Kinetics and Thermochemistry of Cyclohexadienes Reactions with Hydroxyl Radicals

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Colloquium: Gas-Phase Reaction Kinetics

Total length of paper: 5894 words (Method 1)
Main text: 3705 words
Equations: 60 words
References: 682 words
Tables: 440 words
Figures and Captions: 1007 words

This manuscript contains Supplementary Material.
Abstract
Cyclohexadienes (CHDs) are important intermediates in the pyrolysis and oxidation of many C₆ cyclic hydrocarbons. Under combustion relevant conditions, these dienes may either eliminate H₂ directly or lose H atoms sequentially to produce the first aromatic ring, i.e., benzene. This is one of the major reaction pathways for the formation of benzene from C₆ cyclic hydrocarbons. Despite its importance in PAH and soot formation process, the chemistry of CHD has attracted less attention from the scientific community. In this work, we have investigated hydrogen abstraction reactions of 1,3- and 1,4-CHD by OH radicals using a shock tube and UV laser absorption over the temperature range of 900 – 1100 K and pressures of ~ 1 – 3 atm. Reaction kinetics was followed by monitoring OH radicals near 307 nm. At high temperatures, both isomers of CHDs are found to exhibit comparable reactivity with OH radicals. These reactions show a weak positive temperature dependence. Measured rate coefficients can be represented by the following Arrhenius expressions in units of cm³ molecule⁻¹ s⁻¹:

\[
k_1(1,3-\text{CHD} + \text{OH}) = 1.76 \times 10^{-10} \exp \left( \frac{-1761 K}{T} \right) \\
k_2(1,4-\text{CHD} + \text{OH}) = 2.23 \times 10^{-10} \exp \left( \frac{-1813 K}{T} \right)
\]

To gain further insights into these reactions, various *ab initio* methods were employed to compute relevant thermochemical data. This study reports the first high-temperature kinetic data for cyclohexadienes which will be beneficial to improve the performance of the oxidation kinetic models of C₆ cyclic hydrocarbons.

**Keywords:** Cyclohexadiene; Aromatic ring formation; Hydroxyl radical; Shock tube; Laser absorption
1. Introduction

Olefins are vital intermediates formed during the pyrolysis and oxidation of hydrocarbon fuels. A wide spectrum of olefinic compounds, including cyclic and acyclic dienes, have been detected in vehicle exhaust or fuel vapor [1]. Olefins are known to have a tendency to enhance soot formation. Diolefinic compounds, such as 1,3-cyclic hexadiene (1,3-CHD) and 1,4-cyclic hexadiene (1,4-CHD) may either eliminate H₂ or undergo sequential H loss to form the first aromatic ring “benzene”, soot precursor in combustion environment. These CHDs are observed as important intermediates during the oxidation and pyrolysis of cyclic and acyclic C₆ hydrocarbon fuels (see [2-6] and the references cited therein). Detailed knowledge of their oxidation chemistry is, therefore, important for combustion and atmospheric environments.

Chemical pathways forming benzene are key to the understanding of polycyclic aromatic hydrocarbon (PAH) growth rates and soot formation processes [6]. Small resonantly stabilized radicals (RSRs), like propargyl (C₃H₃), allyl (C₃H₅), butadienyl or methyl-substituted propargyl radicals (i-C₄H₅), are well-known to be largely responsible for benzene formation. However, several authors have now proposed an alternative route leading to the first aromatic ring which involves the stepwise dehydrogenation of C₆-cyclic hydrocarbons. This route is considered as a significant pathway to benzene for these cyclic molecules under fuel-rich combustion [2-6], which clearly differs from that of acyclic species. This highlights the importance of CHDs and their reactions with important combustion radicals such as OH under combustion conditions.

One of the important dehydrogenation steps in CHDs is the allylic H-abstraction reaction by OH radicals producing resonantly stabilized 2,5-cyclohexadien-1-yl radical (c-C₆H₇). The incipient c-C₆H₇ radical can either lose an H-atom to produce benzene by overcoming an energy barrier of 26.7 kcal/mol [7] or react with O₂ to form HO₂ + benzene [8]. Despite the importance of CHDs +
OH reactions in combustion, high-temperature data are not yet available. Previous studies are confined to low temperatures [9-11]. These reports revealed a higher reactivity of OH radicals with 1,3-CHD compared to 1,4-CHD by almost a factor of 1.7. In a previous work [12], we made a similar observation for the reactions of acyclic counterparts (1,3-pentadiene vs 1,4- pentadiene) with OH radicals at low temperatures, while an opposite trend was observed at high temperatures. These trends can be understood by considering the relative thermodynamic stability of the parent molecules and the stabilization of incipient radicals. The reactivity difference arises from the higher thermodynamic stability of 1,3-pentadiene as compared to 1,4-pentadiene. Due to the presence of conjugated double bonds, 1,3-pentadiene has ~ 30 kJ/mol more stability than 1,4- pentadiene [13]. In contrast, both 1,3- and 1,4-CHDs are reported to have similar stability with identical allylic C-H bond dissociation enthalpies (BDEs) of ~325 kJ/mol [13]. This would then imply that, unlike open chain 1,3- and 1,4-dienes + OH reactions, 1,3 and 1,4-cyclic dienes should exhibit similar reactivity with OH radicals at high temperatures. However, such chemical systems are of complex nature, and often show unpredictable Arrhenius behavior due to many competing channels. For deeper insights into such convoluted system, a combined experimental and theoretical work is warranted.

In this work, we employed shock tube and laser diagnostics techniques to investigate the reactions of OH radicals with 1,3- and 1,4-CHD at high temperatures.

\[
1,3\text{-CHD} + \text{OH} \rightarrow \text{Products} \quad \text{(R1)}
\]

\[
1,4\text{-CHD} + \text{OH} \rightarrow \text{Products} \quad \text{(R2)}
\]

Additionally, various \textit{ab initio} methods were used to compute thermochemical data for plausible reaction pathways. To our knowledge, this is the first high-temperature kinetic study on the reactions of OH radicals with CHDs. These results will prove beneficial to improve the combustion modeling of C6-cyclic hydrocarbons.
2. Methodologies

2.1 Ab Initio Calculations

With some exceptions, the reactions of OH radicals with unsaturated hydrocarbons undergo exclusively via addition to the double bond at low temperatures, whereas hydrogen abstraction reactions prevail at high temperatures. These reactions often display complex kinetic behaviors due to several competing channels (see our earlier experimental work [12] and references cited therein). The reactivity trends of olefins with OH radicals and the relative importance of various channels are greatly influenced by the thermodynamic stability of the parent molecule and the incipient radicals as they eventually influence the relative position of the transition states responsible for various channels in their reactive potential energy surface. To improve our understanding of the cyclohexadienes + OH reactions, thermodynamic properties, e.g., zero-point corrected reaction energy ($\Delta_{\text{rxn}}E_0$), bond dissociation energy ($\text{BDE}_0$), standard enthalpy of reaction ($\Delta_{\text{rxn}}H^0$), and standard enthalpy of formation ($\Delta_fH^0$), were computed in this work. Atomization scheme (AS) was applied to access highly accurate standard enthalpies of formation, $\Delta_{f,0\text{K}}H^0$ and $\Delta_{f,298.15\text{K}}H^0$, for the relevant species. Within AS, the essential highly accurate atomization enthalpies were obtained from Ruscic’s Active Thermochemical Tables (ATcT) [14]. Additionally, $\Delta_{f,298.15\text{K}}H^0$ values were calculated via isodesmic reactions, CBS-QB3 electronic structure calculations and the ATcT “experimental” database by using an in-house code. These thermodynamic properties are key to the understanding of the molecular-reactivity relationship.

To assess the method dependency of the calculated thermochemistry, various composite ab initio methods such as CBS-QB3 [15], G2MP2 [16] and G2 [17] were chosen. The reason is that the standard enthalpy of formation obtained by AS is sensitive to the chosen basis set, and G2MP2 and G2 use more extended basis sets (6-311G(d,p)) for the post-Hartree-Fock single point
calculations than those in G3 [18] and G4 [19]. However, the results from highly accurate CCSD(T)/cc-pV(T,Q)Z//MP2/aug-cc-pVDZ level of theory were taken as the thermodynamic reference (abbreviated as Xpol). The harmonic vibrational frequencies obtained at MP2/aug-cc-pVDZ were scaled by a factor of 0.959 [20] for better accuracy of the computed thermodynamic properties (the molecular properties are listed in Table S1 and S2 of Supplementary Material). The CCSD(T) energies at the infinite basis set limit were obtained as the sum of the Hartree-Fock limit ($\Delta E_{HF}^{\infty}$) and correlation energies ($\Delta E_{corr}^{\infty}$). Here, $E_{HF}^{\infty}$ was obtained by applying Feller three-point exponential extrapolation [21] according to $E_{HF}(X) = E_{HF}^{\infty} + b \exp(-cX)$ using cc-pVXZ ($X = Q, 5, 6$) basis sets. As for $\Delta E_{corr}^{\infty}$, two-point extrapolation of the form $E_{corr}^{\infty}(X) = E_{corr}^{\infty} + b X^{-3}$ was used, where $X$ was 3 and 4 for cc-pV(T,Q)Z basis sets. Frozen core approximation was applied for all CCSD(T) calculations. $T_1$ diagnostics [22] and TAE% [23] were also computed to assess the contribution of higher excitations. The largest $T_1$ diagnostics value was < 0.04 obtained at CCSD/cc-pVQZ level of theory, and the largest TAE was < 1.9%, inferring that the chemical systems studied here are all dominated by dynamical correlation [22]. All calculations were performed using Gaussian09 software package [24].

2.2 Thermochemical Data.

Calculated values of the standard enthalpy of formation ($\Delta H^0$) at various model chemistries are tabulated in Table 1. As can be seen, $\Delta H^0$ values for both isomers of CHD are almost identical ($\Delta f_{298.15} H^0 \sim 120$ kJ/mol at Xpol). Other model chemistries also predicted similar thermodynamic stability for these isomers. Among the model chemistries employed here, G2 values appear to match reasonably well with that of Xpol for all species within an absolute deviation of 6 kJ/mol. The largest deviation was with CBS-QB3 values, being -16.3 kJ/mol for cyclohexa-1,3-dien-2-yl.
Also, G2MP2 values show significant deviations by overpredicting the enthalpies of formation in all cases. Clearly, $\Delta_f H^0$ values obtained \textit{via} atomization scheme showed large method dependency. Compared to the experimental values of 104.6 ± 0.6 kJ/mol and 104.8 ± 0.6 kJ/mol reported by Steele et al. [25] for 1,3- and 1,4-CHD, respectively, even our Xpol predictions seem to be off somewhat. Therefore, we further employed isodesmic reaction schemes to compute enthalpies of formation as such schemes allow cancellation of errors from \textit{ab initio} methods to yield more accurate values than those determined \textit{via} atomization scheme. $\Delta_f,298.15K H^0$ values obtained by isodesmic reaction schemes for CHD isomers match excellently with those of Steele et al. [25]. For cyclohexa-2,5-dien-1-yl radical, our isodesmic $\Delta_f,298.15K H^0 = 193.7 \pm 1.0$ kJ/mol value comes close to the experimental value of 208.0 ± 3.96 kJ/mol reported by Gao et al. [26]. Noteworthy, earlier reports for $\Delta_f,298.15K H^0$ of cyclohexa-2,5-dien-1-yl spanned a range of more than 25 kJ/mol (see the discussion in Gao et al. [26]).

\textbf{Table 1.} Standard enthalpy of formation at 298 K, $\Delta_f,298.15K H^0$ in kJ/mol, obtained from various model chemistries using atomization scheme ($\Delta_f,0K H^0$ values are provided in Table S3 of the Supplementary Materials). The deviations from the reference CCSD(T)/cc-pV(T,Q)Z//MP2/aug-cc-pVDZ level of theory (abbreviated as Xpol) are provided in parenthesis. Also, isodesmic reaction scheme was employed using the top-10\% similarity-based isodesmic reactions \textsuperscript{[a]} and averaged values of all isodesmic reactions \textsuperscript{[b]} (see Table S4 in the Supplementary Materials).

<table>
<thead>
<tr>
<th>Species</th>
<th>G2MP2</th>
<th>G2</th>
<th>CBS-QB3</th>
<th>Isodesmic Scheme at CBS-QB3</th>
<th>Xpol</th>
<th>Burcat</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3-CHD</td>
<td>126.8(7.5)</td>
<td>121.8(2.5)</td>
<td>122.1(2.8)</td>
<td>105.5 ± 1.0 \textsuperscript{[a]} 104.2 ± 0.9 \textsuperscript{[b]}</td>
<td>119.3</td>
<td>109.2(-10.1)</td>
</tr>
<tr>
<td>cyclohexa-1,3-dien-1-yl</td>
<td>386.1(6.1)</td>
<td>379.6(-0.5)</td>
<td>365.0(-15.0)</td>
<td>344.4 ± 0.7 \textsuperscript{[a]} 343.5 ± 1.0 \textsuperscript{[b]}</td>
<td>380.0</td>
<td></td>
</tr>
<tr>
<td>cyclohexa-1,3-dien-2-yl</td>
<td>389.0(5.0)</td>
<td>382.4(-1.6)</td>
<td>367.7(-16.3)</td>
<td>347.1 ± 0.7 \textsuperscript{[a]} 346.3 ± 1.0 \textsuperscript{[b]}</td>
<td>384.0</td>
<td></td>
</tr>
<tr>
<td>cyclohexa-2,5-dien-1-yl</td>
<td>238.9(12.4)</td>
<td>232.0(5.5)</td>
<td>215.1(-11.4)</td>
<td>194.5 ± 0.7 \textsuperscript{[a]} 193.7 ± 1.1 \textsuperscript{[b]}</td>
<td>226.5</td>
<td>210.815(-15.7)</td>
</tr>
<tr>
<td>2-hydroxycyclohex-3-en-1-yl</td>
<td>51.1(0.5)</td>
<td>48.2(-2.4)</td>
<td>46.9(-3.7)</td>
<td>12.2 ± 1.5 \textsuperscript{[a]} 27.3 ± 1.0 \textsuperscript{[b]}</td>
<td>50.6</td>
<td></td>
</tr>
<tr>
<td>6-hydroxycyclohex-2-en-1-yl</td>
<td>-17.5(5.8)</td>
<td>-21.2(2.2)</td>
<td>-28.3(-4.9)</td>
<td>-63.0 ± 1.5 [a]</td>
<td>-47.9 ± 1.0 [b]</td>
<td>-23.4</td>
</tr>
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</tr>
<tr>
<td><strong>1,4-CHD</strong></td>
<td>129.2(10.2)</td>
<td>124.2(5.3)</td>
<td>122.4(3.5)</td>
<td>106.0 ±1.0 [a]</td>
<td>103.4 ±1.0 [b]</td>
<td>118.9</td>
</tr>
<tr>
<td>cyclohexa-1,4-dien-1-yl</td>
<td>379.0(5.6)</td>
<td>373.3(-0.1)</td>
<td>362.3(-11.1)</td>
<td>326.8 ±1.5[a]</td>
<td>342.7 ±1.0[b]</td>
<td>373.4</td>
</tr>
<tr>
<td>6-hydroxycyclohex-3-en-1-yl</td>
<td>44.5(0.9)</td>
<td>41.7(1.8)</td>
<td>37.9(-5.7)</td>
<td>22.9 ± 0.8[a]</td>
<td>18.3 ± 1.0[b]</td>
<td>43.6</td>
</tr>
</tbody>
</table>

**Figure 1.** C-H Bond dissociation enthalpies (BDE) of 1,3-cyclohexadiene and 1,4-cyclohexadiene obtained at CCSD(T)/cc-pV(T,Q)Z//MP2/aug-cc-pVDZ level of theory.

Figure 1 provides bond dissociation energies (BDEs) of various C-H bonds in CHD isomers. Allylic C-H BDEs for both isomers of CHD are almost equal (BDE<sub>298.15K</sub> ≈ 325.0 kJ/mol) within the chemical accuracy of the model chemistry Xpol. Our values show an excellent agreement with that of Gao et al. [26] (BDE<sub>298.15K</sub> ≈ (321.7 ± 2.9) kJ/mol) and Agapito et al. [13] (BDE<sub>298.15K</sub> ≈ 325.0 kJ/mol). The authors employed a high-level coupled-cluster-based approach to compute these values. This small difference of the allylic C-H BDEs appears to stem from the relative stability of the two isomers. Apparently, 1,4-CHD is about 1 kJ/mole more stable than 1,3-CHD which has nicely translated into the difference of their corresponding bisallylic C-H bond enthalpies because the resulting radical after allylic C-H bond cleavage is cyclohexa-2,5-dien-1-yl radical in either case. Interestingly, allylic C-H bonds in CHDs are found to be drastically weaker, by ≈46 kJ/mol, as compared to that of the corresponding bond in propene [13]. In both cases, the resulting radicals are resonantly stabilized, however, the bisallyl resonance of cyclohexa-2,5-dien-1-yl arising from the extended delocalization of unpaired electron lowers the allylic C-H
bond enthalpy dramatically. The resonance stabilization energy (RSE) of cyclohexa-2,5-dien-1-yl is calculated to be $90.7 \pm 4.2$ kJ/mol which is obtained from the difference in the BDEs of C-H bond in cyclohexane ($\text{BDE}_{298.15K} = 416 \pm 5$ kJ/mol [27]) and bisallylic C-H bond in cyclohexadienes ($\text{BDE}_{298.15K} = 325.6$ kJ/mol, this work). Our calculated value of RSE for cyclohexa-2,5-dien-1-yl radical agrees excellently with the values tabulated by Senosiain et al. [28], while RSE for allyl radical is reported to be $\sim 61$ kJ/mol [28]. This shows that cyclohexa-2,5-dien-1-yl radical, the conjugated cyclic-bisallyl radical, exhibits higher stabilization as compared to the allyl radical. The vinylic C-H $\text{BDE}_{298.15K}$ are found to be 478.7 and 482.8 kJ/mol for 1,3-CHD, whereas it is somewhat lower for 1,4-CHD ($\text{BDE}_{298.15K} = 472.1$ kJ/mol). These values are found to be comparable to the vinylic C-H bonds of propene ($\text{BDE}_{298.15K} = 464.8$ kJ/mol) or other alkenes [27].

From the discussion above, it appears that both CHDs are expected to exhibit similar reactivity with OH radicals at high temperatures because: (i) Unlike other 1,3- and 1,4-acyclic dienes e.g., pentadienes, both CHDs do have identical thermodynamic stabilities because of their similar values of heat of formation, and the incipient radical after bisallylic C-H bond cleavage is cyclohexa-2,5-dien-1-yl radical in each case. The corresponding BDE for 1,4-pentadiene is lower by 28 kJ/mol than that of 1,3-pentadiene owing to the difference in their thermodynamic stabilities; (E)-1,3-pentadiene is $\sim 30$ kJ/mole more thermodynamically stable than 1,4-pentadiene [13]. These two pentadiene isomers differed significantly in their kinetic behavior with OH radicals by exhibiting very interesting temperature dependence [12]). (ii) BDEs for vinylic CH-H are quite high, therefore, one expects that the bisallylic H-abstraction reactions dominate at high temperatures. (iii) Allylic C-H BDE for both CHD isomers is $\sim 46$ kJ/mol which is 17 kJ/mol lower than that of the corresponding BDEs of propene and (E)-1,3-pentadiene [13].
An important kinetic implication of these observations is that unlike OH reactions with monoalkenes and open-chain conjugated dienes, CHDs can undergo significant H-abstraction by OH radicals even at low temperatures. For both CHDs + OH reactions, the abstraction rate coefficients were reported to be as high as \((2.5\pm1.0)\times10^{-11}\) cm\(^3\)/molecule/s near ambient temperatures [29].

2.3 Experimental Details

The reaction of OH radicals with 1,3- and 1,4-CHDs was investigated using a low-pressure shock tube (LPST) and UV laser diagnostics. A brief description of the experimental set up is provided here (see reference [12] for details). The LPST is made of stainless steel which has a 9 m long driven section and a variable-length driver section to achieve the desired test time behind reflected shock waves. Both sections have an internal diameter of 14.2 cm. Shock waves were generated by pressure-bursting of the polycarbonate diaphragm of different thicknesses. Five piezoelectric transducers (PCB 113B26) placed over the last 1.3 m of the driven section were used to measure incident shock speeds. Using the thermodynamic data of the test gas mixture and incident shock speed as inputs, pressure \((P_s)\) and temperature \((T_s)\) behind reflected shock waves were calculated by employing shock-jump relations embedded in the Frosh code [30]. Uncertainties associated in the calculated values of \(T_s\) and \(P_s\) are ±0.7\% and ±1\%, respectively.

Hydroxyl radicals were generated via fast thermal decomposition of tert-butyl hydroperoxide (TBHP), a well-known clean precursor of OH radicals [31]. Tunable UV light was generated by a narrow linewidth cw laser system comprising of an Nd:YAG 532 nm pump laser, a ring-dye visible laser and a frequency doubler. The laser was tuned precisely to the center (306.6868 nm) of the
well-characterized R1(5) absorption line in the (0,0) vibrational band of the A2Σ+ ← X2Π electronic system of OH. Mole fraction was calculated using the Beer-Lambert Law, \( I/I_0 = \exp(-X_{\text{OH}} k_{\text{OH}} P L) \); here, \( I_0 \) and \( I \) refer to the incident and transmitted beam intensities recorded by photodetectors; \( X_{\text{OH}} \) and \( k_{\text{OH}} \) are mole fraction and absorption coefficient of OH radical, respectively; \( P \) and \( L \) are the total pressure and absorption pathlength (14.2 cm), respectively.

Gas mixtures were prepared in a 24-litre teflon-coated stainless-steel vessel equipped with a magnetically-driven stirrer. Prior to mixture preparation, the mixing vessel was turbo-pumped to \(< 10^{-5} \) Torr. The mixture was left for ~ 2 hours for homogeneity. The chemicals used were: 1,4-CHD and 1,3-CHD (97 % purity), 70 % TBHP solution in H2O from Sigma-Aldrich, helium (99.99%) and argon (99.999%) from AH Gases. The driven section was pumped down to ~10^{-5} Torr between successive measurements using a turbomolecular pump.

3. Results and Discussion

3.1 Experimental Results

All experiments were run in excess of CHD concentration to achieve pseudo-first-order conditions. Figure 2 depicts a representative time-history of OH radicals measured at 1027 K and 1.12 atm for 1,4-CHD + OH reaction. As expected, the OH decay follows first-order kinetics, and the overall rate coefficient can be extracted from the slope of \( \ln[\text{OH}] \) vs time plot. However, this methodology does not take into account intereference from secondary reactions, such as OH + CH3, and the slow decomposition of TBHP at low temperatures. Therefore, a detailed kinetic model comprising of the base mechanism for CHD isomers from Wang et al. [32] and the TBHP sub-mechanism from Pang et al. [33] was assembled. Kinetic simulations were carried out in ChemkinPro [34] using a zero-dimensional batch reactor and constant UV constraints. Rate coefficient for allylic H-abstraction of CHD was iteratively varied until a best fit, as shown by the red line in Fig. 2, was
obtained. For this example case, best fit $k_2$ (1027 K, 1.12 atm) = $3.8 \times 10^{-11}$ cm$^3$/molecule/s, and the dashed lines indicate ±50% perturbation from $k_2$. Clearly, the target reaction shows strong sensitivity to the decay of OH radicals. Hydroxyl sensitivity analysis was carried out which showed that secondary reactions are unimportant (see Fig. 1S in Supplementary Material). The overall uncertainty (2σ) of our measured rate coefficients was estimated to be ±17% that transpired from various sources of errors, such as temperature (±0.7%), determination of time zero (±0.5 µs), mixture composition (±5%), OH absorption cross-section (±3 %), the detection wavelength (± 0.002 cm$^{-1}$), and fitting of the measured OH profile (±5%).

Figure 2. A typical OH mole fraction time-profile for 1,4-CHD + OH reaction at 1027 K and 1.12 atm. Mixture composition: 300 ppm 1,4-CHD / 17 ppm TBHP in argon. Lines represent simulated profiles. Inset shows the linearity of ln[OH] vs time plot validating pseudo-first order kinetics.

Rate coefficients for the reactions of OH radicals with both CHD isomers are plotted Fig. 3 (and complied in Table S5) along with available literature data. These data are also compared with our earlier experimental work on 1,3- and 1,4-pentadienes + OH reactions [12]. Measured rate coefficients can be expressed in the following Arrhenius expressions (cm$^3$/molecule/s) over $T = 900 – 1090$ K and $p = 1.0 – 2.9$ bar:

$$k_1(1,3 – \text{CHD} + \text{OH}) = 1.76 \times 10^{-10} \exp\left(-\frac{1761 K}{T}\right)$$  \hspace{1cm} \text{Eq. (1)}

$$k_2(1,4 – \text{CHD} + \text{OH}) = 2.23 \times 10^{-10} \exp\left(-\frac{1813 K}{T}\right)$$  \hspace{1cm} \text{Eq. (2)}
3.2 Reactivity of OH Radicals with 1,3- and 1,4-CHD

Aiming to discriminate among various reaction channels, the standard enthalpy of the reaction ($\Delta_r H^0$) was computed using CCSD(T)/cc-pV(T,Q)Z//MP2/aug-cc-pVDZ level of theory. The computed reaction enthalpies at 0 K and at 298.15 K are presented in Fig. 4. As can be seen, $\Delta_{r,298.15k} H^0$ are found to be in the range of -16.4 and -26.8 kJ/mol for vinylic hydrogen abstraction of CHDs by OH radicals. These values are less exothermic than that of the corresponding reaction of propene and OH radicals [35]. This difference in the reaction enthalpies can be attributed to Pitzer strain of the incipient radicals (cyclohexa-1,3-dien-1-yl, cyclohexa-1,3-dien-2-yl and cyclohexa-1,4-dien-1-yl) formed after the cleavage of vinylic C-H bond. This would imply that the barrier heights for these vinylic abstraction channels will be higher than that of propene + OH reaction ($\Delta E_0 = 19.6$ kJ/mol) according to Bell-Evans-Polanyi principle, and, therefore, vinylic channels are expected to be less important than that of propene + OH. For the current chemical systems, most probably vinylic H-abstraction channel remains inactive until very high temperature.
is reached.

**Figure 4** Abstraction and addition pathways for OH reactions with 1,3-CHD and 1,4-CHD. The standard enthalpies of the reaction were computed at CCSD(T)/cc-pV(T,Q)Z//MP2/aug-cc-pVDZ level of theory.

Since only H-abstraction channels prevail at high temperatures, hydrogen abstraction from allylic C-H leading to resonantly stabilized cyclohexa-2,5-dien-1-yl radical + H₂O remains the only common and active channel for both CHDs + OH reactions at high temperatures. This channel is highly exothermic ($\Delta_r^{298.15K} H^0 \sim -174.0 \text{ kJ/mol}$) and found to be only slightly larger than the corresponding reaction of 1,4-pentadiene + OH ($\Delta_r^{298.15K} H^0 = -167.9 \text{ kJ/mol}$ in Ref. [36]). These observations led us to conclude that both CHDs should exhibit similar reactivity with OH radicals as the barrier height for the abstraction reaction yielding cyclohexa-2,5-dien-1-yl radical + H₂O is expected to be roughly similar to that of 1,4-pentadiene + OH reaction. For the latter reaction, our unpublished work indicated a submerged barrier of $\Delta E_0 = -5.0 \text{ kJ/mol}$ relative to the reactants (see Fig. 2S). Indeed, our measured data show similar reactivity for both CHDs + OH (within the experimental uncertainty). Both CHDs exhibit a weak positive temperature dependence, and 1,3-CHD is found to react slightly slower than its counterpart with OH radicals (see Fig. 3). This
difference may probably originate from the difference in the barrier heights for vinylic abstraction even though these channels are minor. Note that the bond enthalpy of vinylic C-H of 1,4-CHD is at least 7 kJ/mol lower compared to 1,3-CHD.

Both CHDs are expected to exhibit twice the reactivity with OH radicals as compared to that of 1,4-pentadiene. However, the ratio of rate coefficients (k_{CHD}/k_{1,4-PTD}) at a given temperature is ~1.5. This enhanced reactivity of 1,4-pentadiene stems from more labile vinylic C-H bonds (see Fig. 2S) as compared to similar bonds in propene + OH [35] and also from the higher number of abstractable vinylic hydrogen atoms. As seen in Fig. 3, (E)-1,3-pentadiene displayed the slowest reactivity which can be understood from its relative thermodynamic stability. (E)-1,3-pentadiene is about 30 kJ/mol more stable than 1,4-pentadiene [13] due to conjugated double bonds which will ultimately alter the reaction exogercity or the barrier height for a given reaction.

Interestingly, both isomers of CHDs exhibit different reactivity toward OH radicals at low temperatures. Unlike high-temperature chemistry, 1,4-CHD displays slower reactivity with OH radicals than that of 1,3-CHD. For 1,3-CHD + OH reaction, the low-temperature rate coefficients reported by Ohta [3, 10] and Atkinson et al. [9] agree very well, \(k_1(298 \text{ K}) \approx 1.56 \times 10^{-10} \text{ cm}^3/\text{molecule/s}\); whereas their reports show significantly lower values of the rate coefficients for 1,4-CHD + OH reaction, \(k_2(298 \text{ K}) = (9.86\pm0.31)\times10^{-11} \text{ and } (9.48\pm0.39)\times10^{-11} \text{ cm}^3/\text{molecule/s}\), respectively. This trend can be understood by looking into the reaction enthalpy of various channels. At low temperatures, it is well known that OH radicals exclusively undergo addition to the double bond of alkenes with some exceptions. Hydroxyl addition to 1,3-CHD resulting in 6-hydroxycyclohex-2-en-1-yl is highly exothermic. Its exothermicity (\(\Delta_r298.15K\text{H}^0=-179.2 \text{ kJ/mol}\)) is
comparable to that of the allylic H-abstraction reaction (see Fig. 4) due to the fact that the ensuing radical is resonantly stabilized. The addition of OH radical to other sites produces radicals that will lack resonance stabilization resulting in much lower enthalpy of reaction ($\Delta_{r,298.15}H^0 = -105.2$ and -119.9 kJ/mol). These values of the enthalpy change for OH addition are comparable to that observed for OH + 1,4-pentadiene addition reaction ($\Delta_{r,298.15}H^0 = -111.3$ kJ/mol and -118.2 kJ/mol) [36]. Here, OH addition to 1,4-CHD does not seem as favorable as in 1,3-CHD because of low reaction exogercity or plausible higher lying transition states for such processes.

As discussed above, abstraction reactions of allylic C-H of CHDs and 1,4-pentadiene should have a comparable rate coefficient on per C-H bond basis because these chemical systems are expected to have a similar negative energy barrier for bisallylic H-abstraction as in 1,4-pentadiene + OH reaction (see Fig. 2S). For 1,3-CHD + OH reaction, a comparable negative energy barrier of $\sim\Delta E_0 = -6.9$ kJ/mole relative to the reactants’ energy was computed at G2 level of theory. As for 1,4-CHD + OH reaction, the corresponding transition state lies even lower ($\sim\Delta E_0 = -13.7$ kJ/mole relative to the reactants’ energy). As the transition state is submerged below the reactants, a large percentage of the reaction flux can lead to abstraction reactions, and thus not favoring the OH addition channel even at low temperatures. Interestingly, our unpublished theoretical work indicates that bisallylic H-abstraction reaction can constitute as high as 60% for 1,4-pentadiene + OH system at 298 K. The difference in the room temperature values of $k_2(1,4\text{CHD}+\text{OH}) = (9.86\pm0.31)\times10^{-11}$ cm$^3$/molecule/s from Ohta[10] and $k(1,4\text{-pentadiene}+\text{OH}) = 5.92\times10^{-11}$ cm$^3$/molecule/s from our recent work [12] reveals that the abstraction reactions can be the dominant channel at low temperatures for such 1,4-polyenes + OH chemical systems. To fully understand such complex systems, a quantitative kinetic analysis combining high level ab initio
and master equation computations is required which will appear in a future publication.

4. Conclusions

We conducted the first high-temperature kinetic study for the reaction of OH radicals with 1,3- and 1,4-cyclohexadienes. Rate coefficients measured over 900 – 1100 K exhibited positive temperature dependence and were fit with two-parameter Arrhenius expression. Our rate data over 1 – 3 bar did not show pressure dependence. Our thermochemistry calculations showed that both CHDs should exhibit similar reactivity with OH radicals at high temperatures, which is nicely demonstrated by our experimental data. Unlike monoalkenes and conjugated alkenes + OH systems, 1,4-polyenes display peculiar reactivity with OH radicals by undergoing reactions significantly via bisallylic hydrogen abstraction channel even at low temperatures. We recommend these new rate data to be implemented for the improvement of the oxidation models of C₆-cyclic hydrocarbons.

5. Acknowledgment

Research reported in this publication was funded by the Office of Sponsored Research at King Abdullah University of Science and Technology (KAUST). MZ thanks the grant GINOP-2.3.4-15-2016-00004.
References

List of Supplementary Material

**Fig. 1S**: OH radical sensitivity for 1,4-CHD + OH reaction at 1027 K and 1.12 atm. Mixture: 300 ppm CHD, 17 ppm TBHP (~54 ppm H₂O) in argon. The hydroxyl sensitivity is defined as $S_{OH} = \left( \frac{\partial X_{OH}}{\partial k_i} \right) \times \left( \frac{k_i}{X_{OH}} \right)$, where $k_i$ is the rate coefficient for the $i^{th}$ reaction and $X_{OH}$ is the mole fraction of OH radical.

**Fig. 2S**: Simplified version of the potential energy surface (PES) of OH + 1,4-pentadiene reaction system (unpublished work, manuscript under preparation). Zero-point corrected energies relative to the reactants (14PTDN + OH) were obtained at QCISD(T)/cc-pVTZ//BH&HLYP/6-31G(d) level of theory.

**Table S1**: Calculated MP2/aug-cc-pVDZ harmonic vibrational wavenumbers (scaled by 0.959) and rotational constants of the calculated stationary points for the 1,3- and 1,4-CHD + OH reactions.

**Table S2**: Calculated MP2/aug-cc-pVDZ geometries in Cartesian coordinates of the calculated stationary points for the 1,3- and 1,4-CHD + OH reactions.

**Table S3** Standard enthalpy of formation at 0 K, $\Delta_f^{0K}H^0$ in kJ/mol, obtained from various model chemistries for the species specified. The deviations from the reference model CCSD(T)/cc-pV(T,Q)Z//MP2/aug-cc-pVDZ level of theory (abbreviated as Xpol) are provided in parenthesis. Atomization scheme was employed to obtain the values of the standard enthalpy of formation.

**Table S4**: Generated isodesmic reactions for calculating standard enthalpy of formation at 298 K, $\Delta_f^{298.15K}H^0$.

**Table S5**: Measured rate coefficients for 1,3- and 1,4 -CHD + OH at the specified experimental conditions.