

The Thermal Decomposition of 1,7 Octadiyne as
A Source of Propargyl Radicals

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ABSTRACT

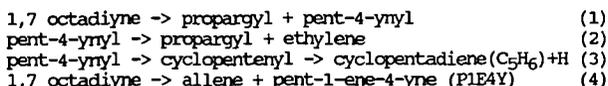
Dilute concentrations of 1,7 octadiyne have been decomposed in single pulse shock tube experiments. At temperatures between 1000-1200K and pressures of 2-7 atm argon, the products are consistent with the main reaction involving the breaking of the propargylic carbon-carbon. The rate expression for bond breaking is $1.6 \times 10^{16} \exp(-35760/T) \text{ s}^{-1}$. The newly formed pent-4-ynyl radical can cyclize or decompose via beta bond cleavage to form another propargyl radical and ethylene. The ratio of rate constants for the two processes is $5.4 \times 10^{-4} \exp(6700/T)$. A parallel retroene reaction proceeds with the rate expression, $5.6 \times 10^{12} \exp(-27860/T) \text{ s}^{-1}$. The propargyl radicals recombine to form a large number of linear C_6 isomers. As the temperature is increased fulvene and benzene are among the main products. The use of 1,7 octadiyne as a thermal source of propargyl radicals for studying reactions with other reactive species will be discussed.

INTRODUCTION

Recent studies^{1,2} have demonstrated the important role that propargyl radicals may play as a precursor for the formation of benzene and other C_6H_6 isomers in hydrocarbon combustion systems. Except for the work on Kern and coworkers³ at very high temperatures, there have been no direct quantitative studies involving the reactions of propargyl radicals with other organic molecules under conditions that lead to results that can be used in combustion systems. A prerequisite for making such studies is a method for the generation of propargyl radicals in known quantities. This paper reports on the results of efforts in this direction and on the nature of the products from propargyl radical combination.

Stein et al¹ have confirmed⁴ that one of the possible products of propargyl radical combination, 1,5 hexadiyne will easily rearrange through molecular processes to form fulvene and benzene. Alkemade and Homann² have generated propargyl radicals through reaction of propargyl bromide with sodium and reported on the formation of a variety of recombination products, 1,5 hexadiyne, 1,3 hexadien-5-yne, 1,2 hexadien-5-yne, 1,2,4,5-hexatetraene and benzene at temperatures between 623-673K. They distinguish between initial and secondary products with benzene and 1,3-hexadien-5-yne being in the latter category. To some degree these results are discordant with that of Stein et al, since one would have thought that with the low energy molecular decomposition channel for 1,5 hexadiyne, most of this compound would have been immediately converted upon recombination in the low pressure system used by Alkemade and Homann. In addition, they were not able to detect the well known characteristic products of 1,5 hexadiyne decomposition, bis-methylenecyclobutene and fulvene.

The focus of this study is 1,7 octadiyne decomposition. Previously, extensive studies⁵ on the decomposition of the larger acetylenes have been carried out. The important reaction pathways were the breaking of the propargyl C-C bond and a molecular process (retro-ene reaction) leading to the production of allene and the appropriate olefin. On this basis it is expected that the mechanism for 1,7 octadiyne decomposition will be



The desired reactions are (1) and (2) and it will be noted that every ethylene that is formed leads to the creation of two propargyl radicals. Reactions (3) and (4) are possible interfering processes. The consequence of (4) is not important since all that occurs is the release of two stable species into the system. Reaction (3) releases hydrogen atoms. This can lead to the formation of other radicals and to complications in the interpretation of the data. Such effects can be eliminated through the use of a chemical inhibitor. In addition, major contributions from this channel will mean that the 2 to 1 relation between propargyl and ethylene will be violated unless it is taken into consideration.

From another point of view the detection of cyclopentadiene is quite important since pent-4-ynyl is the result of the addition of propargyl to ethylene. Any products that are formed is indicative of ring closing becoming competitive with beta C-C bond cleavage leading to smaller molecular fragments. It is the competition between these two processes that is a key determinate of whether soot can be formed in any particular system.

In the course of this work experiments have also been carried out on the decomposition of 1,5 hexadiyne, 1-hexyne and 2,4 hexadiyne. All of these studies are aimed at providing confirmation for the surmise that a number of the gas chromatographic peaks that are observed arise from propargyl radical combination. This is necessary because it was not possible to identify specific compounds with these peaks.

Experiments are carried out in a single pulse shock tube. Such studies have unique capabilities for determining the stability characteristics (in the sense of unimolecular decompositions) of volatile organics at high temperatures. We have used the method for studying the thermal unimolecular decomposition processes of many organic compounds⁶. More recently, the mechanisms and rate constants for hydrogen-atom attack on unsaturated compounds⁷ have been determined. For these studies, the hydrogen atoms were generated through the thermal decomposition of organic molecules in a manner similar to the generation of propargyl radicals in this study.

EXPERIMENTAL

The details of the single pulse shock tube and the experimental procedure⁶ used in carrying out experiments on the thermal decomposition of organics have been described in earlier publications. Summarizing briefly, trace quantities of the organic in question, 100-1000 ppm, are decomposed by the reflected shock in the presence of large amounts of a thermally stable

chemical inhibitor such as mesitylene. Reactive radicals such as hydrogen atoms will attack the inhibitor leading to the formation of a less reactive, resonance stabilized species, 3,5 dimethylbenzyl radical. In the short time scale of shock tube experiments these can only recombine with itself and other long lived radicals and therefore can not play a role in the overall reaction. Analysis was by gas chromatography using flame ionization detection. The light gases were eluted isothermally using a 12 ft Poropak N⁸ column while the heavier compounds, from C₄ on up, were eluted using a wide bore 30-meter dimethylsiloxane column in the programmed temperature mode. All products were identified on the basis of retention times of neat samples.

The experiments were carried out using the internal standard method. This eliminated the possibility of errors arising from uncertainties in the reaction temperature. The internal standard used in these experiments was the decomposition of 4-methylcyclohexene to form propene and butadiene. The rate expression for this reverse Diels-Alder reaction has previously been found to be

$$k(4\text{-methylcyclohexene} \rightarrow \text{propene} + \text{butadiene}) = 2 \times 10^{15} \exp(-33400/T) \text{ s}^{-1}$$

The use of the inhibitor makes impossible chain processes. Thus the only decomposition process must be the initial unimolecular reactions. It is expected that resonance stabilized radicals such as propargyl should not be particularly reactive with trimethylbenzene in the time scale of the experiments. Of course it can react with the benzylic type radicals that are generated in the course of the inhibition reactions. These are chain terminating processes.

DISCUSSION

The important products bearing on decomposition mechanisms for dilute quantities of 1,7 octadiyne in mesitylene and argon are listed in Table 1. It is clear that the dominating channels are the breaking of the propargylic C-H bond and the retroene reaction leading to the formation of allene and pent-1-ene-4-yne (P1E4Y). It can be seen that the concentration of the specific products formed; ethylene, cyclopentadiene, and P1E4Y is very close to the amount of the 1,7 octadiyne that is destroyed. Significant quantities of allene and propyne were also found. A large portion of the former is due to the retroene reaction. The excess quantities may be formed through a variety of other mechanisms. Note that as discussed subsequently, under certain conditions substantial quantities of propargyl radicals actually survive the heating period and it is possible that propargyl radical may undergo a variety of other unspecified reactions. Small quantities of meta-xylene was also found. This is evidence that hydrogen atoms are present in the system. Since the branching ratio for hydrogen atom attack on mesitylene have been determined, the total number of hydrogen atom released into the system can be placed on a quantitative basis. The concentrations found here are somewhat larger than that which can be accounted for by cyclopentadiene formation. However, any hydrogen atom in the system will in fact reveal its presence through the presence of meta-xylene.

In the time range where one expects C₆H₆ compounds to elute under the

present conditions a large number of peaks were detected. Unfortunately, it was not possible to obtain the neat samples that would lead directly to the identification of many of these compounds. Typical chromatograms in this elution region can be found in Figure 1. At low conversions (and temperatures) one sees the initial formation of a plethora of products. At high conversions and temperatures one notes increasingly the formation of fulvene and benzene as well as smaller quantities of other unidentified products.

An important question is whether these peaks can actually be attributed to the combination of propargyl radicals. The results of ancillary experiments with 1,5 hexadiyne, 1-hexyne and 2,4 hexadiyne are as follows. In the case of 1-hexyne, where the mechanism involve formation of the propargyl radical, many of the same peaks that were found in the decomposition of 1,7 octadiyne were also present. Unfortunately the parent hexyne-1 peak eluted at the same time as the fulvene peak. In the case of 1,5 hexadiyne the situation is similar to that found by Stein and coworkers, dimethylenecyclobutene is first formed, followed by conversion into fulvene and benzene. Typical chromatograms can be found in Figure 2. It is interesting to note that in the studies with 1,7 octadiyne and 1-hexyne, 1,5 hexadiyne could barely be detected. Nevertheless the pattern of products, in these studies were very much similar to that found in the direct 1,5 hexadiyne decomposition. The obvious interpretation is that 1,5 hexadiyne is an important intermediate. The existence for this molecule of very low energy decomposition channels mean that at the high temperatures of these studies they are almost immediately converted into the stable decomposition products, fulvene and benzene. 2,4 Hexdiyne is a minor product. Its decomposition product was found to be chiefly benzene and a small quantity of fulvene. These results clearly establish that from the linear C_6H_6 isomers there must be a variety of pathways to form benzene. In the present instance benzene must be formed after various hydrogen shifts.

Quantitative results can give a better picture of the rate at which propargyl radicals are generated in this system. The analysis of this data and the determination of the appropriate rate constants and expressions follow from earlier publications. In the present case the propargyl C-C bond cleavage is monitored by the yield of ethylene and cyclopentadiene. The contribution from the molecular retro-ene reaction is determined from the yields of the pent-1-ene-4-yne (P1E4Y). The rate constants can be related to the measured yields on the basis of the following relations

$$k(1) = \log(1 - X * C_2H_4 + \text{cyclopentadiene} / (1,7\text{cyclooctadiyne})_i) / X * t$$

$$k(4) = k(1) * (P1E4Y) / C_2H_4 + \text{cyclopentadiene}$$

where $X = 1 + (P1E4Y) / C_2H_4 + \text{cyclopentadiene}$, t is the total heating time of approximately 500 microsec. A plot of these results can be found in Figure 1. The rate expressions for the two initial processes are therefore

$$k(1) = 1.6 \times 10^{16} \exp(-35760/T) \text{ s}^{-1}$$

$$\text{and } k(4) = 5.6 \times 10^{12} \exp(-27860/T) \text{ s}^{-1}$$

It should be noted that the reaction temperature is calculated on the basis of the propene yields from 4-methylcyclohexene decomposition and is derived from the relation $1/T = (\log k(4\text{-methylcyclohexene-propene-1,3butadiene}) -$

LogA)/E, where the A and E are rate parameters for 4-methylcyclohexene decomposition decomposition given earlier.

It is interesting to compare these rate expressions with that for 1-hexyne decomposition. The rate expressions are

$$k(\text{hexyne-1=propargyl} + \text{n-propyl}) = 8 \times 10^{15} \exp(-36300/T) \text{ s}^{-1} \text{ and} \\ k(\text{hexyne-1=allene} + \text{C}_3\text{H}_6) = 5 \times 10^{12} \exp(-28400/T) \text{ s}^{-1}.$$

At the reaction temperature the differences in rate constants are factors of 3.3 and 1.8 respectively. For the latter this is very close to the reaction pathway degeneracy. On the other hand for the bond breaking process the rate constant for 1,7 octadiyne decomposition is a factor of 1.7 higher than would be dictated by the two propargyl bond. From the rate expressions, it would appear that this is an activation energy effect, although this claim cannot be completely justified in terms of the uncertainties in deriving the rate expression. It appears that propargyl substitution in the beta position has a larger than expected effect on rate constants for bond cleavage. Studying octyne-1 decomposition will be very worthwhile.

The ratio of cyclopentadiene to ethylene yields a measure of the branching ratio for pent-4-ynyl decomposition. An Arrhenius plot of this ratio can be found in Figure 2. The rate expression is

$$k(3)/k(2) = 5.4 \times 10^{-4} \exp(6700/T)$$

In the temperature range of these experiments this is equivalent to 25% cyclization at the lowest temperatures and decreasing to 10% at the other extreme. Cyclization is thus favored at the lower temperatures and the activation energy for cyclization is about 50 kJ/mol smaller than that for beta C-C bond fission. This is a surprisingly large number since with an estimated activation energy for C-C bond fission of about 120 kJ/mol will lead to an activation energy for cyclization in the 80 kJ/mol range. It is also possible that this process is not kinetically controlled and that the ratio given above is a reflection of the equilibrium properties of the cyclic and linear radicals. Obviously further work is required. For the present purposes it is clear that optimum yields of propargyl radicals will be achieved at the highest temperatures. At 900 K cyclization and beta bond cleavage will be equally important.

With this data there is now sufficient information to deduce the temporal history of propargyl in the present system. Using a rate expression for propargyl combination similar to that for allyl³, it was found that at lower concentrations, 200 ppm level and 2 atm pressure, a large portion of the radical remain unreacted during the entire heating period and much of the products are thus presumably formed at somewhat lower temperatures. On the other hand for the higher concentrations 1000 ppm and 7 atm. recombination is substantially completed in during the heating period. Despite this difference the chromatograms are substantially similar. In addition, recovery in the form of the C₆H₆ compounds is no more than 50% of all the propargyls that are released into the system. Here again the results appear to be independent of the concentration of radicals released into the system. The former may be a reflection of the low energy pathways available for decomposition and the formation of hot molecules from

propargyl recombination. Propargyl radicals can of course also be removed from the system by combination with 3,5 dimethylbenzyl and methyl radicals. These pathways cannot account for all the deficit.

The results are in general confirmatory of the observations of Stein et al regarding the nature of the decomposition products of 1,5 hexadiyne decomposition and that of Homann and Alkemade regarding the wide variety of linear C_6H_6 compounds that can be formed. Indeed the present results suggest many more peaks than the latter reported. It is difficult to account for the failure of Alkemade and Homann to find two of the decomposition products of 1,5 hexadiyne pyrolysis, dimethylenecyclobutene and fulvene. This is particularly serious for fulvene since it apparently is quite stable as the temperature is increased. It is possible from the reported retention times of Alkemade and Homann the 1,3 hexadiyne-5 and fulvene peaks may actually be coincident.

A system for the controlled release of propargyl radicals have now been described. The next step in this work must be studies where the propargyl radicals are allowed to react with other unsaturated compounds or radicals that may be present in high temperature reactive systems. A major problem in so far as single pulse shock tube studies are concerned is that the reaction time is very short and if truly quantitative results are to be obtained concentration of propargyl or reactants must be maintained at a sufficiently high level so that all the reactions occur during the heating period. With such a scenario, measurements of the concentration of one of the direct propargyl combination products, for example, benzene, and the product of addition or combination with another species can now be used as a means of determining relative rate constants. This can lead to a scale of propargyl reactivities and predictions regarding the quantity and distribution of the aromatic products formed in high temperature pyrolytic systems. Comparison with actual measurements will then lead to an assessment of the actual importance of propargyl radical in soot forming systems.

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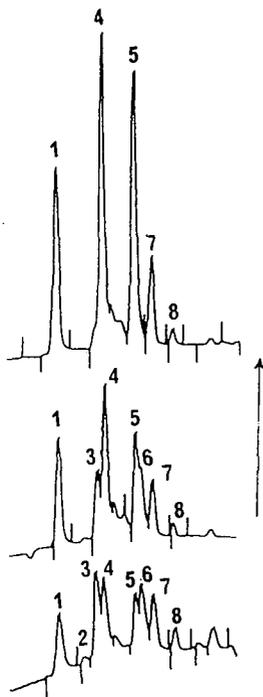


Figure 1. Typical chromatograms in the C_6 region from 1,7 Octadiyne decomposition. Peaks 1,6-8 were not identified. (2)=1,5hexadiyne (3)=dimethylenecyclobutene (4)=fulvene (5)=benzene. Arrow points to higher temperature.

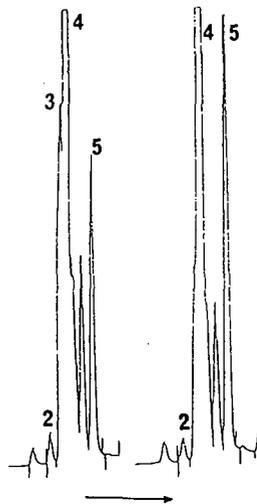


Figure 2. Typical chromatograms in the C_6 region from 1,5 hexadiyne decomposition (2)=1,5hexadiyne, (3)=dimethylenecyclobutene (4)=fulvene, (5)=benzene. Arrow points to higher temperature.

Figure 3. Arrhenius plots for the decomposition of 1,7 octadiyne. (○) propargyl C-C bond cleavage. (●) retroene reaction

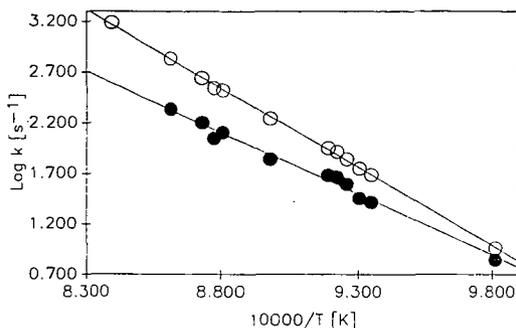


Figure 4. Arrhenius plot for the ratio of rate constants for cyclization vs beta bond cleavage during the decomposition of pent-4-ynyl

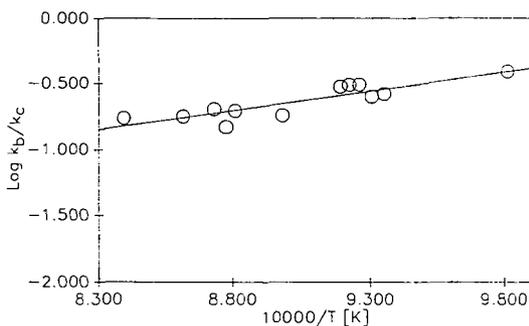


Table 1. Reactant and Product Distribution formed from 1,7 Octadiyne Decomposition in the Presence of Excesses of Mesitylene

Temp.	Pressure (atm)	C ₂ H ₄	Allene	Compounds (%conversion)			1,7oct
				Propyne	PIE4Y	C ₅ H ₆	
a. 200 ppm 1,7 octadiyne in 0.5% Mesitylene and Argon							
1080	1.8	1.1	.9		.7	.2	100
1101	2.1	6.1	4.3	.6	4.1	1.5	87
1131	1.8	13.7	8.2	1.3	6.7	2.5	72
1150	1.9	21.9	11.1		10.1	4.9	52
1166	2.2	31.0	15.4	4.7	10.8	5.5	44
b. 1000 ppm 1,7 octadiyne and 1.0% Mesitylene and Argon							
1034	1.8	.8	.8	.1	.8	.3	92
1101	2.1	6.1	4.3	.6	3.9	1.3	75
1141	6.2	17.7	10.5	3.0	8.8	3.7	65
1183	6.7	43.1	19.3	7.4	11.8	7.4	27