Pyrolysis of 1,7-Octadiene and the Kinetic and Thermodynamic Stability of Allyl and 4-Pentenyl Radicals

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Dilute mixtures of 1,7-octadiene in argon have been decomposed in single-pulse shock tube experiments. The main reaction is the breaking of the carbon-carbon allylic bond leading to the formation of allyl and 4-pentenyl radicals. A minor pathway involving a retroene reaction yielded propene and 1,5-pentadiene. Most of the 4-pentenyl radical decomposes to form another allyl and ethylene. Contributions from a cyclization process resulting in the formation of cyclopentene have also been observed. Allyl radical decomposition rate constants have been measured. The following rate expressions have been determined: $k(1,7-\text{octadiene} \rightarrow \text{allyl} + 4-\text{pentenyl}) = 1.2 \pm 0.8 \times 10^{16} \exp(-35700 \pm 400/T) \text{ s}^{-1}, k(1,7-\text{octadiene} \rightarrow \text{propene} + 1,4-\text{pentadiene}) = (3 \pm 1.5) \times 10^{12} \exp(-27900 \pm 250/T) \text{ s}^{-1}, k(4-\text{pentenyl}) \rightarrow \text{cyclopentene} + H)/k(4-\text{pentenyl}) \rightarrow \text{allyl} + ethylene) = (6.9 \pm 4) \times 10^{-3} \exp(2118 \pm 500/T)$, and $k(\text{allyl} \rightarrow \text{allene} + \text{H}) = 40 \pm 10 \text{ s}^{-1} \text{ at 1080 K}$. When compared with lower temperature literature data on hydrogen addition to allene to form allyl, the present results are consistent with a resonance energy of $51 \pm 4 \text{ kJ/mol}$ for the allyl radical, a step-size down for collisional deactivation in argon of 500 cm⁻¹, and lead to the high-pressure rate expression $k(\text{allyl} \rightarrow \text{allene} + \text{H}) = 1.5 \times 10^{11} T^{0.84} \exp(-30053/T) \text{ s}^{-1}$ and $k(\text{H} + \text{allene} \rightarrow \text{allyl}) = 1.2 \times 10^8 T^{0.69}$ exp(-1513/T) L mol⁻¹ s⁻¹ over the temperature range 350-1200 K. The uncertainty for the decomposition reaction, is estimated to be a factor of 1.3 at 1100 K, but may increase to 1 order of magnitude at the lower temperatures. For the addition reaction, the estimated uncertainties are a factor of 1.5 at 350 K increasing to a factor of 2.5 at 1100 K. The disproportionation to combination ratio for allyl radical under high-temperature conditions is considerably less than 0.005.

Introduction

This paper is concerned with the mechanisms and rate constants for decomposition of allyl and 4-pentenyl radicals. In order to generate these radicals, dilute mixtures of 1.7-octadiene in mesitylene and argon are decomposed in single-pulse shock tube experiments. Allyl radical is especially interesting because resonance energy renders it much more thermally stable than alkyl radicals. Lifetimes for thermal decomposition are longer, and concentrations in high-temperature reactive systems will be larger. It can be expected to play a role different from alkyl radicals in high-temperature environments. For example, through its increased stability, it can react with active radicals and thus terminate chain decompositions. Addition to ethylene will lead to the formation of 4-pentenyl. This process can be expected to be reversed under most high-temperature conditions. However, a competitive cyclization reaction can also occur. This may be prototypical of the processes that lead to cyclization, aromatization, and ultimately soot formation. Sakai et al.¹ have observed the cyclization product, cyclopentene, in the course of studying allyl radical addition to ethylene.

On the basis of past work,² it is expected that the initial mechanism for the decomposition of 1,7-octadiene involves the following pathways:

1.7-octadiene = allvl + 4-pentenvl (a)

= propene + 1,4-pentadiene (b)

$$4-pentenyl = allyl + ethylene$$
(c)

= cyclopentene + H (d)

Reaction a is the main decomposition process and releases the two radicals of interest into the system. Reaction b can be considered to be an interfering process. It is a molecular reaction and leads to the formation of a unique species, 1,4-pentadiene. Its importance can be directly inferred. No active radicals are formed, and there will not be any subsequent interfering reactions. Reactions c and d deal with the decomposition and cyclization processes mentioned earlier.

Particular interest is focused on the decomposition of allyl radical. The most likely pathway is the ejection of a hydrogen atom, leading to the formation of allene

$$allyl \rightarrow allene + H$$
 (e)

There have been no previous determinations of the rate constants

or rate expression for this process. From thermochemistry the reaction is endothermic by $\sim 230 \text{ kJ/mol.}^3$ This is a minimum value for the limiting high-pressure activation energy and contrasts with 159 kJ/mol for the activation energy for the removal of a β -hydrogen from ethyl radical.⁴ This change in activation energy is mainly responsible for the thermal stability of the allyl radical in contrast to that for alkyl radicals. Wagner and Zellner⁵ have determined the mechanism and rate expressions for hydrogen atom addition to allene in the temperature range 272–470 K. They found, for addition to the nonterminal position, the rate expression, $k(H + \text{allene} \rightarrow \text{allyl}) = 4 \times 10^9 \exp(-1360/T) \text{ L mol}^{-1} \text{ s}^{-1}$. Using this measurement and the thermochemistry for allyl leads to the rate expression³

$$k(e) = 1.4 \times 10^{13} \exp(-30192/T) \text{ s}^{-1}$$

There are a number of problems in addition to possible experimental errors in the use of this expression for high-temperature applications. Unlike stable compounds, the thermodynamic properties of the allyl radical must be estimated. The entropies used in the present study are those given in an earlier review on allyl radical reactions.³ They have been estimated in the usual manner and therefore should not have larger uncertainties. It is estimated³ that the uncertainty in the heat of formation of the allyl radical leads to possible errors in the activation energy of ~6 kJ/mol. Roth et al.⁶ have recently summarized the many measurements on this quantity and presented new data. The results of the present study will yield additional data on this issue. Strictly speaking, the rate expressions given above are only applicable in the temperature range covered. An Arrhenius extrapolation over 700 K and covering 25 orders of magnitude in rate constants may well lead to serious errors. The present study can therefore yield information on the nature and magnitude of the curvature in the Arrhenius plots for this type of reaction. This is the most direct information on the nature of the transition state for such processes and is particularly valuable for the extrapolation of lower temperature results. For isobutenyl radicals⁷ the rate expression for the ejection of the methyl group is k(isobutenyl \rightarrow allene + methyl) = 2 × 10¹³ exp(-24000/T) s⁻¹. Here again one sees the drastic effect of the double bond in raising the activation energy from 126 kJ/mol⁸ for n-propyl radical decomposition to 200 kJ/mol for isobutenyl.

The determination of accurate rate constants and expressions for the decomposition of organic radicals is experimentally difficult.

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Since they are unstable, the first prerequisite is their reproducible generation in a well-understood environment. Until recently, the best rate constants were from systems where the ratio of decomposition and combination products was measured and the most accurate rate expressions are derived through the equilibrium constant and the rate expression of the reverse radical addition process.8 More recently Gutman and co-workers9 have generated alkyl radicals in a lower temperature flow system and followed their decay directly with a mass spectrometer. As noted earlier, allyl radical is much more stable than alkyl radicals and higher temperatures are required to induce thermal decomposition. It is thus not surprising that there have been no previous attempts at studying its rates and mechanisms for decomposition. A special problem with studying the decomposition of organic radicals is that at the high temperatures of interest their rates are usually in the falloff region. The limiting high-pressure rate expression, the fundamental quantity in so far as it characterizes the transition-state structure and energetics, can only be obtained through extrapolation. This becomes increasingly unreliable for data that are deep into the pressure-dependent region. Indeed, at sufficiently low pressures, one is measuring collisional efficiencies and the reaction threshold. A particular advantage of single-pulse shock tube experiments, unlike low-pressure flow tube studies, for example, is that they are carried out at much higher pressures (2-7 atm in the present case), and the rate constants are thus closer to the high-pressure limit than those derived using other methods. They are also in the range where they can be directly used in practical applications.

There has been no previous study on the kinetics of the decomposition of 1,7-octadiene. If it is assumed that vinyl substitution γ to the bond being broken will have negligible effect on the rate expression for allylic-*n*-alkyl bond cleavage, then one expects that the rate constant will be twice that for the breaking of the allylic-*n*-propyl bond in 1-hexene² or 2k(1-hexene \rightarrow allyl + n-propyl) = $2 \times 10^{16} \exp(-36200/T) \text{ s}^{-1}$. There is also a molecular channel similar to that for 1-hexene decomposition, and its rate expression can be expected to be 2k(1-hexene \rightarrow 2propene) = $(2 \times 4) \times 10^{12} \exp(-28900/T) \text{ s}^{-1}$. Thus, in addition to data on radical stability, this study should yield information regarding the transferability of rate data from smaller to larger organic structures.

Experimental Section

The experiments are carried out in a heated single-pulse shock tube. Details of the instrument and experimental procedures can be found in an earlier publication.¹⁰ The experimental temperatures ranged from 1040 to 1200 K, and the pressures were from 2 to 7 atm. The heating times were in the 500- μ s range. Analysis of the products was by gas chromatography using a 30-m dimethylsiloxalane wide-bore capillary column in the programmed-temperature mode for the analysis of the larger species and a 12-ft Poropak N¹¹ column under isothermal conditions for the lighter components. Flame ionization was used for detection. Experiments were carried out with large excess concentrations of an inhibitor, mesitylene, that captures the more reactive fragments that may be formed during the decomposition process. The strategy is to change the reactive fragments into more unreactive large polyatomic benzylic radicals, which can only recombine with other radicals under the reaction conditions. In particular, such radicals under the present conditions cannot initiate or take part in chain processes. Allyl radicals have some of these properties. However, when they decompose H atoms are produced. Quantitative data are based on the internal standard method. This removes the major uncertainty from single-pulse and many other shock tube studies, possible errors in the reaction temperature. The internal standard used in this study is the reverse Diels-Alder reaction involving 1-methylcyclohexene decomposition to form isoprene and ethylene. The rate expression for this reaction has been previously found to be¹⁰ k(1-methylcyclohexene \rightarrow isoprene + ethylene) = $10^{15} \exp(-33500/T) \text{ s}^{-1}$.

Experiments were carried out with the following mixtures: 33 ppm 1,7-octadiene in 0.33% mesitylene and argon; 100 ppm



Figure 1. Product distribution from the decomposition of 1,7-octadiene as a function of temperature: (O) ethylene, (\odot) propene, (\blacksquare) cyclopentene, (\Box) 1,4-pentadiene, (Δ) allene, (Δ) propyne, (∇) 1,5-hexadiene, and (∇) 1,7-octadiene. (A) Data from 100 ppm 1,7-octadiene and 1% mesitylene at 2.2 atm argon. (B) Data from 1000 ppm 1,7-octadiene and 1% mesitylene at 2.5 atm argon.

1,7-octadiene in 1% mesitylene and argon; 1000 ppm 1,7-octadiene in 1% mesitylene and argon; 150 ppm 1,7-octadiene/150 ppm 1-methylcyclohexene in 1% mesitylene and argon. The wide variation in octadiene concentration was necessary in order to quantitatively relate allene formation to the elementary process of allyl radical decomposition in the face of competing processes that consume the latter. Experiments using the 33 ppm samples were carried out under conditions where the pressure was ~3 times that of the other studies. This was used to check for pressure effects. All the chemicals were purchased from Chemical Samples. Gas chromatographic analysis did not reveal significant amounts of any impurities. Thus, except for vigorous degassing, the samples were used without further purification.

Results

Typical product distributions from the decomposition of trace quantities of 1,7-octadiene in mesitylene can be found in Figure 1A,B. These confirm the postulated mechanism given earlier. Ethylene is the main product. Other significant products include allene, propene, propyne, 1,5-hexadiene, 1,4-pentadiene, m-xylene, and cyclopentene. 1-Butene was also present, but due to experimental problems, quantitative measurements of its concentrations were not made. Allene becomes an important product at high extent of decomposition. Note the very strong temperature dependence for the formation of allene and propyne. Panels A and B of Figure 1 are qualitatively similar. The agreement is in fact quantitative for products such as ethylene, 1,4-pentadiene, and cyclopentene. However, the higher concentration mixture led to larger yields of hexadiene and smaller yields of allene. Allene to ethylene ratios are summarized in Figure 2 and will be used in the subsequent analysis. Also of interest is the dependence of the allene to ethylene ratio on the initial concentration. These results clearly indicate that allene is formed as a secondary product and that its formation is retarded as reactant concentration is increased. The presence of large quantities of 1,5-hexadiene suggests that allyl combination must be an important channel that

TABLE I: Rate Expressions Used in Modeling Allene to Ethylene Ratios during 1,7-Octadiene Decomposition⁴

	log A	n	E/R	ref	
1. 1,7-octadiene = 4 -pentenyl + allyl	16.1	0	35.7	Ь	
2. 1,7-octadiene = 1,4-pentadiene + propene	12.5	0	27.9		
3. 4-pentenyl = allyl + ethylene	fast ^c				
4. 4-pentenyl = cyclopentene + H	fast				
5. allyl = allene + H		see text			
6. allyl + allyl = $1,5$ -hexadiene	10.0	0	-0.3	14	
7. $allyl + allyl = allene + propene$		see text			
8. 1,5-hexadiene = $allyl + allyl$		see text			
9. H + mesitylene = H_2 + 3,5-dimethylbenzyl	11.6	0	4.3	15	
10. H + mesitylene = methyl + m -xylene	10.8	0	3.3	15	
11. allyl + 3,5-dimethylbenzyl = $4-(3,5-dimethylphenyl)$ butene	10.2	0	0	est	
12. $allyl + 3.5$ -dimethylbenzyl = $allene + mesitylene$	7.6	0	0	est	
13. $4-(3,5-dimethylphenyl)$ butene = allyl + 3,5-dimethylbenzyl	15.4	0	30.7	est	
14. $allyl + methyl = 1$ -butene	10.3	0	0	3	
15. allyl + methyl = CH_4 + allene	8.9	0	0	3	
16. $H + allyl = propene$	11.3	0	0	3	
17. $H + allyl = allene + H_2$	10.3	0	0	3	
18. $H + 3.5$ -dimethylbenzyl = mesitylene	11.3	0	0	est	
19. $H + methyl = methane$	10.5	0	0	4	
20. $methyl + methyl = ethane$	10.0	0	0	4	
21. methyl + $3,5$ -dimethylbenzyl = 1 -ethyl, $3,5$ -dimethylbenzene	10.3	0	0	est	
22. methyl + mesitylene = $3,5$ -dimethylbenzyl	9.1	0	4.8	17	
23. $2(3,5-dimethylbenzyl) = (3,5-dimethylbenzyl)_2$	9.9	0	0	est	
24. $(3,5-dimethylbenzyl)_2 = 2(3,5-dimethylbenzyl)$	15.0	0	31.7	est	

^a In units of s⁻¹ and L mol⁻¹ s⁻¹. ^b This work. ${}^{c}k_{4}/k_{3} = 6.9 \times 10^{-3} \exp(2118/T)$.



Figure 2. Allene to ethylene yields as a function of temperature for various reaction mixtures: (O) 100 ppm 1,7-octadiene and 1% mesitylene at 2.2 atm argon, (\Box) 1000 ppm 1,7-octadiene and 1% mesitylene at 2.5 atm argon, and (\diamond) 33 ppm 1,7-octadiene and 0.33% mesitylene at 6.6 atm argon.

may cause a retarding of allene formation in higher concentration mixtures. In addition, small amounts of m-xylene have also been detected. This is derived from the hydrogen atom induced displacement of methyl from mesitylene, the inhibitor in the system. Most of the methyl radicals so formed probably abstract a benzylic hydrogen and form methane. Methane is a reaction product but quantitative measurements were not made, since at the low concentrations used here background methane makes a significant contribution.

Also of interest is the detection of propyne at $\sim^1/_{10}$ the concentration of allene. The temperatures of these experiments are too low for appreciable quantities of this compound to be formed via the known isomerization process.¹² Indeed, the relative independence of the propyne to allene ratio with temperature and reaction extent is indicative of its formation coincident with allene.

Another important feature of the results is the ratio of allene to 1,5-hexadiene. Results are summarized in Figure 3. At the lowest temperature, this ratio drops to values as low as 0.005. James and Kambanis¹³ found at lower temperatures a disproportionation to combination ratio of 0.008. In the present case, allene can also be formed from allyl decomposition. Therefore one expects that if disproportionation should make an important contribution, then the allene to 1,5-hexadiene ratio should level off with decreasing temperature. Even at the lowest values this does not occur. Thus the present results suggest that, at the temperatures appropriate to these experiments, the lower tem-



Figure 3. Allene to hexadiene yields as a function of temperature: (•) 100 ppm 1,7-octadiene in 1% mesitylene and argon and (O) 1000 ppm 1,7-octadiene in 1% mesitylene and argon; pressure, 2.5 atm. Dashed line is for disproportionation to combination ratio of 0.005.

perature number is not applicable.

The data in Figure 2 also contain results at the same concentration as that for the 100 ppm 1,7-octadiene studies but at an argon pressure that is a factor of ~ 3 larger. The results are very similar to the lower pressure studies. On this basis it would appear that any pressure dependence is less than $p^{0.1}$. Nevertheless, as will be seen in a subsequent section, it does appear that the rate constants for allyl radical decomposition, although close, are not at the high-pressure limit and a small correction factor is needed to obtain results at this limit.

Analysis of the data in Figure 1 demonstrates very satisfactory mass balance. Specifically, the sum of the ethylene, 1,4-pentadiene, and cyclopentene is very close to the 1,7-octadiene that has disappeared. The presence of large quantities of allene and 1,5-hexadiene is clear evidence of allyl radicals. As expected, these do not account for all the allyl radicals that must be released into the system as deduced from the ethylene yield. This is expected since allyl can also recombine with the other radicals such as methyl and 2,4-dimethylbenzyl that are presumed to be present in the system. Note that the yield of propene is in excess of the 1,4-pentadiene. Thus some of the propene must have been formed from the allyl radicals that are present in the system. Some of the possible processes are listed in Table I. Since some of the allyl radicals actually survive the heating period, there are many other processes that may make contributions. The earlier discussion on the disproportionation process of allyl radicals would seem to rule this out as a major source of the excess propene.



Figure 4. Arrhenius plots for decomposition of 1,7-octadiene: (O) bond breaking and (\bullet) retroene process. Results are from a mixture containing 150 ppm 1,7-octadiene and 150 ppm 1-methylcyclohexene in 1% mesitylene in argon; pressure, 2.5 atm. Dotted lines represent 2× results for 1-hexene decomposition.



Figure 5. Ratio of rate constants for cyclization (k_d) to bond breaking (k_c) during the decomposition of the 4-pentenyl radical.

Quantitative analysis of the results will be divided into two parts. The first will consider the initial bond-breaking unimolecular steps. This is straightforward, and the procedure has been utilized in previous studies. The results are very important for the subsequent work since this yields information regarding the release of allyl radicals into the system. Note that in so far as C-C bond breaking is concerned (reaction a), quantitative conversion to ethylene and cyclopentene means that the concentration measurements can be used to calculate unimolecular rate constants. Similarly, the yield of 1,4-pentadiene is a direct measure of the contribution from the molecular process, reaction b. The relevant relations are

$$k(a) =$$

$$\log (1 - X[C_2H_4 + cyclopentene]/[1,7-octadiene]_i)/tX$$

where t, the total heating time for these experiments, is 500 μ s and $X = 1 + [1,4\text{-pentadiene}]/[C_2H_4 + cyclopentene]$ and

$$k(b) = k(a)([1,4-pentadiene]/[C_2H_4 + cyclopentene])$$

In addition, the ratio of the yield of the cyclopentene and ethylene is a measure of the branching ratio for the decomposition of 4-pentenyl radicals via cyclization, reaction d, or bond breaking, reaction c. The experimental results can be found in Figures 4 and 5. They lead to the following rate expressions:

$$k(a) = (1.2 \pm 0.8) \times 10^{16} \exp(-35700 \pm 400/T) \text{ s}^{-1}$$

$$k(b) = (3 \pm 1.5) \times 10^{12} \exp(-27900 \pm 270/T) \text{ s}^{-1}$$

$$k(d)/k(c) = (6.9 \times 4) \times 10^{-3} \exp(2118 \pm 500/T)$$

It is not possible to derive the rate constant for allyl radical decomposition in an analytical fashion directly. Aside from the fact that it is being formed in the course of the reaction, there are a variety of processes in addition to its decomposition to allene that may remove it from the system. The most important of these is direct combination to form 1,5-hexadiene, and as noted earlier, large quantities of this compound are in fact found. On the other hand, 1,5-hexadiene is not completely stable under the present conditions, so the reverse decomposition must also be factored into the analysis. Furthermore, combination processes can occur not only with allyl itself but also with any other radicals that may be present in the system. A complicating feature is the disproportionation reaction. In an earlier section it was noted that the measured product distribution indicates a lower disproportionation to combination ratio than that determined at room temperature. In this work the analysis has been carried out by assuming the lowest value obtained here and also for a value of zero. From the earlier discussion it can be seen that the value of 0.005 must be an overestimate. It will be seen in the subsequent discussion that the experiments are in fact being carried out at sufficiently high levels of allene yield from allyl radical decomposition, so that quantitative results are probably unaffected by the contribution from the disproportionation process.

Due to the above complicating features, rate constants for allyl radical decomposition have been extracted on the basis of chemical kinetic modeling using the set of reactions and rate expressions given in Table I. Most of these are fairly well established. In the course of fitting the results, it turned out that the only important complicating process is that of combination of the allyl and the subsequent decomposition of the 1,5-hexadiene. Reactions 11-24 could therefore have been neglected without affecting the quantitative results. Thus a key variable is the equilibrium constant for this process, $K_{eq}(1,5-hexadiene = 2allyl)$. A consequence of the present work is a redetermination of this quantity and through it the heat of formation of the allyl radical.

In this analysis, the rate expression for combination of allyl is taken from Tulloch et al.¹⁴ It is very similar to that determined more recently by Roth et al.⁶ At the temperatures of these experiments, 1,5-hexadiene rapidly decomposes. For this process, the rate expression has been calculated through the equilibrium constant. Indeed, in the present situation the latter is the key variable. Assuming, as was done earlier, that the entropy change can be accurately estimated, then the remaining uncertainty is the bond dissociation energy and through it the heat of formation of the allyl radical. In an earlier review, a value for the heat of formation of allyl of $169 \pm 6 \text{ kJ/mol}$ was recommended. This leads to an activation energy for 1,5-hexadiene decomposition of $238.5 \pm 12 \text{ kJ/mol}$. Due to the consequent large uncertainty in the heat of formation of allyl, values ranging from 164.8 to 177.4 kJ/mol have been considered. This should cover all the likely possibilities with respect to possible rate expressions for allyl decomposition.

The fitting procedure involves exactly reproducing the observed allene to ethylene ratio as given in Figure 2 for the 100 ppm 1.7-octadiene mixture using a number of possible heats of formation of the allyl radical. A check of the assumptions is furnished by satisfactory fits for the 1000 ppm 1,7-octadiene results. The lines in Figure 2 are an example of a typical case with the heat of formation of allyl set at 169 kJ/mol. The lines are given in pairs, and the higher values are for a disproportionation to combination ratio of 0.005, which, as noted earlier, is undoubtedly an overestimate. The lower line is for a value of zero and is used to derive the expressions given here. These lines clearly encompass all the results. It is estimated that in the context of the data the uncertainty is ~ 4 kJ/mol in the activation energy and a factor of 1.5 in the A-factor. Aside from these trials, fits have also been made in which 1,5-hexadiene decomposition and allyl combination rate constants are varied by the same amount (factor of 2). This leaves the allene/ethylene ratio completely unchanged and clearly establishes the importance of the equilibrium constant as opposed to the individual rate constants. Unfortunately the fits of the present data by themselves do not have sufficient sensitivity to permit discrimination between the various trial heats of formation. Instead, one obtains for each heat of formation of allyl a rate expression for allyl decomposition under the present reaction conditions. The results are summarized in Table II. A plot of the rate expressions can be found in Figure 6.

From the data in Table II, it is clear that the derived rate expressions are strongly dependent on the equilibrium constant that is selected. The actual rate constants, particularly at the

 TABLE II: Derived Rate Expressions, Assuming Various Values for 1,5-Hexadiene Decomposition

		H _e (allyi)			allyl decomp ⁶			
A (s ⁻¹)	E/T	(kJ/mol)	A (s ⁻¹)	E/T	$\overline{A(s^{-1})}$	E/T		
8×10^{14}	-27 700	164.8	2.5×10^{12}	-26 888	2.0×10^{14}	-31 668		
8×10^{14}	-28 700	169.0	1.3×10^{13}	-28 600	1.0×10^{14}	-30937		
8×10^{14}	-29 200	171.1	2.7×10^{13}	-29 406	7.2×10^{13}	-30 557		
8×10^{14}	-29710	173.2	6.3×10^{13}	-30 363	5.4×10^{13}	-30 206		
8×10^{14}	-30715	177.4	3.1×10^{14}	-32125	2.8×10^{13}	-29 475		

^a From experimental allene/ethylene ratios. ^b From shock tube measurement at 1080 K and H + allene result at 350 K.



Figure 6. Arrhenius plots of rate constants for allyl decomposition for various heats of formation of allyl radicals: (A) 177.4, (B) 173.2, (C) 171.1, (D) 169.0, and (E) 164.8 kJ/mol. Dashed line is based on rate expression of Wagner and Zellner for H + allene \rightarrow allyl and 169.0 kJ/mol heat of formation of allyl.

lowest temperatures, are much less sensitive. This can be seen in Figure 6. Thus, from the present experiment it is possible to state that $k(\text{allyl} \rightarrow \text{allene} + \text{H}) = 40 \pm 10 \text{ s}^{-1}$ at 1080 K. Physically this means that at the lowest temperatures and conversions not enough allyl radicals are being formed to trigger the equilibrium and the measured allene/ethylene ratio is a direct reflection of the decomposition process.

Note, from Figure 6, that the rate constants at 1080 K from this study are a factor of 4 higher than that extrapolated from the results of Wagner and Zellner on the basis of the equilibrium constant with a heat of formation of allyl of 169.0 kJ/mol. Originally, it was thought that this was a manifestation of the expected curvature of the Arrhenius plot. However, transition-state calculations showed that the data could not be fitted in this manner with any reasonable transition-state structure. Instead, it seems that the choice of the heat of formation of allyl as well as uncertainties in the rate expression of Wagner and Zellner must be the source of the discrepancy.

The possibilities for Arrhenius rate expressions as a function of various heats of formation of the allyl radical are summarized in the last column in Table II. This is based on the measured number at 1080 K and a calculated value at 350 K derived from the low-temperature hydrogen atom addition rate constant of Wagner and Zellner and converted to a decomposition rate constant through the appropriate equilibrium constant. Obviously, for each allyl heat of formation a different expression is determined. It should be realized that the present and subsequent analysis involving the low-temperature data assumes that all the allene that is detected at the high temperatures originates from the ejection of the β -hydrogen from the allyl radical. On the other hand, note that the low- and high-temperature points span 25 orders of magnitude in decomposition rate constants. Therefore considerable errors in the two values upon which the expressions are determined are tolerable. Since the shock tube data have been shown to be near the high-pressure limit, it is clear that the data are not consistent with the lowest value of the heat of formation used in the present trials (164.8 kJ/mol), since a 2 orders of magnitude larger A-factor implies that the reaction would be strongly pressure dependent. This will be demonstrated below. Similarly, the highest value is also unlikely since this will imply an extremely strong curvature in the Arrhenius plot.

TABLE III: Rate Expressions for Allyl Decomposition on the Basis of Best Fits of Low-Temperature Data and High-Pressure Results at 1080 K, and Pressure Dependence between 2 and 7 atm Argon²

model	ing ^b	step-size	step-size RRKM calcns (s ⁻¹)		
$A(s^{-1})$	E/T	down (cm ⁻¹)	$A (s^{-1})$	E/T	dependence
2.5×10^{12}	-26 888	400	3.7×10^{13}	-29738	0.2
(164.8)		600	6.5×10^{13}	-30 361	0.15
		800	8.7×10^{13}	-30 684	0.12
1.3×10^{13}	-28 600	400	2.6×10^{13}	-29 450	0.15
(169.0)		600	4.3×10^{13}	-29 930	0.1
		800	5.3 × 10 ¹³	-30 226	0.08
2.5×10^{13}	-29 406	300	1.4×10^{13}	-28 906	0.14
(171.1)		400	2.1×10^{13}	-29 283	0.11
		500	2.5×10^{13}	-29 525	0.10
		600	3.3×10^{13}	-29713	0.08
		800	4.3×10^{13}	-29 982	0.07
		300	1.2×10^{13}	-28 638	0.14
6.3×10^{13}	-30 363	400	1.8×10^{13}	-29 070	0.1
(173.2)		600	2.6×10^{13}	-29 473	0.07
		800	3.3×10^{13}	-29715	0.06
3.1×10^{14}	-32125	300	9 × 10 ¹²	-28 315	0.1
(177.4)		400	1.3×10^{13}	-28 665	0.08
		600	1.7×10^{13}	-29015	0.05
		800	2×10^{13}	-29 203	0.04

^aAssuming various values for the heat of formation of allyl and step-sizes down. ^bNumbers in parentheses are the assumed heats of formation of allyl (kJ/mol).

Although the data in Table II are suggestive, a more valid and complete treatment will be through a transition-state model and the determination via RRKM calculations of rate expressions that can be compared with the experimentally determined quantities. One can then determine the heat of formation of allyl that will actually reproduce the rate expression determined from the shock tube experiments. For this purpose, a vibrator transition-state model is used to fit the results from Wagner and Zellner at 350 K (converted to a decomposition rate constant through the equilibrium constant for a given heat of formation of allyl) and the experimental data on allyl decomposition at 1080 K. For a variety of step-sizes down, rate expressions are then derived for the temperature range of 1080-1190 K and compared with that deduced on the basis of chemical kinetic modeling. Although there are elements of ambiguity in arriving at a transition-state structure. it is well-known that details are relatively unimportant as long as the correct A-factors are obtained. Attention is also paid to the calculated pressure dependence, and it is assumed that the present results forbid a dependence greater than $p^{0.1}$

The results of these calculations in terms of the deduced rate expressions are summarized in Table III. They confirm the earlier conclusions that the shock tube data are incompatible with allyl heats of formation of 164.2 and 177.4 kJ/mol. As noted earlier, for the former choice, matching of the rate expressions will lead to very strong pressure dependencies. For the latter, no match of the rate expression is possible, and the deviation in the activation energies is of the order of 25 kJ/mol. This is far larger than any conceivable error. The best match of results and calculations is with a heat of formation of 171 kJ/mol or an allylic resonance energy of 51 kJ/mol and a step-size down of 500 cm⁻¹.

It is difficult to assign uncertainties to these values. For the allyl heat of formation, clearly the expressions from values of 164.8 and 177.4 kJ/mol do not match the experimental results. In view of the possible uncertainties in the low-temperature measurements and the contributions from the disproportionation reaction, an estimated uncertainty of ± 4 kJ/mol in the heat of formation of allyl would seem to be appropriate. The uncertainty in the step-size-down parameter is tied to the high-pressure rate expression used. As a rough estimate, an uncertainty of ± 200 cm⁻¹ may be appropriate.

On this basis, the high-pressure rate expression for allyl radical decomposition is

$$k(\text{allyl} \rightarrow \text{allene} + \text{H}) = 1.5 \times 10^{11} T^{0.84} \exp(-30053/T) \text{ s}^{-1}$$

TABLE IV: Falloff Characteristics for Allene Decomposition

(a) log k/kinf for Anyr Docomposition as a renotion of remperature and resourc, Assuming Strong Com	osition as a Function of Temperature and Pressure, Assuming St	trong Collisio
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log	<i>T</i> (K)											
(density)	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16	-0.01	-0.04	-0.15	-0.33	-0.57	-0.82	-1.10	-1.37	-1.64	-1.91	-2.16	-2.41
16.5		-0.02	-0.08	-0.20	-0.38	-0.59	-0.82	-1.06	-1.30	-1.54	-1.77	-1.99
17		-0.01	-0.04	-0.11	-0.23	-0.39	-0.58	-0.78	-0.98	-1.19	-1.40	-1.61
17.5			-0.01	-0.05	-0.13	-0.24	-0.38	-0.54	-0.71	-0.89	-1.07	-1.25
18			-0.01	-0.02	-0.06	-0.13	-0.23	-0.35	-0.48	-0.62	-0.77	-0.92
18.5				-0.01	-0.03	-0.07	-0.13	-0.20	-0.30	-0.41	-0.52	-0.64
19					-0.01	-0.03	-0.06	-0.11	-0.17	-0.24	-0.32	-0.41
19.5						-0.01	-0.03	-0.05	-0.08	-0.13	-0.18	-0.24
20							-0.01	-0.02	-0.04	-0.06	-0.09	-0.12
20.5								-0.01	-0.01	-0.02	-0.04	-0.05
21										-0.01	-0.01	-0.02

(b)	Collision	Efficiency	for	Allene	Decomposition	as a	Function of	f Step-	Size	Down a	and	Temperature
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			step-size (cm ⁻¹)		
T (K)	50	100	200	400	800
300	2.6×10^{-2}	7.7×10^{-2}	1.9 × 10 ⁻¹	3.7×10^{-1}	5.7×10^{-1}
500	1.0×10^{-2}	3.3×10^{-2}	9.5×10^{-2}	2.2×10^{-1}	4.1×10^{-1}
700	4.8×10^{-3}	1.7×10^{-2}	5.3×10^{-2}	1.4×10^{-1}	3.0×10^{-1}
900	2.6×10^{-3}	9.3 × 10 ⁻³	3.1×10^{-2}	9.0×10^{-2}	2.1×10^{-1}
1100	1.5×10^{-3}	5.5×10^{-3}	1.9×10^{-2}	5.9 × 10 ⁻²	1.5×10^{-1}
1300	8.8×10^{-4}	3.3×10^{-3}	1.2×10^{-2}	3.8×10^{-2}	1.1×10^{-1}
1500	5.5 × 10 ⁻⁴	2.1×10^{-3}	7.6×10^{-3}	2.6×10^{-2}	7.7×10^{-2}
1700	3.6 × 10 ⁻⁴	1.4×10^{-3}	5.2×10^{-3}	1.8×10^{-2}	5.7×10^{-2}
1900	2.6×10^{-4}	1.0×10^{-3}	3.8×10^{-3}	1.4×10^{-2}	4.4×10^{-2}
2100	2.1×10^{-4}	8.0 × 10 ⁻⁴	3.1×10^{-3}	1.1×10^{-2}	3.7×10^{-2}
2300	1.7×10^{-4}	6.8 × 10 ⁻⁴	2.6×10^{-3}	9.5×10^{-3}	3.2×10^{-2}
2500	1.6 × 10 ⁻⁴	6.1×10^{-4}	2.4×10^{-3}	8.7×10^{-3}	3.0×10^{-2}

(c) k/k_{inf} as a Function of Temperature (0.1, 1.0, and 10 atm Argon)

 $log (k(Ar,0.1)/k(inf)) = -0.2296 + 1.0949 \times 10^{-3}T - 1.2605 \times 10^{-6}T^2 + 7.9536 \times 10^{-11}T^3 + 4.4410 \times 10^{-14}T^4 log (k(Ar,1.0)/k(inf)) = -0.0303 + 5.5148 \times 10^{-6}T + 4.1868 \times 10^{-7}T^2 - 6.1874 \times 10^{-10}T^3 + 1.4013 \times 10^{-13}T^4$

 $\log \left(k(\text{Ar},10)/k(\text{inf}) \right) = 0.0811 - 4.9765 \times 10^{-4}T + 9.6629 \times 10^{-7}T^2 - 6.8737 \times 10^{-10}T^3 + 1.2663 \times 10^{-13}T^4$

or alternatively it could be equally well represented in the Arrhenius form

$$k(\text{allyl} \rightarrow \text{allene} + \text{H}) = 8 \times 10^{13} \exp(-30567/T) \text{ s}^{-1}$$

As expected this is very similar to that derived earlier (see Table III). Through the equilibrium constant with a heat of formation of allyl of 171 kJ/mol, one obtains

$$k(H + allene \rightarrow allyl) =$$

1.2 × 10⁸ T^{0.69} exp(-1513/T) L mol⁻¹ s⁻¹

In the temperature range covered by Wagner and Zellner this is equivalent to

$$k(H + allene \rightarrow allyl) =$$

2.1 × 10¹⁰ exp(-1935/T) L mol⁻¹ s⁻¹

In comparison to the published expression of Wagner and Zellner, the present results suggest larger rate parameters and emphasize the contribution of the activation energy in retarding nonterminal addition of hydrogen to allene. Similar effects have been noted in studies of methyl⁹ and hydrogen¹⁶ addition to isobutene.

It should be noted that these rate expressions, although they are self-consistent over the entire temperature range covered, must be used with caution outside the range where measurements have been made. It is estimated that the uncertainty in the decomposition rate constant should not exceed a factor of 1.3 near 1100 K. At 350 K however it may be as large as 1 order of magnitude. In this region the uncertainty in the heat of formation of allyl becomes particularly important. Fortunately, in this temperature region the rate constant for allyl decomposition is so small that errors of this amgnitude are unimportant under practically all conceivable situations. For the addition reaction, it is estimated that the uncertainty in the direct measurement will be of the order of a factor of 1.5. This will increase to a factor of 2.5 at 1100 K and is, as before, a reflection of the uncertainty in the heat of formation of allyl.

As an aid to those who may need to use these rate constants, we present, in Table IV, k/k_{inf} values as a function of temperature and pressure assuming strong collisions. They are meant to supersede earlier recommendations which are based on smaller rate parameters.³ The actual changes are however not very large. Also in Table IV are collision efficiencies as a function of step-size down and temperature. Starting with the high-pressure rate expression given above and these two tables, a user should be able to calculate decomposition rate constants or the reverse under all conditions. For further details the reader is referred to ref 3. Finally we give k/k_{inf} as a closed expression as a function of temperature for 0.1, 1, and 10 atm argon over the temperature range 300-2500 K. These expressions are also recommended for reactions in nitrogen. The k_{inf} expression is that given above. The step-size down is taken to be 500 cm⁻¹ at 1150 K and assumed to follow a linear temperature dependence. It should be noted that the real significant change from the earlier recommendation is in the high-pressure rate expression.

Discussion

It has been shown that the thermal decomposition of 1,7-octadiene is a well-controlled source for the production under high-temperature conditions of allyl radicals. It is interesting to compare the rate expressions derived here for this dissociation with earlier results on the most closely comparable system, 1-hexene decomposition. The results in the form of 2× the rate constants can be found in Figure 4, the dotted lines. Agreement with the new results is extraordinarily good. The implication is that γ substitution of a vinyl group is too remote to have any effect on the bond being broken. Thus the data for small systems can be confidently extrapolated to more complex molecules. A consequence of this observation is that the bond dissociation energy of the primary bond in 1-pentene can be taken to be that of propane to within 2 kJ/mol.

The detection of cyclopentene in small amounts is a clear demonstration that cyclization after allyl addition to ethylene is

TABLE V: Rate Expressions for Allyl and Ethyl Decomposition at Various Temperatures

	allyl	l	ethy	l
<i>T</i> (K)	$\log A(s^{-1})$	E/R	$\log A (s^{-1})$	E/R
300	13.6	30272	13.1	18800
500	13.8	30471	13.3	19000
700	13.9	30649	13.5	19200
900	14.0	30806	13.6	19400
1100	14.1	30952	13.7	19600

^a Allyl expressions based on vibrator model with frequencies of 200, 300, 500, 1100 (5), 1300 (3), 1450 (2), and 3100 (2) cm^{-1} .

making a contribution. It is however dwarfed by β -bond fission, and the temperature dependence is such it will be even less important as the temperature is increased. The rate expression 6 $\times 10^6 \exp(-5776/T)$ L mol⁻¹ s⁻¹ for the formation of cyclopentene from the reaction of allyl + ethylene determined by Sakai et al.¹ is not a true elementary reaction; instead it deals with the complex process

allyl + ethylene \leftrightarrow 4-pentenyl \leftrightarrow cyclopentene + H

Since the present measurement has led to the determining of the partitioning of the 4-pentenyl radical with the reverse bond breaking being overwhelmingly favored, then

$$k(\text{allyl} + \text{ethylene}) = 8.4 \times 10^8 \exp(-8000/T) \text{ L mol}^{-1} \text{ s}^{-1}$$

This can be compared with the published value for n-propyl addition to ethylene near 430 K¹⁸

$$k(n-\text{propyl} + \text{ethylene}) =$$

1.6 × 10⁷ exp(-3120/T) L mol⁻¹ s⁻¹

ľ

The calculated rate parameters appear to be very large. Part of the problem undoubtedly is due to the fact that the results of Sakai et al. are in the 700 K region. The cyclization to bond breaking ratio determined here is for the
$$1050-1190$$
 K regime, and the *n*-propyl rate quoted here is at 430 K. With this caveat, it should be noted that a larger *A*-factor for reactions of allyl in comparison to that of alkyl radicals can be expected since the former has a

to much "stiffer" structure (no free rotors).

This explanation is also in line with the apparently larger A-factor for allyl decomposition in comparison to that for alkyl radicals. Table V gives calculated rate expressions at various temperatures. These may be compared with comparable expressions for ethyl radical decomposition. These are based on the work of Pilling and co-workers, 19,20 converted to the decomposition rate constant through the equilibrium constant and fitted to a transition-state model in a manner similar to that used here. Note that in the case of allyl there is only one hydrogen compared to three in ethyl or nine in tert-butyl. Thus, on a per hydrogen basis there are differences of between 0.5 and 1 order of magnitude in the A-factor. It is probably not accidental that the entropies of the free methyl rotor (in alkyl radicals) are considerably larger than that of a 400-cm⁻¹ vibrator. Qualitatively the A-factors for radical decomposition are all in the "normal" range and in contrast to that for bond breaking leading to the formation of two radicals. Note that the vibrator model leads to an increasing A-factor with temperature. However, the positive curvature for these cases is considerably smaller than the negative curvature for bond breaking, and as for allyl, the rate expression can be represented to good accuracy by an Arrhenius expression.

The 500-cm⁻¹ step-size down is very much in line with other measurements that have been made under similar conditions.¹⁹ They are however somewhat higher than values determined at lower temperatures and pressures on the decomposition of alkyl radicals. The activation energy for this process is however much higher than that for alkyl decomposition. It should be noted that for this type of measurement the step-size down is very sensitive

to the A-factor. Thus a lower A-factor would have led to a smaller value for this parameter.

The mechanism for propyne formation during allyl decomposition is uncertain. Allyl decomposition is a very high activation energy process. Thus some comparatively high activation processes can make contributions. For example, it is possible that a 1,2 hydrogen shift is the precursor to propyne formation. In the case of the decomposition of alkyl radicals such as isopropyl and tert-butyl, small concentrations of ethylene and propylene, respectively, in comparison to the main products, propene and isobutene, have always been detected in single-pulse shock tube experiments. These must have been formed as a consequence of 1,2 hydrogen shifts followed by β -carbon bond scission. However, if the 2-propenyl radical is formed, then one would expect that some of the allene that is detected must have also arisen from this reaction channel. This may have some effect on the rate expressions derived earlier. Fortunately, as noted earlier, the large rate constant range used in deriving these expressions means that this should not be a large source of error. Finally, the lower than expected disproportionation to combination ratio for allyl radicals suggests that the rate constant for the disproportionation has a stronger negative temperature dependence than the combination reaction. Unfortunately, there does not appear to be any precedent for such an observation.

Registry No. CH2=CH(CH2)4CH=CH2, 3710-30-3; CH2= CHCH₂*, 1981-80-2; CH₂=CH(CH₂)₂CH₂*, 7313-97-5; CH₂=CH₂, 74-85-1; CH₂=CHCH₃, 115-07-1; CH=CCH₃, 74-99-7; CH₂=CH(C-H₂)₂CH=CH₂, 592-42-7; CH₂=CHCH₂CH=CH_∞, 591-93-5; CH₂= CHCH₂CH₃, 106-98-9; CH₃C₆H₄-m-CH₃, 108-38-3; cyclopentene, 142-29-0; mesitylene, 108-67-8.

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