Computational and Theoretical Chemistry 1090 (2016) 88–93

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc

Ozonolysis mechanism of heterocyclic organic sulfides: A computational study

Hanlu Wang *, Rujin Zhou *, Minjie Jiang, Zhigeng Lin, Yiqiang Deng

College of Chemical Engineering, Guangdong University of Petrochemical Technology, Maoming 525000, PR China

ARTICLE INFO

Article history:
Received 13 May 2016
Received in revised form 13 June 2016
Accepted 13 June 2016
Available online 14 June 2016

Keywords:
Ozonation
Benzothiophene
Reaction mechanism
Density functional theory
Solvation effect
Oxidation activity

ABSTRACT

The reaction mechanism of the ozonation of benzothiophene (BT) and its derivatives was explored by using the density functional theory (DFT) considering the solvation effect in acetonitrile using both the COSMO implicit solvent approach and SMD solvent model with and without D3 corrections. Two pathways are proposed for ozonation of BT. The path through Criegee mechanism was found to be more favorable. Furthermore, we also calculated the ozonation of the derivatives of BT such as dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT). The reaction mechanisms of DBT and 4,6-DMDBT are different from that of BT. Based on the activation energies, the reactivity of BT and its derivatives to ozone are in the following order: BT > 4, 6-DMDBT > DBT.

1. Introduction

As global environmental problems have become increasingly prominent, the voice to protect the environment is also growing. Sulfur compounds are extremely undesirable in fuels. The atmospheric emission of sulfur combustion products contributes to generation of acid rain and smog. Moreover, their presence has been related to the corrosion of refining equipment and with premature breakdown of combustion engines [1].

Various desulfurization techniques such as hydrodesulfurization (HDS) [2], adsorptive desulfurization [3], extractive desulfurization [4,5], biodesulfurization [6,7] and oxidative desulfurization (ODS) [8,9] have been extensively investigated. In widely used HDS, polycyclic aromatic sulfurs such as BT, DBT and their derivatives in fuel oils are more difficult to remove than thiols, sulfides, and disulfides [10–12]. ODS is one of the most interesting options for these refractory sulfur compounds. In ODS method, the hydrogen peroxide is widely used. However, it can decompose into water, forming an oil–water biphasic system reduces the fuel quality and leads to the difficult recovery of the oil phase. Using a gas as an oxidizing agent, oil–water biphasic problems can be avoided. Ozone possesses a very high oxidation potential, which is 2.07 V. It is higher when compared to 1.77 V for hydrogen peroxide or 1.4 V for chlorine. Ozone is a very strong oxidant and can be used to oxidize the organic sulfur compounds in fuel [13–16].

Zhang [17] have carried a series of experiments on the ozonation of the sulfur compounds, such as BT, DBT and 4,6-DMDBT in acetonitrile. As shown in Fig. 1, the final oxidation product of BT is 2-mercapto-benzoic acid, and those of DBT and 4,6-DMDBT are their corresponding sulfones $DBTO_2$ and 4,6-$DMDBTO_2$, respectively, by GC-MS spectrum analysis. The oxidation product of BT and DBT sulfur compounds are of different types, it can be inferred that they follow different ozonation mechanisms. Then, the detailed mechanism and intermediates involved in the reaction are unclear. Here, based on the previous work [17], we focus on the ozonation mechanisms of these refractory sulfur compounds using DFT-D3 calculations both in gas phase and acetonitrile solution.

2. Computational methods

All the reactants, intermediates, transition states in oxidation reaction of the sulfides using O_3 as oxidants were fully optimized employing B3LYP [18,19] functional and 6-311++G(d, p) basis set was used throughout this work for geometry optimizations and frequency calculations in vacuo. Frequency calculations were used to confirm the correct character of all reported structures at 1 atm and 298.15 K. Only one imaginary frequency and one negative eigenvalue is for the transition states. The intrinsic reaction coordinate (IRC) calculations were conducted to confirm the pres-

---

* Corresponding authors.
E-mail addresses: wanghlu@mail2.sysu.edu.cn (H. Wang), rujinzhou@126.com (R. Zhou).

http://dx.doi.org/10.1016/j.comptc.2016.06.015

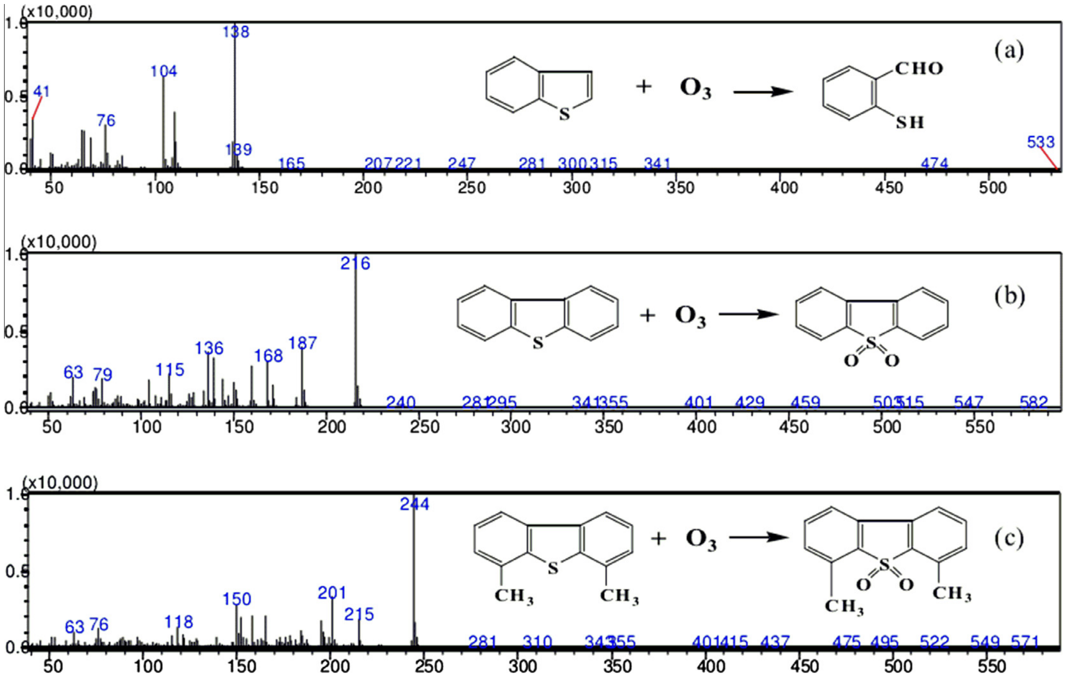

Fig. 1. Mass spectra and reaction scheme of three sulfur compounds (a) oxidation product of BT; (b) oxidation product of DBT; (c) oxidation product of 4,6-DMDBT.

ence of transition states along the reaction path [20,21]. BT and its derivatives are polycyclic aromatic sulfurs and there should be weak interactions between molecules, and requires an empirical treatment of dispersion. Because the standard B3LYP functional cannot describe the weak interactions well, dispersion corrected scheme (B3LYP+D3) [22–25] at the same level was used to calculate the interaction energy. Thermal energies were extracted from the vibrational frequency calculations. Moreover, single-point energies at the same level were further calculated in acetonitrile using both the classical COSMO implicit solvent approach [26] and new SMD solvent model [27] with and without D3 corrections. The relative free energies of the oxidation reaction of the sulfides with different methods are listed in Table S1. The calculated reaction barriers are qualitatively similar to each other (within a few kcal mol^{-1}) with the two different solvation models, while the reaction barriers determined using the new SMD method with D3 correction seems to give the better agreement with experimental results. Therefore, throughout the paper, we used SMD+D3 model to make the computations more tractable. All calculations were completed using the Gaussian 09 program [28].

The calculated S—C bond lengths are in the range 1.72–1.74 Å for BT, and 1.78–1.80 Å for BTO and BTO$_2$. Comparing the computed results with the experimental data of S—C (in thiophene is 1.71 Å and in sulfoxides and sulfones are 1.80 Å), we can find that all of the computed selective bond lengths are slightly longer than the corresponding experimental ones [29]. The minor differences from the experimental data aroused from systematic errors caused by the computation method/basis set and environment factors. Therefore, the computations here should be reliable, and we can further carry out the study on the structures as well as energies, thermodynamic and kinetic properties for the ozonation of sulfur compounds.

3. Results and discussion

3.1. Ozonation of the BT

In this section, the reaction of BT with ozone is investigated. As depicted in Fig. 2, ozone bond to BT with different orientations resulted in two intermediates (IM_1 and IM_6) corresponding to two possible reaction mechanisms. The one is through Criegee mechanism, which is originally put forward by R. Criegee [30]. In this process, the O1 and O3 of ozone attack the C1=C2 π bond in the thiophene ring of BT. The other is O1 of ozone straightly attacking S atom of BT to produce sulfoxide, then further ozonized to produce sulfone.

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are very important for understanding the reactivity of the molecules. The HOMO and LUMO energy levels of BT and ozone calculated by Hartree-Fock method [31] at 6-31G(d, p) level are displayed in Fig. 3. According to the frontier molecular orbital theory (FMO), the reactivity between two molecules is inversely proportional to the energy difference ($\Delta\varepsilon$) between HOMO of one molecule and the LUMO of the other [32]. The smaller the value of the energy difference is, the more reactive the chemical reaction will be. The energy difference between HOMO$_{BT}$ and LUMO$_{O3}$ (7.17 eV) is smaller than that between HOMO$_{O3}$ and LUMO$_{BT}$ (16.22 eV). Therefore, the ozonation of BT possibly proceeds via the HOMO$_{BT}$–LUMO$_{O3}$ interaction. The HOMO of BT is a π orbital, largely localized at S atom and C=C bonds, and the LUMO of O$_3$ is a π^* orbital, largely localized at O1 and O3 atoms. These areas are expected to be the active sites in the following reaction.

In the path 1, the O1 and O3 of ozone approach the C1=C2 π bond in the thiophene ring of BT to produce IM_1, endothermic by 4.2 kcal mol^{-1}. As shown in Fig. 4, O$_3$ succeeded to bind BT forming a five-membered ring complex IM_2 through the transition state TS1. The distances of O1—C1 and O3—C2 gradually decrease from 2.716 Å, 2.985 Å (IM_1) to 1.782 Å, 1.745 Å (TS1), to 1.442 Å, 1.429 Å (IM_2), respectively. While in this process, the distances of O1—O2 and O2—O3 of ozone correspondingly become longer. This process only requires 2.7 kcal mol^{-1} free energy, and exothermically by −34.7 kcal mol^{-1}. Then, both of the O1—O2 and C1—C2 bonds are being broken in TS2, lengthened from 1.441 Å and 1.566 Å to 2.095 Å and 1.883 Å, respectively. The resulted IM_3 bearing an aldehyde group is an intermediate that the five-ring is completely broken in which O1—O2 and C1—C2