



Density functional theory study on the mechanism of OH-initiated atmospheric photooxidation of ethylbenzene

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ABSTRACT

The reaction mechanism for ethylbenzene with OH radical and O₂ was investigated by density functional theory (DFT) method. The structures, energetics, and relative stability of OH-ethylbenzene reaction intermediate radicals have been determined, and their activation barriers have been analyzed to assess the energetically favorable pathways to propagate the ethylbenzene oxidation. The results of the theoretical study indicate that OH addition is predicted to occur dominantly at the ortho position, with branching ratios of 0.53, 0.31, 0.10, and 0.06 for ortho, para, meta, and ipso additions, respectively, and the calculated overall rate constant is $1.24 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, showing a very good agreement with available experimental data. Under atmospheric conditions, oxygen is expected to add to the ethylbenzene-OH adducts forming ethylbenzene peroxy radicals. And subsequent ring closure of the peroxy radicals to form bicyclic radicals. With relatively low barriers, isomerization of the ethylbenzene bicyclic radicals to more stable epoxide radicals likely occurs, competing with O₂ addition to form bicyclic peroxy radicals. The study provides thermochemical data for assessment of the photochemical production potential of ozone and formation of toxic products and secondary organic aerosol from ethylbenzene photooxidation.

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1. Introduction

Ethylbenzene is an important constituent of aromatic hydrocarbons, also a harmful environmental pollutant and toxicant in atmosphere [1]. In addition to its high atmospheric photochemical reactivity and their consequent major influence on the formation of tropospheric ozone and on the oxidizing capacity of the atmosphere, there is now strong evidence that the photochemistry of ethylbenzene can lead to the formation of secondary organic aerosol (SOA) [2,3], which are known to be harmful to human and ecosystem health [4–6]. As emissions of ethylbenzene are concentrated in urban areas, where many people live and work, the formation of SOA becomes a more acute problem.

In the atmosphere, the reaction of ethylbenzene with hydroxyl radicals (OH) corresponds to the major atmospheric loss process during daylight hours. The OH-ethylbenzene reaction results in minor H-atom abstraction from the ethyl group and major OH addition to the aromatic ring [7]. Under atmospheric conditions, the OH-ethylbenzene adduct reacts with O₂ either by O₂ addition to form (primary) peroxy radicals or by H-abstraction to yield phenolic compounds. The fate of the peroxy radicals is governed by competition between reaction with NO to form alkoxy radicals

and cyclization to form bicyclic radicals. The bicyclic radicals can undergo unimolecular rearrangement to form epoxide radicals or bimolecular reaction with O₂ to form (secondary) bicyclic peroxy radicals [2]. The mechanistic complexity of the ethylbenzene oxidation further arises from multiple isomeric pathways at each reaction stage. Initial OH addition to ethylbenzene results in four distinct structural OH-ethylbenzene adduct isomers (i.e., ipso, ortho, meta, and para) (Fig. 1(a)). Subsequent reactions of OH-ethylbenzene adducts with O₂ and cyclization of aromatic peroxy radicals also incur additional isomeric branching. Fig. 1(b)–(e) illustrates the likely pathways of ethylbenzene oxidation following OH addition to the ipso, ortho, meta, and para position, respectively. For the ortho OH-ethylbenzene adduct, for example, O₂ addition to the aromatic ring occurs at C1, C3, or C5 on the ring, forming three possible structural isomers of the peroxy radicals. The next step involves formation of bicyclic radicals with an O–O bridge across the benzene ring, forming five possible isomers.

The room-temperature rate constant for ethylbenzene reported by Ohta is $7.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, much higher than that of OH-toluene reaction [8]. Environmental chamber studies have identified several major products consisting of both ring-retaining and fragmentation compounds [9,10]. In the experiment study of OH-initiated reactions of ethylbenzene using GC/MS detection, Forstner and co-workers [9] observed aromatic aldehydes products as well as ring fragmentation products, such as glyoxal, 2-butenedial,

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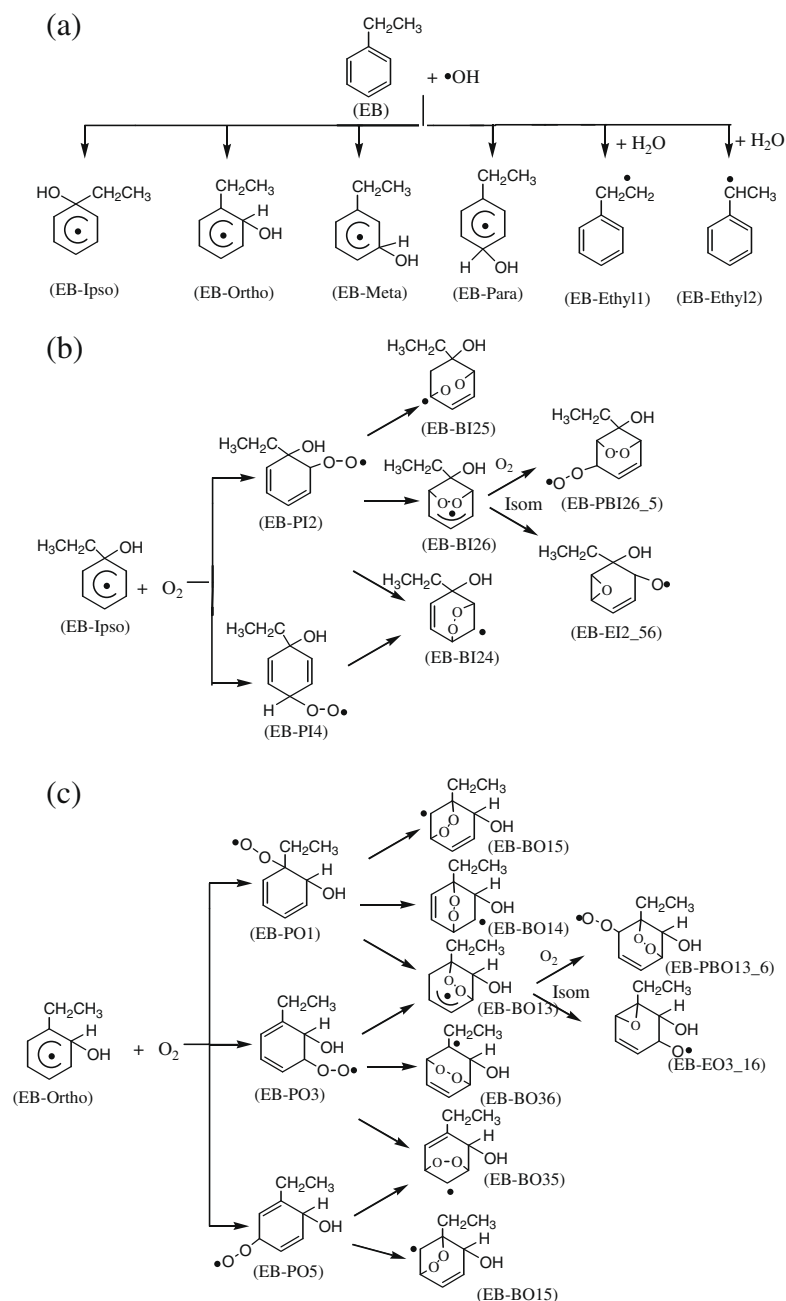


Fig. 1. (a) Suggested pathways of the reaction of OH with ethylbenzene; (b) suggested pathways of the reaction of EB-Ipso with O₂; (c) suggested pathways of the reaction of EB-Ortho with O₂; (d) suggested pathways of the reaction of EB-Meta with O₂; (e) suggested pathways of the reaction of EB-Para with O₂.

and 3-heptene-2,5-dione. However, in previous experimental product study of ethylbenzene, less than 50% of the reacted carbon has been typically identified in product distribution [9]. Interpretation of the identified reaction products is hindered because of the existence of multiple reaction pathways and steps. On the other hand, theoretical studies can be extremely useful in evaluating the possible mechanisms of the aromatic oxidation. In previous studies by Zhang and co-workers [11–13], some of intermediate species of OH with toluene, and xylene have been theoretically investigated using DFT (B3LYP) methods. At present, however, the detailed mechanism of ethylbenzene oxidation following the initial OH attack remain highly uncertain. So, in this work, we present a comprehensive theoretical investigation of the reaction of OH with ethylbenzene and the subsequent reactions, including the formation of aromatic peroxy, bicyclic, epoxide and bicyclic peroxy

radicals. Reaction energies for the formation of the aromatic radicals have been obtained to determine their relative stability and reversibility, and the activation barriers have been analyzed to assess the energetically favorable pathways to propagate the ethylbenzene oxidation.

2. Computational methods

As pointed out by Schreiner et al. [14], DFT method has recently come under some serious disrepute especially concerning description of radicals, and MP2 often works better than DFT functionals especially when energies are concerned. In fact, as García-Cruz et al. [15] had noted, in several cases, that MP2 method consistently emphasizes the positive interactions in compounds where

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