

**The Formation of Soot and Polynuclear Aromatic Compounds in the  
Low-Temperature Pyrolysis of Alkynes**

by

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**Abstract**

The pyrolysis of vinylacetylene ( $\text{CH}_2=\text{CH}-\text{C}\equiv\text{CH}$ ), 2-methylbut-1-ene-3-yne ( $\text{CH}_2=\text{C}(\text{CH}_3)-\text{C}\equiv\text{CH}$ ), acetylene-vinylacetylene mixtures and acetylene-styrene mixtures at 300-550°C produced polymer and adducts (or dimers) in parallel independent homogeneous second-order reactions. At the temperatures of the studies, the polymerization reaction dominates, but because the Arrhenius parameters are smaller for the polymerization process, it should become relatively less important above  $\approx 850\text{K}$ . The respective Arrhenius A factors are about  $10^{6.5}$  and  $10^{8.0} \text{ M}^{-1} \text{ sec}^{-1}$  for polymerization and adduct formation (or dimerization) and the respective activation energies are about 90 and 125 kJ/mole.

The adducts (or dimers) are cyclic compounds some of which are aromatic. With continued heating they can lose hydrogen and condense to higher polynuclear aromatic compounds. The polymer chars on heating, presumably because of hydrogen evolution. The second-order removal processes dominate over unimolecular decomposition at the temperatures studied and can remain significant for temperatures in excess of 1200K. Both second-order processes should be important in soot formation.

### Early Work

Soot and the aromatic compounds are well-known products of the low-temperature pyrolysis of hydrocarbons. They include polynuclear aromatic compounds, some of which are carcinogenic.

The pyrolysis of  $C_2H_2$  has been studied for over 50 years, an early work being done by Pease (1929) who reported only polymerization at 400-600°C. Munson and Anderson (1963) studied the reaction in a flow reactor between 500 and 850°C. Apparently they were the first to show that the exclusive initial product is vinylacetylene. In a companion study, Hou and Anderson (1963) found that no free radicals were formed at temperatures up to 700°C in the pyrolysis of acetylene, vinylacetylene or diacetylene.

Cullis and Franklin (1964) studied the pyrolysis of  $C_2H_2$  from 500-1000°C and confirmed that the sole initial product was vinylacetylene. The diacetylene seen comes from the heterogeneous decay of the vinylacetylene. They found the reaction to be second order in  $C_2H_2$ , and to be unaffected by the presence of other hydrocarbons. By comparing their results with earlier work, they concluded that a single mechanism prevails for the pyrolysis of  $C_2H_2$  from 350-2500°C. The reaction is second order with  $\log(k, M^{-1} s^{-1}) = 10.8 - 41,600/\theta$  where  $\theta = 4.575 T$  (Cullis and Read, 1970). Palmer and Cullis (1965) have pointed out that vinylacetylene is the sole initial product at temperatures at least up to 1300°C. Subsequent work by Ogura (1977) of the shock decomposition of  $C_2H_2$  gave  $\log(k, M^{-1} sec^{-1}) = 11.39 + 0.26 - (46,000 + 1400/\theta)$  from 1000-1670K.

Extended pyrolysis of  $C_2H_2$  does produce many other products. Stehling et al (1962) studied the reaction at 600-900°C and found benzene as the main product at 600°C with some vinylacetylene and styrene present. At 700°C, indene, naphthalene, and other unidentified products were seen. Above 800°C,  $H_2$  and  $C_2H_4$  became important, though they were seen along with  $CH_4$  for very extended conversions at 600°C. The aromatic compounds are produced at temperatures up to 800°C, at which temperature they start dehydrogenating. The vinylacetylene reached a maximum concentration at 600-650°C. The aromatic compounds formed must come from reactions of vinylacetylene, either by itself or with  $C_2H_2$ .

The first study on vinylacetylene pyrolysis was done by Ikegami (1963). He studied the reaction at 300-400°C and found two processes, a rapid polymerization and a slow decomposition to produce mainly  $H_2$ ,  $C_2H_4$ ,  $C_2H_6$ ,  $CH_4$ , and small amounts of  $C_2H_2$ . The rate was second order in  $C_4H_4$  with a rate coefficient of  $1.85 \times 10^8 \exp(-25,300/1.987T) M^{-1} s^{-1}$ .

The pyrolysis of vinylacetylene was also studied by Cullis et al (1967) and Cullis and Read (1970). They studied the reaction between 300 and 620°C and found it to be quite different below and above 500°C. Below 500°C only polymerization occurred in a second order reaction with an activation energy of 28 kcal/mole. These results agree with those of Ikegami (1963). Above 500°C it was found that polymerization was accompanied by large amounts of low molecular weight products, mainly  $H_2$  and  $C_2H_2$ , though  $CH_4$ ,  $C_2H_4$ , and soot were also formed. Diacetylene and methylacetylene were not produced under any conditions.

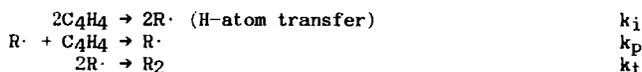
Cullis and Read (1970) found that the addition of  $C_2H_2$  to vinylacetylene had no effect on the vinylacetylene pyrolysis at  $478^\circ C$ , even for an acetylene concentration twice that of vinylacetylene. On the other hand, Yampol'skii et al (1968) found that at  $800-950^\circ C$ , vinylacetylene removal was slower in a mixture of 0.5% vinylacetylene and 99.5%  $C_2H_2$  than in a mixture of 0.5% vinylacetylene and 99.5% Xe, and they reported the respective rates in terms of first order removal coefficients. Furthermore in the presence of  $C_2H_2$ , though the vinylacetylene removal rate was reduced, benzene was produced.

### Polymer Formation

The pyrolyses of several alkyne systems have been studied in our laboratory from  $300-550^\circ C$ . The dominant product in all cases is a yellow polymer which settles on the wall of the reaction vessel. This polymer is stable at  $\approx 300^\circ C$ , but slowly becomes black over a period of weeks at higher temperatures. Presumably hydrogen is being evolved from the polymer and it becomes soot.

The systems studied include pure vinylacetylene ( $CH_2=CH-C\equiv CH$ ), pure 2-methylbut-1-ene-3-yne ( $CH_2=C(CH_3)-C\equiv CH$ ), vinylacetylene-acetylene ( $C_2H_2$ ) mixtures and acetylene-styrene ( $C_6H_5CH=CH_2$ ) mixtures. In all cases the rate of disappearance of reactants was homogeneous, second order, and unaffected by the addition of excess  $N_2$  or He. For the pure  $C_4H_4$  and  $C_5H_6$  systems the reaction was second order in the reactant, whereas for the mixed systems, the removal rate for  $C_2H_2$  or  $C_8H_8$  was first order in each reactant. The rate coefficients and temperature ranges used are summarized in Table 1.

Presumably the polymerization occurs through a free-radical addition mechanism. For the pure  $C_4H_4$  system the basic mechanism would be:



which leads to the rate law

$$-d[C_4H_4]/dt = (2k_i + k_p(k_i/k_t)^{1/2})[C_4H_4]^2$$

The mechanism and rate law for the  $C_5H_6$  system is analogous. Since  $2k_i$  is small compared to  $k_p(k_i/k_t)^{1/2}$ , the overall Arrhenius A factor for the reaction is given by  $A_p(A_i/A_t)^{1/2}$ . The expected values for  $A_i$  and  $A_p$  are  $\approx 10^8 M^{-1} \text{sec}^{-1}$  since these are typical second-order reactions. Radical-radical termination reactions occur near collision frequency, and since  $R\cdot$  is a large radical, we expect  $A_t \approx 10^{11} M^{-1} \text{sec}^{-1}$ . Thus the overall A factor should be  $10^8 \times (10^8/10^{11})^{1/2} = 106.5 M^{-1} \text{sec}^{-1}$  in agreement with the observation of Lundgard and Heicklen (1984) for  $C_4H_4$  and Chanmugathas and Heicklen (1985) for  $C_5H_6$ . The overall activation energy is  $E_p + E_i/2$  since  $E_t \approx 0$  and is about 90 kJ/mole.

For the  $C_2H_2-C_4H_4$  system the initiation and termination steps are the same as for pure  $C_4H_4$ , since  $C_2H_2$  self polymerization was negligibly slow under the conditions of the study. However an additional propagation step is needed:



so that

$$-d[C_2H_2]/dt = k_p(k_i/k_t)^{1/2}[C_2H_2][C_4H_4]$$

in agreement with the observations. The values for the overall Arrhenius A factor and activation energy should be similar to those for the one-compound polymerizations, as indeed they are.

The C<sub>2</sub>H<sub>2</sub>-C<sub>8</sub>H<sub>8</sub> polymerization is considerably more complex and not completely understood. The polymerization of either compound alone was negligibly slow under the conditions studied, yet copious amounts of polymer were produced in the mixed system. A tentative mechanism has been suggested (Chanmugathas and Heicklen, 1987) in which initiation occurs by the interaction of 2C<sub>8</sub>H<sub>8</sub> molecules:



The R<sub>1</sub>· radical presumably does not add readily to styrene, but does add readily to C<sub>2</sub>H<sub>2</sub>



where the distinction between R<sub>1</sub>· and R<sub>2</sub>· radicals is that the former has a styrene end group, whereas the latter has an acetylene end group. The R<sub>1</sub>· radicals can also terminate:



The R<sub>2</sub>· radicals add preferentially to C<sub>2</sub>H<sub>2</sub> to regenerate R<sub>2</sub>· type radicals, but occasionally they generate a different radical, R<sub>3</sub>·, which adds preferentially to styrene to give an R<sub>1</sub>· type radical:



This mechanism leads to the rate laws

$$-d[C_8H_8]/dt = 2k_1[C_8H_8]^2 + k_2(k_1/k_3)^{1/2}[C_2H_2][C_8H_8]$$

$$-d[C_2H_2]/dt = k_2(k_1/k_3)^{1/2}[(k_4 + k_{4b})/k_{4b}][C_2H_2][C_8H_8]$$

If  $2k_1 \ll k_2(k_1/k_3)^{1/2}$ , then C<sub>8</sub>H<sub>8</sub> removal is first-order in both reactants and the rate coefficient parameters should be similar to those for the other systems in agreement with the observations. The C<sub>2</sub>H<sub>2</sub> removal rate is first-order in both reactants but is much larger than that for C<sub>8</sub>H<sub>8</sub> by the factor  $(k_4 + k_{4b})/k_{4b}$ .

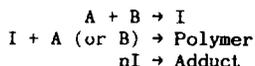
Many addition polymers have a ceiling temperature at which their rate of depolymerization equals their rate of polymerization, and the polymer is not produced at higher temperatures. Usually this occurs because the polymerization process produces C-C single bonds which are the weakest bonds in the polymer and are ruptured on heating. This does not appear to

be the case with polymers produced from acetylenes. C-C single bonds are formed but they are sandwiched between C=C double bonds giving rise to a conjugation effect. Thus the C-C single bond energies are strengthened to >400 kJ/mole while the tertiary vinylic C-H bonds are weakened to ≈335 kJ/mole. Therefore instead of depolymerization at high temperature, C-H bond scission occurs and hydrogen is released leaving behind a char (or soot). Thus the polymerization followed by charring could be an important soot-producing process in the low-temperature pyrolysis of hydrocarbons.

It is interesting to see at what temperatures the polymerization process is important. This can be computed precisely for C<sub>4</sub>H<sub>4</sub> since its first-order decomposition rate has been measured recently by Hidaka et al (1986) to be  $6.1 \times 10^{13} \exp(-335 \text{ kJ/mole-RT}) \text{ sec}^{-1}$ . With this expression and the Arrhenius parameters obtained by Lundgard and Hecklen (1984) for total C<sub>4</sub>H<sub>4</sub> removal at low temperatures where polymerization predominates, we can obtain  $[\text{C}_4\text{H}_4]^{1/2}$ , the concentration of C<sub>4</sub>H<sub>4</sub> where equal amounts of it disappear by unimolecular decomposition and polymerization. The curve marked polymerization in Fig. 1 shows a plot of  $\log([\text{C}_4\text{H}_4]^{1/2})$  vs. temperature. From this curve it can be seen that the polymerization dominates over decomposition at 1000K for C<sub>4</sub>H<sub>4</sub> pressures in excess of 0.1 Torr or at 1200K for C<sub>4</sub>H<sub>4</sub> pressures in excess of 20 Torr. Soot formation through polymerization is important at temperatures up to at least 1200K and may be significant at temperatures up to 1400K.

#### Adduct Formation

Adduct formation occurs along with polymerization. Thus in the single reactant systems dimers are produced along with polymer, but no trimers or tetramers were seen. In the mixed systems adducts of the two reactants were observed. Both polymerization and adduct formation (dimerization) are initial processes as determined by examining time histories of the curves of growth. Furthermore they are completely independent of each other and do not proceed through a common intermediate. This conclusion comes from the rate laws by the following argument. Let us assume that the two processes have some common intermediate I. Then the general mechanism would be



where A and B are the two reactants. This general mechanism requires that the rate law for polymer formation be of higher order than for adduct formation, contrary to observation. Therefore the two processes cannot have a common intermediate. The adduct formation occurs by a concerted or diradical process. Presumably the polymerization occurs via a mono radical chain mechanism.

In our laboratory, acetylene and vinylacetylene mixtures were pyrolyzed at 400-500°C in the absence and presence of O<sub>2</sub> or NO (Chanmugathas and Hecklen, 1986). The major product of the interaction between C<sub>2</sub>H<sub>2</sub> and C<sub>4</sub>H<sub>4</sub> was polymer, but benzene was also produced. Both the C<sub>2</sub>H<sub>2</sub> removal and C<sub>6</sub>H<sub>6</sub> formation rates were first-order in C<sub>2</sub>H<sub>2</sub> and C<sub>4</sub>H<sub>4</sub>. The rate coefficient parameters are listed in Tables 1 and 2, respectively. Benzene formation occurred by two processes: a concerted molecular mechanism (≈60%) and a singlet diradical mechanism (≈40%).

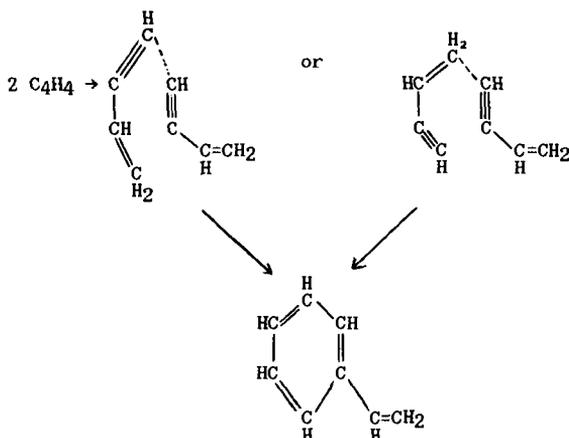
In order to investigate the low temperature (below 500°C) pyrolysis of vinylacetylene as an avenue for polynuclear aromatic hydrocarbon formation, it is essential to look at the formation of higher molecular weight products. Due to experimental limitations, however, the two early studies (Ikegami, 1963; and Cullis and Read, 1970) in this temperature range were only able to monitor lower molecular weight products such as H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub> and in one case benzene. Also, kinetic data were limited to vinylacetylene removal rates as a function of temperature.

Therefore, a study was undertaken in our laboratory in order to obtain more detailed kinetic information about the low-temperature pyrolysis of vinylacetylene, paying particular attention to higher molecular weight products formed during the early stages of reaction. Thus we have examined the pyrolysis of vinylacetylene at 300-450°C (Lundgard and Heicklen, 1984). Vinylacetylene removal was found to be second-order with rate coefficients similar to those reported by Ikegami (1963) and Cullis and Read (1970). In agreement with the earlier work, we found no effect of added gases (N<sub>2</sub>, He in our case) and that the main product was polymer which coated the reaction vessel walls. However, in addition we found that 20% of the vinylacetylene was converted to styrene, a dimer of vinylacetylene. This provided the first direct evidence of how aromatics are produced from the pyrolysis of smaller hydrocarbons.

The reaction for vinylacetylene removal and C<sub>8</sub>H<sub>8</sub> formation is homogeneous, second-order in reactant, and independent of the presence of a large excess of N<sub>2</sub> or He. However C<sub>8</sub>H<sub>8</sub> formation is about half-suppressed by the addition of the free radical scavengers NO or O<sub>2</sub>. The major reaction for C<sub>4</sub>H<sub>4</sub> removal is polymerization. In addition four C<sub>8</sub>H<sub>8</sub> isomers, carbon, and small hydrocarbons are formed. The three major C<sub>8</sub>H<sub>8</sub> isomers are styrene, cyclooctatetraene (COT), and 1,5-dihydropentalene (DHP).

The C<sub>8</sub>H<sub>8</sub> compounds are formed by both molecular and free radical processes in a second-order process with an overall  $k \approx 3 \times 10^8 \exp(-122 \text{ kJ/mole RT}) \text{ M}^{-1}\text{-sec}$  (average of packed and unpacked cell results). The molecular process occurs with an overall  $k = 8.5 \times 10^7 \exp(-188 \text{ kJ/mole RT}) \text{ M}^{-1}\text{-sec}$ . The COT, DHP, and an unidentified isomer (d), are formed exclusively in molecular processes with respective rate coefficients of  $4.4 \times 10^4 \exp(-77 \text{ kJ/mole RT})$ ,  $1.7 \times 10^5 \exp(-89 \text{ kJ/mole RT})$ , and  $3.1 \times 10^9 \exp(-148 \text{ kJ/mole RT}) \text{ M}^{-1}\text{-sec}$ . The styrene is formed both by a direct free-radical process and by isomerization of COT.

Lundgard and Heicklen (1984) pointed out that the mechanism for styrene formation could involve a modified Diels-Alder reaction with either of two intermediates:



With either of the transition states it is necessary to transfer a hydrogen atom before ring closure.

In order to distinguish which intermediate is involved in styrene formation a study was made of the pyrolysis of 2-methylbut-1-ene-3-yne:  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{C}\equiv\text{CH}$  (hereafter referred to as  $\text{C}_5\text{H}_6$ ). For this molecule the two intermediates will give different products. The head-to-head addition will give a meta-substituted product, while the head-to-tail addition will give a para-substituted product.

The pyrolysis of 2-methylbut-1-ene-3-yne ( $\text{C}_5\text{H}_6$ ) has been studied from 375–450°C in a quartz reaction vessel in the absence and presence of  $\text{O}_2$  or  $\text{NO}$  (Chanmugathas and Heicklen, 1985). From 375–425°C, the rates of disappearance of reactant and of formation of dimers are second order in  $\text{C}_5\text{H}_6$ . The major product is polymer, with the dimers accounting for about 3% of the  $\text{C}_5\text{H}_6$  consumed. In addition toluene and p-xylene are produced, their production coming, at least in part, from decomposition of the  $\text{C}_5\text{H}_6$  dimers ( $\text{C}_{10}\text{H}_{12}$ ). Also trace amounts of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ , and  $\text{C}_3\text{H}_6$  are formed. The rate coefficient parameters for  $\text{C}_5\text{H}_6$  removal and  $\text{C}_{10}\text{H}_{12}$  formation in the absence of  $\text{O}_2$  or  $\text{NO}$  are listed in Tables 1 and 2, respectively.

The reaction mechanism for dimer formation is analogous to that in vinylacetylene ( $\text{C}_4\text{H}_4$ ) pyrolysis (Lundgard and Heicklen, 1984), except that in the  $\text{C}_4\text{H}_4$  system cyclooctatetraene is seen as an unstable product that isomerizes to styrene, whereas in the  $\text{C}_5\text{H}_6$  system, the dimethylcyclooctatetraene apparently is too unstable to be detected. The dimers detected were 2,6-dimethylstyrene (P4), p-isopropenyltoluene (P5), and 2 other unidentified dimers (P3) with nearly identical gas chromatographic retention times. From the effect of the radical scavengers and by comparison of the  $\text{C}_4\text{H}_4$  and  $\text{C}_5\text{H}_6$  systems, the following mechanistic characteristics were determined:

- 1) The direct formation of styrene in the  $\text{C}_4\text{H}_4$  system comes from a

head-to-head "modified Diels-Alder" 6-member cycloaddition which proceeds through a diradical intermediate.

2) There is no conclusive evidence for a direct head-to-tail "modified Diels-Alder" 6-member cycloaddition. However, if it does occur, it does not involve diradicals, but must be concerted. Presumably this is how the unquenchable  $C_6H_6$  is formed in the  $C_2H_2-C_4H_4$  reaction.

3) Cyclooctatetraene is formed in concerted, non-free radical mechanisms which may proceed both by head-to-head and head-to-tail 8-member cycloadditions. For the  $C_5H_6$  system, the head-to-head adduct isomerizes to P3, whereas the head-to-tail adduct isomerizes to P3, P4, and/or P5. Kinetic data suggest that P3 is not produced from the cyclooctatetraene intermediate, in which case, head-to-head addition would not occur.

It appears that the head-to-head additions are free radical in nature and proceed mainly through a 6-membered ring intermediate, while head-to-tail additions are a concerted molecular process and proceed mainly through an 8-membered ring intermediate.

Chanmugathas and Hecklen (1987) have found that styrene adds to acetylene in a homogeneous second-order reaction with a rate coefficient of  $\log(k[C_{10}H_{10}], M^{-1}\text{-sec}^{-1}) = 8.24 \pm 0.62 - (143 \pm 9)\text{kJ/mole-RT}$  from 450-550°C to produce methyl indene and 1,2-dihydronaphthalene as initial products. These products then decay to produce indene and naphthalene, respectively.



1,2 dihydronaphthalene



naphthalene



methylindene



indene

These experiments suggest how larger polynuclear aromatic systems may be produced. Presumably if vinylacetylene were added to styrene, then vinylnaphthalene might be produced, which in turn could add to acetylene to product anthracene and phenanthrene.

In summary we have discovered a new class of reactions: the second-order homogeneous reaction of alkynes to form adducts. There are three pieces of evidence that these reactions are homogeneous. First, all four systems studied give normal homogeneous second-order Arrhenius preexponential factors of  $\log(A, M^{-1}\text{sec}^{-1}) \approx 8$ . Second the addition of a large excess of inert gas ( $N_2$  or He) had no effect on the rate coefficients. Third, for the one system in which packed vessels were used, the rate constants for vinylacetylene dimerization was unaffected by a change in surface-to-volume ratio of 59.

At the temperatures for which these systems were studied, the polymerization process was much more important than adduct formation. However its Arrhenius parameters are smaller than those for adduct formation (see Tables 1 and 2). Thus at higher temperatures the relative importance of adduct formation will become greater. We can use the rate coefficients for adduct formation for  $C_4H_4$  obtained by Lundgard and Hecklen (1984) and for  $C_4H_4$  unimolecular decomposition of  $6.1 \times 10^{13} \exp(-335 \text{ kJ/mole-RT}) \text{ sec}^{-1}$  obtained by Hidaka et al (1986) to obtain  $[C_4H_4]_{1/2}$  when the two processes

for C<sub>4</sub>H<sub>4</sub> removal are equal. This C<sub>4</sub>H<sub>4</sub> pressure is shown in Fig. 1 as a function of temperature by the curve marked dimerization. The dimerization becomes more important than polymerization at temperatures above 860K. It is equal to unimolecular decomposition at 10 Torr pressure of C<sub>4</sub>H<sub>4</sub> at 1250K and can play a significant role at even higher temperatures.

The dimerization or adduct formation forms aromatic compounds which can continue to add acetylenic compounds to form polynuclear aromatic compounds which become more and more graphitic as the number of aromatic rings grow. Thus this may be an important, or even the major, path to soot formation at temperatures of  $\geq 1200\text{K}$ .

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Table 1: Summary of Total Removal Rate Coefficients

Reactant 1	Reactant 2	$\text{Log}(A_1)$ $M^{-1}\text{sec}^{-1}$	$\text{Log}(A_2)$ $M^{-1}\text{sec}^{-1}$	$E_1$ , kJ/mole	$E_2$ , kJ/mole	Temp. °C	Reference
C <sub>4</sub> H <sub>4</sub>	C <sub>4</sub> H <sub>4</sub>	8.57	-	105	-	300-400	Ikegami (1963)
"	"	9.32	-	117	-	336-475	Cullis and Read (1970)
"	"	6.22	-	79	-	300-450	Lundgard and Heicklen (1984) <sup>a</sup>
"	"	7.10	-	91	-	300-450	Lundgard and Heicklen (1984) <sup>b</sup>
C <sub>5</sub> H <sub>6</sub>	C <sub>5</sub> H <sub>6</sub>	6.79	-	80	-	375-450	Chanmugathas and Heicklen (1985)
C <sub>2</sub> H <sub>2</sub>	C <sub>4</sub> H <sub>4</sub>	6.26	-	71	-	400-500	Chanmugathas and Heicklen (1986)
C <sub>2</sub> H <sub>2</sub>	C <sub>8</sub> H <sub>8</sub>	7.53	6.63	91	99	450-550	Chanmugathas and Heicklen (1987)

a) Unpacked cell.  
b) Packed cell.

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Table 2: Summary of Adduct Formation Rate Coefficients

Reactant 1	Reactant 2	$\text{Log}(A, M^{-1}\text{sec}^{-1})$	$E, \text{kJ/mole}$	Temp. °C	Reference
C <sub>4</sub> H <sub>4</sub>	C <sub>4</sub> H <sub>4</sub>	8.50	122	300-450	Lundgard and Heicklen (1984)
C <sub>5</sub> H <sub>6</sub>	C <sub>5</sub> H <sub>6</sub>	7.40	111	375-450	Chanmugathas and Heicklen (1985)
C <sub>2</sub> H <sub>2</sub>	C <sub>4</sub> H <sub>4</sub>	8.65	126	400-500	Chanmugathas and Heicklen (1986)
C <sub>2</sub> H <sub>2</sub>	C <sub>8</sub> H <sub>8</sub>	8.27	143	450-550	Chanmugathas and Heicklen (1987)

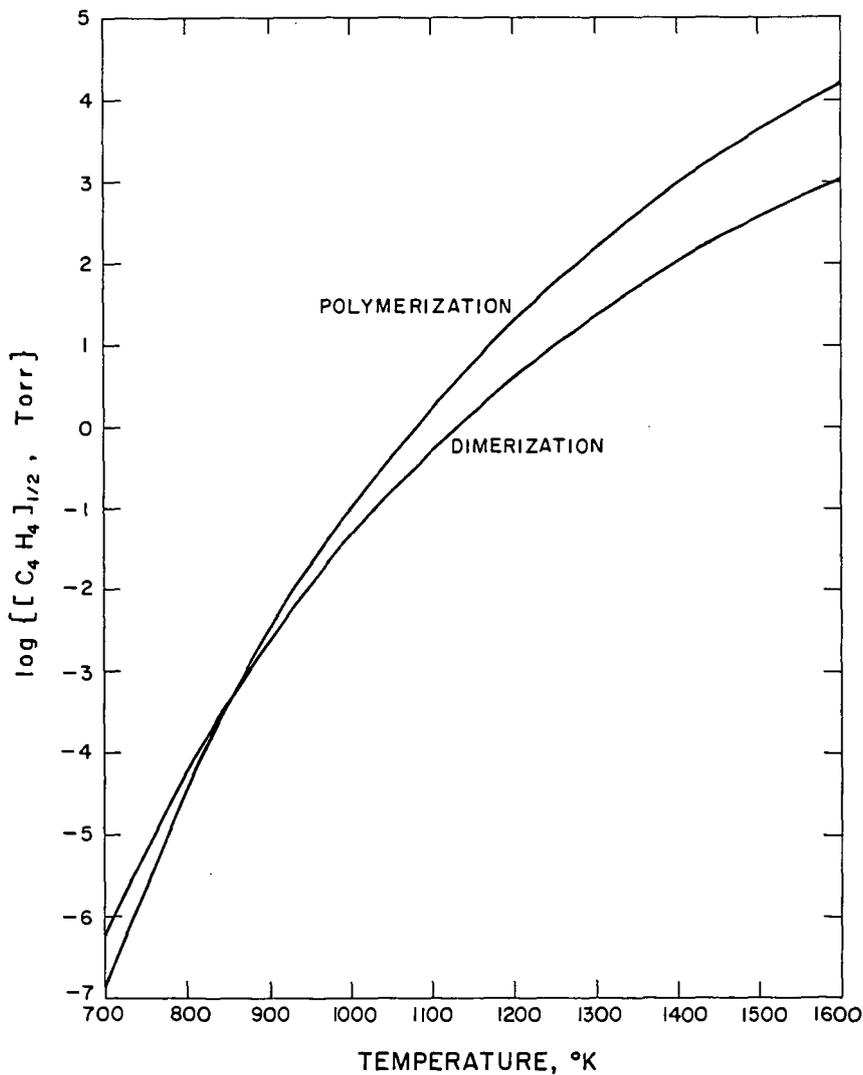


Fig. 1: Plot of the  $C_4H_4$  pressure where unimolecular decay is equal to second-order removal vs. temperature.