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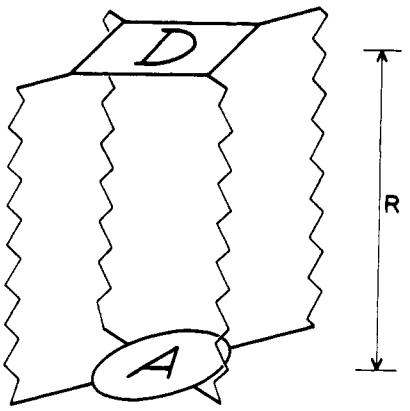

Figure 9. Schematic view of constrained donor-acceptor complex.

clear that the famous Thouless conditions[16] are decisive when the symmetry-breaking takes the form of a bifurcation, but are not very useful when multistability is concerned.

B. Possible Guidelines for Bistability Conditions in DA Complexes. The model study of a DA complex (Li_2···F) was purely academic since it would lead to a strongly bound complex. A stable DA system should first involve a rigid chemical structure, i.e., chemical bonds maintaining the D and A partners at the appropriate intersystem distance R such that $R^{-1} \simeq$ IP(D) - EA(A) (see Figure 9).

R should be large enough so that

$$|h| = |\langle \text{homo}_D|F|\text{lumo}_A\rangle_R| = \langle (\text{IP} - \text{EA})^{\text{vert}} - (\text{IP} - \text{EA})^{\text{adiab}} = 4\Delta E$$

The h integral may be rather small, even for relatively small R distances, if the highest occupied MO (homo) of D and lowest empty MO (lumo) of A are of different spatial symmetries.

Of course, these desires are somewhat contradictory. The ionization potential of conjugated molecules decreases with the size of the π system (8.15 eV for naphthalene, 7.04 eV for tetracene for instance[21]), but the difference between vertical and adiabatic ionization potentials also decreases with that size. The quantity $IP^{vert} - IP^{adiab}$ is only 0.10 eV for naphthalene and falls to 0.04 eV in tetracene.[22] The use of properly substituted (conjugated) molecules should be considered to solve the conflict between the smallness of IP - EA and the amplitude of $\Delta(\text{IP} - \text{EA})^{\text{vert-adiab}}$. Work is in progress in that direction, considering the (D,A) molecular pairs which organic conductors are built of, and for the localization of which the condition $2\Delta E > h$ was proposed by Shaik and Whangbo.[23]

Registry No. H_4^+, 12184-94-0; LiF, 7789-24-4; Li_2, 14452-59-6; F, 14762-94-8; HF, 7664-39-3.

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Kinetics and Mechanisms of the Reactions of CH_3S, CH_3SO, and CH_3SS with O_3 at 300 K and Low Pressures

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The reactions of $CH_3S + O_3 \rightarrow$ products (1), $CH_3SO + O_3 \rightarrow$ products (2), and $CH_3SS + O_3 \rightarrow$ products (3) were investigated at 300 K in a discharge flow tube reactor coupled to a photoionization mass spectrometer. The measured value of k_1 is (5.7 ± 1.4) × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} in 1 Torr He. We observed that OH was produced in this reaction or in subsequent steps and that complex branched chain reactions, which generate CH_3S from its precursor molecule, took place in our flow tube reactor. We found that CH_3SO was a product of reaction 1 and the branching ratio for this channel was 15 ± 4%, between 0.7 and 2.2 Torr He, independent of pressure. A preliminary value of $k_2 = (6 \pm 3) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} was measured. CH_3S was not a major product of reaction 2. These results suggest that the reaction with O_3 is a major CH_3S removal process in the atmosphere. The rate coefficient for the reaction of CH_3SS with O_3 (3) was measured to be $k_3 = (4.6 \pm 1.1) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}.

Introduction

Dimethyl sulfide (CH_3SCH_3, DMS) is estimated to make up between 50 and 90% of the total biogenic sulfur released to the atmosphere.[1] The CH_3S radical is thought to be an important intermediate in the atmospheric oxidation of DMS and of other biogenic sulfur compounds, such as methanethiol (CH_3SH) and dimethyl disulfide (CH_3SSCH_3, DMDS).[2-4] Therefore, several groups have investigated the reactions of CH_3S with the abundant tropospheric oxidants O_2, NO_2, and O_3.[5-9] Three groups have reported rate coefficients for the reaction of CH_3S with NO_2[5-7] and obtained results in the range (5-11) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}. Even though this reaction is fast, there generally is not enough NO_2 in the marine troposphere, where most of the DMS, and hence CH_3S, is present, to make this reaction an important CH_3S removal. An earlier measurement suggested that the reaction of O_3 with CH_3S was slow[8] ≤8 × 10^{-14} cm^3 $molecule^{-1}$ s^{-1}. The reaction of CH_3S with O_2 is very slow and an upper limit has been

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placed on its rate coefficient: $k \leq 2.5 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}.[6] It is therefore uncertain as to what species or processes remove CH_3S from the atmosphere.

Recently, measurements by Tyndall and Ravishankara[9] showed that the CH_3S reaction with O_3

$$CH_3S + O_3 \rightarrow \text{products} \quad (1)$$

was fast with $k_1 = (4.1 \pm 2.0) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. However, some aspects of the CH_3S/O_3 chemistry still need to be clarified before the atmospheric importance of this reaction can be fully understood. Tyndall and Ravishankara observed regeneration of CH_3S but could not identify the chemistry responsible for it in their pulsed photolysis laser-induced fluorescence experiment. Based on the analogous $HS/HSO + O_3$ reaction mechanism,[10,11] they suggested that reaction 1a could produce CH_3SO

$$CH_3S + O_3 \rightarrow CH_3SO + O_2$$

$$\Delta H^\circ_{298} = -59.1 \text{ kcal mol}^{-1} \quad (1a)$$

which may subsequently react with O_3 to regenerate CH_3S

$$CH_3SO + O_3 \rightarrow CH_3S + 2O_2$$

$$\Delta H^\circ_{298} = -9.1 \text{ kcal mol}^{-1} \quad (2a)$$

The ΔH values for reactions 1a and 2a were obtained using heats of formation of 31 kcal mol^{-1} for CH_3S[12] and 6 kcal mol^{-1} for CH_2SO.[7] If this reaction scheme were correct, and if CH_3SO does not react with O_2, reactions 1a and 2a will not result in a net loss of CH_3S. On the other hand, reaction 1 is fast enough to be the major atmospheric loss process for CH_3S, if the products of (1) were removed from the atmosphere without regenerating CH_3S in subsequent steps.

The objectives of the present study are (a) to examine the kinetics and mechanisms of the reactions of CH_3S and CH_3SO radicals with O_3, (b) to determine what process or processes are responsible for the chain reactions observed by Tyndall and Ravishankara, and (c) to identify and quantify as many of the products and intermediates in the reaction scheme as possible. Our emphasis on the elucidation of the mechanism is facilitated by the use of a photoionization mass spectrometer which is capable of detecting many of the species we expect to be present in the reaction mixture, including CH_3, CH_3S, CH_3SO, CH_2S, CH_3SS, and CH_3SSO.

The CH_3SS radical was formed by secondary chemistry in our source reactor and may be an intermediate in the atmospheric oxidation of DMDS. We have also measured the rate coefficient of its reaction with O_3

$$CH_3SS + O_3 \rightarrow \text{products} \quad (3)$$

Experimental Section

The experimental system used in this study was a discharge flow tube with a photoionization mass spectrometer, which has been described previously.[7] Therefore, it will not be described in detail here. The flow tube, with a 2.2 cm i.d., had a 50 cm long reaction region, and the average gas flow velocity, v, in the tube was approximately 2800 cm s^{-1}. All experiments were carried out under pseudo-first-order conditions, with the excess reactant, O_3, added through a movable injector. The free radicals CH_3S, CH_3SO, and CH_3SS were produced in a side arm reactor. A fraction of the flow tube effluents were sampled into a differentially pumped ion source, where they were ionized by hydrogen Lyman α radiation (10.2 eV), obtained by flowing pure hydrogen at 0.6 Torr through a microwave discharge. The ions were then electrostatically focused into a second chamber, where they were mass selected with a quadrupole mass filter and detected by an electron multiplier.

During this study an accident occurred which damaged several components of the detection system. The rebuilt system suffered from increased background noise due to scattered UV light from the ion source. As a result, the detection limit for the present study was about 10^9 molecules cm^{-3} for the sulfur compounds.

In this study, CH_3S radicals were produced by either of the following two reactions:

$$Cl + CH_3SH \rightarrow CH_3S + HCl \quad (4)$$

$$O + CH_3SSCH_3 \rightarrow CH_3S + CH_3SO \quad (5)$$

The source chemistry of these radicals has been described previously.[7] It should be noted that the self-reaction of CH_3S produced DMDS, CH_2S, and CH_3SH, which are detectable in our system. The slower self-reaction of CH_3SO produces $CH_3S(O)S(O)CH_3$, CH_2SO, and CH_3SOH, which were also detected. Reaction 5 produced equal amounts of CH_3S and CH_3SO and was used to calibrate the response ratio of the instrument to CH_3S and CH_3SO, detected at masses 47 and 63. We found that the (mass 47)/(mass 63) signal ratio was 1.73. It was observed that CH_3SS was generated in the side arm reactor whenever CH_3S was produced. This was attributed[7] to a heterogeneous reaction

$$CH_3S + S_{wall} \rightarrow CH_3SS \quad (6)$$

which was used as a source of CH_3SS. We produced CH_3SO radicals by the reaction of ethyl methyl sulfide ($C_2H_5SCH_3$, EMS) with O atoms (7), as described previously[7]

$$O + C_2H_5SCH_3 \rightarrow C_2H_5 + CH_3SO$$
$$\rightarrow CH_3 + C_2H_5SO \quad (7)$$

We tested for the possibility of radical generation by reaction of the precursor gases with O_3 by turning off the microwave discharge and searching for radicals with the mass spectrometer. No detectable background signals were observed, indicating that no significant radical generation occurred when the source discharge was off.

The helium (≥99.999%), hydrogen (≥99.999%), oxygen (≥99.97%), DMDS (≥99%), EMS (≥99%), and CCl_4 (≥99.9%) were used without further purification. The CH_3SH (≥99.5%) was purified by distillation. O_3 was stored on silica gel at 196 K and was eluted from the trap with a measured flow of He. The O_3–He mixture then flowed through an absorption cell where the O_3 partial pressure was measured by the absorption at 254 nm, using a cross section of 1.15×10^{-17} cm^2 molecule^{-1}.[13]

Results

a. OH Production by the CH_3S/O_3 System. In the study of the $CH_3S + O_3$ reaction, CH_3S regeneration was observed. We have attempted to understand the chemistry responsible for this regeneration by using both reactions 4 and 5 as sources of CH_3S.

When CH_3S was produced by the reaction of Cl with CH_3SH (4), it was observed that in the presence of excess O_3, the CH_3S signal showed an initial decay followed by an increase at longer reaction time, as shown in Figure 1. A signal at mass 63, assigned to CH_3SO produced by the reaction of CH_3S with O_3, was also observed to increase with time. At a reaction time greater than 8 ms, with $[O_3] = 2.2 \times 10^{14}$ molecules cm^{-3}, the sum of the concentrations of CH_3S and CH_3SO was greater than the initial concentration of CH_3S. Since the first-order-order wall loss rate coefficients of CH_3S and CH_3SO are about 6 s^{-1}, these reactions can be neglected. This observation shows that the number of radicals in our reactor increases with time and that some complex chemistry with one or more branched chain reactions is taking place.

We suspected that OH might be involved in the chain branching. However, OH cannot be directly detected in our apparatus because its ionization potential is higher than the Lyman α energy, 10.2 eV. Therefore we added C_2F_3Cl, an efficient OH scavenger, to our reactor. The OH adds to C_2F_3Cl with a rate coefficient of 6×10^{-12} cm^3 molecule^{-1} s^{-1} at 296 K in 1 Torr He.[14]

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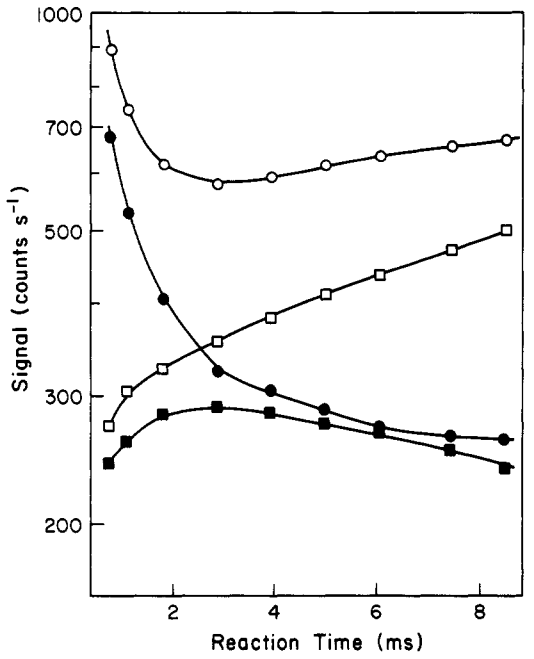

Figure 1. Plot of $[CH_3S]$ and $[CH_3SO]$ vs time, with $[O_3] = 2.2 \times 10^{14}$ molecule cm^{-3}: source, Cl + CH_3SH, with $[CH_3SH] = 2.7 \times 10^{12}$ molecule cm^{-3}; (○) CH_3S, (□) CH_3SO, with $[C_2F_3Cl] = 0$; (●) CH_3S, (■) CH_3SO, with $[C_2F_3Cl] = 2.3 \times 10^{14}$ molecules cm^{-3}.

We found that CH_3S, CH_3SS, and CH_3SO did not react with C_2F_3Cl on the time scale of our experiments. As can be seen in Figure 1, in the presence of C_2F_3Cl the CH_3S signal did not show any increase with reaction time, although the CH_3S decay plot was still nonexponential. The CH_3SO signal showed an initial increase followed by a decay, indicating that CH_3SO was a product of the O_3 and CH_3S reaction and that it reacted with O_3. It also appears that in the presence of C_2F_3Cl the sum of the concentrations of CH_3S and CH_3SO does not increase with reaction time.

The above observations are consistent with the following interpretation: (i) OH is formed in the reaction of CH_3S with O_3 or in some subsequent step. (ii) A branched chain reaction, which increases the number of radicals in the absence of C_2F_3Cl, takes place. (iii) OH reacts with CH_3SH to form CH_3S.[9] (iv) In the presence of C_2F_3Cl, the first-order CH_3S decay plot shows some curvature, which is probably due mainly to the fragmentation of a heavier compound in the flow tube or in the ionization region, to give a CH_3S radical or a CH_3S^+ ion. This complication will be detailed later.

To test this interpretation, we used the O + DMDS reaction as a source of CH_3S and CH_3SO. This source reaction eliminated the chlorine precursor and employed a different sulfur reagent. In the presence of O_3, the CH_3S signal showed an initial decay followed by an increase as shown in Figure 2a. No initial decay was observed in the CH_3SO signal, which rose continuously over the time range investigated. A signal at mass 64 was observed to rise and was assigned to CH_3SOH, although we believe, as detailed below, that there is a minor contribution from S_2. The rate of formation of CH_3SOH increased 5-fold between 3 and 18 ms. When C_2F_3Cl was added to the flow tube, the CH_3S and CH_3SO signals were found to decrease with time, as shown in Figure 2b. The first-order decay of CH_3S was slightly curved, probably due to heavy compound fragmentation, while the decay of CH_3SO was exponential. Since the reaction of CH_3S with O_3 produces CH_3SO, some curvature in its decay might be expected. However, considering that the CH_3SO was formed mainly in the O + DMDS source because the yield of CH_3SO from reaction 1 is small, as shown below, it is not surprising that a significant initial increase was not observed. The signal at mass 64 was found to decay with time and was much lower than when C_2F_3Cl was absent.

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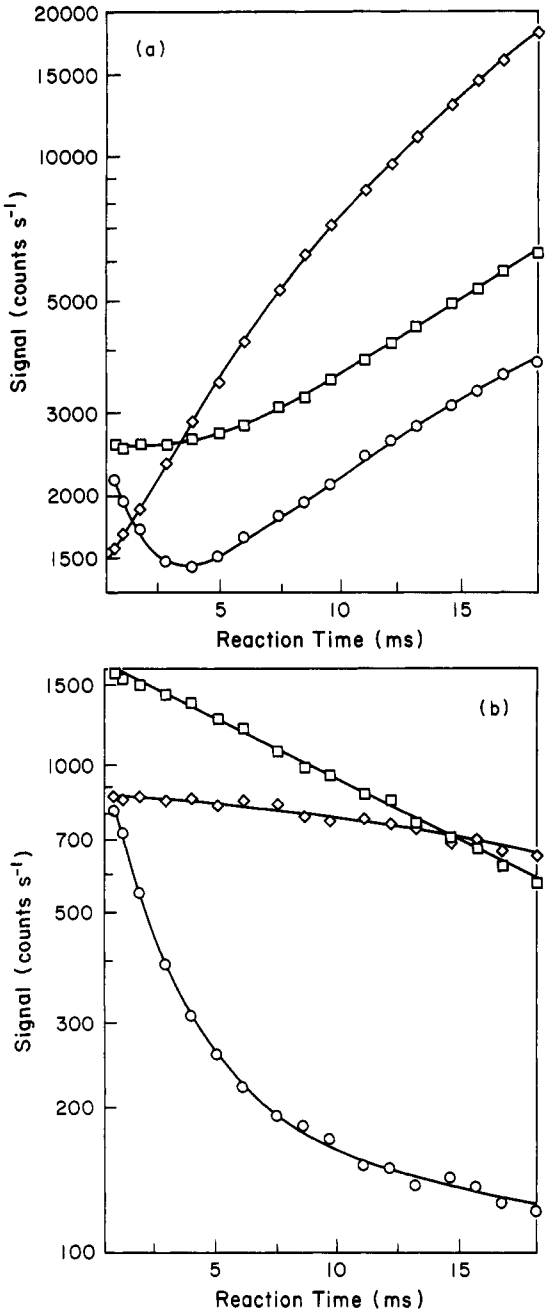

Figure 2. (a) Plot of $[CH_3S]$ (○), $[CH_3SO]$ (□), and $[CH_3SOH]$ (◇) vs time, with $[O_3] = 1.05 \times 10^{14}$ molecules cm^{-3}. Source was O + DMDS, with $[DMDS] = 1.6 \times 10^{12}$ molecules cm^{-3}. (b) Same as part a with $[C_2F_3Cl] = 1.02 \times 10^{15}$ molecules cm^{-3} added to the flow tube. Note different scales on the ordinates in parts a and b.

These observations are consistent with interpretations i, ii, and iv above and with the occurrence of reaction 8

$$OH + CH_3SSCH_3 \rightarrow CH_3S + CH_3SOH$$
$$\rightarrow \text{other products} \qquad (8)$$

which generates CH_3S and CH_3SOH. In the presence of C_2F_3Cl, no CH_3SOH should be formed via reaction 8, although it is possible that some is made in the self-reaction of CH_3SO radicals to account for the residual signal observed at mass 64. Alternatively this signal may be due to S_2. Since S_2 does not react with O_3, $k < 4 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1},[15] the decay of the mass 64 signal may be due to a reaction between the S_2 precursor and O_3.

We have tried to understand the mechanism responsible for the formation of OH. Reaction 1e

(15) Hills, A. J.; Cicerone, R. J.; Calvert, J. G.; Birks, J. W. *J. Phys. Chem.* **1987**, *91*, 1199.

$$CH_3S + O_3 \rightarrow OH + CH_2S + O_2$$

$$\Delta H^\circ_{298} = -31.5 \text{ kcal mol}^{-1} \quad (1e)$$

forms OH and could take place in our reactor. Since we cannot detect OH, this was tested by monitoring CH_2S at mass 46 in the presence of C_2F_3Cl. The fact that CH_2S is also formed in the source reactor by the self-reaction of CH_3S made this test difficult to perform. However, the CH_2S signals in the presence and in the absence of O_3 were the same, within the precision of our measurements. Assuming equal instrument responses for CH_2S and CH_3S, we conclude that the branching ratio for channel 1e is <4%. We believe that this assumption is reasonable, because we observed that the instrument response depended primarily upon the number of sulfur atoms in small organic species.[7]

Reactions involving some of the products of reaction 1 could also lead to the formation of OH. Reaction 2b

$$CH_3SO + O_3 \rightarrow OH + CH_2SO + O_2$$

$$\Delta H^\circ_{298} = -42.8 \text{ kcal mol}^{-1} \quad (2b)$$

is a possibility that was investigated by monitoring the rise of CH_2SO product at mass 62. The ΔH value for reaction 2b was obtained using heats of formation of -12 kcal mol^{-1} for CH_2SO[16] and 6 kcal mol^{-1} for CH_3SO.[7] Even though there are large uncertainties on both of these values, reaction 2b is definitely exothermic. To minimize interference from the $CH_3S + O_3$ chemistry, CH_3SO was produced by the reaction of EMS with O atoms (7). Figure 3a shows that, in the presence of O_3, the mass 63 (CH_3SO) signal, after an initial decay, increased with reaction time to an intensity greater that the initial value. The mass 29 (C_2H_5) and mass 64 (CH_3SOH with a possible contribution from S_2) signals showed a similar pattern, while signals were observed to increase at masses 62 (CH_2SO) and 47 (CH_3S). In the presence of O_3 and C_2F_3Cl (Figure 3b), the signals at masses 63, 29, and 64 showed nonexponential decays and the CH_3S and CH_2SO signals were observed to increase, although they did so more rapidly in the absence of C_2F_3Cl.

These observations are consistent with the following interpretation: (i) OH, CH_3S, and CH_2SO are formed when CH_3SO reacts with O_3. The formation of CH_2SO suggests that OH may be formed in this reaction, although subsequent reactions also could also produce OH, or even CH_2SO. (ii) The increase in the number of radicals indicates that a branched chain reaction take place. (iii) OH reacts with EMS to regenerate C_2H_5 and produce CH_3SOH

$$CH_3SC_2H_5 + OH \rightarrow CH_3SOH + C_2H_5 \quad (9a)$$

Other channels are possible for the reaction of EMS with OH. These include

$$CH_3SC_2H_5 + OH \rightarrow CH_3 + C_2H_5SOH \quad (9b)$$

$$CH_3SC_2H_5 + OH \rightarrow CH_3SC_2H_4 + H_2O \quad (9c)$$

$$\Delta H^\circ_{298} = -18 \text{ kcal mol}^{-1}$$

$$CH_3SC_2H_5 + OH \rightarrow CH_3S + C_2H_4 + H_2O \quad (9d)$$

$$\Delta H^\circ_{298} = -9.3 \text{ kcal mol}^{-1}$$

$$CH_3SC_2H_5 + OH \overset{M}{\rightleftharpoons} CH_3S(OH)C_2H_5 \quad (9e)$$

$$\Delta H^\circ_{298} < 0$$

Heats of formation values of -14.3 and 31 kcal mol^{-1} have been used for EMS[17] and CH_3S,[12] respectively. The ΔH for reactions 9a, 9b, and 9e are not given because the heats of formation of CH_3SOH, C_2H_5SOH, and $CH_3S(OH)C_2H_5$ are not known. The sulfur radical formed in reaction 9c will likely decompose to CH_3S and C_2H_4 (9d), as this process is endothermic by only about 9 kcal mol^{-1}. The adduct formation (9e) has been hypothesized by

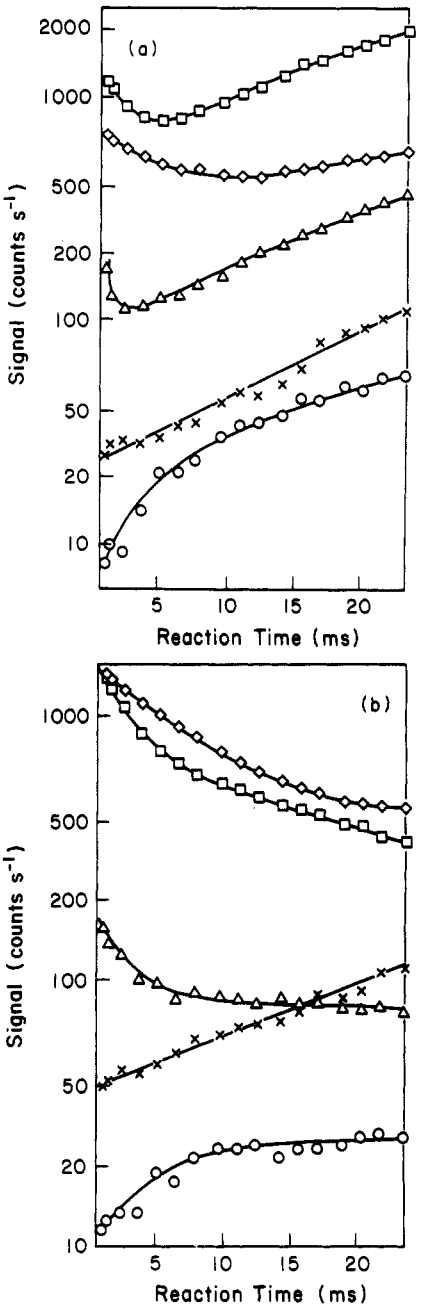

Figure 3. (a) Plot of $[CH_3SO]$ (□), $[CH_3SOH]$ (◇), $[C_2H_5]$ (△), $[CH_2SO]$ (×), and $[CH_3S]$ (○) vs time, with $O_3 = 3.0 \times 10^{14}$ molecules cm^{-3}. Source was $O/C_2H_5SCH_3$ with $[C_2H_5SCH_3] = 2.1 \times 10^{12}$ molecules cm^{-3}. (b) Same as part a with $[C_2F_3Cl] = 1.26 \times 10^{14}$ molecules cm^{-3} added to the flow tube. Note different scales on the ordinates in parts a and b.

Hynes et al.[18] and channels 9a and 9b correspond to the decomposition of the adduct. (iv) CH_3S reacts with O_3 to generate some CH_3SO. (v) In the presence of C_2F_3Cl and O_3, CH_3SO shows a nonexponential decay. This deviation from exponentiality is probably due to the fragmentation of heavier compounds to produce CH_3SO in the flow tube or to produce CH_3SO^+ ions in the ionization region. The decay of the mass 64 signal may be explained by reaction of the S_2 precursor with O_3, while no CH_3SOH is being formed.

In summary, we have identified the reaction of CH_3SO with O_3 to be a possible source of OH. However, this chemical system is very complex and there may be other sources of OH. The branched chain reaction has not been identified but some possibilities are suggested in the discussion section.

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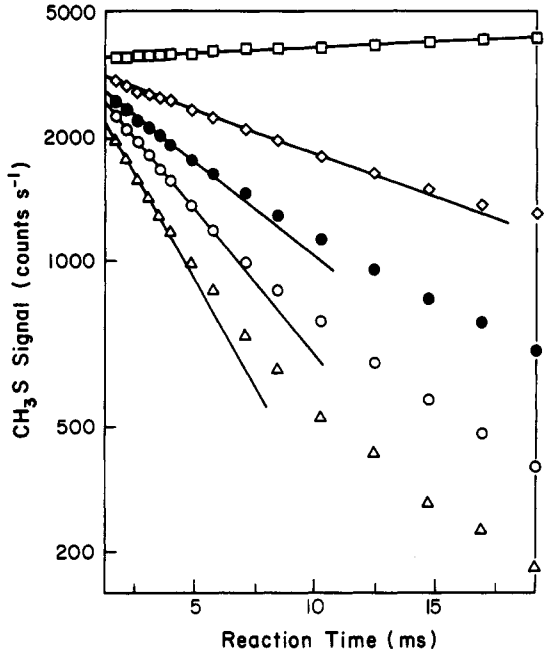

Figure 4. $CH_3S + O_3$ decay plots: source, $Cl + CH_3SH$; $T = 300 \pm 1$ K; $P = 1$ Torr; $v = 2850$ cm s^{-1}; $[O_3]$ (10^{13} molecules cm^{-3}) = 0 (□), 0.96 (◇), 2.01 (●), 3.44 (○), 5.48 (△).

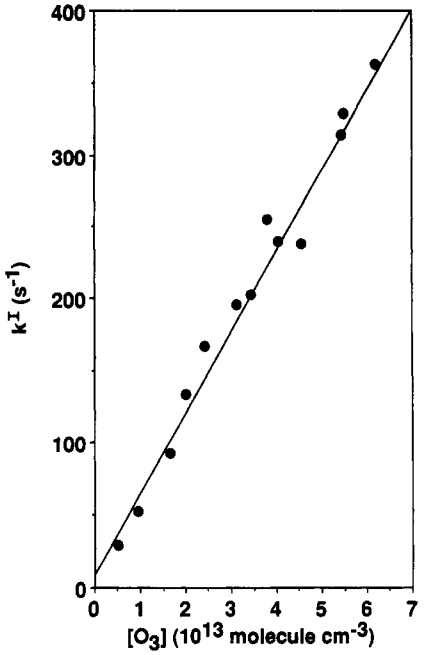

Figure 5. Plot of k^I versus $[O_3]$ for the $CH_3S + O_3$ reaction data: $T = 300 \pm 1$ K; $P = 1$ Torr; slope = 5.7×10^{-12} cm^3 $molecule^{-1}$ s^{-1}.

b. Measurement of the Rate Coefficients of the Reactions of CH_3S and CH_3SS with O_3. To measure the rate coefficient of the reaction of CH_3S with O_3 at 300 K and 1 Torr, CH_3S radicals were produced in the side arm reactor by the reaction of Cl atoms with CH_3SH. Assuming similar instrument responses to CH_3SH and CH_3S, the initial concentrations of CH_3S used in the flow tube were estimated to be between 2×10^{10} and 5×10^{10} molecule cm^{-3}. The decays of CH_3S in the presence of O_3 were measured under pseudo-first-order conditions in CH_3S. The $[CH_3SH]$ was about 2×10^{12} molecules cm^{-3}, while $[C_2F_3Cl]$ was about 3×10^{14} molecules cm^{-3}. This ensured that OH was effectively scavenged by C_2F_3Cl and thus that the regeneration of CH_3S by the reaction of OH with CH_3SH was suppressed. The plots of log (CH_3S signal at mass 47) vs time, shown in Figure 4, showed an initial linear decay followed by a curved decay. Such a curvature could be due to the regeneration of CH_3S by reactions other than by OH with CH_3SH. Indeed, Tyndall and Ravishankara[9] observed the regeneration of CH_3S in their flash-photolysis laser-induced fluorescence study of the $CH_3S + O_3$ reaction. They suggested that this reaction produced CH_3SO with a yield of unity and that CH_3SO reacted with O_3 to regenerate CH_3S, also with a yield of unity. However, as detailed in the discussion section, the regeneration of CH_3S by these reactions is not large enough (about 2%) to explain the curvature shown in Figure 4. Another possible explanation would be that CH_3SH reacts with O_3, leading to a substantial loss of $[O_3]$ in the reaction zone. However, since the $[CH_3SH]$ was always much smaller than the $[O_3]$, a substantial decrease in $[O_3]$ due to such a reaction is unlikely, unless a chain reaction takes place. Moreover, we searched for, but did not detect, any reaction between CH_3SH and O_3 in our flow tube, and we place an upper limit of 1×10^{-15} cm^3 $molecule^-$ s^{-1} on its rate coefficient. These possibilities being eliminated, we believe that the curvature shown in Figure 4 can be explained by a set of reactions similar to those described in our study of the $CH_3S + NO_2$ reaction.[7] In that study CH_3SS was produced in the CH_3S source. The CH_3SS reacted with NO_2 to produce CH_3SSO, which was dissociatively ionized by Lyman α radiation in the ionization region to yield a CH_3S^+ fragment. This fragment was detected at mass 47, thus interfering with the detection of CH_3S. As shown below, CH_3SS also reacts with O_3 and it is likely that CH_3SSO is a product of this reaction

$$CH_3SS + O_3 \rightarrow CH_3SSO + O_2 \qquad (3a)$$

The fragmentation of CH_3SSO in the ionization region would then result in the curvature observed on the plots of Figure 4. The CH_3S radical may also be a direct product of the CH_3SS reaction with O_3

$$CH_3SS + O_3 \rightarrow CH_3S + SO + O_2 \qquad (3b)$$

$$\Delta H^\circ_{298} = -19.2 \text{ kcal mol}^{-1}$$

In our study of the $CH_3S + NO_2$ reaction, the curved decay plots were corrected by subtracting the contribution of the CH_3SSO fragmentation from the CH_3S^+ signal. The resulting decay plots were exponential. However, taking the initial slopes of the curved plots or the slopes of the corrected decay plots gave first-order rate constant values different by less than 2%, which showed that such a correction was not essential. In the present case, the initial slopes of the decay plots were taken as a measurement of the first-order rate coefficients, k^I.

A plot of k^I versus $[O_3]$ is shown in Figure 5, and its slope yields the second-order rate coefficient for reaction 1: $k_1 = (5.74 \pm 0.25) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} with an intercept of 8 ± 9 s^{-1}, which is not statistically significant. The error limits are 1σ based on precision only. Using uncertainties at the 95% confidence level for the gas flow rates (±3%), temperature (±1%), pressure (±1%), and flow tube radius (±1%) and taking into account an estimate of systematic errors which include errors due to the decay plots curvature, we suggest, $k_1 = (5.7 \pm 1.4) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}.

The CH_3SS radical was generated in our source whenever the CH_3S radical was produced. We believe that CH_3SS was formed by the reaction of CH_3S with elemental sulfur deposited on the walls of the source reactor. It is possible that some CH_3SS was also generated by this reaction taking place on the flow tube walls. However, this source of CH_3SS is probably negligible in the reaction zone because both the S and CH_3S react rapidly with O_3. To measure k_3, the rate coefficient of the CH_3SS reaction with O_3, the decay of CH_3SS was measured in the presence of O_3 under conditions similar to those used for CH_3S. The decay plots were linear and their least-squares slopes gave the first-order rate coefficient of reaction 3. The plot of the first-order rate coefficient vs $[O_3]$ is shown in Figure 6 and yields $k_3 = (4.63 \pm 0.12) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} with an intercept 5 ± 3 s^{-1}. The error limits are 1σ based on precision only. With an estimate of the total errors similar to that detailed for k_1, we obtain $k_3 = (4.6 \pm 1.1) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at the 95% confidence level.

c. Yield of CH_3SO from the $CH_3S + O_3$ Reaction. The following procedures were used to measure the yield of CH_3SO from

TABLE I: CH_3SO Yield from the $CH_3S + O_3$ Reaction

pressure, Torr	$[O_3]$, 10^{14} molecules cm^{-3}	$[CH_3SO]_{max}/[CH_3S]_0e^{-(k_w+k_i)L/v}$	t_{max}, ms calcd	t_{max}, ms measd	CH_3SO yield
0.703	1.59	0.133	2.84	3.26	0.170
1.014	1.41	0.110	3.22	2.95	0.141
1.277	1.62	0.124	2.79	2.88	0.159
1.292	1.45	0.110	3.13	2.84	0.141
2.184	0.623	0.108	7.58	7.06	0.135
2.193	1.29	0.094	3.53	4.11	0.120
2.194	1.14	0.117	3.95	4.32	0.149
2.200	1.62	0.133	2.79	2.77	0.171
					0.15 ± 0.04[a]

[a] Average. Error is 95% confidence limit including an estimate for systematic error.

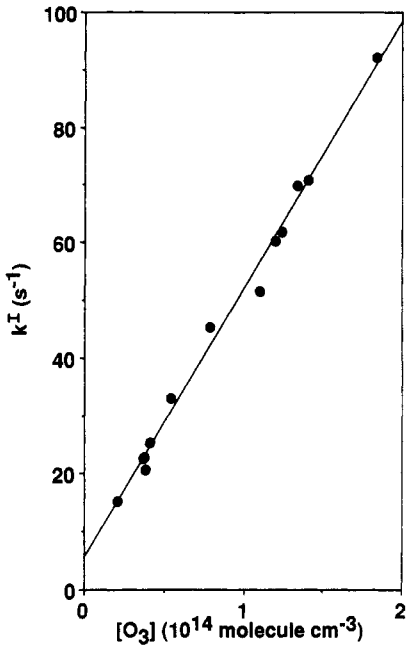

Figure 6. Plot of k^1 versus $[O_3]$ for the $CH_3SS + O_3$ reaction data: T = 300 ± 1 K; P = 1 Torr; slope = 4.6×10^{-13} cm^3 $molecule^{-1}$ s^{-1}.

reaction 1: (1) the temporal profiles of CH_3S and CH_3SO were measured; (2) a rate equation describing the temporal variations of $[CH_3SO]$ was derived; (3) the rate constants of the reactions of CH_3SO with O_3 and of the wall losses of CH_3S and CH_3SO were measured; (4) these measured values, the measured value of k_1, and the response ratios of the instrument to CH_3S and CH_3SO were used to fit the rate equation to obtain the yield of CH_3SO.

CH_3S radicals were produced by the $Cl + CH_3SH$ reaction in the side arm reactor and reacted with O_3 in the flow tube in the presence of C_2F_3Cl, and the temporal profiles of CH_3S and CH_3SO were measured. The $[CH_3SH]$ and $[C_2F_3Cl]$ used were similar to those used for the measurement of k_1. We assumed the following reaction sequence to define the CH_3SO temporal profile:

$$CH_3S + O_3 \xrightarrow{\alpha k_1} CH_3SO + O_2 \qquad (1a)$$

$$\xrightarrow{(1-\alpha)k_1} \text{products}$$

$$CH_3S \xrightarrow{k_i} \text{injector wall loss}$$

$$CH_3S \xrightarrow{k_w} \text{flow tube wall loss}$$

$$CH_3SO \xrightarrow{k_w'} \text{flow tube wall loss}$$

$$CH_3SO + O_3 \xrightarrow{k_2} \text{products} \qquad (2)$$

The regeneration of CH_3S by reaction 2 is neglected, as will be justified later. The following integrated rate equation gives the concentration of CH_3SO

$$[CH_3SO] = \frac{\alpha k_1[CH_3S]_0[O_3]e^{-(k_w+k_i)L/v}}{k_1[O_3] - k_2[O_3] - k_w' + k_w}\left(e^{-(k_2[O_3]+k_w'-k_w-k_i)t} - e^{-(k_1[O_3]-k_i)t}\right) \qquad (10)$$

The parameters of eq 10 are defined as follows: $[CH_3S]_0$, concentration of CH_3S, where the side arm reactor and the flow tube intersect; d, length of the reaction region, where O_3 and CH_3S are in contact; L, distance between the end of the flow tube and the side arm reactor; v, average flow velocity in the flow tube, assuming that v is not changed by the presence of the injector; t: reaction time between CH_3S and O_3. $t = d/v$. The quantity $[CH_3S]_0e^{-(k_w+k_i)L/v}$ was measured independently, at $[O_3] = 0$ and with $d = 0$. The k_i was measured by flowing CH_3S in the absence of O_3 and monitoring the CH_3S signal as a function of injector position; a value of 6 s^{-1} was found. Since the flow tube and the injector were both coated with halocarbon wax, we assumed that the surface loss of CH_3S was proportional to the surface area and we calculated k_w = 17 s^{-1} based on the measured value of k_i. Similarly, by producing CH_3SO by reaction 7 and measuring its injector loss, we obtain k_w' = 17 s^{-1}. We need the value of k_2 to obtain α from eq 10. A few measurements made using reaction 7 as a source of CH_3SO yielded $k_2 = (6.0 \pm 3.0) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}, where the large error limit reflects the small number of measurements. A sensitivity analysis performed by using k_2 values of (6 and 3) $\times 10^{-13}$ in eq 10 showed that a 50% change in k_2 results in a change of only 6.5% in α, so a very accurate value of k_2 is not critical.

As expected, the plot of ln (CH_3SO signal) versus t showed a maximum, $[CH_3SO]_{max}$, which, according to eq 10, occurred at t_{max} given by

$$t_{max} = \frac{\ln(k_1[O_3] - k_i) - \ln(k_2[O_3] + k_w' - k_w - k_i)}{k_1[O_3] + k_w - k_2[O_3] - k_w'} \qquad (11)$$

The time origin needed to determine the experimental values of t_{max} was taken as the point where the decay plots of Figure 4 intersect. The location of this point is consistent with the geometry of our flow tube reactor. Measured and calculated values of t_{max} are reported in Table I. Considering that the CH_3SO signal was measured only at discrete time intervals, the agreement between these two sets of values is reasonable.

Eight runs were performed at different pressures and O_3 concentrations. The yield of CH_3SO, $\alpha = k_{1a}/k_1$, was derived for each run by using the measured value of $[CH_3SO]_{max}$ and the calculated value of t_{max} in eq 10. The calculated value, rather than the measured value, of t_{max} was used because $[CH_3SO]$ was measured only at discrete time intervals. The data used for and obtained from these eight runs are reported in Table I. We find no systematic variation of the yield with pressure and we conclude that between 0.7 and 2.2 Torr He, α is independent of pressure. The average value of α is 15%, and with an estimate of various errors, we get $\alpha = 15 \pm 4\%$.

A few measurements of the yield of CH_3S from the $CH_3SO + O_3$ reaction were made in 1 Torr He, using reaction 7 as a source of CH_3SO. An analysis similar to the one described above was

performed, and the yield of CH_3S was found to be 13 ± 6%.

Discussion

The reaction of CH_3S with O_3 has previously been studied by Black and Jusinski[8] and by Tyndall and Ravishankara[9]. Black and Jusinski did not observe any reaction between CH_3S and O_3 in their flash-photolysis laser-induced fluorescence system and estimated $k_1 \leq 8 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. However, it seems likely that under their experimental conditions, the regeneration of CH_3S was too fast to observe its decay, as pointed out by Tyndall and Ravishankara.[9] Tyndall and Ravishankara used a system similar to Black and Jusinski and obtained $k_1 = (4.1 \pm 2.0) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, which agrees with our value, within the quoted error limits. Tyndall and Ravishankara observed some CH_3S regeneration. To obtain the above value of k_1, they performed a correction which assumed that CH_3SO from the $CH_3S + O_3$ reaction reacted with O_3 to give CH_3S with a yield of unit. Here we find that the yield of CH_3SO from the $CH_3S + O_3$ reaction is 15% independent of pressure between 0.7 and 2.2 Torr helium. Our preliminary results on the $CH_3SO + O_3$ reaction show that the yield of CH_3S from this reaction is 13 ± 6%. If the yields of CH_3SO and CH_3S from reactions 1 and 2 measured here at low pressure are valid at the pressures used by Tyndall and Ravishankara, 50–200 Torr He and 70–100 Torr SF_6, then the corrections made by these authors are unwarranted. The value of k_1, that they measured without correction, $k_1 = 5.1 \times 10^{-12}$ cm^3 molecule^{-1} s$^-$ would be the appropriate value. In that case, the agreement between their value and our value is very good.

On the basis of known thermochemistry[7,12,16] some of the possible channels for reaction 1 are shown in channels 1a–f.

$$CH_3S + O_3 \rightarrow CH_3SO + O_2 \quad \Delta H°_{298} = -59.1 \text{ kcal mol}^{-1} \tag{1a}$$

$$\rightarrow CH_3 + SO + O_2 \quad \Delta H°_{298} = -28.5 \text{ kcal mol}^{-1} \tag{1b}$$

$$\rightarrow CH_2SO + H + O_2 \quad \Delta H°_{298} = -25.0 \text{ kcal mol}^{-1} \tag{1c}$$

$$\rightarrow CH_2SO + HO_2 \quad \Delta H°_{298} = -74.1 \text{ kcal mol}^{-1} \tag{1d}$$

$$\rightarrow CH_2S + OH + O_2 \quad \Delta H°_{298} = -31.5 \text{ kcal mol}^{-1} \tag{1e}$$

$$\rightarrow CH_3O + SO_2 \quad \Delta H°_{298} = -129.9 \text{ kcal mol}^{-1} \tag{1f}$$

Channels 1a and 1e have been investigated here. Although we observed signals at mass 15 (CH_3) and 62 (CH_2SO), we cannot quantify channels 1b, 1c, and 1d because, as shown below, CH_3 and CH_2SO could also be products of reaction 2. Moreover, CH_3 reacts rapidly with O_3,[19] $k = 7 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, and our detection limit for CH_3 is quite high (probably $>5 \times 10^9$ molecules cm^{-3}). We also cannot detect SO, produced in channel 1b. Channels 1a, 1b, and 1c are likely to be coupled. A large fraction of the 59 kcal mol^{-1} energy from the highly exothermic channel 1a is likely to be deposited in the CH_3SO product. Indeed, the HSO product formed in the analogous $HS + O_3$ reaction[10,11] is known to be highly excited.[20,21] Since the bond dissociation energies $D(CH_3\text{–}SO) \approx 30$ kcal mol^{-1} and $D(H\text{–}CH_2SO) \approx 34$ kcal mol^{-1} are relatively small, these dissociation processes may be the major paths, particularly at low pressures. At higher pressures the excited CH_3SO may be substantially deactivated and the distribution of products may be quite different from our low pressure observations. Channel 1d involves a tight transition state and is probably slow. Channel 1e has been shown to be unimportant (<4%). This is not surprising because O_3 is expected to react at the radical site of the CH_3S. The reactions of HS and CH_3S with O_3 have similar rate constants, $k(HS + O_3) = 4.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, and the reaction of HS with O_3 is known to produce HSO.[10,11] Reaction 1f seems unlikely, because it involves extensive rearrangement.

The products of the reaction of CH_3SO with O_3 are not all known. Some possibilities are given in channels 2a–g. Channel 2a has been identified here and we obtained a value of 13 ± 6% for the branching ratio of this channel. If we assume that the CH_2SO detected here is formed by reaction 2b and that our instrument responses to CH_3SO and CH_2SO are the same, the branching ratio for (2b) is 10%. However, channel 2b involves a hydrogen abstraction by ozone, and for reasons similar to those given above for reaction 1e, channel 2b seems to be an unlikely pathway. The CH_2SO detected in our reactor may come from reaction 1c, and CH_2SO would then be an important product of reaction 1. Regardless of its origin, CH_2SO is a new species that could be of atmospheric interest.

$$CH_3SO + O_3 \rightarrow CH_3S + 2O_2 \quad \Delta H°_{298} = -9.1 \text{ kcal mol}^{-1} \tag{2a}$$

$$\rightarrow CH_2SO + OH + O_2 \quad \Delta H°_{298} = -42.8 \text{ kcal mol}^{-1} \tag{2b}$$

$$\rightarrow CH_3SO_2 + O_2 \quad \Delta H°_{298} = -95.1 \text{ kcal mol}^{-1} \tag{2c}$$

$$\rightarrow CH_3 + SO_2 + O_2 \quad \Delta H°_{298} = -75.7 \text{ kcal mol}^{-1} \tag{2d}$$

$$\rightarrow CH_2SO_2 + H + O_2 \quad \Delta H°_{298} = \text{unknown} \tag{2e}$$

$$\rightarrow CH_2SO_2 + HO_2 \quad \Delta H°_{298} = \text{unknown} \tag{2f}$$

$$\rightarrow CH_3O + SO_3 \quad \Delta H°_{298} = -131.2 \text{ kcal mol}^{-1} \tag{2g}$$

By analogy to the HS/HSO system[10,11] and to the $CH_3S + O_3$ reaction, we expect reactions 2c, 2d, and 2e to be major routes. These channels are probably coupled. Reaction 2c is highly exothermic and a large fraction of this energy is probably deposited on the CH_3SO_2 product; therefore collisional deactivation of the energetic CH_3SO_2 product may affect the yields for channels 2c, 2d, and 2e. Reactions 2d and 2e represent the unimolecular dissociations of the energetic CH_3SO_2. Channel 2f, like reaction 1d, involves a tight transition state and is probably insignificant. Channel 2g involves extensive rearrangement and seems unlikely as an elementary reaction.

Since reactions 1e and 2b seem unlikely, the source of the OH present in our reactor is unclear. A likely possibility is that channel 1c and/or channel 2e is important. The H atoms produced in these reactions will then react rapidly, $k = 2.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1},[22] to form OH

$$H + O_3 \rightarrow OH + O_2 \tag{12}$$

$$\Delta H°_{298} = -76.9 \text{ kcal mol}^{-1}$$

The OH formed in this reaction is known to be vibrationally excited,[23] up to $v = 9$, and reacts rapidly with O_3, $k \approx 2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1},[24] in a chain branching reaction[25]

$$OH(v=9) + O_3 \rightarrow OH + O + O_2 \tag{13}$$

This reaction could be the chain branching reaction responsible for the increase in the number of radicals observed in our reactor. Both OH and O react with the sulfur radical precursors to regenerate CH_3S and/or CH_3SO.

The CH_3 produced in channels 1b and 2d might also be involved in a chain branching reaction. Washida et al.[19] report that CH_3 reacts rapidly with O_3. A possible channel mentioned by these authors is

$$CH_3 + O_3 \rightarrow HCOOH + OH \tag{14a}$$

$$\Delta H = -148.5 \text{ kcal mol}^{-1}$$

(19) Washida, N.; Akimoto, H.; Okuda, M. *J. Chem. Phys.* **1980**, *73*, 1673.
(20) Schurath, U.; Weber, M.; Becker, K. H. *J. Chem. Phys.* **1977**, *67*, 110.
(21) Kendall, D. J. W.; O'Brien, J. J. A.; Sloan, J. J. *Chem. Phys. Lett.* **1984**, *110*, 183.
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(23) Polanyi, J. C.; Sloan, J. J. *Int. J. Chem. Kinet.* **1975**, *Symp. 1*, 51.
(24) Greenblatt, G. D.; Wiesenfeld, J. R. *J. Geophys. Res.* **1982**, *87*, 11145.
(25) Slanger, T. G.; Huestis, D. L. *Int. J. Chem. Kinet.* **1985**, *17*, 713.

The HCOOH is probably formed highly excited, and we could also have

$$CH_3 + O_3 \rightarrow HCO + OH + OH \qquad (14b)$$

$$\Delta H = -41.9 \text{ kcal mol}^{-1}$$

Although this would help explain the observed OH generation, the amount of molecular rearrangement is formidable.

The rate coefficient for the reaction of CH_3SS with O_3 has not been reported previously. CH_3SS reacts with O_3 about 40 times slower than with NO_2.[7] For CH_3S this ratio is about 10. Considering that the mechanisms of the CH_3S reactions with NO_2 and O_3 are an oxygen transfer,[7] it is likely that an oxygen transfer is also involved in the $CH_3SS + O_3$ reaction

$$CH_3SS + O_3 \rightarrow CH_3SSO + O_2 \qquad (3a)$$

$$\rightarrow CH_3S + SO + O_2 \qquad (3b)$$

$$\rightarrow CH_3 + SSO + O_2 \qquad (3c)$$

$$\rightarrow CH_2SSO + H + O_2 \qquad (3d)$$

These four channels are probably coupled, in a manner, similar to that described for reactions 1 and 2. The production of CH_3S by channel 3b, and of CH_3SSO, which can be photodissociated by Lyman α radiation to CH_3S^+ and SO,[7] is consistent with the curvature of the CH_3S decay plots, in the presence of C_2F_3Cl.

Most of the products of reactions 1, 2, and 3 are still not accounted for. Further work is under way in our laboratory to elucidate this chemistry.

Atmospheric Implications. The fate of CH_3S radical in the atmosphere depends on the rates at which it reacts with different oxidizers, O_3, NO_2, and O_2. Using nominal mole fractions of 4×10^{-8}, 1×10^{-10}, and 0.21 for O_3, NO_2, and O_2 to represent conditions in the clean troposphere and the rate coefficients reported here and elsewhere[6,7,9] for the CH_3S reactions, we estimate first-order rate coefficients of 6 s^{-1}, 0.15 s^{-1}, and ≤ 13 s^{-1} for reactions of CH_3S with O_3, NO_2, and O_2. Tyndall and Ravishankara[6,9] have suggested that the rate coefficient for the O_2 reaction is possibly an order of magnitude lower than the upper limit they derived. If this were the case, then the reaction with O_3 is the major loss process for CH_3S in the atmosphere, under most conditions. The results from our study show that, at low pressures, the regeneration of CH_3S in the O_3 reaction scheme is negligible, although it is possible that at atmospheric pressure the yield of CH_3SO is higher. Furthermore, the reaction of CH_3SO with O_2 could be enhanced in the atmosphere, if the CH_3SO formed by reaction 1 is excited. If the rate coefficient for the reaction of CH_3SO with O_2 is faster than even 1×10^{-19} cm^3 $molecule^{-1}$ s^{-1}, the major loss process for CH_3SO would be reaction with O_2. Therefore, it is very likely that the reaction of CH_3S with O_3 leads to the loss of CH_3S from the atmosphere.

All the product information obtained here is strictly applicable to pressures lower than ~5 Torr. Although the yield of CH_3SO does not vary with pressure in the small range that was tested, our result may not be valid at pressures up to 760 Torr. The excited CH_3SO and CH_3SO_2 formed in the $CH_3S + O_3$ and $CH_3SO + O_3$ reactions may be quenched and stabilized in the atmosphere. However, if we assume that our observations are valid in the atmosphere, it is clear that the oxidation of CH_3S by O_3 primarily leads to cleavage of the C–S bond. For the formation of methanesulfonic acid (MSA, CH_3SO_3H) the CH_3S moiety must remain intact. This may explain the high yields of MSA from DMS oxidation found in the presence of NO_x[3,4] in chamber experiments. When CH_3S is oxidized by NO_2, we expect CH_3SO and CH_3SO_2 to be formed. These species may lead to formation of MSA. One possibility is that CH_3SO adds O_2 forming CH_3SO_3 which leads to MSA.[26] If the C–S bond is cleaved, oxidation of SO to SO_2 will be rapid.

Our observation of C_2H_5 and CH_3SOH in (9a), the reaction of OH and $C_2H_5SCH_3$, has some interesting implications. There is evidence that the reaction of OH with CH_3SCH_3 in the atmosphere[20] proceeds via either H atoms abstraction or OH addition to sulfur followed by reaction of the adduct with O_2.[18] Hynes et al.[18] have assessed the branching ratios for these channels by measuring the loss rate coefficient for OH under various conditions of temperature, pressure, and composition and by assuming a two-channel model. Our observation of C_2H_5 and CH_3SOH production indicates that the C–S bond may be cleaved by OH addition to CH_3SCH_3 as well

$$OH + CH_3SCH_3 \xrightarrow{M} CH_3S(OH)CH_3 \qquad (15a)$$

$$\rightarrow CH_3SOH + CH_3 \qquad (15b)$$

where a third body (M) may be involved in one or both of these steps. This reaction could appear as an abstraction, when OH loss is monitored. The interpretation of the kinetic isotope effect reported by Hynes et al. is complex, because the reaction has a negative activation energy and involves the formation of an adduct. Furthermore, if the OH reaction pathway does indeed cleave the C–S bond, it will require a reanalysis of the observed variation of the OH loss rate coefficient with pressure and O_2 composition. In any case, further studies on the OH reaction with DMS aimed at elucidating the mechanism are necessary.

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Registry No. CH_3S, 7175-75-9; CH_3SO, 25683-64-1; CH_3SS, 29245-72-5; O_3, 10028-15-6.

(26) Jensen, N. R.; Hjorth, J.; Lohse, C.; Skov, H.; Restelli, G. *J. Atmos. Chem.*, in press, and references cited therein.