The reaction paths for the thermal interconversion of the various \( \text{C}_3\text{H}_4 \) isomers have been studied by the MNDO method and the activation barriers to the various isomerizations have been estimated. The transition state structures have been analyzed in terms of the orbital compositions of the frontier molecular orbitals and the overlap populations of the various bonds involved in the transition states. These have been interpreted to understand the mechanisms of the various interconversions. Vinylmethylene is found to play a central role in the isomerizations as its formation from the stable isomers, and subsequent rearrangement to the other isomers, is the most facile process among the various other competing reactions. The anti nonplanar geometry of vinylmethylene is found the intermediate in the interconversions.

The \( \text{C}_3\text{H}_4 \) system is interesting since there are many stable and unstable isomers, which interconvert by mechanisms involving carbenes and radicals. We have previously examined the structures and stabilities of the various isomers on the \( \text{C}_3\text{H}_4 \) surface\(^1\). In the present work, an attempt has been made to study the interconversion of the stable isomers, allene, methylacetylene and cyclopropene.

Many experiments and theoretical calculations have been performed to elucidate the kinetics and mechanisms of the various reactions\(^1\text{--}^{19} \). The gas phase pyrolysis\(^2\text{--}^{23} \) of cyclopropene yields methylacetylene. Bailey and Walsh\(^1\) found a small amount of allene, too, as a minor product. Shock-tube studies\(^4\text{--}^5 \) on the allene to methylacetylene interconversion indicated a unimolecular mechanism. It was presumed by the authors\(^4\text{--}^5 \) that the interconversion occurs via a direct 1,3-hydrogen shift. Walsh\(^4 \) had proposed that cyclopropene might be an intermediate in the isomerization of allene to methylacetylene. The cyclopropene isomerization is known\(^7 \) to involve vinylmethylene. If vinylmethylene is also involved in the allene to methylacetylene isomerization, the mechanism requires two 1,2-hydrogen shifts rather than the 1,3-hydrogen shift proposed\(^4\text{--}^5 \). The ring closure of vinylmethylene to cyclopropene has also been observed\(^8\text{--}^9 \).

In view of all this evidence, we have carried out a systematic and detailed study of the reaction paths for the various interconversions:

\[
\text{Allene} \leftrightarrow \text{Cyclopropene} \\
\text{Allene} \leftrightarrow \text{Methylacetylene} \\
\text{Cyclopropene} \leftrightarrow \text{Methylacetylene}
\]

These reactions have been investigated earlier by SCF, MCSCF and CI calculations\(^10 \). The aim of the present work was also to compare our semi-empirical MNDO\(^20 \) calculations of reaction paths with the \text{ab initio} results, although we have already confirmed that equilibrium geometries are calculated reliably by the MNDO method\(^20 \).

Results and Discussion

The interconversion of the stable isomers may involve several unstable species as intermediates. The possible intermediates have been already investigated\(^1 \). Thus, eight possible intermediate reactions have been studied here. These reactions and results for their activation barriers are given in Figure 1 and the optimized geometries of the transition states are depicted in Figure 2.

The first reaction investigated is the conversion of allene to cyclopropene, which involves ring closure and a 1,2-hydrogen shift. If the ring closure occurs first, cyclopropylidene is the intermediate, and, on the other hand, if the 1,2-hydrogen shift should occur first, the intermediate would be vinylmethylene. Both the possibilities were considered.

The allene to cyclopropylidene reaction has earlier been studied theoretically concerning the synthesis, structure and chemical reactivity of allene\(^12\text{--}^{13} \). This and its reverse reaction have been thoroughly investigated by Ruedenberg's group\(^14\text{--}^{17} \), which also mapped out this part of the \( \text{C}_3\text{H}_4 \) potential energy hypersurface. Bettinger \text{et al.}\(^18 \) used density functional theory.
Figure 1—Interconversion of various C$_3$H$_4$ isomers. The numbers refer to the partial charge densities on the corresponding atoms.

Figure 2—Structures of transition states and the partial charge densities on the various atoms.

and obtained a barrier of 3-6 kcal/mol for the ring opening of cyclopropyldiene. From their ab initio studies, Pasto et al.$^{11}$ determined a barrier height of 18 kcal/mol and an exothermicity of 74 kcal/mol for the reverse reaction. Honjou et al.$^{10}$ reported a barrier height of 74.2 kcal/mol for the forward reaction, 11.3 kcal/mol for the reverse reaction, and a bent, twisted, allene transition state.

Our calculations indicate that, until about a C$_3$C$_6$C$_6$ bond angle of 90°, the hydrogen H$_6$ (see Figure 2) remains in the plane of the carbons, after which a rotation of the in-plane CH$_2$ group occurs. The other CH$_2$ group (perpendicular to the plane) undergoes a disrotatory motion, maintaining C$_5$ symmetry till about 90°. After this, a conrotatory motion begins, leading to a twisted allene structure for TS1, in which
the C₆C₅C₆ plane is no longer a plane of symmetry. However, the C₆ symmetry is retained arising from a perpendicular plane passing through C₅. While the H₂C₆C₅C₆ and H₁C₅C₆C₇ torsion angles are 58.1°, the H₂C₇C₈C₉ and H₂C₈C₉C₁₀ torsion angles are -128.5°. The transition state has a three-center-like structure and C₆ symmetry. The C₅C₆ bond length increases to 1.407 Å from 1.306 Å in allene, but is much smaller than the C₅C₆ bond length in cyclopropylidene (1.511 Å). The bond angle at C₅ is 87.5°, which reduces to 60.8° in cyclopropylidene. The C₅C₆ bond distance is quite large (1.945 Å, see Figure 2). While the C₅C₆ and C₅C₇ bond orders reduce from 1.956 in allene to 1.318 in TS1, the incipient C₅C₈ bond has a bond order of 0.624. The calculated geometry of the transition state agrees well with the ab initio geometry.¹⁰

Thus the geometry of the transition state and the mechanism are correctly predicted by MNDO calculations, but the barrier height is grossly over-estimated. This is a well-known shortcoming of the MNDO method which disfavors non-classical structures and hence over-estimates barriers to 1,2 hydrogen shifts.

Subsequently, cyclopropylidene may undergo a 1,2-hydrogen shift to form cyclopropene. This reaction has been investigated in order to gain insight into experimental evidence that photolysis of cyclopropylidene always produces allene but not cyclopropene.⁶

Thus, the overall barrier to the allene to cyclopropene rearrangement is calculated as 121.1 kcal/mol, and that for the reverse reaction is 96.7 kcal/mol. Both barriers are high and the overall reaction may be written as:

\[
\begin{align*}
\text{Allene} & \rightleftharpoons \text{Cyclopropylidene} \\
102.1 & \rightarrow 44.2 \\
25.2 & \rightarrow 96.7 \\
\text{(TS1)} & \rightarrow \text{(TS2)} \\
\text{Cyclopropene} & \rightarrow \text{(1)}
\end{align*}
\]

Figure 2 gives the structure of the transition state for the 1,2-hydrogen shift (TS2). The C₅C₆ bond distance decreases from its value of 1.512 Å in cyclopropylidene to 1.424 Å, while the C₅C₇ bond distance decreases from 1.530 Å in cyclopropylidene to 1.509 Å, which is close to its value in cyclopropene. The C₅C₈C₉ bond angle in the transition state is 63.6°, which is almost equal to its value in cyclopropylidene (64.0°). The C₅C₈H₉ bond angle is 56.8°. Hence, the transition state has a three-center-like structure. The migrating hydrogen H₉ is below the plane of the carbon skeleton and is almost midway between the two carbons C₅ and C₆. The hydrogen H₉ is almost in the plane of the carbon skeleton. There is a strong resemblance between the transition state structure and cyclopropene, except for the location of H₉. The Mulliken overlap populations of 0.527 and 0.423, respectively, for the C₅H₉ and C₇H₉ bonds show that the new C₅H₉ bond is almost half formed at the transition state, while the C₅C₆ bond also acquires some double bond character (bond order = 1.368).

Another possible conversion of allene to cyclopropene is through vinylmethylene. The structure of the transition state (TS3) is given in Figure 2. Both C-C bond distances increase slightly to 1.320 Å and 1.329 Å from their value in allene (1.306 Å). This transition state also has a three-center-like structure, in which the C₅C₇H₈ bond angle is 55.3° (see Figure 2). This step is endothermic. Both the cyclopropylidene-cyclopropene and allene-vinylmethylene reactions involve the migration of H₉ from C₅ to C₆ (see Figure 2). However, compared to the 1,2 hydrogen shift in Step II of Equation (1), the transition state here occurs much later in the reaction path, as the C₅-H₉ bond distance in TS3 (1.442 Å) is considerably larger than in TS2 (1.391 Å). This is so because the allene to vinylmethylene reaction involves migration of the hydrogen over a double bond to give a single bond, while in the cyclopropylidene to cyclopropene reaction, there is a migration of the hydrogen over a single bond resulting in a carbon-carbon double bond. Also, as the hydrogen H₉ migrates over the C₅C₆ double bond, a rotation of the CH₃ group occurs simultaneously, the torsion angles changing from 90° and -90°, respectively, to 22.9° and -156.2°, respectively. The fact that this transition state occurs late in the reaction path is also borne out by the calculated bond orders of 0.385 and 0.583, respectively, for the C₅H₉ and C₇H₉ bonds. The C₅C₆ bond order also reduces to 1.510 in the transition state. The barrier to the reverse reaction is much smaller as only a slight rotation of the CH₃ group is required to reach the transition state.

The intermediate is the trans nonplanar isomer of vinylmethylene, which undergoes ring closure to form cyclopropene. The activation energy for this step is only 9.6 kcal/mol, and it is exothermic (ΔH = -40.8 kcal/mol). The transition state (TS4) structure is given in Figure 2. The C₅C₆ bond distance decreases to 1.404 Å from its value of 1.428 Å in vinylmethylene, and the C₅C₇ bond distance increases to 1.377 Å.
KAKKAR et al.: \( \text{C}_3\text{H}_4 \): INTERCONVERSION OF ISOMERS

from 1.352 Å in vinylmethylene. This is because there is a shift of the double bond from C\(_6\)C\(_c\) in vinylmethylene to C\(_4\)C\(_b\) in the product cyclopropene. The C\(_6\)C\(_b\) and C\(_6\)C\(_c\) bond orders are 1.267 and 1.682, respectively, while the incipient C\(_6\)C\(_c\) bond has a bond order of 0.252. The barrier to the reverse reaction is much smaller as only a slight rotation of the CH\(_2\) group occurs up to the transition state. The CaCbCc and CbCc bond orders are 1.267 and 1.682, respectively, while the incipient CaCc bond has a bond order of 0.252. The barrier to the reverse reaction is much smaller as only a slight rotation of the CH\(_2\) group occurs up to the transition state. The CaCbCcHc and CaCbCcHcHd torsion angles in TS4 are \(-21.6^\circ\) and \(158.3^\circ\), respectively. The mechanism involves the gradual rotation of the CH\(_2\) group of vinylmethylene until the transition state is reached, after which the C\(_4\)C\(_c\) bond is formed with a shift of the double bond to C\(_4\)C\(_b\).

The overall reaction is thus:

\[
\text{Allene} \xrightarrow{68.5} \text{Vinylmethylene} \xrightarrow{9.6} \text{Cyclopropene} \quad \text{(TS3)}
\]

Hence, Equation (2) represents a more feasible pathway for the isomerization of allene to cyclopropene, as compared to Equation (1). Also, since the barrier to the direct isomerization of cyclopropylidene to cyclopropane is higher (44.2 kcal/mol) than that to the formation of allene (25.2 kcal/mol), an indirect pathway involving allene would be preferred, i.e.,

\[
\text{Cyclopropylidene} \xrightarrow{TS1} \text{Allene} \quad \text{TS3}
\]

Vinylmethylene \( \xrightarrow{TS4} \) Cyclopropene \quad \ldots \quad (3)

in which the transition state of highest energy is TS1, having a heat of formation of 145.9 kcal/mol, and hence the activation energy is only 25.2 kcal/mol, while the direct path [see Eqn(1)] involves TS2, which has a higher heat of formation (164.9 kcal/mol). The same conclusions were drawn by Honjou et al.\(^{10}\) from their \textit{ab initio} calculations.

We next calculated the reaction path for conversion of allene to methylacetylene. This may proceed by two 1,2-hydrogen shifts, the first shift producing vinylmethylene via TS3 as in Equation (2), and the second step involving another transition state, TS5. Another alternative for the reaction is a direct 1,3-hydrogen shift. The optimized geometry of the transition state, TS5, for the vinylmethylene to methylacetylene conversion is given in Figure 2. It can be seen that this transition state resembles vinylmethyl-ene with the C\(_6\)H\(_b\) bond being only slightly weakened. The C\(_6\)H\(_b\) bond distance is quite large, i.e. 1.842 Å, and the C\(_6\)C\(_b\)H\(_b\) bond angle is \(40.9^\circ\). The incipient C\(_6\)H\(_b\) bond has a bond order of only 0.019. The C\(_6\)H\(_b\) bond, which should become a triple bond in methylacetylene, still has a bond order of only 1.182, while the C\(_6\)C\(_b\) bond is still almost a double bond (bond order = 1.795). Thus, this transition state occurs very early in the reaction path. As this step is highly exothermic (\(\Delta H = -68.1\) kcal/mol) with a relatively low activation energy, this transition state resembles the reactant in accordance with Hammond's postulate\(^{21}\).

A three-centered transition state with bonding between C\(_b\), C\(_c\) and H\(_b\) would have been highly strained, as it would have involved doubly bonded carbons. This is in contrast to the situation encountered in TS3 in which the reverse reaction involves transfer of H\(_b\) from C\(_6\) to the other carbon, i.e. C\(_a\), to which C\(_b\) is singly bonded in vinylmethylene. The H,C,C\(_b\)H\(_b\) and H,C,C\(_a\),C\(_b\)H\(_b\) torsion angles are \(175.2^\circ\) and \(-2.7^\circ\), respectively, indicating that all atoms, except H\(_a\), lie almost in the same plane (see Figure 2), as in vinylmethylene. Thus, the rotation of the CH\(_2\) group occurs after the transition state is formed. Thus:

\[
\text{Allene} \xrightarrow{88.5} \text{Vinylmethylene} \xrightarrow{16.5} \text{Methylacetylene} \quad \text{(TS3)}
\]

The first step is the rate-determining one, and the overall activation energy for the forward reaction is 88.5 kcal/mol, while that for the reverse reaction is 91.5 kcal/mol.

For the direct 1,3-hydrogen shift from allene, the calculated activation energy is 137.2 kcal/mol, which is much higher than the activation energy obtained for reaction via vinylmethylene.

\[
\text{Allene} \xrightarrow{137.2} \text{Methylacetylene} \quad \text{(TS6)}
\]

The geometry of the transition state TS6, is given in Figure 2. Hence, the conversion of allene to methylacetylene must proceed via vinylmethylene, as this path requires lower activation energy (88.5 kcal/mol). This concerted mechanism for the allene to methylacetylene isomerization via a 1,3-hydrogen shift had been proposed earlier\(^4,5\), but was rejected by Walsh et
who suggested the involvement of cyclopropene as an intermediate. Figure 2 shows that the transition state has a four-center-like structure with the CH2 group rotated out of the plane of the other atoms. The migration of H$_2$ from C$_a$ to C$_c$ involves the formation of a partial bond between C$_a$ and C$_c$ in the transition state (bond order = 0.335). The C$_a$H$_4$ and C$_c$H$_4$ bond orders are 0.357 and 0.546, respectively.

The conversion of cyclopropene to methylacetylene was also considered. This may proceed by ring opening, followed by a 1,2-hydrogen shift. Ring opening yields propenylidene as an intermediate, via TS7. This step has an activation energy of 85.4 kcal/mol and is highly endothermic ($\Delta H = 41.6$ kcal/mol). The optimized geometry of the transition state, given in Figure 2, shows that it has a four-center-like structure. The hydrogen H$_b$ is unsymmetrically placed, the C$_b$H$_4$ and C$_c$H$_4$ bond distances being 1.251 Å and 1.430 Å, respectively, and the bond orders being 0.506 and 0.425. TS7 also has Cs symmetry. The C$_a$C$_c$H$_b$ bond angle is 88.5°. There is a synchronous transfer of H$_b$ to C$_c$, while the C$_b$C$_c$ bond weakens (bond order = 0.552) and eventually breaks after the transition state.

In the second step of the reaction, propenylidene undergoes a 1,2-hydrogen shift to produce methylacetylene via a three-center-like transition state, TS8. The first step, i.e., conversion of cyclopropene to propenylidene, is the rate-determining step of the reaction and the overall activation energy is 85.4 kcal/mol for the forward reaction and 112.7 kcal/mol for the reverse reaction.

\[
\begin{array}{c|c|c}
\text{Cyclopropene} & 85.4 & \text{Propenylidene} \\
\text{TS7} & 43.8 & \text{Methylacetylene} \\
\text{Propenylidene} & 25.8 & \text{Methylacetylene} \\
\text{TS8} & 94.7 & \text{Methylacetylene} \\
\end{array}
\]

The transition state (TS8, see Figure 2) has Cs symmetry. The C$_a$C$_c$H$_4$ bond angle is 60.5°. The C$_a$C$_c$C$_c$ bond is almost linear in the transition state, the bond angle being 166.6°. Although the C$_b$H$_4$, C$_c$H$_4$, and C$_c$H$_4$ bond lengths are equal, i.e., 1.111 Å, the C$_c$C$_a$H$_4$ bond angle is 110.1°, while the bond angles with H$_a$ and H$_d$ are 111.4°. The H$_a$C$_c$H$_b$ and H$_d$C$_c$H$_b$ torsion angles are −119.8° and 119.8°, respectively. As observed by Honjou et al., the transition state lies closer to methylacetylene than to propenylidene as the C$_b$C$_c$ bond is almost linear and the C$_c$C$_c$ bond length (1.453 Å) is almost the same as in methyla-

cetylene (1.445 Å). However, the migrating hydrogen, H$_a$, is almost equally bonded to the two carbons, C$_a$ and C$_b$ (C$_a$H$_4$ and C$_c$H$_4$ bond orders = 0.526 and 0.447, respectively).

It can be seen from Figure 1 that the most favorable reaction paths from the three stable species, allene, methylacetylene and cyclopropene involve conversion to vinylmethylene. The respective activation barriers are 88.5 kcal/mol, 84.6 kcal/mol and 50.4 kcal/mol, and the transition states are TS3, TS5 and TS4. Thus, vinylmethylene plays a central role in the interconversions. The reverse reactions, i.e., the conversion of vinylmethylene to one of these stable isomers are very facile, the activation energies being, respectively, 22.8 kcal/mol, 16.5 kcal/mol and 9.6 kcal/mol. This is in agreement with the experimental observation that the gas phase pyrolysis of cyclopropene at temperatures above 193°C yields methylacetylene as the major product along with small amounts of allene. This reaction can be summarized as:

\[
\begin{align*}
\text{Cyclopropene} & \xrightarrow{50.4} \text{Propenylidene} \\
\text{TS7} & \xrightarrow{25.8} \text{Methylacetylene} \\
\text{Vinylmethylene} & \xrightarrow{9.6} \text{Allene} \\
\end{align*}
\]

Since TS3 and TS5 have higher energies than TS4, the rate-determining step for the formation of products is the second one. Hence, the overall activation energy for the formation of allene is 64.1 kcal/mol, while that for methylacetylene formation is 57.2 kcal/mol.

The cyclopropene to vinylmethylene reaction and the reverse reaction have both been observed. Our calculations suggest that the latter should be extremely facile. The activation energy of 88.5 kcal/mol obtained for the allene to methylacetylene interconversion via vinylmethylene is in agreement with the data of Bradley and West, who obtained an activation energy of 92.7 kcal/mol at temperatures between 1440 and 1700 K. The intermediacy of cyclopropene in the reaction pathway, as suggested by Walsh, is possible, as the activation barrier to the formation of cyclopropene (9.6 kcal/mol) is lower than that for methylacetylene formation. This would then involve propenylidene to give methylacetylene. However, the activation barrier to the formation of propenylidene...
(85.4 kcal/mol) is high enough to preclude its involvement. This explains why Bailey and Walsh\(^2\) could not find any evidence for the existence of this pathway.

**Charge density distributions**

Figures 1 and 2 give the partial charge distributions along the reaction paths for the various reactions investigated and Table I gives the orbital component analysis of the frontierorbitals of the transition states. For the reaction represented by Equation (1), it can be seen that the bending of the C\(_a\)C\(_b\)C\(_e\) moiety and formation of the C\(_a\)C\(_b\) bond with concomitant reduction of the C\(_b\)C\(_e\) and C\(_a\)C\(_e\) bond orders is accompanied by a withdrawal of charge density from C\(_b\) by C\(_a\) and C\(_e\). This results in a vacant orbital on C\(_b\) in cyclopropylen. However, in the transition state, C\(_b\) is still negatively charged. In the second step of the reaction, C\(_b\) again becomes negatively charged, accepting electron density from C\(_a\) and C\(_e\).

For the reactions represented by Equation (2), C\(_a\) and C\(_b\) first gain electron density from C\(_b\) to form the transition state after which they donate it back to C\(_b\) to form vinylmethylene, which has a carbene center at C\(_a\). For the vinylmethylene to cyclopropene reaction, it is found that the formation of a new C\(_a\)C\(_b\) bond with a shift of the double bond from C\(_b\)C\(_e\) to C\(_a\)C\(_b\) is accomplished by the donation of electron density to C\(_a\) and C\(_e\) by C\(_a\), H\(_b\), and H\(_h\).

In the case of the vinylmethylene to methylacetylene reaction, up to the transition state, there is not much change in the charge distribution. After this, the formation of a new bond between C\(_a\) and H\(_b\) is accomplished by the donation of charge by these two atoms to C\(_a\), which now becomes triply bonded to C\(_b\) (see Figure 2).

In the direct isomerization of allene to methylacetylene [Eqn (5)], there is transfer of the hydrogen H\(_b\) from C\(_a\) to C\(_b\) (see Figure 2). The carbon C\(_a\) loses a proton, itself becoming negatively charged, while the other two carbons donate charge to the proton.

In the isomerization of cyclopropene to methylacetylene via propenylidene [see Eqn (6)], first the hydrogen H\(_b\) migrates to C\(_b\) and the C\(_b\)C\(_e\) bond breaks with the transfer of electron density from C\(_b\) to C\(_a\). In the second step of this reaction, there is formation of a bond between C\(_b\) and H\(_b\) while the C\(_b\)H\(_b\) bond breaks. The carbon C\(_a\) donates charge to C\(_b\) through the migrating hydrogen H\(_b\).

To understand the nature of the frontier orbital and the mechanisms of the various reactions, we have carried out an orbital component analysis of this orbital. The results are given in Table I. Comparison of the

<table>
<thead>
<tr>
<th>System Atom</th>
<th>MO#11</th>
<th>MO#12</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_a)</td>
<td>8a'</td>
<td>4a''</td>
</tr>
<tr>
<td>C(_b)</td>
<td>17.74</td>
<td>55.87</td>
</tr>
<tr>
<td>C(_e)</td>
<td>52.79</td>
<td>78.63</td>
</tr>
<tr>
<td>H(_a)</td>
<td>77.37</td>
<td>48.21</td>
</tr>
<tr>
<td>H(_b)</td>
<td>73.55</td>
<td>54.07</td>
</tr>
<tr>
<td>H(_c)</td>
<td>7.57</td>
<td>2.13</td>
</tr>
<tr>
<td>H(_d)</td>
<td>12.14</td>
<td>28.73</td>
</tr>
<tr>
<td>H(_e)</td>
<td>4.73</td>
<td>2.13</td>
</tr>
<tr>
<td>e</td>
<td>-8.440</td>
<td>-8.306</td>
</tr>
</tbody>
</table>

*see Figure 2. Orbital energies are in electron Volts.*
energies of this orbital for allene, cyclopropylidene\textsuperscript{1} and TS1 shows that the transition state has the largest electron affinity and the smallest ionization potential (8.44 eV) calculated based on Koopmans' theorem\textsuperscript{22}. This is because the lone pair is centered mainly on C\textsubscript{b}, while the vacant orbital is delocalized over C\textsubscript{a} and C\textsubscript{c} which are equivalent (see Figure 2). Thus the mechanism of this step involves the donation of electronic charge by C\textsubscript{a} and C\textsubscript{c} to C\textsubscript{b}, resulting in the formation of the transition state, TS1. After this, C\textsubscript{b} donates back the charge to form cyclopropylidene in which the carbene lone pair and the vacant orbital are both located on C\textsubscript{b}. It is also interesting to note that the overlap populations of the C\textsubscript{a}C\textsubscript{b} and C\textsubscript{b}C\textsubscript{c} bonds reduce to 1.318 from 1.956 in allene and finally become 1.011 in cyclopropylidene. Thus the carbon atom, C\textsubscript{b}, has a valency of 2.636 in the transition state. The incipient CC bond has an overlap population of 0.624 in the transition state.

For the cyclopropylidene to cyclopropene reaction, it is found that there is no significant change in the highest occupied molecular orbital in going from the reactant to the transition state (see reference 1 and Table I), but the vacant orbital partly shifts from C\textsubscript{b} to C\textsubscript{a}. Thus the mechanism involves donation of electronic charge by C\textsubscript{a} through the migrating hydrogen H\textsubscript{b}, resulting in a vacant orbital on C\textsubscript{b}. Although this transition state has a very high heat of formation.

For the allene to vinylmethylene rearrangement, it is seen that there is a shift in electron density from the C\textsubscript{a}C\textsubscript{b} \pi bond of allene to C\textsubscript{a} resulting in a lone pair on C\textsubscript{a} (see Figure 2 and Table I). At the same time, C\textsubscript{a} donates charge to C\textsubscript{b} through the migrating hydrogen H\textsubscript{a}, resulting in a vacant orbital on C\textsubscript{a}. Although this transition state has a three-center-like structure, the C\textsubscript{a}C\textsubscript{b} bond also is weakened and its bond order reduces to 1.761. The C\textsubscript{a}C\textsubscript{b} bond order is 1.510, while the C\textsubscript{a}H\textsubscript{a} and C\textsubscript{b}H\textsubscript{b} bond orders are, respectively, 0.385 and 0.583. Thus, the transition state occurs after the midpoint of the reaction path. The total overlap population of C\textsubscript{a} with other atoms is 2.833.

For the vinylmethylene to cyclopropene rearrangement, it is found that first both the lone pair and vacant orbital are delocalized over C\textsubscript{a} and C\textsubscript{c} (see Figure 2) in TS4. However, the C\textsubscript{a}C\textsubscript{c} bond order is only 0.252, while the C\textsubscript{a}H\textsubscript{a} and C\textsubscript{b}H\textsubscript{b} bond orders in TS4 are 1.267 and 1.682, respectively. This indicates that first the C\textsubscript{a}C\textsubscript{b} double bond is partially formed and the C\textsubscript{b}C\textsubscript{c} double bond weakened, making both carbons C\textsubscript{a} and C\textsubscript{c} trivalent (total bond orders for C\textsubscript{a} and C\textsubscript{c} are 2.472 and 2.855, respectively) in the transition state, after which the C\textsubscript{a}C\textsubscript{b} bond is formed.

TS5, the transition state for the isomerization of vinylmethylen to methylacetylene has a structure that closely resembles that of vinylmethylene. As noted before, this is in accord with Hammond's postulate\textsuperscript{23} as the reaction is highly exothermic with relatively low activation energy. The only difference is a slight decrease in the overlap populations of the C\textsubscript{a}C\textsubscript{b} and C\textsubscript{b}H\textsubscript{b} bonds and the greater delocalization of the vacant orbital over C\textsubscript{a} and C\textsubscript{c}. There is also a greater localization of the lone pair on C\textsubscript{a} making this carbon, which has a small positive charge (0.016) in vinylmethylene, neutral in the transition state.

The transition state for the 1,3 hydrogen shift from allene to methylacetylene, TS6, contains a four membered ring involving C\textsubscript{a}, C\textsubscript{b}, C\textsubscript{c} and H\textsubscript{b} (see Figure 2), but there are partial bonds only between C\textsubscript{a}C\textsubscript{c} and H\textsubscript{b}. The C\textsubscript{b}H\textsubscript{b} partial bond order is 0.335, 0.357 and 0.546, respectively. Thus the transition state occurs after the midpoint of the reaction path, since at this stage the C\textsubscript{b}C\textsubscript{c} bond has already become a single bond (bond order = 0.895) and C\textsubscript{b} has become trivalent. Because of its strained nature, this transition state has a high energy. The HOMO (see Table I) is a lone pair on C\textsubscript{b} while the vacant orbital is delocalized over C\textsubscript{a} and C\textsubscript{c} (see Figure 2).

The transition state, TS7, for the isomerization of cyclopropene to propenyldiene also involves partial bonding between three atoms, C\textsubscript{a}, C\textsubscript{b} and H\textsubscript{b}. The C\textsubscript{b}H\textsubscript{b} and C\textsubscript{b}H\textsubscript{b} bond overlap populations are, respectively, 0.552, 0.506 and 0.425, indicating that this transition state occurs about midway in the reaction path. The overall bond order of C\textsubscript{b} with other atoms is 2.963, which is again in between its value in cyclopropene and propenyldiene. Both the HOMO and LUMO contain large coefficients for C\textsubscript{a} and C\textsubscript{b} (see Table I).

TS8, which is the transition state for the propenyldiene to methylacetylene reaction, also has a three-center-like structure involving partial bonding between C\textsubscript{a}, C\textsubscript{b} and H\textsubscript{b} (see Figure 2). The bond orders for the C\textsubscript{a}C\textsubscript{b}, C\textsubscript{b}H\textsubscript{b} and C\textsubscript{b}H\textsubscript{b} bonds are, respectively, 2.211, 0.526 and 0.447. Again the transition state occurs a little before the midpoint of the reaction.
path and the overall bond order of 2.658 of C3, with the other atoms is in between its value of 2 in propenylidene and 4 in methyla cetylene. The HOMO is the C3C2 π bonding molecular orbital.

Conclusions

In conclusion, we may state that our calculations indicate that vinylmethy lene seems to play a central role in the interconversions of the three stable isomers, as reactions involving other pathways have much higher activation energies. The trans nonplanar geometry of vinylmethylene is the one involved in the isomerizations. The isomerization of allene to methyla cetylene must involve vinylmethylene and the calculated activation energy is in agreement with the data of Bradley and West\(^4\). The data on the pyrolysis of cyclopropene\(^2-3\) to form primarily methyla cetylene is also explained because of the higher activation energy for the formation of allene.

The transition state structures are found very interesting. The transition from divalent to tetravalent carbons and vice versa is found to occur, in most cases, via transition states containing trivalent carbons. The orbital composition analyses of the transition states has given an insight into the mechanisms for the interconversions.

However, the activation barriers to some of the reactions are predicted to be much higher than those calculated by \textit{ab initio} MCSCF methods\(^10\), although the structures of the transition states are by-and-large similar. Although the prediction of higher activation energies for 1,2 hydrogen shifts is an artifact of the MNDO method, in some cases the difference is very large. For example, in the propenylidene to methyla cetylene reaction, while the present calculations predict a significant barrier, Honjou \textit{et al.}\(^10\) predicted a negligible barrier (0.6 kcal/mol), which, on zero-point energy corrections, becomes negative. However, since they found the transition state to closely resemble methylacetylene, with the migrating hydrogen already transferred to its new site, their findings seem contrary to Hammond's postulate\(^21\), according to which a low barrier would be associated with a transition state resembling the product of higher energy, i.e. propenylidene.

Thus, if we extend our calculations to larger systems for which \textit{ab initio} calculations are difficult, the MNDO equilibrium geometries and relative energies may be expected to be correct. The transition state geometries and the progress of the reaction along the reaction path, i.e. the mechanism, are correctly estimated. However, the activation barriers must be accepted with a degree of reservation as they are generally overestimated.

Acknowledgement

One of the authors (BSP) thanks the University Grants Commission (UGC), New Delhi, for a Senior Research Fellowship.

References