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Ab Initio Studies of the C_3H_4 Surface. 3. Thermal Isomerization

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Abstract: SCF, MCSCF, and CI calculations have been carried out to study thermal interconversions occurring on the singlet C_3H_4 surface. Transition states and reaction paths between the pairs of possible isomers, methylacetylene, allene, cyclopropene, propenylidene, vinylmethylene, and cyclopropylidene were determined. In addition, the zero-point energies were calculated, and the activation energies for pertinent reactions were evaluated. The thermal rearrangement of allene to methylacetylene was found to proceed in four steps via vinylmethylene, cyclopropene, and propenylidene with the activation energy of 65.8 kcal/mol, which is in good agreement with the observed values of 60.5 and 63.8 kcal/mol. The same reaction paths can also apply to pyrolysis of cyclopropene, in which it undergoes conversion to methylacetylene via propenylidene more easily than to allene via vinylmethylene; the calculated activation energies are 38.1 and 43.4 kcal/mol, respectively. These are again in excellent agreement with the observed values of 37.5 and 43.3 kcal/mol. The activation energies for the allene to cyclopropylidene and the reverse conversions were calculated to be 72.2 and 10.2 kcal/mol. This indicates that cyclopropylidene may not be involved in the interconversion of allene, cyclopropene, and methylacetylene. One of the significant findings in this study is the reaction path for the cyclopropene to methylacetylene conversion via propenylidene, which is less energy demanding than that via vinylmethylene. This made the calculated mechanisms in accord with the experimental data. Furthermore, we will present and discuss reaction mechanisms for pyrolysis of singly and doubly substituted cyclopropene in which this particular reaction path is expected to play a dominant role.

I. Introduction

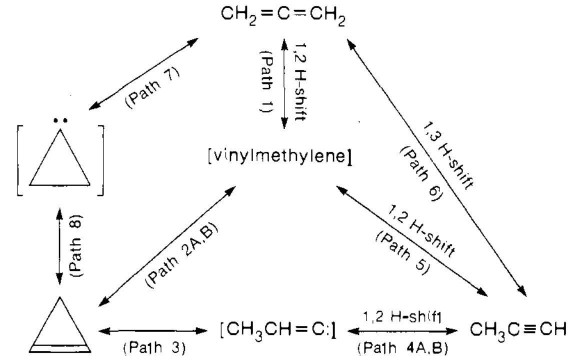
Many of the mechanisms for the thermal interconversion of isomers on the C_3H_4 surface play a central role in organic chemistry. Thus, they not only serve as models for much larger systems but also provide a fundamental basis for reactions of hydrocarbons.

In Scheme I (see also Figure 1) a number of possible thermal reactions are shown that provide the basis for our ab initio study. These mechanisms for thermal interconversions of cyclopropene, allene, and methylacetylene involve ring opening and closure reactions, 1,2- and 1,3-hydrogen shifts, formation of double and triple bonds, and reactive intermediates like the carbene and diradical forms of vinylmethylene.

Although many experiments[1-3] have been conducted to elucidate kinetics and mechanisms for the possible reactions shown in Scheme I, their details have not been established.[4] For example, gas-phase pyrolysis experiments indicate that the conversion of allene and methylacetylene goes through cyclopropene and that cyclopropene undergoes bond fission to form an intermediate that produces allene and methylacetylene.[2d,e] A convenient structure for this intermediate, proposed by Bailey et al.,[2e] is the 1,3-diradical form of vinylmethylene. Photochemical interconversion of the C_3H_4 isomers in low-temperature matrices indicated that the stable isomers also interconvert through a common intermediate, for which the bisected diradical form of vinylmethylene has been proposed.[3a] Consequently, since a number of experimental studies propose a "vinylmethylene" intermediate, then a key to understanding the chemistry on the C_3H_4 surface may be to characterize the structure of vinylmethylene.

As Steinmetz et al.[4] have pointed out, the experimental evidence for the involvement of vinylmethylene is indirect, and its structure and bonding are not well established due to the possibility of equilibration among various structures and electronic states possible for vinylmethylene. On the other hand, previous theoretical studies[5-10] which employed SCF, GVB, and simple CI wave functions indicated that the stable structures for both triplet and singlet are planar carbene species. However, our extensive MCSCF and multireference CI study on the potential energy surface[11,12] located six local minima which are different from the previous results. The lowest two of these minima belong to the $^3A''$ states of trans and cis planar vinylmethylene and are isoenergetic lying 46 kcal/mol above the $^1A_1$ state of methylacetylene. Their structures are allylic with the C–C bond lengths of 1.39

Scheme I



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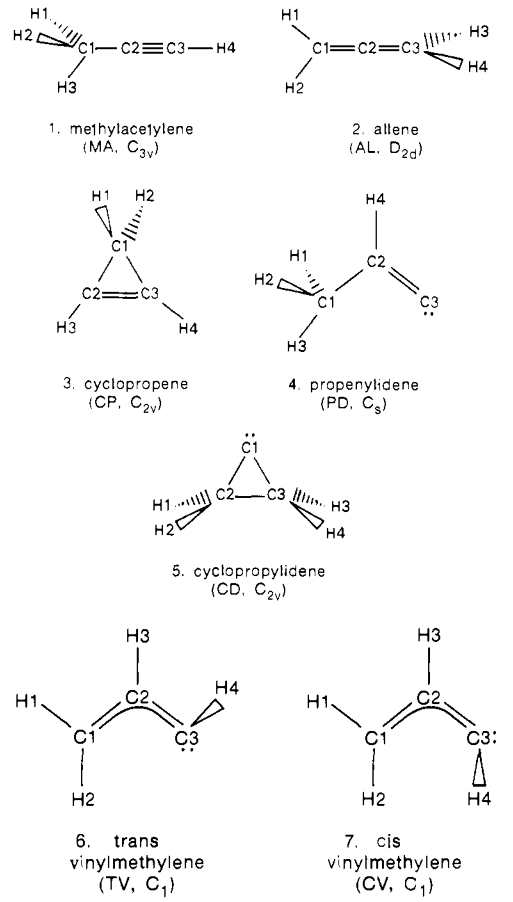

1. methylacetylene (MA, C_{3v})

2. allene (AL, D_{2d})

3. cyclopropene (CP, C_{2v})

4. propenylidene (PD, C_s)

5. cyclopropylidene (CD, C_{2v})

6. trans vinylmethylene (TV, C_1)

7. cis vinylmethylene (CV, C_1)

Figure 1. Structures of possible C_3H_4 isomers. Abbreviation and symmetry of each isomers are given in parentheses.

Å and are global minima. The other four minima belong to singlet *trans*- and *cis*-vinylmethylenes (plus their steroisomers) and are also isoenergetic to each other lying 12 kcal/mol above triplet vinylmethylene. These singlet species also have allylic-like structures with the terminal hydrogen above or below the plane of the three carbon atoms (see **6** and **7** in Figure 1). It is also found that the potential energy barriers for the ring closure reaction to cyclopropene are small (1–5 kcal/mol) implying that singlet vinylmethylenes are thermally unstable. Thus, if these were the intermediates involved in the allene to methylacetylene isomerization, then the ring closure to cyclopropene is also a highly competitive process.

It has been conjectured that the possible mechanism[2e] for the interconversion of allene and methylacetylene would be via vinylmethylene with the ring closure to cyclopropene as a competing reaction. Gas-phase pyrolysis experiments[2e] of cyclopropene indicated that the cyclopropene to methylacetylene conversion to be a faster process, as the experimental activation energies in kcal/mol are shown below. Therefore, the overall rate-deter-

$$\text{allene} \xleftarrow{43.3} \text{cyclopropene} \xrightarrow{37.5} \text{methylacetylene}$$

mining process would be the conversion of vinylmethylene to allene or vice versa. We shall label this path 1 and we have investigated two parts of path 1, the first involves a transition state with a C_1 symmetry (path 1A) and the second with a C_s symmetry (path 1B). the ring closure reaction paths which are designated as path 2A and 2B initiate at *cis*- and *trans*-vinylmethylenes, respectively.

Because propenylidene was found to lie 15 kcal/mol below vinylmethylene,[10] one must consider two possible paths for the cyclopropene to methylacetylene conversion. The most likely one, the lowest energy path, would be via propenylidene

$$\text{cyclopropene} \xrightarrow{\text{path 3}} \text{propenylidene} \xrightarrow{\text{path 4}} \text{methylacetylene}$$

and the other

$$\text{cyclopropene} \xrightarrow{\text{path 2}} \text{vinylmethylene} \xrightarrow{\text{path 5}} \text{methylacetylene}$$

In addition, we also investigated a direct path from allene to methylacetylene (path 6) involving a 1,3-H shift, which was proposed as the reaction mechanism for this interconversion before the cyclopropene involvement was discovered. The paths are labeled in Scheme I.

Another interconversion of interest of the C_3H_4 surface involves cyclopropylidene. This ring-opening reaction to allene has been studied theoretically in connection with the synthesis, structure, and chemical reactivity of allene.[9] We have also studied this path (path 7), and, furthermore, the conversion of cyclopropylidene to cyclopropene (path 8) was investigated in order to gain insight into experimental evidence that photolysis of cyclopropylidene always produces allene but not cyclopropene.[3a]

In this paper we report the details of SCF, MCSCF, and CI calculations on the reaction paths, transition-state structures, potential energy barriers, and activation energies for the interconversions mentioned above and illustrated in Scheme I. The mechanistic details of the various reactions occurring on the C_3H_4 surface are also discussed and summarized. Finally, generalization of the mechanism for pyrolysis of cyclopropene emerged from the present study to methyl-substituted cyclopropene are presented.

Before embarking onto a detailed discussion on the C_3H_4 surface, a few comments on the notation used are pertinent. Structures of possible isomers and intermediates are sketched in Figure 1, where the abbreviation and symmetry of each isomer are given. In the text and tables, the isomers will be referred by a number or by an abbreviation written in capitalized italic letters. A number of points are computed along reaction paths and are listed in tables and discussed in the text. These are labeled by a capitalized italic letter or letters for a particular reaction path followed by a number indicating the particular point on the path. Thus, the points computed along the path 1A listed in Table I are *1A.1* for the first, *1A.2* for the second, etc. Transition states are also labeled by the path name prefixed by TS in capitalized italic letters as *TS1A*, *TS1B*. In addition, acronyms are used to specify a particular ab initio method (e.g., SCF, MCSCF), and these are also capitalized in nonitalicized letters to distinguish them from the computed structures.

II. Computational Procedure

In order to locate transition states, we first selected an appropriate reaction coordinate for each rearrangement, and then a path was determined by optimizing the geometry at selected values of the reaction coordinate with all other geometrical parameters relaxed. When an approximate transition-state structure was located, its structure was refined using the SADDLE POINT program in the GAMESS program system.[13,14] The force constants were also calculated in order to assure that the structure so determined has at the least the necessary conditions for a transition state; that is, all gradients are zero (less than 0.001) and only one vibrational frequency is imaginary.

In the path determinations we used two types of wave functions, MCSCF and SCF. The MCSCF functions were used for those paths that involve vinylmethylene (paths 1, 2, and 5; designated as MCSCF paths). The SCF functions were used for the rest of the paths studied where the transition states were well represented by a single configuration (SCF paths). The 4-31G basis set[15] (431G) was employed for the

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Table I. Geometrical Parameters[a] and Energies for Selected Points on the Lowest Energy Path between Allene and Vinylmethylene (Path 1A)

point state	*1A.1* *AL* $^1A_1$	*1A.2* ^1A	*1A.3* ^1A	*1A.4* *TS1A* ^1A	*1A.5* ^1A	*1A.6* ^1A	*1A.7* *TSCT* ^1A
C1C2	1.302	1.315	1.317	1.317	1.317	1.325	1.327
C2C3	1.302	1.345	1.361	1.385	1.393	1.425	1.454
H1C1	1.077	1.075	1.074	1.075	1.075	1.078	1.076
H2C1	1.077	1.073	1.073	1.074	1.074	1.079	1.074
H3C2		1.231	1.188	1.154	1.142	1.114	1.087
H3C3	1.077	1.387	1.469	1.598	1.640	1.809	2.085
H4C3	1.077	1.089	1.091	1.093	1.094	1.094	1.096
C1C2C3	180.0	169.7	165.2	157.2	154.4	145.0	130.9
H1C1C2	121.0	119.9	119.4	120.0	120.3	120.5	122.2
H2C1C2	121.0	121.4	121.6	121.1	121.0	121.3	120.4
H3C2C3	26.2	65.0	70.0	77.4	79.9	90.0	109.5
H4C3C2	121.0	111.4	109.9	108.1	107.5	109.7	109.4
H1C1C2C3		29.4	13.4	11.0	10.2	7.3	2.9
H2C1C2C3		150.9	166.3	169.1	170.0	172.9	175.0
H3C2C3C1		144.2	163.0	167.5	169.1	172.3	175.2
H4C3C2C1		125.4	109.8	107.1	106.1	103.2	85.5
Total Energies[b] (hartrees)							
SCF(DZP)	0.88887	0.78056	0.78116	0.78373	0.78486	0.78982	0.79454
SDCI(DZP)	0.26704	0.15791	0.15649	0.15621	0.15639	0.15836	0.16065
C(1)	0.93774	0.93736	0.93749	0.93766	0.93773	0.93788	0.93809
SDQCI(DZP)	0.31266	0.20370	0.20195	0.20120	0.20122	0.20273	0.20458
Relative Energies (kcal/mol) with Respect to Methylacetylene							
SDQCI(DZP)	0.7	69.1	70.2	70.7	70.7	69.7	68.6

[a] Bond lengths are in Å and bond angles are in deg. [b] Only fractional parts are given; integer parts are −115 and −116 for SCF and CI, respectively. C(1) is the dominant CI coefficients.

MCSCF paths and the DZP basis set[16] was used in addition to the 431G basis set for the SCF paths. In both cases, few points in the vicinity of the transition state are calculated to study polarization function and correlation energy effect on the transition state and their potential energy barrier heights.

Our best estimates on the potential energy profile of the reaction paths thus determined were obtained by performing CI calculations with the DZP basis set on the selected points on the paths. Interpolation between points yielded our estimates for the transition-state structures and potential energy barrier heights. The CI wave function used for the SCF paths includes all singly and doubly excited configurations with respect to an SCF configuration (SDCI(DZP)). Quadruple excitation corrections were estimated by Davidson's formula[17] (SDQCI(DZP)). For the MCSCF paths multireference CI wave functions (MRCI) were employed, and a description of these and MCSCF functions will be given below. For both cases, the inner atomic shells, the 1s orbitals of three carbons, were frozen, and the corresponding core complement orbitals are excluded from the virtual orbital space.

Calculations using MRCI(DZP) functions, which in fact are based on MCSCF(DZP) functions, did yield a very reasonable potential energy surface for vinylmethylene and also for the ring closure reactions to cyclopropene.[12] The MCSCF functions include all configurations generated by distributing four electrons in the four active orbitals. The active orbitals selected are a σ lone-pair orbital and three π orbitals for the planar carbene structure (see Figure 1). We shall designate this function as MC4 function. For determination of paths 1 and 5 we used an MCSCF function of six electrons in six orbitals (MC6) that is constructed by adding two orbitals to the MC4 function. The added orbitals are bonding and antibonding ones of a C–H bond where a migrating hydrogen is involved. We noticed however that the dominant configurations involve only four orbitals even at the transition-state structures. Therefore, we repeated MC4(DZP) calculations, and the resultant natural orbitals and six CSF's with CI coefficients greater than 0.05 are used in constructing MRCI(DZP) wave functions for paths 1B and 5. We note here that SCF and SDCI functions are used for path 1A because MC6(431G) calculations indicated only one configuration would dominate throughout the path, particularly around the transition state.

MRCI energies were further improved by the empirical formula[12]

$$\text{MRCI*(DZP)} = \text{MRCI(DZP)} - 0.2(1.0 - \text{NORM})$$

where NORM is a sum of the squares of the MC4 CI coefficients of those used for reference configurations in the MRCI wave functions. Thus, the MRCI* energies represent an estimated limit of a MRCI calculation in which all the CSF's in the MC4 function are included as reference configurations. The formula was derived from the results of the investigation, carried out at several points on the vinylmethylene surface, on a convergence pattern for the MRCI energy as a function of NORM by deleting least important configurations one at a time. We found that the formulae most likely gives the limit within 0.2 kcal/mol if NORM is greater than 0.99 (see ref 12 for details).

Our best estimates are SDQCI(DZP) and MRCI*(DZP) potential energy profiles for the SCF and MCSCF paths, respectively. Total energies calculated in these two types of profiles are qualitatively different although the relative energies among the profiles of the same type are expected to be consistent and reasonably accurate. Therefore, in order to get a consistent overall picture of the potential energy surface for C_3H_4, these two potential surfaces are aligned at the trans planar carbene structure determined by the SCF(DZP) wave function.[10] This structure was chosen because it is the most stable conformer of vinylmethylenes in the SDQCI(DZP) approximation, and the energy separation between this structure and methylacetylene should be the most reliable one. SDQCI(DZP) and MRCI*(DZP) energies at this structure are −116.21787 and −116.18573 hartrees, respectively. The MRCI*(DZP) energy for the $^1A_1$ state of methylacetylene resulted from this alignment of the two potential surfaces is −116.28168 hartrees, with respect to which all the MRCI*(DZP) relative energies are evaluated.

The ALCHEM II program[18] was used for the MCSCF and CI calculations in this study.

III. Reaction Paths

In this section results are presented for the reaction paths, 1–8, defined in Scheme I. The energy profiles, transition-state structures and potential energy barriers are presented separately for each of the paths. Subsequently, the zero-point energies for pertinent structures and resultant activation energies are presented and discussed.

A. Allene–Vinylmethylene Interconversion (Path 1). For this interconversion two possible pathways were investigated. Calculated geometrical parameters and energies for selected points on the lowest energy path, path 1A, are listed in Table I, and those for path 1B in which the transition state had been constrained to have a C_s symmetry are given in Table II. For both cases, ∠H3C2C3 is taken to be a reaction coordinate.

The results for path 1A are summarized in Figure 2 where relevant geometrical parameters are also shown. We note first that the transition state (*TS1A* or *1A.4* in Table I) still retains a vinylmethylene-like structure, that is, the migrating hydrogen

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Table II. Geometrical Parameters[a] and Energies for Selected Points on the Path between Allene and Vinylmethylene Constrained to a C_s Symmetry (Path 1B)

point	*1B.1*	*1B.2*	*1B.3* *TS1B*	*1B.4*	*1B.5*	*1B.6*
state	$^1A'$	$^1A'$	$^1A'$	$^1A'$	$^1A'$	$^1A'$
C1C2	1.373	1.393	1.433	1.456	1.460	1.463
C2C3	1.289	1.298	1.319	1.350	1.343	1.333
H1C1	1.073	1.073	1.074	1.070	1.073	1.073
H2C1	1.073	1.073	1.074	1.070	1.073	1.073
H3C2	1.287	1.239	1.169	1.121	1.103	1.068
H3C3	1.514	1.524	1.603	1.755	1.946	2.145
H4C3	1.063	1.066	1.070	1.076	1.075	1.073
C1C2C3	170.0	166.5	155.5	133.8	120.6	106.9
H1C1C2	119.9	119.3	118.5	120.4	119.5	120.0
H2C1C2	119.9	119.3	118.5	120.4	119.5	120.0
H3C2C3	72.0	73.8	80.0	90.0	105.0	126.1
H4C3C2	145.1	142.7	140.7	136.3	134.0	133.4
H1C1C2C3	99.6	102.1	104.8	84.4	78.1	79.0
			Total Energies[b] (hartrees)			
MC6(431G)	0.62317	0.62233	0.62751	0.64497	0.67124	0.68389
MC6((DZP)		0.81997	0.82163	0.83588	0.86232	0.87642
MC4((DZP)	0.79184	0.79215	0.79699	0.81424	0.84270	0.85876
MRCI(DZP)	0.14479	0.14351	0.14250	0.15331	0.18104	0.19907
NORM	0.99964	0.99974	0.99990	0.99988	0.99983	0.99976
MRCI*(DZP)	0.14487	0.14357	0.14252	0.15334	0.18107	0.19912
			Relative Energies (kcal/mol) with Respect to Methylacetylene			
MRCI*(DZP)	85.9	86.7	87.4	80.6	63.2	51.8

[a] Bond lengths are in Å and bond angles are in deg. [b] Only fractional parts are given; integer parts are −115 and −116 for MC6 (or MC4) and CI, respectively. NORM is the sum of the squares of the MC4 CI coefficients of those used as the reference configurations.

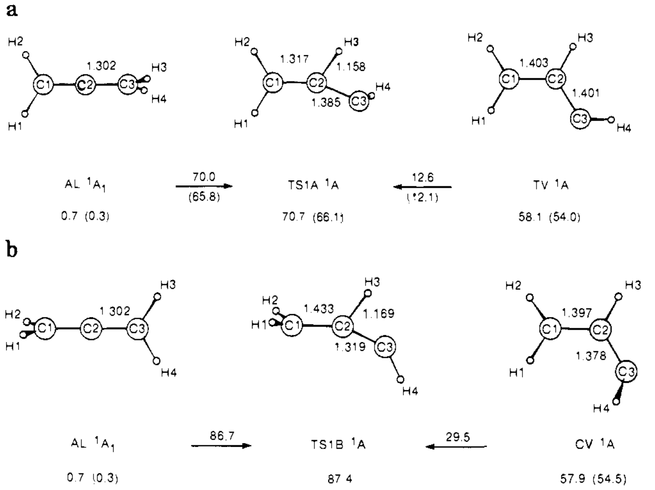

Figure 2. Schematic reaction paths for the allene–vinylmethylene interconversion. The potential energy barriers and relative energies in kcal/mol are given with the corresponding energies with the zero-point energy correction in parentheses: (a) allene–*trans*-vinylmethylene interconversion (path 1A) and (b) allene–*cis*-vinylmethylene interconversion with a C_s symmetry constrain (path 1B).

H3 is still attached to the central carbon C2 (the H3–C2 bond length is 1.158 Å). Consequently, the potential energy barrier is only 12.6 kcal/mol for the vinylmethylene-to-allene conversion. On the other hand, the barrier for the allene-to-vinylmethylene conversion is 70.7 kcal/mol indicating the amount of energy needed not only for the 1,2-H shift over the double bond but also for the internal rotation about the double bond involved. We note also H4 which does not participate in the migration is relatively unperturbed.

The structure of *TS1A* indicates that the H4–C3 bond is slightly trans with respect to the C1–C2 bond. In fact, an SCF(431G) optimization of the geometry starting from structures which are slightly perturbed from that of the corresponding transition state did yield either *trans*-vinylmethylene or the ground-state allene. Therefore, the allene-to-vinylmethylene conversion most likely produce *trans*-vinylmethylene rather than the cis species, as indicated in Figure 2a. However, allene could convert itself to cis vinylmethylene along a reaction path that would go through *TS1A* and the transition state for the cis–trans conversion of vinylmethylene (*TSCT* in Table I), which is indicated as a dashed line in Figure 3. This is a possible path because the energy for *TSCT* is lower than that for *TS1A*, and the structure at ∠H3C2C3 = 90° is quite similar to that of *TSCT*. In particular, when changes in ∠H3C2C3 and ∠H4C3C2C1 are coupled, then we expect a small barrier if any between these points, as shown Figure 3. Thus, it is most likely that *TS1A* is the lowest and the only transition state for the allene–vinylmethylene interconversion.

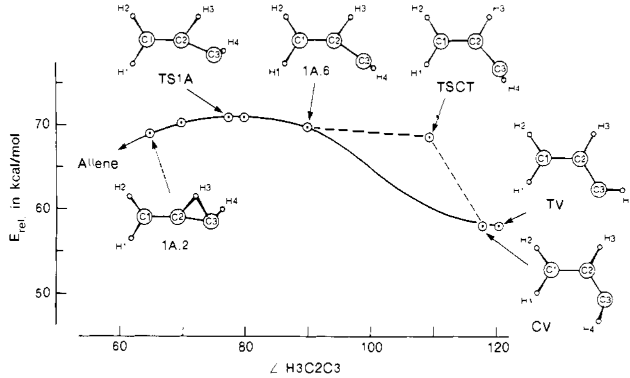

Figure 3. MRCI*(DZP) potential energy profiles for the lowest energy path between vinylmethylene and allene. See Tables I and III for geometrical parameters.

Another path we have investigated is path 1B where the transition state is constrained to have a C_s symmetry. As shown in Figure 2b in which the calculated results are summarized, the transition state (*TS1B*) lies 17 kcal/mol above *TS1A* showing that it is not the lowest energy path. From a geometrical point of view this path appears to be most favorable since no rotation of the CH_2 group is necessary, but the transition state has a bisected diradical structure as shown in Figure 2b (the C1–C2 bond length is 1.433 Å and ∠C1C2C3 is 155.5°). Consequently, not only the 1,2-shift of hydrogen but also the breaking of the C1–C2 double bond are involved resulting in a high barrier for the allene rearrangement to vinylmethylene. When the transition

Table III. Geometrical Parameters[a] and Energies for Isomers and Transition States on the Isomerization Path from Vinylmethylene (*CV*, *TV*) to Methylacetylene (*MA*) via Cyclopropene (*CP*) and Propenylidene (*PD*) (Paths 2, 3, and 4)

point	*2A.1*	*2A.2*	*2B.1*	*2B.2*	*2B.3*	*3.1*	*3.2*	*4A.1*	*4B.1*	*4.2*
	CV	*TS2A*	*TV*	*TS2B*	*CP*	*TS3*	*PD*	*TS4A*	*TS4B*	*MA*
state	^1A	^1A	^1A	^1A	$^1A_1$	$^1A'$	$^1A'$	$^1A'$	$^1A'$	$^1A_1$
C1C2	1.397	1.467	1.403	1.509	1.500	1.474	1.510	1.474	1.867	1.472
C2C3	1.378	1.338	1.401	1.336	1.281	1.320	1.298	1.243	1.245	1.191
H1C1	1.069	1.067	1.071	1.071	1.084	1.077	1.084	1.083	1.078	1.084
H2C1	1.077	1.083	1.071	1.074	1.084	1.077	1.084	1.083	1.078	1.084
H3C2	1.079	1.075	1.078	1.075	1.070	1.061	1.085	1.418	1.067	
H3C3								1.185		1.060
H4C3	1.081	1.074	1.082	1.065	1.070	1.364	2.686			
H4C1						1.472	1.083	1.085	1.087	1.084
C1C2C3	122.9	122.2	121.2	115.0	64.7	85.4	127.2	178.4	64.6	180.0
H1C1C2	120.6	117.9	121.2	118.5	119.7	119.7	110.1	111.4	119.2	110.2
H2C1C2	123.1	119.4	120.1	119.2	119.7	119.7	110.1	111.4	119.2	110.2
H3C2C3	118.0	119.6	120.4	124.6	150.1	136.6	112.5	52.4	175.4	
H4C3C2	120.2	132.5	119.4	139.3	150.1	101.1	52.3			
H4C1C2							111.1	107.0	85.1	110.2
H1C1C2C3	9.1	6.8	1.7	37.2	105.6	101.6	120.2	118.3	71.7	
H2C1C2C3	162.8	143.7	169.5	117.9	105.6	101.6	120.2	118.3	71.7	
H3C2C3C1	167.9	169.2	179.1	176.3	180.0	0.0	0.0	0.0	180.0	
H4C3C2C1	41.9	27.1	146.1	164.6	180.0	0.0	0.0	0.0	180.0	
Total Energies[b] (hartrees)										
SCF(DZP)					0.84946		0.83086	0.81993	0.78789	0.89261
SDCI(DZP)					0.23286		0.20000	0.19797	0.16621	0.26947
C(1)					0.93941		0.93795	0.93790	0.93733	0.93931
SDQCI(DZP)					0.27791		0.24439	0.24346	0.21215	0.31383
MC4(DZP)	0.84769	0.84703	0.84763	0.84295		0.82550				
NORM	0.99828	0.99668	0.99911	0.99851		0.99919				
MRCI(DZP)	0.18907	0.18676	0.18902	0.18127		0.17944				
MRCI*(DZP)	0.18942	0.18742	0.18920	0.18157	(0.24576)	0.17961	(0.21223)	(0.21131)		(0.28168)
Relative Energies (kcal/mol) with Respect to Methylacetylene										
MRCI*(DZP)	57.9	59.2	58.1	62.8	22.6	64.1	43.6	44.2	63.8	0.0

[a] Bond lengths are in Å and bond angles are in deg. [b] Only fractional parts are given; integer parts are −115 and −116 for SCF (or MC4) and CI, respectively. C(1) is the dominant CI coefficients and NORM is the sum of the squares of the MC4 CI coefficients of those used as the reference configurations.

state is reached, it appears to transform itself directly to cyclopropene (see points *1B.5* and *1B.6* in Table II), but a reaction path via *cis*-vinylmethylene is also possible as indicated in Figure 2b, since *cis*-vinylmethylene is located slightly below the cis bisected potential surface. This point will be discussed below in connection with the ring-closure reaction of vinylmethylene.

B. Vinylmethylene–Cyclopropene Interconversion (Path 2). The results for the highly reversible ring-closure mechanisms of vinylmethylene intermediates have been reported in detail.[12] For completeness, we shall present here the salient features. Table III lists the structures and energies for the intermediates and transition states for the ring closure, and Figure 4 summarizes the mechanisms for the reversible ring closure of vinylmethylene to cyclopropene.

For singlet vinylmethylene, allylic-like structures with the terminal hydrogen above or below the plane of the three carbon atoms (stereoisomers) represent local minima for both trans (*TV*) and cis (*CV*) species. Schematic structures are shown in Figure 1, and geometrical parameters for the trans species with H4 below and the cis species with H4 above the plane are given in Table III. The structures with the equivalent C–C bonds indicate stabilization due to a resonance reaction between the carbene (C1–C2 double bond) and diradical (C2–C3 double bond) structures. These stereoisomers interconvert via a planar carbene structure with the potential energy barriers of 1.3 and 2.1 kcal/mol for the cis and trans species, respectively (carbene structures are designated as *CPC* in Figure 5a and *TPC* in Figure 5b). These four minima are isoenergetic lying 35 kcal/mol above the $^1A_1$ state of cyclopropene, but the potential energy barriers for the conversion of cis and trans species to cyclopropene are found to differ significantly, our best estimates being 1.3 and 4.7 kcal/mol, respectively.

The conversions of both *cis*- and *trans*-vinylmethylenes to cyclopropene were found to proceed in two steps. The first step is to reach a bisected diradical structure by bond reorganization and rotation of the CH_2 group. The second step is a downhill process in which the bisected diradical undergoes ring-closure reaction to form cyclopropene with no energy barrier. Therefore, transition states are expected to be located in the first step, and the barrier

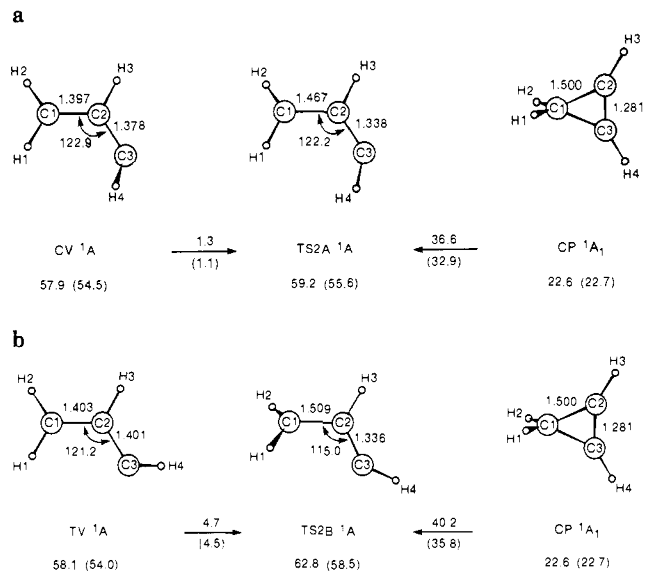

Figure 4. Schematic reaction paths for the vinylmethylene–cyclopropene interconversion. The potential energy barriers and relative energies in kcal/mol are given with the corresponding energies with the zero-point energy correction in parentheses: (a) *cis*-vinylmethylene–cyclopropene interconversion (path 2A) and (b) *trans*-vinylmethylene–cyclopropene interconversion (path 2B).

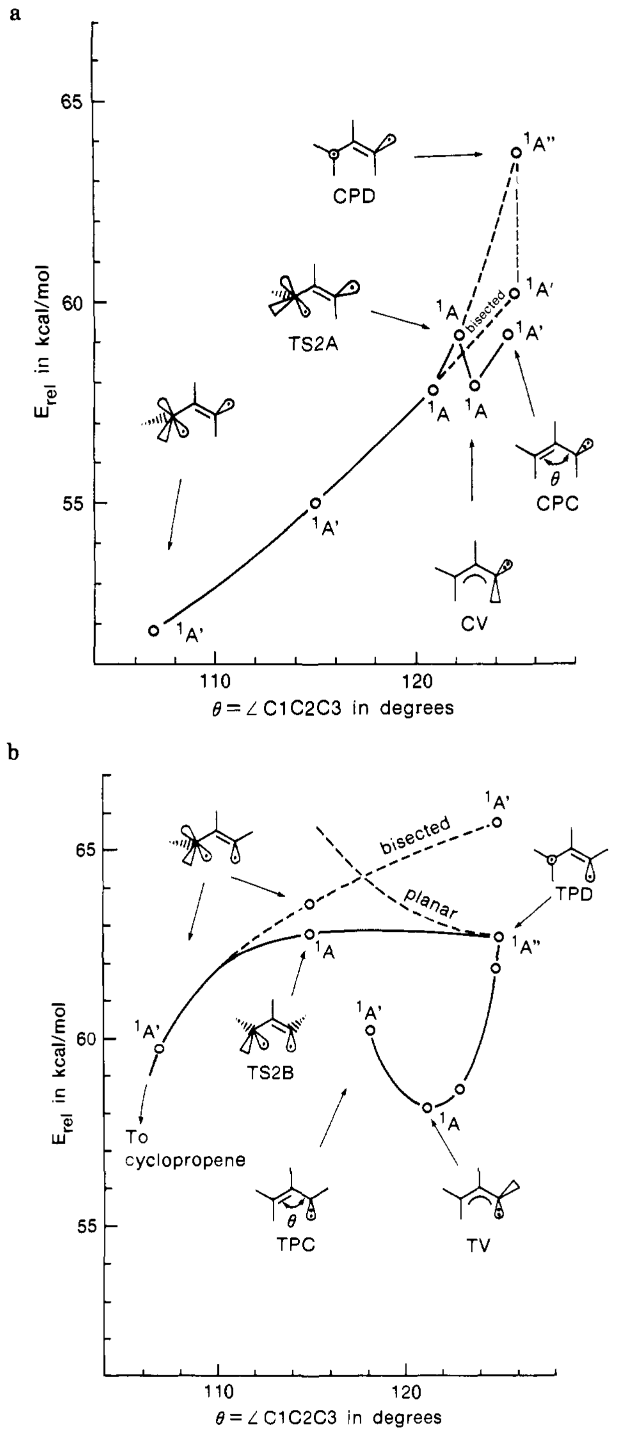

Figure 5. MRCI*(DZP) potential energy profiles for the vinylmethylene–cyclopropene conversion: (a) *cis*-vinylmethylene (CV)–cyclopropene conversion (path 2A) and (b) *trans*-vinylmethylene (TV)–cyclopropene conversion (path 2B). See Table III and ref 12 for geometrical parameters.

heights may depend on the relative positions of the cis and trans bisected potential surfaces with respect to the corresponding local minima. As shown in Figure 5a, the cis bisected potential surface is located very close to the cis stable species, and, consequently, a transition state (*TS2A*) occurs early, and the barrier is low; the transition-state structure is similar to that of *cis*-vinylmethylene except that its electronic structure shows a diradical character indicating formation of the C2–C3 double bond (see Figure 4a). The cis bisected diradical surface was found to merge into the trans surface without any energy barrier around $\angle$C1C2C3 = 80°, indicating *TS2A* is indeed the transition state for the conversion of *cis*-vinylmethylene to cyclopropene. As shown in Figure 5b, the trans bisected surface, on the other hand, is located rather high above the stable structure. Consequently, *trans*-vinylmethylene first transforms to a planar diradical structure indicated as *TPD* in Figure 5b, and the transition state (*TS2B*) is located in the planar to bisected transition, resulting in the relatively high barrier of 4.7 kcal/mol. In addition, the potential energy barrier for a direct cis–trans interconversion by rotation of the C3–H4 bond about the C2–C3 bond was estimated to be about 11 kcal/mol which is higher than those for the conversion to cyclopropene. This suggested that both *cis*- and *trans*-vinylmethylenes should be directly involved as intermediates in the highly reversible ring-opening reaction of cyclopropene with the calculated potential barriers of 36.6 and 40.2 kcal/mol, respectively.

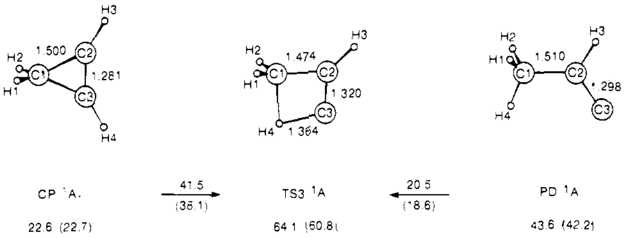

Figure 6. Schematic reaction path for the cyclopropene–propenylidene interconversion. The potential energy barriers and relative energies in kcal/mol are given with the corresponding energies with the zero-point energy correction in parentheses.

We also found a potential energy surface crossing located at 12 kcal/mol above *trans*-vinylmethylene; the excited surface is connected to the singlet excited state of cyclopropene, and the other is the lowest potential surface of vinylmethylene which is connected to the ground state of cyclopropene. This provided a radiationless deexcitation mechanism for cyclopropene and suggested that isomerizations should occur on the ground-state surface of C_3H_4 upon photolysis of cyclopropene. It is known that the photolysis of cyclopropene at 8 K in an argon matrix produces allene and methylacetylene in the ground state.[3a] However, there is, to our knowledge, no experimental data showing that the photoisomerization is occurring on the ground-state surface.

C. Cyclopropene–Propenylidene Interconversion (Path 3). The detailed results for this interconversion have also been reported.[12] We shall present here the main results, which are summarized in Figure 6, and the structure of the transition state is given in Table III. The conversion of cyclopropene to propenylidene involves a synchronous 1,2-hydrogen shift for H4 to C1 occurring with the cleavage of the bond C1C3. This results in a tight transition-state structure (*TS3*) in which H4 is bridging C1 and C3. The potential energy barrier is calculated to be 41.5 kcal/mol which is comparable to those for the ring opening of cyclopropene to vinylmethylene species. However, the potential energy barrier for the reverse reaction is 20.5 kcal/mol indicating that this conversion is not highly reversible. In fact, propenylidene is not a stable isomer, and it converts easily to methylacetylene by a 1,2-hydrogen shift for H3 to C3, as discussed below.

D. Propenylidene-to-Methylacetylene Conversion (Path 4). The reaction path for this conversion was determined by using $\angle$H3C2C3 as the reaction coordinate and SCF(DZP) wave function. The results are summarized in Figure 7. The interesting result is that propenylidene is not a stable isomer in the cyclopropene–methylacetylene rearrangement. The hydrogen migration coupled with linearization of the carbon skeleton essentially requires no energy; the calculated potential energy barrier height is 0.6 kcal/mol. We also note that the transition-state structure *TS4A* is closer to methylacetylene than propenylidene. This can be seen from the fact that $\angle$C1C2C3 is 178.4°, the C1–C2 bond length is unchanged, and the migrating hydrogen H3 is already attached to C3 (H3–C3 and H3–C2 bond lengths are 1.185 and 1.418 Å, respectively; see Figure 7a and Table III).

It is instructive to compare the propenylidene–methylacetylene conversion with the vinylidene–acetylene conversion, which should provide some information on the substitution effect. Since propenylidene is a singly substituted vinylidene, the transition-state

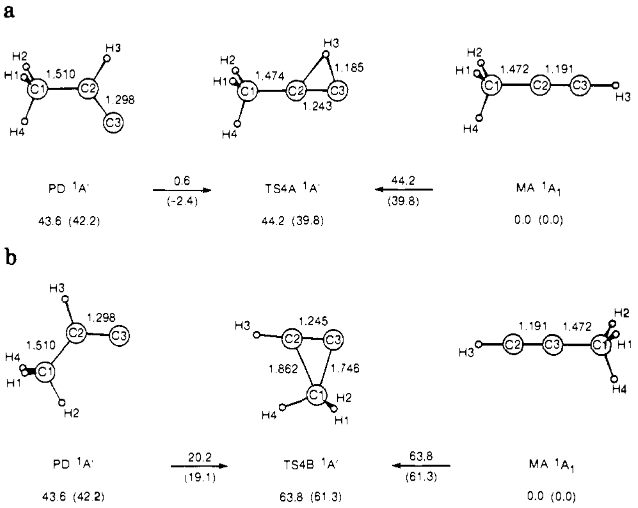

Figure 7. Schematic reaction paths for the propenylidene–methylacetylene interconversion. The potential energy barriers and relative energies in kcal/mol are given with the corresponding energies with the zero-point energy correction in parentheses: (a) path with a 1,2-H migration (path 4A) and (b) path with a 1,2-CH$_3$ migration (path 4B).

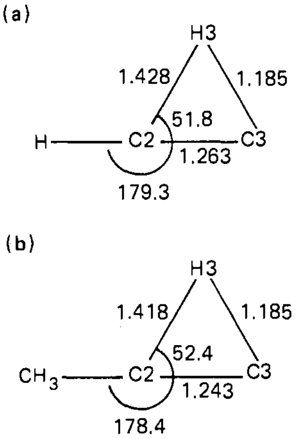

Figure 8. Comparison of transition-state structures, bond lengths in Å and angles in deg: (a) vinylidene-to-acetylene conversion and (b) propenylidene-to-methylacetylene conversion.

Table IV. Comparison of the Relative Potential Energies in kcal/mol for Acetylene and Methylacetylene Systems

substituent	H[a]	CH$_3$
acetylene	0	0
transition state	46.7	44.2
vinylidene	39.6	43.6

[a] Taken from ref 19.

structure and the barrier heights are expected to be similar. Indeed, the transition-state structures for these conversions are very similar, as compared in Figure 8, where the previous results for the vinylidene–acetylene conversion reported by Osamura et al.[19] are used. The geometries of the active sites are almost identical, the largest difference being 0.02 Å for the C–C bond length. The hydrogen atom or the methyl group that does not participate in the reaction is unperturbed and acts as a spectator. There are few kcal/mol differences in the relative energies as shown in Table IV. The substitution effect is to decrease the energy of the transition state by 2.5 kcal/mol, while the energy of substituted vinylidene (propenylidene) is increased by 4 kcal/mol. The important point is that the methyl substitution did not increase the activation energy for the methylacetylene-to-propenylidene conversion.

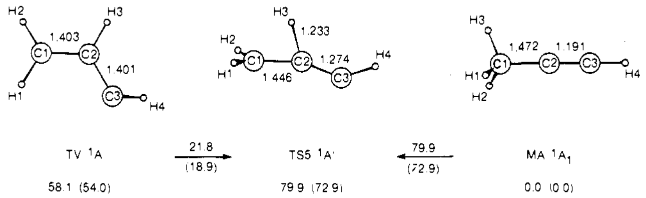

Figure 9. Schematic reaction path for the *trans*-vinylmethylene–methylacetylene interconversion. The potential energy barriers and relative energies in kcal/mol are given with the corresponding energies with the zero-point energy correction in parentheses.

We also studied the CH$_3$ migration instead of hydrogen. The results are summarized in Figure 7b, and the transition-state structure (*TS4B*) is given in Table III. In this case the potential energy barrier for the propenylidene–methylacetylene conversion is calculated to be 20.2 kcal/mol, which is about the same as that for the conversion to cyclopropene (20.5 kcal/mol). We note that in this reaction mechanism shown in Figure 7b, H3 acts as a spectator during the entire reaction. Therefore, replacing it by a methyl group may not alter the mechanism appreciably. Thus, dimethylvinylidene should be stable by about 20 kcal/mol against rearrangements to both dimethylacetylene and methylcyclopropene. We shall discuss this point more fully later on when we consider generalization of the mechanisms obtained in the present study to larger systems. We also note that the methyl group is in a staggered conformation with respect to the H3–C2 bond for propenylidene, while it is in an eclipsed conformation for the transition state. Since these conformations are lowest in energy, the reaction is a concerted one in which the methyl group migration is accompanied by its rotation around the C1–C2 bond to reach the transition state.

E. Vinylmethylene-to-Methylacetylene Conversion (Path 5). An indirect reaction pathway via cyclopropene and propenylidene for this arrangement has been discussed in previous sections. In this section we present results for a direct pathway (path 5) which turned out to be more energy demanding than the indirect pathway. The reaction coordinate for this path is assumed to be $\angle$H3C2C1, and the path was determined by the MC6(431G) function. The geometrical parameters and energies for the selected points on this path are listed in Table V and summarized in Figure 9.

This conversion proceeds as follows. First, *trans*-vinylmethylene which has a resonance structure transforms to a bisected species (see *5.1* in Table V) by a rotation of the CH$_2$ group, and then a hydrogen migration takes place. A transition state (*TS5*) is reached when the reaction coordinate becomes 74.4°. *TS5* still retains the bisected diradical structure with the H3–C2 bond length of 1.233 Å. Thereafter, it is a downhill process where the hydrogen migration and linearization of the carbon skeleton continue until the methylacetylene structure is reached.

The geometry of *TS5* indicates a trans conformation, which does transform to *trans*-vinylmethylene. We have located another transition state which has a cis conformation. However, it lies 5 kcal/mol above *TS5*. Considering that the barrier for the cis–trans conversion for vinylmethylene is 11 kcal/mol which is less than that of 21.8 kcal/mol for the conversion to methylacetylene via *TS5*, it is most likely that the conversion of *cis*-vinylmethylene also proceeds via *TS5* by first converting to trans species. We mention here that these two are only low-lying transition states and we could not find any low-lying transition states in C_1 symmetry such as *TS1A* which we found for the vinylmethylene-to-allene conversion mentioned in section A. Thus, the relative energy of 79.9 kcal/mol for *TS5* implies that the vinylmethylene–methylacetylene conversion must proceed via cyclopropene and propenylidene.

F. Direct Path between Allene and Methylacetylene (Path 6). A concerted mechanism for the allene-to-methylacetylene thermal isomerization has been proposed,[2c] which assumes a 1,3-hydrogen shift and a four-center transition-state structure. Because the

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(18) Lengsfield III, B. H. *J. Chem. Phys.* **1980**, *73*, 382. Lengsfield, B. H.; Liu, B. *Ibid.* **1981**, *75*, 478. Liu, B.; Yoshimine, M. *Ibid.* **1981**, *74*, 612.

(19) Osamura, Y.; Schaefer III, F. H.; Gray, S. K.; Miller, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 1904.

Table V. Geometrical Parameters[a] and Energies for Selected Points on the Direct Path between Vinylmethylene and Methylacetylene Constrained to the C_s Symmetry (Path 5)

point	*5.1*	*5.2*	*5.3*	*5.4* *TS5*	*5.5*
state	$^1A'$	$^1A'$	$^1A'$	$^1A'$	$^1A'$
C1C2	1.480	1.489	1.463	1.446	1.401
C2C3	1.331	1.330	1.283	1.274	1.214
H1C1	1.073	1.074	1.071	1.070	1.070
H3C1		1.849	1.664	1.629	1.651
H3C2	1.106	1.095	1.188	1.233	1.821
H4C3	1.070	1.069	1.065	1.063	1.051
C1C2C3	125.9	144.0	155.3	158.5	175.8
H1C1C2	120.0	116.9	118.5	119.5	119.5
H3C2C3	116.5	90.0	77.0	74.4	60.0
H4C3C2	131.6	132.2	136.3	138.5	176.9
H1C1C2C3	99.0	107.6	101.3	96.2	79.2
		Total Energies[b] (hartrees)			
MC6(431G)	0.67099	0.65905	0.63958	0.63859	0.68688
MC4((DZP)	0.84026	0.82354	0.80618	0.80293	0.83362
MRCI(DZP)	0.17688	0.16437	0.15540	0.15422	0.17528
NORM	0.99992	0.99977	0.99927	0.99902	0.99928
MRCI*(DZP)	0.17690	0.16442	0.15555	0.15441	0.17542
		Relative Energies (kcal/mol) with Respect to Methylacetylene			
MRCI*(DZP)	65.8	73.6	79.2	79.9	66.7

[a] Bond lengths are in Å and bond angles are in deg. [b] Only fractional parts are given; integer parts are −115 and −116 for SCF (or MC4) and CI, respectively. NORM is the sum of the squares of the MC4 CI coefficients of those used as the reference configurations.

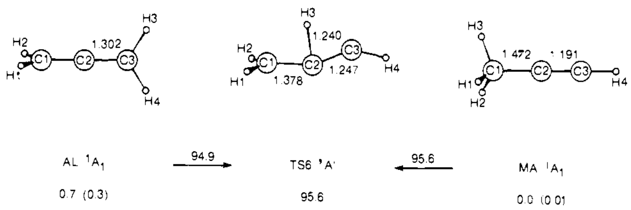


Figure 10. Schematic reaction path for the allene–methylacetylene interconversions. The potential energy barriers and relative energies in kcal/mol are given with the corresponding energies with the zero-point energy correction in parentheses.

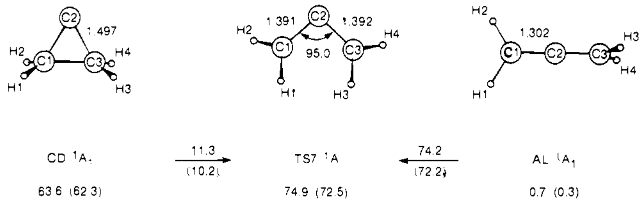


Figure 11. Schematic reaction path for the allene–cyclopropylidene interconversion. The potential energy barriers and relative energies in kcal/mol are given with the corresponding energies with the zero-point energy correction in parentheses.

involvement of cyclopropene in this isomerization has been established,[2e] this mechanism is no longer in favor. Nevertheless, it would be of interest to know how high the potential energy barrier would be if this particular reaction path exists. Our calculation with SCF(DZP) wave functions assuming ∠H3C2C3 as a reaction coordinate did locate an extremum which has characteristics of a transition state, namely, all gradients are zero and it has one negative force constant. The transition state (*TS6*) has a four-center structure as shown in Figure 10 and Table VI; but its energy is quite high, 95 kcal/mol above allene. Thus, it is a possible path, but not a lowest energy path.

However, we believe that this four-center transition state does not exist in the ground-state C_3H_4 surface. In fact, that *TS6* is an artifact due to the use of a closed-shell SCF wave function can be seen from the following observations. We note first that the *TS6* geometry is similar to that of a bisected diradical which has an open-shell electronic structure. Secondly, the potential surface for diradical species (for example, path 1B and 5) lies well below it. If an MCSCF wave function which included open-shell electronic configurations is employed with the C_s symmetry constraint, then its energy will be lower, and optimization of this path would eventually produce a path which was composed of path 1B and path 5. Therefore, this concerted isomerization path does not exist on the ground-state potential surface of C_3H_4.

G. Cyclopropylidene-to-Allene Conversion (Path 7). The reaction path was determined by the SCF(DZP) wave function using ∠C1C2C3 as the reaction coordinate. The detailed results for the path are given in Table VI, and the reaction is summarized in Figure 11. The SDQCI(DZP) potential energy profile is also depicted in Figure 12.

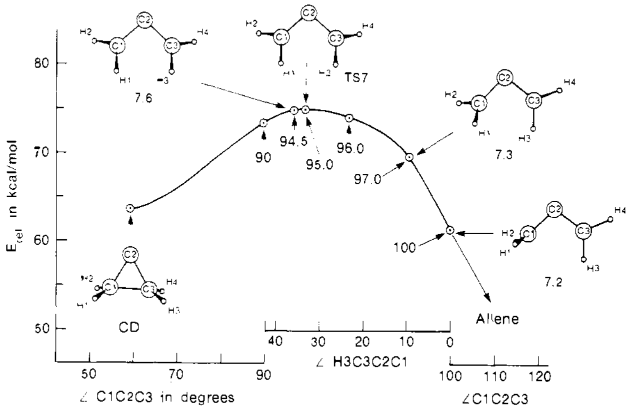


Figure 12. MRCI*(DZP) potential energy profiles for the lowest energy path between cyclopropylidene and allene. See Table VI for geometrical parameters.

The cyclopropylidene-to-allene rearrangement proceeds as follows. As the ring opens, the CH_2 groups go through a disrotatory motion keeping a C_s symmetry until the ring opens to 94.5° and the CH_2 groups have rotated about 30° along the C1–C2 and C2–C3 bonds. At this point, a conrotatory motion of the CH_2 groups commences thereby destroying the C_s symmetry. This conrotatory motion continues until the ring opens to about 100°, and a bent twisted allene structure is reached (see Figure 12). A transition state (*TS7*) is located at ∠C1C2C3 = 95° and very close to the onset of conrotatory motion. Although we used ∠C1C2C3 as the reaction coordinate, a proper one around *TS7* may be a combination of ∠C1C2C3 and the rotation angle for the conrotatory motion. This can be seen from the fact that the change in energy is relatively large for a small change of 5° in

Table VI. Geometrical Parameters[a] and Energies for Selected Points on the Direct Path between Methylacetylene and Allene (Path 6) and Paths between Allene and Cyclopropylidene (Path 7), and between Cyclopropylidene and Cyclopropene (Path 8)

point	*6.1*	*6.2*	*7.1*	*7.2*	*7.3*	*7.4*	*7.5*	*7.6*	*7.7*	*7.8*	*8.1*	*8.2*
	MA	*TS6*	*AL*				*TS7*			*CD*	*TS8*	*CP*
state	$^1A_1$	^1A	$^1A_1$	^1A	^1A	^1A	^1A	^1A	^1A	$^1A_1$	^1A	$^1A_1$
C1C2	1.472	1.378	1.302	1.368	1.379	1.387	1.391	1.391	1.395	1.497	1.567	1.500
C2C3	1.191	1.247	1.302	1.364	1.386	1.392	1.392	1.391	1.395	1.497	1.363	1.281
C1C3				2.093	2.071	2.064	2.052	2.043	1.971	1.483	1.454	1.500
H1C1	1.084	1.075	1.077	1.084	1.084	1.085	1.086	1.087	1.084	1.079	1.076	1.084
H2C1	1.084	1.075	1.077	1.084	1.084	1.083	1.082	1.082	1.082	1.079	1.078	1.084
H3C1	1.084	1.656										
H3C2		1.240								2.194	1.245	1.070
H3C3		1.532	1.077	1.080	1.085	1.085	1.086	1.087	1.084	1.079	1.322	2.272
H4C3	1.060	1.067	1.077	1.085	1.083	1.083	1.082	1.082	1.082	1.079	1.075	1.070
C1C2C3	180.0	154.3	180.0	100.0	97.0	96.0	95.0	94.5	90.0	59.4	59.0	64.7
H1C1C2	110.2	119.5	121.0	122.3	124.5	125.6	126.1	126.0	126.7	115.9	111.7	119.7
H2C1C2	110.2	119.5	121.0	122.1	120.7	119.8	119.6	119.5	118.9	115.9	123.5	119.7
H3C2C3		76.0								26.3	60.7	150.1
H3C3C2			121.0	126.4	126.4	126.2	125.9	126.0	126.7	115.9		
H4C3C2	180.0	146.7	121.0	120.6	120.1	119.7	119.7	119.5	118.9	115.9	145.0	150.1
H1C1C2C3		96.3		91.8	57.4	44.2	36.1	35.7	42.0	111.0	108.5	105.6
H2C1C2C3		97.6		96.2	125.9	134.3	139.3	140.0	134.5	111.0	107.1	105.6
H3C3C2C1		0.2		0.1	9.3	23.1	33.3	35.7	42.0	111.0	116.3	180.0
H4C3C2C1		179.4		179.6	163.0	149.6	141.3	140.0	134.5	111.0	177.8	180.0
	Total Energies[b] (hartrees)											
SCF(DZP)	0.89261	0.71838	0.88887	0.77724	0.77153	0.77140	0.77178	0.77192	0.77323	0.79591	0.75529	0.84946
SDCI(DZP)	0.26947	0.11110	0.26704	0.16530	0.15391	0.14913	0.14836	0.14855	0.15059	0.16867	0.13986	0.23286
C(1)	0.93931	0.93359	0.93774	0.93220	0.93383	0.93591	0.93672	0.93678	0.93699	0.93925	0.93827	0.93941
SDQCI(DZP)	0.31383	0.16153	0.31266	0.21613	0.20284	0.19599	0.19452	0.19467	0.19665	0.21258	0.18587	0.27791
	Relative Energies (kcal/mol) with Respect to Methylacetylene											
SDQCI(DZP)	0.0	95.6	0.7	61.3	69.7	74.0	74.9	74.8	73.6	63.6	80.3	22.6

[a] Bond lengths are in Å and bond angles are in deg. [b] Only fractional parts are given; integer parts are −115 and −116 for SCF (or MC4) and CI, respectively. C(1) is the dominant CI coefficients.

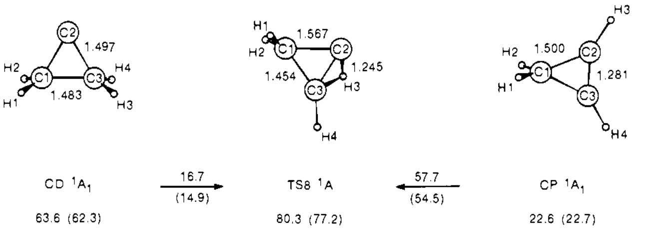


Figure 13. Schematic reaction path for the cyclopropylidene–cyclopropene interconversion. The potential energy barriers and relative energies in kcal/mol are given with the corresponding energies with the zero-point energy correction in parentheses.

∠C1C2C3. In Figure 12 the energy profile for this part is given as a function of the dihedral angle between planes of (H3C3C2) and (C3C2C1).

The potential energy barrier for the cyclopropylidene-to-allene rearrangement is calculated to be 11.3 kcal/mol, while that for the reverse reaction is 74.2 kcal/mol. We note that *TS7* lies 4.5 kcal/mol above that for the allene-to-vinylmethylene rearrangement. We also note that our reaction path is essentially the same as that obtained by a SCF(431G) study of Pasto et al.[9c] But the barrier height for the ring opening is reduced from 18 to 11.3 kcal/mol.

H. Cyclopropylidene-to-Cyclopropene Conversion (Path 8). ∠H3C2C3 was used as the reaction coordinate for determination of the reaction path for the 1,3-hydrogen shift of cyclopropylidene to produce cyclopropene. SCF(DZP) calculations yielded a very tight transition-state structure (*TS8*, as shown in Figure 13 and Table VI), where the migrating hydrogen H3 is out the plane and midway between C3 and C2, while the nonmigrating hydrogen is already in the plane of the carbon skeleton. We note that although the C1–C2 bond is lengthened by 0.07 Å at the transition-state structure, no C–C bonds were broken on the entire reaction path. Thus, this reaction appears to proceed by simply rotating one of the CH_2 groups around the C1–C3 bond without ring opening. This indicates that this reaction does not go through a vinylmethylene structure.

The potential energy barrier was calculated to be 16.7 kcal/mol for this conversion which is 5.4 kcal/mol higher than that for cyclopropylidene-to-allene conversion. Thus, this implies that an indirect path via allene is less energy demanding than this direct path since the barrier for the conversion of allene to cyclopropene is lower than that to cyclopropylidene as mentioned in the previous section.

I. Activation Energies. In order to compare with the experimental activation energy (E_a), the potential energy barriers we have calculated must be modified by corrections for zero-point energy. For this purpose we calculated the harmonic vibrational frequencies for all of the isomers, intermediates, and pertinent transition states, using the SCF(431G) wave functions except for vinylmethylenes (*CV* and *TV* structures) and transition states, *TS2A*, *TS2B*, and *TS5*, where the MC4(431G) wave functions were employed. To be consistent, the SCF(431G) calculations were carried out at the geometries optimized by the SCF(431G) wave functions (these are slightly different from those given in the tables), and the MC4(431G) force constants were calculated at those geometries given in this paper.

The calculated zero-point energies (E_z), estimated as a half of the sum of harmonic vibrational frequencies (imaginary frequencies are left out), are listed in Table VII together with the relative energies with and without the zero-point energy corrections (E_{r0} and E_{re}). We note that the zero-point energies for the isomers and intermediates are in general a few kcal/mol larger than those for the transition states, as expected. It is of interest to note that the zero-point energies for the carbenes are about 1.5 kcal/mol less than those for the stable isomers, which are about 38 kcal/mol. Those for vinylmethylene with a resonance structure are about 2 kcal/mol less than those for other carbenes.

Zero-point corrections on potential energy barriers for the important reactions are given in Table VIII, together with potential energy barriers and activation energies. As expected, the effect of the zero-point energy corrections is to lower the energy barriers. The energy lowerings are quite significant ranging from 0.2 to 7 kcal/mol. In fact, with the zero-point energy correction propenylidene is no longer an intermediate, and the 1,2-hydrogen shift to produce methylacetylene requires no energy.

The calculated activation energies for the cyclopropene conversion to methylacetylene and allene are 38.1 and 43.4 kcal/mol, respectively, which are in excellent agreement with the experi-

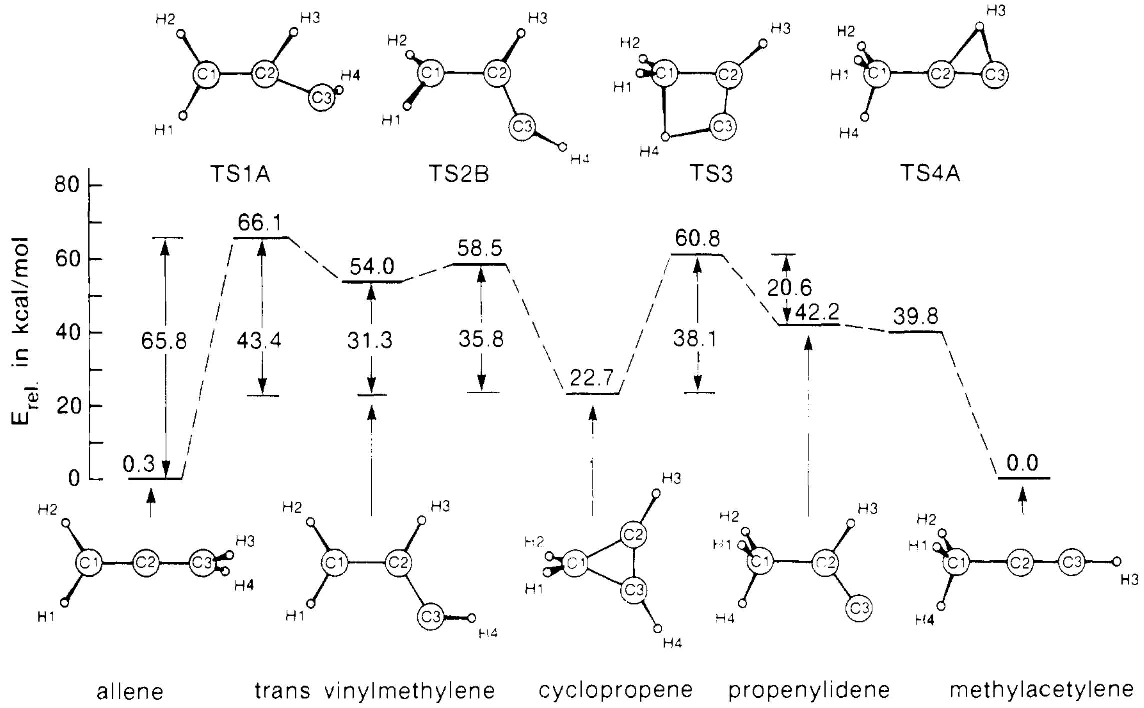


Figure 14. Summary of the reaction mechanism for the allene–methylacetylene interconversion.

Table VII. Zero-Point Energies (E_z) and Relative Energies without and with the Zero-Point Energy Corrections (E_{re} and E_{r0}) in kcal/mol for Isomers and Transition States

isomers or trans. state	E_z	E_{re}	E_{r0}
methylacetylene (MA)	38.1	0.0	0.0
allene (AL)	37.7	0.7	0.3
cyclopropene (CP)	38.2	22.6	22.7
propenylidene (PD)	36.7	43.6	42.2
cis-vinylmethylene (CV)	34.7	57.9	54.5
trans-vinylmethylene (TV)	34.0	58.1	54.0
cyclopropylidene (CD)	36.8	63.6	62.3
TS1A (AL-TV)	33.5	70.7	66.1
TS2A (CV-CP)	34.5	59.2	55.6
TS2B (TV-CP)	33.8	62.8	58.5
TS3 (CP-PD)	34.8	64.1	60.8
TS4A (PD-MA)	33.7	44.2	39.8
TS4B (PD-MA)	35.6	63.8	61.3
TS5 (TV-MA)	31.1	79.9	72.9
TS7 (AL-CD)	35.7	74.9	72.5
TS8 (CD-CP)	35.0	80.3	77.2

Table VIII. Potential Energy Barriers (E_p), Zero-Point Energy Corrections (ΔE_z), and Activation Energy (E_a) in kcal/mol for Various Thermal Isomerization Reactions on the C_3H_4 Surface

	reaction	path	E_p	ΔE_z	E_a	remarks
1	AL → CP	(1A,2B)	70.0	4.2	65.8	(63.8)[a]
	CP → AL	(2B,1A)	48.1	4.7	43.4	(43.3)[a]
2	CP → MA	(3,4A)	41.5	3.4	38.1	(37.5)[a]
	MA → CP	(4A,3)	64.1	3.3	60.8	
3	AL → TV	(1A)	70.0	4.2	65.8	
	TV → AL	(1A)	12.6	0.5	12.1	
4	AL → CV	(1A)	70.0	4.2	65.8	
	CV → AL	(1A)	12.8	1.2	11.6	
5	CV → CP	(2A)	1.3	0.2	1.1	
	CP → CV	(2A)	36.6	3.7	32.9	
6	TV → CP	(2B)	4.7	0.2	4.5	
	CP → TV	(2B)	40.2	4.4	35.8	
7	PD → CP	(3)	20.5	1.9	18.6	
	CP → PD	(3)	41.5	3.4	38.1	
8	PD → MA	(4A)	0.6	3.0	−2.4	H migration
	MA → PD	(4A)	44.2	4.4	39.8	
9	PD → MA	(4B)	20.2	1.1	19.1	CH_3 migration
	MA → PD	(4B)	63.8	2.5	61.3	
10	TV → MA	(5)	21.8	2.9	18.9	
	MA → TV	(5)	79.9	7.0	72.9	
11	CD → AL	(7)	11.3	1.1	10.2	
	AL → CD	(7)	74.2	2.0	72.2	
12	CD → CP	(8)	16.7	1.8	14.9	
	CP → CD	(8)	57.7	3.2	54.5	

[a] Experimental values taken from ref 2e.

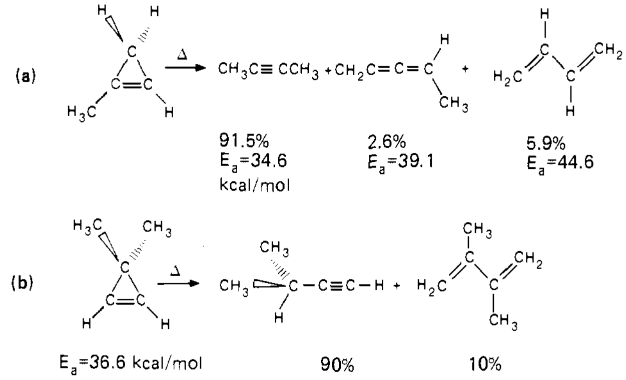
mental values of 37.5 and 43.3 kcal/mol reported by Hopf et al.[2f] The calculated activation energy for the allene-to-cyclopropene isomerization is 65.8 kcal/mol, while the experiment gives 63.8 kcal/mol[2f] for it. This difference of 2 kcal/mol is most likely due to the error in the relative energy calculations. Our relative energy between allene and cyclopropene is 22.7 kcal/mol while thermochemical data gives 20.4 kcal/mol for it.

The almost exact agreement of the calculated activation energies with the observed values may be fortuitous, but it does give a strong support for the reliability of the reaction paths we have determined. In particular, the lowest energy reaction path for the cyclopropene to methylacetylene conversion which proceeds via propenylidene is most likely correct though it is rather complicated and differs from the one normally assumed (via vinylmethylene). We shall see in the next section that the isomerizations occurring on not only the simple C_3H_4 surface but also some methyl-substituted systems could be explained by this mechanism.

IV. Mechanisms for Thermal Isomerization

The calculated minimum energy path for the reversible thermal isomerization of allene to methylacetylene is summarized in Figure 14. According to our results, this isomerization process consists of four steps. In the first step allene rearranges itself to the intermediate, vinylmethylene (preferably to the *TV* structure), by the 1,2-hydrogen shift via the transition state, *TS1A*. The second step is a highly reversible ring-closure process of vinylmethylene to reach cyclopropene via the transition state, *TS2B*. The third step is ring opening of cyclopropene coupled with the 1,2-hydrogen migration to reach propenylidene via *TS3*. The fourth step is transformation of propenylidene to methylacetylene by the 1,2-hydrogen shift via *TS4A* without any energy barrier. The rate-determining step is the first, the 1,2-H shift of allene to reach vinylmethylene. The calculated activation energy for this isomerization is 65.8 kcal/mol which is in good agreement with the experimental values of 60.5[2c] and 63.8[2d] kcal/mol. Thus, this is a direct confirmation of the experimental evidence obtained by Hopl, Priebe, and Walsh[2f] which suggested that cyclopropene

Scheme II



is the intermediate in the reversible thermal isomerization of allene and methylacetylene.

Figure 14 also provides a mechanism for pyrolysis of cyclopropene which produces mostly methylacetylene and a small amount of allene. The calculated activation energies in kcal/mol for this pyrolysis are in excellent agreement with the experimental values (in parentheses) reported by Bailey et al.[2e] as shown below

$$AL \xleftarrow{43.4\ (43.3)} CP \xrightarrow{38.1\ (37.5)} MA$$

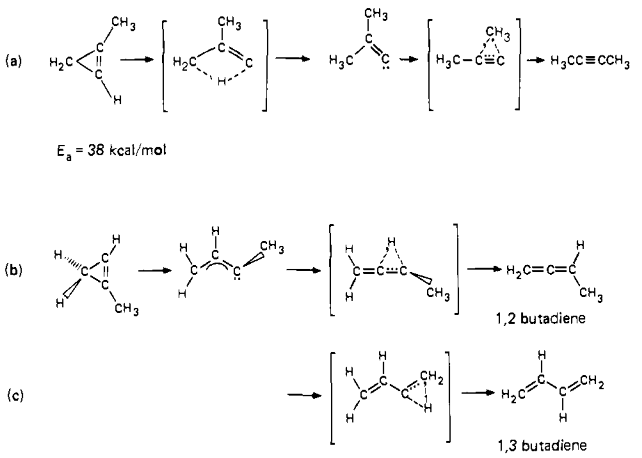
This implies that the isomerization of cyclopropene to allene is via vinylmethylene but to methylacetylene is via propenylidene, which involves two 1,2-hydrogen shifts. Thus, vinylmethylene is not a common intermediate in the pyrolysis of cyclopropene, in which methylacetylene is a dominant product. If vinylmethylene is a common intermediate, which has been generally assumed, then methylacetylene could not be a dominant product as our results indicate

$$AL \xleftarrow{12.1} TV \xrightarrow{18.9} MA$$

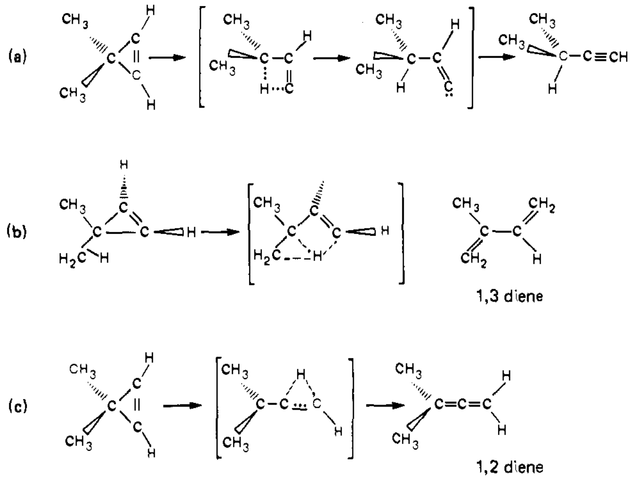
Although we indicated *trans*-vinylmethylene as the preferred intermediate, *cis*-vinylmethylene may also be involved with similar activation energies. Thus, we have shown that for unsubstituted cyclopropene the conversion to methylacetylene must proceed via propenylidene. Because of the complexity of the reaction mechanisms proposed above, in particular that for the pyrolysis of cyclopropene, generalization to larger systems may be questioned. However, generalization to certain substituted cyclopropenes is possible, and, to prove this point, we shall examine pyrolysis of methyl-substituted cyclopropenes.

Before discussing the generalization, we shall state the following observations on the reaction paths obtained in this study. In the allene-to-vinylmethylene path shown in Figure 2a, H4 which does not participate in the migration is essentially a spectator,[20] and, thus, the activation energy would be the same if H4 is replaced by a substituent R such as a methyl group. Similarly, H3 in the cyclopropene-to-propenylidene path shown in Figure 6 is also a spectator and can be replaced by R without changing the activation energy. For the propenylidene-to-methylacetylene conversion, we determined two possible paths: one with the hydrogen migration and another with the methyl group migration, shown in Figures 7a and 7b, respectively. In these two cases, we also notice that either hydrogen or the methyl group is a spectator. Thus, the substitution may not change the activation energies appreciably.

Scheme III



Scheme IV



The thermal isomerization of methyl-substituted cyclopropenes has been extensively studied.[4] Of these, singly and doubly substituted cyclopropenes are of interest since upon thermolysis over 90% of products are the corresponding methylacetylene (alkyne) for both cases; experimental data[4] on products, activation energies, and yields are given in Scheme II. On the basis of the present study we propose reaction mechanisms shown in Scheme III for pyrolysis of 1-methylcyclopropene. The alkyne formation proceeds in two steps via dimethylvinylidene. In the first step the methyl group is essentially a spectator, and the transition-state structure and activation energy are expected to be similar to those for the C_3H_4 case. The methyl migration in the second step is similar to that of the path 4B (see Figure 7b), and the activation energy was estimated to be about 19.1 kcal/mol which is about the same as that of 18.6 kcal/mol for the 1,3-hydrogen migration to produce cyclopropene (see Figure 7a). If we assume that the activation energies do not change by the methyl substitution, then we will find that dimethylvinylidene is a stable intermediate and the activation energy for the 1-methylcyclopropene-to-dimethylacetylene conversion should be about 38 kcal/mol which is in good agreement with the experimental value of 34.6 ± 0.7 kcal/mol.[21] The diene formation should proceed via vinylmethylene species as shown in Scheme III. The geometrical circumstances are quite similar for the 1,2-hydrogen migrations to produce the 1,2-butadiene or the 1,3-butadiene and are analogous to the vinylmethylene-to-allene conversion, which is the rate-determining step. Thus, our estimate for the activation energy is 43 kcal/mol for both cases, which is in good agreement with the observed values of 39.1 ± 5.6[21] and 44.6 ± 2.5[21] kcal/mol for formation of the 1,3- and 1,2-butadiene, respectively.

In a similar fashion we may explain the isomerization of dimethylcyclopropene as shown in Scheme IV. The alkyne formation proceeds via a substituted vinylidene which is expected to be unstable (see Scheme IVa). The rate-determining step is

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[20] An atom or a group of atoms will be called a spectator if it is not directly involved in a reaction and if its geometrical relationship within the group and with respect to the rest of the molecular frame change little during the reaction. For example, in the reaction depicted in Figure 2a, the H4–C3 bond lengths are 1.077, 1.093, and 1.081 Å and the H4C3C2 bond angles are 121, 110, and 120° for allene, TS1A, and *trans*-vinylmethylene, respectively. Note that the H1C1H2 group is also a spectator in the reaction.

[21] Srinivasan, R. *J. Am. Chem. Soc.* **1969**, *91*, 6250.

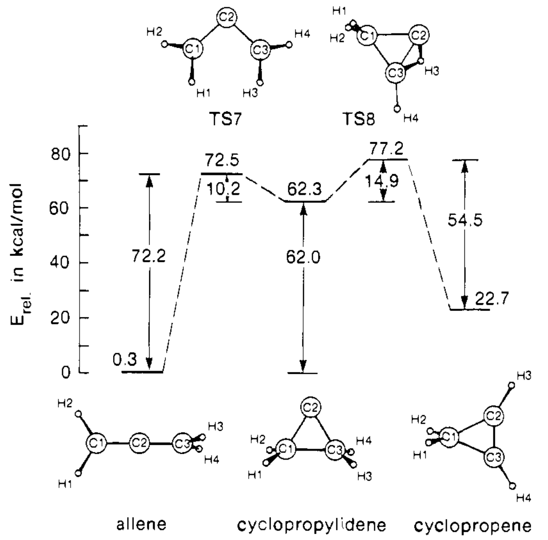

Figure 15. Summary of the reaction mechanism for the cyclopropylidene-to-allene and -to-cyclopropene conversions.

therefore the first step, and the activation energy is estimated to be 38 kcal/mol, which is in good agreement with the experimental value of 36.6 ± 0.85 kcal/mol.[22] However, the only other product is a 1,3-diene, and its formation appears not to go through a vinylmethylene species as an intermediate. As Srinivasan[22] pointed out, the most likely path may involve a concerted reaction in which a 1,3-hydrogen migration accompanied by ring opening and rotation along the single C–C bond as indicated in Scheme IVb. We believe that this is less energy demanding than another possible path involving a ring opening followed by a 1,4-hydrogen migration. Furthermore, if the latter is the path, then a 1,2-diene (allene) should be produced rather than a 1,3-diene since the 1,2-diene can be formed by a 1,2-hydrogen shift from a vinylmethylene intermediate. In fact, since no 1,2-diene is produced, the reaction path to the 1,2-diene most likely involves a bisected transition state with a high barrier as indicated in Scheme IVc; the barrier is 66 kcal/mol for unsubstituted cyclopropene. This is conceivable because the barrier for the internal rotation of the $C(CH_3)_2$ group may be high enough so that dimethylcyclopropene cannot afford planar vinylmethylene.

Figure 15 summarizes the thermal reaction mechanism for cyclopropylidene to allene and to cyclopropene. Our calculations indicate that cyclopropylidene should undergo conversion more easily to allene than to cyclopropene; the activation energies are 10.2 and 14.9 kcal/mol, respectively. This is contrary to the previous prediction based on the MINDO/2 calculation by Bodor et al.[23] that the activation energies are 6.3 and 13.7 kcal/mol for the conversion to cyclopropene and to allene, respectively. However, if we assume that the isomerization takes place on the ground-state surface, then our prediction is in accord with the experimental finding that only allene results upon photochemical isomerization of cyclopropylidene.[1c] At any rate, cyclopropylidene is most likely not involved in the thermal interconversion between allene and methylacetylene since the activation energy for allene to undergo conversion to cyclopropene via cyclopropylidene would be 76.9 kcal/mol which is much higher than the activation energy of 65.8 kcal/mol for the conversion via vinylmethylene.

V. Conclusion

From the results discussed above, we draw the following conclusions about the mechanisms for thermal isomerization reactions occurring on the singlet C_3H_4 surface. (1) The thermal allene-to-methylacetylene isomerization proceeds in four steps via vinylmethylene, cyclopropene, and propenylidene, confirming the involvement of cyclopropene as a stable intermediate. (2) Vinylmethylene is a very reactive intermediate with a nonplanar structure which shows stabilization by resonance interactions. It is not necessarily a common intermediate for the thermal interconversions. The activation energy for the conversion by the 1,2-hydrogen shift to methylacetylene is higher than that to allene, and the least energy path to methylacetylene is via cyclopropene. (3) The cyclopropene-to-methylacetylene isomerization proceeds via propenylidene, while it rearranges to allene via vinylmethylene. The activation energy for the former is less than that for the latter. (4) The direct pathway for the allene to methylacetylene isomerization does not exist on the ground-state surface. The isomerization always proceeds via cyclopropene. (5) Cyclopropylidene does not play a role in the thermal interconversions of allene, cyclopropene, and methylacetylene. (6) In photolysis of cyclopropene the isomerization to methylacetylene and allene most likely occurs on the ground-state surface after excited cyclopropene undergoes interconversion to the lowest singlet vinylmethylene species.

We note that some of these conclusions have been inferred from experimental observations and from theoretical calculations. The conclusions (1)–(3) are new findings that gave a fresh insight into the thermal isomerization mechanisms on the C_3H_4 surface. Furthermore, we have demonstrated that the new mechanisms emerged from the present study could be used to explain the reaction mechanisms for pyrolysis of methyl-substituted cyclopropene.

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[22] Srinivasan, R. *J. Chem. Soc., Chem. Commun.* **1971**, 1041.

[23] Bodor, N.; Dewar, M. J. S.; Maksic, Z. B. *J. Am. Chem. Soc.* **1973**, *95*, 5245.