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Theoretical Study of Decomposition of Thiophenic Compounds in Accidental and Spontaneous Fires of Coal

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ABSTRACT

This study investigates the thermochemical data and rate parameters for facile routes involved in combustion of fossil fuels, particularly in case of coal fires, using the density functional theory (DFT). We have studied mechanisms for the decomposition and oxidation reactions of cyclic organosulfur compounds including tetrahydrothiophene, 2-methyltetrahydrothiophene, 2,5-dimethyltetrahydrothiophene and 1,4-thioxane. The results show a pleasing consistency and considerably expand the available data for these important compounds. CBS-QB3 based calculations predict that thiophene family decomposes via two types of bond breakages, namely, C-S and C-C β bond-scission with C-S bond cleavage to be the preferred pathway on account of lower barrier heights. However, reaction of a model compound from thiophene group with O₂ offers significantly large barriers (i.e., > 20 kcal/mol) indicating that direct oxidation of thiophenes by ground state oxygen might be important only in case of high temperature combustion processes. Decomposition of 1,4-thioxane (TO) is observed to be favoured by ring opening processes with β -CH₂-O scission, based on the DFT calculations. Further decomposition of thioxane radicals leads to two heavy atom species and generation of doubly unsaturated four heavy atom segments with reasonable endothermicity. Although TO radicals react readily with oxygen, the resulting intermediate formed requires considerable activation barriers to be overcome for ring opening reactions. The implication of current theoretical results sheds new light on further pyrolytic and oxidative mechanisms for these particular compounds.

KEYWORDS: Coal fires, oxidation, pyrolysis, thermochemical properties

INTRODUCTION

Emissions from open burning on a mass pollutant per mass fuel (emission factor) basis are far greater than those from well controlled combustion sources [1, 2]. Open burnings, including fossil fuels, poses a serious threat to environment as well as to human health. Uncontrolled fires of coal have been considered one of the most important contributors in toxic emissions on account of increasing use of fossil energy in the world [3]. As coal is a major source of energy in many countries, emission of pollutants from fires of coal is a serious environmental predicament on a global scale. Coal fires refers to the burning/smouldering of coal storage piles or coal seams. Spontaneous ignition of coal constitutes the most prominent cause of coal fires in many parts of the world including China, Russia, USA and Australia [4]. It is after-human influence the second most common cause for coal fires of large extent, second only to anthropogenic combustion. Emissions from coal combustion span inorganic species (CO_x, NO_x, SO_x), polycyclic aromatic hydrocarbons (PAHs), and polycyclic aromatic sulfur hydrocarbons (PASHs) [5].

PASHs are sourced from sulfur-bound constituents in organic and inorganic forms in coal. The inorganic forms are mostly pyrite and marcasite minerals with small amounts of sulfatessulphates, depending on the level of oxidation of coal. The organic sulfur exists either in aromatic rings or in aliphatic functional groups, usually categorised as thiols, thiophenes, and disulfides [6]. This study focuses on addressing decomposition of major aromatic sulfur carriers in coal; namely, tetrahydrothiophenes (THT), 2-methyltetrahydrothiophenes (MTHT), 2,5-dimethyltetrahydrothiophenes (DMTHT) and 1,4-thioxane (TO) [7,8]. It is well known that, these compounds have carcinogenic and mutagenic effects on human health as well as notorious impacts on all environmental matrices; notably, via the formation of the acid rain as a consequence of combustion of these compounds.

Thiophenic species are often regarded as surrogates for aromatic sulfur content in various types of fuels; including coal and oil shale [9]. Various studiesPrevious studies have suggested the emergence of H₂S as a major gaseous product during pyrolysis of thiophene above 1000 K [10]. It follows that, an atomic-base understanding of the decomposition of thiophenic compounds would be instrumental in the effort to reduce emission of sulfur species from accidental fires of coal. In the present investigation, the pyrolytic and oxidative

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decomposition of the above said cyclic organosulfur compounds are studied. Pathways for the reactions of four compounds under conditions encountered in a real fire environment were modelled using density functional theory (DFT) methods. Since virtually all basic thermochemical data are absent for these compounds, the objective of this work is to provide a reliable framework, as prerequisites for future experimental, modelling, and simulation studies.

METHODS

Gaussian suit of programs [11] was used to perform structural optimisations and energy calculations at the accurate chemistry model of CBS-QB3 and M052X/6-311+G(d,p) level of theories. Transition structures were tracked to link to reactants and products via calculations of intrinsic reaction coordinate (IRC). M052X [12] is a new hybrid meta exchange correlation functional that was proven to outperforms all other DFT methods in predicting reaction and activation enthalpies in general applications of to C/H/O molecules. Potential energy surfaces in the systems of the 1,4 thioxane (TO) molecule were mapped out at the M052X/6-311+G(d,p) level of theories; , while systems of other compounds were carried out at the CBS-QB3. Reaction rate constants were evaluated by applying the conventional transition state theory as implemented in the “TheRate” code [13].

RESULTS AND DISCUSSION

Pyrolysis and oxidation of thiophenes

Unimolecular decomposition of four thiophene-type compounds was investigated for two types of radicals, A and B, depending on the position of the radical centre with respect to the S atom. Barrier heights and reaction enthalpies for all possible β bond-scission reactions of THT, MTHT and DMTH radicals were evaluated and found to be endothermic with modest activation enthalpies. Potential energy surface (PES) is depicted in Figs. 1 and 2 for the initial decomposition for the four A and B plausible radicals in the four thiophen-type compounds.

As shown in Fig. 1, bond scission for parent THT radical proceeds via two channels, one involving scission of C-S bond (TS1) and the other the cleavage of C-C bond (TS2). Decomposition of A-THT radical exhibits comparable activation enthalpies for both channels. Ring opening processes are found to be associated with high enthalpy barriers and noticeable endothermicity. Formation of carbon centred radicals in both types of cleavages may be one of the possible reasons of higher enthalpies. Pyrolytic reactions of THT, MTHT and DMTH leads to the formation of P1 (a-d) due to C-S bond breakage with reaction enthalpies ranging between 23.2-25.2 kcal/mol and activation energies between 24.7-27 kcal/mol. Similarly C-C bond cleavage forms P2 (a-d) with a difference of 10 ± 1 kcal/mol in comparison to the corresponding P1 product.

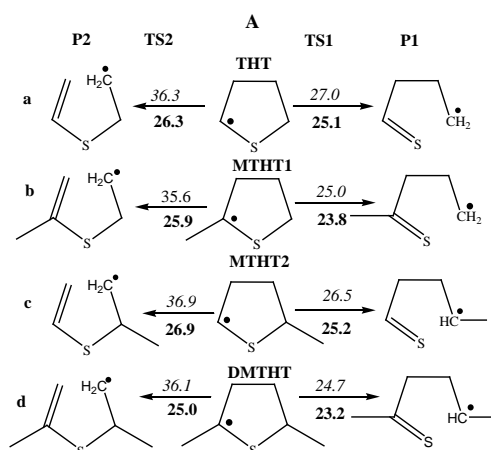


Figure 1. β bond-scissions of A-THT, -MTHT1, -MTHT2 -DMTHT radicals. Values in bold and italic signify reaction and activation enthalpies respectively. All values are in kcal/mol at 298.15 K.

On the contrary, C-S bond cleavage (TS3) is thermodynamically preferred over the C-C bond scission (TS4) in case of B-THT, as shown in Fig. 2. Parent B-THT radical undergoes ring opening to form a carbon-centred propenylthioxymethyl propenethioxymethyl radical ($\text{CH}_2\text{SCH}_2\text{CHCH}_2$) with an activation enthalpy of 30.6 kcal/mol. However, formation of sulfur centred radical intermediates encounters a rather shallow enthalpic barrier of 12.8 kcal/mol. This indicates that, position of radical in the thiophene ring plays an important role in mapping out the thermochemical parameters of the products. A similar pattern arises for the other three B-radicals of MTHT and DMTH as well, with reaction enthalpies ranging between 28.6-30.2 kcal/mol for C-C bond fission and 11.1 to 12.7 kcal/mol for C-S bond cleavage.

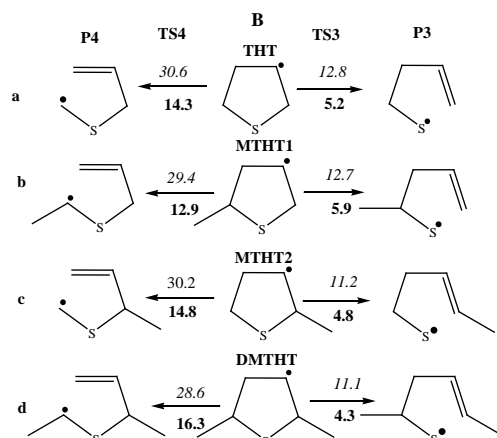


Figure 2. β bond-scissions of B-THT, -MTHT1, -MTHT2 -DMTHT radicals. Values in bold and italic signify reaction and activation enthalpies respectively. All values are in kcal/mol at 298.15 K.

Oxidation processes of thiophenes and their derivatives are of great significance because of the presence of atmospheric oxygen as the sole oxidising agent in fires. A-MTHT2 is chosen as a model compound to represent the oxidation pathways for the thiophene family. Initial pathways for the reaction of the triplet oxygen with M moiety are illustrated in Fig. 3.

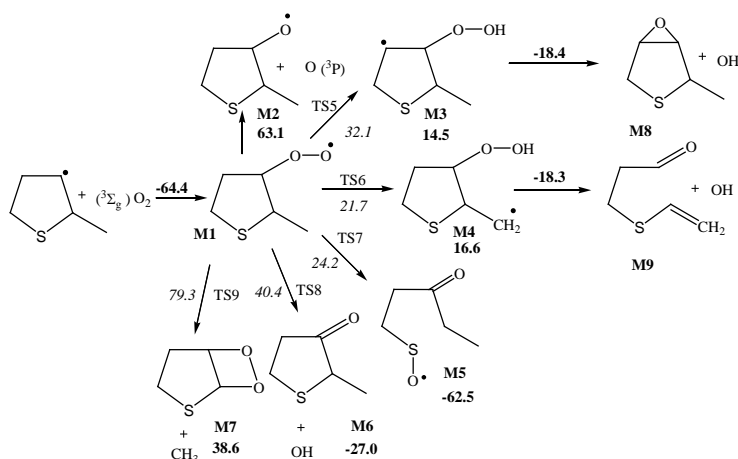


Figure 3. Reaction pathways for O_2 addition to 2-methylthiophenyl radicals. Values in bold and italic signify reaction and activation enthalpies respectively. All values are in kcal/mol at 298.15 K.

Oxygen addition to C3 of MTHT forms M1 which has six plausible rearrangement routes leading to the formation of six types of structures labelled M2, M3, M4, M5, M6, and M7. The optimised geometrical transition structures for the thiophenes are illustrated in Fig. 4. M5 is the most stable of all the six initial adducts that is produced, as a result of oxygen bond cleavage from M1. M1 can rearrange into another intermediate via

Comment [BD1]: Tajwar – if you have (say) $\text{M1} \rightarrow \text{M4} \rightarrow \text{M9} + \text{OH}$, are the reaction and activation enthalpies for the final reaction given with respect to M4 or M1?

Also, could you double check the reaction enthalpy to produce M5. -62.5 kcal appears to me to be very small.

shifting of H atom from C4 to terminal O atom forming M3 via activation energy of 32.1 kcal/mol. The relative reaction energy is 14.5 kcal/mol. M3 can react further by O-O bond breaking and simultaneous C-O bond formation to produce M8. This reaction is exothermic by -18.4 kcal/mol. Formation of M4 is predicted to be the most favourable channel with minimum energy barrier of 21.7 kcal/mol. This pathway involves migration of one of the methyl H's to the terminal oxygen atom. As shown in Fig. 3, further decomposition of M3 and M4 affords the propagating OH radicals in highly exothermic barrierless reactions. M1 undergoes unimolecular rearrangement either by OH or CH₃ elimination to form M6 and M7 respectively with significant barriers. In view of the sizable barriers of TS8 and TS9, formation of M6 and M7 should be a rather negligible exit channel for M1. Overall, intramolecular H transfer from the methyl group to the terminal O atom (M1 → M4) and migration of the outer peroxy oxygen to the S-site should control the fate of M1.

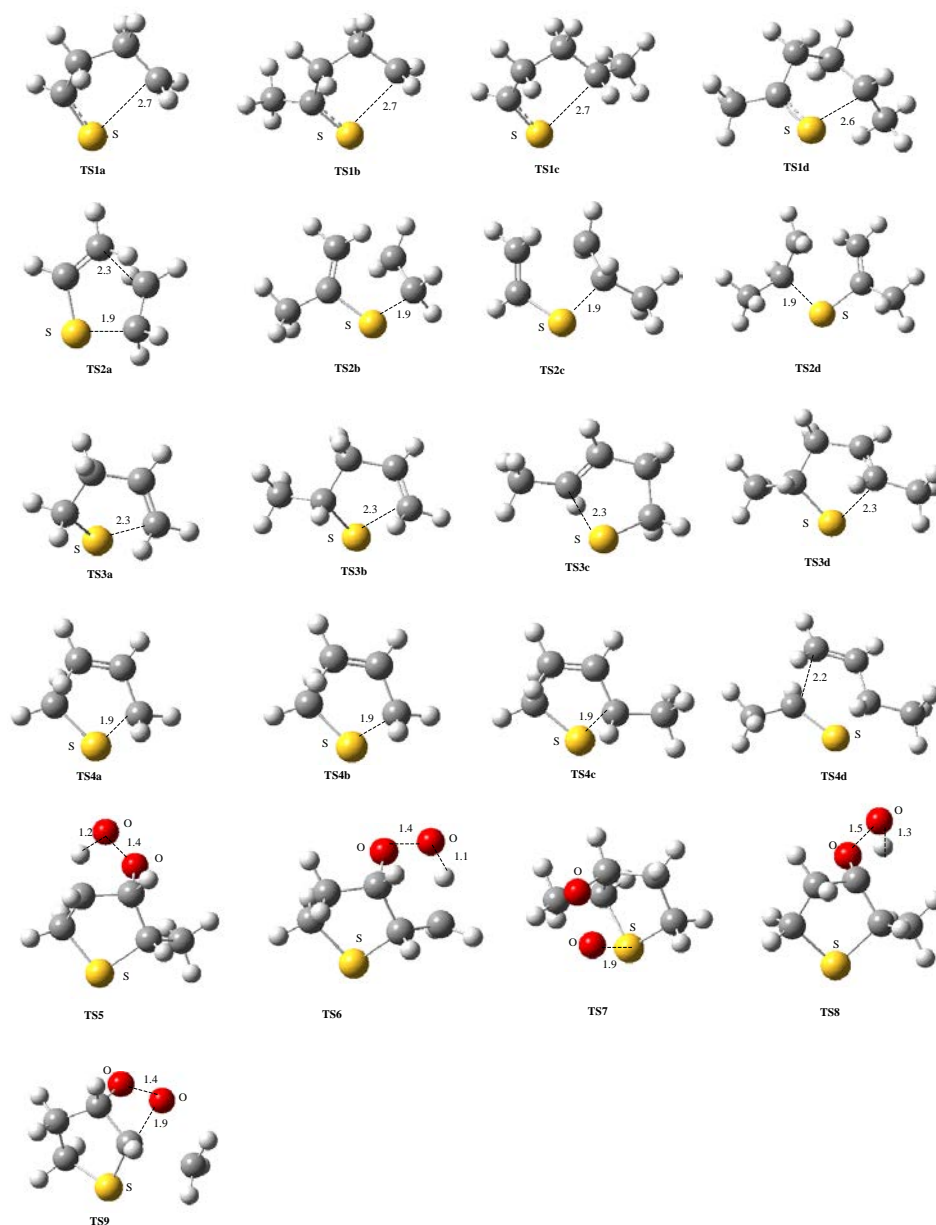


Figure 4. Optimised geometries for transition structures of A, B-THT, -MTHT1, -MTHT2, -DMTHT radicals. All distances are in Å.

Pyrolysis and oxidation of 1,4-thioxane (TO)

Ring opening processes in pyrolysis of cycloalkanes have been studied both experimentally and theoretically [14-16]. In an analogy to the well-documented pathways in the decomposition of cycloalkanes, we investigate in this section, channels pertinent to the unimolecular decomposition of 1,4-thioxane (TO). Under real combustion conditions, initial oxidation of 1,4-thioxane commences with H cleavage from the two distinctive sites C-H bonds to yield 1,4-thioxan-2-yl (D2) and 1,4-thioxan-3-yl (D1). Direct fission of C-H bonds from 1,4-thioxane

leading to the formation of D1 and D2 demands endothermicity of 95.6 kcal/mol and 93.6 and 95.9 kcal/mol respectively.

Decomposition of TO via 1, 3-hydrogen shift affords two structures D3 (2-(vinylthio)ethanol) and D4 (2-(vinylthio)ethanethiol). Formation of both structures D3 and D4 is found to be endoergic by 12.1 and 17.0 kcal/mol respectively, and associated with very significant reaction enthalpies of 74.0 and 80.7 kcal/mol. Further decomposition of D3 offers ethenol and ethenethiol via a reaction enthalpy of 74.5 kcal/mol (TS11).

Three singlet biradical species can be sourced from the TO molecule via barrierless bond cleavage reactions. These structures are D5 (β -CH₂-S scission), D6 (β -CH₂-CH₂ scission) and D7 (β -CH₂-O scission). Formation of D5 and D7 constitutes the most favourable exit channel in the decomposition of the TO molecule with comparable endothermicity of 59.1 and 56.9 kcal/mol.

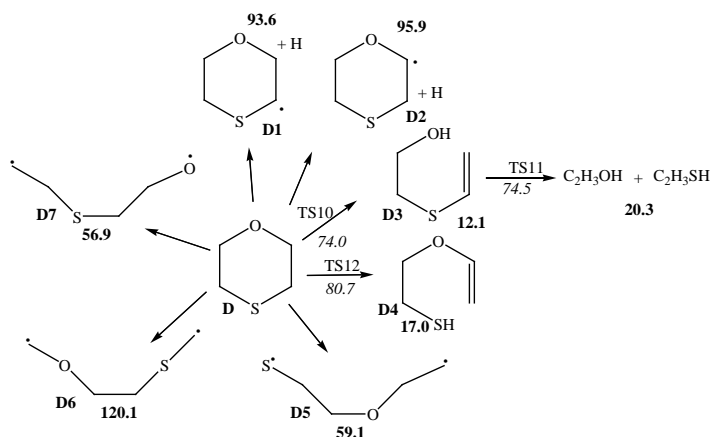


Figure 5. Potential energy surface for the initial decomposition of 1, 4-thioxane. Values in bold are reaction enthalpies and values in italic are activation enthalpies. All values are calculated at 298.15 K.

In Fig. 6, we investigate the further unimolecular decomposition of TO radicals, D1 and D2. As shown in Fig. 6a, bond breakage of D2 occurs via two channels, β -CH₂-S or β -CH₂-O bond scission that leads to the formation of D9 and D8 respectively. The two structures D8 and D9 are slightly endothermic by 7.6 and 5.3 kcal/mol, with more likely formation of D9 on account of lower activation energy (TS13). D8 and D9 undergo further decomposition by two channels, either by H elimination or by expulsion of two heavy molecules. H elimination occurs by two endothermic reactions that result in the formation of D11 (2-(vinylthio) acetaldehyde) and D12 (2-(vinylthio)ethenethiol). Methanethial and ethene molecules, formed with D10 and D13, respectively, are sourced from D8 and D9 via endoergicity of 10.7 and 41.4 kcal/mol respectively. Further decomposition results in (H₂CS+HCO) formation from D10 and (C₂H₃+H₂CO) from D13.

A similar pattern is observed for D1, where comparable difference in enthalpic barriers between TS16 and TS17 (31.8 kcal/mol versus 27.4 kcal/mol) entails equally likely opportunities of reaction to proceed via β -CH₂-S and β -CH₂-O bond scission,; respectively. As shown in Fig. 6b, the two intermediates D14 and D15 undergo further dissociation to yield D12 and D13 via H expulsion, and D16 and D17 with elimination of other smaller fragments. D16 further splits into (C₂H₃ + H₂CO + H₂CS) after climbing a high energy barrier of 63.9 kcal/mol (TS20). However, decomposition of D17 proceeds with much lower barrier height (TS21) with endothermicity of 15.9 kcal/mol.

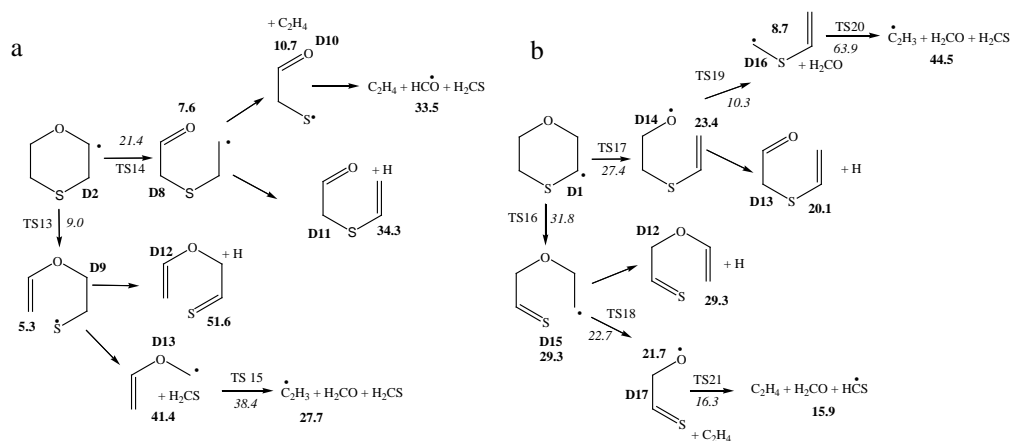


Figure 6. Potential energy surface for the decomposition of the radicals D1 and D2. Values in bold are reaction enthalpies and values in italic are activation enthalpies. All values are calculated at 298.15 K.

In order to illustrate the conditions encountered in real fire environment, temperature dependant reaction rate constants are calculated for the four ring opening reactions of D1 and D2, namely (D2 → D8, D2 → D9, D1 → D14 and D1 → D15). Figure 7 shows the Arrhenius plots for these reactions at the high-pressure limit. These Arrhenius parameters are obtained based on conventional transition state theory (TST) [17] over a temperature range of 300-2000 K. Modified Arrhenius expressions for the formation of the two segments D8 and D9 from D2 were fitted to expressions of $2.75 \times 10^{11} T^{0.71} \exp(-10\,080/T) \text{ s}^{-1}$ and $6.55 \times 10^{12} T^{0.16} \exp(-4\,700/T) \text{ s}^{-1}$, respectively. The two-ring opening reactions of D1 into D14 and D13 were fitted to $1.28 \times 10^{12} T^{0.50} \exp(-14\,000/T) \text{ s}^{-1}$ and $3.90 \times 10^{12} T^{0.49} \exp(-16\,300/T) \text{ s}^{-1}$, respectively. As shown in Fig. 7a, formation of D8 is the sole important channel from the initial decomposition of D2. Figure 7b reveals that, formation of D14 and D15 incurs practically comparable importance throughout the temperature of interest. For instance the branching ratio for the formation of D15 is found to amount to 0.10, 0.23 and 0.36 at 700 K, 1000 K and 1400 K, respectively.

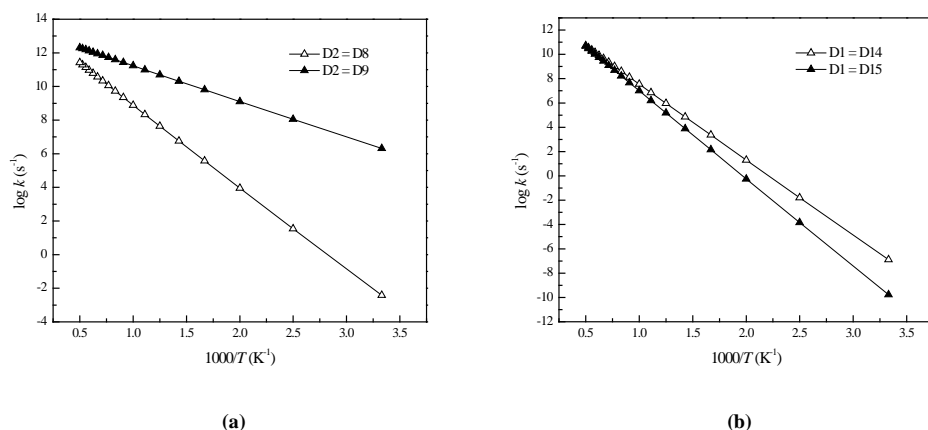


Figure 7. Arrhenius plots for calculated reaction constants for the ring opening of two TO radicals D2 (a) and D1 (b)

Pathways to ring opening begin with molecular oxygen addition to thioxane radicals D1 and D2 as illustrated in Fig. 8 embedded with reaction and activation enthalpies. Fig. 8a depicts potential energy surface for subsequent steps following an oxygen molecule addition to the D1 radical. Oxygen addition at the radical site results in the

formation of the peroxy adduct of D18 in an exothermic reaction of 67.9 kcal/mol. A metastable hydroperoxy radical D19 is produced in an intramolecular endothermic hydrogen abstraction (isomerisation) reaction via TS22 with barrier energy of 33.6 kcal/mol. Geometries of all transition structures in the TO system are shown in Fig. 9. D19 can in turn lose an OH radical over TS23 with an activation enthalpy of 23.4 kcal/mol to form highly stable cyclic epoxy intermediate, D20. Ring opening barrier (TS24) of this cyclic epoxy intermediate is very high (56.6 kcal/mol) despite high exothermicity of ring opening. This suggests that this cyclic epoxy intermediate may accumulate in combustion environment including TO, as related compounds have been reported in low temperature combustion of cyclic hydrocarbons [18].

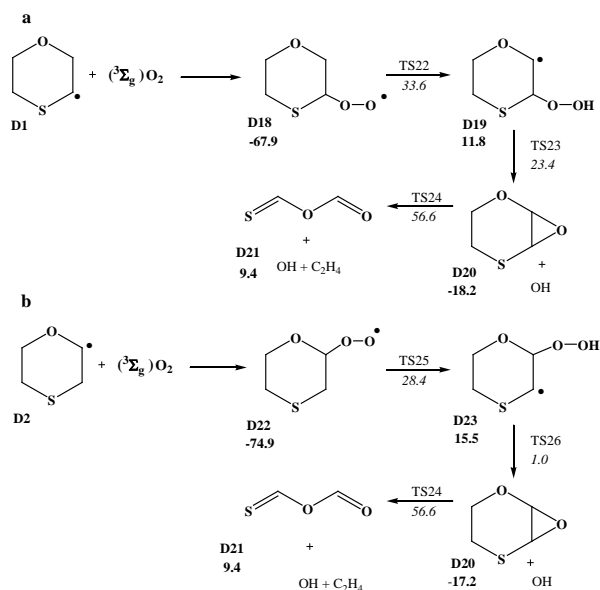


Figure 8. Reaction pathways for O_2 addition to 1,4-thioxane radicals. Values in bold and italic signify reaction and activation enthalpies respectively. All values are in kcal/mol at 298.15 K.

A similar reaction pathway is depicted in Fig. 8b for reaction of D2 with oxygen. Initial addition of oxygen molecule forms D22 in a barrierless and highly exothermic (by -74.9 kcal/mol) reaction. The isomerisation via TS25 to D23 and OH elimination via TS26 occur with substantially lower barrier in comparison to analogous reactions of D1. This finding suggests that D23 to be extremely short-lived species. OH elimination from D23 provides alternative pathways for cyclic epoxide D20. In general, cyclic epoxy species are found to be important in low-temperature oxidation of various hydrocarbons [19].

In a nutshell, calculated mechanistic pathways for the pyrolysis of tetrahydrothiophenes and their derivatives show facile routes for the C-S bond cleavages followed by formation of short sulfur-containing alkyl radicals (i.e., CH_2SH). Initial oxidation channels produce stable S-molecules and the propagating OH radicals. Further oxidative decomposition of these initial products affords the formation of smaller fragments including SO and H_2S ; the two major S-containing products from the decomposition of coal. However, in case of thioxanes, among the two radicals, D1 is found to be more stable in accord with the energy calculations. Both radicals have strong tendency to react with oxygen, as addition reactions of O_2 to TO radicals have no apparent barrier. However, highly stable cyclic epoxy intermediate formed by 1,4-H shift isomerisation signifies a considerable energy barrier for ring opening reactions. Kinetic and thermochemical data provided herein should be useful in the pursuit to understand the transformation of sulfur-containing species in burning of coal, especially involving the formation of sulfates and oxygenates that comprise two to four heavy atoms.

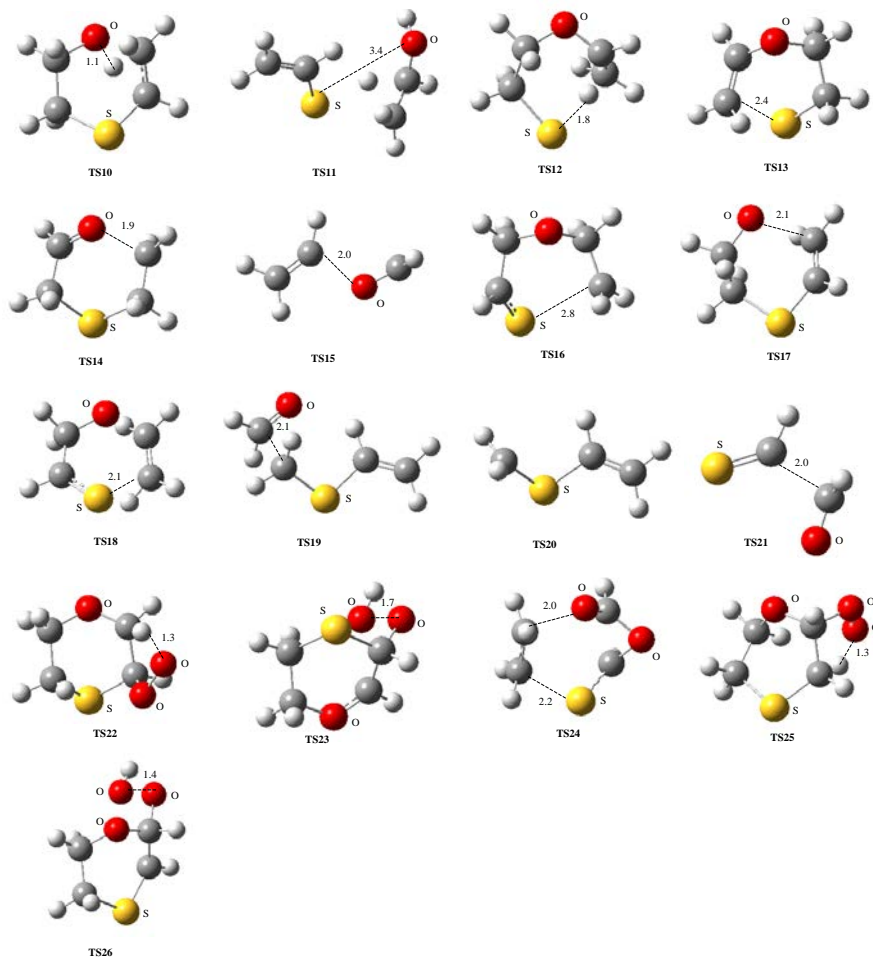


Figure 9: Optimised geometries for transition structures of 1,4-thioxane. All distances are in Å.

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