

Rate Constants for Hydrogen Abstraction Reactions by the Hydroperoxyl Radical from Methanol, Ethenol, Acetaldehyde, Toluene and Phenol

¹M. Altarawneh, ²B.Z. Dlugogorski*, ²E. M. Kennedy, ²J.C. Mackie*[†]

¹Chemical Engineering Department, Al-Hussein Bin Talal University, Ma'an, Jordan

²School of Engineering, The University of Newcastle, Callaghan, NSW 2308, Australia
Process Safety and Environment Protection Research Group

Abstract

An important step in the initial oxidation of hydrocarbons is the abstraction of H by hydroperoxyl radical (HO₂). In this study, reaction rate constants are derived for H abstraction by HO₂ from the weakest H bond in methanol, ethenol, acetaldehyde, toluene and phenol. Rate constants are provided in the simple Arrhenius form. Reasonable agreement was obtained with the limited literature data available for acetaldehyde and toluene. For the case of phenol, direct abstraction of the hydroxyl H was found to dominate over HO₂ addition to the ring. The results presented herein should be useful in modelling the lower temperature oxidation of the five compounds considered.

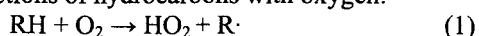
Keywords: HO₂ radical, Toluene, Acetaldehyde, TST.

1. Introduction

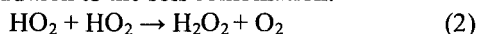
Hydrogen atom transfer (HAT) reactions with hydrogen atom, hydroxyl radical and oxygen atom have been extensively studied both experimentally and theoretically for large numbers of species, ranging from simple alkanes to aromatic compounds. In spite of the importance of the hydrogen abstraction reactions by the hydroperoxyl radical (HO₂), there have been very limited experimental measurements of their rate constants, presumably due to the difficulty in finding a suitable source for the HO₂ radicals [1]. Furthermore, theoretical approaches have not been widely applied on HAT by HO₂.

Hydroperoxyl radical plays an important role in atmospheric chemistry and low temperature oxidation phenomena such as autoignition and engine knock. In the case of benzene, for example, HO₂ is partially responsible for the observed negative temperature coefficient (NTC) behaviour where the oxidation rate is decreasing with temperature at intermediate temperatures [2]. For instance, the reaction of formaldehyde with HO₂ provides chain propagation steps that are important in the decomposition of hydrocarbons in the atmosphere [3].

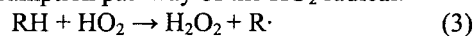
HO₂ is produced in the early stages of oxidation by reactions of hydrocarbons with oxygen:



in addition to the self combination:



direct abstraction of H from hydrocarbons, is a major consumption pathway of the HO₂ radical:



Relatively little kinetic information is available for reaction (3) for the majority of compounds. Due to the difficulty associated with studying reaction (3) experimentally, this reaction is an excellent candidate for a theoretical investigation. In this study, we investigate reaction (3) by density functional theory (DFT) for five compounds, viz., methanol, ethenol, acetaldehyde, toluene and phenol. These five compounds have a distinct feature, namely, one of the O-H or C-H bonds is weaker than the other H bonds. For example, abstraction of H from the ring in toluene and phenol will be of negligible importance when compared with abstraction from the methyl group and the hydroxyl group, respectively. The results of this study will add useful information to the library of combustion kinetics.

2. Computational details

Electronic structure calculations were carried out with the Gaussian 03 suite of programs [4]. Optimized geometries and harmonic vibrational frequencies of reactants, transition states and products have been calculated using the density functional theory (DFT) of BB1K [5]. The BB1K method is a meta hybrid DFT method in which the deployment of an HF exchange fraction is coupled with the abstraction of kinetic energy density from Kohn-Sham orbitals [6]. BB1K functional has been shown to significantly outperform all hybrid DFT methods including B3LYP in determination of saddle-point geometries and barrier

* Corresponding authors: Phone: (+61 2) 4921 6176. Email: Bogdan.Dlugogorski@newcastle.edu.au

[†] Also at School of Chemistry, University of Sydney.

heights, especially for hydrogen transfer reactions [7]. Optimizations were carried out with the 6-311++G(2d,p) basis set [8]. The stationary points located were either minima or transition states (TS) determined by analysis of the vibrational frequency where first order saddle points contain one and only one imaginary frequency along the reaction coordinate.

Rate constants, $k(T)$, have been calculated according to:

$$k(T) = \kappa(T) \times k_{\text{TST}}(T)$$

where $k_{\text{TST}}(T)$ is the rate constant derived by conventional transition state theory (TST) [9]:

$$k_{\text{TST}}(T) = \frac{\sigma k_b T}{h} \exp\left(\frac{\Delta S^{\text{act}}}{R}\right) \exp\left(\frac{-\Delta H^{\text{act}}}{RT}\right)$$

and $\kappa(T)$ is the transmission coefficient that accounts for the quantum tunnelling corrections calculated by the Wigner functional [10]:

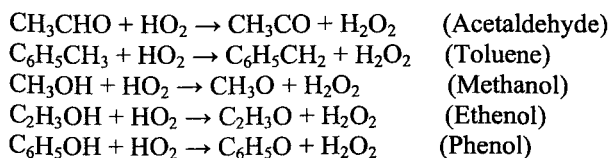
$$\kappa(T) = 1 + \frac{1}{24} \left[\frac{h\nu^{\text{TS}}}{k_b T} \right]$$

where ΔS^{act} is the entropy of activation, ΔH^{act} is the enthalpy of activation, σ is the reaction symmetry number, h is Planck constant, k_b is the Boltzmann constant and ν^{TS} is the imaginary vibrational frequency in the transition state. Thermochemical parameters (ΔS^{act} , ΔH^{act}) needed for the (TST) calculations were evaluated using the STATHERM program [11]. STATHERM uses ideal gas statistical mechanical principles to evaluate the thermochemical parameters by using the vibrational frequencies, rotational constants, standard enthalpy of formation, and the overall symmetry number. Low-frequency vibrations corresponding to internal rotation in phenol, toluene and ethenol have been treated as hindered internal rotations. In this treatment, the low-frequency vibrations have been replaced by barriers for internal rotations, their moments of inertia and symmetry numbers. Enthalpy of formation for transition states were calculated as the summation of the experimental enthalpies of formation of the reactant and the calculated enthalpy of activation.

3. Results and Discussions

3.1 Geometries and Energetics

The five considered reactions are:



Transition structures for these reactions are depicted in Fig.1. Reaction energies (ΔE) and activation energies (ΔE^\ddagger) at 0 K are given in Table 1. The five transition structures have a common feature that the O-O bond in the HO_2 is elongated by nearly 4.6% from the 1.300 Å

equilibrium distance in HO_2 . The hydroxyl O-H bonds in TS_Phenol, TS_Methanol and TS_Ethenol are shortened by 4.2%, 2.0% and 5.6%, respectively from their corresponding equilibrium molecular distances. The phenyl-methyl bond in TS_Toluene is shortened by 0.05 Å from the equilibrium distance in toluene.

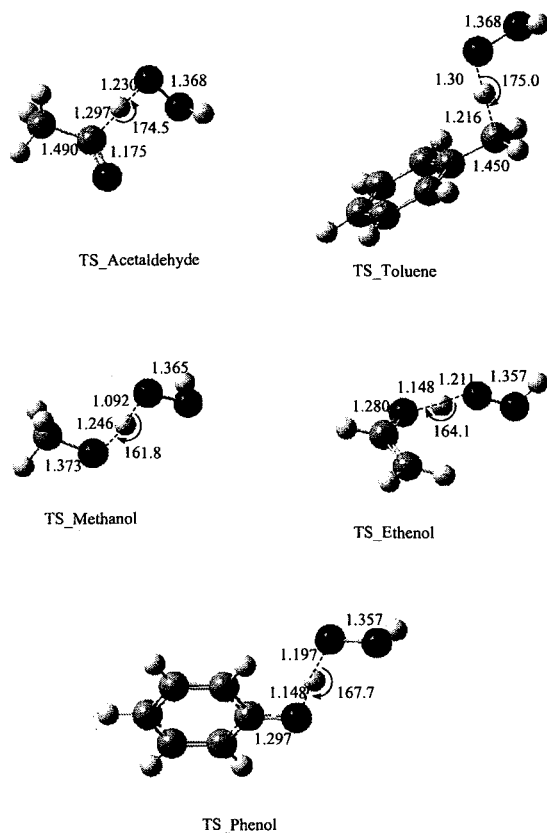


Fig. 1. Optimized transition structures at the BB1K/6-311++G(2d,p). Distances are in angstrom (Å) and angles are in degree.

Table 1. Reaction energies (ΔE) and activation energies (ΔE^\ddagger) at 0 K in kcal/mol.

	ΔE	ΔE^\ddagger
Acetaldehyde	4.5	12.0
Toluene	6.6	18.6
Methanol	17.7	21.7
Ethenol	0.8	14.4
Phenol	3.7	13.7

Except for methanol, the reactions are weakly endoergic. This slight endoergicity of reactions with toluene and phenol originates from the production of the resonance stabilized radicals benzyl and phenoxy, respectively. The five reactions require rather modest activation energies in the range of 12.0 to 21.7 kcal/mol. However, the calculated ΔE^\ddagger for HAT by HO_2 are significantly greater than well-established ΔE^\ddagger values for HAT by the hydroxyl radical or H atom.

3.2 Rate Constants

Rate constant calculations using TST require accurate values for standard entropies of formation S_{298}° for the initial reactants and for TSs. The calculated STATHERM S_{298}° for phenol, toluene, acetaldehyde and hydroperoxyl are, 75.31, 76.50, 62.70 and 54.46 cal/mol.K, respectively. These values are in good agreement with the literature values of 75.26, 76.77, 63.00 and 54.75 cal/mol.K, respectively [12].

Rate constants were fitted to the simple Arrhenius formula:

$$k(T) = A \exp\left(\frac{-E_a}{RT}\right)$$

where A is the pre-exponential factor and E_a is the fitted enthalpy of activation. The Arrhenius parameters of the five abstraction reactions are given in Table 2.

Table 2. Reaction rate parameters for the five title reactions.

	A ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	E_a/R (K)
Acetaldehyde	1.02×10^{-11}	7 500
Toluene	2.87×10^{-11}	10 900
Methanol	5.89×10^{-12}	12 000
Ethenol	9.30×10^{-12}	8 800
Phenol	4.26×10^{-12}	8 200

From the literature, experimental measurements only exist for reaction with toluene. Eng et al. [13], measured $k(T) = 4.98(\pm 1.66) \times 10^{10} \exp(-11000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $T = 1150\text{-}1250$ K. Scott et al. obtained $9.13 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 773 K. The A factor measured by Eng et al. is larger than any other known A factor for H abstraction by HO_2 by at least one order of magnitude. However, our calculated E_a agrees well with their value. Scott et al. described their value at 773 K as the first reliable kinetic data for the abstraction of H from any aromatic compound by HO_2 . They conducted the experiment by adding trace amount of toluene to a mixture of $\text{H}_2 + \text{O}_2$. Scott et al. [14], attributed the unexpectedly low rate constant in reference to the alkanes to a combination of lower A factor with a slightly higher activation energy.

Baulch et al. [15], following an extensive review of the high temperature kinetics data for toluene give $k(T) = 6.59 \times 10^{13} \exp(-7000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Fig.2, shows the Arrhenius plot of the two measured rate constants and the recommended values by Baulch together with our calculated values. The calculated rate constant is four times slower than the experimental value of Scott et al. As can be seen from Fig.2, there is good agreement between the calculated rate constant and the recommended values by Baulch et al, especially at $T = 800\text{-}1000$ K.

Acetaldehyde, ethenol and methanol are important intermediates in the oxidation of alcohols which are increasingly being used in automobile fuels. Reaction of acetaldehyde with the hydroperoxyl radical was found to be important to model the combustion of acetaldehyde in the temperature range of 1000-1700 K in a recent study [15]. The only available rate constant for the reaction of acetaldehyde with HO_2 comes from a detailed review by Baulch et al who give $k(T) = 2.82 \times 10^{-12} \exp(-5350/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in the temperature range of 600-1000 K. In Fig.3, our calculated rate constant is compared with the value by Baulch et al. Our calculated values are within a factor 1.71-2.60 of the values by Baulch et al.

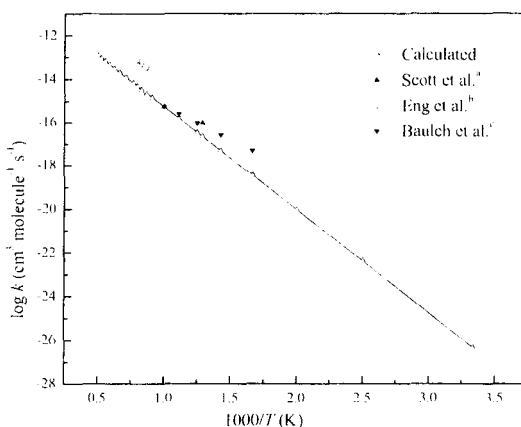


Fig. 2. Comparison between the calculated rate constant for the reaction $\text{C}_6\text{H}_5\text{CH}_3 + \text{HO}_2 \rightarrow \text{C}_6\text{H}_5\text{CH}_2 + \text{H}_2\text{O}_2$ and the experimental values. ^a Ref 13, ^b Ref 14, ^c Ref 15.

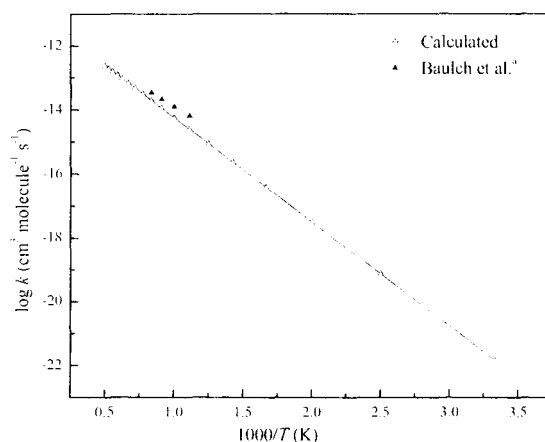


Fig. 3. Comparison between the calculated rate constant for the reaction $\text{CH}_3\text{CHO} + \text{HO}_2 \rightarrow \text{CH}_3\text{CO} + \text{H}_2\text{O}_2$ and the value provided by Baulch et al. ^a Ref 15.

Due to the higher enthalpy of activation, reaction of HO_2 with methanol is the slowest calculated rate constant in the selected group of the five compounds.

The rate constant for HO₂ abstraction from ethenol has a larger *A* factor than that for methanol due to the fact that the transition structure for ethenol exhibit a more-product like characters (*i.e.*, shorter C-O bond)

Reaction of HO₂ with phenol is relevant to the oxidation of the polyphenolic constituents in biomass and the formation of the phenoxy radical - a direct precursor for the highly toxic dioxins compounds. For the case of phenol, abstraction of the phenoxy H was compared with addition to the phenolic ring. Fig.4, shows energetics for the addition of HO₂ to the three possible sites, *ortho*-C, *ipso*-C and *para*-C.

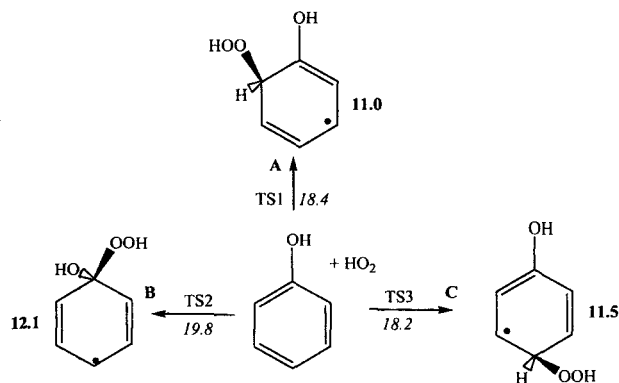


Fig. 4. Energetics for HO₂ addition to phenol. Values in italics and bold are the activation energies and the reaction energies, respectively.

The located transition structures (TS1, TS2, TS3) were used to evaluate reaction rate constants for the addition reactions. Arrhenius rate parameters for these reactions are given in Table 3.

Table 3. Reaction rate parameters HO₂ addition to phenol.

	<i>A</i> (cm ³ molecule ⁻¹ s ⁻¹)	<i>E_a</i> /R (K)
Phenol-HO ₂ (A)	2.16 × 10 ⁻¹³	11 000
Phenol-HO ₂ (B)	9.35 × 10 ⁻¹⁴	11 800
Phenol-HO ₂ (C)	7.78 × 10 ⁻¹⁴	11 000

In comparison to the calculated rate constant for the abstraction reaction (C₆H₅OH + HO₂ → C₆H₅O + H₂O₂) in Table 1, the addition reaction is slower than the abstraction process by at least two orders of magnitude over the entire temperature range. Thus, the addition channel is of negligible importance, even at low temperature. This behaviour is different from that of the OH + aromatics systems where addition dominates at temperatures as high as 400 K [17].

4. Conclusions

While a great deal of research has been carried out to study HAT with radicals such as OH and H, there is limited information on HAT with the hydroperoxyl radical in the literature despite their agreed importance. We investigated the abstraction reaction of H from five

selected compounds by the hydroperoxyl radical, namely, acetaldehyde, toluene, methanol, ethenol and phenol. The present study could serve in building comprehensive kinetics databases for HAT by the hydroperoxyl radical.

Acknowledgments

This research has been supported by a grant from the Australian Research Council.

5. References

- [1] R.W. Walker. Reaction Kinetics; Ashmore, P. G., (Ed) The Chemical Society: London, 1975; Vol. 1, p 161.
- [2] R.W. Walker, C. Morely, M.J Piling (Ed.), Low-Temperature Combustion and Autoignition. Elsevier, Amsterdam, 1997, p.1.
- [3] M. Evleth, C. F. Melius, Rayez, T, C. Rayez, W. Forst, J. Phys. Chem. **97** (1993), pp. 5040-5045.
- [4] M.J. Frisch, et al., Gaussian03, Revision B.05. Gaussian Inc., Pittsburgh, PA, 2003.
- [5] Y. Zhao, B. J. Lynch and D. G. Truhlar, J. Phys. Chem. A. **108** (2004), pp. 2715-2719.
- [6] W. Kohn and L. J. Sham, Phys. Rev. A. **140** (1965), pp. 1133-1138.
- [7] Y. Zhao, N. Gonzalez-Garcia and D. G. Truhlar, J. Phys. Chem. A. **109** (2005), pp. 2012-2018.
- [8] J.A. Montgomery, J.W. Ochterski, G. Petersson, J. Chem. Phys. **101** (1994) 5900-5909.
- [9] H. Eyring, J. Chem. Phys. **3** (1935), pp. 107-111.
- [10] E. P. Wigner, Phys. Chem. **19** (1932), pp. 203-206.
- [11] J.C. Mackie, STATHERM. Private Communications
- [12] S. W. Benson, Thermochemical Kinetics; Wiley-Interscience: New York, 1976.
- [13] R. A. Eng, C. Fittschen, A. Gebert, P. Hibomvski, H. Hippler and Unterreiner, Proc. Combust. Inst **27** (1998), pp. 211-218.
- [14] M. Scott, R. W. Walker, Combust. Flame. **129** (2002), pp. 365-377.
- [15] D.L. Baulch, C.J. Cobos, R.A. Cox, C. Esser, P. Frank, Th. Just, J.A. Kerr, M.J. Pilling, J. Troe, R.W. Walker, J. Warnatz, J. Phys. Chem. Ref. Data, **21**(1992) pp.411-429.
- [16] Y. Kenji, K. Satoshi, H. Hiroki, K. Takashi and H. Yoshiaki, Int. J. Chem. Kinet. **40** (2008), pp. 73-102.
- [17] I. V. Tokmakov and M. C. Lin. J, Phys. Chem. A. **106** (2002), pp. 11309-11326.