.01 ± 0.06	1.37 ± 0.05	
	374	17	5.96	6.55	2.24 ± 0.03	1.25 ± 0.02	
	421	17	5.42	6.26	2.69 ± 0.04	1.12 ± 0.03	
	474	17	4.88	6.50	3.40 ± 0.09	0.95 ± 0.06	
	475	7	4.87	6.36	3.63 ± 0.09	1.02 ± 0.06	
	537	17	5.93	7.20	4.27 ± 0.09	0.84 ± 0.03	
	C ₂ H ₅ SH	300	16	7.26	2.87	2.43 ± 0.10	1.79 ± 0.07
300		16	16.2	1.82	2.38 ± 0.09	1.57 ± 0.05	
300 ^b		16	6.83	2.17	2.49 ± 0.08	1.89 ± 0.06	
337		17	8.26	2.11	2.55 ± 0.09	1.88 ± 0.07	
375		16	5.70	2.96	2.86 ± 0.08	1.43 ± 0.06	
428		16	6.30	3.01	3.42 ± 0.10	1.26 ± 0.05	
475		16	5.71	3.96	4.20 ± 0.22	1.12 ± 0.08	
574		16	5.66	4.66	6.15 ± 0.31	0.90 ± 0.07	
CH ₃ SCH ₃		296	14	18.2	5.26	50.2 ± 3.9	1.28 ± 0.17
	297	16	7.21	5.75	50.2 ± 4.2	1.14 ± 0.38	
	297	13	7.29	4.05	50.2 ± 3.5	1.88 ± 0.43	
	297	16	17.4	5.36	53.4 ± 2.5	1.34 ± 0.09	
	298 ^b	15	7.20	5.51	51.6 ± 2.1	1.36 ± 0.17	
	333	17	6.58	4.64	44.6 ± 2.0	1.40 ± 0.23	
	370	18	7.23	6.70	39.5 ± 1.2	1.08 ± 0.10	
	422	17	6.36	7.34	32.7 ± 0.7	1.04 ± 0.07	
	479	18	7.85	9.85	29.9 ± 1.1	0.65 ± 0.08	
	557	18	6.65	8.28	24.1 ± 1.2	0.71 ± 0.12	
	CH ₃ SSCH ₃	298	12	7.09	3.60	102 ± 5	1.41 ± 0.06
		298	14	6.90	2.77	103 ± 5	1.94 ± 0.08
		299	12	15.6	1.82	97 ± 6	1.94 ± 0.08
333		14	8.26	2.95	91 ± 4	1.62 ± 0.05	
373		14	7.49	2.90	82 ± 5	1.49 ± 0.08	
425		14	6.76	2.57	78 ± 4	1.55 ± 0.10	
475		14	6.04	3.25	77 ± 2	1.02 ± 0.05	
571		13	5.93	4.24	64 ± 2	1.20 ± 0.04	

^a The indicated uncertainties are the 95% confidence limits for the appropriate number of degrees of freedom. ^b The incident 253.7-nm light intensity was reduced to 30% of its usual value.

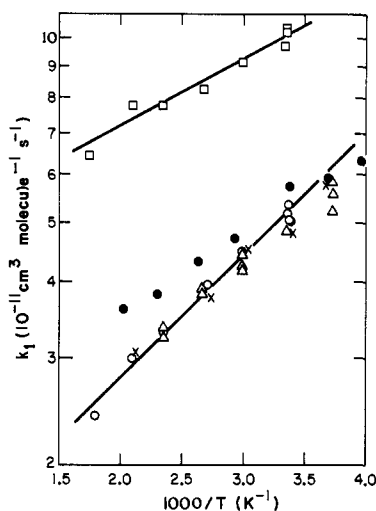


Figure 3. Arrhenius plots for the reaction of O(³P) with methyl sulfide and dimethyl disulfide. CH₃SCH₃: ○, this work; ●, ref 12; ▲, ref 15; × ref 16. CH₃SSCH₃: □, this work. The lines are the weighted least-squares analyses of this work.

[RSR'] at constant [NO] and [M]. Examples of the plots of CH₃SH and CH₃SSCH₃ are given in Figures 1 and 2. Good linearity was always observed, supporting the form of eq I. Values of k₁ at different temperatures for the four sulfur compounds

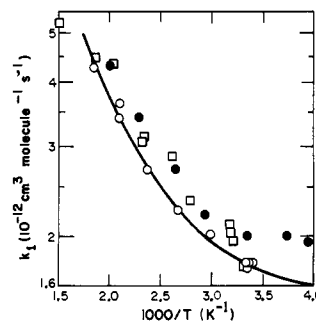


Figure 4. Arrhenius plot for the reaction of O(³P) with CH₃SH: ○, this work; ●, ref 12; □, ref 17. The value of ref 17 at the lowest temperature is the average of 10 values between 300 and 307 K.

studied are given in Table I. Variation of the pressure from 24 to between 50 and 60 torr did not affect the values of k₁ at room temperature, nor did reduction of the incident 253.7-nm intensity to 30% of its usual value of 7 × 10¹² quanta s⁻¹.

The Arrhenius plots in Figure 3 for k_{CH₃SCH₃} and k_{CH₃SSCH₃} exhibit negative temperature dependence and can be satisfactorily represented by expressions 4 and 5 (in units of cm³ molec⁻¹ s⁻¹),

$$k_{\text{CH}_3\text{SCH}_3} = (1.11 \pm 0.12) \times 10^{-11} \exp[(460 \pm 41)/T] \quad (4)$$

$$k_{\text{CH}_3\text{SSCH}_3} = (4.35 \pm 0.70) \times 10^{-11} \exp[(251 \pm 61)/T] \quad (5)$$

which were obtained by weighted (1/σ_k²), nonlinear, least-squares treatment of the rate constants in Table I. The indicated uncertainties are the 95% confidence limits for eight and six degrees of freedom, respectively.

The Arrhenius plots for k_{CH₃SH} and k_{C₂H₅SH} are curves, as seen in Figures 4 and 5. Although the temperature range of the

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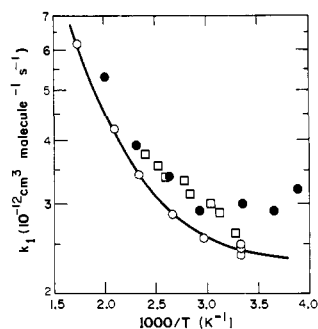


Figure 5. Arrhenius plot for the reaction of O(³P) with C₂H₅SH: ○, this work; ●, ref 12; □, ref 17. The value of ref 17 at the lowest temperature is the average of four values between 304 and 306 K.

measurements is not large, the usual Arrhenius expression would be clearly inadequate to represent the data, given the experimental uncertainties. The rate constants can be fitted (by the least-squares method) to other nonlinear functions, for example to the following relatively simple empirical expressions of eq 6 and 7 (in units of cm³ molec⁻¹ s⁻¹), where the indicated uncertainties are the 95%

$$k_{\text{CH}_3\text{SH}} = (1.52 \pm 0.17) \times 10^{-12} + (64 \pm 40) \times 10^{-12} \exp[(-1673 \pm 322)/T] \quad (6)$$

$$k_{\text{C}_2\text{H}_5\text{SH}} = (2.28 \pm 0.11) \times 10^{-12} + (145 \pm 74) \times 10^{-12} \exp[(-2075 \pm 268)/T] \quad (7)$$

confidence limits for eight and six degrees of freedom, respectively.

Values of the rate constant, k_2 , for the reaction O + NO + M → NO₂ + M (M = N₂O) could in principle be obtained from the intercepts of the plots of eq I. The values obtained are given in Table I and are generally 30–50% larger than the values obtained previously.²² An impurity of NO₂ of 150 ± 50 ppm in the NO and N₂O used in the present work would be required to account for the difference, but it would not affect the slopes of plots such as those in Figures 1 and 2 and hence would not affect the values of k_1 . A higher than usual concentration of NO₂ impurity was indicated by the more rapid discoloration of the mercury in the system. A day to day variation in concentration of any NO₂, caused perhaps by different rates of consumption by mercury, could explain the somewhat large variation in values of k_2 at some temperatures.

Relative Rate Constants. Experiments in which 1-butene competed for oxygen atoms with either CH₃SCH₃ or CH₃SSCH₃ were performed to obtain relative rate constants based on the yield of products of reaction 3, according to eq II. At room temperature, $k_{\text{CH}_3\text{SCH}_3}/k_{1-\text{C}_4\text{H}_8} = 13.8 \pm 0.9$ and $k_{\text{CH}_3\text{SSCH}_3}/k_{1-\text{C}_4\text{H}_8} = 24.5 \pm 1.5$, where the uncertainties are the 95% confidence limits for three determinations in each case. Using our previously determined value²⁴ for $k_{1-\text{C}_4\text{H}_8}$, we obtain the following absolute values with their 95% confidence limits: $k_{\text{CH}_3\text{SCH}_3} = (5.51 \pm 0.42) \times 10^{-11}$ and $k_{\text{CH}_3\text{SSCH}_3} = (9.82 \pm 0.61) \times 10^{-11}$ cm³ molec⁻¹ s⁻¹, in excellent agreement with the values in Table I obtained by the phase-shift method.

Discussion

Potential sources of systematic errors in the values of the absolute rate constants could be the presence of reactive impurities and the reaction of oxygen atoms with products of the primary reaction. For CH₃SH, the most significant impurities were determined by gas chromatography to be CH₃SCH₃ (0.038%) and CH₃SSCH₃ (0.061%), which would increase the rate constants 1.1% and 3.5%, respectively, at room temperature and less at higher temperatures. The rate constants were not corrected for this contribution.

No organic sulfide or disulfide impurities were detected in C₂H₅SH, but small amounts of CH₃SCH₃ would not be detected because of the similarity of its retention time with that of C₂H₅SH. The small amount of impurities in CH₃SCH₃ and CH₃SSCH₃ would not affect the rate constant measurements for these very fast reactions.

The products of the reaction of oxygen atoms with CH₃SH or with C₂H₅SH include CH₃SSCH₃ or C₂H₅SSC₂H₅. Because the disulfides react so much faster than the mercaptans, they could interfere with the rate measurements if their concentrations were allowed to build up too high. However, under the experimental conditions used, the interference can be shown to be very small. If r_1' is the rate of reaction of oxygen atoms with disulfide and r_1 is the rate with mercaptan, then $r_1'/r_1 = r_1'[\text{disulfide}]/k_1[\text{mercaptan}]$. Since $[\text{disulfide}]/[\text{mercaptan}] < I_a/F$, where I_a is the rate of 253.7-nm light absorption and F is the flow rate of mercaptan, $r_1'/r_1 < k_1'I_a/k_1F$. A value of k_1' for C₂H₅SSC₂H₅ is not available, but it is likely that the ratio k_1'/k_1 is about the same for CH₃SSCH₃/CH₃SH and C₂H₅SSC₂H₅/C₂H₅SH. At the minimum flow rate of mercaptan used at room temperature, where the error would be greatest, $r_1'/r_1 < 0.06\%$ for CH₃SH and is $< 0.18\%$ for C₂H₅SH. Likewise, secondary reactions of oxygen atoms with other products such as might arise from reactions of radicals with NO would be insignificant, even if the rate constant of the secondary reaction were 10 times greater than the already large value of k_1 used above. Other potential systematic errors, including those in the phase shift, flow rate, and pressure measurements, are probably less than 15%.

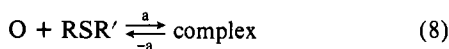
Comparison with Literature Values. The results of the present study are compared with other reported rate constants in Figures 3–5. The present results for CH₃SCH₃ are very similar to the flash photolysis–resonance fluorescence results of Lee, Timmons, and Stief¹⁵ and the discharge flow–resonance fluorescence results of Lee, Tang, and Klemm¹⁶ shown in Figure 3. The values reported by Slagle et al.¹² are slightly larger, particularly at higher temperatures, but the differences are not excessive. The value 5.5×10^{-13} cm³ molec⁻¹ s⁻¹ reported in ref 25 is considerably smaller and is probably in error.

The room-temperature rate constant for O + CH₃SSCH₃ determined by Lee and Tang,²⁶ using the discharge flow–resonance fluorescence technique, is about twice as large as the present value. Although they reported no variation in $k_{\text{CH}_3\text{SSCH}_3}$ between 270 and 329 K, the present Arrhenius expression indicates that there would be less than a 20% variation over this relatively narrow temperature interval. The cause of the discrepancy in the magnitude of $k_{\text{CH}_3\text{SSCH}_3}$ in the two studies is not apparent and is surprising in view of the excellent agreement for the O + CH₃SCH₃ rate constants determined in both laboratories. A careful search was made for systematic errors in the present work, including independent calibrations of N₂O and NO flowmeters, but none was found. Five different mixtures of N₂O and CH₃SSCH₃ were used, with a different mixture for each of the three values near room temperature. In these three cases the rate measurements were made from 1 to 2 days after making a mixture. The values at 298 K were measured before and the value at 299 K after the determinations at higher temperatures, with good consistency in the values. Furthermore, the very good agreement between the relative and absolute values of the rate constant for O + CH₃SCH₃ (as well as for O + CH₃SSCH₃) determined in the present work is indicative of the absence of systematic errors.

The values determined for CH₃SH and C₂H₅SH must be considered to be in reasonably good agreement with those reported by Slagle et al.¹² and by Kirchner et al.,¹⁷ although the latter results do not indicate any curvature in the Arrhenius plots. Both groups used a discharge flow–mass spectrometry method with pressures in the reactor in the 1-torr region and with an excess of oxygen atoms over thiol, and Kirchner et al. also studied the influence of the initial ratio [O]/[RSH] on the observed rate constant. Of particular interest in Figures 4 and 5 is our confirmation of the curvature in the Arrhenius plots reported by Slagle et al.¹² for the thiols, which will be discussed below.

Interpretation of Arrhenius Plots. The negative temperature dependence observed for CH₃SCH₃ and CH₃SSCH₃ is similar to that reported for the O plus tetramethylethylene reaction.²² The temperature dependences obtained in the present work of $T^{-1.2}$ for CH₃SCH₃ and $T^{-0.6}$ for CH₃SSCH₃ are somewhat larger than

the limiting negative temperature dependence of $T^{-0.5}$ calculated from transition state theory for bimolecular reactions. By analogy with the olefin reactions, a reversible formation of an oxygen atom-sulfide complex could be postulated to account for the observed negative temperature dependence (eq 8 and 9). The



products of the reactions $\text{O} + \text{CH}_3\text{SCH}_3$ and $\text{O} + \text{CH}_3\text{SSCH}_3$ are consistent with a mechanism involving addition of oxygen to sulfur, followed by fragmentation of the energy-rich adduct, which is discussed in detail in the accompanying paper.

The general nature of the complex could be similar to that suggested for the $\text{O} + \text{olefin}$ reactions.²⁴ Transition-state theory can be used to adequately reproduce the observed Arrhenius behavior of plots of k_{298}/k_T if appropriate values are chosen for the two S-O bending frequencies, ω , in the transition state and for $E = E_a - E_{-a} + E_b$, as described previously.²⁴ Because a single pair of ω, E values does not provide a unique fit to the Arrhenius plots, reasonable values of ω are assumed, and the best value of E is then chosen to fit the experimental data. The bending frequencies²⁷ in gaseous $(\text{CH}_3)_2\text{SO}$ are 376 and about 333 cm^{-1} , which could be considered upper limits for the bending frequencies in the transition state. For the usual simplifying assumptions that both frequencies are identical and harmonic²⁴ for $\text{O} + \text{CH}_3\text{SCH}_3$, the pair of ω, E values, 200 cm^{-1} and -1300 cal mol^{-1} , leads to an adequate fit of the data, as does the pair 200 cm^{-1} and -1000 cal mol^{-1} for $\text{O} + \text{CH}_3\text{SSCH}_3$. If a higher value of ω were chosen,

for example, 300 cm^{-1} , values of E would be -1100 and -800 cal mol^{-1} for CH_3SCH_3 and CH_3SSCH_3 , respectively. The values of E required to fit the data are somewhat more negative than for the case of $\text{O} + \text{tetramethylethylene}$,²⁴ due in part to the restriction of lower S-O bending frequencies in the assumed sulfoxide structure of the transition state in comparison with the epoxide structure for the olefin reactions.

On the other hand, the curvature of the Arrhenius plots for the thiols ($T^{1.5}$ for CH_3SH and $T^{1.2}$ for $\text{C}_2\text{H}_5\text{SH}$) is about the maximum temperature dependence ($T^{1.5}$) of the preexponential factor allowed by transition-state theory.²⁴ Also, at least some of the curvature may be due to two concurrent mechanisms: addition to the sulfur atom and abstraction of hydrogen, which would be expected to have low and high activation energies, respectively. The hydrogen bound to sulfur is more weakly bound (92 kcal mol^{-1} ;²⁸ on the basis of spectroscopic evidence, $\leq 87.4 \text{ kcal mol}^{-1}$)²⁹ and is expected to be more readily abstracted than the alkyl hydrogens ($\sim 94\text{--}98 \text{ kcal mol}^{-1}$). The product analysis experiments²⁰ indicate that abstraction may account for about 10% of the total reaction at 300 K, with addition of oxygen to sulfur followed by fragmentation of the adduct accounting for the remainder. If the temperature-dependent term, $A_2 \exp(-B/T)$, in the modified form of the Arrhenius expression for the thiols given in the Results [$k = A_1 + A_2 \exp(-B/T)$] is identified with the abstraction path, then at 300 K abstraction would make up 14% of the total calculated value of k , which is close to the value of 10% obtained from product analysis results. However, it should be emphasized that the particular functional form used was arbitrarily chosen in that it assumes a zero activation energy for one of the two routes.

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Gas-Phase Reactions of $\text{O}(^3\text{P})$ Atoms with Methanethiol, Ethanethiol, Methyl Sulfide, and Dimethyl Disulfide. 2. Reaction Products and Mechanisms¹

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Abstract: In conjunction with the determinations of the rate constants of reactions of the ground-state oxygen atoms, $\text{O}(^3\text{P})$, with methanethiol, ethanethiol, methyl sulfide, and dimethyl disulfide described in the preceding paper,³ a parallel study was carried out of the products and mechanisms of the same reactions at 300 K. Oxygen atoms were generated by the mercury-photosensitized decomposition of N_2O , used in large excess, and the recovered products were analyzed by gas chromatography. The total pressure was varied from 300 to 1200 torr. Nitrogen formed in the photosensitized decomposition of N_2O provided a direct measure of the number of O atoms generated and allowed determination of the yields of some of the products per oxygen atom reacting with the sulfur organic compounds. From a detailed analysis of the experimental results obtained with single sulfur organics and their mixtures, it is possible to derive substantial quantitative information on the reaction mechanisms. The postulated overall reaction mechanisms include some novel features common to the thiols, sulfide, and disulfide studied, which provide a simple explanation for some unexpected experimental trends observed.

Introduction

The present study of the products and mechanisms of the reactions of the ground-state oxygen atoms, $\text{O}(^3\text{P})$, with CH_3SH , $\text{C}_2\text{H}_5\text{SH}$, CH_3SCH_3 , and CH_3SSCH_3 has been carried out in parallel with the determinations for the same reactions of the rate constants and Arrhenius parameters, described in the preceding paper.³ There is no quantitative information in the literature on

the mechanisms of these reactions, in spite of their relevance to some important industrial, environmental, and biochemical problems, although some useful qualitative information has been obtained.⁴⁻⁶ Gutman and his co-workers have found an ap-

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