



Oxidation of cyclopentadienyl radical with molecular oxygen: A theoretical study

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ABSTRACT

The potential energy surface for the reaction of cyclopentadienyl radical with O_2 has been studied using ab initio calculations at the CCSD(T)-F12/cc-pVTZ-f12//B3LYP/6-311G(d,p) level and the RRKM-Master Equation approach has been employed to compute reaction rate constants and product branching ratios at various temperatures and pressures pertinent to combustion. The results show that at low temperatures from 500 to 800–1250 K (depending on pressure), the reaction predominantly forms a collisionally-stabilized C_5H_5-OO complex and then, the thermalized complex rapidly decomposes back to the reactants establishing a $C_5H_5 + O_2/C_5H_5-OO$ equilibrium. At higher temperatures, typically above 1000 K, the mechanism is different and the $C_5H_5 + O_2$ reaction proceeds to form various bimolecular products. Cyclopentadienone $C_5H_4O + OH$ are predicted to be the predominant product (63.5–83.3%). Relatively minor products include $H_2CCHCHC(H)O + CO$ (20–3%), vinylketene + HCO (12–2%), and $OC(H)CHCHCHCO + H$ (3–5%), which are formed via the $OC(H)CHCHCHC(H)O$ intermediate residing in a deep potential well, and highly endothermic $C_5H_5O + O$ (up to 6.5% at 2500 K) produced directly by the O–O bond cleavage in the initial complex. The calculated rate constants for the formation of $C_5H_4O + OH$ and $C_5H_5O + O$ are shown to be independent of pressure above 800 K, but the rate constants for the reaction channels resulting in CO, HCO, and H eliminations show some pressure dependence in the low end of the high-temperature regime and decrease with the pressure growing from 10 to 100 atm. The CO_2 loss channel leading to the formation of 1,3-butadien-1-yl C_4H_5 is shown to be negligible. The total reaction rate constants at all considered pressures from 0.03 to 100 atm merge at 1375 K and show no pressure dependence at higher temperatures, as only the bimolecular products are formed. Overall, the rate constant of the $C_5H_5 + O_2$ reaction at combustion-relevant temperatures is predicted to be very slow, 10^{-16} – 10^{-15} cm^3 molecule⁻¹ s⁻¹, that is typically ~5 orders of magnitude lower than those for the oxidation reactions of cyclopentadienyl with OH and $O(^3P)$. A comparison of the rates of the $C_5H_5 + O_2/OH/O$ reactions allowed us to conclude that molecular oxygen can play only a small role in oxidation and removal of five-member rings in combustion and only when the concentration of O_2 is orders of magnitude higher than the concentrations of O and OH.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAH) and their aggregates in the form of soot particles [1] are major pollutants produced during incomplete combustion of fossil fuels. The formation of soot consists of a number of sequential steps, such as soot precursor formation at the molecular level, particle nucleation, and particle coagulation [2,3]. In competition to the molecular PAH growth, re-

actions take place at the edges of PAHs and soot [3,4], which involve removal of carbon [5] resulting in degradation of the size of a PAH molecule or a soot particle via e.g., their oxidation with such common oxidants as O_2 , O, and OH abundant in flames. In particular, the reactions of (poly)aromatic radicals with molecular oxygen play an important role in combustion of hydrocarbon fuels because they compete with the growth of PAH in flames and produce smaller species. On the other hand, the oxidation products often contain five-member rings, such as cyclopentadienyl and indenyl, which may propagate further PAH synthesis and thus contribute to the formation of a large variety of cyclopentafused PAH. Additionally, the oxidation reactions generate energy for further growth processes. In order to develop reliable kinetic models for

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the formation and degradation of PAH and soot in combustion, detailed information is required on the mechanism, rate constants, and product branching ratios of elementary chemical reactions involved in these processes.

In recent years, a significant progress has been made in understanding the mechanism of oxidation of aromatic radicals and in quantifying rate constants and branching ratios for the relevant reactions. In particular, we computed potential energy surfaces as well as temperature- and pressure-dependent rate constants and relative product yields for the $C_6H_5 + O_2$ and $C_{10}H_7 + O_2$ reactions [6–8]. The results showed that radicals containing five-member rings, such as cyclopentadienyl and indenyl, are the major reaction products, especially at high temperatures. The conclusions from the theoretical calculations were generally confirmed by experimental measurements of the products of the $C_6H_5 + O_2$ reaction in a pyrolytic reactor using photoionization spectroscopy [9]. Klippenstein and coworkers have recently generated more precise high pressure limit rate constants for the association of phenyl and naphthyl radicals with O_2 using variable reaction coordinate-transition state theory (VRC-TST) [10]. Raj et al. [11] studied structural effects on the oxidation of soot particles both experimentally and computationally. In particular, they performed quantum chemical B3LYP and Hartree–Fock calculations of the reaction pathways of 4-pyrenyl and 1-corannulenyl with O_2 . The results suggested a mechanism in which the six-member ring of the pyrenyl radical is oxidized by molecular oxygen and is eventually converted into a five-member ring, similar to the reactions of phenyl and naphthyl radicals with O_2 . The ensuing oxidation of a five-member ring with a second O_2 molecule results in the full destruction of the five-member ring with the formation of the phenanthryl radical, i.e. a PAH radical with one less six-member ring than the starting material, the pyrenyl radical. The oxidation mechanism of 1-corannulenyl was found to be similar, but with lower activation energies, which corroborated the experimentally observed higher reactivity of curved PAH structures. In our recent study [12] we confirmed the mechanism of the 4-pyrenyl + $2O_2$ reaction by higher-level G3(MP2,CC) calculations and predicted temperature- and pressure-dependent rate constants for both stages, oxidation of a six-member ring radical and oxidation of a five-member ring radical embedded in three six-member rings. The computed oxidation mechanisms of six- and five-member rings and relevant rate constants were then utilized in kinetic Monte Carlo simulations of oxidation of a graphene “molecule” evolving in flame-like environments.

While the aforementioned studies clearly suggest a two-stage process of oxidative carbon removal from an edge of a PAH molecule or a soot particle via degradation of a six-member ring to a five-member ring followed by destruction of the latter, the oxidation mechanism of the prototype five-member ring aromatic radical, cyclopentadienyl C_5H_5 , remained largely unknown. An experimental study of cyclopentadiene combustion in a plug flow reactor near 1150 K by Butler and Glassman [13] provided some results on oxidation of C_5H_5 . The authors emphasized the critical role of the $C_5H_5 + O$ reaction in the oxidation process, which competes with the PAH formation pathways via combination of two C_5 rings and concluded that the major oxidative consumption path of cyclopentadienyl is the formation of 2,4-cyclopentadienoxyl radical followed by ring opening to produce *n*-butadienyl + CO. Almost two decades ago, Zhong and Bozzelli [14] studied the $C_5H_5 + O_2/O/HO_2/OH/H$ reactions using molecular thermodynamic parameters obtained from group additivity and semi-empirical PM3 and ab initio MP4 and G2 calculations, with empirical estimation of activation energies. Employing kinetic computations based on QRRK theory, Zhong and Bozzelli suggested in particular that the $C_5H_5 + O_2$ reaction leads to two major product pairs, 2-pentenedialdehyde radical plus H and vinylketene plus formyl

radical. More recently, Robinson and Lindstedt [15], within their extended study of oxidation of cyclopentadienyl by various oxidizers, calculated a portion of the $C_5H_5 + O_2$ potential energy surface (PES) and computed temperature- and pressure-dependent rate constants using a simplified Rice–Ramsperger–Kassel–Marcus Master Equation (RRKM-ME) treatment with a ChemRate code [16]. On the contrary to Zhong and Bozzelli, they suggested $C_5H_4O + OH$ to be the predominant reaction products. However, their exploration of the $C_5H_5O_2$ PES was far from complete.

In view of the importance of cyclopentadienyl oxidation for modeling of C_5H_5 contribution to soot formation and in propagation and extinction of cyclopentadiene flames [17], it is necessary to reconsider the PESs, mechanisms, and rate constants of the oxidation reactions of cyclopentadienyl at a modern level of ab initio and theoretical kinetic calculations. The a priori RRKM-ME theoretical approach now allows us computing temperature- and pressure-dependent rate constants with ‘kinetic accuracy’, i.e., with accuracies comparable to that of experiment [18]. For instance, the recently developed Master Equation System Solver (MESS) program [19,20] greatly facilitates the evaluation of temperature- and pressure-dependent rate coefficients for complex reactions. Recently, we reported detailed ab initio/RRKM-ME studies on the mechanism and kinetics of the $C_5H_5 + O$ and $C_5H_5 + OH$ reactions [21,22]. In this paper, we complete systematic investigations aimed to generate reliable rate constants and product branching ratios for the oxidation of cyclopentadienyl with various oxidizers present in flames with a study of the $C_5H_5 + O_2$ reaction.

2. Theoretical methods

Geometries of the reactants, various intermediates, transition states, and products involved in the $C_5H_5 + O_2$ reaction were optimized at the density functional B3LYP/6-311G(d,p) level of theory [23,24]. Vibrational frequencies were computed at the same theoretical level and were used to evaluate zero-point vibrational energy corrections (ZPE) and were also utilized in calculations of rate constants. Energies were refined by single-point calculations using the explicitly-correlated coupled clusters CCSD(T)-F12 method [25,26] with Dunning’s correlation-consistent cc-pVTZ-f12 basis set [27,28]. The CCSD(T)-F12/cc-pVTZ-f12 approach is expected to closely approximate 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. It is anticipated 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 or better [29]. The ab initio calculations were performed using the GAUSSIAN 09 [30] and MOLPRO 2010 [28] program packages.

Temperature- and pressure-dependent phenomenological rate constants were computed by solving the one-dimensional master equation employing the MESS package [19,20]. We used collision parameters calculated by Jasper and Hansen for the methylcyclopentadienyl radical ($C_5H_4CH_3$) + Kr reaction [31], which is representative of the system considered here. Specifically, the Lennard–Jones parameters were taken as $(\epsilon/\text{cm}^{-1}, \sigma/\text{Å}) = (230, 4.01)$ and the temperature dependence of the range parameter α for the deactivating wing of the energy transfer function was expressed as $\alpha(T) = \alpha_{300}(T/300\text{ K})^n$, with $n = 0.7$ and $\alpha_{300} = 333\text{ cm}^{-1}$, where the collisional energy transfer in the master equation was described using the “exponential down” model [32]. Jasper and Miller [33] have shown that results for other heavy atomic and diatomic baths are likely to be very similar to those for Kr, with differences within the accuracy of the approach for predicting collisional energy transfer parameters for master equation calculations. The Rigid-Rotor, Harmonic-Oscillator (RRHO) model was generally utilized in the calculations of the densities of states and partition

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