Pressure dependent kinetic analysis of pathways to naphthalene from cyclopentadienyl recombination

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ABSTRACT

Cyclopentadiene (CPD) and cyclopentadienyl radical (CPDyl) reactions are known to provide fast routes to naphthalene and other polycyclic aromatic hydrocarbon (PAH) precursors in many systems. In this work, we combine literature quantum chemical pathways for the CPDyl + CPDyl recombination reaction and provide pressure dependent rate coefficient calculations and analysis. We find that the simplified 1-step global reaction leading to naphthalene and two H atoms used in many kinetic models is not an adequate description of this chemistry at conditions of relevance to pyrolysis and steam cracking. The $C_{10}H_{10}$ species is observed to live long enough to undergo H abstraction reactions to enter the $C_{10}H_9$ potential energy surface (PES). Rate coefficient expressions as functions of T and P are reported in CHEMKIN format for future use in kinetic modeling.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of molecules comprised of hundreds of chemicals produced from various anthropogenic sources, such as the incomplete combustion of fuels in boilers and heating devices, oil refining processes, and the combustion of transportation fuels (in particular diesel). Many PAHs are known to be carcinogenic or mutagenic as well as important precursors to soot [1–5]. Increasing energy demands and more stringent emission regulations have spurred research into various new technologies that reduce PAH emissions [6–8]. Despite the attention that these PAHs have attracted, many questions related to their formation remain not fully understood, i.e. what are the key reactions responsible for the formation of PAHs and what are the main PAH precursors? Researchers have developed extensive kinetic mechanisms describing low and high temperature fuel oxidation, but few exist that are able to predict the PAH growth and subsequent soot formation [9–11]. Some key efforts toward the latter have come from Frenklach, Appel et al., and Richter and Howard [12–15]. However, these studies focused primarily on the chemistry at high temperature flame conditions, at which the HACA mechanisms first proposed by Frenklach in 1991 as well var-

ious similar pathways summarized in the review article by Richter and Howard [12,14] dominate. The radicals involved in these reactions are highly reactive or energetic and thus not present in sufficient concentrations at lower temperatures. Given their increased stability, resonantly stabilized radicals such as allyl, propargyl and cyclopentadienyl (CPDyl) have been suggested as possible precursors of aromatic products at low or moderate temperatures [16–19]. However, most of these reactions lead to mono-aromatic hydrocarbons. Several experimental pyrolysis studies at lower temperatures detected CPD as an important product and Melton et al. showed that PAH formation was most sensitive to the CPD concentration [20–23]. Since CPD is easily converted to CPDyl this suggests that CPDyl radicals play a crucial role in PAH formation. In this work, the focus is on the development of a detailed kinetic network for cyclopentadienyl recombination that is relevant at pyrolytic and low-temperature combustion conditions to describe the formation of naphthalene, the simplest PAH and an important PAH precursor.

As briefly indicated above, a number of researchers have explored the thermal decomposition of CPD experimentally. In an attempt to obtain bond dissociation energies, the decomposition of CPD under pyrolytic conditions was studied by Szwarc in 1950 [24]. This led to a complicated decomposition spectrum, containing H_2, CH_4, C_2 hydrocarbons and other species hinting at the complexity of the CPD reaction network. In 1972 Spielman and Cramers
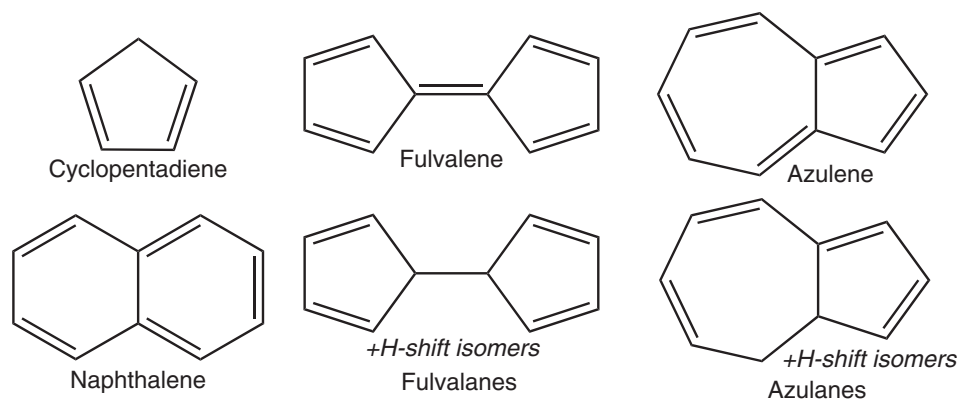
Fig. 1. Primary structures of this study. An ending of –yl added to a species indicates a radical of that species formed by hydrogen loss.

first proposed a potential role of CPD in the formation of the initial aromatics, observing products such as styrene, indene, and naphthalene under pyrolytic conditions [25]. This was then validated by studies of the pyrolysis and hydrogenolysis of phenol [26–28]. Burcat et al. studied the high-temperature decomposition reactions of CPD in a shock-tube in 1996, and modeled it with a simple model of 36 reactions. Roy et al. also studied CPD reactions using shock tube experiments and reported rate coefficients for the C–H bond scission and the reaction between CPD and a hydrogen atom [29,30]. While the Spielman study and others showed qualitatively that naphthalene appears to be produced from CPD, in 2003, Murakami et al. first experimentally derived a rate expression for a net reaction from CPDyl to naphthalene, assuming CPD initially forms its relatively stable radical [31]. More recently, experimental efforts to understand CPD pyrolysis chemistry have shifted toward flow reactor studies [32,33]. Djokic et al. and Kim et al. identified and quantified numerous pyrolytic products from CPD up to anthracene, phenanthrene and fluorene supporting the important role of CPD and CPDyl in PAH formation. The crucial role of CPDyl radicals in PAH formation is additionally confirmed by pyrolysis studies of anisole (which forms CPDyl by methyl loss and carbon monoxide ejection) and dimethylfuran [20,34,35]. More recently, in 2015, Knyazev and Popov experimentally investigated the total self-reaction rate of CPDyl, finding it to show significantly faster kinetics when compared with other similar radical self-reactions. Naphthalene and Azulene were detected as final products with the former being the major product [36].

The first quantum chemical exploration of the potential energy surface (PES) for CPDyl recombination was reported by Melius et al. in 1996. This study used the BAC-MP4 and MP2 levels of theory to characterize pathways in which two CPDyl radicals recombine, subsequently lose an H atom to form a fulvalanyl radical (Fig. 1), which then isomerizes and ejects an additional H atom to yield naphthalene. The importance of hydrogen atom mobility for PAH formation was emphasized by this work as was the role of resonantly stabilized intermediates [37]. A 2006 paper by Wang et al. extended the surface using the B3LYP level to incorporate pathways to benzene and indene as well as naphthalene. However, that work focused on initial reactions between CPD and CPDyl rather than two CPDyl radicals. It was observed that C–C β scission routes tended to be favored at high temperatures [38]. A 2007 paper by Kislov and Mebel used the RCCSD(T)/6-311G(d,p) level to investigate the $C_{10}H_9$ potential energy surface. Routes to naphthalene, azulene, and fulvalene were compared. Assuming unimolecular reactions in the high pressure limit, fulvalene was computed to be the dominant product above 1500 K, while naphthalene was the primary species at lower temperatures, and azulene was always a minor product. Kislov and Mebel extended their work in 2008

to incorporate the relevant portion of the $C_{10}H_{11}$ surface consisting principally of routes to indene calculated at the G3 level [39]. Subsequent work by Kislov and Mebel elucidated the poor likelihood of reaction pathways that would produce molecular hydrogen along the way to naphthalene from two CPDyl radicals as had been proposed as a global step for the pathway and incorporated into some kinetic mechanisms [40,41]. A 2012 paper by Cavallotti et al. revisited routes from the reaction of CPD with CPDyl using the B3LYP level for most calculations and ROCBS-QB3 for important flux determining steps along the pathways analyzed. Additional routes were located for the formation of indene, benzene, vinylfulvene, and phenyl butadiene [42]. In 2013 Cavallotti et al. analyzed the $C_{10}H_{10}$ surface at the CBS-QB3 level, focusing on the formation of the fulvalanyl and azulanyl radicals. Routes to the azulanyl radical were reported to dominate up to 1450 K [43]. This result in turn added relevance of the spiran and methyl walk pathways from azulene to naphthalene shown by Alder et al. in 2003 [44]. Some additional discussion of many of these quantum chemical studies can be found in a recent paper by Mebel et al. [45].

Rate coefficients are needed to quantitatively model PAH formation kinetics. A number of the previously noted studies presented high pressure limit rate coefficients and global step rate constants. Wang et al. reported only high-pressure limit Arrhenius expressions for the primary reaction pathway branching reactions they studied [38]. The 2007 and 2008 Kislov and Mebel papers reported rate coefficients and equilibrium constants for all important reactions they located. These were reported at various relevant temperatures in table format [39,46]. Global overall Arrhenius expressions were reported by Cavallotti et al. in 2012 and 2013 for the formation of the terminal species of interest in those studies [42,43]. However, none of these studies incorporated pressure dependence in their reported rate expressions. While the C_{10} species of interest are relatively large molecules, they are not large enough to be sure their unimolecular reactions are at the high pressure limit at pyrolysis and combustion conditions. This follows from a 2003 paper by Wong et al. which developed convenient criteria for determining the relevance of pressure dependent kinetics for a system [47]. Following this criteria, a recent model of propene pyrolysis includes a set of pressure dependent rate expressions for the progression of CPDyl to naphthalene first described by Melius et al. Rather than calculating the individual rates for the network directly, they are assigned based on analogy to similar reaction whose rate constants are readily available [48]. A brief comparison with this estimated network is presented in the supporting information of this work.

The objective of the current study is two-fold. First it aims to combine the most promising pathways previously studied and use this information to calculate a set of pressure-dependent rate expressions that will be easily used in future kinetic mechanisms.