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Photooxidation of Dimethyl Sulfide and Dimethyl Disulfide. I: Mechanism Development

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Abstract. Detailed theoretical (Part I, this article) and experimental (Part II) investigations are presented for the mechanism of the atmospheric photooxidation of dimethyl sulfide (CH_3SCH_3) and dimethyl disulfide (CH_3SSCH_3). In this paper, comprehensive mechanisms for the atmospheric chemistry of CH_3SCH_3 and CH_3SSCH_3 are developed based on fundamental considerations of all available kinetic and mechanistic information.

Key words: Dimethyl sulfide, dimethyl disulfide, photooxidation mechanism.

1. Introduction

Reduced sulfur compounds, including hydrogen sulfide (H_2S), carbonyl sulfide (COS), carbon disulfide (CS_2), methanethiol (CH_3SH), dimethyl sulfide (CH_3SCH_3), and dimethyl disulfide (CH_3SSCH_3), are released from the ocean to the atmosphere. Among these compounds, dimethyl sulfide (CH_3SCH_3) is of major importance in the global sulfur cycle, with an estimated flux of about 40 Tg S yr^{-1} from the oceans and a mean concentration of about 100 ppt in the marine atmosphere (Andreae and Raemdonck, 1983; Andreae *et al.*, 1985). Thus, a better understanding of the atmospheric chemistry of reduced sulfur compounds, including dimethyl sulfide and dimethyl disulfide, is directly relevant to a number of important issues such as SO_2 formation, deposition acidity, and global tropospheric sulfur budget.

In an earlier study (Yin *et al.*, 1986), we proposed reaction mechanisms for the atmospheric oxidation of several organosulfur compounds including dimethyl sulfide. These mechanisms accounted for the major features of the few experimental studies then available (e.g., Hatakeyama *et al.*, 1983; 1985; Grosjean and Lewis, 1982; Grosjean, 1984) and outlined major areas of uncertainty in the tropospheric chemistry of organosulfur compounds. As more experimental studies have become available in recent years, especially regarding the kinetics of initial reactions of reduced sulfur compounds and the subsequent reactions of the CH_3S radical, it is now possible to develop and test updated mechanisms of the atmospheric oxidation of dimethyl sulfide and dimethyl disulfide. These new mechanisms are summarized conceptually in Figures 1 and 2, respectively. In this article, Part I, we present, based on chemical considerations, a theoretical investigation of the possible

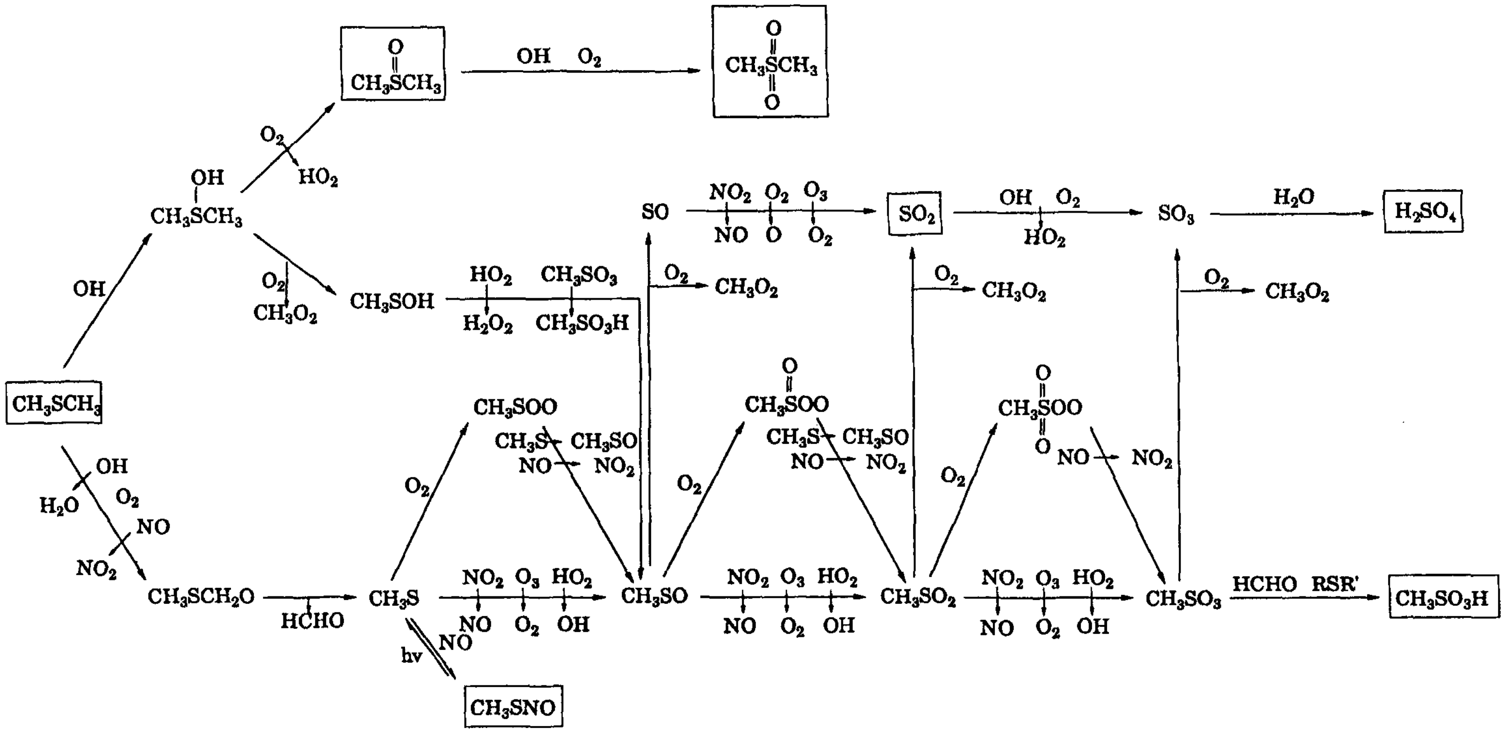


Fig. 1. CH_3SCH_3 Atmospheric photooxidation mechanism.

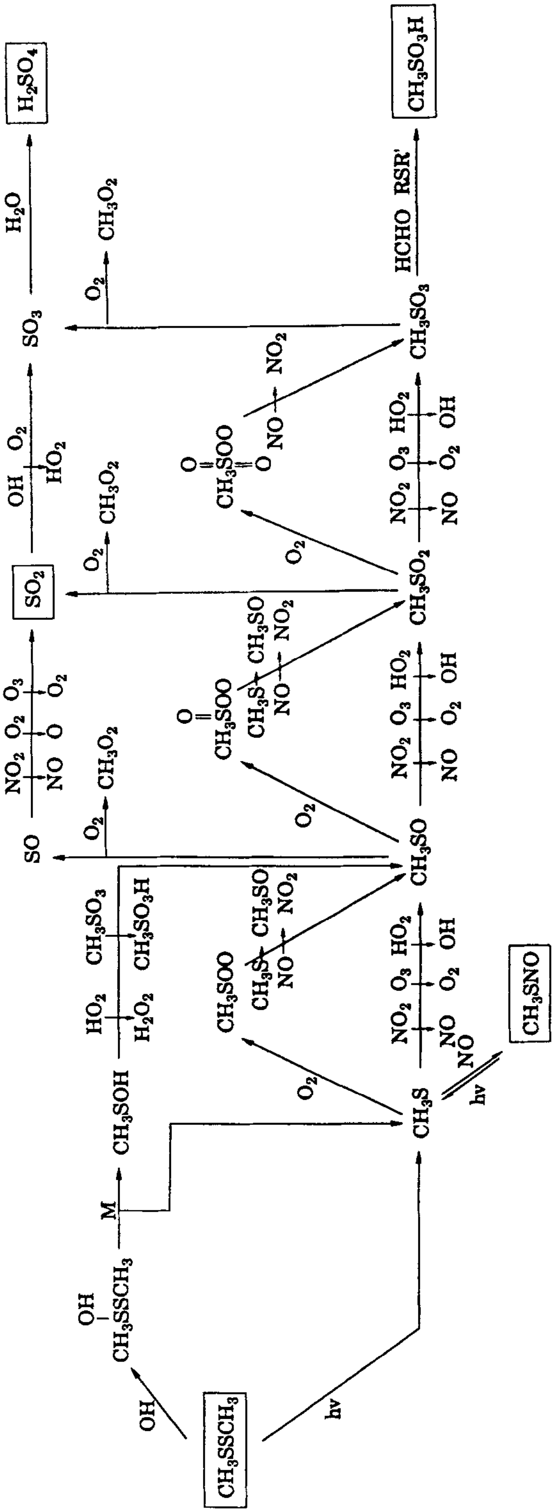


Fig. 2. CH_3SSCH_3 Atmospheric photooxidation mechanism.

CH_3SCH_3 and CH_3SSCH_3 oxidation pathways that are consistent with kinetic and mechanistic information now available. The proposed mechanisms are evaluated in a companion article, Part II (Yin *et al.*, 1990), with new experimental data obtained in sunlight-irradiated CH_3SCH_3—NO_x—air, CH_3SSCH_3—air and CH_3SSCH_3—NO_x—air mixtures.

In the following sections, a comprehensive analysis of all available experimental information relevant to the chemistry of CH_3SCH_3 and CH_3SSCH_3 is carried out along the reaction sequences shown in Figures 1 and 2, i.e., initial reactions with OH, NO_3, $O(^3P)$ and IO radicals, unimolecular decomposition and bimolecular reactions of the corresponding adducts, structures of CH_3SO_x and $CH_3S(O)_xOO$ radicals, detailed reactions of CH_3SOH and $CH_3S(O)_xCH_3$, oxidations of CH_3SO_x radicals and reductions of $CH_3S(O)_xOO$ radicals, and major formation pathways of SO_2 and CH_3SO_3H products and possible 'missing' products. Finally, the new mechanisms are contrasted to those developed in earlier studies.

2. Initial Reactions

Atmospheric removal of organosulfur compounds is initiated by their reactions with OH, NO_3, IO and $O(^3P)$ radicals. The critical issue regarding these initial reactions is the extent of competition between addition and abstraction pathways. Although numerous kinetic studies of these reactions have been carried out, these studies have shed little light on the corresponding reaction mechanisms, especially as to the trends of observed rate constants and to the various 'effects' due to secondary reactions. In this section, the general character of the initial reactions, i.e., addition and/or abstraction, will be analyzed in terms of fundamental chemistry, as well as on the basis of available experimental data. Although our study focuses on CH_3SCH_3 and CH_3SSCH_3, initial reactions of other reduced sulfur compounds including H_2S and CH_3SH will also be included for comparison.

2.1. *Initial Reaction Mechanisms*

The initial reactions of reduced sulfur compounds with free radicals may involve two pathways, abstraction and addition. Hydrogen atom abstraction may proceed through C–H or S–H bond scission. Alternatively, the initial reaction may involve electrophilic addition onto the S atom. The corresponding energy-rich adduct may be collisionally stabilized or may unimolecularly decompose, either back to the reactants or to yield new products. These initial reactions can be represented by

$$\begin{array}{rcll} \mathrm{RSR'} + \mathrm{X} & \longrightarrow & \mathrm{RSR''} + \mathrm{HX} & k_{\mathrm{abs}} \\ & \xrightarrow{M} & \mathrm{Adduct} & k_{\mathrm{add}},\ k_{-\mathrm{add}} \\ \mathrm{Adduct} & \xrightarrow{M} & \mathrm{Product} & \\ \mathrm{Adduct} + \mathrm{Y} & \longrightarrow & \mathrm{Products} & \end{array}$$

(R = H, CH_3; R′ = H, CH_3, CH_3S; X = OH, NO_3, $O(^3P)$, IO; Y = reactive species such as O_2, NO_2 in the system.)

From the trend of the bond dissociation energy (BDE) of C—H and S—H bonds (Hwang and Benson, 1979; Shum and Benson, 1983; 1985):

	CH_3S—H,	HS—H <	H—CH_2SH,	H—CH_2SCH_3,	H—CH_2SSCH_3
BDE (kcal/mole):	88.6 ± 1	90.5 ± 1.1	96 ± 1	96.6 ± 1.0	97 (estimated)

the order of rate constants for the abstraction pathway can be expected to be

$$k_{CH_3S—H},\ k_{HS—H} > k_{H—CH_2SH},\ k_{H—CH_2SCH_3},\ k_{H—CH_2SSCH_3}.$$

Importantly, the rate constants for the abstraction pathways involving C—H and S—H bond scission are not expected to span several orders of magnitude (see Table I), since the difference of bond dissociation energies for C—H and S—H bonds is about 6–8 kcal/mole although the H atoms bonded to S could be more readily abstracted than those bonded to C.

The relative reactivity of different radicals towards reduced sulfur compounds by H-atom abstraction can be evaluated from the strength of the newly formed H—X bond (Kerr, 1985; Baulch *et al.*, 1984),

	HO—H >	H—O >	H—ONO_2,	H—OI
BDE (kcal/mole):	119 ± 1	102.2	101.2 ± 0.5	(101)

that is,

$$k_{OH} > k_{O(^3P)} > k_{NO_3},\ k_{OI}.$$

Considering the difference of bond dissociation energy between broken and formed bonds, it is anticipated that, among the four radicals, OH will be the most likely to react with reduced sulfur compounds by H-atom abstraction.

The addition pathway can be envisioned as involving two steps, adduct formation and subsequent unimolecular decomposition. Adduct formation involves an electrophilic addition reaction, and is mainly determined by the electron density on the S atom. The electron-donating capability of substituted groups on the S atom is in the order of

$$CH_3S > CH_3 > H$$

Thus, the tendency for radical addition to the S atom is in the order of

$$CH_3SSCH_3 > CH_3SCH_3 > CH_3SH > H_2S.$$

The rate and selectivity of the subsequent adduct unimolecular decomposition step depend on the bond dissociation energies of broken and formed bonds as well as on the stability of the radicals produced. The overall addition reaction rate may be controlled by addition, unimolecular decomposition, or both. The adduct may also react with other reactive species in the system, thus affecting the observed rate constants; see Section 2.4.

Table I. Summary of kinetic data for reduced sulfur compounds

Initial reaction			$k_{298} \times 10^{11}$ (cm^3 $molecule^{-1}$ s^{-1})
$O(^3P) + H_2S$	$\rightarrow HS + OH$		0.0022
$+ CH_3SH$	$\rightarrow CH_3S + OH$		0.18
	$\rightarrow CH_3S(O)H$	$\rightarrow HSO + CH_3$	
		$\rightarrow CH_3SO + H$	
$+ CH_3SCH_3$	$\rightarrow CH_3S(O)CH_3$	$\rightarrow CH_3SO + CH_3$	5.0
$+ CH_3SSCH_3$	$\rightarrow CH_3S(O)SCH_3$	$\rightarrow CH_3SO + CH_3S$	10–13
$OH + H_2S$	$\rightarrow HS + H_2O$		0.48
$+ CH_3SH$	$\rightarrow CH_3S + H_2O$		3.3
	$\rightarrow CH_3S(OH)H$		
$+ CH_3SCH_3$	$\rightarrow CH_3SCH_2 + H_2O$		0.44–0.63
	$\rightarrow CH_3S(OH)CH_3$		
$+ CH_3SSCH_3$	$\rightarrow CH_3S(OH)SCH_3$	$\rightarrow CH_3SOH + CH_3S$	21
$NO_3 + H_2S$	$\rightarrow HS + HONO_2$		<0.00008–0.003
	$\rightarrow HS(ONO_2)H$		
$+ CH_3SH$	$\rightarrow CH_3S + HONO_2$		0.077–0.109
	$\rightarrow CH_3S(ONO_2)H$		
$+ CH_3SCH_3$	$\rightarrow CH_3SCH_2 + HONO_2$		0.075–0.106
	$\rightarrow CH_3S(ONO_2)CH_3$		
$+ CH_3SSCH_3$	$\rightarrow CH_3SSCH_2 + HONO_2$		0.0739
	$\rightarrow CH_3SS(ONO_2)CH_3$		
$IO + CH_3SSCH_3$	$\rightarrow CH_3S(OI)CH_3$	$\rightarrow CH_3S(O)CH_3 + I$	1.5–3.0

Notes:

1. The rate constants are measured at room temperature and at both low or high pressure by various techniques.
2. Usually both abstraction and addition pathwas are presented. In the case where the information on the mechanism is available, the dominant reaction is given.

References:

$O(^3P)$:

Nip *et al.* (1981), Cvetanović *et al.* (1981), Baulch *et al.* (1984).

OH:

Atkinson *et al.* (1977), Wine *et al.* (1981), Wine *et al.* (1984), Hynes and Wine (1987), Baulch *et al.* (1984), Martin *et al.* (1985), Wallington *et al.* (1986a), Nielsen *et al.* (1986), Hynes *et al.* (1986), Hsu *et al.* (1987), Barnes *et al.* (1988), Cox and Sheppard (1980).

NO_3:

Atkinson *et al.* (1984), MacLeod *et al.* (1986), Wallington *et al.* (1986b), Wallington *et al.* (1986c), Tyndall *et al.* (1986), Dlugokencky and Howard (1988).

IO:

Barnes *et al.* (1987a), Martin *et al.* (1987).

2.2. *Observed Rate Constant Trends*

Rate constants for the reactions of OH, NO_3, IO and $O(^3P)$ with reduced sulfur compounds are given in Table I. These rate constants may include contributions from both abstraction and addition pathways. The rate constant trends are discussed below with respect to the relative importance of these two pathways.

2.2.1. *Reaction with $O(^3P)$ Radical*

The observed rate constants for the reactions of RSR′ with $O(^3P)$ are in the order of

$$k_{H_2S} \ll k_{CH_3SH} < k_{CH_3SCH_3} < k_{CH_3SSCH_3}$$

and span some four orders of magnitude (Cvetanović *et al.*, 1981; Baulch *et al.*, 1984). This trend is consistent with addition being the major pathway. Cvetanović *et al.* (1981) studied the reactions of $O(^3P)$ with CH_3SH, CH_3SCH_3 and CH_3SSCH_3 and found that addition of $O(^3P)$ to the S atom followed by rapid unimolecular decomposition (see Table I) was the dominant pathway, although abstraction may account for as much as 10% of the total reaction in the case of CH_3SH. The small negative activation energy for the reaction of $O(^3P)$ with CH_3SCH_3 and CH_3SSCH_3 is also consistent with an addition mechanism. The $H_2S + O(^3P)$ reaction is believed to proceed mostly by abstraction; this is supported by the positive activation energy of about 3.8 kcal/mole (Baulch *et al.*, 1984).

2.2.2. *Reaction with OH Radical*

The trend of rate constants for the RSR′ + OH reaction is similar to that for $O(^3P)$, with the exception of CH_3SCH_3

$$k_{H_2S} < k_{CH_3SCH_3} < k_{CH_3SH} < k_{CH_3SSCH_3}.$$

Hynes *et al.* (1986) estimated that, for the $OH + CH_3SCH_3$ reaction under atmospheric conditions at 300 K, the *effective* branching ratio is 0.75 abstraction, and 0.25 addition.

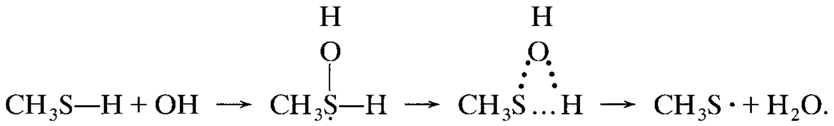
It will be shown below, however, that the observed trend of OH rate constants is consistent with addition being the dominant pathway, even for the $OH + CH_3SCH_3$ reaction. Although the *effective or apparent* pathway (considering only the formed adducts that are scavenged by O_2) for the $OH + CH_3SCH_3$ reaction is dominated by abstraction, 0.75 at 300 K as estimated by Hynes *et al.* (1986), the *actual or intrinsic* branching ratios of abstraction vs. addition (i.e., without considering the reverse reaction of addition) are 0.12 to 0.88 for CD_3SCD_3 at 261 K (Hynes *et al.*, 1986), and 0.33 to 0.67 for CH_3SCH_3 at 298 K (Barnes *et al.*, 1988), indicating that addition is the dominant pathway for the $OH + CH_3SCH_3$ reaction, although the abstraction pathway is not negligible. Furthermore, despite the fact that the observed $k_{OH+CH_3SCH_3}$ is almost a factor of 10 lower than the observed k_{OH+CH_3SH}, the difference is much smaller if we define $k_{initial} = k_{abs} + k_{add}$ and remove the effect of the reverse reaction of addition pathway. Estimates of k_{add} and k_{-add} have been made by Hynes *et al.* (1986) and Barnes *et al.* (1988). For the CD_3SCD_3 + OH reaction at 261 K in 700 torr $N_2 + O_2$ (Hynes *et al.*, 1986),

$$\begin{aligned} k_{OH} &= (1.6 \pm 0.2) \times 10^{-12} + (1.15 \pm 0.20) \times 10^{-11} \\ &= (1.31 \pm 0.22) \times 10^{-11} \quad (\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}) \end{aligned}$$

and for CH_3SCH_3 + OH at 298 K in 760 torr air (Barnes *et al.*, 1988),

$$\begin{aligned} k_{OH} &= (4.4 \pm 0.4) \times 10^{-12} + (9.0 \pm 0.5) \times 10^{-12} \\ &= (1.34 \pm 0.09) \times 10^{-11} \quad (\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}). \end{aligned}$$

Comparing with the corresponding value of $k_{OH+CH_3SH} = 3.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K (Hynes and Wine, 1987), both rate constants are now of the same magnitude, although k_{OH+CH_3SH} is still larger than $k_{OH+CH_3SCH_3}$. Since the trend for the abstraction pathway is $CH_3SH > CH_3SCH_3$ (see Section 2.1), and the contribution of H-atom abstraction by the OH radical is increased relative to that by the O(^{3}P) radical and also is comparable to that from addition, therefore, the reason that $k_{OH+CH_3SH} > k_{OH+CH_3SCH_3}$ can be explained by the contribution from the abstraction pathway, or more likely through the following mechanism:



$$CH_3S{-}H + OH \longrightarrow CH_3\overset{\overset{\displaystyle H}{\overset{\displaystyle O}{|}}}{S}{-}H \longrightarrow CH_3\overset{\overset{\displaystyle H}{\overset{\displaystyle O}{\vdots}}}{S}\ldots H \longrightarrow CH_3S\cdot + H_2O.$$

Intramolecular H-bonding as well as the weaker S—H bond than C—H bond by 6–8 kcal/mole BDE facilitates the H-atom abstraction by OH radical, and the contribution of reverse decomposition is small compared to that for CH_3SCH_3. The formation of such a nonlinear transient state is consistent with the near-zero isotopic effect observed by Wine *et al.* (1984) for the CH_3SD + OH reaction. The lack of O_2 effect observed for $CH_3S(OH)H$ by Hynes and Wine (1987) is consistent with a relatively short lifetime for the $CH_3S(OH)H$ adduct and also supports the above mechanism. For CH_3SSCH_3, the effect of the reverse reaction is negligible, since the tendency of OH addition toward CH_3SSCH_3, whose rate constant is almost a factor of 10 higher, is much stronger than that for other reduced sulfur compounds.

In summary, the reaction of OH with organosulfur compounds involves addition as the dominant pathway, although abstraction also contributes to the overall reaction in the case of CH_3SH and CH_3SCH_3. Due to the reverse reaction of the adduct $CH_3S(OH)CH_3$, the OH + CH_3SCH_3 reaction is apparently dominated by abstraction at temperature larger than 285 K in the atmosphere (estimated by Hynes *et al.*, 1986).

2.2.3. *Reactions with NO_3 and IO Radicals*

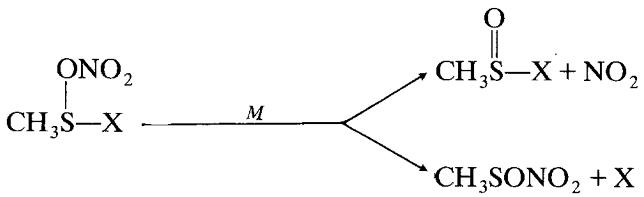
As discussed in Section 2.1, the NO_3 reaction is expected to involve abstraction only as a minor pathway, i.e., much smaller than that for OH and similar to that of $O(^3P)$. However, NO_3 reaction rate constants exhibit a totally different trend from those for $O(^3P)$ and OH; see Table I. The NO_3-organosulfur rate constants are similar with the exception of that for $k_{NO_3 + CH_3SSCH_3}$ (MacLeod *et al.*, 1986), which will be discussed later. The rate constant of $H_2S + NO_3$ is at least three orders of magnitude smaller (Dlugokencky and Howard, 1988), indicating that in this case abstraction may be the dominant pathway. From Table I, it can be seen that the rate constant for NO_3 radical is always a factor of 10 or more lower than that for other radicals. One possible explanation is that the unpaired electron on O atom of NO_3 is delocalized and forms a large π bond over the whole NO_3 radical, leading to its lower reactivity, while for other radicals the unpaired electron is localized on the O atom of each radical.

Comparison of CH_3SCH_3 and CH_3OCH_3 also supports the fact that addition is the dominant pathway for $NO_3 + RSR'$ (Wallington *et al.*, 1986b, 1986c; Dlugokencky and Howard, 1988):

	k_{298} (cm^3 molecule^{-1} s^{-1})
$NO_3 + CH_3SCH_3 \longrightarrow$ Product	$7.7 - 10.9 \times 10^{-13}$
$NO_3 + CH_3OCH_3 \longrightarrow HNO_3 + CH_3O\dot{C}H_2$	$< 0.03 \times 10^{-13}$

although C—H BDE are similar for the two compounds, i.e., 96.6 ± 1.0 and 93 ± 1 kcal/mole for $CH_3SCH_2—H$ and $CH_3OCH_2—H$, respectively (Shum and Benson, 1985; McMillen and Golden, 1982).

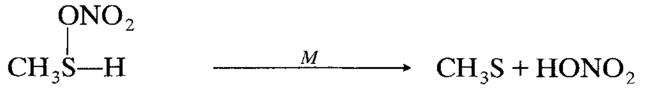
The observed similarity among NO_3 rate constants is not inconsistent with addition being the dominant reaction pathway if the observed rate constants are actually determined by the subsequent reactions of the adducts and the energy changes associated with them are of similar magnitude. Basically, the formed adducts, $CH_3S(ONO_2)X$ where X = H, CH_3 or SCH_3, can undergo unimolecular decomposition,



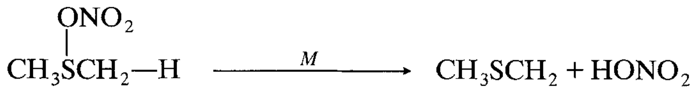
$$CH_3\overset{\displaystyle ONO_2}{\overset{|}{S}}—X \xrightarrow{M} CH_3\overset{\displaystyle O}{\overset{\|}{S}}—X + NO_2 \qquad (1)$$

$$CH_3\overset{\displaystyle ONO_2}{\overset{|}{S}}—X \xrightarrow{M} CH_3SONO_2 + X \qquad (2)$$

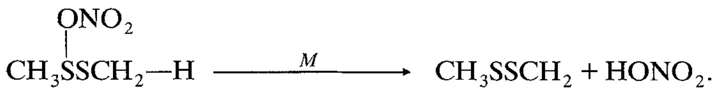
or intramolecular H-atom abstraction.



$$CH_3\overset{ONO_2}{\overset{|}{S}}—H \xrightarrow{M} CH_3S + HONO_2 \qquad (3a)$$



$$CH_3\overset{ONO_2}{\overset{|}{S}}CH_2—H \xrightarrow{M} CH_3SCH_2 + HONO_2 \qquad (3b)$$



$$CH_3\overset{ONO_2}{\overset{|}{S}}SCH_2—H \xrightarrow{M} CH_3SSCH_2 + HONO_2. \qquad (3c)$$

For pathway (1), the rates of adduct decomposition are expected to be similar for CH_3SH, CH_3SCH_3 and CH_3SSCH_3 since each of them involves similar O—NO_2 bond scission. Since it is difficult to evaluate the bond dissociation energies of adducts for pathway (2), a rough comparison of bond dissociation energy from the corresponding reactants can be made as follows (Benson, 1978; Shum and Benson, 1983):

	CH_3—S—H	H_3C—S—CH_3	CH_3S—S—CH_3
BDE (kcal/mole):	74.2 ± 1 88.6 ± 1	75.0 ± 1	67.8 ± 2 57 ± 1.5

If the broken bonds are C—S in the CH_3SH and CH_3SCH_3 adducts and S—S in the CH_3SSCH_3 adducts, the difference between those bond dissociation energies is small and similar rate constants will be expected. C—S bond scission is indeed expected for the CH_3SH adduct. In order to explain the decomposition of the CH_3SSCH_3 adduct, the small bond dissociation energy of the C—S bond in CH_3SSCH_3 must be explained first. The bond dissociation energy of the C—S bond in CH_3SSCH_3 is about 18 kcal/mole less than that in CH_3SCH_3. This is due to the higher stability of the produced radical, $CH_3S\dot{S}$, because of the partial double or π bond formed in the radical (Benson, 1978; Shum and Benson, 1983). However, if the adduct, $CH_3SS(ONO_2)CH_3$, decomposes by C—S bond scission instead of forming the $CH_3S\dot{S}$ radical, the molecule $CH_3SS—ONO_2$ will be formed, that is

$$\begin{aligned} CH_3S\dot{S}(ONO_2)CH_3 &\rightarrow CH_3SS—ONO_2 + CH_3 \quad \text{S—C bond scission} \\ &\rightarrow CH_3S—ONO_2 + CH_3\dot{S} \quad \text{S—S bond scission} \end{aligned}$$

and the corresponding special stability of $CH_3S\dot{S}$ is no longer involved. Although no thermodynamic data are available for $CH_3SS—ONO_2$ and $CH_3S—ONO_2$, their bond dissociation energies are expected to be in the order

$$BDE(CH_3S—ONO_2) > BDE(CH_3SS—ONO_2)$$

since $BDE(CH_3S—CH_3) > BDE(CH_3SS—CH_3)$, and S—S bond scission in $CH_3SS(ONO_2)CH_3$ is therefore expected to be dominant.

The energy change for reaction pathway (3) is not available at the present, since the bond dissociation energies of C—H and S—H bonds of the *adducts* are unknown. It is expected that the adduct $CH_3S(ONO_2)H$ may undergo intramolecular

H-atom abstraction faster than either $CH_3S(ONO_2)CH_3$ or $CH_3SS(ONO_2)CH_3$ due to its weaker S—H bond. However, other factors including the stability of the formed products and the energy strain between five-, six- and seven-member rings may compensate the favourable BDE for $CH_3S(ONO_2)H$. In summary, the observed trend of rate constants alone cannot distinguish the proposed three possible reaction pathways for the adduct $CH_3S(ONO_2)R'$, since each of them could lead to similar rate constants for $CH_3S(ONO_2)H$, $CH_3S(ONO_2)CH_3$ and $CH_3S(ONO_2)SCH_3$ adducts.

Why the rate constants for NO_3 + RSR′ reactions appear to be determined by the unimolecular decomposition step rather than by the addition step is not evident. One possible explanation is the relatively large size of the NO_3 adduct, which would allow for easy dispersion of this excess energy over the whole radical.

Turning now to IO, only one reaction rate constant has been measured, that for CH_3SCH_3 (Martin *et al.*, 1987; Barnes *et al.*, 1987a). Both studies showed that addition of IO to the S atom is the dominant pathway, followed by unimolecular decomposition through I—O bond cleavage. The trend of the rate constants for the IO radical is expected to be similar to that for $O(^3P)$ radical if the addition of IO to the S atom is the rate-limiting step.

In summary, analysis of observed reaction rate constant trends strongly suggests that addition is the dominant pathway for the initial reactions of $O(^3P)$, OH, NO_3 and IO radicals with organosulfur compounds, which is mainly due to the unsaturated nature of the S atom and the relatively high electron density on the S atom of organosulfur compounds.

2.3. *Unimolecular Decomposition of the Adducts*

Reactants and the corresponding adducts are listed in Table II. The discussion in this section will focus on the elucidation of the dominant adduct decomposition pathways, which depend on the relative strength of the bonds in the adducts and on the stability of the radicals and molecules produced.

The unimolecular decomposition of the $O(^3P)$ + RSR′ adducts is reasonably well understood from the work of Cvetanović *et al.* (1981). The dominant decomposition reaction is C—S bond scission for $CH_3S(O)H$ and $CH_3S(O)CH_3$, and S—S bond scission for $CH_3SS(O)CH_3$, although S—H bond cleavage is also important for $CH_3S(O)H$. No experimental observations are available for the decomposition of all other adducts listed in Table II. Therefore the fate of those adducts is discussed here based mainly on thermodynamic considerations. Indirect experimental evidence will also be examined when available.

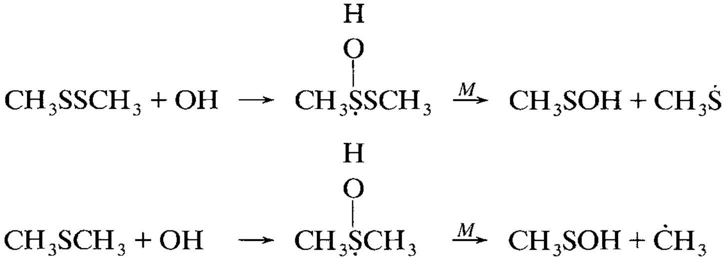
With respect to the adducts produced from the reactions between RSR′ and OH radical, it is generally assumed that the adduct $CH_3S(OH)SCH_3$ undergoes rapid unimolecular decomposition to CH_3SOH and CH_3S (Wine *et al.*, 1981; Hatakeyama and Akimoto, 1983; Atkinson, 1985), although no direct evidence is yet avail-

Table II. Structures of initial reaction adducts

	H_3C-S-H	$H_3C-S-CH_3$	$CH_3-S-S-CH_3$
BDE: (kcal/mole)	74.2 88.6	75.0	67.8 57
	$CH_3-\overset{O}{\overset{\vert}{S}}-H$	$CH_3-\overset{O}{\overset{\vert}{S}}-CH_3$	$CH_3-\overset{O}{\overset{\vert}{S}}-S-CH_3$
	$CH_3-\overset{O-H}{\overset{\vert}{S}}-H$	$CH_3-\overset{O-H}{\overset{\vert}{S}}-CH_3$	$CH_3-\overset{O-H}{\overset{\vert}{S}}-S-CH_3$
	$CH_3-\overset{O-NO_2}{\overset{\vert}{S}}-H$	$CH_3-\overset{O-NO_2}{\overset{\vert}{S}}-CH_3$	$CH_3-\overset{O-NO_2}{\overset{\vert}{S}}-S-CH_3$
	$CH_3-\overset{O-I}{\overset{\vert}{S}}-H$	$CH_3-\overset{O-I}{\overset{\vert}{S}}-CH_3$	$CH_3-\overset{O-I}{\overset{\vert}{S}}-S-CH_3$

Note: The bond dissociation energies of organosulfur compounds are from Benson (1978) and Shum and Benson (1983).

able. The fate of $CH_3S(OH)CH_3$ may be examined by comparison with that of the adduct $CH_3SS(OH)CH_3$:



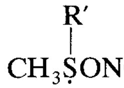
$$CH_3SSCH_3 + OH \longrightarrow CH_3\overset{\overset{H}{O}}{\overset{\vert}{\underset{\cdot}{S}}}SCH_3 \xrightarrow{M} CH_3SOH + CH_3\dot{S}$$

$$CH_3SCH_3 + OH \longrightarrow CH_3\overset{\overset{H}{O}}{\overset{\vert}{\underset{\cdot}{S}}}CH_3 \xrightarrow{M} CH_3SOH + \dot{C}H_3$$

The energy changes of decomposition for above two adducts depend on the bond dissociation energies as well as the stability of the formed radicals. The difference in the formation enthalpy between CH_3S (31.0 kcal/mole) and CH_3 (34.8 kcal/mole) (Shum and Benson, 1983; Baulch *et al.*, 1984) is small, and the bond dissociation energies between S—C and S—S bonds of the *adducts* are not expect to be very large (considering their corresponding reactants and the similar reasoning discussed in Section 2.2.3). Thus, the unimolecular decomposition of $CH_3S(OH)CH_3$ to CH_3SOH and CH_3 is probably not negligible, and may contribute partially to $k_{CH_3SCH_3+OH}$ measured in the *absence* of O_2. Also the mechanism

$$CH_3S(OH)CH_3 + O_2 \longrightarrow CH_3SOH + CH_3O_2$$

proposed by Hynes and Wine (1989) is more likely to proceed first through unimolecular decomposition of $CH_3S(OH)CH_3$ followed by addition of CH_3 to O_2, i.e., same as that in the absence of O_2. The adduct $CH_3S(OH)H$ may mainly undergo unimolecular decomposition to CH_3S and H_2O via intramolecular H-bonding. Given the structural similarity of all four CH_3SH adducts, one may also expect the $O(^3P)$, NO_3 and IO adducts to form intramolecular H-bonding and to decompose further to CH_3S and HO, $HONO_2$ or HOI, respectively, although the ability to form such H-bonding and to abstract an H atom is quite different among those four radicals. In fact, the observed 10% S—H bond cleavage for the $O(^3P) + CH_3SH$ reaction may be explained in terms of such H-bonding formation rather than by direct H-atom abstraction.

As discussed in Section 2.2.3, the $NO_3 + RSR'$ reaction adduct,  $CH_3\overset{\overset{R'}{|}}{S}ONO_2$, may undergo three possible reaction pathways. Since no NO_2 was observed by Tyndall *et al.* (1986) and Dlugokencky and Howard (1988) in the time scale of 100–200 ms, and no $CH_3S(O)CH_3$ was detected in FT–IR product studies (Tyndall *et al.*, 1986; MacLeod *et al.*, 1986), the adduct appears to decompose by pathways other than those involving O—N bond scission. In addition to the reaction between adducts and other species, another possible reaction for the adduct $CH_3S(ONO_2)R'$ is decomposition by breaking S—H, C—S and S—S bonds to produce $R'SONO_2$. It is interesting to note that an unidentified product containing a nitrate group was observed for the $NO_3 + CH_3SCH_3$ reaction (Tyndall *et al.*, 1986) although it may also be formed through secondary reactions. The product, $R'SONO_2$, may be thermally unstable and further decompose to R'SO and NO_2, which is also mentioned by Dlugokencky and Howard (1988) for the HSO—NO_2 adduct. Finally, the adduct $CH_3S(ONO_2)R'$ may undergo intramolecular H-atom abstraction through a five-, six- or seven-member ring, which is more favourable since only $HONO_2$, not NO_2, is formed. The simulation of smog chamber data also supports this pathway as dominant (see Part II, Yin *et al.*, 1990).

The dominant reaction for adduct $CH_3S(OI)CH_3$ is the unimolecular decomposition to $CH_3S(O)CH_3$ by breaking the O—I bond since the yield of $CH_3S(O)CH_3$ was observed to be close to unity for the $IO + CH_3SCH_3$ reaction by Barnes *et al.* (1987a).

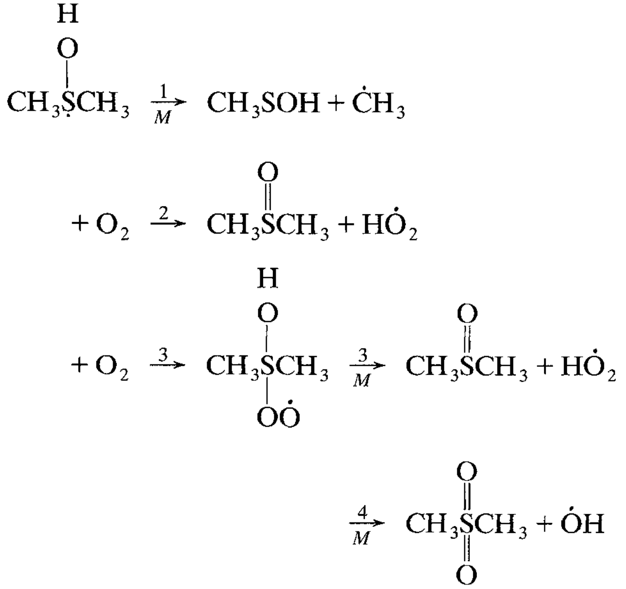
2.4. *Adduct Bimolecular Reactions*

Depending on adducts lifetime and on the time resolution of the experimental techniques used, secondary reactions may contribute to the observed rate constants. Possible adduct bimolecular reactions are discussed in this section along with other secondary reactions and their possible effects on the observed reaction rate constants.

2.4.1. *Adduct Reaction with Oxygen*

Rate constants for the reactions of free radicals with organosulfur compounds have been observed to vary with oxygen concentration. This 'O_2 effect' usually refers to the reaction Adduct + O_2 ⟶ Product.

The 'O_2 effect' has been confirmed experimentally for only one reaction among H_2S, CH_3SH, CH_3SCH_3 and CH_3SSCH_3, that of OH with CH_3SCH_3 (Hynes *et al.*, 1986; Barnes *et al.*, 1988), although it has also been reported in studies of other organosulfur compounds (Barnes *et al.*, 1986a). The following possible reactions have been proposed for the $CH_3S(OH)CH_3$ adduct



$$
\begin{aligned}
CH_3\overset{\overset{\displaystyle H}{O}}{\underset{\cdot}{S}}CH_3 &\xrightarrow[M]{1} CH_3SOH + \dot{C}H_3 \\
+O_2 &\xrightarrow{2} CH_3\overset{O}{\overset{\|}{S}}CH_3 + H\dot{O}_2 \\
+O_2 &\xrightarrow{3} CH_3\overset{\overset{\displaystyle H}{O}}{\underset{O\dot{O}}{S}}CH_3 \xrightarrow[M]{3} CH_3\overset{O}{\overset{\|}{S}}CH_3 + H\dot{O}_2 \\
&\xrightarrow[M]{4} CH_3\overset{O}{\underset{O}{S}}CH_3 + \dot{O}H
\end{aligned}
$$

Note that reaction (1) is not related to 'O_2 effect'. Reaction (3) may proceed by addition to the S atom followed by H-atom abstraction via a five-member intramolecular ring. Although $CH_3S(O)_2CH_3$ has been observed (Barnes *et al.*, 1988), it is not likely to form directly through reaction (4) since it is less likely to be a one-step reaction. The production of $CH_3S(O)_2CH_3$ in the CH_3SCH_3—H_2O_2—air system may result from the further oxidation of $CH_3S(O)CH_3$, which is supported by the fact that $k_{OH+CH_3S(O)CH_3} = 5.8 \pm 2.3 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} and by a preliminary product study of the $CH_3S(O)CH_3 + OH$ reaction in which $CH_3S(O)_2CH_3$ was found to be one of the major products (Barnes *et al.*, 1986b).

No O_2 effect should be observed for the $CH_3S(OH)H$ adduct because of the formation of intramolecular H-bonding, which is consistent with the experimental observation by Hynes and Wine (1987). The reason that no O_2 effect was observed for the $CH_3SS(OH)CH_3$ adduct may be that the *observed* rate constant for the $OH + CH_3SSCH_3$ reaction is already near the collision limit or may be that the adduct decomposition is fast enough that the reaction of adduct with O_2 cannot compete with it.

No data are available for the adducts formed in the reactions of RSR′ with radicals other than OH. An 'O_2 effect' may also exist, depending mainly on the lifetime of the adduct.

2.4.2. *NO_x Effect*

Rate constants of initial reactions for organosulfur compounds have also been found to depend on the NO_x concentration. The observed increase of the rate constant due to NO_x, observed only for OH + RSR′ reactions, is usually associated with conditions of high concentrations of NO_x, RSR′ and O_2, and with long reaction times (Cox and Sheppard, 1980; Atkinson *et al.*, 1984; Barnes *et al.*, 1984, 1986a; Nielsen *et al.*, 1986; Wallington *et al.*, 1986a). More specifically, rate constants for the reactions of OH with CH_3SH, CH_3SCH_3 and $C_2H_5SC_2H_5$ were found to increase with increasing NO concentration (Barnes *et al.*, 1986a; Nielsen *et al.*, 1986). Many secondary reactions may be responsible for this NO_x or NO effect. Of these, the reaction between CH_3SO_3 and RSR′ is probably the most important in view of the high reactivity of the CH_3SO_3 radical

$$\begin{aligned} CH_3SO_3 + RSR' &\longrightarrow CH_3SO_3H + RSR'' \\ &\longrightarrow \text{Adduct} \end{aligned}$$

The detailed mechanism relating NO and CH_3SO_3 will be discussed in Section 7. The adduct $CH_3S(OH)(OO)CH_3$ formed from reaction (3) in Section 2.4.1 may also react with NO. Other species that may contribute to the NO_x effect include $O(^3P)$, CH_3O_x, NO_3, Criegee radicals (when an alkene is used as reference reactant) and CH_3SO_x radicals. Although many of these species will mainly react with O_2 under atmospheric conditions, their reactions with RSR′ may become important at high concentrations of RSR′.

2.4.3. *RS Effect*

The reaction between RS and RSR′ is another possible secondary reaction responsible for the observed rate constant enhancement. However, considering the enthalpy changes of all the possible reactions of CH_3SH, CH_3SCH_3 and CH_3SSCH_3 with CH_3S (Benson, 1978; Baulch *et al.*, 1984; Shum and Benson, 1983, 1985), the reactions between RS and RSR′ are all endothermic (6.9–20.7 kcal/mole) except that of CH_3SSCH_3 with $CH_3S\cdot$ (whose enthalpy change cannot be estimated due to the lack of data on formation enthalpies for CH_3SOH, CH_3SSCH_2 and CH_3SSSCH_3). Compared to the large negative enthalpy change [(−22.6)–(−30.7) kcal/mole] for the OH + CH_3SH and OH + CH_3SCH_3 reactions, the reactions between CH_3S and CH_3SH or CH_3SCH_3 are expected to be negligible under both laboratory and atmospheric conditions, especially considering the competition between CH_3S + RSR′ and OH + RSR′ and between CH_3S + RSR′ and CH_3S + NO_x. The effect of secondary reactions due to the $CH_3S\cdot$ radical has been found to be negligible for CH_3SCH_3 by Nielsen *et al.* (1986), who observed no additional loss of CH_3SCH_3 when photolyzing CH_3SSCH_3 in the presence of CH_3SCH_3 in either N_2 or air.

While the reaction between RS and RSR′ is negligible, the RS radical will have an effect on the observed rate constants when an alkene is used as a reference reactant. This is due to the addition of RS to the alkene double bond, a reaction well-documented in the liquid phase. An alkene has been used as reference reactant in both OH and NO_3 kinetic measurements by the relative rate method (Cox and Sheppard, 1980; Atkinson *et al.*, 1984, 1988; Barnes *et al.*, 1984, 1986a, 1988; MacLeod *et al.*, 1986; Nielsen *et al.*, 1986) and in product studies (Hatakeyama and Akimoto, 1983). The following mechanism is proposed to explain the possible effect of the RS radical in these studies (NO_3 radical and $CH_2 = CH_2$ are used as examples).

$$\begin{array}{llll}
NO_3 + RSR' & \longrightarrow & \text{Adduct} & k_1 \\
\quad + CH_2 = CH_2 & \longrightarrow & \text{Product} & k_2 \\
CH_3S + CH_2 = CH_2 & \longrightarrow & CH_3SCH_2\dot{C}H_2 & k_3 \\
\quad + NO_2 & \longrightarrow & CH_3SO + NO & k_4 \\
\quad + NO & \longrightarrow & CH_3SNO & k_5
\end{array}$$

Since studies involving the NO_3 radical are carried out in the dark, the photolysis of CH_3SNO is negligible. Usually the equation used to analyse the experimental data obtained by a relative rate technique is expressed as

$$\ln \frac{[RSR']_0}{[RSR']} = \frac{k_1'}{k_2} \ln \frac{[C_2H_4]_0}{[C_2H_4]}, \tag{a}$$

where k_1' is the observed rate constant without considering reaction (3). If reaction (3) is included,

$$\ln \frac{[RSR']_0}{[RSR']} = \frac{k_1}{k_2} \left(\ln \frac{[C_2H_4]_0}{[C_2H_4]} - C \right), \tag{b}$$

where k_1 is the rate constant when reaction (3) is considered, and

$$C = \int_{[RSR']}^{[RSR']_0} \frac{d[RSR']}{k_3[C_2H_4] + k_4[NO_2] + k_5[NO]} > 0.$$

Dividing Equation (a) by Equation (b),

$$\frac{k_1'}{k_1} = \frac{\ln[C_2H_4]_0/[C_2H_4] - C}{\ln[C_2H_4]_0/[C_2H_4]} < 1,$$

i.e., the observed rate constant k_1' is smaller than the actual rate constant k_1 if reaction (3) is important compared to reaction (2). The following conditions need to be satisfied in order for reaction (3) to be important:

(1) CH_3S (or RS) radical has to be generated. For the reactions between OH

and RSR′, the CH_3S radical is generated from CH_3SH, CH_3SCH_3 and CH_3SSCH_3. For reactions of NO_3 with RSR′, CH_3S may be generated only from CH_3SSCH_3.

(2) k_2/k_3 is close to one, or smaller than one. Since $k_{OH+RSR'}$ is much larger than $k_{NO_3+RSR'}$, the effect of the CH_3S radical on observed rate constants will be much larger for the NO_3 + RSR′ reactions than for the OH + RSR′ reactions.

(3) $[Alkene]/[NO_x]$ is close to one, or larger than one, which is usually the case at the beginning of the experiment.

Based on the above considerations, the $NO_3 + CH_3SSCH_3$ reaction is the most likely candidate to exhibit a CH_3S effect, in agreement with the observation of MacLeod *et al.* (1986) and Akinson *et al.* (1988). MacLeod *et al.* (1986) measured the rate constants of the $CH_3SH + NO_3$ and $CH_3SSCH_3 + NO_3$ reactions, and obtained a much smaller $k_{NO_3+CH_3SSCH_3}$ than those measured by an absolute method (Wallington *et al.* 1986c; Dlugokencky and Howard, 1988), however the rate constant of $k_{NO_3+CH_3SH}$ agrees reasonably well with other measurements (Wallington *et al.*, 1986c; Rahman *et al.*, 1988; Dlugokencky and Howard, 1988). Another study showed that the observed rate constant for the $NO_3 + CH_3SSCH_3$ reaction increased in the later stages of the reaction (Atkinson *et al.*, 1988), indicating that the competitive reaction of CH_3S + alkene, i.e., reaction (3), was important in the early stage of the experiment. The alkenes used in these experimental studies were propene and trans-2-butene. The rate constants listed below for the CH_3S + alkene reactions are compared to those for the NO_3 + alkene reactions (MacLeod *et al.*, 1986; Graham *et al.*, 1964a; Atkinson, 1985; Balla *et al.*, 1987):

		k_{298} (cm^3 molecule^{-1} s^{-1})
$CH_3CH=CH_2 + NO_3$	→ Product	7.6×10^{-15}
$+ OH$	→ Product	2.63×10^{-11}
$+ CH_3S$	→ Adduct	$1.0 \pm 0.4 \times 10^{-14}$
trans-2-butene + NO_3	→ Product	3.8×10^{-13}
$+ OH$	→ Product	6.37×10^{-11}
2-butene + CH_3S	→ $CH_3CH(CH_3S)CHCH_3$	3.32×10^{-14}
cis-2-butene + CH_3S	→ Adduct	$<5.5 \times 10^{-15}$.

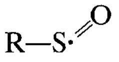
Therefore, the effect of the CH_3S radical on the measured $CH_3SSCH_3 + NO_3$ rate constant cannot be neglected. The competition between reactions of OH and CH_3S with alkenes is dominated by the OH radical since the OH rate constants are much larger than those for CH_3S. Finally, the addition of the CH_3SO_2 radical to alkene double bonds, similar to the addition of the CH_3S radical, may also have similar effects on the observed rate constants.

3. Structure of RSO_x and $RS(O)_xOO$ Radicals

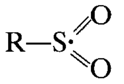
The sulfinyl radical, RSO, sulfonyl radical, RSO_2, sulfur peroxyl radicals, $RS(O)_x$—OO, and possibly several other oxygen-containing sulfur radicals are involved as intermediates in the photooxidation of organosulfur compounds. In order to better understand the reactions of these species, it is necessary to discuss the structures of the following radicals and to estimate their reactivity from the corresponding structural properties:

$R-S$

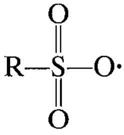
(I)



(II)



(III)

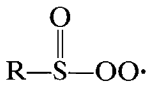


$R-\overset{O}{\overset{\|}{\underset{\underset{O}{\|}}{S}}}-O\cdot$

(IV)

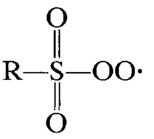
$R-S-OO\cdot$

(V)



$R-\overset{O}{\overset{\|}{S}}-OO\cdot$

(VI)



$R-\overset{O}{\overset{\|}{\underset{\underset{O}{\|}}{S}}}-OO\cdot$

(VII)

Sulfinyl radicals, RSO (II), are formal analogues of peroxyl (ROO) and perthiyl (RSS) radicals. The π nature of the RSO radical results in enhanced stability relative to that of either the thiyl RS (I) or sulfonyl RSO_2 (III) radicals. This is reflected in the corresponding bond dissociation energies, i.e., $BDE(CH_3S(O)—CH_3) = 55 \pm 2$ kcal/mole is about 13–20 kcal/mole lower than $BDE(CH_3S—CH_3) = 75.0 \pm 1$ kcal/mole and $BDE(CH_3S(O)_2—CH_3) = 68$ kcal/mole (Benson, 1978; Shum and Benson, 1983).

Considering the sulfur peroxyl radicals, some confusion has been caused by the radical representation. The methanethiyl peroxyl radical, the adduct of methanethiyl radical (CH_3S) to molecular oxygen, should be represented as CH_3SOO rather than CH_3SO_2, which is the methanesulfonyl radical (III). Evidence for the thiol peroxyl radical (RSOO) has been recently observed by electron spin resonance in the liquid phase (Swarts *et al.*, 1989). Likewise, the adducts of O_2 to CH_3SO and CH_3SO_2 should be represented as $CH_3S(O)OO$ and $CH_3S(O)_2OO$, respectively. This distinction between sulfur and sulfur peroxy radicals is very important since these radicals have quite different chemical properties. The enthalpy change for the reaction $CH_3S + O_2$, which was incorrectly based on the formation enthalpy of the CH_3SO_2 radical (Hatakeyama and Akimoto, 1983), is about −89 kcal/mole. However, the *correct* enthalpy change for this reaction is in fact much less than −89 kcal/mole since CH_3SOO is much less stable than CH_3SO_2. This downward revision is entirely consistent with experimental observations of a very slow reaction between CH_3S and O_2 (Balla *et al.*, 1986; Tyndall and Ravishankara, 1988).

4. Reactions of CH_3SOH and $CH_3S(O)_xCH_3$

Although CH_3SOH, $CH_3S(O)CH_3$ and $CH_3S(O)_2CH_3$ are proposed to be the addition pathway products of the $OH + RSR'$ reaction, only $CH_3S(O)_2CH_3$ has been observed experimentally (Barnes *et al.*, 1988). $CH_3S(O)CH_3$ and $CH_3S(O)_2CH_3$ have been detected in marine air and rain water (Harvey and Lang, 1986), suggesting that both are possible oxidation products of CH_3SCH_3. Only one kinetic study has been carried out for the reaction of $OH + CH_3S(O)CH_3$ (Barnes *et al.*, 1986b) and no kinetic data are available for CH_3SOH and $CH_3S(O)_2CH_3$. Therefore, the following discussion is based mainly on thermochemistry and on comparison of reactivity in the gas phase and liquid phase.

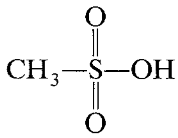
4.1. *Reactions of CH_3SOH*

Methanesulfenic acid, CH_3SOH, has not been directly detected but is believed to form by unimolecular decomposition of the adducts of $CH_3S(OH)CH_3$ and $CH_3SS(OH)CH_3$. It was proposed first by Hatakeyama and Akimoto (1983) that CH_3SOH reacts with O_2 to form CH_3SO_3H

$$CH_3SOH + O_2 \xrightarrow{M} CH_3SO_3H.$$

However, this one-step reaction is not consistent with the structural difference between CH_3SOH and CH_3SO_3H

$CH_3—S—OH$

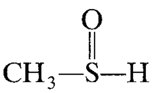


$$CH_3—\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}—OH$$

The structure of CH_3SOH has been confirmed by microwave spectroscopy to have form (A) rather than form (B) [Penn *et al.*, 1978],

$CH_3—S—O—H$

(A)



$$CH_3—\overset{\overset{\displaystyle O}{\|}}{S}—H$$

(B)

By further examining the possibility of the reactions between CH_3SOH and O_2, it is concluded that O_2 cannot abstract a hydrogen from CH_3SOH to produce two radicals from two molecules since the H—OO bond is about 10[★] kcal/mole weaker than the $CH_3SO—H$ bond (see discussion later). Also the addition of O_2 to the S atom on CH_3SOH will not be important since the similar reactions between O_2 and CH_3SCH_3 should be faster because of the electrophilic nature of O_2.

[★] Since the BDE($CH_3SO—H$) is estimated from the BDE(HOSO—H), the absolute value is less accurate than the relative trend. The importance of the $O_2 + CH_3SOH$ reaction will be determined by the relative strength of $CH_3SO—H$ and OO—H bonds, which is unknown at this time.

However, due to the extremely large O_2/radicals concentration ratio in the atmosphere, the reaction between O_2 and CH_3SOH cannot be ruled out completely, although it is clear that CH_3SO_3H cannot be formed directly from $CH_3SOH + O_2$.

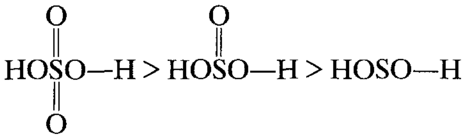
Although the importance of sulfenic acid (RSOH) intermediate in mechanistic organic sulfur chemistry is well recognized, simple alkanesulfenic acids are extremely reactive and unstable and only a few of them have been isolated and detected (Davis *et al.*, 1981). Sulfenic acids readily undergo hydrogen atom transfer to free radicals and they have been found to be active radical scavengers for peroxy radicals (Koelewijn and Berger, 1972), indicating that the bond dissociation energy of the RSO—H bond is less than that of the ROO—H bond, about 87 kcal/mole. The efficiency of sulfenic acids as hydrogen atom donors is undoubtedly a consequence of the appreciable stability of the sulfinyl radical, RSO, due to its delocalized π-structure.

In the liquid phase, both sulfenic acids and sulfinic acids undergo facile H-atom abstraction by either alkoxy or OH radicals (Gilbert *et al.*, 1975b; Block, 1978; Lunazzi and Pedulli, 1985). Based on these experimental studies in the liquid phase, we propose that H-atom abstraction is also a dominant atmospheric reaction pathway for both CH_3SOH and CH_3SO_2H (a possible product of the $CH_3S(O)CH_3 + OH$ reaction). Thus, possible H-atom abstraction reactions for CH_3SOH and the bond dissociation energies of the corresponding formed H—X bonds are listed below:

			BDE (kcal/mole)
$CH_3SOH + OH$	→	$CH_3SO + H_2O$	119
$+ CH_3SO_3$	→	$CH_3SO + CH_3SO_3H$	(104)
$+ CH_3O$	→	$CH_3SO + CH_3OH$	104.4
$+ O(^3P)$	→	$CH_3SO + OH$	102.2
$+ NO_3$	→	$CH_3SO + HONO_2$	101.2
$+ CH_3O_2$	→	$CH_3SO + CH_3OOH$	87.2
$+ HO_2$	→	$CH_3SO + H_2O_2$	87.2
$+ NO_2$	→	$CH_3SO + HONO$	78.3

(Benson, 1978; McMillen and Golden, 1982; Baulch *et al.*, 1984; Kerr, 1985). Of the reactions listed above, those with OH and CH_3SO_3 radicals, and with peroxy radicals at low NO_x concentration are important. These reactions may in fact be quite fast, since the bond dissociation energy of $CH_3SO—H$ is expected to be much less than 87 kcal/mole.

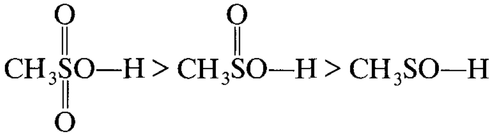
Although no data are available for the BDE of O—H bond in $CH_3S(O)_xO—H$ compounds, some estimates can be obtained from the structurally similar species $HOS(O)_xO—H$ (Benson, 1978):



$$\mathrm{HO}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\overset{\|}{\underset{\|}{\mathrm{S}}}}}\mathrm{O{-}H} > \mathrm{HO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}\mathrm{O{-}H} > \mathrm{HOSO{-}H}$$

BDE (kcal/mole): 104 ± 3 81 59

Therefore, a similar bond strength trend can be expected for $CH_3S(O)_xO{-}H$ acids, i.e.,



$$\mathrm{CH_3}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\overset{\|}{\underset{\|}{\mathrm{S}}}}}\mathrm{O{-}H} > \mathrm{CH_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}\mathrm{O{-}H} > \mathrm{CH_3SO{-}H}$$

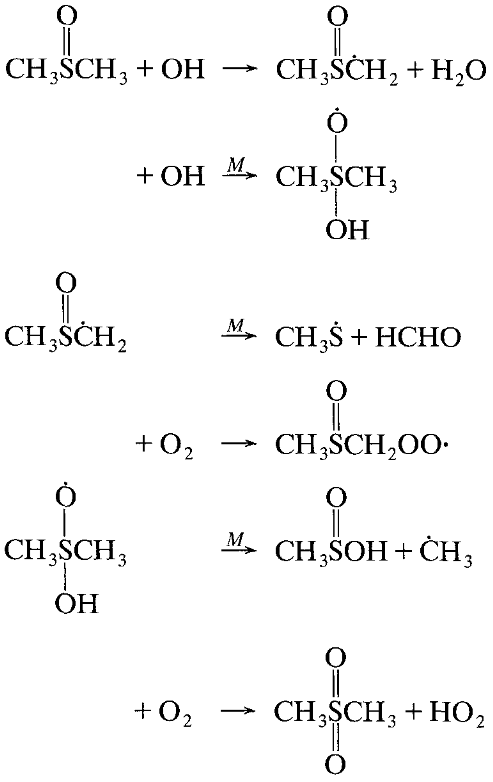
and the effect of CH_3 and OH groups on the bond dissociation energy is expected to be small compared to that of the group $S(O)_x$, since the bond dissociation energy of $HOS(O)_x{-}H$ species varies about 44 kcal/mole from HOSO—H to $HOS(O)_2O{-}H$, although an OH group is attached to each of $HOS(O)_x{-}H$. As a starting point, the bond dissociation energy of $CH_3S(O)_x{-}H$ can be assumed to be the same as that for the corresponding acids of $HOS(O)_x{-}H$. This would assign 59 kcal/mole to the $CH_3SO{-}H$ bond, a value consistent with our earlier estimate, i.e., much less than 87 kcal/mole. Since the bond dissociation energy of $CH_3S(O)O{-}H$ is higher than that of $CH_3SO{-}H$, the H-atom abstraction from $CH_3S(O)OH$ is expected to be correspondingly slower. However, the O—H bond in $CH_3S(O)_2OH$ is much stronger than those in $CH_3S(O)OH$ and CH_3SOH; thus these compounds are expected to react rapidly with CH_3SO_3 by H-atom abstraction.

It should be pointed out that the electrophilic addition of radicals such as OH and NO_3 to the S atom in CH_3SOH, although it is minor, may not be negligible since the adduct of OH + CH_3SOH is stabilized by the resonance effect of OH in CH_3SOH, although the weak electron-withdrawing resulting from OH inductive effect could decrease the tendency of OH addition to CH_3SOH.

4.2. *Reaction of* $CH_3S(O)_xCH_3$

While $CH_3S(O)CH_3$ was not observed as a product by Barnes *et al.* (1988), they suggested that $CH_3S(O)CH_3$ was likely to be produced and further oxidized rapidly to $CH_3S(O)_2CH_3$ and SO_2. The rate constant for OH + $CH_3S(O)CH_3$ has been measured to be $(5.8 \pm 2.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} and $(6.2 \pm 2.2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (Barnes *et al.*, 1986b, 1989), with SO_2 and $CH_3S(O)_2CH_3$ yields of 60% and 30%, respectively (Barnes *et al.*, 1988). The formation of SO_2 indicates that the addition pathway is not necessarily related only to the formation of CH_3SO_3H, but could also lead to the production of SO_2 as well. The same reaction has been studied by Meissner *et al.* (1967) in aqueous solutions of sulfoxides and a similar reaction rate constant of 1.2×10^{-11} cm^3 molecule^{-1} s^{-1} has been reported (Gilbert *et al.*, 1975a).

While $CH_3S(O)CH_3$ and $CH_3S(O)_2CH_3$ may react with a number of radicals in the atmosphere, their reaction with OH is likely to be the most important chemical loss process, and their reactions with NO_3 could also be important at nighttime in the atmosphere. The reaction of $CH_3S(O)CH_3$ with OH may involve abstraction or addition as follows:



$$
\begin{aligned}
CH_3\overset{\overset{O}{\|}}{S}CH_3 + OH &\longrightarrow CH_3\overset{\overset{O}{\|}}{S}\dot{C}H_2 + H_2O \\
+ OH &\xrightarrow{M} CH_3\underset{\underset{OH}{|}}{\overset{\overset{\dot{O}}{|}}{S}}CH_3 \\
CH_3\overset{\overset{O}{\|}}{S}\dot{C}H_2 &\xrightarrow{M} CH_3\dot{S} + HCHO \\
+ O_2 &\longrightarrow CH_3\overset{\overset{O}{\|}}{S}CH_2OO\cdot \\
CH_3\underset{\underset{OH}{|}}{\overset{\overset{\dot{O}}{|}}{S}}CH_3 &\xrightarrow{M} CH_3\overset{\overset{O}{\|}}{S}OH + \dot{C}H_3 \\
+ O_2 &\longrightarrow CH_3\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}CH_3 + HO_2
\end{aligned}
$$

In turn, methanesulfinic acid, $CH_3S(O)OH$, may be further oxidized to SO_2 or CH_3SO_3H. Although no information is available regarding the relative importance of addition and abstraction pathways for the $OH + CH_3S(O)CH_3$ reaction, some indication can be obtained from studies in the liquid phase. For H-atom abstraction by the phenyl radical, the relative reactivity per H-atom is (Block, 1978):

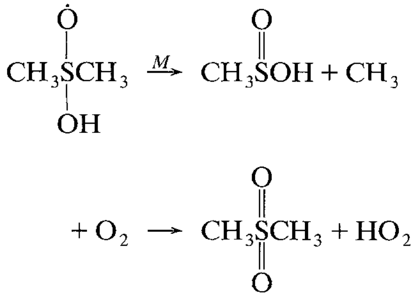
$$
\begin{array}{ccccc}
CH_3SCH_2\text{—}H & > & CH_3SSCH_2\text{—}H & > & CH_3S(O)CH_2\text{—}H \\
1.89 & & 1.2 & & 0.08
\end{array}
$$

This indicates that the bond dissociation energy of $CH_3S(O)CH_2$—H is much higher than that of CH_3SCH_2—H of 96.6 ± 1.0 kcal/mole (Shum and Benson, 1985), but lower than that of Ph—H of 110.9 ± 2 kcal/mole (McMillen and Golden, 1982). This is also true for $CH_3S(O)_2CH_3$, since the reaction

$$CH_3S(O)_2CH_3 + C_6H_5 \longrightarrow CH_3S(O)_2CH_2 + C_6H_6$$

takes place readily in the liquid phase. Thus, H-atom abstraction by OH is expected to be much slower for $CH_3S(O)CH_3$ and $CH_3S(O)_2CH_3$ than for CH_3SCH_3. Since the observed rate constant of $CH_3S(O)CH_3$ with OH is about a factor of 10 higher than that of CH_3SCH_3 + OH, addition is therefore expected to be the major pathway for $CH_3S(O)CH_3$ + OH.

Studies by Norman and Pritchett (1965) and Lagercrantz and Forshult (1969) indicate that the reaction of OH with dialkyl sulfoxides involves addition onto the sulfur atom rather than H-atom abstraction. Gilbert *et al.* (1975a) studied the reaction of OH with $CH_3S(O)CH_3$ in aqueous solution at ambient temperature and found that the addition of OH to $CH_3S(O)CH_3$, followed by rapid decomposition of the adduct $CH_3S(O\cdot)(OH)CH_3$ is the dominant pathway. The adduct, $CH_3S(O\cdot)(OH)CH_3$, once formed, may either react with O_2 to produce $CH_3S(O)_2CH_3$ or undergo unimolecular decomposition to $CH_3S(O)OH$:



$$CH_3\overset{\dot{O}}{\underset{OH}{S}}CH_3 \xrightarrow{M} CH_3\overset{O}{\overset{\|}{S}}OH + CH_3$$

$$+ O_2 \longrightarrow CH_3\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}CH_3 + HO_2$$

The above decomposition may be faster than that of the adduct $CH_3S(OH)CH_3$ since $BDE(CH_3S(O){-}CH_3) = 55 \pm 2$ is much smaller than $BDE(CH_3S{-}CH_3) = 75.0 \pm 1$ (Benson, 1978; Shum and Benson, 1983). This may be one of the reasons that $k_{CH_3S(O)CH_3 + OH}$ is about a factor of 10 higher than $k_{CH_3SCH_3 + OH}$. The rate constant of decomposition of the adduct, $CH_3S(\dot{O})(OH)CH_3$, is 1.5×10^7 s^{-1} (Veltwisch *et al.*, 1980) in aqueous solution. Thus, if the aqueous phase rate constant is used as a guide for estimating gas phase reactivity, the rate constant for $O_2 + CH_3S(\dot{O})(OH)CH_3$ would need to be about 3×10^{-12} cm^3 $molecule^{-1}$ s^{-1} to be competitive with the unimolecular decomposition of adduct $CH_3S(\dot{O})(OH)CH_3$ to form $CH_3S(O)_2CH_3$ in the atmosphere.

The hypothesis of addition being the dominant pathway for the $OH + CH_3S(O)CH_3$ reaction is consistent with the fact that $CH_3S(O)_2CH_3$ was observed as one of the major product only when O_2 was present for CH_3SCH_3 + OH reaction (Barnes *et al.*, 1988). The independence of the rate constant for the reaction of $CH_3S(O)CH_3$ with OH on O_2 concentration, observed by Barnes *et al.* (1986b), indicates that the reverse reaction of the adduct $CH_3S(O)(OH)CH_3$ is much slower than its decomposition to $CH_3S(O)OH + CH_3$. Notice that the observation of SO_2 as the major product for the $CH_3S(O)CH_3$ + OH reaction does not necessarily support the abstraction pathway since addition can also lead to SO_2 formation. The high yield of $CH_3S(O)_2CH_3$ observed by Barnes *et al.* (1988) indicates that $CH_3S(O)_2CH_3$ is relatively unreactive toward OH. This is not unexpected, since (a) the S atom in $CH_3S(O)_2CH_3$ is hexavalent and no further addition of OH to S is possible, and (b) H-atom abstraction is expected to be slow as a result of the polar effects of the $CH_3S(O)_2$ group.

The rate constant for $NO_3 + CH_3S(O)CH_3$ has been measured to be $(1.7 \pm 0.3) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} (Barnes *et al.*, 1989), and $CH_3S(O)_2CH_3$ and $HONO_2$ were observed from a preliminary product study on system $CH_3S(O)CH_3$—N_2O_5—air in the dark. Elucidation of the $CH_3S(O)CH_3 + NO_3$ reaction is not possible at present, and further experimental studies are needed.

The above discussion indicates that CH_3SOH does not necessarily lead to the formation of CH_3SO_3H, and that both SO_2 and CH_3SO_3H can be produced by further oxidation of CH_3SOH and $CH_3S(O)_xCH_3$. Thus, there is no direct relation between the yields of SO_2 and CH_3SO_3H and the relative importance of OH addition and abstraction pathways.

5. Reactions of RSO_x Radicals

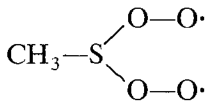
CH_3SO_x and $CH_3S(O)_xOO$ radicals have not been detected in product studies. Only indirect evidence suggests their existence. That of CH_3S is suggested by the observation of CH_3SNO (Niki *et al.*, 1983b; Hatakeyama and Akimoto, 1983; MacLeod *et al.*, 1986; Barnes *et al.*, 1987b). The tentative identification of $CH_3S(O)OO$—NO_2 by Barnes *et al.* (1987b) suggests that CH_3SO and $CH_3S(O)OO$ radicals are involved as well. The recent study of the $CH_3S + NO_2$ reaction by Tyndall and Ravishankara (1988) suggests the formation of both CH_3SO and CH_3SO_2 radicals. In the present sections, possible reactions of CH_3SO_x radicals are discussed, with focus on their further oxidation and unimolecular decomposition.

5.1. *Reactions of RSO_x Radicals with O_2*

The addition of molecular oxygen to CH_3S is arguably the most important reaction for CH_3S in the atmosphere. It is also the least characterized reaction of the CH_3S radical. Balla and Heicklen (1985) studied the photolysis of CH_3SSCH_3 in the presence of O_2 and proposed the following mechanism to explain the formation of SO_2,

$$\begin{aligned} CH_3S + O_2 &\rightarrow CH_3SOO \\ CH_3SOO + O_2 &\rightarrow CH_3SO_4 \\ CH_3SO_4 &\rightarrow HO + HCHO + SO_2 \end{aligned}$$

with the structure of the CH_3SO_4 radical given as



This structure is not correct, i.e., there should be another single unpaired electron (plus a pair of lone electrons) on the S atom. The CH_3SO_4 radical structure proposed by Balla and Heicklen would therefore include three single unpaired electrons, which is very unlikely. The structurally correct adduct of O_2 to CH_3SOO should be $CH_3SOO—OO$, which is very unstable and thermodynamically unfavorable. Furthermore, Tyndall and Ravishankara (1988) did not detect OH as a product in the reaction of CH_3S with O_2, thus suggesting that SO_2 is not produced from the CH_3SO_4 radical.

The rate constant of the $CH_3S + O_2$ reaction has been measured, and only upper limits have been determined. These range from 2×10^{-17} to 2.5×10^{-18} cm^3 $molecule^{-1}$ s^{-1} (Balla *et al.*, 1986; Tyndall and Ravishankara, 1988). Considering $k_{CH_3 + O_2} = 1.0 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, and the strong electrophilic character of O_2, the reaction of CH_3S with O_2 seems unexpectedly slow. Before we attempt to explain this result, let us consider in more detail the bonding between S and O atoms in CH_3SOO. The isoelectronics of CH_3SOO are CH_3OOO and CH_3SSS, with estimated BDE of -22 to -11.8 kcal/mole for the $CH_3O—OO$ bond and $+41$ kcal/mole for the $CH_3S—SS$ bond (Benson and Shaw, 1970; Francisco and Williams, 1988; Benson, 1978). It can be seen that the adduct CH_3OOO is unstable and decomposes rapidly to CH_3O and O_2, which may be consistent with observation of the fast reaction between CH_3 and O_3 (Paltenghi *et al.*, 1984) since this reaction may also involve the adduct CH_3OOO. The relatively strong bond of $CH_3S—SS$ may reflect more resonance structures. Therefore the S—O bond in CH_3SOO is expected to be weak and the lifetime of the $CH_3S + O_2$ adduct will correspondingly be short. Based on these considerations, we suggest the following mechanism for the reaction between CH_3S and O_2:

$$\begin{aligned} CH_3S + O_2 &\longrightarrow CH_3SOO \\ CH_3SOO &\xrightarrow{M} CH_3S + O_2 \\ &\xrightarrow{M} CH_3SO_2 \\ + CH_3S &\longrightarrow CH_3SO + CH_3SO \\ + NO &\longrightarrow CH_3SO + NO_2 \end{aligned}$$

Further reactions of CH_3SO produce SO_2 and CH_3SO_3H. In the above scheme, the addition of O_2 to CH_3S is fast (with a rate constant about one order of magnitude smaller than that for the $CH_3 + O_2$ reaction), but the unstable adduct CH_3SOO, either rapidly decomposes back to CH_3S and O_2 or oxidizes reduced species in the system including CH_3S (or NO when NO_x is used). The rearrangement from CH_3SOO to CH_3SO_2 is slower than all other reactions.

The above mechanism is speculative, but is consistent with many experimental observations. For example, the apparent slow reaction observed by Balla *et al.* (1986) and Tyndall and Ravishankara (1988) is consistent with fast decomposition of the adduct back to the reactants. The observed decay of CH_3S is the net effect of adduct decomposition and adduct reactions with other species. Our mechanism also predicts that the observed reaction rate should *increase* with *increasing* concentrations of species consuming the adduct and/or with any factor that stabilize the adduct, i.e., that decreases its rate of reverse decomposition. Balla and Heicklen (1985) reported increasing SO_2 yields with increasing light intensity, which is inconsistent with their mechanism. The observed SO_2 yield increase may be simply due to the increased steady-state concentration of CH_3S. Black *et al.* (1988b) studied the reaction between C_2H_5S and O_2 by laser induced fluorescence and estimated an upper limit of 2×10^{-17} cm^3 molecule^{-1} s^{-1} for the rate constant. In contrast, the liquid phase rate constant for this reaction is 5.6×10^{-13} cm^3 molecule^{-1} sec^{-1} (Schäfer *et al.*, 1978), which is comparable to the rate constant for addition of O_2 to C_2H_5, 1.0×10^{-12} cm^3 molecule^{-1} s^{-1} (Atkinson and Lloyd, 1984). The observed high rate constant in solution may reflect solvent stabilization of the adduct and/or rapid removal by other species, in this case, possibly by C_2H_5SH as follows,

$$C_2H_5SOO + C_2H_5SH \longrightarrow C_2H_5SOOH + C_2H_5S.$$

The large rate constants for the i-$C_3H_7S + O_2$ reaction (1.1×10^{-14} cm^3 molecule^{-1} s^{-1}, (Black *et al.*, 1988a)) and the $C_6H_5S + O_2$ reaction (2.52×10^{-12} cm^3 molecule^{-1} s^{-1}, (Shibuya *et al.*, 1988)) are also consistent with stabilization of the RSOO adduct by the substituted groups, although abstraction may also be involved in the i-$C_3H_7S + O_2$ reaction.

The attachment of electron-withdrawing groups to the adduct S atom stabilizes the adduct and increases its lifetime. The tentative identification of $CH_3S(O)OO$—NO_2 in the CH_3SSCH_3—NO_2—air system (Barnes *et al.*, 1987b) suggests a reasonably long lifetime for the $CH_3S(O)OO$ radical. Interestingly, the same set of IR peaks assigned to $CH_3S(O)OONO_2$ by Barnes *et al.* (1987b) was also detected by MacLeod *et al.* (1986) in mixtures of both CH_3SSCH_3—N_2O_5—NO_2—air and CH_3SH—N_2O_5—NO_2—air, indicating $CH_3S(O)OO$—NO_2 may also be involved. The adduct $CH_3S(O)_2OO$ should be even more stable, and the *apparent* addition of O_2 to CH_3SO_2 should be faster. A bond strength of about 16 kcal/mole can be estimated for the $CH_3S(O)_2$—OO bond by comparison with the similar bond in $HOS(O)_2$—OO (BDE($HOS(O)_2$—OO = 16 kcal/mole (Benson, 1978)), which is stronger than the S—O bond in CH_3SOO radical. The reaction mechanisms for CH_3SO and CH_3SO_2 radicals with O_2 are similar to the mechanism for CH_3S with O_2 as discussed above.

CH_3SOO may also rearrange to form the CH_3SO_2 radical. However, this rearrangement is expected to be unimportant. No decay of CH_3S was observed by Tyndall and Ravishankara (1988) in the CH_3SSCH_3—O_2 system on the time scale of milliseconds. This intramolecular rearrangement, proceeding by a three-member ring, should be hindered by ring string and by the large lone-pair repulsion involving six lone-pairs of electrons in the CH_3SOO radical. Another point that argues against such intramolecular conversion is that similar rearrangement from $CH_3S(O)OO$ to $CH_3S(O)_2O$ is expected to be faster due to the effect of electron-withdrawing by attached oxygen on sulfur in $CH_3S(O)OO$ radical, and CH_3SO_3H is predicted to be the major product from reactions $CH_3SO_x + O_2$, which is contrary to the experimental results (Hatakeyama and Akimoto, 1983; Yin *et al.*, 1990).

5.2. *Reaction of RSO_x Radicals*

CH_3SO_x radicals can be readily oxidized in the atmosphere,

$$CH_3S + O\text{—}Y \longrightarrow [CH_3SO\text{—}Y]^* \longrightarrow CH_3SO + Y$$
$$CH_3SO + O\text{—}Y \longrightarrow [CH_3S(O)O\text{—}Y]^* \longrightarrow CH_3SO_2 + Y$$
$$CH_3SO_2 + O\text{—}Y \longrightarrow [CH_3S(O)_2O\text{—}Y]^* \longrightarrow CH_3SO_3 + Y$$

and undergo direct or intramolecular (via six-member ring) H-atom abstraction

$$CH_3S + O\text{—}Y \longrightarrow [CH_3SO\text{—}Y]^* \longrightarrow CH_2S + H\text{—}OY$$
$$CH_3SO + O\text{—}Y \longrightarrow [CH_3SOO\text{—}Y]^* \longrightarrow CH_2SO + H\text{—}OY$$
$$CH_3SO_2 + O\text{—}Y \longrightarrow [CH_3S(O)_2O\text{—}Y]^* \longrightarrow CH_2SO_2 + H\text{—}OY$$

(H—OY will be HO + Y for O_3) or regenerate CH_3S and CH_3SO. (Notice that the resonance structures of $CH_3\dot{S}O$ and $CH_3\dot{S}O_2$ are $CH_3S\dot{O}$ and $CH_3S(O)\dot{O}$):

$$CH_3SO\cdot + O\text{—}Y \longrightarrow [CH_3SOO\text{—}Y]^* \longrightarrow CH_3S + O_2 + Y$$
$$CH_3S(O)O\cdot + O\text{—}Y \longrightarrow [CH_3S(O)OO\text{—}Y]^* \longrightarrow CH_3SO + O_2 + Y,$$

where Y includes NO for ONO, NO_2 for ONO_2, OH for HOO, CH_3O for CH_3OO, O_2 for O_3, and $CH_3S(O)_xO$ for $CH_3S(O)_xOO$, respectively. The relative importance of these oxidative species will depend on their ambient concentrations.

Several experimental studies have recently become available regarding the reactions of CH_3SO_x radicals. Tyndall and Ravishankara (1988) identified NO as the major product of the $CH_3S + NO_2$ reaction, with a yield of 0.80 ± 0.20. They also observed a secondary production of NO and suggested that the CH_3SO radical formed could be oxidized further to CH_3SO_2 by NO_2. The CH_3SO radical was indeed detected in another study of the $CH_3S + NO_2$ reaction by mass spectrometry (Mellouki *et al.*, 1988). Regarding the reactions of CH_3S with O_3, Domine *et al.* (1989) have identified CH_3SO as one of the products with a yield of (0.156 ± 0.04). Also CH_2SO and OH were detected in the CH_3S/O_3 system, possibly via H-atom abstraction as shown above. Their preliminary data also indicated that CH_3SO reacts with O_3 to regenerate CH_3S with a yield of about 0.22. Furthermore, both our experimental observations and computer simulation for CH_3SSCH_3 photooxidation (see detailed discussion in Part II) indicate that the reactions of CH_3SO_x with O_3 are very important, and the rate constant of $CH_3S + O_3$, 6×10^{-12} cm^{-3} $molecule^{-1}$ s^{-1} estimated entirely from the simulation of our experimental data, agrees reasonably well with the first reported rate constant, $(4.1 \pm 2.0) \times 10^{-12}$ cm^{-3} $molecule^{-1}$ s^{-1} (Tyndall and Ravishankara, 1989) and better with the more recently reported value $(5.7 \pm 1.5) \times 10^{-12}$ cm^{-3} $molecule^{-1}$ s^{-1} (Domine *et al.*, 1989).

With the exception of limited data for the $RSO_x + NO_2$ and $RSO_x + O_3$ reactions, kinetic data are not available for RSO_x reactions. In order to estimate the reactivity of CH_3S, CH_3SO and CH_3SO_2 radicals towards oxidants, let us compare the reaction enthalpies between the analogous reactions. Table III lists enthalpy changes for all oxidation reactions except those for $CH_3S(O)_xOO$ radicals, which will be discussed later. Examination of the data in Table III reveals two important features. First, for a given oxidant species the reaction enthalpy decreases from CH_3S to CH_3SO_2 radicals, indicating that the tendency of CH_3SO_x radicals toward oxidation is in the order

$$CH_3S > CH_3SO > CH_3SO_2.$$

Second, for a given sulfur radical all oxidation reactions are considerably exo-

Table III. Summary of reaction enthalpies for CH_3SO_x oxidation

Oxidation reaction	ΔH°_{298} (kcal/mole)
$CH_3S + O{-}NO \rightarrow CH_3SO + NO$	−32
$+ O{-}OH \rightarrow CH_3SO + OH$	−39
$+ O{-}OCH_3 \rightarrow CH_3SO + OCH_3$	−46
$+ O{-}OO \rightarrow CH_3SO + O_2$	−80
$+ O{-}NO_2 \rightarrow CH_3SO + NO_2$	−55
$CH_3SO + O{-}NO \rightarrow CH_3SO_2 + NO$	−26
$+ O{-}OH \rightarrow CH_3SO_2 + OH$	−33
$+ O{-}OCH_3 \rightarrow CH_3SO_2 + OCH_3$	−40
$+ O{-}OO \rightarrow CH_3SO_2 + O_2$	−74
$+ O{-}NO_2 \rightarrow CH_3SO_2 + NO_2$	−49
$CH_3SO_2 + O{-}NO \rightarrow CH_3SO_3 + NO$	−13
$+ O{-}OH \rightarrow CH_3SO_3 + OH$	−20
$+ O{-}OCH_3 \rightarrow CH_3SO_3 + OCH_3$	−27
$+ O{-}OO \rightarrow CH_3SO_3 + O_2$	−61
$+ O{-}NO_2 \rightarrow CH_3SO_3 + NO_2$	−36

Note: The formation enthalpies of CH_3SO_x radicals are estimated from the bond dissociation energies of corresponding species estimated by Benson (1978) and Kerr and Calvert (1984). The formation enthalpies of other species are from Shum and Benson (1983) and Baulch *et al.* (1984).

thermic with similar enthalpy changes, thus suggesting that all these reactions are expected to proceed rapidly in the atmosphere. For comparison, Table IV presents the rate constants as well as the reaction enthalpies for CH_3SO_x oxidation by NO_2 and O_3 and for HSO_x reactions. For both CH_3SO_x and HSO_x radicals, the observed trend in kinetic data is quite consistent with that predicted from thermodynamic considerations. The rate constants for CH_3SO_x radicals are similar to those for HSO_x radicals, and so are the corresponding enthalpy changes. Therefore, rate constants for CH_3SO_x oxidation can be estimated from those of the corresponding HSO_x reactions. While no rate constant is available, the oxidation of the CH_3SO_2 radical by NO_2 may be fast since the similar reaction

$$HOSO_2 + NO_2 \longrightarrow HOS(O)_2{-}ONO \longrightarrow HOS(O)_2O + NO$$

was estimated to be relatively fast at 300 K (Benson, 1978). Although no rate constants are available for the reactions of peroxy radicals with CH_3SO_x, they should be of a similar magnitude as those for the reaction with NO_2 since reaction enthalpies for the analogous reactions between NO_2 and peroxy radicals are similar. The observations of a high SO_2 yield in the photolysis of $CH_3SCH_3{-}H_2O_2$ mixtures in air (Barnes *et al.*, 1988) and in the photolysis of CH_3SSCH_3 in air (Hatakeyama and Akimoto, 1983; Yin *et al.*, 1990) are consistent with a rapid oxidation of CH_3S and CH_3SO by HO_2 and CH_3OO. Furthermore, the enthalpy changes listed in Table IV for all the possible pathways of $CH_3SO_x + O_3$ reactions indicate that oxidation is thermodynamically most favourable, although H-atom abstraction is also significantly exothermic.

In experiments carried out at high NO_x concentrations (Hatakeyama *et al.*, 1982; Hatakeyama and Akimoto, 1983; Grosjean, 1984; Barnes *et al.*, 1987b), CH_3SO_x radicals are oxidized mainly by NO_2. At much lower NO_x concentrations, e.g., in the marine atmosphere, reactions of CH_3SO_x with ozone may become the most important pathway for CH_3SO_x radicals.

Finally, the addition of NO_2 (or NO_3) to CH_3SO_x may also be a minor pathway for CH_3SO_x radicals. Although CH_3SNO_2 has been tentatively identified as a reaction product in several studies (Niki *et al.*, 1983a; Grosjean, 1984; MacLeod *et al.*, 1986; Barnes *et al.*, 1987b), the corresponding addition pathway is probably only a minor component of the $CH_3SO_x + NO_2$ reaction, which proceeds mainly via oxidation. Comparing the NO_2 reactions of CH_3O and CH_3S:

$$\begin{array}{llll} CH_3O + NO_2 & \longrightarrow & CH_3O{-}NO_2 & \text{major} \\ & \longrightarrow & CH_3O{-}ONO & \text{negligible} \\ CH_3S + NO_2 & \longrightarrow & CH_3S{-}NO_2 & \text{minor} \\ & \longrightarrow & CH_3S{-}ONO & \text{major} \end{array}$$

the $CH_3O{-}ONO$ bond is very weak and no CH_3OONO has been observed to form. In contrast, the $CH_3S{-}ONO$ bond is expected to be stronger than that in $CH_3S{-}NO_2$ because of the larger difference of electronegativity. Thus, the domi-

Table IV. Summary of kinetic data for NO_2 and O_3 reaction

Reaction		$k \times 10^{11}$ (cm^3 $molecule^{-1}$ s^{-1})	ΔH°_{298} (kcal/mole)
NO_2 *Reaction*			
$NO_2 + HS$	$\rightarrow HSO + NO$	2.4–8.6	−25.0
$+ CH_3S$	$\rightarrow CH_3SO + NO$	5.1–11.0	−32
$+ C_2H_5S$	$\rightarrow C_2H_5SO + NO$	9.2	~ −30
$+ i\text{-}C_3H_7S$	$\rightarrow i\text{-}C_3H_7SO + NO$	5.9	~ −30
$NO_2 + HSO$	$\rightarrow HSO_2 + NO$	0.41–0.96	−23.3
$+ CH_3SO$	$\rightarrow CH_3SO_2 + NO$	0.8–3	−26
$NO_2 + HSO_2$	$\rightarrow$ Product		
$+ CH_3SO_2$	$\rightarrow CH_3SO_3 + NO$		−13
$O_3 + HS$	$\rightarrow HSO + O_2$	0.29–0.32	−72.7
$+ CH_3S$	$\rightarrow CH_3SO + O_2$	0.41–0.57	−80
	$\rightarrow CH_2S + O_2 + OH$		−31
$O_3 + HSO$	$\rightarrow HSO_2 + O_2$	0.001–0.01	−71
	$\rightarrow HS + 2O_2$		+5.9
$+ CH_3SO$	$\rightarrow CH_3S + O_2 + O_2$	~0.06	+12
$+ CH_3SO$	$\rightarrow CH_3SO_2 + O_2$		−74
	$\rightarrow CH_2SO + OH + O_2$		−22
$O_3 + HSO_2$	$\rightarrow$ Product		
$+ CH_3S(O)O$	$\rightarrow CH_3SO + O_2 + O_2$		+6
$+ CH_3SO_2$	$\rightarrow CH_3SO_3 + O_2$		−61
$+ CH_3SO_2$	$\rightarrow CH_2SO_2 + OH + O_2$		−39

Notes:

1. The rate constants were measured at room temperature and at low or high pressure by various techniques.
2. Only the dominant pathway is given for each reaction.

References:

NO_2 *reactions:*

Black (1984), Bulatov *et al.* (1984), Friedl *et al.* (1985), Wang *et al.* (1987), Schönle *et al.* (1987), Stachnik and Molina (1987), Lovejoy *et al.* (1987), Balla *et al.* (1986), Tyndall and Ravishankara (1988), Black *et al.* (1988a, b), Mellouki *et al.* (1988), Domine *et al.* (1989).

O_3 *reactions:*

Friedl *et al.* (1985), Schönle *et al.* (1987), Tyndall and Ravishankara (1987), Tyndall and Ravishankara (1989), Domine *et al.* (1989).

Reaction enthalpy:

The formation enthalpies of CH_3SO_x radicals are estimated from the bond dissociation energies of corresponding species estimated by Benson (1978) and Kerr and Calvert (1984). The formation enthalpy of HSO radical is uncertain within the range of (-5 ± 4)–(-0.4 ± 2) kcal/mole (Slagle *et al.*, 1978; Benson, 1978; Davidson *et al.*, 1982; Luke and McLean, 1985) and the value estimated by Benson (1978) was used. The formation enthalpies of other species nant pathway in this case is the formation of the adduct CH_3SONO, which is thermally unstable and further decomposes rapidly to CH_3SO and NO. This may explain the relative difficulty of detecting CH_3SNO_2 in the experiments, which may also be true for the analogous species of $CH_3S(O)NO_2$ and $CH_3S(O)_2NO_2$.

5.3. *Decomposition of RSO$_x$ Radicals*

Unimolecular decomposition reactions of CH_3SO_x radicals and the corresonding estimated bond dissociation energies are given below,

	ΔH°_{298} (kcal/mole)
$CH_3SO \xrightarrow{M} CH_3 + SO$	50 ± 2
$CH_3SO_2 \xrightarrow{M} CH_3 + SO_2$	17.2
$CH_3SO_3 \xrightarrow{M} CH_3 + SO_3$	22

(Benson, 1978; Kerr and Calvert, 1984). Examination of BDE values suggests that the CH_3SO radical should be stable with respect to its decomposition, and that CH_3SO_2 and CH_3SO_3 radicals should decompose rapidly. According to the above mechanism, the CH_3 radical is postulated to form, but experimental studies so far have yield conflicting results. On the one hand, MacLeod *et al.* (1986) studied the reactions of $CH_3SH + NO_3$ and $CH_3SSCH_3 + NO_3$ in the dark and observed CH_3ONO_2 in both systems, strongly suggesting that the CH_3 radical was the intermediate species. CH_3ONO_2 was also observed in the $CH_3SSCH_3 + NO_2$ study of Barnes *et al.* (1987b), clearly indicating the formation of CH_3 radicals. On the other hand, the absence of CH_3ONO in the photolysis of CH_3SNO in air with light above 500 nm (Hatakeyama and Akimoto, 1983; Hatakeyama, 1987) was cited as an evidence for lack of CH_3 formation in their system, where CH_3ONO would be formed by:

$$CH_3 + O_2 \xrightarrow{M} CH_3O_2$$
$$CH_3O_2 + NO \longrightarrow CH_3O + NO_2$$
$$CH_3O + NO \xrightarrow{M} CH_3ONO$$

However, the same authors observed CH_3ONO in the system of $CH_3SSCH_3 + C_2H_5ONO + NO + h\nu$ (Hatakeyama and Akimoto, 1983). In this system, CH_3ONO is unlikely to form from CH_3CHO since in the analogous system of $CH_3SCH_3 + C_2H_5ONO + NO + h\nu$ Niki *et al.* (1983b) measured a lower limit of 25% of CH_3ONO without consuming the formed CH_3CHO.

It should be pointed out that lack of observation of CH_3ONO and CH_3ONO_2 does not necessarily indicate the absence of the formation of the CH_3 radical since

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are obtained from Benson (1978), Hwang and Benson (1979), Shum and Benson (1983), and Baulch *et al.* (1984). The enthalpy changies for $C_2H_5S + NO_2$ and i-$C_3H_7S + NO_2$ reactions are estimated by Balck *et al.* (1988a, b).

the rate constants of $CH_3O + NO_x$ are uncertain and the competitive reaction of $CH_3O + O_2$ is the major loss pathway for CH_3O radical.

Another observation which has been used to argue against the formation of CH_3 radical by Hatakeyama and Akimoto (1983) is that little CH_3OH was formed from the photolysis of CH_3SSCH_3 in air although HCHO yield was more than 90% because from following mechanism and available rate constants,

$$\begin{aligned} CH_3 + O_2 &\xrightarrow{M} CH_3O_2 \\ CH_3O_2 + CH_3O_2 &\rightarrow 2\,CH_3O + O_2 \\ &\rightarrow HCHO + CH_3OH + O_2 \\ CH_3O + O_2 &\rightarrow HCHO + HO_2 \end{aligned}$$

a yield of 46% CH_3OH was expected. However, such result not only was consistent with the generation of CH_3 radical in the system, but also was a clear evidence that $CH_3O_2 + CH_3S$ reaction occurred, i.e.,

$$CH_3O_2 + CH_3S \rightarrow CH_3O + CH_3SO$$

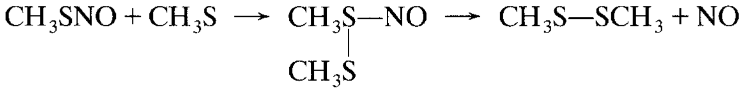
therefore, HCHO should be expected to form, but not CH_3OH.

Mellouki *et al.* (1988) studied the decomposition of the CH_3SO_2 radical by a discharge flow-EPR-mass spectrometric technique and estimated $k_{CH_3SO_2}$ to be about 10 s^{-1} at room temperature and 0.33 Torr pressure. This rate constant may be higher in the atmosphere since the reaction is probably pressure dependent. Moreover, the decomposition rate of CH_3SO_2 radical may be enhanced in sunlight because CH_3SO_2 absorbs strongly in the 300–600 nm region with a maximum at ca. 350 nm (Chatgilialogou *et al.*, 1987).

In summary, thermodynamic, kinetic and some (but not all) product data indicate that unimolecular decomposition is an important loss process for CH_3SO_x radicals.

5.4. *Formation of CH_3SSCH_3*

The formation of CH_3SSCH_3 has been observed in the systems of CH_3SNO—air—$h\nu$ (Niki *et al.*, 1983a), CH_3SNO—NO_x—air—$h\nu$ (Hatakeyama, 1987) and CH_3SH—N_2O_5—air in the dark (MacLeod *et al.*, 1986). The formation of CH_3SSCH_3 is puzzling since CH_3S radical recombination to produce CH_3SSCH_3 ($k = 4.1 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} (Graham *et al.*, 1964b)) is too slow to compete with the $CH_3S + NO_2$ reaction ($k = 6.1 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} (Tyndall and Ravishankara, 1987)) at the high level of NO_2 used in the above studies. Therefore, there must be other routes to produce CH_3SSCH_3. Based on thermochemistry considerations, the following reaction is proposed to account for the formation of CH_3SSCH_3,



$$CH_3SNO + CH_3S \longrightarrow \underset{\displaystyle CH_3S}{CH_3S{-}NO} \longrightarrow CH_3S{-}SCH_3 + NO$$

Since BDE($CH_3S{-}NO$) = 25 ± 1 kcal/mole is much less than BDE($CH_3S{-}SCH_3$) = 74 ± 2 kcal/mole (Benson, 1978), the above reaction is expected to be fast. In fact, from the experimental data of $CH_3S^{14}NO + {}^{15}NO + N_2$ system obtained by Niki *et al.* (1983a) and using a simple mechanism including CH_3S radical, NO, CH_3SNO and CH_3SSCH_3 species, we estimate a value of 5.5×10^{-12} cm^3 molecule^{-1} s^{-1} for the rate constant of the $CH_3S + CH_3SNO$ reaction. The validity of our proposed mechanism for formation of CH_3SSCH_3 can be further tested using Hatakeyama's (1987) experimental data for the $CH_3SNO{-}NO_x{-}\text{air}{-}h\nu$ system. Assuming CH_3S is mainly consumed by the following two reactions,

$$\begin{aligned} CH_3S + CH_3SNO &\longrightarrow CH_3SSCH_3 + NO && \text{(a)} \\ + NO_2 &\longrightarrow CH_3SO + NO && \text{(b)} \end{aligned}$$

and that the reaction between CH_3S and CH_3SNO is the sole reaction responsible for the production of CH_3SSCH_3, the CH_3SSCH_3 yield is therefore proportional to the ratio of reaction rates, R_a/R_b, or to the ratio of $[CH_3SNO]/[NO_2]$, i.e.,

$$\frac{R_a}{R_b} = \frac{5.5 \times 10^{-12}}{6.1 \times 10^{-11}} \times \frac{[CH_3SNO]}{[NO_2]}$$

As a first approximation, the yield of CH_3SSCH_3 should be roughly proportional to the initial concentration ratio, $[CH_3SNO]_o/[NO_2]_o$ (no time profiles of CH_3SNO and NO_2 were available). Initial concentration and CH_3SSCH_3 yields are listed in Table V, and indeed show a high degree of correlation. It should be pointed out that the CH_3SSCH_3 yield does not anticorrelate with the initial O_2 concentration directly, which was interpreted by Hatakeyama originally, because the consumption of CH_3S due to $CH_3S + O_2$ reaction is minor under such high concentration of NO_2 (1.3–10.5 ppm) according to the apparent rate constant of 2.5×10^{-18} cm^3 molecule^{-1} s^{-1} (Tyndall and Ravishankara, 1988). However, the presence of high O_2 concentration in the system is necessary to reconvert NO to NO_2 and maintain the high NO_2 concentration by the following reactions,

$$\begin{aligned} CH_3 + O_2 &\xrightarrow{M} CH_3O_2 \\ CH_3O_2 + NO &\longrightarrow CH_3O + NO_2 \\ CH_3O + O_2 &\longrightarrow HCHO + HO_2 \\ HO_2 + NO &\longrightarrow OH + NO_2 \\ CH_3SSCH_3 + OH &\longrightarrow CH_3S + CH_3SOH \end{aligned}$$

and also the reaction of $CH_3SSCH_3 + OH$ decreases the production yield of CH_3SSCH_3. The high CH_3SSCH_3 yield observed in the absence of O_2 (which is shown in Table V at last line), despite the relatively low ratio of $[CH_3SNO]_o/$

Table V. Correlation between CH_3SSCH_3 yield and initial concentration

$[CH_3SNO]_0/[NO_2]_0$	CH_3SSCH_3 Yield	$[O_2]_0$ (Torr)
7.97	0.67	152
6.75	0.52	76
6.24	0.54	152
4.94	0.42	380
4.09	0.20	760
1.85	0.18	152
1.09	0.13	152
0.74	–	152
5.96	0.71	~0

Note: The CH_3SSCH_3 yield is measured from the photolysis of $CH_3SNO—NO_x$—air mixtures by Hatakeyama (1987).

$[NO_2]_0$, is not inconsistent with our mechanism since the competition cannot be maintained in this case.

In the dark reaction of CH_3SH with N_2O_5 in air (MacLeod *et al.*, 1986), several reactions may be responsible for the formation of CH_3SSCH_3. The formation of CH_3SSCH_3 was only observed in the presence of O_2 and CH_3 was also produced, as indicated by the observation of CH_3ONO_2. Thus, it is likely that OH was produced from CH_3O_2. Therefore, CH_3S could have formed by reaction of CH_3SH with OH, and could have further reacted with CH_3SNO_x or CH_3SONO_2 to produce CH_3SSCH_3:

$$\begin{aligned} CH_3S + CH_3SNO &\rightarrow CH_3SSCH_3 + NO \\ + CH_3SNO_2 &\rightarrow CH_3SSCH_3 + NO_2 \\ + CH_3SONO_2 &\rightarrow CH_3SSCH_3 + NO_3 \end{aligned}$$

Although no bond dissociation energies are available for $CH_3S—NO_2$ and $CH_3S—ONO_2$ bonds, the S—N and S—O bonds in the above three species are expected to be weaker than the S—S bond of $CH_3S—SCH_3$.

Due to the rapid photolysis of CH_3SNO, CH_3SSCH_3 formation by the reaction of CH_3S with CH_3SNO will *not* be important in the daytime atmosphere.

6. Reaction of $RS(O)_xOO$ Radicals

The reactivity of $CH_3S(O)_xOO$ radicals may be more similar to that of peroxy radicals than to that of sulfur radicals. This is consistent with the prediction, from a recent *ab initio* molecular orbital calculation, that the electron spin density on O atoms in CH_3SOO is similar to that in CH_3OO (Swarts *et al.*, 1989). In fact, $CH_3S(O)_xOO$ radicals may be even more reactive than peroxy radicals by virtue of the weaker O—O bonds. Although no thermodynamic data are available, the relative reactivity of $CH_3S(O)_xOO$ radicals is expected to be

$$CH_3SOO > CH_3S(O)OO > CH_3S(O)_2OO$$

since the relative strength of O—O bond is in the order of

$$CH_3SO\text{—}O < CH_3S(O)O\text{—}O < CH_3S(O)_2O\text{—}O.$$

The major loss process for $CH_3S(O)_xOO$ radicals will be reduction reactions involving NO or CH_3SO_x, although self-reaction and H-atom abstraction may also be important. Thus, for NO and CH_3S:

$$\begin{aligned}
CH_3SOO + NO &\rightarrow CH_3SO + NO_2\\
+ CH_3S &\rightarrow CH_3SO + CH_3SO\\
CH_3S(O)OO + NO &\rightarrow CH_3SO_2 + NO_2\\
+ CH_3S &\rightarrow CH_3SO_2 + CH_3SO\\
CH_3S(O)_2OO + NO &\rightarrow CH_3SO_3 + NO_2\\
+ CH_3S &\rightarrow CH_3SO_3 + CH_3SO
\end{aligned}$$

These reactions are expected to be fast and comparable to the reaction of CH_3O_2 with NO, $k = 7.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. At high NO concentration, $CH_3S(O)_xOO$ will oxidize NO to NO_2; at low NO_x concentration, the reactions between $CH_3S(O)_xOO$ and CH_3SO_x radicals become importat, competing with the reactions between other peroxy radicals and CH_3SO_x radicals.

The tentative identification of $CH_3S(O)OONO_2$ by Barnes *et al.* (1987b) suggests that the competition reaction of NO_2 for $CH_3S(O)OO$ is important; this may also hold true for the $CH_3S(O)_2OO$ radical.

7. Formation of SO_2 and CH_3SO_3H

Although SO_2 and CH_3SO_3H have been identified as major reaction products in several studies (Grosjean and Lewis, 1982; Hatakeyama *et al.*, 1982, 1985; Hatakeyama and Akimoto, 1983; Grosjean, 1984; Barnes *et al.*, 1987b, 1988), their formation pathways are still poorly characterized. In this section, we discuss SO_2 and CH_3SO_3H formation pathways, and examine the effects of high or low NO_x concentration on the yield distribution of SO_2 and CH_3SO_3H.

The analysis presented in the preceding sections makes it clear that SO_2 and CH_3SO_3H can be produced in both addition or abstraction pathways. The major formation pathways for SO_2 and CH_3SO_3H are compiled below:

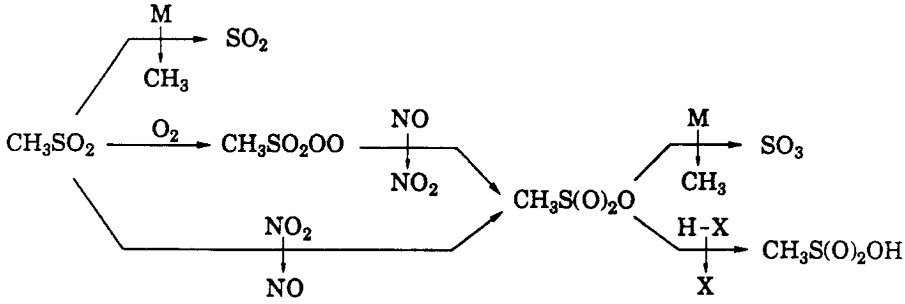
$$\begin{aligned}
CH_3SO_2 &\xrightarrow{M} SO_2 + CH_3\\
CH_3SO_3 + HCHO &\rightarrow CH_3SO_3H + HCO\\
+ CH_3SCH_3 &\rightarrow CH_3SO_3H + CH_3SCH_2\\
+ CH_3SH &\rightarrow CH_3SO_3H + CH_3S\\
+ CH_3SOH &\rightarrow CH_3SO_3H + CH_3SO
\end{aligned}$$

$$\begin{aligned}
&+CH_3SO_2H &&\rightarrow CH_3SO_3H + CH_3SO_2\\
&+HONO &&\rightarrow CH_3SO_3H + NO_2\\
&+H_2O_2 &&\rightarrow CH_3SO_3H + HO_2\\
&+CH_3OH &&\rightarrow CH_3SO_3H + CH_2OH\\
&+HO_2 &&\rightarrow CH_3SO_3H + O_2
\end{aligned}$$

The unimolecular decomposition of CH_3SO_2 is the dominant pathway for SO_2 production, and may be enhanced in sunlight as discussed earlier. The bond dissociation energies of the C—H, S—H and O—H bonds in the H-donors listed above are in the range 49–96 kcal/mole (Benson, 1978; McMillen and Golden, 1982; Shum and Benson, 1983, 1985; Kerr, 1985) and are much smaller than that for $CH_3S(O)_2O$—H bond of about 104 kcal/mole or more. In smog chamber experiments, especially at high concentrations of RSR′, the reactions of CH_3SO_3 with RSR′ (including CH_3SOH) and with HCHO will be the dominant pathways for CH_3SO_3H formation compared with the decomposition of the CH_3SO_3 radical.

The relative importance of addition and abstraction is still uncertain for the reaction of CH_3SO_3 with organosulfur compounds. Considering the relatively strong C—H bonds in CH_3SCH_3 and CH_3SSCH_3 (about 97 kcal/mole) and the relatively high electron density on S atom, electrophilic addition of CH_3SO_3 to CH_3SCH_3 and CH_3SSCH_3 is probably more important than H-atom abstraction, as is the case for other free radicals including OH, NO_3, $O(^3P)$ and IO.

Since SO_2 and CH_3SO_3H are produced mainly from CH_3SO_2, the competition between CH_3SO_2 decomposition and further oxidation to CH_3SO_3 will determine their yield distribution, which is shown schematically as follows:



In the absence of NO_x or at very low NO_x concentration, neither the oxidation of CH_3SO_2 by peroxy radicals nor the reduction of $CH_3S(O)_2OO$ by CH_3SO_x radicals will be fast since the concentrations of those radicals are very low. In this case, the competition is dominated by the unimolecular decomposition of the CH_3SO_2 radical to form SO_2. This is consistent with the observation of high SO_2 yield in the systems of CH_3SCH_3—H_2O_2—air—$h\nu$ (Barnes *et al.*, 1988), and CH_3SSCH_3—air—$h\nu$ (Hatakeyama and Akimoto, 1983; Yin *et al.*, 1990). At higher NO_x concentrations (>0.1 ppm), the reactions $CH_3SO_2 + NO_2$ and $CH_3S(O)_2OO + NO$, especially the later, compete effectively with CH_3SO_2 decomposition. In this case, the yield of SO_2 decreases and that of CH_3SO_3H increases, in agreement with experimental observations (Grosjean and Lewis, 1982; Hatakeyama *et al.*, 1982, 1985; Hatakeyama and Akimoto, 1983; Grosjean, 1984; Barnes *et al.*, 1987b, Yin *et al.*, 1990).

The effects of NO_x on the yield distribution of SO_2 and CH_3SO_3H can be used to explain the NO_x effects on the observed rate constants of initial reactions mentioned in section 2.4.2. As the NO_x concentration increased in the systems, the formation rate of CH_3SO_3 is increased, and so is the rate of CH_3SO_3H formation. Also in those experiments, the concentration of CH_3SH and CH_3SCH_3 were very high and the reaction between CH_3SO_3 and CH_3SH or CH_3SCH_3 should be the dominant one for CH_3SO_3H formation. Therefore, the observed decay rate of CH_3SH or CH_3SCH_3 will be enhanced and the measured rate constants of the initial reactions will depend on the NO_x concentration. It should be mentioned that, although the difference between the bond dissociation energy of $CH_3S(O)_2O$—H and CH_3SCH_2—H bonds is relatively small (about 8 kcal/mole or more), the addition of CH_3SO_3 to CH_3SCH_3 may also contribute to the enhanced decay rate of CH_3SCH_3 since the CH_3SO_3 radical is analogous to NO_3 radical.

It should be pointed out that the formation mechanisms of SO_2 proposed by Balla and Heicklen (1985) and Hatakeyama (1987) do not predict SO_2 production in the absence of O_2, in contradiction with the observations of Barnes *et al.* (1987b) for the CH_3SSCH_3—NO_2—N_2 system.

8. Missing Products

Experimental studies of organosulfur oxidation have so far yielded poor sulfur, nitrogen and carbon mass balances. Although concentrations of many measured compounds, including H_2SO_4, CH_3SO_3H, HNO_3 and HCHO, may usually be underestimated due to wall losses, other unidentified products may also be produced, especially condensible species with high molecular weight. A speculative list of such products is given below:

$$\begin{aligned}
CH_3S(O)OO + NO_2 &\xrightarrow{M} CH_3S(O)OONO_2\\
CH_3S(O)_2OO + NO_2 &\xrightarrow{M} CH_3S(O)_2OONO_2\\
CH_3SO_2 + RSR' &\xrightarrow{M} \text{Adduct}\\
CH_3SO_3 + RSR' &\xrightarrow{M} \text{Adduct}\\
+ NO &\xrightarrow{M} CH_3S(O)_2ONO\\
+ NO_2 &\xrightarrow{M} CH_3S(O)_2ONO_2\\
CH_3SO_2 + NO_2 &\xrightarrow{M} CH_3S(O)_2ONO
\end{aligned}$$

The peroxynitrate compounds may be thermally unstable and serve as a reservoir for both sulfur and nitrogen compounds. The CH_3SO_3 radical, which is analogous to NO_3, may not only abstract hydrogen from RSR′ or hydrocarbons but also add to RSR′ or unsaturated hydrocarbons in the atmosphere. The adduct may undergo unimolecular decomposition to form condensible species. The possible $CH_3S(O)_2ONO_x$ products, which are similar to $HOS(O)_2ONO_x$ discussed by Benson (1978), may be easily absorbed on the reactor surfaces and exothermically hydrolyzed to CH_3SO_3H, HONO, or $HONO_2$. Two other condensible species, CH_3SOH and CH_3SO_2H, may also be lost on the reactor walls, although they could be further oxidized to SO_2 and CH_3SO_3H.

9. New Mechanisms for Atmospheric Oxidation of CH_3SCH_3 and CH_3SSCH_3

Based on the comprehensive analysis presented in the preceding sections, new mechanisms have been developed to describe the atmospheric chemistry of CH_3SCH_3—NO_x—air—*hv* (Tables VI, VII and IX) and CH_3SSCH_3—NO_x—air—*hv* (Table VIII). The difference between these two mechanisms lies mostly in their initial reactions. A detailed mechanism for CH_3SH photooxidation in the atmosphere could readily be developed using the appropriate initial reactions, with subsequent reactions identical to those presented here for CH_3SSCH_3.

Major differences between the mechanisms presented here and those developed in our earlier work (Yin *et al.*, 1986) including the following:

(1) Detailed description of the reactions of $CH_3S(O)CH_3$, $CH_3S(O)_2CH_3$ and CH_3SOH.
(2) Clear distinction between CH_3SO_x and $CH_3S(O)_xOO$ radicals.
(3) Detailed elucidation of CH_3SO_x reaction mechanisms.
(4) Delineation of the major pathways for SO_2 and CH_3SO_3H formation.

In order to evaluate the proposed new mechanisms and to determine the yield distribution of SO_2 and CH_3SO_3H under low NO_x conditions, a series of outdoor smog chamber experiments has been carried out for CH_3SCH_3—NO_x—air—*hv* and CH_3SSCH_3—(NO_x)—air—*hv* mixtures. The results of these experiments are presented in our companion paper, Part II.

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Table VI. Inorganic and aldehyde chemistry common to mechanisms of organosulfur species

Reaction	Rate constant[a]	Activation energy (K)	Ref.*	Note*
Inorganic Reactions				
1. $NO_2 + h\nu \longrightarrow NO + O(^3P)$				(1)
2. $O(^3P) + O_2 \xrightarrow{M} O_3$	1.5×10^{-14}	-5.60×10^2	2, 17	
3. $O_3 + NO \longrightarrow NO_2 + O_2$	1.8×10^{-14}	1.43×10^3	2	
4. $O(^3P) + NO \xrightarrow{M} NO_2$	2.1×10^{-12}		3	
5. $O(^3P) + NO_2 \longrightarrow NO + O_2$	9.7×10^{-12}	-1.2×10^2	3	
6. $O(^3P) + NO_2 \xrightarrow{M} NO_3$	1.8×10^{-12}	-4.2×10^2	6, 17	
7. $O(^3P) + NO_3 \longrightarrow NO_2 + O_2$	1.0×10^{-11}		3	
8. $O(^3P) + O_3 \longrightarrow 2\ O_2$	8.0×10^{-15}	2.06×10^3	3	
9. $O_3 + NO_2 \longrightarrow NO_3 + O_2$	3.2×10^{-17}	2.45×10^3	3	
10. $O_3 + NO_2 \longrightarrow NO + 2\ O_2$	9.7×10^{-19}	2.45×10^3	17	
11. $O_3 + OH \longrightarrow HO_2 + O_2$	6.7×10^{-14}	1.0×10^3	3	
12. $O_3 + HO_2 \longrightarrow OH + 2\ O_2$	2.0×10^{-15}	6.0×10^2	3	
13. $O_3 + h\nu \longrightarrow O(^3P) + O_2$	$4.0 \times 10^{-2}\ k_{NO_2}$		1, 19	
14. $O_3 + H_2O + h\nu \longrightarrow 2\ OH + O_2$	$9.34 \times 10^{-22}\ k_{NO_2}$		1,9	(3)
15. $HO_2 + OH \longrightarrow O_2 + H_2O$	1.1×10^{-10}	-2.5×10^2	3	
16. $HO_2 + HO_2 \longrightarrow H_2O_2 + O_2$	1.8×10^{-12}	-6.2×10^2	2	(2)
16. $HO_2 + HO_2 \longrightarrow H_2O_2 + O_2$	1.8×10^{-12}	-6.2×10^2	2	(2)
17. $HO_2 + HO_2 \longrightarrow H_2O_2 + O_2$	1.3×10^{-12}	-9.8×10^2	2	(2)
18. $HO_2 + HO_2 + H_2O \longrightarrow H_2O_2 + O_2 + H_2O$	4.0×10^{-30}	-2.8×10^3	2	(2)
19. $HO_2 + HO_2 + H_2O \longrightarrow H_2O_2 + O_2 + H_2O$	2.8×10^{-30}	-3.2×10^3	2	(2)
20. $H_2O_2 + OH \longrightarrow HO_2 + H_2O$	1.7×10^{-12}	1.6×10^2	3	
21. $H_2O_2 + h\nu \longrightarrow 2\ OH$	$7.1 \times 10^{-4}\ k_{NO_2}$		1	
22. $NO + HO_2 \longrightarrow NO_2 + OH$	8.3×10^{-12}	-2.4×10^2	3	
23. $NO + NO + O_2 \longrightarrow 2\ NO_2$	2.0×10^{-38}	-5.3×10^2	3	
24. $NO + OH \xrightarrow{M} HONO$	6.6×10^{-12}		2	
25. $HONO + h\nu \longrightarrow NO + OH$	$1.7 \times 10^{-1}\ k_{NO_2}$		1	
26. $HONO + OH \longrightarrow NO_2 + H_2O$	4.9×10^{-12}	3.9×10^2	3	
27. $HNO + O_2 \longrightarrow NO + HO_2$	2.1×10^{-20}	5.0×10^3	17	
28. $NO_2 + OH \xrightarrow{M} HONO_2$	1.1×10^{-11}		2, 17	
29. $NO_2 + HO_2 \xrightarrow{M} HO_2NO_2$	1.4×10^{-12}		2	
30. $HO_2NO_2 \xrightarrow{M} HO_2 + NO_2$	8.5×10^{-2}	1.042×10^4	2	
31. $HO_2NO_2 + OH \longrightarrow NO_2 + H_2O + O_2$	5.0×10^{-12}	-3.6×10^2	3, 17	
32. $NO_3 + OH \longrightarrow NO_2 + HO_2$	2.3×10^{-11}		3	
33. $NO_3 + NO \longrightarrow 2\ NO_2$	2.7×10^{-11}	-1.5×10^2	3	
34. $NO_3 + NO_2 \longrightarrow NO + NO_2 + O_2$	4.0×10^{-16}	1.23×10^3	2	
35. $NO_3 \xrightarrow{M} NO + O_2$	3.0×10^{-3}	6.84×10^3	17	
36. $NO_3 + HO_2 \longrightarrow HONO_2 + O_2$	4.3×10^{-12}		3	
37. $NO_3 + h\nu \longrightarrow 0.3\ NO + 0.7\ NO_2 + 0.7\ O(^3P)$	$1.55 \times 10^{1}\ k_{NO_2}$		18	
38. $NO_3 + NO_2 \xrightarrow{M} N_2O_5$	1.2×10^{-12}	6.0×10^1	2, 17	

Table VI. (*continued*)

Reaction	Rate constant[a]	Activation energy (K)	Ref.*	Note*
39. $N_2O_5 \xrightarrow{M} NO_2 + NO_3$	5.2×10^{-2}	1.084×10^{4}	5, 17	
40. $N_2O_5 + H_2O \longrightarrow 2\ HONO_2$	2.0×10^{-21}		3	
41. $HONO_2 + OH \longrightarrow NO_3 + H_2O$	1.5×10^{-13}	-7.78×10^{2}	2, 3, 6	
42. $CO + OH \xrightarrow{O_2} CO_2 + HO_2$	2.4×10^{-13}		3	
43. $H_2 + OH \xrightarrow{O_2} HO_2 + H_2O$	6.7×10^{-15}	2.10×10^{3}	3	
Aldehyde Reactions				
44. $HCHO + h\nu \longrightarrow H_2 + CO$	$3.3 \times 10^{-3}\ k_{NO_2}$		19	
45. $HCHO + h\nu \xrightarrow{O_2} 2\ HO_2 + CO$	$2.3 \times 10^{-3}\ k_{NO_2}$		19	
46. $HCHO + OH \xrightarrow{O_2} HO_2 + CO + H_2O$	1.1×10^{-11}	1.1×10^{2}	3	
47. $HCHO + NO_3 \xrightarrow{O_2} CO + HONO_2 + HO_2$	6.0×10^{-16}		3	
48. $HCHO + O(^3P) \xrightarrow{O_2} OH + HO_2 + CO$	1.6×10^{-13}	1.550×10^{3}	2	
49. $HCHO + HO_2 \xrightarrow{M} O_2CH_2OH$	7.0×10^{-14}	-6.25×10^{2}	3	
50. $O_2CH_2OH \xrightarrow{M} HCHO + HO_2$	1.5×10^{2}	7.0×10^{3}	3	
51. $O_2CH_2OH + NO \xrightarrow{O_2} HCOOH + NO_2 + HO_2$	7.6×10^{-12}	-1.8×10^{2}	2, 17	
52. $O_2CH_2OH + HO_2 \longrightarrow HO_2CH_2OH + O_2$	7.2×10^{-12}	-2.3×10^{3}	24, 25	
53. $O_2CH_2OH + HO_2 \longrightarrow HCOOH + H_2O + O_2$	4.8×10^{-12}	-2.3×10^{3}	24, 25	
54. $2\ O_2CH_2OH \longrightarrow HCOOH + CH_2(OH)_2 + O_2$	7.0×10^{-13}	-7.5×10^{2}	24, 25	
55. $2\ O_2CH_2OH \longrightarrow 2\ HCOOH + 2\ HO_2 + O_2$	5.5×10^{-12}		24, 25	
56. $HCOOH + OH \xrightarrow{O_2} H_2O + HO_2 + CO_2$	4.8×10^{-13}	7.7×10^{1}	3, 17	
57. $CH_3 + O_2 \xrightarrow{M} CH_3O_2$	1.0×10^{-12}		2	
58. $CH_3 + O_2 \longrightarrow HCHO + OH$	5.0×10^{-17}		6	
59. $CH_3O_2 + NO \longrightarrow NO_2 + CH_3O$	7.6×10^{-12}	-1.80×10^{2}	3	
60. $CH_3O_2 + NO_2 \xrightarrow{M} CH_3O_2NO_2$	4.1×10^{-12}		3	
61. $CH_3O_2NO_2 \xrightarrow{M} CH_3O_2 + NO_2$	1.8	1.06×10^{4}	3	
62. $CH_3O_2 + HO_2 \longrightarrow CH_3OOH + O_2$	4.9×10^{-12}	-1.0×10^{3}	3	
63. $CH_3O_2H + OH \longrightarrow CH_3O_2 + H_2O$	3.9×10^{-12}	-1.9×10^{2}	26	
64. $CH_3O_2H + OH \longrightarrow HCHO + OH + H_2O$	1.5×10^{-12}	-1.9×10^{2}	26	
65. $CH_3O_2 + CH_3O_2 \longrightarrow CH_3OH + HCHO + O_2$	2.1×10^{-13}	-2.2×10^{2}	3	
66. $CH_3O_2 + CH_3O_2 \longrightarrow 2\ CH_3O + O_2$	1.3×10^{-13}	-2.2×10^{2}	3	
67. $CH_3O_2 + CH_3O_2 \longrightarrow CH_3OOCH_3 + O_2$	3.0×10^{-14}	-2.2×10^{2}	3	
68. $CH_3O + O_2 \longrightarrow HCHO + HO_2$	1.9×10^{-15}	1.08×10^{3}	3	
69. $CH_3O + NO_2 \xrightarrow{M} CH_3ONO_2$	1.5×10^{-11}		2	
70. $CH_3O + NO_2 \longrightarrow HCHO + HONO$	3.0×10^{-13}		3	
71. $CH_3O + NO \xrightarrow{M} CH_3ONO$	3.0×10^{-11}		2	
72. $CH_3ONO + h\nu \longrightarrow CH_3O + NO$	$0.17\ k_{NO_2}$		E	(4)
73. $CH_3O + NO \longrightarrow HCHO + HNO$	1.3×10^{-12}		2	
74. $CH_3OH + OH \xrightarrow{O_2} HCHO + HO_2 + H_2O$	9.0×10^{-13}	6.9×10^{2}	3, 17	

* References and notes are listed at the foot of Table IX.

Table VII. Atmospheric photooxidation mechanism for dimethyl sulfide

Reaction	Rate constant[a]	Activation energy (K)	Ref.*	Note*
Initial Reactions				
75. $CH_3SCH_3 + OH \rightarrow CH_3SCH_2 + H_2O$	4.4×10^{-12}	2.34×10^2	3	(6)
76. $CH_3SCH_3 + OH \xrightarrow{M} CH_3S(OH)CH_3$	1.7×10^{-12}		3	(6)
77. $CH_3SCH_3 + O(^3P) \rightarrow CH_3SO + CH_3$	5.0×10^{-11}	-4.09×10^2	3, 8, 20	
78. $CH_3SCH_3 + O(^3P) \rightarrow CH_3S + CH_3O$	0.0		E	(7)
79. $CH_3SCH_3 + NO_3 \rightarrow CH_3SCH_2 + HONO_2$	0.0		E	(6)
80. $CH_3SCH_3 + NO_3 \xrightarrow{M} CH_3S(ONO_2)CH_3$	7.5×10^{-13}	-5.00×10^2	3, 27	(6)
81. $CH_3SCH_3 + NO_2 \rightarrow CH_3S(O)CH_3 + NO$	9.0×10^{-21}		4	
82. $CH_3SCH_3 + O_3 \rightarrow$ Product	0.0		E	(7)
Adduct Reactions and other Radical Reactions				
83. $CH_3S(OH)CH_3 \xrightarrow{M} CH_3SOH + CH_3$	5.0×10^5		E	(6)
84. $CH_3S(OH)CH_3 + O_2 \rightarrow CH_3S(O)CH_3 + HO_2$	2.0×10^{-12}		E	(6)
85. $CH_3S(OH)CH_3 + O_2 \xrightarrow{M} CH_3S(OH)(OO)CH_3$	1.0×10^{-12}		E	(6)
86. $CH_3S(OH)(OO)CH_3 \xrightarrow{M} CH_3S(O)CH_3 + HO_2$	1.0×10^1		E	(6)
87. $CH_3S(OH)(OO)CH_3 + NO \rightarrow CH_3S(OH)(O)CH_3 + NO_2$	5.0×10^{-12}		E	(6)
88. $CH_3SCH_2 + O_2 \xrightarrow{M} CH_3SCH_2OO$	7.3×10^{-13}		15	
89. $CH_3SCH_2OO + NO \rightarrow CH_3SCH_2O + NO_2$	8.0×10^{-12}		E	(11)
90. $CH_3SCH_2OO + CH_3S \rightarrow CH_3SCH_2O + CH_3SO$	6.1×10^{-11}		E	(11)
91. $CH_3SCH_2OO + CH_3SO \rightarrow CH_3SCH_2O + CH_3SO_2$	4.0×10^{-12}		E	(11)
92. $CH_3SCH_2OO + CH_3SO_2 \rightarrow CH_3SCH_2O + CH_3SO_3$	2.5×10^{-13}		E	(11)
93. $CH_3SCH_2OO + HO_2 \rightarrow CH_3SCH_2OOH + O_2$	1.5×10^{-12}		E	(11)
94. $CH_3SCH_2OO + CH_3O_2 \rightarrow CH_3SCH_2O + CH_3O + O_2$	1.8×10^{-13}		E	(11)
95. $2\ CH_3SCH_2OO \rightarrow 2\ CH_3SCH_2O + O_2$	8.6×10^{-14}		E	(11)
96. $CH_3SCH_2O \xrightarrow{M} CH_3S + HCHO$	1.0×10^1		E	(8)
97. $CH_3S(ONO_2)CH_3 \xrightarrow{M} CH_3SCH_2 + HONO_2$	1.0×10^2		E	(6)
98. $CH_3S(ONO_2)CH_3 + O_2 \rightarrow$ Product	0.0		E	(7)
99. $CH_3SONO_2 \xrightarrow{M} CH_3SO + NO_2$	1.0×10^0		E	(8)
$CH_3S(O)CH_3$ Reactions				
100. $CH_3S(O)CH_3 + OH \rightarrow CH_3S(O)CH_2 + H_2O$	0.0		E	(7)
101. $CH_3S(O)CH_3 + OH \xrightarrow{M} CH_3S(OH)(O)CH_3$	5.8×10^{-11}		14	(6)
102. $CH_3S(OH)(O)CH_3 \xrightarrow{M} CH_3SO_2H + CH_3$	1.5×10^7		22	(6)

Table VII. (*continued*)

Reaction	Rate constant[a]	Activation energy (K)	Ref.*	Note*
103. $CH_3S(OH)(O)CH_3 + O_2 \longrightarrow CH_3S(O)_2CH_3 + HO_2$	1.2×10^{-12}		E	(6)
104. $CH_3S(O)CH_2 \xrightarrow{M} CH_3S + HCHO$	1.0×10^{2}		E	(8)
105. $CH_3S(O)CH_2 + O_2 \xrightarrow{M} CH_3S(O)CH_2OO$	1.0×10^{-12}		E	(10)
106. $CH_3S(O)CH_2OO + NO \longrightarrow CH_3S(O)CH_2O + NO_2$	6.0×10^{-12}		E	(11)
107. $CH_3S(O)CH_2OO + CH_3S \longrightarrow CH_3S(O)CH_2O + CH_3SO$	5.0×10^{-11}		E	(11)
108. $CH_3S(O)CH_2OO + CH_3SO \longrightarrow CH_3S(O)CH_2O + CH_3SO_2$	4.0×10^{-12}		E	(11)
109. $CH_3S(O)CH_2OO + CH_3SO_2 \longrightarrow CH_3S(O)CH_2O + CH_3SO_3$	2.5×10^{-13}		E	(11)
110. $CH_3S(O)CH_2OO + HO_2 \longrightarrow CH_3S(O)CH_2OOH + O_2$	1.5×10^{-12}		E	(11)
111. $CH_3S(O)CH_2OO + CH_3O_2 \longrightarrow CH_3S(O)CH_2O + CH_3O + O_2$	1.8×10^{-13}		E	(11)
112. $2\,CH_3S(O)CH_2OO \longrightarrow 2\,CH_3S(O)CH_2O + O_2$	8.6×10^{-14}		E	(11)
113. $CH_3S(O)CH_2O \xrightarrow{M} CH_3SO + HCHO$	1.0×10^{2}		E	(8)
$CH_3S(O)_2CH_3$ Reactions				
114. $CH_3S(O)_2CH_3 + OH \longrightarrow CH_3S(O)_2CH_2 + H_2O$	1.0×10^{-14}		E	(6)
115. $CH_3S(O)_2CH_2 + O_2 \xrightarrow{M} CH_3S(O)_2CH_2OO$	7.3×10^{-13}		E	(10)
116. $CH_3S(O)_2CH_2OO + NO \longrightarrow CH_3S(O)_2CH_2O + NO_2$	5.0×10^{-12}		E	(11)
117. $CH_3SO)_2CH_2OO + CH_3S \longrightarrow CH_3S(O)_2CH_2O + CH_3SO$	5.0×10^{-11}		E	(11)
118. $CH_3S(O)_2CH_2OO + CH_3SO \longrightarrow CH_3S(O)_2CH_2O + CH_3SO_2$	4.0×10^{-12}		E	(11)
119. $CH_3S(O)_2CH_2OO + CH_3SO_2 \longrightarrow CH_3S(O)_2CH_2O + CH_3SO_3$	2.5×10^{-13}		E	(11)
120 $CH_3S(O)_2CH_2OO + HO_2 \longrightarrow CH_3S(O)_2CH_2OOH + O_2$	1.5×10^{-12}		E	(11)
121. $CH_3S(O)_2CH_2OO + CH_3O_2 \longrightarrow CH_3S(O)_2CH_2O + CH_3O + O_2$	1.8×10^{-13}		E	(11)
122. $2\,CH_3S(O)_2CH_2OO \longrightarrow 2\,CH_3S(O)_2CH_2O + O_2$	8.6×10^{-14}		E	(11)
123. $CH_3S(O)_2CH_2O \xrightarrow{M} CH_3SO_2 + HCHO$	1.0×10^{1}		E	(8)
CH_3SOH and CH_3SO_2H Reactions				
124. $CH_3SOH + OH \longrightarrow CH_3SO + H_2O$	1.1×10^{-10}		E	(6)

Table VII. (*continued*)

Reaction	Rate constant[a]	Activation energy (K)	Ref.*	Note*
125. $CH_3SOH + CH_3SO_3 \rightarrow CH_3SO + CH_3SO_3H$	3.4×10^{-12}		E	(6)
126. $CH_3SOH + CH_3O \rightarrow CH_3SO + CH_3OH$	3.4×10^{-12}		E	(5)
127. $CH_3SOH + O(^3P) \rightarrow CH_3SO + OH$	3.4×10^{-12}		E	(5)
128. $CH_3SOH + NO_3 \rightarrow CH_3SO + HONO_2$	3.4×10^{-12}		E	(5)
129. $CH_3SOH + HO_2 \rightarrow CH_3SO + H_2O_2$	8.5×10^{-13}		E	(6)
130. $CH_3SOH + CH_3O_2 \rightarrow CH_3SO + CH_3OOH$	8.5×10^{-13}		E	(6)
131. $CH_3SOH + NO_2 \rightarrow CH_3SO + HONO$	0.0		E	(7)
132. $CH_3SOH + O_3 \rightarrow CH_3SO + OH + O_2$	0.0		E	(7)
133. $CH_3SOH + CH_3SOH \rightarrow CH_3SS(O)CH_3 + H_2O$	3.6×10^{-18}		E	
134. $CH_3SO_2H + OH \rightarrow CH_3SO_2 + H_2O$	1.6×10^{-11}		E	(6)
135. $CH_3SO_2H + CH_3SO_3 \rightarrow CH_3SO_2 + CH_3SO_3H$	1.0×10^{-13}		E	(6)
136. $CH_3SO_2H + CH_3O \rightarrow CH_3SO_2 + CH_3OH$	1.0×10^{-13}		E	(5)
137. $CH_3SO_2H + O(^3P) \rightarrow CH_3SO_2 + OH$	1.0×10^{-13}		E	(5)
138. $CH_3SO_2H + NO_3 \rightarrow CH_3SO_2 + HONO_2$	1.0×10^{-13}		E	(5)
139. $CH_3SO_2H + HO_2 \rightarrow CH_3SO_2 + H_2O_2$	1.0×10^{-15}		E	(5)
140. $CH_3SO_2H + CH_3O_2 \rightarrow CH_3SO_2 + CH_3OOH$	1.0×10^{-15}		E	(5)
CH_3SO_x and $CH_3S(O)_xOO$ Reactions				
141. $CH_3S + O_2 \xrightarrow{M} CH_3SOO$	5.8×10^{-17}		E	(6)
142. $CH_3SOO \xrightarrow{M} CH_3S + O_2$	6.0×10^{2}		E	(6)
143. $CH_3S + NO_2 \rightarrow CH_3SO + NO$	6.1×10^{-11}		21	(6)
144. $CH_3S + NO_2 \xrightarrow{M} CH_3SNO_2$	6.1×10^{-13}		E	(6)
145. $CH_3S + NO_3 \rightarrow CH_3SO + NO_2$	6.4×10^{-11}		E	(5)
146. $CH_3S + O_3 \rightarrow CH_3SO + O_2$	6.0×10^{-12}		E	(6)
147. $CH_3S + HO_2 \rightarrow CH_3SO + OH$	3.0×10^{-11}		E	(6)
148. $CH_3S + CH_3O_2 \rightarrow CH_3SO + CH_3O$	6.1×10^{-11}		E	(6)
149. $CH_3S + NO \xrightarrow{M} CH_3SNO$	2.87×10^{-11}		10	
150. $CH_3SNO + h\nu \rightarrow CH_3S + NO$	$0.5\ k_{NO_2}$		E	
151. $CH_3S + CH_3S \xrightarrow{M} CH_3SSCH_3$	4.15×10^{-11}		11	
152. $CH_3S + CH_3SNO \rightarrow CH_3SSCH_3 + NO$	1.4×10^{-12}		E	(6)
153. $CH_3S + OH \xrightarrow{M} CH_3SOH$	5.0×10^{-11}		E	(5)
154. $CH_3SOO + NO \rightarrow CH_3SO + NO_2$	1.4×10^{-11}		E	(11)
155. $CH_3SOO + CH_3S \rightarrow CH_3SO + CH_3SO$	8.0×10^{-11}		E	(11)
156. $CH_3SOO + CH_3SO \rightarrow CH_3SO + CH_3SO_2$	9.0×10^{-12}		E	(11)
157. $CH_3SOO + CH_3SO_2 \rightarrow CH_3SO + CH_3SO_3$	3.0×10^{-13}		E	(11)
158. $CH_3SOO + HO_2 \rightarrow CH_3SOOH + O_2$	4.0×10^{-12}		E	(11)
159. $CH_3SOO + CH_3O_2 \rightarrow CH_3SO + CH_3O + O_2$	5.5×10^{-12}		E	(11)

Table VII. (*continued*)

Reaction	Rate constant[a]	Activation energy (K)	Ref.*	Note*
160. $CH_3SOO + CH_3SOO \rightarrow 2\ CH_3SO + O_2$	6.0×10^{-12}		E	(11)
161. $CH_3SO \xrightarrow{M} SO + CH_3$	5.0×10^{-5}	2.52×10^4	E	(6)
162. $CH_3SO + O_2 \xrightarrow{M} CH_3S(O)OO$	7.7×10^{-18}		E	(6)
163. $CH_3S(O)OO \xrightarrow{M} CH_3SO + O_2$	1.7×10^2		E	(6)
164. $CH_3SO + NO_2 \rightarrow CH_3SO_2 + NO$	3.0×10^{-12}		E	(6)
165. $CH_3SO + NO_2 \xrightarrow{M} CH_3S(O)NO_2$	0.0		E	(7)
166. $CH_3SO + NO_3 \rightarrow CH_3SO_2 + NO_2$	8.0×10^{-12}		E	
167. $CH_3SO + O_3 \rightarrow CH_3SO_2 + O_2$	2.0×10^{-12}		E	(6)
168. $CH_3SO + HO_2 \rightarrow CH_3SO_2 + OH$	1.5×10^{-12}		E	(6)
169. $CH_3SO + CH_3O_2 \rightarrow CH_3SO_2 + CH_3O$	3.0×10^{-12}		E	(6)
170. $CH_3SO + NO \xrightarrow{M} CH_3S(O)NO$	0.0		E	(7)
171. $CH_3SO + CH_3SO \rightarrow CH_3S + CH_3SO_2$	7.5×10^{-12}		E	
172. $CH_3SO + CH_3SNO \rightarrow CH_3S(O)SCH_3 + NO$	6.8×10^{-13}		E	
173. $CH_3SO + OH \xrightarrow{M} CH_3SO_2H$	5.0×10^{-11}		E	(5)
174. $CH_3S(O)OO + NO \rightarrow CH_3SO_2 + NO_2$	8.0×10^{-12}		E	(11)
175. $CH_3S(O)OO + CH_3S \rightarrow CH_3SO_2 + CH_3SO$	7.0×10^{-11}		E	(11)
176. $CH_3S(O)OO + CH_3SO \rightarrow CH_3SO_2 + CH_3SO_2$	8.1×10^{-12}		E	(11)
177. $CH_3S(O)OO + CH_3SO_2 \rightarrow CH_3SO_2 + CH_3SO_3$	3.0×10^{-13}		E	(11)
178. $CH_3S(O)OO + HO_2 \rightarrow CH_3S(O)OOH + O_2$	3.0×10^{-12}		E	(11)
179. $CH_3S(O)OO + CH_3O_2 \rightarrow CH_3SO_2 + CH_3O + O_2$	5.5×10^{-12}		E	(11)
180. $CH_3S(O)OO + CH_3S(O)OO \rightarrow 2\ CH_3SO_2 + O_2$	6.0×10^{-12}		E	(11)
181. $CH_3S(O)OO + NO_2 \xrightarrow{M} CH_3S(O)OONO_2$	1.0×10^{-12}		E	(11)
182. $CH_3S(O)OONO_2 \xrightarrow{M} CH_3S(O)OO + NO_2$	4.2×10^{-3}		E	(9)
183. $CH_3S(O)OO + CH_3SOH \rightarrow CH_3S(O)OOH + CH_3SO$	4.0×10^{-13}		E	(11)
184. $CH_3SO_2 \xrightarrow{M} SO_2 + CH_3$	1.1×10^1	8.656×10^3	E	(6)
185. $CH_3SO_2 + O_2 \xrightarrow{M} CH_3S(O)_2OO$	2.6×10^{-18}		E	(6)
186. $CH_3S(O)_2OO \xrightarrow{M} CH_3SO_2 + O_2$	3.3×10^0		E	(6)
187. $CH_3SO_2 + NO_2 \rightarrow CH_3SO_3 + NO$	1.0×10^{-14}		E	(6)
188. $CH_3SO_2 + NO_2 \xrightarrow{M} CH_3S(O)_2NO_2$	0.0		E	(7)
189. $CH_3SO_2 + NO_3 \rightarrow CH_3SO_3 + NO_2$	1.0×10^{-14}		E	(5)
190. $CH_3SO_2 + O_3 \rightarrow CH_3SO_3 + O_2$	5.0×10^{-15}		E	(6)
191. $CH_3SO_2 + HO_2 \rightarrow CH_3SO_3 + OH$	2.5×10^{-13}		E	(6)
192. $CH_3SO_2 + CH_3O_2 \rightarrow CH_3SO_3 + CH_3O$	2.5×10^{-13}		E	(6)
193. $CH_3SO_2 + NO \xrightarrow{M} CH_3S(O)_2NO$	0.0		E	(7)
194. $CH_3SO_2 + CH_3S \rightarrow CH_3S(O)_2SCH_3$	4.2×10^{-11}		E	(5)
195. $CH_3SO_2 + CH_3SO_2 \rightarrow CH_3SO + CH_3SO_3$	7.5×10^{-12}		E	(5)

Table VII. (*continued*)

Reaction	Rate constant[a]	Activation energy (K)	Ref.*	Note*
196. $CH_3SO_2 + CH_3SNO \rightarrow CH_3S(O)_2SCH_3 + NO$	6.8×10^{-13}		E	
197. $CH_3SO_2 + OH \xrightarrow{M} CH_3SO_3H$	5.0×10^{-11}		E	(5)
198. $CH_3S(O)_2OO + NO \rightarrow CH_3SO_3 + NO_2$	1.0×10^{-11}		E	(11)
199. $CH_3S(O)_2OO + CH_3S \rightarrow CH_3SO_3 + CH_3SO$	6.0×10^{-11}		E	(11)
200. $CH_3S(O)_2OO + CH_3SO \rightarrow CH_3SO_3 + CH_3SO_2$	8.0×10^{-12}		E	(11)
201. $CH_3S(O)_2OO + CH_3SO_2 \rightarrow CH_3SO_3 + CH_3SO_3$	3.0×10^{-13}		E	(11)
202. $CH_3S(O)_2OO + HO_2 \rightarrow CH_3S(O)_2OOH + O_2$	2.0×10^{-12}		E	(11)
203. $CH_3S(O)_2OO + CH_3O_2 \rightarrow CH_3SO_3 + CH_3O + O_2$	5.5×10^{-12}		E	(11)
204. $CH_3S(O)_2OO + CH_3S(O)_2OO \rightarrow 2\,CH_3SO_3 + O_2$	6.0×10^{-12}		E	(11)
205. $CH_3S(O)_2OO + NO_2 \xrightarrow{M} CH_3S(O)_2OONO_2$	1.0×10^{-12}		E	(11)
206. $CH_3S(O)_2OONO_2 \xrightarrow{M} CH_3S(O)_2OO + NO_2$	4.2×10^{-3}		E	(9)
207. $CH_3S(O)_2OO + CH_3SOH \rightarrow CH_3S(O)_2OOH + CH_3SO$	4.0×10^{-13}		E	(11)
CH_3SO_3H Formation				
208. $CH_3SO_3 \xrightarrow{M} SO_3 + CH_3$	1.6×10^{-1}		E	(6)
209. $CH_3SO_3 + HCHO \xrightarrow{O_2} CH_3SO_3H + HO_2 + CO$	1.6×10^{-15}		E	(6)
210. $CH_3SO_3 + CH_3SCH_3 \rightarrow CH_3SO_3H + CH_3SCH_2$	6.8×10^{-14}		E	(6)
211. $CH_3SO_3 + CH_3SCH_3 \xrightarrow{M}$ Adduct	0.0		E	(6)
212. $CH_3SO_3 + HO_2 \rightarrow CH_3SO_3H + O_2$	5.0×10^{-11}		E	
213. $CH_3SO_3 + HONO \rightarrow CH_3SO_3H + NO_2$	6.6×10^{-16}		E	
214. $CH_3SO_3 + H_2O_2 \rightarrow CH_3SO_3H + HO_2$	3.0×10^{-16}		E	
215. $CH_3SO_3 + CH_3OOH \rightarrow CH_3SO_3H + CH_3O_2$	3.0×10^{-16}		E	
216. $CH_3SO_3 + CH_3OH \xrightarrow{O_2} CH_3SO_3H + HO_2 + HCHO$	1.0×10^{-16}		E	
217. $CH_3SO_3 + NO_2 \xrightarrow{M} CH_3S(O)_2ONO_2$	3.0×10^{-15}		E	(6)
218. $CH_3S(O)_2ONO_2 + H_2O \rightarrow CH_3SO_3H + HONO_2$	1.0×10^{-15}		E	(5)
219. $CH_3SO_3 + NO \xrightarrow{M} CH_3S(O)_2ONO$	3.0×10^{-15}		E	(6)
220. $CH_3S(O)_2ONO + H_2O \rightarrow CH_3SO_3H + HONO$	1.0×10^{-15}		E	(5)

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* References and notes are listed at the foot of Table IX.

Table VIII. Atmospheric photooxidation mechanism for dimethyl disulfide

Reaction	Rate constant[a]	Activation energy (K)	Ref.*	Note*
Initial Reactions				
221. $CH_3SSCH_3 + OH \longrightarrow CH_3SSCH_2 + H_2O$	0.0		E	(6)
222. $CH_3SSCH_3 + OH \longrightarrow CH_3SOH + CH_3S$	2.0×10^{-10}	-3.80×10^2	3	(6)
223. $CH_3SSCH_3 + O(^3P) \longrightarrow CH_3SO + CH_3S$	1.3×10^{-10}	-2.50×10^2	3, 8, 20	
224. $CH_3SSCH_3 + NO_3 \longrightarrow CH_3SSCH_2 + HONO_2$	0.0		E	(7)
225. $CH_3SSCH_3 + NO_3 \xrightarrow{M} CH_3S(ONO_2)SCH_3$	7.0×10^{-13}	0.0	3	(6)
226. $CH_3SSCH_3 + h\nu \longrightarrow CH_3S + CH_3S$	$5.0 \times 10^{-3}\ k_{NO_2}$		E	(6)
Adduct Reactions and other Radical Reactions				
227. $CH_3S(ONO_2)SCH_3 \xrightarrow{M} CH_3SONO_2 + CH_3S$	1.0×10^2		E	(8)
228. $CH_3S(ONO_2)SCH_3 + O_2 \longrightarrow$ Product	0.0		E	(7)
229. $CH_3SONO_2 \xrightarrow{M} CH_3SO + NO_2$	1.0×10^0		E	(8)
CH_3SOH and CH_3SO_2H Reactions				
230. $CH_3SOH + OH \longrightarrow CH_3SO + H_2O$	1.1×10^{-10}		E	(6)
231. $CH_3SOH + CH_3SO_3 \longrightarrow CH_3SO + CH_3SO_3H$	3.4×10^{-12}		E	(6)
232. $CH_3SOH + CH_3O \longrightarrow CH_3SO + CH_3OH$	3.4×10^{-12}		E	(5)
233. $CH_3SOH + O(^3P) \longrightarrow CH_3SO + OH$	3.4×10^{-12}		E	(5)
234. $CH_3SOH + NO_3 \longrightarrow CH_3SO + HONO_2$	3.4×10^{-12}		E	(5)
235. $CH_3SOH + HO_2 \longrightarrow CH_3SO + H_2O_2$	8.5×10^{-13}		E	(6)
236. $CH_3SOH + CH_3O_2 \longrightarrow CH_3SO + CH_3OOH$	8.5×10^{-13}		E	(6)
237. $CH_3SOH + NO_2 \longrightarrow CH_3SO + HONO$	0.0		E	(7)
238. $CH_3SOH + O_3 \longrightarrow CH_3SO + OH + O_2$	0.0		E	(7)
239. $CH_3SOH + CH_3SOH \longrightarrow CH_3SS(O)CH_3 + H_2O$	3.6×10^{-18}		E	
240. $CH_3SO_2H + OH \longrightarrow CH_3SO_2 + H_2O$	1.6×10^{-11}		E	(6)
241. $CH_3SO_2H + CH_3SO_3 \longrightarrow CH_3SO_2 + CH_3SO_3H$	1.0×10^{-13}		E	(6)
242. $CH_3SO_2H + CH_3O \longrightarrow CH_3SO_2 + CH_3OH$	1.0×10^{-13}		E	(5)
243. $CH_3SO_2H + O(^3P) \longrightarrow CH_3SO_2 + OH$	1.0×10^{-13}		E	(5)
244. $CH_3SO_2H + NO_3 \longrightarrow CH_3SO_2 + HONO_2$	1.0×10^{-13}		E	(5)
245. $CH_3SO_2H + HO_2 \longrightarrow CH_3SO_2 + H_2O_2$	1.0×10^{-15}		E	(5)
246. $CH_3SO_2H + CH_3O_2 \longrightarrow CH_3SO_2 + CH_3OOH$	1.0×10^{-15}		E	(5)
CH_3SO_x and $CH_3S(O)_xOO$ Reactions				
247. $CH_3S + O_2 \xrightarrow{M} CH_3SOO$	5.8×10^{-17}		E	(6)
248. $CH_3SOO \xrightarrow{M} CH_3S + O_2$	6.0×10^2		E	(6)
249. $CH_3S + NO_2 \longrightarrow CH_3SO + NO$	6.1×10^{-11}		21	(6)
250. $CH_3S + NO_2 \xrightarrow{M} CH_3SNO_2$	6.1×10^{-13}		E	(6)
251. $CH_3S + NO_3 \longrightarrow CH_3SO + NO_2$	6.4×10^{-11}		E	(5)
252. $CH_3S + O_3 \longrightarrow CH_3SO + O_2$	6.0×10^{-12}		E	(6)
253. $CH_3S + HO_2 \longrightarrow CH_3SO + OH$	3.0×10^{-11}		E	(6)

Table VIII. (*continued*)

Reaction	Rate constant[a]	Activation energy (K)	Ref.*	Note*
254. $CH_3S + CH_3O_2 \longrightarrow CH_3SO + CH_3O$	6.1×10^{-11}		E	(6)
255. $CH_3S + NO \xrightarrow{M} CH_3SNO$	2.87×10^{-11}		10	
256. $CH_3SNO + h\nu \longrightarrow CH_3S + NO$	$0.5\ k_{NO_2}$		E	
257. $CH_3S + CH_3S \xrightarrow{M} CH_3SSCH_3$	4.15×10^{-11}		11	
258. $CH_3S + CH_3SNO \longrightarrow CH_3SSCH_3 + NO$	1.4×10^{-12}		E	(6)
259. $CH_3S + OH \xrightarrow{M} CH_3SOH$	5.0×10^{-11}		E	(5)
260. $CH_3SOO + NO \longrightarrow CH_3SO + NO_2$	1.4×10^{-11}		E	(11)
261. $CH_3SOO + CH_3S \longrightarrow CH_3SO + CH_3SO$	8.0×10^{-11}		E	(11)
262. $CH_3SOO + CH_3SO \longrightarrow CH_3SO + CH_3SO_2$	9.0×10^{-12}		E	(11)
263. $CH_3SOO + CH_3SO_2 \longrightarrow CH_3SO + CH_3SO_3$	3.0×10^{-13}		E	(11)
264. $CH_3SOO + HO_2 \longrightarrow CH_3SOOH + O_2$	4.0×10^{-12}		E	(11)
265. $CH_3SOO + CH_3O_2 \longrightarrow CH_3SO + CH_3O + O_2$	5.5×10^{-12}		E	(11)
266. $CH_3SOO + CH_3SOO \longrightarrow 2\ CH_3SO + O_2$	6.0×10^{-12}		E	(11)
267. $CH_3SO \xrightarrow{M} SO + CH_3$	5.0×10^{-5}	2.52×10^{4}	E	(6)
268. $CH_3SO + O_2 \xrightarrow{M} CH_3S(O)OO$	7.7×10^{-18}		E	(6)
269. $CH_3S(O)OO \xrightarrow{M} CH_3SO + O_2$	1.7×10^{2}		E	(6)
270. $CH_3SO + NO_2 \longrightarrow CH_3SO_2 + NO$	3.0×10^{-12}		E	(6)
271. $CH_3SO + NO_2 \xrightarrow{M} CH_3S(O)NO_2$	0.0		E	(7)
272. $CH_3SO + NO_3 \longrightarrow CH_3SO_2 + NO_2$	8.0×10^{-12}		E	
273. $CH_3SO + O_3 \longrightarrow CH_3SO_2 + O_2$	2.0×10^{-12}		E	(6)
274. $CH_3SO + HO_2 \longrightarrow CH_3SO_2 + OH$	1.5×10^{-12}		E	(6)
275. $CH_3SO + CH_3O_2 \longrightarrow CH_3SO_2 + CH_3O$	3.0×10^{-12}		E	(6)
276. $CH_3SO + NO \xrightarrow{M} CH_3S(O)NO$	0.0		E	(7)
277. $CH_3SO + CH_3SO \longrightarrow CH_3S + CH_3SO_2$	7.5×10^{-12}		E	
278. $CH_3SO + CH_3SNO \longrightarrow CH_3S(O)SCH_3 + NO$	6.8×10^{-13}		E	
279. $CH_3SO + OH \xrightarrow{M} CH_3SO_2H$	5.0×10^{-11}		E	(5)
280. $CH_3S(O)OO + NO \longrightarrow CH_3SO_2 + NO_2$	8.0×10^{-12}		E	(11)
281. $CH_3S(O)OO + CH_3S \longrightarrow CH_3SO_2 + CH_3SO$	7.0×10^{-11}		E	(11)
282. $CH_3S(O)OO + CH_3SO \longrightarrow CH_3SO_2 + CH_3SO_2$	8.1×10^{-12}		E	(11)
283. $CH_3S(O)OO + CH_3SO_2 \longrightarrow CH_3SO_2 + CH_3SO_3$	3.0×10^{-13}		E	(11)
284. $CH_3S(O)OO + HO_2 \longrightarrow CH_3S(O)OOH + O_2$	3.0×10^{-12}		E	(11)
285. $CH_3S(O)OO + CH_3O_2 \longrightarrow CH_3SO_2 + CH_3O + O_2$	5.5×10^{-12}		E	(11)
286. $CH_3S(O)OO + CH_3S(O)OO \longrightarrow 2\ CH_3SO_2 + O_2$	6.0×10^{-12}		E	(11)
287. $CH_3S(O)OO + NO_2 \xrightarrow{M} CH_3S(O)OONO_2$	1.0×10^{-12}		E	(11)
288. $CH_3S(O)OONO_2 \xrightarrow{M} CH_3S(O)OO + NO_2$	4.2×10^{-3}		E	(9)
289. $CH_3S(O)OO + CH_3SOH \longrightarrow CH_3S(O)OOH + CH_3SO$	4.0×10^{-13}		E	(11)

Table VIII. (*continued*)

Reaction	Pate constant[a]	Activation energy (K)	Ref.*	Note*
290. $CH_3SO_2 \xrightarrow{M} SO_2 + CH_3$	1.1×10^{1}	8.656×10^{3}	E	(6)
291. $CH_3SO_2 + O_2 \xrightarrow{M} CH_3S(O)_2OO$	2.6×10^{-18}		E	(6)
292. $CH_3S(O)_2OO \xrightarrow{M} CH_3SO_2 + O_2$	3.3×10^{0}		E	(6)
293. $CH_3SO_2 + NO_2 \longrightarrow CH_3SO_3 + NO$	1.0×10^{-14}		E	(6)
294. $CH_3SO_2 + NO_2 \xrightarrow{M} CH_3S(O)_2NO_2$	0.0		E	(7)
295. $CH_3SO_2 + NO_3 \longrightarrow CH_3SO_3 + NO_2$	1.0×10^{-14}		E	(5)
296. $CH_3SO_2 + O_3 \longrightarrow CH_3SO_3 + O_2$	5.0×10^{-15}		E	(6)
297. $CH_3SO_2 + HO_2 \longrightarrow CH_3SO_3 + OH$	2.5×10^{-13}		E	(6)
298. $CH_3SO_2 + CH_3O_2 \longrightarrow CH_3SO_3 + CH_3O$	2.5×10^{-13}		E	(6)
299. $CH_3SO_2 + NO \xrightarrow{M} CH_3S(O)_2NO$	0.0		E	(7)
300. $CH_3SO_2 + CH_3S \longrightarrow CH_3S(O)_2SCH_3$	4.2×10^{-11}		E	(5)
301. $CH_3SO_2 + CH_3SO_2 \longrightarrow CH_3SO + CH_3SO_3$	7.5×10^{-12}		E	(5)
302. $CH_3SO_2 + CH_3SNO \longrightarrow CH_3S(O)_2SCH_3 + NO$	6.8×10^{-13}		E	
303. $CH_3SO_2 + OH \xrightarrow{M} CH_3SO_3H$	5.0×10^{-11}		E	(5)
304. $CH_3S(O)_2OO + NO \longrightarrow CH_3SO_3 + NO_2$	1.0×10^{-11}		E	(11)
305. $CH_3S(O)_2OO + CH_3S \longrightarrow CH_3SO_3 + CH_3SO$	6.0×10^{-11}		E	(11)
306. $CH_3S(O)_2OO + CH_3SO \longrightarrow CH_3SO_3 + CH_3SO_2$	8.0×10^{-12}		E	(11)
307. $CH_3S(O)_2OO + CH_3SO_2 \longrightarrow CH_3SO_3 + CH_3SO_3$	3.0×10^{-13}		E	(11)
308. $CH_3S(O)_2OO + HO_2 \longrightarrow CH_3S(O)_2OOH + O_2$	2.0×10^{-12}		E	(11)
309. $CH_3S(O)_2OO + CH_3O_2 \longrightarrow CH_3SO_3 + CH_3O + O_2$	5.5×10^{-12}		E	(11)
310. $CH_3S(O)_2OO + CH_3S(O)_2OO \longrightarrow 2\ CH_3SO_3 + O_2$	6.0×10^{-12}		E	(11)
311. $CH_3S(O)_2OO + NO_2 \xrightarrow{M} CH_3S(O)_2OONO_2$	1.0×10^{-12}		E	(11)
312. $CH_3S(O)_2OONO_2 \xrightarrow{M} CH_3S(O)_2OO + NO_2$	4.2×10^{-3}		E	(9)
313. $CH_3S(O)_2OO + CH_3SOH \longrightarrow CH_3S(O)_2OOH + CH_3SO$	4.0×10^{-13}		E	(11)
CH_3SO_3H Formation				
314. $CH_3SO_3 \xrightarrow{M} SO_3 + CH_3$	1.6×10^{-1}		E	(6)
315. $CH_3SO_3 + HCHO \xrightarrow{O_2} CH_3SO_3H + HO_2 + CO$	1.6×10^{-15}		E	(6)
316. $CH_3SO_3 + CH_3SSCH_3 \longrightarrow CH_3SO_3H + CH_3SSCH_2$	0.0		E	(6)
317. $CH_3SO_3 + CH_3SSCH_3 \xrightarrow{M}$ Adduct	0.0		E	(6)
318. $CH_3SO_3 + HO_2 \longrightarrow CH_3SO_3H + O_2$	5.0×10^{-11}		E	
319. $CH_3SO_3 + HONO \longrightarrow CH_3SO_3H + NO_2$	6.6×10^{-16}		E	

Table VIII. (*continued*)

Reaction	Rate constant[a]	Activation energy (K)	Ref.★	Note★
320. $CH_3SO_3 + H_2O_2 \longrightarrow CH_3SO_3H + HO_2$	3.0×10^{-16}		E	
321. $CH_3SO_3 + CH_3OOH \longrightarrow CH_3SO_3H + CH_3O_2$	3.0×10^{-16}		E	
322. $CH_3SO_3 + CH_3OH \xrightarrow{O_2} CH_3SO_3H + HO_2 + HCHO$	1.0×10^{-16}		E	
323. $CH_3SO_3 + NO_2 \xrightarrow{M} CH_3S(O)_2ONO_2$	3.0×10^{-15}		E	(6)
324. $CH_3S(O)_2ONO_2 + H_2O \longrightarrow CH_3SO_3H + HONO_2$	1.0×10^{-15}		E	(5)
325. $CH_3SO_3 + NO \xrightarrow{M} CH_3S(O)_2ONO$	3.0×10^{-15}		E	(6)
326. $CH_3S(O)_2ONO + H_2O \longrightarrow CH_3SO_3H + HONO$	1.0×10^{-15}		E	(5)

★ References and notes are listed at the foot of Table IX.

Table IX. Reactions common to all organosulfur reaction mechanisms: SO_x chemistry and chamber wall reactions

Reaction	Rate constant[a]	Activation energy (K)	Ref.	Note
SO_x Reactions				
327. $SO + O_2 \longrightarrow SO_2 + O(^3P)$	6.7×10^{-17}	2.275×10^3	3	
328. $SO + NO_2 \longrightarrow SO_2 + NO$	1.4×10^{-11}		3	
329. $SO + O_3 \longrightarrow SO_2 + O_2$	8.9×10^{-14}	1.17×10^3	3	
330. $SO + O(^3P) \xrightarrow{M} SO_2$	2.2×10^{-11}		12	
331. $SO + OH \xrightarrow{O_2} SO_2 + HO_2$	1.1×10^{-10}		12	
332. $SO + SO_3 \longrightarrow SO_2 + SO_2$	2.0×10^{-15}		12	
333. $SO_2 + OH \xrightarrow{M} HOSO_2$	1.1×10^{-12}	-2.31×10^2	3, 17	(12)
334. $SO_2 + O(^3P) \xrightarrow{M} SO_3$	3.4×10^{-14}	1.0×10^3	6, 17	
335. $SO_2 + HO_2 \longrightarrow SO_3 + OH$	1.0×10^{-18}		2, 3	
336. $SO_2 + CH_3O_2 \longrightarrow CH_3O + SO_3$	5.0×10^{-17}		2, 3	
337. $SO_2 + CH_3O \xrightarrow{M} CH_3OSO_2$	5.5×10^{-13}		7	
338. $SO_2 + CH_3 \xrightarrow{M} CH_3SO_2$	2.9×10^{-13}		12	
339. $SO_2 + h\nu \longrightarrow SO_2^*$	$2.0\ k_{NO_2}$		12	
340. $SO_2^* \xrightarrow{M} SO_2$	3.7×10^6		12	
341. $SO_2^* + SO_2 \longrightarrow SO_3 + SO$	6.3×10^{-13}		12	
342. $SO_2^* + CO \longrightarrow SO + CO_2$	1.1×10^{-14}		12	
343. $HOSO_2 + O_2 \longrightarrow SO_3 + HO_2$	4.0×10^{-13}	1.0×10^3	3, 17	
344. $HOSO_2 + OH \xrightarrow{M} H_2SO_4$	1.0×10^{-11}		E13[b]	
345. $SO_3 + H_2O \xrightarrow{M} H_2SO_4$	9.1×10^{-13}		2, 17	
346. $SO_3 + O(^3P) \longrightarrow SO_2 + O_2$	7.0×10^{-13}		28	
Wall Effects				
347. $CH_3SCH_3 \longrightarrow$ Wall	1.5×10^{-6}		23	
348. $CH_3SSCH_3 \longrightarrow$ Wall	1.6×10^{-6}		23	
349. $SO_2 \longrightarrow$ Wall	3.0×10^{-6}		23	
350. $O_3 \longrightarrow$ Wall	4.5×10^{-6}		23	
351. $HNO_3 \longrightarrow$ Wall	5.8×10^{-5}		16	
352. $NO_2 + H_2O +$ Wall $\longrightarrow HONO$	6.8×10^{-24}		19	
353. $NO_2 +$ Wall $\longrightarrow HONO$	6.5×10^{-7}		19	
354. $N_2O_5 +$ Wall (or aerosol) $\longrightarrow 2\ HONO_2$	8.3×10^{-3}		E	

[a] Rate constants are at 298 K, 1 atm in units of molecule, cm^3 and sec. See Part II for detailed discussion.

[b] 'E' is used to indicate the rate constant was estimated in the reference whose number follows 'E'. In the absence of a number following 'E', the rate constant has been estimated in the present work.

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1. Atkinson *et al.* (1980); 2. Atkinson and Lloyd (1984); 3. Atkinson *et al.* (1989); 4. Balla and Heicklen (1984); 5. Baulch *et al.* (1982); 6. Baulch *et al.* (1984); 7. Calvert and Stockwell (1984); 8. Cvetanović *et al.* (1981); 9. Demore *et al.* (1982); 10. Balla *et al.* (1986); 11. Graham *et al.* (1964a); 12. Graedel (1977); 13. Graedel (1979); 14. Barnes *et al.* (1986b); 15. Schäfer *et al.* (1978); 16. Grosjean (1985); 17. Kerr and Calvert (1984); 18. Leone and Seinfeld (1984); 19. Leone *et al.* (1985); 20. Nip *et al.* (1981); 21. Tyndall and Ravishankara (1988); 22. Veltwisch *et al.* (1980); 23. Yin *et al.* (1990); 24. Veyret *et al.* (1989); 25. Burrows *et al.* (1989); 26. Vaghjiani and Ravishankara (1989); 27. Wallington *et al.* (1986b); 28. Calvert *et al.* (1978).

Notes:

1. k_{NO_2} was estimated theoretically (Demerjian *et al.*, 1980) for simulation of the experiments. See Part II for discussion.
2. The rate constant data of reaction between HO_2 and HO_2 were fit by the expression (Atkinson and Lloyd, 1984),

$$k = [2.2 \times 10^{-13} \exp(620/T) + 1.9 \times 10^{-33} [M] \exp(980/T)] \times [1 + 1.4 \times 10^{-21} [H_2O] \exp(2200/T)]$$

cm^3 molecule^{-1} s^{-1}, which can be expressed by reactions of (16)–(19).

3. Reaction (14) is the combination of the following three reactions,

$$O_3 + h\nu \rightarrow O(^1D) + O_2$$
$$O(^1D) + O_2 \rightarrow O(^3P) + O_2$$
$$O(^1D) + H_2O \rightarrow 2\,OH$$

4. CH_3ONO is assumed to have the same photolysis rate as HONO
5. The system reactivity and the product distribution are not sensitive to the values of these reactions.
6. See text of Part I and II for detailed discussion.
7. These reactions are assumed to be negligible.
8. These unimolecular reactions are assumed to decompose rapidly and the simulations are not sensitive to them.
9. These unimolecular reactions are assumed to decompose rapidly, however, the system reactivity and the product distribution are sensitive to these rate constants, which are estimated mainly based on the product studies.
10. The rate constants are estimated from the similar reactions of R + O_2.
11. These rate constants are basically estimated from the corresponding reactions of similar peroxy radicals. Also the structural difference of the peroxy radicals is considered.
12. The temperature coefficient, which is a function of the total pressure, has been expressed for the temperature range 200–300 K by Kerr and Calvert (1984) as

$$-(E/R)/K = 3.6896 \times 10^{-4} \times (P/\mathrm{Torr})^2 - 6.793 \times 10^{-1} \times (P/\mathrm{Torr}) + 5.3374 \times 10^2.$$

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