

# 1,2-Pentadiene Decomposition

JUERGEN HERZLER, JEFFREY A. MANION, WING TSANG

National Institute of Standards and Technology, Gaithersburg, Maryland 20899

Received 16 May 2001; accepted 18 June 2001

ABSTRACT: 1,2-Pentadiene has been decomposed in single pulse shock tube experiments. There appear to be a large number of parallel decomposition and isomerization channels. The following rate expressions for isomerization in the temperature range 1100–1250 K and pressures between 200 and 300 kPa have been obtained

$$k(1,2\text{-pentadiene} \rightarrow 1\text{-pentyne}) = 1.0 \times 10^{13} \exp(-32300 \pm 900 \text{ K/T}) \text{ s}^{-1}$$

$$k(1,2\text{-pentadiene} \rightarrow \textit{cis/trans}\text{-}1,3\text{-pentadiene}) = 2.2 \times 10^{14} \exp(-33900 \pm 900 \text{ K/T}) \text{ s}^{-1}$$

$$k(1,2\text{-pentadiene} \rightarrow \text{cyclopentene}) = 1.8 \times 10^{11} \exp(-26080 \pm 900 \text{ K/T}) \text{ s}^{-1}$$

Overall, we estimate the  $2\sigma$  uncertainty in the absolute rate constants to be about 30%. From detailed balance the rate expression for 1,3 to 1,2-pentadiene isomerization has been found to be

$$k(1,3\text{-pentadiene} \rightarrow 1,2\text{-pentadiene}) = 1.2 \times 10^{15} \exp(-42070 \pm 900 \text{ K/T}) \text{ s}^{-1}$$

The significance of the 1,3 to 1,2 isomerization process as a bridge between the two-carbon and three-carbon species in high temperature hydrocarbon decomposition systems is discussed.

The decomposition processes involve bond breaking and retroene reactions. The rate expression for the latter has been found to be

$$k(1,2\text{-pentadiene} \rightarrow \text{propyne} + \text{ethylene}) = 6.6 \times 10^{12} \exp(-29240 \pm 900 \text{ K/T}) \text{ s}^{-1}$$

The rate constants for fission of the  $\text{C}_3\text{—C}_4$  and  $\text{C}_4\text{—C}_5$  bonds appear to be close to each other. Our results indicate that the resonance energy of the 1,3-butadiene-2-yl radical is smaller than that of allyl radical by an amount equal to the  $\pi$  bond conjugation energy of butadiene. © 2001 John Wiley & Sons, Inc.\*Int J Chem Kinet 33: 755–767, 2001

## INTRODUCTION

This paper is concerned with the decomposition and isomerization of 1,2-pentadiene. Interest in this molecule arises from the possibility of new reaction

channels becoming important as the degree of unsaturation is increased. For example, when one compares 1-pentene with *n*-pentane, it is found that the former species undergoes much faster unimolecular decomposition. Not only does allylic resonance energy weaken the 3,4 C—C bond, but 1-pentene can also decompose via a retroene reaction [1]. In a similar fashion, unimolecular stability decreases rapidly in the series cyclohexane, cyclohexene [1], and 1,4-cyclohexadiene [2], where the respective initial products are 1-hexene, butadiene and ethylene, and benzene. The common

Correspondence to: Jeffrey A. Manion; e-mail: jeffrey.manion@nist.gov.

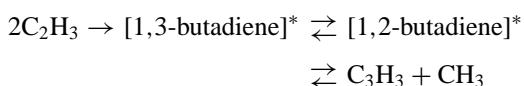
© 2001 John Wiley & Sons, Inc.\*This article is a US Government work and, as such, is in the public domain in the United States of America.

characteristic in these rate progressions is the increasing importance of molecular channels involving the direct elimination of stable molecules.

In the case of homolytic bond breaking, knowledge of the thermodynamics of the process together with analogies regarding radical combination rate constants leads to a certain degree of predictability [3]. By contrast, the situation is much less certain for molecular reactions where there are simultaneous bond breaking and bond forming processes. A particularly interesting class of reactions is isomerization of highly unsaturated molecules. Such species tend to be formed under severe pyrolytic conditions, for example, in fuel-rich combustion regions of flames. Reactions of such compounds are of particular importance immediately prior and subsequent to the formation of aromatics and soot. Our interest in such processes is the main rationale for the present study.

1,2-Pentadiene can be formed in high temperature systems from the combination of methyl and 1,3-butadienyl radicals or ethyl and propargyl radicals. Both propargyl and methyl radicals are extremely stable in the unimolecular sense, and hence tend to adopt relatively high concentrations and undergo a variety of such combination processes. We are especially interested in the rate expression for transformation of the 1,2-diene structure to the 1,3-diene and the reverse. The prototypical example of this reaction is the conversion of 1,2-butadiene to 1,3-butadiene. Although the present experiments directly concern the five carbon compound, it is expected that isomerization rate for the diene structure should be similar to that of analogous hydrocarbons. Hence, with the present results and detailed balance it should be possible to estimate a rate expression for 1,3-butadiene  $\rightarrow$  1,2-butadiene, a process difficult to study directly but likely to be of considerable importance in a variety of high temperature combustion systems.

Vinyl and propargyl radicals are important species in many high temperature organic systems. Mechanisms for their reaction to form benzene and higher aromatics have been proposed [4,5]. Combination of two vinyl radicals will lead to the formation of "hot" 1,3-butadiene that can isomerize to 1,2-butadiene and thereafter decompose to propargyl and methyl radicals [6]:



At high temperatures, despite its endothermicity, the reverse process may also play a role. Information on these interconversion processes will permit a proper

assessment of the role of each of the radicals in high temperature situations.

The starting point for the prediction of the rate constants for these processes under all conditions is the determination of the unimolecular rate expressions at the high-pressure limit. We chose to study the 1,2-pentadiene instead of 1,2-butadiene directly because the latter compound is no longer commercially available short of custom synthesis. As will be seen subsequently, this choice leads to some interesting and unexpected new information. The use of 1,2-pentadiene does, however, make the data analysis more complex since competitive C—C bond fission becomes a more important process.

Despite their importance, there has been little work on the isomerization reactions of larger polyunsaturated compounds. The interconversion of allene and propyne is a well-studied [7] reaction, however. It has been suggested that the reaction proceeds by way of cyclopropene and involves a carbene intermediate [8]. Hidaka et al. [9] have recently used the shock tube to study the decomposition of 1,2-butadiene at temperatures between 1100 and 1600 K and pressures of 120–230 kPa. They analyzed the results on the basis of a 82-step reaction mechanism. Because of the complexity of the reaction, the authors were forced to fit their data on the basis of *assumed* activation energies for the main two processes. On this basis they obtained the following rate expressions:

$$k(1,2\text{-butadiene} \rightarrow 1,3\text{-butadiene}) \\ = 2.5 \times 10^{13} \exp(-31702 \text{ K}/T) \text{ s}^{-1} \\ k(1,2\text{-butadiene} \rightarrow \text{propargyl} + \text{methyl}) \\ = 2.0 \times 10^{15} \exp(-37741 \text{ K}/T) \text{ s}^{-1}$$

The authors warn the reader that the results are valid only under their specific conditions and should not be extrapolated or imprudently applied to other conditions.

Unlike the allene to propyne conversion, which is essentially thermoneutral, the 1,2 to 1,3 isomerization reactions are highly exothermic. The reverse reaction consequently has a large activation energy and is likely to be important only at high temperatures, for example, in combustion processes. Following up on their initial suggestion [9], Hidaka et al. [10] appear to confirm the importance of the isomerization mechanism in studies on 1,3-butadiene decomposition. Here again the results must be extracted on the basis of a complex mechanism. A very important consequence of the work of Hidaka et al. [10] is that it suggests that propargyl radicals could be an important product arising from butadiene

decomposition. In their study of this reaction, Kiefer et al. [11,12] originally attributed their surprisingly low experimental activation energy to a low heat of formation of vinyl radical, where they assumed that the process under study involved the direct formation of two vinyl radicals. It is now clear that this cannot be the case, however, since subsequent work has now firmly established the "higher" heat of formation of vinyl radical [13]. There is therefore a need for an alternative decomposition channel for 1,3-butadiene. Our initial analysis of the present data led us to carry out more detailed modeling of the 1,3-butadiene system. That work is presented elsewhere [14] and shows that the decomposition channel to propargyl and methyl radicals is not sufficient to account for the results of Kiefer et al. There is in fact the need to invoke a direct molecular channel. Nevertheless it is clear that the vinyl radical production channel does not contribute to 1,3-butadiene decomposition and that the propargyl radical channel is the main radical production pathway.

Although the original intention was to obtain information on the isomerization reactions, it will be seen subsequently that bond breaking processes are also important. There are two carbon-carbon single bonds in 1,2-pentadiene which must be considered. The thermodynamic parameters relevant to scission of the propargyl-ethyl bond ( $\text{CH}_2=\text{C}=\text{CH}-\text{CH}_2\text{CH}_3 \rightarrow \text{C}_3\text{H}_3 + \text{C}_2\text{H}_5$ ), are available [1,15] and we find

$$\begin{aligned} \text{BDE} &= \Delta_f H(\text{C}_3\text{H}_3) + \Delta_f H(\text{C}_2\text{H}_5) \\ &\quad - \Delta_f H(1,2\text{-pentadiene}) \\ &= 347 [1] + 119 [1] - 146 [15] = 320 \text{ kJ/mol} \end{aligned}$$

For fission of the butadienyl-methyl bond ( $\text{CH}_2=\text{C}=\text{CHCH}_2-\text{CH}_3 \rightarrow \text{C}_4\text{H}_5 + \text{CH}_3$ ) there is an element of uncertainty in the bond energy that arises since butadienyl radical can be expressed in the following two resonance forms



To estimate the heat of formation of the radical one can modify prototypical C-H bond energies of the respective parent hydrocarbons of each of the above resonance forms, assuming in each case that the butadienyl radical has the same resonance energy as allyl radical, 50 kJ/mol [1]. Using this procedure, we derive the heat of formation of the left-most form to be 313 kJ/mol, whereas that on the right is calculated as 294 kJ/mol. Clearly, the above approach is not completely satisfactory. Nonetheless, if the true heat of formation of butadienyl radical is in this range, the C-methyl bond

energy is calculated to be between 295 and 314 kJ/mol. This leads to the conclusion that the energies of the two C-C bonds are not very far apart, despite the fact that in the first case a vinyl-carbon bond is being broken.

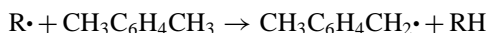
## EXPERIMENTAL\*

We have studied 1,2-pentadiene decomposition using the comparative rate single pulse shock tube methodology. The single pulse shock tube [1] has unique capabilities for studying the kinetic stability of intermediate or large sized organic molecules. Heating is by a shock wave, thus the walls are cold. The heating time is short, about 500  $\mu\text{s}$  for the present configuration. Hence reactants cannot migrate to or from the cold wall. Thus all reactions must occur in the gas phase. Subsequent to the heating pulse, samples can be removed for detailed analysis. In the present case, gas chromatography with flame ionization is used, thus making it possible to work with very dilute mixtures. It also means that chemical inhibitors, which will capture all reactive radicals, can be added in vast excess. Thus only unimolecular reactions are observed. This also means that it is possible to simultaneously study two unimolecular process at once. If the rate expression of one is well known, then that of the other can be determined with great accuracy since the known reaction can now serve as the internal standard. Our focus on isomerization reactions means that small amounts of several similar products need to be simultaneously determined with quantitative precision. Chromatographic analysis is probably the only technique by which this can be achieved and the present type of studies the only means to obtain reliable rate data.

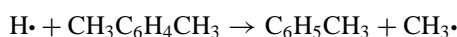
The reaction mixtures that were studied contained 280 and 400 ppm of 1,2-pentadiene in the presence of a 2% mixture of *m*-xylene (the inhibitor) together with 100 ppm of cyclohexene serving as the internal standard. The diluent gas was argon. Some experiments were also carried out in the absence of cyclohexene. This permitted an estimate to be made of the quantities of ethylene and butadiene formed in the absence of the standard. The reaction temperature ranged from 1100 to 1250 K and the pressure during reaction was between 200 and 300 kPa. The presence of the inhibitor serves as a sink for reactive radicals through the metathesis

\*Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the material or equipment is necessarily the best available for the purpose.

reaction:



This process quickly converts highly reactive radicals ( $R\cdot$ ) such as H-atoms or methyl radicals into resonance stabilized benzyl-type radicals. Under the present conditions such stabilized radicals cannot abstract hydrogen atoms or add to the 1,2-pentadiene but instead only recombine with other radicals. This is thus another route for the inhibition of radical reactions. In addition to reacting as above, hydrogen atoms can also displace methyl groups attached to the aromatic ring:



Near 1100 K this reaction is about 50% the rate of abstraction of the benzylic hydrogens [16]. Because this is the only realistic route to toluene in our system, this product will serve as a convenient marker for the presence of hydrogen atoms.

Analysis was by gas chromatography with 30 m Q-plot and alumina columns in the programmed temperature mode. Identification of the listed major products was made by comparison with authentic samples. All products up to  $C_9$  aromatics were determined with flame ionization detection. Cyclohexene decomposition was the internal standard. This is the substance that is added to the reaction mixture as a means of determining the reaction temperature. The rate expression for cyclohexene decomposition is well established [1] as

$$\begin{aligned} k(\text{cyclohexene} \rightarrow \text{butadiene} + \text{ethylene}) \\ = 1.41 \times 10^{15} \exp(-33500/T) \text{ s}^{-1} \end{aligned}$$

If we now determine its extent of decomposition, the reaction temperature can be readily determined from the relation

$$1/T = (15.15 - \log k)/33500$$

with

$$k = t^{-1} \ln [1/(1 - (\text{butadiene})_f/(\text{cyclohexene})_i)]$$

where the subscripts refer to initial and final concentrations and  $t$  is the heating time of 500  $\mu$ s.

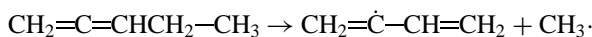
The 1,2-pentadiene and cyclohexene were obtained from Chemical Samples and were of stated purity of 99.9%. *m*-Xylene was from Aldrich and was of 99+% purity. Gas chromatographic analysis did not reveal the presence of any significant impurities. The argon was Matheson High-purity Grade.

## RESULTS

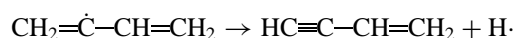
### Mechanisms and General Observations

Typical product yields at several temperatures can be found in Table I. Also found but not tabulated are small amounts of unsaturated compounds such as acetylene, propene, butene, butyne, and benzene. Except for benzene their yields were smaller than those from the minor isomerization channels. For benzene, the concentration levels are near the levels of the latter. These minor products are treated only in a qualitative manner. To a large extent this is because it is difficult to exclusively associate their formation with a single reaction channel. This is not to say that all the other compounds can be so associated. These problems will be discussed subsequently. The complex distribution of products clearly demonstrates that many reactions are occurring in parallel and in series. It appears that along with isomerization, direct molecular decomposition as well as bond breaking processes all make contributions. In fact, the decomposition processes are more important than the isomerizations.

The general proposed mechanism is illustrated in Fig. 1. Aside from the isomerization reactions, propargyl-ethyl and butadienyl-methyl bonds are being broken. This is demonstrated by the presence of methane and ethane, toluene, *m*-ethylmethylbenzene and, as will be seen subsequently, the excess of ethylene over that formed from what will be identified as direct molecular channels. From the product spectrum it is clear that hydrogen atoms and methyl radicals are released into the system. The former can be definitively established from the presence of toluene which, as noted before, can only be formed as a result of the displacement of the methyl radical from the *m*-xylene inhibitor by hydrogen atoms. Methyl radicals from this source, as well as those directly ejected from bond fission in 1,2-pentadiene, lead to the formation of methane, ethane, and *m*-ethylmethylbenzene. Ethane, of course, is the product of methyl radical recombination whereas the latter species is derived from combination of methyl radical with *m*-methylbenzyl radical, a primary species formed in the radical inhibition pathway. The presence of significant quantities of vinylacetylene is suggestive of a sequence of reactions that begin with the breaking of a C-methyl bond leading to the formation of the 2-butadienyl radical and methyl radical.



The decomposition of the former leads to the formation of vinylacetylene:



**Table I** Typical Product Yields in ppm

Products	Mixtures and Conditions		
	283 ppm 1,2-pentadiene 2% <i>meta</i> -xylene at 1213 K and 250 kPa	400 ppm 1,2-pentadiene 100 ppm cyclohexene 2% <i>meta</i> -xylene at 1231 K and 250 kPa	400 ppm 1,2-pentadiene 100 ppm cyclohexene 2% <i>meta</i> -xylene at 1171 K and 250 kPa
Methane	34.9	66.1	N.A. <sup>a</sup>
Ethane	2.2	13.4	N.A. <sup>a</sup>
Ethylene	53.2	143	51.1
Allene	3.1	6.1	N.A. <sup>a</sup>
Propyne	25.6	44.7	16.3
1,3-Butadiene	4.1	56.7	21.5
Vinyl Acetylene	16.6	27.2	5.2
1,2-Pentadiene	172.4	195	286
1-Pentyne	N.A. <sup>a</sup>	3.7	N.A. <sup>a</sup>
1,3-Pentadiene- <i>cis</i>	4.8	9.6	2.3
1,3-Pentadiene- <i>trans</i>	8.7	16.4	6.2
Cyclopentene	9.4	14.9	5.6
Cyclohexene	N.A. <sup>a</sup>	38.9	79.5
Toluene	N.A. <sup>a</sup>	54.4	16.5
Ethylmethylbenzene	N.A. <sup>a</sup>	50.2	N.A. <sup>a</sup>

<sup>a</sup> Not analyzed.

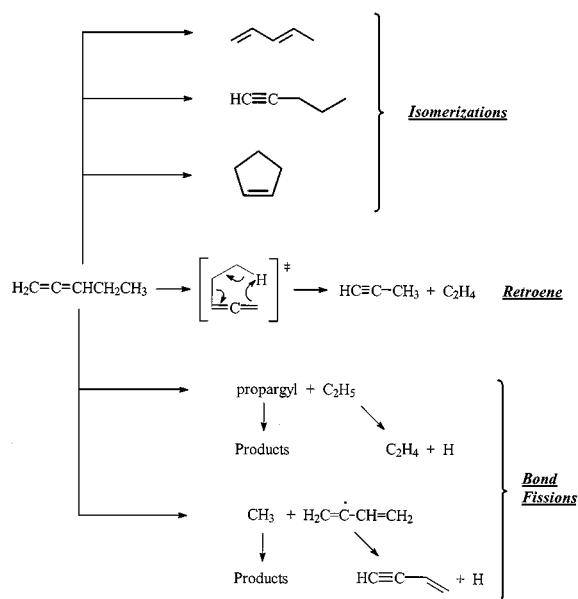
One direct source of ethylene in the present system is the retroene reaction: 1,2-pentadiene  $\rightarrow$  propyne + C<sub>2</sub>H<sub>4</sub>. However, comparison of the molar quantities of ethylene with the C<sub>3</sub> species attributable to the retroene reaction shows that there is a significant excess of ethylene. This indicates an additional source of ethylene. It is almost certainly ethyl radicals that

rapidly decompose, C<sub>2</sub>H<sub>5</sub>  $\rightarrow$  C<sub>2</sub>H<sub>4</sub> + H, thus also releasing H atoms into the system.

All of the minor products can be explained in similar fashion. For example, the presence of acetylene can be attributed to the decomposition of the 2-butadienyl radical which, upon isomerization to 1-butadienyl radical, will then decompose to form acetylene and vinyl radicals. The vinyl radical can then decompose to form another acetylene and a hydrogen atom or abstract a hydrogen to form ethylene. As our main interest is in the initial steps in 1,2-pentadiene decomposition, we have not attempted to develop a detailed model of such secondary processes, and note only that the processes are consistent with the current understanding of radical hydrocarbon chemistry.

The major portion of the propyne that is found apparently arises from the retroene decomposition: 1,2-pentadiene  $\rightarrow$  HC $\equiv$ CCH<sub>3</sub> + C<sub>2</sub>H<sub>4</sub>. Of course, propyne can also arise from propargyl radicals that are formed. It is highly likely that the observed allene is derived from propargyl radicals [17]. It cannot be derived from propyne if we use the published kinetic results on propyne to allene conversion [7].

The benzene that is found arises from the combination of propargyl radicals [4,5]. Finally, it is suspected that the small amounts of other olefins are due either to the hydrogen-atom induced decomposition of 1,2-pentadiene or radical combination reactions involving the vinyl radical.

**Figure 1** Primary processes during the thermal decomposition and isomerization of 1,2-pentadiene.

Finally, it should be noted that although 1-pentyne was observed, 2-pentyne was not detected as a product. In the work of Hidaka et al. [9] on 1,2-butadiene decomposition both 1-butyne and 2-butyne were found. A rationale for this difference will be offered in the Discussion section.

If one follows the general line of reasoning given here it will be possible to make some estimate of the contributions from bond breaking on the basis of the yields of methane, ethane, ethylene, toluene, and *m*-ethylmethylbenzene. These will have limited accuracy because most of the numbers are derived from differences. What is found is that the recovered product yields from the breaking of the butadienyl–methyl and propargyl–methyl bonds are very close to each other. It is suspected, however, that all the products from the bond breaking reactions have not been recovered. Specifically, some of the precursor to vinylacetylene, 1,3-butadien-2-yl, has been converted to unidentified products. Combination with methylbenzyl radical (present in large amounts as part of the radical chain inhibition chemistry) may be responsible.

### Rate Expressions for Overall Reaction

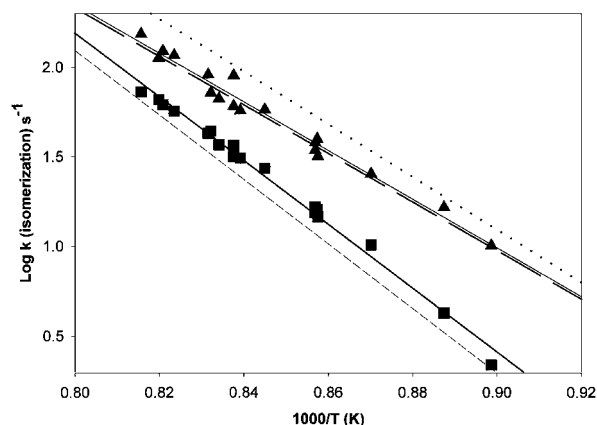
As previously derived [18] for a mathematically analogous system, rate constants for individual channels can be calculated from our data using the following relation:

$$k_i = (\alpha t)^{-1} \ln [1/(1 - \alpha X_i)],$$

where  $X_i$  is the fractional conversion to a particular species and  $\alpha = 1 + \sum X_{\neq i}$ .

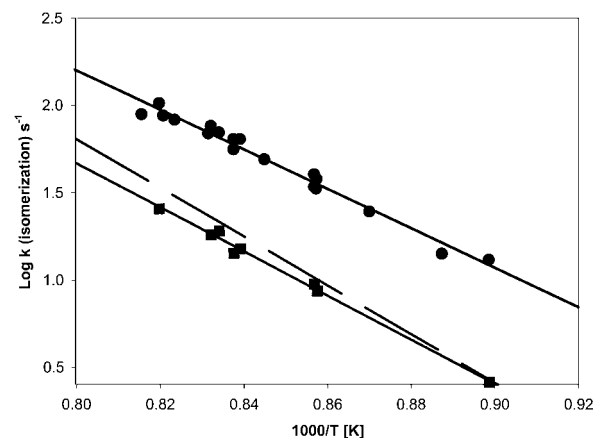
In the present case, the compounds that we consider are the major direct stable products or those products that are directly formed from sequences of unimolecular reactions. Specifically, these compounds are propyne, *cis*- and *trans*-1,3-pentadiene (*Z*- and *E*-1,3-pentadiene), cyclopentene, 1-pentyne, and vinylacetylene. At high extents of decomposition they total only about half of the 1,2-pentadiene that has disappeared. The missing compounds are treated as a group for the purposes of the calculations using the equation given above. This does not introduce serious errors because from an examination of the relation given above it can be seen that at low conversions where the 50% unaccounted compounds value used here may be in error, the uncertainty of the unaccounted reaction channels becomes very small.

The results are given in the Arrhenius plots in Figs. 2–4. These primary data have not been adjusted for subsequent chemistry of the products. Regarding

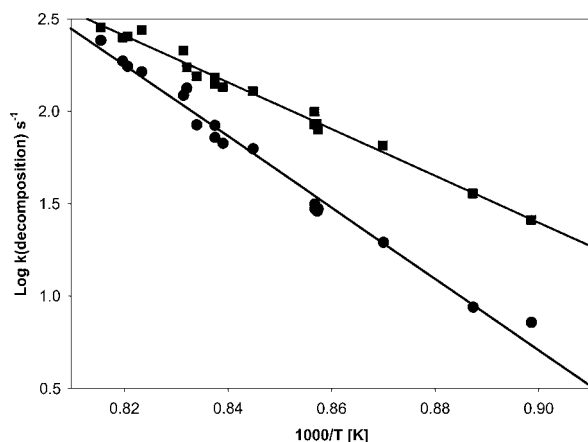


**Figure 2** Rate constants pertinent to the isomerization of 1,2-pentadiene to 1,3-pentadiene. Triangles (▲) represent data from yields of *trans*-1,3-pentadiene. Squares (■) are from yields of *cis*-1,3-pentadiene. The dotted line is the result from the sum of both 1,3-pentadiene isomers. The solid lines represent the least squares fits to the experimental points. The dashed lines are results derived from the assumption that the *trans*-isomer is the sole product and that the *cis*-isomer is formed subsequently through the isomerization process. See text.

the retroene decomposition of 1,2-pentadiene, which leads directly to formation of ethylene and propyne, we have slightly modified the raw data to account for a secondary source of product. Ethylene formation is a poor marker for this channel, as it is formed primarily via bond fission. We therefore rely on production of propyne to obtain rate constants for this pathway. However an additional minor source of propyne is from



**Figure 3** Rate constants pertinent to the isomerization of 1,2-pentadiene to form cyclopentene (●) and 1-pentyne (■). The solid lines represent the least squares fits to the experimental points. The dashed line indicates the rate expression derived for 1-pentyne formation after correction for its decomposition. See text.



**Figure 4** Rate constants pertinent to the retroene decomposition of 1,2-pentadiene to form propyne and ethylene (■) and vinylacetylene (●).

propargyl radicals. To correct for this we make use of previous studies [17], which suggest that reactions of propargyl radicals should result in about equal yields of allene and propyne. Hence to obtain the amount of propyne formed from the retroene reaction we have subtracted the allene yield from the total formation of propyne. This adjustment is in the range of 10–15%. As shown in Fig. 4, after this small correction, we obtain

$$k(1,2\text{-pentadiene} \rightarrow \text{propyne} + \text{ethylene}) \\ = 6.6 \times 10^{12} \exp(-29240 \pm 900 \text{ K}/T) \text{ s}^{-1}$$

The Arrhenius rate expressions for the other processes are as follows:

$$k(1,2\text{-pentadiene} \rightarrow \text{trans-1,3-pentadiene}) \\ = 1.6 \times 10^{13} \exp(-31283 \pm 900 \text{ K}/T) \text{ s}^{-1}$$

$$k(1,2\text{-pentadiene} \rightarrow \text{cis-1,3-pentadiene}) \\ = 2.7 \times 10^{16} \exp(-41000 \pm 900 \text{ K}/T) \text{ s}^{-1}$$

$$k(1,2\text{-pentadiene} \rightarrow 1\text{-pentyne}) \\ = 6.3 \times 10^{11} \exp(-29164 \pm 900 \text{ K}/T) \text{ s}^{-1}$$

$$k(1,2\text{-pentadiene} \rightarrow \text{cyclopentene}) \\ = 1.8 \times 10^{11} \exp(-26080 \pm 900 \text{ K}/T) \text{ s}^{-1}$$

$$k(1,2\text{-pentadiene} \rightarrow \text{vinylacetylene}) \\ = 1.3 \times 10^{18} \exp(-44550 \pm 900/T) \text{ s}^{-1}$$

The uncertainties in the activation energies are a factor of 3 larger than those usually obtained from similar single pulse shock tube experiments [1]. Part of the problem is due to the large number of isomerization

products produced in small amounts. Indeed the main reactions involve bond breaking. Overall, we estimate the  $2\sigma$  uncertainty in the absolute rate constants to be about 30%.

### Rate Expressions for Elementary Processes

In the subsequent discussion we convert several of the above overall rate expressions to true elementary rate expressions. In all cases we have considered the possible disappearance of the products used as a markers for the particular reaction channels. This has been done by modeling the subsequent reactions using rate constants derived from appropriate literature data. At times this has led to some changes in the rate expressions and in other cases proved to be unnecessary. These effects are all noted in the course of the subsequent discussion.

The rate expression for conversion of 1,2-pentadiene to *cis*-1,3-pentadiene appears to have a disproportionately large A-factor and activation energy, whereas the parameters for the *trans* isomer are smaller than might be expected. We suspect that this is due to the initial product being the *trans* isomer and that interconversion to the *cis* compound occurs from this source as opposed to formation directly from 1,2-pentadiene. This *cis*–*trans* isomerization of 1,3-pentadiene was studied by Marley and Jeffers [19] many years ago. Results of calculations using their rate constants for *cis*–*trans* isomerization where it is assumed that the *trans* compound is the first product and that the *cis* compound is formed from it are given in Fig. 2 (dotted line). It can be seen that the experimental distribution of *cis* and *trans* compounds is reproduced. Note that the equilibrium constant for this reaction is near 1 under our conditions [15] so the product distribution is still kinetically controlled even at the highest temperatures studied. Although we cannot rule out that some minor fraction of the product is initially the *cis* species, the data are consistent with isomerization of 1,2-pentadiene to 1,3-pentadiene being stereospecific for the *trans* isomer. This leads to the following corrected rate expression for the conversion of 1,2-pentadiene to *trans*-1,3-pentadiene.

$$k(1,2\text{-pentadiene} \rightarrow \text{trans-1,3-pentadiene}) \\ = 2.2 \times 10^{14} \exp(-33900 \text{ K}/T) \text{ s}^{-1}$$

Note that the above parameters comprise the transferable rate expression. The individual rate parameters for the *cis* and *trans* isomers derived directly from our data are valid only in our system and should not be used elsewhere. Because the 1,3-pentadienes are much more thermodynamically stable than 1,2-pentadiene,

the reverse isomerization to 1,2-pentadiene is very slow and it is not necessary to correct the data for that process.

The rate constant for the 1-pentyne formation channel is affected by the subsequent decomposition of 1-pentyne to form propargyl and ethyl radicals as well as allene and ethylene. The rate constants for the decomposition of 1-pentyne have been taken as equal to those found [1] for 1-hexyne decomposition, and we estimate  $k(1\text{-pentyne} \rightarrow \text{propargyl} + \text{ethyl}) = 7.9 \times 10^{15} \exp(-36300/T) \text{ s}^{-1}$  and  $k(1\text{-pentyne} \rightarrow \text{allene} + \text{ethylene}) = 5.0 \times 10^{12} \exp(-28400/T) \text{ s}^{-1}$ . When these reactions are taken into account one obtains the Arrhenius plot given in Fig. 3. The new rate expression is

$$k(1,2\text{-pentadiene} \rightarrow 1\text{-pentyne}) \\ = 1.0 \times 10^{13} \exp(-32300/T) \text{ s}^{-1}$$

Although the equilibrium constants of formation of 1,2-pentadiene and 1-pentyne are very close to each other, and hence the above reaction is reversible, the low degree of conversion to 1-pentyne assures that the reverse process may be ignored.

As noted above, in the case of the 1,3-pentadiene product it proved unnecessary to correct the data for the reverse isomerization. This is also the case for cyclopentene, which is much more thermodynamically stable than 1,2-pentadiene. Cyclopentene, in any case, would preferentially undergo the well-studied conversion to cyclopentadiene rather than reform 1,2-pentadiene. That process is also too slow to be important, however, in agreement with the literature data [20] and the absence of this species in the product spectrum.

We have suggested that vinylacetylene arises through fission of the butadienyl-methyl bond of 1,2-pentadiene followed by  $\beta$  fission of H from the radical intermediate (Fig. 1). The rate expression for this process is characterized by extraordinarily large parameters, however, much larger than would be expected for a "normal" C-C bond fission. What must be happening is that, unlike simple alkyl radicals, the butadienyl radical intermediate is stable enough that it does not immediately eject a hydrogen atom. At low temperatures in particular its unimolecular lifetime is long enough that bimolecular reaction channels become important. The large activation energy is thus a reflection of an ever increasing fraction of the radical intermediate undergoing decomposition to vinyl acetylene as the temperature is increased. Clearly the directly determined rate expression is a composite value and should not be used in other systems.

## Relative Importance of C-C Bond Fission Channels

As indicated in Fig. 1, the two possible C-C bond fissions in 1,2-pentadiene lead to production of methyl and ethyl radicals, respectively. To the extent that we are able to count the number of these species formed directly from 1,2-pentadiene, we can gauge the relative importance of the two channels. Table II summarizes the results in terms of methyl and ethyl radicals formed during the decomposition process. These numbers are not very precise because it is necessary to derive these values by taking into account multiple sources and sinks for these radicals. For example, methyl radicals are formed by fission of a C-C bond in the starting compound, but also by the reaction of H atoms with the inhibitor. Although this latter channel is conveniently marked by toluene formation, the correction adds to the uncertainty. Thus the quantity of methyl radicals directly attributable to bond fission in 1,2-pentadiene is derived from the sum of methane, ethane, and *m*-ethylmethylbenzene yields and reduced by the amount of toluene formed. It is also necessary to subtract the small amount of background methane. The alternate C-C bond fission leads to ethyl radicals, which rapidly decompose to ethylene. However, ethylene is also formed in the retroene decomposition of 1,2-pentadiene. Further we cannot simply account for this based on propyne formation, since propargyl radicals also lead to some propyne (see previous mechanistic discussion). Following our earlier discussion, propargyl radical decomposition gives approximately equal amounts of allene and propyne. Thus for the ethyl radical channel we use

$$\text{Ethyl}_{\text{C-C}} \approx \text{Ethylene}_{\text{Total}} \\ - (\text{Propyne} - \text{Allene}) - \text{Butadiene}$$

The butadiene correction is only necessary in the cases where the retroene reaction of cyclohexene ( $\rightarrow \text{C}_4\text{H}_6 + \text{C}_2\text{H}_4$ ) has been used as the standard. It is estimated that the uncertainties in the ratios of contributions from each channel may be as large as a factor of 1.3. Nevertheless, the observation that the ratios of

**Table II** Methyl and Ethyl Radical Yields from 1,2-Pentadiene Decomposition

Temperature (K)	Percent Methyl Radicals from 1,2-Pentadiene	Percent Ethyl Radicals from 1,2-Pentadiene
1170	28	22
1174	32	23
1199	31	27
1204	32	34



methyl to ethyl radicals are fairly close to each other is suggestive that the two bonds must have similar strengths.

## DISCUSSION

### Rates of Isomerization

Comparison of the present result on the conversion of 1,2-pentadiene to 1,3-pentadiene with that estimated by Hidaka et al. [9] for the analogous butadiene compound can be found in Fig. 5A. Agreement is very good except for a small difference in the activation energy. This strongly suggests that methyl substitution has a minimal effect on the kinetics of the isomerization process. On the basis of detailed balance, the present results on the isomerization reactions of 1,2-pentadiene can be used to calculate the rate expressions for the reverse reactions. For this purpose we use the thermodynamics of the stable compounds from Stull et al. [15] The following rate expressions, valid for 1100–1250 K, are derived:

$$k(\text{trans-1,3-pentadiene} \rightarrow \text{1,2-pentadiene})$$

$$= 1.2 \times 10^{15} \exp(-42070 \text{ K}/T) \text{ s}^{-1}$$

$$k(\text{1-pentyne} \rightarrow \text{1,2-pentadiene})$$

$$= 2.0 \times 10^{13} \exp(-32700 \text{ K}/T) \text{ s}^{-1}$$

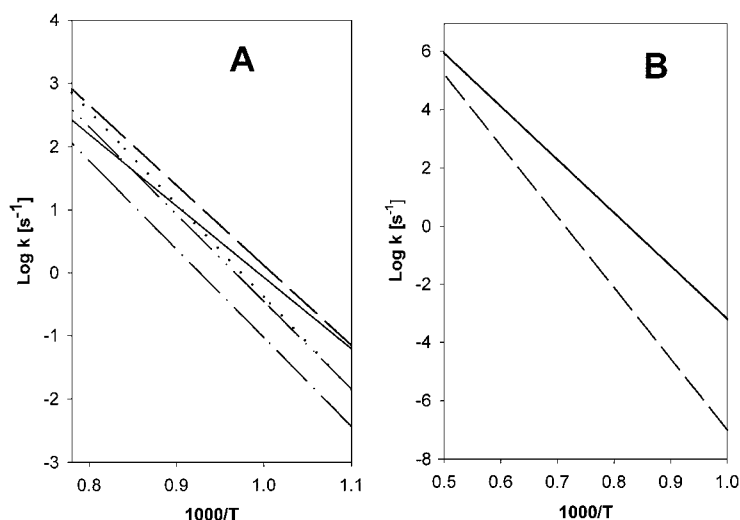
$$k(\text{cyclopentene} \rightarrow \text{1,2-pentadiene})$$

$$= 4.8 \times 10^{14} \exp(-40950 \text{ K}/T) \text{ s}^{-1}$$

If the first of these rate expressions can be taken to be that for the conversion of 1,3-butadiene to 1,2-butadiene, then some conclusions can be drawn regarding the decomposition chemistry of 1,3-butadiene. Specifically the rate of isomerization can be compared with that for C–C bond fission to give two vinyl radicals. The rate expression for this latter process can be derived from the reported recombination rate of vinyl radicals [21] and the now established thermochemistry of  $\text{C}_2\text{H}_3$  [13]. We find

$$\begin{aligned} k(\text{1,3-butadiene} \rightarrow 2\text{C}_2\text{H}_3) \\ = 2.8 \times 10^{17} \exp(-56300 \text{ K}/T) \text{ s}^{-1}. \end{aligned}$$

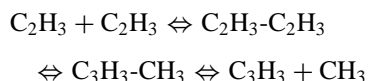
The comparison is shown graphically in Fig. 5B. Clearly the isomerization must be favored under all applicable conditions. Thus in the decomposition of 1,3-butadiene, isomerization to 1,2-butadiene must be more important than direct formation of vinyl radical. Once formed, 1,2-butadiene can decompose by C–C bond cleavage to form propargyl and methyl radicals. This latter reaction is endothermic by 335 kJ/mol. Because 1,3-butadiene is more stable than the 1,2 compound by 55 kJ/mol [15] the net conversion of 1,3-butadiene to propargyl and methyl radicals will require a total energy of 390 kJ/mol. This is very close to the activation energy,  $E_\infty = 391\text{--}393$  kJ/mol, determined by Kiefer et al. [11,12] for 1,3-butadiene decomposition. Although on the surface this appears compatible, there remain some problems. To fit the data of Kiefer et al. with the above mechanism it would require that the



**Figure 5** Some rate constant comparisons. Graph A: (1) dashed line, the retroene decomposition: 1,2-pentadiene → propyne + ethylene; (2) dash-dot-dash line, 1,2-pentadiene → 1-pentyne; (3) dotted line, 1,2-pentadiene → 1,3-pentadiene; (4) solid line, 1,2-butadiene → cyclopentene; (5) dash-dot-dot-dash line, 1,2-butadiene → 1,3-butadiene from Hidaka et al. [9]. Graph B: solid line, 1,3-pentadiene → 1,2-pentadiene; dashed line, estimated rate constant for 1,3-pentadiene →  $\text{C}_2\text{H}_3$  + 1-propenyl.

isomerization 1,2-butadiene  $\rightarrow$  1,3-butadiene be much slower than the decomposition process 1,2-butadiene  $\rightarrow$  propargyl + methyl. Although the latter process has a much larger A-factor, this is compensated for by the 45 kJ/mol lower activation energy of the isomerization. The end result is that the overall process for formation of propargyl and methyl radicals cannot be the main channel observed by Kiefer et al. As noted earlier, more detailed calculations [14] have confirmed this and suggest that the main channel in 1,3-butadiene decomposition involves a molecular channel which directly forms acetylene and ethylene.

The present analysis is compatible with the mechanism given by Hidaka and coworkers for 1,3-butadiene decomposition since propargyl and methyl radicals are the important radicals released into the system during 1,3-butadiene decomposition. These results should also permit the determination of the branching ratio for the reactions



We are carrying out such calculations as the present time.

The rate expressions given above for formation of 1,2-pentadiene from 1-pentyne and cyclopentene can be compared in a similar fashion with known rate expressions for other decomposition or isomerization processes. These are

$$\begin{aligned} k(1\text{-pentyne} \rightarrow \text{propargyl} + \text{C}_2\text{H}_5) \\ &= 7.9 \times 10^{15} \exp(-36300 \text{ K}/T) \text{ s}^{-1} [1] \\ k(\text{cyclopentene} \rightarrow \text{cyclopentadiene} + \text{H}_2) \\ &= 2.24 \times 10^{13} \exp(-30193 \text{ K}/T) \text{ s}^{-1} [21] \end{aligned}$$

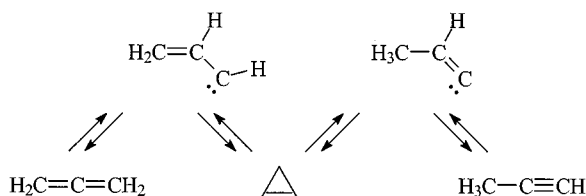
It can be seen that the rate constants for both of these processes are larger than the ones calculated for isomerization to 1,2-pentadiene, at least under higher temperature conditions. Thus the two isomerization reactions are not likely to be of importance in most applications.

We have assigned the propyne yields predominantly to the retroene reaction. The activation energy for this process is very much like those for the retroene reactions of other alkenes and alkynes. A direct comparison of the rate the retroene channel relative to some of the isomerization pathways of 1,2-pentadiene can be found in Fig. 5A.

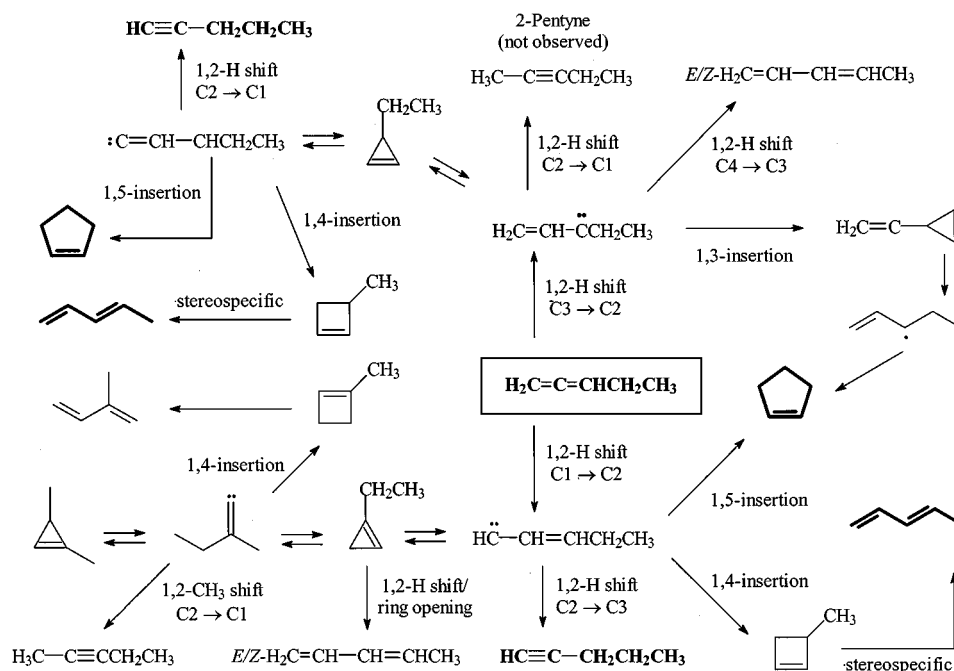
## Mechanism of Isomerization

In the Introduction we mentioned the possibility of a carbene mechanism for the allene to propyne isomerization reaction. Historically, the postulated mechanism for this reaction has evolved from direct H transfer, to the participation of first diradical and then carbene intermediates. Consequently, mechanistic discussion in the past literature should be treated cautiously and, indeed, the issues are still not fully settled. The current thinking was largely established in a series of papers in the mid to late 1980s by Honjou et al. [22–24] in which they used ab initio calculations to explore the  $\text{C}_3\text{H}_4$  surface in detail. They proposed that the dominant mechanism is that shown in Fig. 6, involving carbene and cyclopropene intermediates. Subsequent theoretical [25–27] and experimental [28,29] work seem to broadly support this view. A mechanism of the same general type can obviously accommodate the interconversion of 1,2-pentadiene and 1-pentyne. A general scheme is given Fig. 7. It is immediately apparent how complex the  $\text{C}_5\text{H}_8$  surface is in comparison to that of  $\text{C}_3\text{H}_4$ . Note that the cyclopropenes and cyclobutenes are proposed as intermediates only and are far too unstable at our temperatures to survive as end products. The gas phase decomposition of one of the possible intermediates, 1-ethylcyclopropene, has been studied at much lower temperatures (472 K) by Hopf et al. [28]. They obtained mass balances of  $(100 \pm 2)\%$  and found 2-pentyne, *trans*- and *cis*-1,3-pentadiene in near-equilibrium proportions, and 1,3-dimethylcyclopropene as major products. Traces of isoprene (2-methylbutadiene) and 1,2-pentadiene were also observed, but cyclopentene was not a product. Hopf et al. discussed formation of 2-pentyne and 1,3-dimethylcyclopropene, but did not propose a mechanism for production of the 1,3-pentadienes.

A detailed discussion of the full mechanism would be speculative and beyond the intended scope of this work but some comments are in order. First, the observation that in our system formation of *trans*-1,3-pentadiene is heavily favored over the *cis* isomer is suggestive that the primary route to this product is via 3-methylcyclobutene, which is known to isomerize



**Figure 6** Mechanism proposed by Honjou et al. [22–24] for the allene  $\rightleftharpoons$  propyne isomerization reaction.



**Figure 7** Suggested mechanism for the isomerization reactions of 1,2-pentadiene. The main observed isomerization products are indicated in bold. See text for discussion.

stereospecifically to *trans*-1,3-pentadiene [30]. Two other possible routes are put forth in Fig. 7: both involve 1,2-hydrogen shifts, either from a carbene intermediate or from the ethyl group of 1-ethylcyclopropene. These latter paths would be expected to generate a less stereospecific product distribution, contrary to what is observed. In this regard it is noteworthy that Hopf et al. [28] observed a near-equilibrium proportion of 1,3-pentadienes in the low temperature decomposition of 1-ethylcyclopropene. The gas phase isomerization rate of 1,3-pentadienes has been measured [18,31] and is far too slow to account for the equilibrium product distribution found by Hopf et al. Although it is possible that the long time scale (15 h) of the Hopf et al. studies could lead to surface mediated isomerization, the 1,2-hydrogen shift proposed in Fig. 7 would equally well explain their results. Hopf et al. did not find any cyclobutenes as products, but these compounds have half-lives of only about 10 s under their conditions [30]. A second noteworthy observation is that we did not observe 2-pentyne as a product, while it would perhaps be expected on the basis of the Hidaka et al. studies, as well as the Hopf et al. work, if 1-ethylcyclopropene were an important intermediate. A third observation is that Hopf et al. report no cyclopentene while we find it to be a relatively major pathway. An examination of the mechanism of Fig. 7 presents a possible rationale for the above observations. The differences with the low temperature data of Hopf et al. are suggestive that in the high temperature isomerization of 1,2-pentadiene the

1-ethylcyclopropene part of the  $C_5H_8$  energy surface is minimally sampled. This would require either that the initial  $C3 \rightarrow C2$  H shift is heavily favored over the  $C1 \rightarrow C2$  shift in 1,2-pentadiene (see Fig. 7) and thus that the chemistry of 3-ethylcyclopropene dominates, or that competing 1,3-, 1,4- and 1,5-insertion reactions dominate the chemistry of the initially formed carbene. This latter suggestion is not fully satisfying as the current thinking from low temperature experiments [28,29] is that the insertion reactions of carbenes are somewhat slower than 1,2-H transfer reactions, which are in turn slower than simple closure to cyclopropenes. The former suggestion, on the other hand, seems to be supported by the work of Hopf et al. [28,29]. This postulate would not be at odds with the Hidaka et al. work provided that in the  $C_5$  system the initially formed carbene preferentially undergoes ring closure to 3-ethylcyclopropene, or, again, that insertion reactions are dominant.

To summarize, our best explanation, at present, is that the principal isomerization chemistry we observe is channeled through the 3-ethylcyclopropene portion of the energy surface. This suggests that secondary hydrogens preferentially undergo the initial H shift reaction. Such patterns would be expected to be general in nature and should help predict the reactivity of larger 1,2-dienes. A more detailed examination of the  $C_5H_8$  energy surface would seem warranted and could perhaps clarify the situation. A secondary issue that we have not considered in detail is the possible role of

1,2-alkyl transfers in the carbenes, a process that may be important in some instances [29]. A better understanding of the  $C_5H_8$  surface would again be helpful.

It is interesting that all the isomerization activation energies are in the 240–280 kJ/mol range. This is very close to the  $\pi$ -bond energy of olefins and is consistent with the mechanisms involving fission or rearrangement of this bond in some manner. This may well be a general feature of the isomerizations of polyunsaturated hydrocarbons.

The cyclopentene formation reaction is characterized by a low A-factor,  $1.8 \times 10^{11} \text{ s}^{-1}$ . Presumably this is a reflection of a tighter transition state structure than that for conversion to *trans*-1,3-pentadiene ( $A = 2.2 \times 10^{14} \text{ s}^{-1}$ ). However, the proposed transition states both involve carbene insertions and it is not clear how these structures may be so different. We have investigated the possibility that secondary decomposition of cyclopentene to form cyclopentadiene [20] could be perturbing our derived rate expression for cyclopentene formation. The published rate constants are not large enough to make a significant contribution, however, and it is not obvious what other reaction could play a role.

### Bond Fission Reactions—Bond Energies

The relative equality in the yields of products from the breaking of the two C—C single bond strongly suggests that these reactions will be characterized by nearly the same rate expressions. Subject to the uncertainties that have been mentioned earlier, the bond dissociation energies would therefore have to be similar. Note that possible differences in the A-factors are unlikely, since it has been found [1] that bond breaking reactions leading to the formation of a stiffened resonance stabilized radical have completely “typical” values. This then leads to a butadienyl- $CH_3$  bond dissociation energy of  $318 \pm 6$  kJ/mol or a heat of formation of butadienyl radical (at 298 K) of  $317 \pm 6$  kJ/mol. This means that the secondary hydrogens in butadiene have bond strengths of 418 kJ/mol. We estimate that the bond strength of the vinyl C—H bond in 1-butene is 452 kJ/mol. The resonance energy of butadienyl radical is therefore only 34 kJ/mol. This is consistent with the 13–20 kJ/mol stabilization energy of butadiene (due to the conjugated  $\pi$  bonds) being lost in the radical. Classical molecular orbital theory provides a ready explanation: the sp-hybridized carbon in the radical contains two orthogonal p orbitals, only one of which can overlap with the adjacent  $\pi$  bond. Thus the radical must make a “choice” of forms and the net observed stabilization is the allylic resonance energy minus the  $\pi$  bond conjugation energy.

### Conclusion—Some Implications Regarding Hydrocarbon Decomposition

The greater importance of the fragmentation reactions in comparison to the isomerization processes is of considerable importance in the context of general mechanisms for hydrocarbon decomposition. It means that alkyl groups that are appended to sites of unsaturation will be rapidly released into the reacting system. This is brought about by the resonance stabilization of the propargyl radical. This sets definite limitations on the numbers and types of species that are important in high temperature hydrocarbon environments even for the largest and most complex of mixtures. A limit can then be set on the number and types of species that must be considered in complex models of such systems.

### BIBLIOGRAPHY

1. Tsang, W. In *Shock Waves in Chemistry*; Lifshitz, A. (Ed.); Marcel Dekker: New York, 1981; pp. 59–129.
2. Benson, S. W.; O'Neal, H. E. NSRDS-NBS 21; U. S. Government Printing Office, 20402, 1970.
3. Tsang, W.; Kiefer, J. H. In *The Chemical Dynamics and Kinetics of Small Radicals*; Liu, K.; Wagner, A. (Eds.); 1995; p. 58.
4. Frenklach, M.; Clary, D. W.; Gardiner, W. C.; Stein, S. E. In *20th Symp (Int) on Combustion, The Combustion Institute, Pittsburg, PA, 1984*; p. 887.
5. Stein, S. E.; Walker, J. A.; Suryan, M. M.; Fahr, A. In *23rd Symp (Int) on Combustion, The Combustion Institute, Pittsburg, PA, 1990*; p. 85.
6. Kubitz, C. *Das Vinylradikal—Massenspektrometrische Untersuchungen seiner Radikal-Radikal-Reaktionen und seiner Additionsreaktionen mit ungesättigten Kohlenwasserstoffen in der Gasphase*; PhD Dissertation; Technischen Hochschule Darmstadt, 1995.
7. Lifshitz, A.; Frenklach, M.; Burcat, A. *J Phys Chem* 1975, 79, 1148.
8. Bailey, I. M.; Walsh, R. *J Chem Soc Faraday Trans I* 1978, 74, 1146.
9. Hidaka, Y.; Higashihara, T.; Nimomiya, N.; Oki, T.; Kawano, H. *Int J Chem Kinet* 1995, 27, 331.
10. Hidaka, Y.; Higashihara, T.; Nimomiya, N.; Masaoka, H.; Nakamura, T.; Kawano, H. *Int J Chem Kinet* 1996, 28, 137.
11. Kiefer, J. H.; Wei, H. C.; Kern, R. D.; Wu, C. H. *Int J Chem Kinet* 1985, 17, 225.
12. Kiefer, J. H.; Mitchell, K. I.; Wei, H. C. *Int J Chem Kinet* 1988, 20, 787.
13. Kaiser, E. W.; Wallington, T.; *J Phys Chem* 1995, 99, 10549.
14. Tsang, W.; Mokrushin, V. In *28th Symp (Int'l) on Combustion, The Combustion Institute, Pittsburg, PA, Part 2, 2000*, 28, 1717.

15. Stull, D. R.; Westrum, E. F. Jr.; Sinke, G. C. *The Chemical Thermo dynamics of Organic Compounds*; Wiley: New York, 1969.
16. Robaugh, D.; Tsang, W. *J Phys Chem* 1986, 90, 4159.
17. Tsang, W. *Int J Chem Kinet* 1970, 2, 23.
18. Tsang, W. *J Chem Phys* 1965, 43, 352.
19. Marley, W. M.; Jeffers, P. M. *J Phys Chem* 1975, 79, 2085.
20. Lewis, D. K., Bergmann, J.; Manjoney, R.; Paddock, R.; Kaira, B. L. *J Phys Chem* 1984, 88, 4112.
21. Fahr, A.; Laufer, A.; Klein, R.; Braun, W. *J Phys Chem* 1991, 95, 3218.
22. Honjou, N.; Pacansky, J.; Yoshimine, M. *J Am Chem Soc* 1984, 106, 5361.
23. Honjou, N.; Pacansky, J.; Yoshimine, M. *J Am Chem Soc* 1985, 107, 5332.
24. Yoshimine, M.; Pacansky, J.; Honjou, N. *J Am Chem Soc* 1985, 107, 5332.
25. Kakumoto, T.; Ushirogouchi, T.; Saito, K.; Imamura, A. *J Phys Chem* 1987, 91, 183.
26. Melius, C. F.; Miller, J. A.; Evleth, E. M. 24th Symp (Int'l) on Combustion, The Combustion Institute, Pittsburg, PA, 1992; p. 621.
27. Davis, S. G.; Law, C. K.; Wang, H. *J Phys Chem* 1999, 103, 5889.
28. Hopf, H.; Plagens, A.; Walsh, R. *Liebigs Ann* 1996, 825.
29. Hopf, H.; Plagens, A.; Walsh, R. *Angew Chem Int Ed Engl* 1996, 36, 381.
30. Frey, H. M. *Trans Faraday Soc* 1964, 60, 83.
31. Frey, H. M.; Lamont, A. M.; Walsh, R. *J Chem Soc A* 1971, 2642.