Quantum chemical and kinetic study of the oxidation mechanisms of thiophene initiated by hydroxyl radicals



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Abstract

The oxidation mechanisms of thiophene by OH radicals under inert conditions (Ar) have been studied using density functional theory (DFT) in conjunction with various exchange-correlation functionals. Comparison has been made with benchmark CBS-QB3 theoretical results. Kinetic rate constants were correspondingly estimated by means of variational TST and RRKM theory. Effective rate constants have been calculated according to a steady state analysis upon a two-step model reaction mechanism. In line with experiment, the computed branching ratios indicate that the kinetically most efficient process corresponds to OH addition onto a carbon atom which is adjacent to the sulfur atom. Because of negative activation energies, pressures larger than 10⁴ bar are required to reach the high-pressure limit. Nucleus independent chemical shift indices and natural bond orbital analysis show that the computed activation energies are dictated by alterations of aromaticity and charge transfer effects due to the delocalization of sulfur lone pairs to empty π^* orbitals.

Introduction

- Kinetic reactions of sulfur compounds with important oxidant species such as OH, O₃, and NO₃ are required in order to evaluate their atmospheric residence times as well as the ultimate fates of these compounds.
- 4 The major gas-phase chemical loss processes in the atmosphere are via reactions with O₃ and OH radicals.
- 4 OH radicals are the main oxidant species during day time.
- **4** Studies of the oxidation processes of thiophene are essential for understanding the atmospheric

Table 1. Internal energies, standard enthalpies and Gibb's free energies (in kcal/mol) of pre-reactive, and products relative to the reactants along chemical pathways 1-3 at different levels of theory. (P = 1 atm)

Method	Method @B97XD/aug-cc-pVTZ		UM06-2 <i>x</i> /aug-cc-pVTZ	CBS-QB3		
Species	$\Delta E_{0\mathrm{K}}$ $\Delta H^{\circ}_{298\mathrm{K}}$ ΔG	ΔE_{0K} ΔH°_{298K} ΔG°_{298K}	$\Delta E_{0 m K}$ $\Delta H^{\circ}_{298 m K}$ $\Delta G^{\circ}_{298 m K}$	$\Delta E_{0 m K}$ $\Delta H^{\circ}_{298 m K}$ $\Delta G^{\circ}_{298 m K}$		
Thiophene +OH•	0.00 0.00 0	.00 0.00 0.00 0.00	0.00 0.00 0.00	0.00 0.00 0.00		
IM <i>x</i> (<i>x</i> =1,2)	-2.73 -2.84 4	.27 -3.11 -3.29 3.87	-3.82 -3.81 2.71	-2.63 -2.77 4.40		
IM3	-2.10 -2.11 4	.40 -3.20 -3.31 3.65	-3.71 -3.71 3.07	-1.70 -1.89 5.38		
P1	-27.22 -28.17 -1	8.51 -27.08 -28.03 -18.35	-26.30 -27.25 -17.58	-26.18 -27.12 -17.46		
P2	-15.80 -16.57 -7	.32 -15.74 -16.47 -7.31	-15.46 -16.24 -6.94	-15.80 -16.56 -7.28		
Р3	-2.10 -2.11 4	.38 -3.20 -3.31 3.65	-3.76 -3.79 3.20	-1.70 -1.89 5.38		

Table 2. Internal energies, standard enthalpies and Gibb's free energies (in kcal/mol), and activation entropies (in cal/mol K) of transition states relative to the reactants along chemical pathways 1–3 at different levels of theory. (P = 1 atm)

Method			UM05-	UM05-2 <i>x</i> /aug-cc-pVTZ		UM06-2 <i>x</i> /aug-cc-pVTZ			CBS-QB3			
Species	$\Delta E_{0\mathrm{K}}^{\dagger}$	$\Delta H^{\circ}_{298\mathrm{K}^{\dagger}}$	$\Delta G^{\circ}_{298\mathrm{K}^{\dagger}}$	$\Delta E_{0\mathrm{K}}^{\dagger}$	$\Delta H^{\circ}_{298\mathrm{K}}^{\dagger}$	$\Delta G^{\circ}_{298\mathrm{K}^{\dagger}}$	$\Delta E_{0\mathrm{K}}^{\dagger}$	$\Delta H^{\circ}_{298\mathrm{K}}^{\dagger}$	ΔG° 298K †	$\Delta E_{0\mathrm{K}}^{\dagger}$	$\Delta H^{\circ}_{298\mathrm{K}}^{\dagger}$	$\Delta G^{\circ}_{298\mathrm{K}^{\dagger}}$
Thiophene +OH•	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TS1	-1.93	-2.65	6.22	-0.81	-1.58	7.47	-0.07	-0.82	8.20	-2.18	-2.90	6.00
TS2	-0.41	-1.20	7.90	0.68	-0.10	8.99	1.37	0.59	9.70	-1.18	-1.98	7.20
TS3	-2.10	-2.58	5.13	-0.82	-1.48	6.93	0.10	-0.63	8.23	-1.57	-2.28	6.51

4 Reaction pathways 1–2 are *exoergic processes* ($\Delta G < 0$), whereas pathway 3 is found to be endogenic ($\Delta G > 0$) at ambient temperature and pressure.

Table 5. Kinetic parameters for the reported reaction channels using RRKM theory (P=133 mbar), according to the computed CBS-QB3 energy profiles. (x=1,2)

Т		Rate constants							io (%)
(K)	$IMx \rightarrow P1 k_2(1)$	$IMx \rightarrow P2 k_2(2)$	$IM3 \rightarrow P3$ k ₂ (3)	$\begin{array}{c} R \rightarrow P1 \\ k_{eff}(1) \end{array}$	$R \rightarrow P2$ $k_{eff}(2)$	$R \rightarrow P3$ $k_{eff}(3)$	<i>R</i> (1)	<i>R</i> (2)	<i>R</i> (3)
298	1.05×10 ⁹	7.81×10 ⁸	1.11×10 ⁹	2.29×10 ⁻¹⁵	1.69×10 ⁻¹⁵	3.58×10 ⁻¹⁶	52.79	38.96	8.25
322	1.00×10 ⁹	8.04×10 ⁸	1.04×10 ⁹	1.99×10 ⁻¹⁵	1.59×10 ⁻¹⁵	3.25×10 ⁻¹⁶	50.96	40.72	8.32
353	9.43×10 ⁸	8.11×10 ⁸	9.65×10 ⁸	1.73×10 ⁻¹⁵	1.49×10 ⁻¹⁵	2.92×10 ⁻¹⁶	49.26	42.43	8.31
380	8.94×10 ⁸	8.04×10 ⁸	9.09×10 ⁸	1.56×10 ⁻¹⁵	1.40×10^{-15}	2.70×10^{-16}	48.30	43.34	8.36
400	8.60×10 ⁸	7.93×10 ⁸	8.72×10 ⁸	1.47×10^{-15}	1.35×10 ⁻¹⁵	2.57×10^{-16}	47.77	43.87	8.35
425	8.22×10 ⁸	7.75×10 ⁸	8.30×10 ⁸	1.37×10 ⁻¹⁵	1.30×10 ⁻¹⁵	2.43×10 ⁻¹⁶	47.03	44.63	8.34
442	7.97×10 ⁸	7.61×10 ⁸	8.04×10 ⁸	1.32×10 ⁻¹⁵	1.26×10^{-15}	2.35×10 ⁻¹⁶	46.89	44.76	8.35
457	7.77×10 ⁸	7.48×10 ⁸	7.83×10 ⁸	1.28×10 ⁻¹⁵	1.24×10^{-15}	2.29×10 ⁻¹⁶	46.56	45.11	8.33
471	7.59×10 ⁸	7.35×10 ⁸	7.64×10 ⁸	1.25×10 ⁻¹⁵	1.21×10^{-15}	2.24×10^{-16}	46.57	45.08	8.35

4 Since VTST calculations cannot be performed for practical reasons in conjunction with CBS-QB3 method, it is preferable to consider the RRKM approach for evaluating kinetic rate constants, since in this case it is possible to rely upon more quantitative estimates for activation and reaction energies. Besides, pressure effects need to be taken into account for a reliable interpretation of the experimentally available kinetic rate constants (Fig. 3).



- sulfur cycle.
- 4 The overall rate constants of the oxidation reaction between thiophene and OH radicals are separated into individual processes involving OH addition onto the C=C double bond and onto the sulfur atom.
- Witte and Zetzsch used a flash photolysis-resonance fluorescence apparatus to investigate the temperature dependence of the reaction between 298 and 471 K at a total pressure of 133 mbar with argon (Ar) as inert gas.
- 4 Since thiophene is stabilized by resonance, one may assume that the kinetics of the reaction should be similar to the kinetics of the reactions of OH radicals with other aromatic hydrocarbons.
- The negative temperature dependence of experimental rate constants for the oxidation processes of thiophene by OH radicals over the temperature range 255-471 K indicates negative activation energies.
- 4 Three different pathways (Fig. 1) have been suggested in the gas phase to explain these findings.



4 the formation of **P1** will be thermodynamically favored, since the reaction is strongly exothermic (ΔH =-27.0 kcal/mol) and exoergic (ΔG =-17.5 kcal/mol).



- Fig. 2. CBS-QB3 potential energy profile of reaction pathways 1–3.
- **4** The TSs and IMs are characterized by nucleus independent chemical shift (NICS) indices: $[TS1=-12.2, TS2=-11.0, TS3=-11.8] \rightarrow most aromatic nature of the TS1 \rightarrow its higher stability.$ $[IMx = -13.5, IM3 = -12.1] \rightarrow$ more aromatic nature of the IM_x complex \rightarrow its higher stability.
- 4 Natural bond orbital (NBO) analysis upon TS1 and TS2 reveals that a strong interaction prevails in between a sulfur lone pair and the unoccupied $\pi^*(C_4-C_5)$ orbital; charge transfer delocalization contributes to the greater stability of TS1.

Kinetic analysis

 \downarrow Effective rate constants for the reaction pathways 1–3 have been computed upon a two-step mechanism, involving first a fast and reversible preequilibrium between the reactants and a pre-reactive complex $[C_4H_4S...OH]^{\bullet}$ (IMz with z=1-3), followed by an irreversible dissociation step leading to the products:



Fig. 3. Arrhenius plot of the obtained RRKM bimolecular rate constants using the CBS-QB3 approach (P=133 mbar).

- 4 Due to the involved negative energy barriers, RRKM effective rate constants decrease with increasing temperatures. Because the equilibrium constants for the first reversible reaction step $(K_{\rm c}=K_{\rm p}/RT)$ do not depend very much on the site of addition, this results in turn into a larger effective rate constant, by about one order of magnitude, for the OH• addition process onto the C_2 atom, compared with the effective rate constants obtained for OH[•] addition onto the C_3 and S_1 atoms.
- 4 Branching ratios for pathways 2–3 increase with increasing temperatures, whereas the branching ratio for pathway 1 decreases as T increases.
- 4 In line with the computed energy profiles, the RRKM data (Fig. 3) indicate that the production of the P1 species will dominate the overall reaction mechanism, and this down to extremely low pressures, larger than 10^{-10} bar.
- **4** RRKM effective rate constants obtained from the CBS-QB3 energy profiles for the fastest chemical reaction pathway ($R \rightarrow P1$, i.e., OH addition at the C₂ position) underestimate the experimental ones by about 2 to 3 orders of magnitude only (Table 5), which correspond to errors of the order of 3 to 4.5 kcal/mol on the computed activation energies.
- \blacksquare Both the experimental and theoretical rate constants for OH addition at the C₂ position reaction decrease with increasing temperatures, confirming the idea of a negative activation energy.
- **4** With reaction enthalpies (ΔH°) and Gibb's free reaction (ΔG°) energies below -24.4 and -21.9 kcal/mol, respectively, the second reaction steps in pathways 1 and 2 are highly exothermic and exoergic, and, therefore, most clearly irreversible.
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Fig. 1. Reaction pathways for the oxidation of thiophene by OH radicals.

Theory and Computational Details

- 4 The molecular structures and harmonic vibrational frequencies of all stationary points were calculated using Density Functional Theory along with a variety of exchange-correlation functionals (ω B97XD, UM05-2x and UM06-2x), in conjunction with the aug-cc-pVTZ basis
- Our most accurate calculations were conducted at the CBS-QB3 level.
- **t** The CBS-QB3 approach involves five steps:
- B3LYP/6-311G(2d,d,p) geometry optimization.
- B3LYP/6-311G(2d,d,p) frequency calculation with a 0.99 scale factor for the ZPE
- CCSD(T)/6-31+G^{*} energy calculation.
- MP4(SDQ)/6-31+G(d(f),p) energy calculation.
- UMP2/6-311+G(3d2f,2df,2p) energy calculation and extrapolation to a complete basis set.
- **4** Kinetic parameters were evaluated using transition state theory (TST) using CBS-QB3 values for activation energies:

$$k_{\text{TST}} = \kappa(T) \frac{\sigma k_{\text{B}} T}{h} V_{\text{m}}(T) \frac{Q_{\text{TS}}^{\dagger}(T)}{Q_{\text{A}}(T) Q_{\text{B}}(T)} \exp(-E_a/R)$$
$$k_{\text{TST}} = \kappa(T) \frac{\sigma k_{\text{B}} T}{h} \frac{Q_{\text{TS}}^{\dagger}(T)}{Q_{\text{A}}(T)} \exp(-E_a/R)$$

where σ is the reaction pathway degeneracy, and $\kappa(T)$ is the Wigner's tunneling factor.

- **W** Statistical RRKM has been used along with the strong collision approximation to evaluate pressure effects on a microcanonical basis, both in the fall-off regime and towards the highpressure limit frequencies.
- All supplied values for unimolecular kinetic rate constants (k_2) are the results of calculations that were performed using the implementation of canonical variational TST, and statistical RRKM theory in the Kinetic and Statistical Thermodynamical Package (KiSThelP).

Results and Discussion

$$C_{4}H_{4}S + OH^{\bullet} \xrightarrow{k_{R} \to IM_{z}} [C_{4}H_{4}S...OH]^{\bullet} \xrightarrow{k_{IMz} \to P_{z}} [C_{4}H_{4}S-OH]^{\bullet}$$

4 A steady-state analysis upon the above chemical mechanism yields the following effective rate constants for the three studied chemical pathways:

$$k_{\text{eff}}(i) = \frac{k_{\text{R} \to \text{IM}_i} k_{\text{IM}_i \to \text{P}_i}}{k_{\text{IM}_i \to \text{R}} + k_{\text{IM}_i \to \text{P}_i}} \approx K_{\text{c}(\text{R} \rightleftharpoons \text{IM}_i)} k_{\text{IM}_i \to \text{P}_i} = (RT) K_{\text{p}(\text{R} \rightleftharpoons \text{IM}_i)} k_{\text{IM}_i \to \text{P}_i}; i = 1-3$$

4 Branching ratios have been obtained according to VTST and RRKM estimates of rate constants, as follows:

$$R(i) = \frac{k_{eff}(i)}{k_{eff}(1) + k_{eff}(2) + k_{eff}(3)} ; i = 1 - 3$$

- \downarrow These rate constants are based upon UM06-2*x*/aug-cc-pVTZ calculations of activation energies (ZPEs included). Note that the UM06-2x exchange-correlation functional is most generally considered to be the best one for applications involving main-group thermochemistry, kinetics, noncovalent interactions, and electronic excitation energies to valence and Rydberg states.
- \downarrow Kinetic parameters obtained at P = 1 bar using the VTST and RRKM approaches do not appreciably differ (Tables 3–4). The largest discrepancy is found for the rate constant characterizing the second reaction step in pathway 3 $[k_2(3)]$, and this discrepancy does not exceed a factor 3.

Table 3. Kinetic parameters for the reported reaction channels using VTST theory (P = 1 bar), according to the computed UM06-2*x* energy profiles. (x=1,2)

Т		Branching ratio (%)							
(K)	$IMx \rightarrow P1 k_2(1)$	$IMx \rightarrow P2 \\ k_2(2)$	IM3→P3 <i>k</i> ₂ (3)	$\begin{array}{c} R \rightarrow P1 \\ k_{eff}(1) \end{array}$	$R \rightarrow P2$ $k_{eff}(2)$	$\begin{array}{c} R \rightarrow P3 \\ k_{eff}(3) \end{array}$	<i>R</i> (1)	<i>R</i> (2)	<i>R</i> (3)
298	3.03×10 ⁸	2.13×10 ⁷	3.48×10 ⁸	2.27×10^{-14}	1.60×10 ⁻¹⁵	1.49×10 ⁻¹⁴	57.91	4.08	38.01
322	4.81×10 ⁸	4.08×10 ⁷	5.66×10 ⁸	2.78×10^{-14}	2.36×10 ⁻¹⁵	1.89×10 ⁻¹⁴	56.67	4.81	38.52
353	7.96×10 ⁸	8.28×10^{7}	9.60×10 ⁸	3.53×10^{-14}	3.67×10 ⁻¹⁵	2.48×10^{-14}	55.36	5.76	38.89
380	1.15×10 ⁹	1.39×10 ⁸	1.41×10 ⁹	4.25×10^{-14}	5.14×10^{-15}	3.06×10 ⁻¹⁴	54.32	6.57	39.11
400	1.47×10 ⁹	1.96×10 ⁸	1.82×10 ⁹	4.85×10 ⁻¹⁴	6.46×10 ⁻¹⁵	3.54×10^{-14}	53.67	7.15	39.18
425	1.92×10 ⁹	2.86×10 ⁸	2.41×10 ⁹	5.63×10 ⁻¹⁴	8.39×10 ⁻¹⁵	4.19×10 ⁻¹⁴	52.82	7.87	39.31
442	2.27×10 ⁹	3.61×10 ⁸	2.86×10 ⁹	6.22×10^{-14}	9.89×10 ⁻¹⁵	4.66×10 ⁻¹⁴	52.41	8.33	39.26



Fig. 4. Pressure dependence of the RRKM bimolecular rate constants for the reaction pathways 1–3 according to the CBS-QB3 energy profiles.

In line with negative activation energies, pressures larger than 10⁴ bar are required for ensuring the saturation of RRKM kinetic rate constants to their high-pressure (TST) limit. Pressure effects need therefore to be taken into account on RRKM grounds for consistent insights (Table 5) into the experimental rate constants by Witte and Zetzsch (P = 133 mbar). Compared with the highpressure limit, pressure effects result then indeed into a decrease of the computed rate constants, by ~4 orders of magnitude.

Thermodynamical analysis

The CBS-QB3 results show that:

- 4 The oxidation process via reaction pathway 2 appears also to be a rather strongly exothermic process, whereas pathway **3** appears to be only slightly exothermic (Table 1).
- 4 Canonical VTST including Wigner's tunneling corrections has been used mainly for the sake of validating the RRKM approach at P = 1 bar. Indeed, when studying reaction mechanisms involving shallow energy wells and loose transition states, VTST is most commonly regarded as the most reliable approach for estimating kinetic rate coefficients with an accuracy approaching the limits of the assumptions inherent in transition state theory.
- With VTST, the position of the transition state is varied until the maximum value of the Gibbs free activation energy (ΔG^{\dagger}) is found for reactions in the gas phase and at gas surface interfaces.
- Transition state on pathway 1 (TS1) as the lowest transition state, and locate it at ~2.2 kcal/mol below the reactants (Table 2).
- **4** The activation barrier for pathway **1** is lower by 1.0 and 0.6 kcal/mol than the barrier for pathways 2 and 3, respectively.
- + This difference in activation energies for the bimolecular reactions $R \rightarrow P1$, $R \rightarrow P2$ and $R \rightarrow P3$ indicates that the formation of product P1 will be kinetically favored over the formation of the products P2 and P3.
- **4** Reaction pathways **1–3** are *exothermic* processes.

 $457 \quad 2.60 \times 10^9 \quad 4.38 \times 10^8 \quad 3.29 \times 10^9 \quad 6.74 \times 10^{-14} \quad 1.14 \times 10^{-14} \quad 5.09 \times 10^{-14} \quad 51.97 \quad 8.79 \quad 39.24$ 471 2.92×10^9 5.17×10^8 3.73×10^9 7.26×10^{-14} 1.28×10^{-14} 5.53×10^{-14} 51.60 9.10 39.30

Table 4. Kinetic parameters for the reported reaction channels using RRKM theory (P=1 bar) according to the computed UM06-2*x* energy profiles. (x=1,2)

Т				Branc	hing ra	tio (%)			
(K) $\frac{IMx \rightarrow P1}{k_2(1)}$	$IMx \rightarrow P2 \\ k_2(2)$	IM3→P3 <i>k</i> ₂ (3)	$\begin{array}{c} R \rightarrow P1 \\ k_{eff}(1) \end{array}$	$R \rightarrow P2$ $k_{eff}(2)$	$R \rightarrow P3$ $k_{eff}(3)$	<i>R</i> (1)	<i>R</i> (2)	R(3)
29	8 1.52×10 ⁸	2.18×10 ⁷	1.16×10 ⁸	1.14×10 ⁻¹⁴	1.63×10 ⁻¹⁵	4.96×10 ⁻¹⁵	63.37	9.06	27.57
32	2 2.10×10 ⁸	3.90×10 ⁷	1.67×10 ⁸	1.21×10^{-14}	2.25×10 ⁻¹⁵	5.58×10 ⁻¹⁵	60.71	11.29	28.00
35	3 2.88×10 ⁸	7.09×10 ⁷	2.40×10 ⁸	1.28×10^{-14}	3.15×10 ⁻¹⁵	6.20×10 ⁻¹⁵	57.79	14.22	27.99
38	0 3.52×10 ⁸	1.07×10 ⁸	3.03×10 ⁸	1.30×10 ⁻¹⁴	3.95×10 ⁻¹⁵	6.57×10 ⁻¹⁵	55.27	16.79	27.93
40	0 3.95×10 ⁸	1.37×10 ⁸	3.47×10 ⁸	1.30×10 ⁻¹⁴	4.52×10^{-15}	6.75×10 ⁻¹⁵	53.56	18.62	27.81
42	5 4.41×10 ⁸	1.78×10^{8}	3.96×10 ⁸	1.29×10 ⁻¹⁴	5.22×10^{-15}	6.88×10 ⁻¹⁵	51.60	20.88	27.52
442	2 4.68×10 ⁸	2.06×10 ⁸	4.25×10 ⁸	1.23×10^{-14}	5.43×10 ⁻¹⁵	6.66×10 ⁻¹⁵	50.43	22.26	27.31
45	7 4.87×10 ⁸	2.31×10 ⁸	4.48×10 ⁸	1.26×10 ⁻¹⁴	5.99×10 ⁻¹⁵	6.93×10 ⁻¹⁵	49.37	23.47	27.16
47	l 5.03×10 ⁸	2.54×10 ⁸	4.66×10 ⁸	1.25×10 ⁻¹⁴	6.31×10^{-15}	6.91×10 ⁻¹⁵	48.60	24.53	26.87

4 In line with the experimental data, the RRKM results for the effective rate constants of the reaction pathways 1–3 are negatively dependent on the temperature (Fig. 3). The production of the P1 radical therefore dominates the overall reaction mechanism under atmospheric pressure and at temperatures ranging from 298 to 471 K in the absence of O_2 .

Conclusions

- 4 The best agreement with the CBS-QB3 energy barriers is obtained with the UM06-2x exchange-correlation functional.
- \downarrow In line with experiment, due to the formation of a pre-reactive complex[C₄H₄S...OH], transition states lie below the reactant, hence effective negative activation energies.
- 4 In line with experiment, the obtained branching ratios indicate that the kinetically most efficient process at temperatures ranging from 298 to 471 K corresponds to OH addition onto a carbon atom which is adjacent to the sulfur atom.
- 4 NICS indices and NBO analysis show that the computed activation energies are largely dictated by aromaticity and, to a lesser extent, charge transfer effects.
- 4 The regioselectivity of the reaction decreases with increasing temperatures and decreasing pressures.
- **4** A comparison with VTST results validates RRKM theory for all investigated reaction channels.
- 4 The TST approximation breaks down at ambient pressure (1 bar) for the first bimolecular reaction steps.
- \downarrow Due to low and negative activation energies, pressures larger than 10⁴ bar are required for reaching the high pressure limit.
- **4** RRKM enables semi-quantitative insights into the available experimental kinetic rate constants, with discrepancies in the range of 2 to 3 orders of magnitude between theory and experiment.

References

[1] A. Shiroudi, M.S. Deleuze, J. Mol. Model., 21 (2015) 301.