ISSN: 2639-7455

Review Article

Earth & Environmental Science Research & Reviews

Thermodynamic Study and Oxidation Productsfor the Reaction of Methyl Ethyl Sulfide $CH_3SCH_2CH_3$with O_2 at Standard Conditions.

*Hebah Abdel-Wahab,Tamara Gund

*Delaware County College, 901 Media Line Rd, Media, PA 19063. New Jersey Institute of Technology, Newark

*Corresponding author
Hebah Abdel-Wahab, Delaware County College, 901 Media Line Rd, Media, PA 19063. New Jersey Institute of Technology, Newark.

Submitted: 04 Mar 2022;Accepted: 16 Mar 2022;Published: 20 Mar 2022.

Citation: *Hebah Abdel-Wahab, Tamara Gund (2022) Thermodynamic Study and Oxidation Products for the Reaction of Methyl Ethyl Sulfide $CH_3SCH_2CH_3$ with O_2 at Standard Conditions, Eart &Envi Scie Res & Rev. 5(1): 01-05.*

Abstract
Entropyand Gibb's free energy change for all possible reaction pathways of oxidation of radicals of methyl ethyl sulfide radicals 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 radicals 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. There 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].

$CH_3SCH_2CH_3$ + HO • → CH_2• SCH_2CH_3
$CH_3SCH_2CH_3$+ HO • → CH_3SCH•CH_3
$CH_3SCH_2CH_3$ + HO • → $CH_3SCH_2CH_2$ •

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

CH_2• SCH_2CH_3+ O_2 → • $OOCH_2SCH_2CH_3$
CH_3SCH•CH_3+ O_2 → $CH_3SCH(OO$ •$)CH_3$
$CH_3SCH_2CH_2$ • + O_2 → $CH_3SCH_2CH_2OO$ •

The reaction pathway for oxidation of each radical, CH_2•$SCH_2CH_3$10, CH_3SCH•$CH_3$11and $CH_3SCH_2CH_2$ •12_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 ± 2 % SO_2, 46 ± 4 % HCHO, 57±3 % CH_3CHO and 0.07% OCS. And the Photooxidation products by OH in the presence of oxygen at atmospheric pressure of diethyl sulfide are 50 ± 3 % SO_2, 91±3 % CH_3CHO and 0.14% OCS, and of dimethyl sulfide are 80 ± 10 % SO_2 (Barnes et al. 1996), 90 ± 6 % HCHO, 0.7% ± 0.2 %OCS, and 95 ± 4 % SO_2 (Arsene at al., 1999) [7].

In 2010, studies made by Zheng and Bozzelli show that pyrolysis and oxidation of ethyl methyl sulfide at 630-740°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 1atm pressure, these thermodynamic quantities can also be used to predict favored products at different temperatures. These thermodynamic quantities arestandard enthalpy change (ΔHrxn), Standard entropy change (ΔSrxn), and standard Gibbs free energy change (ΔGrxn) 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 calculated 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 ($\Delta H°rxn$), can be calculated using tabulated standard enthalpy of formation of species involved in the reaction at 25°C and 1 atm pressure,

$\Delta Hrxn° = \Sigma n\ \Delta Hf°$ (products)- $\Sigma m\ \Delta Hf°$ (reactants) [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 ($\Delta S°rxn$) can be calculated using from standard entropy values of reactants and products,

$\Delta Srxn° = \Sigma n\ \Delta S°$ (products)- $\Sigma m\ \Delta S°$ (reactants) [15].

Standard free energy change ($\Delta G°$), it's free energy change that occurs when products in their standard states are formed from reactants in their standard states. Standard states referrers 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,

$\Delta G°r = \Delta H° - T\ \Delta S°$.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 are58, 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 -69.2kcal/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 favorthe 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, andstandard 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_3CH=O), Thioformaldehyde (CH_2=S),Thio-acetaldehyde (CH_3CH=S), Formaldehyde (CH_2=O). And some short lived, unstable and reactive radicals, CH_3S•=O, CH_3CH_2S•=O, CH_3S(=O)CH_2CO•, and OH are also formed under standard conditions.
Two of these products, Acetaldehyde (CH_3CH=O) and Formaldehyde (CH_2=O) were identified as major photooxidation products of ethyl methyl sulfide at atmospheric pressure, it was found that 46 ± 4 % of CH2=O and 57±3 % of CH_3CH=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_2=CH_2), Thioformaldehyde (CH_2=S), S=CHCOOH, and CH_2=CHOOH and some short-lived stable radicals, HO2, CH3•, HOOCH2S •, and CH3S•. are also formed at high temperatures.
Two of these products, Ethylene (CH_2=CH_2), and water (H_2O) were identified as products of pyrolysis and oxidation of ethyl methyl sulfide ate 630-740° Cand 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 ΔHrxn[a]	Calculated ΔHrxn[a]	Calculated ΔSrxn[b]	Calculated ΔGrxn[a]
Reaction 1	$CH_3SCH_2CH_2$ • + O_2 → C $_3$ SCH_2CH2OO • CH2•SCH2COOH → → CH2=CH2 + HO2 + CH2=S	28.2	31.5	58	26.2
2	CH3SCH•COOH → CH3• + S=CHCOOH	27.7	27.2	41.5	15.3
3	CH3SCH2COO• → CH3S(=O) CH2CO•	-23.2	-23.1	1.7	-23.7
Reaction	CH_2•SCH_2CH_3 + O_2 → • OOCH-2SCH_2CH_3				
4	• OOCH2SCH2CH3 → CH 2 = O + CH 3 CH 2 S • = O	-49.7	-49.7	20.9	-55.9
5	HOOCH2SCH • CH3 → CH2CH = S CH 2 = O + OH	-6.9	-6.9	54.6	-23.2
6	HOOCH2SCH2CH2 • → HOOCH2S • + CH2 = CH2	9.0	9.0	20.7	1.4
7	HOOCH2S • → HO 2 + CH 2 = S	19.9	20.9	41.4	7.6
8	• OOCSCC → CH 2 • OO • + CH 3 CH 2 S •	46.2	47.8	27.7	37.9
Reaction	CH3SCH•CH3 + O2 → CH3SCH(OO •) CH3				
9	CH2•SCH(OOH)CH3 → CH2=S+ CH3CH=O + OH	-7.0	-7.4	87.3	-33.0

10	CH3SCH(OOH)CH2• → CH3S•+ CH2=CHOOH	8.5	8.5	55.6	-8.0
11	CH3SCH(OO•)CH3 → CH3CH=O + CH3S•=O	-53.3	-53.3	-53.3	-69.2
bcal/mol.K					

Summery and Conclusion

Three thermodynamic quantities are used to predict the spontaneous reaction pathways and the reaction pathways thatenergetically favors products at standard conditions, Gibbs free change for reaction, standard enthalpy change for reaction, and standard entropy change for reaction. TheEnergetically favorable stable products formed from oxidation of ethyl methyl sulfide at standard conditions, 298 K and 1 atm pressure are acetaldehyde (CH3CH=O), thioformaldehyde (CH2=S) , thio-acetaldehyde (CH_3CH=S), andformaldehyde (CH2=O). The favored reactive and unstable radicals formed under standard conditions are CH3S•=O, CH3CH2S•=O, CH3S(=O)CCO•, and OH.The Energetically favorable stable products formed from oxidation of ethyl methyl sulfide at high temperatures and 1 atm pressureare Ethylene (CH2=CH2), Thioformaldehyde (CH2=S), S=CHCOOH, and CH2=CHOOH, the favored reactive and unstable radicals formed at high temperatures and 1 atm pressure are HO2, CH3•, HOOCH2S •, and CH3S•.

Acknowledgement

The authors wish to acknowledge NJIT Academic and Research Computing Systems resources and stafffor computational Facilities.

References

1. Pillai, S., & Bozzelli, J. W. (2012). Computational study on structures, thermochemical properties, and bond energies of disulfide oxygen (S–S–O)-bridged CH3SSOH and CH3SS (= O) H and radicals. *Journal of Physical Organic Chemistry, 25*(6), 475-485.
2. Hindiyarti, L., Glarborg, P., & Marshall, P. (2007). Reactions of SO3 with the O/H radical pool under combustion conditions. *The Journal of Physical Chemistry A, 111*(19), 3984-3991.
3. Cao, J., Wang, W., Zhang, Y., Wang, W., Zhang, T., Lv, J., & Li, C. (2011). Computational study on the reaction of CH3SCH2CH3 with OH radical: mechanism and enthalpy of formation. T*heoretical Chemistry Accounts, 129*(6), 771-780.
4. Pillai, S., & Bozzelli, J. W. (2012). Computational study on structures, thermochemical properties, and bond energies of disulfide oxygen (S–S–O)-bridged CH3SSOH and CH3SS (= O) H and radicals. *Journal of Physical Organic Chemistry, 25*(6), 475-485.
5. Oksdath-Mansilla, G., Peñéñory, A. B., Barnes, I., Wiesen, P., & Teruel, M. A. (2012). Photodegradation of (CH3CH2) 2S and CH3CH2SCH3 initiated by OH radicals at atmospheric pressure. Product yields and mechanism in NOx free air. *Atmospheric environment, 55,* 263-270.
6. Hynes, A. J., Wine, P. H., & Semmes, D. H. (1986). Kinetics and mechanism of hydroxyl reactions with organic sulfides. *The Journal of Physical Chemistry, 90*(17), 4148-4156.
7. Oksdath-Mansilla, G., Peñéñory, A. B., Barnes, I., Wiesen, P., & Teruel, M. A. (2012). Photodegradation of (CH3CH2) 2S and CH3CH2SCH3 initiated by OH radicals at atmospheric pressure. Product yields and mechanism in NOx free air. *Atmospheric environment, 55,* 263-270.
8. Atkinson, R., & Arey, J. (2003). Atmospheric degradation of volatile organic compounds. *Chemical reviews, 103*(12), 4605-4638.
9. Oksdath-Mansilla, G., Peñéñory, A. B., Albu, M., Barnes, I., Wiesen, P., & Teruel, M. A. (2009). FTIR relative kinetic study of the reactions of CH3CH2SCH2CH3 and CH3CH2SCH3 with OH radicals and Cl atoms at atmospheric pressure. *Chemical Physics Letters, 477*(1-3), 22-27.
10. Song, G., & Bozzelli, J. W. (2019). Reaction pathways, kinetics and thermochemistry of the chemically-activated and stabilized primary methyl radical of methyl ethyl sulfide, CH3CH2SCH2•, with 3O2 to CH2CH3SCH2OO•. *Combustion and Flame, 204*, 368-379.
11. Song, G., Bozzelli, J., & Abdel-Wahab, H. (2021). Thermochemistry and Reaction Kinetics of Secondary Ethyl Radical of Methyl Ethyl Sulfide, CH3SCH• CH3, with 3 O2 to CH2SCH (OO•) CH3. *American Journal of Physical Chemistry, 10*(4), 74-87.
12. Song, G., & Bozzelli, J. W. (2019). Reaction kinetics and thermochemistry of the chemically activated and stabilized primary ethyl radical of methyl ethyl sulfide, CH3SCH2CH2•, with O2 to CH3SCH2CH2OO•. I*nternational Journal of Chemical Kinetics, 51*(8), 618-633.
13. Gammon, Ebbing, General Chemistry 11th edition, Boston MA, Cengage Learning, 2017, pp 630-631.
14. Gammon, Ebbing, General Chemistry 11th edition, Boston MA, Cengage Learning, 2017, pp 608-610.
15. Gammon, Ebbing, General Chemistry 11th edition, Bos-

ton MA, Cengage Learning, 2017, pp 618-620.
16. Kotz, J. C., Treichel, P. M., Townsend, J. R., & Treichel, D. A. (2015). Chemistry and chemical reactivity 9th edn. *Ch,* 17, 630-677.
17. https://en.wikipedia.org/wiki/Radical_(chemistry).
18. Zheng, X., Fisher, E. M., Gouldin, F. C., & Bozzelli, J. W. (2011). Pyrolysis and oxidation of ethyl methyl sulfide in a flow reactor. *Combustion and flame, 158*(6), 1049-1058.

Copyright: *©2022* Hebah Abdel-Wahab. *This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.*