experiments.^{18,20,40} Therefore, the observed Chla^T must originate from the internal antenna. Indeed the magnetic parameters calculated from the spectra are very similar to those obtained for LHC II β^{48} which are attributed to antenna Chla^T. The triplet state of Chla should sensitize the β -carotene to its triplet state (reaction 2); however, this is not experimentally observed in the unblocked system, and its absence is attributed to an annihilation process already described.^{33,35,36,49} For example, the reaction

$$Chla^{T} + \beta$$
-carotene^T \rightarrow $Chla^{*} + \beta$ -carotene (3)

was suggested in other LHC II photosystem complexes.³³ This reaction should decrease the triplet yield of β -carotene so that it is below the detection level. The observed $Chla^T$ results from the large excess of Chla over β -carotene (ratio of Chla to β -carotene is, at least, 40:1). It should be pointed out that the relatively low light intensity prevents the formation of high triplet concentrations of Chla to undergo self-annihilation.

In the LM experiments (modulation frequency 500 or 800 Hz), prereduction of the acceptors enforces the excitation path to proceed via P_{700}^{T} (Scheme II) without disturbance because the cycling time is about 1 ms.^{18,20,30} This will be accompanied by a reduction of the $Chla^T$ yield in the internal antenna. As [Chla] \gg [β -carotene] in CC I, the relatively low concentration of Chla^T is still sufficient to sensitize β -carotene to its triplet state without allowing reaction 3 to occur. On the other hand, the energy within the laser excitation pulse (10-ns pulse width) is sufficient to populate P₇₀₀ to its triplet as well as to maintain high triplet concentration of Chla. Under these conditions reaction 3 will occur, resulting in a decrease of β -carotene^T and a relative increase of $Chla^{T}$ compared to the results of the LM experiments. The poor S/N ratio of the DD spectra (Figures 3 and 4) warrant some further comments. Such a S/N ratio, which is not characteristic of the DD method, suggests that the effective concentration of paramagnetic species in CC I (blocked system) is low due to the annihilation processes that occur in the early steps. The semiquantitative analysis should be considered as lending support to our conclusions from the DD experiments, where we assume the species and processes that are responsible for the experimental observations occur at early times of 300-2000 ns.

We have demonstrated in this study that time-resolved EPR detection in the submillisecond range (LM, low-power light excitation) fully complements that in the submicrosecond range (DD, high-power light excitation). This is of importance in studying in vivo photosynthetic systems in which several biochemical species are involved in the light excitation pathway. These species exhibit different magnetic and spin dynamics parameters, thereby having different responses to the LM and DD methods. Moreover, time-evolved spectra obtained by the latter method can be compared with the integrated first derivative spectra generated in the LM experiments. We believe that this analysis will lead to a better future understanding of the β -carotene sensitization mechanism and the triplet disappearance via triplet-triplet annihilation.

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Kinetics and Mechanism of the Reactions of CH_3S with O_2 and NO_2 at 298 K^T

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Rate coefficients for the reactions $CH_3S + O_2 \rightarrow products$ (1) and $CH_3S + NO_2 \rightarrow products$ (2) have been measured at 298 K by laser induced fluorescence detection of CH₃S which was generated by pulsed 248-nm laser photolysis of CH₃SSCH₃. k_1 was found to be less than 2.5 × 10⁻¹⁸ cm³ s⁻¹. k_2 was measured to be (6.10 ± 0.90) × 10⁻¹¹ cm³ s⁻¹. The mechanism of reactions 1 and 2 was investigated. The major product in reaction 2 is NO, with a yield of 0.80 ± 0.20 . Secondary production of NO was observed, indicating that CH₃SO formed in reaction 2 also reacts with NO₂, with a rate coefficient of (8 ± 5) \times 10⁻¹² cm³ s⁻¹. At long reaction times laser excited fluorescence was detected from a product, possibly CH₃SO₂.

Introduction

The tropospheric oxidation of dimethyl sulfide (DMS, CH₃SCH₃), methyl mercaptan (CH₃SH), and dimethyl disulfide (DMDS, CH₃SSCH₃), the most widely emitted naturally occurring organosulfur compounds in the atmosphere, is initiated

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cation.48

by reaction with OH radicals and, to a lesser extent, NO₃ radicals.^{1,2} The products of these reactions have not been identified, but there is a fairly compelling body of evidence from indirect studies that the OH-initiated oxidation of these sulfur compounds (DMS, CH₃SH, DMDS) can lead to production of the methylthiyl

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radical, CH₃S, in the atmosphere.³⁻⁶
OH + CH₃SCH₃
$$\rightarrow$$
 H₂O + CH₃SCH₂
CH₃SCH₂ + O₂ \xrightarrow{M} CH₃SCH₂O₂
CH₃SCH₂O₂ + NO \rightarrow NO₂ + CH₃SCH₂O
CH₃SCH₂O \xrightarrow{M} HCHO + CH₃S
OH + CH₃SH \rightarrow H₂O + CH₃S
OH + CH₃SSCH₃ \rightarrow CH₃SOH + CH₃S

If CH₃S is indeed produced in the atmosphere, it is desirable to have a consistent set of kinetics data on its reactions with atmospheric species (O2, O3, NO2, NO, hydrocarbons, etc.). We report rate coefficients for the reactions of CH₃S with O₂ and NO₂.

$$CH_3S + O_2 \rightarrow products$$
 (1)

$$CH_3S + NO_2 \rightarrow products$$
 (2)

Much of the information on the oxidation of DMS, DMDS, and CH₃SH is derived from environmental chamber studies, which show the major products to be SO_2 , methanesulfonic acid (MSA, CH_3SO_3H), and formaldehyde.⁶⁻¹³ However, there is no quantitative agreement on the product yields from these studies. Particularly, the yield of SO₂ found at low NO_x concentrations is always much higher than when NO_x is present. The differences are undoubtedly due to the chemistry of the secondary radicals produced in the system. Since the fates of SO_2 and MSA in the atmosphere may be different, it is necessary to identify the pathways by which the products are formed.

The chamber studies provided the first estimates of rate coefficients for CH₃S reactions,^{7,8,10} based on mechanisms in which O_2 added to CH₃S leads ultimately to SO₂ formation.

$$CH_3S + O_2 \rightarrow SO_2 + CH_3 \text{ or HCHO}$$
 (1)

Grosjean⁷ and Hatakeyama and Akimoto⁸ estimated k_1 relative to the addition of NO_2 or NO to CH_3S .

$$CH_3S + NO_2 \rightarrow CH_3SNO_2$$
 (2a)

$$CH_3S + NO \rightarrow CH_3SNO$$
 (3)

Grosjean found $k_{2a}/k_1 = 2 \times 10^6$ and Hatakeyama derived a value of 2 \times 10³ for the ratio k_3/k_1 .

Balla and Heicklen photolyzed DMDS in the presence of O₂ and found that SO₂ was produced in a chain mechanism.¹⁰ They proposed that O₂ adds to CH₃S, yielding finally SO₂ and OH.

$$\begin{array}{c} \mathrm{CH}_{3}\mathrm{S} + \mathrm{O}_{2} \xrightarrow{\mathrm{M}} \mathrm{CH}_{3}\mathrm{S}(\mathrm{O}_{2}) \\ \mathrm{CH}_{3}\mathrm{S}(\mathrm{O}_{2}) + \mathrm{O}_{2} \xrightarrow{\mathrm{M}} \mathrm{CH}_{3}\mathrm{S}(\mathrm{O}_{2})_{2} \\ \mathrm{CH}_{3}\mathrm{S}(\mathrm{O}_{2})_{2} \xrightarrow{\mathrm{M}} \mathrm{H}\mathrm{CHO} + \mathrm{SO}_{2} + \mathrm{OH} \\ \mathrm{OH} + \mathrm{CH}_{3}\mathrm{SH} \xrightarrow{} \mathrm{H}_{2}\mathrm{O} + \mathrm{CH}_{3}\mathrm{S} \end{array}$$

They concluded that the reaction of O2 with CH3S dominates over CH₃S recombination and derived $k_1 > 2 \times 10^{-16}$ cm³ s⁻¹.

Following the discovery by Suzuki et al.¹⁴ of the laser induced fluorescence (LIF) spectrum of CH₃S, Balla et al. directly measured the rate coefficients for the reactions of CH₃S with NO,

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Figure 1. Schematic of the apparatus: 2ν , second-harmonic generator; λ_1 , output of dye laser (564-574 nm); L, lens; A, variable aperture; F, filter; PC, personal computer.

NO₂, and O₂¹⁵ and several unsaturated hydrocarbons,¹⁶ detecting CH_3S under pseudo-first-order conditions. k_2 was measured to be 1.1×10^{-10} cm³ s⁻¹ while k_1 was found to be less than 2×10^{-17} $cm^3 s^{-1}$. Black and Jusinski also used LIF detection of CH_3S and derived upper limits for the reactions of CH₃S with O₃ and O₂ of 8×10^{-14} and 2×10^{-16} cm³ s⁻¹, respectively.¹⁷

The reaction of O_2 with CH_3S is thus very slow in comparison with the NO₂ reaction. However, in the marine troposphere, where most CH₃S production occurs, the mole fractions of O₂ and NO₂ differ typically by a factor of 10^{11,18} Furthermore, it is not clear whether the production of SO₂, the major S-containing product observed in the atmosphere, originates in the reaction of CH₃S with O₂ or not. Because of these uncertainties in the CH₃S oxidation scheme, we have initiated a systematic study of the kinetics and mechanism of CH₃S oxidation using pulsed laser photolysis to generate CH₃S radicals and pulsed laser induced fluorescence for their detection. The rate coefficient for the reaction of CH₃S with O₂ was found to be less than 2.5×10^{-18} $cm^3 s^{-1}$. No evidence was found for formation of a $CH_3S(O_2)$ adduct. The rate coefficient for the $CH_3S + NO_2$ reaction was determined to be $(6.10 \pm 0.70) \times 10^{-11}$ cm³ s⁻¹, and NO was identified as the major product. A rate coefficient of $(8 \pm 5) \times$ 10⁻¹² cm³ s⁻¹ was derived for the reaction between CH₃SO and NO₂:

$$CH_3SO + NO_2 \rightarrow CH_3SO_2 + NO$$
 (4)

Experimental Section

In the course of this work CH₃S, OH, and NO were detected via pulsed laser induced fluorescence. CH₃S was monitored to measure k_1 and k_2 , and OH was monitored to check for secondary reactions. NO produced in reaction 2 was detected to obtain product yields and mechanistic information. In all cases, CH₃S was produced by pulsed 248-nm KrF laser photolysis of CH₃S-SCH₃ (DMDS) in excess bath gas (He, N₂, or O₂). Conditions were chosen to ensure that the reactant CH₃S and products OH and NO were thermalized prior to detection.

Both photolysis and probe lasers were pulsed, with pulse widths of ~ 20 and 8 ns, respectively. The delay time between the photolysis and probe lasers could be varied from 100 ns to ~ 98 ms. The lower limit was set by the scattered light from the photolysis laser interfering with the detector and thermalization of CH₃S and OH, while the upper limit was dictated by the 10-Hz

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TABLE I: Experimental Conditions Used for Detection of CH₃S, OH, and NO and the Photophysical Parameters of the Detected Species

	excitation		fluorescence			filter (band-pass	detection
species	transition	λ, nm	transition	λ, nm	$\tau_{\rm R}$, ns	or cutoff)	limit, ^a cm ⁻³
CH ₃ S	$\tilde{A}(^{2}A) \leftarrow \tilde{X}(^{2}E)$		$\tilde{A}(^{2}A) \rightarrow \tilde{X}(^{2}E)$				
-	$v_{3}' = 1$	371.4	$v_3' = 0 \rightarrow v_3'' = n$	450 ± 30	760 ⁶	$450 \pm 12 \text{ or } \lambda > 400$	2×10^{10}
	$v_{3}' = 0$	377.0					1×10^{11}
ОН	$A(^{2}\Sigma) \leftarrow X(^{2}\Pi)$		$A(^{2}\Sigma) \rightarrow X(^{2}\Pi)$				
	v' = 1	282.0	$v' = 1 \rightarrow v'' = 1$ $v' = 0 \rightarrow v'' = 0$	~310	740 ^c	308 ± 5	3×10^{9}
NO	$A(^{2}\Sigma) \leftarrow X(^{2}\Pi)$		$A(^{2}\Sigma) \rightarrow X(^{2}\Pi)$				
	v' = 0	226.2	$v' = 0 \rightarrow v'' = 3$	259	218 ^d	259 ± 5	1×10^{9}

^a Detection limit is for 100-s average in 100 Torr of N₂. ^b From ref 21. ^c From ref 20. ^d From ref 19.

repetition rate of the two lasers and the electronics used to time the lasers. Fluorescence from the transient of interest (i.e., CH_3S , OH, or NO) was detected at some delay time for 100–1000 laser shots, and then the delay time was varied to construct a temporal profile of the species. This mode of data acquisition requires that the energies of both the photolysis and probe lasers be constant or known precisely during the entire data acquisition period. In general, the laser energies were constant; if the energy drifted, the signals were normalized for the variations.

A schematic of the apparatus is shown in Figure 1. The reaction vessel was a glass sphere blackened on the outside, 10-cm diameter, with 15-cm side arms fitted with Brewster angle windows. The photolysis and probe laser beams were combined with a dielectric-coated mirror and copropagated through the cell. The dielectric mirror used in a particular experiment was chosen to reflect a sufficient amount of the 248-nm radiation, while transmitting the probe beam. The energies of the exiting laser beams were measured by a power meter and used to check for drifts in the laser energy and, when necessary, to normalize the fluorescence signal to variations in laser power. The energy of the photolysis beam was kept below 4 mJ per pulse to minimize secondary chemistry. Red-shifted fluorescence was collimated by a 5-cm focal length UV quartz lens and passed through a variable aperture and a band-pass or cutoff filter before being imaged onto a slit in front of the photomultiplier tube. The combination of the aperture, filter, and slit allowed minimization of scattered light from the photolysis and probe lasers.

The probe laser was a Nd:YAG laser pumped dye laser, whose output was passed through a nonlinear optics module (wavelength extender) for frequency doubling and mixing. Using this module, we could generate the wavelengths required for detecting CH₃S, OH, and NO. CH₃S was detected via its $\tilde{A}(^{2}A_{1}) \leftarrow \tilde{X}(^{2}E)$ electronic transition either at 377.1 nm ($v_3' = 0$ band) or at 371.4 nm $(v_3' = 1 \text{ band})$.¹⁴ OH and NO were detected by pumping their $A(^{2}\Sigma) \leftarrow X(^{2}\Pi)$ transitions at 282 and 226 nm, respectively. Detection of OH by LIF is quite routine and need not be described further. Detection of NO has been discussed by Greenblatt and Ravishankara,¹⁹ and our procedure was very similar. The detection conditions are summarized in Table I. The radiative lifetimes and quenching rate coefficients by various gases of the different vibrational levels of the \tilde{A} state of CH₃S have recently been characterized by Black and Jusinski.^{17,21} We have also measured the radiative lifetimes and quenching rate coefficients for the gases used in this work; our results, which support Black and Jusinski's measurements of the radiative lifetime, will be reported in a forthcoming paper.

The pulse height from the photomultiplier tube was proportional to the concentration of CH₃S, OH, or NO in the cell and was measured by a gated charge integrator triggered in synchronization with the dye laser pulse. For experiments carried out in helium the integrator was triggered between 20 and 70 ns after the dye laser pulse, to discriminate against scattered light. In O₂ or N₂, however, fluorescence quenching of CH₃S occurs very efficiently,¹⁷

and the length of the fluorescence pulse is reduced to nearly that of the probe laser pulse. In these cases scattered light from the dye laser was also detected. The background signal due to scattered laser light was measured in an experiment with the excimer laser blocked and subtracted from the total signal to obtain the fluorescence signal. In studies on reaction 2 a small amount of NO was always present, since the cell could not be swept out completely in the time between laser shots (100 ms). This background fluorescence was accounted for by setting the delay between the two lasers to 85 ms. In this time most NO produced by the reaction had dissipated throughout the cell, and the remaining signal was due to background NO and scattered light.

The main paths by which CH_3S is lost in the absence of added reactant are diffusion from the detection zone, reaction with impurities in the diluent gas, and the recombination reaction 5.

$$CH_3S + CH_3S \xrightarrow{M} CH_3SSCH_3$$
 (5)

To obtain good upper limits on k_1 , it is very important to minimize these background losses and to keep them constant such that any increase in loss rate in the presence of O_2 is easily detected. Particular care was taken to optimize the overlap of the laser beams to minimize diffusion of the radicals out of the detection region. The photolysis beam was normally limited to a diameter of 6-8 mm, with the concentric probe beam 4-6 mm in diameter. Pure gases were used to minimize loss of CH₃S by reaction with impurities.

The carrier gas (O₂, N₂, or He) and the DMDS-containing mixture (usually $\sim 1\%$ in He) were mixed in a glass manifold and flowed into the reaction vessel. NO₂ (1% in He or air) was added down a movable injector, to minimize contact with the DMDS and suppress heterogeneous reactions. All experiments were carried out with the gases flowing slowly through the reaction vessel perpendicular to the plane of the laser beams and detection system. The flow rate was fast enough to prevent depletion of the reaction mixture but slow enough that the mixture could be considered static during the measurement of a kinetics decay curve. For the NO experiments, a small flow of carrier gas was added through the side arms to minimize accumulation of NO in the reaction region and reduce the background signal. The side-arm purge also reduced scattered light originating from elemental sulfur which deposited on the Brewster windows at the points where the lasers entered and exited the cell.

Carrier gases He (U.S. Bureau of Mines), O_2 , and N_2 (both from Scott Gases) all had stated purities better than 99.999% and were used without further purification. NO was obtained from Scott Gases as a mixture of 11.1 ppmv NO in N₂ whose composition was checked against a primary standard. DMDS (Aldrich) was outgassed and made into a 1% mixture in He. NO₂ (prepared by reacting UHP NO with excess O₂) was made into 1% mixture in He or air. The mole fractions of the mixtures were checked periodically by UV absorption. The DMDS was measured at 254 nm (mercury line), with an absorption cross section of 1.13×10^{-18} cm² (estimated from ref 22 and checked independently), and NO₂ at 366 nm (mercury line), with a cross section of 5.75×10^{-19} cm².²³ H₂O₂ (90% from FMC Corp.) had N₂

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TABLE II: Summary of Experimental Data on k1 at 298 K

		• •				
press., Torr	carrier gas	[DMDS], 10 ¹⁴ cm ⁻³	[CH ₃ S] ₀ , 10 ¹¹ cm ⁻³	k′, s⁻¹	$\frac{\Delta k'+2\sigma}{\mathrm{s}^{-1}}$	$k_1, 10^{-18}$ cm ³ s ⁻¹
38	N ₂	1.4	5.0	130 ± 13		
	O_2	1.4	6.4	124 ± 6	32	≤26
91	N_2	1.1	4.5	88 ± 7		
	O_2	1.2	4.3	95 ± 7	35	≤12
90	N_2	0.4	8.0	108 ± 6		
	02	0.4	8.3	125 ± 5	39	≤13
101	N_2	1.4	4.4	101 ± 6		
	O_2	1.6	4.8	98 ± 5	19	≤6
165	N_2	0.65	9.9	43 ± 13		
	0,	0.69	10.5	51 ± 8	50	≤9
245	N_2	0.71	12	70 ± 6		
	0,	0.71	12	71 ± 5	23	≤3
300	N_2	0.68	9.2	47 ± 5		
	0 ₂	0.61	8.2	50 ± 5	23	≤2.5

bubbled through to remove water vapor. It was introduced into the reaction vessel by bubbling a stream of carrier gas through the sample. Before reaching the reaction vessel, it passed through a 1-m absorption cell, where its concentration was measured by absorption of zinc atomic emission at 214 nm.²⁴ Concentrations of all reactive gases in the mixtures were calculated from known mass flow rates, the total pressure, and, in the case of mixtures, the mixing ratio of the reactive component.

Results and Discussion

In view of the complexity of the investigation, the results and discussion section has been divided into subsections. The measurements of k_1 and k_2 will be presented first, each followed by a discussion. The investigations on the mechanism of reaction 2 follow.

Reaction of CH₃S with O_2 . As pointed out in the Introduction, it is known that CH₃S does not react rapidly with O_2 . Large concentrations of O_2 are therefore needed to obtain a useful estimate of the upper limit for k_1 . The rate of decay of CH₃S radicals was measured in back-to-back experiments in O_2 and N_2 . Up to 300 Torr of ultrahigh-purity O_2 and N_2 was used. The DMDS concentration and the photolysis laser power were kept constant. Increasing the total pressure of O_2 and N_2 led to decreases in the decay rates. As noted earlier, the decay rates were controlled by diffusion out of the probe beam, reaction with impurities, and CH₃S recombination. Initial CH₃S concentrations were kept below 10^{12} cm⁻³ to minimize recombination. Although the rate coefficients for quenching of the $v_3' = 0$ level of the Ã state by O_2 and N_2 are reasonably fast (5.5 × 10⁻¹² and 6.4 × 10^{-12} cm³ s⁻¹, respectively),¹⁷ our system was sensitive enough to follow the CH₃S decay over 2–3 lifetimes in 300 Torr of O_2 or N_2 .

At lower pressures of carrier gas lower radical concentrations could be used, and the decays appeared logarithmic. At higher pressures fluorescence quenching forced us to use higher radical concentrations, and because of the slower diffusion, second-order kinetic processes dominated at short times. In these cases the early parts of the decays (<2 ms) were excluded from the analysis. An attempt was made to fit the decay curves using a Gear iteration program to account for the mixed-order decays, but the quality of the data was not sufficiently good to allow unambiguous results. We were able to estimate a value for the limiting high-pressure rate coefficient for CH₃S recombination of 7×10^{-11} cm³ s⁻¹ (with an uncertainty of a factor of 2), which is in reasonable agreement with the value obtained by Graham et al.²⁵

The results of the experiments are collated in Table II. It can be seen that at all pressures the decay rates in O_2 and N_2 were equal, within error limits, and that the O_2 data are not system-



Figure 2. CH₃S temporal profiles in 300 Torr of O₂ and N₂. [CH₃S]₀ = 8×10^{11} cm⁻³. Line fitted to data for t > 3 ms. Decay rates: $50 \pm 5 \text{ s}^{-1}$ in O₂ and $47 \pm 5 \text{ s}^{-1}$ in N₂.

atically higher than the N_2 data. The data at the highest pressure used are shown in Figure 2, for an initial CH₃S concentration calculated to be 8×10^{11} cm⁻³. The initial part of the plot shows some recombination, due to the relatively high radical concentration used, but for the longer, logarithmic decay the apparent first-order loss rates were 47 \pm 5 and 50 \pm 5 s⁻¹ in N₂ and O₂, respectively. The error limits are 1σ values obtained from the $1/\sigma$ -weighted linear least-squares analyses of 1n (signal) vs time data. If the entire loss rate in O_2 is assigned to a chemical reaction, we obtain a rate coefficient 6×10^{-18} cm³ s⁻¹. In our experiments the major loss process for CH₃S in N₂ should be diffusion out of the detection region, since the N_2 contains less than 0.5 ppmv of gases that could possibly react with CH₃S. The first-order loss rate was found to decrease when the N_2 pressure was increased, but if impurities are a major contributor to the loss of CH₃S, then the loss rate should increase with total pressure. The diffusion rates of CH₃S in N₂ and O₂ should be nearly identical, and there is less than 0.5 ppmv of reactive gases in O₂ also. Therefore, the loss observed in O_2 must also be due to diffusion, and it is appropriate to use the difference in loss rate between the two bath gases for the reactive loss of CH_3S . When the uncertainties in the measurements are included, a maximum rate coefficient of $2.5 \times 10^{-18} \text{ cm}^3 \text{ s}^{-1}$ is obtained at the 2σ confidence level.

The absence of observable CH₃S loss in our experiments does not automatically prove the absence of a reaction for two reasons. First, CH₃S and O₂ could react rapidly and reversibly to form an adduct, which does not react on the time scale of our measurements. In such a case, unless the equilibration process is observed, the CH₃S loss rate would be very close to the loss rate in the absence of a reaction. Observations made within the first $2 \mu s$ after the photolysis pulse showed no significant curvature in the CH₃S decays, so adduct formation must occur on a time scale shorter than this. (On this time scale reaction 5 cannot contribute significantly to the CH₃S loss.) Although the CH₃S signals were not equal in magnitude for measurements in O₂ and N₂, the differences could be satisfactorily accounted for by quenching. We conclude that CH₃S and O₂ do not form an adduct or that such an adduct must be very weakly bound.

The second possible explanation for our low rate coefficient is that CH_3S could be regenerated due to formation of OH radicals in secondary reactions. Balla and Heicklen investigated the dependence of the SO₂ yield on O₂ pressure in the CW photolysis of DMDS-O₂ mixtures.¹⁰ They found that chain reactions were occurring and postulated that OH radicals could be generated following a reaction between CH₃S and O₂:

$$CH_{3}S + O_{2} \xrightarrow{M} CH_{3}S(O_{2})$$
$$CH_{3}S(O_{2}) + O_{2} \xrightarrow{M} CH_{3}S(O_{2})_{2}$$
$$CH_{3}S(O_{2})_{2} \xrightarrow{M} SO_{2} + HCHO + OH$$

If such a process is fast enough to produce OH on the time scale

⁽²³⁾ Wine, P. H.; Kreutter, N. M.; Ravishankara, A. R. J. Phys. Chem. 1979, 83, 3191.

⁽²⁴⁾ DeMore, W. B.; Margitan, J. J.; Molina, M. J.; Watson, R. T.; Golden, D. M.; Hampson, R. F.; Kurylo, M. J.; Howard, C. J.; Ravishankara, A. R. Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, JPL-85-37.

Modeling, JPL-85-37. (25) Graham, D. M.; Mieville, R. L.; Pallen, R. H.; Sivertz, C. Can. J. Chem. 1964, 42, 2250.

of our CH₃S detection, no loss of CH₃S would be observed, since OH is believed to react rapidly with DMDS to regenerate CH₃S radicals.^{3,8}

$$OH + CH_3SSCH_3 \rightarrow CH_3S + CH_3SOH$$
(6)

We carried out experiments in which DMDS was photolyzed in the presence of O_2 and looked for OH production; none was observed. If we assume that OH is produced in a reaction between CH₃S and O_2 , and removed by its reaction with DMDS, then the instantaneous OH concentration is given by

$$[OH]_t = \frac{k_1[O_2]}{k_6[DMDS]}[CH_3S]$$

if the rate $(k_1[O_2] + k_6[DMDS])$ is much greater than the rates for CH₃S and OH loss.

Assuming that photolysis of DMDS at 248 nm leads to production of two CH_3S radicals, the initial CH_3S concentration was calculated from the DMDS concentration and photolysis laser fluence:

$$[CH_{3}S]_{0} = 2\sigma_{DMDS}F_{DMDS}[DMDS]$$

where F_{DMDS} is the laser fluence in photons cm⁻² at 248 nm and σ_{DMDS} is the absorption cross section for DMDS at 248 nm, which is approximately equal to that at 254 nm.²² (The absolute magnitude of the cross section is therefore not critical, since the same cross section is used for both the DMDS concentration measurement and the calculation of the CH₃S concentration.)

The sensitivity for OH detection was determined in a calibration experiment in which H_2O_2 was photolyzed, without changing the total pressure or detection geometry. $[OH]_0$ was calculated from the analogous equation:

$$[OH]_0 = 2\sigma_{H_2O_2}F_{H_2O_2}[H_2O_2]$$

We calculated a detection sensitivity for OH in 100 Torr of O_2 of 8×10^8 cm⁻³ for 100-s integration, i.e., 1000 shots.

The OH fluorescence signal was monitored for 1000 shots, first with and then without the 248-nm excimer laser radiation entering the reactor. After many pairs of measurements at different delay times it could be shown that the concentration of OH did not differ significantly from the detection limit of 8×10^8 cm⁻³ for a total pressure of 100 Torr of O₂ and an initial CH₃S concentration of 3.5×10^{12} cm⁻³. From this observation we calculate that the rate coefficient for the reaction between CH₃S and O₂ to give OH is 3.5×10^{-18} cm³ s⁻¹ or less. This upper limit is consistent with our measured upper limit for CH₃S removal. Regeneration of CH₃S following OH formation therefore cannot be responsible for our observed low loss rate of CH₃S.

The results of our experiments confirm earlier findings, that the reaction between CH₃S and O₂ is very slow. In direct studies at 298 K, Balla et al.¹⁵ obtained $k_1 < 2 \times 10^{-17}$ cm³ s⁻¹ and Black and Jusinski¹⁷ obtained $k_1 < 1 \times 10^{-16}$ cm³ s⁻¹. By performing back-to-back experiments under carefully controlled conditions, we have been able to reduce the upper limit by approximately an order of magnitude.

Three indirect studies that used CW photolysis and end-product analysis produced values for k_1 larger than our value. Hatakeyama and Akimoto measured the yields of SO₂ and CH₃SNO following the reaction of OH + DMDS.⁸ High NO_x was used in these experiments to catalyze the formation of OH. They found that the CH₃SNO yield increased with NO and proposed the following mechanism for SO₂ and CH₃SNO formation.

$$OH + CH_3SSCH_3 \rightarrow CH_3S + CH_3SOH$$
(6)

$$CH_3S + NO \xrightarrow{M} CH_3SNO$$
 (3)

$$CH_3S + O_2 \rightarrow SO_2$$
 (1)

They deduced the ratio $k_3/k_1 = 2 \times 10^3$ at 760-Torr total pressure. When used in conjunction with the rate coefficient for CH₃S + NO measured by Balla et al.,¹⁵ one obtains $k_1 = 2 \times 10^{-14}$ cm³ s⁻¹. It is clear that the measurements were not sensitive to this particular ratio and that the SO_2 was probably being formed from another reaction.

Grosjean studied the photooxidation of several organosulfur compounds in natural sunlight.⁷ He found that the rates of production of SO₂ and sulfur tied up as an unidentified compound, presumed to be CH₃SNO₂, were equal at NO₂ mixing ratios of about 0.1 ppm.

$$CH_3S + NO_2 \xrightarrow{M} CH_3SNO_2$$
 (2a)

$$CH_3S + O_2 \rightarrow CH_3 + SO_2 \tag{1}$$

This yielded $k_{2a}/k_1 = 2 \times 10^6$. In light of our findings this mechanism is obviously inadequate. It is questionable whether SO₂ is generated from the CH₃S + O₂ reaction, and the yield of CH₃SNO₂ in the CH₃S + NO₂ reaction is very low (see section on mechanism of reaction 2).

The experiments of Hatakeyama and Grosjean illustrate a serious problem in dealing with the study of these systems under conditions where individual reactions are not isolated. The observed end products may be formed from multiple pathways, and the derivation of kinetics data from relative product measurements can be unreliable.

Balla and Heicklen photolyzed DMDS in the presence of O_2 and measured the SO₂ yield as a function of [DMDS], [O₂], and light intensity.¹⁰ They proposed that the addition of O_2 to CH₃S radicals can compete effectively with CH₃S radical recombination and generate SO₂, HCHO, and OH.

$$CH_{3}S + 2O_{2} \rightarrow \rightarrow HCHO + OH + SO_{2}$$
$$CH_{3}S + CH_{3}S \rightarrow CH_{3}SSCH_{3}$$
(5)

If OH reacts with DMDS to regenerate CH₃S, this reaction could lead to large yields of SO₂ in CW experiments, but no loss of CH₃S would be observed in pulsed experiments. As described earlier, we found no evidence for OH production in the first few milliseconds following the photolytic pulse, during which time CH₃S would not have decayed appreciably, and we can deduce that any such reaction must proceed with a rate coefficient less than 3.5×10^{-18} cm³ s⁻¹. Balla and Heicklen's mechanism predicts a decrease of the SO₂ yield with increasing light intensity, but they actually observed an increase, implying that CH₃S radical recombination does not occur in the presence of ~5 Torr of O₂. This leads to the inequality

$$k_1^2/2k_5 > 6 \times 10^{-22} \text{ cm}^3 \text{ s}^{-1}$$

(In Balla and Heicklen's paper the factor of 2 was omitted.) Balla and Heicklen calculated their lower limit for k_1 using $k_5 = 4.1 \times 10^{-14}$ cm³ s⁻¹. The k_5 value was apparently wrongly converted from the original work of Graham et al.²⁵ When the correct value for Graham's rate coefficient $(4.1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1})$ is used, a lower limit of $2.3 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ is obtained for k_1 . This is approximately 2 orders of magnitude higher than our upper limit for this reaction.

One explanation for the discrepancy between our upper limit and Balla and Heicklen's lower limit is that CH_3S does form an adduct with O_2 and that the chemistry of this adduct is rate limiting in the CW photolysis experiments. Indeed the mechanism proposed by Balla and Heicklen relies on the addition of a second O_2 molecule followed by a rearrangement, which may not be observed on the time scale of our experiment.

A second interpretation is implied in Balla and Heicklen's observation that the SO₂ yield increased with light intensity. It is possible that CH₃S is not the only radical present in the system and that peroxy radicals, for instance, could lead to production of SO₂ via a chain reaction that regenerates CH₃S. It is known that photolysis of DMDS does not lead exclusively to CH₃S radical production at 248 nm. Akimoto and co-workers detected laser induced fluorescence signals due to S₂ at short delay times following 248-nm photolysis of DMDS.¹⁴ If the 254-nm photolysis of DMDS also leads to production of S₂, and hence CH₃, a sequence of reactions can be proposed in which peroxy radicals produce the observed enhancement in the SO₂ yields.

$$CH_{3}SSCH_{3} + h\nu \rightarrow 2CH_{3}S \qquad \lambda \leq 421 \text{ nm}$$

$$\rightarrow 2CH_{3} + S_{2} \qquad \lambda \leq 272 \text{ nm}$$

$$\rightarrow CH_{3}SS + CH_{3} \qquad \lambda \leq 498 \text{ nm}$$

$$CH_{3} + O_{2} \rightarrow CH_{3}O_{2}$$

$$CH_{3}O_{2} + CH_{3}S \rightarrow CH_{3}O + CH_{3}SO \qquad \Delta H^{\circ}_{298} = -45 \text{ kcal mol}^{-1}$$

$$CH_{3}O + O_{7} \rightarrow HCHO + HO_{7}$$

 $HO_2 + CH_3S \rightarrow OH + CH_3SO$ $\Delta H^{\circ}_{298} = -40 \text{ kcal mol}^{-1}$ $CH_3SO + O_2 \rightarrow \rightarrow SO_2$

$$OH + CH_3SSCH_3 \rightarrow CH_3S + CH_3SOH$$

The enthalpies of formation of sulfur-containing species were taken from ref 26 except for that of CH₃S.²⁷ Recent literature values were taken for HO_2 ,²⁸ CH₃O₂,²⁹ OH, CH₃O, and CH₃.³⁰

The suggestion that other radicals are responsible for SO₂ formation is consistent with results reported in another paper by Balla and Heicklen, in which mixtures of CH₃SH and CH₃SSCH₃ in O_2 were photolyzed at wavelengths greater than 280 nm.³¹ Under these conditions only DMDS photolysis should yield free radicals, since the cross section for CH₃SH is very small at 280 nm. However, the thermodynamic threshold for production of $2CH_3 + S_2$ from DMDS is around 270 nm, so in these experiments only CH₃S radicals should be produced. If the above sequence of reactions is responsible for SO₂ formation, SO₂ formation would be suppressed; these authors reported such an effect.

The explanation for the production of SO_2 in the CW photolysis experiments at low NO_x remains problematic, and the mechanism by which it occurs may still be very relevant to the atmosphere. Experiments at low temperatures may give some hint as to the extent of adduct formation. Even if an adduct is formed, it cannot react rapidly with O_2 , since we do not observe a loss of CH_3S . Potential mechanisms for reaction 1 are

 $CH_3S + O_2 \rightarrow CH_3O + SO$ $\Delta H^{\circ}_{298} = -26 \text{ kcal mol}^{-1}$ \rightarrow CH₃ + SO₂ $\Delta H^{\circ}_{298} = -68 \text{ kcal mol}^{-1}$ \rightarrow CH₂S + HO₂ $\Delta H^{\circ}_{298} = -4$ kcal mol⁻¹ \rightarrow CH₂SO + OH $\Delta H^{\circ}_{298} = -34 \text{ kcal mol}^{-1}$ \rightarrow CH₃SO₂ $\Delta H^{\circ}_{298} = -85 \text{ kcal mol}^{-1}$ → adduct

Detailed experiments should be carried out to determine the rate coefficient and products of this reaction more accurately.

Reaction of CH_3S with NO_2 . Measurements of the rate coefficient for the reaction $CH_3S + NO_2$ were made using He, N_2 , and O_2 as bath gases. The most extensive measurements were made in He, since CH₃S fluorescence is quenched only weakly by He.¹⁷ At a pressure of 40 Torr, a rate coefficient of $(5.98 \pm 0.21) \times 10^{-11}$ cm³ s⁻¹ was obtained. The error is 1σ based on precision only. The NO_2 concentration was varied in the range $(0.9-7.8) \times 10^{14}$ cm⁻³, and the initial CH₃S was in the range $(0.2-1.4) \times 10^{12}$ cm⁻³, so that $[NO_2]/[CH_3S]_0 \ge 200$ and pseudo-first-order conditions were always maintained. Changes in the CH₃S concentration (varied over a factor of 7) or the residence time (varied by a factor of 3) led to a maximum change in the rate coefficient of 15%. Semilogarithmic plots of [CH₃S] vs time were found to be linear over a factor of 20-30 in [CH₃S], irrespective of whether the $v_{3}' = 0$ or $v_{3}' = 1$ band was excited.

We also carried out experiments using a fast flow rate (450 sccm and a pressure of 40 Torr) using N_2 as the bath gas, with NO_2 added through the movable injector just before the reaction



Figure 3. Dependence of pseudo-first-order rate coefficient k' on NO₂ concentration for $CH_3S + NO_2$. Data for He and N_2 displaced upward by 10^4 s^{-1} . Symbols: (\Box) He, 40 Torr; (\blacksquare) He, 100 Torr; (\diamondsuit) N₂, 40 Torr; (\blacklozenge) N₂, 85 Torr; (O) O₂, 40 Torr; (+) O₂, \ge 85 Torr.



Figure 4. Temporal profiles of CH₃S in the presence of NO₂ in 40 Torr of O_2

TABLE III: Summary of Experimental Data on k2 at 298 Ka

gas	press., Torr	$[NO_2],$ 10 ¹⁴ cm ⁻³	no. of decays	[DMDS], 10 ¹³ cm ⁻³	flow rates, sccm	$k_{obsd}, 10^{-11} \ cm^3 s^{-1}$
He	34-140	0.9-7.8	17	2.8-12.5	75-250	5.98 ± 0.21
N_2	40	0.8-4.5	4	6.4	450	6.31 ± 0.20
-	87	3.1	1	8.7	250	6.00 ± 0.10
02	40	0.9-5.4	8	5.8	450	6.14 ± 0.14
	17	5.6	1	10.9	300	6.48 ± 0.14
	44	5.5	1	11.4	340	6.45 ± 0.17
	77	5.2	1	11.0	390	5.00 ± 0.22
	85	2.85	1	8.7	250	4.94 ± 0.16
	95	1.6-3.1	4	9.9	250	4.75 ± 0.2
	125	2.3-8.9	3	7.0	460	4.96 ± 0.15
	140	5.2-10.7	3	22.2	122	4.3 ± 0.4

"If only one decay, error is from weighted fit to decay-otherwise weighted fit to k' vs [NO₂].

vessel. The rate coefficient was the same as in helium with longer residence times. The upper graph of Figure 3 is a first-order plot for all the data obtained in He and N_2 , displaced upward by 10000 s⁻¹. The regression line shown was obtained from a $1/\sigma$ -weighted linear least-squares fit to the data and yields $k_1 = (6.10 \pm 0.10)$ $\times 10^{-11}$ cm³ s⁻¹, where the error is a single standard deviation based on precision alone. We estimate a maximum systematic error of approximately 15% and recommend a rate coefficient of (6.10 \pm 0.90) \times 10⁻¹¹ cm³ s⁻¹ at 95% confidence level. The error limits have been chosen to encompass all the measurements, although significant deviations were observed only below the mean (when the residence time was very long).

As a test for secondary reactions in this system, experiments were carried out in O₂, in which we looked for regeneration of CH₃S at longer reaction times. We found that the decays were logarithmic but, surprisingly, that the rate coefficient decreased

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(31) Balla, R. J.; Heicklen, J. J. Photochem. 1985, 29, 314.

as the O₂ concentration was increased. The apparent value of the rate coefficient in 100 Torr of O_2 was 20% less than in the absence of O_2 . Back-to-back experiments in O_2 and N_2 confirmed this observation (see points at ~ 85 Torr in N_2 and O_2 in Table III), and it was also found that if increasing amounts of O_2 were added to a mixture initially containing 100 Torr of He, the rate coefficient fell off when 70 Torr or more of O₂ was present. Figure 4 shows a series of CH_3S decays in 40 Torr of O_2 . The decays are clearly exponential. In the lower part of Figure 3, the dependence of the pseudo-first-order rate coefficient on NO2 in 40 and ~ 100 Torr of O₂ is shown. The results and experimental conditions are summarized in Table III.

Balla et al. recently reported the first direct measurements of the rate coefficient for this reaction.¹⁵ Their value, (1.08 ± 0.10) \times 10⁻¹⁰ cm³ s⁻¹ independent of pressure at 298 K, is higher than ours. We measured the rate coefficient for this reaction to be $(6.10 \pm 0.90) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ at 298 K. This value was obtained independent of the residence time (t_{res}) in the vessel and the initial $[CH_3S]$. And the value was the same in He and N₂ at pressures less than 100 Torr. The variation of $[CH_3S]_0$ and t_{res} was important to ascertain that we were measuring the correct, homogeneous rate coefficient. Balla et al. found a dependence of the rate coefficient on the flow rate, which they interpreted as being due to a heterogeneous reaction between DMDS and NO₂.

$$CH_3SSCH_3 + 4NO_2 \rightarrow (CH_3SO_2)_2 + 4NO_2$$

We did see a slight decrease in the rate coefficient at very long residence times (~ 20 s) but did not observe substantial production of NO when DMDS and NO₂ were flowed together in the dark (<4% of the DMDS). We think that the variation of the rate coefficient was due to depletion of NO_2 by reaction, since up to three molecules of NO₂ can be consumed for every CH₃S formed (see discussion of mechanism later). Balla et al. appear not to have changed the photolysis energy, which was 18 mJ per pulse. It is quite possible that the high radical concentrations used in their study could account for the difference between their rate coefficient and ours. We feel that we have satisfactorily eliminated such systematic errors. (See also section on product formation later.)

Although no other measurements of the rate coefficient for CH₃S with NO₂ have been made, Black and co-workers have recently measured the rate coefficients for C₂H₅S and *i*-C₃H₇S with NO_2 ^{32,33} Both of these rate coefficients are of similar magnitude, $(9.2 \pm 0.9) \times 10^{-11}$ and $(5.9 \pm 0.6) \times 10^{-11}$ cm³ s⁻¹, respectively, to the measurements of $CH_3S + NO_2$. In addition, the analogous reaction between HS and NO₂ has been the subject of several investigations. The measured rate coefficients fall in the range $(2.4-12) \times 10^{-11}$ cm³ s⁻¹.³⁴⁻³⁹ The two most reliable determinations are probably those of Stachnik and Molina³⁸ (4.9 $\times 10^{-11}$ cm³ s⁻¹) and Wang et al.³⁹ (6.7 $\times 10^{-11}$ cm³ s⁻¹).

The reason for the decrease of the rate coefficient in the presence of oxygen is not entirely clear. One possibility is that OH is produced in the presence of O_2 , and this leads to regeneration of CH₃S. Two experiments were carried out to see whether OH radicals were produced, with NO₂ concentrations of 1.6 \times 10^{14} and 3.6×10^{14} cm⁻³, in 100 Torr of O₂. OH radicals were detected, although the concentration was not large, due to the rapid reaction between OH and DMDS. However, the OH concentration appeared to pass through a maximum and then decay to zero, with the time to reach the maximum shorter at the higher NO_2 concentration. It was estimated at the lower NO_2 concen-

(39) Wang, N. S.; Lovejoy, E. R.; Howard, C. J. J. Phys. Chem. 1987, 91, 5743.

tration and an initial CH₃S concentration of 1.8×10^{12} cm⁻³ that the maximum OH concentration was approximately 4×10^9 cm⁻³, occurring at a delay time of 200 μ s. Under these conditions, the first-order loss rate for CH₃S removal was 10⁴ s⁻¹. Further analysis proved difficult, since the data were scattered and very close to the detection limit $(1 \times 10^9 \text{ cm}^{-3})$ for OH. If regeneration of CH_3S by OH + DMDS is the reason for the lower rate coefficient, then some curvature in the CH₃S decays may have been anticipated. Within the precision of the data curvature was not observed, but we cannot rule it out. The apparent value of the rate coefficient is probably dependent on both the O_2 pressure and the DMDS concentration, which is why the decrease in k_2 with O_2 does not appear uniform.

A second possibility is that a $CH_3S(O_2)$ adduct is formed which does not react with NO₂ as rapidly as CH₃S does and so reduces the apparent loss rate for CH_3S . However, this would imply that at least 25% of CH₃S is tied up as the adduct at 100 Torr of O_2 , which is not consistent with our observations on the $CH_3S + O_2$ reaction.

Mechanism of the $CH_3S + NO_2$ Reaction: Formation of NO. Balla et al.¹⁵ found that the rate coefficient of the reaction between CH₃S and NO₂ is independent of pressure from 2 to 300 Torr, and that it has a weak negative temperature dependence, and proposed that the reaction proceeds not by addition

$$CH_3S + NO_2 + M \rightarrow CH_3SNO_2 + M$$
 (2a)

but by a rapid atom transfer.

$$CH_3S + NO_2 \rightarrow CH_3SO + NO$$
 (2b)

$$CH_3S + NO_2 \rightarrow CH_2S + HONO$$
 (2c)

Lovejoy et al.,⁴⁰ Bulatov et al.,³⁵ and Schönle et al.³⁷ have reported the formation of HSO in the analogous reaction of HS.

$$HS + NO_2 \rightarrow HSO + NO$$

However, there are no direct measurements of the product yields of reaction 2. We carried out time-resolved measurements of the production of NO following pulsed laser photolysis of DMDS-NO₂ mixtures.

The NO rise had two components, with their time constants separated roughly by a factor of 10, as depicted in Figure 5a,b. We interpret this as showing that the CH₃SO produced in the reaction between CH₃S and NO₂ reacts further with NO₂ to produce NO.

$$CH_3SO + NO_2 \rightarrow CH_3SO_2 + NO$$
 (4)

A preliminary analysis of the data could be made by fitting the slow loss of NO out of the detection region to an exponential form and correcting the rise for the calculated NO loss. The corrected signal was then fitted to a biexponential form. This could be safely done if the time constant for the NO loss was less than 10% of the slower of the two rising exponentials, which turned out often to be the case. When the rate coefficient for CH_3S + NO_2 was fixed at the value measured, a rate coefficient $k_4 = (7)$ \pm 2) × 10⁻¹² cm³ s⁻¹ was obtained.

In order to place the NO yield on a quantitative basis, two approaches were used, one absolute and the other relative. In the absolute experiments, a standard mixture of NO was used to calibrate the system for NO fluorescence. Measurements were made under conditions identical with those in the kinetic measurements-that is, with the NO₂-air mixture also flowing. This meant that the background signal from NO produced from 226-nm photolysis of NO₂ was present and that any quenching of the NO fluorescence by O_2 present in the NO₂ mix (to stabilize the NO_2) was the same as in the kinetics experiments. Addition of NO caused an increase in fluorescence proportional to the amount of NO added. Two such experiments were carried out. The initial CH₃S concentration was calculated from the DMDS and laser flux to be 6×10^{11} cm⁻³. The overall yield of NO was

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Phys. Chem. 1987, 91, 66. (38) Stachnik, R. A.; Molina, M. J. J. Phys. Chem. 1987, 91, 4603.

⁽⁴⁰⁾ Lovejoy, E. R.; Wang, N. S.; Howard, C. J. J. Phys. Chem. 1987, 91, 5749.

 1.65 ± 0.25 (single standard deviation including estimated systematic errors). A large uncertainty arises in determining the laser fluence, so a relative method was performed in which O₃ photolysis was used for actinometry.

The relative experiments were carried out to measure both the overall NO yield and the ratio of the yields of reactions 2 and 4. Back-to-back experiments were carried out in which either O_3 or DMDS was photolyzed in the presence of NO₂ in up to 300 Torr of N₂. The predominant reactions occurring are

$$O_{3} + h\nu \rightarrow O(^{3}P) + O_{2}$$

$$\rightarrow O(^{1}D) + O_{2}$$

$$O(^{1}D) + N_{2} \rightarrow O(^{3}P) + N_{2}$$

$$O(^{3}P) + NO_{2} \rightarrow O_{2} + NO$$
(7)

or

 $CH_3SSCH_3 + h\nu \rightarrow 2CH_3S$ $CH_3S + NO_2 \rightarrow CH_3SO + NO$ $CH_3SO + NO_2 \rightarrow CH_3SO_2 + NO$

High pressures of N₂ were chosen to deactivate the O(¹D) initially formed in the photolysis, without quenching of the NO- $(\tilde{A}\rightarrow \tilde{X})$ fluorescence. High pressures of N₂ were also essential to relax any NO molecules formed vibrationally excited. The reactions of NO₂ with both O(³P) ($\Delta H^{\circ}_{298} = -45.9$ kcal mol⁻¹)³⁰ and CH₃S ($\Delta H^{\circ}_{298} = -32 \pm 2$ kcal mol⁻¹)^{26,27} are considerably exothermic, and it is possible that NO could be produced in vibrational levels up to v'' = 8 and, 6, respectively. The rate coefficient for deactivation of NO(v''=1) by N₂ has been measured to be 1.4 × 10⁻¹⁶ cm³ s⁻¹,⁴¹ so at total pressures of 300 Torr relaxation should have been nearly complete on the time scale of the experiment.

The experiments using O₃ photolysis were analyzed by using a nonlinear least-squares fit to a biexponential form and gave a value for k_7 in good agreement with the literature value. For the final fits k_7 was fixed, and the program calculated values for the initial O-atom concentration (expressed as NO) and the rate coefficient for diffusion of NO out of the detection region. For the CH₃S experiments, an analytical form for the NO kinetics curve was derived following the method outlined by Benson for consecutive reactions.⁴² The expression for the time dependence of the NO concentration is

$$[NO]_{t} = \frac{f_{2}k_{2}'[CH_{3}S]_{0}}{DET} \{ (k_{4}' - k_{d})[(1 + f_{4})k_{4}' - k_{2}'] \exp(-k_{2}'t) + (k_{d} - k_{d}')[(1 + f_{4})k_{4}' - k_{d}] \exp(-k_{d}t) \}$$

where $DET = k_2'k_4'(k_2' - k_4') + k_4'k_d(k_4' - k_d) + k_dk_2'(k_d - k_2')$, with $k_2' = k_2[NO_2]$, $k_4' = k_4[NO_2]$, f_2 = branching ratio for NO production in reaction 2, f_4 = branching ratio for NO production in reaction 4, and k_d = first-order rate coefficient for diffusion of NO out of probe beam.

The NO data were fitted to this equation by using a nonlinear least-squares program, inputting k_2 , $[NO_2]$, and the value of k_d derived from the O₃ photolysis. The program returned values for k_4 , f_4 , and $f_2[CH_3S]_0$. The relative $[CH_3S]_0$ (expressed as NO) could be calculated from the relative laser fluence, concentration, and absorption cross section for both the DMDS and O₃ photolysis. Thus, f_2 could be determined. It was found that at 300 Torr f_4 was approximately equal to 1.0, and a value for k_4 of $(9.5 \pm 3.0) \times 10^{-12}$ cm³ s⁻¹ was obtained. Figure 5 shows the fit to the NO produced in one such experiment. However, at lower pressure the fitted value of f_4 increased above 1.0 and k_4 decreased to $\sim 5 \times 10^{-12}$ cm³ s⁻¹. We believe this is due to the effect of vibrationally



Figure 5. (a) Production of NO in pulsed photolysis of DMDS-NO₂ mixtures at 300 Torr of N₂. Line fitted to data with $k_4 = (6.8 \pm 1.3) \times 10^{-12}$ and $f_4 = 1.1 \pm 0.1$. (b) Initial part of rise, showing biexponential rise of NO fluorescence.

excited NO, which appears "late", i.e., in the second exponential, and reduces the apparent yield of reaction 2. For the experiments in which quantitative measurements of the NO were made, the yields varied between 1.0 and 1.6 NO per CH₃S. It was not possible to see a systematic dependence of the yields or rate coefficients on the [NO₂] or total pressure. A further complication in the analysis is that some O₂ was present in the NO₂ mixture; otherwise, a large background NO signal was observed. There is evidence that CH₃SO adds to O₂,⁴³ and this may also be occurring here.

$$CH_3SO + O_2 \xrightarrow{M} CH_3SO \cdot O_2$$
 (8)

However, the reaction cannot be very fast $(k_8 \le 5 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1} \text{ at } 300 \text{ Torr})$; otherwise, we would not have seen NO yields greater than 1.0. All of these factors make an unambiguous analysis of the data impossible. Even if the kinetics scheme were "clean", i.e., only reactions 2 and 4 and diffusion, a meaningful fit would be hard to achieve, but with the added uncertainty of vibrational quenching and further reactions taking place, it is difficult to be very exact. However, the results of all these different kinds of experiments are consistent with the NO yields of reactions 2 and 4 both being 0.8 ± 0.2 and k_4 being $(8 \pm 5) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$.

The measurements of NO reported here are the first quantitative measurements of the products of reaction 2 under isolated conditions. Barnes et al. have shown in a CW experiment that

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⁽⁴²⁾ Benson, S. W. The Foundations of Chemical Kinetics; McGraw-Hill: New York, 1960; p 36.

⁽⁴³⁾ Barnes, I.; Bastian, V.; Becker, K. H.; Niki, H. Chem. Phys. Lett. 1987, 140, 451.

NO is a major product of the photooxidation of DMDS in the presence of NO₂.⁴³ They reported that approximately two molecules of NO were formed per molecule of DMDS photolyzed in N₂ and that one molecule of NO was formed in air. This result is quite similar to our finding, that 1.6–2.0 molecules of NO are produced for every CH₃S radical. Other reactions must however have been occurring in their system. They also noted a minor reaction channel leading to production of CH₃SNO₂. Our experiments show that the yield of NO is possibly as high as 100% and that other channels, to form e.g. CH₂S + HNO₂ or CH₃SNO₂, must be relatively minor. The secondary production of NO indicates a reaction between CH₃SO and NO₂ to form CH₃SO₂ + NO.

The analysis of the NO profiles yields a rate coefficient of $(8 \pm 5) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ for the reaction of CH₃SO with NO₂. This rate coefficient has not been previously measured. The analogous reaction

$$HSO + NO_2 \rightarrow HSO_2 + NO_2$$

has been studied by Bulatov et al., using intracavity dye laser absorption,³⁵ and Lovejoy et al., by laser magnetic resonance.⁴⁰ These groups measured rate coefficients of 4×10^{-12} and 9.6×10^{-12} cm³ s⁻¹, respectively. These rate coefficients are very similar in magnitude to that for CH₃SO + NO₂, and presumably the mechanism is analogous, as proposed by Lovejoy et al.

Product Formation: Detection and Effect on k_2 . The observation of a dependence of the rate coefficient k_2 on the O₂ pressure led us to look further into the mechanism of the reaction. The CH₃S decays were examined at long reaction times, to see whether they decayed to zero or whether a residual signal was present which would indicate that other radicals were cycling to regenerate CH₃S. On close examination of the CH₃S decays in He, it was found that the signal did not always decay to zero at longer times, indicating possible regeneration of CH₃S. When the signals were measured at longer times and averaged for a greater number of shots to enhance the signal, the "tail" resembled a product growing and decaying. Two experiments were carried out which show that this fluorescence was due to a separate chemical species. First, the delay time of the gated integrator was extended to 700 ns after the dye laser pulse. Since the lifetime of excited CH₃S in helium is ~ 800 ns, it was still possible to detect CH₃S with this gate delay. In these experiments the CH₃S temporal profile was strictly logarithmic, and no residual signal was seen at the end. Second, the dye laser was tuned to 370.7 nm, i.e., between the $v_{3}' = 1$ and $v_3' = 2$ bands. CH₃S fluorescence was always detected, but at a greatly reduced level. The residual signal was not reduced, though, and it was possible to fully resolve the temporal profile. Figure 6 shows the composite fluorescence signal, obtained with a gate delay of 40 ns. It is clear that the residual signal is not due to a direct product of the $CH_3S + NO_2$ reaction, since it has a substantial "induction" time, and continues to be produced after the CH_3S has decayed away.

An attempt was made to measure the fluorescence excitation spectrum of the product by exciting fluorescence ~ 1 ms after the photolysis pulse. In 200 μ s all the CH₃S is reacted away, and only the new species remains, as shown in Figure 6. Although the signal to noise was not very good, it was clear that the spectrum contans many very sharp lines and no further measurements were made at this time. We estimate that the radiative lifetime of the state that we excited must be of the order of 100 ns. Further work is planned to try to determine the identity of the product.

One possibility is that the product is CH_3SO_2 , formed from the consecutive reaction of CH_3SO with NO_2

$$CH_3SO + NO_2 \rightarrow CH_3SO_2 + NO$$
 (4)

 CH_3SO_2 is known from liquid-phase studies to absorb at $350 \pm 30 \text{ nm.}^{44}$ The effect of varying the NO₂ concentration on the profile was determined. Increasing the [NO₂] led to an increase in both the production rate and the loss rate of the species, in-



Figure 6. Fluorescence signal following excitation at 374 nm in pulsed laser photolysis of DMDS-NO₂ mixture in 100 Torr of He. Boxcar delay: 40 ns. [NO₂] = 3.5×10^{14} cm⁻³. Full line shows fit to CH₃S decay, yielding $k_2 = 5.9 \times 10^{-11}$ cm³ s⁻¹. Dashed lines show results of simulations assuming fluorescence is due to CH₃SO₂. (---) $k_4 = 1.0 \times 10^{-11}$ and $k_9 = 7.0 \times 10^{-12}$ cm³ s⁻¹; (---) $k_4 = 8.0 \times 10^{-12}$ and $k_9 = 5.0 \times 10^{-12}$ cm³ s⁻¹.

dicating that it, too, reacts with NO₂. Computer simulations were carried out to test whether CH_3SO_2 could be responsible for the fluorescence. The reaction scheme consisted of reactions 2, 4, and 9:

$$CH_3SO_2 + NO_2 \rightarrow products$$
 (9)

 k_2 was fixed at the value measured, and k_4 and k_9 were varied. It was not possible to fit the data exactly by any particular pair of rate coefficients. Notably, the induction time could not be reproduced, and the actual rise was always much slower than modeled. Figure 6 shows this effect for different values of k_4 and k_9 . The disappearance of this species is best reproduced by the pair of values 1.0×10^{-11} and 7.0×10^{-12} cm³ s⁻¹. However, the maximum signal occurs at too short a time. Reducing both values leads to a delayed maximum, but also to a slower decay. In neither case is the initial rise well-described. It should be noted that since k_4 and k_9 are similar in magnitude, it is not possible to decide unambiguously which rate coefficient corresponds to which reaction from this analysis. If the value of k_2 used in the model was reduced to less than 10^{-11} cm³ s⁻¹, the fit improved, since this delayed production of this product. Therefore, we cannot say conclusively at this stage whether CH₃SO₂ is responsible for the fluorescence or not. It is possible that CH₃SO₂ is produced vibrationally excited and that we observe a convolution of its production and relaxation kinetics, as in the case of NO. On the other hand, we may be observing a different species produced further along the reaction sequence.

Effect of the Product on CH_3S Kinetics. As stated earlier, the product fluorescence was discovered while checking to see whether CH₃S was regenerated. The occurrence of a residual signal obviously affects the analysis for k_2 . If the residual signal is due to a product formed directly from CH₃S, the correct way to analyze the data is to use the residual signal as the base line, as discussed for the case of absorption by Sander and Watson.⁴⁵ However, since the product is not formed in reaction 2, and is therefore kinetically "decoupled" from CH₃S, it is appropriate to use the true background, obtained either prior to the photolysis laser flash or with the photolysis laser blocked. The presence of a residual signal will, of course, lead to curvature as it grows in, but the rate coefficient obtained for the CH₃S decay from the early part will be correct. To verify that our conditions were appropriate for measuring only CH₃S, a few decays were analyzed taking the maximum of the residual signal as the background level.

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The decays were found to be strongly curved, and the fit to the initial part yielded a rate coefficient of $\sim 7 \times 10^{-11}$ cm³ s⁻¹, approximately 15% higher than when the "true" background was used. On the other hand, using the pretrigger background resulted in a rate coefficient identical with that obtained when the boxcar delay was extended so that only CH₃S was detected. Product formation is a potential reason for the higher value of the rate coefficient obtained by Balla et al.,¹⁵ depending on the exact wavelength and boxcar delay they used.

Implications for Atmospheric Chemistry. The upper limit for the $CH_3S + O_2$ reaction rate coefficient determined here is an order of magnitude lower than previous estimates. We still cannot rule out this reaction in the atmosphere, though. O_2 has a mole fraction of 0.21, and this implies a loss rate for CH₃S of $\leq 15 \text{ s}^{-1}$ in the lower troposphere. Even though the NO_2 reaction rate coefficient is 6×10^{-11} cm³ s⁻¹, the maximum NO₂ mixing ratio observed in the background troposphere is around 100-300 ppt $((2.5-7.5) \times 10^9 \text{ cm}^{-3})$,¹⁸ giving a loss rate of 0.2–0.5 s⁻¹. In the marine boundary layer, where most of the atmospheric CH₃S oxidation occurs, the NO₂ concentration may be as low as 10 ppt $(3 \times 10^8 \text{ cm}^{-3})$. The upper limit for the O₂ reaction is therefore still 3 orders of magnitude higher than we need to rule this reaction out.

Our results indicate that CH₃S and O₂ do not form a strongly bound adduct and that such an adduct, if formed at all, does not react rapidly with O_2 . Therefore, the loss rate for CH₃S which we observe will correspond to the actual loss rate in the atmosphere, provided the adduct does not react with other trace molecules, such as NO, NO₂, or O₃, substantially faster than CH₃S does.

> $CH_3S(O_2) + NO \rightarrow CH_3SO + NO_2$ $CH_3S(O_2) + NO_2 \rightarrow products$ $CH_3S(O_2) + O_3 \rightarrow CH_3SO + 2O_2$

The most pressing problem remains the identification of the mechanisms by which CH₃S is converted to SO₂ and MSA at low NO_r. Simultaneous measurements of the DMS flux and SO₂ in the marine troposphere suggest that SO_2 is the major product of DMS oxidation, maybe accounting for 90% of the oxidized sulfur.46 However, the laboratory studies have consistently shown reduced SO₂ yields and a predominance of MSA. It is not clear whether this reflects the mode of attack on CH₃S or subsequent reactions of radicals with the precursor.^{9,13} Our experiments show that oxidation of CH₃S to CH₃SO and presumably CH₃SO₂ occurs rapidly in the presence of NO2, and Hatakeyama et al. have recently shown that if ¹⁸O-labeled NO₂ is used, some of the SO₂ produced contains ¹⁸O,⁴⁷ indicating the importance of the CH₃S + NO_2 reaction in the production of SO_2 in chambers. The formation of MSA, CH₃SO₃H, could also follow CH₃SO₂ production.⁴³ However, under atmospheric conditions of low NO₂ different considerations may apply, and an oxidation chain initiated by $CH_3S + O_2$ could give a different product distribution. These questions can only be resolved by a thorough study of CH₃SO and CH₃SO₂ chemistry and more mechanistic information on the $CH_3S + O_2$ reaction.

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Ab Initio Study of the Addition Reaction of the Methyl Radical to Ethylene and Formaldehyde

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A detailed study of the potential energy surfaces for methyl radical plus ethylene and methyl radical plus formaldehyde has been carried out with the 3-21G and 6-31G* basis sets at the Hartree-Fock level. Heats of reaction and barrier heights have been computed with the Møller-Plesset perturbation theory up to the fourth order with and without annihilation of spin contamination. The results of the calculations indicate the formation of an early transition state with reactant-like structure for both reactions. In the case of methyl radical plus ethylene, spin annihilation lowers the barrier height by 7 kcal/mol, while in the reaction between methyl radical and formaldehyde the barrier is lowered by 6 kcal/mol when spin annihilation is considered. A comparison between the calculated and experimental values of the barrier height for the methyl addition to ethylene (6.9 kcal/mol vs 7.9 kcal/mol) and formaldehyde (6.3 kcal/mol vs 6.8 kcal/mol) indicates very good agreement between theory and experiment.

Introduction

Although radical additions to double bonds have been extensively studied experimentally,^{1,2} there is still some controversy about the nature of the transition states. While experimental data lead to the conclusion that these reactions have tight transition states with productlike structures,³⁻⁵ the low activation energies and high exothermicities of these reactions would suggest early, reactant-like transition states.^{1,6,7}

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