Recombination of propargyl radicals to form benzene: A computational study

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Present study involves QCISD(T)/6-311G(d,p) level calculations to analyze reaction pathways during the recombination of propargyl radicals leading to the formation of benzene. A new path on the C\textsubscript{3}H\textsubscript{3} recombination potential energy surface that connects 3,4-dimethylenecyclobutene (34DMCB) to benzene involving four-membered bicyclic compounds such as bicycle[2.2.0]hexa-1(4),2-diene and bicycle[2.2.0]hexa-2,5-diene have been determined. Geometries of all the species are optimized at HF/6-31G(d) level. All the stationary points along this path on the potential energy surface have been characterized. Single point energy calculation have been performed using QCISD(T) with 6-311G(d,p) basis set. Transition states are determined and characterized by the observation of only one imaginary frequency. Intrinsic Reaction Coordinate (IRC) calculation has also been performed in order to ascertain the existence of the transition states.

Keywords: Propargyl radical, HF, IRC, PES, 3,4-dimethylene-cyclobutene

One of the intriguing problems always faced by combustion chemists during the flame or high temperature pyrolytic studies of hydrocarbon fuels is to find an explanation for the formation of aromatics and soot from low molecular weight gaseous species such as C\textsubscript{2}H\textsubscript{2}, C\textsubscript{2}H\textsubscript{4}, etc. Propargyl radical C\textsubscript{3}H\textsubscript{3} (m/z 39) has been found abundantly in flames and it has also been detected during time-of-flight mass spectroscopic studies of many aliphatic fuels\textsuperscript{1,2}. The latter studies also detected peak at m/z 78. Modeling calculations performed on the m/z 78 profile envisaged the species as benzene. Thus, the main question raised is how do these aliphatic fuels which breakup to smaller fragments mostly C\textsubscript{2} and C\textsubscript{3} species at high temperature say 1500-2000 K undergo cyclization and form benzene. C\textsubscript{3}H\textsubscript{3} is a resonantly stabilized free radical and is believed to play a critical role in the formation of aromatic hydrocarbons and soot\textsuperscript{5-8}. The unpaired electron present in C\textsubscript{3}H\textsubscript{3} radical is delocalized and spread out over two or more sites. As a result of the delocalization of the unpaired electron, these free radicals are stabilized and normally form weaker bonds with stable molecules\textsuperscript{9,10}. Such weakly bonded addition complexes are not easily stabilized by collisions at high temperature, nor do they readily undergo rearrangement. In such a situation such radicals are relatively non-reactive and can reach high concentrations in flames. High concentrations and rapid rates at which such radicals may react with another constituent make an important route for the formation of higher hydrocarbons in flames. There is a possibility of the formation of other C\textsubscript{3}H\textsubscript{3} isomers. Four such isomers viz., 2-propynyl (propargyl), 1-propynyl, cycloprop-1-enyl and cycloprop-2-enyl have been proposed to be thermally stable\textsuperscript{11}. Additional isomers may also be formed but these have been ruled out, being kinetically unstable\textsuperscript{11}. A recent computational study performed at a very high level utilizing electron correlation via second order Z-Averaged Perturbation Theory (ZAPT2) and primarily through coupled cluster theory by Wheeler et al.\textsuperscript{11} reported the heat of formation of the different isomers of C\textsubscript{3}H\textsubscript{3} and the calculated isomerization energies. The results show that propargyl has the lowest energy and thus the most stable amongst the four C\textsubscript{3}H\textsubscript{3} isomers\textsuperscript{11}. The recombination of propargyl radicals is proposed to be one of most important reactions occurring in hydrocarbon flames\textsuperscript{5,6}. Depending on the reaction conditions, they may lead to the formation of a number of cyclic and chain hydrocarbons. It may be shown to exist in the following two resonating structural forms:

\[ \text{C} = \text{C} \equiv \text{C} \quad \text{H} \text{H} \quad \text{H} \text{H} \]

Out of these two resonating structures the structure marked as H is accepted to have a dominant one\textsuperscript{12}. These stabilized free radicals can combine in three
possible ways\textsuperscript{12-16} leading to the formation of \( C_6H_6 \) as shown below:

1. Head to head (HTH) \( \rightarrow HC=\text{C}—\text{CH}—\text{CH}—\text{C}=\text{CH} \)
   1.5-hexadiyne (15HD)

2. Tail to tail (TTT) \( \rightarrow H_2\text{C}=\text{C}=\text{CH}=\text{C}=\text{CH}_2 \)
   1,2,4,5-hexatetraene (1245HT)

3. Head to tail (HTT) \( \rightarrow H_2\text{C}=\text{C}=\text{CH}—\text{CH}=\text{C}=\text{CH} \)
   1,2-hexadiene-5-yne (12HD5Y)

In the above recombination reactions \( \text{CH}_2 \) end of the propargyl is designated as the head (H) and CH as the tail (T) end. The path shown for the benzene formation via HTT recombination forming 12HD5Y has been extensively studied by Miller and Klippenstein\textsuperscript{15} and various transition states in the path following have been characterized. Thus, attention was focused to explore the path following HTH and TTT leading to the formation of benzene. Both HTH and TTT reaction paths lead to the formation of 3,4-dimethylene-cyclobutene (34DMCB) as a stable species which has been reported to be the dead end.

In the present study it is attempted to explore the path for the formation of benzene from 3,4-dimethylenecyclobutene (34DMCB) using computational methods. The structures of all the species involved in the path are optimized and transition states characterized. Reaction energetics has also been studied.

**Computational Details**

\textit{Ab-initio} calculations\textsuperscript{17} performed during the course of present investigation are done using the G03 package\textsuperscript{18}. The geometries of all the species and the transition states involved have been optimized at Hartree-Fock\textsuperscript{19} level of theory using 6-31G(d) basis set\textsuperscript{20}. In order to get a refined and more accurate value of electronic energy of the molecule single point energy calculations are performed at quadratic configuration interaction \text{QCISD(T)/6-311G(d,p)}\textsuperscript{21,22} method which includes singles and doubles excitations and the contribution from triples excitations taken in a perturbative manner. \text{QCISD(T)} calculation is performed on geometries optimized at \text{HF/6-31G(d)} level. Electronic energies of various species involved are calculated and corrected for zero-point energies. The latter are obtained at \text{HF/6-31G(d)} level of theory. A scaling factor of 0.9135 is used for zero-point energy correction\textsuperscript{23}. In order to characterize the stationary points, vibrational frequencies were calculated on the optimized geometries. Absence of any imaginary frequency during the frequency calculation shows that the stationary point obtained on the corresponding potential energy surface is the minimum that corresponds to the optimized structure. Transition states are identified by the presence of only one imaginary frequency. Intrinsic reaction coordinate (IRC) calculations\textsuperscript{24} are performed at HF/6-31G(d) level of theory to ascertain the existence of the transition states.

**Results and Discussion**

The recombination products of propargyl following three different paths \textit{viz.}, TTT, HTH and HTT forming 1245HT, 15HD and 12HD5Y respectively are shown in Figure 1. Optimized geometries of various species obtained at HF/6-31G(d) respectively are shown in Figure 1. There is a plausibility of sigmatropic [1,3] H-transfer between these three recombined products and the path may follows 15HD \( \rightarrow \) 12HD5Y \( \rightarrow \) 1245HT. This possibility is ruled out with the fact that in thermal reactions 1,3 H shift must be antarafacial and this shift is impossible because a three-carbon chain is too rigid to allow the H atom to migrate in such cases\textsuperscript{25}. Therefore, the possibility of 15HD to undergo cyclization is minimum. Thus, the only path left for 15HD is to undergo isomerization to form 1245HT and this has been explored during the present study. The experimental studies performed by Tang \textit{et al.}\textsuperscript{16} showed that all three isomers of \( C_6H_6 \) were present during the propargyl recombination with branching ratios of 44\% (15HD), 38\% (12HD5Y) and 18\% (1245HT). In another experimental study Fahr and Nayk\textsuperscript{26} showed that the formation of 15HD to the extent of 60\%. The path following HTT forming 12HD5Y and subsequently to benzene on the propargyl recombination surface has been studied by Miller \textit{et al.}\textsuperscript{15} and therefore this path has not been taken into consideration during the present study. One of the species formed by the path following HTH and TTT is 3,4-dimethylenecyclobutene (34DMCB). The subsequent isomerization and/or transformation of 34DMCB to other species/products have not been studied so far. In an earlier computational study performed on the PES of propargyl recombination it has been shown to be the dead end\textsuperscript{6,15}. In the present work the path from 34DMCB to benzene is explored. Zero point energy and electronic energy at HF/6-31G(d) level for the various species and transition states are recorded in Table I. Zero point energy corrected total energies for various species and transition states calculated at \text{QCISD(T)/6-311G(d,p)}
Table I — Zero point energy and electronic energy at HF/6-31G(d) for various species and transition states (Unit: hartrees)

<table>
<thead>
<tr>
<th>Species/Transition states</th>
<th>ZPE</th>
<th>E_{ele}</th>
</tr>
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<tbody>
<tr>
<td>Propargyl Radical</td>
<td>0.042571</td>
<td>-115.2506017</td>
</tr>
<tr>
<td>1,5-Hexadiyne(15HD)</td>
<td>0.102156</td>
<td>-230.5670522</td>
</tr>
<tr>
<td>1,2,4,5-Hexatetraene(1245HT)</td>
<td>0.100930</td>
<td>-230.5739857</td>
</tr>
<tr>
<td>3,4-Dimethylenecyclobutene(34DMCB)</td>
<td>0.103732</td>
<td>-230.5960778</td>
</tr>
<tr>
<td>Bicyclo[2.2.0]hexa-1(4),2-diene</td>
<td>0.103618</td>
<td>-230.4631333</td>
</tr>
<tr>
<td>Bicyclo[2.2.0]hexa-2,5-diene</td>
<td>0.105555</td>
<td>-230.5653187</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.107674</td>
<td>-230.7031370</td>
</tr>
<tr>
<td>TS1</td>
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<td>-230.4650172</td>
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<tr>
<td>TS2</td>
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</tr>
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<td>-230.4013948</td>
</tr>
<tr>
<td>TS4</td>
<td>0.098444</td>
<td>-230.4001192</td>
</tr>
<tr>
<td>TS5</td>
<td>0.100337</td>
<td>-230.4826819</td>
</tr>
</tbody>
</table>

Figure 1 — Reaction pathways involved during the recombination of propargyl radicals and the path following 34DMCB to benzene

level are recorded in Table II. Energy barriers for different transition states along the present path are calculated from the data recorded in Table II. The barrier heights are recorded in Table III. Propargyl radical following HTH path directly combine to form 15HD. This further isomerizes to 1245HT involving a transition state TS1. The barrier to this transition is determined to be 37.6 kcal mol$^{-1}$. The stabilized open chain 1245HT undergoes cyclization forming a four-membered ring compound (34DMCB) through a transition state TS2. The optimized structures of TS1 and TS2 are shown in Figure 1. The barrier for the isomerization involving TS2 is calculated to be 30.8 kcal mol$^{-1}$. These isomerizations involving TS1 and TS2 were also shown by Miller et al.$^{15}$ showing barriers to transitions as 35.4 and 29.6 kcal mol$^{-1}$ at
The path following 3,4-Dimethylenecyclobutene (34DMCB) to benzene which remained unexplored in earlier works is studied extensively during the present investigation and are shown in Figure 1. In a particular study the formation of a four-membered bicyclo compound, bicyclo[2.2.0]hexa-1(4),2-diene had been shown to be involved from 34DMCB as an intermediate but the structural parameters of transition states involved in the path could not be determined. During the course of the present study extensive search was made to find the transition state for the formation of benzene from bicyclo[2.2.0]hexa-1(4),2-diene as proposed by Miller and Melius but such a transition state could not be found on the potential energy surface. On the other hand the present investigation reveals that the path following 34DMCB to benzene does not proceed in a single step, instead it involves two steps as depicted in Figure 1. The additional intermediate during the second step has been determined to be bicycle [2.2.0]hexa-2,5-diene also shown in Figure 1. This is in contradiction to the work proposed by Miller and Melius. The transition states TS3, TS4 and TS5 involved during the path following 34DMCB → Benzene are optimized. Figure 1 also contains the optimized structures of these transition states. Frequency calculation performed on the optimized structures of each transition state shows the existence of only one imaginary frequency and these are TS3 (-932.1 cm⁻¹), TS4 (-1507.7 cm⁻¹) and TS5 (-1078.3 cm⁻¹). Vibrations pertaining to these imaginary frequencies were visualized by GaussView Program and found to correspond to valid transition states. In order to ascertain the existence of transition state on the potential energy surface along the reaction path IRC calculations were also performed for each one of the transition states. IRC plots for TS3, TS4 and TS5 are shown in Figures 2-4. These plots clearly show that transition states connect the reactant and the product and there is a smooth transition.

The energy diagram for rearrangement of 15HD and 1245HT formed via HTH and TTT paths ultimately leading to the formation of benzene is shown in Figure 5. Energy barriers to various transitions as given in Table III are determined from the calculated electronic energy data of various species recorded in Table II. Energy barrier involved during the transition of 34DMCB to the first intermediate bicyclo[2.2.0]hexa-1(4),2-diene is determined to be 96.6 kcal mol⁻¹ while in an earlier study Miller and Melius determined it to be

![Figure 2](image-url)
The process $34\text{DMCB}$ $\rightarrow$ bicyclo[2.2.0]hexa-1(4),2-diene (Intermediate I) will be highly endothermic and it is probably thermally driven. In such a case the transition state would correspond to more like the product that is intermediate I. An energy diagram for transition from propargyl radical recombination to benzene formation involving various transition states is shown in Figure 5. The most notable contribution of the present study is the exploration of the path connecting $34\text{DMCB}$ to benzene and the characterization of transition states involved during this transition.

**Conclusion**

The study of potential energy surface and structural determination of various species involved during the recombination reaction of propargyl radicals are quite informative because they provide an understanding of the possible reaction paths along with energies involved during the transformation. The potential energy diagram for the isomerization of $34\text{DMCB}$ to benzene explored during the present investigation elucidates a new path with the identification of transition states. Two new intermediates along the path following $34\text{DMCB}$ to benzene have been determined and transition states involved during this transformation are characterized.

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**References**