

# Rate constants for Reactions of Ethylbenzene with Hydroperoxyl Radical and Oxygen Molecule

M. Altarawneh<sup>\*†</sup>, B.Z. Dlugogorski, E. M. Kennedy, J.C. Mackie<sup>‡</sup>  
Priority Research Centre for Energy, Faculty of Engineering & Built Environment  
The University of Newcastle, Callaghan NSW 2308, Australia

## Abstract

A central step in the low-temperature oxidation of hydrocarbons is the abstraction of H by hydroperoxyl radical ( $\text{HO}_2$ ). In this study, reaction rate constants are derived for H abstraction by  $\text{HO}_2$  from the three distinct locations of H in ethylbenzene (primary, secondary and aromatic H, with H on the ortho carbon taken as an example of unreactive aromatic H) as well as for the addition of H at the four possible sites. Rate constants are provided in the simple Arrhenius form. The dominant channel at all temperatures is found to be H abstraction from the secondary C-H bonds of the ethyl chain, whereas abstractions from the primary C-H bonds also contribute significantly at higher temperatures. Reasonable agreement was obtained with the limited literature data. Addition at the four sites of the aromatic ring and abstraction of one of the C-H aromatic bonds are rather unimportant for all temperatures. The results presented herein should be useful in modeling the lower temperature oxidation of alkylbenzenes.

*Keywords:*  $\text{HO}_2$ , Alkylbenzene, TST, Ethylbenzene.

## 1. Introduction

Reaction rate constants are commonly available for the faster elementary reactions for hydrogen atom abstractions by hydrogen atom, hydroxyl radical and oxygen atom for a wide range of hydrocarbon species. In contrast, there have been very limited experimental measurements of rate constants for the hydrogen abstraction reactions by the hydroperoxyl radical ( $\text{HO}_2$ ). Hydroperoxyl radical plays a key-determining task in the autoignition region (600 – 1200 K) observed in the negative temperature coefficient (NTC) behavior [1]. It is well-documented that  $\text{HO}_2$  plays a significant role in the reactive oxidation cycle operating at low temperatures or the so called “cool flame” reactions [2]. For instance, global sensitivity analysis of the mechanism of ethylene oxidation proved that the product yields are very sensitive to H abstraction reactions by  $\text{HO}_2$  in the intermediate temperature region [3]. For the case of benzene, this reaction is found to be faster by 4-5 orders of magnitude than H abstraction by the oxygen molecule, expressing its importance in the early oxidation process of aromatics [4]. The addition reaction of methylbenzyl radical +  $\text{HO}_2$  was found to be the most sensitive reaction in the ignition delays of xylene [5]. Due to the intricacy associated with studying this reaction experimentally in view of the difficulty in finding suitable sources for  $\text{HO}_2$  radicals, this reaction serves as an excellent case for a purely theoretical exploration. In recent studies, we calculated theoretically reaction rate constants for  $\text{HO}_2$  reactions with various compounds including benzene [4], phenol and toluene [6].

Alkylbenzenes in forms of xylene ( $\text{C}_6\text{H}_5(\text{CH}_3)_2$ ) and ethylbenzene ( $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$ ) constitute a large portion of

the total aromatic content in commercial fuels such as kerosene, gasoline and diesel, therefore, alkylbenzenes have been proposed as components for fuel surrogates [7]. Self-ignition of low alkylbenzene was studied with the aim of providing chemical kinetic model for gasoline surrogate groups [8]. It was found that the rate controlling step in the ethylbenzene oxidation is the recombination reaction between the oxygen molecule and ethylphenyl radicals [9]. Reactions of ethylbenzene with  $\text{HO}_2$  and  $\text{O}_2$  at low and intermediate temperatures are a major source for the formation of ethylphenyl radicals. In the current submission, reaction with ethylbenzene is addressed as a model compound for alkylbenzene.

## 2. Computational details

Electronic structure calculations were performed with the Gaussian 03 suite of programs [10]. Optimized geometries and harmonic vibrational frequencies of reactants, transition states and products have been calculated using the composite theoretical methods of CBS-QB3[11]. The CBS-QB3 method performs initial geometry optimization and frequency calculations at the B3LYP/CBS7B method followed by several successive single point energy calculations to obtain very accurate energies. Energies for certain reactions are also calculated at the G4 level of theory [12]. 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) and  $\kappa(T)$  is the transmission coefficient that accounts for the quantum tunnelling corrections calculated by the Eckart functional. Rate constants calculations are carried out with the aid of the “TheRate” program [13].

\* Corresponding author: Phone: (+61) 2 4985-4286, Email: [Mohammednoor.Altarawneh@newcastle.edu.au](mailto:Mohammednoor.Altarawneh@newcastle.edu.au)

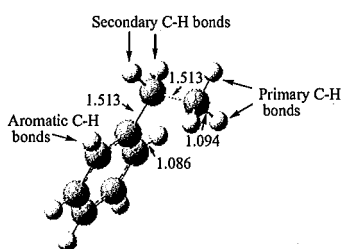
† Also at Chemical Engineering Department, Al-Hussein Bin Talal University, Ma'an, Jordan

‡ Also at School of Chemistry, The University of Sydney, Australia

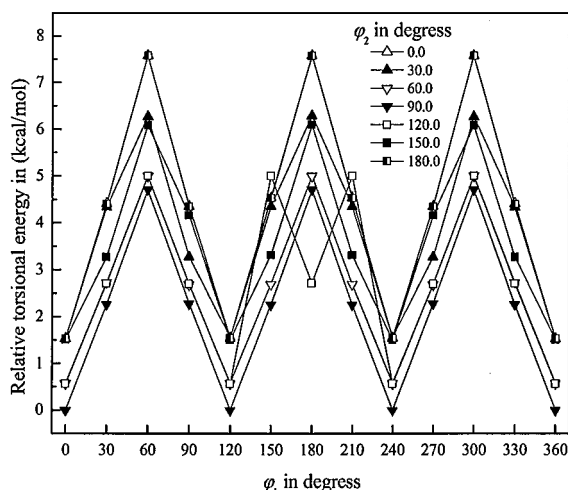
## 2. Results and discussion

### 2.1. Internal rotations and bond energies in ethylbenzene

Optimized structure of ethylbenzene is shown in Fig. 1. Most theoretical work on ethylbenzene has targeted its unique coupled internal rotations in which the rotation of the methyl group concurs with the rotation of the entire ethyl group [14]. Fig. 2 depicts the two internal rotations in ethylbenzene, i.e., the rotation of methyl group ( $\varphi_1$ ) and the rotation of the entire ethyl chain ( $\varphi_2$ ). In line with the consensus in literature, the global minimum is found to occur when the ethyl group is perpendicular with respect to the phenyl ring ( $\varphi_1 = 0.0^\circ$  and  $\varphi_2 = 90.0^\circ$ ). Ethylbenzene possesses three distinct C-H bonds; namely, the aromatic bonds on the phenyl ring, secondary ethyl bonds and primary methyl bonds. The calculated CBS-QB3 bond energies are found to be 113.7 kcal/mol, 87.0 kcal/mol and 100.6 kcal/mol, respectively. The corresponding G4 values are reported to be 112.1 kcal/mol, 86.0 kcal/mol and 98.3 kcal/mol. Accordingly, radical attack under oxidative conditions is most likely to commence by abstractions of the secondary H atoms.



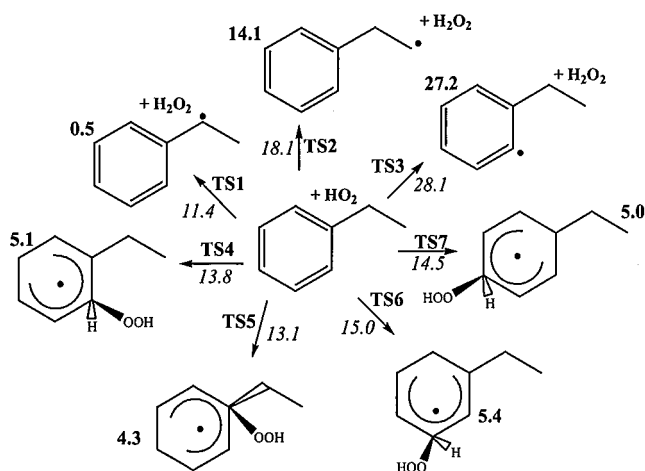
**Fig. 1.** Optimized geometries of ethylbenzene at the B3LYP/CBS7B level of theory. Distances are in angstrom (Å)



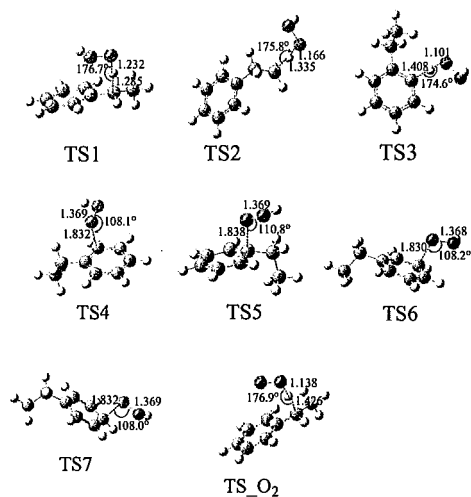
**Fig. 2.** Internal rotations in ethylbenzene.  $\varphi_1$  signifies the rotation of the methyl group and  $\varphi_2$  signifies the internal rotation of ethyl chain ( $\varphi_2$ ). Relative torsional energies with respect to the global minimum ( $\varphi_1 = 0.0^\circ$  and  $\varphi_2 = 90.0^\circ$ ).

### 2.2. Reaction of ethylbenzene with $\text{HO}_2$

All possible reactions between  $\text{HO}_2$  and ethylbenzene are shown in Fig. 3. Geometries of transition structures are given in Fig. 4. The O...O distance in all transition structures are elongated by 5–8% with respect to the equilibrium distance in the  $\text{HO}_2$  radical (1.328 Å). As shown,  $\text{HO}_2$  could add at the four plausible sites on the phenyl ring. It is found that the four addition channels have very comparable activation barriers (13.1–15.0 kcal/mol) and reaction energies (4.3–5.4 kcal/mol). Addition at the *ipso*-site is as endoergic as addition to other sites on the aromatic sites. The formation of the four  $\text{HO}_2\text{-C}_6\text{H}_5\text{CH}_2\text{CH}_3$  adducts is found to be slightly endoergic with relatively sizable reverse reaction barriers. This indicates that these adducts - if formed - could be long-lived species and may act as a source for the chain-propagating OH radicals, in an analogy to the reaction mechanism of  $\text{HO}_2$  + benzene. Abstractions of H atom from aromatic C-H bonds are associated with the highest energy barrier (28.1 kcal/mol) through the transition structure TS3. This barrier is very close to the corresponding barrier for H abstraction from benzene (28.9 kcal/mol) [4]. This indicates that the presence of the ethyl chain has a rather minimal effect on the reaction barrier, and thus barriers of abstractions from other aromatic C-H bonds are expected to be very similar. The energy barrier of this channel is only 0.9 kcal/mol above the separated products ( $\text{H}_2\text{O}_2$  and 1-ethylphenyl radical ( $\text{C}_6\text{H}_4\text{CH}_2\text{CH}_3$ )). As expected in view of the difference in the bond energies of the C-H bonds, abstraction of secondary H atoms is associated with the most accessible energy barrier which amounts to 11.4 kcal/mol through the transition structure TS1. Abstraction of a primary H atom incurs an activation barrier of 18.1 kcal/mol.



**Fig. 3.** Plausible pathways in the reaction of  $\text{HO}_2$  with Ethylbenzene. Values in bold and italic are reaction and activation energies respectively. All values are relative to the entrance channel.



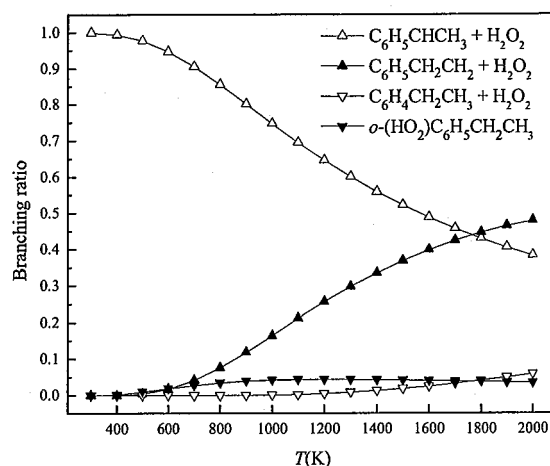
**Fig. 4.** Optimized transition structures at the B3LYP /6-CBSB7. Distances are in angstrom (Å) and angles are in degree.

### 2.3. Reaction rate constants

Reaction rate constants are evaluated using the seven bimolecular channels. Simple Arrhenius parameters are given in Table 1. Contribution from corrections of tunneling is more profound in the three abstraction reactions than the addition reactions. For example, Eckart coefficients for the abstraction reaction from the secondary H atoms amount to 3.06 and 1.64 at 600 K and 1000 K, respectively, whilst the corresponding values for the addition reaction at the *ortho* position are found to be 1.23 and 1.12 respectively. Branching ratios is given in Fig. 5. Abstraction of secondary H atoms is predicted to be dominant through the low and intermediate temperature regions. Abstraction of primary H atoms also contributes significantly. For instance, the branching ratio for the formation of the ethylphenyl radical ( $C_6H_5CH_2CH_2$ ) is calculated to be 7.6%, 16.4% and 37.0%, respectively at 800 K, 1000 K and 1500 K. Abstractions of aromatic H and additions at the phenyl ring are found to be of negligible importance at all temperatures. The presence of a weak C-H bond in ethylbenzene diminishes the role of addition channels in reference to the system of  $HO_2$  + benzene in which the addition channel was found to be the sole dominant channel at all temperatures. .

**Table 1:** Simple Arrhenius parameters for reactions of  $HO_2$  with ethylbenzene fitted in the temperature range of 300-2000 K.

	$A$ ( $cm^3$ $molecule^{-1} s^{-1}$ )	$E_a/R$ (K)
$C_6H_5CHCH_3 + H_2O_2$	$1.93 \times 10^{-12}$	6 500
$C_6H_5CH_2CH_2 + H_2O_2$	$2.30 \times 10^{-11}$	10 600
$C_6H_4CH_2CH_3 + H_2O_2$	$4.60 \times 10^{-11}$	16 000
$o-(HO_2)C_6H_5CH_2CH_3$	$4.63 \times 10^{-13}$	8 500
$ipso-(HO_2)C_6H_5CH_2CH_3$	$7.66 \times 10^{-14}$	8 000
$m-(HO_2)C_6H_5CH_2CH_3$	$3.35 \times 10^{-13}$	9 000
$p-(HO_2)C_6H_5CH_2CH_3$	$5.12 \times 10^{-13}$	8 800



**Fig. 5.** Branching ratios for products from the reactions of  $HO_2$  with ethylbenzene. Contributions from additions at *m*-, *ipso*- and *p*- sites are very similar to that of additions at the *o*- sites and not shown in the figure.

Experimentally, rate constants for the reaction of  $HO_2$  with ethylbenzene were measured only at 773 K by Baulch *et al.* [15] and Scott and Walker [16]. Both studies found that the overall reaction of  $HO_2$  with ethylbenzene proceeds at a rate of  $3.0 \times 10^{-16} cm^3 molecule^{-1} s^{-1}$  at 773 K. The authors described this value as the first reliable kinetic data measured for the abstraction of an H atom from any aromatic compound by  $HO_2$  radicals.

The unexpected low rate constant was explained based on a lower  $A$ -factor with a slightly higher enthalpy of activation in reference to alkanes. Based on an analogy with  $(HO_2 + (CH_3)_3CC(CH_3)_3)$  for the  $A$  factor and adjustment for the enthalpies of activations, Baulch *et al.* [15] recommended the following rate expressions for the three abstraction reactions between 600 and 1000 K:

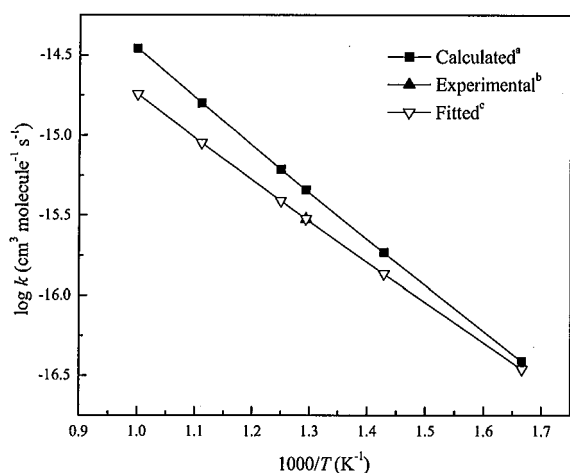
$$k = 4.41 \times 10^{-13} \exp\left(\frac{-5\ 600}{T}\right) cm^3 molecule^{-1} s^{-1} \text{ (secondary H atoms)}$$

$$k = 5.31 \times 10^{-12} \exp\left(\frac{-9\ 700}{T}\right) cm^3 molecule^{-1} s^{-1} \text{ (primary H atoms)}$$

$$k = 9.12 \times 10^{-13} \exp\left(\frac{-14\ 500}{T}\right) cm^3 molecule^{-1} s^{-1} \text{ (aromatic H atoms)}$$

A comparison between our calculated values with the single experimental value and the recommended values by Baulch *et al.* [15] is given in Fig. 6. Our calculated combined rate for abstraction from primary and secondary H atoms differ from the experimental value by only a factor of 1.50. Also, calculated values are in good agreement with the recommended values. Estimated  $A$ -factors and energies of activation in Table 1 are in a good agreement with the recommended values. As demonstrated by Scott and Walker, reactions of  $HO_2$  with alkylbenzenes have very much in common with

those of alkanes; thus rate constant expressions obtained herein could be extended for alkanes.



**Fig. 6.** Comparisons between the calculated reaction rate for HO<sub>2</sub> + ethylbenzene and other literature values calculated in this work, <sup>b</sup>experimental values in references 15 and 16, <sup>c</sup>recommended values in reference 15.

#### 2.4. Reaction of ethylbenzene with the oxygen molecule.

Despite the importance of oxygen molecule as the sole initiator of the onset of the oxidation process, relatively few rate constants have been obtained for this reaction. Ingham *et al.* [17] discussed in details the factors that contributed to the difficulty of obtaining reliable rate constants for this reaction. Theoretically, transition structures for the reaction of the triplet oxygen molecule often reside below the separated products. Thus, reactions rate constants must be calculated within the formalisms of vibrational transition state theory. Reaction and activation barriers for the reaction (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH<sub>3</sub> + O<sub>2</sub> → C<sub>6</sub>H<sub>5</sub>CHCH<sub>3</sub> + HO<sub>2</sub>) are calculated by CBS-QB3 and G4 composite methods. The transition structure is shown in Fig. 4 (TS<sub>O<sub>2</sub></sub>). The CBS-QB3 method yields similar values for activation and reaction energies at 37.9 kcal/mol. Activation energy by the G4 method amounts to 37.6 kcal/mol while the reaction energy is found to be 1.0 kcal/mol above the transition structure. A lower estimate of the reaction rate constant thus can be obtained by setting the activation energy at the value of the reaction energy. A rate constant based on the G4 values is fitted in the temperature range of [300 - 2000 K] to:

$$k = 2.85 \times 10^{-11} \exp\left(\frac{-20300}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The only literature estimate for this reaction rate constant comes from a database compiled by Ingham *et al* for the general reaction (RH + O<sub>2</sub> → R + HO<sub>2</sub>). Our calculated values for this reaction are within a factor of 2.3 from the recommended values by Ingham *et al.*

### 3. Conclusions

Reaction rate constants are obtained for all possible reactions channels between HO<sub>2</sub> and ethylbenzene. Throughout the NTC region in which there exists appreciable concentrations of HO<sub>2</sub> radicals, abstractions reactions from the secondary C-H bonds are the dominant channel. Reaction rate expressions presented herein should be useful in the pursue to construct a reliable kinetic database for HO<sub>2</sub> reactions pertinent to low temperature oxidation.

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