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Reaction mechanism, rate constants, and product yields for the oxidation of Cyclopentadienyl and embedded five-member ring radicals with hydroxyl

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ABSTRACT

Potential energy surfaces for the C_5H_5 + OH and $C_{15}H_9$ + OH reactions have been studied by ab initio calculations at the CCSD(T)-F12/cc-pVTZ-f12//B3LYP/6-311G(d,p) and G3(MP2,CC)//B3LYP/6-311G(d,p) levels of theory, respectively, in order to unravel the mechanism of oxidation of the cyclopentadienyl radical and five-member-ring radicals embedded in a sheet of six-member rings with OH. The VRC-TST approach has been employed to compute high-pressure-limit rate constants for barrierless entrance and exit reaction steps and multichannel/multiwell RRKM-ME calculations have been utilized to produce phenomenological pressure- and temperature-dependent absolute and individual-channel reaction rate constants. The calculations allowed us to quantify relative yields of various products in a broad range of conditions relevant to combustion and to generate rate expressions applicable for kinetic models of oxidation of aromatics. The C_5H_5 + OH reaction is shown to proceed either by well-skipping pathways without stabilization of C_5H_6O intermediates leading to the bimolecular products *ortho*-C_5H_5O + H, C_5H_4OH (hydroxycyclopentadienyl) + H, and C_4H_6 (1,3-butadiene) + CO, or via stabilization of the C_5H_6O intermediates, which then undergo unimolecular thermal decomposition to *ortho*-C_5H_5O + H and C_4H_6 + CO. The well-skipping and stabilization/dissociation pathways compete depending on the reaction conditions; higher pressures favor the stabilization/dissociation and higher temperature favor the well-skipping channels. For the $C_{15}H_9$ + OH reactions, the results demonstrate that embedding decreases the oxidation rate constants and hinder the decarbonylation process; the removal of CO grows less likely as the number of common edges of the five-member ring with the surrounding six-member rings increases.

1. Introduction

The oxidation of aromatic radicals plays an important role in combustion chemistry because their parent aromatic molecules are present in substantial amounts in all practical hydrocarbon fuels [1,2]. Therefore, reliable data on the oxidation mechanism and kinetics of the aromatics are critical for developing accurate and trustworthy kinetic models of combustion flames. The cyclopentadienyl radical, C_5H_5, has been established as a key transition species while considering the oxidation mechanisms of aromatic and acyclic molecules [3–7]. This is so because an initial step in oxidation of a six-member aromatic ring normally results in its contraction to a five-member ring and a subsequent oxidation step produces an acyclic hydrocarbon molecule or a radical. For instance, oxidation of benzene involves formation of the phenyl radical, C_6H_5, via H abstraction by others radicals present in flames (H, OH, CH_3, etc.) [8–10] and then, C_6H_5 reacts with molecular oxygen producing C_5H_5 as one of the major products [11–24]:

$$C_6H_6 + R \rightarrow C_6H_5 + RH$$

$$C_6H_5 + O_2 \rightarrow C_6H_5OO \rightarrow C_6H_5O + O \rightarrow C_5H_5 + CO + O$$

$$\rightarrow C_5H_5 + CO_2$$

The next oxidation step, the reactions of cyclopentadienyl with a variety of oxidizers (O_2, O, OH, and HO_2) were first studied in detail theoretically by Zhong and Bozzelli [25], who utilized thermodynamic parameters from group additivity and semi-empirical

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PM3 and ab initio MP4 and G2 calculations and empirical estimates for activation energies to compute reaction rate constants using QRRK theory. More recently, Robinson and Lindstedt [26] revisited the same reactions employing more advanced G4MP2 and G3B3 calculations of pertinent potential energy surfaces (PES) and generated temperature- and pressure-dependent rate constants using a simplified Rice–Ramsperger–Kassel–Marcus Master Equation (RRKM–ME) treatment. However, the RRKM-ME calculations by Robinson and Lindstedt with the ChemRate code [27] have not taken into account multiwell/multichannel effects in the master equation set-up and treated rather approximately barrierless channels, such as the entrance $C_5H_5 + O$ and $C_5H_5 + OH$ channels and the exit $C_5H_6O \rightarrow C_5H_5O + H$ channels.

To our knowledge, no direct experimental measurements of rate constants for the oxidation reactions of C_5H_5 are available. The current kinetic models for oxidation of aromatics mostly rely upon evaluations of rate constants for the C_5H_5 reactions based on hypothetical mechanisms derived from fitting experimental flame results on concentration profiles for the key species [28-33] or use rate expressions proposed by Robinson and Lindstedt [26]. Among the experimental/modeling studies, Butler and Glassman [34] presented the cyclopentadienyl oxidation data sets measured in a flow reactor, which provided a foundation for further investigation of the major oxidation and mass growth channels of C_5H_5. One of the most important findings by Butler and Glassman is the key role of the 2,4-cyclopentadienoxy C_5H_5O radical, which can be formed, in particular, via the $C_5H_5 + O$ reaction and further decompose by ring opening producing *n*-butadienyl, C_4H_5, + CO as the major products. On the contrary, 2,4-cyclopentadienone C_5H_4O was not detected. Ji et al. [32] have studied propagation and extinction of cyclopentadiene flames and modeled their experimental data using recent kinetic models. Their results indicated that both flame propagation and extinction are controlled by the fuel kinetics and the formation and consumption of such intermediates as cyclopentadienyl, cyclopentadienone, and cyclopentadienoxy. For instance, the authors concluded that among the potential consumption pathways of cyclopentadienyl radicals, two relevant reactions could improve the high temperature oxidation kinetic model of cyclopentadiene – unimolecular decomposition, $C_5H_5 \rightarrow C_3H_3 + C_2H_2$, and oxidation of cyclopentadienyl with hydroxyl, $C_5H_5 + OH \rightarrow C_4H_6 + CO$.

In view of the importance of the C_5H_5 oxidation reactions, we began systematic theoretical studies of their mechanism and kinetics employing up-to-date methods of the electronic structure to unravel their PESs and using modern kinetic theories to generate more reliable rate constants and product branching ratios for kinetic models of oxidation of the aromatics and five-member rings. In our previous paper [35], we discussed the $C_5H_5 + O$ reaction along with unimolecular and H-atom assisted decomposition of cyclopentadienone occurring on the C_5H_4O and C_5H_5O surfaces. The goal of the present study is to map out in detail the C_5H_6O PES and to utilize its features for RRKM-ME calculations of temperature- and pressure-dependent rate constants for the $C_5H_5 + OH$ reaction. The development of the non-empirical RRKM–ME theoretical scheme implemented in the MESMER package [36] and more recently in the MESS program [37,38] greatly facilitated theoretical evaluations of rate constants for complex reactions and opened an opportunity to compute them close to 'kinetic accuracy', i.e., with accuracies comparable to that of experiment [39], providing that the energies of the relevant species on the PES and their densities and numbers of states or partition functions are calculated with sufficient accuracy.

After considering the $C_5H_5 + OH$ reaction, we extend our study to the reactions of hydroxyl radicals with PAH radicals containing a five-member ring embedded in a sheet of six-member rings, emulating oxidation of the five-member ring at the edges of a graphene sheet, a large PAH molecule, or a soot particle. Soot and PAHs are known to be the major pollutants from combustion of fossil fuels and hence their growth and decay in flames occurring via the addition and removal of carbon, respectively, remain an active area of both experimental and theoretical research [10,40]. Previously, we simulated the oxidation at the edges of PAH with molecular oxygen using the pyrene molecule (more precisely, the pyrenyl radical produced by H abstraction from pyrene) as a model system for the PAH surface [41]. Earlier, similar studies of the O_2 reaction with pyrenyl and corannulenyl radicals were reported by Raj et al. [42,43]. The results showed that, similarly to the phenyl and naphthyl [23,44] reactions with O_2, oxidation of a six-member ring in pyrenyl predominantly contracts it into a five-member ring giving a $C_{15}H_9$ radical. We have also investigated the subsequent reactions of $C_{15}H_9$ with O_2 and O and used our results to generate rate constants for oxidation of the embedded five-member ring with molecular and atomic oxygen at the edges of PAHs and soot. The derived oxidation mechanisms and the calculated rate constants for six- and five-member rings were then utilized in kinetic Monte Carlo simulations of oxidation of a graphene "molecule" evolving in flame-like environments [41]. Along with O_2 and O, the hydroxyl radical has been experimentally identified as one of the major soot oxidizers [45]. Theoretically, Edwards et al. have studied the reaction of OH with phenanthryl radicals and showed that the conversion of a six-member ring to a five-member ring is the prevailing reaction outcome [46]. However, the consequent reaction of the embedded five-member ring radical with OH has not been investigated so far. In the present work, we fill this gap and generate the PES and rate constants for the $C_{15}H_9 + OH$ reactions, thus simulating the oxidation of five-member rings with OH at the PAH and soot edges. In addition, we compare the mechanisms and kinetics of the reactions of a five-member ring with hydroxyl radicals when such a ring is isolated as in C_5H_5 or is embedded in a sheet of six-member rings as in different isomers of our model $C_{15}H_9$ radical containing three six- and one five-member rings.

2. Theoretical methods

Geometries of the reactants, various intermediates, transition states, and products participating in the $C_5H_5 + OH$ reaction on the C_5H_6O PES and in the $C_{15}H_9 + OH$ reactions on the $C_{15}H_{10}O$ surface were optimized at the hybrid density functional B3LYP/6-311G(d,p) level of theory [47,48]. Vibrational frequencies were computed at the same theoretical level and were utilized in calculations of zero-point vibrational energy corrections (ZPE) and rate constants. Energies of various C_5H_6O species were refined by single-point calculations using the explicitly-correlated coupled clusters CCSD(T)-F12 method [49,50] with Dunning's correlation-consistent cc-pVTZ-f12 basis set [51,52]. The CCSD(T)-F12/cc-pVTZ-f12 approach closely approximates CCSD(T)/CBS energies, i.e. the energies within the coupled clusters theory with single and double excitations with perturbative treatment of triple excitations in the complete basis set limit. We expect that the accuracy of the CCSD(T)-F12/cc-pVTZ-f12//B3LYP/6-311G(d,p) + ZPE(B3LYP/6-311G(d,p)) relative energies should be within 1 kcal/mol based upon the assessment by Zhang and Valeev [53], who reported the mean unsigned errors in reaction energies and barrier heights for a broad range of reactions calculated at the CCSD(T)-F12/cc-pVTZ-f12 level to be 0.55 and 0.28 kcal/mol, with the maximal unsigned errors being 1.53 and 0.78 kcal/mol, respectively. For $C_{15}H_{10}O$ species, the refinement of single-point energies was carried out employing the modified G3(MP2,CC)//B3LYP [54,55] composite scheme where the energies were computed as

$$E_0[G3(MP2,CC)] = E[CCSD(T)/6-311G^{**}] + \Delta E_{MP2} + E(ZPE),$$