



## Theoretical derivation for reaction rate constants of H abstraction from thiophenol by the H/O radical pool

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### ABSTRACT

Reaction and activation energy barriers are calculated for the H abstraction reactions ( $C_6H_5SH + X \cdot \rightarrow C_6H_5S + XH$ ,  $X = H, OH$  and  $HO_2$ ) at the BB1K/GTLarge level of theory. The corresponding reactions with  $H_2S$  and  $CH_3SH$  are also investigated using the G3B3 and CBS-QB3 methods in order to demonstrate the accuracy of BB1K functional in finding activation barriers for hydrogen atom transfer reactions. Arrhenius parameters for the title reactions are fitted in the temperature range of 300 K–2000 K. The calculated reaction enthalpies are in good agreement with their corresponding experimental reaction enthalpies. It is found that H abstraction by OH radicals from the thiophenol molecule proceed in a much slower rate in reference to the analogous phenol molecule.  $\Delta_f H_{298}^0$  of thiophenoxy radical is calculated to be 63.3 kcal/mol. Kinetic parameters presented herein should be useful in describing the decomposition rate of thiophenol; i.e., one of the major aromatic sulfur carriers, at high temperatures.

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### 1. Introduction

Fossil fuels contain organic and inorganic sulfur. For example the sulfur content in coal varies between 0.5% and 11% depending on the location, type and origin of coal [1]. Organic sulfur in oil shale could be as high as 6% [2]. The presence of these compounds in solid or liquid fuels causes the release of large quantities of sulfur dioxide ( $SO_2$ ) during combustion, which contributes to air pollution and is a reason for the formation of acid rain [3]. Therefore, it is necessary to remove these sulfur compounds from oil or solid fossil fuels prior to combustion to avoid sulfur dioxide emission. During the pyrolysis or combustion, significant concentrations of organic sulfur are emitted as thiols; especially alkylthiophenes [4–6]. Thiophenol ( $C_6H_5SH$ ) in particular is regularly utilized as a surrogate compound for thio-alcohol structural entities in coal [7,8].

A great deal of recent research has targeted reducing sulfur emission from the various types of fossil fuels; including coal, natural gas and oil shale. For instance, a number of desulphurization techniques are employed for sulfur removal from fuels, including chemical desulphurization [7–10], biological desulphurization [3,11] for solid fossil fuels, and hydrodesulphurization [12] for liquid fuels.

Central to this effort is to understand the main reactions involved in the decompositions of sulfur-containing aromatic com-

pounds; i.e., a major entity of sulfur-bearing compounds in coal and oil shale. However, there is scarcity in experimental or theoretical measurements for reactions involving thiolic compounds in general and thiophenol in particular at temperature relevant to combustion. In particular, reactions of thiophenol with the H/O radical pools are not yet determined, neither experimentally nor theoretically. However, significant amount of experimental data are available for these reactions with hydrogen sulfide ( $H_2S$ ), and to a lesser extent for methyl sulfide ( $CH_3SH$ ) under atmospheric conditions. Particularly, the reaction of  $H_2S$  with OH radicals has attracted increasing interest due its primary role in explosive and atmospheric chemistry of  $H_2S$  [13]. Recently, Ellingson and Truhlar [14] studied theoretically the reaction ( $H_2S + OH \rightarrow HS + H_2O$ ) with emphasis on describing the observed unusual temperature dependence at elevated temperatures.

On the same line, the reactions of OH with aliphatic compounds have been studied theoretically with the aim of providing an explanation for a two stepwise mechanism observed experimentally under low temperatures [15]. Interestingly, experimental reaction rate constant for the reaction of the propagating radical  $HO_2$  are only available at 298.15 K for  $H_2S$  and  $CH_3SH$  [16]. Any attempt to satisfactorily model the low-temperature oxidation mechanism of thiol compounds would be hindered by the lack of accurate rate constant involving  $HO_2$ .

To this end, we report in this study theoretical derivation of the reaction rate constants of thiophenol with H, OH and  $HO_2$  radicals. The corresponding reactions with  $H_2S$  and  $CH_3SH$  are also studied to fulfill two aims. Firstly to set a benchmark for the accuracy of

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our titled reactions with thiophenol and secondly to provide temperature-dependent rate constants for those reactions whose rate constants are only available at normal ambient temperatures. The kinetic parameters presented herein should be instrumental in building a robust kinetic model not only the decomposition of thiophenol but also for the fate of sulfur-containing at temperatures relevant to combustion conditions.

## 2. Computational details

All geometrical optimizations, harmonic vibrational frequencies have been calculated using the Gaussian 03 suite of programs [17]. For the system of thiophenol, calculations are carried out using the meta hybrid density functional theory (DFT) of BB1K [18] with the GTLarge basis set [19]. The BB1K functional is found to significantly surpass the accuracy of all hybrid DFT methods including B3LYP in determination of saddle-point geometries and their associated barrier heights [20]. For hydrogen transfer reactions, BB1K method has been proven to show very comparable performance with ab initio methods such as MP2 and the chemistry models methods such as G3B3 [21]. In order to further test the accuracy of the BB1K/GTLarge methodology, reaction and activation energies for the three corresponding reactions in hydrogen sulfide ( $H_2S$ ) and methyl sulfide ( $CH_3SH$ ) systems are also calculated and compared with the corresponding results from the composite methods of G3B3 and CBS-QB3.

The transmission coefficient that accounts for the quantum tunneling corrections is calculated with the one-dimensional Eckart functional [22]. Rate constants are fitted to simple Arrhenius parameters as  $k(T) = A \exp(-E^{\ddagger}/RT)$ , where  $A$  is the pre-exponential  $A$ -factor and  $E^{\ddagger}$  is the calculated energy of activation. Rate constants are calculated using TheRate code [23]. TheRate code is installed online and it is available free of charge at the CSEO resource (<http://www.cseo.net>).

## 3. Results and discussions

### 3.1. Structure and thermochemistry of thiophenol and thiophenoxy

Optimized structure of the planar thiophenol and its derived thiophenoxy radical are depicted in Fig. 1 at the BB1K/GTLarge. The calculated C–S and S–H bond lengths are 1.770 Å and 1.330 Å, i.e., in a fairly close agreement with the corresponding experimental values of 1.775 Å and 1.300 Å; respectively [24]. Our structural geometries for thiophenol and thiophenoxy are almost equivalent to those optimized at the B3LYP/6-311++G(d,p) [25] and CASPT2 [26] levels. The C–S bond in thiophenol is longer than the corresponding bond in thiophenoxy by only 3%. In comparison with the phenoxy/phenol ( $C_6H_5O/C_6H_5OH$ ) system, the corresponding calculated C–O bond is significantly shortened by 9% in phenoxy radical in reference to the phenol molecule. The Mulliken charge

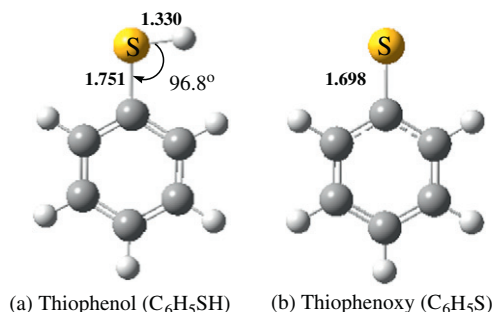


Fig. 1. Optimized structures of thiophenol (a) and thiophenoxy (b) at the BB1K/GTLarge. Distances are in Å.

at the S atom in thiophenoxy is determined to be  $-0.378 e$  in comparison with  $-0.728 e$  of located charge on the O atom in phenoxy. This indicates that the thiophenoxy radical exhibit less radical character at the S atom in comparison with the radical character at the O atom of the phenoxy radical.

Literatures values of the bond enthalpy of dissociation (BDH) of  $C_6H_5S-H$  bond shows significant disparity in the range of 77.5 kcal/mol–85.9 kcal/mol [27]. Herein, BDH of  $C_6H_5S-H$  is reevaluated using isodesmic work reactions as:



where X is considered to be one of the sulfur-centered radicals of HS,  $CH_3S$ . This method is shown to provide accurate BDH values by deploying reference species with well-known enthalpies of formation (errors not greater than  $\pm 0.50$  kcal/mol) while maintaining the same number of radical species on both sides of the reaction [28]. The reaction (Rx) utilizes the literature experimental enthalpy values ( $\Delta_f H_{298}^0$ ) [29] listed in Table 1 and total electronic energies for species and as given in Table 2. The BDH value is calculated as:

$$BDH(C_6H_5S-H) = \Delta_{rxn} H_{298}^0 + \Delta_f H_{298}^0(H) + \Delta_f H_{298}^0(X) - \Delta_f H_{298}^0(XH)$$

The calculated values for  $\Delta_{rxn} H_{298}^0$  and  $BDH(C_6H_5S-H)$  are listed in Table 3 using the two campsite methods of G3B3 and CBS-QB3. These two methods yield a BDH value of 88.0–98.0 kcal/mol. The value calculated herein is significantly higher than any other literature value by at least 2.1 kcal/mol. Accordingly; H expulsion from the thiol group in thiophenol is as endoergic as H expulsion from the hydroxyl group in phenol [28]. Utilizing the  $\Delta_f H_{298}^0$  values for H atom (52.1 kcal/mol) and the thiophenol (57.96 kcal/mol); in addition to the calculated BDH of  $C_6H_5S-H$  as 88.5 kcal/mol,  $\Delta_f H_{298}^0$  for thiophenoxy radical is calculated to be 63.3 kcal/mol. This value is higher than the available corresponding experimental [27] value by 3.3 kcal/mol. The difference between the experimental and the calculated  $\Delta_f H_{298}^0$  for thiophenoxy can be partially attributed to the uncertainty in  $\Delta_f H_{298}^0$  for reference species ( $\pm 1.1$  kcal/mol) and the small margin errors in the theoretical predictions ( $\pm 1.0$  kcal/mol).

In the calculations of  $S^\circ(298.15 K)$  for thiophenol, torsional frequency corresponding to the rotation of H about the C–S bond in thiophenol was treated as a hindered rotor and its thermochemical contribution is replaced by its corresponding rotational barrier, symmetry numbers and moment of inertia. The calculated internal barrier of rotation about the C–S bond is calculated to be 0.67 kcal/mol, in good agreement with the reported experimental value of 0.76 kcal/mol measured by microwave spectroscopy [30]. The calculated  $S^\circ(298.15 K)$  values for thiophenol and thiophenoxy are 81.13 cal/K mol and 76.76 cal/K mol, respectively in a satisfactorily agreement with the corresponding experimental values, i.e., 80.48 cal/K mol and 76.66 cal/K mol, respectively [31].

Table 1

Literature enthalpies of formation ( $\Delta_f H_{298}^0$ ) used in the estimation of BDH of  $C_6H_5S-H$  and the experimental values of  $\Delta E$  in Table 3. Values are in kcal/mol sourced from Ref. [29].

Species	$\Delta_f H_{298}^0$
H	52.1
OH	9.3
$H_2O$	-57.8
$HO_2$	2.9
$H_2O_2$	-32.4
$H_2S$	$-4.9 \pm 0.1$
HS	$34.2 \pm 0.2$
$CH_3SH$	$-5.4 \pm 0.1$
$CH_3S$	$29.8 \pm 0.4$
$C_6H_5SH$	26.8
$C_6H_5S$	$58.0 \pm 1.1$

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