Thermochemistry and Reaction Paths for Dimethyl Sulfide Radical with O2

Fei Jin and Joseph w Bozzelli

Chemistry, New Jersey Institute of Technology, Newark, NJ 07102

Abstract

The thermo property data on CH_3SCH_2OOH and two radicals $CH_3SCH_2OO\cdot$ and $C\cdot H_2SCH_2OOH$ are important to understand the stability, reaction paths and kinetics of reactions of sulfur hydrocarbons (sulfides) in atmospheric and combustion processes. Thermochemical properties for species and transition states in the methylthiomethyl ($CH_3SC\cdot H_2$) radical + O_2 reaction system are analyzed to evaluate reaction paths and kinetics. Isodesmic working reaction are employed to determine enthalpies of formation ($\Delta H_f^o{}_{298}$) using density functional (B3LYP/6-311G(d,p)) and complete basis set (CBS-QB3) computational methods. Entropy ($S°_{298}$) and heat capacities $C_p(T)$ ($300 \leq T/K \leq 1500$) are determined using geometric parameters and vibration frequencies obtained at B3LYP/6-311G(d,p) level of theory. $\Delta H_f^o{}_{298}$ values estimated at the CBS-QB3 level (unit in kcal/mol): $CH_3SC\cdot H_2$ (32.66±0.50), CH_3SCH_2OOH(–29.14±0.12), $CH_3SCH_2OO\cdot$ (5.17±0.36), $C\cdot H_2SCH_2OOH$ (11.48±1.44). Quantum Rice-Ramsperger-Kassel(QRRK) analysis is used to calculate energy- dependent rate constants, $k(E)$ and master equation analysis is used to account for collisional stabilization of adduct and isomer. The methylthiomethyl radical adds to O_2 to form a methylperoxy racial with a 37.82 kcal/mol well depth. The peroxy radical can undergo dissociation back to reactants, isomerize via hydrogen shift (TS1,E_a=17.06kcal/mol) to form a hydroperoxide methyl radical $C\cdot H_2SCH_2OOH$, decompose via hydrogen transfer (TS2, E_a=37.79kcal/mol) to form $CH_3SC(=O)H$ plus OH radical , or the peroxy radical can also attack the sulfur atom via TS3(E_a=32.92kcal/mol) to form $CH_3S(=O)$ + CH_2O. The $C\cdot H_2SCH_2OOH$ isomer can decompose via TS4 (E_a=24.09kcal/mol) to CH_2O+CH_2S+OH, or through a four-member ring transition state (TS5, E_a =30.77kcal/mol) to form 1,3-Oxathietane + OH.

Introduction

Dimethyl sulfide (DMS) has been recognized as the main natural source of sulfur in the atmosphere[1], which emitted into the atmosphere over the global oceans has a range of effects upon atmospheric composition (mediated through various oxidation products) that may be significant with regard to issues as important as climate regulation. The roles played by DMS oxidation products within these contexts are diverse and complex, and in many instances are not well understood.

At present, the main step of the DMS oxidation in the atmosphere is the reaction with OH radical during daylight and the reactions with NO_3 radical and Cl radical, which will lead to the formation of the $CH_3SC\cdot H_2$ radical.

The $CH_3SCH_2OO\cdot$ peroxy radical is an important intermediate in the atmospheric degradation of dimethyl sulfide. The $CH_3SCH_2OO\cdot$ peroxy radical is produced through the addition of O_2 to the CH_3SCH_2 radical.

$$CH_3SC\cdot H_2 + O_2 \rightarrow CH_3SCH_2OO\cdot$$

It is believed that the reaction of the $CH_3SCH_2OO\cdot$ with the HO_2 radical will lead to the following products:

$$CH_3SCH_2OO\cdot + HO_2 \rightarrow CH_3SCH_2OOH + O_2$$

In this chapter, reaction pathways of the addition of O_2 atoms to $CH_3SC\cdot H_2$ radical are analyzed. CBS-QB3 and density functional methods are utilized estimate thermodynamic properties ($\Delta\Delta H_f^o{}_{298}$, $S°_{298}$ and $C_p(T)$) for reactant $CH_3SC\cdot H_2$, intermediate radicals $CH_3SCH_2OO\cdot$, $C\cdot H_2SCH_2OOH$ and transition states:

TS1: $\overbrace{CH_3SCH_2OO\cdot}$ Intramolecular hydrogen shift to form a hydroperoxy radical.

TS2: $CH_3S\overbrace{CH_2OO\cdot}$ Intramolecular hydrogen shift to form $CH_3S\cdot CHOOH$ radical, and $CH_3S\cdot CHOOH$ rapidly dissociates $CH_3SC(=O)H$ + OH.

TS3: $CH_3\overbrace{SCH_2OO\cdot}$ The peroxy radical can also attack the sulfur atom form $CH_3S(=O)H$ + CH_2O.

TS4: $C\cdot H_2S$-CH_2O-OH β,γ-scission reaction to form a thioformaldehyde plus a formaldehyde and OH.

TS5: $\overbrace{CH_2SCH_2O}$-OH 1,3-Oxathietane + OH.

Isodesmic working reactions are applied to evaluate enthalpies of formation. Contributions to entropy and heat capacities from internal rotation are estimated using direct integration over energy level of the intermolecular rotation potential energy curve, with B3LYP/6-311g(d,p) level calculations for rotation barrier. Activation energies for the transition states are determined and the kinetic analysis is detailed on the base of the thermodynamic properties.

Quantum Rice-Ramsoerger-Kassel (QRRK) analysis is used to calculate the energy dependent rate constant $k(E)$, and master equation analysis is applied to account for collisional stabilization in the $CH_3SCH_2\cdot$ + O_2 adduct and isomers. The thermochemical and kinetic data at relevant pressures and temperatures should be useful to both atmospheric and combustion models

Calculation Methods

Density functional B3LYP/6-311g(d,p) is utilized to calculate structures and vibrational frequencies and potentials for internal rotors. CBS-QB3 methods are utilized to calculate enthalpy in working reaction analysis.

Entropy ($S^o{}_{298}$) and Heat Capacities($C_p(T)$, $300 \leq T/K \leq 1500$)

Entropies and heat capacities (T) were calculated using the rigid – rotor-harmonic – oscillator approximation based on scaled vibrational frequencies and moments of inertia of the optimized BLYP/6-311G(d,p) structures. Contribution to entropy and heat capacity from internal rotation are determined using Pitzer et al,'s treatment based on rotational barrier height and corresponding moments of inertia for the rotors.

High-Pressure Limit *A* Factors(*A*) and Rate Constant (k_∞)

For the reactions where thermochemical properties of transition states are calculated by density functional methods and CBS-QB3 methods. k_∞ values are fit by three parameters, A, n, and E_a over the temperature range from 200k to 2000k, expressed by:

$$k_\infty = A(T)^n \exp(-E_a/RT)$$

Activation energies of reactions are calculated as follows:

$$E_a = [\Delta H_f^o{}_{298,TS} - \Delta H_f^o{}_{298,reactant}]$$

Entropy differences between reactant and transition state are used to determine the pre-exponential factor A, via classical, cannonical TST for a unimolecular reaction, $A = (\kappa_b T/h_p)\exp(\Delta S^{\neq}/R)$ where h_p is the Planck constant and κ_b is Boltzman's constant.

Results and Discussion

Enthalpies of Formation ($\Delta H_f^o{}_{298}$)

The enthalpies of formation ($\Delta H_f^o{}_{298}$) are estimated using total energies and calculated ΔH_{rxn298} for the listed reactions. The total

energies are determined at the CBS-QB3 level; scaled ZPVE's and thermal corrections to 298.15K are listed in Table 1.2.

Thermochemical Kinetic Analysis of the Reaction $CH_3SC{\cdot}H_2 + O_2 \rightarrow (CH_3SCH_2OO{\cdot})^* \rightarrow$ Products

A potential energy diagram for the methylthiomethyl radical with O2 is illustrated in Figure 1.6; energies are calculated at the CBS-QB3 level. Addition of oxygen to the $CH_3SC{\cdot}H_2$ radical forms an energized adduct.

$$CH_3SC{\cdot}H_2 + O_2 \rightarrow CH_3SCH_2OO{\cdot}^* \rightarrow \text{Products}$$

Possible reactions for this activated adduct are described as follows:

Rxn1: $CH_3SCH_2OO{\cdot}^* \rightarrow$ rev rxn - to reactants $CH_3SC{\cdot}H_2 + O_2$

Rxn2: Stabilization ($CH_3SCH_2OO{\cdot}^* \rightarrow CH_3SCH_2OO.$)

Rxn3: Hydrogen atom shift from the methyl group to form a hydroperoxide methyl radical:

$$CH_3SCH_2OO{\cdot}^* \rightarrow C{\cdot}H_2SCH_2OOH \text{ isomer (TS1).}$$

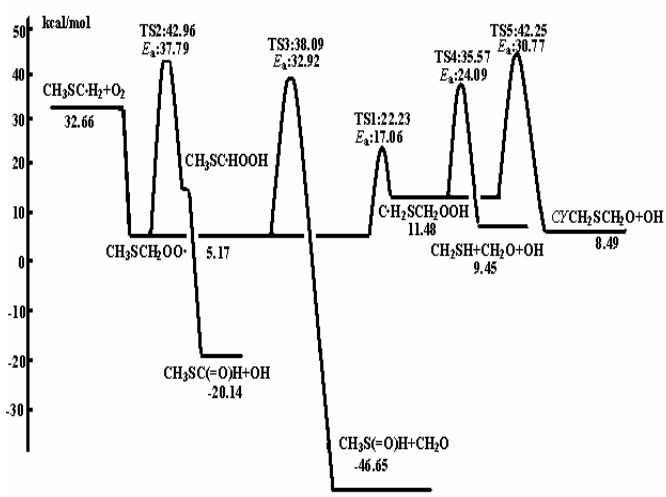
Rxn4: Hydrogen atom transfer from peroxy carbon (TS2)

$$CH_3SCH_2OO{\cdot}^* \rightarrow CH3SC{\cdot}HOOH \rightarrow CH_3SC(=O)H + OH$$

Note CH3SC·HOOH is unstable and immediately dissociates to $CH_3SC(=O)H$ plus OH radical (TS2)

Rxn5: The peroxy radical can also attack the sulfur atom to form a cyclic transition state structure (TS3, a 4-member ring) where the relatively strong S=O bond (near double bond) starts to form; and the weak (SO—OC) peroxide bond in the transition state starts to cleave (ring opening). The initial product from this reaction: a radical intermediate $CH_3S(=O)CH_2O{\cdot}$ will undergo beta scission (carbonyl formation) resulting in $CH_3S(=O) + CH_2O$

The methylthiomethyl radical ($\Delta H_f^o{}_{298}$ =32.66 kcal/mol) adds to O_2 to form $CH_3SCH_2OO{\cdot}$ peroxy radical. The activation energy of TS1 is 17.06 kcal/mol, and TS1 is below the reactants. The $\Delta H_f^o{}_{298}$ for the $CH_3SC{\cdot}HOOH$ radical in Reaction VI are estimated on the base of the result of $C{\cdot}H_2SCH_2OOH$ and their difference of total energy calculated under MP2/6-31G(d,p) level. The activated $CH_3SCH_2OO{\cdot}^*$ adduct crossed TS2, which then undergoes OH elimination to form $CH_3SC(=O)H$, with the barrier 37.79kcal/mol. Reaction V has a barrier of 32.92 kcal/mol.



$CH_3SCH_2OO{\cdot} \rightarrow$ Products

The energized $C{\cdot}H_2SCH_2OOH$ can undergo four different reactions, which include reverse reaction back to $CH_3SCH_2OO{\cdot}$ radical, stabilization, CH_2S+CH2O+OH forming through TS4 and reaction through a four-member ring transition state (TS5) to form 1,3-Oxathietane + OH. The activation energy of TS4 and TS5 are respectively 24.09 and 30.77 kcal/mol, based on the CBS-QB3 level of theory.

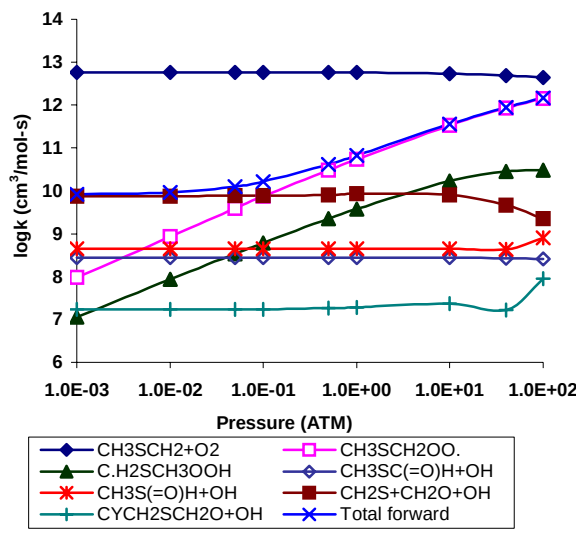
High-Pressure Limit Rate Constants,
- Input Parameters for QRRK Calculations

	Reaction	$A(s^{-1})$	n	E_a (kcal/mol)
k_1	$CH_3SC{\cdot}H_2 + O_2 \rightarrow CH_3SCH_2OO{\cdot}$	5.82E+12	0.00	0.00
k_{-1}	$CH_3SCH_2OO{\cdot} \rightarrow CH_3SC{\cdot}H_2 + O_2$	4.28E+14	0.00	26.90
k_2	$CH_3SCH_2OO{\cdot} \rightarrow C{\cdot}H_2SCH_2OOH$	1.2231E+07	1.20	17.06
k_{-2}	$C{\cdot}H_2SCH_2OOH \rightarrow CH_3SCH_2OO{\cdot}$	7.5535E+10	-0.26	10.75
k_3	$CH_3SCH_2OO{\cdot} \rightarrow CH_3SC(=O)H + OH$	8.3158E+09	0.92	37.79
k_4	$CH_3SCH_2OO{\cdot} \rightarrow CH_3S(=O)H + CH_2O$	1.7013E+10	0.53	32.92
k_5	$C{\cdot}H_2SCH_2OOH \rightarrow CH_2S$+CH2O+OH	6.4507E+13	-0.47	24.09
k_6	$C{\cdot}H_2SCH_2OOH \rightarrow CYCH_2SCH_2O$+OH	3.7282E+13	-0.70	30.77

Lennard-Jones paramenters : σ =5.54Å,ϵ/k=460 Geometric mean frequency (from CPFIT, :
$CH_3SCH_2OO{\cdot}$ (904.0cm^{-1} ×22.5), $C{\cdot}H_2SCH_2OOH$(736.9 cm^{-1} ×23.0)

k_{-1}, k_{-2} : microscopic reversibility

CH3SCH2. + O2 => Products



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