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Theoretical Study of the Straight-Chain C_4H_7 Radical Isomers and Their Dissociation and Isomerization Transition States

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We use the G3//B3LYP method to calculate structures, harmonic vibrational frequencies, and energies at selected local minima and saddle points on the C_4H_7 potential energy surface. These include the straight-chain C_4H_7 radical isomers (of which there are twelve conformers of five structural isomers: 1-buten-1-yl, 2-buten-2-yl, 1-buten-2-yl, 1-methylallyl, and 3-buten-1-yl), sets of dissociation products, and dissociation, isomerization, and conformational transition states. Analogy with smaller hydrocarbon systems reveals why, for some reaction channels, more than one transition state may be accessed from the conformers of a structural isomer en route to the corresponding products. We compare results of the G3 and G3//B3LYP methods for selected C_4H_7 species.

Introduction

Gaining predictive ability with regard to the progress of chemical reactions is one of the primary goals of the field of chemical dynamics. Toward this end, it is important to have both theoretical and experimental results of high quality. In recent years, theoretical methods have been developed (G3//B3LYP[1] and G3[2] are the ones we consider here) that allow for the calculation of the energy of a species, to within chemical accuracy, with a modest computational effort for a system of substantial size. These methods allow for the characterization not only of minima on a potential energy surface but also of transition states connecting these minima, an understanding of which is necessary for the calculation of rate constants and branching ratios.

Unsaturated hydrocarbon radicals play important roles as intermediates in combustion reactions,[3−6] so an understanding of their unimolecular reaction dynamics is necessary to achieve an understanding of combustion. This work was motivated by recent experiments on the dissociation and isomerization channels of the three noncyclic C_3H_5 isomers. Those experiments used a new method, introduced by Mueller et al.,[7] to form selected radical isomers, dispersed by their internal energies, and measure the branching between radical dissociation product channels as a function of internal energy.[8−10] The complete theoretical characterization of the noncyclic C_3H_5 isomers and their dissociation and isomerization channels, appearing in Davis et al.,[3] has proved invaluable in the analysis of these experiments. Also, Osborn et al.[11] have determined that the allyl radical can isomerize to the cyclopropyl radical with a relatively low barrier, and that the cyclopropyl radical can isomerize to the 1-propenyl radical, but with a much higher barrier. The barrier for the cyclopropyl radical to dissociate to form cyclopropene plus H is also prohibitively high.[12] Therefore, the isomerization from the allyl to the cyclopropyl radical does not alter the unimolecular dynamics of the straight-chain species on the C_3H_5 potential energy surface.

Isolated theoretical and experimental values for the energies of some C_4H_7 radicals and transition states appear in the literature,[4,13−16] and extensive computational studies have been performed on other four-carbon systems,[17−19] but thus far, there has been no complete theoretical study of the straight-chain C_4H_7 radicals as has been done for the C_3H_5 system.[3,11,12] It is such a study that we provide here. Laskin et al.[4] have recognized the complexity of the C_4H_7 potential energy surface, and it is upon their preliminary enumeration of the C_4H_7 dissociation and isomerization channels that this work is based.

The reactions we consider here are not limited in usefulness to the unimolecular dissociation of C_4H_7 radicals. For example, the addition of a carbon-centered radical to an unsaturated carbon−carbon bond (the reverse of the C−C fission reactions discussed herein) is of great importance as a C−C bond-forming reaction in polymer chemistry and in synthetic organic chemistry,[20] so the knowledge of the rate constants of such reactions is of practical interest.

Computational Methods

For all calculations, we used the Gaussian 98 program, revision A.11.3.[21] Optimized molecular geometries and vibrational frequencies were found using the B3LYP density functional with the 6-31G(d) basis set. Full G3//B3LYP energy calculations[1] were performed on these B3LYP/6-31G(d) optimized geometries. For the purposes of computing the zero-point vibrational energies (ZPVE), we scale the vibrational frequencies by 0.96, as recommended by Scott and Radom[22] and required by the G3//B3LYP method.[1] Wave functions for doublet species were spin-unrestricted, and spin contamination was found to be low ($\langle S^2 \rangle \leq 0.8$ for all radicals and transition states.) Wave functions for singlet species were spin-restricted. All energies are presented as zero-point corrected enthalpies of formation at zero Kelvin ($\Delta H^{\circ}_{f,0K}$), calculated using atomic energies from Baboul et al.[1] and atomic enthalpies of formation from Curtiss et al.[23]

For selected species, we also present $\Delta H^{\circ}_{f,0K}$ values calculated using the G3 method, for which the ZPVE is calculated at the HF/6-31G(d) level and scaled by 0.8929, and a geometry optimized at the MP2(Full)/6-31G(d) level is used for the single-point energy calculations.[2] Geometry optimizations for two of the transition states we consider, C−H fission from *trans*- and

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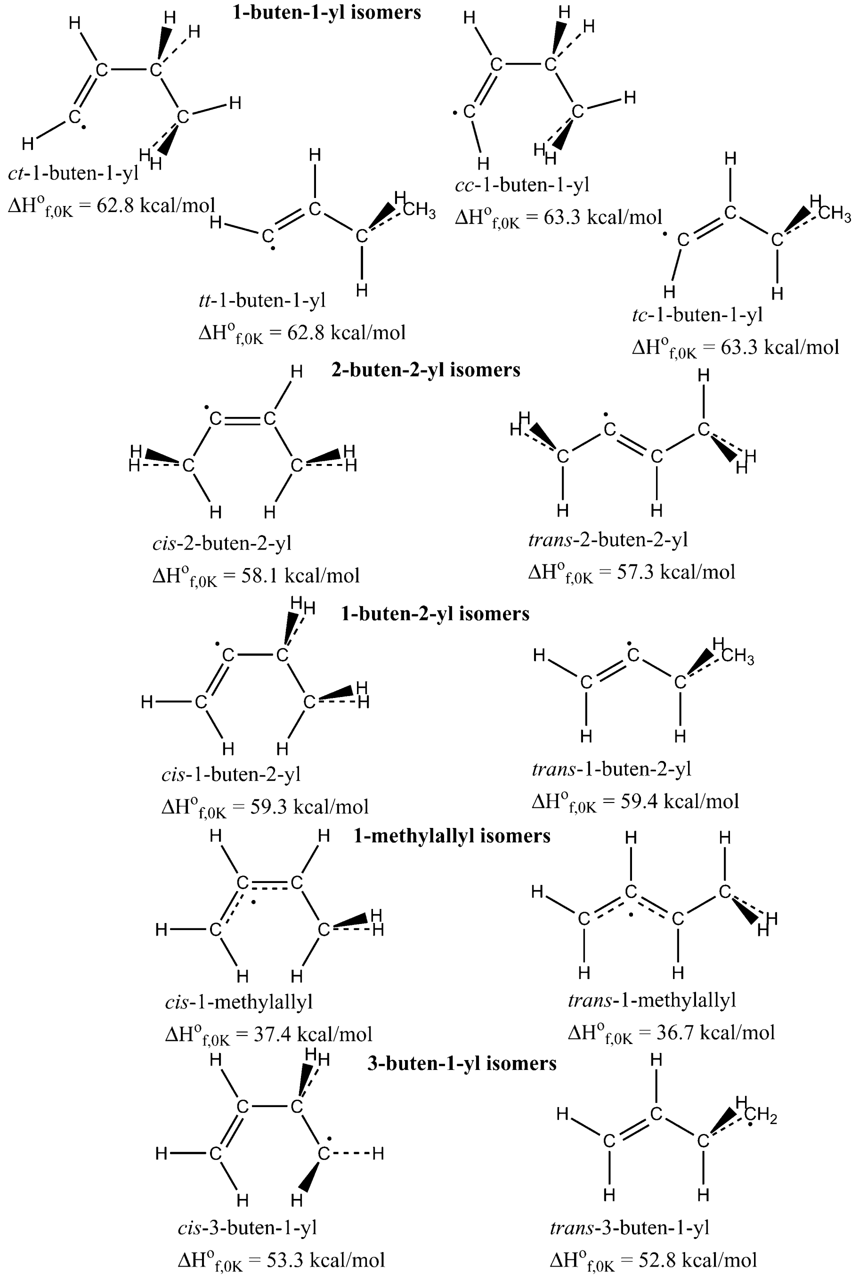


Figure 1. Schematic structures of the butenyl radicals investigated. Values of $\Delta H^{\circ}_{f,0K}$ are from G3//B3LYP calculations. In the names of the 1-buten-1-yl conformers, t and c stand for trans and cis, respectively, and refer to the geometry of the CCCC backbone and the orientation of the H atom on the 1-carbon, in that order.

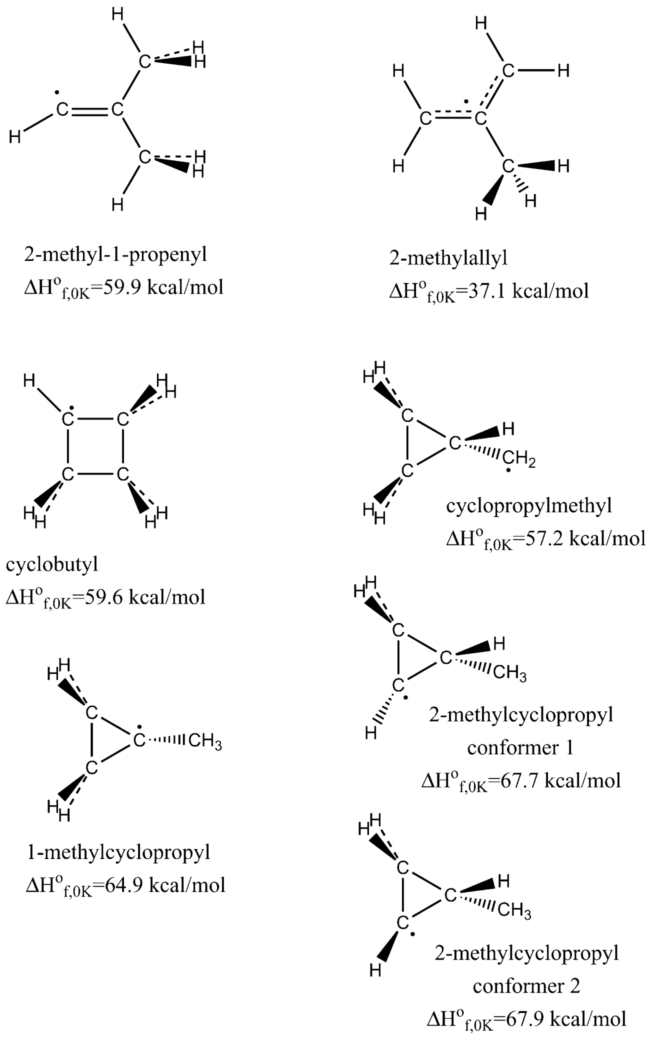
cis-1-methylallyl to give *trans*- and *cis*-1,3-butadiene, respectively, did not converge at the B3LYP/6-31G(d) level; the dissociative bond length for each of them at the final, nonoptimized step was greater than 4 Å, which suggests that the reverse barriers to these dissociation reactions are extremely small. For these species, we present G3 results only.

We report results for all five straight-chain C_4H_7 structural isomers. The dissociation reactions examined all involve the cleavage of a single bond between a carbon atom adjacent to the radical center and a neighboring carbon or hydrogen atom. The isomerization reactions considered all involve the migration of a hydrogen atom to the carbon atom containing the radical center from another carbon atom. We have performed a preliminary investigation of isomerizations between straight-chain radicals and cyclic radicals, to address the question of whether such isomerizations might provide a route by which one straight-chain radical could isomerize to another. We provide a brief summary of our findings here; the results will be reported in detail in future work.

All transition state structures were confirmed by having only one imaginary frequency with motion along the reaction coordinate. In cases where the identities of the reactant or product(s) were in doubt, an intrinsic reaction coordinate (IRC) calculation was performed as an additional check to establish the nature of the transition state.

Results

Radicals. There are five structural isomers in the straight-chain C_4H_7 radical system. One of these (1-buten-1-yl) has four conformers, whereas the other four each have two. Schematic structures of these conformers are shown in Figure 1; full optimized structures are provided in Z-matrix form in the Supporting Information. Not all structures have planar CCCC geometry; for the structural isomers derived from 1-butene (1-



2-methyl-1-propenyl
$\Delta H^{o}_{f,0K}$=59.9 kcal/mol

2-methylallyl
$\Delta H^{o}_{f,0K}$=37.1 kcal/mol

cyclobutyl
$\Delta H^{o}_{f,0K}$=59.6 kcal/mol

cyclopropylmethyl
$\Delta H^{o}_{f,0K}$=57.2 kcal/mol

1-methylcyclopropyl
$\Delta H^{o}_{f,0K}$=64.9 kcal/mol

2-methylcyclopropyl
conformer 1
$\Delta H^{o}_{f,0K}$=67.7 kcal/mol

2-methylcyclopropyl
conformer 2
$\Delta H^{o}_{f,0K}$=67.9 kcal/mol

Figure 2. Schematic structures of cyclic and branched C_4H_7 radical isomers, along with G3//B3LYP heats of formation at 0 K, presented for comparison.

buten-1-yl and 1-buten-2-yl, as well as 3-buten-1-yl, which could also be called 1-buten-4-yl), the CCCC dihedral angle of the "trans" conformer is approximately 120°, whereas for the 2-buten-2-yl and 1-methylallyl radicals, the CCCC dihedral angle of the "trans" conformer is exactly 180°. The CCCC dihedral angle of the "cis" conformers of all structural isomers is exactly 0°, except for the 3-buten-1-yl isomer, for which it is 11.8°. The nonplanar geometry of this conformer is presumably a result of steric hindrance between the CH_2 groups at opposite ends of the molecule. For both conformers of the 3-buten-1-yl radical, the CH_2 group on the terminal carbon containing the radical center is rotated out of plane by approximately 40°.

The four conformers of the 1-buten-1-yl radical exist because the terminal CCCH chain can also have either trans or cis geometry. It might be expected that other conformers of the 3-buten-1-yl radical could be obtained by rotating the CH_2 group on the terminal carbon containing the radical center, with respect to the rest of the molecule. We searched for these but found only one energy minimum for each of the possible CCCC geometries.

The most stable of the straight-chain C_4H_7 structural isomers, by about 20 kcal/mol, is the 1-methylallyl radical (resonance structures of which may be called 2-buten-1-yl and 1-buten-3-yl), which is, as expected, due to the delocalization of spin. The other four structural isomers are comparable in energy to one another (values for $\Delta H^{\circ}_{f,0K}$ are also given in Figure 1), all

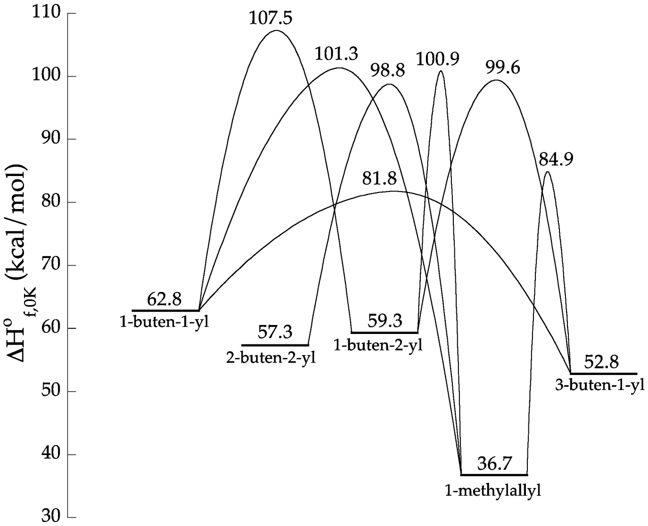


Figure 3. Energy diagram summarizing the possible isomerization channels that involve a change of connectivity. Values of $\Delta H^{\circ}_{f,0K}$ were calculated using the G3//B3LYP method and represent the lowest energy conformer of each radical, and the lowest energy transition state connecting each reactant−product pair. Note that there is a second isomerization channel connecting the 2-buten-2-yl and 1-methylallyl radicals, with a barrier some 3 kcal/mol higher than the one shown here. Both channels are shown in Figures 6 and 8; this figure includes only the lowest energy transition state.

lying within a range of approximately 10 kcal/mol. For comparison, Figure 2 depicts the structures and energies of the six branched and cyclic structural isomers of the C_4H_7 system (only one of which has more than one conformer.) The 2-methylallyl radical is comparable in energy to the 1-methylallyl radical, and the other five branched and cyclic structural isomers are comparable in energy to one another and to the higher energy straight-chain structural isomers.

Isomerizations and Dissociations. The possible isomerization and dissociation channels considered for the five straight-chain radical structural isomers are summarized in Figures 3 and 4, respectively. In these figures, the energies given represent the lowest energy conformer of each species (radical, set of dissociation products, or transition state) for which more than one conformer exists. RRKM parameters (unscaled vibrational frequencies and rotational constants) are provided in the Supporting Information.

For the most part, the barriers to isomerization are substantially higher than the barriers to dissociation. Also, the isomerization transition states are qualitatively much tighter than the dissociation transition states. Therefore, most of the isomerization channels are not expected to compete effectively with the available dissociation channels. There are two exceptions to this: the isomerization between 1-buten-1-yl and 3-buten-1-yl, and the isomerization between 1-methylallyl and 3-buten-1-yl. The barriers to both these isomerizations are lower than the barrier to any dissociation channel available to 3-buten-1-yl. The barrier to isomerization from 1-buten-1-yl to 3-buten-1-yl is also lower than either of the dissociation channels available to 1-buten-1-yl. (However, 1-methylallyl can dissociate to 1,3-butadiene + H with a lower barrier than the barrier to isomerization to 3-buten-1-yl.) We conclude that isomerizations may safely be neglected in many cases for the 2-buten-2-yl, 1-buten-2-yl, and 1-methylallyl radicals but should always be taken into account for 1-buten-1-yl and 3-buten-1-yl.

In contrast, Davis et al.[3] found that on the straight-chain C_3H_5 potential energy surface, all of the isomerization transition states are higher in energy than any of the dissociation transition states.

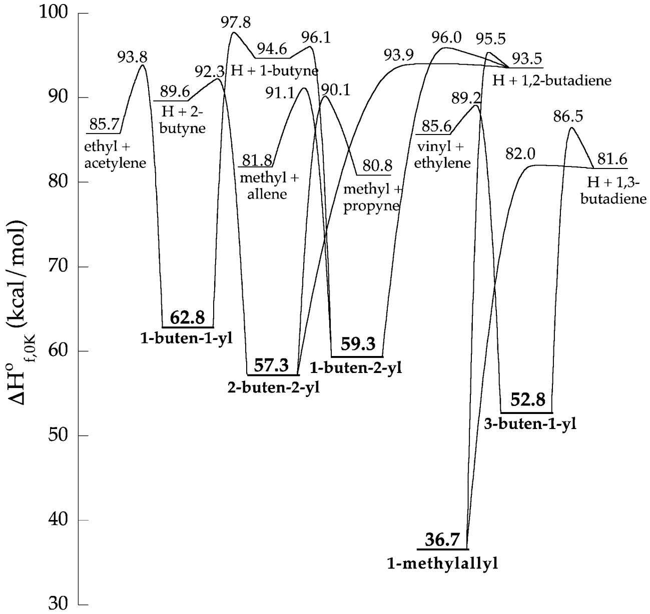


Figure 4. Energy diagram summarizing the possible dissociation channels. Values of $\Delta H^\circ_{f,0K}$ represent the lowest energy conformer of each species. The transition state between the 1-methylallyl radical and 1,3-butadiene was calculated using the G3 method; all other species were calculated via the G3//B3LYP method.

The reason for this qualitative difference between C_3H_5 and C_4H_7 is that there is no C_3H_5 isomer analogous to the 3-buten-1-yl radical. A more detailed explanation of the reason for the existence of two low-energy isomerization transition states involving the 3-buten-1-yl radical is provided below.

Figures 5−9 depict more detailed information for each of the five radicals, taking care to keep track of the conformers of each species involved. In nearly all cases, all possible conformers of a structural isomer (radical, set of dissociation products, or transition state) lie within 1.5 kcal/mol of one another (the exceptions being H + 1,3-butadiene and transition states leading to it). Also, in all cases, any barrier to conversion between the different conformers of a C_4H_7 structural isomer is much lower than any barrier to dissociation or isomerization.

The reason, then, for distinguishing between the conformers is that some dissociation and isomerization channels result from only one conformer of a particular radical structural isomer, and some channels result from more than one conformer. What we mean by this is *not* that the radical conformers function as distinct chemical species; all conformers of each structural isomer interconvert quickly enough that it is obviously not correct to treat the individual conformers as frozen structures. Instead, we use this terminology as a convenient way of enumerating the possible transition states. For example, as shown in Figure 6, there exist two distinct transition state structures connecting the 2-buten-2-yl radical to the dissociation products H + 1,2-butadiene. Both of these transition states must be taken into account in an RRKM analysis of this dissociation reaction. On the other hand, there exists only a single transition state structure between the 2-buten-2-yl radical and dissociation products H + 2-butyne. It so happens that this transition state structure more closely resembles the geometry of *trans*-2-buten-2-yl than that of *cis*-2-buten-2-yl. To indicate this fact, we say that the H + 2-butyne channel results from *trans*-2-buten-2-yl but not from *cis*-2-buten-2-yl, whereas the H + 1,2-butadiene channel may result from both conformers.

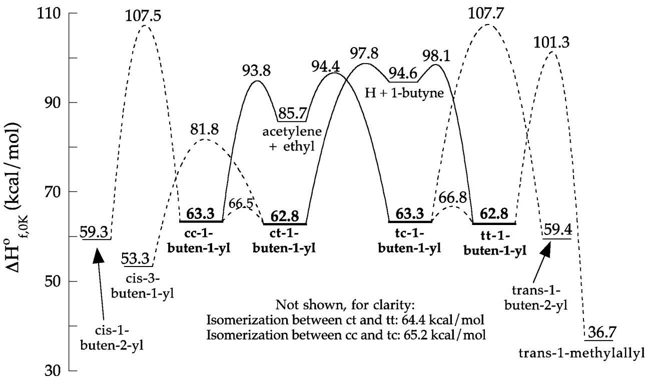


Figure 5. Energy diagram of the dissociation channels (solid lines) and isomerization channels (dashed lines) of the 1-buten-1-yl conformers. All values of $\Delta H^\circ_{f,0K}$ are from G3//B3LYP calculations. Note that all four of the conformers can readily interconvert; two of the conformational transition states are not depicted for clarity.

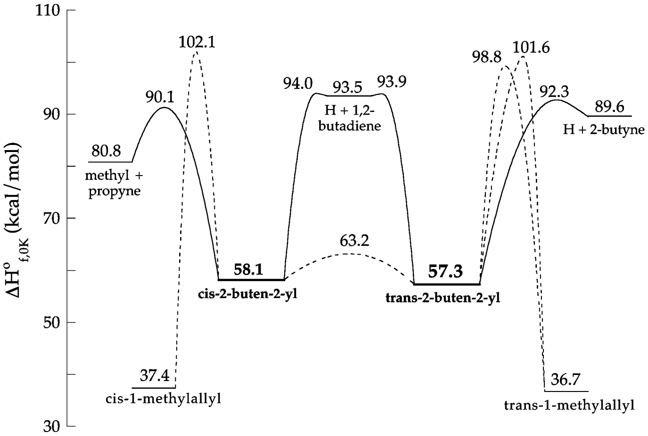


Figure 6. Energy diagram of the dissociation channels (solid lines) and isomerization channels (dashed lines) of the 2-buten-2-yl conformers. All values of $\Delta H^\circ_{f,0K}$ are from G3//B3LYP calculations. The two barriers connecting *trans*-2-buten-2-yl with *trans*-1-methylallyl represent two distinct channels by which this reaction can proceed (see text).

Isomerization Transition States. Figure 3 depicts the energies of the barriers to the possible isomerization channels. Each isomerization involves the migration of a hydrogen atom to the carbon atom containing the radical center from one of the other carbon atoms. The 2-buten-2-yl radical is not able to isomerize directly to any of the structural isomers derived from 1-butene, but the 1-methylallyl radical, because of its two resonance structures that behave like 2-buten-1-yl and 1-buten-3-yl, is able to isomerize to the 2-buten-2-yl radical, as well as the three 1-butenyl isomers.

We consider several isomerization channels that were not depicted by Laskin et al. in Figure 2 of their work.[4] This is because those authors included only those isomerizations that involve migration of an H between two adjacent C atoms, whereas we include the possibility of the migration of an H between nonadjacent C atoms.

The two 2-butenyl isomers (2-buten-2-yl and 1-methylallyl, behaving as 2-buten-1-yl) have the interesting property of being able to isomerize to themselves via H-migration: from the 3-carbon to the 2-carbon, in the case of 2-buten-2-yl, and from the 4-carbon to the 1-carbon, in the case of 1-methylallyl. For clarity, these channels are not included in Figures 3, 6, and 8, but their structures and RRKM parameters are provided in the Supporting Information. The $\Delta H^\circ_{f,0K}$ values for these transition states are 104.1 kcal/mol (for 2-buten-2-yl) and 76.3 kcal/mol (for 1-methylallyl.) The existence of these self-isomerization

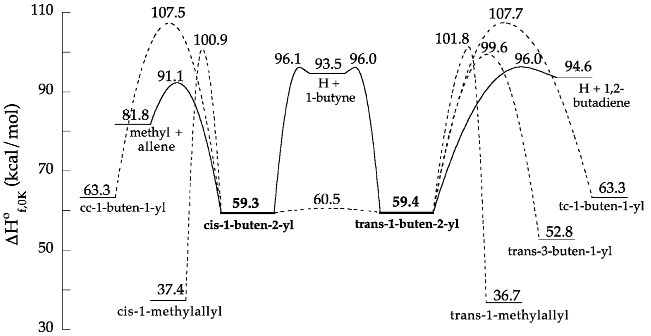


Figure 7. Energy diagram of the dissociation channels (solid lines) and isomerization channels (dashed lines) of the 1-buten-2-yl conformers. All values of $\Delta H^\circ_{f,0K}$ are from G3//B3LYP calculations.

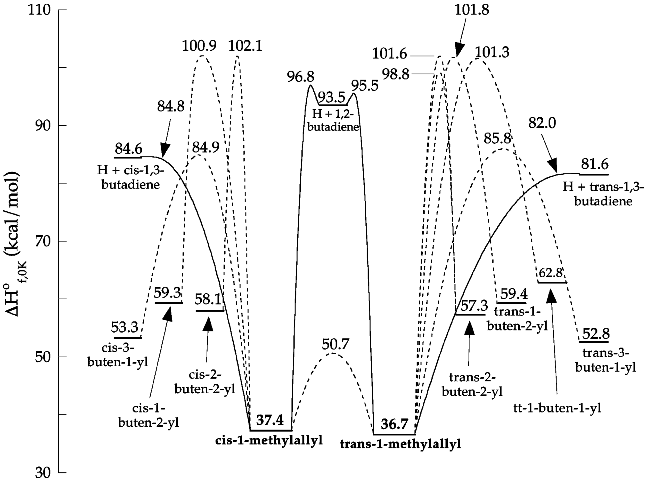


Figure 8. Energy diagram of the dissociation channels (solid lines) and isomerization channels (dashed lines) of the 1-methylallyl conformers. The energies of the two C−H fission transition states leading to *trans*- and *cis*-1,3-butadiene were calculated using the G3 method; all other energies are from G3//B3LYP calculations. The two barriers connecting *trans*-1-methylallyl with *trans*-2-buten-2-yl represent two distinct channels by which this reaction can proceed (see text).

channels should have no effect on the observed dissociation products of any radical under normal circumstances but may become important in experiments on isotopically labeled species.

The isomerization from 2-buten-2-yl to 1-methylallyl can proceed in two different ways: via H-migration from the 1-carbon to the 2-carbon, or from the 4-carbon to the 2-carbon. Only the latter, which has the lower barrier, is shown in Figure 3; both channels are shown in Figures 6 and 8.

The available isomerization channels can be classified according to the proximity of the carbon atoms between which the H atom migrates. Two isomerizations involve H-migration between the 1-carbon and the 4-carbon: the self-isomerization of 1-methylallyl, and the isomerization between 1-buten-1-yl and 3-buten-1-yl. These are the two lowest energy isomerization transition states, because of the minimal strain on the five-membered ring. Both require cis geometry of the carbon backbone. Three isomerizations involve H-migration between the 1-carbon and 3-carbon or between the 2-carbon and 4-carbon: the isomerization between 1-buten-2-yl and 3-buten-1-yl and between 1-buten-1-yl and 1-methylallyl and one of the channels for isomerization between 2-buten-2-yl and 1-methylallyl. All three of these transition states are comparable in energy, and all require a trans geometry of the carbon backbone. The remaining isomerizations all involve the migration of an H atom between two adjacent carbons. With the exception of the self-isomerization of the 2-buten-2-yl radical, which requires cis geometry, all of them can proceed through either the cis or the trans geometry. Two of these, the self-isomerization of 2-buten-2-yl, and the isomerization between 1-buten-1-yl and 1-buten-2-yl, involve the migration of an H atom across the double bond. These transition states are higher in energy than the others. All of the other 1,2 H atom migration transition states, in which an H atom bridges a single bond, are comparable in energy to one another, with the exception of the transition state between 1-methylallyl and 3-buten-1-yl, which is much lower in energy.

In general, our results are in agreement with the observations made for alkyl radicals: that 1,2 and 1,3 H atom migrations proceed with high barriers, whereas the barriers to 1,4 H atom migrations are lower.[24] The exception to this trend is the isomerization from the 1-methylallyl radical to the 3-buten-1-yl radical, a 1,2 H atom migration, which proceeds with a much lower barrier than the rest. The reason for this anomaly has to do with the resonance energy of the 1-methylallyl radical. When the 1-methylallyl radical isomerizes to the 3-buten-1-yl radical, it behaves as the 1-buten-3-yl resonance structure, with the radical center on the 3-carbon, because the migrating H atom moves from the 4-carbon to the 3-carbon. One might expect, then, that at the transition state structure, the unpaired electron spin density would be localized on the two carbon atoms involved in the H atom migration. In actuality, we find that there is also substantial α spin density on the 1-carbon, which suggests that at the transition state, the resonance between the 2-buten-1-yl and 1-buten-3-yl structures is still partially intact, thus lowering the energy of the transition state.

Dissociation Transition States. Figure 4 depicts the energies of the barriers to the possible dissociation channels. Again, only the lowest energy conformers are shown; all conformers are shown in Figure 5−9. Of the dissociation products, the only one that can exist in multiple conformers is 1,3-butadiene. The $\Delta H^\circ_{f,0K}$ of H + *trans*-1,3-butadiene (which has planar CCCC geometry) is 81.6 kcal/mol, whereas the $\Delta H^\circ_{f,0K}$ of H + *cis*-1,3-butadiene (with a CCCC dihedral angle of 30°) is 84.6 kcal/mol. The difference is significant and may be attributed to the greater degree of overlap between the π orbitals on the two double bonds of the trans conformer, as well as the steric hindrance between the H atoms on the two terminal carbons.

The dissociation reactions are all highly endothermic, with endothermicities ranging from 22.5 to 32.8 kcal/mol for C−C fission channels, and from 28.8 to 56.8 kcal/mol for C−H fission channels. Therefore, the transition states bear more resemblance to the products than to the reactants. In particular, the dissociative bond lengths (the lengths of the partially broken C−C and C−H bonds of the transition states) are long, ranging from 2.33 to 2.45 Å for C−C fissions and from 1.96 to 2.23 Å for C−H fissions.

The conformer dependence of the different dissociation channels is less obvious here than it was with the isomerization channels, but may be understood by analogy with two smaller systems, namely, C−H fission from the vinyl radical to form H + acetylene, and C−H fission from the 2-propenyl radical to form H + allene. These analogies provide restrictions on which dissociation channels may result from each conformer of a C_4H_7 structural isomer. All dissociation channels that are not restricted by either of these two analogies may result from any existing conformer of a structural isomer.

Analogy with the Vinyl Radical. When the vinyl radical loses an H atom to form H + acetylene, the H that is lost is the one that is instantaneously cis to the H on the far C atom, and trans to the radical electron, as shown in Figure 10a (which H

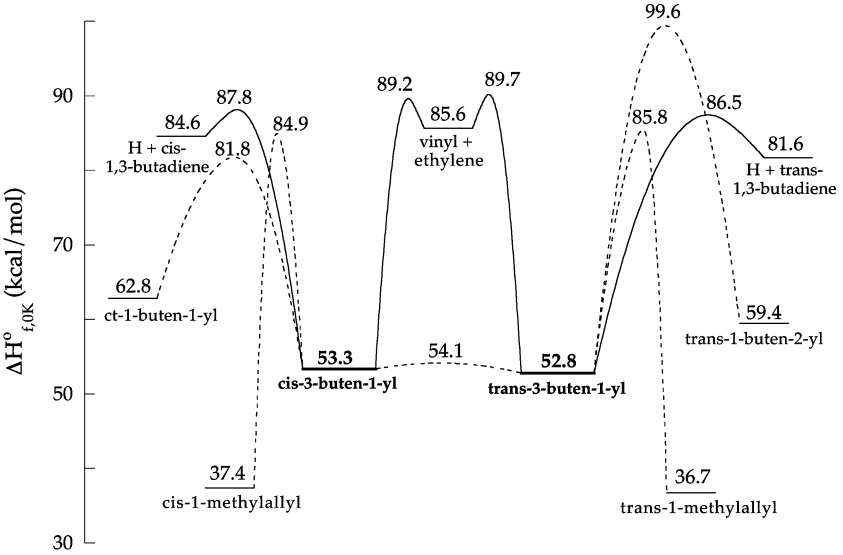


Figure 9. Energy diagram of the dissociation channels (solid lines) and isomerization channels (dashed lines) of the 3-buten-1-yl conformers. All values of $\Delta H^\circ_{f,0K}$ are from G3//B3LYP calculations.

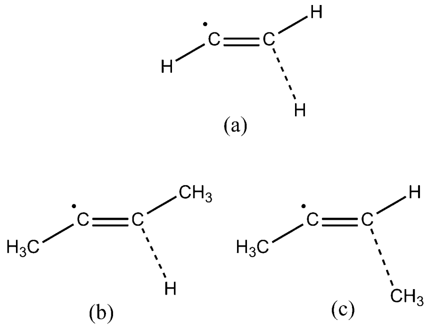

(a)
(b)
(c)

Figure 10. Schematic structures of (a) the vinyl C−H fission transition state, (b) the *trans*-2-buten-2-yl C−H fission transition state to form 2-butyne + H, and (c) the *cis*-2-buten-2-yl C−C fission transition state.

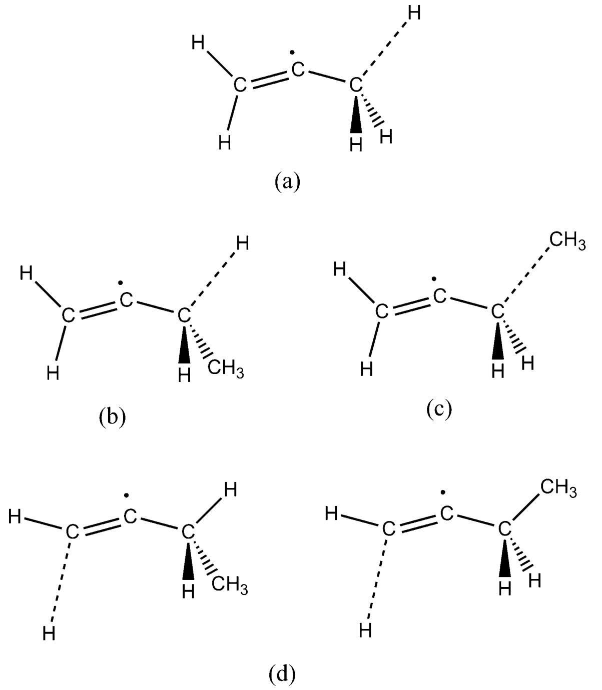

(a)
(b)
(c)
(d)

Figure 11. Schematic structures of (a) the 2-propenyl C−H fission transition state to form allene + H, (b) the *trans*-1-buten-2-yl C−H fission transition state to form 1,2-butadiene + H, (c) the *cis*-1-buten-2-yl C−C fission transition state, and (d) the C−H fission transition states to form 1-butyne + H from either *trans*- or *cis*-1-buten-2-yl. The transition states in (b) and (c) are analogous to the 2-propenyl transition state in (a), whereas the transition states in (d) are analogous to the vinyl transition state in (a).

atom is cis and which is trans changes as the CCH angle bends). Loss of the H that is cis to the radical electron must be preceded by a bending of the CCH bond angle so that the H that is lost becomes trans to the radical electron. That is, there exists a C−H fission transition state in which the two remaining H atoms are trans to each other, but there is no such transition state in which they are cis to each other. The reason for this is because the trans bending mode of acetylene has a lower frequency than the cis bending mode. Thus, it is energetically favorable for the acetylene-like portion of the C−H fission transition state to have trans geometry, rather than cis geometry.[25]

In the case of the vinyl radical, where both of these H atoms are equivalent, this fact is of less consequence than it is for the C_4H_7 radicals, some of which can behave as substituted vinyl radicals. Consider, for example, the 2-buten-2-yl radical, which may be characterized as a vinyl radical with two of the H atoms replaced by methyl groups. Two of the dissociation reactions of this radical, leading to H + 2-butyne and methyl + propyne, both involve fission of bonds on the 3-carbon, and may be considered in analogy with the vinyl C−H fission dissociation. When the 2-buten-2-yl radical exists in the trans geometry, the H on the 3-carbon is trans to the radical electron, whereas the methyl group is cis to the radical electron. Therefore, C−H fission to form H + 2-butyne, but not C−C fission to form methyl + propyne, may result from the trans conformer of the 2-buten-2-yl radical. Likewise, methyl + propyne, but not H + 2-butyne, may result from *cis*-2-buten-2-yl. The third dissociation channel of the 2-buten-2-yl radical, C−H fission from the 1-carbon to form H + 1,2-butadiene, is subject to no such restriction. In fact, two distinct transition states exist for this channel; IRC calculations confirm that one results from the cis conformer and the other results from the trans conformer (though these, of course, can interconvert.) Note, however, that the analogy with the 2-propenyl radical, described below, dictates which H atom is lost in this channel.

Analogy with the 2-Propenyl Radical. When the 2-propenyl radical loses an H atom to form H + allene, the H that is lost is the one that is instantaneously in the plane of the CCC backbone (and also in the plane of the CH_2 group on the far end of the molecule), as shown in Figure 11a. This is due to

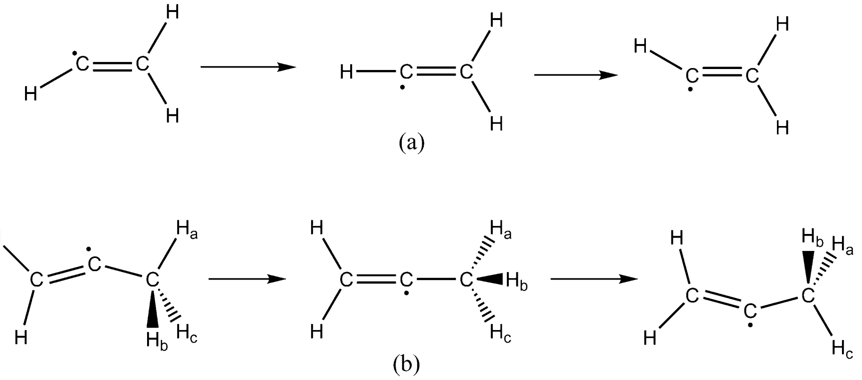


Figure 12. Schematic structures of (a) the CCH bend conformation of the vinyl radical and (b) the CCC bend conformation of the 2-propenyl radical. The CCC bend of the 2-propenyl radical is accompanied by a rotation of the methyl group on the 3-carbon.

the structure of allene, with the two CH_2 groups at opposite ends of the molecule in perpendicular planes.

Some of the C_4H_7 radicals can behave as substituted 2-propenyl radicals. Figure 11b,c shows two transition states of the 1-buten-2-yl radical that may be understood in analogy with the 2-propenyl radical. When 1-buten-2-yl is in the trans (or nonplanar) conformer, the H atom that is lost is one of those on the 3-carbon that is instantaneously in the plane of the CH_2 group on the 1-carbon. Therefore, C−H fission to form H + 1,2-butadiene, but not C−C fission to form methyl + allene, may result from the *trans*-1-buten-2-yl radical. Likewise, C−C fission, but not C−H fission to form H + 1,2-butadiene, may result from *cis*-1-buten-2-yl. Loss of an H atom from the 1-carbon to form H + 1-butyne (shown in Figure 11d) is not subject to this restriction, so this dissociation channel may result from either *trans*- or *cis*-1-buten-2-yl. (However, due to the analogy with the vinyl radical the H atom that is lost in this channel is the one that is instantaneously cis to the 3-carbon, and trans to the radical electron.)

Conformational Transition States. Also shown in Figures 5−9 are the calculated barriers connecting the different conformers of each structural isomer. All of these transition states are much lower in energy than any transition state leading to a dissociation or isomerization channel, which is as we expect. However, it is interesting to note that there is considerable variation in the conformational barrier heights among the different structural isomers, ranging from 1 kcal/mol or less for the 1-buten-2-yl and 1-buten-4-yl radicals to 14 kcal/mol for the 1-methylallyl radical.

Table 1 lists these barrier heights, as well as all the other conformational barrier heights that we were able to locate on the straight-chain C_4H_7 potential energy surface. The conformations are organized into groups, according to the smallest system to which they are analogous. For example, as far as the methyl rotations of the 1-buten-1-yl and 1-buten-2-yl radicals are concerned, these radicals behave like substituted ethanes. The conformational barriers of these analogous systems are presented, in italics, for comparison.

TABLE 1: G3//B3LYP Calculated Barriers to the Conformational Transition States of the Straight-Chain C_4H_7 Radical Isomers[a]

radical	conformation	barrier height(s) (kcal/mol)
1-buten-1-yl	ct methyl rotation	3.0
1-buten-1-yl	cc methyl rotation	3.4
1-buten-1-yl	tc methyl rotation	3.0
1-buten-1-yl	tt methyl rotation	3.0
1-buten-2-yl	cis methyl rotation	3.0
1-buten-2-yl	trans methyl rotation	2.8
ethane	*methyl rotation*	*2.6*
1-buten-1-yl	ct to tt CCCC rotation	1.7; 1.6
1-buten-1-yl	cc to tc CCCC rotation	1.9; 1.9
1-buten-1-yl	tc to tc CCCC rotation	1.7
1-buten-1-yl	tt to tt CCCC rotation	1.5
3-buten-1-yl	cis to trans CCCC rotation	0.8; 1.4
3-buten-1-yl	trans to trans CCCC rotation	1.1
2-buten-2-yl	cis methyl rotation on 4-carbon	1.3
2-buten-2-yl	trans methyl rotation on 4-carbon	1.4
1-methylallyl	cis methyl rotation	−0.2
1-methylallyl	trans methyl rotation	0.8
propene	*methyl rotation*	*1.7*
3-buten-1-yl	cis CH_2 rotation	−0.1
3-buten-1-yl	trans CH_2 rotation	0.3
ethyl	*CH_2 rotation*	*−0.1*
2-buten-2-yl	cis methyl rotation on 1-carbon	0.7
2-buten-2-yl	trans methyl rotation on 1-carbon	1.1
1-buten-2-yl	cis to trans CCCC rotation	1.2; 1.1
1-buten-2-yl	trans to trans CCCC rotation	1.2
2-propenyl	methyl rotation	1.0
1-methylallyl	cis to trans CCCC rotation	13.3; 14.0
1-methylallyl	cis CH_2 rotation	13.6
1-methylallyl	trans CH_2 rotation	14.0
allyl	*CH_2 rotation*	*13.7*
1-buten-1-yl	ct to cc CCH bend	3.8; 3.2
1-buten-1-yl	tc to tt CCH bend	3.5; 3.9
1-buten-2-yl	cis to trans CCC bend	5.3; 5.2
2-buten-2-yl	cis to trans CCC bend	5.0; 5.9
vinyl	*CCH bend*	*3.7*
2-propenyl	*CCC bend*	*5.3*

[a] The conformations are organized into groups according to the smallest hydrocarbon system to which they are analogous. Conformations analogous to the vinyl CCH bend and the 2-propenyl CCC bend are grouped together, although it is more accurate to consider these groups to be nonanalogous. When the two minima connected by a conformational transition state are structurally identical, only one barrier height is given; when the minima are structurally distinct, both barrier heights are given. A barrier to an internal rotation must necessarily be positive, but some of these calculated values are slightly negative; this is due to the limitations in accuracy of the G3//B3LYP calculational method.

With a few notable exceptions, the conformational barriers for the C_4H_7 radicals agree with the barriers for the smaller analogous molecules to within 1 kcal/mol. Though one might initially expect that the CCH bend of the vinyl radical and the CCC bend of the 2-propenyl radical (see Figure 12) are analogous to each other, there is a significant difference between the barriers to these two conformations, so it is more accurate to consider them separately. The CCH bends of the 1-buten-1-yl radical are consistent with the former, whereas the CCC bends of the 1-buten-2-yl and 2-buten-2-yl radicals are consistent with the latter. The CCC bend conformation of the 2-propenyl radical also involves the rotation of the terminal methyl group; by analogy, the CCC bend conformation of the 1-buten-2-yl radical involves the rotation of the CCCC backbone from the

TABLE 2: $\Delta H^\circ_{f,0K}$ Values (kcal/mol) Calculated at the G3 Level of Theory, for Selected C_4H_7 Species, with the Corresponding Values Calculated at the G3//B3LYP Level of Theory Presented for Comparison

species	$\Delta H^\circ_{f,0K}$ G3	$\Delta H^\circ_{f,0K}$ G3//B3LYP	diff
ct-1-buten-1-yl	62.9	62.8	0.1
cc-1-buten-1-yl	63.4	63.3	0.1
tc-1-buten-1-yl	63.3	63.3	0.0
tt-1-buten-1-yl	62.9	62.8	0.1
cis-2-buten-2-yl	58.2	58.1	0.1
trans-1-buten-1-yl	57.4	57.3	0.1
cis-1-buten-2-yl	59.5	59.3	0.2
trans-1-buten-2-yl	59.6	59.4	0.2
cis-1-methylallyl	36.7	37.4	−0.7
trans-1-methylallyl	36.1	36.7	−0.6
cis-3-buten-1-yl	54.0	53.3	0.7
H + 1-butyne	94.9	94.6	0.3
H + 1,2-butadiene	93.5	93.5	0.0
H + *cis*-1,3-butadiene	84.7	84.6	0.1
H + *trans*-1,3-butadiene	81.8	81.6	0.2
H + 2-butyne	89.7	89.6	0.1
methyl + allene	81.5	81.8	−0.3
methyl + propyne	80.8	80.8	0.0
vinyl + ethylene	85.9	85.6	0.3
ethyl + acetylene	86.2	85.7	0.5

transition states	$\Delta H^\circ_{f,0K}$ G3	$\Delta H^\circ_{f,0K}$ G3//B3LYP	diff
cis-1-buten-2-yl to *trans*-1-buten-2-yl	60.7	60.6	0.1
cis-1-buten-2-yl to *cc*-1-buten-1-yl	107.2	107.5	−0.3
cis-1-methylallyl to *cis*-3-buten-1-yl	84.7	84.9	−0.2
cc-1-buten-1-yl to ethyl + acetylene	94.3	93.8	0.5
cis-2-buten-2-yl to methyl + propyne	90.8	90.1	0.7
cis-2-buten-2-yl to H + 1,2-butadiene	95.3	94.0	1.3
trans-2-buten-2-yl to H + 1,2-butadiene	95.2	93.9	1.3
trans-2-buten-2-yl to H + 2-butyne	91.7	92.3	−0.6
cis-1-buten-2-yl to methyl + allene	91.2	91.1	0.1
cis-1-buten-2-yl to H + 1-butyne	96.3	96.1	0.2
trans-1-buten-2-yl to H + 1-butyne	96.3	96.2	0.1
trans-1-buten-2-yl to H + 1,2-butadiene	96.1	96.0	0.1

cis conformer to the trans conformer. We believe that there should also be a CCC bend transition state of the 1-buten-2-yl radical that connects the trans conformer with itself, but we were unable to find it.

The barrier to the methyl rotation of the *cis*-1-methylallyl radical is not consistent with the analogous propene methyl rotation. Because of the resonance of the 1-methylallyl radical, we could have classified this conformation as either propene-like or ethyl-like; we chose the former because the minimum energy structure of 1-methylallyl is more similar to that of propene than that of ethyl, in that one of the H atoms of the methyl group is in the plane of the rest of the molecule. However, the barrier to the methyl rotation is more consistent with that of the ethyl radical.

Comparison of G3//B3LYP and G3 Methods. Geometry optimizations of the *trans*- and *cis*-1-methylallyl C−H fission transition states to give H + *trans*- and *cis*-1,3-butadiene did not converge at the B3LYP/6-31G(d) level, so we were unable to calculate G3//B3LYP energies for these species. Instead, the $\Delta H^\circ_{f,0K}$ values reported for these species are calculated using the G3 method. In this section, we discuss the validity of comparing results of these two theoretical methods as applied to the C_4H_7 system.

Table 2 lists G3 values of $\Delta H^\circ_{f,0K}$ for selected species on the C_4H_7 potential energy surface, including all radical conformers (except for *trans*-3-buten-1-yl, for which we were unable to obtain an MP2 optimized geometry) and all sets of dissociation products. G3//B3LYP energies are presented for comparison. In most cases the agreement between the two methods is excellent, with energies differing by 0.2 kcal/mol or less for many species. The only species that present a discrepancy of greater than 0.7 kcal/mol are the transition states between *trans*- and *cis*-2-buten-2-yl and H + 1,2-butadiene. Notice that although these transition states are analogous to C−H fission from the 2-propenyl radical to form H + allene, the transition state connecting the *cis*-1-buten-2-yl radical and H + 1,2-butadiene, also analogous to the same 2-propenyl dissociation, does not exhibit such a discrepancy.

TABLE 3: Calculated Lengths (Å) of the Dissociative C−C or C−H Bonds of Selected Dissociation Transition States, at Three Different Levels of Theory[a]

reactant	products	HF	MP2	B3LYP
cc-1-buten-2-yl	ethyl + acetylene	2.31	2.14	2.34
cis-2-buten-2-yl	methyl + propyne	2.29	2.14	2.36
cis-1-buten-2-yl	methyl + allene	2.29	2.21	2.33
cis-2-buten-2-yl	H + 1,2-butadiene	1.97	1.76	2.22
trans-2-buten-2-yl	H + 1,2-butadiene	1.97	1.76	2.23
trans-2-buten-2-yl	H + 2-butyne	1.87	1.67	2.00
cis-1-buten-2-yl	H + 1-butyne	1.90	1.69	2.13
trans-1-buten-2-yl	H + 1-butyne	1.90	1.69	2.14
trans-1-buten-2-yl	H + 1,2-butadiene	1.95	1.75	2.02
cis-1-methylallyl	H + *cis*-1,3-butadiene	2.39	1.82	
trans-1-methylallyl	H + *trans*-1,3-butadiene	2.29	1.93	

[a] All structural calculations utilized the 6-31G(d) basis set. The HF and MP2 structures are used in the G3 energy calculation, and the B3LYP structures are used in the G3//B3LYP energy calculation. No B3LYP values are available for the two 1-methylallyl transition states because geometry optimizations of these transition states did not converge at the B3LYP level of theory.

Also worthy of consideration is the fact that there is a 1.9 kcal/mol difference between the results of the G3 and G3//B3LYP methods of the relative barrier heights of the two C−H fission channels of the 2-buten-2-yl radical (resulting in H + 1,2-butadiene and H + 2-butyne), and a 1.3 kcal/mol difference between the relative barrier heights of the C−C fission channel and the lower energy C−H fission channel of the same radical. Differences of this magnitude will certainly affect the RRKM branching ratios among these three channels. To assess which method gives more accurate relative barrier heights, our group plans to investigate experimentally the competition between these dissociation channels of the 2-buten-2-yl radical using the same methodology as our group has used for the competing C−H fission channels of the 2-propenyl radical.[7]

For the dissociation transition states listed in Table 2, Table 3 lists the dissociative bond lengths at three levels of theory: HF/6-31G(d) (for which the ZPVE is calculated in the G3 method), MP2(Full)/6-31G(d) (for which the single-point energy calculations are performed in the G3 method), and B3LYP/6-31G(d) (for which both the ZPVE and the single point energies are calculated in the G3//B3LYP method.) HF and MP2 values are also listed for the two 1-methylallyl transition states that we were unable to optimize at the B3LYP level. The B3LYP level consistently gives looser transition states than either the HF or MP2 level, but this fact alone does not imply that the G3//B3LYP transition state energies are consistently too low, because the trend also holds for the C−H fission transition state from 2-buten-2-yl to H + 2-butyne, for which the G3 method gave a lower value of $\Delta H^\circ_{f,0K}$ than did the G3//B3LYP method.

At both the HF and MP2 levels, the dissociative bonds of the two 1-methylallyl C−H fission transition states are considerably longer than those for any other C−H fission transition state. This suggests that at the B3LYP level, the dissociative bond lengths of these transition states would be even longer than 2.23 Å, and may even be too long to give a sensible convergent transition state structure. Indeed, this is what we found to be the case.

Reactions Involving Branched and Cyclic Isomers. It is necessary to address the question of whether a cyclic C_4H_7 isomer might serve as an intermediate by which one straight-chain isomer can efficiently isomerize to another, or whether the branched and cyclic isomers might play some other important role in the unimolecular reaction dynamics of the straight-chain isomers. On the basis of our calculations using the G3//B3LYP method, we have found three isomerizations between straight-chain and non-straight-chain isomers for which the value of $\Delta H^\circ_{f,0K}$ at the transition state is not prohibitively high: 1-methylallyl to 2-methylcyclopropyl ($\Delta H^\circ_{f,0K} = 87.7$ kcal/mol), 3-buten-1-yl to cyclopropylmethyl (65.1 kcal/mol), and 3-buten-1-yl to cyclobutyl (87.8 kcal/mol).

The first of these isomerizations is of little consequence for the reaction dynamics of the 1-methylallyl radical, because no other dissociation or isomerization of the 2-methylcyclopropyl radical has a transition state with an enthalpy of formation of less than 105 kcal/mol. Similarly, all the other dissociations and isomerizations of the cyclopropylmethyl radical have transition states with $\Delta H^\circ_{f,0K}$ values of at least 105 kcal/mol. However, because there are two ways in which the cyclopropylmethyl radical may isomerize back to the 3-buten-1-yl radical, this isomerization channel serves as a means of interchanging the 1- and 2-carbons of the 3-buten-1-yl radical, which can affect the results of experiments on isotopically labeled species.

The cyclobutyl radical can dissociate to cyclobutene plus H, with a $\Delta H^\circ_{f,0K}$ at the transition state of 95.8 kcal/mol. This is substantially higher than some of the dissociation channels available to the 3-buten-1-yl radical and the other radicals to which it can readily isomerize but may contribute as a minor channel at high internal energies. The isomerization between the 3-buten-1-yl and cyclobutyl radicals also serves as a means of permuting the carbon atoms of the 3-buten-1-yl radical, which must again be taken into account when studying isotopically labeled species.

Discussion

Applications. We are interested in the theoretical results contained herein primarily because of their usefulness in modeling the dissociation and isomerization of C_4H_7 radical species. However, we expect our results also to be of interest in modeling bimolecular reaction kinetics. For example, the vinyl + ethylene reaction currently under study by Taatjes et al.[26] proceeds through a 3-buten-1-yl radical intermediate, as shown in Figures 4 and 9. Also, the methyl + propyne reaction is expected to occur via a 2-buten-2-yl intermediate. (In principle, it is also possible for the methyl radical to attack the middle C atom of the propyne molecule, forming the 2-methyl-1-propenyl radical, but the barrier to this reaction is not included in our results here. Fischer and Radom[27] argue that when a methyl radical adds to a carbon−carbon double or triple bond, the dominant channel is expected to be the one in which the methyl attacks the less substituted carbon.) Our calculated entrance barrier to the formation of the 2-buten-2-yl intermediate is 9.3 kcal/mol. Fischer and Radom present experimental activation energies of 8.8 and 9.5 kcal/mol, corresponding to entrance barriers of 8.3 and 9.0 kcal/mol, respectively, derived from two different analyses with the same set of gas-phase kinetics data; the latter analysis is subject to certain assumptions regarding the preexponential factor in the Arrhenius equation, whereas the former analysis makes no such assuptions.

These theoretical results can also aid in predicting the product branching for bimolecular reactions. In the case of the methyl + propyne reaction, Figures 4 and 6 show that there should exist two competing product channels, H + 1,2-butadiene and H + 2-butyne. Our results suggest that H + 2-butyne should be the favored channel, for two reasons. First, the barrier to forming H + 2-butyne is significantly lower than the barrier to forming H + 1,2-butadiene. Second, the transition state leading to H + 1,2-butadiene freezes one of the two methyl rotors present in the 2-buten-2-yl radical, whereas the transition state leading to H + 2-butyne does not.

In the attached document, we present RRKM parameters (rotational constants and harmonic vibrational frequencies) for every transition state structure to aid in such predictions. Note that in some cases, it is more accurate to treat a mode of internal motion as a free or hindered rotor rather than as a harmonic vibration. Moments of inertia for such free internal rotors may be calculated from the Z-matrices provided in the Supporting Information.

Validity of the G3//B3LYP Results. Recent calculations presented in Michael et al.[28] on the entrance barrier to the H + acetylene reaction show that the G3//B3LYP method underestimates this barrier height by about 2 kcal/mol and gives too loose a transition state structure, as compared with the full CI (configuration interaction) calculation. (It is not feasible at this time to carry out such a high-level calculation on a four-carbon system.) It is likely that this trend extends to larger analogous systems, and that our results underestimate the absolute barrier heights, at least to C−H fission channels, by approximately 2 kcal/mol. However, recent work in our group on the dissociation of the 2-propenyl radical,[7] as well as preliminary results on the dissociation of the 1-buten-2-yl radical,[29] have shown that calculated values of the relative barrier heights to different dissociation channels are in excellent agreement with experiment. Interestingly, the comparisons shown in Tables 2 and 3 show that although the G3 method consistently gives tighter transition state structures than the G3//B3LYP method, the barrier heights are not substantially different. Thus, a full CI calculation of one of the C_4H_7 isomers would be valuable.

As noted above, our calculated value for the entrance barrier to the methyl + propyne reaction is in excellent agreement with the experimental results presented in Fischer and Radom.[27] In addition, Fischer and Radom present an extensive comparison of theoretical values, calculated at different levels of theory, for the barrier to the methyl + ethylene reaction. They find that all high-level theoretical methods give barriers in the range 4.9−6.9 kcal/mol, and the current experimental barriers also lie within this range. (Note, however, that a full CI calculation was not carried out on this system.) In particular, the G3//B3LYP method gives an entrance barrier of 6.4 kcal/mol, and the gas-phase experimental data give an entrance barrier of 6.2 kcal/mol. Although such a good agreement is certainly coincidental, we conclude from this that the G3//B3LYP method gives accurate estimates of the $\Delta H^\circ_{f,0K}$ values of C−C fission transition states.

Future Work. Plans for future work on the C_4H_7 radical system in our group include the experimental study of the 1-buten-2-yl and 2-buten-2-yl radicals, as well as a complete computational study of the branched and cyclic C_4H_7 radical isomers.

We have already obtained a large amount of data on the photofragment translational spectroscopy of 2-bromo-1-butene, a photolytic precursor to the 1-buten-2-yl radical. Preliminary data analysis has shown that the photodissociation of 2-bromo-

1-butene at 193 nm produces the 1-buten-2-yl radical with a range of internal energies both above and below the barriers to the three available dissociation channels. There is excellent agreement between theory and experiment with regard to the barrier height to the C−C fission channel, and the lowest of the barrier heights to C−H fission.[29]

Our group plans to undertake a similar experimental study of 2-chloro-2-butene, expected to be a photolytic precursor to the 2-buten-2-yl radical. We hope that this investigation may resolve the ambiguity between the G3 and G3//B3LYP results for the barrier heights to the dissociation channels of this radical.

In a future study of the branched and cyclic C_4H_7 radical isomers, we plan to provide as complete a characterization of the dissociation and isomerization channels available to the branched and cyclic isomers as we have done here for the straight-chain isomers. That work may also address the question of whether branched radicals play a significant, albeit minor, role as intermediates in bimolecular reactions.

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Supporting Information Available: Optimized geometries in Z-matrix form, along with rotational constants and tables of vibrational frequencies, are provided for all radicals and transition states considered in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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