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

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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 (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 HO_2 plays a significant role in the reactive oxidation cycle operating at low temperatures or the so called "cool flame" reactions [2]. Alkylbenzenes in forms of xylene ($C_6H_4(CH_3)_2$) and ethylbenzene ($C_6H_5CH_2CH_3$) 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 [3]. Reactions of ethylbenzene with HO_2 and 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. Reaction rate constants are derived for H abstraction by 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.

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.
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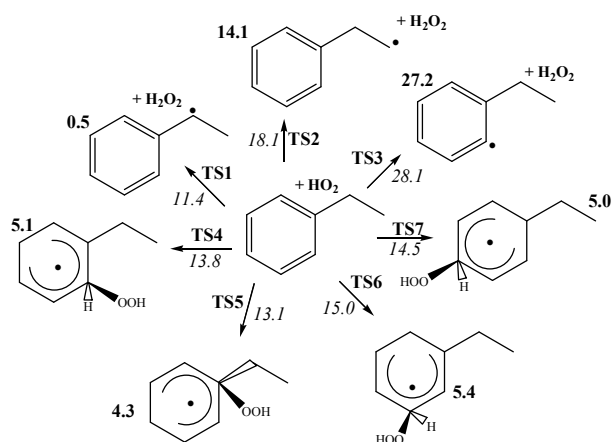
Simple Arrhenius parameters for reactions of HO_2 with ethylbenzene fitted in the temperature range of 300-2000 K.

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

Plausible pathways in the reaction of HO_2 with Ethylbenzene.
Values in bold and italic are reaction and Activation energies respectively. All values are relative to the entrance channel.