

Predictive kinetics on the formation and decomposition of ethylbenzene

Lili Ye^{a,*}, Lili Xing^b, Wenhao Yuan^b, Yuyang Li^a, Lidong Zhang^b,
Fei Qi^a

^a Key Laboratory for Power Machinery and Engineering of MOE, Shanghai Jiao Tong University, Shanghai 200240, PR China

^b National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, PR China

Received 4 December 2015; accepted 26 May 2016
Available online 13 June 2016

Abstract

The kinetics of reactions over the ethylbenzene surface were studied by using ab initio transition state theory (TST) based master equation methodologies. The variable reaction coordinate TST (VRC-TST) approach was employed to obtain high pressure limit rates for barrierless channels, including $C_7H_7 + CH_3$, $C_6H_5 + C_2H_5$, $C_6H_5CHCH_3 + H$, and $C_6H_5CH_2CH_2 + H$. Interaction potentials between each pair of fragments were simply simulated with CASPT2/cc-pVDZ calculations and scaled by reference to QCISD(T)/CBS energies. The larger basis set, cc-pVTZ, was tested to have only a very limited improvement on the final kinetics. For benzyl + CH_3 recombination, addition to benzylic-site forming ethylbenzene dominates overwhelmingly over addition to *ortho*- and *para*-sites forming *o*-methylbenzyl and *p*-methylbenzyl, respectively. For $C_6H_5CHCH_3 + H$ recombination, addition to benzylic-site also dominates over addition to sites at the aromatic ring. Present predictions, from a theoretical perspective, demonstrate strong preference for the C–C dominance in ethylbenzene decomposition. The quite good agreement with earlier studies lend confidence to present predictions. More importantly, our kinetic predictions imply that it could probably introduce large uncertainties if simply using kinetic parameterizations of toluene in modeling study of larger alkylbenzenes. The ethylbenzene system should serve as a better and safer reference.

© 2016 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

Keywords: Ethylbenzene; Decomposition and recombination; VRC-TST; Master equation; Rate constants

1. Introduction

Alkylbenzenes are major aromatic constituents in practical fuels such as gasoline, diesel and jet fuels. As the simplest alkylbenzene after toluene,

ethylbenzene is attracting growing attention due not only to the increasing use in commercial fuels but also to its significant role in PAHs formation [1,2]. Available studies on ethylbenzene have mostly centered on applying experiments and/or kinetic models to investigate its pyrolysis/oxidation behavior [2–5]. Of key importance at the early stage are the unimolecular decomposition of ethylbenzene [6], and in particular for oxidation also the recom-

* Corresponding author.

E-mail address: yell@sjtu.edu.cn (L. Ye).

bination of its derived radicals with molecular oxygen [7–9]. Recently, the kinetic mechanism of ethylbenzene oxidation has advanced considerably. Husson et al. [5] have performed a jet-stirred reactor experiment and the new mechanism proposed therein satisfactorily predicted the measured species profiles. As an important sub-mechanism, the unimolecular decomposition of ethylbenzene therein provides very useful reference for the present study.

With respect to its dissociation, a solid consensus has been reached that ethylbenzene mainly decomposes by β C–C bond fission at lower temperatures [10,11]. At high temperatures, the controversy about dominance of C–H or C–C bond fission was once aroused by Brouwer et al. [12], who claimed styrene to be the major product via two successive direct H-loss steps at $T > 1000$ K. After that, a variety of discussions had been performed and reached the agreement that C–C bond fission yielding benzyl + CH_3 is the most favored pathway with styrene being identified only as a minor product [13–16]. Unfortunately, available experimental measurements all date back to the last century, and the reported rate constants either covered very limited ranges of temperature and/or pressure, or were obtained by rather indirect means. Furthermore, large dispute still remains in branching ratios of products.

Previous experiments together with proposed models have improved our understanding of ethylbenzene system, but information about the detailed kinetics, such as the falloff behavior, is far from complete and more effort is certainly desirable. Compared with experimental progress, a priori theoretical predictions of this system seem severely lacking in spite of recent great advances in quantum chemistry and computing power. One available study we notice on its unimolecular dissociation is that of Matsugi and Miyoshi [17], in which the authors made rate predictions for the two C–C bond fissions. Therein, the geometric mean rule was used to get infinite-pressure recombination rates, which were then converted to dissociation rates using equilibrium constants computed at CBS-QB3. The microscopic rate constants were achieved via inverse Laplace transform. Due to the simplifications the authors employed, it is perhaps not that surprising if considerable uncertainties were found. Altarawneh et al. [8,18] have presented a number of theoretical analysis on several important reactions in the low temperature oxidation, e.g., ethylbenzene with HO_2 , α -phenylethyl + O_2 , and β -phenylethyl + O_2 . Detailed kinetics of these reactions threw useful light on the importance of different H atoms and the chemical role of the aromatic ring.

Theoretical investigations into kinetics of larger alkylbenzenes often present a number of complexities. First, the primary dissociation is often governed by the kinetics of C–C bond

fissions. Accurate treatment for these barrierless reactions remains fairly challenging. Next, the potential energy surfaces are often characterized by interconnected wells and multiple channels. Also, secondary reactions of products give rise to different mechanisms, and the problem becomes particularly complicated under combustion conditions. Furthermore, the rate constants of competing channels and their branching ratios are typically pressure dependent, and the falloff curves might have some sensitivity on the collisional energy transfer. The ab initio transition-state-theory based master-equation (AITSTME) methodology provides an effective way to address this problem.

The present study involves an exhaustive AITSTME analysis of the kinetics for key reactions on ethylbenzene surface, including decomposition, isomerization, and recombination. One main feature of the analysis is the implementation of VRC-TST approach for the reactive flux of barrierless channels. Another feature lies in the generation of phenomenological rate constants from master equation for multi energy-well reactions. Also, high-level schemes employed here allow for reliable predictions for the properties of stationary points. The current AITSTME analysis is aimed for a better understanding of the kinetics of reactions occurring over ethylbenzene surface.

2. Theoretical methodologies

2.1. Reaction kinetics

Direct bond fissions in side chain of ethylbenzene leads to a number of radical pairs, namely, C–C fissions lead to benzyl + CH_3 , or $\text{C}_6\text{H}_5 + \text{C}_2\text{H}_5$, while C–H fissions lead to $\text{C}_6\text{H}_5\text{CHCH}_3 + \text{H}$, or $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2 + \text{H}$. Also, C–C fission in ethylbenzene isomer, methylcycloheptatriene, leads to the cyclic-C7 triene radical and CH_3 . Bond fissions at cyclic aryl rings are generally thought to be ignorable comparing those at side chains, and therefore are not involved. Direct bond-fission reactions are often characterized by the transformation of transitional modes from free-rotor to hindered-rotor to harmonic-oscillator as the two interacting fragments get closer, and accurate treatment is rather complicated. The VRC-TST approach has proved to be an effective tool in making predictions of flux contribution from transitional modes of radical–radical reactions [19,20].

The most distinctive feature of the VRC-TST approach lies in the multifaceted diving surface devised to separate reactants and products. Detailed description of constructing such dividing surface can be found elsewhere [20,21]. Briefly, a set of pivot points are selected for each fragment, and the reaction coordinate is defined as the distance

Download English Version:

<https://daneshyari.com/en/article/6478007>

Download Persian Version:

<https://daneshyari.com/article/6478007>

[Daneshyari.com](https://daneshyari.com)