Mechanistic and kinetic study on the reaction of thiophene with hydroxyl radical

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ABSTRACT

In order to understand the thiophene with hydroxyl reaction mechanism and kinetics, we carried out a detailed potential energy surface (PES) on the title reaction at the M06-2X/6-311++G(d,p) and G3 (MP2) (single-point) levels. Two possible reaction mechanisms including addition-elimination and H-abstract were revealed. The hydrogen abstraction of thiophene by OH produces H_2O along with the 2-thienyl (h-P1) or 3-thienyl (h-P2) radicals via a barrier of 7.9 and 2.2 kcal/mol, respectively. The addition of OH to the carbon atoms of the thiophene ring (at either α or β reaction sites) proceeds to intermediates IM1 and IM2 via barrier of 3.4 and 4.7 kcal/mol, and then decompose to the final products, respectively. Multichannel RRKM calculations have been carried out for the total and individual rate constants for all the channels over a wide range of temperatures and pressures. At atmospheric pressure with Ar, N_2 and He as bath gases, IM1 formed by collisional stabilization is dominated at T $\leqslant$ 600 K, whereas P1 produced by addition/elimination pathway are the major products at the temperatures between 700 and 1000 K; the direct hydrogen abstraction leading to H_2O with 3-thienyl (h-P2) plays an important role at higher temperatures.

1. Introduction

A multitude of the oxygen- or sulphur-containing organic compounds are produced from the combustion of fossil oil or coal, fuel refining, from burning plants and other biomasses and from petroleum refining which have been identified as being aliphatic or heterocyclic in nature [1–3]. Thiophene is a heterocyclic aromatic molecule that has been detected in fluid catalytic cracking (FCC) and residue fluid catalytic cracking (RFCC) gasoline [4]. The accelerated increasing emissions of sulphur compounds into the atmosphere produce acid rains, thus resulting in an increased atmospheric burden of the sulphur-containing organic compounds and creating a very acute problem in industrial countries. Oxidation processes of thiophene are of great important in the atmospheric chemistry and combustion of hydrocarbons. In the atmosphere, the main sink for thiophene is reaction with OH, O_3, and NO_3 radicals, which have been extensively studied [5–17], especially for investigated kinetic rate constants. The hydroxyl

radical is believed to be one of the important oxidizing agents that play an important role in the chemistry of atmospheric and photochemical air pollution reactions, and combustion processes. The hydroxyl radical is mainly responsible for the gas-phase chemical loss of most organics.

Until now, kinetic studies on the chemical reaction of thiophene + OH have been performed by several groups. In 1982, Lee and Tang [7] estimated the rate constant of thiophene with OH reaction using the discharge flow-resonance fluorescence technique, $k = (4.77 \pm 0.63) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K and total pressures of 1–5 Torr (Helium buffer gas). In the next year, Atkinson et al. [8] determinate the rate constants by using a competitive kinetics technique at 298 ± 2 K and 1 atm air with an assumed rate constant of 9.58×10^{-12} cm^3 $molecule^{-1}$ s^{-1} as bath gas of N_2. Subsequently, MacLeod and Jourdain et al. [9,10] reported the results of a discharge flow-EPR study of the title reaction in 0.45–2 Torr helium over a temperature range 293–473 K. The rate constant at 293 K is agreement with the 298 K results of Lee. This rate constant had also been determined by Barnes et al. [11] Martin et al. [12] Wallington [13] and Wine and Thompson [14] using different experimental technique, respectively. The rate

constants measured by Barnes et al., Martin et al. are 9.58×10^{-12} cm^3 molecule^{-1} s^{-1} as bath gas N$_2$ and 1.20×10^{-11} cm^3 molecule^{-1} s^{-1} as bath gas of He, respectively. The rate constants were measured by Wallington et al. in the pressure range 25–100 Torr pressure of Ar and over temperatures range 274–382 K and the Arrhenius expression obtained was $(1.2^{+1.0}_{-0.6}) \times 10^{-12}$ exp[(584 ± 217)/T] cm^3 molecule^{-1} s^{-1}, with the rate constants at 298 ± 2 K of $k = (8.7 \pm 0.70) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The rate constant expression which studied by Wine et al. is $(3.20 \pm 0.70) \times 10^{-12}$ exp[(325 ± 71)/T] cm^3 molecule^{-1} s^{-1} at the 30–150 Torr pressure of Ar and over the temperature range of 254–425 K. Evidently, different experimental conditions and methods might lead to different results. A systematic formula or explanation that may combine sets of the scattered experimental data is apparently desired. There is no theoretical study for mechanism and kinetics for the title reaction up to date. In this paper, we present the ab initio calculations of potential energy surface for the reaction of thiophene with OH radicals. Multichannel RRKM theory and transition state theory has been used to calculate the rate constants over a wide range of temperatures and pressures.

2. Computational methods

All calculations reported in this paper are carried out using the Gaussian 09 programs packages [18]. Geometry optimizations and frequency calculations are performed using M06-2X [19,20] with the standard 6-311++G(d,p) basis set. It is very important to test the reliability of these methods to model the title reaction. Therefore, the intermediates and transition states are also optimized using the MP2 [21] and B3LYP [22,23] methods with the same basis set. It appears that neither B3LYP nor MP2 is appropriate for the calculations of the thiophene + OH reaction because (1) B3LYP usually gives transition states that are too early and activation energies that are too low, even worse, some important species cannot be located, for example, pre-reactive complex (CR1), entrance transition state (TS1); (2) the MP2 method shows the significant spin contamination for the wave function of the transition states. However, the M06-2X functional show much better performance. As a matter of fact, M06-2X method has been employed successfully to investigate the addition reactions of OH to the unsaturated compounds [24]. All stationary points are characterized by harmonic vibrational frequency analysis (number of imaginary frequencies, NIMAG, 0 for minima and 1 for transition states). Moreover, for each transition state the intrinsic reaction coordinate (IRC) calculations were employed at the same level to confirm the connections between the corresponding reactants and products [25]. The energies of the stationary points were calculated using the G3(MP2) [26] method. In addition to the G3(MP2) single point energies, CCSD(T)/cc-pVTZ method was also performed for the thiophene + OH reaction using the M06-2X/6-311++G(d,p) optimized geometries. As seen from Table 1, there is a good linear correlation between the two sets of data.

The rate constants for all the pathways have been calculated statistically using the transition-state theory (TST) and the multichannel RRKM theory [27] that had been successfully used to deal with the complex reactions [28–32].

3. Results and discussion

The optimized structures of reactants, products, complexes, intermediates and transition states at M06-2X/6-311++G(d,p) level of theory are shown in Fig. 1. The profile of the potential energy profile for the OH with thiophene reaction is plotted in Fig. 2 in order to clarify the reaction mechanism. Table 1 summarizes

Table 1
ZPE corrections, relative energies (ΔE), reaction enthalpies (ΔH), and gibbs free energy (ΔG) at 298 K for all the species in the OH + thiophene reaction (energies in kcal/mol).

Species	ZPE	ΔE^a	ΔE^b	ΔE^c	$\Delta H^0_{298}{}^d$	$\Delta H^0_{298}{}^e$	ΔG^f
Thiophene + OH	47.6	0.0	0.0	0.0	0.0	0.0	0.0
h-TS1	45.3	6.6	7.9	8.1	7.6	7.5	15.1
h-TS2	45.4	5.4	2.2	7.8	7.3	1.7	9.6
TS1	49.2	−0.6	1.1	1.5	0.7	0.3	9.1
TS2	49.2	1.2	2.4	2.8	2.0	1.6	10.4
TS3	51.2	−14.8	−7.8	−9.4	−10.6	−9.1	0.6
TS4	50.8	−7.6	−1.5	−2.9	−4.0	−2.6	6.9
TS5	49.5	4.2	8.4	7.4	6.8	7.9	15.9
TS6	46.0	10.3	13.0	13.8	12.9	12.1	21.6
TS7	46.3	11.4	13.3	14.1	13.1	12.2	21.8
CR1	48.8	−4.2	−2.3	−4.2	−1.9	−2.4	3.9
IM1	51.2	−29.2	−25.1	−26.3	−27.3	−26.1	−16.8
IM2	51.0	−17.8	−15.8	−16.0	−16.9	−16.8	−7.6
P1	51.3	−23.7	−15.5	−18.2	−18.7	−16.0	−8.1
P2	51.5	−30.5	−22.3	−24.9	−25.8	−23.2	−14.5
P3 + H	44.7	5.9	6.2	8.1	8.4	6.6	8.8
P4 + H	44.7	3.0	3.0	4.9	5.2	3.4	5.6
h-P1 + H$_2$O	47.9	0.4	0.5	2.2	2.6	0.8	−0.7
h-P2 + H$_2$O	47.8	−2.2	−2.0	−0.1	0.2	−1.6	−3.2

[a] M06-2X/6-311++G(d,p) level.
[b] G3(MP2)//M06-2X/6-311++G(d,p) level.
[c] CCSD(T)/cc-PVTZ//M06-2X/6-311++G(d,p) level.
[d] CCSD(T)/cc-PVTZ//M06-2X/6-311++G(d,p) level.
[e] G3(MP2)//M06-2X/6-311++G(d,p) level.
[f] G3(MP2)//M06-2X/6-311++G(d,p) level.

relative energies, reaction enthalpies and Gibbs free energy. The moment of inertia, harmonic vibrational frequencies and the Cartesian coordinates of all species involved in this reaction are deposited in Tables S1 and S2, respectively. The frequencies of thiophene, OH and water are in agreement with experimental data [33]. Unless otherwise specified, the geometric parameters and energies used in the following discussion are at G3(MP2)//M06-2X/6-311++G(d,p) level.

3.1. Thiophene + OH reaction

As for the title reaction, there are two kinds of pathways, including the OH addition to the carbon atoms of C=C double bonds in the thiophene ring and direct H-abstraction mechanisms. In the C_{2v} symmetry thiophene molecule, both two types of pathways may occur at the sites of the α (C1) or β (C2) position of thiophene. We now consider them individually.

3.1.1. Addition/elimination pathways

The hydroxyl radical addition to the α (C1) or β (C2) sites of thiophene form a pre-reactive complex CR1 with no barrier at the reaction entrance. In CR1, the distances between the oxygen atom of OH moiety and two carbon atoms (C1 and C2) of thiophene moiety are very long (i.e., 2.872 and 2.831 Å). Similar complexes have been found for the reactions of OH radicals with furan [31]. The calculated binding energy ΔE (see Table 1) of CR1 is 2.3 kcal/mol.

After forming CR1, it could transform to intermediate IM1 and IM2 via TS1 and TS2, respectively, which depending on the orientation of the attack of OH radical. If the OH radical attacks the to the α (C1) site of thiophene, then IM1 will be formed. If the OH radical attacks the β (C2) site of thiophene, then IM2 will be formed. The corresponding barrier heights are calculated to be 3.4 and 4.7 kcal/mol, respectively. The geometries of TS1 and TS2 are illustrated in Fig. 1. Both TS1 and TS2 show a conserved character of the C=C double bond, and the distance between the C1 (TS1) or C2 (TS2) and oxygen atoms are long (2.079 or