

THE REACTIONS OF PROPARGYL CHLORIDE AND 1,5 HEXADIYNE
BEHIND REFLECTED SHOCK WAVES

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INTRODUCTION

Several reports have appeared which describe the reactions of C_3H_3 and the subsequent formation of benzene. These investigations have been conducted using a variety of experimental techniques and precursor compounds to form propargyl radicals: allene,¹ 1,2 butadiene² (shock tube); 1,5 hexadiyne³ (flow reactors); ethylacetylene⁴ (microjet reactor); rich acetylene flames;^{5,6} C_3H_3Cl or $C_3H_3Br + Na$ ⁷ (flow reactor); allene and propyne⁸ (shock tubes). Although there is general agreement that the reaction of $2 C_3H_3 \rightarrow C_6H_6$ is an efficient route to benzene, there are several C_6H_6 isomers such as bisallene, 3,4 dimethylenecyclobutene, and fulvene that have been proposed to participate in the sequence of reactions that precede benzene formation⁹ and consensus is lacking on the details of the conversion.

Furthermore, reactions of C_3H_3 with allene and propyne have been proposed¹ as routes to benzene via the sequence $C_3H_3 + C_3H_4 \rightarrow C_6H_7 \rightarrow C_6H_6 + H$. The single pulse shock tube results of Hidaka et al. indicate that benzene yields are greater in the pyrolysis of allene compared to those recorded from a mixture containing an equivalent amount of propyne.⁸

There has been considerable effort expended on the allene \rightleftharpoons propyne isomerization by experimentalists and theoreticians which is described in a recent review.¹⁰ The energetics of various intermediates involved in the isomerization such as trans-vinylmethylene, cyclopropene, and propenylidene have been calculated and the highest energy barrier, 65.8 kcal/mol, identified.¹¹

The object of this work is to examine the reactions of two possible precursors for C_3H_3 , propargyl chloride and 1,5 hexadiyne, and to study the reactions of C_3H_3 with itself and with allene (C_3H_4A) and propyne (C_3H_4P) with particular emphasis on the formation of benzene. This latter point is important since a correlation between benzene production and soot yield has been proposed.¹²

EXPERIMENTAL

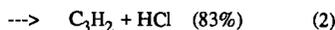
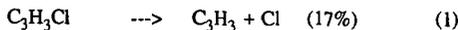
A shock tube coupled to a time-of-flight (TOF) mass spectrometer is employed to analyze dynamically the reflected shock zone containing various mixtures of gases. The apparatus and experimental procedures have been described recently.¹⁰ The mixture compositions and reaction conditions are listed in Table 1.

The sources of reactants are as follows: C_3H_3Cl (Aldrich, 98%); C_3H_4A (Matheson, 93%); C_3H_4P (Farchan); 1,5 C_6H_6 (Alpha); D_2 (Matheson, 99.5%); H_2 (Linde, 98.5%); Ne (Matheson, 99.999%). Ionization was achieved by 32 eV electron bombardment. The mass spectral range covers m/e 12 - 120. Peak heights were converted to concentrations using calibration plots obtained under no-reaction temperatures. The following mixtures diluted with neon were prepared for the calibration of the corresponding species: 3% C_3H_3Cl ; 3% C_3H_4A ; 3% C_3H_4P ; 2% 1,5 C_6H_6 ; 3.2% C_2H_2 ; 2% HCl; 2% C_4H_2 ; 2% C_6H_6 ; and 3% CH_4 . The mass spectral factor for C_6H_2 was obtained from previous work in which a carbon atom balance procedure was employed.¹³

RESULTS AND DISCUSSION

Mixtures A, B, and C: 3% C_3H_3Cl decomposes readily at temperatures above 1400 K. Major products are C_2H_2 , HCl, and C_4H_2 which were observed to form at the same reaction time. The amount of HCl formed is equal to the amount of dissociation of propargyl chloride, indicating that Cl atom is balanced. However, carbon atom balance is only 60 - 80%. Concentration plots for 3% C_3H_3Cl pyrolysis at 1411 K are shown in Figures 1 - 4. Solid lines represent model calculations using the mechanism listed in Table 2. The C_3H_3Cl mass spectral cracking pattern displays a substantial peak at m/e 39 ($C_3H_3^+$). At late reaction times, m/e 39 disappears but m/e 74 remains, indicating the formation of C_6H_2 .

Benzene was not recorded in the thermal decomposition of 3% C_3H_3Cl . However, upon addition of 5% H_2 (mixture B), benzene was detected. The major products distribution and the carbon balance are the same as in the decomposition of 3% C_3H_3Cl ; Cl atoms are balanced. The results from 3% C_3H_3Cl - 5% D_2 (mixture D) are interesting. HCl and DCl are formed almost at the same time; the temporal HCl/DCl ratio is ~ 5. The following two parallel initiation reactions are proposed to account for the experimental results:

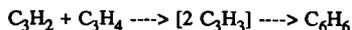


Mixtures D and E: Compared to the pyrolysis of 3% C_3H_3Cl , 1,5 hexadiyne decomposes at relatively higher temperatures. The major products are C_2H_2 , C_4H_2 , and C_6H_2 . Carbon balance for 2% 1,5 C_6H_6 pyrolysis is 75 - 80% in the temperature range 1657 - 1800 K. Adding 5% H_2 does not change the product distribution but results in 100% carbon balance due to the increased amount of observable products. Benzene production was difficult to determine here due to the overlap of the parent molecule and benzene.

Mixtures F and G: The TOF results for a 4.3% allene mixture are published in ref. 1. We employed 3% allene or propyne mixtures here in order to maintain the same carbon atom concentrations as most other mixtures in Table 1 and to compare the respective benzene yields. 3% allene and 3% propyne mixtures were shocked at the same experimental conditions to determine if there are any kinetic differences as claimed in the single pulse shock tube work.⁸ Benzene is formed in amounts of $2.3 - 3.2 \times 10^{-9}$ mol/cm³, about the same levels as in mixtures H and I. CH_4 is a minor product. The carbon atom balance is ~90%. The reaction profiles were modeled by the mechanism of ref. 1. Figures 5 - 8 show 3% propyne decomposition at 1770 K. Examining the C_3H_4 and the product concentrations, it is concluded that there are little or no observable differences between these two isomers at high temperatures which confirms that the isomerization reaction is faster than the decomposition.

Mixtures H and I: There are no significant differences in comparing the reaction profiles for these two mixtures. Benzene appears in amounts of 2.5×10^{-9} to 4.0×10^{-9} mol/cm³ for the temperature range 1325 - 1735 K. Major products are C_2H_2 , C_4H_2 , HCl. Comparison of the respective profiles reveals that propargyl chloride decomposes much faster than allene or propyne. The C_3H_3Cl profile is obtained by Cl atom balancing, since its mass spectral sensitivity is low and interference from C_6H_2 at high temperatures is severe. The reaction profiles for mixtures H and I at 1458 and 1492 K are displayed in Figures 9 - 16.

The mechanism in Table 2 is composed of the previous allene mechanism¹ and reactions of propargyl chloride. Benzene appears at lower temperatures in H and I compared to F and G and is formed mainly from the overall net reaction



Benzene production predicted by the model is about 4 times higher than the experimental data as shown in Figures 12 and 16. The carbon atom balance for the two mixtures are about 70% at ~ 1450 K. This carbon deficiency is due to the formation of high molecular weight polyaromatic

hydrocarbons (PAH) and solid carbon; these steps are not included in our mechanism. The model describes reasonably well the observable species except for benzene. The overall reactions (3) and (4) are highly exothermic. It is likely that benzene or its isomers, some of which are highly reactive, are apparently consumed in a series of reactions leading to PAH and soot. The mechanism is tentative; extensive modeling of the experimental data is ongoing.

Mixtures J and K: C_2H_2 , C_4H_2 , and C_6H_2 are the detectable products. Reaction profiles and product distributions are the same as for mixtures J and K at similar reaction conditions. Carbon balance is around 70%. Information relevant to benzene formation is obscured due to the overlap of the parent peak.

CONCLUSIONS

The main decomposition channel for propargyl chloride pyrolysis is through the elimination of HCl to form C_3H_2 . C_3H_2 plays an important role in producing benzene in reactions with allene or propyne. Benzene is not observed in the pyrolysis of C_3H_3Cl but it is formed readily in mixtures of C_3H_3Cl and allene or propyne.

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Table 1: Summary of Experimental Conditions

Mixture	Composition	T ₅ , K	P ₅ , atm
A	3% C ₃ H ₃ Cl	1411 - 1608	0.24 - 0.29
B	3% C ₃ H ₃ Cl - 5% H ₂	1394 - 1633	0.24 - 0.31
C	3% C ₃ H ₃ Cl - 5% D ₂	1364 - 1616	0.23 - 0.31
D	2% 1,5 C ₆ H ₆	1530 - 1800	0.28 - 0.37
E	2% 1,5 C ₆ H ₆ - 5% H ₂	1367 - 1827	0.24 - 0.39
F	3% C ₃ H ₄ A	1564 - 2136	0.27 - 0.45
G	3% C ₃ H ₄ P	1549 - 2131	0.27 - 0.44
H	1.5% C ₃ H ₃ Cl - 1.5% C ₃ H ₄ A	1295 - 1698	0.20 - 0.32
I	1.5% C ₃ H ₃ Cl - 1.5% C ₃ H ₄ P	1304 - 1793	0.20 - 0.35
J	1.5% 1,5 C ₆ H ₆ - 1.5% C ₃ H ₄ A	1316 - 1931	0.22 - 0.43
K	1.5% 1,5 C ₆ H ₆ - 1.5% C ₃ H ₄ P	1438 - 1823	0.26 - 0.39

Table 2. Reaction Mechanism

Reactions	A	E
1. $C_3H_3Cl = C_3H_3 + Cl$	1.0E13	65.5
2. $C_3H_3Cl = C_3H_2 + HCl$	5.0E13	65.5
3. $C_3H_2 + C_3H_4A = C_6H_6$	4.0E11	0.0
4. $C_3H_2 + C_3H_4P = C_6H_6$	4.0E11	0.0
5. $C_3H_2 + C_3H_4A = 3 C_2H_2$	1.7E13	15.0
6. $C_3H_2 + C_3H_4P = 3 C_2H_2$	1.7E13	15.0
7. $2 C_3H_2 = C_2H_2 + C_4H_2$	2.0E13	8.5
8. $2 C_3H_2 = C_6H_2 + H_2$	2.0E13	8.5
9. $Cl + H_2 = HCl + H$	8.3E13	5.5
10. $C_3H_4A = C_3H_4P$	2.0E13	62.0
11. $C_3H_4A + M = C_3H_3 + H + M$	1.0E17	70.0
12. $C_3H_4P + M = C_3H_3 + H + M$	1.0E17	70.0
13. $C_3H_4A + H = C_2H_2 + CH_3$	2.0E13	2.4
14. $C_3H_4P + H = C_2H_2 + CH_3$	2.0E13	2.4
15. $C_3H_4P = C_2H + CH_3$	4.2E16	100
16. $C_3H_4P + H = C_3H_3 + H_2$	1.0E12	1.5
17. $C_3H_4A + H = C_3H_3 + H_2$	1.0E12	1.5
18. $C_3H_4P + C_2H = C_3H_3 + C_2H_2$	1.0E13	0.0
19. $C_3H_4A + C_2H = C_3H_3 + C_2H_2$	1.0E13	0.0
20. $C_3H_4P + CH_3 = C_3H_3 + CH_4$	2.0E12	7.7
21. $C_3H_4A + CH_3 = C_3H_3 + CH_4$	2.0E12	7.7
22. $C_3H_3 + CH_3 = C_2H_5 + C_2H$	1.0E13	37.5
23. $2 CH_3 = C_2H_6$	2.0E13	0.0
24. $C_3H_3 + CH_3 = C_4H_6$	5.0E12	0.0
25. $C_3H_4A + C_3H_3 = C_6H_6 + H$	2.2E11	2.0
26. $2 C_3H_3 = C_6H_6(L)$	6.0E13	0.0
27. $2 C_3H_3 = C_6H_6$	3.0E11	0.0
28. $2 C_3H_3 = 3 C_2H_2$	5.0E11	0.0

Units are: cm^3 , mol, sec, kcal. Reactions 10 - 28 taken from ref. 1.

FIGURE 1

3% C₃H₃Cl T = 1411 K

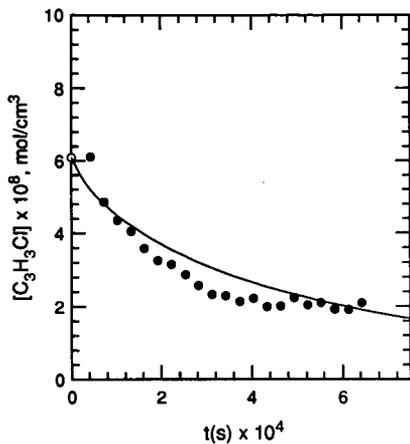


FIGURE 2

3% C₃H₃Cl T = 1411 K

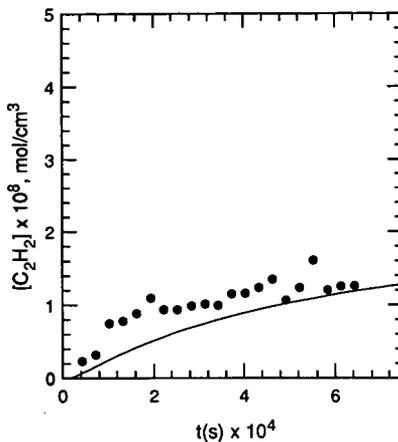


FIGURE 3

3% C₃H₃Cl T = 1411 K

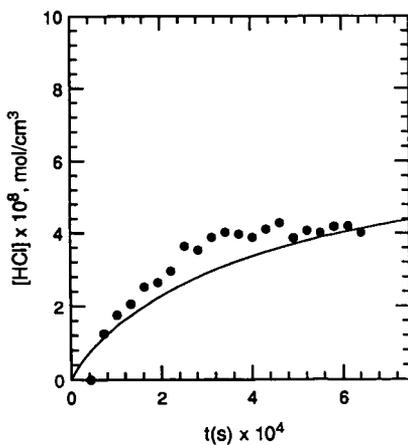


FIGURE 4

3% C₃H₃Cl T = 1411 K

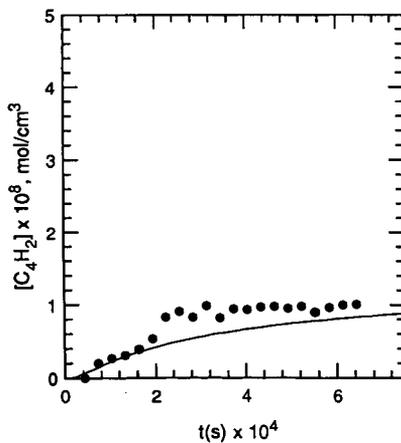


FIGURE 5

3% C₃H₄P T = 1770 K

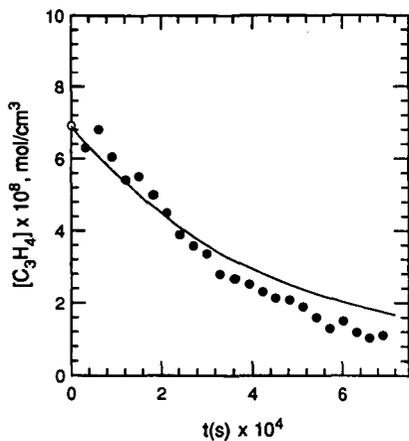


FIGURE 6

3% C₃H₄P T = 1770 K

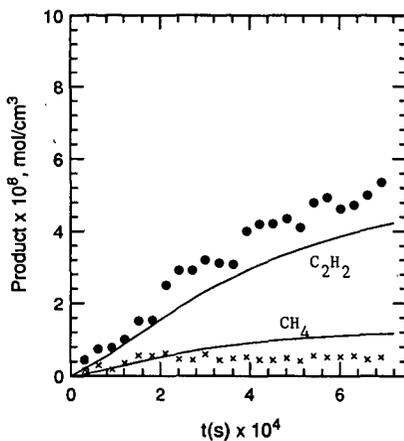


FIGURE 7

3% C₃H₄P T = 1770 K

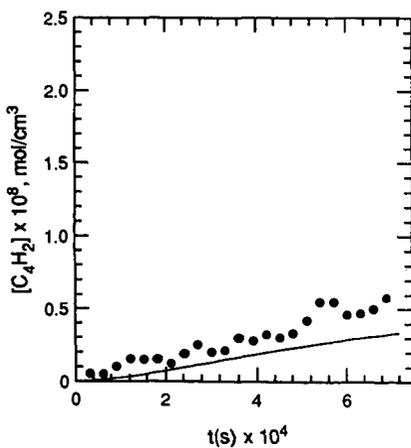


FIGURE 8

3% C₃H₄P T = 1770 K

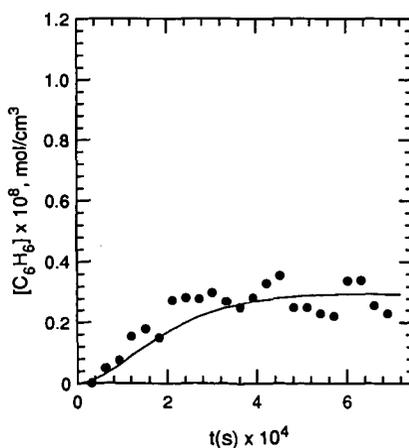


FIGURE 9

1.5% C_3H_3Cl - 1.5% C_3H_3A T = 1458 K

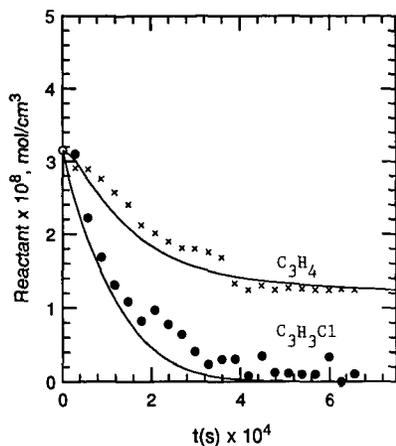


FIGURE 10

1.5% C_3H_3Cl - 1.5% C_3H_4A T = 1458 K

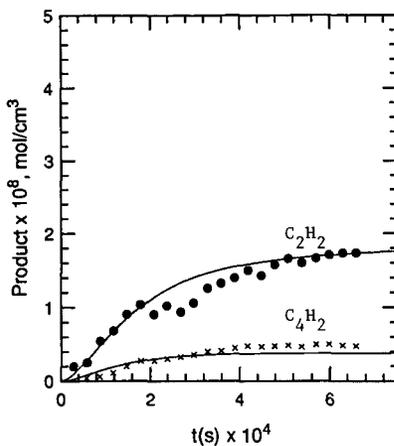


FIGURE 11

1.5% C_3H_3Cl - 1.5% C_3H_4A T = 1458 K

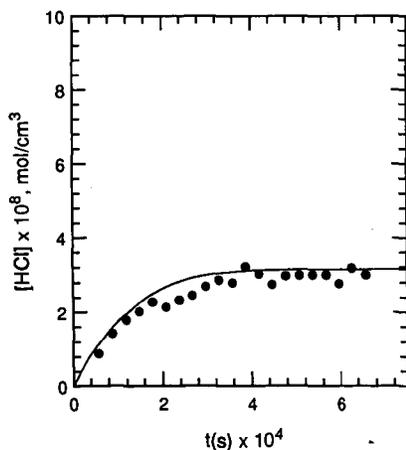


FIGURE 12

1.5% C_3H_3Cl - 1.5% C_3H_4A T = 1458 K

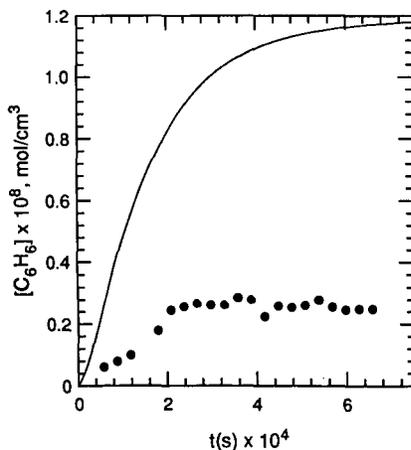


FIGURE 13

1.5% C₃H₃Cl - 1.5% C₃H₄P T = 1492 K

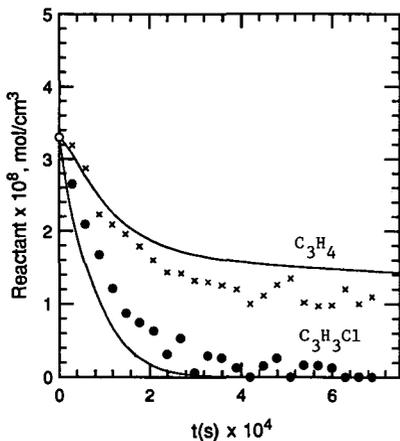


FIGURE 14

1.5% C₃H₃Cl - 1.5% C₃H₄P T = 1492 K

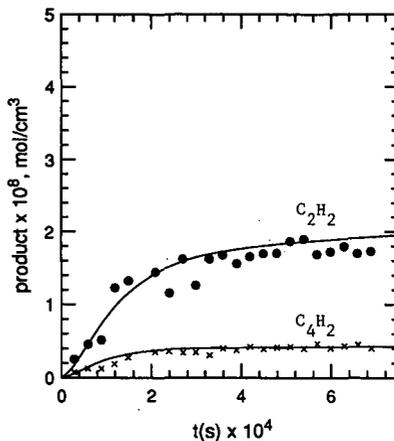


FIGURE 15

1.5% C₃H₃Cl - 1.5% C₃H₄P T = 1492 K

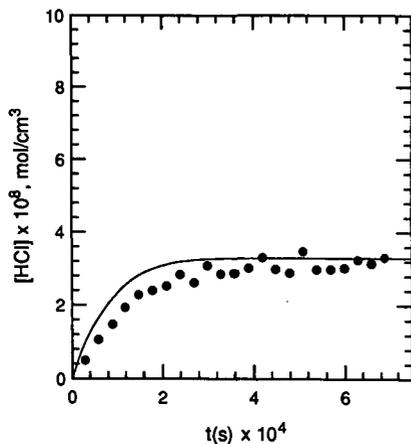


FIGURE 16

1.5% C₃H₃Cl - 1.5% C₃H₄P T = 1492 K

