

# Thermodynamic Study and Oxidation Products for the Reaction of Methyl Ethyl Sulfide $\text{CH}_3\text{SCH}_2\text{CH}_3$ with $\text{O}_2$ at Standard Conditions.

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## Abstract

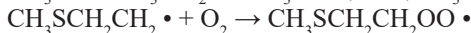
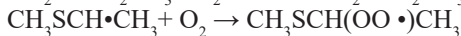
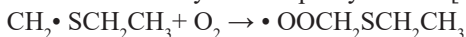
Entropy and Gibbs free energy change for all possible reaction pathways of oxidation of radicals of methyl ethyl sulfide were calculated. Enthalpy change for the reaction pathways was also calculated and compared to the values calculated using CBS-QB3 DFT method. Energetically favorable products for the oxidation of radicals of methyl ethyl sulfide at 298 K and 1 atm pressure, and under high temperatures were determined.

## Introduction

Methyl ethyl sulfides are used in organic synthesis and scientific research. These compounds have a negative effect on the atmosphere and the environment by generating sulfuric oxides [1]. Understanding the oxidation of sulfur compounds is important for the reduction and the prevention of sulfur oxides, as they are harmful to human health, building, and the environment [2]. Due to biological activity in the sea, a significant amount of ethyl methyl sulfide is emitted, the concentration of ethyl methyl sulfide in the atmosphere is the result of anthropogenic and human activity. 3. Methyl ethyl sulfides has a negative effect on the atmosphere as it produces sulfuric oxides in the environment. 4. Recent studies show that the partial oxidation of methyl ethyl sulfide begins with the abstraction of a hydrogen atom from each of its carbon sites [5,6,7-9].



The unstable radical products would subsequently be oxidized and form unstable alkyl sulfide proxy radicals [3,8].



The reaction pathway for oxidation of each radical,  $\text{CH}_2 \cdot \text{SCH}_2\text{CH}_3$ ,  $\text{CH}_3\text{SCH} \cdot \text{CH}_3$ , and  $\text{CH}_3\text{SCH}_2\text{CH}_2 \cdot$  has been studied.

The study of methyl ethyl sulfide oxidation products is of value to know the fate of its oxidation products in the atmosphere. In the past several studies were conducted to detect and identify the oxidation products ethyl methyl sulfide at different reaction conditions.

In 2012, studies made by Gabriela Oksdath-Mansilla group show that hydroxyl radical initiated oxidation of ethyl methyl sulfide at 1 atm pressure and 298 K in a borosilicate glass photoreactor and quartz-glass photoreactor in synthetic air, yielded  $51 \pm 2\%$   $\text{SO}_2$ ,  $46 \pm 4\%$   $\text{HCHO}$ ,  $57 \pm 3\%$   $\text{CH}_3\text{CHO}$  and  $0.07\%$   $\text{OCS}$ . And the Photooxidation products by OH in the presence of oxygen at atmospheric pressure of diethyl sulfide are  $50 \pm 3\%$   $\text{SO}_2$ ,  $91 \pm 3\%$   $\text{CH}_3\text{CHO}$  and  $0.14\%$   $\text{OCS}$ , and of dimethyl sulfide are  $80 \pm 10\%$   $\text{SO}_2$  (Barnes et al. 1996),  $90 \pm 6\%$   $\text{HCHO}$ ,  $0.7\% \pm 0.2\%$   $\text{OCS}$ , and  $95 \pm 4\%$   $\text{SO}_2$  (Arsene et al., 1999) [7].

In 2010, studies made by Zheng and Bozzelli show that pyrolysis and oxidation of ethyl methyl sulfide at  $630\text{--}740^\circ\text{C}$  and 1 atm pressure in a turbulent flow reactor, yielded ethylene, methane, and ethane at significant level, other species were also formed and detected, carbon dioxide, carbon monoxide, formaldehyde, and sulfur dioxide [18].

Three thermodynamic quantities can be used to predict the spontaneity of a reaction, therefore predict the favored products formed at certain set of conditions, e.g. standard conditions 298 K and 1 atm pressure, these thermodynamic quantities can also be used to predict favored products at different temperatures. These thermodynamic quantities are standard enthalpy change ( $\Delta H_{\text{rxn}}$ ), Standard entropy change ( $\Delta S_{\text{rxn}}$ ), and standard Gibbs free energy change ( $\Delta G_{\text{rxn}}$ ) for a reaction. It's known that if the sign for both calculated standard enthalpy change and standard entropy change for a reaction are negative, regardless of the sign of calcu-

lated Gibbs free energy change for the reaction, the reaction would be spontaneous only at low temperatures, therefore the reaction would favor the formation of products only at low temperatures. If the sign for both calculated standard enthalpy change and standard entropy change for a reaction are positive, regardless of the sign of calculated Gibbs free energy change for the reaction, the reaction would be spontaneous only at high temperatures. If the sign for the calculated standard enthalpy change for a reaction is negative, the sign for the calculated standard entropy change for a reaction is positive, and the sign for the calculated Gibbs free energy change for the reaction is negative, the reaction would be spontaneous at all temperatures. If the sign for the calculated standard enthalpy change for a reaction is positive, the sign for the calculated standard entropy change for a reaction is negative, and the sign for the calculated Gibbs free energy change for the reaction is positive, the reaction would be non-spontaneous at all temperatures, therefore the reaction wouldn't favor the formation of products at all temperatures [13].

Enthalpy of reaction (H) is a thermodynamic quantity and it's the heat involved in chemical or physical change at constant temperature and pressure.,  $q = \Delta H$ . Standard enthalpy change for a reaction ( $\Delta H^{\circ}_{rxn}$ ), can be calculated using tabulated standard enthalpy of formation of species involved in the reaction at 25°C and 1 atm pressure,

$$\Delta H_{rxn}^{\circ} = \sum n \Delta H_f^{\circ} (\text{products}) - \sum m \Delta H_f^{\circ} (\text{reactants}) \quad [14].$$

Entropy (S) is a measure of entropy dispersal of a system and it's another is a thermodynamic quantity. In a spontaneous process, entropy of system and the surroundings would increase, energy has been dispersed. Entropy change for a reaction ( $\Delta S^{\circ}_{rxn}$ ) can be calculated using from standard entropy values of reactants and products,

$$\Delta S_{rxn}^{\circ} = \sum n \Delta S^{\circ} (\text{products}) - \sum m \Delta S^{\circ} (\text{reactants}) \quad [15].$$

Standard free energy change ( $\Delta G^{\circ}$ ), it's free energy change that occurs when products in their standard states are formed from reactants in their standard states. Standard states refers to 1 atm partial pressure, for gases, 1M concentration for solutions, 1 atm pressure for solutions and liquids, and the temperature is 25°C or 298K. The standard free energy for a reaction can be calculated using the equation,

$$\Delta G^{\circ}_r = \Delta H^{\circ} - T \Delta S^{\circ} \quad [16]$$

Free radicals are ions, molecules or atoms containing at least one unpaired electron in the valance shell. These unpaired valance electrons make radicals unstable and chemically reactive. Most radicals have short lifetimes. Radicals can be generated by an ionizing radiation, electrical discharge, electrolysis, and heat. In many chemical reactions, free radicals are intermediates. Free radicals are important in many chemical processes, atmospheric chemistry, combustion, polymerization, plasma chemistry and biochemistry [17].

## Calculation Methods

Standard entropy and Standard Gibbs free energy change for possible pathways of oxidation of methyl ethyl sulfide radicals has been calculated using the method described in the introduction and the calculated values are used to predict the spontaneity of reaction pathways and are also used to determine thermionically favored products at 25°C/ 298 K and 1 atm pressure.

## Results and Analysis

The calculated enthalpy change for the reaction were comparable to the calculated enthalpy change for the reaction using CBS-QB3 DFT method, with values differing in range of 0.1- 3.3 Kcal/mol, indicating that the CBS-QBS DFT method is an accurate method in calculating enthalpy change for a reaction.

The standard entropy change for possible pathways of oxidation of methyl ethyl sulfide radicals has been calculated using thermochemical properties for species involved and previously calculated using CBS-QB3 DFT method. The standard entropy change for reaction pathways 1-11 are 58, 41.5, 1.7, 20.9, 54.6, 20.7, 41.4, 27.7, 87.3, 55.6, and 53.3 cal/mol.K, table 1.

The standard Gibbs free energy change for possible pathways of oxidation of methyl ethyl sulfide radicals has been calculated using thermochemical properties for species involved and previously calculated using CBS-QB3 DFT method. The standard Gibbs free energy change for reaction pathways 1-11 are 26.2, 15.3, -23.7, -55.9, -23.2, 1.4, 7.6, 37.9, -33.0, -8.0, and -69.2 kcal/mol, table 1.

For a reaction to spontaneous and form Energetically favorable product at all temperatures, the sign of both enthalpies change of the reaction and Gibbs free energy of reaction must be negative and the sign of entropy change of the reaction must be positive. Reaction pathway numbers 3,4,5, 9 and 11 show a negative sign for both the calculated standard enthalpy and standard Gibbs free energy change for the reaction, but a positive sign for entropy change for reactions, therefore, these reaction pathways occur spontaneously at all temperatures including standard conditions, and the reactions would favor the formation of products.

Reaction pathway numbers 1,2,6,7, and 8 show a positive sign for all calculated thermolytic properties; standard entropy, standard enthalpy, and standard Gibbs free energy change for the reaction pathways, therefore, these reaction pathways are spontaneously only at high temperatures. These reaction pathways are nonspontaneous at standard conditions. Reaction pathway numbers 10, show a positive sign for calculated standard entropy and standard enthalpy change for the reaction, but a negative sign for the calculated standard Gibbs free energy change for the reaction, therefore, this reaction pathway is also spontaneously only at high temperatures, and non-spontaneous at standard conditions.

The Energetically favorable oxidation products formed at standard conditions, 1 atm pressure and 298K, are Acetaldehyde

(CH<sub>3</sub>CH=O), Thioformaldehyde (CH<sub>2</sub>=S), Thio-acetaldehyde (CH<sub>3</sub>CH=S), Formaldehyde (CH<sub>2</sub>=O). And some short lived, unstable and reactive radicals, CH<sub>3</sub>S•=O, CH<sub>3</sub>CH<sub>2</sub>S•=O, CH<sub>3</sub>S(=O)CH<sub>2</sub>CO•, and OH are also formed under standard conditions.

Two of these products, Acetaldehyde (CH<sub>3</sub>CH=O) and Formaldehyde (CH<sub>2</sub>=O) were identified as major photooxidation products of ethyl methyl sulfide at atmospheric pressure, it was found that 46 ± 4 % of CH<sub>2</sub>=O and 57±3 % of CH<sub>3</sub>CH=O was present in the reaction mixture in 2012. 7.

The Energetically favorable oxidation products formed at 1 atm pressure and at high temperatures are Ethylene (CH<sub>2</sub>=CH<sub>2</sub>), Thioformaldehyde (CH<sub>2</sub>=S), S=CHCOOH, and CH<sub>2</sub>=CHOOH and some short-lived stable radicals, HO<sub>2</sub>, CH<sub>3</sub>•, HOOCH<sub>2</sub>S•, and CH<sub>3</sub>S•. are also formed at high temperatures.

Two of these products, Ethylene (CH<sub>2</sub>=CH<sub>2</sub>), and water (H<sub>2</sub>O) were identified as products of pyrolysis and oxidation of ethyl methyl sulfide at 630-740° C and at 1 atm pressure in 2010. 18,

**Table1: Calculated Entropy and Gibbs Free Energy Change for All Possible Pathways of Oxidation of Methyl Ethyl Sulfide Radicals.**

Number	Reaction Pathway	CBS-QB3 ΔH <sub>rxn</sub> <sup>a</sup>	Calculated ΔH <sub>rxn</sub> <sup>a</sup>	Calculated ΔS <sub>rxn</sub> <sup>b</sup>	Calculated ΔG <sub>rxn</sub> <sup>a</sup>
Reaction 1	CH <sub>3</sub> SCH <sub>2</sub> CH <sub>2</sub> • + O <sub>2</sub> → C <sub>3</sub> SCH <sub>2</sub> CH <sub>2</sub> OO•  CH <sub>2</sub> •SCH <sub>2</sub> COOH → → CH <sub>2</sub> =CH <sub>2</sub> + HO <sub>2</sub> + CH <sub>2</sub> =S	28.2	31.5	58	26.2
2	CH <sub>3</sub> SCH•COOH → CH <sub>3</sub> • + S=CHCOOH	27.7	27.2	41.5	15.3
3	CH <sub>3</sub> SCH <sub>2</sub> COO• → CH <sub>3</sub> S(=O) CH <sub>2</sub> CO•	-23.2	-23.1	1.7	-23.7
Reaction	CH <sub>2</sub> •SCH <sub>2</sub> CH <sub>3</sub> + O <sub>2</sub> → •OOCH- 2SCH <sub>2</sub> CH <sub>3</sub>				
4	•OOCH <sub>2</sub> SCH <sub>2</sub> CH <sub>3</sub> → CH 2 = O + CH <sub>3</sub> CH <sub>2</sub> S• = O	-49.7	-49.7	20.9	-55.9
5	HOOCH <sub>2</sub> SCH•CH <sub>3</sub> → CH <sub>2</sub> CH = S CH <sub>2</sub> = O + OH	-6.9	-6.9	54.6	-23.2
6	HOOCH <sub>2</sub> SCH <sub>2</sub> CH <sub>2</sub> • → HOOCH <sub>2</sub> S• + CH <sub>2</sub> = CH <sub>2</sub>	9.0	9.0	20.7	1.4
7	HOOCH <sub>2</sub> S• → HO <sub>2</sub> + CH <sub>2</sub> = S	19.9	20.9	41.4	7.6
8	•OOCSCC → CH <sub>2</sub> •OO• + CH <sub>3</sub> CH <sub>2</sub> S•	46.2	47.8	27.7	37.9
Reaction	CH <sub>3</sub> SCH•CH <sub>3</sub> + O <sub>2</sub> → CH <sub>3</sub> SCH(OO•) CH <sub>3</sub>				
9	CH <sub>2</sub> •SCH(OOH)CH <sub>3</sub> → CH <sub>2</sub> =S+ CH <sub>3</sub> CH=O + OH	-7.0	-7.4	87.3	-33.0

10	$\text{CH}_3\text{SCH}(\text{OOH})\text{CH}_2\bullet \rightarrow \text{CH}_3\text{S}\bullet + \text{CH}_2=\text{CHOOH}$	8.5	8.5	55.6	-8.0
11	$\text{CH}_3\text{SCH}(\text{OO}\bullet)\text{CH}_3 \rightarrow \text{CH}_3\text{CH}=\text{O} + \text{CH}_3\text{S}\bullet=\text{O}$	-53.3	-53.3	-53.3	-69.2
<b>bc/mol.K</b>					

## Summary and Conclusion

Three thermodynamic quantities are used to predict the spontaneous reaction pathways and the reaction pathways that energetically favors products at standard conditions, Gibbs free change for reaction, standard enthalpy change for reaction, and standard entropy change for reaction. The energetically favorable stable products formed from oxidation of ethyl methyl sulfide at standard conditions, 298 K and 1 atm pressure are acetaldehyde ( $\text{CH}_3\text{CH}=\text{O}$ ), thioformaldehyde ( $\text{CH}_2=\text{S}$ ), thio-acetaldehyde ( $\text{CH}_3\text{CH}=\text{S}$ ), and formaldehyde ( $\text{CH}_2=\text{O}$ ). The favored reactive and unstable radicals formed under standard conditions are  $\text{CH}_3\text{S}\bullet=\text{O}$ ,  $\text{CH}_3\text{CH}_2\text{S}\bullet=\text{O}$ ,  $\text{CH}_3\text{S}(=\text{O})\text{CCO}\bullet$ , and OH. The energetically favorable stable products formed from oxidation of ethyl methyl sulfide at high temperatures and 1 atm pressure are Ethylene ( $\text{CH}_2=\text{CH}_2$ ), Thioformaldehyde ( $\text{CH}_2=\text{S}$ ),  $\text{S}=\text{CHCOOH}$ , and  $\text{CH}_2=\text{CHOOH}$ , the favored reactive and unstable radicals formed at high temperatures and 1 atm pressure are  $\text{HO}_2$ ,  $\text{CH}_3\bullet$ ,  $\text{HOOCH}_2\text{S}\bullet$ , and  $\text{CH}_3\text{S}\bullet$ .

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