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Rate Constant Calculations Of H-Atom Abstraction Reactions From Ethers By HO_2 Radicals

Jorge Mendes, Chong-Wen Zhou,^{*} and Henry J. Curran

Combustion Chemistry Centre, National University of Ireland, Galway, Ireland.

E-mail: chongwen.zhou@nuigalway.ie

^{*}To whom correspondence should be addressed

Abstract

In this work, we detail hydrogen atom abstraction reactions from six ethers by the hydroperoxyl radical, including dimethyl ether, ethyl methyl ether, propyl methyl ether, isopropyl methyl ether, butyl methyl ether and isobutyl methyl ether in order to test the effect of the functional group on the rate constant calculations. The Møller–Plesset (MP2) method with the 6-311G(d,p) basis set has been employed in the optimizations and frequencies calculation of all of the species involved in the above reaction systems. The 1-D hindrance potentials for the reactants and transition states have been described by intrinsic reaction coordinate calculations which were used to connect each transition state to the corresponding local minima. Energies are reported at the CCSD(T)/cc-pVTZ level of theory and include the zero-point energy corrections. As a benchmark in the electronic energy calculations, the CCSD(T)/CBS extrapolation was used for the reactions of dimethyl ether + HO₂ radicals. A systematic calculation of the high-pressure limit rate constants has been performed using conventional transition state theory, including asymmetric Eckart tunneling corrections, in the temperature range 500–2000 K. Herein, we report the calculated individual, average and total rate constants. A branching ratio analysis for every reaction site has also been performed.

Keywords

ab-initio, potential energy surface, hydroperoxyl radical, oxygenated fuels, theoretical, chemical kinetics

Introduction

In order to increase the octane rating of unleaded gasoline, ethers have been used as additives. They have also been studied as alternative fuels in order to decrease CO and NO_x emissions, without loss of performance.¹ Due to their solvating properties, ethers are also solvents commonly used in the laboratory and industry.² An understanding of their ignition properties is important due to their low ignition temperature.² Dimethyl ether (DME) is being explored as an alternative to diesel fuel due to its high cetane number and favorable oxygen to carbon ratio.² The petroleum product and biomass ethanol can be used to easily synthesize ethyl *tert*-butyl ether (ETBE).³ ETBE is considered a "carbon neutral" fuel.³ As the use of ethers as an alternative fuel increases, their combustion kinetics and mechanisms become more important.

During combustion, H-atom abstraction by \ddot{O} and \dot{H} atoms and hydroxyl ($\dot{O}H$), hydroperoxyl ($H\dot{O}_2$) and methyl ($\dot{C}H_3$) radicals are very important in fuel oxidation.⁴ H-atom abstraction of an ether when reacting with an $H\dot{O}_2$ radical will form hydrogen peroxide (H_2O_2) and an ether radical. The formation of two highly reactive $\dot{O}H$ radicals follows when H_2O_2 decomposes.

We have determined in our previous study on ketones that abstraction by $\dot{O}H$ radicals at the alpha and beta sites relative to the functional group leads to the formation of two conformers with similar chemical properties.⁵ In our previous work on the reactions of esters with an $H\dot{O}_2$ radical⁶ we have also reported that in the case of methyl pentanoate, the energy of the *trans* reactant conformer is lower by 4 kcal mol⁻¹ when compared to the energy of the *gauche* reactant conformer. In the same work, the *trans* reactant conformer of methyl pentanoate has energy barriers of 4.5 and 5.7 kcal mol⁻¹ for the $\alpha'-\beta'$ and $\beta'-\gamma'$ hindrance potentials, respectively.⁶ Therefore, as with our previous work with ketones^{4,5} and esters,⁶ we only consider the *trans* reactant conformers in our calculations. Figure 1 shows a 2D representation of the conformers of a reactant in this study, *trans* (Figure 1(a)) and *gauche* (Figure 1(b)).

This work focuses on investigating the effect that the ether functional group ($R'OR$) has on the abstraction of each of the H-atoms present, primary (1°), secondary (2°) and tertiary (3°), at each position (α' , α , β , γ and δ), when reacting with an $H\dot{O}_2$ radical, Figure 2, Table 1.

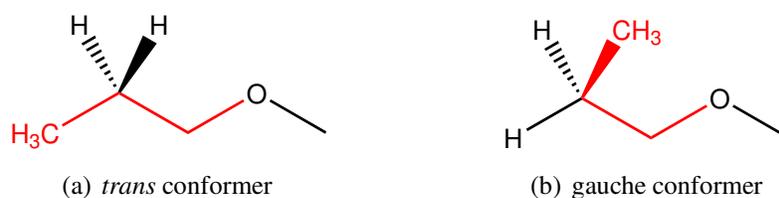


Figure 1: 2D representation of a *trans* and a *gauche* reactant conformer in this study.

In this work we detail a systematic *ab-initio* and rate constants calculation investigation of the reactions of H-atom abstraction on ethers by the HO_2 radical, in the temperature range from 500 to 2000 K. To the best of our knowledge these have not been previously determined.

Computational methods

All of the geometry optimizations, frequency calculations and treatment of the hindrance potentials of each reactant and transition state have been performed with the use of the Møller–Plesset⁷ (MP2) method employing the 6-311G(d,p) basis set. The confirmation of the connection between each transition state and the corresponding local minima for each transition state, was performed with the use of intrinsic reaction coordinate⁸ (IRC) calculations. Vibrational frequency analyses was used in order to determine the first-order saddle points (local minima). As with our previous work on ketones⁴ and esters,⁶ we have used the CCSD(T) method⁹ with the cc-pVXZ ($X = \text{D, T, Q}$) basis set, extrapolated to the complete basis set limit (CCSD(T)/CBS), in order to more accurately calculate the energies of each species on the potential energy diagram of dimethyl ether + HO_2 radicals. The CCSD(T)/CBS extrapolation was performed using the three parameter equation from Peterson *et al.*¹⁰

The electronic energies obtained using the CCSD(T)/cc-pVTZ method were benchmarked against the energies obtained by the complete basis set limit (CCSD(T)/CBS) extrapolation and are within 1 kcal mol^{-1} . As the CCSD(T)/cc-pVTZ method is computationally less expensive than the CCSD(T)/CBS method, the electronic energies for all of the species involved in the title reactions were obtained with the use of the CCSD(T)/cc-pVTZ method with zero-point corrections.

As recommended by Merrick *et al.*,¹¹ a scaling factor of 0.9496 was used for all of the harmonic frequencies. Gaussian-09¹² was used for all quantum chemistry calculations and ChemCraft¹³ was used for the visualization and determination of geometrical parameters.

Potential Energy Surface

To detail all of the different types of H-atoms studied and the labeling we use in this work, we provide Figure 2 and Table 1. At the sites adjacent to the functional group of the ether (α' and α), the electronic lone pair on the oxygen atom delocalizes to the α' and α C–H anti-bonding orbital (CH^*) which weakens the C–H bond at those positions. This lowers the relative energy required to undergo abstraction by the HO_2 radical and, consequently, increases the rate constants for those reaction channels. This influence of the oxygen atom at the sites further from the functional group (β , γ and δ) is negligible. We observed that even though the H-atom might be the same type (1° , 2° or 3°) at the different positions of the ether (α' , α , β , γ and δ), they will behave differently depending on their position relative to the R'OR group. Herein, we study the influence of the R'OR group in the reactivity of these different H-atoms at the different positions of the ethers. Figure 3 shows the optimized geometries of all of the ethers in this work (Figure 3(a) for dimethyl ether, Figure 3(b) for ethyl methyl ether, Figure 3(c) for propyl methyl ether, Figure 3(d) for isopropyl methyl ether, Figure 3(e) for butyl methyl ether and Figure 3(f) for isobutyl methyl ether). Table S1 in the Supporting Information (SI) shows the CCSD(T)/cc-pVDZ (TZ, QZ) and CCSD(T)/CBS electronic energy calculations for all of the species involved in the reactions of dimethyl ether when an hydroperoxyl radical abstracts a H-atom; Table S2 gives all of the geometry co-ordinates for each species in the title reactions and the corresponding frequencies.

As some of the species formed in this study have similar energies, geometries, and frequencies, only one is shown in the calculated potential energy surfaces (PES).

Most of the reactant (RC) and product (PC) complexes formed in the entrance and exit channels, respectively, form a hydrogen bond between the oxygen atom of the ether and the H-atom of

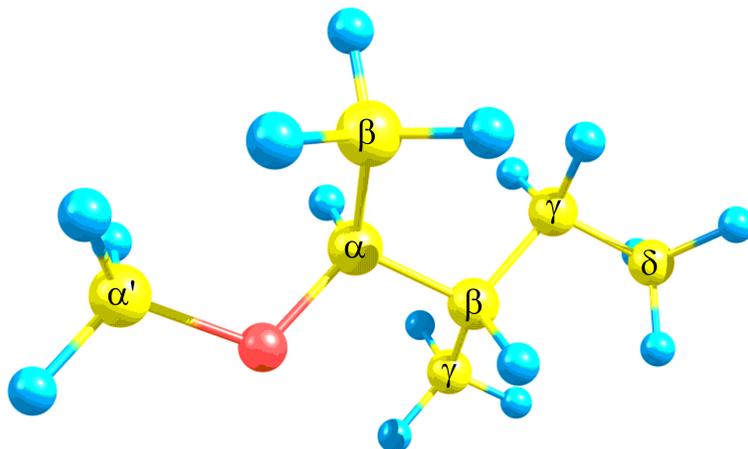


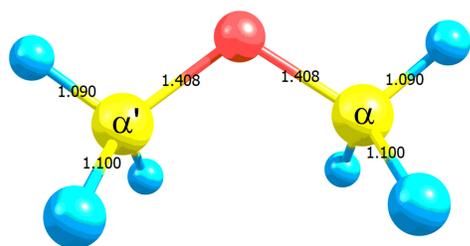
Figure 2: Labeling in use in this work.

Table 1: Relative electronic energies of the transition states for ethers + HO_2 radicals in this work (in kcal mol^{-1}).

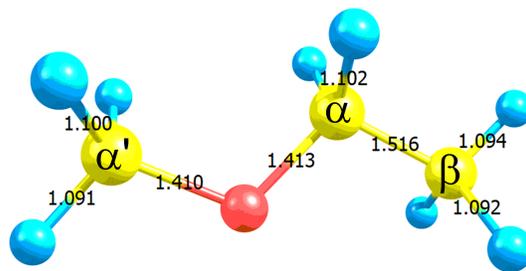
Species	Adjacent to the functional group		Alkane like		
	α'	α	β	γ	δ
(a) CH_3OCH_3 (DME)	16.2 (1°)	16.2 (1°)			
(b) $\text{CH}_3\text{OCH}_2\text{CH}_3$ (EME)	15.8 (1°)	14.2 (2°)	19.9 (1°)		
(c) $\text{CH}_3\text{O}(\text{CH}_2)_2\text{CH}_3$ (PME)	15.7 (1°)	13.6 (2°)	16.9 (2°)	20.2 (1°)	
(d) $\text{CH}_3\text{OCH}(\text{CH}_3)_2$ (iPME)	15.0 (1°)	13.0 (3°)	19.9 (1°)		
(e) $\text{CH}_3\text{O}(\text{CH}_2)_3\text{CH}_3$ (BME)	15.6 (1°)	13.5 (2°)	16.3 (2°)	16.9 (2°)	20.2 (1°)
(f) $\text{CH}_3\text{OCH}_2\text{CH}(\text{CH}_3)_2$ (iBME)	15.6 (1°)	13.4 (2°)	14.0 (3°)	20.2 (1°)	

the hydroperoxyl radical. This is comparable to our previous work on the ketones⁴ and esters.⁶ Their relative electronic energies range from -10.0 to $-9.3 \text{ kcal mol}^{-1}$ for RC and from 2.7 to $11.9 \text{ kcal mol}^{-1}$ for PC.

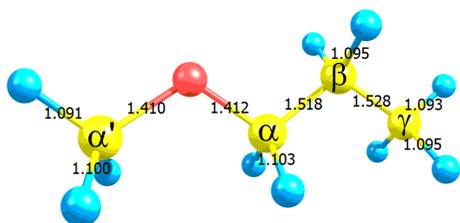
Figure 4 details the PES for dimethyl ether (DME) + HO_2 radicals and was obtained using the CCSD(T)/cc-pVTZ method and corresponding extrapolation to the complete basis set limit (CBS), with energies in kcal mol^{-1} . The relative electronic energies obtained by these two methods are within 1 kcal mol^{-1} of one another. Due to the computational cost involved in the CBS extrapolation when used for the larger reaction systems in this work, we considered the computationally cheaper CCSD(T)/cc-pVTZ method in order to calculate the relative electronic energies for all of the reaction systems. The remaining energy potentials are shown in Figure 5 for ethyl methyl ether (EME), in Figure 6 for propyl methyl ether (PME), in Figure 7 for isopropyl methyl ether (iPME),



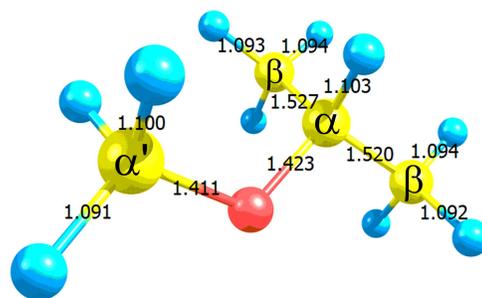
(a) Dimethyl ether (DME)



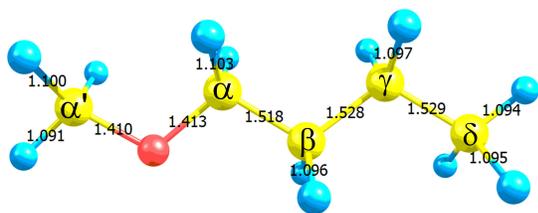
(b) Ethyl methyl ether (EME)



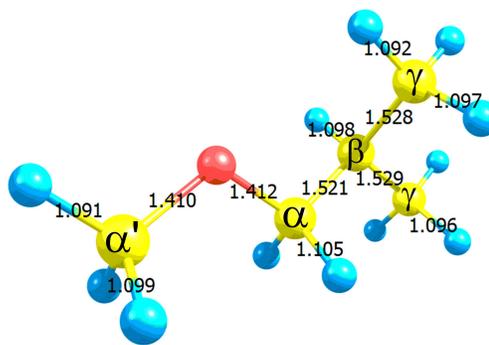
(c) Propyl methyl ether (PME)



(d) Isopropyl methyl ether (iPME)



(e) Butyl methyl ether (BME)



(f) Isobutyl methyl ether (iBME)

Figure 3: Geometries of the ethers in this work optimized at MP2/6-311G(d,p) level of theory and detailing the different types of H-atoms present.

in Figure 8 for butyl methyl ether (BME) and in Figure 9 for isobutyl methyl ether.

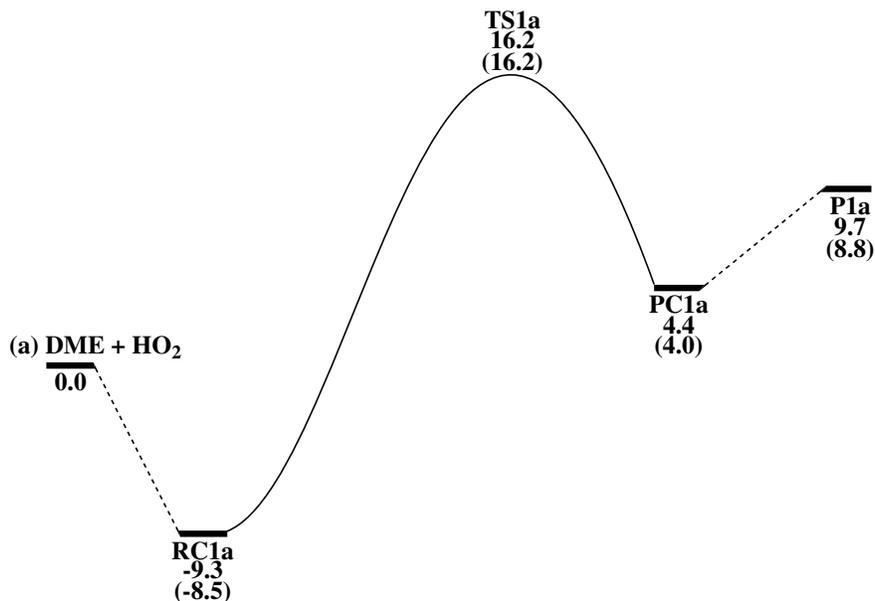


Figure 4: Potential electronic energy diagrams for the reactions of H-atom abstraction of dimethyl ether + HO₂ radicals, in kcal mol⁻¹, obtained with the use of the CCSD(T)/cc-pVTZ and CCSD(T)/CBS (in parentheses) levels of theory.

The calculated electronic energy of the transition states relative to the reactants for the H-atom abstraction of a 1° H-atom at the α' position is very similar for all of the ethers studied and they range from 15.0 to 16.2 kcal mol⁻¹. RC1a–f goes through the corresponding transition states: TS1a–f for DME, EME, PME, iPME, BME and iBME, respectively. Subsequent abstraction of a H-atom occurs and will form the corresponding product complexes followed by an α' 1° radical and H₂O₂, with relative electronic energies ranging from 9.3 to 9.8 kcal mol⁻¹.

Similarly to the α' position, the formation of the complexes in the entrance and exit channels also occurs at the α position when a H-atom is abstracted by an HO₂ radical. At this position the H-atoms are 2° for EME, PME, BME and iBME, with relative energies for the transition states ranging from 13.4 to 14.2 kcal mol⁻¹. At this same position, the H-atom is 3° for iPME and has a relative energy of 13.0 kcal mol⁻¹. Abstraction will subsequently occur, forming H₂O₂ and the corresponding α radical, with relative energies ranging from 8.6 to 9.2 kcal mol⁻¹.

At the remaining sites (β , γ and δ positions) the relative energies for H-atom abstraction are

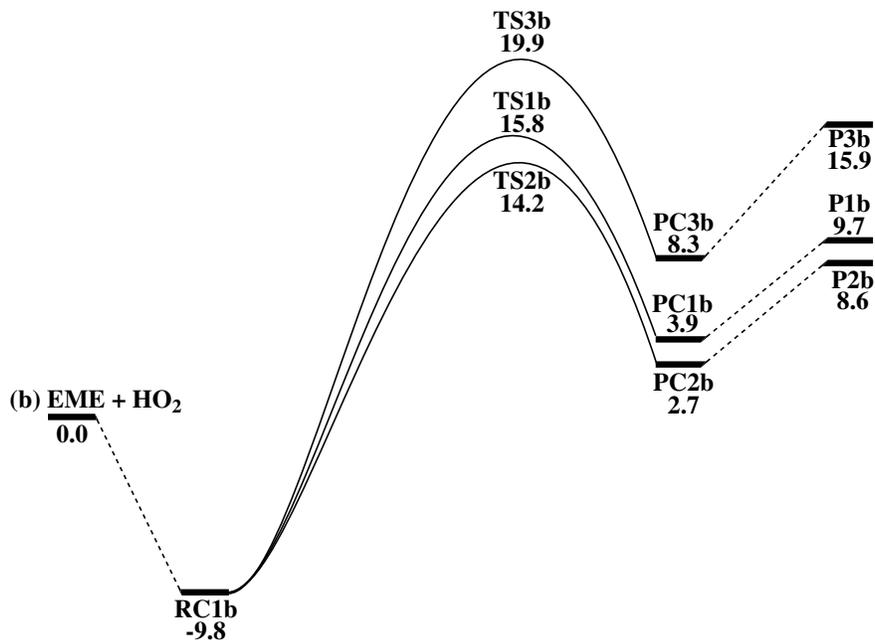


Figure 5: Potential electronic energy diagrams for the reactions of H-atom abstraction of ethyl methyl ether + HO₂ radicals, in kcal mol⁻¹, obtained with the use of the CCSD(T)/cc-pVTZ level of theory.

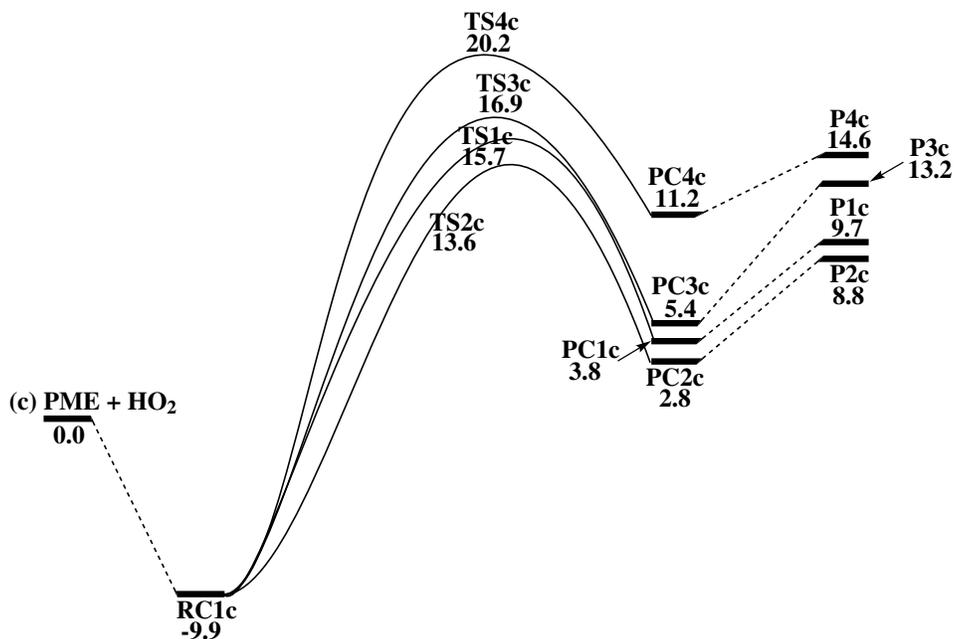


Figure 6: Potential electronic energy diagrams for the reactions of H-atom abstraction of propyl methyl ether + HO₂ radicals, in kcal mol⁻¹, obtained with the use of the CCSD(T)/cc-pVTZ level of theory.

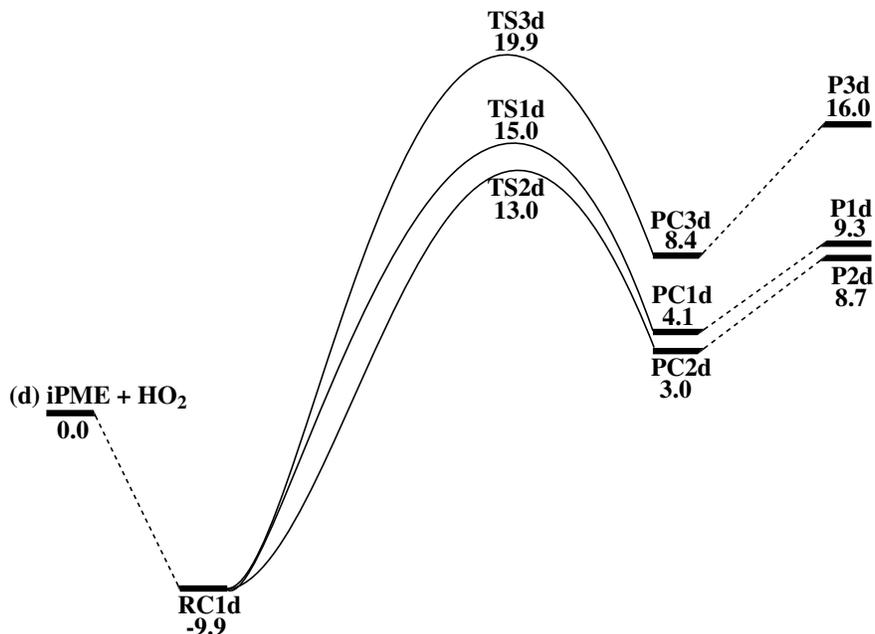


Figure 7: Potential electronic energy diagrams for the reactions of H-atom abstraction of isopropyl methyl ether + HO₂ radicals, in kcal mol⁻¹, obtained with the use of the CCSD(T)/cc-pVTZ level of theory.

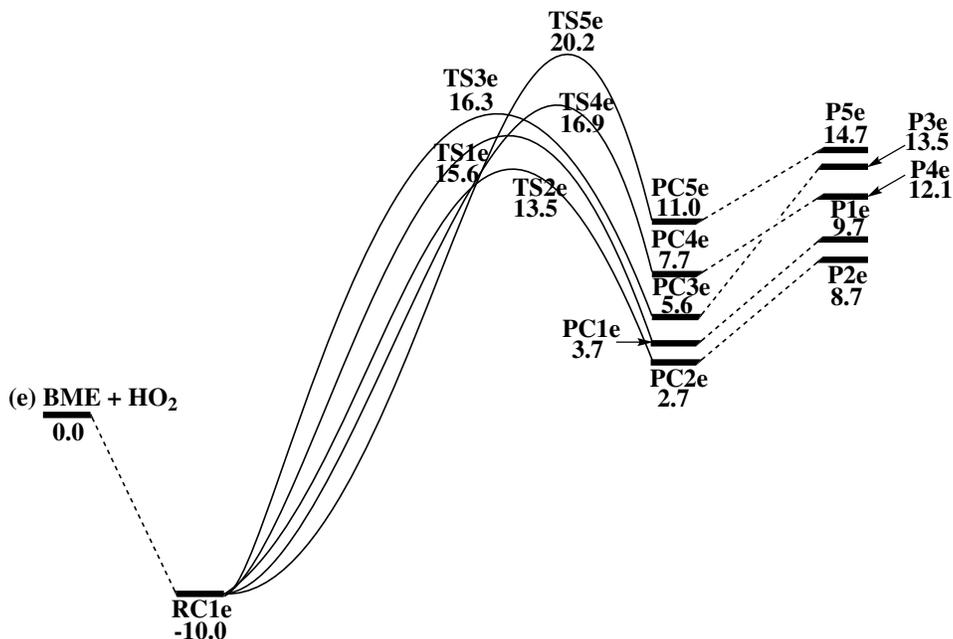


Figure 8: Potential electronic energy diagrams for the reactions of H-atom abstraction of butyl methyl ether + HO₂ radicals, in kcal mol⁻¹, obtained with the use of the CCSD(T)/cc-pVTZ level of theory.

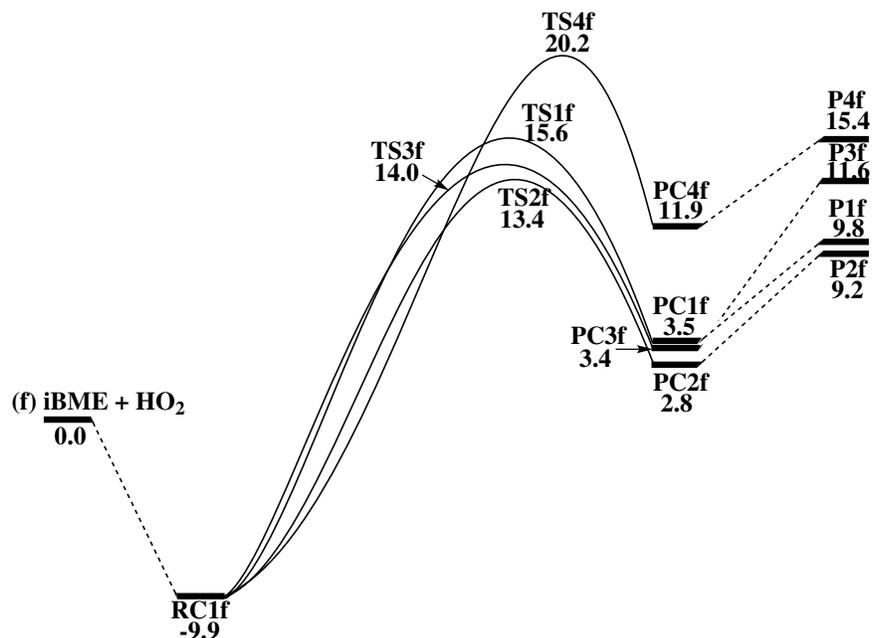


Figure 9: Potential electronic energy diagrams for the reactions of H-atom abstraction of isobutyl methyl ether + HO₂ radicals, in kcal mol⁻¹, obtained with the use of the CCSD(T)/cc-pVTZ level of theory.

similar to the corresponding sites in our previous work on the ketones⁴ and esters⁶ (Table 1). At the β position, a 1° H-atom has a relative electronic energy of 19.9 kcal mol⁻¹ for EME and iPME. At the same position of PME and BME, a 2° H-atom has a relative energy of 16.9 and 16.3 kcal mol⁻¹, respectively. A β 3° H-atom in iBME has a relative electronic energy of 14.0 kcal mol⁻¹. At the γ position, 1° and 2° H-atoms have energies of 20.2 kcal mol⁻¹ for both PME and iBME and 16.9 kcal mol⁻¹ for BME, respectively. At the δ position, a 1° H-atom has a relative energy of 20.2 kcal mol⁻¹.

Rate constant calculations

Considering the above reaction mechanisms and potential electronic energy diagrams, the rate constants (high-pressure limit) have been determined for the abstraction of a H-atom when ethers react with an HO₂ radical. Individual rate constant comparisons for each ether, on a per site

basis in $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$, are detailed on Figure S1 in the SI. The rate constants are calculated, in the temperature range 500–2000 K, with the use of conventional transition state theory with an asymmetric Eckart tunneling correction¹⁴ as implemented in Variflex v2.02m.¹⁵ The formation of the complexes in the entrance and exit channels narrows the tunneling barrier which, at low temperatures, accelerates the effect of tunneling and, subsequently, the rate constants. The Pitzer–Gwinn-like¹⁶ approximation was used in order to treat the low-frequency torsional modes as one dimensional hindered rotors. Occasionally, the coupling that occurs between internal rotations that are adjacent to each other and between external and internal rotations can't be separated. This makes the torsional treatment difficult. However, as we can separate all of the internal rotations in this work, the one dimensional torsional treatment is the best we can do, at present. This was also observed in our previous work with ketones⁴ and esters.⁶ Truhlar and co-workers^{17,18} used a multi-structure method to deal with the problem of torsional coupling. When applying their multi-structure method to the H-atom abstraction reactions of n-butanol + $\text{H}\dot{\text{O}}_2$ radicals, it is shown that their results are quite similar to our rate constant results using the one dimensional hindered rotor treatment at the α and γ sites.¹⁹ A modified three parameter Arrhenius equation [$k = A \times T^n \times \exp(-E/T)$], reported in $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$, has been used to fit our rate constants (Tables 2–4). Table 3 shows the calculated average high-pressure limit rate constants at each different position relative to the R'OR group. These have an average error of 4.5% with no more than 9.4% maximum error in the fit.

Figures 10–12 detail the calculated rate constants for the reactions of $\text{H}\dot{\text{O}}_2$ radicals when abstracting a H-atom from the following positions of the ethers: α' (1°), α (2° and 3°), β (1° , 2° and 3°), γ (1° and 2°) and δ (1°). We have performed a comparison to the rate constants from our previous work on the reactions of ketones⁴ and esters⁶ + $\text{H}\dot{\text{O}}_2$ radicals, and with alkanes + $\text{H}\dot{\text{O}}_2$ radicals determined by Aguilera-Iparraguirre *et al.*²⁰

Figure 10 shows the calculated rate coefficients at the α' position of the ether (1° H-atom). A trend is observed for all of the ethers, where the calculated rate constants are a factor of 436 and 252 faster when compared to the ketones⁴ and esters⁶ at 500 K, respectively, at the corresponding

reaction site. At 2000 K they are faster than the ketones⁴ and esters⁶ by about a factor of 9 and 6, respectively. When comparing to the alkanes²⁰ they are very similar at high temperatures (2000 K) and faster by about a factor of 41 at 500 K. The same trend is observed for a 2° and 3° H-atom located at the α position where the calculated rate constants are similar to alkanes²⁰ at 2000 K and faster by about a factor of 15 and 3 at 500 K, respectively.

When abstraction of a 2° H-atom at the α reaction site is compared to the corresponding site in the ketones⁴ and esters⁶ from our previous work, it is faster by about a factor of 191 and 120 at 500 K, respectively. At 2000 K they are faster than ketones⁴ and esters⁶ by about a factor of 12. At 500 K, a 3° H-atom at the same reaction site is about a factor of 36 and 17 faster than the ketones⁴ and esters,⁶ respectively. At 2000 K they are faster than ketones⁴ and esters⁶ by a factor of 10 and 8, respectively. A trend is observed at the remaining positions of the ethers (β , γ and δ) where the rate constants are similar to the ones calculated in our previous work for the ketones⁴ and esters⁶ and they are slower than the alkanes.²⁰

In order to understand these results, we have compared the geometries and relative electronic energies of the transition states for H-atom abstraction from the β position (1°, 2° and 3° H-atoms) of the ethers in this study with calculations from our previous studies on several ketones⁴ and esters,⁶ Table 5. We observed a similarity in the geometrical parameters and relative energies of the different transition states found. This, as well as the multiple hydrogen bond interactions between the two reactants, are the reasons for the similarity of the rate constants when comparing to the ketones⁴ and esters.⁶

Rate constants have been calculated in our previous work for the abstraction reactions of a H-atom from the different sites of n-butanol by $\dot{\text{C}}\text{H}_3$ radicals.²¹ It was shown that the results obtained using VariFlex, CanTherm and MultiWell are within a factor of 2.5. In this work we have performed a similar and consistent kinetics treatment. Goldsmith *et al.* suggest that for simple abstraction reactions, an overall uncertainty of a factor of 2–3 can be achieved.²² Based on the comparison of our results using the three kinetics programs²¹ and also based on the suggestion by Goldsmith *et al.*,²² we estimate the overall uncertainty of our calculations to be a factor of 2.5.

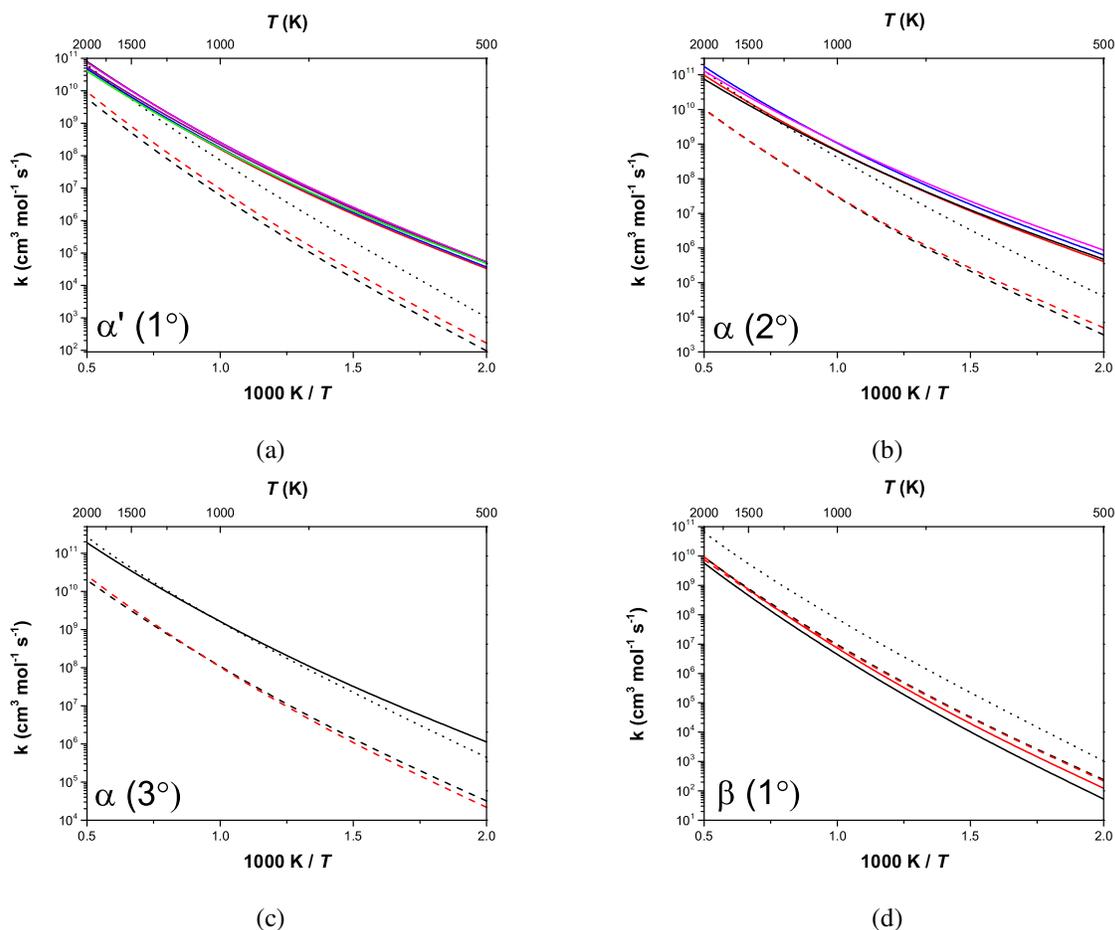


Figure 10: Rate constants comparison, in $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$, for the reactions of ethers + HO_2 radicals at the α' position (1° H-atom), α position (2° and 3° H-atoms) and at the β position (1° H-atom). (a) DME (black), EME (red), PME (blue), iPME (magenta), BME (purple) and iBME (green); (b) EME (blue), PME (red), BME (magenta) and iBME (black); (c) iPME (black); (d) EME (red) and iPME (black); ketones + HO_2 ⁴ (dashed black); esters + HO_2 ⁶ (dashed red) and alkanes + HO_2 ²⁰ (dotted).

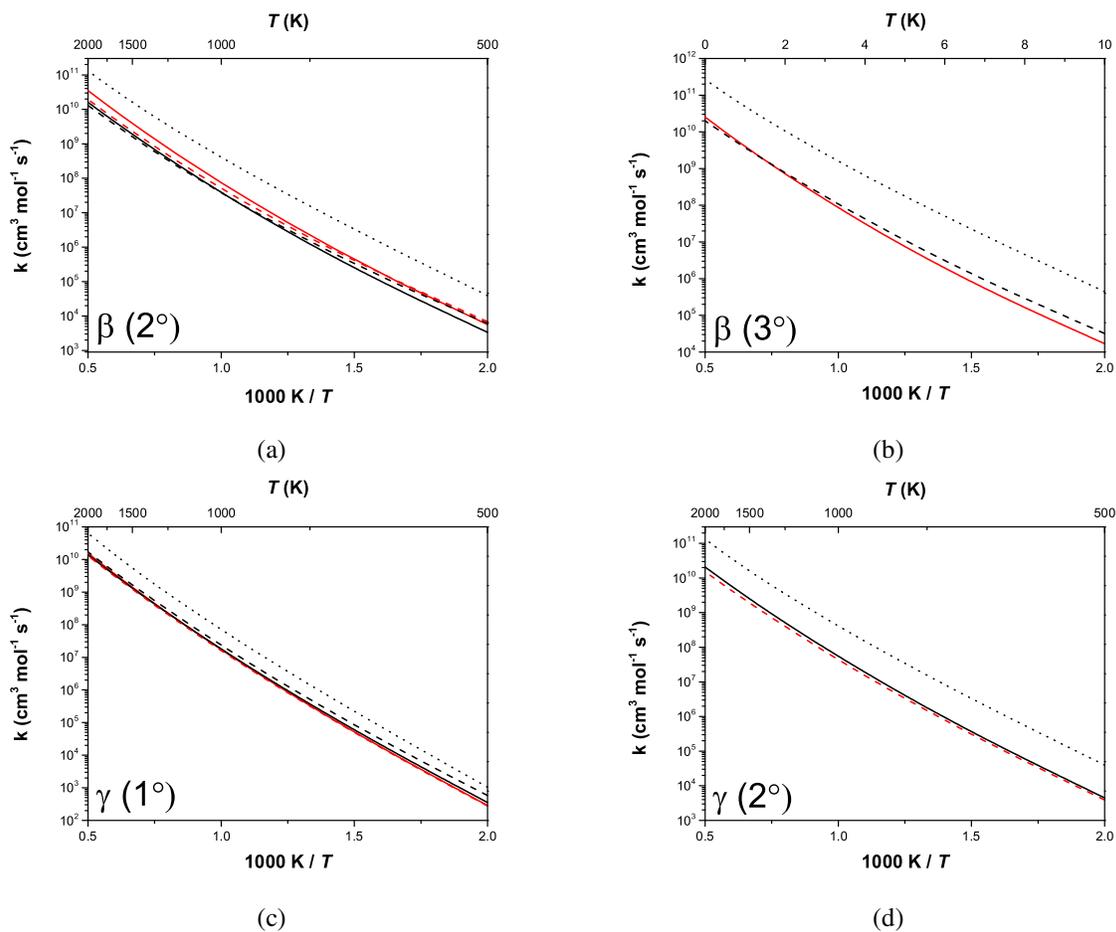


Figure 11: Rate constants comparison, in $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$, for the reactions of ethers + HO_2 radicals at the β position (2° and 3° H-atoms) and at the γ position (1° and 2° H-atoms). (a) PME (red) and BME (black); (b) iBME (red), (c) PME (red) and iBME (black); (d) BME (black); ketones + HO_2^4 (dashed black); esters + HO_2^6 (dashed red) and alkanes + HO_2^{20} (dotted).

Table 2: Rate constants, in $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$, at each position of the ethers in this work, on a per H-atom basis.

(a) dimethyl ether: CH_3OCH_3

(1) $k(\alpha') = 5.28 \times 10^{-4} T^{4.64} \exp(-5312/T)$

(b) ethyl methyl ether: $\text{CH}_3\text{OCH}_2\text{CH}_3$

(2) $k(\alpha') = 5.85 \times 10^{-4} T^{4.57} \exp(-5359/T)$

(3) $k(\alpha) = 1.91 \times 10^{-2} T^{4.23} \exp(-4541/T)$

(4) $k(\beta) = 5.32 \times 10^{-6} T^{5.12} \exp(-7484/T)$

(c) propyl methyl ether: $\text{CH}_3\text{O}(\text{CH}_2)_2\text{CH}_3$

(5) $k(\alpha') = 5.52 \times 10^{-3} T^{4.29} \exp(-5543/T)$

(6) $k(\alpha) = 3.43 \times 10^{-2} T^{4.08} \exp(-4583/T)$

(7) $k(\beta) = 7.52 \times 10^{-3} T^{4.28} \exp(-6581/T)$

(8) $k(\gamma) = 1.45 \times 10^{-1} T^{3.90} \exp(-8345/T)$

(d) isopropyl methyl ether: $\text{CH}_3\text{OCH}(\text{CH}_3)_2$

(9) $k(\alpha') = 2.17 \times 10^{-3} T^{4.46} \exp(-5442/T)$

(10) $k(\alpha) = 8.60 T^{3.46} \exp(-4898/T)$

(11) $k(\beta) = 2.21 \times 10^{-4} T^{4.61} \exp(-8191/T)$

(e) butyl methyl ether: $\text{CH}_3\text{O}(\text{CH}_2)_3\text{CH}_3$

(12) $k(\alpha') = 2.29 \times 10^{-2} T^{4.12} \exp(-5588/T)$

(13) $k(\alpha) = 7.85 \times 10^{-1} T^{3.71} \exp(-4614/T)$

(14) $k(\beta) = 8.05 \times 10^{-3} T^{4.17} \exp(-6513/T)$

(15) $k(\gamma) = 3.05 \times 10^{-1} T^{3.74} \exp(-6858/T)$

(16) $k(\delta) = 5.88 \times 10^{+1} T^{3.18} \exp(-8655/T)$

(f) isobutyl methyl ether: $\text{CH}_3\text{OCH}_2\text{CH}(\text{CH}_3)_2$

(17) $k(\alpha') = 2.22 \times 10^{-3} T^{4.36} \exp(-5187/T)$

(18) $k(\alpha) = 4.99 \times 10^{-1} T^{3.70} \exp(-4657/T)$

(19) $k(\beta) = 1.83 \times 10^{-3} T^{4.36} \exp(-5567/T)$

(20) $k(\gamma) = 4.07 \times 10^{-1} T^{3.74} \exp(-8270/T)$

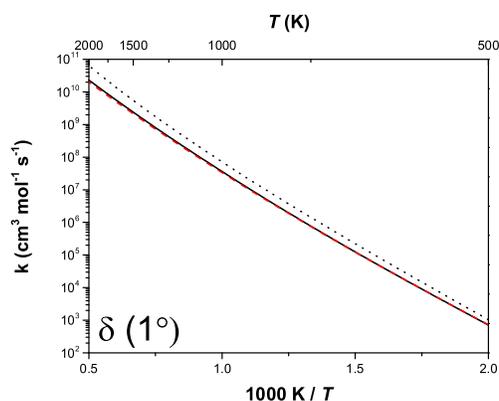


Figure 12: Rate constants comparison, in $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$, for the reactions of ethers + HO_2 radicals at the δ position (1° H-atom). BME (black); ketones + HO_2^4 (dashed black); esters + HO_2^6 (dashed red) and alkanes + HO_2^{20} (dotted).

Table 3: Recommended fit parameters, A , n and E , per type of H-atom and per position relative to the oxygen atom of the ether, on a per-H-atom basis in $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$.

H-atom type	A	n	E
Primary, α'	1.99×10^{-3}	4.44	5389.
Secondary, α	9.05×10^{-2}	3.98	4558.
Tertiary, α	8.60	3.46	4898.
Primary, β	1.73×10^{-5}	4.95	7721.
Secondary, β	6.86×10^{-3}	4.25	6550.
Tertiary, β	1.83×10^{-3}	4.36	5567.
Primary, γ	2.23×10^{-1}	3.83	8295.
Secondary, γ	3.05×10^{-1}	3.74	6858.
Primary, δ	$5.88 \times 10^{+1}$	3.18	8655.

$$k = A \times T^n \times \exp(-E/T)$$

Table 4: Total rate constants fit parameters, A , n and E , in $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$.

	A	n	E
DME	3.17×10^{-3}	4.64	5312.
EME	3.44×10^{-3}	4.59	4417.
PME	5.00×10^{-4}	4.83	4367.
iPME	1.11×10^{-2}	4.42	4490.
BME	5.14×10^{-3}	4.54	4301.
iBME	1.06×10^{-3}	4.70	4247.

$$k = A \times T^n \times \exp(-E/T)$$

This is due to uncertainties in the electronic energy determination, tunneling effects, treatment of some critical internal rotation modes, *etc.*

Table 5: Geometries and relative electronic energies of the transition states obtained at CCSD(T)/cc-pVTZ//MP2/6-311G(d,p) levels of theory for abstraction of a β H-atom (1° , 2° and 3°).

		$r(\text{C-H})/\text{\AA}$	$r(\text{H-O})/\text{\AA}$	$\angle(\text{C-H-O})/\text{\AA}$	Hydrogen bond length	E/kcal mol ⁻¹
β 1°	EMK	1.300	1.166	167.628	2.025	18.6
	MP	1.300	1.167	165.599	2.005	18.6
	EME	1.300	1.171	160.780	2.018	19.9
β 2°	nPMK	1.277	1.188	171.483	2.044	15.5
	MB	1.277	1.189	169.989	2.020	15.5
	PME	1.279	1.192	162.989	2.029	16.9
β 3°	iBMK	1.269	1.199	177.462	2.035	13.0
	iBME	1.267	1.211	164.522	2.044	14.0

EMK: ethyl methyl ketone; nPMK: n-propyl methyl ketone; iBMK: isobutyl methyl ketone
 MP: methyl propanoate; MB: methyl butanoate

Branching Ratios

Figure 13 details a branching ratio analysis for each reaction channel of the ethers over the temperature range from 500 to 2000 K.

The branching ratio for ethyl methyl ether is shown in Figure 13(a) and abstraction from the α position dominates from 500–2000 K. Figure 13(b) shows the branching ratio for propyl methyl ether where H-atom abstraction from the α position dominates from 500–2000 K. As the temperature increases, abstraction from both the α' and α positions become closer in reactivity. For isopropyl methyl ether (Figure 13(c)), abstraction from the α position dominates from 500 to 1800 K. Above 1800 K abstraction from the α' position becomes dominant. Figure 13(d) and 13(e) show the branching ratios for butyl methyl ether and isobutyl methyl ether, respectively. Abstraction from the α position dominates from 500 K to 2000 K and, as the temperatures increases, abstraction from the α' position becomes more important. The reactivity at the β positions of PME and BME, even though they are also 2° H-atoms, is slower than at the α' and α positions.

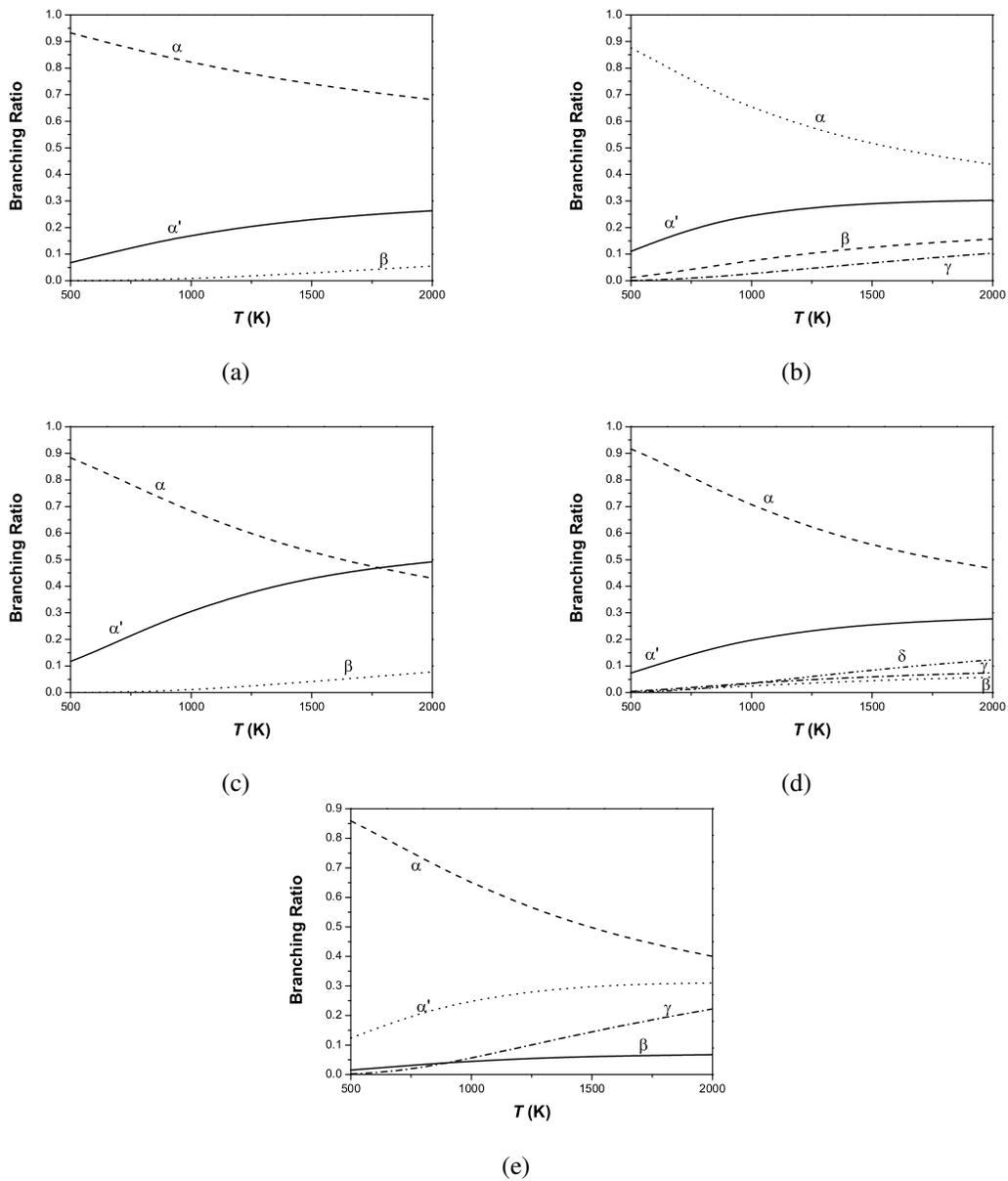


Figure 13: Predicted branching ratios for the different sites of each ether in this study, between 500 and 2000 K. (a) EME; (b) PME; (c) iPME; (d) BME; (e) iBME.

Conclusions

We have performed a systematic and detailed investigation of the potential electronic energy diagrams, high-pressure limit rate constants and branching ratio analyses of the reactions of $\text{H}\dot{\text{O}}_2$ radicals abstracting a H-atom from six ethers. As with our previous work on ketones⁴ and esters,⁶ we have identified a reaction mechanism involving complexes in the entrance and exit channels. We observed the formation of a hydrogen bond between the oxygen atom of the ether and the H-atom of the hydroperoxyl radical for most of the complexes formed. It was also observed that the formation of a similar hydrogen bond in the transition states occurs mainly when abstracting a H-atom at the β positions of the ethers. When abstracting a H-atom from the α' and α positions of the ether, the hydroperoxyl radical is too close to the oxygen atom of the ether and hence the transition states are too strained to allow its formation. At the remaining sites (γ and δ), the hydroperoxyl radical is too far from the oxygen atom of the ether to allow a hydrogen bond to be formed.

The rate constants were determined for all of the reaction channels of each ether and a detailed comparison with our previous work on ketones⁴ and esters,⁶ and alkanes + $\text{H}\dot{\text{O}}_2$ ²⁰ calculated by Aguilera-Iparraguirre *et al.* has also been carried out.

The electronic lone pair on the oxygen atom delocalizes to the adjacent C–H anti-bonding orbitals (CH^*) at the α' and α positions, weakening the C–H bond. Consequently, the relative energy for abstraction by the $\text{H}\dot{\text{O}}_2$ radical is lowered which increases the rate constants for those reaction channels. This influence of the ether functional group at the β , γ and δ positions is negligible. We observed that even though the H-atom might be the same type (1° , 2° or 3°) at the different positions of the ether (α' , α , β , γ and δ), they will behave differently depending on their position relative to the R'OR group. At the δ position the oxygen atom of the ether has the least influence on the reactivity of the H-atom that is being abstracted. As with our previous work,^{4,6} at this position the rate constants are most similar to an alkane.²⁰

A branching ratio analysis for every reaction channel of all of the ethers when reacting with an $\text{H}\dot{\text{O}}_2$ radical has been performed from 500 to 2000 K. We observe that the reactivity at the α

site, followed by the α' site, dominate over the remaining sites (β , γ and δ) throughout the entire temperature range.

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Supporting Information Available

In the Supporting Information, Table S1 details the CCSD(T)/cc-pVDZ (TZ, QZ) and CCSD(T)/CBS electronic energy calculations for all of the species in the reactions of DME with an HO_2 radical. Table S2 gives all of the geometry co-ordinates for each species in the title reactions and the corresponding frequencies. Figure S1 shows the individual rate constant comparisons for each ether, on a per site basis in $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$.

This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Graphical TOC Entry

