Reaction mechanisms and kinetics of the O₂ addition pathways upon the main thiophene-OH adduct: A theoretical study



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Abstract

Density Functional Theory (DFT) along with the ω B97XD and UM06-2x exchangecorrelation functionals has been used to study the reaction mechanisms and kinetics of atmospheric oxidation of the main (kinetically dominant) thiophene-OH adduct $[C_4H_4S-$ OH]• (R1) by molecular oxygen in its triplet electronic ground state. Kinetic rate constants and branching ratios under atmospheric pressure and in the fall-off regime have been calculated by means of transition state theory (TST), variational transition state theory (VTST) and statistical Rice–Ramsperger–Kassel–Marcus (RRKM) theory. In line with the computed energy profiles, the dominant process under both a thermodynamic and kinetic control of the reaction is O_2 addition at the C_5 position in syn mode. The computed branching ratios indicate that the regioselectivity of the reaction decreases with increasing temperatures and decreasing pressures.

Introduction

- 4 Among all oxidation mechanisms of thiophene which are initiated by OH radicals, the process which dominates under inert conditions (Ar) at temperatures ranging from 298 to 471 K under a kinetic control of the reaction is the OH addition process onto a carbon atom which is adjacent to the sulfur atom ($[C_4H_4S-OH]^{\bullet}$, R1 adduct).
- 4 Under atmospheric conditions, the $[C_4H_4S-OH]^{\bullet}(R1)$ energized adduct is expected to react primarily with triplet molecular oxygen, to form $R1-O_2$ peroxy radicals.
- \downarrow O₂ addition (from syn and anti directions) onto the R1 adduct can occur at the C₃, C₄,

- 4 In this study, we focus only on the formation of the R1-*i*OO-*anti/syn*(*i*=3,5) radicals, yielding the P1–P4 products (Fig. 1).
- Lenergy barriers related to the formation processes of R1-4OO-*anti/syn* radicals are larger than ~37 kcal/mol, hence these processes will be kinetically negligible under atmospheric conditions (Fig.1, Table 2).
- \downarrow The stabilization energy (~2 kcal/mol) for the formation of the R1-5OO-*syn* peroxy radical compared with the R1-500-anti species corresponds to the formation of an intramolecular hydrogen bond.
- + The activation energy (ΔE_{0K}^{\dagger}) for the formation of the R1-500-*syn* radical is lower than that for the R1-3OO-syn radical, because of some extra-stabilization due to the formation of an H-bond between O_9 (peroxy group) and H_7 (hydroxyl group).

Table 2. Activation energies, enthalpies and Gibb's free activation energies (in kcal/mol) for the addition of triplet molecular O₂ on the [C₄H₄S-OH][•] radical, at different levels of theory.

| Method | <i>ω</i> B972 | XD/aug-cc | e-pVTZ | UM06-2 <i>x</i> /aug-cc-pVTZ | | | | |
|--------------------|------------------------------------|--|--|------------------------------------|--|--|--|--|
| Species | $\Delta E_{0\mathrm{K}}^{\dagger}$ | $\Delta H^{\circ}{}_{298\mathrm{K}}^{\dagger}$ | $\Delta G^{\circ}_{298\mathrm{K}}^{\dagger}$ | $\Delta E_{0\mathrm{K}}^{\dagger}$ | $\Delta H^{\circ}_{298\mathrm{K}}^{\dagger}$ | $\Delta G^{\circ}_{298\mathrm{K}}^{\dagger}$ | | |
| $R1 + O_2$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | | |
| TS-300- <i>syn</i> | 5.988 | 5.188 | 16.193 | 5.039 | 4.271 | 15.225 | | |
| TS-400-syn | 37.23 | 36.11 | 48.20 | 39.12 | 38.18 | 49.72 | | |
| TS-500-syn | 0.066 | -0.754 | 10.442 | -1.773 | -2.641 | 8.782 | | |

| Table 3. | Kinetic | rate | constants | for | the | reaction | channels | obtained | using | TST | theory |
|-----------|------------|--------|-----------|------|-----|------------------|------------|------------|----------------|-------|--------|
| (P=1 bar) | r), accord | ling t | o the com | pute | d U | M06-2 <i>x</i> e | energy pro | files (x=1 | or 3, <i>y</i> | =2 or | 4). |

| T | | | Rate co | onstant | Effective rate constant (cm^3 molecule ⁻¹ s ⁻¹) | | | | | | |
|-----|---------------------------------------|-------------------------------|-------------------------------|--|---|-------------------------------|--|--|--|--|--|
| 1 | | <i>anti</i> mode | | | <i>syn</i> mode | | | mode | syn 1 | syn mode | |
| (K) | $IMx \rightarrow R1 + O_2$ (k_{-1}) | $IM2 \rightarrow P2$ $k_2(2)$ | $IM4 \rightarrow P4$ $k_2(4)$ | $\frac{\text{IM}y \rightarrow \text{R}1 + \text{O}_2}{(k_{-1})}$ | $IM1 \rightarrow P1$ $k_2(1)$ | $IM3 \rightarrow P3$ $k_2(3)$ | $R1+O_2 \rightarrow P2$ $[k_{eff}(2)]$ | $R1+O_2 \rightarrow P4$ [$k_{eff}(4)$] | $R1+O_2 \rightarrow P1$ $[k_{eff}(1)]$ | $R1+O_2 \rightarrow P3$ $[k_{eff}(3)]$ | |
| 298 | 6.91×10 ¹⁵ | 8.82×10 ⁵ | 1.97×10⁷ | 8.59×10 ¹⁵ | 5.41×10 ⁴ | 1.38×10 ⁹ | 7.70×10^{-18} | 1.72×10^{-16} | 2.63×10 ⁻¹⁹ | 6.70×10^{-15} | |
| 322 | 4.43×10 ¹⁵ | 2.40×10⁶ | 4.01×10⁷ | 5.42×10 ¹⁵ | 1.86×10 ⁵ | 2.10×10⁹ | 1.41×10^{-17} | 2.35×10^{-16} | 6.00×10 ⁻¹⁹ | 6.78×10 ⁻¹⁵ | |
| 353 | 2.74×10 ¹⁵ | 7.15×10 ⁶ | 8.67×10⁷ | 3.30×10 ¹⁵ | 7.15×10 ⁵ | 3.32×10 ⁹ | 2.80×10^{-17} | 3.39×10 ⁻¹⁶ | 1.51×10^{-18} | 7.01×10^{-15} | |
| 380 | 1.94×10 ¹⁵ | 1.60×10 ⁷ | 1.53×10 ⁸ | 2.30×10 ¹⁵ | 1.93×10 ⁶ | 4.65×10 ⁹ | 4.69×10 ⁻¹⁷ | 4.48×10 ⁻¹⁶ | 3.02×10^{-18} | 7.27×10^{-15} | |
| 400 | 1.55×10 ¹⁵ | 2.70×10^{7} | 2.22×10 ⁸ | 1.82×10 ¹⁵ | 3.69×10 ⁶ | 5.78×10 ⁹ | 6.59×10 ⁻¹⁷ | 5.42×10 ⁻¹⁶ | 4.77×10^{-18} | 7.47×10^{-15} | |
| 425 | 1.21×10 ¹⁵ | 4.86×10⁷ | 3.35×10 ⁸ | 1.41×10 ¹⁵ | 7.62×10 ⁶ | 7.38×10 ⁹ | 9.76×10 ⁻¹⁷ | 6.72×10^{-16} | 8.05×10^{-18} | 7.80×10^{-15} | |
| 442 | 1.04×10^{15} | 6.97×10⁷ | 4.33×10 ⁸ | 1.21×10^{15} | 1.19×10 ⁷ | 8.57×10 ⁹ | 1.25×10^{-16} | 7.74×10^{-16} | 1.11×10^{-17} | 8.00×10^{-15} | |
| 457 | 9.23×10 ¹⁴ | 9.36 ×10 ⁷ | 5.33×10 ⁸ | 1.06×10 ¹⁵ | 1.71×10 ⁷ | 9.68×10 ⁹ | 1.53×10^{-16} | 8.71×10 ⁻¹⁶ | 1.45×10^{-17} | 8.19×10 ⁻¹⁵ | |
| 471 | 8.30×10 ¹⁴ | 1.21×10 ⁸ | 6.39×10 ⁸ | 9.53×10 ¹⁴ | 2.36×10 ⁷ | 1.08×10 ¹⁰ | 1.83×10 ⁻¹⁶ | 9.64×10 ⁻¹⁶ | 1.84×10 ⁻¹⁷ | 8.43×10 ⁻¹⁵ | |

Table 4. Kinetic rate constants for the reaction channels obtained using VTST theory (P = 1 bar), according to the computed UM06-2x energy profiles (x=1 or 3, y=2 or 4).

| | T . | | | Rate c | onstant | Effective rate constant (cm^3 molecule ⁻¹ s ⁻¹) | | | | | |
|----|------------|---------------------------------------|--------------------------------|----------------------------------|--|---|-------------------------------|---|--|--|--|
| | 1 | (| <i>anti</i> mode | | <i>syn</i> mode | | | anti 1 | mode | syn mode | |
| () | () | $IMx \rightarrow R1 + O_2$ (k_{-1}) | $IM2 \rightarrow P2 \\ k_2(2)$ | $IM4 \rightarrow P4$ $k_2(4)$ | $\frac{\mathrm{IM}y \rightarrow \mathrm{R}1 + \mathrm{O}_2}{(k_{-1})}$ | $IM1 \rightarrow P1 \\ k_2(1)$ | $IM3 \rightarrow P3$ $k_2(3)$ | $\begin{array}{c} \text{R1+O}_2 \rightarrow \text{P2} \\ [k_{\text{eff}}(2)] \end{array}$ | $R1+O_2 \rightarrow P4$ $[k_{eff}(4)]$ | $R1+O_2 \rightarrow P1$ $[k_{eff}(1)]$ | $R1+O_2 \rightarrow P3$ $[k_{eff}(3)]$ |
| 2 | 98 | 6.91×10 ¹⁵ | 6.94×10 ⁴ | 2.55×10 ⁶ | 8.59×10 ¹⁵ | 4.94×10 ³ | 2.41×10 ⁸ | 6.06×10 ⁻¹⁹ | 2.23×10^{-17} | 2.40×10^{-20} | 1.17×10^{-15} |
| 32 | 22 | 4.43×10 ¹⁵ | 2.00×10 ⁵ | 5.46×10 ⁶ | 5.42×10 ¹⁵ | 1.79×10 ⁴ | 3.85×10 ⁸ | 1.17×10^{-18} | 3.21×10 ⁻¹⁷ | 5.79×10 ⁻²⁰ | 1.24×10^{-15} |
| 3 | 53 | 2.74×10 ¹⁵ | 6.31×10 ⁵ | 1.25×10 ⁷ | 3.30×10 ¹⁵ | 7.28×10 ⁴ | 6.40×10 ⁸ | 2.47×10^{-18} | 4.88×10 ⁻¹⁷ | 1.54×10^{-19} | 1.35×10^{-15} |
| 3 | 80 | 1.94×10 ¹⁵ | 1.47×10 ⁶ | 2.29 ×10 ⁷ | 2.30×10 ¹⁵ | 2.05×10 ⁵ | 9.29×10 ⁸ | 4.31×10^{-18} | 6.71×10 ⁻¹⁷ | 3.20×10^{-19} | 1.45×10^{-15} |
| 4 | 00 | 1.55×10^{15} | 2.55×10^{6} | 3.40×10⁷ | 1.82×10 ¹⁵ | 4.01×10 ⁵ | 1.18×10 ⁹ | 6.24×10^{-18} | 8.31×10 ⁻¹⁷ | 5.19×10 ⁻¹⁹ | 1.53×10^{-15} |
| 42 | 25 | 1.21×10 ¹⁵ | 4.73×10 ⁶ | 5.29×10 ⁷ | 1.41×10^{15} | 8.52×10 ⁵ | 1.55×10 ⁹ | 9.49×10 ⁻¹⁸ | 1.06×10^{-16} | 9.00×10 ⁻¹⁹ | 1.64×10^{-15} |
| 4 | 42 | 1.04×10^{15} | 6.91×10 ⁶ | 6.94×10 ⁷ | 1.21×10 ¹⁵ | 1.35×10 ⁶ | 1.83×10 ⁹ | 1.24×10^{-17} | 1.24×10^{-16} | 1.26×10^{-18} | 1.71×10^{-15} |
| 4: | 57 | 9.23×10 ¹⁴ | 9.42×10 ⁶ | 8.66×10 ⁷ | 1.06×10 ¹⁵ | 1.98×10 ⁶ | 2.09×10 ⁹ | 1.54×10^{-17} | 1.42×10^{-16} | 1.67×10^{-18} | 1.77×10^{-15} |
| 4 | 71 | 8.30×10 ¹⁴ | 1.24×10⁷ | 1.05×10 ⁸ | 9.53×10 ¹⁴ | 2.75×10 ⁶ | 2.35×10 ⁹ | 1.87×10^{-17} | 1.59×10^{-16} | 2.15×10^{-18} | 1.84×10^{-15} |

and C₅-positions [yielding the R1-*i*OO-*anti/syn*(i=3-5) peroxy radicals] (Fig. 1).



Fig. 1. Computed energy profiles for the considered reaction pathways (UM06-2x/augcc-pVTZ level of theory).

Theory and Computational Details

- 4 The molecular structures and harmonic vibrational frequencies of all stationary points were calculated using DFT along with the ω B97XD and UM06-2x functionals, in conjunction with the aug-cc-pVTZ basis set.
- **W** Transition state theory (TST) has been used to evaluate the global bimolecular kinetic rate constants, using the following equation:

$$k_{\text{overall}} = \kappa(T) \times \frac{\sigma k_{\text{B}} T}{h} \times V_{\text{m}}(T) \times \frac{Q_{\text{TS}}(T)}{Q_{\text{A}}(T) \cdot Q_{\text{B}}(T)} \times \exp\left(-\frac{(E_{\text{TS}} - E_{\text{A}} - E_{\text{B}})}{RT}\right)$$

where σ is the reaction symmetry number, $\kappa(T)$ denotes the Wigner's tunneling factor, $V_{\rm m}(T) = RT/P$ is the molar volume of an ideal gas, and $Q_{\rm A}$, $Q_{\rm B}$, and $Q_{\rm TS}$ correspond to the total molecular partition functions for the isolated reactants (A = R1, B = O_2) and to the transition state, respectively.

| TS-300-anti | 3.874 | 3.144 | 13.977 | 3.206 | 2.497 | 13.188 |
|-------------|--------|--------|--------|--------|--------|--------|
| TS-400-anti | 41.832 | 40.886 | 52.456 | 39.556 | 38.559 | 13.188 |
| TS-500-anti | 2.121 | 1.422 | 12.120 | 0.589 | -0.214 | 10.959 |

- \downarrow O₂ addition at the C₅ position in *syn* mode is both thermodynamically and kinetically favored over O_2 addition in *anti* position.
- \downarrow The formation of the R1-500-syn isomer clearly predominates under a thermodynamic control of the reaction.
- \downarrow Both for the syn and anti modes, O₂ addition in C₅ position is thermodynamically favored over O_2 addition in C_3 position.

Structural characteristics of stationary points

- 4 Geometries of all stationary points in the studied chemical pathways were obtained at the ω B97XD/aug-cc-pVTZ and UM06-2*x*/aug-cc-pVTZ levels of theory.
- **4** The structures describing the R1-300-*anti* and R1-500-*anti* isomers do not allow the formation of an intramolecular H-bond between the hydroxyl (OH) and peroxy (O_2) substituents. This is in sharp contrast with the observations that can be made for the R1-300-syn and R1-500-syn peroxy radical species.
- 4 The H₇ and O₉ atoms exhibit interdistances of 2.16–2.17 Å for the R1-3OO-syn species, of 2.37–2.49 Å for the R1-30O-syn species, of ~4.7 Å for the R1-30O-anti species and of ~5.2 Å for the R1-500-anti radical. It is thus clear that for the anti there can not be any significant enough stabilizing electrostatic interaction through hydrogen bonds.
- \downarrow The transition states TS-30O-syn and TS-50O-syn involve a six-membered cyclic structure $[C_2-O_6-H_7-O_9-O_8-C_i(i=3,5)]$, which is also stabilized by an intramolecular hydrogen bond (H_7-O_9) .



Table 5. Kinetic rate constants for the reaction channels obtained using RRKM theory (P=1 bar), according to the computed UM06-2x energy profiles (x=1 or 3, y=2 or 4).

| T | | | Rate co | onstant | Effective rate constant (cm^3 molecule ⁻¹ s ⁻¹) | | | | | |
|-----|---------------------------------------|-------------------------------|-------------------------------|--|---|-------------------------------|--|--|--|--|
| I | | <i>anti</i> mode | | | <i>syn</i> mode | | anti | mode | syn | mode |
| (K) | $IMx \rightarrow R1 + O_2$ (k_{-1}) | $IM2 \rightarrow P2$ $k_2(2)$ | $IM4 \rightarrow P4$ $k_2(4)$ | $\frac{\mathrm{IM}y \rightarrow \mathrm{R}1 + \mathrm{O}_2}{(k_{-1})}$ | $IM1 \rightarrow P1 \\ k_2(1)$ | $IM3 \rightarrow P3$ $k_2(3)$ | $R1+O_2 \rightarrow P2$ $[k_{eff}(2)]$ | $R1+O_2 \rightarrow P4$ $[k_{eff}(4)]$ | $R1+O_2 \rightarrow P1$ $[k_{eff}(1)]$ | $R1+O_2 \rightarrow P3$ $[k_{eff}(3)]$ |
| 298 | 6.91×10 ¹⁵ | 6.86×10 ⁵ | 1.31×10⁷ | 8.59×10 ¹⁵ | 4.70×10 ⁴ | 2.94×10 ⁸ | 5.99×10 ⁻¹⁸ | 1.14×10 ⁻¹⁶ | 2.28×10 ⁻¹⁹ | 1.43×10^{-15} |
| 322 | 4.43×10 ¹⁵ | 1.83×10 ⁶ | 2.51×10⁷ | 5.42×10 ¹⁵ | 1.61×10 ⁵ | 3.69×10 ⁸ | 1.07×10^{-17} | 1.47×10^{-16} | 5.20×10 ⁻¹⁹ | 1.19×10 ⁻¹⁵ |
| 353 | 2.74×10 ¹⁵ | 5.19×10 ⁶ | 4.90×10⁷ | 3.30×10 ¹⁵ | 6.08×10 ⁵ | 4.53×10 ⁸ | 2.03×10^{-17} | 1.92×10 ⁻¹⁶ | 1.28×10^{-18} | 9.56×10 ⁻¹⁶ |
| 380 | 1.94×10 ¹⁵ | 1.09×10 ⁷ | 7.78×10^{7} | 2.30×10 ¹⁵ | 1.59×10 ⁶ | 5.10×10 ⁸ | 3.19×10 ⁻¹⁷ | 2.28×10^{-16} | 2.49×10^{-18} | 7.98×10 ⁻¹⁶ |
| 400 | 1.55×10 ¹⁵ | 1.75×10 ⁷ | 1.03×10 ⁸ | 1.82×10 ¹⁵ | 2.96 ×10 ⁶ | 5.41×10 ⁸ | 4.27×10^{-17} | 2.51×10^{-16} | 3.83×10^{-18} | 6.99×10 ⁻¹⁶ |
| 425 | 1.21×10 ¹⁵ | 2.90×10⁷ | 1.39×10 ⁸ | 1.41×10^{15} | 5.81×10 ⁶ | 5.70×10 ⁸ | 5.82×10^{-17} | 2.79×10^{-16} | 6.14×10 ⁻¹⁸ | 6.02×10^{-16} |
| 442 | 1.04×10^{15} | 3.91×10⁷ | 1.65×10 ⁸ | 1.21×10 ¹⁵ | 8.73×10 ⁶ | 5.83×10 ⁸ | 6.99×10 ⁻¹⁷ | 2.95×10^{-16} | 8.15×10 ⁻¹⁸ | 5.44×10 ⁻¹⁶ |
| 457 | 9.23×10 ¹⁴ | 4.96×10 ⁷ | 1.88×10 ⁸ | 1.06×10^{15} | 1.21×10 ⁷ | 5.90×10 ⁸ | 8.11×10^{-17} | 3.07×10^{-16} | 1.02×10^{-17} | 4.99×10 ⁻¹⁶ |
| 471 | 8.30×10 ¹⁴ | 6.08×10 ⁷ | 2.09×10 ⁸ | 9.53×10 ¹⁴ | 1.60×10 ⁷ | 5.95×10 ⁸ | 9.18×10 ⁻¹⁷ | 3.15×10^{-16} | 1.25×10^{-17} | 4.64×10 ⁻¹⁶ |

\downarrow O₂ addition [from *syn/anti* directions] at the C₅ position is both thermodynamically and kinetically favored over addition at the C_3 position.



under atmospheric pressure and at temperatures ranging from 298 to 471 K (Fig. 3)

Since reaction pathways involve loose transition states corresponding to small energy barriers, comparison has been made with results obtained by means of Variational TST (VTST). RRKM theory has been used to study the fall-off behavior of canonical kinetic rate constants from the TST (high-pressure) limit $(P \rightarrow \infty)$ towards the lowpressure) limit $(P \rightarrow 0)$. In RRKM theory, energy-dependent microcanonical rate constants k(E) are given by



where $N^{\dagger}(E)$ denotes the ro-vibrational sum of states at the transition state, and $\rho(E)$ represents the (RRHO) density of states of reactants. Canonical rate constants are then obtained through Canonical RRKM rate constants k(T) are then ultimately determined by state integration and Boltzmann averaging.

- 4 All TST, VTST and RRKM rate constants were performed using the KiSThelP package.
- \downarrow Rate constants are based upon UM06-2*x*/aug-cc-pVTZ calculations of activation energies (ZPEs included). Note that the UM06-2x 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 (Zhao and Truhlar, 2008).
- 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.

Results and Discussion

Energetic and thermodynamic parameters

- \downarrow The R1-*i*OO-*anti/syn* (*i*=3,5) peroxy radicals are found to be by far the most stable structures, compared with the R1-4OO-syn/anti species.
- **UFT** results show that the most stable product is the R1-500-syn species (Table 1).

Fig. 2. Optimized geometries of the R1-300 and R1-500 peroxy radicals.

Natural bond orbital (NBO) analysis

- \downarrow In line with the formation of H-bonds between the H₇ (OH group) and O₉ atoms (peroxy substituents), NBO analysis shows that, for both the R1-3OO-syn and R1-500-syn isomers, electron delocalization from the non-bonding lone-pair $[n(O_9)]$ to the σ^*_{O6-H7} anti-bonding orbital result in significant stabilization energies (E_2).
- **Where the set of the** $n(O_9) \rightarrow \sigma^*(O_6 - H_7)$ are in the energy range 0.34-0.41 kcal/mol, whereas for the R1-300-syn radical these interactions do not exceed 0.3 kcal/mol.
- **4** Enhanced delocalization of the $n(O_9)$ lone pair onto the σ^*_{O6-H7} antibonding orbital from the R1-300-syn to the R1-500-syn structures correlates with a decrease of the occupation of one of the non-bonding lone-pair orbitals on the O_9 atom $[n(O_9)]$.

Kinetic parameters

4 Kinetic rate constants for the reaction pathways 1–4 were obtained from the UM06-2x/aug-cc-pVTZ energy profiles (ZPE included), assuming a two-step mechanism, which involves first a fast and reversible pre-equilibrium between the reactants and a pre-reactive complex $[C_4H_4S-OH...O_2]^{\bullet}$ (IM), followed by the irreversible formation of the thiophene peroxy radicals R1-iOO-syn/anti (*i* =3,5):

$$\left[C_{4}H_{4}S-OH\right]^{\bullet}+O_{2}\underset{k_{-1}}{\overset{k_{1}}{\longleftarrow}}\left[C_{4}H_{4}S-OH...O_{2}\right]^{\bullet}\overset{k_{2}}{\longrightarrow}R1-iOO-anti/syn(i=3-5)$$

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

- 4 Branching rations were obtained using TST, VTST and RRKM theories, in conjunction with the UM06-2x estimates for effective rate constants. TST and VTST estimates of branching ratios at a pressure of 1 bar are almost identical.
- \blacksquare Branching ratios significantly differ from the RRKM values obtained at P=1 bar, especially at high temperatures, due to the extreme pressure dependence of the global bimolecular kinetic rate constant characterizing pathway 3 (R1+O₂ \rightarrow R1-5OO-*syn*).
- \downarrow Overall kinetic rate constants obtained at P=1 bar using the TST, VTST and RRKM approaches in conjunction with the same energy profiles do not appreciably differ.



 \downarrow TST approximation breaks down at pressures lower than 100 bar for the global bimolecular rate constant characterizing pathway 3 $[k_{eff}(3)]$ (i.e. R1+O₂ \rightarrow R1-5OOsyn), due to the negative activation energy (-1.77 kcal/mol) characterizing this reaction pathway (Fig. 1).

- \downarrow O₂ addition reactions (from *syn/anti* modes) onto the C₃ and C₅ positions are strongly exothermic processes ($\Delta H_r \le -15$ kcal/mol), whereas formation processes of the R1-4OO-*anti/syn* peroxy radicals are strongly endothermic (Table 1).
- 4 The reaction energy (ΔE_{0K}) characterizing the formation of the R1-5OO-syn radical is lower by about 2.36–2.45 kcal/mol than the reaction energy for the formation of the R1-500-anti peroxy radical.
- 4 The reaction energy for the formation of the R1-3OO-*syn* radical is larger by 0.5–0.9 kcal/mol than the reaction energy for the formation of the R1-3OO-anti species.
- Table 1. Reaction energies, reaction enthalpies and Gibb's free reaction energies (in kcal/mol) for the addition of O_2 on the $[C_4H_4S-OH]^{\bullet}$ radical, at different levels of theory.

| Method | <i>ω</i> B972 | XD/aug-c | c-pVTZ | UM06-2 <i>x</i> /aug-cc-pV7 | | | | |
|---|--------------------------|------------------------------------|------------------------------------|-----------------------------|------------------------------------|------------------------------------|--|--|
| Species | $\Delta E_{0\mathrm{K}}$ | $\Delta H^{\circ}_{298\mathrm{K}}$ | $\Delta G^{\circ}_{298\mathrm{K}}$ | $\Delta E_{0\mathrm{K}}$ | $\Delta H^{\circ}_{298\mathrm{K}}$ | $\Delta G^{\circ}_{298\mathrm{K}}$ | | |
| $R1 + O_2$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | | |
| IM- <i>i</i> OO- <i>syn</i> (<i>i</i> =3,5) | -3.259 | -3.071 | 5.085 | -4.981 | -5.008 | 4.283 | | |
| R1-300-syn | -9.644 | -10.724 | 1.122 | -14.980 | -16.072 | -4.151 | | |
| R1-400-syn | 38.832 | 37.577 | 47.703 | 37.999 | 37.577 | 47.703 | | |
| R1-500-syn | -12.789 | -13.852 | -1.994 | -17.383 | -18.527 | -6.396 | | |
| IM- <i>i</i> OO- <i>anti</i> (<i>i</i> =3,5) | 8.290 | 8.525 | 16.398 | -4.768 | -4.688 | 4.154 | | |
| R1-300-anti | -10.576 | -11.463 | -0.149 | -15.430 | -16.345 | -4.899 | | |
| R1-400-anti | 39.293 | 38.860 | 49.178 | 38.601 | 38.147 | 48.403 | | |
| R1-500-anti | -10.427 | -11.364 | 0.068 | -14.935 | -15.923 | -4.339 | | |

 $k_{(R1+O_2 \rightarrow IM1)} k_{(IM1 \rightarrow R1-3OO-syn)}$ $k_{(R1+O_2 \rightarrow IM2)} k_{(IM2 \rightarrow R1-3OO-anti)}$ $k_{\text{eff}}(1) = \frac{\pi}{1}$ $k_{\rm eff}(2) = \frac{1}{1}$ $k_{(\text{IM2}\rightarrow\text{R1+O}_{2})} + k_{(\text{IM2}\rightarrow\text{R1-300-anti})}$ $k_{(\text{IM1}\rightarrow\text{R1+O})} + k_{(\text{IM1}\rightarrow\text{R1-3OO-syn})}$ $k_{(\text{R1+O}_2 \rightarrow \text{IM4})} k_{(\text{IM4} \rightarrow \text{R1-500-anti})}$ $k_{(\text{R1+O}, \rightarrow \text{IM3})} k_{(\text{IM3} \rightarrow \text{R1-500-syn})}$ $k_{\rm eff}(4) = -\frac{1}{2}$ $k_{\rm eff}(3) = -\frac{1}{2}$ $k_{(IM4\rightarrow R1+O_1)} + k_{(IM4\rightarrow R1-5OO-anti)}$ $k_{(IM3 \rightarrow R1+O_1)} + k_{(IM3 \rightarrow R1-500-syn)}$

- + The effective rate constant $[k_{eff}(3)]$ obtained for the formation of the R1-500-syn radical is larger than the one $[k_{eff}(1)]$ obtained for the formation of the R1-3OO-syn radical, which is in line with a reduction of the activation energy barrier by ~ 6.8 kcal/mol (UM06-2*x*/aug-cc-pVTZ level of theory).
- \downarrow TST, VTST, and RRKM results indicate that the unimolecular $k_2(3)$ kinetic rate constants are larger by factors ranging from ~37 to 4.9×10^4 than the $k_2(1)$ rate constants (Tables 3–5).
- \downarrow The formation of the R1-500-syn species kinetically predominates over the formation of the R1-3OO-syn species. Because of the involved positive energy barriers, these rate constants gradually increase when the temperature increases.
- **4** TST kinetic rate constants overestimate the VTST ones by at most one order of magnitude, which justifies using RRKM theory for studying the fall-off behavior of these rate constants towards the low-pressure limit (Tables 3–5).
- 4 In line with lower activation energies, the $k_2(4)$ rate constants are larger than the $k_2(2)$ rate constants. Therefore, the formation of the R1-5OO-*anti* species kinetically predominates over the formation of the R1-300-*anti* species.

Conclusions

- 4 Reaction mechanisms for the atmospheric oxidation of the main (kinetically dominant) thiophene-OH adduct $[C_4H_4S-OH]^{\bullet}$ (R1) by molecular oxygen in its triplet electronic ground state have been studied using DFT along with the @B97XD and UM06-2x functionals and the aug-cc-pVTZ basis set. All our calculations indicate that, from a thermodynamic viewpoint, the most favorable process is O_2 addition at the C_5 position in syn mode, resulting in the R1-5OO-syn radical.
- 4 A combined structural, energetic and NBO analysis shows that the intramolecular H-bond in the R1-500-*syn* radical is stronger than that in the R1-300-*syn* radical.
- 4 Comparison with the results of calculations employing VTST as benchmark kinetic model indicates that TST and RRKM theories result in overestimation of the obtained kinetic rate constants by, at most, one order of magnitude.
- 4 Under a kinetic control of the reaction, the most abundant product resulting from the oxidation of the $[C_4H_4S-OH]^{\bullet}$ adduct by O₂ is also the R1-5OO-syn radical. For the *anti* modes as well, O_2 addition at the C_5 position is also both thermodynamically and kinetically favored over addition at the C_3 position.
- 4 The computed branching ratios indicate that the regioselectivity of the reaction decreases with increasing temperatures and decreasing pressures.

References

[1] A. Shiroudi, M.S. Deleuze, Chem. Phys. (Submitted)