FORMATION OF LIGHT HYDROCARBONS AND SOOT IN THE PYROLYSIS REACTIONS OF CHLORO, DICHLOROBENZENE, ACETYLENE AND BENZENE IN AN ATMOSPHERE OF HYDROGEN

by

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ABSTRACT

Title of Thesis: Formation of Light Hydrocarbons and Soot in The pyrolysis reactions of Chloro, Dichlorobenzene, Benzene, and Acetylene in an Atmosphere of Hydrogen

Larry J. Zhu, Master of Science in Chemical Engineering, August, 1988.

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The kinetics of thermal decomposition of chlorobenzene and dichlorobenzene in a hydrogen and helium atmosphere were further studied to investigate formation of soot and light hydrocarbons. The experiments were performed at atmosphere pressure with residence times rangeing from 0.2 to 1.2 seconds, and the temperature ranges of 850°C to 925°C for chlorobenzene and 870°C to 910°C for dichlorobenzene. Flame ionization detectors, which were connected to GC columns, were utilized for the qualitative and quantitative analysis of the reaction products. A methyl silicone capillary column was used analyzing of heavy aromatics and a Carbosive G was used to analyze light hydrocarbons. Light hydrocarbon products identified in the pyrolysis reactions of chlorobenzene or dichlorobenzene were CH_4, C_2H_2, C_2H_4, and C_2H_6. While in hydrogen atmosphere, C_2H_4 was formed but no

C_2H_2. In a helium atmospere, C_2H_2 was produced as an end product and less than 0.1% yield of C_2H_4 were converted. All the light hydrocarbons from the pyrolysis of chlorobenzene or dichlorobenzene are less than 5% of the reactant initial concentration. The formation of light hydrocarbons is studied and the reaction pathways are presented.

GC/MS was employed in the quantitative analysis of the soot products. The soot amount is calculated by the difference method of mass balance. Nearly 50% of reactants was found converted to soot in the systems of chloro- and dichlorobenzene pyrolysis reactions at temperatures above 900°C. Meanwhile, larger amount of soot was generated in the system of chloro or dichlorobenzene in helium bath.

The pyrolysis reactions of acetylene and benzene at high temperatures were also conducted so as to investigate the kinetics and reaction pathways of forming those light hydrocarbons and soot products. The reaction conditions used for acetylene was 1 atmosphere pressure at 700 to 900°C. Major products from the pyrolysis of acetylene in hydorgen are CH_4, C_2H_4, C_2H_6 and carbon solids. Over 20% of C_2H_2 was converted to soot at 900°C. No benzene was observed in the pyrolysis reaction of acetylene with hydrogen. A mechanism for the pyrolysis of benzene in hydrogen is proposed. Even though a small amount of benzene was broken down to form light hydrocarbons, the only major product from the pyrolysis of benzene is soot at our reaction temperature range. The pyrolysis of benzene is not a first order reaction.

The kinetic parameters collected for acetylene, chlorobenzene, and dichlorobenzene fit the following Arrhenius equations:

acetylene in H2: $k_{exp} = 5.34 \times 10^{8} \exp(-43.5/RT)$

chlorobenzene in H2: $k_{exp} = 9.1 \times 10^{10} \exp(-62/RT)$

Dichlorobenzene in H2: $k_{exp} = 4.1 \times 10^{12} \exp(-65/RT)$

Here, Ea is in Kcal/mole unit.

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CONTENTS

1. INTRODUCTION

Many efforts have been made in the development of a variety of modern technologies to destroy or convert toxic chlorinated wastes into nontoxic endproducts. Chlorinated organics are generated in the production processes of plastics, solvents and other chemical industries, and present a serious environmental problem. Many of these chlorinated products are carcinogenic or extremely harmful [1].

Among the non-thermal waste treatment technologies, many such as photolytic and microwave plasma destuction methods, are still under active development. However, only Na-based dechlorination has exclusively been put into effective commercial use [2]. The process is costly and can not tolerate presence of water.

The use of landfill is strongly criticized as being shortsighted. Disposal of industrial wastes and toxic chlorinated products by this method would not only risk contaminating groundwater systems, but also damage the natural environment in the society [3], if they eventualy escape their containment.

High temperature incineration, however, has proven to be a practical and ecnomical approach for disposal of a large amount of toxic chlorinated industrial wastes. The mission of high temperature incineration is, to provide a large amount of thermal energy and highly reactive atoms, so that the chlorinated compounds with their high toxicity and stable molecular structure will be broken into lower molecular weight endproducts such as CO2, HCl, and H2O. These products may be readily separated or neutralized.

It is well known that there are two different methods in the incineration or the thermal destruction of toxic chlorinated wastes. One is the so-called incineration method, that is, through a processing in an oxygen rich atmosphere with the combustion of the supplied fuels, where, partially oxygenated chlorocarbon species like phosgene (COCl2) and other incomplete combustion products may be formed. In stead of detoxifying halocarbons in an oxidizing atmosphere, a promising alternative method, for chlorinated wastes, is pyrolysis processing, or implementation of a thermal pyrolysis process in a hydrogen-rich atmosphere with no or little oxygen. The end product for chlorine is HCl, which can be easily neutralized. In addition, the carbon may be converted to useful hydrocarbons.

The advantages on the using hydrogen rich atmosphere pyrolysis for toxic chlorinated compounds were summarized by Chuang [4]. However, it was noticed that a significant amount of soot was formed as an end product on the reactor wall during the experiments on chloroaromatics and others. For example, in the decomposition of dichlorobenzene in hydrogen, 30% to 40% of chlorobenzene was converted to soot by-products at the reaction temperature range of experiment and under 1 atm pressure [4-6].

Soot formation has been persistantly investigated as an important aspect of combustion research for many years; but, only a few researchers have studied soot formation from chloro-aromatics [7]. It is believed that soot formation may involve polymerization of acetylenes and aromatic rings, e.g. phenyls. Our study has covered an extensive range of decomposition with chloro or dichlorobenzene, benzene and acetylene. We specifically focused on the the formation of light hydrocarbons and their relation to the observed soot formation.

Our investigation and results will help further understanding of the reaction pathways leading to formation of high molecular weight soot products, the tendency of forming light hydrocarbons, and the bath gas influence (H2 vs. helium) on decomposition of chlorobenzene and dichlorobenzene.

2. PREVIOUS STUDIES

2.1. CHLOROBENZENE AND DICHLOROBENZENE

. The thermal decomposition of chlorobenzene was earlier studied by Cullis and Priday by using a static (batch) reactor [8]. Afterwards, Cullis and Manton extended this work to a flow system which was operated at a low atmosphere pressure in a flow tank reactor at the temperature range 770°C to 890°C. As a result, they found that addition of hydrogen gas to the system accelerated the decomposion of chlorobenzene. Questions remained, however, about the design of their "tank flow reactor" and non-ideal residence time distribution which was not considered in their analysis [9]. The analytical techniques which were available to them at the time (1957) were in addition less advanced and of less repeatability.

In 1984, Louw, Rothizm and Wegman [10] published their study on the reactions of chlorobenzene with chlorine and hydrogen atoms at 500°C in a tank flow type reactor at an atmosphere pressure. The residence time in the reactor averaged two minutes. Reactant and product information is available and a mechanistic model was proposed.

Recently, Louw, et al. [11] carried out a second study on the decomposition of chlorobenzene by using a tank flow reactor and hydrogen at 1 atm pressure. The residence time ranged from 5 - 10 seconds. The temperatures were 500 to 1000°C. A reaction scheme for the formation of methane through a methyl-cyclopentadiene intermediate was proposed.

In the paper they also mentioned the apparence of C2s (acetylene, ethylene and ethane), and they indicated the formation of soot on the reactor wall. No complete explanation or reaction scheme was proposed. In addition, they discussed the possibility of hydrodechlorination because of the large HCl yield.

In a later study, Louw et al. [12] examined the hydrodechlorination of a mixture of PCB's using a spiralized reactor similar to their earlier study, which was 3.5 meters long and of 6mm ID. The temperatures ranged from 700° C to 925°C with residence times ranging from 7 to 9 seconds. From their results, Louw et al. believed that the hydrodechlorination of PCB's under these reactor conditions yield polychlorinated benzenes which subsequently dechlorinate converting to chlorobenzene and benzene.

In 1987, Ritter [5] studied the thermal decomposition of chlorobenzene in a tubular flow reactor system at an atmosphere pressure and average residence times of 0.02 to 2.5 seconds. He ran the experiment in 3 diameters of quartz reactor tubes, and examined the wall reactions in these reactors by the application of pseudo first order reaction kinetics and assumption of plug flow kinetics (Kaufman equation [13]). The major products he reported were benzene, HCl and significant amount of polycyclic aromatic hydrocarbons (PAHs). But he did not observe any light hydrocarbons such as CH_4. This lack of light hydrocarbon detection was because of his limited GC analysis method for light hydrocarbons. He also studied the pyrolysis of chlorobenzene in a helium atmosphere.

A few groups have studied the high temperature decomposition of dichlorobenzene. Louw et al. provided some data on the decomposition of dichlorobenzene and observed generation of light hydrocarbons [11].

Minta Hung [6] studied the high temperature pyrolysis of dichlorobenzene (DCB) (temperature range from 800°C to 1000°C) at one atmosphere pressure of hydrogen bath gas. He found that the major product are chlorobenzene, benzene, HCl and C(s). The C(s) formation was significant, amounting to 50% reacted DCB. However, because the GC analysis method of his study was still not fit for light hydrocarbon detection, he couldn't report any data on the formation of light hydrocarbons.

2.2. ACETYLENE

Many researches [14-16] have extensively studied the thermal decomposition of acetylene at different temperatures and in various reactors. In 1964, Palmer and Dormish [17] studied the pyrolysis reaction of acetylene in a shock tube at 3 temperatures.

These similar experiments were continuously extended and a number of mechanisms for soot, or carbon(s), formation and growth from acetylene were proposed [18] [19], because of the importance of soot nucleation of acetylene. One study conducted by Frenklach et al [20], concentrated on the reaction pathmays of acetylene to soot under the conditions used in shock tube experiments. The temperature range 1000°K to 2500^{o}K was covered. They reported that fused polycyclic aromatics play a partcularly important role in the soot formation, which involve only carbon and hydrogen containing species. A detailed soot formation reaction mechanism was proposed. His experiment was operated at a very high temperature range in the shock tube. And no data were reported on the identity of other light hydrocarbons rather than polymerization of acetylene.

2.3. BENZENE

Pyrolysis reaction of benzene, have been studied by quite a number of reseachers [21] [22]. The pyrolysis of benzene at 700^{o}C has been researched by Badger and Novotny [22]. Many aromatic products such as biphenyl were reported, with significant amounts of p or m-terphenyl, etc. Methane and ethylene were also identified. Their reactor gas flow was not a tubular flow becaus it was filled with the packing of porcelain chips.

The decomposition of benzene in helium carrier gas has been conducted in a tubular reactor of 5 mm ID in high temperatures from 1173 to 1523 K by Hou and Palmer [23]. They found the reaction kinetics showed mixed order behavior with back reactions and possible wall effects. They offered one reaction scheme to explain the pyrolysis reactions and soot formation from benzene.

Stein and Kafafi recently published an authoritative article about the thermochemistry of soot formation. They believe soot formation involves a sequence of addition and dehydrogenation steps leading to thermodynamically stable carbon structures. They also explained the strong inverse temperature dependence of soot formation [24].

3. THEORY

3.1. PSEUDO-FIRST-ORDER REACTION AND ARRHENIUS LAW

The reactions of chloro-aromatic hydrocarbon decomposition in atmospheres of excess hydrogen or helium are generally initiated by unimolecular reaction and propagated by bimolecular reactions as our study here and previous studies indicate [25]:

$$RCl \longleftrightarrow R\cdot + Cl$$

$$R\cdot + B \longleftrightarrow RB^* \longleftrightarrow \text{products}$$

$$R + B\cdot \longleftrightarrow BH + R\cdot$$

where B = benzene or aromatic stable molecule.

R = hydrocarbons or hydrogen molecules.

When either of the reactants above appears in large excess in comparison with other reactants, its concentration stays constant during the over all reaction. In this case a bimolecular reaction can be simplified to be exhibit first order behavior and pseudo first order reaction kinetics [26]. The reaction kinetics can be written as follows:

$$\ln (C/C0) = kexp * t \qquad (a)$$

where C0 is reactant initial concentration, C is the instant average concentration of the reactant. Kexp is the experimental rate constant; t is residence time in the reactor at a given reaction temperature.

Since our reaction system is complex, an observed or global reaction rate might be the result of many elementary reaction steps. However, a few major steps are usually rate limiting. For instance, in the decomposition of acetylene in hydrogen at the temperature range of 700°C to 900°C, we suggest that the first reaction is a unimolecular step:

(a) $CH \equiv CH \longleftrightarrow CH_2{=}C{:}$

$CH_2{=}C{:} + H_2 \longleftrightarrow [CH_2{=}CH_2]^* \longleftrightarrow C_2H_3 + H$

$\longleftrightarrow C_2H_4$

The result of the observed reaction kinetics from our experiment may reflect this as a rate limiting step or it may depend on the detailed chain reaction processes. The presentation of our mechanestic analysis is found in the Result and Discussion sections (chapter 5).

The temperature dependency of rate constant can be described by modern thermochemical kinetic theories such as collision theory and transition-state theory. Consider A and B colliding and forming an unstable intermediate which then decomposes into products:

(b) $A + B \longleftrightarrow AB^* \longleftrightarrow AB$

Collision theory believes the reaction rate to be governed by the number of energetic collisions between reactants. What happens to the unstable intermediates is not considered. The theory simply assumes that this intermediate breaks down rapidly enough into products so as not to influence the rate of the overall process.

Transition-state theory, constrast, considers the reaction rate to be controlled by the rate of decomposition of intermediate. The rate of formation of intermediate is assumed to be so rapid that it is present in "equilibrium" at all times.

The Arrhrenius Law is a well known equation that expresses the dependency of reaction rate on temperature.

$$k = AT^{n}e^{-Ea/RT}$$

The formula provides a general version of all these theories above. When n = 1/2, it becomes collision theory. But when n = 1, the expression describes transition-state theory. Moreover, when n=0 we get the conventional Arrhenius form.

Because our temperature range is relatively narrow, around 300°K, we can utilize the Arrhenius form as a good approximation to the temperature dependency of the data. Thus, we employ the Arrhenius Law to analyze our experiment data.

3.2. THE TUBULAR REACTOR THEORY AND RELATED ASSUMPTIONS

Experimental measurements of our kinetics study were routinely operated in a tubular flow reactor system, which was made from a quartz tube 36 cm long and 1.05 cm ID.

The validity of the application of the plug flow assumption can be approved through comparisons of the kinetic values obtained by applying the numerical solution of the continuity equation for the first order kinetics with laminar flow, with radial dispersion and bulk reaction [27].

The conservation equation, according to Bird, Stewart and Lightfoot [28] is:

$$-V(r)\,\frac{\partial C}{\partial Z} + D\left\{\frac{\partial^2 C}{\partial r^2} + \frac{1}{r}\,\frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial Z^2}\right\} = K\,C$$

where r is the reactor radius, V(r) the radial velocity distribution, Z distance, D the diffusion coefficient, k the reaction rate constant and C the concentration of the reactant.

Application of a plug flow reactor and its corresponding assumptions help to simplify the analysis of our experimental data, avoiding unnecessary calculational complexity.

3.3. BASIC KINETIC PRINCIPLES FROM THERMOCHEMISTRY AND THE APPLICATION OF QRRK IN THE PREDICTION OF RATE CONSTANT

3.3.1. UNIMOLECULAR REACTION:

The well known Lindemann theory [29] builds the foundation for the modern theories of unimolecular reactions. The main concepts of the theory are as follows:

(a) By collisions, a certain fraction of the molecular become energized. The rate of the energization process depends upon the rate of bimolecular collisions.

$$A + M \xrightarrow{k1} A* + M \qquad (d)$$

M is a third body species, it can represent a product, an inert gas or a second molecule of reactant.

(b) Energized molecules are de-energized by collision. It is the reverse of the process (b):

$$A* + M \xrightarrow{k2} A + M \qquad (e)$$

Constant k2 is energy independent.

(c) There is a time-lag between the energization and unimolecular dissociation or isomerization of the energized molecule:

$$A* \xrightarrow{k3} B + C \qquad (f)$$

The overall reaction rate of the Lindemann mechanism, from the above reaction, can be expressed:

$$R = k3*[A*] = \frac{k1k3[A][M]}{k2[M] + k3} = \frac{(k1k3/k2)[A]}{1 + k3/k2[M]}$$

At high pressures, when k2[M] >> k3,

$$Rinf = \left(\frac{k1k3}{k2}\right)[A] = kinf[A]$$

The reaction exhibits first order behavior.

At low pressures, k2[M] << k3,

$$Rbim = k1[A][M]$$

The rate of reaction follows second-order kinetics.

On the other hand, for the unimolecular reaction rate constant:

$$kuni = \frac{1}{[A]}\left(\frac{-d[A]}{dt}\right) = \frac{k3k1[M]}{k3+k2[M]}$$

At high pressures, k2[M] >> k3,

$$kuni = \frac{k1k3}{k2} = kinf$$

At low pressure, k2[M] << k3,

$$kuni = k1[M]$$

So, we see, kuni is a function of [M]. The common assumption is that the given reaction is at its high pressure limit. Below the transition pressure (Pt), the rate constant Kuni is no longer independent of pressure. We use QRRK theory in this study, however, to determine the fall-off regime.

In 1928, Kassall [30] first demonstrated the equation for the unimolecular rate constants on the quantum - RRK or

QRRK unimolecular reaction theory. He considered the storage of excess energy (relative to the ground state) as quantized vibrational energy. In this theory, it is assummed that the vibrations of the decomposing molecule can be represented by a single frequency ν (the geometric mean vibrational frequency). Each energy E is then divided into vibrational quanta. The quantum levels and the rate processes are illustrated in figure 3.1.a.

The apparent kuni:

$$\text{kuni} = \frac{1}{[A]}\,\frac{d\,[\text{Products}]}{dt}$$

$$= \frac{1}{[A]} \sum_{\substack{E=E_0\\(n=m)}}^{\infty} \text{Krxn}\ (E)\ [A*(E)]$$

$$= \sum_{\substack{E=E_0\\(n=m)}}^{\infty} \text{Krxn}\ (E)\ \frac{\text{Kdeexc}\ [M]\ K[E,T]}{\text{Kdeexc}\ [M] + \text{Krxn}(E)}$$

Where K(E,T) is the thermal-energy distribution function (Kexc/Kdeexc) and M is a third body species. The energy-dependent rate constant is:

$$\text{Krxn}\ (E) = A_{\infty}\frac{n!\,(n-m+\mathcal{L}-1)!}{(n-1)!\,(n+\mathcal{L}-1)!}$$

Where A is the Arrhenius pre-exponential factor for dissociation of A in the high-pressure limit. For the quantized thermal energy distribution K(E,T) (31):

$$K(E,T) = \alpha^{n}(1-\alpha)^{\mathcal{L}}\frac{(n+\mathcal{L}-1)!}{n!\,(\mathcal{L}-1)!}$$

Where α = exp(-H[ν]/kT).

3.3.2. BIMOLECULAR QRRK

For the addition reaction, in which an excited adduct A* is formed, a bimolecular reaction was followed by stabilization, redissociation to reactants, or decomposition of the chemically activated species:

$$\begin{tikzcd} R + R' \arrow[r, Leftrightarrow] & A^* \arrow[r] \arrow[d, dashed, "B\ Z(M)"] & P + P' \\ & A & \end{tikzcd}$$

In the scheme, k1 is the high-pressure limit rate constant for forming adduct A*. f(E.T) is the energy distribution for chemical activation (31):

$$f(E,T) = \frac{k\text{-}1(E)\ k(E,T)}{\sum\limits_{\substack{E=E_{-1}\\(n=m-1)}}^{\infty} k\text{-}1(E)\ k(E,T)}$$

Since Dean [31] derived bimolecular QRRK from the QRRK theory of unimolecular reaction by Kassel, in the expression, K(E,T) is the QRRK thermal distribution from the unimolecular calculating equations.

For a particular product channel, a pseudo steady-state analysis is made in order to get the bimolecular rate constant, in forming the addition / stabilization product A from R + R'(31):

$$Ka/s = \sum_{\substack{E=E_{-1}\\(n=m-1)}}^{\infty} \beta\, Z[M]\ \frac{k1,_{\infty}\ f(E,T)}{\beta\, Z[M] + k\text{-}1(E) + k2(E)}$$

for forming the addition / decomposition products P and P':

$$Ka/d = \sum_{\substack{E=E_{-1} \\ (n=m-1)}}^{\infty} \beta \cdot k2(E) \frac{K1,_{\infty} f(E,T)}{\beta\, Z[Z] + K\text{-}1(E) + K2(E)}$$

When more decomposition channels are available, the Krxn(E) for each channel is added in the denominator in the above two equations.

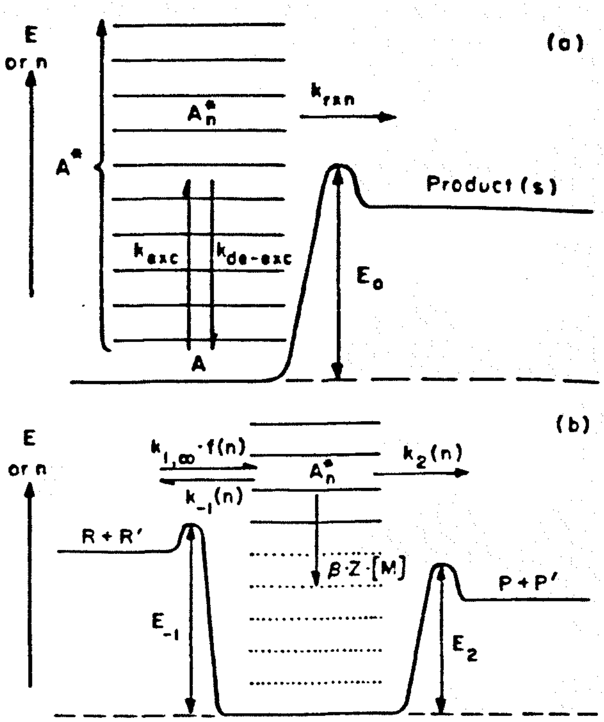


figure 3.3.1.*

Energy diagrams for pressure-dependent reactions.
a. Unimolecular reaction
b. Bimolecular reaction with chemically activated pathway

* from [31]

In our study of the decomposstion of aromatic compounds, we employed a QRRK/ energyzed complex theory to predict of apparent rate constants addition reactions. For further details, please see Chapter 6.

4. EXPERIMENTAL

All the pyrolysis reactions of chlorobenzene, dichlorobenzene, acetylene and benzene in hydrogen and helium were studied in a quartz combustion tube of 10.5 mm i.d. in which plug flow conditions were observed [4]. The flowchart of the experimental equipment in shown in figure 4.1. The apparatus was operated nearly isobarically and isothermally at an atmosphere pressure and temperatures ranging from 700°C - 1000°C, using hydrogen or helium as both diluent and carrier gas.

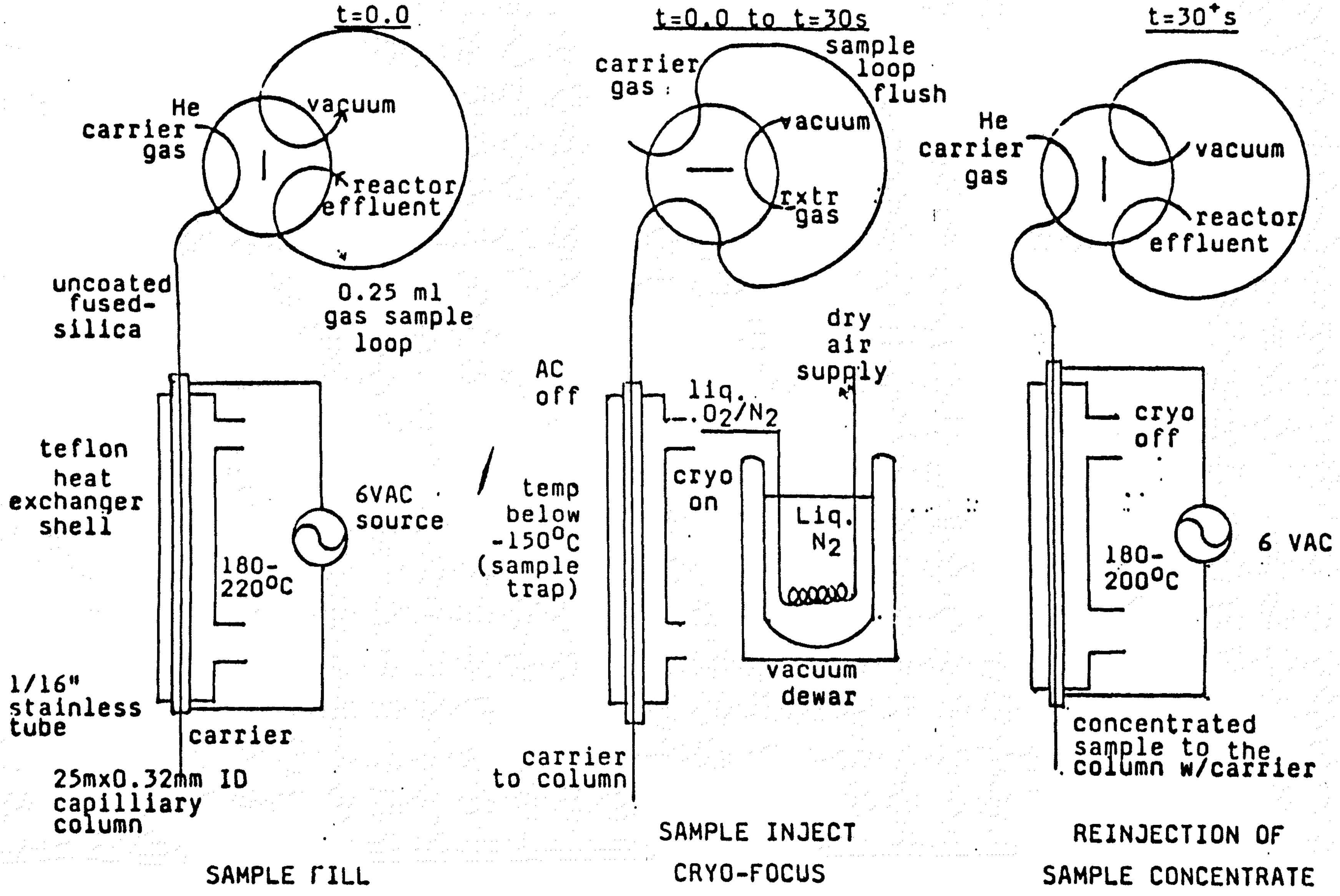
Carrier gas passed through a dual bubbler in which sample reactants chlorobenzene, dichlorobenzene or benzene liquids were moistured and were vaporized into the main gas stream. The chlorobenzene and benzene bubblers were kept at 0°C and the dichlorobenzene was kept at 30°C. The purified acetylene (Matheson Gas Products Company, East Rutherford, NJ.) flowed into and was constantly mixed with the carrier gas before reactor. The concentration of acetylene was adjusted by a needle rotameter. The saturated gas mixture was preheated to nearly 300° before the furnace by a coiled heating tape to prevent condensation and prepare for the high temperature decomposition. The flow rate of carrier gas, which ranged from 2 cc/sec to 44 cc/ sec, was controlled by two sets of rotameters.

The quartz reaction tube was heated within a three-zone Mellen Clamshell type electric furnace. The furnace had an over-all length of 18 inches long and 1.25 inches I.D. The

temperature profile in the quartz reactor chamber was maintained nearly isothermal at the designated temperatures by using the three-zone furnace. The temperature inside the furnace was controlled by three indepenedent Omega CN 300 PI digital temperature controllers. The three K-type thermocouples outside the reactor tube, connected with the controllers, situated inside a second quartz tube with continuous gas flow are in the center of each furnace zone and used to monitor temperature and feedback to the controllors. The actual temperature profile of the reactor chamber was measured by another double shielded K type thermocouple, which significantly minimized the radiation error [33] that could be moved axially within the length of the reactor. While the temperature was measured, helium gas was passed through the reactor to simulate the actual reaction condition. When the desired temperature in the reactor was achieved, the corresponding readouts in the three digital controllors were recorded. During reaction, the corresponding numbers of temperatures were achieved to maintain the desired reactor condition. The temperature profile inside the reactor tube was controlled isothermally within ± 5°C over 90% of the total furnace length. The furnace preheater section operated at a temperature at which reaction could not take place. Above certain reactor temperatures, the vapor/gas mixture reacted and these reactions were monitored.

To obtain the proper initial reagent concentration, the reactant vapor was carried directly to the GC sampler from

Figure 4.2. AUTO-SAMPLER DIAGRAM



the bubbler through the reactor bypass. The GC-FID peak area which corresponded to the initial concentration of the reactant was recorded and used as the C0 for calculations at that temperature.

The reaction effluent gas from the reactor chamber was kept heated at about 200°C by heat transfer lines and drawn to the GC sampler and exhaust system respectively by a vacuum pump. A glass wool filter was set before GC in order to prevent the contamination of the GC sampling system with solids. The HCl gas in the effluent from the reactor was neutralized before most of the reaction gas was exhausted. The design of the exhaust pipe after the reactor chamber and in front of the GC sampler provides a perfect condition for the injection of a sample, by which the pressure of the sampling loop was actually maintained close to the atmospheric pressure. Meanwhile, a vacuum pump was set to draw a fraction of the effluent gas from the bulk through the GC sampler loop to the exhaust system.

The product samples of the reactor effluent were injected into an online Varian 3700 gas chromatograph modified for a flame ionization detection and equiped with a heated 6-port gas sampling valve. A Spectra-physics 4270 integrator was incorporated for quantitative peak area integration. A Chrompack fused silica capillary column, which had an over-all length 25 meters and 0.32 mm ID, was used for channel A to separate the high molecular weight compounds from the reactor effluent. This capillary column features a bonded stationary phase of methyl silicone-CP Sil

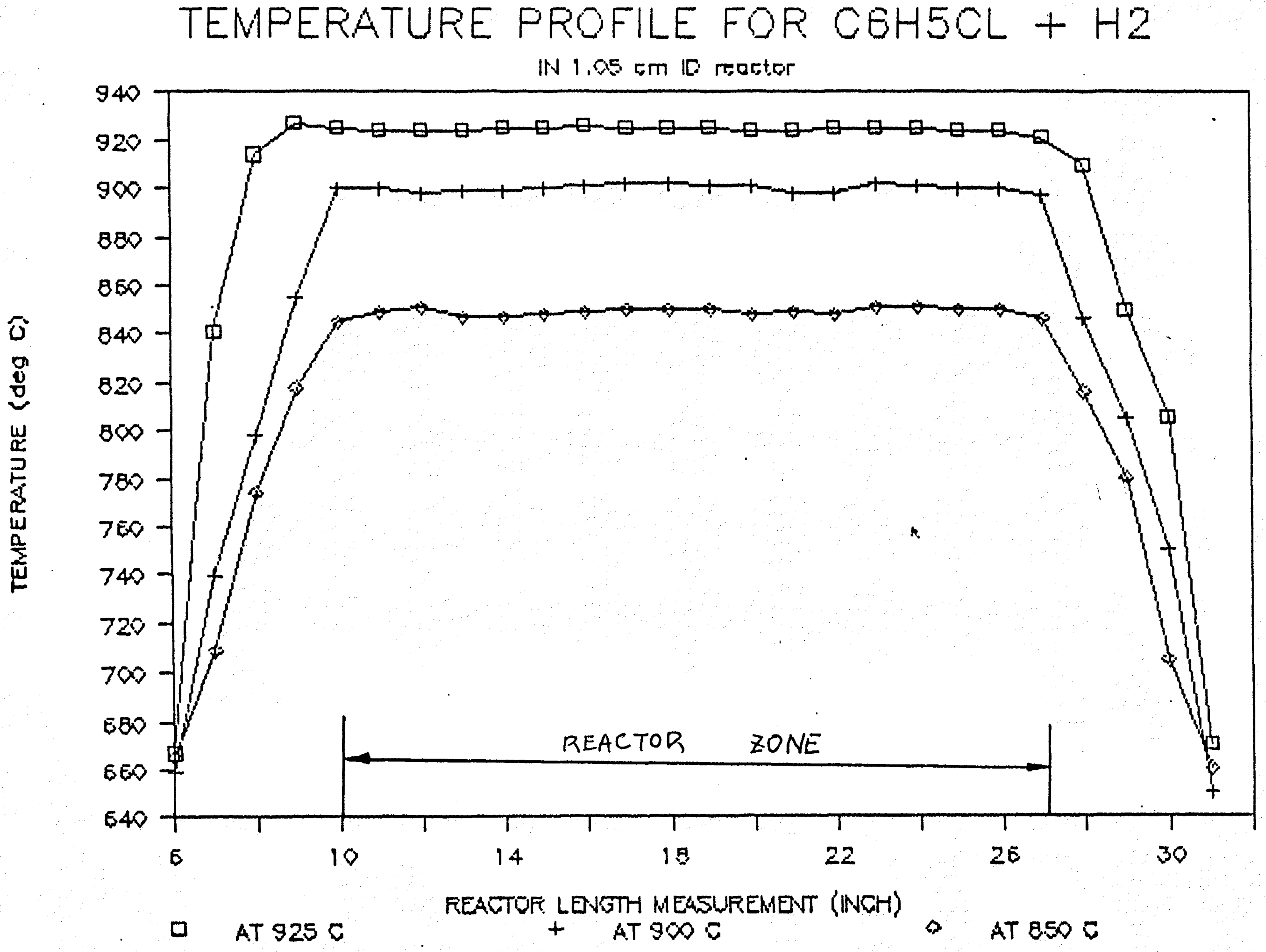

TEMPERATURE PROFILE FOR C6H5CL + H2
IN 1.05 cm ID reactor
TEMPERATURE (deg C)
940
920
900
880
860
840
820
800
780
760
740
720
700
680
660
640
REACTOR ZONE
6
10
14
18
22
26
30
REACTOR LENGTH MEASUREMENT (INCH)
□ AT 925 C
+ AT 900 C
◇ AT 850 C

Figure 4.3

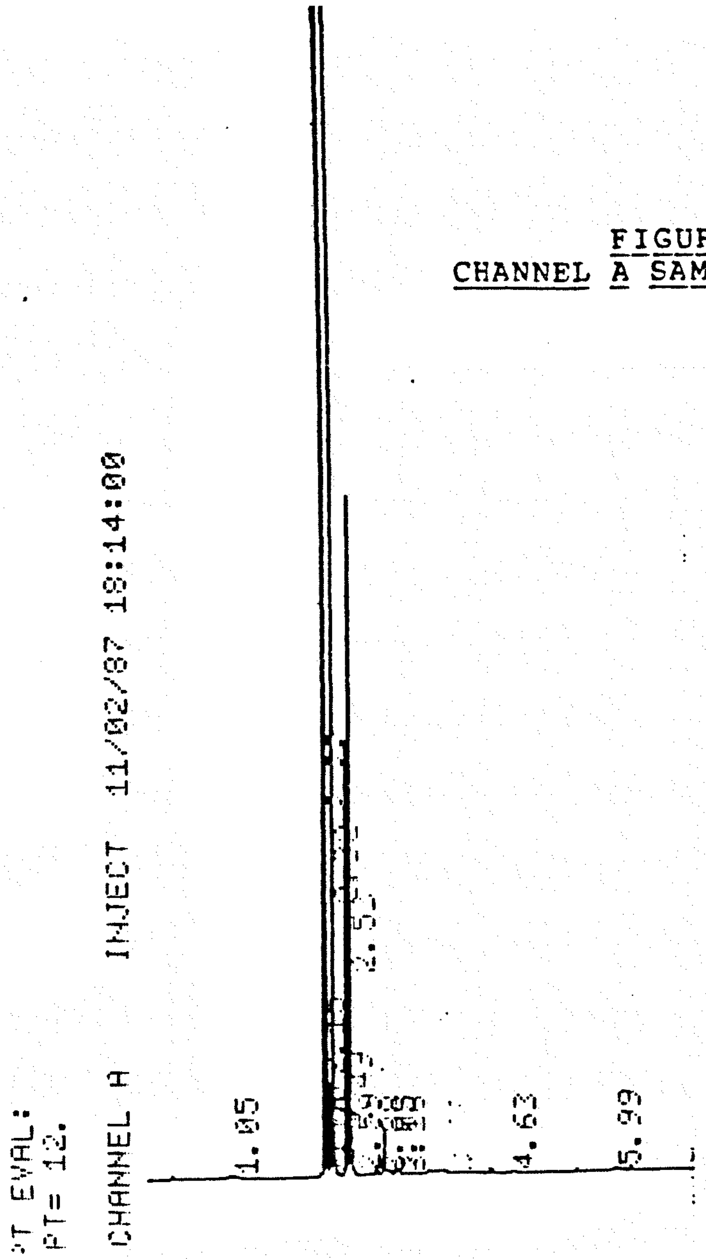
5. This column has good separation characteristics for chloro-aromatic hydrocarbons. Helium gas was used as the carrier gas of column A at an inlet pressure of 10 psig. There are two identical sampling loops for column A and column B. Each loop has a 0.25 ml volume. Gas samples were maintained and injected at 150°C and 1 atm pressure in the both sampling systems. The sampling system structure is shown in figure 4.2.

For the injection of column A, the sample was cryogenically focused at the head of the capillary column by keeping the first 10 cm of the column in a bath of liquid O2 plus N2. Liquid O2 was generatd by passing dry air through a heat exchanger which was immersed in liquid nitrogen. During the injection, cryogenic focusing lasts for 0.5 minutes in order to cool the 10 cm column below -100°C. At the end of the cryofocusing cycle, the sample was reinjected into the carrier gas by rapidly heating it. The time period to heat the sample from -100 to 200°C was approximately 1 minute.

For column A separation of chlorobenzene products, the GC column oven was operated at 70°C for 3 minutes and then programmed at a rate of 35°C/min to a final temperature of 170°C. For the seperation of dichlorobenzene products, the GC oven was mantained at 120°C for 4 minute and programmed at a rate of 35°C/min to a final temperature of 170°C.

In order to separate light hydrocarbons, a Carboseive G column was developed and employedas column B, which was packed with 60/80 mesh Carbosieve G, for 5 ft x 1/8". The

FIGURE 4.4.
CHANNEL A SAMPLE CHROMATOGRAM



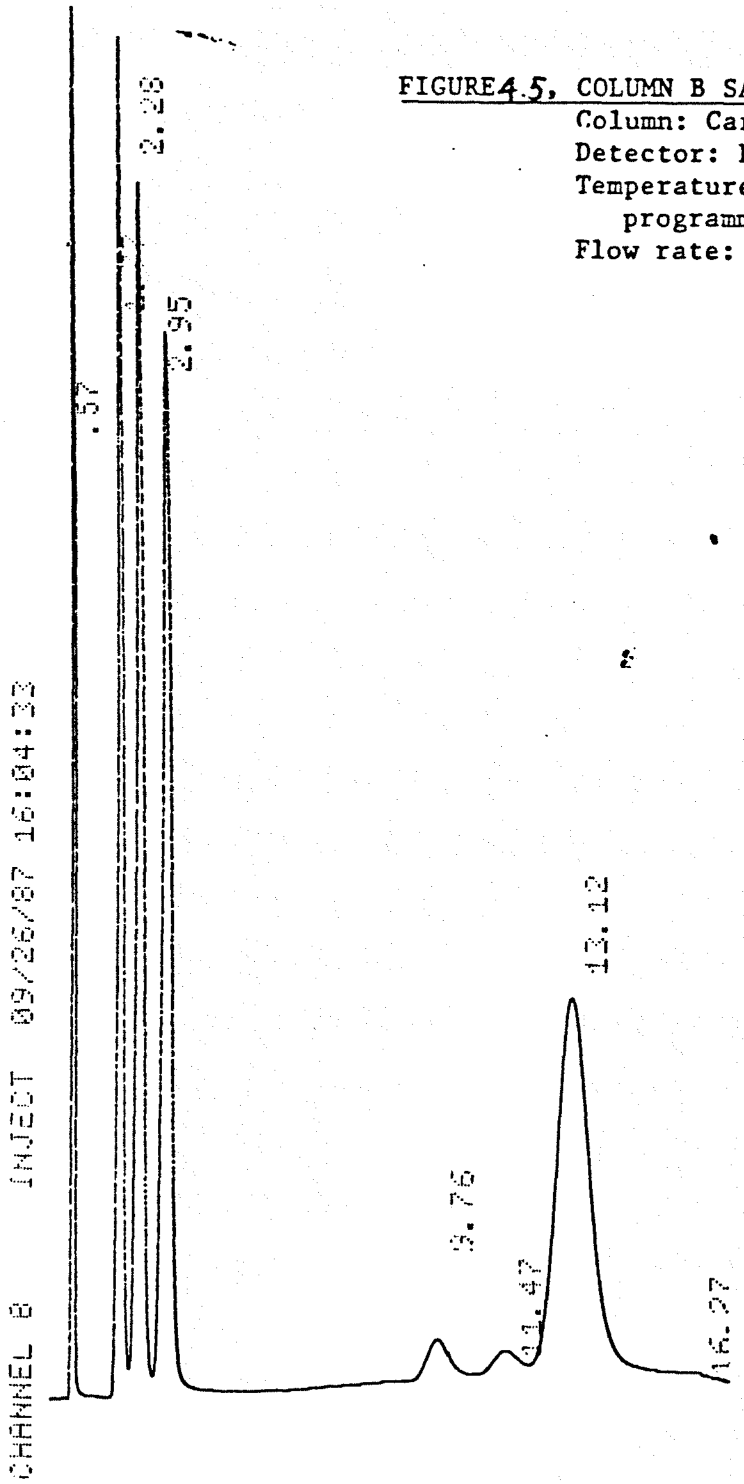
PEAK #	COMPOUND	RETENTION TIME (SEC)
1	ETHYLENE	1.05
2	CYCLOPENTADIENE	1.90
3	BENZENE	2.15
4	TOLUENE	2.22
5	CHLOROBENZENE	2.32
6	O,M,P-DICHLOROBENZENE	2.53
7	NAPHTHALENE	2.88
8	1,1-BIPHENYL	3.78
9	BIPHENYLENE	4.63
10	O,M,P-CHLOROBIPHENYL	5.99

---

column: 25m X 0.32mm ID CP Sil 5 (methyl silicone)
detector: flame ionization detector (FID)
temperature: 120°C (2min): 35°C/min to 170°C
carrier gas: He supplied at 10 psig

FIGURE 4.5, COLUMN B SAMPLE CHROMATOGRAM

Column: Carbosieve G,5ftx1/8"ss
Detector: FID
Temperature: 145°C to 195°C
programmed at 6°C/min, hold 5 min.
Flow rate: 50 cc/min, N2



PEAK #	COMPOUNDS	RETENTION TIME (SEC)
1	CH_4	0.57
2	C_2H_2	1.77
3	C_2H_4	2.28
4	C_2H_6	2.95
5	C_3H_4	9.76
6	C_3H_6	11.47
7	C_3H_8	13.12
8	C_4H_{10}	16.27

oven temperature for column B analyses was ramped between 145°C and 195°C at a rate of 6 °C/min and held for 5 minutes. The flow rate of the carrier gas, nitrogen, was 50 cc/min. Another FID detector was equiped to identify the light hydrocarbon products from channel B.

Both FIDs were set at 280°C. The FID for channel A was supplied with nitrogen make-up gas at a rate of 30 ml/min. Hydrogen and air were provided to the both detectors at the rate of 30 ml/min and 250 ml/min respectivly. The signal amplification sensitivity was set to 10^{-11} amps/mv for column A and 10^{-12} for column B. The corresponding sample chromatograms with retention time and peak identification are shown in figure 4.4. and 4.5.

The response factors for column A are listed in table 4.1.1. The response factors for light hydrocarbons were obtained by the injecting Scotty IV analyzed standard gases. They are listed in table 4.1.2.

TABLE 4.1.1. RESPONSE FACTORS FOR COLUMN A IN GC

COMPOUND	RELATIVE RESPONSE FACTOR
$C_6H_4Cl_2$	1.00
C_6H_5Cl	1.25
C_6H_6	1.34
$C_6H_5CH_3$	1.18

* from [6]

TABLE 4.1.2. RESPONSE FACTORS FOR COLUMN B IN GC

COMPOUND	RELATIVE RESPONSE FACTOR
CH_4	1.0
C_2H_2	1.45
C_2H_4	1.81
C_2H_6	2.01
C_3H_4	2.47
C_3H_6	2.80
C_3H_8	3.44

5. RESULTS AND DISCUSION

5.1 THERMAL DECOMPOSITION OF CHLOROBENZENE IN HYDROGEN AND HELIUM ATMOSPHERE

The high temperature decomposition of chlorobenzene was further studied [5] at 1 atm pressure within 1.05 cm (ID) reactor to focus on observation of light hydrocarbon species. Temperatures were 850°C, 900°C, and 925°C. Chlorobenzene in helium bath gas at 925°C was also run. At each temperature, the carrier gas was varied between the flow rates of 1.1 - 43.7 cc/sec (STP), and the residence time ranged from 0.2 -1.4 seconds in order to maintain the tubular flow reactor condition. The bubbler temperature was kept at 0°C ice bath for a constant saturation vapor pressure in the carrier gas. The initial hydrogen to chlorobenzene mole ratio was maitained at 227:1. The initial concentration of chlorobenzene was 4.44×10^{-3} mole percent concentration.

Figure 5.1.1. shows the normalized concentration $(C_6H_5Cl)/(C_6H_5Cl)_0$ of chlorobenzene versus residence time under the three experimental temperatures. The decomposition of chlorobenzene decreases constantly with residence time. While, increasing temperature resulted in higher decomposition profile of chlorobenzene as shown in figure 5.1.1.

Pseudo first order behavior of the reaction rate kinetics was observed. Figure 5.1.2. shows the linear relationship between the first order rate expression and residence time

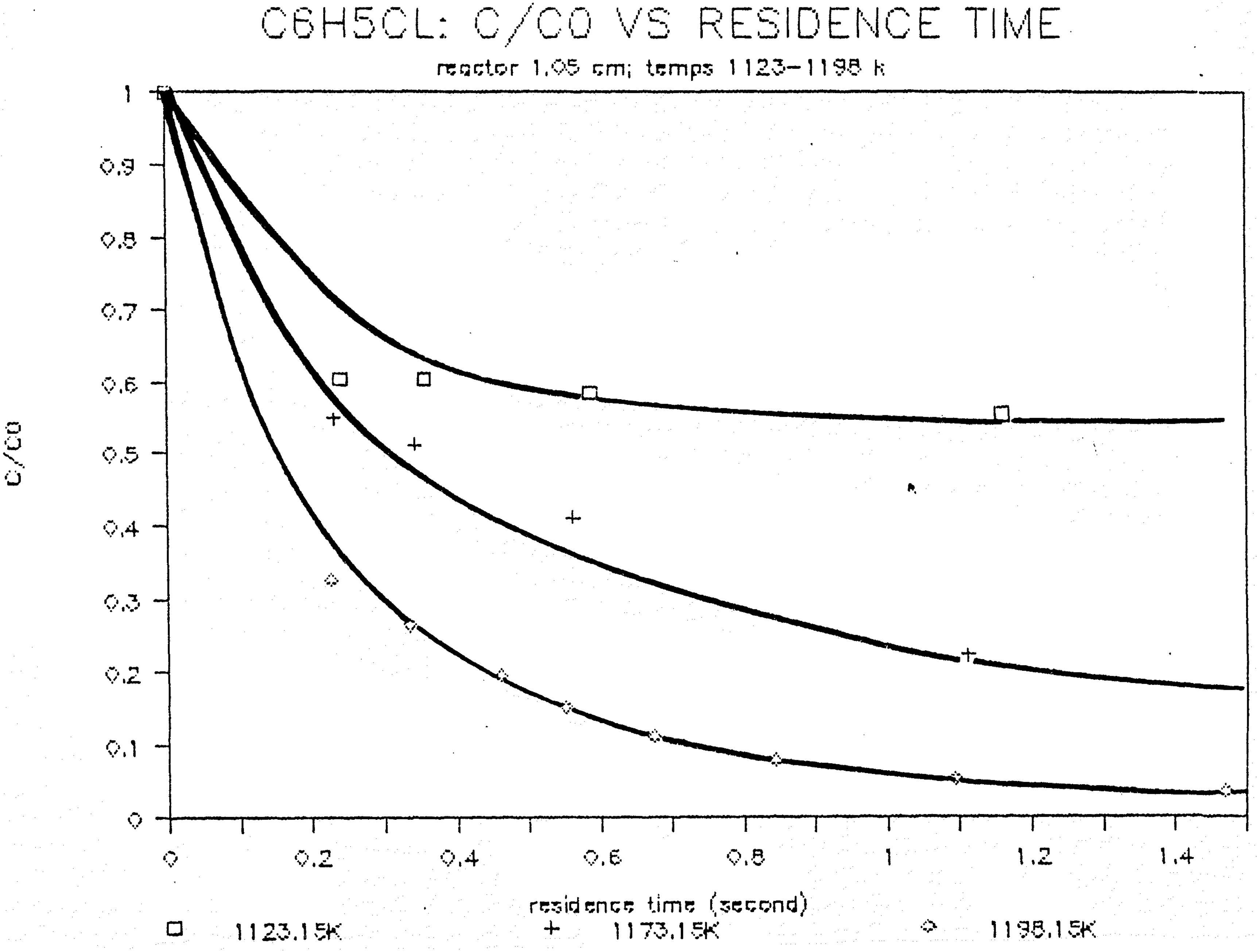

C6H5CL: C/C0 VS RESIDENCE TIME
reactor 1.05 cm; temps 1123-1198 k
C/C0
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.2
0.4
0.6
0.8
1
1.2
1.4
residence time (second)
□ 1123.15K
+ 1173.15K
◇ 1198.15K

Figure 5.1.1.

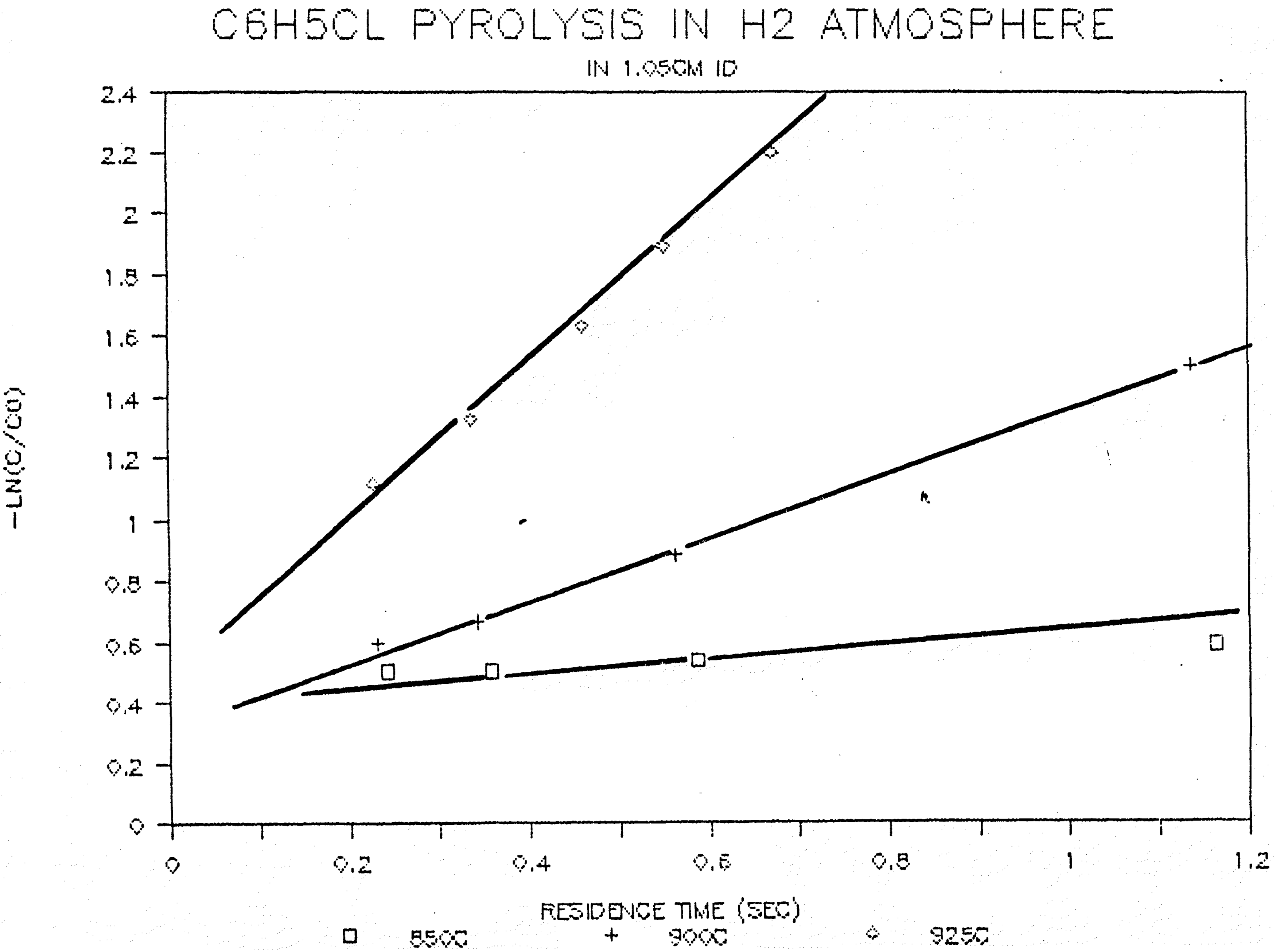
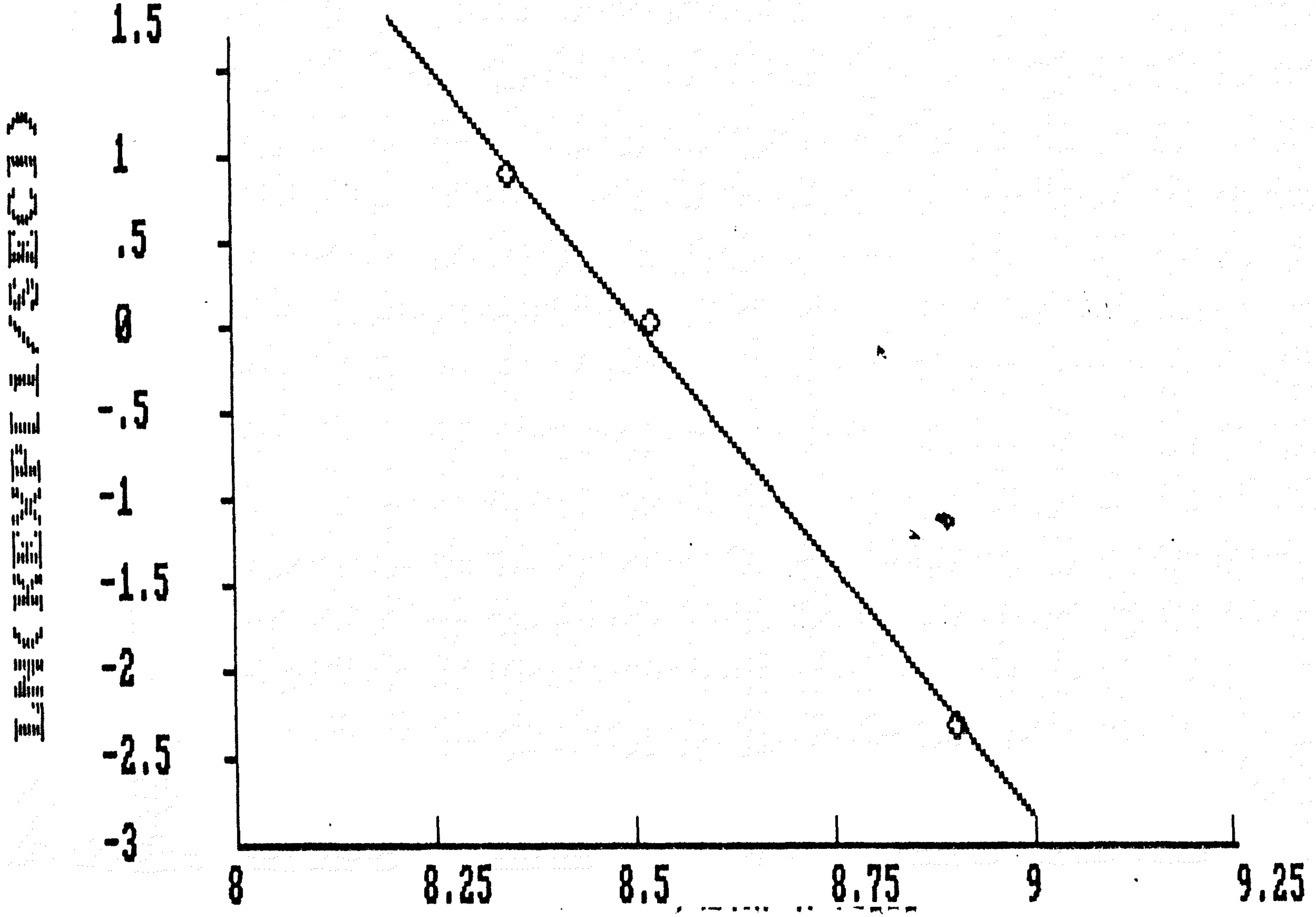

C6H5CL PYROLYSIS IN H2 ATMOSPHERE
IN 1.05CM ID
-LN(C/C0)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
2.2
2.4
0
0.2
0.4
0.6
0.8
1
1.2
RESIDENCE TIME (SEC)
□ 850C
+ 900C
◇ 925C

Figure 5.1.2

Figure 5.1.3. ARRHENIUS BEHAVIOR FOR $C_6H_5CL + H_2$ PYROLYSIS REACTION



for each temperature. The slope of each line was taken as the experimental global rate constant kexp with the unit of sec^{-1} according. The Arrhenius Law expresses the temperature dependency of the global reaction of rate constant kexp:

$$\ln(kexp) = \ln(A) + (-Ea/RT)$$

where A is the frequency factor, a reflection of the percentage of successful collisions. Ea is the Arrhenius activation energy. In figure 5.1.3., the activation energy Ea can be derived from the slope, and the pre-exponential factor (A) from the intercept. The experiment conducted on chlorobenzene for the 1.05 cm diameter reactor resulted in the following parameters for the Arrhenius equation. The results are generally in agreement with that of previous study [5].

TABLE 5.1.1 GLOBAL ARRHENIUS PARAMETERS FOR THE DECOMPOSITION OF CHLOROBENZENE IN HYDROGEN

REACTOR ID	A FACTOR	Ea
1.05	9.1×10^{10}	62 Kcal/Mole

5.1.1. PRODUCT DISTRIBUTION FOR THE DECOMPOSITION OF C_6H_5Cl IN HYDROGEN OR IN HELIUM ATMOSPERE.

Analysis of the reactor effluent gases identified a large number of stable chemical products. The major reaction products identified from chlorobenzene within the carrier gas of hydrogen or helium system were chlorobenzene, benzene and soot. Light hydrocarbons such as methane, acetylene, ethylene and ethane were also reported for the first time in our reaction system by the analysis of carbosive G column on the GC.

The product distribution as a function of residence time is shown for different temperatures in figures 5.1.4.-5.1.7. It is noticed that the decomposition to the major products increases with residence time. Higher decomposition of chlorobenzene also yielded higher benzene concentrations.

Figure 5.1.8. and 5.1.9. shows the decomposition of chlorobenzene in helium atmosphere. At 925°C chlorobenzene actually converted to 40% - 78% soot in our tubular reactor system, while, the yield of benzene only reached from 4.1% - 7.9% due to the increase of the residence time at this temperature in helium. The helium bath inhibited the overall conversion of C_6H_5Cl to C_6H_6, but increased soot products in comparison with the decomposition of C_6H_5Cl in H_2 atmosphere.

The minor light hydrogen products identified were CH_4, C_2H_2, C_2H_4, C_2H_6, and $C_{10}H_8$. They are shown in figures 5.1.4.,5.1.7.,5.1.9. These products are observed at low

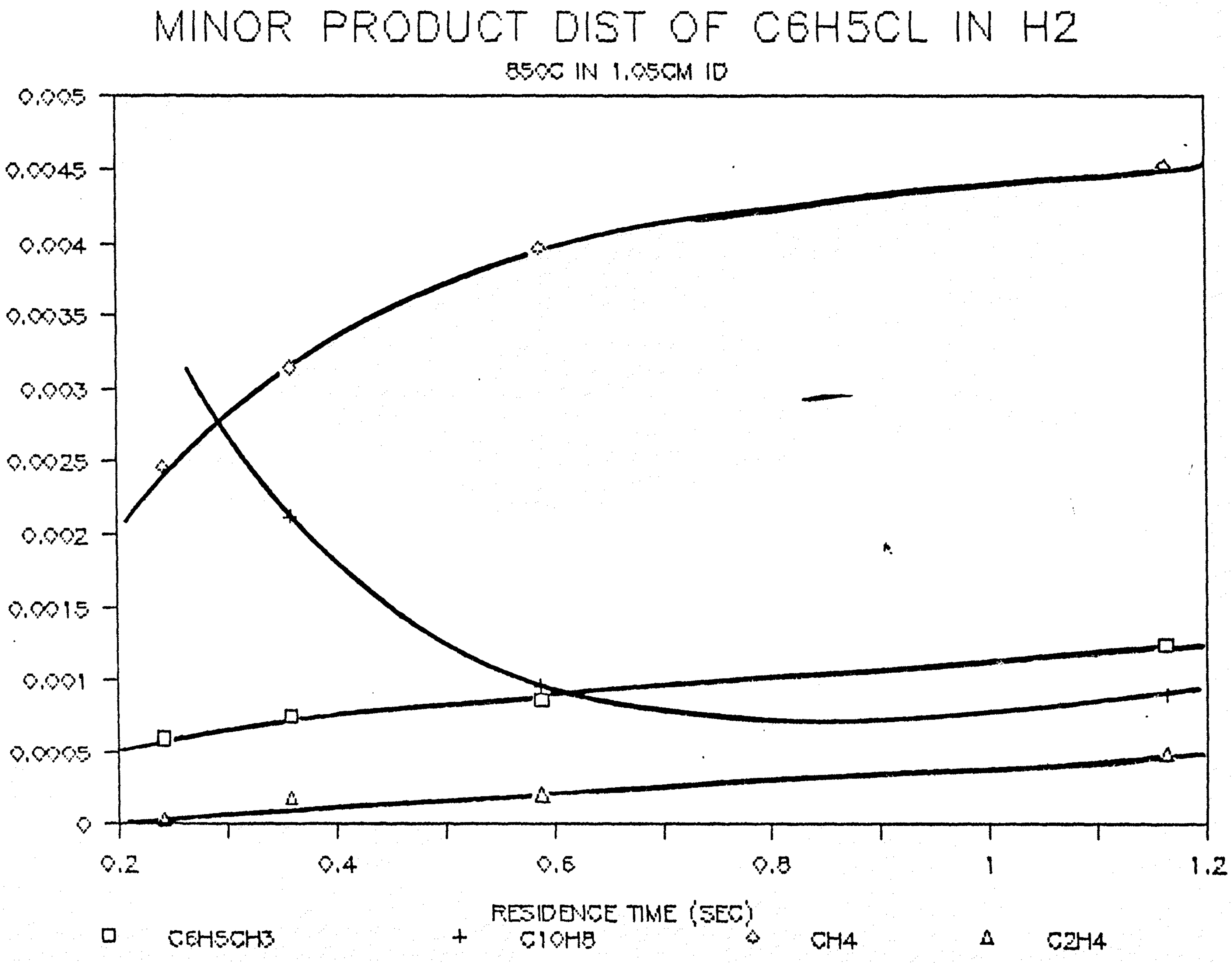

MINOR PRODUCT DIST OF C6H5CL IN H2
850C IN 1.05CM ID
C/C0
0.005
0.0045
0.004
0.0035
0.003
0.0025
0.002
0.0015
0.001
0.0005
0
0.2
0.4
0.6
0.8
1
1.2
RESIDENCE TIME (SEC)
□ C6H5CH3
+ C10H8
◇ CH4
Δ C2H4

Figure 5.1.4.

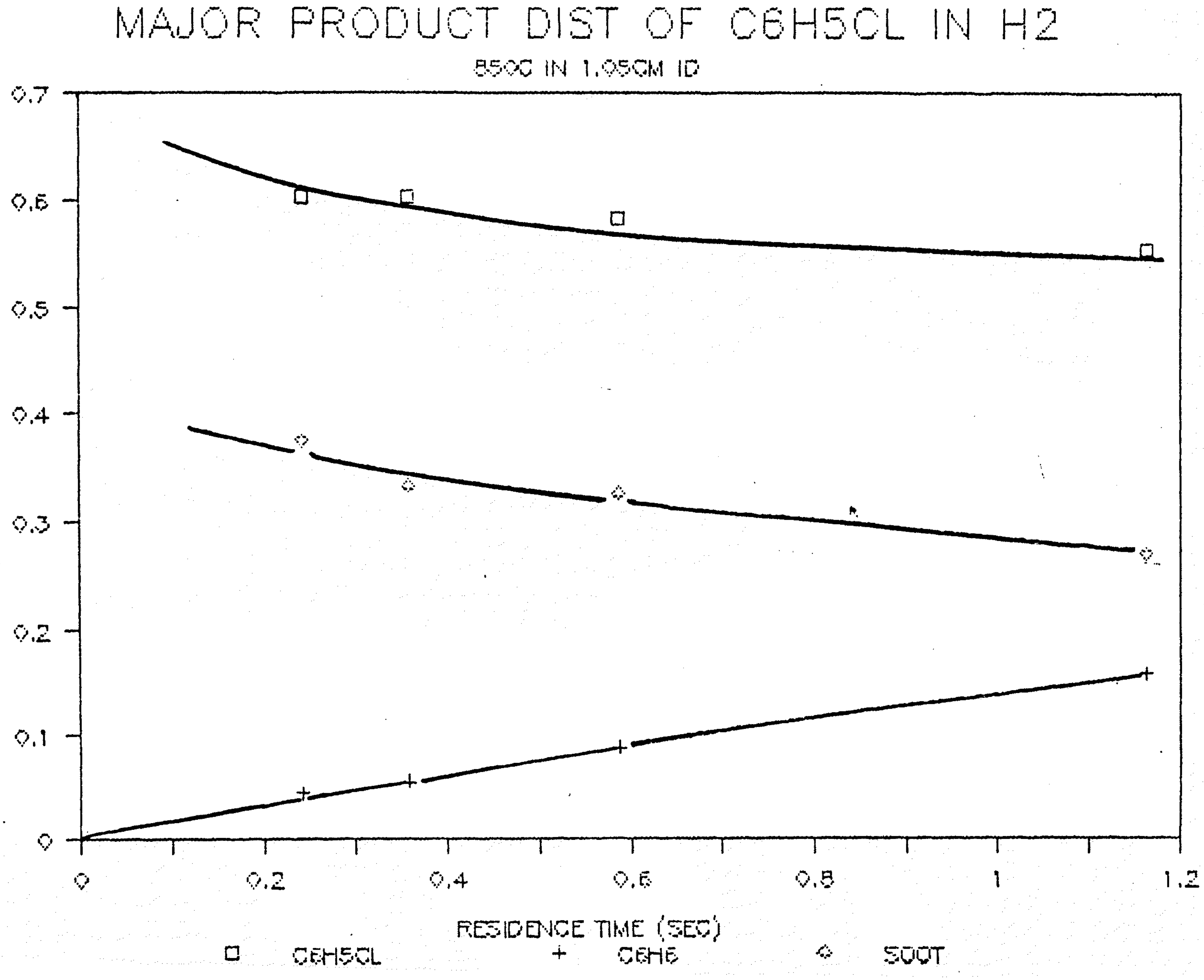

MAJOR PRODUCT DIST OF C6H5CL IN H2
850C IN 1.05CM ID
C/CO
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.2
0.4
0.6
0.8
1
1.2
RESIDENCE TIME (SEC)
□ C6H5CL
+ C6H6
◇ SOOT

Figure 5.1.5.

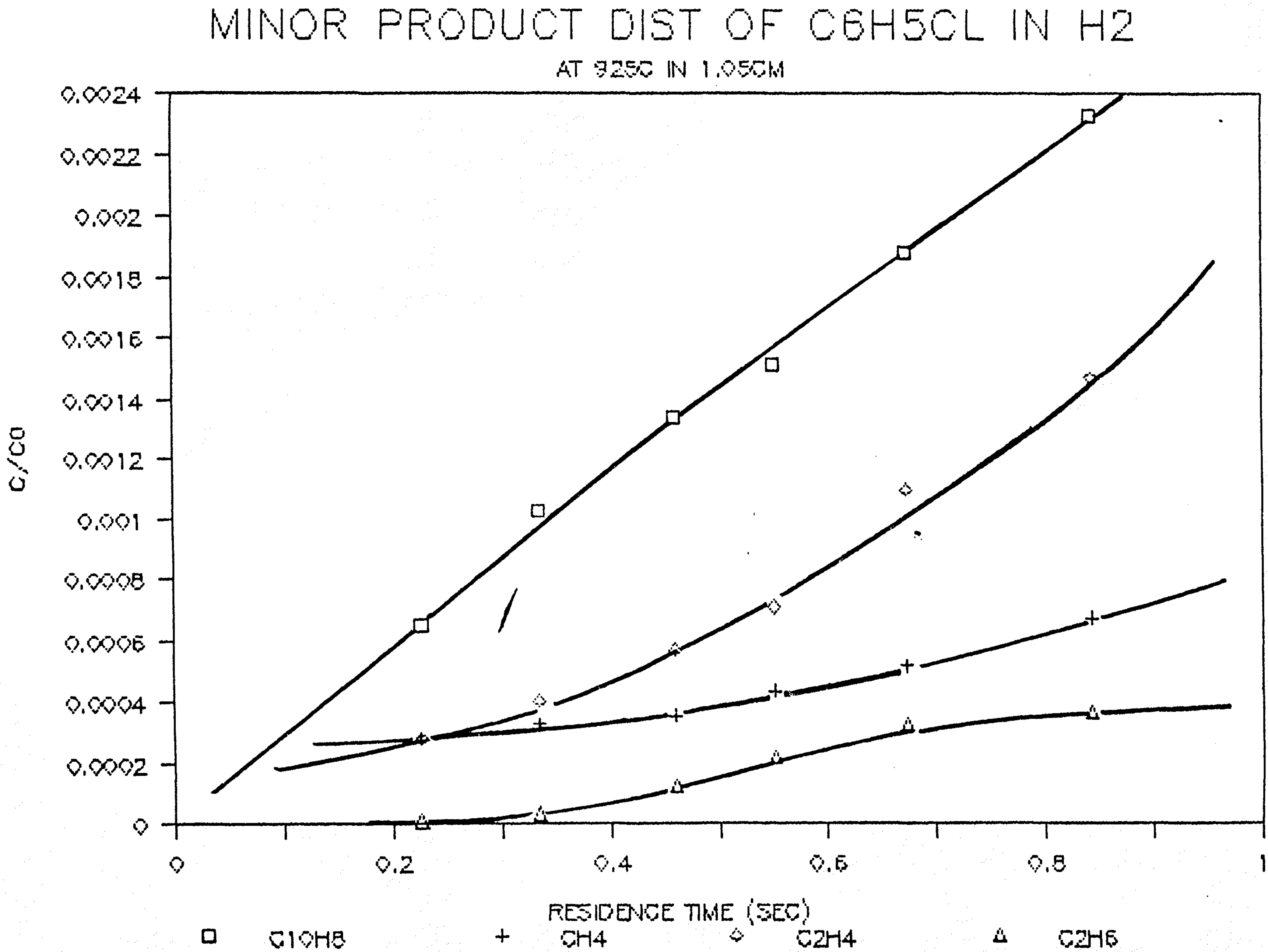

MINOR PRODUCT DIST OF C6H5CL IN H2
AT 925C IN 1.05CM
C/C0
0.0024
0.0022
0.002
0.0018
0.0016
0.0014
0.0012
0.001
0.0008
0.0006
0.0004
0.0002
0
0
0.2
0.4
0.6
0.8
1
RESIDENCE TIME (SEC)
□ C10H8
+ CH4
◇ C2H4
△ C2H6

Figure 5.1.6.

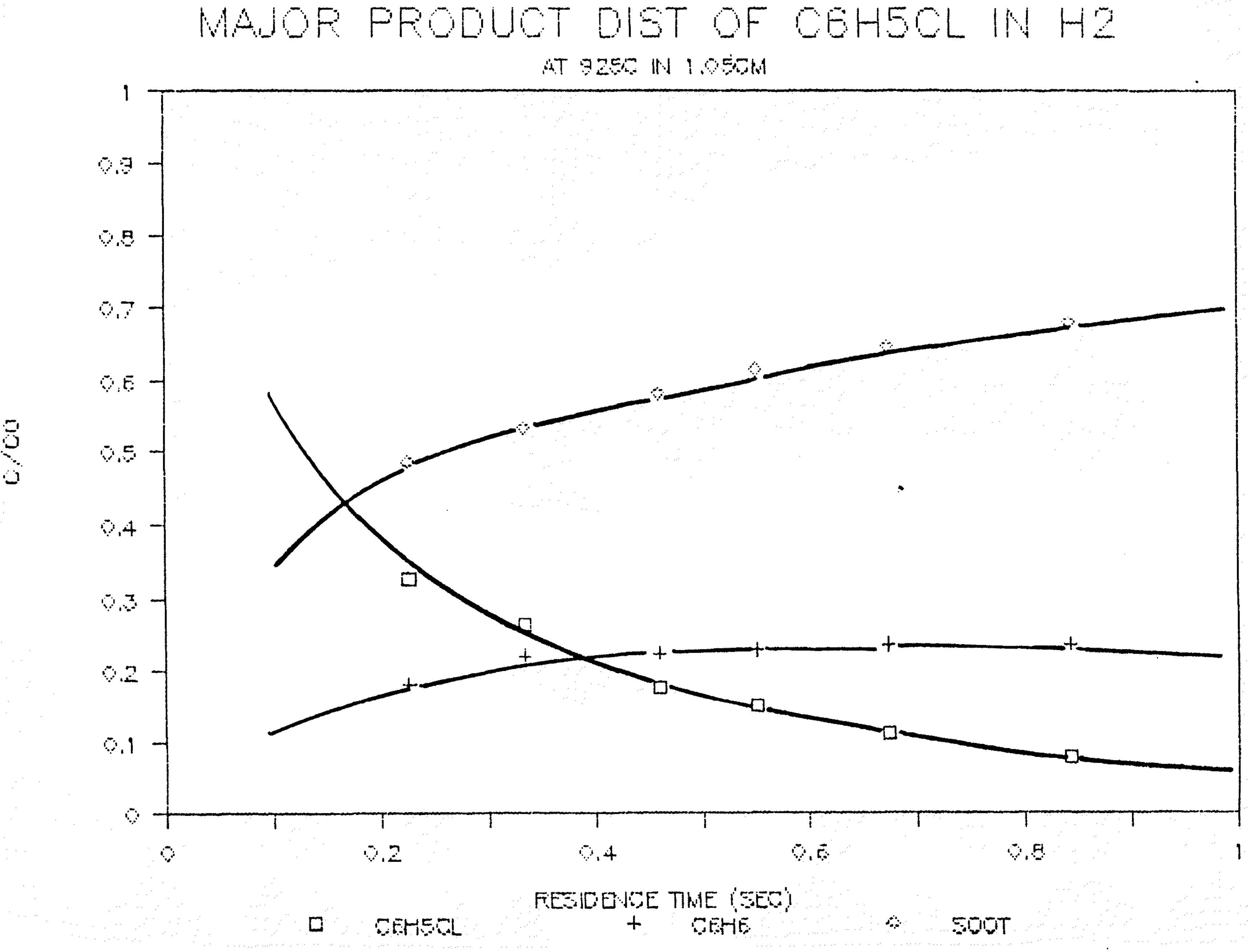

MAJOR PRODUCT DIST OF C6H5CL IN H2
AT 925C IN 1.05GM
C/C0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
0
0.2
0.4
0.6
0.8
1
RESIDENCE TIME (SEC)
□ C6H5CL
+ C6H6
◇ SOOT

Figure 5.1.7.

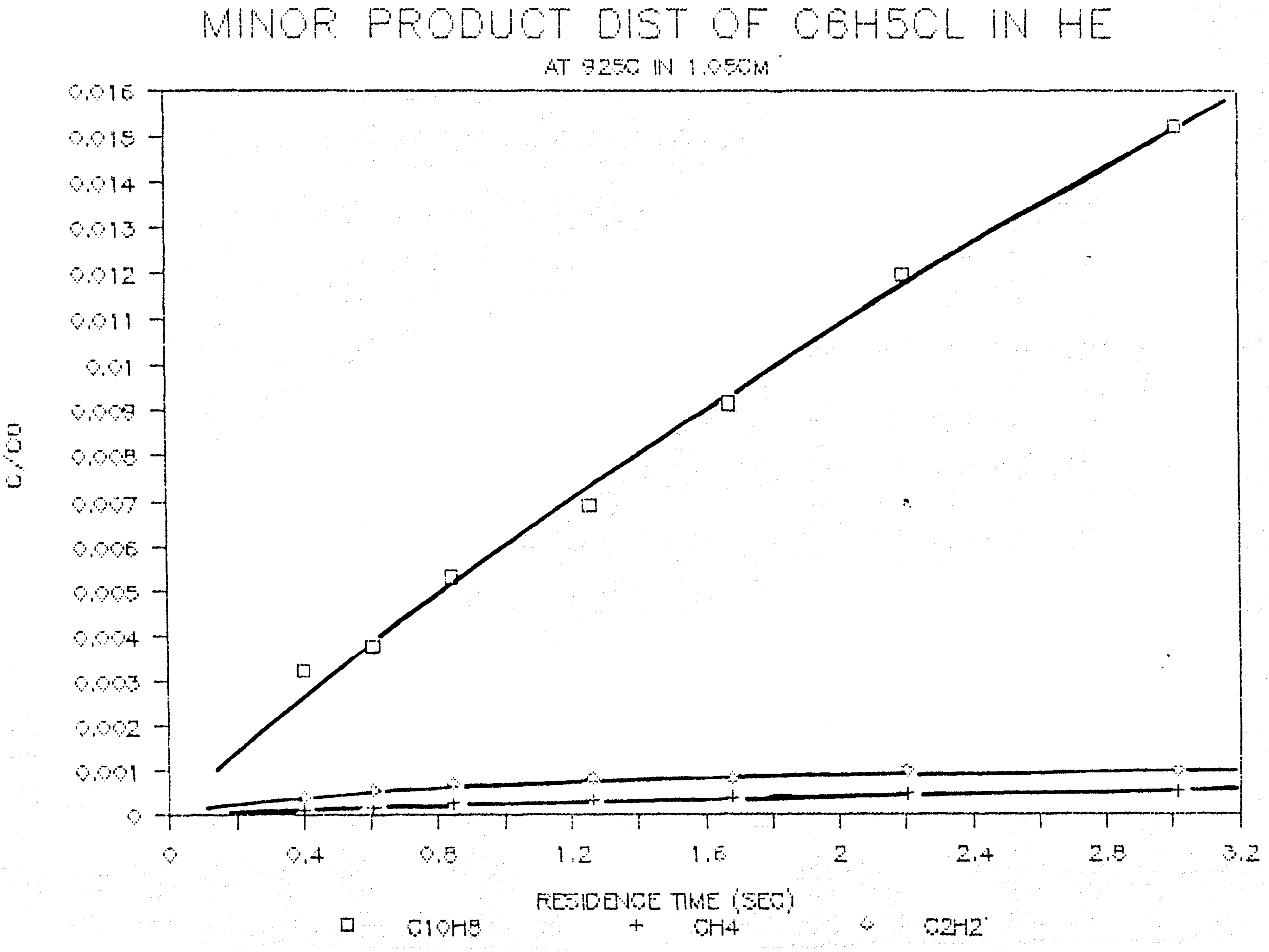

MINOR PRODUCT DIST OF C6H5CL IN HE
AT 925C IN 1.05CM
C/C0
0.016
0.015
0.014
0.013
0.012
0.011
0.01
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
0
0.4
0.8
1.2
1.6
2
2.4
2.8
3.2
RESIDENCE TIME (SEC)
□ C10H8
+ CH4
◇ C2H2

Figure 5.1.8.

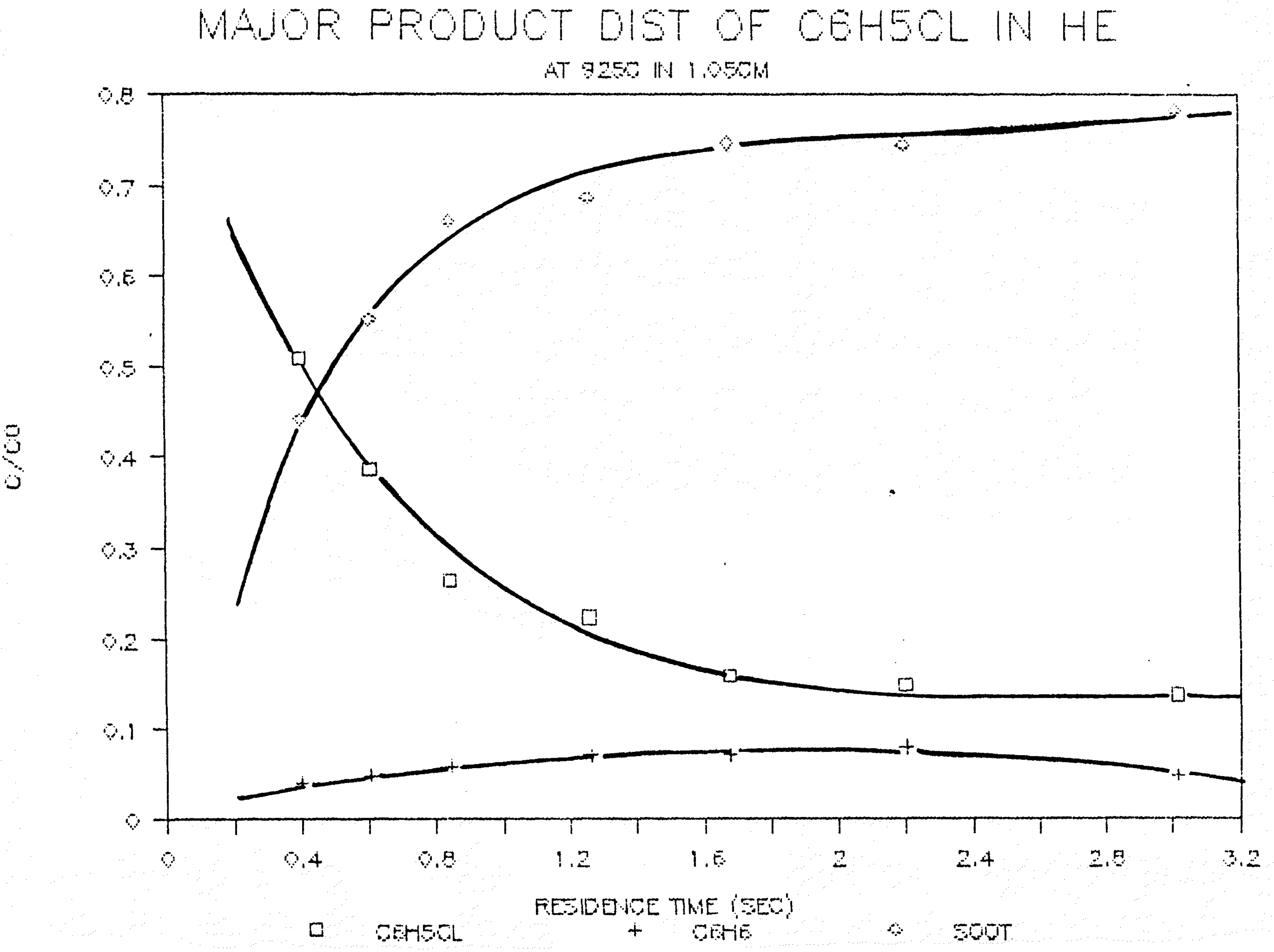

MAJOR PRODUCT DIST OF C6H5CL IN HE
AT 925C IN 1.05CM
C/CO
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0
0.4
0.8
1.2
1.6
2
2.4
2.8
3.2
RESIDENCE TIME (SEC)
□ C6H5CL
+ C6H6
◇ SOOT

Figure 5.1.9.

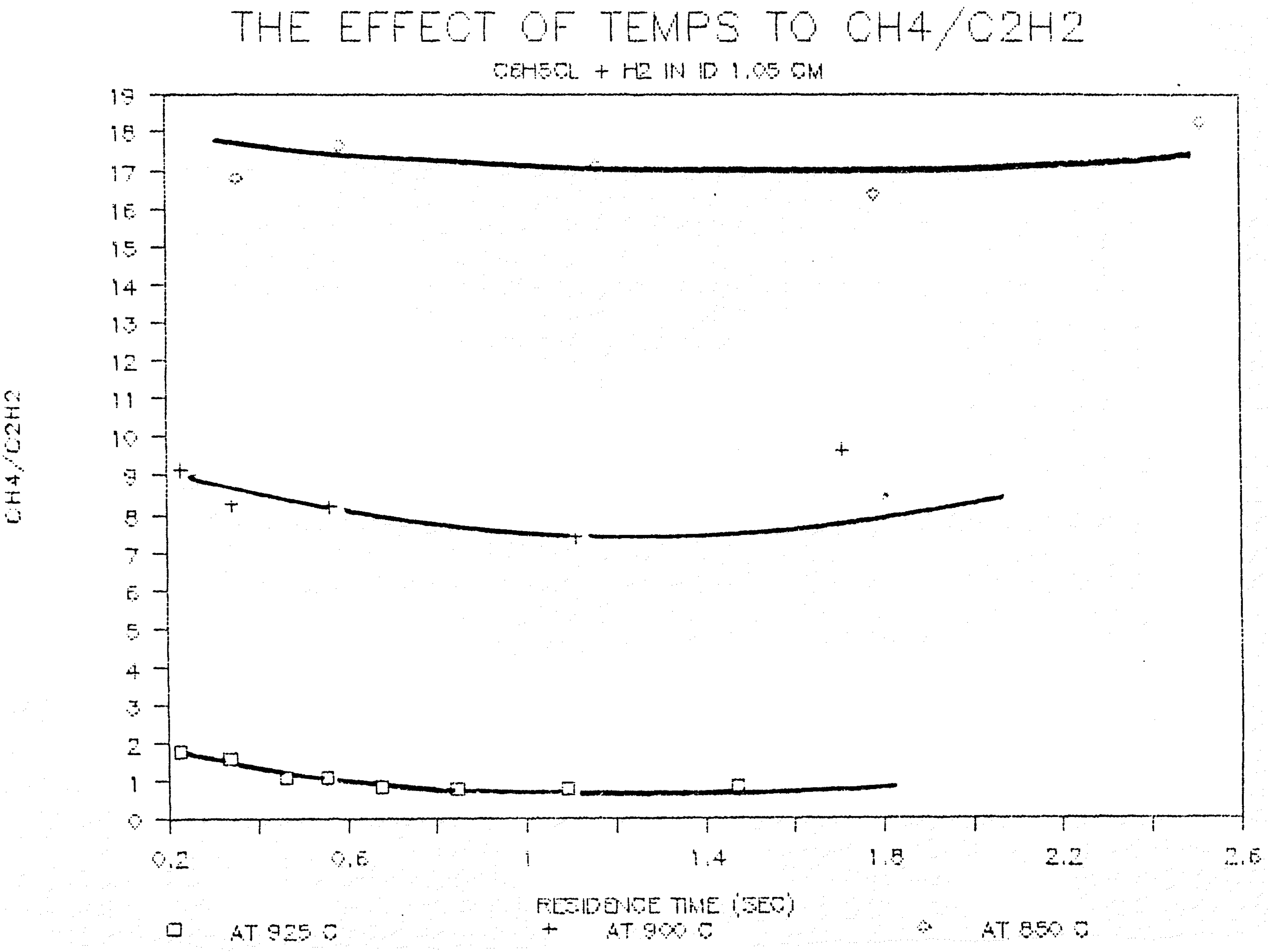
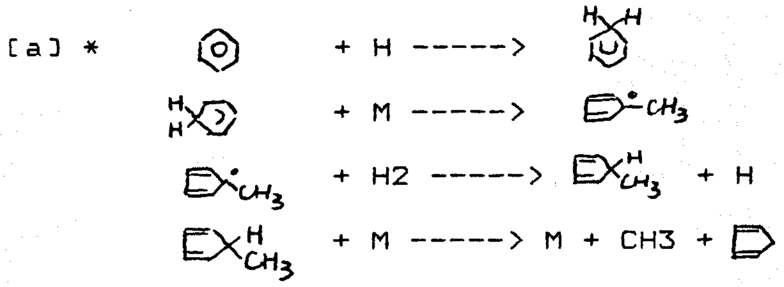

THE EFFECT OF TEMPS TO CH4/C2H2
C6H5CL + H2 IN ID 1.05 CM
CH4/C2H2
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
0.2
0.6
1
1.4
1.8
2.2
2.6
RESIDENCE TIME (SEC)
□ AT 925 C
+ AT 900 C
◇ AT 850 C

Figure 5.1.10.

concentrations of $(C_6H_5Cl)/(C_6H_5Cl)_0 < 5$. Trace amounta of a number of other products were discovered by GC/MS and they are shown in table 5.2.2. Among the light hydrocarbons found, the amount of methane is the highest. Also, it increased with residence time.

The discovery of light hydrocarbons, especially CH_4, was significant. It means that some of the benzene ring is actually broken apart to generate smaller hydrocarbons. It is in good agreement with previous studies [11]. The following reaction scheme and figure 5.1.4, 7, 9. describe the formation of methane.



* from [11]

$$CH_3 + H \longrightarrow CH_4$$

The ring opening reaction of benzene was initiated by the attack of hydrogen radical. Figure 5.1.11. shows the energy diagram of the above ring opening reactions in which C_6H_7 is formed by the attack of H on benzene or chlorobenzene. The identification of cyclopentadiene by our analysis of GC and GC/MS provide strong support that the above reaction route of generating CH_4 is reasonable. A very interesting phenomena was also found in our reaction system. In hydrogen atmosphere, less than 5% ethylene was detected with no acetylene. In helium atmosphere, however, similar amount of

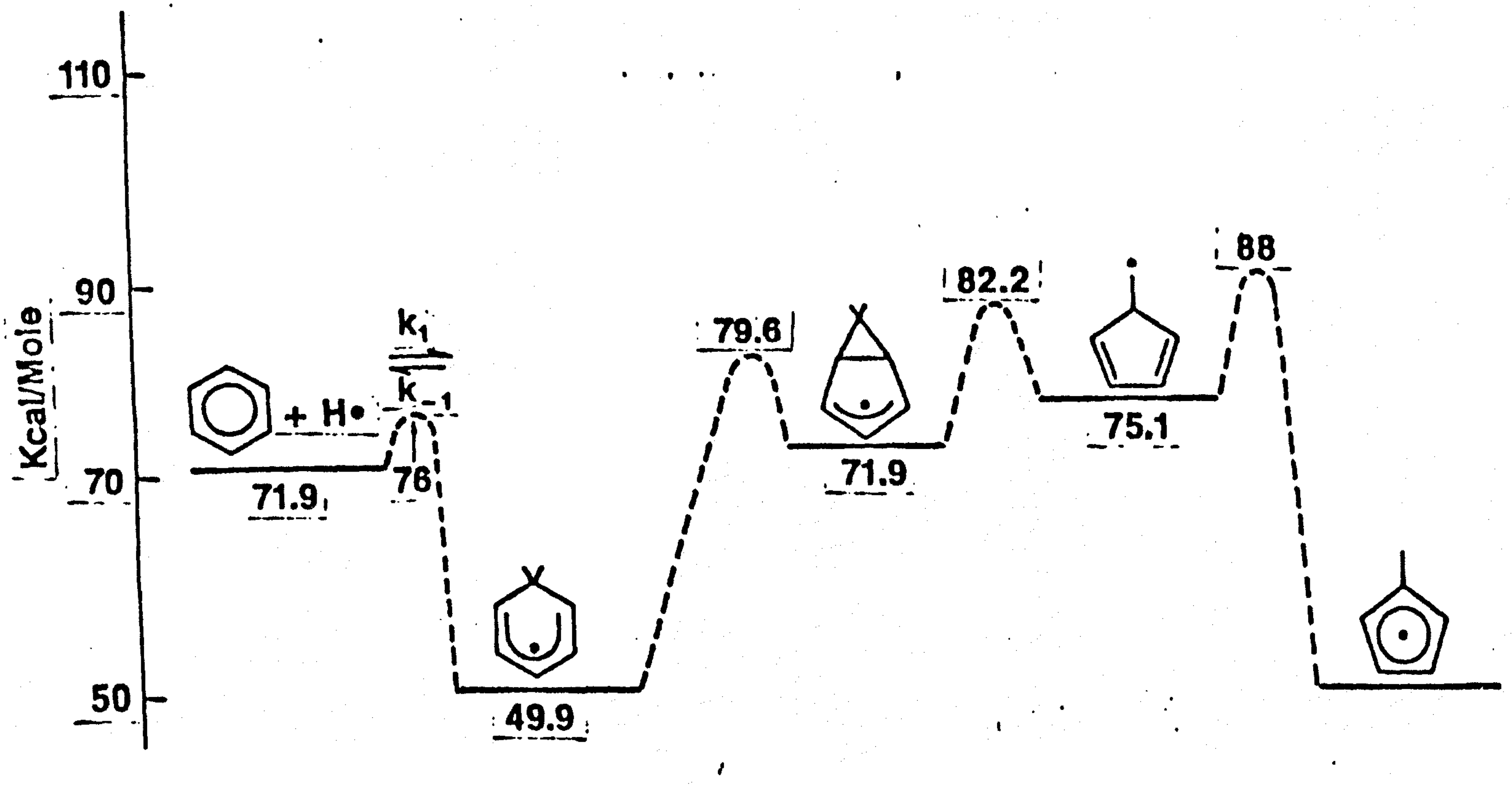


Figure 5.1.11.* The Energy Diagram For Reaction (a)

* from [7]

acetylene was identified with less than 0.1% ethylene. The excess or bath of hydrogen is the reason for this case:

(b) $C_6H_6 + M \longrightarrow C_6H_5 + M + H$

$\longrightarrow CH{\equiv}CCH{=}CHCH{=}C.H$

$CH{\equiv}CCH{=}CHCH{=}C.H \longrightarrow CH{\equiv}CH + CH{\equiv}CCH{=}C.H$

In helium, the reaction almost stops here.

(c) $CH{\equiv}CH \longrightarrow CH_2{=}C\colon \quad \Delta H = 49.99$ Kcal

$CH_2{=}C\colon + H_2 \longrightarrow CH_2{=}CH_2 \quad \Delta H = -91.64$ Kcal

$CH{\equiv}CH + H \longrightarrow CH_2{=}C.H \quad \Delta H = -39.19$ Kcal

$CH_2{=}C.H + H \longrightarrow CH_2{=}CH_2 \quad \Delta H = 12.54$ Kcal

$CH_2{=}CH_2 + H \longrightarrow CH_3{-}C.H_2 \quad \Delta H = -36.35$ Kcal

$CH_3{-}C.H_2 + H \longrightarrow CH_3{-}CH_3 \quad \Delta H = -100.65$ Kcal

$CH_3{-}CH_3 + M \longrightarrow 2CH_3 \quad \Delta H = 89.88$ Kcal

We can see, the last reaction route can produce methyl as well. Also, for these minor products, the energy diagrams for the formation of light hydrocarbons are shown in Chapter 6. $C_{10}H_8$ was observed repeatedly in our GC analysis. It was the lightest soot product that can be found in our GC capilary column.

The temperature dependency of the product distribution is demonstrated in figure 5.1.13 and 5.1.14. at the corresponding constant residence time of 0.5 second.

It is obvious that with the temperature elevation the decomposition of chlorobenzene increases significantly. The conversion of chlorobenzene reached just more than 20% at 0.5 second residence time at temperature 920°C. The

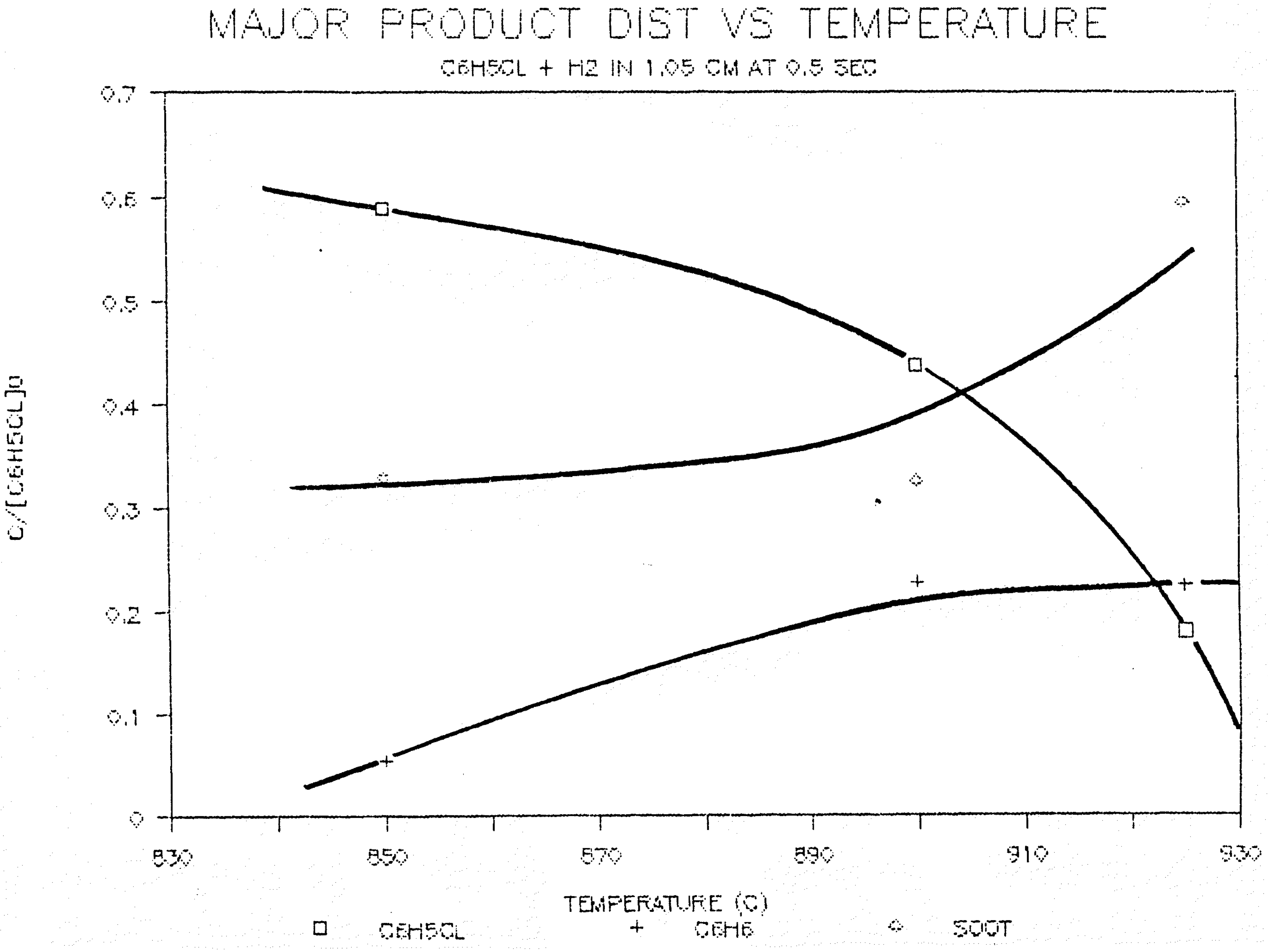

MAJOR PRODUCT DIST VS TEMPERATURE
C6H5CL + H2 IN 1.05 CM AT 0.5 SEC
C/[C6H5CL]0
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
830
850
870
890
910
930
TEMPERATURE (C)
□ C6H5CL
+ C6H6
◇ SOOT

Figure 5.1.13.

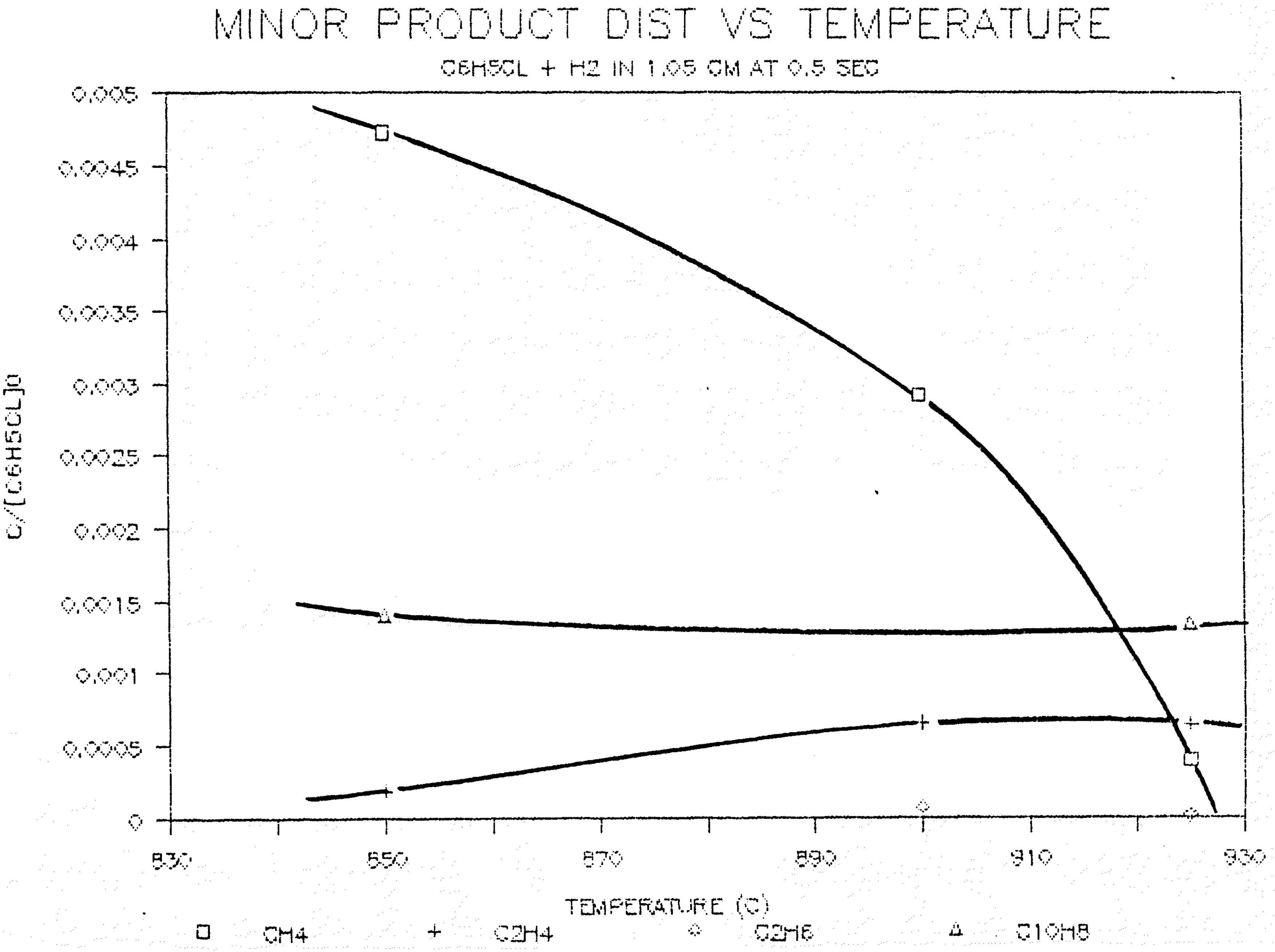

MINOR PRODUCT DIST VS TEMPERATURE
C6H5CL + H2 IN 1.05 CM AT 0.5 SEC
C/[C6H5CL]0
0.005
0.0045
0.004
0.0035
0.003
0.0025
0.002
0.0015
0.001
0.0005
0
830
850
870
890
910
930
TEMPERATURE (C)
□ CH4
+ C2H4
◇ C2H6
△ C10H8

Figure 5.1.14.

concentrations of the two major products, benzene and soot, are increasing due to the rising temperature. C6H6 reaches a stable coversion of nearly 25% since the reaction temperature is over 900°C in the reactor. Soot, however, takes a major conversion, which reaches nearly 60% at 0.5 sec and 900°C, of chlorobenzene and increases significantly with an overall rising temperature profile of. The detailed discussion of soot formation is found in section 5.1.2.

Among the minor products, we notice that the concentration of CH4 dropped while the reaction temperature increases in figure 5.1.14.

Table 5.1.2. shows a material balance calculation result per 600 moles of carbon of C6H5CL + H2 at different temperatures.

TABLE 5.1.2. MATERIAL BALANCE PER 100 MOLES OF CARBON

C6H5CL + H2 IN 1.05 cm ID REACTOR AT 0.5 SECOND

TEMP(°C)	850	900	925	925(HE)
C6H5CL	59.1	44.0	17.6	45.2
C6H6	5.5	22.8	22.5	4.5
C6H5CH3	0.1	/	/	/
C10H8	0.1	/	0.1	/
CH4	2.8	1.8	0.4	0.1
C2H2				0.2
C2H4	0.1	0.2	0.5	0.2
SOOT*	32.8	32.7	59.7	51.7

/ trace amount

* by difference

5.1.2. SOOT YIELD AND FORMATION FROM THE DECOMPOSITION OF CHLOROBENZENE IN HYDROZEN AND IN HELIUM

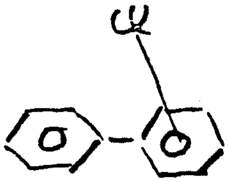
The fact that aromatics form carbon solids or soot at high temprature is well known [11]. Soot formation from aromatics is often considered a result of ring fusing and ring polymerization reactions. Polycyclic aromatic hydrocarbons such as polyphenyls [7] as well as other polyaromaticss [20] are expected to be formed at conditions of our system [24]. For the chlorobenzene decomposition system, chloro and other polycyclic aromatic hydrocarbons were actualy produced and identified by GC/MS analysis. These soot products are usually coated on the reactor wall during the reaction.

Mass spectral analysis of the soot formed in these reactions show a strong evidence of high molecular weight PAHs. The possible molecular structure of the identified PAHs observed in the decomposition of chlorobenzene and dichlorobenzene are shown in table 5.1.3.

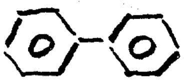
Soot formed from chlorobenzene system increases with both residence time and temperature in figure 5.1.15. i.e. soot increases with the increased decomposition of chlorobenzene.

Figure 5.1.16. shows the comparison of soot yield from chlorobenzene in hydrogen and helium atmosphere at the same temperature of 925°C. It is obvious that more soot was formed from chlorobenzene in a helium atmosphere than in hydrogen atmosphere. This is in an agreement with the

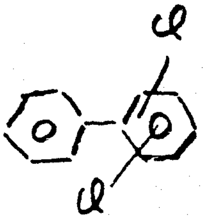
TABLE 5.1.3. POSSIBLE STRUCTURES OF A VARIETY OF SOOT PRODUCTS FROM THE PYROLYSIS REACTIONS OF CHLOROBENZENE AND DICHLOROBENZENE, ODENTIFIED BY GC/MASS



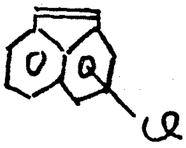
(1)



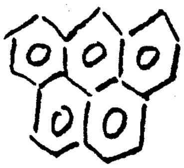
(2)



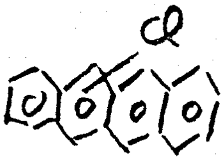
(3)



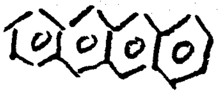
(4)



(5)

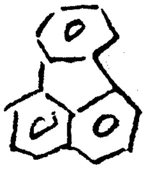


(6)

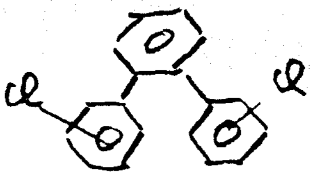


(7)

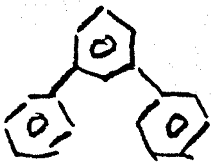
(8)



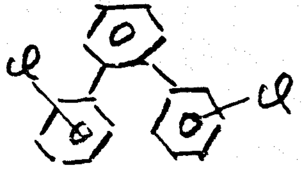
(9)



(10)



(11)



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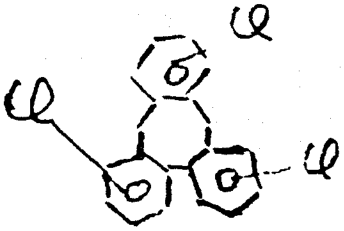
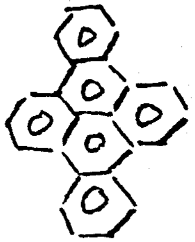


(13)



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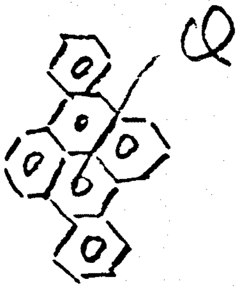


(15)

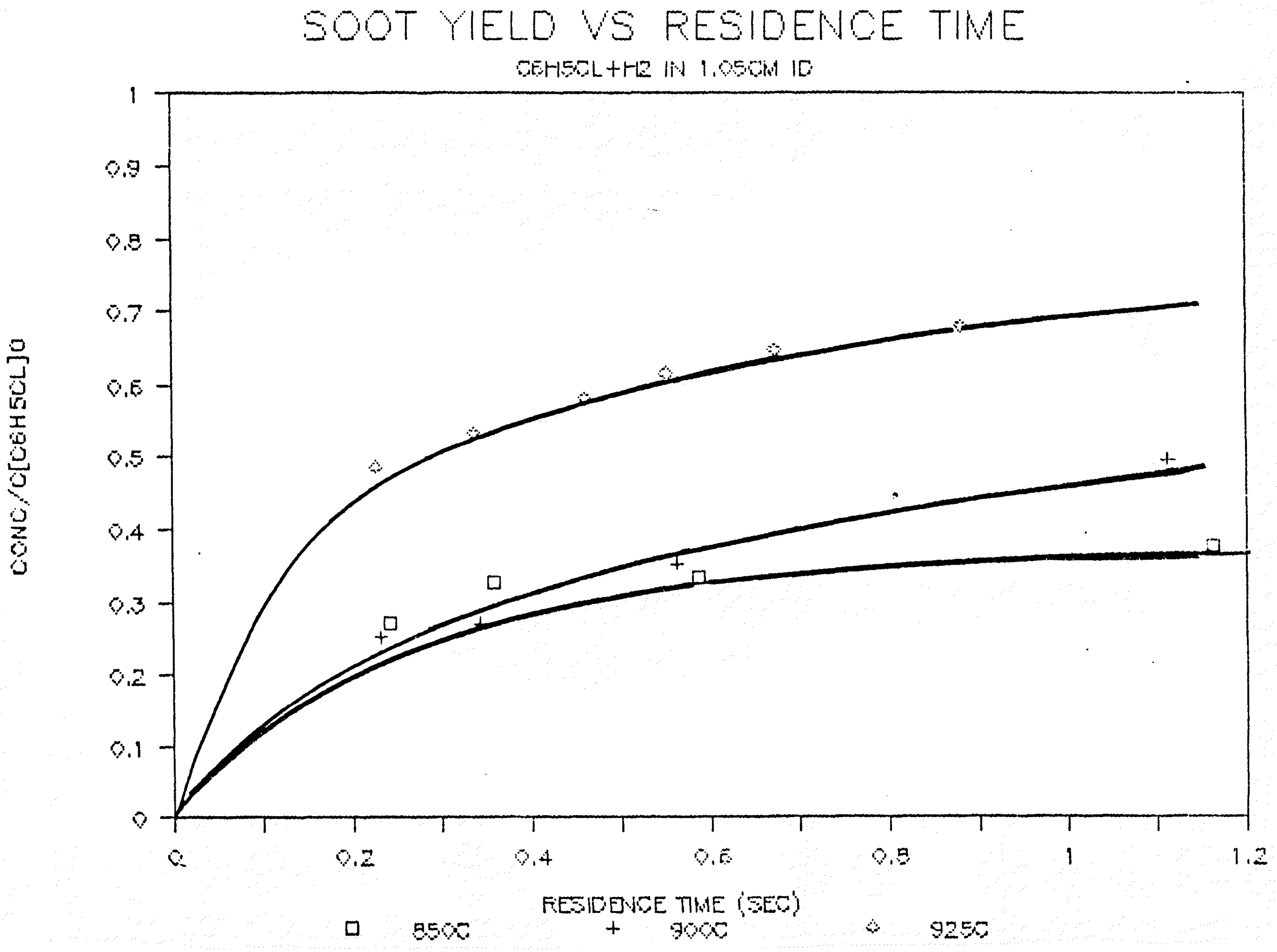

SOOT YIELD VS RESIDENCE TIME
C6H5CL+H2 IN 1.05CM ID
CONC/C[C6H5CL]0
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0.
0.2
0.4
0.6
0.8
1
1.2
RESIDENCE TIME (SEC)
□ 850C
+ 900C
◇ 925C

Figure 5.1.15.

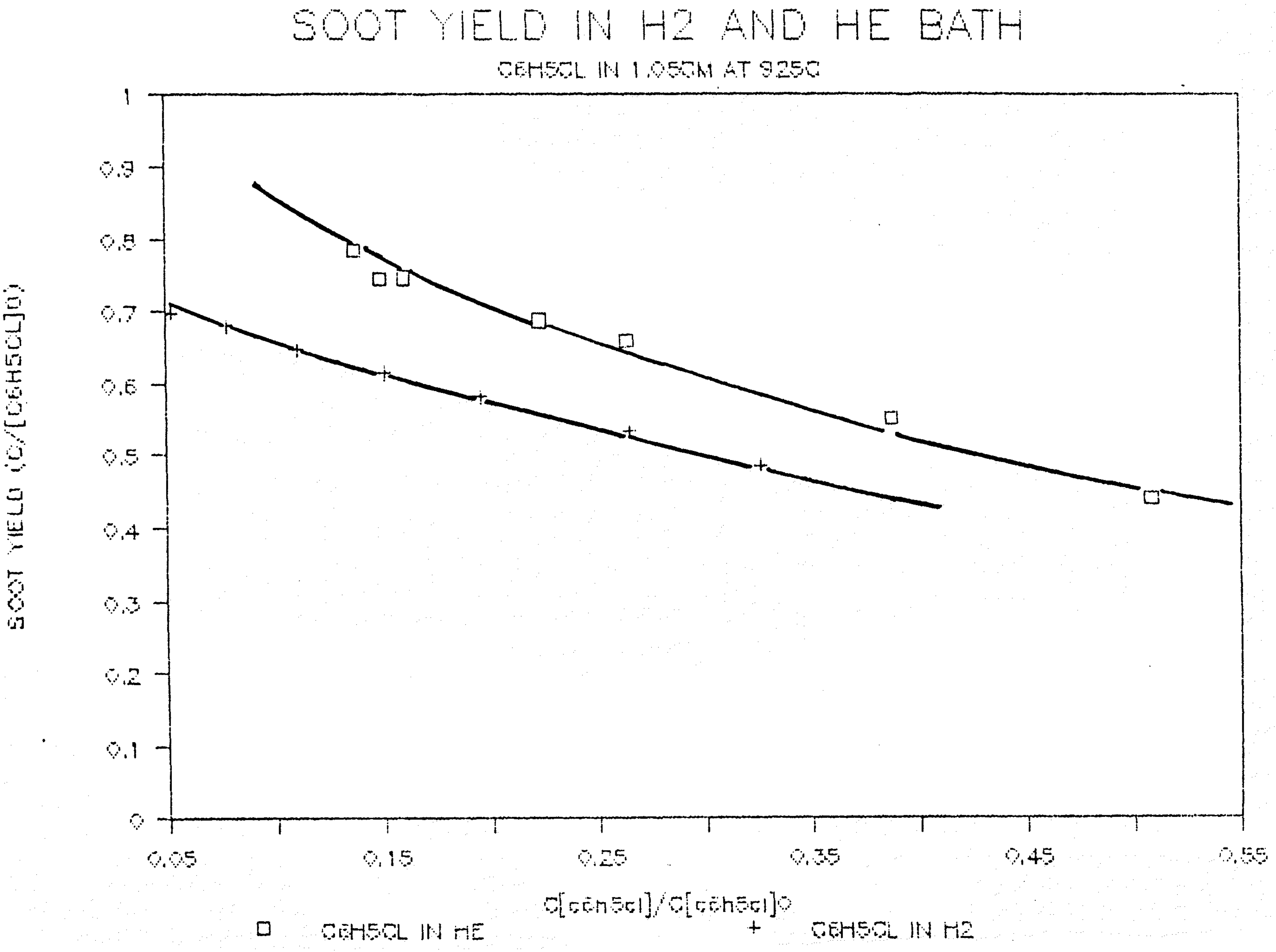
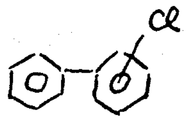

SOOT YIELD IN H2 AND HE BATH
C6H5CL IN 1.05CM AT 925C
SOOT YIELD (C/[C6H5CL]0)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0.05
0.15
0.25
0.35
0.45
0.55
C[c6h5cl]/C[c6h5cl]0
□ C6H5CL IN HE
+ C6H5CL IN H2

Figure 5.1.16.

theoretical result [24] by Stein and Kafafi. The hydrogen atmosphere helps to reverse or limit soot formation. Thus, the lack of hydrogen in the helium atmosphere strongly speeded up the generation of soot. The following reaction scheme explains this situation:

(d) C_6H_5CL + .C_6H_5

OR <----->  + H

C_6H_4CL + C_6H_6

Figure 5.1.17. shows the energy diagram of chloro biphenyl formation from C_6H_5Cl plus .C_6H_5. From reaction scheme (d) we know hydrogen will make the reaction go in the reverse and yield less chlorobiphenyl.

The soot formation mechanism is very complex. Soot from chlorobenzene can be considered to result from high temperature reactions of the major products of dichlorobenzene. This will be further discussed in the chapter of dichlorobenzene.

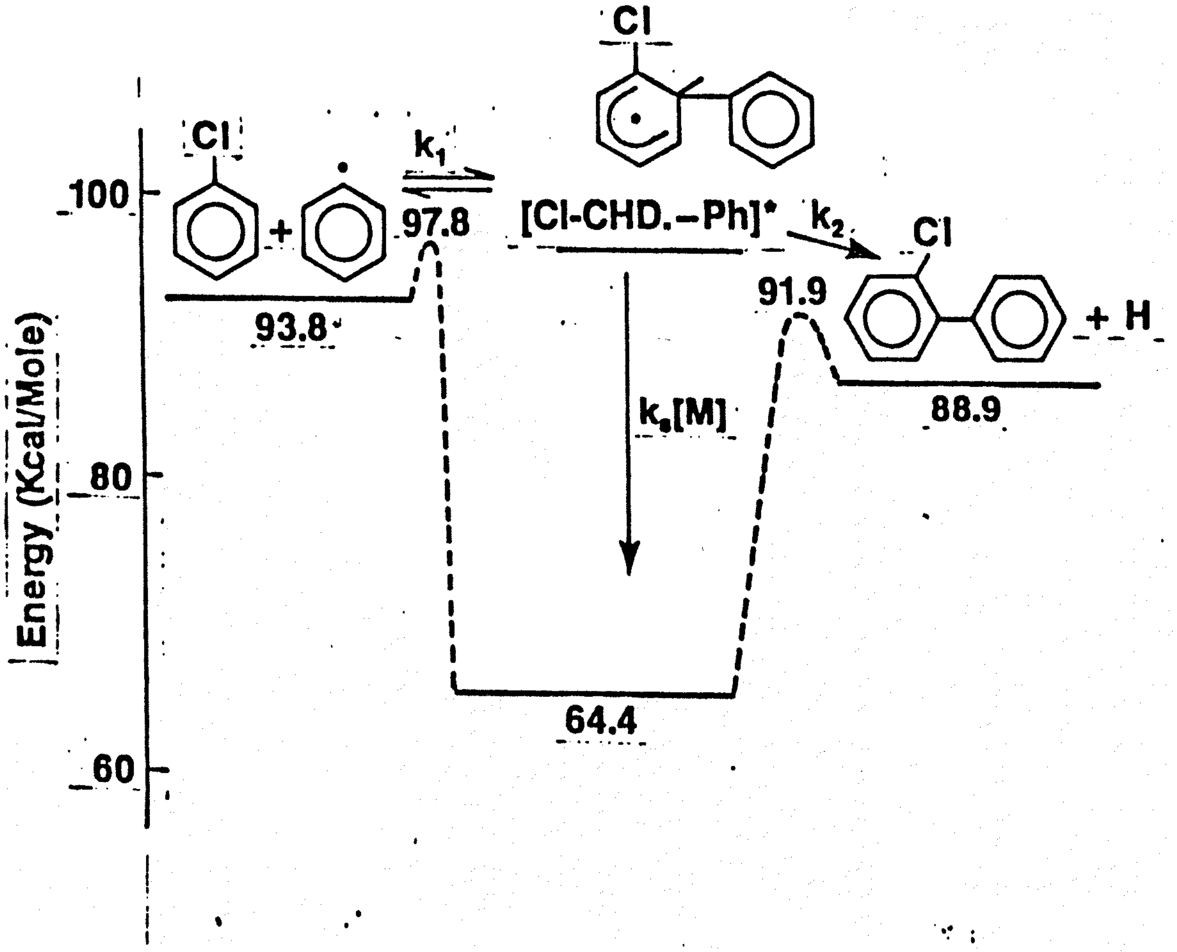


Figure 5.1.17.* The Energy Diagram For Reaction (d)

* from [7]

5.2. THE THERMAL DECOMPOSITION OF C6H4Cl2 IN HYDROGEN OR IN HELIUM ATMOSPHERE

Further studies [6] of decomposition of dichlorobenzne in hydrogen and helium baths were conducted at 1 atm in the 1.05 cm ID reactor. The operational temperatures were 870°C, 890°C, and 910°C. In addition, data for dichlorobensene in helium gas at 870°C was obtained. The experimental range of carrier gas flow rate and residence time is nearly identical to chlorobenzene system. Because of the higher molecular weight of dichlorobenzene, its bubbler system was maintained at 30°C. The ratio of carrier gas to dichlorobenzene was 229:1. The initial concentration of dichlorobenzene is 4.345 x 10^{-3} mole percent concentration.

For dichlorobenzene, we noticed that the decomposition reaches 90% of its initial concentration at 910°C and 0.9 second of residence time as shown in figure 5.2.1. Similarly, the production of other products from dichlorobenzene increased with the residence time inside the reactor. Again, the higher reaction temperature helped to yield higher decomposition rates. Figure 5.2.2. shows the linear relationship from the application of the pseudo first order reaction rate law to the decomposition of dichlorobenzene in hydrogen. It is obvious that for the decomposition of dichlorobenzene in hydrogen the reaction obeys the pseudo first order kinetics. The Arrhenius behavior plot of dichlorobenzene, the decomposition rate constant kexp, the activation energy, and the pre-

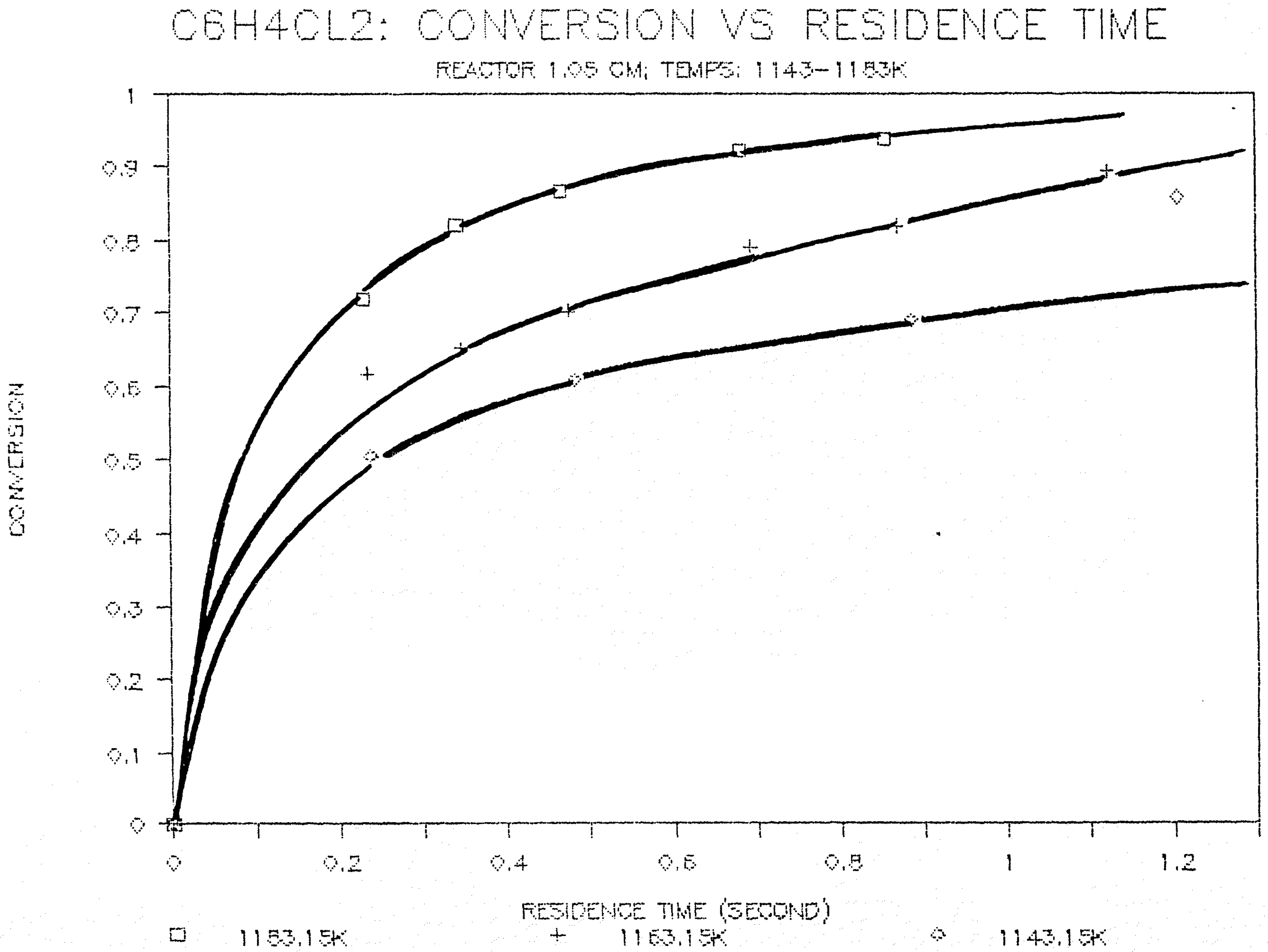

C6H4CL2: CONVERSION VS RESIDENCE TIME
REACTOR 1.05 CM; TEMPS: 1143-1183K
CONVERSION
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.2
0.4
0.6
0.8
1
1.2
RESIDENCE TIME (SECOND)
□ 1183.15K
+ 1163.15K
◇ 1143.15K

Figure 5.2.1.

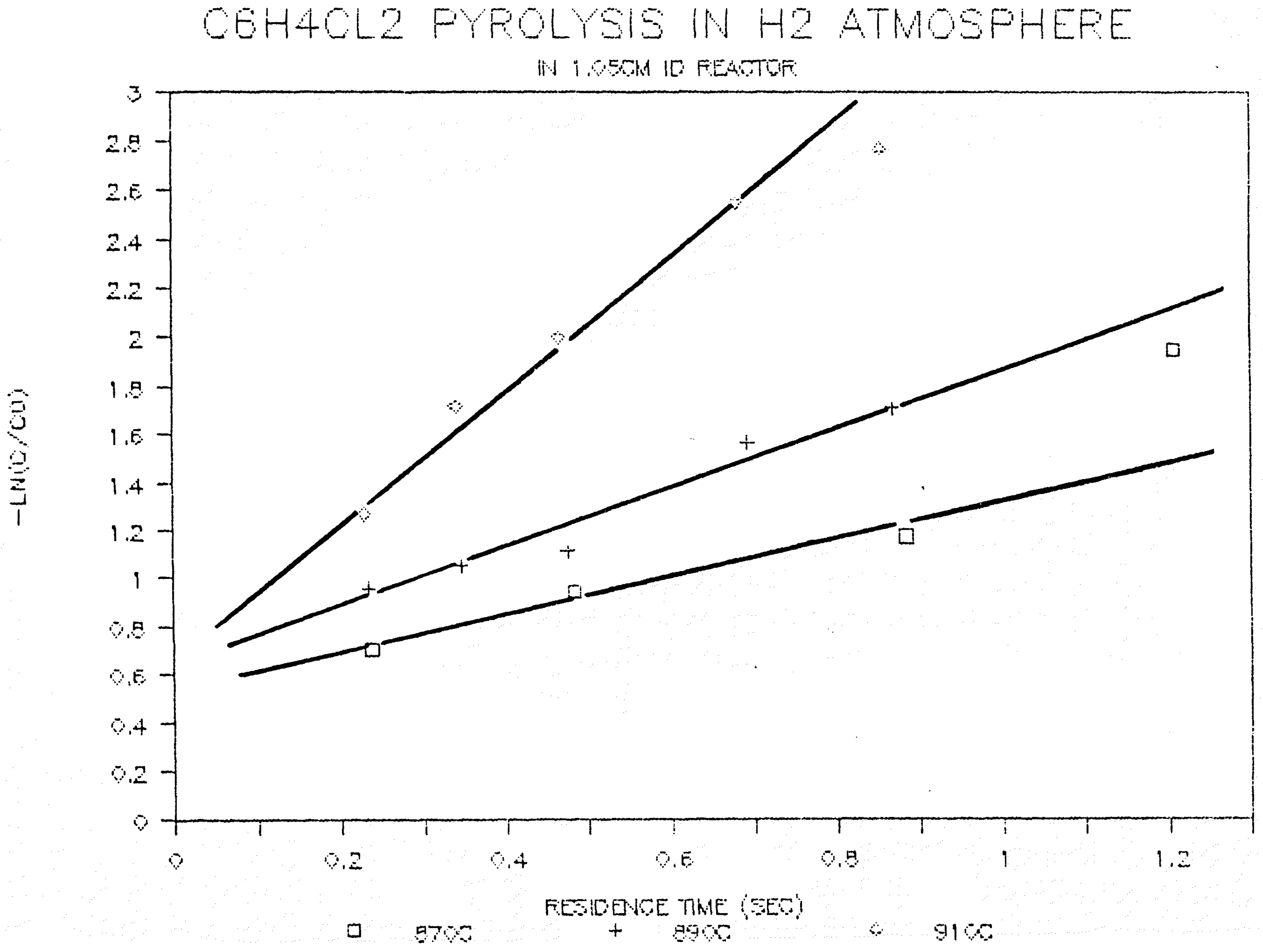
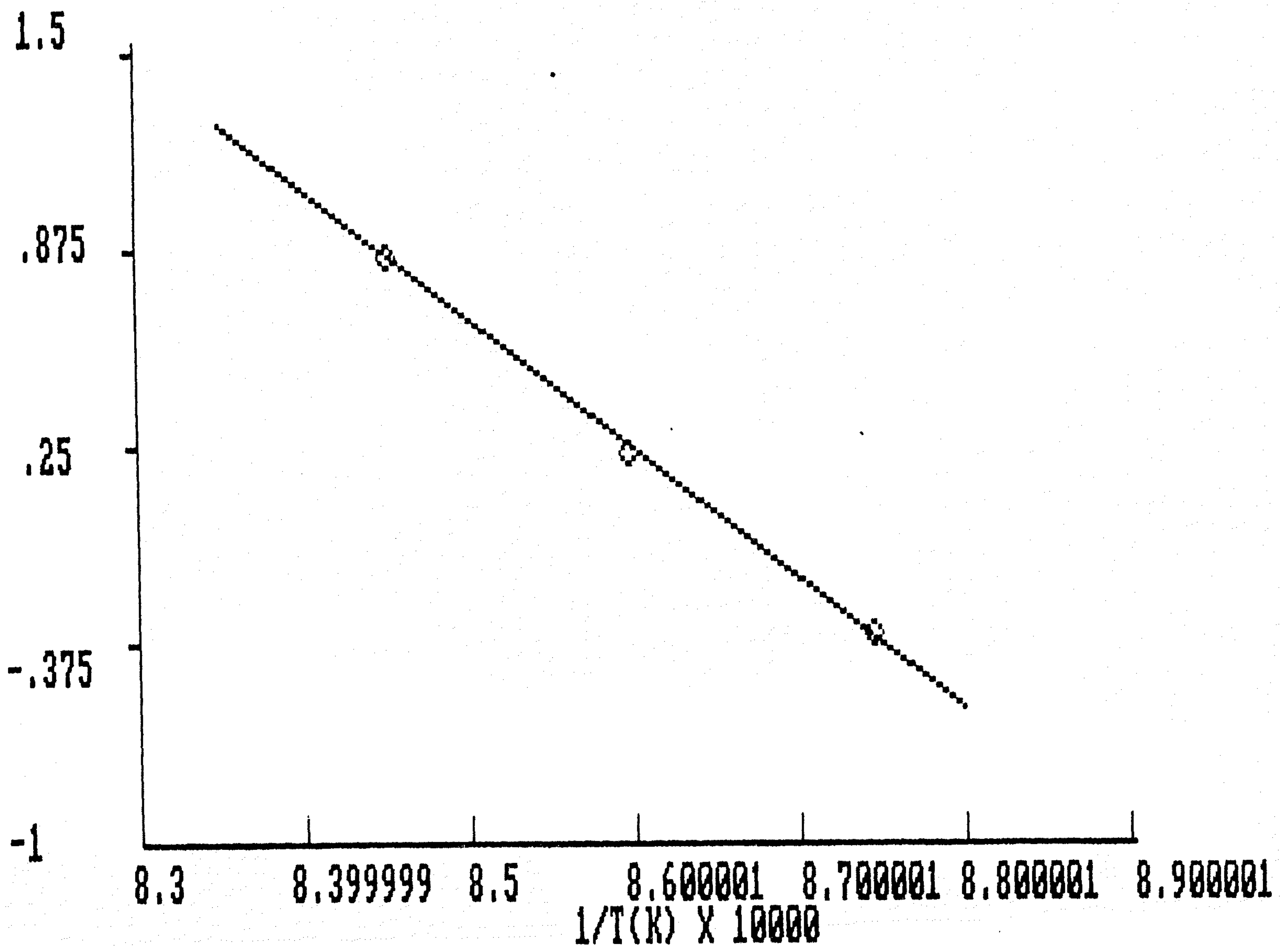

C6H4CL2 PYROLYSIS IN H2 ATMOSPHERE
IN 1.95CM ID REACTOR
-LN(C/C0)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
2.2
2.4
2.6
2.8
3
0
0.2
0.4
0.6
0.8
1
1.2
RESIDENCE TIME (SEC)
□ 870C
+ 890C
◇ 910C

Figure 5.2.2

Figure 5.2.3.


ARRHENIUS BEHAVIOR FOR C6H4CL2 + H2 PYROLYSIS REACTION
LN(KEXPT 1/SEC)
1.5
.875
.25
-.375
-1
8.3
8.399999
8.5
8.600001
8.700001
8.800001
8.900001
1/T(K) X 10000

exponential factor were obtained from figure 5.2.3.

The following table presents the global kinetics parameters of the Arrhenius equation for the decomposition of dichlorobenzene in hydrogen atmosphere, which basically is in agreement with the similar previous study [6].

TABLE 2.2.1. GLOBAL ARRHENIUS PARAMETERS FOR THE DECOMPOSITION OF DICHLOROBENZENE IN HYDROGEN

REACTOR ID	A FACTOR	Ea
1.05	4.1×10^{12}	65

5.2.1. PRODUCT DISTRIBUTION FOR DICHLOROBENZENE IN HYDROGEN OR IN HELIUM ATMOSPERE

The experimental data show that the major products from dichlorobenzene with hydrogen or helium are dichlorobenzene, HCl, chlorobenzene, benzene and soot. The loss of chlorine from the benzene ring is the important initiation reactions [38]:

(e) $C_6H_4Cl_2 \Longleftrightarrow C_6H_4Cl\cdot + Cl$

(f) $Cl + H_2$ (excess) $\Longleftrightarrow H + HCl$

(g) $C_6H_4Cl\cdot + H_2 \Longleftrightarrow C_6H_5Cl + H$

(h) $H + C_6H_4Cl_2 \Longleftrightarrow C_6H_5Cl + Cl$

where as we can see, Cl will always recycle A hydrogen in this H_2 atmosphere from reaction (f).

The product distribution as a function of residence time is demonstrated at different temperatures in Figure 5.2.4 - 5.2.9. It is similar to the decomposition of chlorobenzene, with the increase of the residence time in the conversion to benzene slowly rises. Chlorobenzene concentration achieves a maximum at first and then drops slowly, with the further dcomposition of dichlorobenzene. This phenomenon can be explained on the basis that the reaction rate of the decomposition of chlorobenzene was speeded up with the higher concentration of reactive intermediates while at the same time, the rate of the formation of chlorobenzene from dichlorobenzene was decreased.

A large number of stable gas products from dichlorobenzene were identified by GC/MS. They are shown in

Table 2.2.2. But as we can see, most of the stable species only appeared at a minor or trace amount.

Figure 5.2.5. shows the light hydrocarbon products in the system of dichlorobnzene with hydrogen at 870°C. They are CH_4, C_2H_4, C_2H_6, $C_{10}H_8$ and $C_6H_5CH_3$, the same as for the chlorobenzene system. All the minor products are less than 5% of initial concentration of DCB in the reaction effluents.

The product distribution for the decomposition of dichlorobenzene in helium bath gas at 870°C is shown in figure 5.2.8 - 5.2.9. In helium bath, we notice that the only major products are soot and HCl. The concentration of soot ranges from 20% to nearly 50% (by mass balance diffrence). Other products are C_6H_5Cl and $C_6H_5CH_3$. Their concentrations are only 1% to 5% of the initial reactant concentration. The minor product from decomposition of dichlorobenzene in helium, is primarily acetylene. Also, the concentration of CH_4 is less than C_2H_2 in constrast to that in hydrogen. The lack of hydrogen causes very little acetylene converted to ethylene and nearly no ethane. That is, in a hydrogen atmosphere, hydrogen radicals easily attack acetylene molecules eventually to convert acetylene to both ethylene and ethane, in which ethane might be broken to methyl and make methane. The reaction scheme (c) in chapter 5.1.1. explains the reaction system.

The temperature dependency of the product distribution at the constant residence time of 0.5 seconds is shown in figure 5.2.10 - 5.2.11. Increase of the reaction

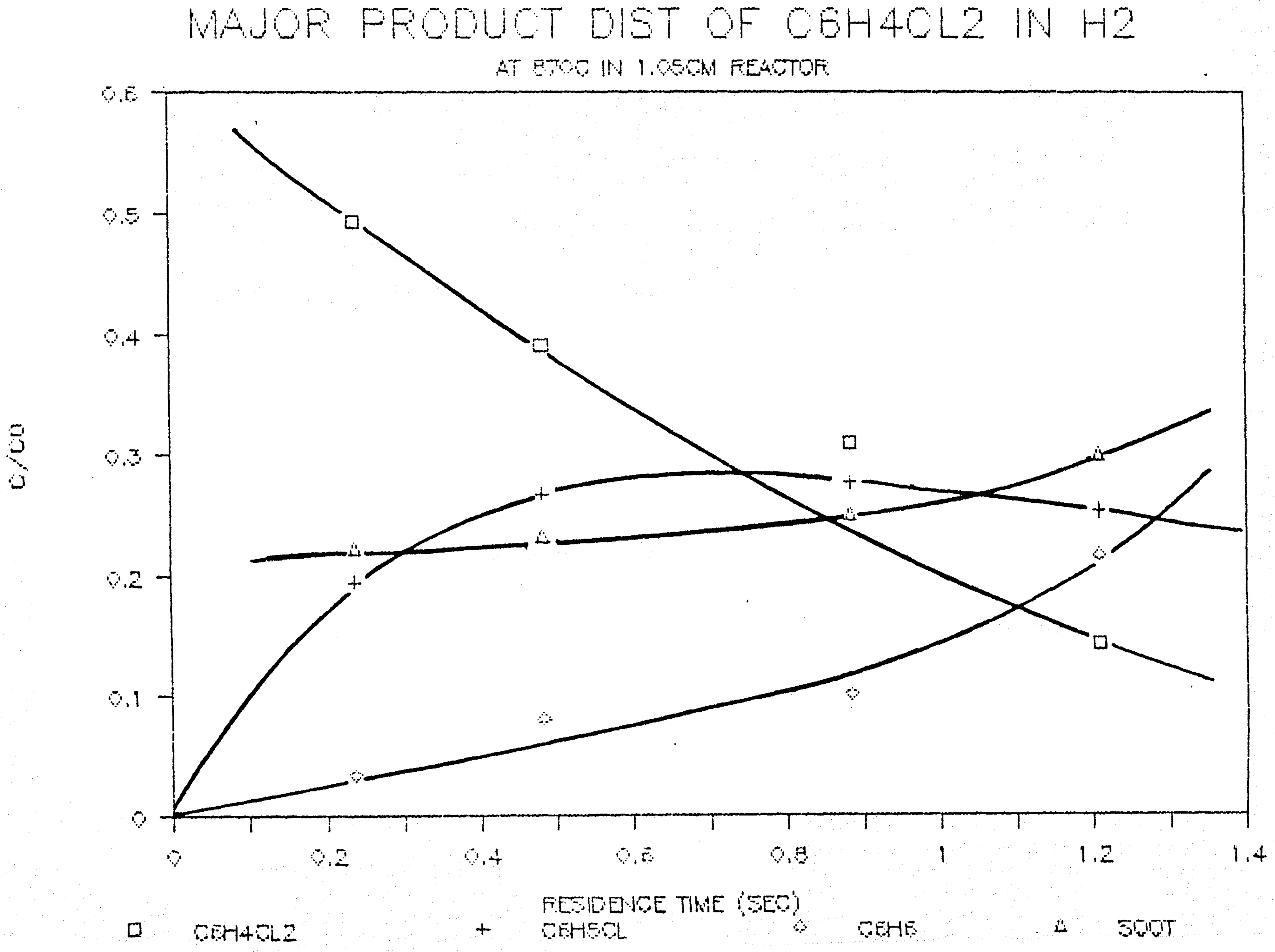

MAJOR PRODUCT DIST OF C6H4CL2 IN H2
AT 870C IN 1.05CM REACTOR
C/C0
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.2
0.4
0.6
0.8
1
1.2
1.4
RESIDENCE TIME (SEC)
□ C6H4CL2
+ C6H5CL
◇ C6H6
△ SOOT

Figure 5.2.4.

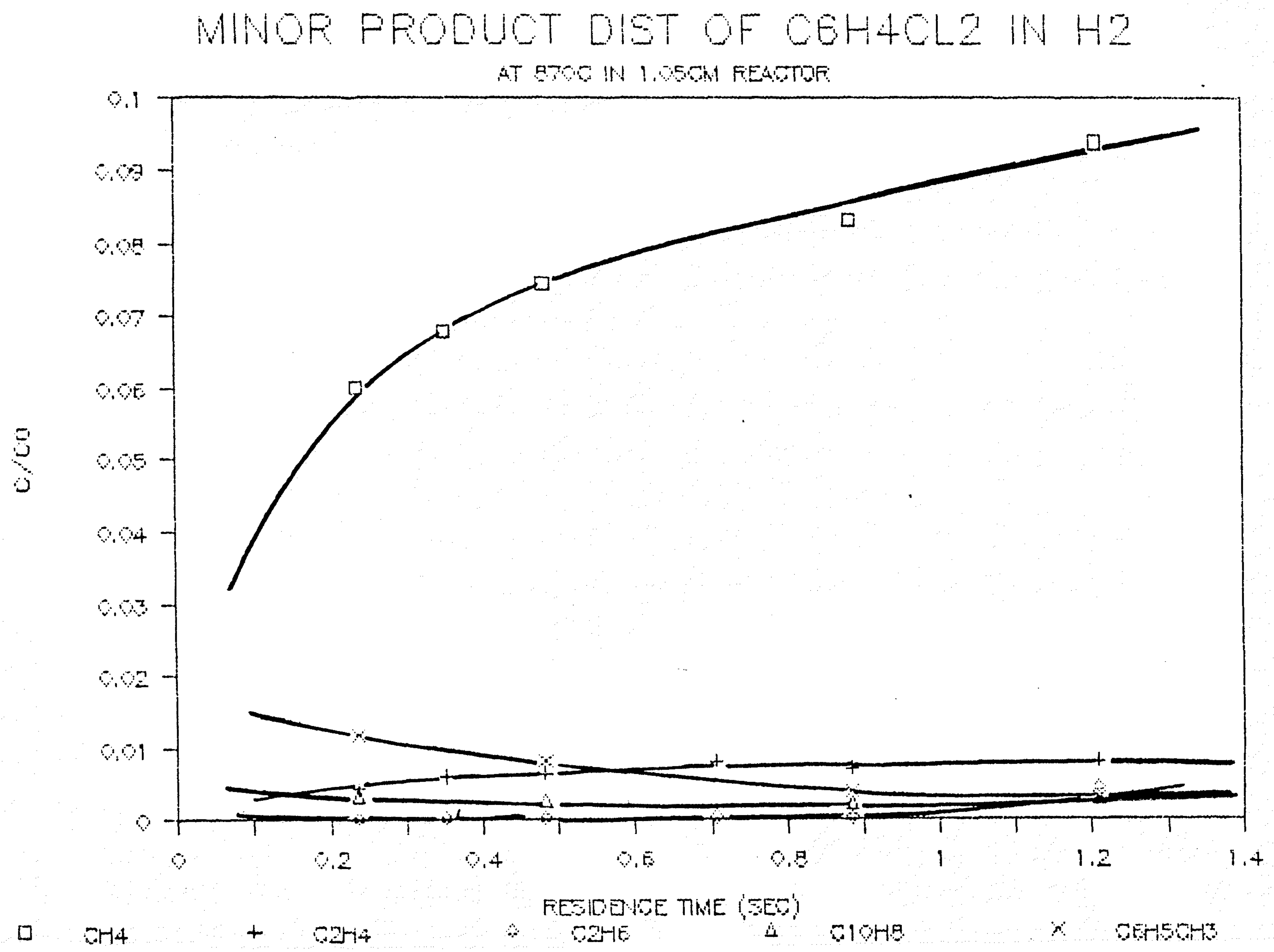

MINOR PRODUCT DIST OF C6H4CL2 IN H2
AT 870C IN 1.05CM REACTOR
C/C0
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0
0.2
0.4
0.6
0.8
1
1.2
1.4
RESIDENCE TIME (SEC)
□ CH4
+ C2H4
◇ C2H6
△ C10H8
× C6H5CH3

Figure 5.2.5.

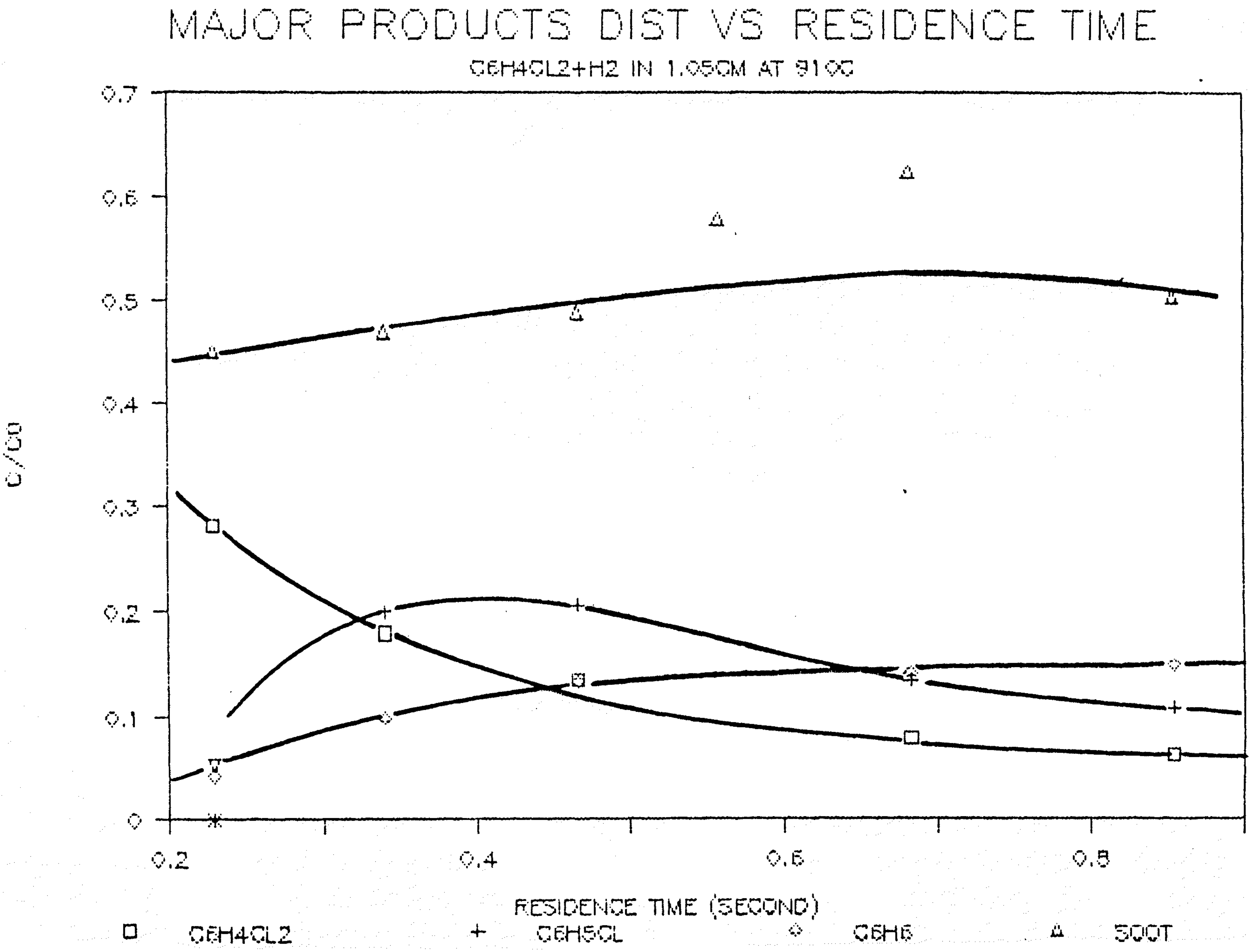

MAJOR PRODUCTS DIST VS RESIDENCE TIME
C6H4CL2+H2 IN 1.05CM AT 910C
C/C0
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0.2
0.4
0.6
0.8
RESIDENCE TIME (SECOND)
□ C6H4CL2
+ C6H5CL
◇ C6H6
△ SOOT

Figure 5.2.6.

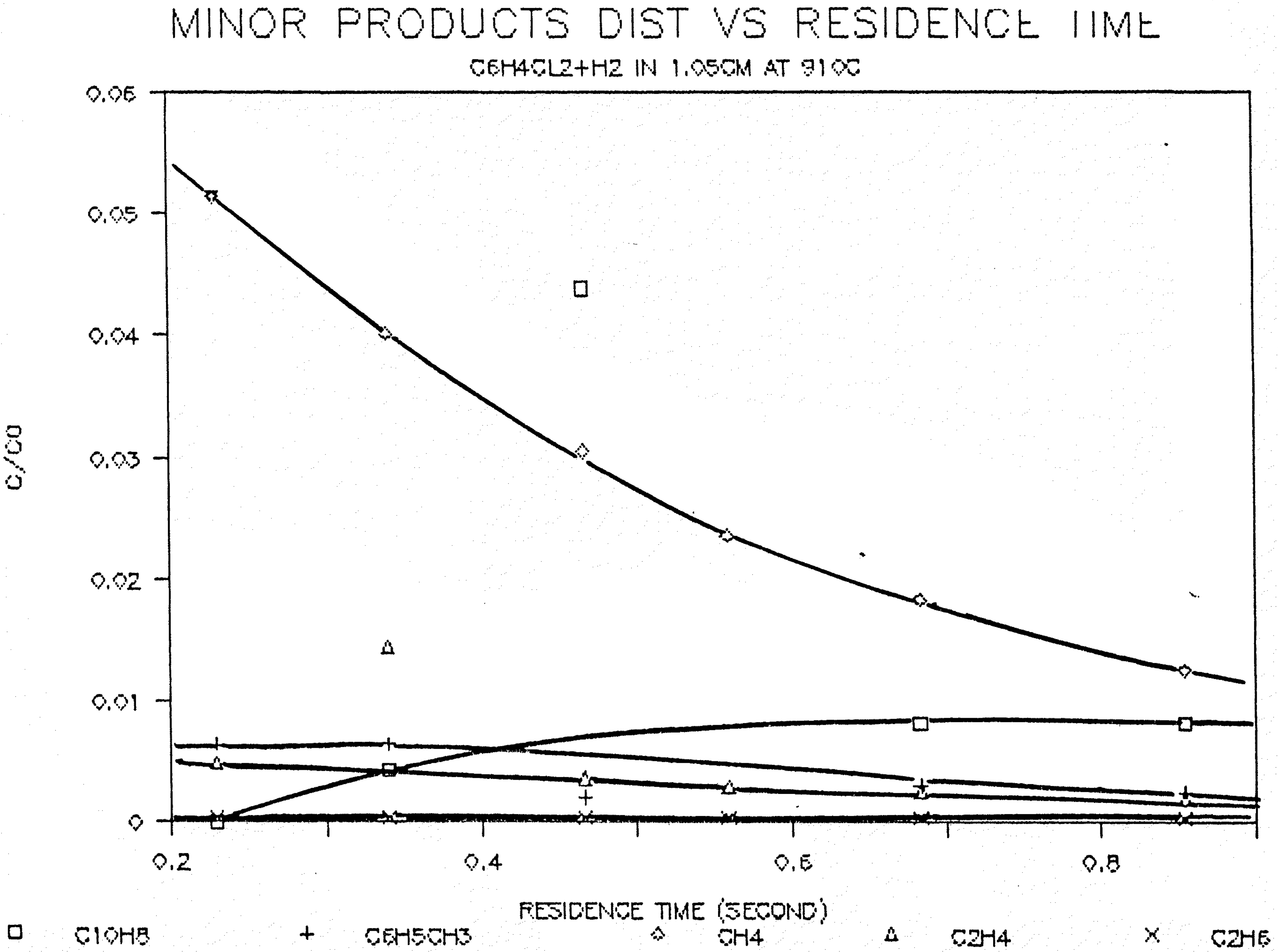

MINOR PRODUCTS DIST VS RESIDENCE TIME
C6H4CL2+H2 IN 1.05CM AT 910C
C/C0
0.06
0.05
0.04
0.03
0.02
0.01
0
0.2
0.4
0.6
0.8
RESIDENCE TIME (SECOND)
□ C10H8
+ C6H5CH3
◇ CH4
△ C2H4
× C2H6

Figure 5.2.7.

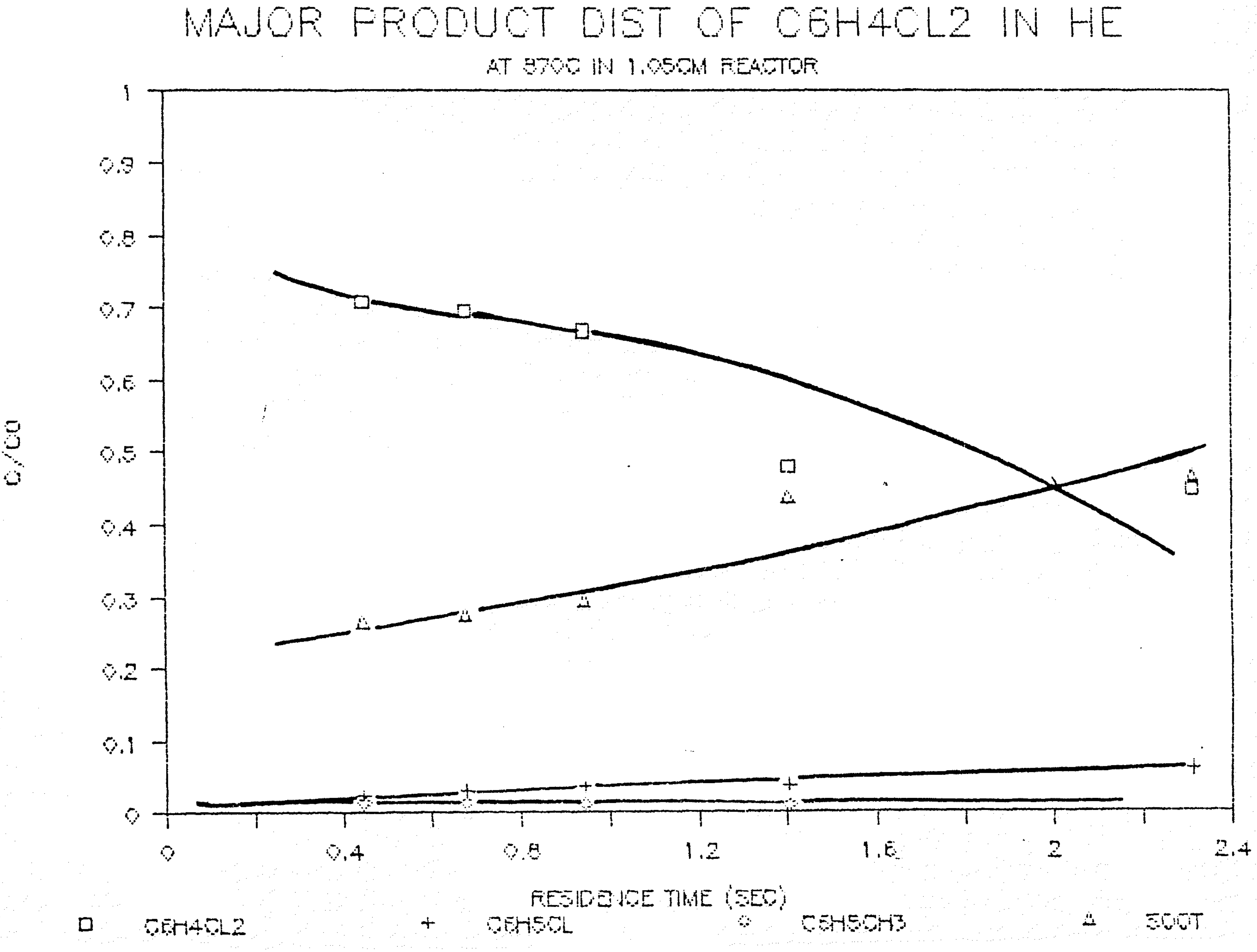

MAJOR PRODUCT DIST OF C6H4CL2 IN HE
AT 870C IN 1.05CM REACTOR
C/C0
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.4
0.8
1.2
1.6
2
2.4
RESIDENCE TIME (SEC)
□ C6H4CL2
+ C6H5CL
◇ C6H5CH3
△ SOOT

Figure 5.2.8.

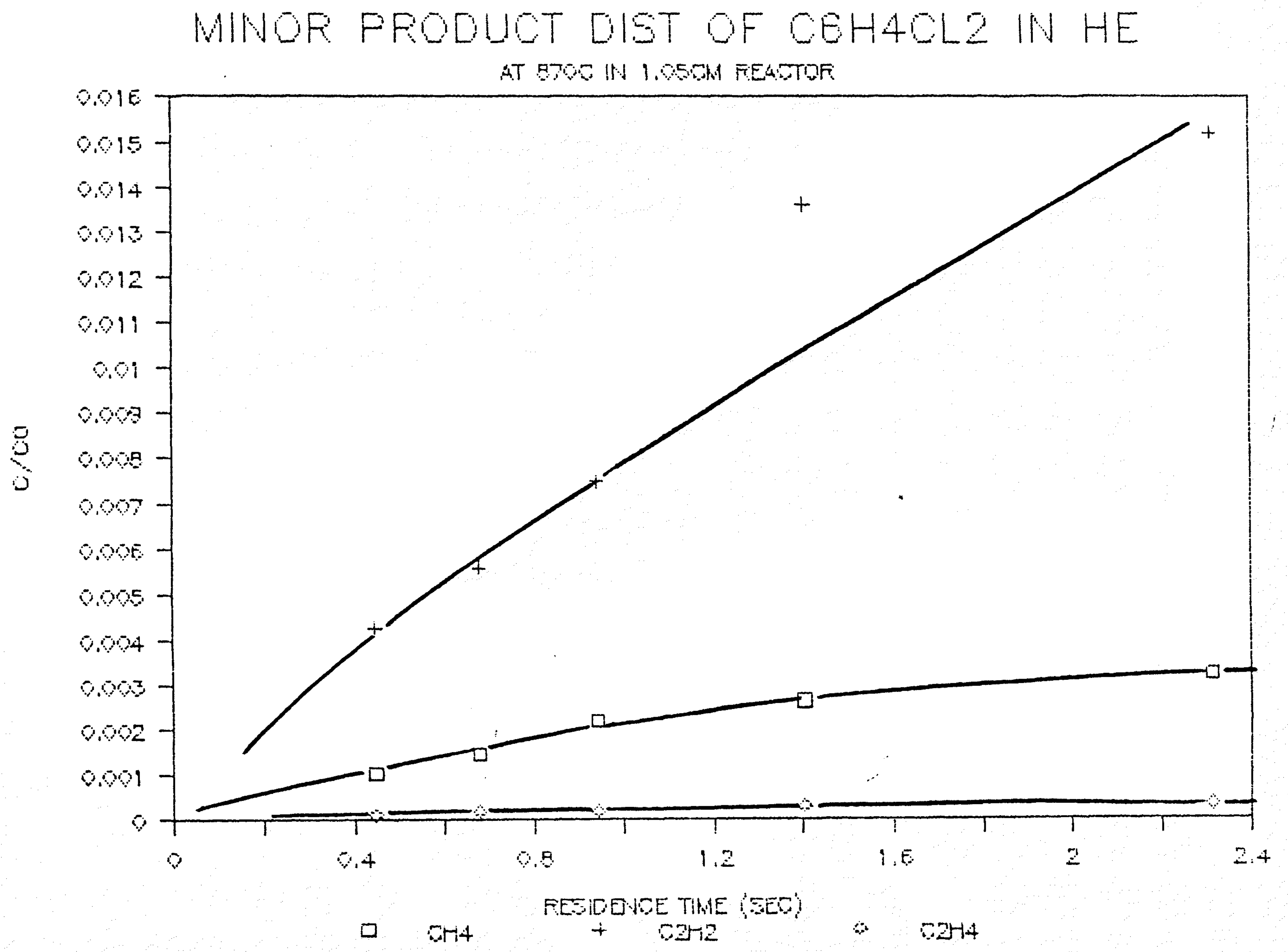

MINOR PRODUCT DIST OF C6H4CL2 IN HE
AT 870C IN 1.05CM REACTOR
C/CO
0.016
0.015
0.014
0.013
0.012
0.011
0.01
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
0
0.4
0.8
1.2
1.6
2
2.4
RESIDENCE TIME (SEC)
□ CH4
+ C2H2
◇ C2H4

Figure 5.2.9.

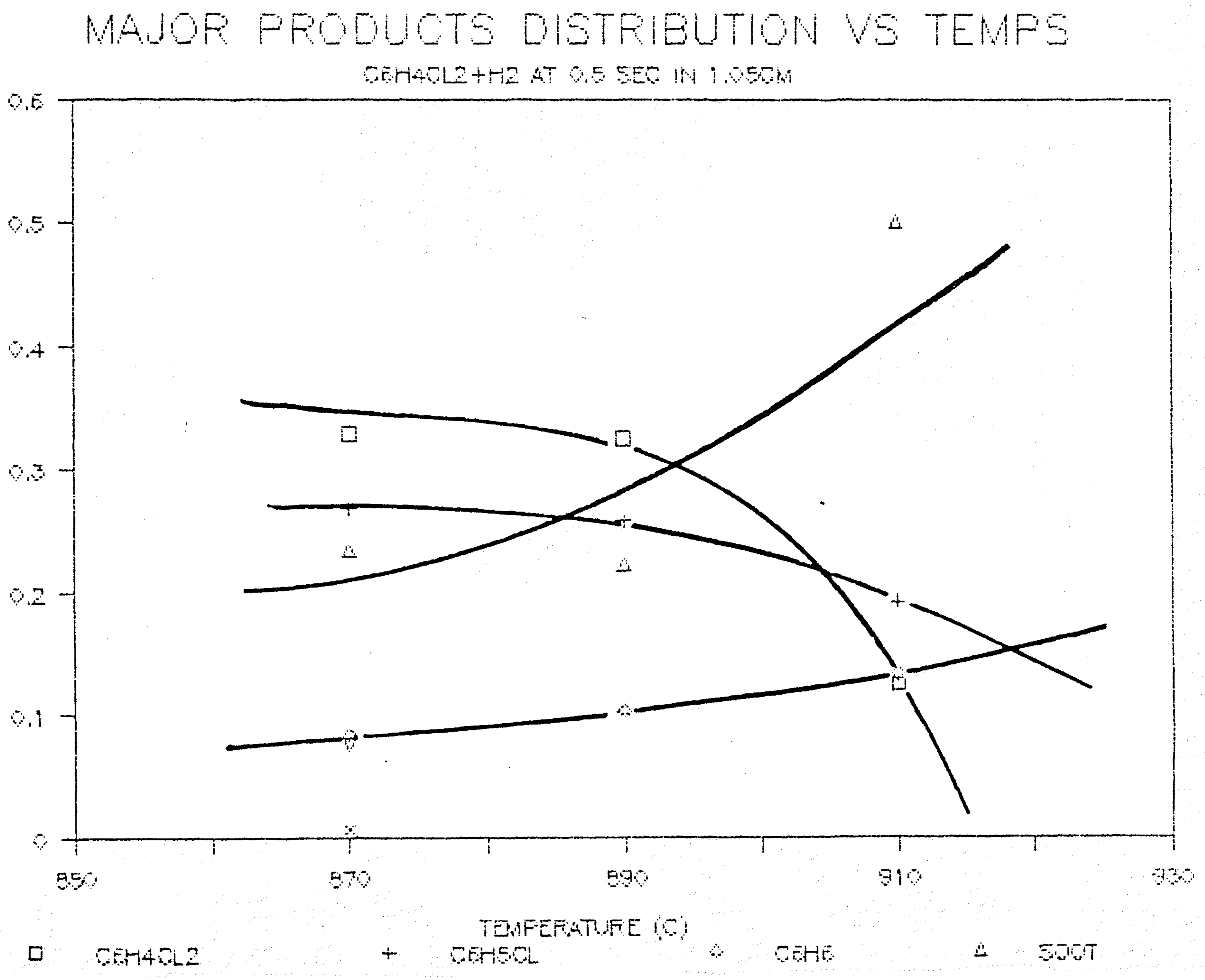

MAJOR PRODUCTS DISTRIBUTION VS TEMPS
C6H4CL2+H2 AT 0.5 SEC IN 1.05CM
0.6
0.5
0.4
0.3
0.2
0.1
0
C/C0
850
870
890
910
930
TEMPERATURE (C)
□ C6H4CL2
+ C6H5CL
◇ C6H6
△ SOOT

Figure 5.2.10.

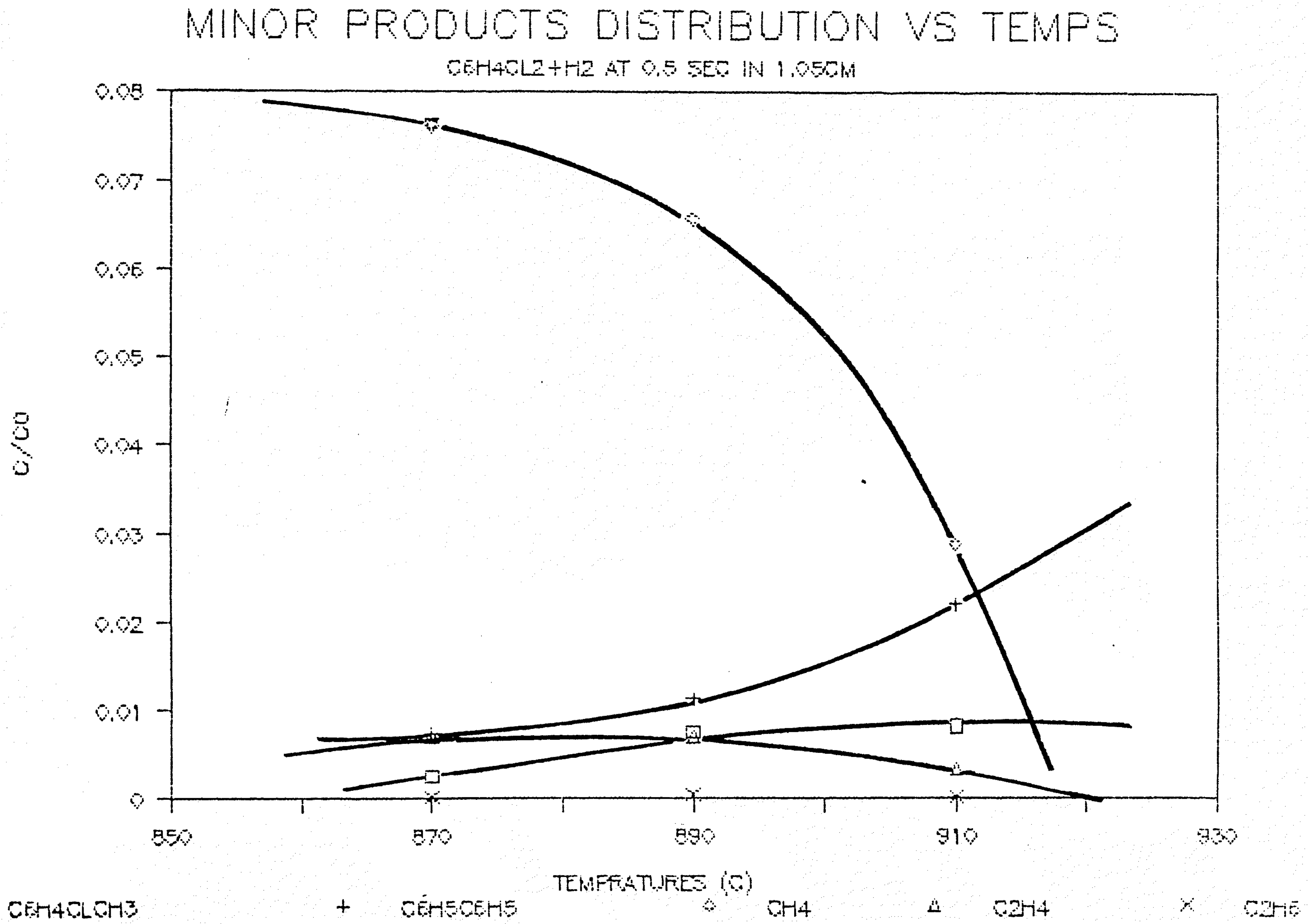

MINOR PRODUCTS DISTRIBUTION VS TEMPS
C6H4CL2+H2 AT 0.5 SEC IN 1.05CM
C/C0
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
850
870
890
910
930
TEMPRATURES (C)
C6H4CLCH3
+ C6H5C6H5
◇ CH4
Δ C2H4
× C2H6

Figure 5.2.11

temperature, increases the decomposition of dichlorobenzene with hydrogen significantly. By 910° the decomposition of $C_6H_4Cl_2$ already is 90%. The concentration of C_6H_5Cl as an intermediate product, reached a maximum and it dropped slowly with the further increase of temperature. the concentration of benzene reached a steady 10% yield when dichlorobenzene achieved 90% conversion. The significant increase of soot formation along with the increase of temperature shows, that most of decomposed dichlorobenzene become a variety of high-molecular-weight products which were mostly coated on the reactor wall. The soot formation increases with the increase of temperature which is in agreement with the result observed in the studies [20] on acetylene by Frenklach.

TABLE 2.2.3. MATERIAL BALANCE PER 100 MOLES OF CARBON

$C_6H_4Cl_2$ + H_2 IN 1.05 CM ID REACTOR AT 0.5 SEC REIDENCE TIME

TEMP (C)	870	890	910	910 (He)
$C_6H_4Cl_2$	33.1	31.6	12.6	70.1
C_6H_5Cl	27.0	25.9	19.4	3.3
C_6H_6	8.4	10.3	27.9	/
$C_6H_5CH_3$	0.3	0.8	0.8	1.3
$C_{10}H_8$	0.7	1.1	0.2	/
CH_4	7.6	6.6	2.9	0.1
C_2H_2				0.5
C_2H_4	0.7	0.7	0.3	0.1
C_2H_6	0.03	0.04	0.03	/

/ trace amount.

TABLE 5.2.2. STABLE GAS PRODUCTS FROM THE DECOMPOSITION OF CHLOROBENZENE AND DICHLOROBENZENE IDENTIFIED BY GC/MASS SPECTROMETRY)

PRODUCT	AMOUNT [CONC/C0]	STATE
HCl	MAJOR PRODUCT (TO 85%)	GAS
CYCLOPENTADIENE	TRACE	GAS
BENZENE	MAJOR PRODUCT	GAS
TOLUENE	MINOR PRODUCT	GAS
CHLOROBENZENE	MAJOR PRODUCT OR REACTANT	GAS
O-DICHLOROBENZENE	TRACE	GAS
M-DICHLOROBNZENE	REACTANT OR TRACE	GAS
P-DICHLOROBENZENE	TRACE	GAS
NAPHTHALENE	TRACE	GAS
METHANE	MINOR PRODUCT	GAS
ETHYLENE	MINOR PRODUCT	GAS
ACETYLENE	MINOR PRODUCT	GAS
ETHANE	MINOR PRODUCT	GAS

5.2.2. THE SOOT YIELD AND FORMATION FROM DICHLOROBENZENE IN HYDROGEN AND HELIUM ATMOSPHERE

As an example of soot formation from the high temperature decomposition of aromatic compounds, dichlorobenzene typically yielded significant carbon solid on the reactor wall. This can build up and subsequently influence the heat exchange from the furnace to the inside reactor tube and also contribute to heterogeneous reactions.

It is noted in chlorobenzene and dichlorobenzene chapters that with increases in residence times, more soot was produced. In addition, at the same residence time, higher temperature in the reactor gave higher yields of soot. In a helium atmosphere, much more soot was coated on the reactor wall than for the same decomposition of chlorobenzene in a hydrogen atmosphere. These observations were reproduced in the decomposition of dichlorobenzene.

For dichlorobenzene decompoition, in figure 5.2.6, we can see that soot yield reached 65% at 0.6 second of 910°C reaction temperature. At 870°C, the soot yield slowly attend to about 30% of dichlorobenzene initial concentration at the residence time of 1.2 second. At the same average reaction residence time, for example, at 0.5 second, 870°C has soot yield of nearly 25%, 890°C has 40%, and 910°C has a soot yield of almost 60%.

For different bath gases, in figure 5.2.12., the soot yield in helium was significantly higher than in hydrogen.

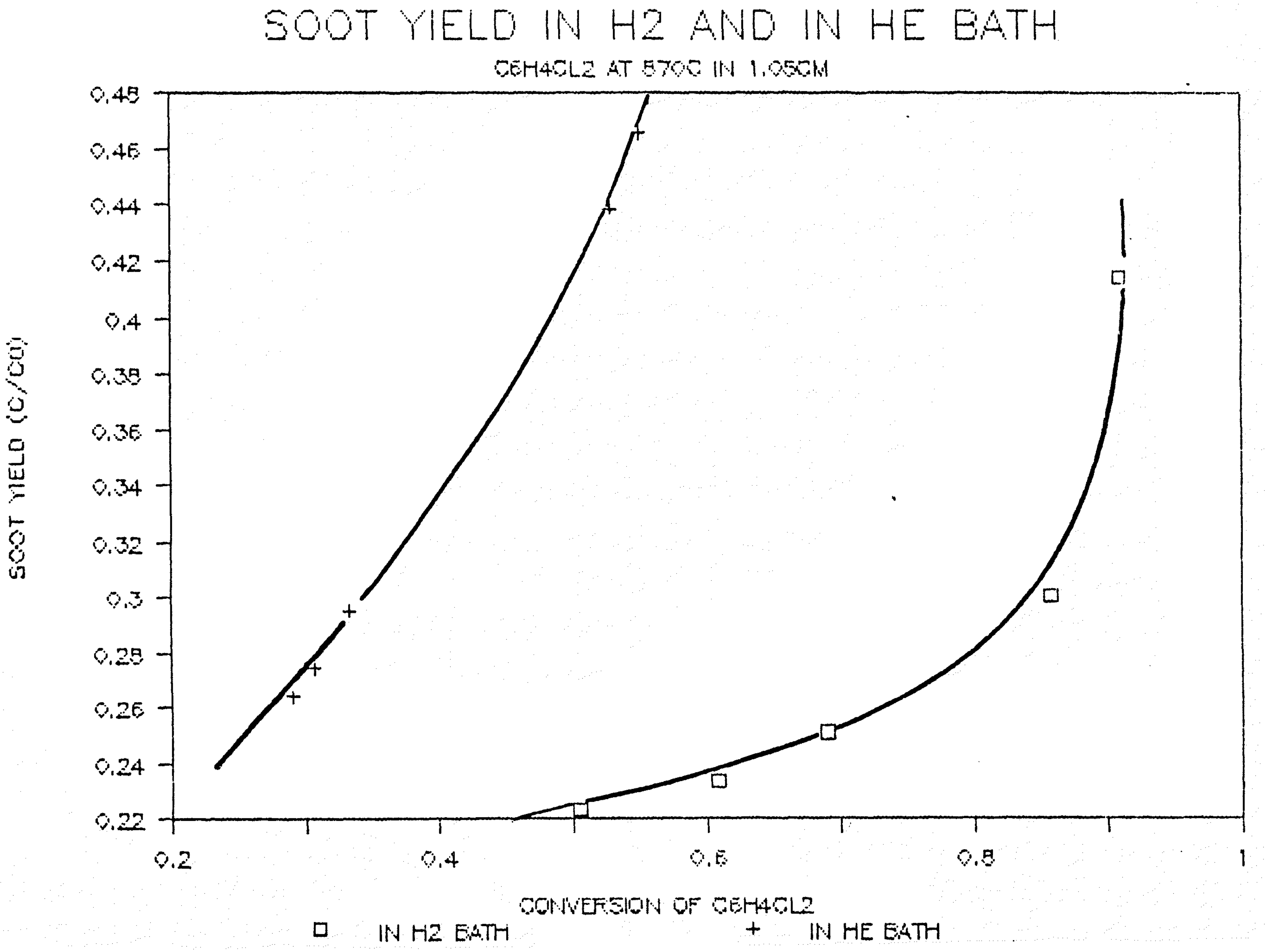

SOOT YIELD IN H2 AND IN HE BATH
C6H4CL2 AT 570C IN 1.05CM
SOOT YIELD (C/C0)
0.48
0.46
0.44
0.42
0.4
0.38
0.36
0.34
0.32
0.3
0.28
0.26
0.24
0.22
0.2
0.4
0.6
0.8
1
CONVERSION OF C6H4CL2
□ IN H2 BATH
+ IN HE BATH

Figure 5.2.12.

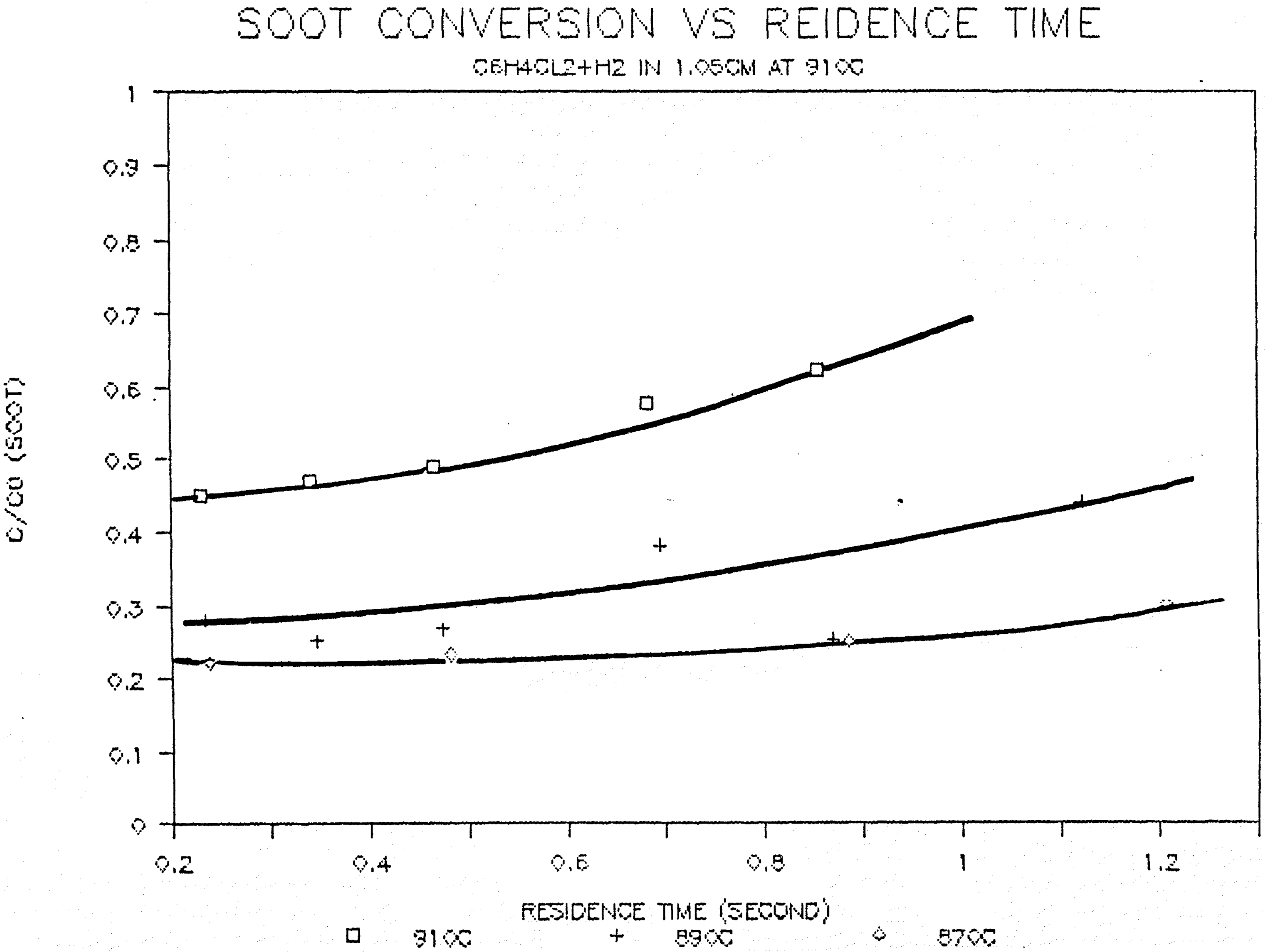

SOOT CONVERSION VS REIDENCE TIME
C6H4CL2+H2 IN 1.05CM AT 910C
C/C0 (SOOT)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0.2
0.4
0.6
0.8
1
1.2
RESIDENCE TIME (SECOND)
□ 910C
+ 890C
◇ 870C

Figure 5.2.13

As we can see, at 910°C, when dichlorobenzene achieved 30% decomposition, 26% of the initial concentration of dichlorobenzene was already converted to soot in helium atmosphere. At the point of 50% conversion, in helium atmosphere, nearly 40% of the initial concentration of C6H4Cl2 became soot, while in a hydrogen atmosphere, only 22% soot was formed.

As we discussed in the chlorobenzene chapter, the soot formation from aromatic compounds appears to occur by an addition process making chloro, dichloro, and other biphenyls, polyphenyls and finally to make carbon solid [7]. The destination of the reaction route is to go to higher ratio of C/H products [24].

The major products from the pyrolysis of dichlorobenzene are chlorobenzene, benzene. It is obvious that these three major species all contribute to the soot formation of dichlorobenzene. In another word, the soot formed in the pyrolysis reaction of dichlorobnzene is also from the initial products: chlorobenzene and benzene.

Table 5.2.4 present some examples of soot products which are from the major products of dichlorobenzene.

5.3. THE DECOMPOSITION OF ACETYLENE IN HYDROGEN ATMOSPHERE

The thermal decomposition of acetylene was studied at one atmosphere pressure in a 1.05 cm ID tubular reactor. Experiments were conducted at seven temperatures: 700°C, 750°C, 800°C, 825°C, 850°C, 875°C, and 900°C. The carrier gas was set between the flow rates of 1.1 - 50 cc/sec for each temperature. Residence time ranged from 0.2 -1.8 seconds. The acetylene used in the experiment was 99.6% purified product, Matheson Gas Products East Rutherford, NJ. The acetylene input to the reactor was controlled by a needle-valve rotameter after passing the through a charcoal purificated filter to remove acetone. Initially, in our cylinder, acetone was almost 10% in the pure acetylene gas, that was added by the manufacter to keep acetylene stable. After purification with activated Charcoal. Acetone was reduced to under 1.5% or lower concentration in acetylene. The initial concentration of acetylene in the reactor ranged from 0.017 to 0.079 mole percent. The percentages of acetylene in the carrier gas, hydrogen was 57.8% to 11.7%.

The decrease of acetylene normalized concentration $[C2H2]/[C2H2]0$, with the increasing residence time and also as a function of different temperatures is demonstrated by figure 5.3.1.

In our reaction system, hydrogen was in large excess, so a pseudo-first-order kinetics model may be applied. Figure 5.3.2 shows the linear relationship between $-\ln(C/C0)$ for the limiting, reagent, acetylene, and residence time at

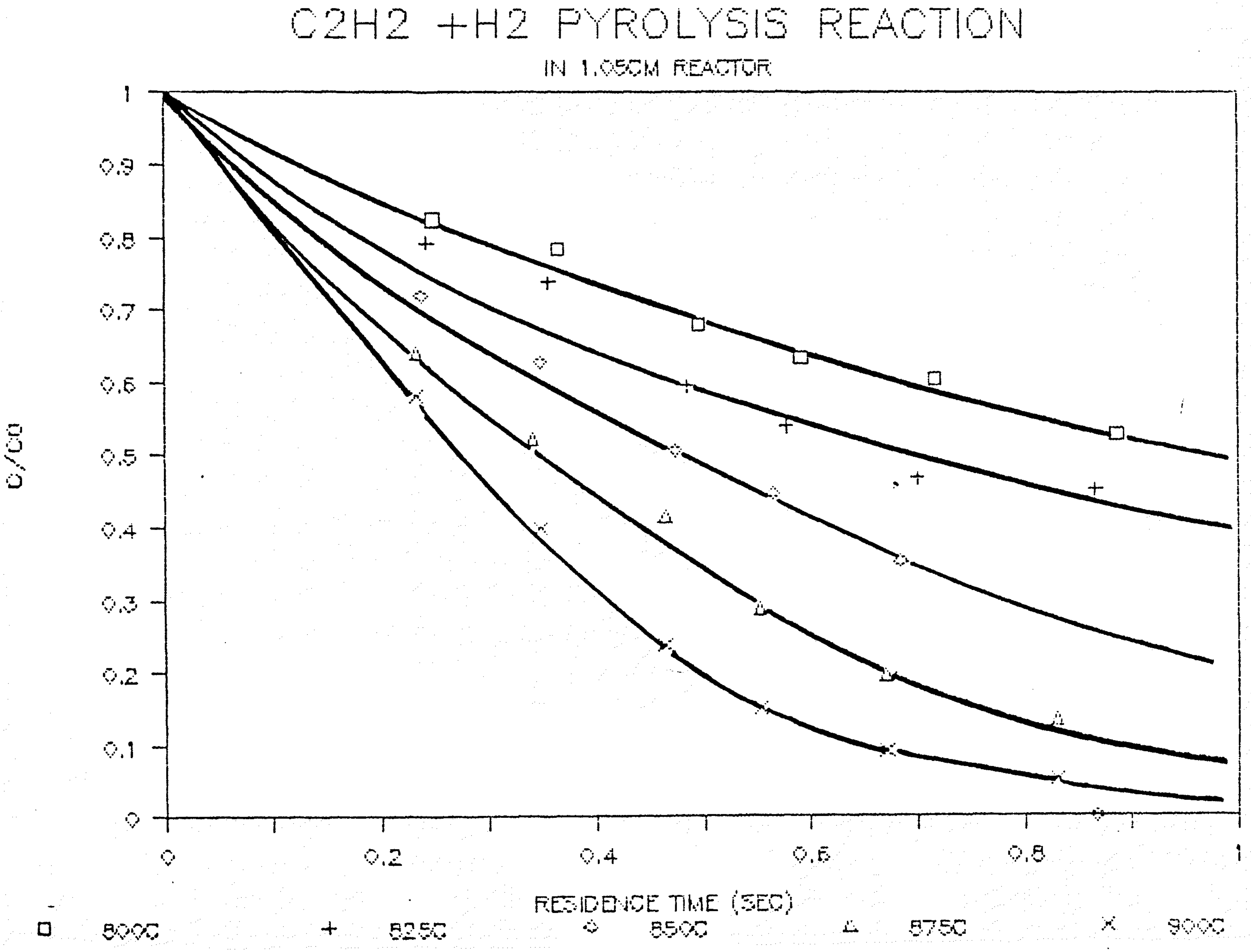
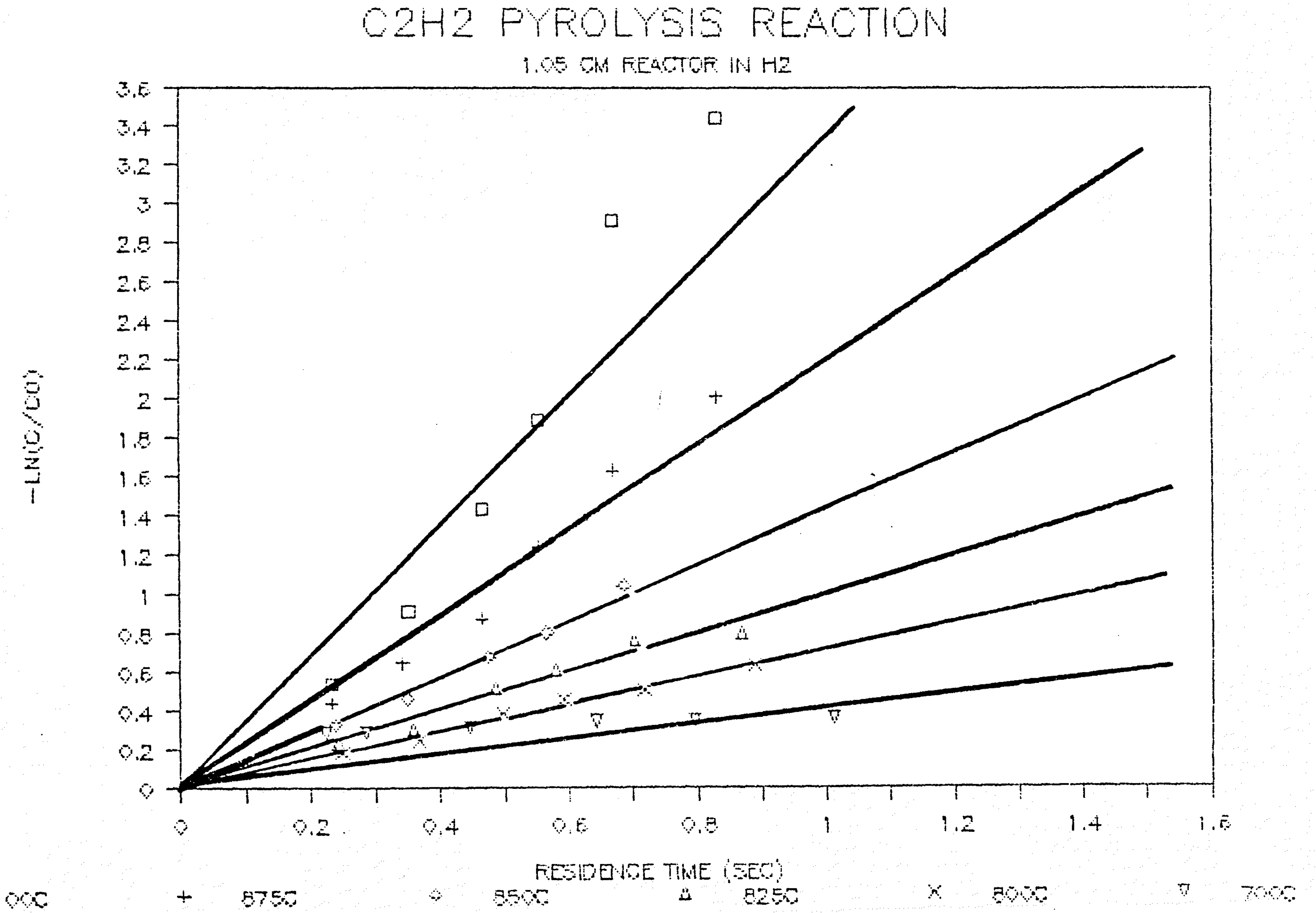

C2H2 +H2 PYROLYSIS REACTION
IN 1.05CM REACTOR
C/CO
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.2
0.4
0.6
0.8
1
RESIDENCE TIME (SEC)
□ 800C
+ 825C
◇ 850C
△ 875C
× 900C

Figure 5.3.1



C2H2 PYROLYSIS REACTION

1.05 CM REACTOR IN H2

Figure 5.3.2.

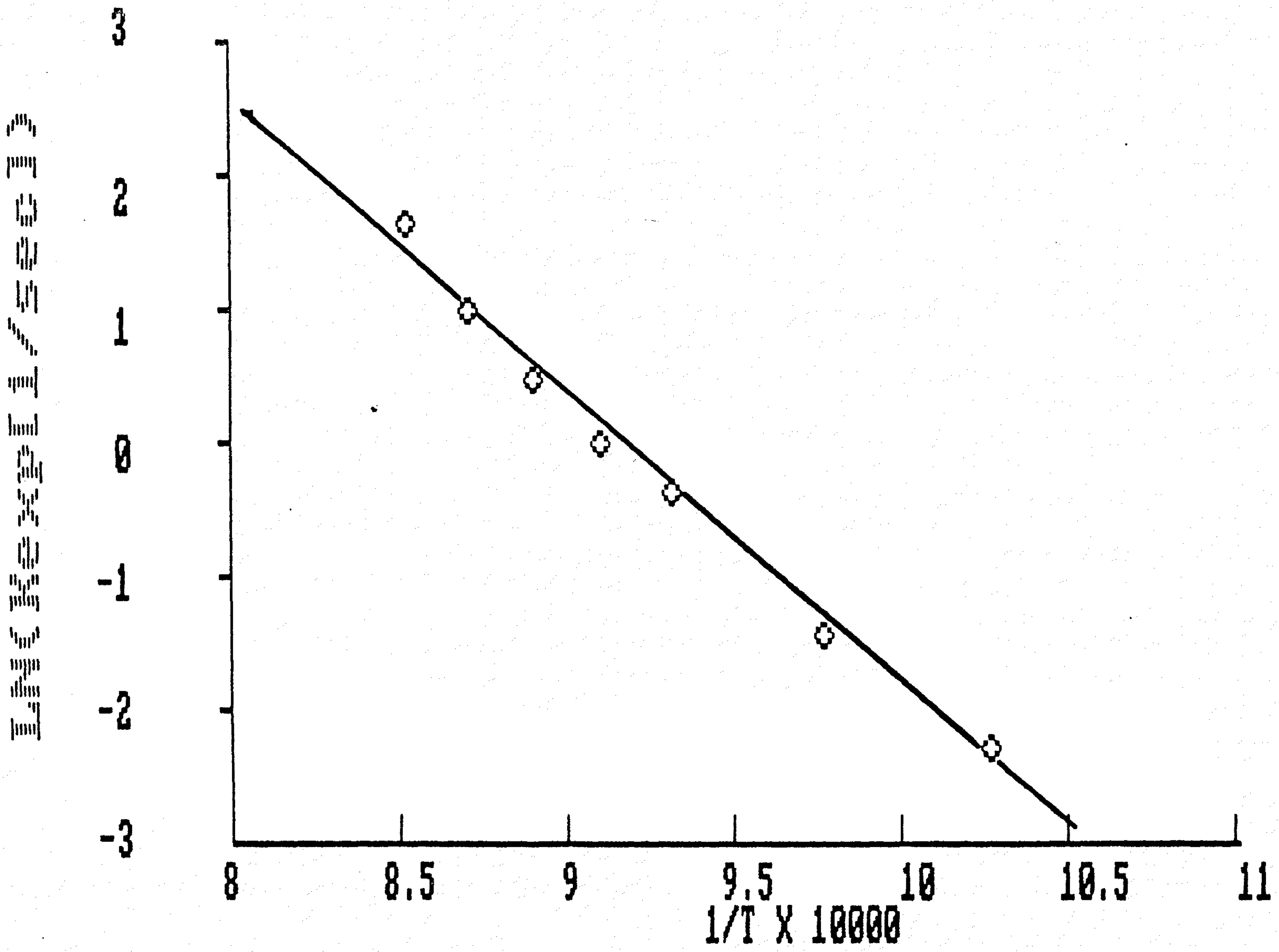


Figure 5.3.3.

different temperatures. The observed global rate constant, kexp for each temperature is calculated from the slope of the corresponding line in the graph. The Arrhenius plot of thefirst order reaction behavior for acetylene is shown in figure 5.3.3.

It is believed that the initial reaction pathways of C2H2 pyrolysis in hydrogen makes products in two categories. One is the generation of light hydrocarbons; The other is the polymerization of acetylene. The reaction scheme (c) in section 3.1. explained how the light hydrocarbons such as methane, ethylene, ethane are formed.

TABLE 5.3.1. GLOBAL ARRHENIUS PARAMETERS FOR THE DECOMPOSITION OF ACETYLENE IN HYDROGEN

REACTOR ID	A FACTOR	Ea
1.05 cm	5.34×10^{8}	43.5 Kcal/mole

5.3.1. PRODUCT DISTRIBUTION FOR ACETYLENE PYROLYSIS IN HYDROGEN ATMOSPHERE

The normalized concentrations of the products from the decomposition of acetylene are given as a function of the residence time at different temperatures in figure 5.3.4. - 5.3.8. The major products from acetylene pyrolysis are CH4, C2H2, C2H4, C2H6 and carbon solids. Figure 5.3.8 shows that the decomposition of C2H2 in hydrogen at 900°C yields nearly 95% conversion at the residence time of 0.85 second. C2H4 is the most significant product among the effluent gases. It reached on apparent steady state value of 45% of the initial C2H2 concentration at 0.6 second residence time.

The second major product is carbon. its yield slowly increased with the decomposition of C2H2. At the residence time of 0.8 second, the yield of soot reached 25% or one fourth of actylene converted to soot at this temperature.

The amount of CH4 and C2H6 are at constant levels. Methane conversion reached about 20% at 0.8 second residence time; while, ethane reached 15% conversion at the same time.

The soot yield and formation from acetylene pyrolysis is different from soot formation of dichlorobenzene or chlorobenzene in hydrogen. The polymerization of acetylene to yield heavy molecules with the high ratio of C/H resulted mostly from addition or insertion reaction of vinylidene, and aromatic ring fusing reactions. The following reaction scheme describes some of our observed products:

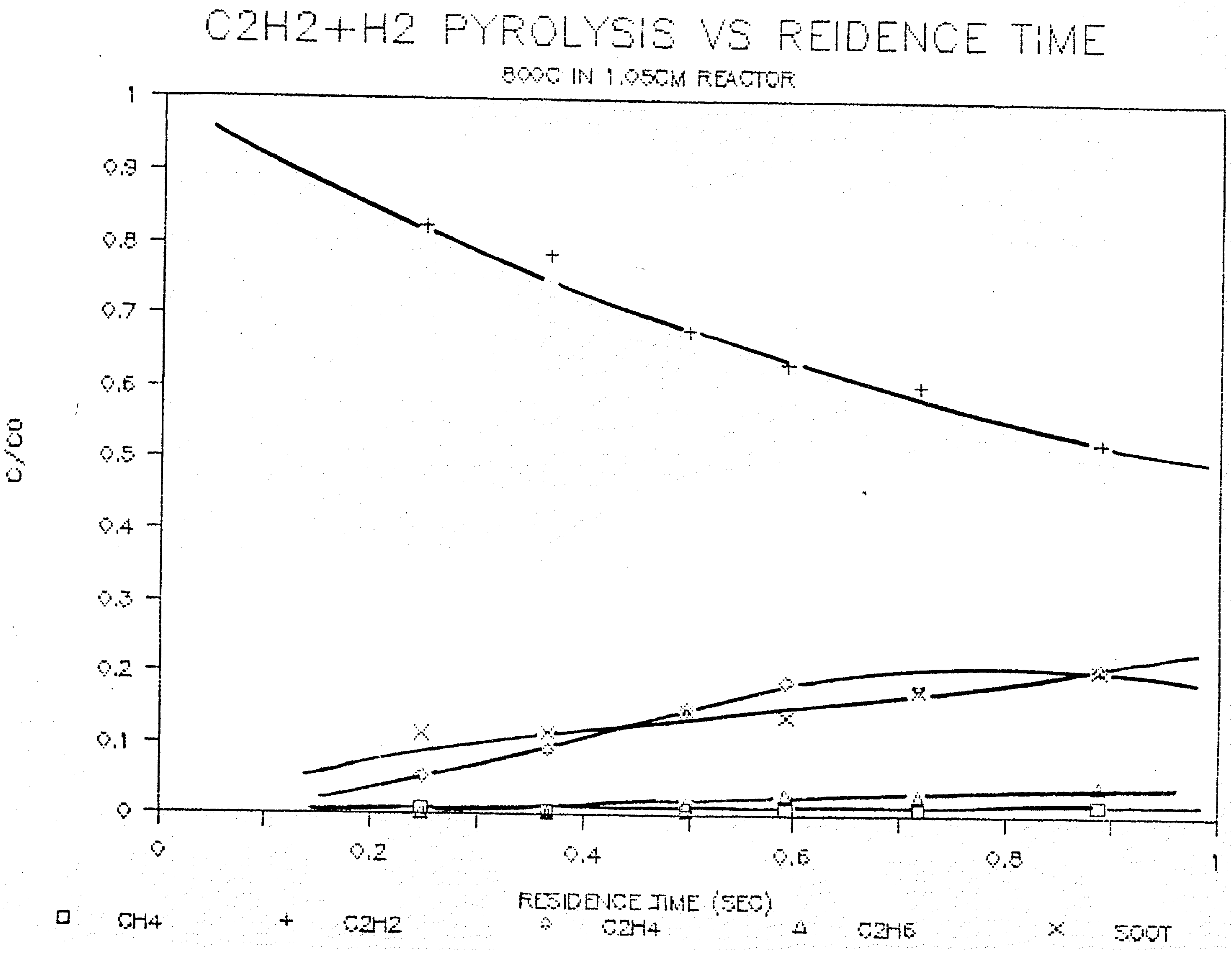

C2H2+H2 PYROLYSIS VS REIDENCE TIME
800C IN 1.05CM REACTOR
C/C0
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.2
0.4
0.6
0.8
1
RESIDENCE TIME (SEC)
□ CH4
+ C2H2
◇ C2H4
△ C2H6
× SOOT

Figure 5.3.4.

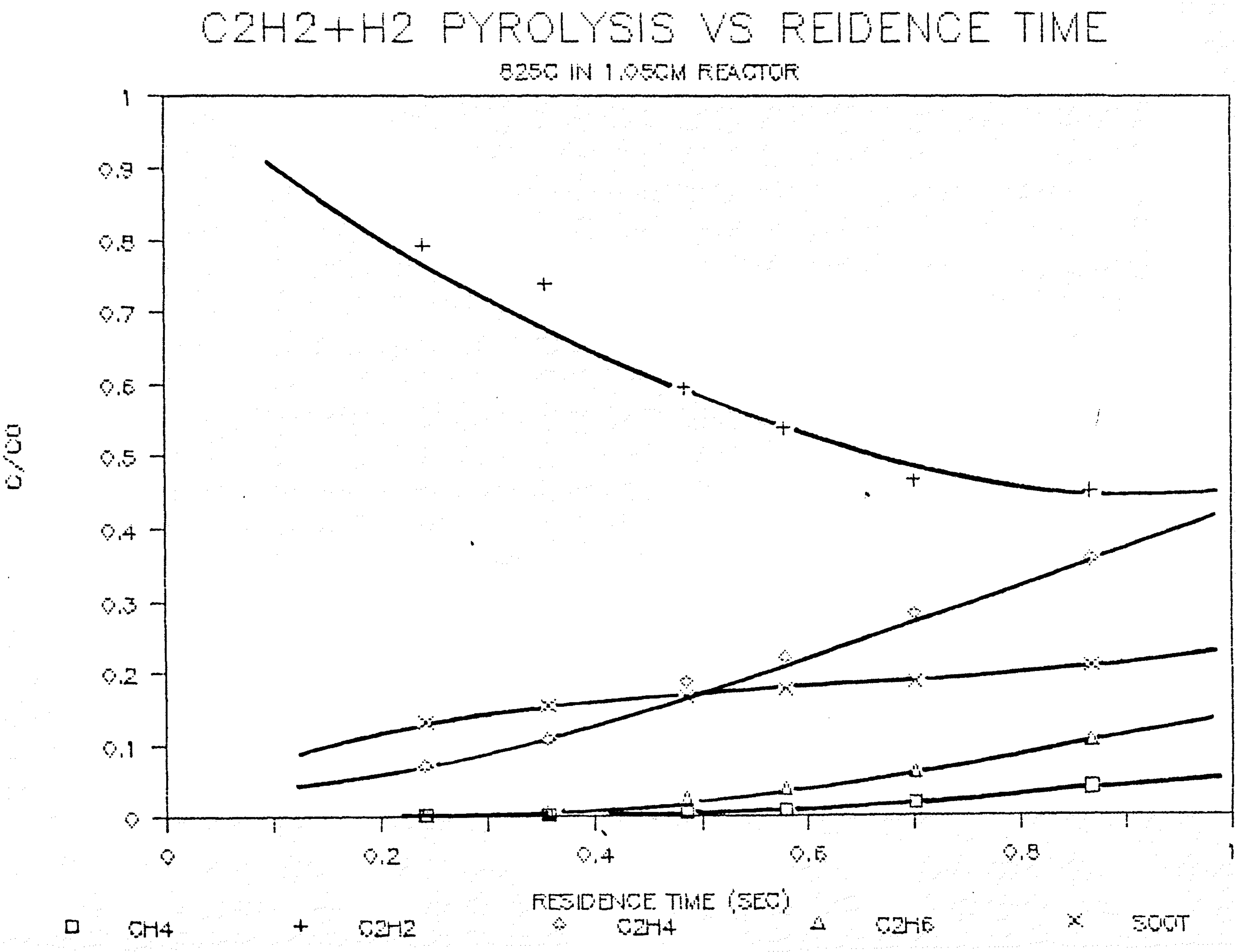

C2H2+H2 PYROLYSIS VS REIDENCE TIME
825C IN 1.05CM REACTOR
C/CO
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.2
0.4
0.6
0.8
1
RESIDENCE TIME (SEC)
□ CH4
+ C2H2
◇ C2H4
△ C2H6
× SOOT

Figure 5.3.5.

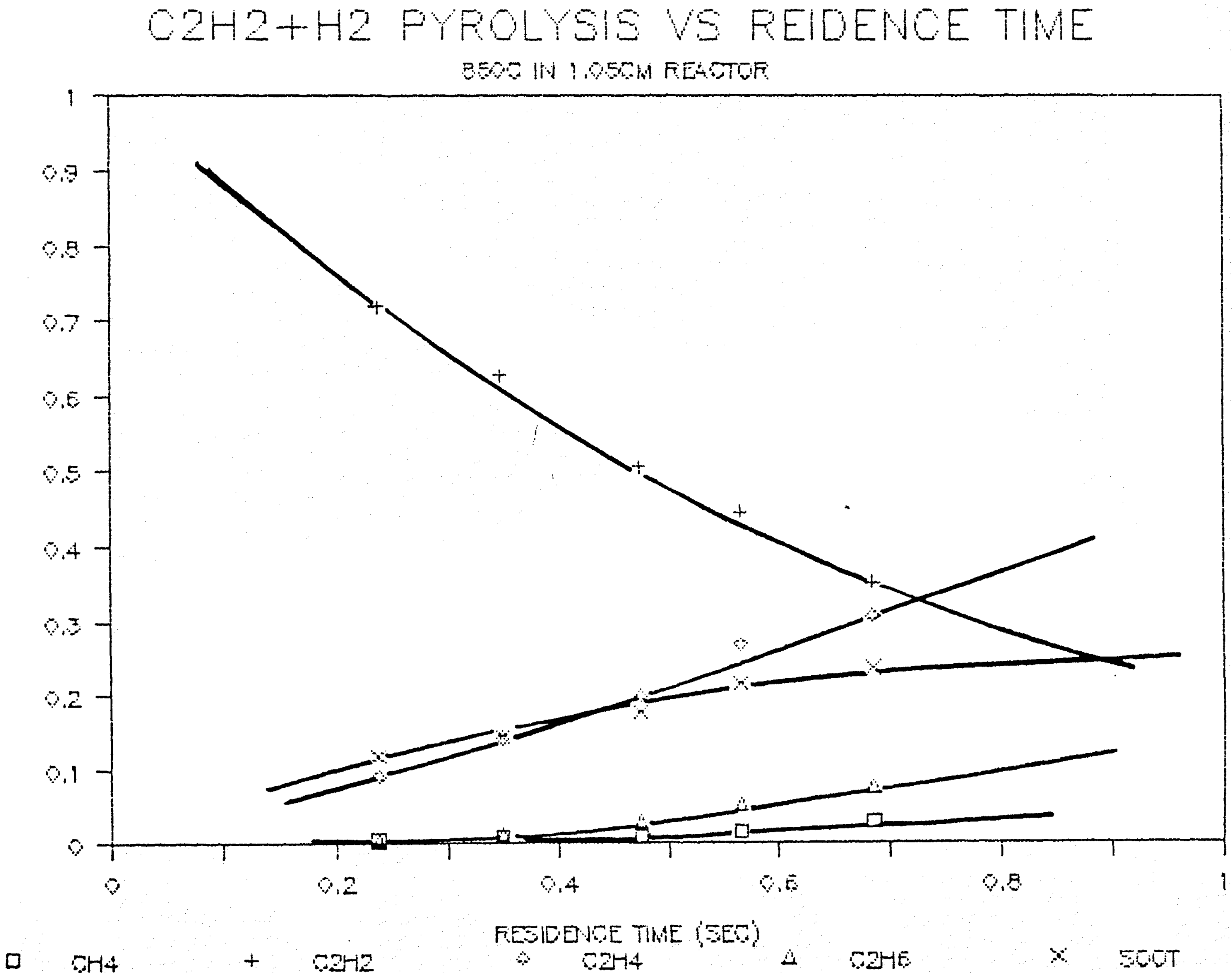

C2H2+H2 PYROLYSIS VS REIDENCE TIME
850C IN 1.05CM REACTOR
C/C0
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.2
0.4
0.6
0.8
1
RESIDENCE TIME (SEC)
□ CH4
+ C2H2
◇ C2H4
△ C2H6
✕ SOOT

Figure 5.3.6.

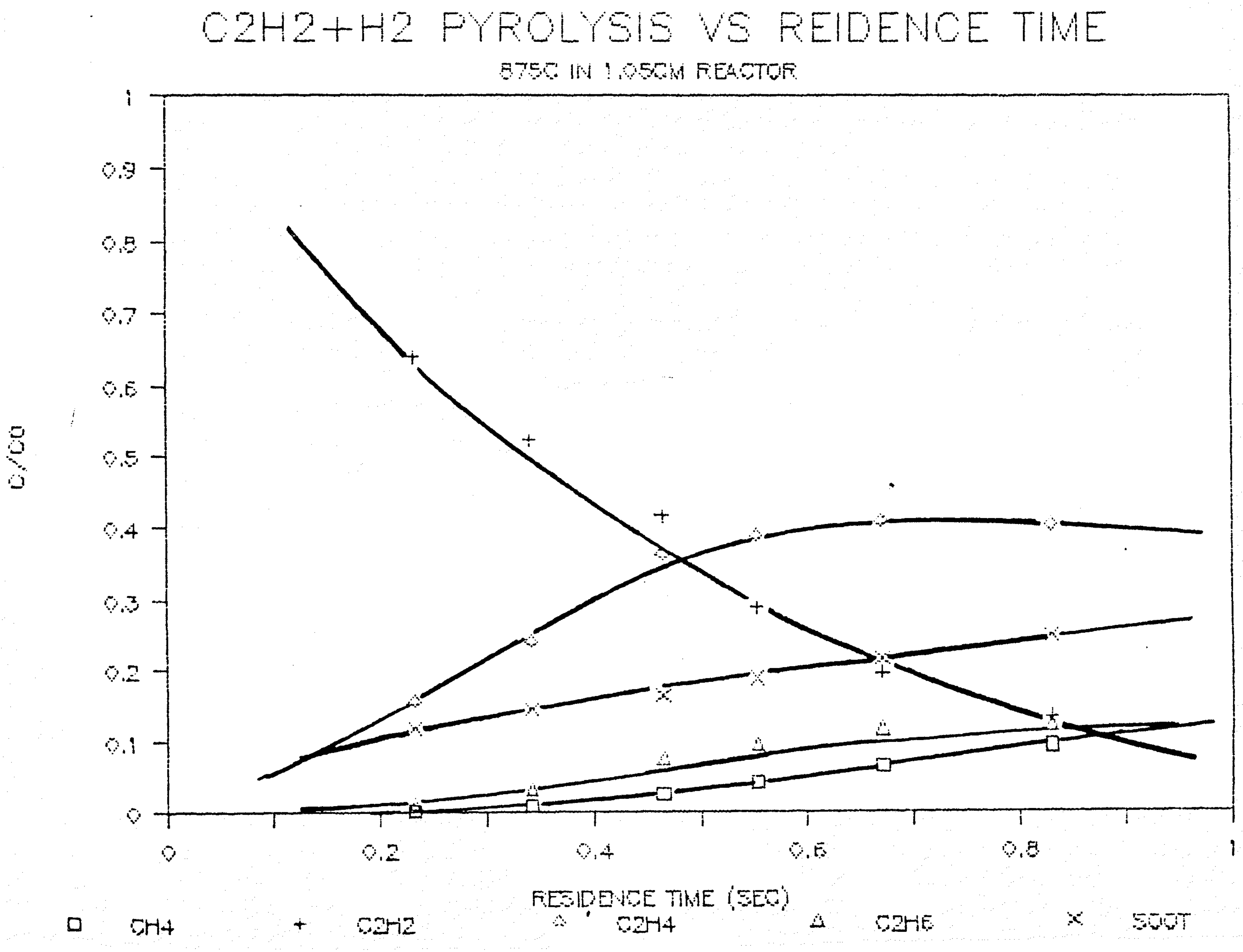

C2H2+H2 PYROLYSIS VS REIDENCE TIME
875C IN 1.05CM REACTOR
C/CO
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.2
0.4
0.6
0.8
1
RESIDENCE TIME (SEC)
□ CH4
+ C2H2
◇ C2H4
△ C2H6
× SOOT

Figure 5.3.7.

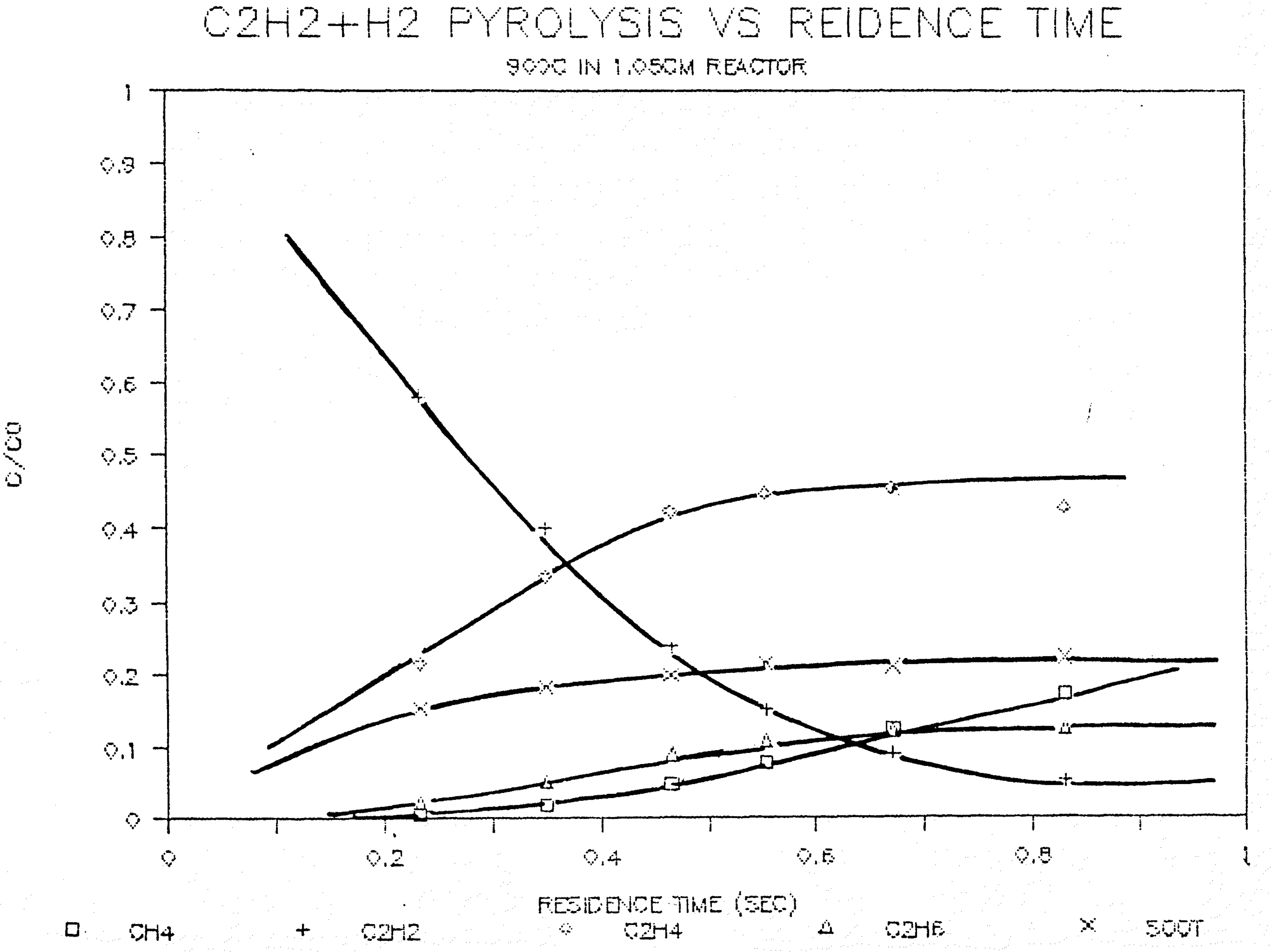
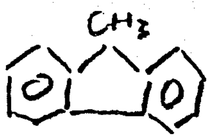
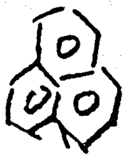

C2H2+H2 PYROLYSIS VS REIDENCE TIME
900C IN 1.05CM REACTOR
C/C0
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.2
0.4
0.6
0.8
1
RESIDENCE TIME (SEC)
□ CH4
+ C2H2
◇ C2H4
△ C2H6
× SOOT

Figure 5.3.8.

TABLE 5.3.2. POSSIBLE STRUCTURES OF A VARIETY OF CARBON PRODUCTS FROM ACETYLENE PYROLYSIS, IDENTIFIED BY GC/MASS

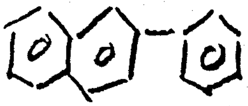


(1)

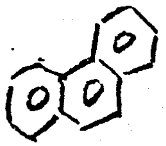


(2)

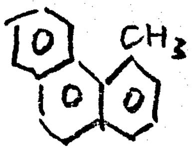
(3)



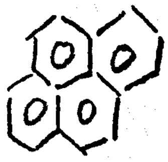
(4)



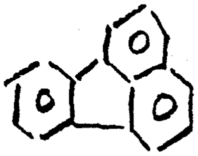
(5)



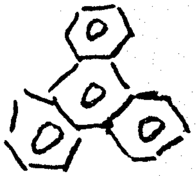
(6)



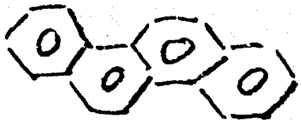
(7)



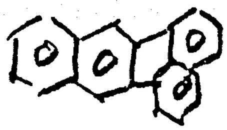
(8)



(9)



(10)



(11)

(d) $CH\equiv CH + M \text{----->} CH_2{=}C{:}$

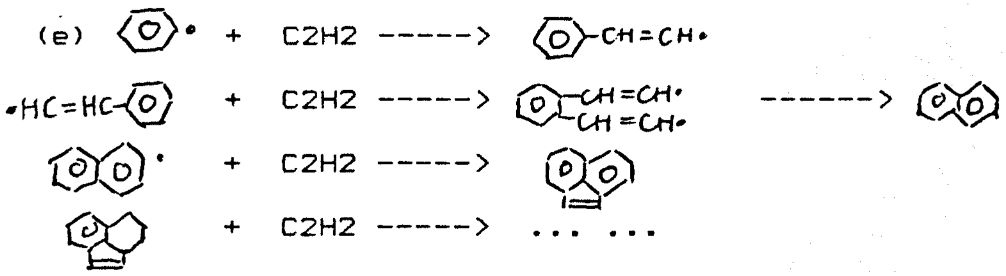
$CH_2{=}C{:} + CH\equiv CH \text{------>} CH_2{=}CHC\equiv CH$

$C.H{=}CH_2 + CH\equiv CH \text{----->} CH_2{=}CHCH{=}C.H$

$CH_2{=}CHCH{=}C.H \text{----->} CH_2{=}CHC\ CH$

$.CH{=}CHC\ CH + C_2H_2 \text{----->} C_6H_6 \text{------>}$ 

(e)



The addition or insertion reactions to polycyclic aromatic hydrocarbons continue usually to form very high molecular weight soot, of which the ratio of C/H is particularly high [24]. Eventually this early soot will become solid carbon. Repeated analysis by GC/MS identified a variety of soot products. They are mostly ring fusion reaction products. This result strongly indicates that the soot formation of acetylene pyrolysis is through ring fusing polymerization reactions. Table 5.3.2. demonstrated a variety of examples of soot products observed from our analysis of acetylene pyrolysis reaction.

5.3.2. THE TEMPERATURE DEPENDENCY OF THE PRODUCT DISTRIBUTION

The major product distribution from the pyrolysis of acetylene in hydrogen at 0.5 second average residence time is presented in figure 5.3.9. As we can see, the decomposition of the reactant acetylene increases slowly with the increase of reaction temperature. At 900°C, its decomposition is 80% of its initial concentration. The most significant product, C2H4, achieved 50% of the initial concentration of acetylene at 900°C. Soot from acetylene pyrolysis also increased with the increase in temperature. This is in a good agreement with the result of acetylene pyrolysis conducted in a shock tube by Frenklach, etc. [20]. Soot yield reached 20% at 900°C. The conversion of acetylene to C2H6 was less than 10% before 900°C. And methane conversion only reached about 8%. The following table presents the material balance per 100 mole of carbons at different temperatures.

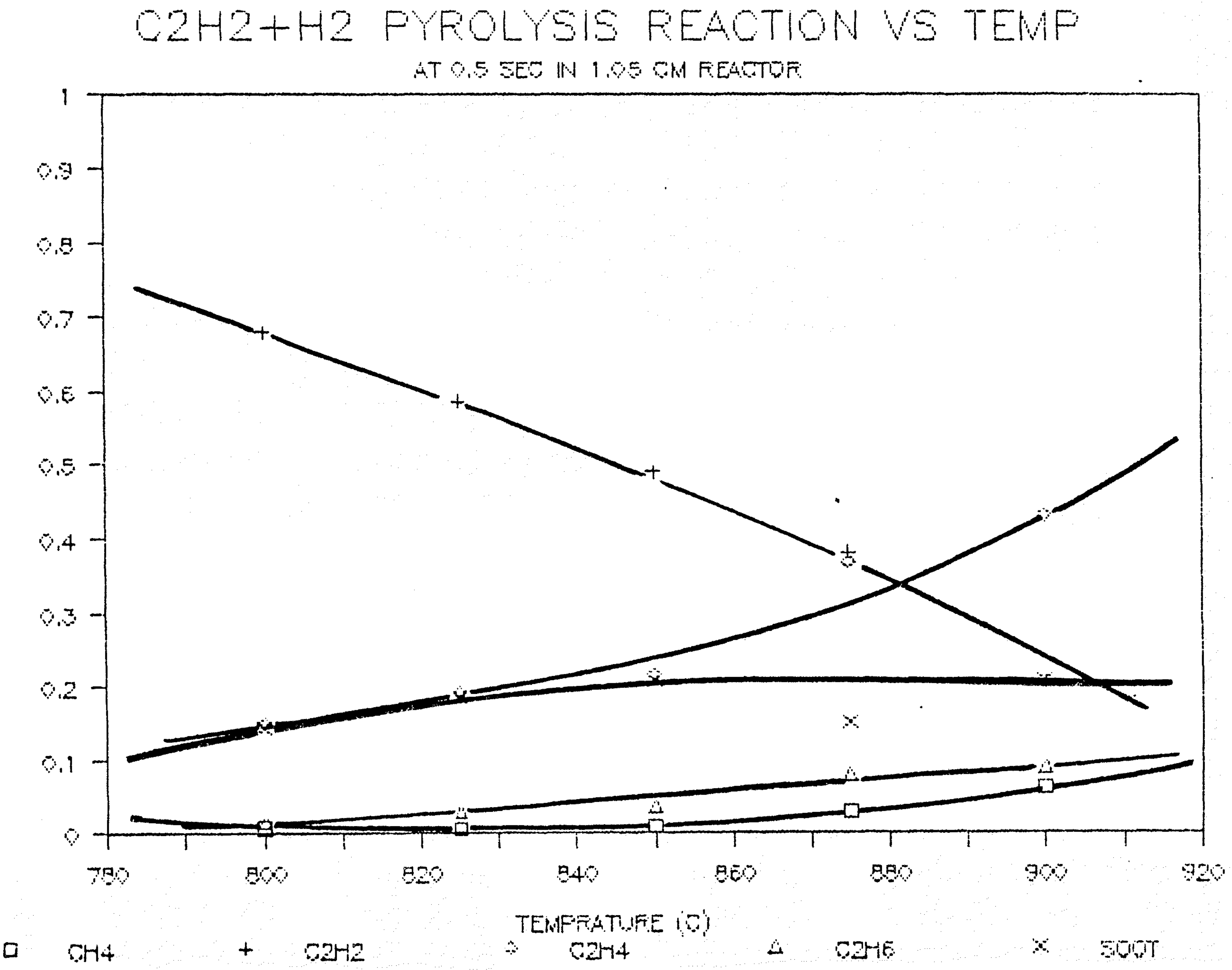

C2H2+H2 PYROLYSIS REACTION VS TEMP
AT 0.5 SEC IN 1.05 CM REACTOR
c/c0
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
780
800
820
840
860
880
900
920
TEMPRATURE (C)
□ CH4
+ C2H2
◇ C2H4
△ C2H6
× SOOT

Figure 5.3 9

TABLE 5.3.3. MATERIAL BALANCE PER 100 MOLES OF CARBONS

C2H2 + H2 IN 1.05 CM REACTOR

TEMP (C)	CH4	C2H2	C2H4	C2H6	SOOT
700	0.4	80.0	9.3	1.2	9.1
750	0.6	75.3	11.1	1.4	11.6
800	0.8	68.0	14.9	1.8	14.6
825	0.7	58.8	19.2	2.8	18.5
850	1.0	49.1	21.7	3.5	21.0
875	3.0	38.1	36.8	7.9	14.2
900	6.1	20.5	43.1	8.7	23.4

5.4. THE THERMAL DECOMPOSITION OF BENZENE IN HYDROGEN AND IN HELIUM ATMOSPERE.

The purpose of studying benzene pyrolysis reaction is to investigate its reaction extent, products, observe soot formation and determing kinetic parameters. In the precious chapters, the pyrolysis of chlorobenzene or dichlorobenzene, carbon solid showed a significant role in the distribution of products. Since benzene is one of major products from the decomposition of chlorobenze or dichlorobenzene, it might also contribute to the soot formation of its reactions.

The high temperature decomposition of benzne was studied at one atmosphere pressure in 1.05 cm ID tubular reactor. Experiments were conducted at the temperatures 875°C, 900°C, 925 °C, 950°C, 975°C, and 1000°C.

The benzene bubbler was maintained at 0 °C. The ratio of benzene to carrier gas was kept constant at 1:27. The initial concentration of benzene was 0.037 mole percent.

Figure 5.4.1. shows the decomposition of benzene at different temperatures as a function of residence time. We note at 875°C, benzene only decomposed 5% at residence time of 0.7 second. With the increase of the reaction temperature, the decomposition increased. At 1000°C, benzene reached 35% decomposition of its initial concentration.

The major product identified from the pyrolysis of benzene is soot. In addition, our experimental data show that less than 0.1% of benzene is converted to light hydrocarbons. These light hydrocarbons observed are CH4,

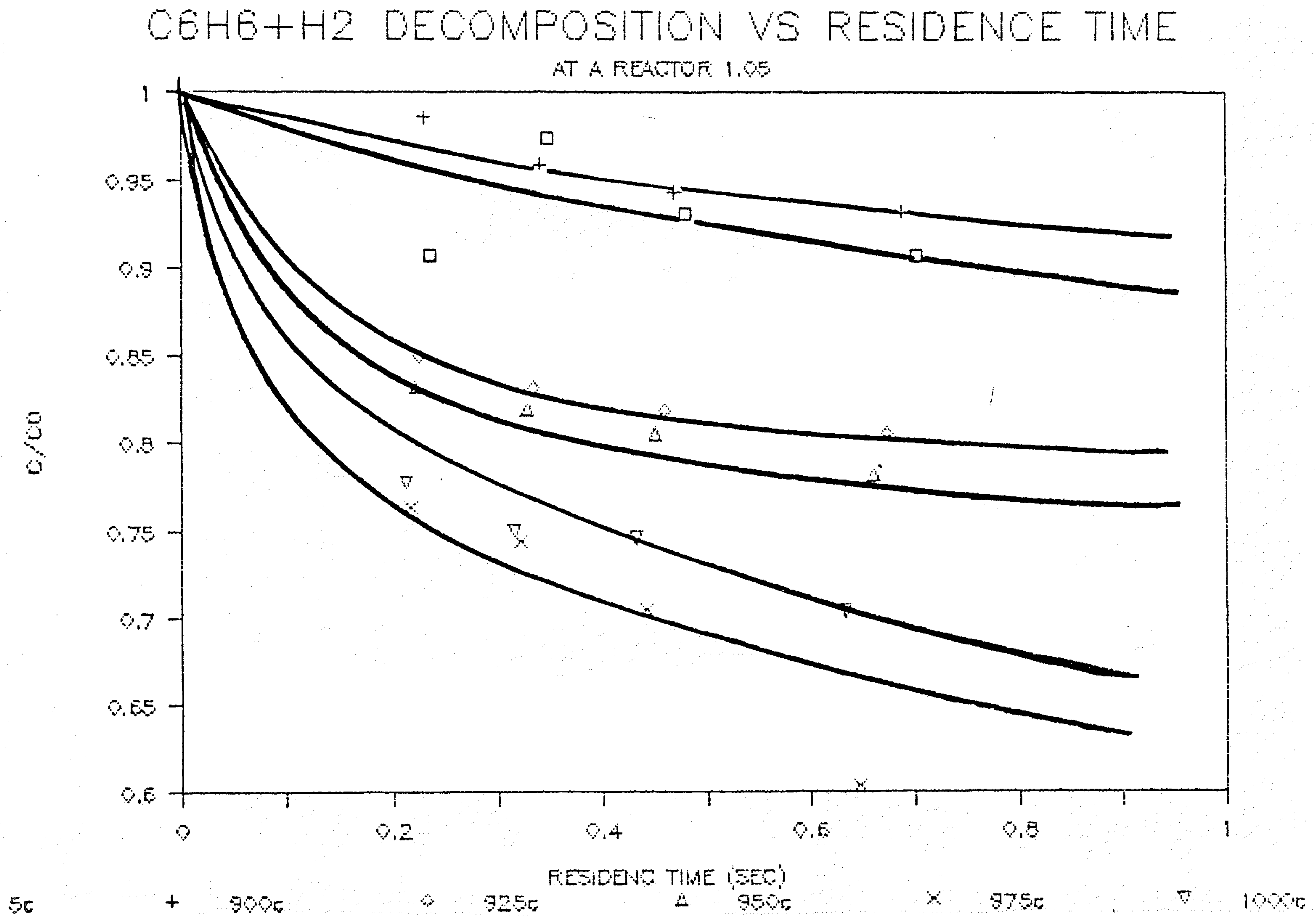

C6H6+H2 DECOMPOSITION VS RESIDENCE TIME
AT A REACTOR 1.05
C/C0
1
0.95
0.9
0.85
0.8
0.75
0.7
0.65
0.6
0
0.2
0.4
0.6
0.8
1
RESIDENC TIME (SEC)
□ 5c
+ 900c
◇ 925c
△ 950c
× 975c
▽ 1000c

Figure 5.4.1.

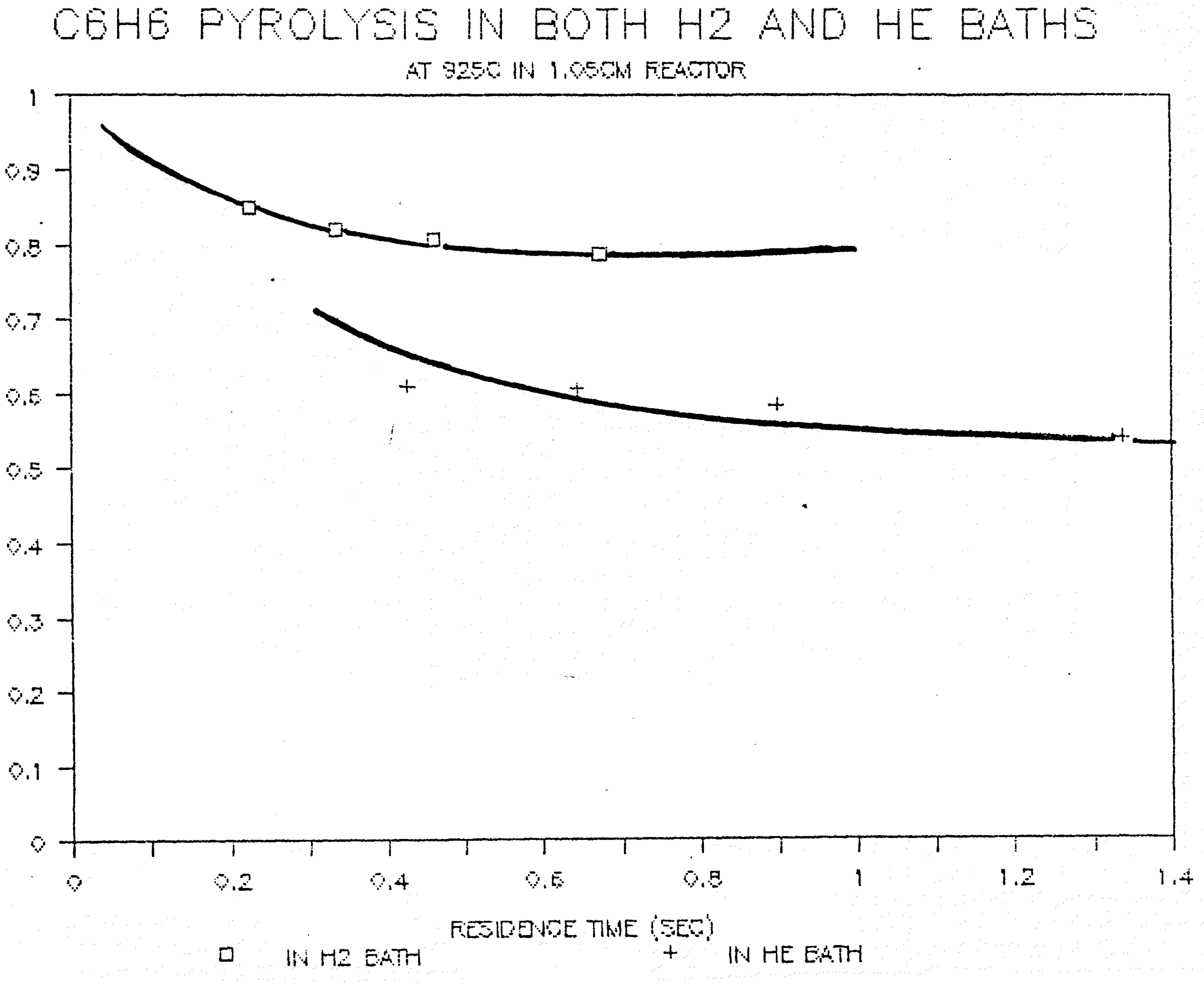

C6H6 PYROLYSIS IN BOTH H2 AND HE BATHS
AT 925C IN 1.05CM REACTOR
C/C0
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.2
0.4
0.6
0.8
1
1.2
1.4
RESIDENCE TIME (SEC)
□ IN H2 BATH
+ IN HE BATH

Figure 5.4.2.

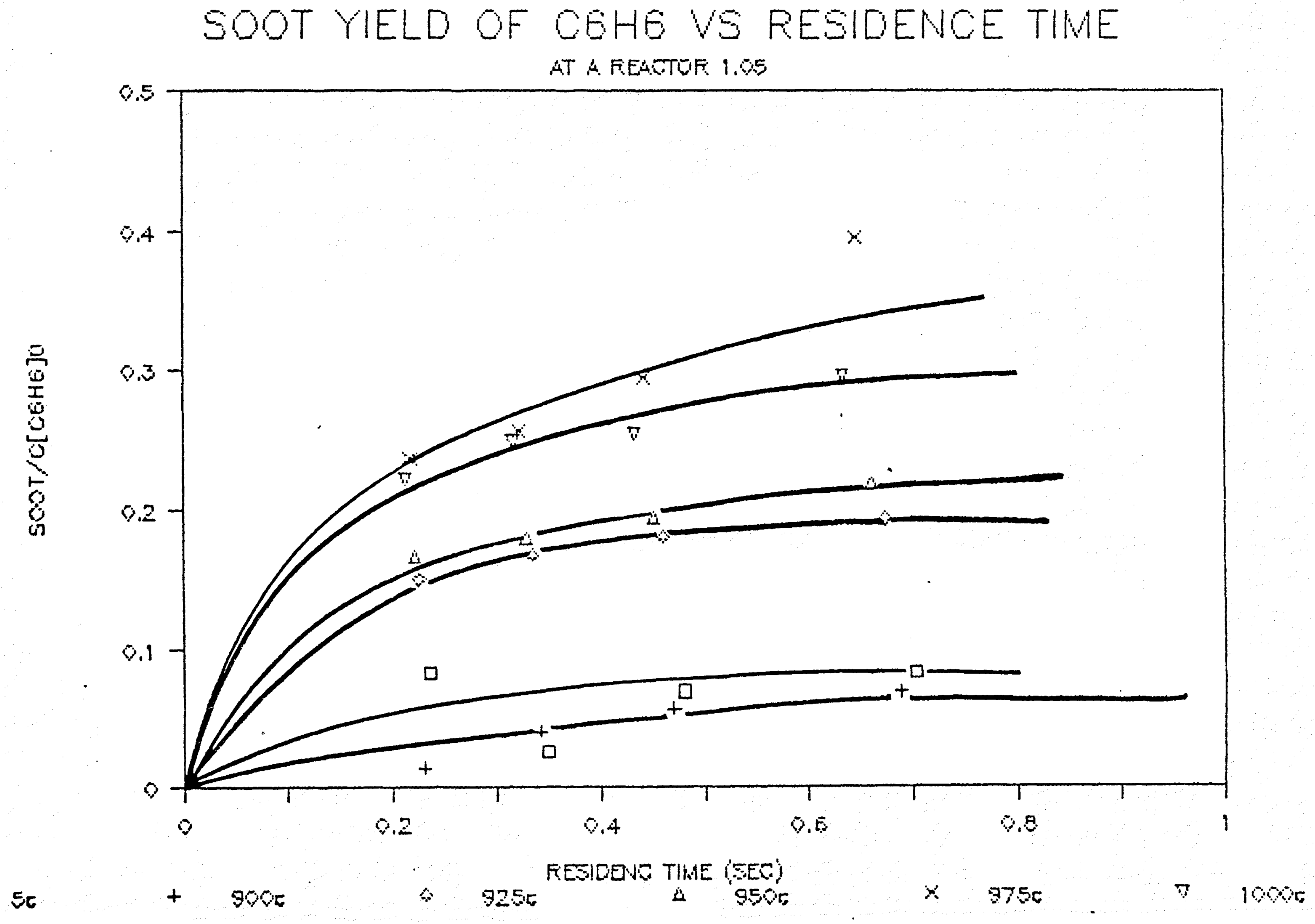

SOOT YIELD OF C6H6 VS RESIDENCE TIME
AT A REACTOR 1.05
SOOT/C[C6H6]0
0.5
0.4
0.3
0.2
0.1
0
0
0.2
0.4
0.6
0.8
1
RESIDENC TIME (SEC)
5c
+ 900c
◇ 925c
△ 950c
× 975c
▽ 1000c

Figure 5.4.3.

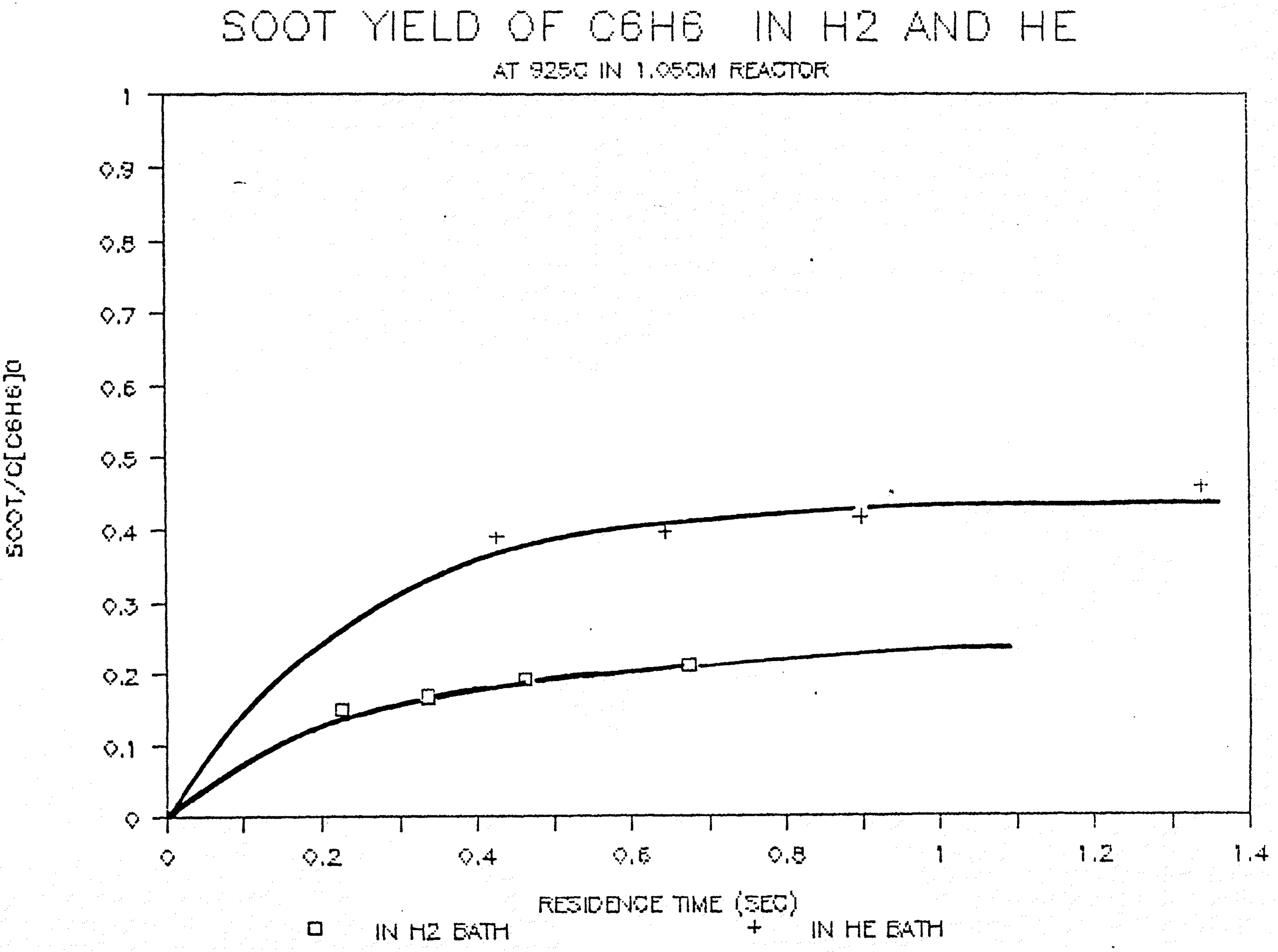

SOOT YIELD OF C6H6 IN H2 AND HE
AT 925C IN 1.05CM REACTOR
SOOT/C[C6H6]0
RESIDENCE TIME (SEC)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
0
0.2
0.4
0.6
0.8
1
1.2
1.4
□ IN H2 BATH
+ IN HE BATH

Figure 5.4.4.

TABLE 5.4.1.

DETAILED KINETICS MECHANISM FOR THE DECOMPOSITION OF BENZENE IN HYDROGEN ATMOSPHERE

REACTIONS	A	Ea (Kcal/mole)	REMARKS
1. C6H6 + H = C6H7	4.87E+56	26.80	a
2. C6H6 + H=C6H5 + H2	2.00E+13	10.0	a
3. C6H6+M=C6H5+M+H	1.67E+16	113.5	a
4. H2 + M = 2H + M	5.26E+8	105.0	a
5. C6H5=HC≡CCH=CHCH=C.H	5.76E+14	55.18	a
6. HC≡CCH=CHCHC.H = CH≡CH + CH≡CCH=C.H	6.09E+14	43.91	a
7. C6H7 = C5H4.CH3	5.0E+12	38.1	a
8. CH≡CH = CH2=C:	8.72E+13*	57.39	b
9. CH2=C: + H2 = C2H4	2.25E+12	5.10	c
10. C2H2 + H = C2H3	1.70E+12	2.50	d
11. C2H3 + H = C2H4	1.96E+12	2.40	d
12. C2H4 + H = C2H5	8.89E+12	36.3	e
13. C2H5 + H = C2H6	3.98E+13	2.60	d
14. C2H2 + M = C2H + H + M	6.10E+12	132.9	f
15. C2H + H2 = H+C2H2	7.41E+13	2.5	g
16. C2H + C2H2 = C4H2 + H	2.00E+13	2.0	g
17. C4H2=C4H+H	3.50E+14	132.0	h
18. C2H + H = C2 + H2	1.00E+12	16.14	g
19. C4H + H = C4 +H2	3.00E+13	0.0	g

20. C4H = C4 + H	7.94E+13	0.0	g
21. C6H5C6H5=C6H5+C6H5	1.90E+16	119.3	a
22. C6H6 + C6H5 = C6H5C6H5 + H	1.60E+45	31.0	a
23. C5H4.CH3 + H2 = C5H5CH3 + H	4.8E+13	32.3	a
24. C5H5CH3 + M = M + CH3 + .C5H5	2.00E+16	61.0	a
25. .C5H5 + H2 = C5H6 + H	2.50E+13	30.2	a
26. CH3 + H2 = CH4 + H	5.0E+12	11.0	a
27. CH3 + H = CH4	8.09E+36	9.2	a
28. CH3 + C6H5 = C6H5CH3	6.17E+11	7.6	i
29. C6H6 + CH3 = C5H5CH3 + H	3.4E+26*	26.4	a
30. C2H3 + H2 = C2H5	2.51E+12	4.0	j
31. C2H5 + H2 = C2H6 + H	6.31E+14	14.1	e
32. C2H + C2H2 = CH$\underline{=}$CCCH + H	3.98E+14	2.5	g
33. C4H2 = C4H + H	7.76E+14	132.0	g
34. C2H + C4H2 = CH$\underline{=}$CC$\underline{=}$CC$\underline{=}$CH + H	3.98E+13	2.5	g
35. C4H + C2H2 = CH$\underline{=}$CC$\underline{=}$CC$\underline{=}$CH + H	3.98E+13	2.5	g
36. C4H + H2 = H + C4H2	2.00E+13	2.5	g

37. $C_2H_4 + H = CH_3+CH_3$	3.55E+14	2.3	k

REMARKS

a. Edward R. Ritter, Joseph W. Bozzelli and Anthony M. Dean, "KINETIC STUDY ON THERMAL DECOMPOSITION OF CHLOROBENZENE DILUTED IN H2", to be published on J. Phys. chem. 1988.

b. A from calculation of QRRK. Ainf = 2 x $10^{13.4}$

$= 2 \times (ekt/n)\exp(\Delta S/R)$, by TST [37].

$Ea=\Delta Hr + 7.4$ [34].

c. A estimated from CH2 radical addition [35].

$Ea = \Delta$ Hr.

d.By the calculation of QRRK. Ainf from A. M. Dean [32].

$Ea = \Delta$ Hr.

e. A factor from A reverse and thermodynamics obtained from Alara and Shaw [36].

f. A factor calculated from Benson [37]. $Ea = \Delta$ Hr.

g. A and Ea factors are from Franklach et al. [20].

h. A factor are from Wanatz et al. Combust. Sci and tech, 1986, vol 1987. Vol 51.pp 265-283. $Ea = \Delta$ Hr.

i. A factor from Kerr, J.A. and Moss, Stephen. " Hand book of bimolecular and thermolecular gas reactions, Vol. I & II", CRC Press, Inc., 1981.

j. A factor calculeted by QRRK. $Ea = 6.5 + \Delta$ Hr.

6. ENERGIZED COMPLEX THEORY QRRK ANALYSIS ON THE FORMATION OF CH≡C:, C2H4 AND C2H6 IN HYDROGEN ATMOSPHERE

6.1 THE FORMATION OF C2H6:

As we discussed in the previous chapters, methyl radical and ethane molecule were repeatedly observed in the system of decomposition of chloro, dichlorobenzene or acetylene in hydrogene.

Ethane is believed as an adduct from C2H5 and H radicals. C2H5 and H radicals form a energized complex $[C2H6]^*$ at the beginning. Some amount of the complexes become stablized ethane, while some other of the complexes further breaks apart to CH3 + CH3, two methyl radicals. As shown in figure 6.2., the fraction of complexes going to CH3 + CH3 will increase with temperature. In addition, at our temperature range and 1 atm pressure, a significant amount of the $C2H6^*$ decomposes to CH3 + CH3; which is a low energy exit channel.

The energy diagram of the reaction channels are shown in figure 6.1.

TABLE 6.1. INPUT PARAMATERS FOR QRRK CALCULATIONS

FOR REACTION:

$C2H5 + H \Longleftrightarrow [C2H6]^*$

$\longrightarrow CH3CH3$

$\longrightarrow CH3 + CH3$

K	A*	Ea**	Ref
1	1.85E+14	0.0	a
-1	1.26E+16	100.65	b
2	5.01E+16	89.88	c

$<v>=1509\ cm^{-1}$

LJ PARAMETERS :

SIGMA = 4.34 A^{o} e/k = $246.79^{o}K$

a. Ainf from A.M.Dean et. al,[32].

b. calculated from thermodynamics by reverse A.

c. from A. M. Dean [32].

Units: * Bimolecular reactions A's in $cm^{3}\ sec^{-1}-mole^{-1}$

Unimolecular reactions A's in sec^{-1}.

** Units are in Kcal/mole.

TABLE 6.2. RATE CONSTANTS FROM THE CALCULATION OF QRRK FOR THE REACTION:

.CH2-C3 + H ------> PRODUCTS

	PRODUCTS	C2H6	CH3 + CH3
	76 TORR	9.70E+10	2.09E+14
A	760 TORR	1.34E+12	3.55E+14
	7600 TORR	1.34E+13	7.45E+14
n	all pressures	0.0	0.0
	76 TORR	-8.20	0.443
Ea	760 TORR	-6.36	2.30
	7600 TORR	-3.69	5.62
(Kcal/mole)			

Rate constant represents a best fit to non linear equation:

$$k = A\ T^{n}\ \exp(-Ea/RT)$$

A units of $cm^{3} mole^{-1} sec^{-1}$ for the biomolecular product channels and sec^{-1} for unimolecular reactions.

Temperature range: 600^{o}K to 2000^{o}K.

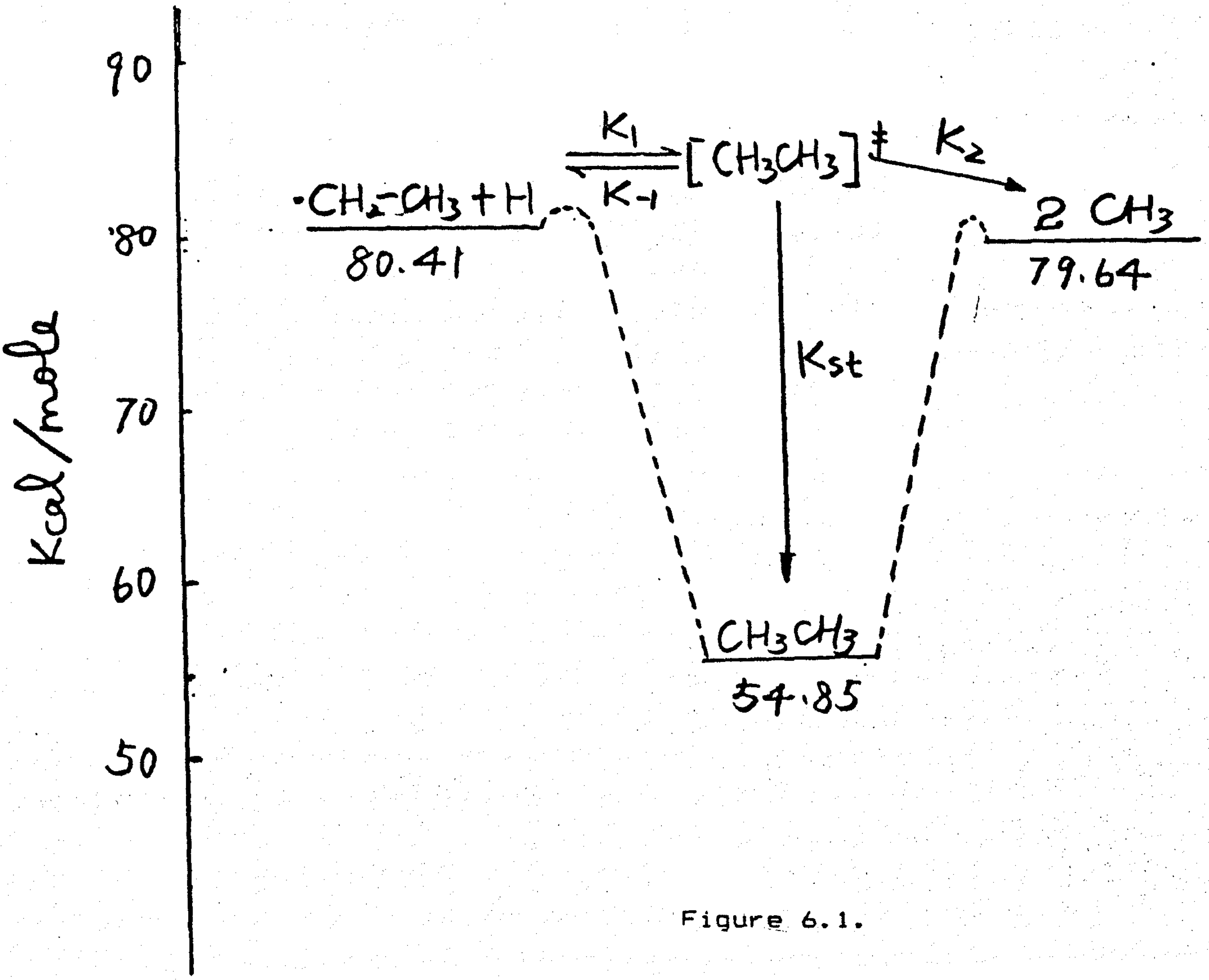

Kcal/mole
90
80
70
60
50
·CH₂-CH₃ + H
80.41
K₁
K₋₁
[CH₃CH₃]‡
K₂
2 CH₃
79.64
Kst
CH₃CH₃
54.85

Figure 6.1.

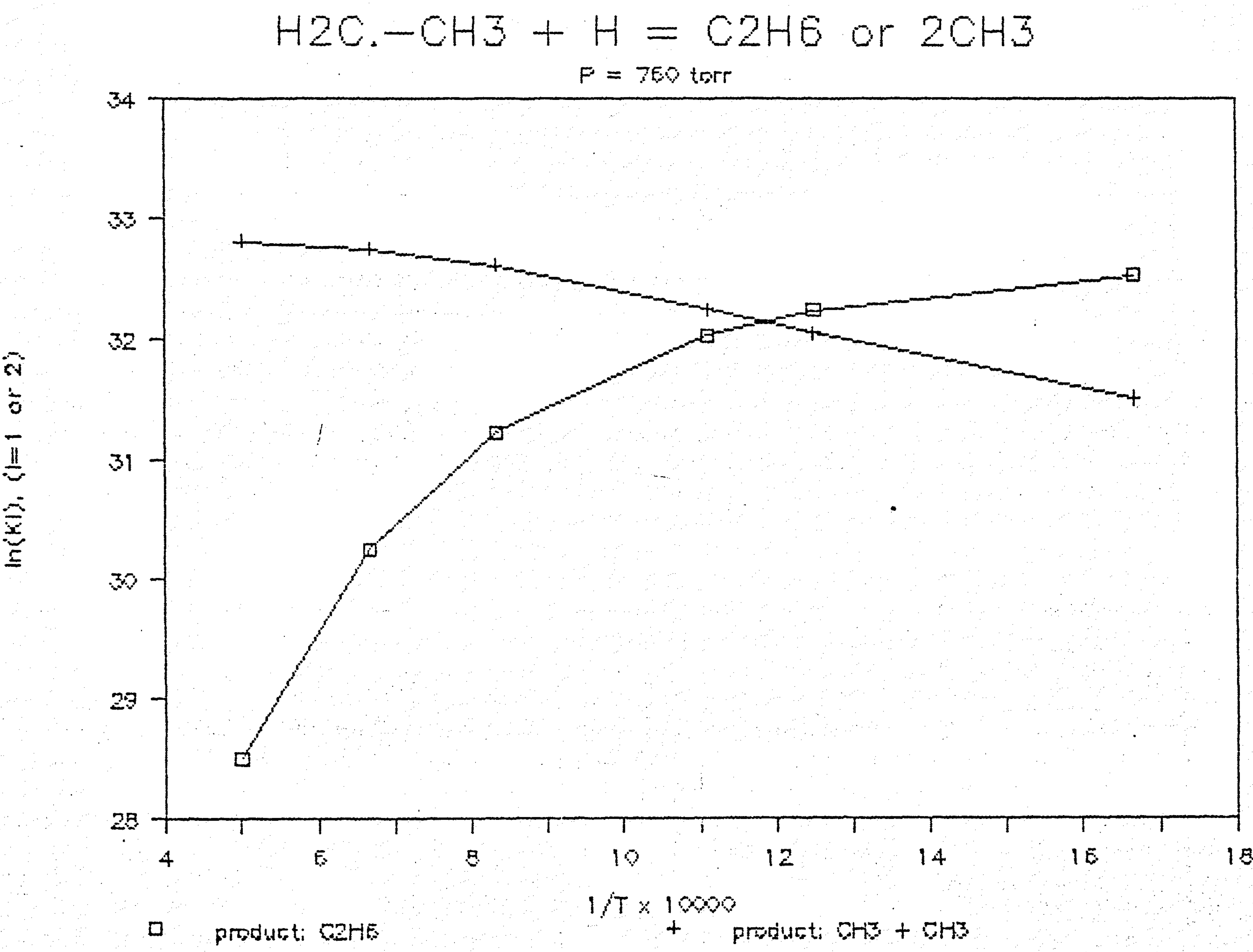

H2C.-CH3 + H = C2H6 or 2CH3
P = 760 torr
34
33
32
31
30
29
28
ln(Ki), (i=1 or 2)
4
6
8
10
12
14
16
18
1/T x 10000
□ product: C2H6
+ product: CH3 + CH3

Figure 6.2.

6.2. THE FORMATION OF ACETYLENE DIRADICALS (VINYLIDENE)

John Tseng et, al. [34] had studied the intramolecular reactions theoretically by using ab initio calculations at the MP2/6-31G* level and experimentally by examing the ring expansion of cyclopentylidene carbene at elevated temperatures, and calculated the the barrier from carbene to bicyclo hex-5-ene, which is 26.4 kcal/mole. Also, they indicated the bicyclo hex-5-ene is more stable than carbene molecule. They believe that carbene or diradicals are very active in the reaction system.

In the decomposition of chlorobenzene and dichlorobenzene, the acetylene from ring opening reactions forms an equilirium with acetylene diradical.

$$CH\equiv CH \Longleftrightarrow CH_2=C:$$

The energy barrier of the reaction is approximately 7.4 kcal above ΔHr [34]. So, the total Ea = Δ Hr + 7.4 kcal.

The reaction channel from C_2H_2 to $HC\equiv C.$ + H is more difficult. As shown in figure 6.3, the energy diagram, we know the barrier to make $.C_2H$ is extremely high. i.e. the bond energy is 132.5 kcal/mole.

Figure 6.4 shows the competition of the two rate constants Ks to form $CH\equiv CH$ and $CH_2=C:$.

TABLE 6.3. INPUT PARAMATERS FOR QRRK CALCULATIONS

FOR REACTION:

$.C_2H + H \Longleftrightarrow [C_2H_2]^*$

$\Longleftrightarrow CH_2{=}C{:}$

$\longrightarrow CH{=}CH$

K	A*	Ea**	Ref
1	1.96E+14	0.0	a
-1	6.10E+12	132.9	b
4	7.96E+13	57.39	c
-4	1.95E+13	7.4	d

$\langle v\rangle = 1236\ cm^{-1}$

LJ PARAMETERS :

SIGMA = 4.023 A^o e/k = 253.62 ^oK

a. Ainf from A. M. Dean et. al, [32]. $C_2H_4 = C_2H_3 + H$

b. calculated from thermodynamics by reverse A.

c. from Benson [37].

d. from the calculation of reverse A. Ea from John Tseng at, el. [34].

Units: * Bimolecular reactions A's in $cm^3\ sec^{-1}$-$mole^{-1}$

Unimolecular reactions A's in sec^{-1}.

** Units are in Kcal/mole.

TABLE 6.4. RATE CONSTANTS FROM THE CALCULATION OF QRRK FOR THE REACTION:

$\cdot C\equiv CH + H \text{ ------> PRODUCTS}$

	PRODUCTS	C_2H_2	$CH_2=C:$
	76 TORR	3.24E+13	1.58E+13
A	760 TORR	8.72E+13	4.50E+13
	7600 TORR	1.19E+14	6.38E+13
n	all pressures	0.0	0.0
	76 TORR	-1.87	-1.76
Ea	760 TORR	-0.615	-0.426
	7600 TORR	-0.179	-0.645
(Kcal/mole)			

Rate constant represents a best fit to non linear equation:

$$k = A\ T^{n} \exp(-Ea/RT)$$

A units of $cm^3 mole^{-1} sec^{-1}$ for the biomolecular product channels and sec^{-1} for unimolecular reactions.

Temperature range: $600^{\circ}K$ to $2000^{\circ}K$.

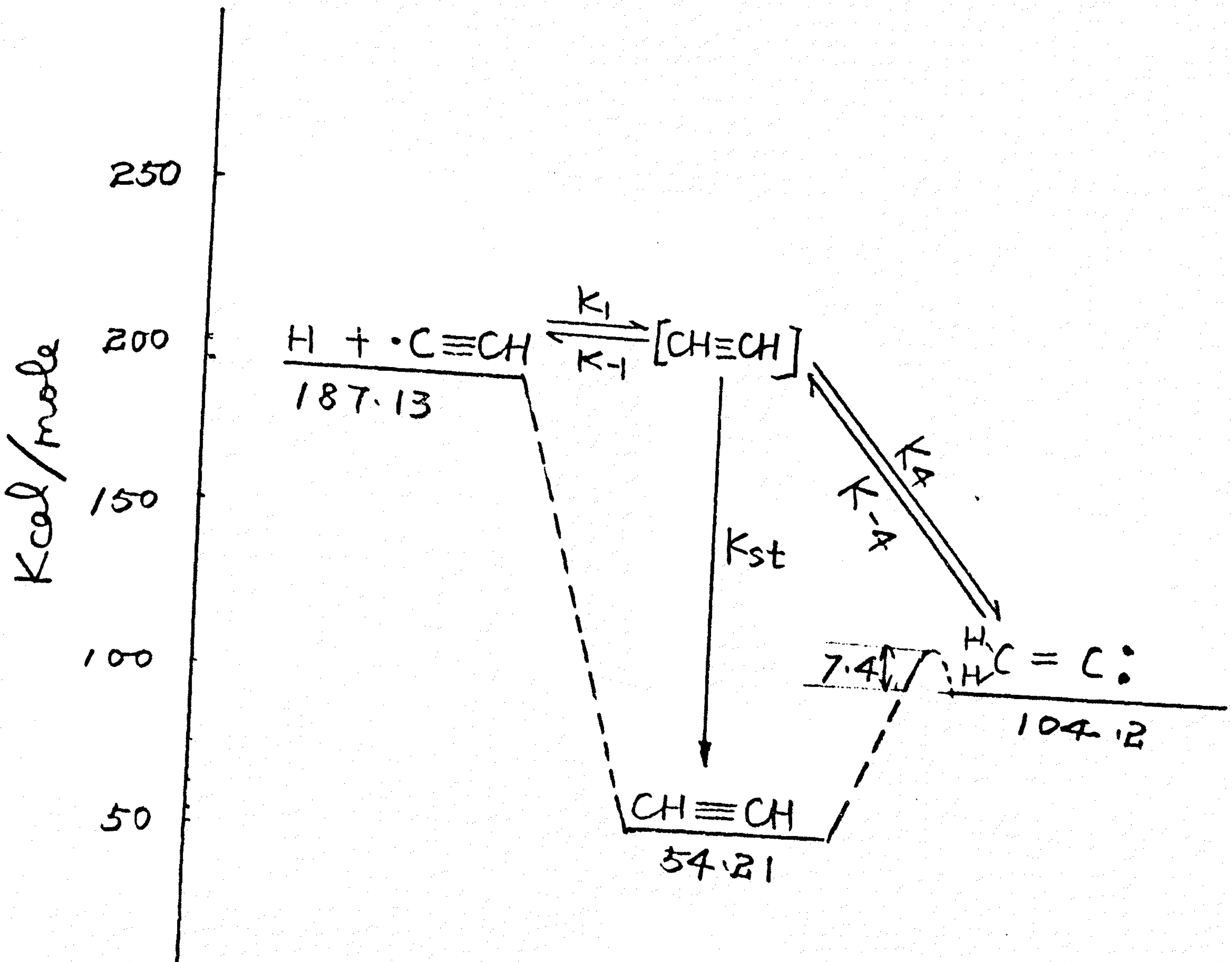

Kcal/mole
250
200
150
100
50
H + ·C≡CH
187·13
K1
K-1
[CH≡CH]
Kst
K7
K-7
7·4
H
H
C = C:
104·2
CH≡CH
54·21

Figure 6.3.

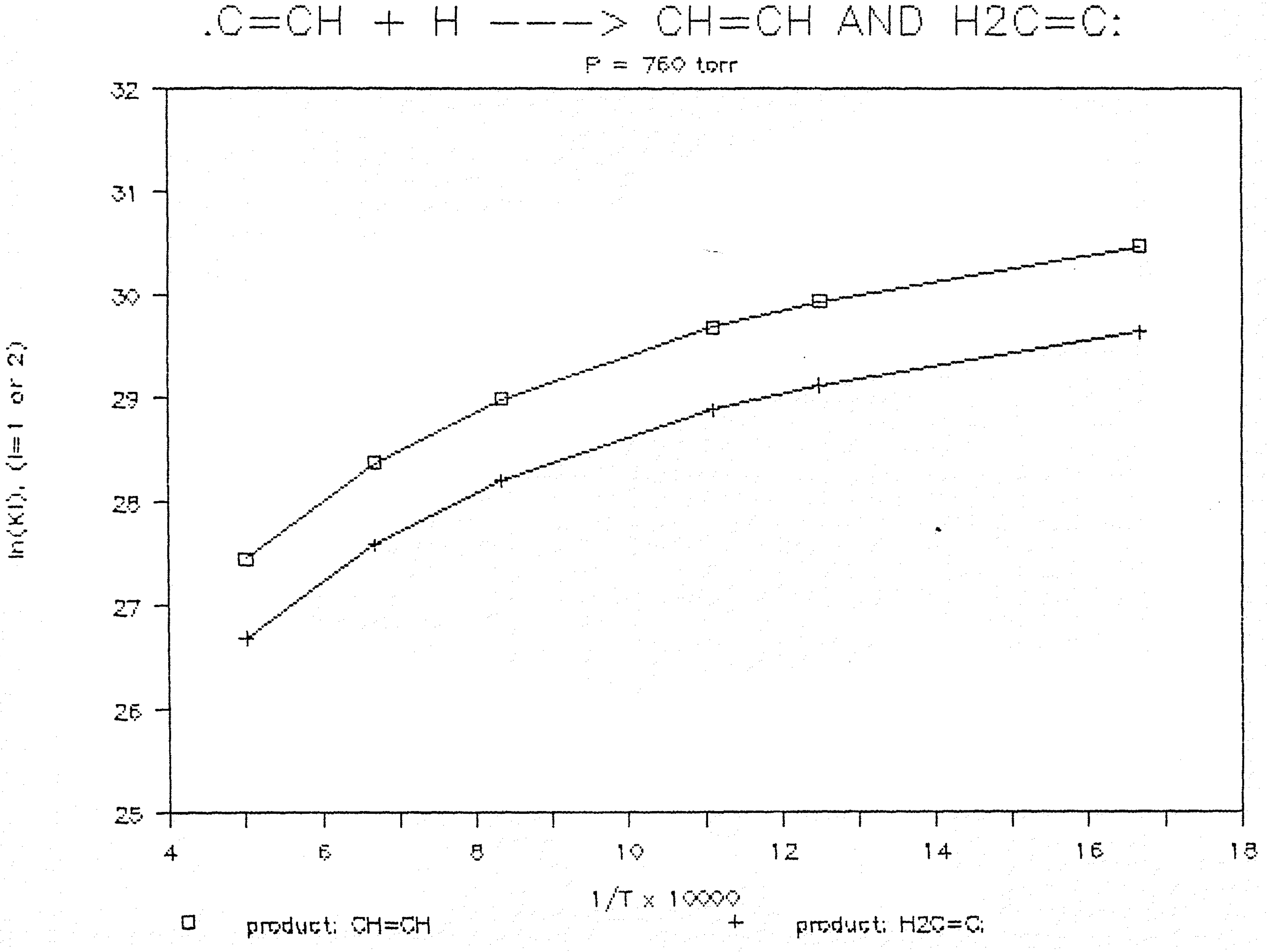

.C=CH + H ---> CH=CH AND H2C=C:
P = 760 torr
ln(Kl), (l=1 or 2)
32
31
30
29
28
27
26
25
4
6
8
10
12
14
16
18
1/T x 10000
□ product: CH=CH
+ product: H2C=C:

Figure 6.4.

6.3. THE FORMATION OF ETHYLENE

The formation of ethylene in our reaction system is very interesting. As we already observed, that in the decomposition of chloro and dichlorobenzene in hydrogene, ethylene was produced instead of acetylene. But in helium atmosphere, only significant amounts of acetylene were formed.

We believe, at our reaction temperature, the ring openning reaction generates acetylene first. However, the carbene diradical, vinylidene, attacks H2 immediately in the hydrogen rich atmosphere. Thus, ethylene is produced. The energy diagram for the reaction is presented in figure 6.5. At high temperature, This reaction can also produce a significant amount of C2H3 + H as shown in figure 6.5 , and 6.6.

TABLE 6.5. INPUT PARAMATERS FOR QRRK CALCULATIONS

FOR REACTION:

$CH_2=C: + H_2 \Longleftrightarrow [C_2H_4]^*$

$\Longleftrightarrow .CH=CH_2 + H$

$\longrightarrow CH_2=CH_2$

K	A*	Ea**	Ref
1	1.50E+14	0.0	a
-1	1.58E+16	91.64	b
2	2.00E+16	106.7	c

$\langle v \rangle = 1588\ cm^{-1}$

LJ PARAMETERS :

SIGMA = 4.23 A° e/k = 227.58°K

a. estimated from CH2 radical addition.

b. reverse calculated from thermodynamics.

C. from A. M. Dean et.al, [32].

Units: * Bimolecular reactions A's in $cm^3\ sec^{-1}\text{-}mole^{-1}$

Unimolecular reactions A's in sec^{-1}.

** Units are in Kcal/mole.

TABLE 6.6. RATE CONSTANTS FROM THE CALCULATION OF QRRK FOR THE REACTION:

$CH_2=C: + H_2 \longrightarrow$ PRODUCTS

	PRODUCTS	C_2H_4	$C_2H_3 + H$
	76 TORR	1.88E+11	2.83E+14
A	760 TORR	2.25E+12	2.86E+14
	7600 TORR	1.74E+13	3.14E+14
n	all pressures	0.0	0.0
	76 TORR	-6.47	17.4
Ea	760 TORR	-5.10	17.4
	7600 TORR	-2.95	17.8
	(Kcal/mole)		

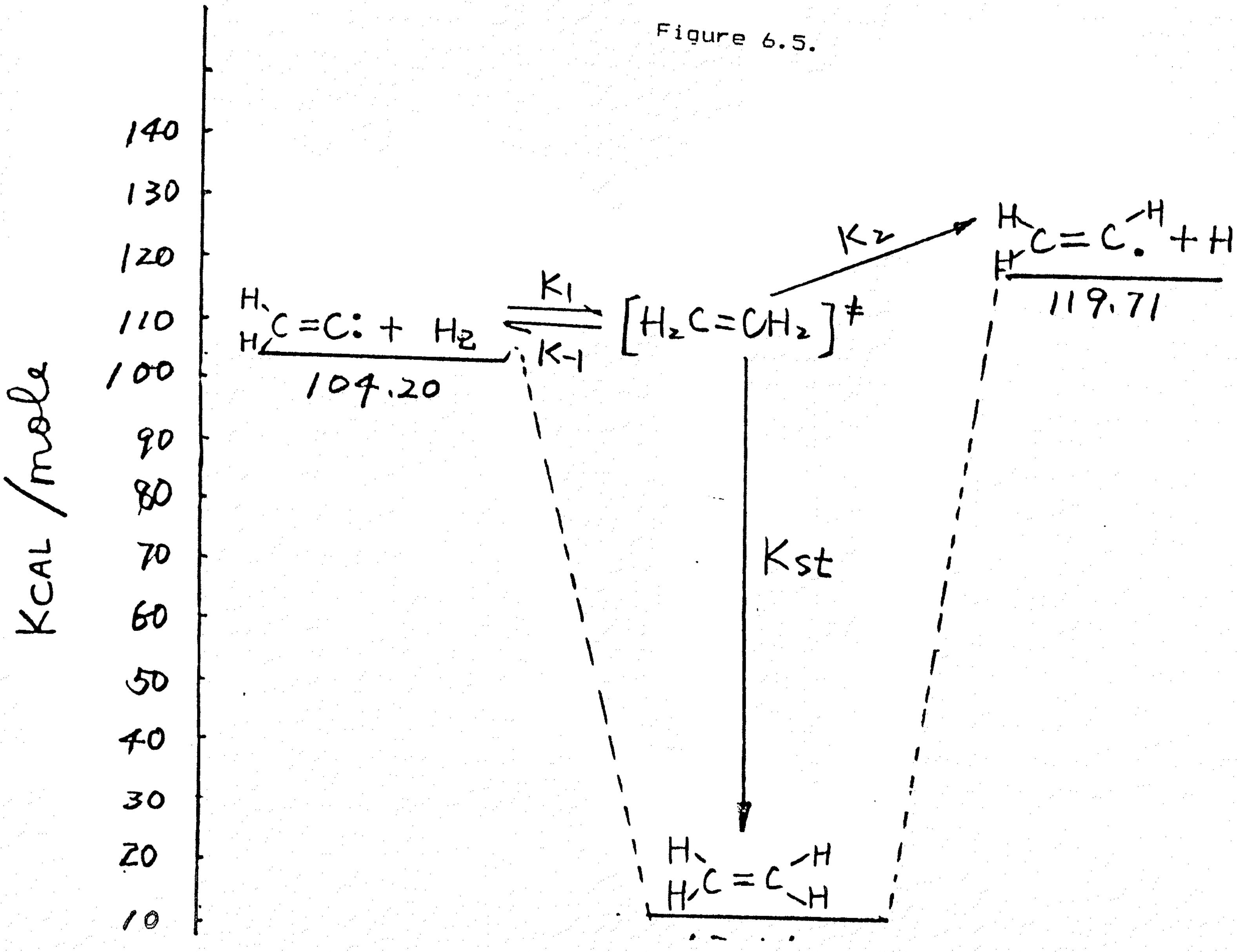
Rate constant represents a best fit to non linear equation:

$$k = A\, T^{n} \exp(-Ea/RT)$$

A units of $cm^{3} mole^{-1} sec^{-1}$ for the biomolecular product channels and sec-1 for unimolecular reactions.

Temperature range: 600^{o}K to 2000^{o}K.

Figure 6.5.


KCAL /mole
140
130
120
110
100
90
80
70
60
50
40
30
20
10
$H_2C=C: + H_2$
104.20
K_1
K_{-1}
$[H_2C=CH_2]^{\neq}$
K_2
$H_2C=\dot{C}H + H$
119.71
Kst
$H_2C=CH_2$

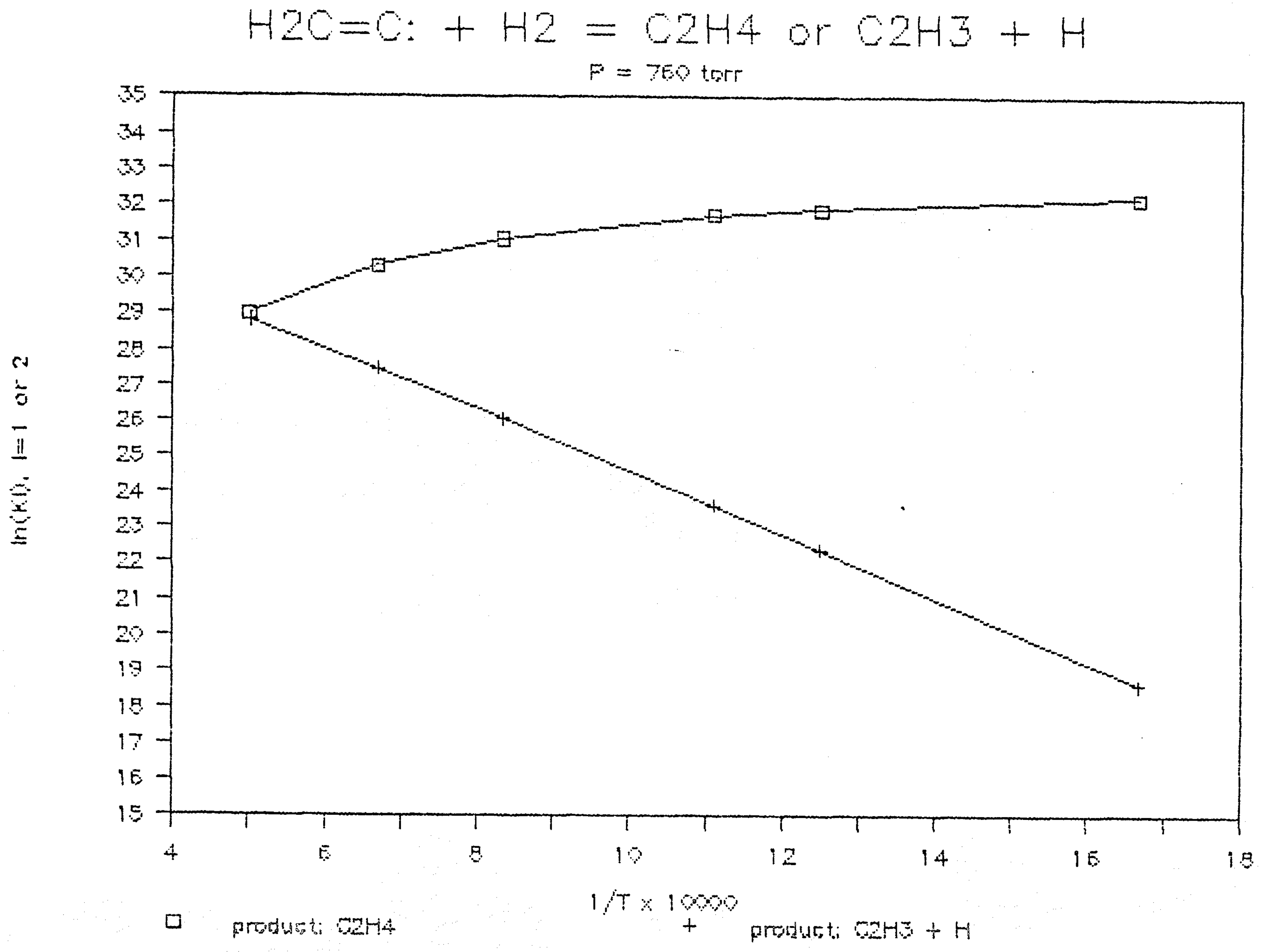

H2C=C: + H2 = C2H4 or C2H3 + H
P = 760 torr
ln(kI), I=1 or 2
35
34
33
32
31
30
29
28
27
26
25
24
23
22
21
20
19
18
17
16
15
4
6
8
10
12
14
16
18
1/T x 10000
□ product: C2H4
+ product: C2H3 + H

Figure 6.6.

6.4. THE FORMATION OF C2H3

TABLE 6.7. INPUT PARAMATERS FOR QRRK CALCULATIONS FOR REACTION:

$C_2H_2 + H \Longleftrightarrow [C_2H_3]^*$

$\longrightarrow .CH{=}CH_2$

K	A*	Ea**	Ref
1	5.01E+12	0.0	a
-1	1.19E+12	39.19	b

$\langle v \rangle = 1412\ cm^{-1}$

LJ PARAMETERS :

SIGMA = 4.108 A^o e/k = 240.62 ^oK

a. Ainf from A.M.Dean et. al,[32].

b. calculated from thermodynamics by reverse A.

Units: * Bimolecular reactions A's in $cm^3\ sec^{-1}$-$mole^{-1}$

Unimolecular reactions A's in sec^{-1}.

** Units are in Kcal/mole.

TABLE 6.8. RATE CONSTANTS FROM THE CALCULATION OF QRRK FOR THE REACTION:

$CH \equiv CH + H$ ------> PRODUCTS

	PRODUCTS	C2H3
A	76 TORR	2.37E+11
	760 TORR	1.70E+12
	2000 TORR	2.74E+12
n	all pressures	0.0
Ea	76 TORR	-3.23
	760 TORR	-1.35
	2000 TORR	-0.781
	(Kcal/mole)	

Rate constant represents a best fit to non linear equation:

$$k = A\,T^{n} \exp(-Ea/RT)$$

A units of $cm^{3} mole^{-1} sec^{-1}$ for the biomolecular product channels and sec^{-1} for unimolecular reactions.

Temperature range: 600^{o}K to 2000^{o}K.

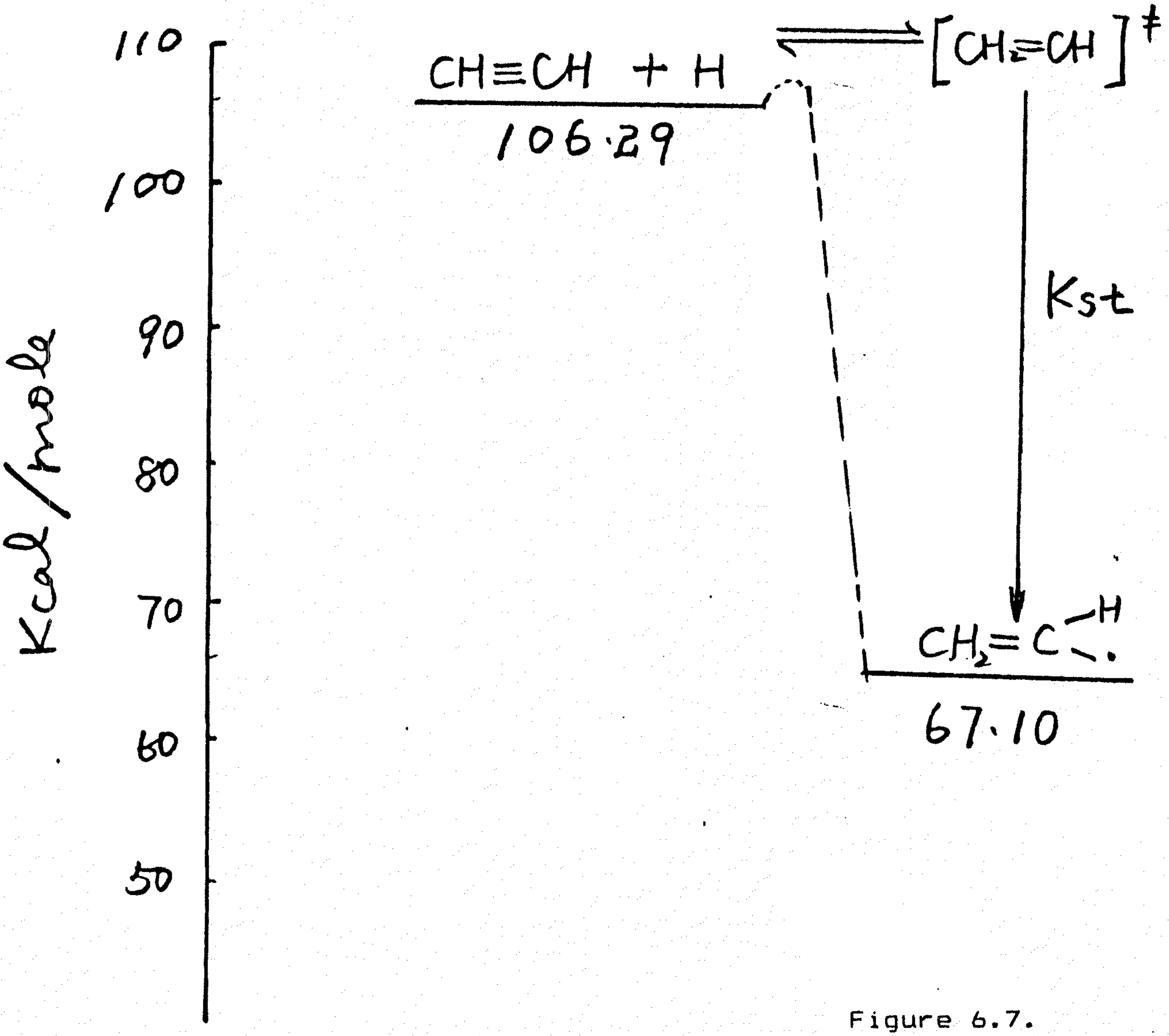

110
100
90
80
70
60
50
Kcal/mole
CH≡CH + H
106.29
[CH₂=CH]‡
Kst
CH₂=C–H
67.10

Figure 6.7.

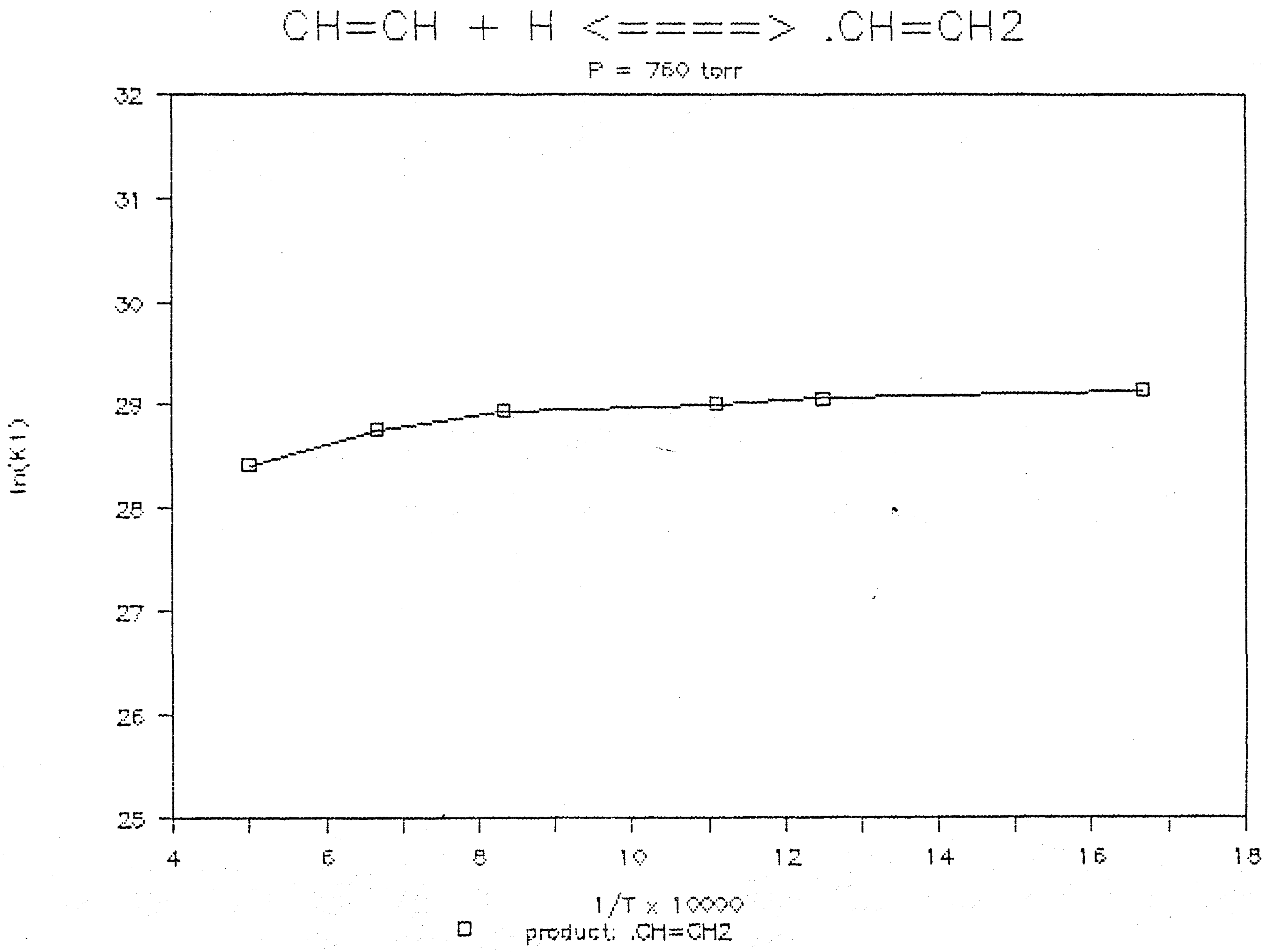

CH=CH + H <====> .CH=CH2
P = 760 torr
ln(k1)
32
31
30
29
28
27
26
25
4
6
8
10
12
14
16
18
1/T x 10000
□ product: .CH=CH2

Figure 6.8.

7. CONCLUSIONS

The pyrolysis reactions of chloro- and dichlorobenzene were conducted in a 1.05 ID tubular flow reactor at the temperature range from 850°c to 925°C under one atmosphere pressure of either hydrogen or helium. The reaction products, especially light hydrocarbons, were analyzed by an on-line FID detection gas Chromatograph. Furthermore, the soot products were analyzed by GC/Mass. Major products were soot and benzene from the chlorobenzene system, and benzene, chlorobenzene, and soot from the dichlorobenzen system, the soot yield reached over 50% at the temperature of 925°C from chloro- or dichlorobenzene. The light hydrocarbon products from the pyrolysis of chloro and dichlorobenzene were identified as CH4, C2H2, C2H4 AND C2H6. C2H2 only appeared in the helium bath gas reaction system. All those light hydrocarbons account for less than 5% of the initial reagent.

It was found that hydrogen bath gas reactions increased the decomposition rate of chlorobenzene and dichlorobenzene and also significantly inhibited the formation of soot products.

A variety of soot products were collected and then analyzed by GC/MS. They were identified as both acetylene polymers fused aromatics and polyphenyls. The Arrhenius kinetic eqauation for the decomposition of chlorobenzene and dichlorobenzene were obtained as follows:

chlorobenzene in H2: $k_{exp} = 9.1\times10^{10}\exp(62/RT)$

dichlorobenzene in H2: $k_{exp} = 4.1 \times 10^{12} \exp(65/RT)$

where Ea is in Kcal/mole unit.

The pyrolysis of acetylene in hydrogen at one atmosphere was also studied in the temperature range from 700°C to 900°C. The destruction of acetylene reached nearly 100% at the residence time of 0.9 seconds and at 900°C. As the light products from the pyrolysis reaction of chloro and dichlorobenzene in hydrogen, the major products are CH_4, C_2H_4, C_2H_6 and soot compounds. No significant amount of benzene or its byproducts were observed. Data from the pyrolysis of acetylene in hydrogen showing the product distribution versus residence time and temperature of the reactions are presented. The Arrhenius rate equation for the decomposition of acetylene was obtanted as follows:

$$k_{exp} = 5.34 \times 10^{8} \exp(-43.5/RT)$$

in which, Ea is in Kcal/mole unit. In addition, the reaction pathways to form these light hydrocarbons are proposed to explain their generation. These pathways are believed to be feasible to describe the formation of the C1 - C2 products from the decomposition of chloro and dichlorobenzene in hydrogen systems. The soot products from acetylene were identified as polyacetylenes (including fused aromatics) and the similar compounds with methyl group. The soot yield reached around 10% at a temperature of 900°C.

The thermal decomposition of benzene was conducted under one atmosphere pressure at the temperature range from 850°C to 1000°C. Up to 30% benzene was converted to soot products, which was the only major product from benzene pyrolysis in hydrogen at our reaction temperatures. These soot products are identified to be polyphenyls and polycyclic aromatic hydrocarbons. A reaction mechanizm is proposed to describe the pyrolysis of benzen in hydrogen at the temperature range of 850°C to 1000°C.

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