THERMAL DECOMPOSITION OF ETHYLENE

by

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PREFACE

The kinetics of the thermal decomposition of olefins are complex and yet most fundamental for the understanding of the problem of thermal decomposition of hydrocarbons. Ethylene, as the simplest member of the olefin homologs, exhibits some unique characteristics. The problem of the ethylene pyrolysis has been investigated since the early 1930's, yet little advance was made in the understanding of the reaction mechanism.

The present investigation of the thermal decomposition of ethylene was made using modern analytical techniques to measure the rates of formation of products. The scope of this study was to establish from the kinetic data reaction steps for the formation of the major products and compose a reaction mechanism for the thermal decomposition of ethylene which is able to interpret both the data of this study and of previous work. The study concluded that the reaction is mainly a radical chain polymerization. The bimolecular reaction of ethylene to form ethyl and vinyl radicals is considered to be the main initiation at first but the secondary decomposition of the olefinic products gradually becomes significant. Other secondary reactions form stable aromatic hydrocarbons. The characteristic of the propagation reactions in ethylene is the ready addition of radicals to ethylene. The propagation steps also include decomposition of radicals and hydrogen abstraction from ethylene. The decomposition of one radical can produce more than one product

and the decomposition of several different radicals may contribute to the formation of the same product. The combinations of ethyl and vinyl radicals are the main termination steps. Secondary initiation of olefins is suggested to explain the unusually long induction periods found in the ethylene pyrolysis in the formation of the major products.

ACKNOWLEDGMENTS

This work was done under the ardent direction of Dr. Margaret Back, who led this work persistently. For this and the valuable discussion during the whole process of the preparation of the thesis, the author wishes to express her appreciation.

I would also like to thank my husband for his encouragement.

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ABSTRACT

The thermal decomposition of ethylene was studied over the pressure range 15 to 60 cm and at 501 to 584°C. The identification and measurements of major products were made by chromatographic analysis incorporated with mass spectrometric analysis. The rates of formation of the major products, including ethane, propylene, butene, butane and butadiene at various conditions, were determined from measurements of the yield as a function of time. The orders and activation energies of the rates of formation of these products were calculated. A radical polymerization mechanism for the thermal decomposition of ethylene is proposed. The experimental order and activation energies of the reaction rates were shown to be consistent with the proposed radical polymerization mechanism.

According to this mechanism the initiation reaction is a bimolecular reaction of ethylene to form ethyl and vinyl radicals. The propagation steps include:

(1) addition of the ethyl and vinyl radical to one or more ethylene molecules to form larger alkyl and alkenyl radicals;

(2) decomposition of the larger alkyl radical to form an olefin and a smaller alkyl radical;

(3) decomposition of the large alkenyl radical to form a diolefin and an alkyl radical, or an olefin and a smaller alkenyl radical, and

(4) hydrogen abstraction by the alkyl radical from ethylene to form a saturated hydrocarbon and a vinyl radical.

Termination of the chain is caused by the combination of radicals. A constant rate for the formation of propylene, butene, butadiene, butane and ethane is reached after an unusually long induction period. The induction period can be explained by the proposition that there is secondary dissociation of major olefinic products, especially butene.

The specific rate constant for the hydrogen abstraction by ethyl radicals from ethylene, k_a, and for the decomposition of the butenyl radical, k'_{2a} , are estimated in this study to be:

$$k_a = 4 \times 10^{10} e^{-13000/RT} \mathrm{cc.mole^{-1}s^{-1}}$$

$$k'_{2a} = 6 \times 10^{14} e^{-35000/RT} \mathrm{sec^{-1}} .$$

INTRODUCTION

History of the Thermal Decomposition of Hydrocarbons

Chemists have been interested in the thermal decomposition of hydrocarbons for almost one hundred years. During this time much knowledge has been accumulated, especially concerning the saturated hydrocarbons. Nevertheless a detailed mechanism expressed as a series of elementary reaction steps has rarely been completely accepted for any compound, at least not until recent years. The mechanisms for unsaturated hydrocarbons are even more uncertain and in fact a quantitative description by a detailed mechanism has not been established for any olefin. Quantitative description of the mechanism is very difficult since the reactions of olefins are more complex than those of paraffins. The thermal decomposition of olefins is more complex because of the unique addition reactions leading to polymerization. The relative instability of the higher molecular weight products may cause secondary initiation. The overall mechanism and the individual reaction steps are still under intensive study by chemists.

Saturated Hydrocarbons

During the past hundred years, many mechanisms for the thermal decomposition of hydrocarbons have been suggested and amended as more accurate data were obtained. The earliest proposal was that of Berthelot in 1866 (1), who suggested the formation of acetylene as an intermediate in every hydrocarbon decomposition together with polymerization to more complex hydrocarbons and their subsequent decomposition. This over-simplified proposition could not be accommodated as more accurate analytical data were obtained.

The next concept in the mechanism of hydrocarbon decomposition was the direct molecular rearrangement (2). By this mechanism decomposition occurred by a break in the hydrocarbon chain accompanied by the simultaneous shift of a hydrogen atom to produce an olefin and a shorter chain saturated hydrocarbon or hydrogen. Some early workers contended that the primary break always occurred at the terminal C-C bond to produce methane (3); later workers thought that in general the hydrocarbon chain might rupture in any position. The molecular mechanism seemed particularly attractive in those cases where the experimental activation energies were somewhat lower than the endothermicity of the bond-breaking reaction. The molecular mechanism (4, 5) is still discussed in some cases although in the thermal decomposition of saturated smaller straight chain hydrocarbons it is now usually considered incompatible with the results of modern technical analysis.

The concept developed next was that of free radical intermediates. This concept was given quantitative expression by Rice and Herzfeld (6), who considered that methyl, ethyl, propyl and similar higher alkyl radicals are the main reaction intermediates in the decomposition of hydrocarbons. They suggested that when saturated hydrocarbons and derivatives such as aldehydes, amines, ethers and ketones were decomposed at atmospheric pressure or lower in the temperature range 450 - 750°C, the reaction was initiated by a homogeneous dissociation of a C-C bond to give two free radicals. All radicals except methyl or ethyl then decomposed rapidly into olefins and either methyl or ethyl radicals or hydrogen atoms. The position of bond breaking is at the weakest bond. The reaction is a chain reaction carried by radicals or hydrogen atoms. This original concept is still widely accepted as a framework for formulating reaction mechanisms.

Some time ago it was proposed (4, 5) that the thermal decomposition of alkanes takes place by two concurrent processes; one a molecular mechanism and the other a free radical chain mechanism. The addition of sufficient quantity of an inhibitor, such as nitric oxide or propylene, was thought to halt the radical chain process without affecting the rate of the molecular reaction. It is now known, however, that in many instances a molecular mechanism is incompatible with the results of mass spectrometric experiments (7), isotope exchange experiments (8) and detailed analytical studies of the reaction products (9). It seems that many of the so-called 'fully inhibited' reactions also involve free radicals, and are variants of the uninhibited reaction mechanism. Free radical processes can satisfactorily describe the fully inhibited reaction.

The kinetics of the thermal decomposition of low molecular weight saturated hydrocarbons have been studied quite extensively (10 - 17). The initial process seems to involve the fission of a carbon-carbon bond to give two radicals. These radicals then abstract hydrogen or decompose as chain propagation reactions, and termination occurs mainly by combination of low molecular weight radicals. The main radicals are saturated radicals, and the products mainly alkanes and alkenes. The energies of activation of these decompositions lie in the range 50 - 80 kcal per mole. There is now general agreement on the mechanism for the uninhibited thermal decomposition of ethane, propane and butane (10, 15, 17).

The thermal decomposition of the simplest hydrocarbon, ethane, is the one most thoroughly studied (10 - 14). From the rates of production of methane and butane in the decomposition of ethane Lin and Back (10) concluded that methane is a measure of the initiation reaction and that the combination and disproportionation of ethyl radicals is the main termination step. The proposed mechanism is:

$$C_2H_6 \rightarrow 2\,CH_3 \tag{1}$$

$$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5 \tag{2}$$

$$C_2H_5 \rightarrow C_2H_4 + H \tag{3}$$

$$H + C_2H_6 \rightarrow H_2 + C_2H_5 \tag{4}$$

$$C_2H_5 + C_2H_5 \rightarrow C_4H_{10} \tag{5a}$$

$$\rightarrow C_2H_4 + C_2H_6 \tag{5b}$$

$$k_1^{\infty} = 1 \times 10^{16}\, e^{-86000/RT} \quad s^{-1}$$

$$k_3^{\infty} = 3.8 \times 10^{13}\, e^{-38000/RT} \quad s^{-1}$$

where k^{∞}'s are the first order rate constants in the high pressure limit. Because ethylene is much more reactive than ethane, secondary reactions occur at an early stage in the reaction of ethane. The secondary products include methane, propylene, butane, butene, butadiene, and acetylene.

The proposed mechanisms for the thermal decomposition of propane and butane are radical chain reactions similar to that of ethane (10 - 13). The initiation step of the propane reaction is:

$$C_3H_8 \rightarrow CH_3 + C_2H_5$$

and the initiation step of the butane reaction is:

$$C_4H_{10} \rightarrow 2\,C_2H_5$$

These chains are carried by abstraction and decomposition reactions of the radicals and terminated by combination of radicals.

In view of the facts that (1) olefins are usually the primary products in the decomposition of saturated hydrocarbons, (2) olefins are often used as a radical trap in kinetic studies, and (3) many olefins are more reactive than saturated hydrocarbons, knowledge of the thermal reactions of olefins is necessary in order to understand more thoroughly the thermal decomposition of hydrocarbons.

Unsaturated Hydrocarbons

The thermal decomposition of alkenes differs from that of the alkanes in many ways. For example, carbon-hydrogen fission can be an important initiating step. In the thermal reaction of propylene and butene-2 the most important primary processes seem to be the fission of the allylicC-H bond.

$$C_3H_6 \rightarrow H + C_3H_5$$

$$CH_3CH = CHCH_3 \rightarrow CH_2CH = CHCH_3 + H$$

With 1-butene and other higher alkenes, two processes are important: the rupture of the allylic C-H bond and the fission of the allylic C-C bond. The allylic C-C bonds in alkenes have bond dissociation energies at least 15 kcal mole^{-1} smaller than that of any other C-C bond in the molecule and their fission is therefore favored. Similarly the allylic C-H bonds in alkenes have dissociation energies smaller than other C-H bonds. The most important primary processes are, therefore:

$$RCH_2CH = CH_2 \rightarrow RCHCH = CH_2 + H$$

and

$$RCH_2CH_2CH = CH_2 \rightarrow RCH_2 + CH_2CH = CH_2$$

Free radical chain mechanisms for the pyrolysis of isobutene (18), butene-1 (19) and butene-2 (20, 21) have been proposed. Molera and Stubbs (22) investigated the kinetics of the thermal decomposition of C_2 to C_4 olefins and of pentene-1, 2-methyl butene-1, 3-methyl butene-1, hexene-1 and heptene-1. The work was done at pressures lower than atmospheric and between 450 - 570°C. The change in pressure of the system was followed. It was reported that in all cases the reactions are first order down to quite low pressures where a transition towards second order occurs. The activation energies for decomposition of the olefins are between 50 and 66 kcal mole^{-1} except that of ethylene which is a unique case. The activation energy for decomposition of butene-1 is 66 kcal mole^{-1} and that for butene-2, 56 kcal mole^{-1}.

Other methyl-substituted butene-1's seem to have very similar activation energies. Among the linear 1-olefins, the activation energy shows a small decrease as the carbon number in the series increases. The rate of polymerization of ethylene was studied by a similar pressure measurement and the reaction was found to be exactly second order in the temperature range 623 - 713°C and at pressures of 50 to 500 mm.

Propylene is the olefin most often investigated. Ingold and Stubbs (23) described the reaction as a homogeneous first order molecular process. Later, Laidler and Wojciechowski (24) observed a reaction order of 3/2 and suggested a free radical chain process. The mechanism proposed was:

$$\begin{aligned}
C_3H_6 &\rightarrow C_3H_5 + H \\
H + C_3H_6 &\rightarrow C_3H_7 \\
C_3H_7 &\rightarrow H_2 + C_3H_5 \\
C_3H_7 &\rightarrow C_2H_4 + CH_3 \\
CH_3 + C_3H_6 &\rightarrow CH_4 + C_3H_5 \\
C_3H_5 + C_3H_6 &\rightarrow \text{Higher Products} + H \\
H + C_3H_5 &\rightarrow C_3H_6
\end{aligned}$$

The mechanism accounted satisfactorily for the observed activation energy and the rates of formation of the individual reaction products.

Purnell and co-workers (25) made a detailed analysis of the products of the thermal decomposition of propylene in the temperature range 555 - 640°C at initial pressures between 7 and 100 mm Hg. From the measurements of pressure change the following expression was obtained:

$$\frac{-d[C_3H_6]}{d\,t} = 10^{14.06}\,[C_3H_6]^{1.4}\,e^{-58600/RT}\ \text{mole.}\,\text{cc}^{-1}.\,\text{s}^{-1}$$

A long chain free radical mechanism was proposed in which reactions of the 1-methyl-4-pentenyl radical are of the prime importance. The main chain termination reaction suggested was the combination of methyl and alkyl radicals, which is the chief difference from the mechanism of Laidler and Wojciechowski. Likely routes to the formation of cyclopentadiene and aromatic compounds were also suggested.

Ethylene

The C-C dissociation energy of ethylene is about 130 kcal mole^{-1} (26). The π bond is relatively strong, as shown by the relatively high activation energy for *cis*-*trans* isomerization. This was measured by Douglas, Rabinovitch and Looney (27) from 450 - 550°C over a pressure range of 0.9 cm to 31 cm Hg. They found a high pressure limit of E_a = 65 kcal, $A = 10^{13}$ sec^{-1}. The ethylene molecule itself has a comparatively high reactivity. The H-C-H bond angle of ethylene observed is 116.7 ± 0.7° rather than the 120° predicted for a pure sp^2 bond. This structure and the high π-bond electron density may be the reason why the ethylenic π-bond is a rather active one.

In 1931 the rate of polymerization of ethylene was measured by Pease (28) at 2.5, 5 and 10 atmospheres and at temperatures from 350 - 500°C. It was found to be a second order reaction. The activation energy was estimated as 35 kcal mole^{-1}, which is abnormally low for a hydrocarbon decomposition. The author also reported that in experiments at atmospheric pressure the decrease in pressure was more rapid than calculated from second order kinetics.

Using an exhaustively purified ethylene sample, Storch studied the kinetics of ethylene polymerization in 1934 (29). He also found that the rate was second order in ethylene with an activation energy of 43.5 kcal mole^{-1}. Furthermore, the polymerization showed an induction period. The author suggested the existence of a moderately stable intermediate compound to explain this induction period.

In 1942 Burnham and Pease (30) observed that the presence of nitric oxide partially inhibited the rate of the thermal decomposition of ethylene. They suggested that the reaction involved free radicals. On the other hand, in 1956 (31) Silcocks proposed the following reaction steps for the thermal decomposition of ethylene:

$$\begin{aligned} 2C_2H_4 &\rightarrow C_4H_8 \\ C_2H_4 + C_4H_8 &\rightarrow 2C_3H_6 \\ &\rightarrow \text{polymer} \end{aligned}$$

The studies before 1956 were made without the benefit of analysis by gas chromatography. The overall reaction rate was determined by following the pressure change in the reactor and the products were analyzed by conventional chemical analysis. By this technique, the composition of primary products and their concentrations during the course of reaction cannot be determined with certainty.

In 1958 Dahlgren and Douglas (32) studied the thermal reactions of ethylene at 480 - 582°C, following the reaction with mass spectrometric analysis. For the first time an important product, butadiene, was found as a primary product together with propylene, butene and ethane. They claimed to have confirmed that free radical processes were involved in forming the primary products. The overall rate was second order in ethylene and the activation energy was 41.1 kcal mole^{-1}. The rate of formation of propylene was second order with respect to ethylene. The mechanism suggested was:

$$2C_2H_4 \rightarrow C_4H_8^*$$

$$C_4H_8^* + C_2H_4 \rightarrow 2C_3H_6$$

$$C_4H_8^* + C_2H_4 \rightarrow C_4H_6 + C_2H_6$$

The decomposition of ethylene has also been studied in the temperature range 1027 - 1527°C by Skinner and Sokoloski in 1960 (33), and in the temperature range 1437 - 1897°C by Gay et al in 1966 (34), both using a shock tube technique. In this temperature range acetylene and hydrogen are the main products and the rate is first order in ethylene.

Recently Halstead and Quinn (35) reported a kinetic investigation of the thermal decomposition of ethylene in the pressure range 1.02 - 26.9 cm and the temperature range 525 - 651°C. They used a gas chromatographic technique to analyze the main reaction products, and suggested a degenerately branched chain mechanism. This mechanism is compared with the proposed mechanism of this thesis in the Discussion section.

Reactions of Alkyl Radicals with Ethylene

Studies on the thermal decomposition of saturated hydrocarbons and radicals by various methods have established much valuable kinetic data. Measurements of rate constants, frequency factors and activation energies of elementary reactions are useful in the understanding of the mechanism of the thermal decomposition of olefins. Unfortunately, the measurements have been mainly limited to saturated alkyl radicals, and these studies have been reviewed by Kerr and Trotman-Dickenson (36). There is little information on unsaturated radicals, such as vinyl, allyl and butenyl radicals.

The additions of alkyl radicals to ethylene have been reported in several studies. The addition of ethyl radicals to ethylene was studied by Lampe and Field (37) who used azoethane photolysis as a source of ethyl radicals and found an activation energy of addition of 5.5 kcal mole^{-1}. This reaction was also studied by Kerr and Trotman-Dickenson (38), who used the photolysis of propionaldehyde as a source of ethyl radicals and reported an activation energy of 8.6 kcal mole^{-1}. The additions of isopropyl and n-butyl radicals to ethylene were studied by the photolysis of isobutyraldehyde and valeraldehyde in the presence of ethylene (39 - 41). Most recently, Watkins and O'Dean (42) have reported a study on the kinetics of the addition of ethyl, isopropyl, n-butyl and isopentyl radicals to ethylene. All the above studies were made in the temperature range of 50 - 300°C. In this temperature range, the polymerization of ethylene was considered to be limited. The activation energies and frequency factors obtained in these studies are not in very close agreement, probably because of the uncertainties in the mechanism of each study and the difficulty in measuring all the products of the subsequent polymerization. The activation energy for the addition of C_1 to C_5 alkyl radicals to ethylene seems to lie in the range between 6.8 - 7.6 kcal mole^{-1} and the frequency factor between 7×10^{10} - 2×10^{11} cc mole^{-1}s^{-1}. This agrees with the prediction that the addition reactions of small alkyl radicals to ethylene have similar reactivity. Watkins and O'Dean concluded that the activation energy and frequency factor are probably independent of the alkyl radicals. The addition reaction of unsaturated radicals to ethylene is equally important in the thermal decomposition of ethylene. Unfortunately not many data on these radicals are available in the literature.

The radicals also undergo hydrogen abstraction from ethylene. This reaction has not been well studied. Hydrogen abstraction from ethylene by methyl radicals has been reported by Trotman-Dickenson and Steacie (43) employing the photolysis of deuteroacetone over the temperature range of 180 - 340°C. The activation energy estimated was 10.0 kcal mole^{-1} and the steric factor ratio was $P_1/P_2 = 9 \times 10^{-4}$, where P_2 is that for methyl combination.

The addition reactions of alkyl radicals to ethylene have lower activation energies than those of hydrogen abstraction from ethylene. The addition reaction may prevail at lower temperatures, but hydrogen abstraction from ethylene will become competitive at higher temperatures.

Purpose and Achievement

The purpose of this investigation was to obtain a general understanding of the reactions involved in the thermal decomposition of ethylene. It was hoped that a reaction mechanism could be proposed which would account for the formation of the major products.

The thermal reactions of ethylene, however, are complex and the reaction mechanism proposed in this thesis is not considered to be complete. Nevertheless the thesis contains new information which aids the understanding of the ethylene reaction and which may be valuable for studies of the thermal reactions of other hydrocarbons.

From the rates of formation of the major products and the existence of constant rates of formation in some cases, the primary products have been distinguished from the secondary products. Unusually long induction periods were observed in the formation of some major products. This was interpreted as caused by the secondary reaction of unstable olefinic products. The rates of formation, orders of reaction, and activation energies of individual major products were determined and a radical polymerization-decomposition mechanism which is compatible with the experimental results is proposed.

EXPERIMENTAL

Apparatus

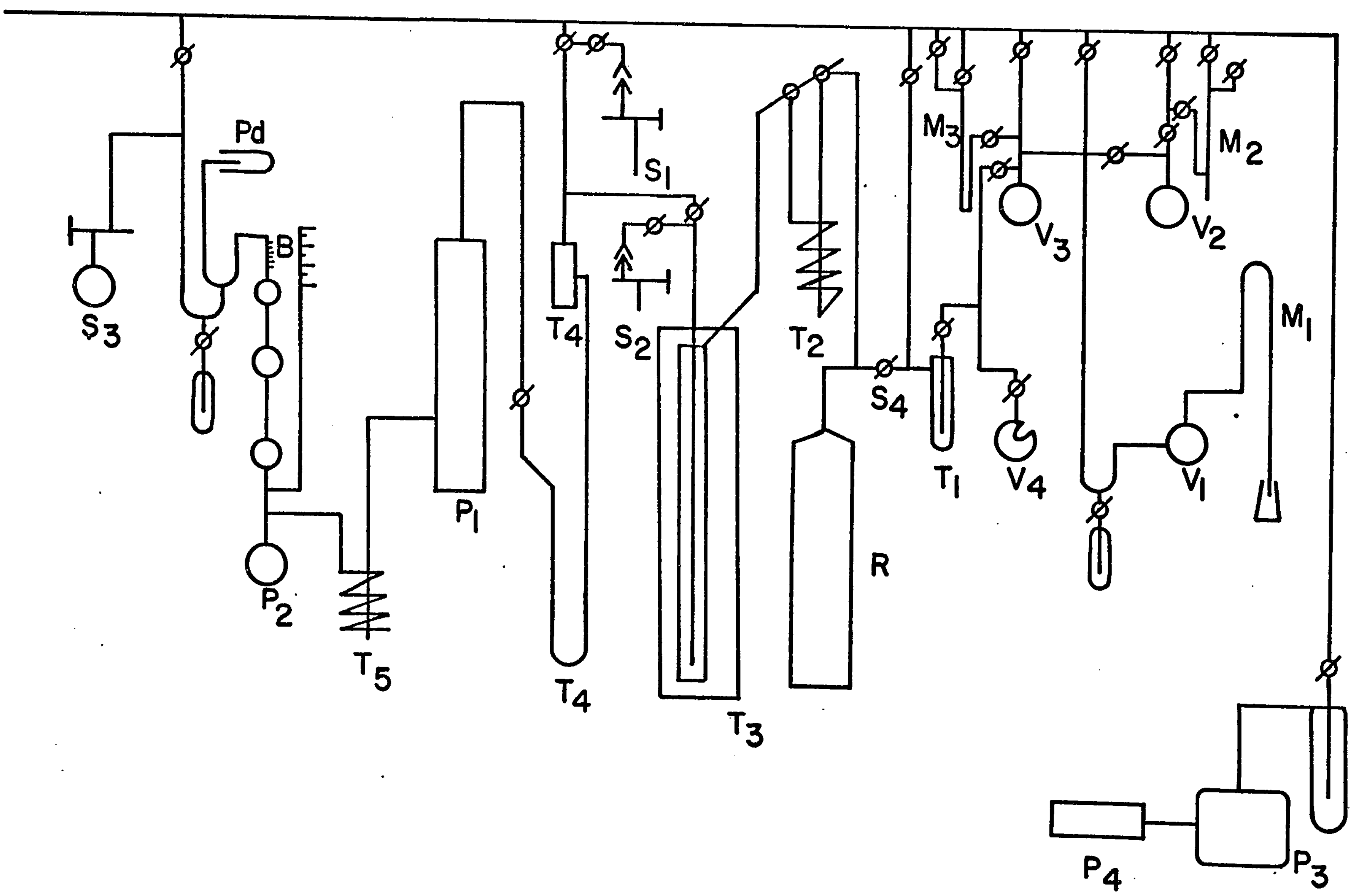
A schematic diagram of the apparatus is shown in Figure 1. The apparatus consisted of storage flasks V_1 and V_2, mixing flasks V_3 and V_4, reaction vessel R and an analytical system. Each portion was joined directly to the vacuum manifold for prompt evacuation. The main vacuum pumping system consisted of an Edwards type 203 oil diffusion pump P_3 backed by a Welch rotary pump P_4 (series no. 446-4) which provided a backing pressure of about 2×10^{-2} mm mercury. This pumping system maintained a vacuum in the whole system of at least 10^{-5} mm Hg.

Ethylene was stored in the 5 liter flask V_1 which was isolated from the rest of the system by a mercury cut-off. Other gases were stored in the 2 liter flask V_2. Before reaction, the required amount of reactant gas was measured into flask V_3, which was equipped with a mercury manometer M_3. Parallel to flask V_3 was a mixing flask V_4 equipped with an inner-sealed cold finger. Gases to be mixed were condensed on the cold finger and, on warming, sufficient convection currents were generated to ensure adequate mixing. Both flasks were joined to a trap T_1 which served as receiver during trap-to-trap distillation. Next to the trap T_1 was the reaction vessel R which was followed by the analytical system.

The analytical system was constructed to collect the reaction products which were condensable in liquid nitrogen and to analyze those which were noncondensable in liquid nitrogen. The condensable gases were collected in the LeRoy still T_3 (44). In between the

Figure 1.

The vacuum system.


S3
Pd
B
P2
T5
P1
T4
S1
S2
T4
T3
T2
R
S4
M3
T1
V4
V3
V2
M2
M1
V1
T
P4
P3

reaction vessel R and the LeRoy still T_3 was a spiral trap T_2 filled with Ascarite which served to remove carbon dioxide when it was added to the reactant. The condensable gases were removed from the system through sampling cells S_1 and S_2 and analyzed by gas chromatography.

The non-condensable gases were collected in gas burette B, aided by the mercury diffusion pump P_1, and the Toepler pump P_2. A U-trap T_4 preceding the mercury diffusion pump P_1, and a spiral trap T_5 following, both packed with copper turnings (1 mm dia.) were used to ensure complete trapping of the ethylene. The traps were of 1 cm diameter tubing and were approximately 1 meter in length. A palladium thimble, Pd, heated to about 300°C, was used to separate hydrogen from methane. The non-condensable gases could be removed from the system through the sampling cell S_3 for further analysis.

Silicone grease was used on stopcocks which came into contact with the products. Absorption of hydrocarbons is very low in silicone grease and loss of products in this way was kept to a minimum. Products were never allowed to stand at room temperature in contact with the grease but were kept frozen in liquid nitrogen except when actually being transferred.

The two reaction vessels were made of quartz tubing, 4.4 cm O.D., with volumes of 266.4 ml and 103.3 ml. The smaller reaction vessel was packed with quartz tubes giving approximately 8.5 times the surface to volume ratio of the unpacked vessel. Each reaction vessel had a central thermocouple well and was connected to the stopcocks with capillary tubing. The dead volume above the unpacked reaction vessel was estimated to be about 3 ml. The temperature of the reaction vessel was measured with a chromel-alumel thermocouple that had been calibrated at the melting points of zinc and lead. The potential of the thermocouple was measured by a Doran thermocouple potentiometer.

The reaction vessel was fitted into a hole drilled axially in a stainless steel cylinder 4 inches in diameter and 10 inches long. Around the steel cylinder was wound the heating coil which was wrapped with asbestos insulation. The power input to the coil was controlled with a Variac and regulated with a Thermo-Electric signalling controller. The sensing thermocouple of this controller was placed in a hole drilled in the stainless steel block close to the coil. The position assured the fastest response of the controller to small changes in the temperature of the block. This arrangement controlled the temperature of the block to within ± 0.5°C.

An F and M Model 720 Dual-Column Temperature-Programmed Gas Chromatography apparatus equipped with a thermal conductivity detector was used to analyze the condensable reaction products. The recorder was a Honeywell Continuous Balance Potentiometer with a calibrated accuracy of 5 microvolt for a span of 2 millivolt or less and a full scale response time of 1 second. At the maximum sensitivity of the bridge a peak height of the full scale of the recorder corresponded to approximately 2×10^{-6} mole of gas, with slightly less sensitivity for the higher molecular weight products. The limit of detection was therefore about 5×10^{-8} mole of gas, which corresponds to a yield of 2×10^{-10} mole cc^{-1}. The apparatus was calibrated by analyzing an accurately measured amount of hydrocarbon gas. Plots of the amount against the peak height were linear for most of the products analyzed. The estimated uncertainty in the calibration curves was about 5%. The uncertainty for ethane was slightly higher probably due to its very short retention time.

Materials

Research Grade ethylene from the Phillips Petroleum Company was used with two methods of purification. In the first method ethylene was degassed once in flask V_1 at -160°C, then two or three times more at -196°C. The purified ethylene was analyzed by gas chromatography using the silica gel-alumina column. The analysis indicated the absence of higher molecular weight compounds but the presence of 0.05 mole % of ethane identified by its retention time. The presence of ethane was not considered to have a significant effect on the rate of pyrolysis of ethylene, but corrections to the yield of ethane were made where necessary. In the second method, ethylene was distilled from V_3 at -160°C to T_1 at -196°C with continuous pumping before storage in V_1. The procedure was repeated with the ethylene used in every experiment just prior to the run. This was considered the best way to remove traces of oxygen and was used in all experiments except a few at 530°C. The average reproducibility using the second purification method was 7% for ethane, 1% for propylene and 0.4% for butene. These percentages include all the errors involved in the measurement.

The same purification procedure was followed for the deuterated ethylene. The isotope content of the deuterated ethylene was tested by mass spectrometric analysis. The mass spectra obtained was compared with the standard taken from "Index of Mass Spectral Data" published by the American Society for Testing and Materials. From the relative peak height analysis, the deuterated ethylene consisted of better than 99% C_2D_4.

Phillips Research Grade ethane was also purified by trap-to-trap distillation at -160°C after degassing at -196°C. No impurities were detected on analysis by gas chromatography.

The carbon dioxide was thoroughly degassed and distilled before use.

Procedure

To start the experiment, the whole system was evacuated to better than 10^{-5} mm Hg. The amount of ethylene needed for the experiment was condensed in the cold finger flask V_3 and then slowly distilled under vacuum into the trap maintained at -196°C. The distillation was an attempt to ensure the absence of oxygen in the reactant. It was then warmed and expanded into the reaction vessel through stopcock S_1 which was then closed after allowing about 5 seconds for equilibration. The pressure was measured on manometer M_3. The electric timer was started simultaneously with the admission of ethylene into the reaction vessel. After the desired reaction time the reaction vessel was opened to the analytical system and the timer stopped.

The reaction mixture was trapped in the LeRoy still at -196°C. The non-condensable gases, hydrogen and methane, were transferred with the aid of the mercury diffusion pump and Toepler pump into the gas burette, until the residual pressure in the LeRoy still or reaction vessel was approximately 5×10^{-4} mm. This procedure usually took not more than half an hour.

In a few experiments the hydrogen-methane mixture was checked for the presence of ethylene. The pumping time was prolonged to two hours and the gases collected were analyzed by gas chromatography on the silica gel column and in a few cases by mass spectrometry. The non-condensable gases were found to contain not more than 0.3 mole % of ethylene and ethane and this fraction was assumed to be negligible.

The total number of moles of hydrogen and methane together were measured in the gas burette B. Hydrogen was then allowed to diffuse out through the Palladium thimble kept at approximately 300°C. This was done by lowering the mercury cut-off connected to the top of the gas burette and admitting the hydrogen-methane mixture into the palladium thimble. Diffusion of hydrogen was continued until the amount of residual gas was constant, as measured on the gas burette. The procedure was checked with known mixtures of hydrogen and methane.

At initial ethylene pressures lower than 30 cm condensable products and unreacted ethylene were transferred without fractionation to the gas chromatography apparatus for analysis. At higher pressures the condensable reaction products together with the excess reactant in the LeRoy still were distilled at -170°C to remove some of the unreacted ethylene. Some ethane, together with about half the ethylene, was separated from most of the higher molecular weight hydrocarbons and collected in trap T_4. Both portions of these condensable gases were then transferred into the respective sampling cells S_1 and S_2 and removed for gas chromatographic analysis. This process reduced the ethylene to ethane ratio and facilitated the analysis of ethane.

The gas sample was introduced into the gas chromatographic apparatus through a U-trap of about 1 cm diam. tubing (Figure 2a). Two three-way stopcocks at either end of the U-trap allowed the trap to be evacuated and filled with the sample, while the flow of helium carrier gas by-passed the trap. The flow of helium could then be quickly switched to the U-trap to pick up the sample for analysis.

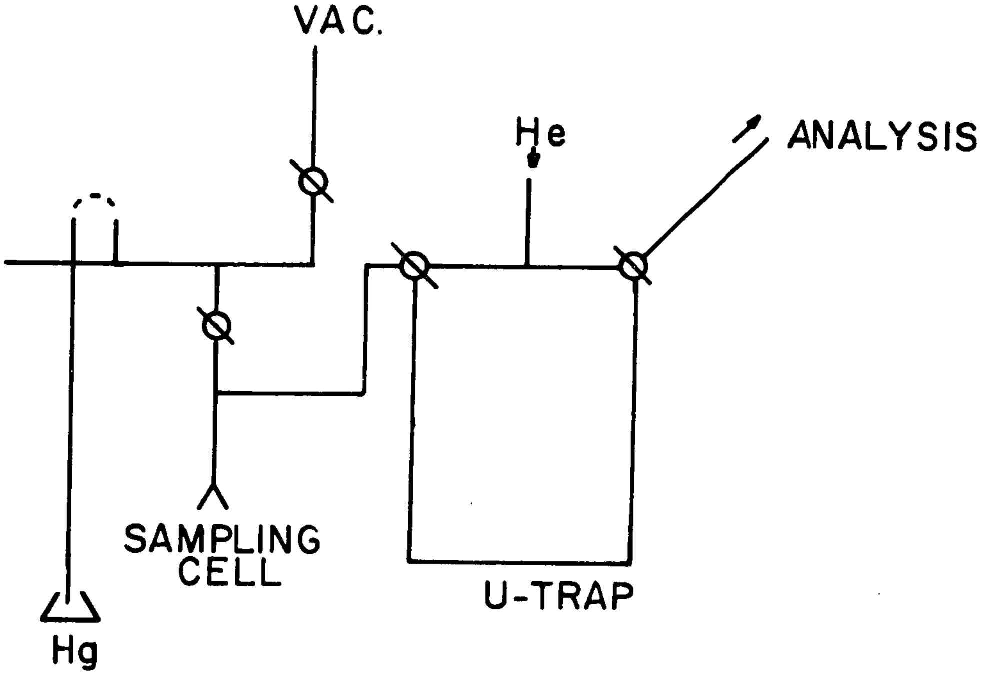
The gas chromatographic instrument was operated as follows. The carrier gas helium, dried by passing through a tube filled with molecular sieves, was maintained at a pressure of 40 psi at the cylinder and the flow controlled at a rate of 75 ml per minute in both reference and sample columns. The current through the detector was adjusted exactly to 150 milliamperes and the temperature of the detector to 150°C. When the gas sample was first introduced, the column was kept at room temperature for the first 6 minutes to facilitate the differentiation of the C_2 and C_3 fractions. Afterwards it was temperature-programmed at a rate of 4°C per minute from room temperature to 300°C. It was held at 300°C until no further products appeared. The highest molecular weight compound detected by this technique was believed to be C_9 or C_{10} hydrocarbons, which illustrates the range and relative amounts of products from an experiment of rather high conversion. Many of these products are secondary.

Figure 2a

Sampling system for gas chromatography analysis

Figure 2b

Trapping system for collection of samples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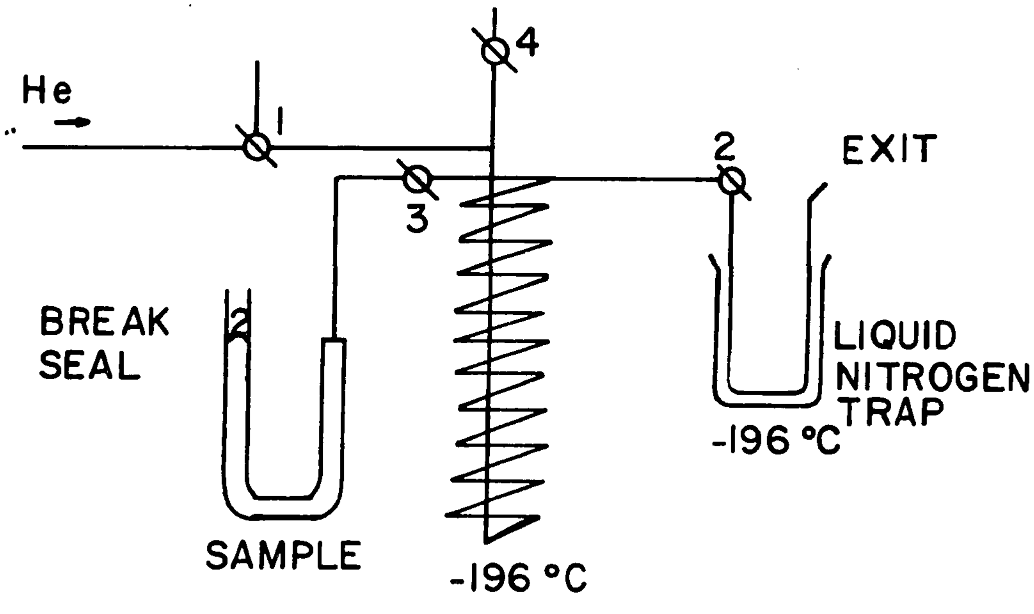
He
ANALYSIS
SAMPLING CELL
U-TRAP
Hg

2 a


He
4
1
2
EXIT
3
BREAK SEAL
2
LIQUID NITROGEN TRAP
-196 °C
SAMPLE
-196 °C

2 b

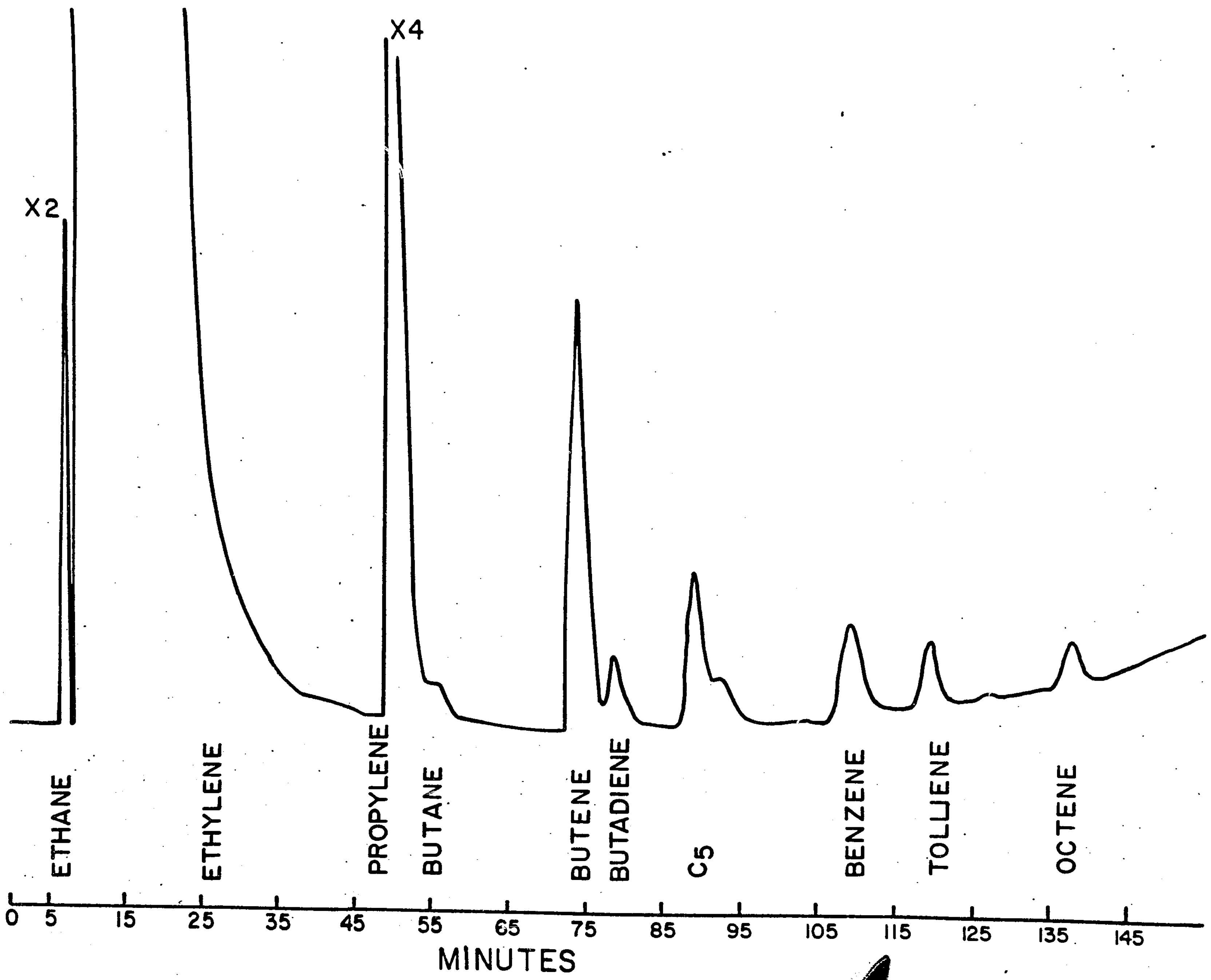
The trapping system to collect samples for mass spectrometric analysis is shown in Figure 2b. The spiral trap was 1 cm in diam. and 1 meter long. A liquid nitrogen trap was used to prevent back condensation of moisture into the system from the outside air. The trapped sample was then transferred, after evacuation of the helium, to another U-trap fitted with a break-seal, and sealed off under vacuum.

Several different columns were tried for separation and analysis of the range of C_2 to C_8 reaction products. The length of the column and flow rate of the carrier gas used were somewhat restricted because the higher temperature of the column required during the programming tended to reduce the flow rate of the carrier gas considerably. A compromise had to be made between the ability to separate isomers and the range of carbon number which could be analyzed within the allowed temperature range. This was achieved with a 35 inch x 1/4 inch silica gel-alumina column with silica gel at the entrance end. The combination of the silica gel and alumina was needed to separate the butenes from butadiene although either silica gel or alumina alone is adequate to separate saturated from unsaturated hydrocarbons through C_4. Typical analysis is shown in Figure 3.

Other columns used occasionally for identification purposes were: (A) a 20 ft. x 1/4 inch column packed with Firebrick coated with 10%, 2,5-hexadione. This column was operated at $0^{o}C$ isothermally. It separated cis and trans-butene-2, butene-1 and butadiene; (B) a 36 inch x 1/4 inch silica gel column was used isothermally at $30^{o}C$ to separate ethane and ethylene mixtures or methane and hydrogen mixtures.

Figure 3

Typical analysis of reaction products


X2
X4
ETHANE
ETHYLENE
PROPYLENE
BUTANE
BUTENE
BUTADIENE
C5
BENZENE
TOLUENE
OCTENE
0
5
15
25
35
45
55
65
75
85
95
105
115
125
135
145
MINUTES

RESULTS

General Description

More than two hundred and fifty pyrolysis experiments were made in order to study the dependence of the rates on pressure, temperature and reaction time. First, the range of reaction products was surveyed using gas chromatography and mass spectrometry to identify all the reaction products. Then quantitative determination of the products was made by gas chromatographic analysis to measure the rates of all the main products and the range of yields of the minor products.

The compounds identified by their mass spectra were ethane, propane, propylene, butane, 1-butene, butadiene, benzene and octene. The important components in the C_5 peak were pentene and 1,4-pentadiene. Preliminary analysis indicated the possible presence of 1-hexene, cyclohexene, cyclohexane, cyclopentene and 3-methyl-pentene-2. Since the single peak observed from the separation on the silica-gel-alumina column of compounds corresponding to C_5 and higher contained many isomers, identification of all these isomers was not possible by mass spectrometric analysis. The amounts of these compounds were generally small and hence their analysis was not pursued further. Toluene was identified by retention time comparison using the silica-gel-alumina column. The distinct separation of some compounds was checked by analyzing known mixtures. This was done for benzene and toluene, butene-1 and butadiene. Octene was also identified mass spectrometrically.

The absence of acetylene in the reaction products was confirmed after analysis of mixtures of small amounts of acetylene with large amounts of ethylene using the main silica-gel-alumina column. Cyclobutane was not separated from n-butane on the silica-gel-alumina column. Mass spectrometric analysis of the n-butane peak, however, showed that cyclobutane was not a major component of this fraction.

Ethane, propylene, butene, butane and butadiene are the major products, and constitute 90% of more of the products. The relative rates of formation of these compounds are shown in Table I for experiments at the highest and lowest reaction temperature investigated. At 501°C the products were ethane, propylene, butene, butane and a small amount of hydrogen. Methane, C_5-compounds, benzene and toluene together made up less than 1% of the products at 501°C. The yield of C_5 and C_6 compounds benzene, toluene, C_8, C_9 and C_{10} higher molecular weight compounds slowly increased with increase of temperature. The total yield of the minor products reached 26% of the total products at 584°C and 60 cm pressure.

The maximum mole percent conversion of ethylene was 3% at 501° and 6% at 584°C, except at the highest reaction pressure and longest reaction time where the data were not used in the measurements of the rates. The total ethylene conversion was obtained from the summation of all measured reaction products. The rates were measured within a much smaller range of percentage conversion. The total reaction rate was obtained from the plot of all ethylene converted to products against reaction time. The total reaction rates for the three reaction temperatures are listed in Table II.

Table I

Relative Rates of Formation of Primary Products

Ethylene Pressure 60 cm

Products	505°C	564°C	584°C
Ethane	1	1	1
Propylene	5.5	1.2	0.8
Butene	1.3	0.34	0.2
Butadiene	none observed	0.2	0.1
Butane	0.7	0.03	0.03

Table II

Total Rate of Conversion of Ethylene

Temp. °C	Maximum Conversion %	Pressure cm	Rate mole. cc^{-1}sec^{-1} x 10^{11}	Order w. r. t. ethylene	E kcal. mole^{-1}
501.6	3	60.7	86.7	2.3	40
		46.5	45.3		
		30.6	17.4		
		15.4	1.67		
563.6	6	60.4	434	1.8	
		30.5	140		
		23.0	77.0		
		15.0	35.7		
584.0	12	60.0	583	1.5	
		45.6	425		
		30.5	234		
		23.0	118		
		15.1	68.2		

From the double logarithm plot of the total reaction rate versus initial ethylene concentration, the reaction order with respect to ethylene at each temperature was obtained. The overall order was about 2 at 501.6°C and decreased to 1.5 at 584°C. This changing reaction order indicates a complex mechanism.

From the slope of the plot of the logarithm of the total rate against the reciprocal of the absolute temperature at 501.6 and 563.6°C, an activation energy of 40 kcal per mole was obtained for the pyrolysis of ethylene. This value for the activation energy is in good agreement with those obtained by other workers using pressure measurements (23).

Typical yield-time plots for the five major products, ethane, propylene, butene, butadiene and butane, are shown in Figures 4 to 9. The yield-time plots for propylene, butene and butadiene show that these products are formed with an induction period. After the induction period, however, the yield-time plots showed a well-defined linear region. The reaction rates of these compounds were defined as the rates when the yield-time curve of each product attained a constant value. A summary of these rates is given in Table III. The induction periods of ethane and butane were less apparent except at the higher temperature. At the initial stage of reaction, the yield-time curves of ethane and butane formation appeared linear, but after a short time curved upwards.

Figure 4.

Yield-time plot for the formation of ethane at 505.4°C

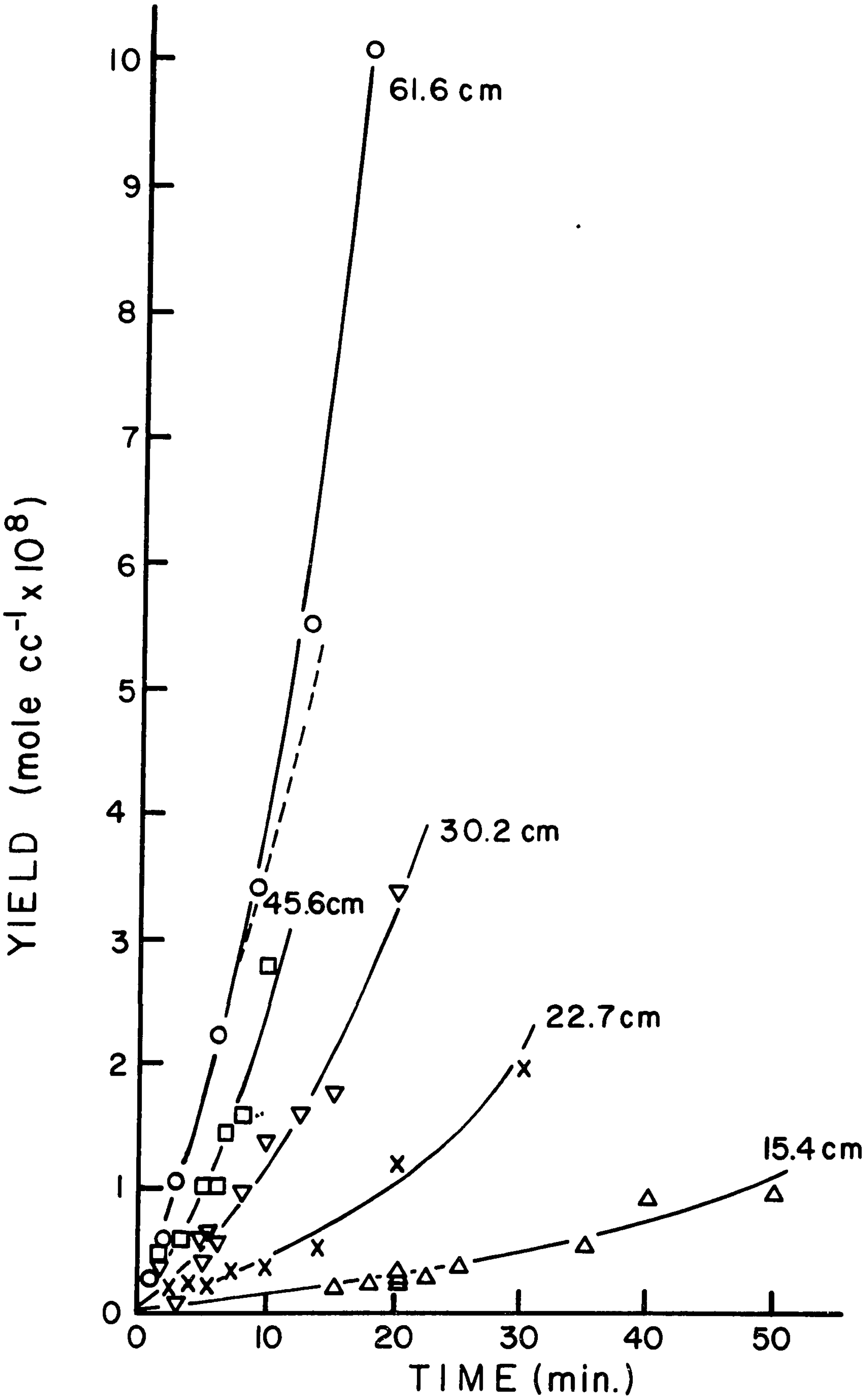

YIELD (mole cc^{-1} x 10^8)
TIME (min.)
61.6 cm
45.6cm
30.2 cm
22.7cm
15.4 cm
0
1
2
3
4
5
6
7
8
9
10
0
10
20
30
40
50

Figure 5.

Yield-time plot for the formation of ethane at 563.4°C

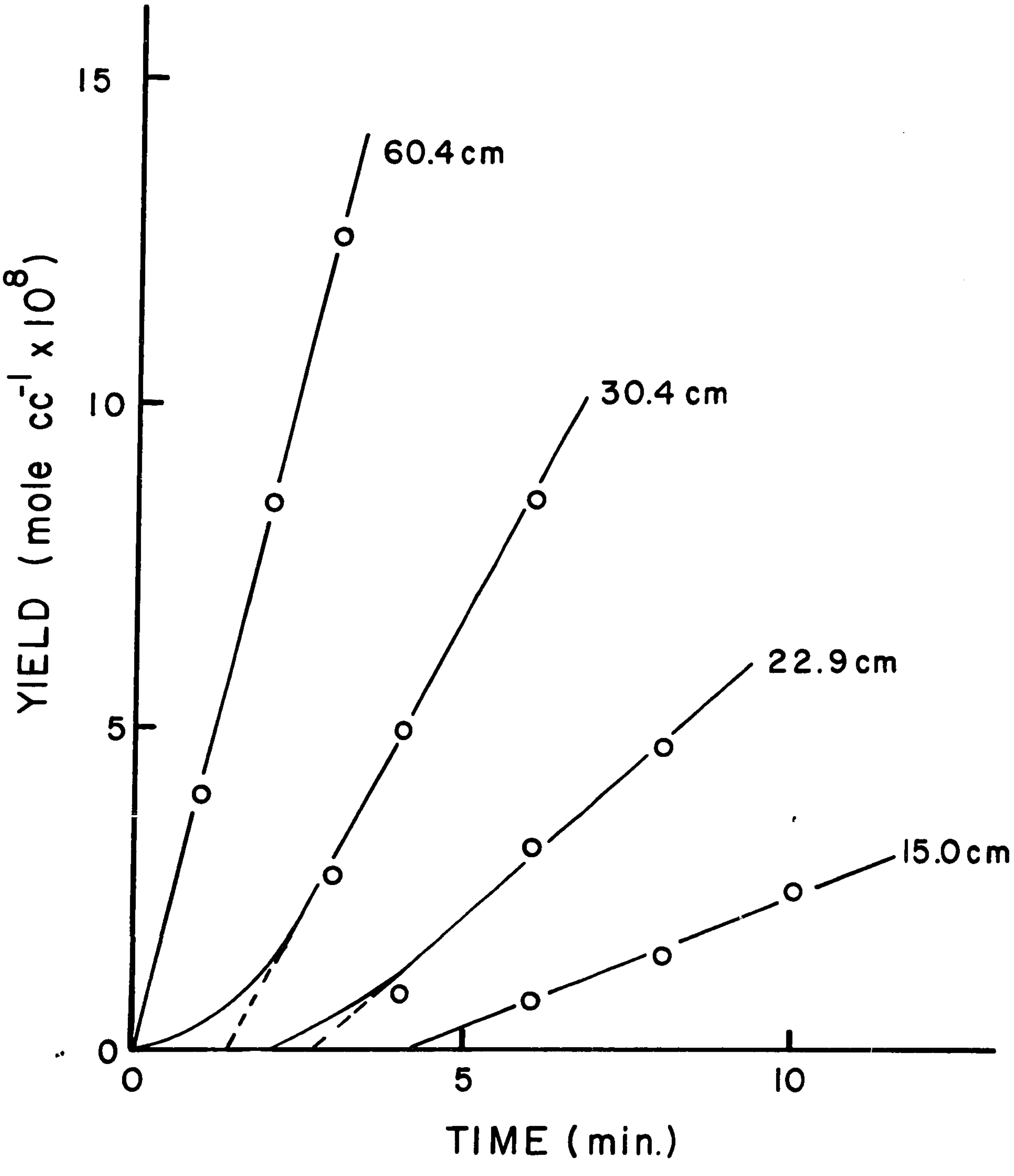

60.4 cm
30.4 cm
22.9 cm
15.0 cm
YIELD (mole cc⁻¹ x 10⁸)
15
10
5
0
0
5
10
TIME (min.)

Figure 6

Yield-time plot for the formation of propylene at 505.4°C

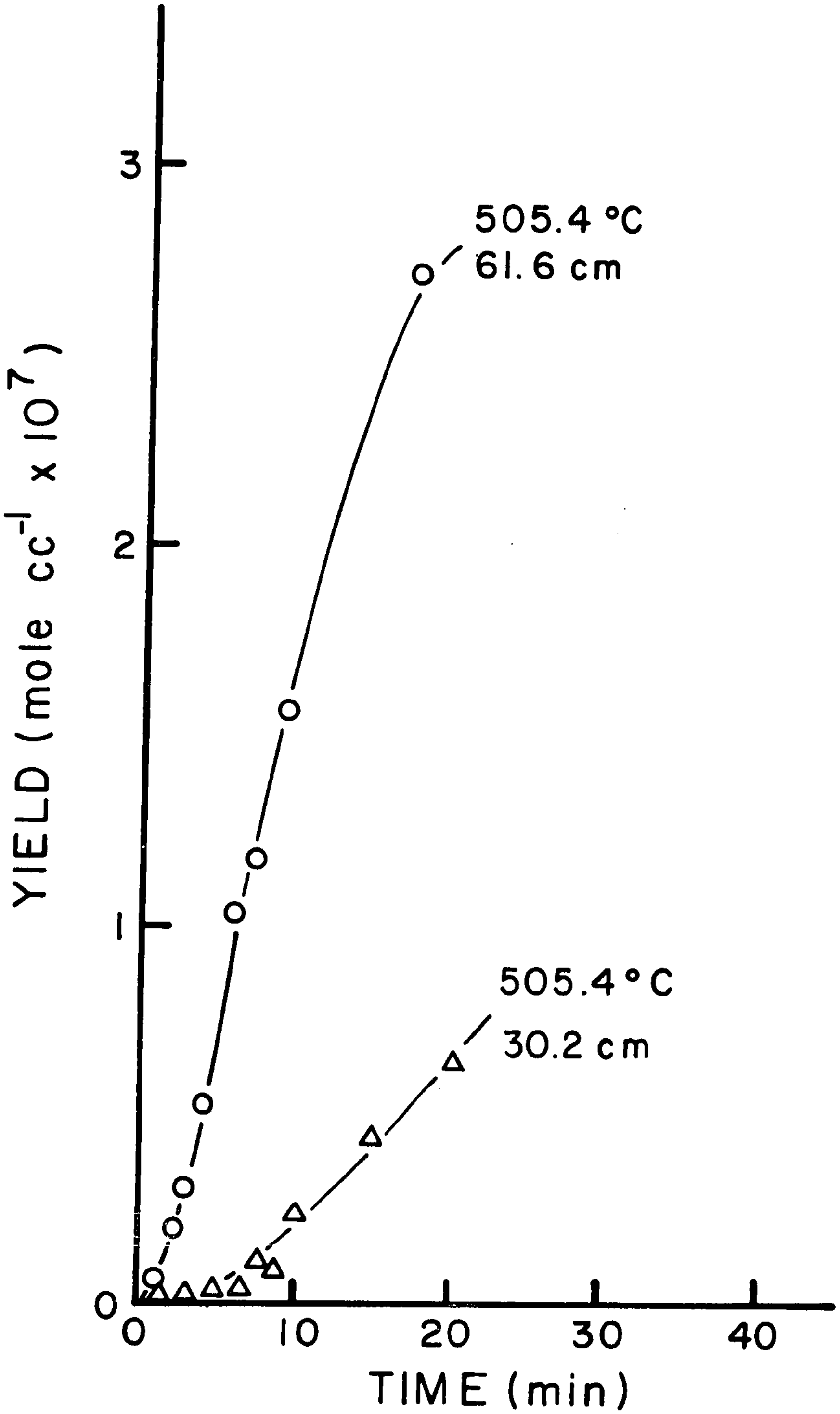

505.4 °C
61.6 cm
505.4 °C
30.2 cm
YIELD (mole cc^{-1} x 10^7)
3
2
1
0
0
10
20
30
40
TIME (min)

Figure 7.

Yield-time plot for the formation of butene at 505.4°C

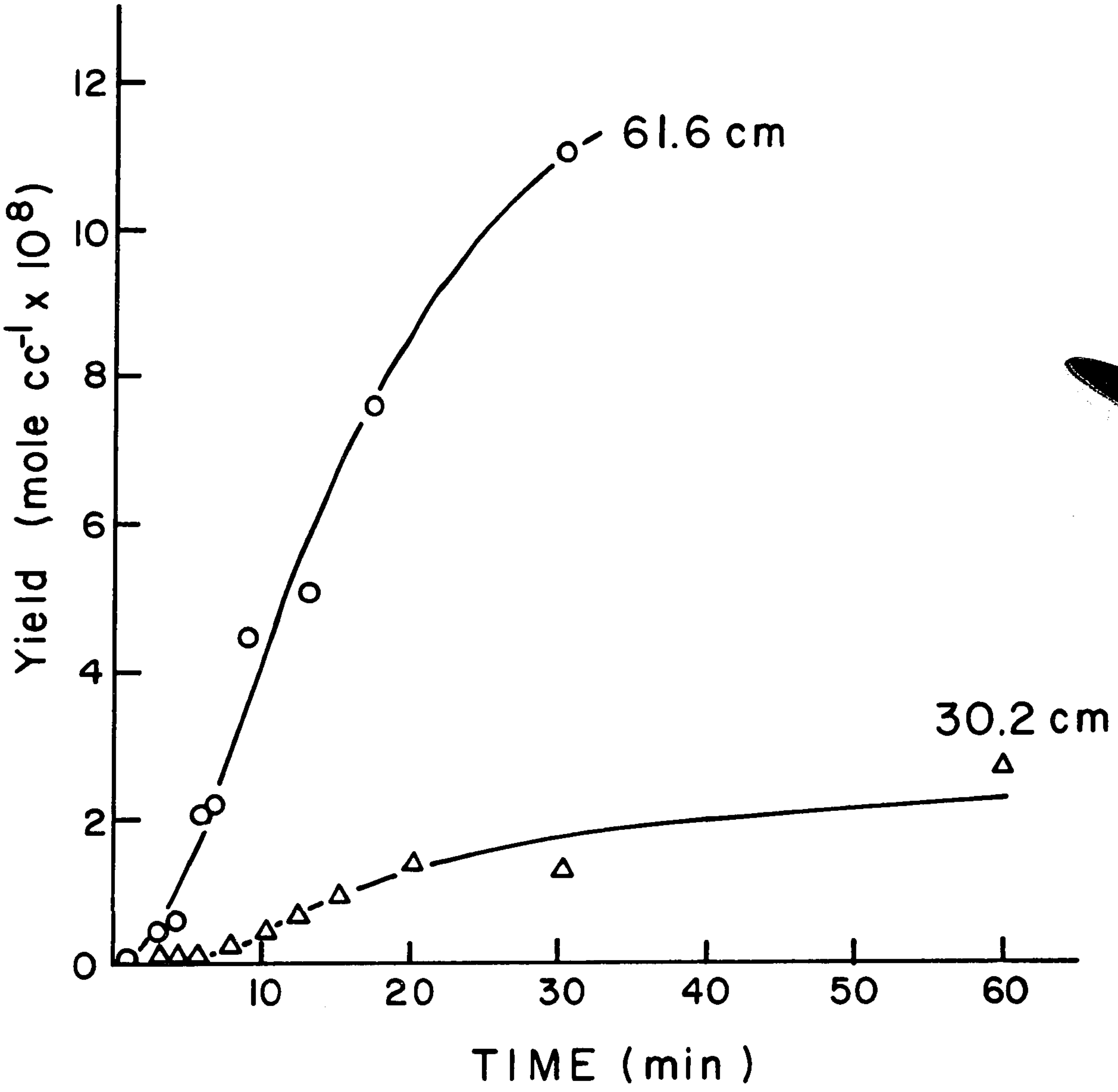

61.6 cm
30.2 cm
Yield (mole cc^{-1} x 10^8)
12
10
8
6
4
2
0
10
20
30
40
50
60
TIME (min)

Figure 8.

Yield-time plot for the formation of butadiene at 584°C.

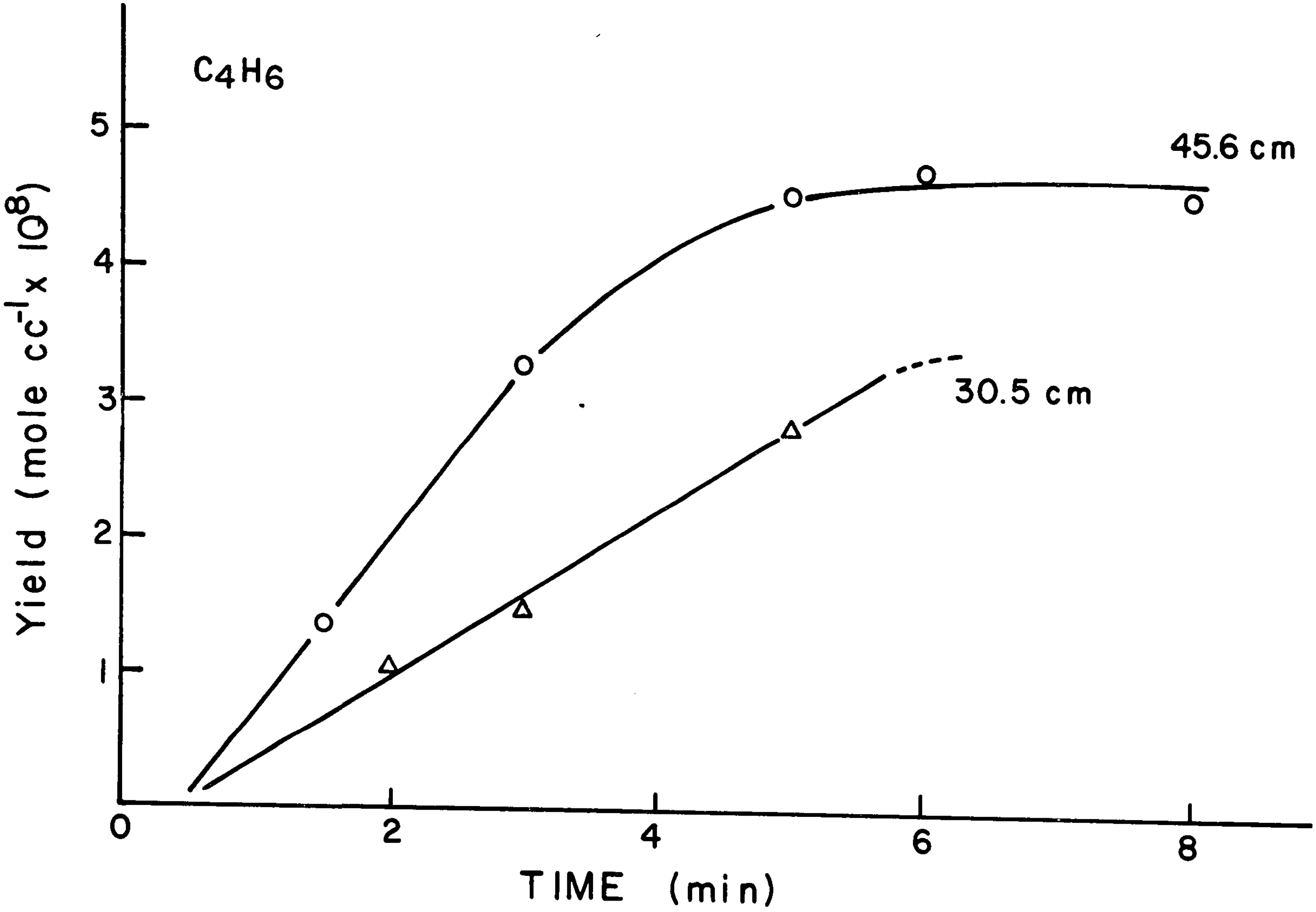

C_4H_6
45.6 cm
30.5 cm
Yield (mole cc^{-1}x 10^8)
5
4
3
2
1
0
2
4
6
8
TIME (min)

Figure 9.

Yield-time plot for the formation of butane at 505.4°C

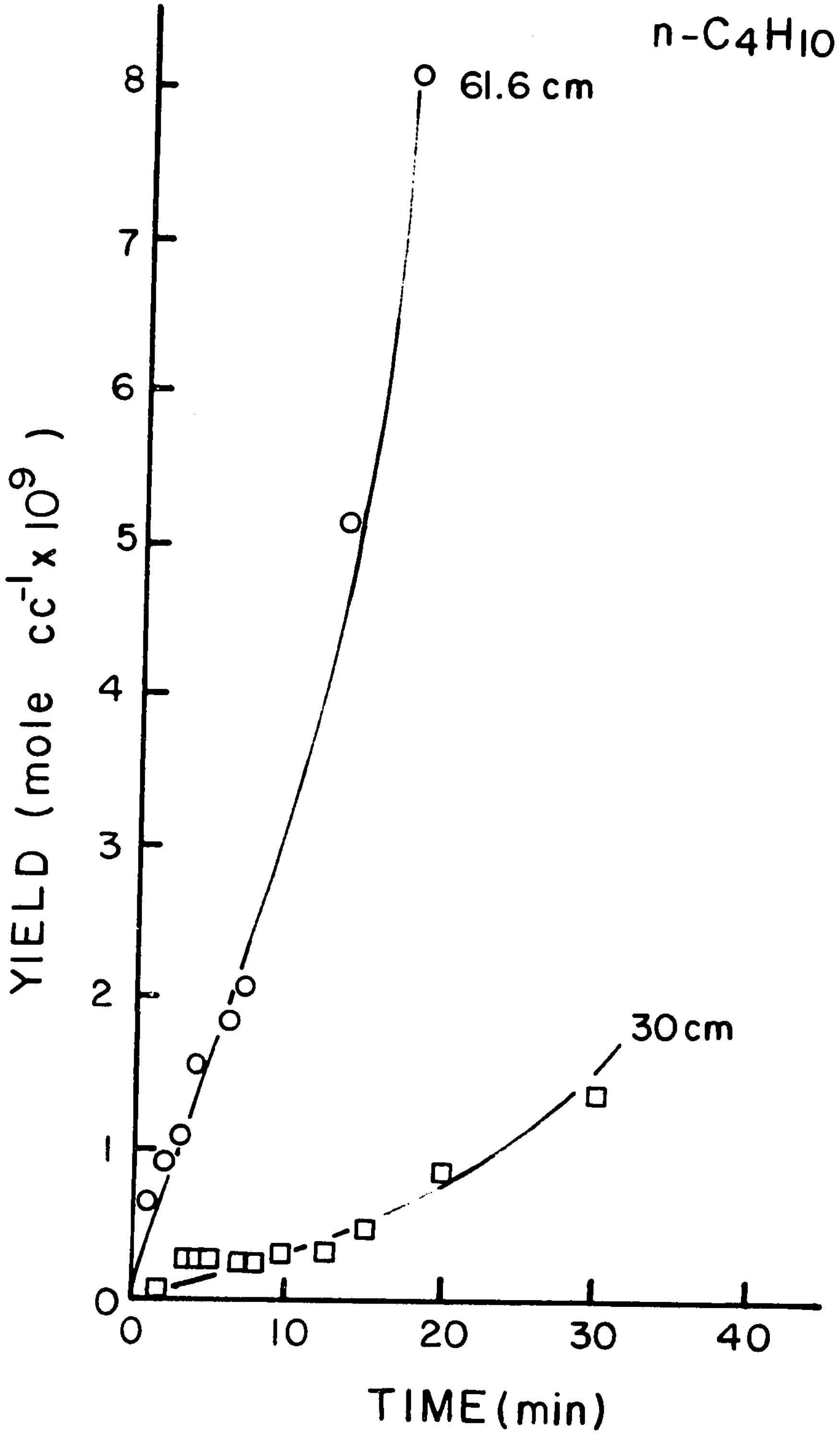

n-C4H10
61.6 cm
30 cm
YIELD (mole cc⁻¹ x 10⁹)
8
7
6
5
4
3
2
1
0
0
10
20
30
40
TIME (min)

Table III

Rates of Product Formation (moles cc^{-1}. sec^{-1}. x 10^{11})

Temperature (^oC ± 0.5^oC)	$P^o_{C_2H_4}$ (cm)	$R_{C_2H_6}$	$R_{C_3H_6}$	$R_{C_4H_8}$	$R_{C_4H_{10}}$	$R_{C_4H_6}$
501.6	60.7	6.92	27.8	5.00	0.58	none observed
	46.5	3.46	14.8	2.45	-	
	30.6	3.08	5.56	0.98	-	
	15.4	-	1.0	0	0	
505.4	61.6	6.3	34.5	8.3	0.4	none observed
	45.5	4.0	17.8	5.1	0.2	
	30.2	2.1	6.7	1.7	0.05	
	22.7	0.8	3.4	1.1	0.03	
	15.3	0.4	1.6	-	-	
530.4	60.7	-	45.6	10.5	0.9	1.2
	47.6	-	25.6	5.6	0.5	1.0
	41.7	10.4	18.2	4.6	0.2	-
	30.9	5.6	9.2	3.0	-	0.5
563.6	60.4	75.0	90.0	25.4	2.3	17.1
	30.4	32.3	26.5	7.9	0.5	-
	22.9	15.5	13.5	4.4	0.3	-
	15.0	6.5	6.3	2.5	-	-
584.0	60.1	161.9	133.3	37.5	5.2	18.4
	45.6	104.0	83.3	25.0	3.5	14.2
	30.5	57.1	40	13.3	1.5	9.9
	23.1	25.6	23.1	12.1	-	-
	15.1	14.9	11.7	4.2	0.2	-

From plots of the logarithm of the rates against the logarithm of the initial concentrations, the order for the rate of formation of each product with respect to ethylene was obtained. These order plots are shown in Figures 10 to 14. From plots of the logarithm of the rate against the reciprocal of the absolute temperature at a constant concentration of ethylene, the activation energy for the rate of formation of each product was determined. These plots are shown in Figures 15 - 19. The reaction orders and activation energies of each product are summarized in Table IV.

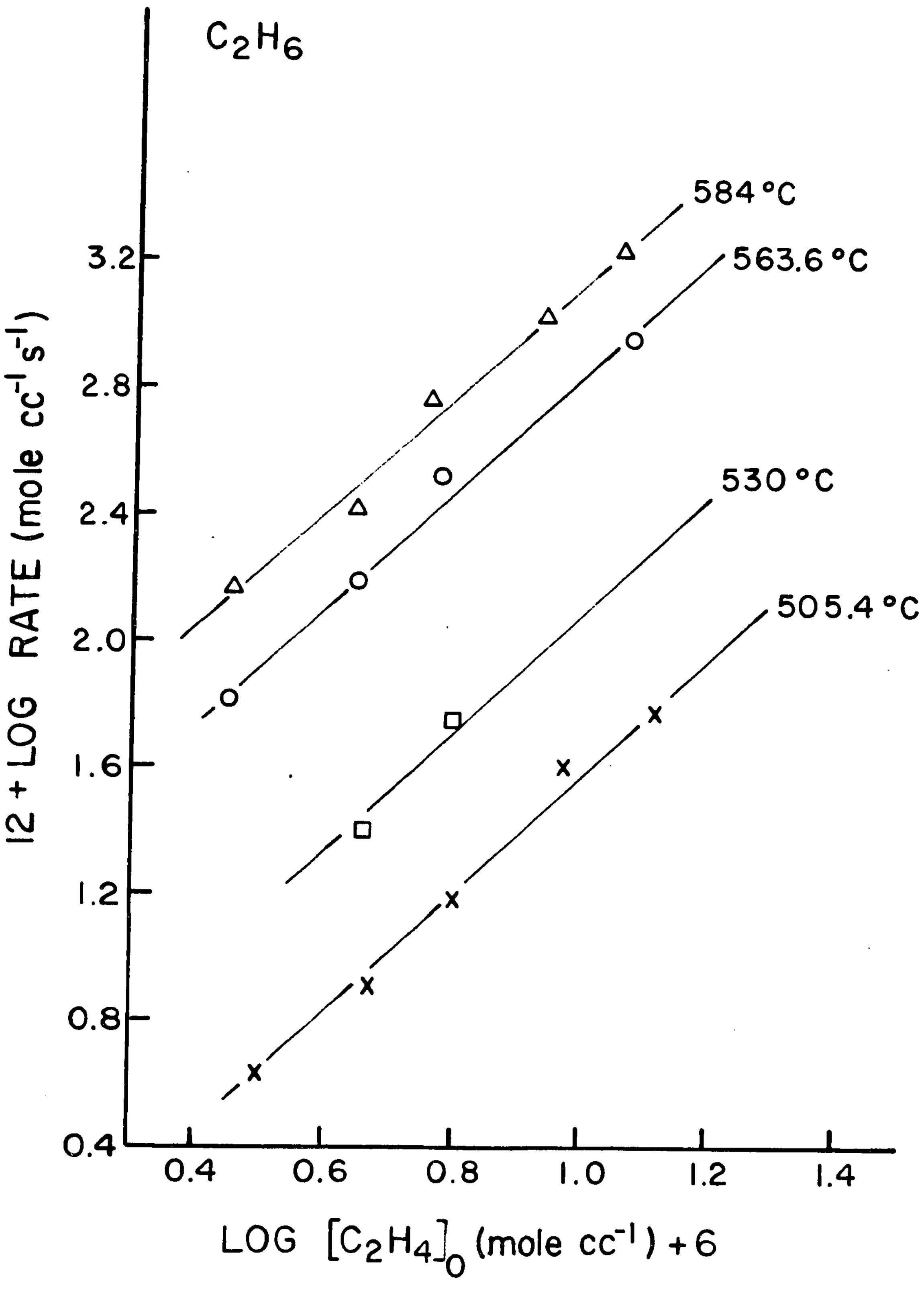
The Induction Period

The yield-time plots of most products showed a well-defined linear portion after a brief acceleration period. The extrapolation of the linear portion to the time axis gives a non-zero starting time which will be defined as the induction period for each compound. These induction periods are listed in Table V.

In general, the induction period decreased with increasing temperature and pressure. At each temperature, the induction period for propylene and butene decreased almost linearly as the pressure was increased except when the pressure was lower than about 25 cm. Under these conditions, the induction period was extremely long, and became very difficult to measure exactly. At 505°C and 30 cm initial pressure of ethylene, several measurements were made with reaction times within the induction period.

Figure 10

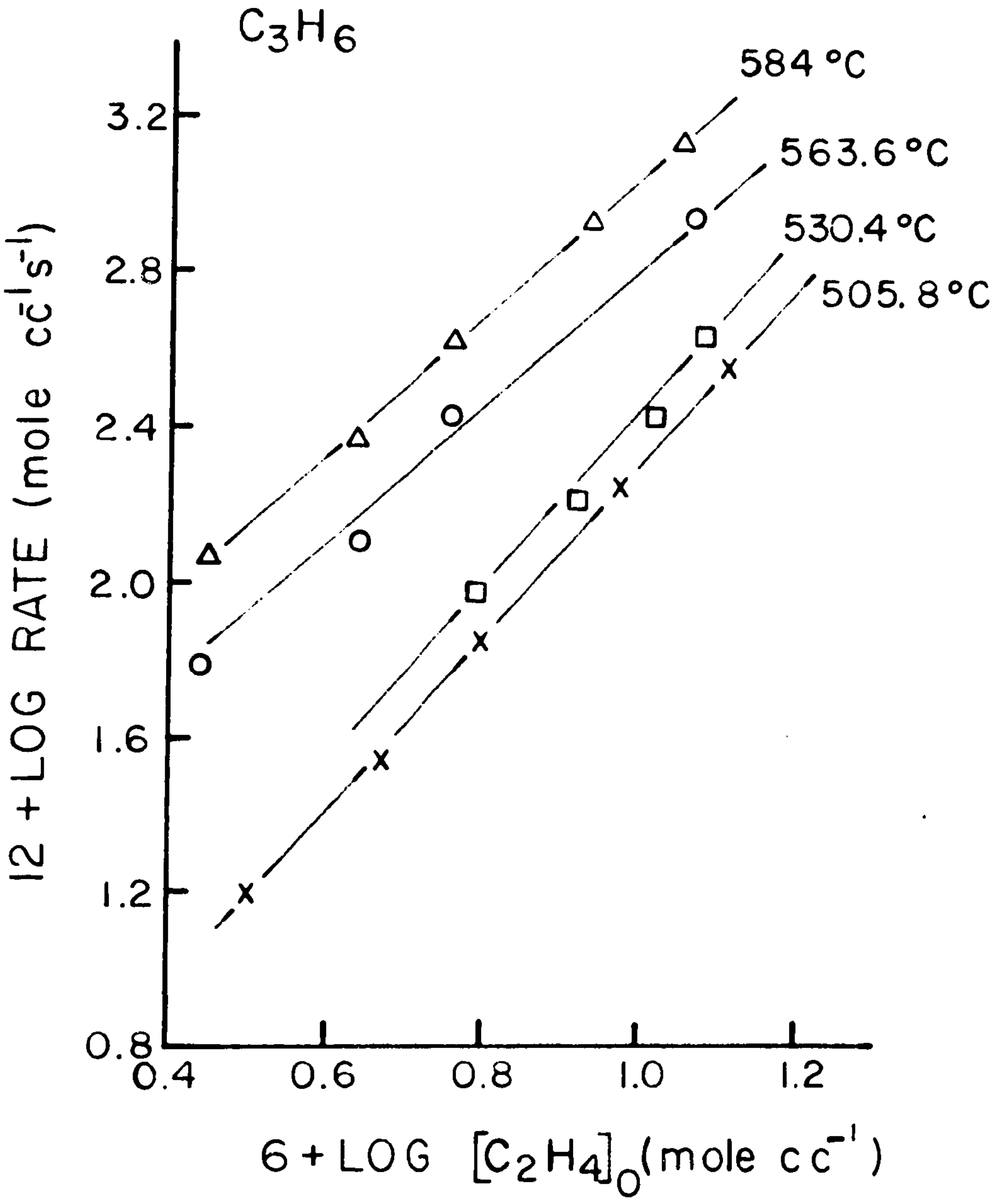
Double logarithmic plot of the rate of formation of ethane against the initial concentration of ethylene



C_2H_6
584 °C
563.6 °C
530 °C
505.4 °C
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.4
0.6
0.8
1.0
1.2
1.4
12 + LOG RATE (mole $cc^{-1}s^{-1}$)
LOG $[C_2H_4]_0$ (mole cc^{-1}) + 6

Figure 11

Double logarithmic plot of the rate of formation of propylene against the initial concentration of ethylene



C_3H_6
584 °C
563.6 °C
530.4 °C
505.8 °C
12 + LOG RATE (mole cc^{-1}s^{-1})
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.6
0.8
1.0
1.2
6 + LOG $[C_2H_4]_0$(mole cc^{-1})

Figure 12

Double logarithmic plot of the rate of formation of butane against the initial concentration of ethylene

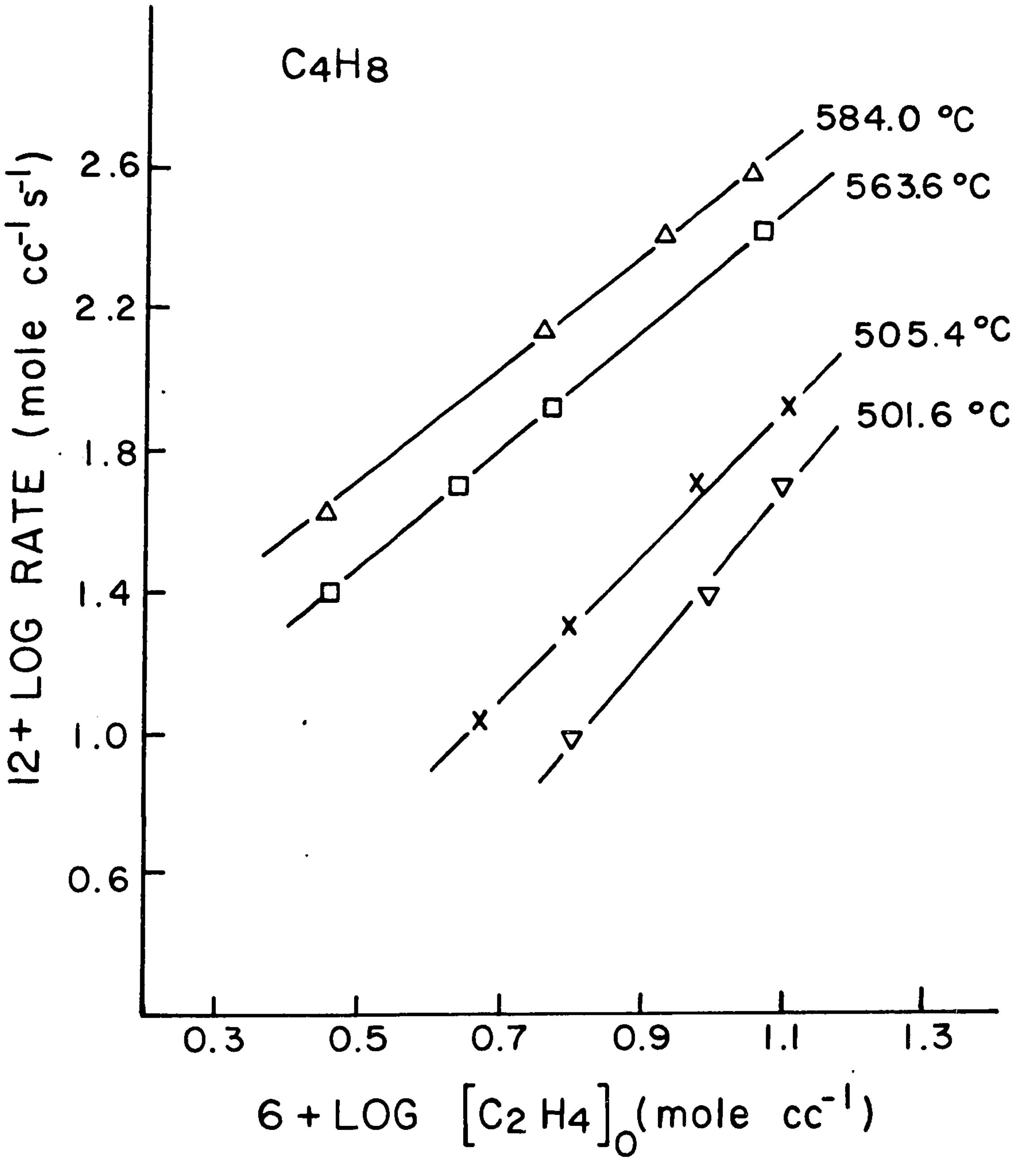

C4H8
584.0 °C
563.6 °C
505.4 °C
501.6 °C
12 + LOG RATE (mole cc⁻¹ s⁻¹)
2.6
2.2
1.8
1.4
1.0
0.6
0.3
0.5
0.7
0.9
1.1
1.3
6 + LOG [C2 H4]0 (mole cc⁻¹)

Figure 13

Double logarithmic plot of the rate of formation of butene against the initial concentration of ethylene

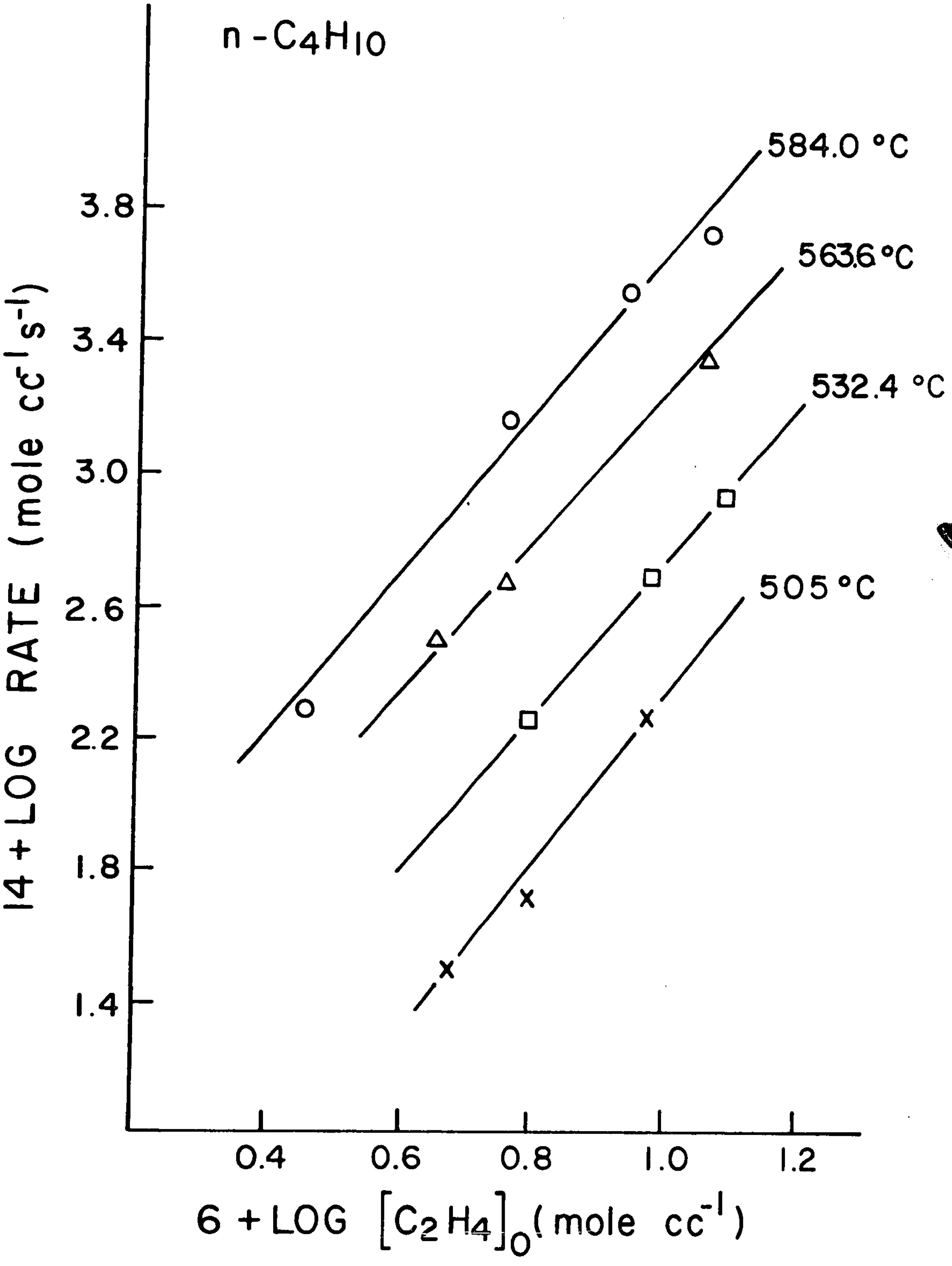

n - C_4H_{10}
584.0 °C
563.6 °C
532.4 °C
505 °C
3.8
3.4
3.0
2.6
2.2
1.8
1.4
0.4
0.6
0.8
1.0
1.2
14 + LOG RATE (mole cc^{-1}s^{-1})
6 + LOG $[C_2H_4]_0$(mole cc^{-1})

Figure 14

Double logarithmic plot of the rate of formation of butadiene against the initial concentration of ethylene

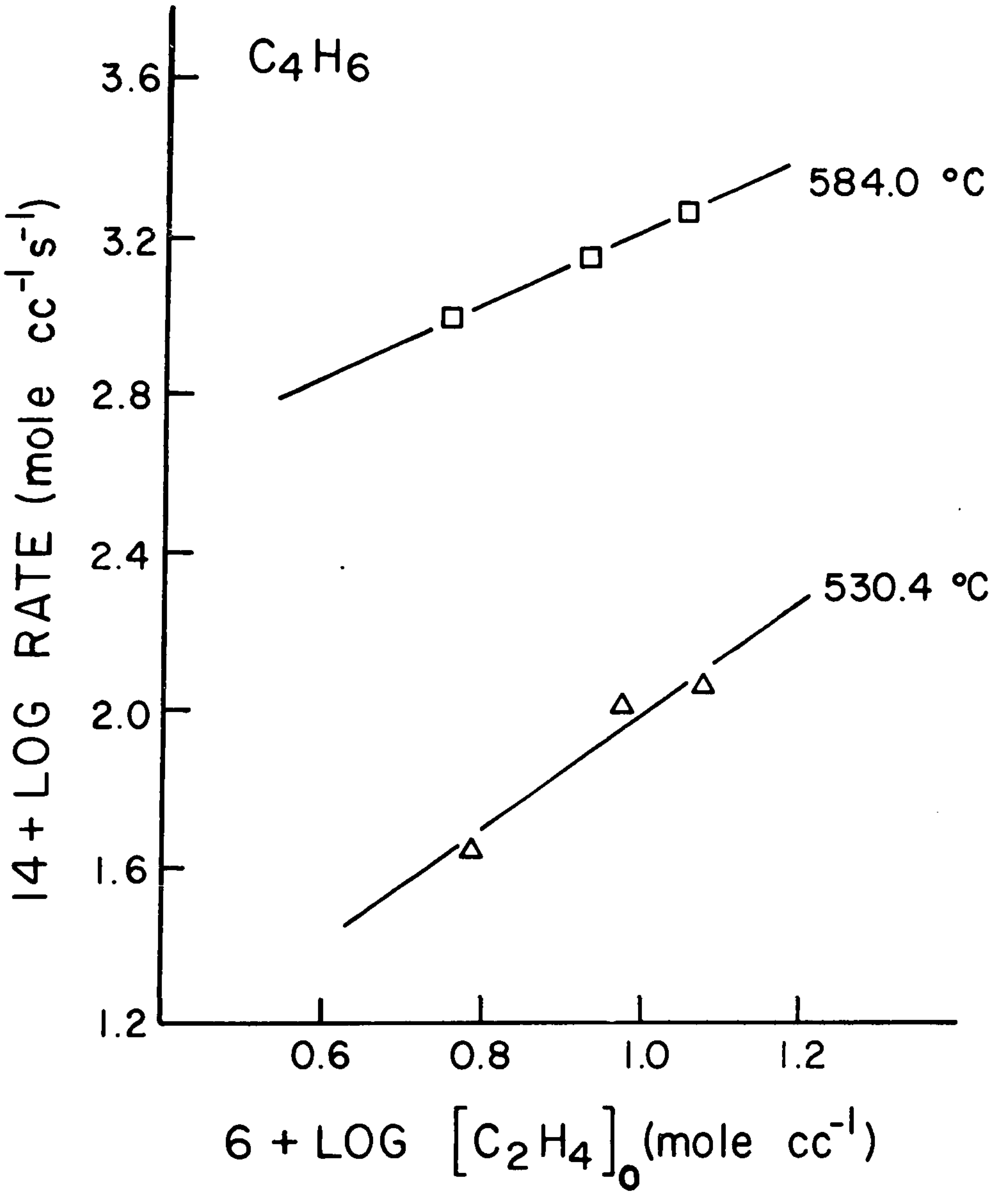

C4H6
584.0 °C
530.4 °C
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.6
0.8
1.0
1.2
14 + LOG RATE (mole cc⁻¹s⁻¹)
6 + LOG [C2H4]0 (mole cc⁻¹)

Figure 15

Arrhenius plot of the rate of formation of propylene.

Initial ethylene pressure 60 cm.

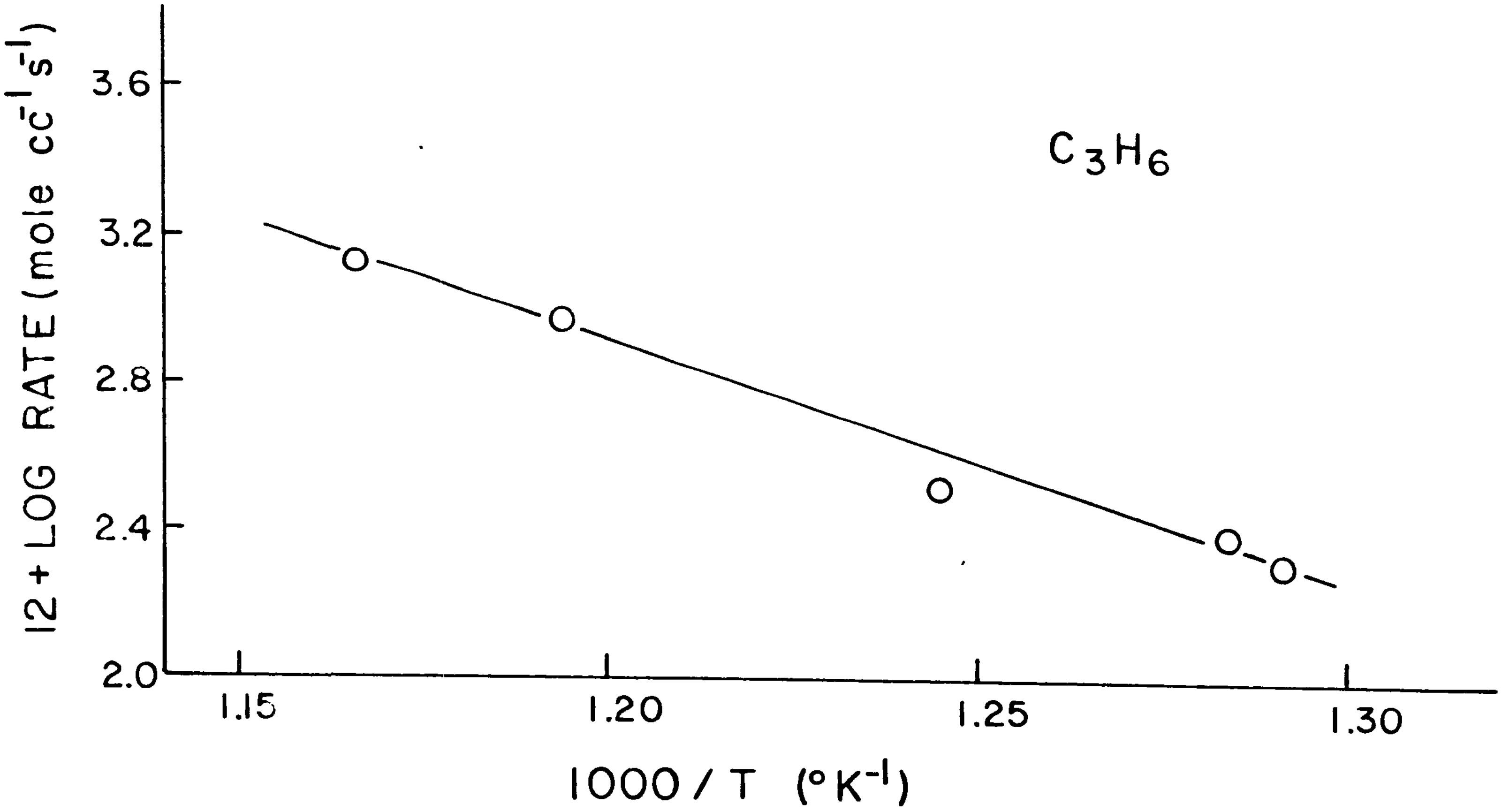
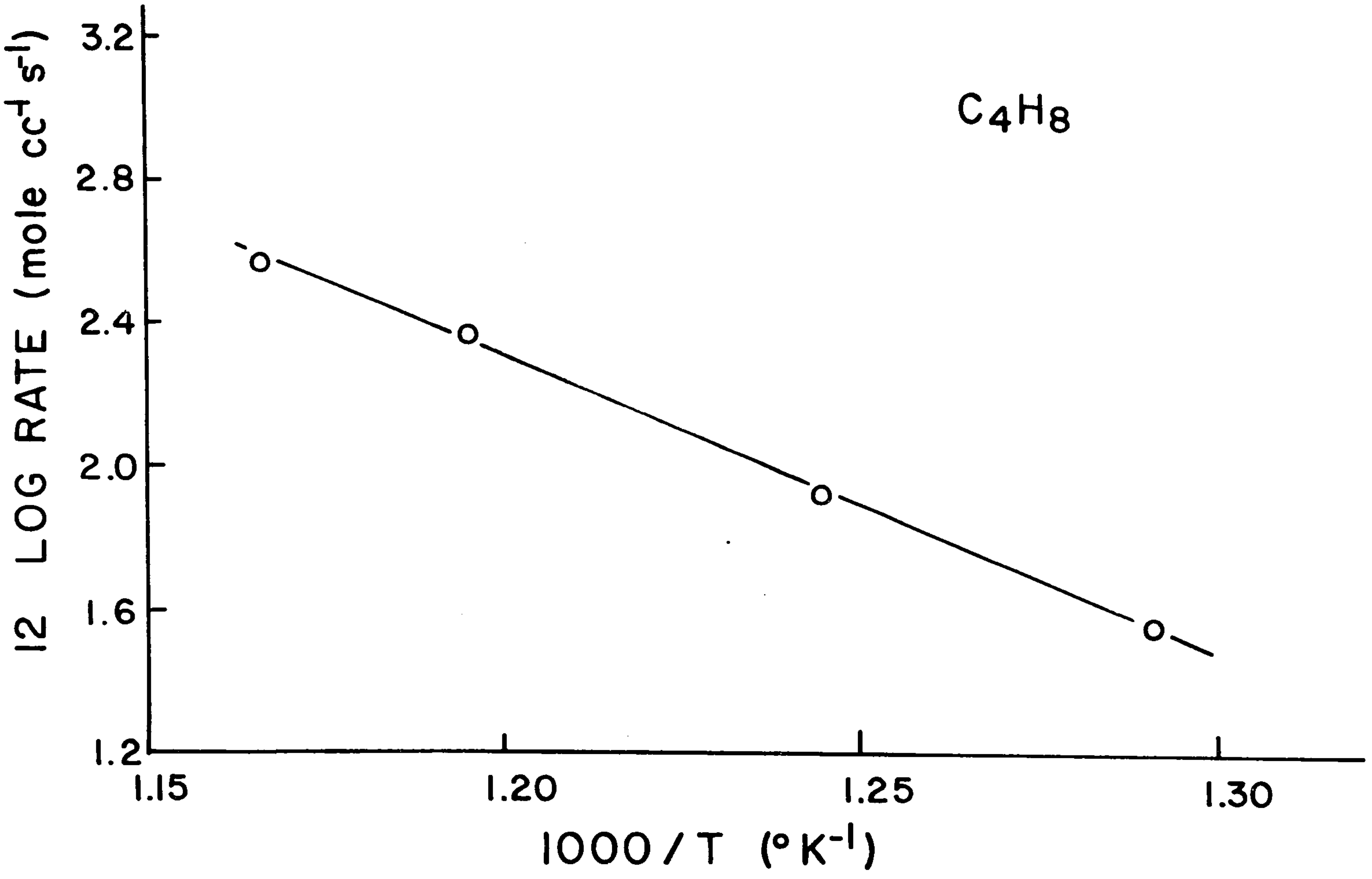

C_3H_6
12 + LOG RATE (mole cc^{-1} s^{-1})
3.6
3.2
2.8
2.4
2.0
1.15
1.20
1.25
1.30
1000 / T (°K^{-1})

Figure 16

Arrhenius plot of the rate of formation of butene.

Initial ethylene pressure 60 cm.

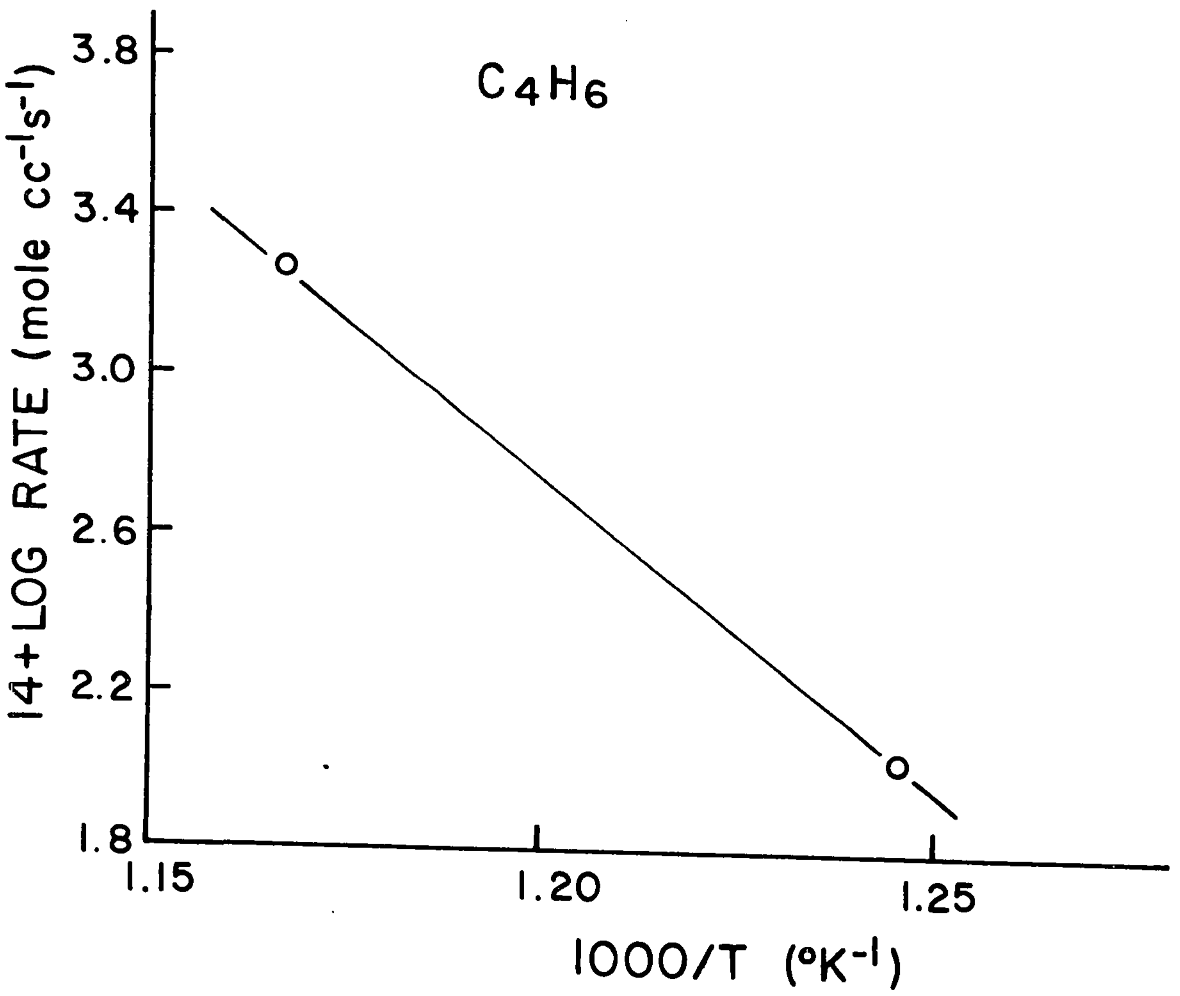


12 LOG RATE (mole cc⁻¹ s⁻¹)
3.2
2.8
2.4
2.0
1.6
1.2
C4H8
1.15
1.20
1.25
1.30
1000/T (°K⁻¹)

Figure 17

Arrhenius plot of the rate of formation of butadiene.

Initial ethylene pressure 60 cm.



C4H6
14+LOG RATE (mole cc-1s-1)
3.8
3.4
3.0
2.6
2.2
1.8
1.15
1.20
1.25
1000/T (°K-1)

Figure 18

Arrhenius plot of the rate of formation of butane.

Initial ethylene pressure 60 cm.

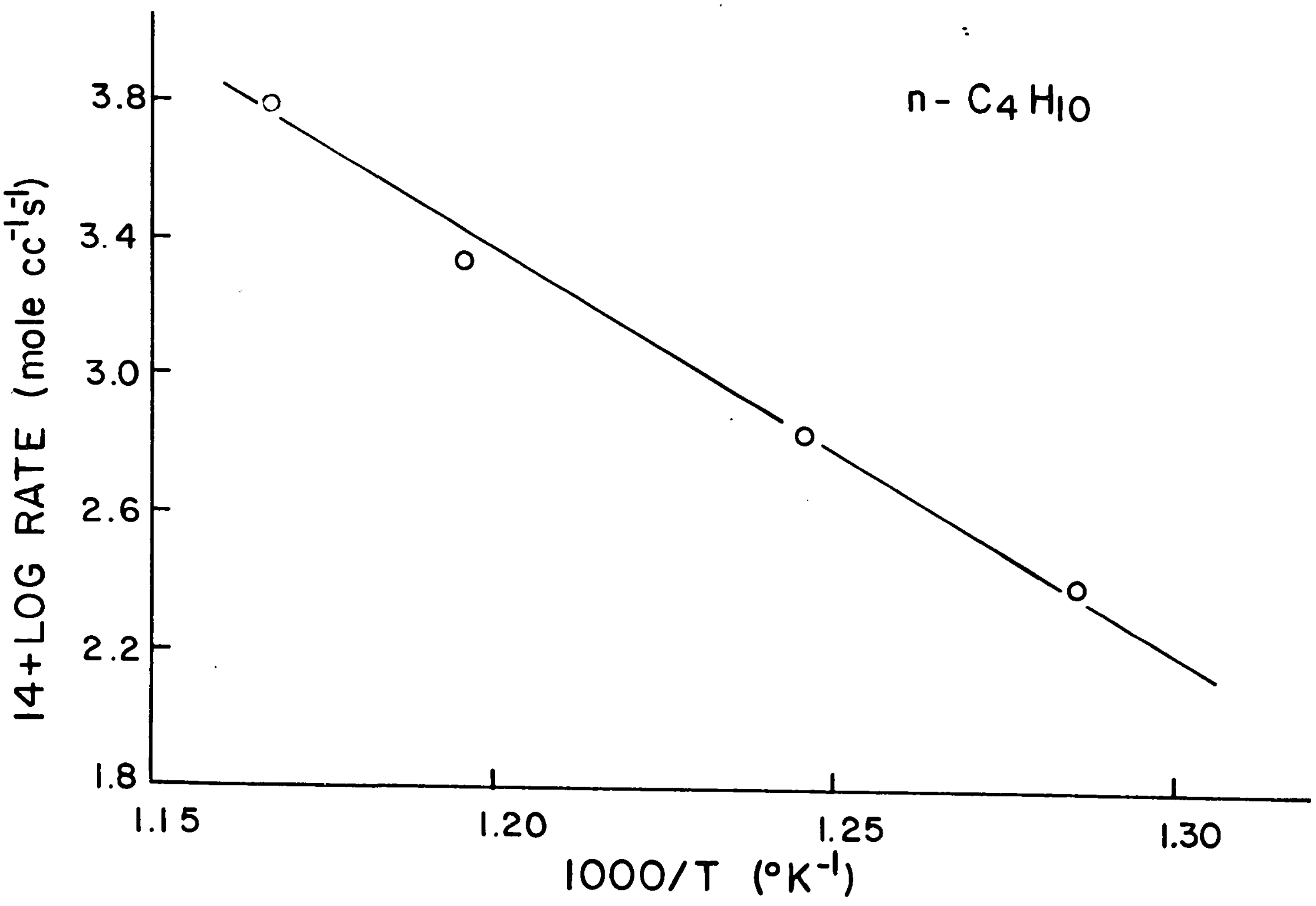

n- C_4H_{10}
14+LOG RATE (mole $cc^{-1}s^{-1}$)
3.8
3.4
3.0
2.6
2.2
1.8
1.15
1.20
1.25
1.30
1000/T (°K^{-1})

Table IV

Summary of the Orders and Activation Energies of the Rates of Formation of the Major Products

Product	Temperature range (^{o}C)	E kcal.mole^{-1}	order w.r.t. ethylene				
			501.6	505.4	530.4	563.6	584.0
Ethane	563 - 584	45.8	1.9	1.9	-	2.0 ± 0.1	1.9
Propylene	501 - 584	29.6 ± 2	-	1.8 ± 0.1	2.0 ± 0.2	1.9 ± 0.1	1.8 ± 0.1
Butene	501 - 584	37.9 ± 2	2.4	2.0 ± 0.1	1.8 ± 0.2	1.7 ± 0.1	1.6 ± 0.1
Butadiene	530 - 584	72	none detectable		1.5 ± 0.2	-	1.0 ± 0.2
n-Butane	501 - 584	53 ± 2.5	-	2.6 ± 0.5	2.2 ± 0.1	2.1 ± 0.1	2.3 ± 0.1

Table V

Induction Period

Temperature (°C)	Pressure (cm)	C_3H_6 (min)	C_4H_8 (min)	C_4H_6 (min)
505.4	61.6	1.0	2	∞
	45.5	3.0	5	
	30.2	5.5	6	
	22.7	7.0	10	
	15.2	16.5	28	
563.6	60.4	0.4	0.3	0.8
	30.4	1.2	1.0	2.5
	23.0	2.0	1.5	-
	15.0	3.0	2.0	3.5
584.0	60.1	0.2	0	0
	45.6	0.5	0	0
	30.5	-	0.2	0.3
	23.0	1.1	1	-
	15.1	2.2	1.8	2

Yields of propylene and butene (Figures 6 and 7) appear to be very small and barely measurable, whereas the yields of ethane were much larger. The rates of formation of propylene and butene accelerate during the induction period and approach the maximum constant rate referred to earlier. The yields of ethane and butane were measurable from the start of the reaction at lower temperatures. At higher initial pressures of ethylene, induction periods were also found for C_5-products and octene at 584°C.

Ethane

At 505 - 530°C the ethane yield increased linearly with time in the initial stages of the reaction (Figure 4). As the reaction progressed, however, the rate of formation of ethane increased rapidly beyond the initial constant value, suggesting that some ethane was produced in secondary reactions. This increase in rate with time made the measurement of the initial rate somewhat uncertain.

At temperatures higher than 563°C, the yield-time plots of ethane formation did not have any well defined linear portion during the initial period corresponding to the induction period of the other primary products. Instead, the rate of formation of ethane, after the brief period of acceleration, attained a nearly constant value (Figure 5). These rates are listed in Table III, and are not the initial rates but are the rates reached after a steady state is established. The activation energy was determined using these rates only since the rates measured at the lower temperatures referred to a different stage of the reaction. The order of the rate of formation of ethane was 1.9. From the rates at 563 and 584°C an activation energy of 45 kcal per mole was obtained.

Propylene

The propylene yield-time plot was linear after the induction period at all reaction temperatures as illustrated in Figure 6. It is clearly shown that extrapolation of the linear yield-time curve for the different initial ethylene pressures does not intersect the time axis at zero, but instead at a finite time, which is called the induction period. In two experiments, with an initial ethylene pressure of 30.2 and 22.2 cm Hg, it was possible to measure the propylene yield during the induction period. In some cases, however the yield during the induction period was too small to be detected by the gas chromatographic method used, which means a yield of product less than about 2×10^{-10} mole/cc. The induction period for propylene decreased as the reaction temperature and initial ethylene pressure increased. The values measured are included in Table IV. The order with respect to ethylene for the rate of production of propylene was between 1.8 and 2.0 for the four temperatures. The Arrhenius plot of log rate against 1/T gave an activation energy of 29.6 ± 2 kcal per mole.

Butene

The yield-time plots for production of butene were similar to those of propylene, and a typical example is shown in Figure 7. At all four temperatures constant rates were obtained after the induction period. At the highest reaction temperature, 584°C, the yield of butene approached a maximum value at long reaction times. The induction period for butene was slightly longer than that for propylene at 505°C, but it was about the same length at higher temperatures. The ratio of butene-1 to butene-2 was greater than 20 at temperatures of 530 and 584°C. This ratio is quite different from that calculated from the thermodynamic equilibrium constant for butene-1 and butene-2. The thermodynamic equilibrium constant calculated from data given by Benson (47) for the reaction:

$$\text{butene-1} \rightarrow \text{trans-butene-2}$$

is 0.59 at 584°C. At 584°C with an initial pressure of ethylene of 15 cm and a reaction time of about seven minutes, the experimental ratio of cis-butene-2 to trans-butene-2 was 3.5, which is a reasonable value for the two compounds in equilibrium.

The order of the rate of production of butene was close to 2.0 at 505°, but gradually decreased to 1.6 at 584°C. The rate of production of butene at the lowest reaction temperature and lowest initial ethylene concentration was anomalously low and may indicate an increasing order at low pressure. On the other hand the amounts analyzed were approaching the limits of detection for the analysis method and the measurement in this range is not very reliable. The temperature coefficient for the rate of production of butene, obtained from the plot of the logarithm of the rate against 1/T for the four temperatures studied was 38 ± 2 kcal per mole.

Butadiene

The presence of butadiene was not detected in the products of the reaction at 501 and 505°C. At 563°C the production of butadiene had a longer induction period than that of butene, while at 584°C the induction periods were very similar. In general, the shapes of the yield-time plots were similar for butadiene and butene. At 584°C and at high pressures of ethylene, there was an observable degree of secondary reaction of butadiene since the yield approached a maximum value at long reaction times. Typical yield-time plots are shown in Figure 8. The butadiene yield was less than 10% of the total reaction products.

The order for the rate of production of butadiene with respect to ethylene was between 1.0 and 1.5. From the plot of the logarithm of the rate against 1/T at 530.4 and 584°C, an activation energy of 72 kcal per mole was obtained.

Butane

The yield of n-butane was not more than 2% of the total reaction products. The yield-time plots of butane (Figure 9) resemble those of ethane both at lower and higher temperatures.

A careful examination was made of the n-butane yield at very short reaction intervals for the initial ethylene pressure of 30.3 cm at 505°C. The results suggest that there was no induction period for the production of n-butane. The measurement of the initial rate at lower temperature was difficult because of the small quantitites involved. Nonetheless, the initial portion of the yield-time plots was linear and the initial rate was obtained from this slope. These initial rates are listed in Table III. Only at 584°C did the formation of butane show an induction period and at this temperature the constant rate after induction period is listed in Table III.

The order for the rate of formation of n-butane was approximately 2. The activation energy for n-butane productinn was estimated to be 53 ± 3 kcal per mole from the plot of the logarithm of the rate against 1/T at four temperatures.

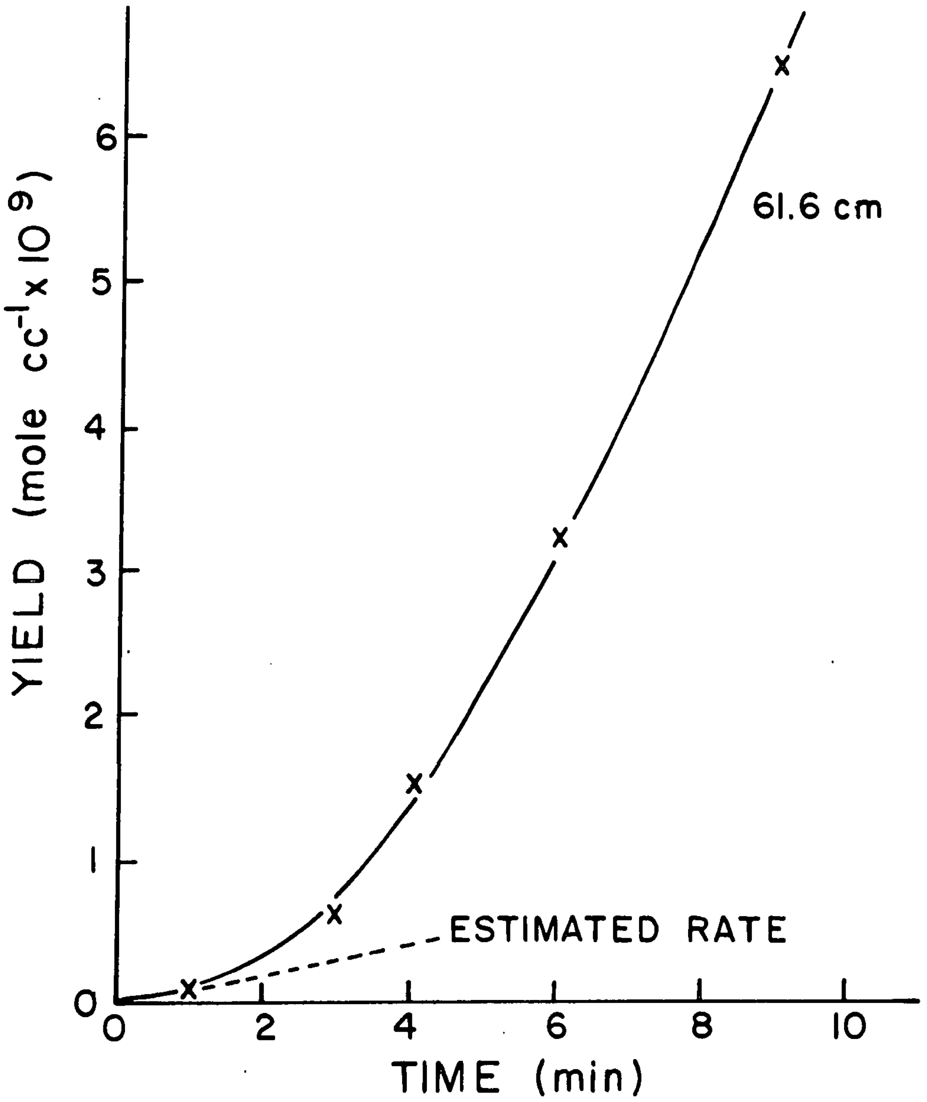
Minor Products:

Methane

The yield of methane was measurable at all four reaction temperatures. The rate of production of methane appeared to increase continuously with reaction time at all temperatures and initial ethylene pressures. The yield of methane as a function of time is shown in Figure 19 for reaction at 505°C. For comparison purposes an initial rate may be estimated as the lowest tangent on the yield-time curve. Such estimated rates relative to the rates of propylene at 505, 563 and 584°C were 0.02, 0.04 and 0.2 respectively, at the highest pressure studied. The order and the activation energy of these rates were 1.5 and 76 kcal/mole for three temperatures and a four-fold change in pressure.

Figure 19

Yield-time plot for the formation of methane at 505°C



YIELD (mole cc^{-1} x 10^{9})
0
1
2
3
4
5
6
61.6 cm
ESTIMATED RATE
0
2
4
6
8
10
TIME (min)

Hydrogen

The yield-time plot was characterized by a very low initial rate over a period longer than the induction periods of other products. The rate increased at longer reaction times. The estimated initial rates were about 1% of the rates of ethane formation at low temperatures and about 10% at high temperatures.

Propane

An increasing rate was also found for the production of propane at all temperature and pressures studied. At 505°C and initial ethylene pressures lower than 30 cm, the amount of propane produced was too small to be detected.

Benzene and Toluene

The yield-time plots for the production of benzene showed a continuous increase in rate as the reaction progressed. The induction periods for the production of benzene were all several minutes longer than the induction periods for propylene under similar conditions. The yield of toluene could be detected only at the highest initial pressures, at all four temperatures. The yield-time plot for toluene resembled that of benzene. For example, at 505°C and initial ethylene pressure of 61. 6 cm, both benzene and toluene have an induction period of 6 minutes, compared to 1 minute for propylene. The yield of both benzene and toluene diminished sharply as the initial ethylene concentration decreased.

Other Hydrocarbons

The C_5 and C_6 hydrocarbons were found in experiments at all four reaction temperatures. The total yield of this fraction was relatively small and analysis of the isomers not complete. The major component of the C_5 fraction was probably 1,4-pentadiene with some pentene. The C_5 compounds were detected in the early stages of the reaction, and the yield increased linearly with reaction time at higher temperature and pressure. Typical yield-time plots are shown in Figure 20. Preliminary analysis of the C_6 peak indicated the presence of hexene, cyclohexene, cyclohexane, cyclopentene, 3-methyl-pentene-2. Typical yield-time plots for the C_6 unsaturated product are shown in Figure 21.

The C_8 compound was C_8H_{16} on the basis of the mass spectrometric analysis. Although the yield of octene was very small at lower temperatures it increased considerably at the higher temperatures. A yield-time plot at 584°C is shown in Figure 22.

The C and H Balance

An average H:C ratio was determined by summing up all the measured products. At the mid-range temperature and pressure studied the ratio was 2.25, and the ratio stayed almost constant over reaction times as long as 30 minutes.

Figure 20

Yield-time plot for the formation of C_5 unsaturated product at 584°C.

Initial pressure of ethylene:

□	60.0 cm
X	30.5 cm
O	23.1 cm
△	15.1 cm

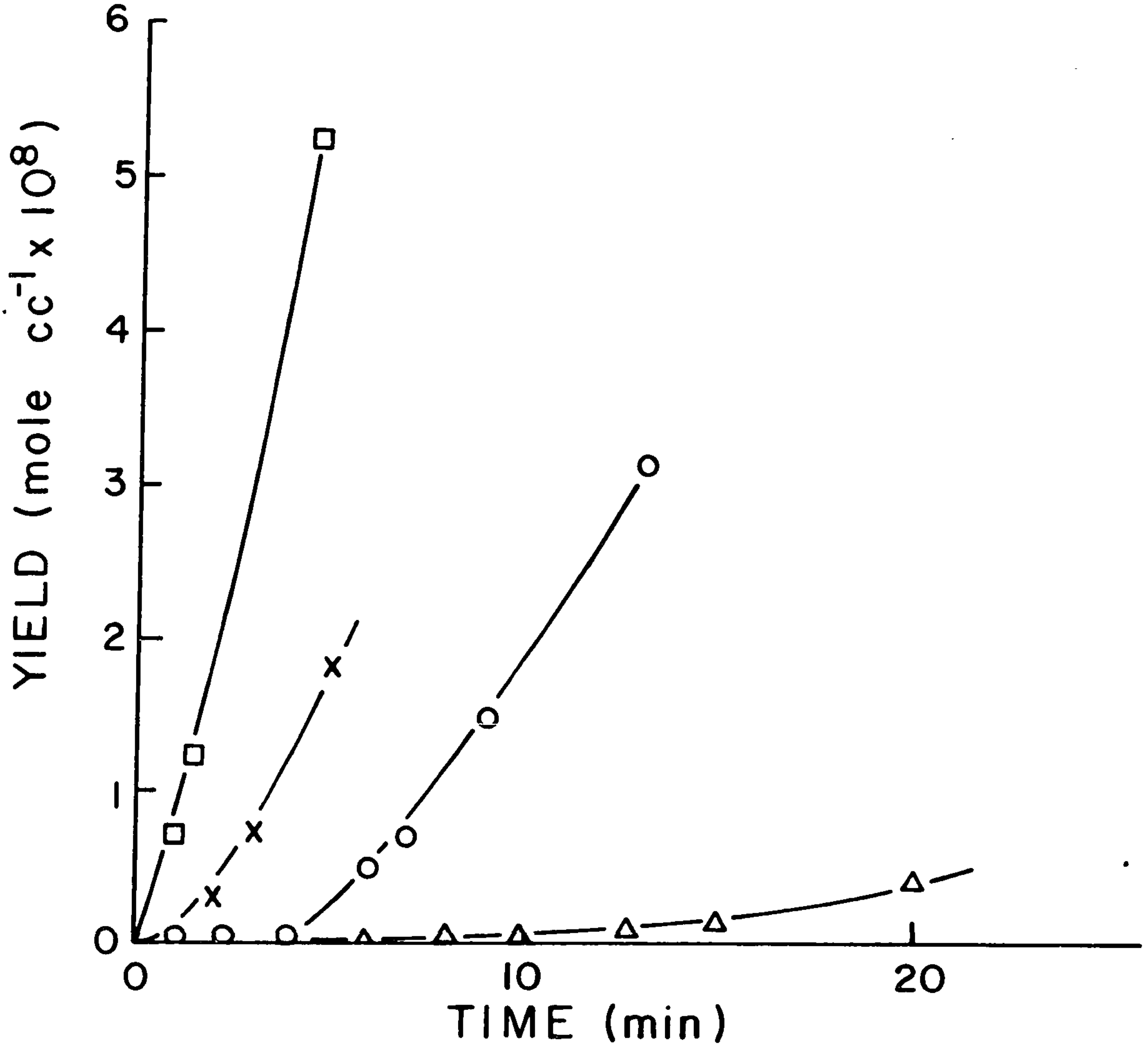

YIELD (mole cc^{-1} x 10^8)
0
1
2
3
4
5
6
TIME (min)
0
10
20

Figure 21

Yield-time plot for the formation of C_6 unsaturated product at 505°C

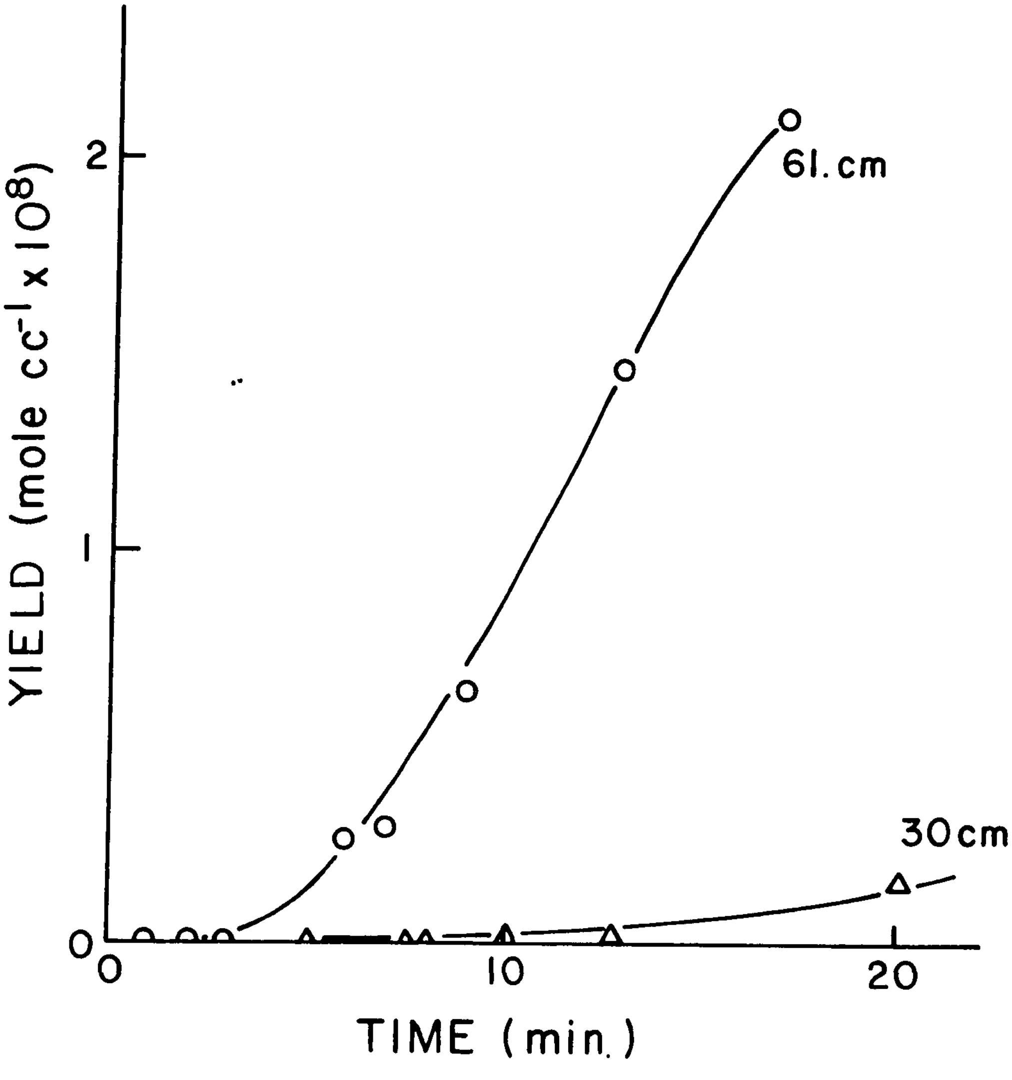
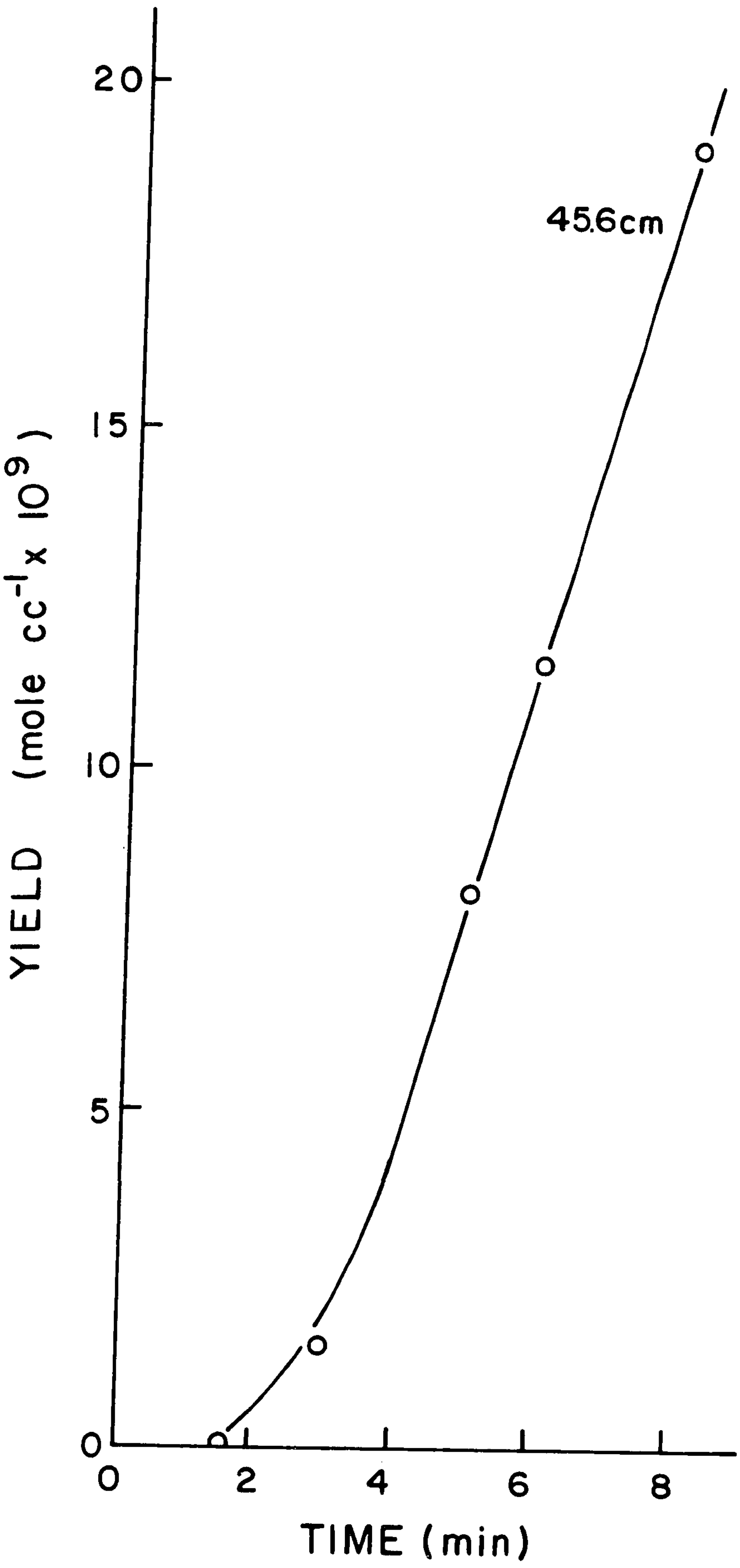

YIELD (mole cc^{-1} x 10^8)
2
1
0
TIME (min.)
0
10
20
61. cm
30 cm

Figure 22

Yield-time plot for the formation of octene

at 584°C


YIELD (mole cc^{-1} x 10^9)
TIME (min)
45.6cm
0
5
10
15
20
0
2
4
6
8

A similar excess of hydrogen in the products was reported by Halstead and Quinn (35). Since the presence of products of carbon number C_9 or higher was not detected by the analytical procedure it must be concluded that higher molecular weight compounds more unsaturated than ethylene are products of the reaction. The relative amount of such products could not be determined in this study. Subsequent work has shown (56) that these products are important in the lower temperature range but become increasingly unimportant as the temperature is raised. The formation of such products is adequately allowed for in the mechanism described in the Discussion section.

Experiments with C_2H_4 - C_2D_4

The products propylene, butene, ethane and the unreacted ethylene from the experiments with ethylene-ethylene-d_4 mixtures at an initial ethylene pressure of 30 cm and 505°C were examined for deuterium content. Reaction times varied from 30 - 60 minutes. The purity of the ethylene-d_4 was rated as 99% deuterium content.

Ethylene: The $C_2H_2D_2$, C_2HD_3 and C_2H_3D were found only in trace amounts in the unreacted ethylene with reaction times of 3 - 60 minutes. This suggests that the formation of a cyclic intermediate $C_4H_4D_4$ is not an important step. Also the reverse reaction of the bimolecular initiation step forming an ethyl and a vinyl radical is not important compared to the forward reaction.

Ethane: The mass spectra showed that isotopic species $C_2H_4D_2$, $C_2H_2D_4$ and $C_2H_3D_3$ were present in very small amounts The C_2H_5D and C_2HD_5 were the major components, indicating a step-wise scrambling of deuterium atoms.

Propylene: All isotopic compositions were present. Essentially complete scrambling of the deuterium took place with odd-numbered deuterium species in abundance.

Butene: The $C_4H_6D_2$ and $C_4H_2D_6$ were in smaller amounts than the other compositions. There was no abundance of $C_4H_4D_4$ over either C_4H_8 or C_4D_8. Again essentially complete scrambling took place with odd-numbered deuterium species in abundance.

Influence of Carbon Dioxide and Oxygen

The pyrolysis of ethylene in the presence of carbon dioxide was studied at 563 and 505°C. The relative yields of products in the presence and absence of carbon dioxide are summarized in Table VI. At 563°C, initial ethylene pressure of 15 cm, the yields of butadiene and butane were not influenced by the presence of a three-fold excess of carbon dioxide. Under the same conditions, the yields of propylene and butene increased nearly 20% while the yield of ethane increased approximately 60%. At 505°C, addition of a two-fold excess of carbon dioxide led to no significant change in

Table VI

Effect of CO_2 on the Product Yields

Temperature (^{o}C)	Pressure (cm) C_2H_4	Pressure (cm) CO_2	Time (min)	Relative Yields C_2H_6	C_3H_6	C_4H_8	C_4H_6	C_4H_{10}
563	15	-	8	1	1	1	1	1
	15	12	8	1.8	1.2	1.4	1	1
	15	33	8	1.4	1.2	1.2	1	1
505	23	-	14	1	1	1		
	23	23	14	1	1.1	-		
	30		15	1	1	1		
	30	30	15	1.4	1	1.1		

the production of propylene and butene, and about a 40% increase in the yield of ethane. It is concluded, therefore, that there was not a large stabilization effect by carbon dioxide on intermediates in the course of the reaction.

A mixture of 30.2 cm ethylene and 10^{-2} cm air was pyrolyzed at 506°C for 15 minutes and the results compared with those from pure ethylene. The yield of propylene increased by 20% but there was no change in the yield of butene. The effect of oxygen on the reaction of ethylene seems insiginificant.

Surface Effect

The surface effect on the formation of major products was studied at 584°C (15 and 46 cm) and 530°C (31 and 61 cm) using the reaction vessel of S/V ratio of 9.8 cm^{-1}. The rates of formation of propylene and butene were practically unchanged at 584°C. The change in rates for ethane production was small (35% decrease). The uncertainty in the ethane measurement was itself large so that it was concluded that the surface effect is not important, and the reaction is largely homogeneous.

Influence of Ethane

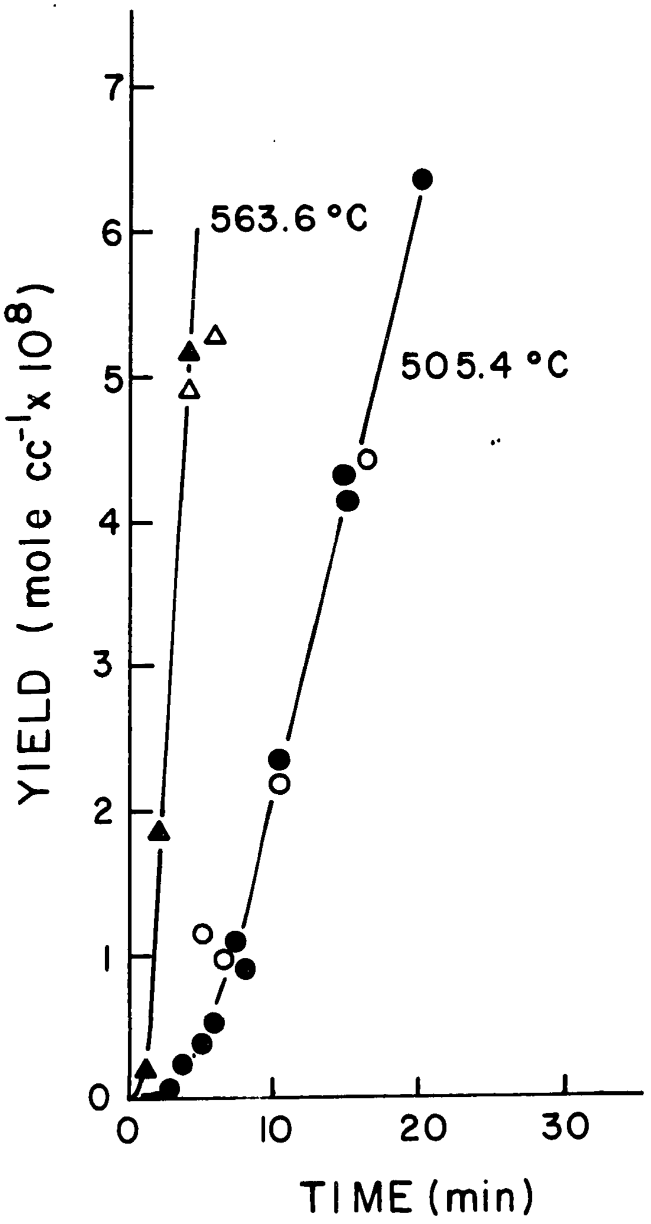
Ethane would be expected to provide a more abstractable hydrogen atom than ethylene and hence the addition of ethane would increase the yield of products which arise from hydrogen-abstraction. The yield-time plots for reaction of pure ethylene are compared with those of a 1:1 ethane-ethylene mixture in Figure 23 to 25. The presence of ethane did not affect the rate of formation of propylene, butene, butadiene, C_5- , C_6- , C_8-olefinic products or benzene. These compounds are, therefore, probably not formed by hydrogen-abstraction reactions of the corresponding radicals. The induction periods for production of propylene and butene at 505.4°C were noticeably shortened, as shown in Figures 23 and 24. The rate of production of butane was about ten times faster in the presence of ethane than the rate with pure ethylene at 563.6°C and about 8.5 times faster than that at 505.4°C. The rate of production of propane was also increased about four to five times at 563.6°, and probably higher at 505°C. Hence butane and propane may be formed by hydrogen-abstraction by the corresponding radicals.

Figure 23

Effect of ethane on the rate of formation of propylene at 563°C and 505°C

Filled points: pure ethylene 30 cm

Open points: added ethane 30 cm.



YIELD (mole cc^{-1} x 10^8)
7
6
5
4
3
2
1
0
563.6 °C
505.4 °C
0
10
20
30
TIME (min)

Figure 24

Effect of ethane on the rate of formation of butene at 563°C and 505°C

Filled points: pure ethylene 30 cm.

Open points: added ethane 30 cm.

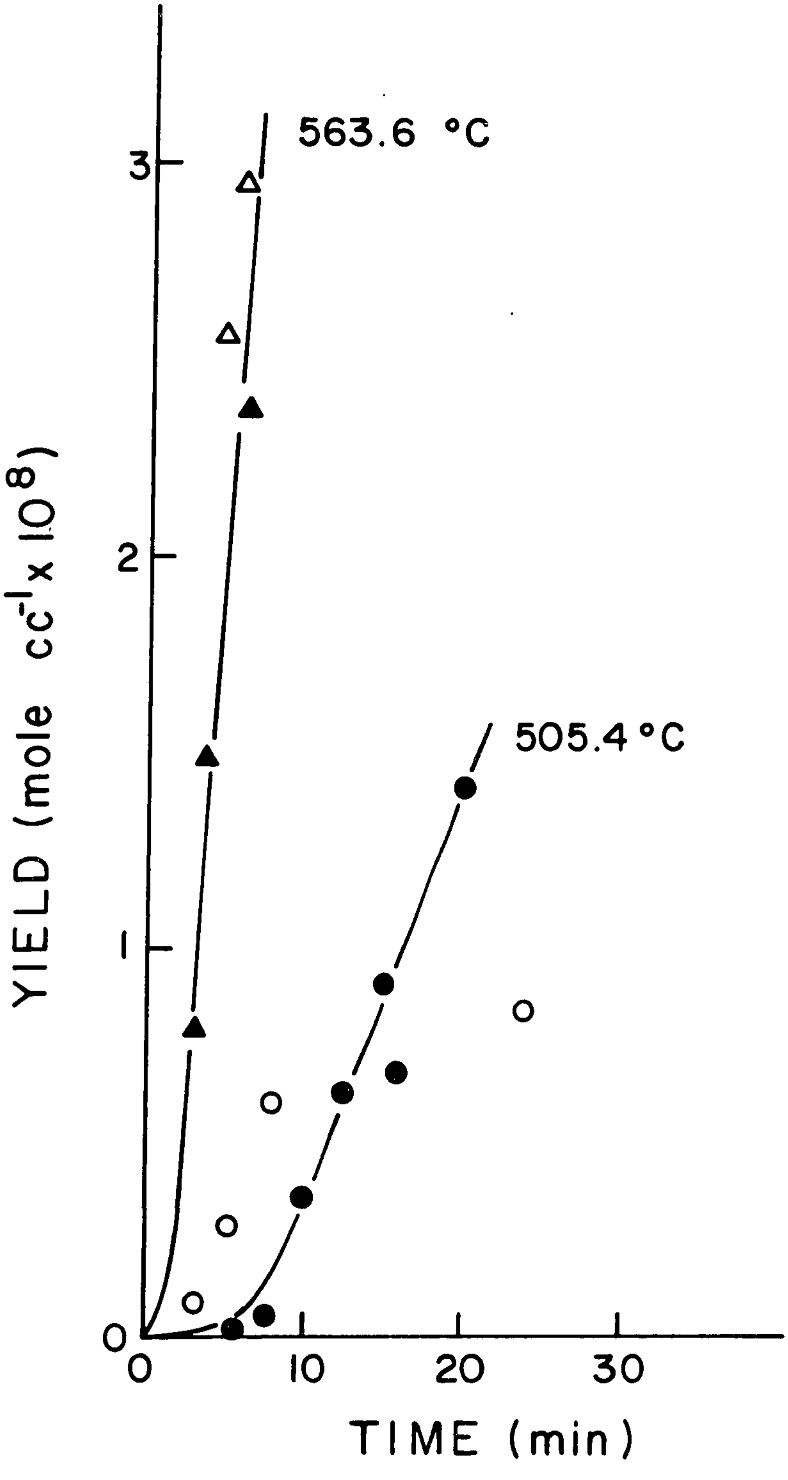
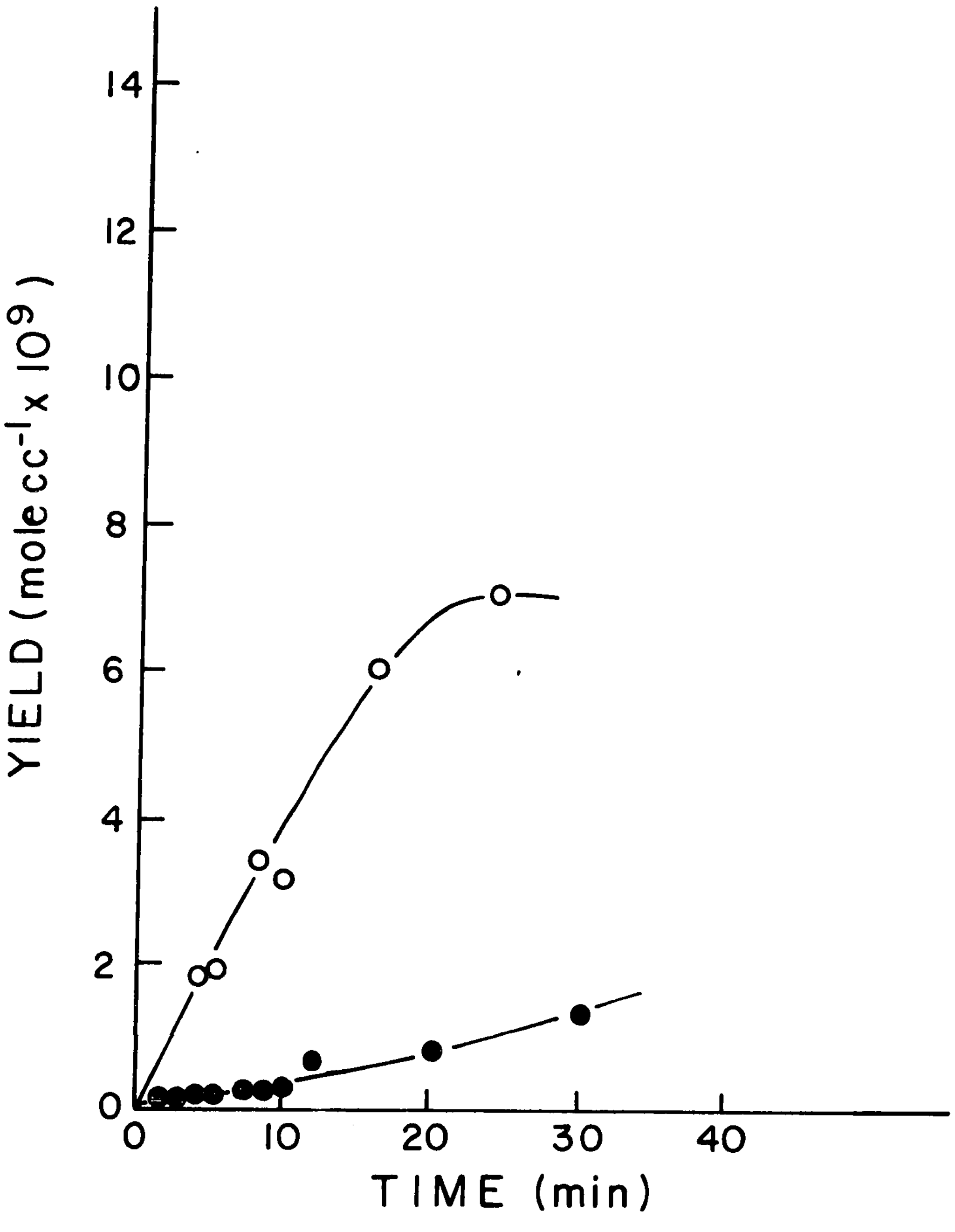

563.6 °C
505.4 °C
YIELD (mole cc^{-1} x 10^8)
0
1
2
3
0
10
20
30
TIME (min)

Figure 25

Effect of ethane on the rate of formation of butane at 505°C.

Filled points: initial pressure of ethylene 30 cm

Open points: additional 30 cm of ethane



14
12
10
8
6
4
2
0
YIELD (mole cc^{-1} x 10^9)
0
10
20
30
40
TIME (min)

DISCUSSION

A central question in the pyrolysis of hydrocarbons is the importance of molecular processes. In many cases, modern analytical techniques have demonstrated that the molecular processes proposed in the earlier investigations are often not as important as the radical processes. This is probably true too in the ethylene pyrolysis. Several observations in this study suggest that radical processes play a major role in the thermal reactions of ethylene.

Firstly, among the products are many compounds with an odd number of carbon atoms, for example methane, propane, propylene, and pentadiene. The formation of such products is most easily accounted for by a radical mechanism. Secondly, the products from the pyrolysis of ethylene-ethylene-d_4 mixtures showed a large extent of mixing of the hydrogen and deuterium. Again such scrambling suggests a radical chain process. Furthermore, several observations suggest the complexity of the ethylene pyrolysis reaction. There are a number of compounds, including saturated hydrocarbons, olefins, diolefins and aromatic compounds, formed even in the early stages of the reaction. There were unusually long induction periods observed for the production of many products. At higher ethylene conversion, about 6 - 10%, the rates of formation of propylene and butene start to decrease, indicating further secondary reactions.

No simple mechanism can be expected to give a quantitative account of the kinetics of the formation of all products, even in the early stages of this complex reaction. The following radical polymerization mechanism, greatly simplified, is intended to give only an outline of the whole picture. It provides, however, a basis for an understanding of the pyrolysis of ethylene.

Free Radical Polymerization

The proposed mechanism for the reaction under the conditions studied is as follows:

[1] $2C_2H_4 \longrightarrow C_2H_5 + C_2H_3$

[2] $C_2H_5 + C_2H_4 \rightleftharpoons n\text{-}C_4H_9$

[2a] $n\text{-}C_4H_9 \longrightarrow s\text{-}C_4H_9$

[2b] $s\text{-}C_4H_9 \longrightarrow C_3H_6 + CH_3$

[2c] $s\text{-}C_4H_9 \longrightarrow C_4H_8 + H$

[4] $n\text{-}C_4H_9 + C_2H_4 \rightleftharpoons n\text{-}C_6H_{13}$

[4a] $n\text{-}C_6H_{13} \longrightarrow C\text{-}C\text{-}C\text{-}C\text{-}\dot{C}\text{-}C \overset{4a1}{\rightarrow} C_3H_6 + C_3H_7$

[4b] $n\text{-}C_6H_{13} \longrightarrow C\text{-}C\text{-}C\text{-}\dot{C}\text{-}C\text{-}C \overset{4b1}{\rightarrow} C_4H_8 + C_2H_5$

$C\text{-}C\text{-}C\text{-}\dot{C}\text{-}C\text{-}C \overset{4b2}{\rightarrow} C_5H_{10} + CH_3$

[6] $\text{n-}C_6H_{13} + C_2H_4 \rightleftharpoons C_8H_{17}$

[2'] $C_2H_3 + C_2H_4 \rightleftharpoons C_4H_7$

[2'a] $C_4H_7 \longrightarrow C_4H_6 + H$

[4'] $C_4H_7 + C_2H_4 \rightleftharpoons \text{n-}C_6H_{11}$

[4'a] $\text{n-}C_6H_{11} \longrightarrow C{=}C{-}C{-}C{-}\dot{C}{-}C{-} \xrightarrow{4'a1} C_3H_6 + C_3H_5$

[4'b] $\text{n-}C_6H_{11} \longrightarrow C{=}C{-}C{-}\dot{C}{-}C{-}C{-} \xrightarrow{4'b1} C_4H_8 + C_2H_3$

$\longrightarrow C{=}C{-}C{-}\dot{C}{-}C{-}C{-} \xrightarrow{4'b2} C_5H_8 + CH_3$

[4'c] $\text{n-}C_6H_{11} \longrightarrow C{=}C{-}\dot{C}{-}C{-}C{-}C{-} \xrightarrow{4'c1} C_4H_6 + C_2H_5$

[6'] $\text{n-}C_6H_{11} + C_2H_4 \rightleftharpoons C_8H_{15}$

[a] $C_2H_5 + C_2H_4 \longrightarrow C_2H_6 + C_2H_3$

[b] $C_4H_9 + C_2H_4 \longrightarrow C_4H_{10} + C_2H_3$
[b'] $C_4H_7 + C_2H_4 \longrightarrow C_4H_8 + C_2H_3$
[c] $C_6H_{13} + C_2H_4 \longrightarrow C_6H_{14} + C_2H_3$

[c'] $C_6H_{11} + C_2H_4 \longrightarrow C_6H_{12} + C_2H_3$

[t] $2C_2H_5 \longrightarrow C_4H_{10}$

The relevant kinetic parameters for these elementary steps are listed in Table VII . In the table and the following text, n refers to the reaction as written and -n to the reverse reaction.

The Initiation and Termination

The following reactions represent the most probable radical initiation steps:

[1] $2C_2H_4 \rightarrow C_2H_5 + C_2H_3$

[1a] $C_2H_4 \rightarrow C_2H_3 + H$

[1b] $C_2H_4 \rightarrow 2CH_2$

From the rate parameters in Table VII., the rates of the three steps at 60 cm and 584°C are estimated. The rates of step [1a] (1.7×10^{-24} mole $cc^{-1}s^{-1}$) and step [1b] (7×10^{-28} mole $cc^{-1}s^{-1}$) are much slower than the rate of step [1] (4×10^{-12} mole $cc^{-1}s^{-1}$). Reaction [1] is hence considered to be the main initiation step.

The isotope analysis of the recovered ethylene from pyrolysis of mixtures of 1:1 ethylene-ethylene-d_4 showed little isotope scrambling, i.e. there was negligible amount of C_2H_3D or C_2HD_3. This suggests that the reverse reaction of the bimolecular initiation is not significant:

$$C_2H_3 + C_2H_5 \rightarrow 2C_2H_4$$

Table VII

Kinetic Parameters of Reactions involved in the Pyrolysis of Ethylene

Reaction	A cc. mole^{-1}s^{-1} or s^{-1}	E kcal. mole^{-1}	k cc. mole^{-1}s^{-1} or s^{-1} at 857°K	Rate at 60 cm. C_2H_4	Reference
1	6.3×10^{14}	64	0.03	4×10^{-12}	67
1a	3.9×10^{16}	104	1.6×10^{-19}	1.7×10^{-24}	58
1b	1×10^{13}	167	6.3×10^{-23}	7×10^{-28}	59
2	1.5×10^{11}	7.5	2×10^{9}		42
-2	3.7×10^{13}	28.5	2×10^{6}		60
2a	10^{7}	10.8	2×10^{4}		estimated, 51
2b	6.3×10^{14}	32.6	4×10^{6}		49
2c	5×10^{13}	39.7	5×10^{3}		49
4	2.2×10^{10}	6.7	3×10^{8}		42
-4	10^{13}	28.7	2×10^{6}		Assumed, 60
4a	2×10^{7}	8.3	1.6×10^{5}		52
4b	2×10^{7}	8.3	1.6×10^{5}		Assumed, 52
2'	1.5×10^{11}	3.3	2.2×10^{10}		Assumed, 61, 42
2'a	5×10^{13}	35	7×10^{4}		This work, assumed 49
4'	1×10^{10}	5	5.5×10^{8}		Estimated
a, b, c	4×10^{10}	10	1.2×10^{8}		43
t			2×10^{13}		59

Table VIII

Thermodynamic Data

Species	S^o (298°K)* cal. deg^{-1}mole^{-1}	Ref.	H^o (298°K) kcal. mole^{-1}	Ref.
C_2H_4	52.45	62	12.5	62
C_2H_3	56.3	63	64.4	64, 65
C_2H_5	59.3	66	26.0	63
H	27.4	62	52.1	63
C_2H_6	54.9	62	-20.2	62

* Standard state: 1 atm. of ideal gas

The bimolecular initiation may take place through the formation of the triplet state or by the interaction of two molecules to form two radicals or one diradical. Evidence to distinguish between these possibilities was not obtained from this study.

The intermediate formation of butene following the bimolecular initiation had been suggested (31);

$$[7] \qquad 2C_2H_4 \rightarrow C_4H_8^*$$

In the present work the formation of butene intermediate through step [7] was considered not to be significant, because of the small percentage (1%) of C_4D_8 found in the product from the pyrolysis of the 1:1 mixture of ethylene-ethylene-d_4. Also, if $(C_4H_8)^*$ were an intermediate, it might be expected to be stabilized by addition of carbon dioxide. The yield of butene, however, was not increased on adding carbon dioxide. The formation of cyclobutane intermediate by the association of two ethylene molecules is also excluded. If such intermediate is formed, some mixing of the unchanged ethylene into $C_2H_2D_2$ would have occurred. The analysis of the unreacted ethylene showed only 0.6% of $C_2H_2D_2$.

Another possible initiation step is the following:

$$[8] \qquad C_2H_4 + C_2D_4 \rightarrow C_2H_4D_2 + C_2D_2$$

Acetylene, however, was not found although it was shown that amounts as small as 0.075 micromole could be detected. Furthermore the percentage of $C_2H_4D_2$ and $C_2H_2D_4$ in the product ethane from the pyrolysis of the mixture of ethylene-ethylene-d_4 was negligible. This result also excludes the molecular process:

[9] $$C_2H_4 \rightarrow C_2H_2 + H_2$$

Since both ethyl and vinyl radicals are the main chain carrying radicals and are in large concentration, the mutual combination of these radicals is considered as the main chain termination step. Whether ethyl or vinyl radicals are the major chain terminating radicals will not affect the conclusions of this study, since both radicals are assumed to disappear by bimolecular reactions.

The Chain Propagation

The stoichiometry of the propagation can be represented by equation [10A] :

[10A] $$R. + n\,C_2H_4 \rightarrow R'. + C_{2n}H_{4n}$$

(where R. and R'. are both alkyl or both alkenyl radicals) for the formation of mono olefins. Equations [10B] and [10C] :

[10B] $$C_2H_3 + n\,C_2H_4 \rightarrow C_{2n}H_{4n-2} + R \text{ (or } C_2H_5)$$

[10C] $$R. + C_2H_4 \rightarrow RH + C_2H_3$$

(where R is limited to alkyl radicals only) represent the equimolar formation of a saturated hydrocarbon and a diolefin from the reaction of vinyl propagation. In a broad sense reaction step [10B] and [10C] are both chain transfer steps, and both alkyl and alkenyl radicals are involved in carrying out the chain cycle.

The addition of ethyl or vinyl radicals to ethylene to form alkyl or alkenyl radicals has a fairly small activation energy and both ethyl and vinyl radicals may start the polymerization represented by equation [10A] to produce many higher olefins. This assumption is supported by the work of Simmons, Rabinovitch and Dorer (45). Since the amount of saturated hydrocarbons and diolefins produced is much greater than can be accounted for from termination steps, there is little doubt that the vinyl radical adds readily to ethylene as represented by equations [10B] and [10C]. In their study on the polymerization of ethylene sensitized by ethyl radicals, Sefton and LeRoy (46) reported that the higher alkyl radicals formed by the addition of ethyl radicals to one or more ethylene molecules have a reactivity comparable to that of the ethyl radical. Thus the reaction represented by equation [10A] may involve more than one step. The larger radicals from the addition of vinyl radicals to one or more molecules of ethylene can be assumed to have reactivity similar to that of vinyl in the addition steps. In this study it can be considered that both vinyl and ethyl radicals add to ethylene, and the subsequent alkenyl and alkyl radicals undergo further addition to ethylene. Such polymerization can proceed until the rate of decomposition of the radicals becomes equal to their rate of addition. Since octene was found among the high molecular weight hydrocarbons, it can be estimated that the size of radicals can be as high as C_{10}.

The building up of large radicals by the addition of ethyl and vinyl radicals to ethylene is a major source of difference between the pyrolysis of ethylene and that of paraffins. It is not possible to discuss the propagation steps in terms of a few chain carrying radicals as has been done with the lower paraffins. In the ethylene pyrolysis each product may be formed from several different radicals and each radical may form more than one product.

From the decomposition of both alkyl and alkenyl radicals mono-olefins such as propylene and butene are produced, and from alkenyl radicals diolefins such as butadiene and pentadiene are produced. The saturated hydrocarbons, such as ethane and butane may come from hydrogen-abstraction or from radical combination. These reaction steps are represented as equations a, b, c, ... t.

Although there are many chain carrying radicals the concentrations of some are much higher than those of others. The predominant production of ethane suggests that the ethyl radical probably is present in large concentration. The ethyl radical may be formed by decomposition of both alkyl and alkenyl radicals such as 4bl and 4cl'. The reaction step 4cl' and similar steps may be called chain transfer steps since the alkenyl radical is transformed to an alkyl radical.

There is also the possibility of direct hydrogen atom transfer from radicals to ethylene:

[11] $$C_nH_{2n+1} + C_2H_4 \rightarrow C_2H_5 + C_nH_{2n}$$

[12] $$C_nH_{2n-1} + C_2H_4 \rightarrow C_2H_5 + C_nH_{2n-2}$$

These steps also regenerate ethyl radicals and will increase the concentration of ethyl radicals. The rate constants of steps [11] and [12] are unknown. These reactions are very likely slightly exothermic because the C-H bond in the ethyl radical is stronger than C-H bonds in higher hydrocarbon radicals.

The rates of formation of hydrogen, methane and propane were much smaller than that of propylene. Hence it is unlikely that the propyl and butyl radicals are the main precursors of propylene production:

[13] $$C_3H_7 \rightarrow C_3H_6 + H$$

[2b] $$C_4H_9 \rightarrow C_3H_6 + CH_3$$

Furthermore, the rate of dissociation of the butyl radical to give butene, $C_4H_9 \rightarrow C_4H_8 + H$, is about 10^{-2} times the rate of dissociation to give propylene in the temperature range of this study. Since the ratio of butene to propylene was about 0.3 at all temperatures and pressures, butene and propylene are probably not formed mainly from the butyl radical decomposition. In agreement with this the butane yield was relatively small. Therefore it seems that the butyl radical is not the main precursor of either propylene or butene and higher radicals must contribute significantly to the formation of these products.

The Induction Period

The induction periods of the major products, especially at low temperature and pressure, were unusually long compared to those observed in the pyrolysis of other hydrocarbons. The induction periods are listed in Table V.

Very small, but detectable yields of propylene were observed during the induction period, as illustrated in Figure 6. This demonstrates that the rate within the induction period gradually increases until the sharp increase in the yield at the end of the induction period. The gradual acceleration is even more obvious for ethane production and in this case it even appears to continue beyond the time of the corresponding induction period, especially at the lower temperature.

The induction period was observed to decrease with increasing temperature and pressure and was reproducible within the accuracy of its measurement. This suggests that inhibition by an impurity in the reactant is probably not the cause of the induction period. Some gas phase pyrolysis reactions which proceed by a radical chain reaction having a relatively slow propagation step have been observed to have induction periods. It has been suggested that the induction period of such reactions is caused by the slow steady state establishment of the radical concentration and the magnitude of this effect has been estimated (47). The length of such induction periods is short compared to those observed in the ethylene pyrolysis and the latter therefore cannot be accounted for by such a cause.

It is proposed that the cause of the induction period in the ethylene pyrolysis is the secondary initiation resulting from the break down of some of the products of the reaction, especially olefins. Many olefinic products are less stable than ethylene under the reaction conditions and small quantities of these products become the source of secondary initiation.

At 584°C the yield time plot of 1-butene showed a linear portion after the induction period but then gradually levelled off as the ethylene conversion increased even though the ethylene had not been appreciably depleted. This was also observed at the lower reaction temperature when the ethylene pressure was high. The yield time plots of propylene formation behave in a similar way at higher temperatures. This suggests secondary decomposition is becoming important at the higher conversion. The rate of dissociation of propylene and butene may be compared to the rate of initiation by ethylene at various times of reaction. The following values were used (Table VII),

[1] $2C_2H_4 \rightarrow C_2H_5 + C_2H_3$ Rate $= 10^{14.82}e^{-64,000/RT}[C_2H_4]^2$

[14] $C_3H_6 \rightarrow CH_3 + C_2H_3$ Rate $= 10^{17.8}e^{-94,000/RT}[C_3H_6]$

[15] $C_4H_8 \rightarrow CH_3 + C_3H_5$ Rate $= 10^{17.8}e^{-77,800/RT}[C_4H_8]$

The rate of dissociation of propylene at 505° and 584°C can be calculated by using the rate equation of Marshall, Purnell and Shurlock (48) and the appropriate propylene concentrations. Since the Arrhenius equation for the dissociation of butene-1 is not known, its rate equation was estimated. The frequency factor of the dissociation of butene-1 was assumed to be about the same as that of propylene and the activation energy was estimated as 77.8 Kcal. mole^{-1} by using the thermochemical data of Benson (47) and Marshall et al (48). In this calculation the combination of methyl and allyl radicals was assumed to have no activation energy. An increase of 3 to 5 Kcal/mole in the estimated activation energy corresponds to a factor of 0.1 in the rate of butene dissociation at these temperatures.

The rates for the secondary dissociation of propylene and butene are compared with the rate of the bimolecular initiation of ethylene in Table IX.

The concentrations of propylene and butene were obtained from the yield time plots shown in Figures 6 and 7. In the experiments at 505°C, the yields of propylene and butene during the first 500 seconds, namely within the induction period, were not measurable and were estimated as less than 10^{-11}mole. cc^{-1}. Compared to the bimolecular initiation of ethylene, the rate of secondary initiation of butene at 505°C is not important until fairly long reaction times. At 505°C the secondary initiation of propylene probably is negligible but at 584°C it also becomes significant. At 584°C the rate of secondary initiation of butene increases rapidly as the reaction proceeds and may be the major source of secondary initiation.

Table IX

Comparison of the Rate of Initiation of Ethylene with the Rates of Secondary Dissociation of Propylene and Butene

Reaction time s	$[C_2H_4]$	$[C_3H_6]$ mole cc.$^{-1}$	$[C_4H_8]$	$R_{C_2H_4}$	$R_{C_3H_6}$ mole cc.$^{-1}$s 1	$R_{C_4H_8}$
505°C						
1	5×10^{-6}	$<10^{-11}$	$<10^{-11}$	10^{-15}	$<10^{-19}$	$<10^{-15}$
500	5×10^{-6}	2×10^{-9}	$<10^{-11}$	10^{-15}	2×10^{-17}	$<10^{-15}$
1000	5×10^{-6}	10^{-8}	5×10^{-9}	10^{-15}	10^{-16}	10^{-13}
584°C						
1	10^{-5}	10^{-9}	4×10^{-9}	3×10^{-12}	10^{-15}	10^{-12}
500	1×10^{-5}	7×10^{-7}	7×10^{-8}	3×10^{-12}	7×10^{-13}	10^{-10}

Decomposition of other olefin products may also be important in the temperature range studied, although the higher olefins were formed in much smaller concentration. The same radicals may be formed by decomposition of the higher olefins and hence the extent of the secondary initiation is difficult to establish.

There are three classes of hydrocarbons in the major products of the ethylene reaction. These are paraffins, olefins and diolefins. The relative stability of these compounds towards thermal decomposition is roughly: diolefins $<$ olefins $<$ paraffin. The thermal decomposition of saturated hydrocarbons, particularly ethane, is negligible relative to that of ethylene itself at low conversions but it cannot be neglected in the reactions of the ethylene-ethane mixtures. Conjugated diolefins may undergo various rearrangement reactions and Diels-Alder additions. These reactions should have little effect on the radical chain process. The most likely secondary initiation is the decomposition of olefins such as propylene, butene, hexene, and the non-conjugated diolefins such as 1,4-pentadiene. Yield time plots of both propylene and butene show definite levelling off after long reaction times (Figures 6, 7). At high temperatures and pressures, C_5 and C_6 unsaturated hydrocarbons and octene appeared in the products at short reaction times. Furthermore, the yield time plots of both C_5 and C_6 unsaturated hydrocarbons show similar levelling off at longer reaction times at 45 cm pressure and 584°C. The thermal stability of higher olefins is similar to that of butene and the thermal decomposition of many olefins may contribute to the secondary initiation. As these decompose the radical concentration increases rapidly. The rate of formation of many products then increases rapidly until a new steady state concentration of radicals is attained. This marks the period of the reaction when many products are formed with constant rates.

It has been experimentally established that the rate of formation of the major primary products maintained constant values for a period of time after the induction period. The constant rate indicates a constant concentration of radicals over this period of time. That so many products, olefins and non-conjugated diolefins showed a constant rate over the same period of time suggests a common reaction mechanism for the formation of the major primary products. According to the reaction steps given in the previous section, many chain carrying radicals are interchangeable and it is the total radical concentration which determines the rates of formation of the products. A steady state treatment for the major precursor radicals is therefore appropriate in this region in order to establish a reaction mechanism for the ethylene reaction.

Steady State Treatment

From the yield-time plots it was shown that all the major products except ethane and butane at low reaction temperatures were formed with an induction period. Nevertheless a well-defined rate of production of propylene, butene, butadiene, and in many cases C_5, C_6 and C_8 unsaturated hydrocarbons was measurable after the induction period. This indicates the concentration of radicals has reached a steady state and the steady state treatment is therefore applicable, using the rates measured after the induction period.

Assuming a steady state concentration for the chain carrying radicals, mainly ethyl and vinyl, and assuming that termination occurs by mutual combination of radicals in the gas phase, the steady state concentration of the ethyl radical may be expressed as follows:

[16] $$[C_2H_5] = (\frac{k_1}{k_t})^{1/2} [C_2H_4]$$

The concentration of all other radicals may be expressed in terms of the concentration of ethyl radicals.

At higher reaction pressure and temperature or long reaction time, initiation may be considerably enhanced by the secondary decomposition of the products, most notably butene. The effect on the ethyl radical concentration of the thermal decomposition of butene is as follows. If butene, X, is formed in a bimolecular radical reaction with ethylene, its rate of formation may be expressed as:

[17] $$\text{Rate X} = k_p (\frac{k_1}{k_t})^{1/2} [C_2H_4]^2$$

where k_p is an average propagation rate constant. (The conditions for the validity of this rate equation will be shown later). Subtracting the rate of decomposition of butene, $k_d[C_4H_8]$, from the Rate X above is the observed experimental constant rate c for butene.

$$\text{Rate X} - k_d[C_4H_8] = c \tag*{[18]}$$

therefore,

$$k_d[C_4H_8] = \text{Rate X} - c \tag*{[18a]}$$

Substituting Rate X in this equation, it becomes:

$$k_d[C_4H_8] = k_p(\frac{k_1}{k_t})^{1/2}[C_2H_4]^2 - c \tag*{[19]}$$

where k_d is the specific rate constant for the dissociation of butene. In cases where secondary initiation is due to other higher molecular weight products, k_d will be the summation of all the characteristic specific rate constants for each or all the compounds. The secondary initiation by other higher molecular weight compounds may be relatively unimportant, since these products were formed in smaller amounts and their rate constants of decomposition are probably about the same as that of butene. The steady state ethyl radical concentration under the influence of secondary initiation of butene can be obtained from the relationship that total initiation equals termination.

$$k_t[C_2H_5]^2 = k_1[C_2H_4]^2 + k_p(\frac{k_1}{k_t})^{1/2}[C_2H_4]^2 - c \tag*{[20]}$$

$$[C_2H_5] = \left\{(\frac{k_1}{k_t})^{1/2}[(\frac{k_1}{k_t})^{1/2} + \frac{k_p}{k_t}][C_2H_4]^2 - \frac{c}{k_t}\right\}^{1/2} \tag*{[20a]}$$

The radicals formed in the secondary initiation eventually will be transformed into the ethyl radical through the propagation chain.

The $k_1[C_2H_4]^2$ term represents the bimolecular initiation, the sum of the next two terms, k_p and c, the rate of radical formation due to butene decomposition. The ethyl concentration will be reduced to the first term $(k_1/k_t)^{1/2}[C_2H_4]$ when the major initiation is the bimolecular reaction of ethylene. In another case, when initiation is largely from dissociation of the products:

$$k_1[C_2H_4]^2 << k_p(\frac{k_1}{k_t})^{1/2}[C_2H_4]^2 - c$$

and when $c \rightarrow 0$, the ethyl concentration becomes:

$$[20b] \qquad [C_2H_5] \rightarrow (\frac{k_1}{k_t})^{1/4} (\frac{k_p}{k_t})^{1/2}[C_2H_4]$$

In both cases, the concentration of the ethyl radical has a first order dependence on ethylene. The condition $c \rightarrow 0$ means the condition under which the butene formed reached a steady state. In the following mathematical treatment, either of the above equations for ethyl radical concentration can be used. It will not affect the order of the reaction. Equation [16] is therefore used in the following description. After the induction period where the rates for product formation have reached constant values, the secondary initiation has reached its maximum effect and does not further increase the number of reaction centres.

The main concern in this discussion is with the propagation reactions which lead to the formation of the products and these reactions were outlined on page 39. The secondary initiation may form radicals different from those formed in the primary initiation yet the main chain carrying radicals will be the ethyl and vinyl radicals since these are regenerated from the abstraction and transfer reactions with ethylene.

The propagation chains may be regarded as consisting of two parallel chains, one carried by ethyl radicals and the other by vinyl radicals. The rate constants of steps involving ethyl radicals are represented by unprimed k's and those involving vinyl radicals by the primed k''s. These two chains are interrelated by regeneration of ethyl or vinyl radicals from the decomposition steps, such as step 4'cl, the decomposition of the hexenyl radical, and from the abstraction reactions (a), (b), and others. The chain transfer steps may be represented by the equations:

[21] $$C_nH_{2n-1} + C_2H_4 \rightarrow C_2H_5 + C_nH_{2n-2}$$

[22] $$C_nH_{2n+1} + C_2H_4 \rightarrow C_2H_3 + C_nH_{2n+2}$$

which may not occur in one step.

Assuming all vinyl radicals are consumed in addition steps and recovered by steps a, b and 4'bl, the following expression is obtained:

[23] $$k'_2[C_2H_3]A = k_a[C_2H_5]A + k_b[C_4H_9]A + \frac{k'_{4b1}\ \ k'_{4a}}{k'_{4b1} + k'_{4b2}}[C_6H_{11}]$$

where A is the ethylene concentration. The fourth term represents only a fraction of the total butene yield while total butene formation was relatively small compared to the second term, $k_a(C_2H_5)A$, the ethane yield. The third term did not exceed one tenth of the second term since the butane production was always less than one tenth of the ethane production. The equation may be simplified to:

[24] $$k'_2[C_2H_3]A = \rho\, k_a[C_2H_5]A$$ and

[25] $$[C_2H_3] = \rho \frac{k_a}{k'_2} [C_2H_5]$$

where $1 < \rho < 2$.

The steady state concentration of the other main radicals may be expressed in terms of the ethyl and vinyl radical concentration:

[26] $$[n\text{-}C_4H_9] = \frac{k_2}{(k_{-2}+k_{2a}+\ldots) + (k_4+k_b)[C_2H_4]}[C_2H_5]A$$

[27] $$[s\text{-}C_4H_9] = \frac{k_{2a}}{k_{2b}+k_{2c}} \cdot \frac{k_2}{(k_{-2}+k_{2a}+\ldots)+(k_4+k_b)A}[C_2H_5]A$$

[28] $$[n\text{-}C_6H_{13}] = \frac{k_4}{(k_{4a}+k_{4b}+k_{-4}\ldots)+(k_6+k_c)A} \cdot \frac{k_2}{(k_{-2}+k_{2a}+\ldots)+(k_4+k_b)A}[C_2H_5]A^2$$

$$[29] \qquad [\text{n-C}_4\text{H}_7] = \frac{k'_2}{(k'_{-2}+k'_{2a}+\ldots)+(k'_4+k'_b)A}\,[\text{C}_2\text{H}_3]A$$

$$[30] \quad [\text{n-C}_6\text{H}_{11}] = \frac{k'_4}{(k'_{-4}+k'_{4a}+k'_{4b}+k'_{4c}+\ldots)+(k'_6+k'_c)A} \cdot \frac{k'_2}{(k'_{-2}+k'_{2a})+(k'_4+k'_b)A}[\text{C}_2\text{H}_3]A^2$$

$$[31] \qquad [\text{n-C}_n\text{H}_{2n+1}] = \frac{k_{n-2}}{(k_{-(n-2)}+k_{(n-2)a}+k_{(n-2)b}+\ldots)+(k_n+k_{ab})A}\cdots\cdots$$

$$\frac{k_2}{(k_{-2}+k_{2a}+\ldots)+(k_4+k_b)A}\,[\text{C}_2\text{H}_5]A^{(n-2)/2}$$

$$[32] \qquad [\text{n-C}_n\text{H}_{2n-1}] = \frac{k_{n-2}}{(k'_{-(n-2)}+k'_{(n-2)a}+k'_{(n-2)b}+\ldots)+(k'_n+k'_{ab})A}\cdots\cdots$$

$$\frac{k'_2}{(k'_{-2}+k'_{2a}+\ldots)+(k'_4+k'_b)A}\,[\text{C}_2\text{H}_3]A^{(n-2)/2}$$

The last two equations are the generalized forms for the concentrations of chain carrying radicals. The first term of the denominator of each fraction, called the unimolecular term, includes all unimolecular modes of decomposition. The second term, the bimolecular term, includes all bimolecular rates of addition to and hydrogen abstraction from ethylene of the radical $C_nH_{2n\pm1}$.

Some assumptions have been made in the derivation of these equations, but these assumptions can be shown to be reasonable approximations. For example, assuming the steady state for butyl radical concentration, the rate of formation of this radical must equal the rate of its decay. From this condition, the following equation can be derived:

$$k_2[C_2H_5][C_2H_4] = (k_{-2}+k_{2a})[n\text{-}C_4H_9] + (k_4+k_b)[n\text{-}C_4H_9][C_2H_4]$$

In this expression the formation of the butyl radical from step -4 is neglected because $k_{-4}[C_6H_{13}]$ is much smaller than $k_2[C_2H_5][C_2H_4]$.

From the data available it may be estimated that the reverse reactions such as (-2) are important relative to the corresponding forward reactions (2) in this system. According to Sefton and LeRoy (46), the higher alkyl radicals in the ethylene polymerization probably have comparable activity to that of the ethyl radicals. The activation energy of vinyl addition to ethylene is very close to that of ethyl addition. It is therefore assumed that the reverse reactions for the alkyl and alkenyl addition reactions are important. These decomposition reactions add a unimolecular rate constant to the denominators of each fraction in the expressions for the radical concentrations. This is an important factor in determining the order of the rate and will also affect the activation energy of the rate. The sequence of addition and abstraction reactions represented by the second parentheses in the denominator, $(k_n + k_{abstraction})A$, has the effect of lowering the order of the rate with respect to ethylene.

The Order of the Total Reaction Rate

The order of the total reaction rate in kinetic studies of the thermal reactions of gaseous hydrocarbons are often derived from pressure measurements. By such measurements a second order reaction rate was reported for the ethylene pyrolysis (31).

The total reaction rate is to a close approximation the rate of consumption of ethylene in the propagation steps. According to the radical polymerization mechanism, the addition and abstraction reactions each consume one molecule of ethylene. The total reaction rate is therefore the sum of the abstraction and addition reactions of all radicals:

$$[33] \qquad \text{Rate} = \sum_{R} \text{abstraction} + \sum_{R} \text{addition}$$

In the ethylene pyrolysis, the chain propagation radicals include all radicals formed by addition reactions of the vinyl, ethyl and other radicals. Inserting the rate equation for each term in equation [33] the total rate may be written:

$$[34] \qquad \text{Rate} = (k_a[C_2H_5] + k_b[C_4H_9] + \ldots)A$$

$$+ (k_2[C_2H_5] + k_4[C_4H_9] + k_2'[C_2H_3] + k_4'[C_4H_7] + \ldots)A$$

Measurements of the time course of the total pressure were made after the induction period. For comparison with this study, the steady state concentration of the radicals may be inserted in this equation.

Referring to the radical concentration of equation [26]-[32], when the first sum of rate constants will be greater than the second sum of specific rates in the denominators and applying such conditions in equations [26] to [32], the total rates in equation [34] can be reduced to:

$$[35] \quad \text{Rate} = \left(\frac{k_1}{k_t}\right)^{1/2}\Big(\underset{(A)}{k_a} + k_b \underset{(B)}{\frac{k_2}{k_{-2}+k_{2a}}} A\Big)A^2$$

$$+\Big\{\Big(\underset{(C)}{k_2A}+k_4 \underset{(D)}{\frac{k_2}{k_{-2}+k_{2a}}} A^2+\ldots\Big)+\Big(\underset{(E)}{k'_2}+k'_4 \underset{(F)}{\frac{k'_2A^2}{k'_{-2}+k'_{2a}}}+\ldots\Big)\Big[\frac{k_a}{k'_2}\Big]\Big\} \left(\frac{k_1}{k_t}\right)^{1/2}A$$

In the above equation the (B) term of the right hand side is the rate of hydrogen-abstraction of the butyl radical which is much smaller than the (A) term, the hydrogen-abstraction of the ethyl radical, since the rate of formation of ethane is ten times that of butane. The (C to (F) terms represent the addition rates of ethyl, butyl, vinyl and butenyl radicals respectively and are of the order between two and three with respect to ethylene. Thus the order of the total reaction rate with respect to ethylene would become higher if larger radicals are involved when the unimolecular term is larger than the bimolecular term for the radicals. The order of the reaction rate measured at 501.6°C was 2.3.

When the bimolecular term will be greater than the unimolecular term in the denominator and applying such a condition in equation [26] to [32], the total rate becomes:

$$[36] \quad \text{Rate} = \left(\frac{k_1}{k_t}\right)^{1/2}\left[k_a + k_b \frac{k_2}{k_4+k_b} \right] A^2$$

$$+ \left[\left(k_2 + k_4 \frac{k_2}{k_4+k_b} + \ldots\right) + \left(k'_2 + k'_4 \frac{k'_2}{k'_4+k'_b} + \ldots\right) \rho \frac{k_a}{k'_2} \right] \left(\frac{k_1}{k_t}\right)^{1/2} A^2$$

This predicts a second order rate which agrees with that reported by Douglas and Dahlgreen (32). It means that the order of the total reaction rate with respect to ethylene remains at two, despite the participation of larger radicals in the polymerization if the bimolecular reaction is faster than the unimolecular decomposition of the radicals. At 563.6 and 584°C the measured order of the total reaction rate was 1.8 and 1.5 respectively.

At lower temperatures, the polymerization is relatively more important than at higher temperatures, because the order of the reaction rate is increased by the contribution of the higher alkyl and alkenyl radicals to the reaction rate. If decomposition of the radicals remainsthe important mode of disappearance, then the steady state concentration of the higher alkyl and alkenyl radicals assumes a high dependence on the ethylene concentration, as expressed in equations [20] to [26] and equation [33]. Since the order measured is only 2.3 at 501°C, the contribution to the rate by large radicals is not very important. It is concluded that radical concentration decreases with increase in radical size. This could be the other reason the major products of ethylene reaction are low molecular weight hydrocarbons.

The Activation Energy of the Total Reaction

The factors $k_2/(k_4+k_b)$ and $k'_2/(k'_4+k'_b)$ in equation [36] will have little effect on the activation energy, since $E_2 \approx E_4$, $E'_2 \approx E'_4$, and $k_4 \gg k_b$ and $k'_4 \gg k'_b$. From Table VII it may be seen that k_4, k'_4, k_b and k'_b have similar frequency factors, while E_b and E'_b are about 10 kcal. mole^{-1} compared to 5 - 7 kcal. mole^{-1} for E_4 and E'_4. The activation energies of the four terms in equation [36], the hydrogen-abstraction reactions of the ethyl and butyl radicals, and the addition reactions of the ethyl and vinyl radicals may be written as follows:

$$\frac{1}{2}(E_1-E_t) + E_a = \frac{1}{2}(64-0) + 10 = 42$$

$$\frac{1}{2}(E_1-E_t) + E_b + (E_2-E_4) = \frac{1}{2}(64-0) + 10 + (7.5-6.7) = 42.8$$

$$\frac{1}{2}(E_1-E_t) + E_2 = \frac{1}{2}(64-0) + 7.5 = 39.5$$

$$\frac{1}{2}(E_1-E_t) + E_a = \frac{1}{2}(64-0) + 10 = 42$$

The average activation energy of the four terms is 41.6kcal. mole^{-1}. The activation energy estimated from equation [35] also gives a low activation energy. The observed activation energy will be a complex combination of these values, as expressed in the total rate equation, depending on the importance of each step. The activation energy estimated from all products measured in this study was about 40 kcal. mole^{-1}. An activation energy of 41 kcal. mole^{-1} has been reported by Dahlgren and Douglas (32). Storch (29) reported a value of 43.5 kcal. mole^{-1} and Pease (28) of 35 kcal. mole^{-1} for the activation energy at relatively high reaction pressure and longer reaction time and the accuracy of their data may be limited by their analytical method.

The origin of Saturated Hydrocarbons

The main saturated hydrocarbon products were ethane and butane and minor ones were methane and propane. The saturated hydrocarbons may be formed in hydrogen-abstraction reactions or in combination and disproportionation reactions of alkyl radicals.

[22] $\text{Alkyl} + C_2H_4 \rightarrow RH + C_2H_3$

[37] $\text{Alkyl} + \text{Alkyl} \rightarrow RR$

or $\rightarrow RH + \text{olefin}$

The ratio k_d/k_c is 0.14 for ethyl and 0. for n-butyl radical. The disproportionation reaction has only a minor role in this mechanism and will not be discussed further.

Ethane

The increasing rate of production of ethane seemed to extend to a longer period than the induction period at 505°C. At this temperature the thermal decomposition of ethane itself may be neglected (10). At 563 and 584°C the yield versus time plot of ethane production was similar to that of propylene and other products. A constant rate was observed after the brief induction period. At the higher temperature the thermal decomposition of ethane may become important as the yield of ethane increases. Ethane is considered to be formed from the reaction of radicals in the chain process. The most probable sources of ethane are hydrogen abstraction by the ethyl radical, R_{ab}, and the combination of methyl radicals R_r .

The relative rates of these two processes may be expressed as:

$$[38] \qquad \frac{R_{ab}}{R_r} = \frac{k_{ab}[C_2H_5][C_2H_4]}{k_r[CH_3]^2}$$

The ethyl radical concentration was calculated from equation [16] and the methyl radical concentration was calculated from the equation $\text{Rate}_{CH_4} = k_{ab}[CH_3][C_2H_4]$, using the measured yield of methane. The disproportionation of ethyl radicals may be neglected since the product from the combination of ethyl radicals, butane, was formed in much smaller amount than ethane. The ratio, R_{ab}/R_r, was calculated to be $10^{8\pm3}$ at all temperatures and pressures studied, using the value of the rate constants listed in Table VII . It can be concluded therefore, that ethane is produced mainly from the ethyl radical abstraction rather than from the combination of methyl radicals.

This conclusion is further supported from the mass spectrometric analysis of the ethane product from experiments with 1:1 ethylene-ethylene-d_4 mixture. If ethane is produced through step 1, which involves transfer of a hydrogen atom, the product ethane would contain predominantly one or two atoms of the other isotope of hydrogen. The sum of C_2H_6, C_2H_5D , $C_2H_2D_4$ and C_2HD_5 amounted to more than 90% of the total product. The small percentage of $C_2H_4D_2$ and C_2D_6 is understandable since the C-D bond is tronger than the C-H bond. The higher percentage of C_2H_5D than that of C_2H_6 and the higher percentage of C_2HD_5 than C_2D_6 probably reflect isotope effect and/or statistical factors in the various rates. The small percentage of $C_2H_3D_3$ may come from methyl radical combination.

The formation of ethane by the molecular proces $2C_2H_4 \rightarrow C_2H_6 + C_2H_2$ can be excluded since acetylene was not found among the reaction products under any conditions.

The equation for the rate of formation of ethane may be written as follows:

$$\frac{dC_2H_6}{dt} = k_a[C_2H_5]A = k_a(\frac{k_1}{k_t})^{1/2} A^2 \qquad [39]$$

Using the estimated value of E_1 and assuming E_a = 10 kcal/mole and E_t = 0, the activation energy for the rate of formation of ethane may be estimated as follows,

$$E_{ethane} = 10 + \frac{1}{2}(64 - 0) = 42 \text{ kcal/mole}.$$

This equation applies under conditions where initiation is mainly by reaction (1). Although the rate of formation of ethane was measured in the post-induction period where considerable secondary initiation may occur the observed activation energy of 45 kcal/mole for ethane formation was close to this value. The conclusion may be either that reaction (1) is still an important initiation reaction in the region where the rate of formation of ethane was measured or that the secondary initiation occurs by a reaction similar to reaction (1) with a similar activation energy. From equation [39] the rate of ethane production would be expected to be second order with respect to ethylene. This order was observed for ethane under all conditions (Table V).

Butane

The two main sources of butane formation are hydrogen abstraction by butyl radical R_{ab}, and the combination of ethyl radicals R_r. The ratio of these two rates is:

$$[40] \qquad \frac{R_{ab}}{R_r} = \frac{k_{ab}[C_4H_9][C_2H_4]}{k_r[C_2H_5]^2}$$

Inserting the steady state concentrations of ethyl and butyl radicals the equation becomes:

$$[40a] \quad \frac{R_{ab}}{R_r} = \frac{k_{ab}}{k_r}\left(1 + \frac{k_{2a}}{k_{2b}+k_{2c}}\right)\frac{k_2}{(k_{-2}+k_{2a}+\ldots)+(k_4+k_b)A}\left(\frac{k_t}{k_1}\right)^{1/2}A$$

It is assumed that both n- and s-butyl radicals lead to butane formation at the same rate. The R_{ab}/R_r obtained is between 10^2 to 10^3 at 501°C and 42 to 142 at 584°C, with the lower value corresponding to the lower pressure. It is therefore reasonable to consider that hydrogen-abstraction by butyl radicals is the main route to butane formation. The increase in the rate of butane production when ethane is added supports this conclusion. The butyl radical disproportionation will be even less significant than the ethyl radical disproportionation, since the concentration of butyl radicals is much less than ethyl radicals in the system. The combination of ethyl radicals may still contribute to the yield of butane especially at low temperatures and low pressures.

The rate of butane formation may be expressed as:

$$[41] \qquad \frac{{}^{d}C_4H_{10}}{dt} = k_b[C_4H_9]A = k_b\left\{ [n\text{-}C_4H_9] + [s\text{-}C_4H_9] \right\} A$$

$$= k_b \, \frac{k_{2a}+k_{2b}+k_{2c}}{k_{2b}+k_{2c}} \, \frac{k_2}{(k_{-2}+k_{2a}+..)+(k_4+k_b)A} \left(\frac{k_1}{k_t}\right)^{1/2} A^3$$

This equation predicts the order of the rate of butane production to be between 2 to 3. At higher temperatures, where $(k_{-2}+k_{2a}) \gg (k_4+k_b)A$, i.e. where the dissociation and the isomerization of the radicals are favored over the addition and abstraction reactions, the rate becomes third order:

$$[42] \qquad \frac{{}^{d}C_4H_{10}}{dt} = k_b \frac{k_{2a}+k_{2b}+k_{2c}}{k_{2b}+k_{2c}} \, \frac{k_2}{k_{-2}+k_{2a}} \left(\frac{k_1}{k_t}\right)^{1/2} [C_2H_4]^3$$

The observed order was between 2.3 and 2.6 (Table V).

The activation energy may be estimated from equation [42] as follows, using the literature values given in Table VII ;

$$E_{\text{butane}} = E_b + [E_2 - E_{-2}] + \frac{1}{2}[E_1 - E_t] = 20.8$$

or

$$E_b + [E_2 - E_{2a}] + \frac{1}{2}[E_1 - E_t] = 38.7.$$

The experimental activation energy was 53 ± 2.5 kcal. mole^{-1}. The activation energy for the rate of butane formation probably has a larger error due to the change in the order of the rate over the temperature range studied.

Taking into account the rate of butane formation from the combination of ethyl radicals, the rate of butane formation becomes:

$$[43] \qquad \frac{d_{C_4H_{10}}}{dt} = [k_b(M_2 + M_{22}M_2)A + k_t(\frac{k_1}{k_t})^{1/2}](\frac{k_1}{k_t})^{1/2}A^2$$

where M_2 and M_{22} are:

$$[44] \qquad M_2 = \frac{k_2}{(k_{-2} + k_{2a}) + (k_4 + k_b)A} \; : \; M_{22} = \frac{k_{2a}}{k_{2b} + k_{2c}}$$

The activation energy estimate for this rate is 64 kcal. mole^{-1}. Comparing the activation energies of these two rates and the experimental value, 53 kcal. mole, it can be suggested that the contribution of ethyl combination to the butane production may be significant. This is not surprising, as the ethyl radical is in the largest concentration.

The ethane and butane came from similar abstraction reactions of the ethyl and butyl radical respectively, yet the activation energies of their rates were very different. Beside the reason mentioned above, a contributing factor may be that a large fraction of ethyl radicals is formed from the chain transfer step reactions (4bl) or (4'cl) , while the contribution of such transfer steps to the formation of the butyl radical may be much less significant.

Methane

The continuous increase in the rate of formation of methane seems to suggest a secondary reaction. The rate was measurable at all temperatures and in the early stages of the reaction. Methane is likely produced both by primary and secondary reactions before the induction period as well as when the steady state has been established.

If methane is produced through hydrogen-abstraction of methyl radical,

$$CH_3 + C_2H_4 \rightarrow CH_4 + C_2H_3$$

the rate of methane formation is expressed as:

$$[45] \qquad \frac{d_{CH_4}}{dt} = k_{ab}[CH_3][C_2H_4]$$

Assuming the methyl radical is formed mostly through steps 2b, 4b2, 4'b2, the steady state methyl radical concentration can be expressed as:

$$[46] \quad [CH_3] = \frac{1}{k_{ab}} \frac{1}{A} \left\{ k_{2b}[C_4H_9] + k_{4b} \frac{k_{4b2}}{k_{4b1}+k_{4b2}} [C_6H_{11}] + k'_{4b} \frac{k'_{4b2}}{k'_{4b1}+k'_{4b2}} [C_8H_{11}] \right\}$$

Inserting the steady state concentration of $[C_4H_9]$, $[C_6H_{13}]$, $[C_6H_{11}]$ from equations [26]-[32], the methyl radical concentration becomes:

$$[46a] \quad [CH_3] = \frac{1}{k_{ab}} \left\{ k_{2b} \frac{k_{2a}}{k_{2b}+k_{2c}} M_2 + k_{4b} \frac{k_{4b2}}{k_{4b1}+k_{4b2}} M_4 M_2 A + k'_{4b} \frac{k'_{4b2}}{k'_{4b1}+k'_{4b2}} M'_4 M'_2 \rho \frac{k_a}{k'_2} A \right\} [C_2H_5]$$

where

$$[47] \quad M_2 = \frac{k_2}{(k_{-2}+k_{2a}+..)+(k_4+k_b)A} \; ; \; M'_2 = \frac{k'_2}{(k'_{-2}+k'_{2a})+(k'_4+k'_b)A}$$

$$M_4 = \frac{k_4}{(k_{4a}+k_{4b}+k_{-4}+..)+(k_6+k_c)A} \; ; \; M'_4 = \frac{k'_4}{(k_{-4}+k'_{4a}+k'_{4b}+k'_{4c})+(k'_6+k'_c)A}$$

Substituting this expression in the rate equation for methane, the rate expression becomes:

$$[48] \qquad \frac{d_{CH_4}}{dt} = \left[\frac{k_{2a}k_{2b}}{k_{2b}+k_{2c}} M_2 + k_{4b} \frac{k_{4b2}}{k_{4b1}+k_{4b2}} M_4 M_2 A \right.$$

$$\left. + k'_{4b} \frac{k'_{4b2}}{k'_{4b1}+k'_{4b2}} M'_4 M'_2 \int \frac{k_a}{k'_2} A \right] \left(\frac{k_1}{k_t} \right)^{1/2} A^2$$

The order of this rate is roughly between 1 and 2. From a plot of the logarithm of the initial rate of methane formation estimated from the initial tangent of yield-time plots of all experimental data at three temperatures - 505, 563, 584°C - against the logarithm of the initial ethylene concentration, the reaction order was estimated to be 1.5.

Propane

The yield of propane is much smaller than that of butane. The most probable source is hydrogen-abstraction by propyl radicals. This is supported by the increase in rate of propane production when ethane was added. A steady state treatment of the rate of formation of propane is not justified because of its small contribution.

Since there will be higher molecular weight alkyl radicals in the system, there may be small amounts of heavier saturated hydrocarbons which were not identified.

The Origin of the Unsaturated Hydrocarbon

Propylene, butene and butadiene together account for most of the unsaturated hydrocarbon products. All these products exhibit constant rates throughout a considerable period after the induction period. Thus propylene, butene and butadiene are all primary products of the main propagation steps and are formed directly from the polymerization of vinyl or ethyl radicals with ethylene.

Propylene and Butene

The ratio of the rates of propylene and butene, $R_{C_3H_6}/R_{C_4H_8}$, remains constant at 3.2 ± 0.4 throughout the whole range of temperature and pressure of this study. This strongly suggests that both propylene and butene are produced by processes of similar activation energy and presumably of similar type. The most reasonable of such reactions is the C-C split of radicals with carbon number of at least five. The most likely radicals are hexyl, hexenyl, octyl and octenyl which are successive adducts of ethyl or vinyl radicals to ethylene.

There is also the possibility that the precursor radicals of propylene and butene production are alkyl or alkenyl radicals of carbon number greater than eight, since octene was detected in the products at all temperatures.

The relative concentration of radicals of more than eight carbon atoms must, however, be rather small. If such radicals composed a large percentage of radicals, then there should be a comparable production of C_5 and C_6 olefins along with propylene and butene. Experimentally, propylene and butene are the major products among the olefins. The contribution of C_8 or large radicals to the formation of propylene and butene is therefore probably minor. Thus it may be concluded that butyl, butenyl, hexyl and hexenyl radicals, the first few adducts of ethyl and vinyl radical to ethylene, are the most important precursor radicals of propylene and butene formation and the reaction steps 4a1, 4b1, 4'a1, 4'b1 and 2b are considered to represent the main processes of propylene and butene production.

The rate equation of propylene production is:

$$[49] \qquad \frac{d[C_3H_6]}{dt} = k_{2b}[s\text{-}C_4H_9] + k_{4a1}[n\text{-}C_6H_{13}] + k'_{4a1}[n\text{-}C_6H_{11}]$$

$$= [k_{2b}M_{22}M_2+(k_{4a1}M_4M_2+..)A+(k'_{4a1}M'_4M'_2+...)A\int\frac{k_a}{k'_2}]\,(\frac{k_1}{k_t})^{1/2}A^2$$

where

$$[50] \qquad M_{22} = \frac{k_{2a}}{k_{2b}+k_{2c}}$$

From equation [49] when $(k_{-2}+k_{2a}) \gg (k_4+k_b)A$, $(k_{-4}+k_{4a}+k_{4b}) \gg (k_6+k_c)A$

and the same for the corresponding primed rate constants in M'_2 and

M'_4 , i.e. when decomposition is faster than addition and abstraction, equation [49] predicts that the order of the rate of formation of propylene will be between 2 and 3. When addition and abstraction are faster than the decomposition, i.e.,

$$(k_4+k_b)A \gg k_{-2}+k_{2a} \text{ and } (k_6+k_c)A \gg (k_{-4}+k_{4a}+k_{4b}) \text{in } M_2 , M_4$$

and the same for M'_2 and M'_4 in equation [49], the order of the rate will be two. The observed order was 2 ± 0.2 at all temperatures.

If hydrogen-abstraction of the C_3H_5 radical, which is formed in step 4'a1, contributed to propylene formation, the following term should be added to the rate equation [49], assuming steady state for C_3H_5 :

$$k_{ab}[C_3H_5][C_2H_4] = k_{ab} \frac{k'_{4a}}{k'_{4a1}} [n\text{-}C_6H_{11}][C_2H_4]$$

$$= k_{ab} \frac{k'_{4a}}{k'_{4a1}} M'_4 M'_2 \rho \frac{k_a}{k'_2} \left(\frac{k_1}{k_t}\right)^{1/2} [C_2H_4]^4$$

This term will give a high order dependence of the rate.

The same high order effect from allyl radical formed by secondary butene initiation can be predicted. The formation of propylene through this step is hence probably not large, since addition of ethane has been shown to have little effect on the rate of propylene formation and the order of the rate measured was 2 ± 0.2.

The activation energy for propylene production can be estimated from the second term in the rate equation [49] as follows:

$$E_{C_3H_6} = E_{4a}+E_4-E_{-4}+E_2-E_{-2}+\frac{1}{2}(E_1-E_t) = 8.3+6.7-28.7+7.5-28.5+\frac{1}{2}(64-0)$$

$$= -2.7.$$

or

$$E_{C_3H_6} = E_{4a}+E_4-E_{4a}+E_2-E_{2a}+\frac{1}{2}(E_1-E_t) = 8.3+6.7-8.3+7.5-10.8+\frac{1}{2}(64-0)$$

$$= 35.4 \text{ kcal. mole}^{-1}.$$

The isomerization of n-C_4H_9, n-C_6H_{13}, i.e. step (2a), (4a) and the reverse reaction (-2), (-4) are the ones which lower the activation energy. The experimental activation energy is 29.6 ± 2. This is the lowest value of the activation energy among the products of this study, which probably is the reason why propylene is produced in the largest quantity, especially at 501°C.

Assuming that butene comes mainly from decomposition of butyl, hexyl and hexenyl radicals, the rate equation of butene production is :

$$[51] \quad \frac{d_{C_4H_8}}{dt} = k_{2c}[s\text{-}C_4H_9] + k_{4b1}\frac{k_{4b}}{k_{4b1}+k_{4b2}}[n\text{-}C_6H_{13}] + \frac{k'_{4b}k'_{4b1}}{k'_{4b1}+k'_{4b2}}[n\text{-}C_6H_{11}]$$

$$= [(k_{2c}M_{22}M_2+k_{4b1}M_{44}M_4M_2+..) + (k'_{4b1}M'_{44}M'_4M'_2+..)\int \frac{k_a}{k'_2}](\frac{k_1}{k_t})^{1/2}A^2$$

where

$$[52] \quad M_{44} = \frac{k_{4b}}{k_{4b1}+k_{4b2}} \quad ; \quad M'_{44} = \frac{k'_{4b}}{k'_{4b1}+k'_{4b2}}$$

This equation is similar to that for the rate of production of propylene, and predicts that the order of the rate of formation of butene will be between 1 and 2. That the butene production relied more heavily on step (4bl) and (4'bl) than (2c) would be expected from the relative rates of the C-C and C-H bond fission (49). The pressure and temperature dependence of the order of the rate of butene formation can be explained by the competing addition and abstraction reactions of the precursor radicals. The observed order for the rate of butene formation was between 1.5 and 2 (Figure 12).

The activation energy for the rate of production of butene may be estimated taking the second term from equation [51] :

$$E_{butene} = E_{4b}+E_{4}-E_{4a}+E_{2}-E_{2a}+\frac{1}{2}(E_{1}-E_{t}) = 8.3+6.7-8.3+7.5-10.8+\frac{1}{2}(64)$$
$$= 35.4 \text{ kcal. mole.}$$

It is obvious that if the reverse reaction of the addition process is important the activation energy will be lowered by the activation energy of this reaction. The actual E_a will be a combination of all terms in the rate equation. The experimental value was 37.9 ± 2 kcal. mole^{-1}, which is about the same as the activation energy of the overall reaction.

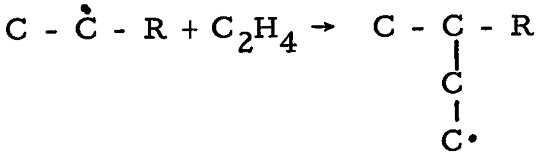
In the treatment of this radical polymerization mechanism it is also assumed that the concentration of branched radicals is relatively small compared to that of normal radicals. In this study this is demonstrated in the amount of butene-2 produced. The butene-2 is always less than 20% of total butene found. The butene-2 is likely produced through decomposition of 2-alkyl or 2-alkenyl radicals with at least six carbon atoms.

The process can be represented as follows:

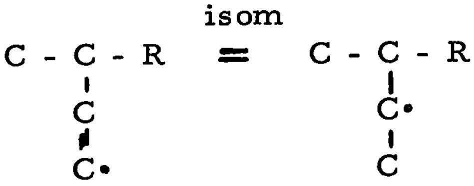
[53] $H_2C = CH_2 + C_2H_5 \text{ or } C_2H_3 \rightarrow \cdot C - C - R$

[54] $\cdot C - C - R \overset{\text{isom}}{\rightleftharpoons} C - \dot{C} - R$ (terminal radical $\rightleftharpoons$ non-terminal radical)

where R is ethyl or vinyl

[55] 

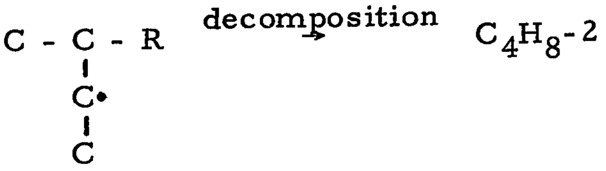
$$C - \dot{C} - R + C_2H_4 \rightarrow \begin{array}{l} C - C - R \\ \quad\;\; | \\ \quad\;\; C \\ \quad\;\; | \\ \quad\;\; C\cdot \end{array}$$

[56] 

$$\begin{array}{l} C - C - R \\ \quad\;\; | \\ \quad\;\; C \\ \quad\;\; | \\ \quad\;\; C\cdot \end{array} \overset{\text{isom}}{\rightleftharpoons} \begin{array}{l} C - C - R \\ \quad\;\; | \\ \quad\;\; C\cdot \\ \quad\;\; | \\ \quad\;\; C \end{array}$$

(branched terminal radical → branched non-terminal radical)

2-alkyl or
2-alkenyl radical

[57] 

$$\begin{array}{l} C - C - R \\ \quad\;\; | \\ \quad\;\; C\cdot \\ \quad\;\; | \\ \quad\;\; C \end{array} \xrightarrow{\text{decomposition}} C_4H_8\text{-}2$$

2-alkyl or 2-alkenyl

The direct isomerization of 1-butene to 2-butene may take place to some degree. The experimental ratio of 2-butene/1-butene was far smaller than the thermodynamic value. In this study there seems to be a temperature dependence of the ratio of butene-1 to butene-2 and this is interpreted as the result of the decomposition of different precursor radicals for the formation of the two compounds. Since butene-2 was much smaller in amount than butene-1, it is assumed that branched radicals are relatively small in concentration compared to the n-radicals. The identification of the isomers of other higher molecular weight products may be useful to decide on this point but is not included in this study.

Butadiene

The order of the rate of butadiene production is about 1 and the activation energy of the rate is 72 kcal. mole^{-1}. The high activation energy suggests that butadiene may originate from a radical decomposition reaction, either butenyl or higher alkenyl radicals.

At 505°C butadiene was not found among the products, indicating that polymerization of unsaturated radicals is faster than decomposition at this temperature. The yield-time plots of butadiene at 530°C showed an induction period, but a constant rate was obtained over a considerable period. In other words, at this temperature, the yield-time plot of butadiene showed behavior similar to propylene and butene. At 584°C the yield approached a maximum value as did the yield of butene, showing that butadiene disappears in secondary reactions. Butadiene may undergo a Diels-Alder type of addition to form cyclic hydrocarbons (50). This reaction does not involve free radicals. The secondary reaction of butadiene therefore probably does not add new radicals to the reaction system and should have no effect on the propagation steps.

The most probable reactions leading to formation of butadiene are the decompositions of butenyl and hexenyl radicals. The rate equation may be written as:

$$[58] \qquad \frac{d_{C_4H_6}}{dt} = k'_{2a}[C_4H_7] + k'_{4c}[C_6H_{11}]$$

$$= [k'_{2a}M'_2 + k'_{4c}M'_4M'_2A] \int \frac{k_a}{k'_2} \left(\frac{k_1}{k_t} \right)^{1/2} [C_2H_4]^2$$

where

$$M'_4 = \frac{k'_4}{(k'_{-4}+k'_{4a}+k'_{4b}+k'_{4c})+(k'_6+k'_c)A} \quad ; \quad M'_2 = \frac{k'_2}{(k'_{-2}+k'_{2a})+(k'_4+k'_b)A}$$

When

$$(k'_4+k'_b)A \gg k'_{-2}+k'_{2a} \text{ and } (k'_c+k'_6)A \gg k'_{4a}+k'_{4b}+k'_{4c}+k'_{-4}$$

the rate equation can be simplified to:

$$[59] \qquad \frac{d_{C_4H_6}}{dt} = \left[k'_{2a}+k'_{4c}\frac{k'_4}{(k'_6+k'_c)A}\right] \frac{k'_2}{(k'_4+k'_b)A} \int \frac{k_a}{k'_2} \left(\frac{k_1}{k_t} \right)^{1/2} A^2$$

From equation [59] the order of the rate of production of butadiene is between 2 and 0, depending on whether decomposition is mainly from the butenyl or the hexenyl radical. The order of reaction rate at 530°C was 1.5 and was slightly lower than 1 at 584°C. The predicted order and experimental order are in close agreement if we assume that at lower temperature butadiene is formed mainly from butenyl and at higher temperature it is also considerably formed from higher alkenyl radicals.

The activation energy of the first term is

$$E'_{2a}-E'_{4}+E_{a}+\frac{1}{2}(E_{1}-E_{c}) = E'_{2a} + 37,$$

using the values of E'_{act} from Table VII. With the experimental activation energy of 72 kcal. mole^{-1}, the activation energy E'_{2a} of the step $C_4H_7 \rightarrow C_4H_6 + H$ is calculated to be 35 kcal. mole^{-1}. This value is reasonable compared to a value of $E_{2c} = 39.7$ calculated by Lin and Laidler (49) for the reaction of $C_4H_9 \rightarrow C_4H_8 + H$. The activation energy for the hexenyl radical decomposition, represented by the 2nd term in the rate equation [59], is

$$E'_{4c}+E_{a}-E'_{6}+\frac{1}{2}(E_{1}-E_{t}) = 43 \text{ kcal. mole}^{-1}.$$

This is much lower than the value of 72 kcal. mole^{-1} and it may be concluded that the first term represents the reactions leading to the formation of butadiene. The experimental values of the activation energy and the order of the rate are in good agreement with that predicted by equation [59], with the assumption that

$$(k'_{4}+k'_{b})[C_{2}H_{4}] \gg (k'_{-2}+k'_{2a})$$

and $$(k'_6+k'_c)[C_2H_4] \gg (k'_{4a}+k'_{4b}+k'_{4c}+k'_{-4}),$$

namely additions of alkenyl radicals are more efficient than their reverse decomposition or isomerization. It is concluded that butadiene is formed by the decomposition of alkenyl radicals under the conditions where reverse dissociation of the radicals is not important. This is the reason why the rate of formation of butadiene is of lower order and has a high activation energy.

The fact that $R_{C_4H_6}$ never exceeds $R_{C_4H_8}$ in all experiments suggests that butenyl radical addition to ethylene may be faster than the corresponding addition of butyl radical. Nevertheless, even this larger concentration of higher alkenyl radicals does not increase the yield of butadiene over that of propylene or butene. This suggests that the hexenyl radical does not readily decompose to form butadiene. It is likely that the 1-hexenyl-3 radical, the one most likely to form butadiene, is in smaller concentration than the other two isomers, 1-hexenyl-4 and 1-hexenyl-5 radicals, because it is formed from the more difficult isomerization of the 1-hexenyl-6 radical. Studies of the isomerization of the n-pentyl (51) and n-hexyl radicals (52) show that the isomerization involving a smaller ring in the activated complex will have the larger activation energy due to strain of the ring. Furthermore, the unsaturated radical can decompose in many ways to give, for example, a saturated radical plus a diolefin,

$$C_6H_{11} \rightarrow C_2H_5 + C_4H_6 ,$$

an unsaturated radical and an olefin,

$$C_6H_{11} \rightarrow C_2H_3 + C_4H_8,$$

or $$C_6H_{11} \rightarrow C_3H_5 + C_3H_6.$$

Thus it is probable that decomposition of the hexenyl radical to propylene and the allyl radical, which has resonance stabilization, is faster than decomposition to butadiene and the ethyl radical. The latter process involves the resonance stabilized 1-hexenyl-3 radical.

Moreover, the same view can be extended to the decomposition of other higher alkenyl radicals. The decomposition of C_8 unsaturated radicals probably favors the formation of pentadiene and propyl radical over the formation of butadiene and butyl radical because the latter reaction will again require an allyl-type resonance stabilized precursor radical. Thus, the decomposition of unsaturated radicals will favor the formation of C_5, C_6 ... diolefins rather than butadiene. It could explain the experimental observation that among the diolefin products there is a large percentage of pentadiene, relative to butadiene, while among the mono olefins the predominant ones are the low molecular weight olefins, propylene and butene.

Higher Molecular Weight Unsaturated Hydrocarbons

Pentadiene is the major component of the C_5 products and hexene of the C_6 products. Pentadiene may be formed from decomposition of the 1-hexenyl-4 or its radical homologs. The pentenes are expected to be present from the decomposition of the 3-hexyl radical or combination of vinyl and propyl radicals. The yield versus time plots of the total C_5 and total C_6 products showed a longer induction period than those of propylene and butene. At 505°C and

60 cm pressure, after a long induction period the rate of formation of C_6 products attained a constant value. The mechanism for formation of the C_6 products is probably similar to that discussed for propylene and butene except that higher radicals must be involved.

Other likely heavier compounds are cyclohexene, cyclohexadienes, 4-vinyl-cyclohexene and their methyl or dimethyl derivatives. These are the products of the dimerization of butadiene or condensation of ethylene with butadiene and higher diolefins and would be secondary products. Some of these compounds have been identified in the thermal reactions of butadiene and ethylene or of butadiene alone (50). Analysis of these alicyclic polyolefine and cyclic olefins is extremely difficult, and was not attempted in this study.

Benzene and toluene were predominant among the secondary products. A probable mechanism for their formation is condensation reaction of the primary product butadiene with olefins. Aromatic compounds have been observed from the thermal reaction of 1, 3-butadiene at 550°C (53) and a mechanism for their formation has been proposed. In the ethylene system, condensation of butadiene and ethylene would be the most likely process. The initial condensation would produce cyclohexene and vinyl cyclohexene which may react further to form benzene and alkyl benzene through structural isomerization and dehydrogenation. There may also be reaction between butadiene and other product olefins. It has been shown (50) that carbon skeleton isomerization and carbon-carbon splitting to form benzene, toluene, and xylenes may follow such condensation.

Experiments under high pressure and temperature show that linear rates of octene production follow the brief initial accelerating rate. The octene production is reduced when ethane is present in large amounts, which indicates that octene may not come from reaction of octyl or octenyl radicals. Instead, octene might come from the decomposition of larger radicals of more than eight carbon number as well as from radical recombinations.

The detection of C_{10} and higher hydrocarbons was not attempted. There is little doubt that small concentrations of many large unsaturated hydrocarbons are produced in the thermal reaction of ethylene. It is conceivable that the increase in H/C ratio of the low molecular weight product is balanced by the presence of unsaturated polymers which have a H/C ratio of less than 2.

Addition of Ethane

In the presence of ethane, hydrogen abstraction reactions should be favored because of the smaller C-H bond energy in ethane as compared to ethylene. The rate of products formed by hydrogen abstraction should be greatly increased. This was the case for propane and butane. These compounds are probably produced from hydrogen abstraction reactions of the propyl and butyl radicals.

The rates of production of propylene and butene hardly changed in the presence of a large amount of ethane (Figures 23 and 24). The induction periods were, however, noticeably shortened and almost disappeared. This may be due to the pyrolysis of ethane itself providing a rapid initiation reaction. This would shorten the induction period, as observed, but would not affect the rate of formation of propylene and butene, since these compounds are formed in the chain propagation.

The yields of butadiene, C_5 and C_6 hydrocarbons and benzene are not changed in the presence of excess ethane. They are probably not produced from hydrogen abstraction reactions. The yield of C_8 compounds seemed to decrease, possibly because smaller radicals react to form saturated compounds instead of adding to ethylene while C_8 compounds come from larger radicals.

From the effect of the excess ethane on the rates of formation of saturated hydrocarbon and on the unchanged rates of the unsaturated hydrocarbon products, it is likely that addition of the unsaturated radicals is faster than abstraction under these conditions, whereas this may not be the case for the alkyl radicals. In other words the addition reactions of alkenyl radicals are faster than similar reactions of alkyl radicals under the conditions of this study, as suggested in the butadiene section.

Comparison with Previous Studies

It may be considered that there are four main propagation processes in the thermal reactions of ethylene. The four processes may co-exist in various degrees depending on the experimental conditions. The dominating propagation steps change gradually with changes in temperature and pressure.

Depending on the experimental conditions, in general one propagation step will predominate over the others. These main steps can be summarized for the four extreme cases:

(1) When n = 1, $C_{2n}H_{4n-2} = C_2H_2$ and the propagation is:

[60] $$C_2H_3 \rightarrow H + C_2H_2$$

This is the highest energy propagation and occurs in shock tube reactions in the neighborhood of 1500°K and a few atmospheres pressure (33) where olefinic C-H bond fission is the initiation, $C_2H_4 \rightarrow C_2H_3 + H$, and hydrogen and acetylene are the main products .

(2) When n = 2, $C_{2n}H_{4n-2} = C_4H_6$

and

[61] $$[C_2H_4]_2C_2H_3 \rightarrow C_2H_2 + C_4H_6 + H_2 + H \, .$$

This occurs between temperatures 600 to 1000°C and a low pressure range. The important products are acetylene, hydrogen and butadiene. The bimolecular dissociation step (1) is the main initiation.

(3) When $5 > n > 2$, this is the medium temperature propagation which occurs in our study and that of Halstead and Quinn (35). The $[C_2H_4]_nC_2H_3$ may react to form either olefin or diolefin:

(a) Both $[C_2H_4]C_2H_3$ and $[C_2H_4]_nC_2H_5$ react to produce olefins :

[62] $C_2H_3 + nC_2H_4 \rightarrow [C_2H_4]_nC_2H_3 \ ; \ [C_2H_4]_nC_2H_3 \rightarrow C_2H_3 + C_{2n}H_{4n}$

[63] $C_2H_5 + nC_2H_4 \rightarrow [C_2H_4]_nC_2H_5 \ ; \ [C_2H_4]_nC_2H_5 \rightarrow C_2H_5 + C_{2n}H_{4n}$:

(b) The $[C_2H_4]_nC_2H_3$ reacts to yield diolefin as well as ethane :

[64] $[C_2H_4]_nC_2H_3 \rightarrow C_{2n}H_{4n-2} + C_2H_5$

[65] $C_2H_5 + (n+1)\ C_2H_4 \rightarrow C_2H_6 + [C_2H_4]_nC_2H_3$

This is the region where bimolecular initiation to yield ethyl and vinyl radicals is most probable. The result is large yields of ethane, propylene, butene, butadiene, together with other saturated hydrocarbons, unsaturated olefins, and diolefins. This medium temperature propagation occurs at temperatures between 400 - 600°C. In this temperature range, all the primary products, especially olefins and non-conjugated diolefins, are susceptible to secondary decomposition especially at higher temperatures. The secondary initiation increases the radical concentration and increases the production of all the low molecular weight products. This is the cause of the induction period.

(4) When n > 5, the reaction can be designated as pure polymerization:

[66] $[C_2H_4]_nC_2H_3 \rightarrow C_2H_3 + C_{2n}H_{4n}$ and $[C_2H_4]_nC_2H_5 \rightarrow C_2H_5 + C_{2n}H_{4n}$

This probably occurs up to a temperature of about 500°C.

In the early papers of Storch (29) and Taniewski (54), general propositions were made regarding the origin of the lower primary reaction products in the thermal decomposition of olefins. Storch suggested that a stable intermediate compound was formed which caused the observed induction period. Taniewski also proposed an intermediate of polymeric nature as the origin of other reaction products. He assumed that the difference between the decrease in total reaction pressure and the concentration of ethane formed must correspond to the formation of the polymeric intermediate. His measurements, however, could not identify such an intermediate.

Recent studies by Boyd, Wu and Back (55), and Simon and Back (56), showed a rapid pressure decrease in the initial stages of the reaction. A plot of pressure versus time showed an S-shaped curve. The rapid initial rate slowed to a minimum value and then increased to a constant value which was less than the initial rate. The time of the minimum rate corresponded roughly to the induction period observed for the major products, propylene, butene and butadiene. This pressure decrease was interpreted as due to a rapid radical chain polymerization. Since the yields of many products before the induction period were much smaller than the yields after the induction period, it is almost impossible to determine how many products were formed and at what rates they were formed. The H/C ratio larger than 2 indicates that some diolefinic product has not been recovered as the correct ratio should be 2. An attempt was made in this study to search for high molecular weight compounds formed during the induction period, which could decompose to form low molecular weight products, by means of temperature-programmed gas chromatography. None could be found.

The observation that the initial decrease in pressure was greater than that calculated from the products measured is consistent with the radical chain polymerization mechanism proposed in this thesis. The decomposition of alkyl and alkenyl radicals produce paraffins, olefins and diolefins of various molecular weight depending on the size of the radicals. All products of the ethylene reaction, except hydrogen, methane and ethane, can be considered as polymerization products and their formation should cause a decrease in total pressure. The effects would be even greater when liquid products such as hexene and octene were formed. Since it has been shown that both butene and propylene can undergo secondary initiation it is likely that any polymeric olefins formed will also be the source of secondary initiation. This could be the reason why low molecular weight products are predominant in the reaction of ethylene in the temperature range of this study.

Recently Halstead and Quinn (35) studied the thermal reactions of ethylene in the temperature range 525 - 651°C and at pressure between 10 and 270 torr. This corresponds to the high temperature propagation range mentioned previously and the products would be expected to be slightly different from those observed in this study. The mechanism was suggested to be a degenerately branched chain reaction with the dissociation of butene-1 as the primary initiation. A degenerately branched chain reaction is one in which the primary chain is unbranched and additional reaction centers are produced by reactions of the products of the primary chain.

The suggestion by Halstead and Quinn of the initiation by butene-1,and the proposed secondary initiation of olefinic products in this thesis, are the same in many respects. Both suggestions can explain the long induction periods of the major products. High temperature and low pressure will greatly reduce the length of the radical chain polymerization and the main source of secondary initiation could be limited to butene and possibly propylene.

Consistent with this view is the difference in the distribution of products found in the two studies. For example, the formation of methane was more important relative to the other products in the study by Halstead and Quinn and hydrogen, which is a minor product in this study, was a primary product under some of their conditions. Propylene, which is an important major product at lower temperatures, was considered to be a secondary product in their study.

Halstead and Quinn attempted a quantitative explanation of the yields of ethane, n-butane and butadiene. They made the assumptions that the chain propagation step was :

$$C_2H_5 + C_2H_4 \rightarrow C_2H_6 + C_2H_3 \qquad \text{(D)}$$

that the initiation step was :

$$C_4H_8 \rightarrow CH_3 + C_3H_5 \qquad \text{(E)}$$

and that the main chain termination step was :

$$2C_2H_5 \rightarrow C_4H_{10} \; .$$

No explanation was given to link the initiation step (E) with the chain propagation step (D). According to this mechanism, equimolar quantities of ethane and butadiene should be produced disregarding secondary and minor products. This was not observed in their experiments, nor in ours. The accelerating effect of butene-1 under the reaction conditions is not sufficient evidence to support the suggestion that butene-1 is the only source of secondary initiation in the thermal reactions of ethylene. Evidence from this study suggests that higher molecular weight compounds also are important in secondary initiation even at temperatures as high as 600°C.

From their mechanism Halstead and Quinn obtained the following relation:

$$\log_{10} k_E = (13.9 \pm 0.5) - (69500 \pm 2000)/2.3RT \text{ sec}^{-1}$$

where k_E is the rate constant of step (E).

The value of E_E = 69.5 kcal is much higher than that of 59.1 kcal. mole^{-1} obtained by Trotman-Dickenson et al (57) from the butene-1 pyrolysis. The activation energy is very close to the activation energy for the initiation step $2C_2H_4 \rightarrow C_2H_5 + C_2H_3$ proposed here.

In conclusion, the data of Halstead and Quinn from the higher temperature and lower pressure range, can also be explained by the radical chain propagation proposed in this thesis. In the primary processes, ethane is produced by hydrogen abstraction of the ethyl radical. Olefins, including propylene and butene, are formed mainly by the decomposition of alkyl and alkenyl radicals. Diolefins, such as butadiene, are formed mainly by decomposition of alkenyl radicals.

There are two main features which emerge as the most important characteristic of the present chain mechanism. First, this mechanism suggests two parallel chain reactions initiated by ethyl and vinyl radicals. The subsequent reactions produce a variety of olefin and diolefin products. This parallel treatment of the chains of ethyl and vinyl radicals gives a good material balance as a whole of the ethylene pyrolysis system. Secondly, this mechanism emphasizes that each product may be formed from several sources, and each radical may give many products. The reactions proposed, together with the secondary initiation, explain the simultaneous formation of multiple primary products with constant rates and the induction periods.

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CLAIMS TO ORIGINAL RESEARCH

1. The pyrolysis of ethylene was studied over the pressure range 150 to 600 Torr and the temperature range 501 to 584°C.

2. Using a temperature-programmed gas chromatograph, an analysis was developed for the products of the reaction, ranging from C_2 to C_8 hydrocarbons. The identity of most of the products was confirmed by mass spectrometric analysis.

3. In the majority of the experiments, ethane, propylene, butene, butane and butadiene made up more than 90% of the products. The minor products were hydrogen, methane, propane, pentadiene, hexene, benzene, toluene and octene. Acetylene and cyclobutane were not found.

4. From the yield of the five major products, the order and activation energy of the rate of formation of each product were determined. The sum of the yields of all reaction products gave the over-all rate of reaction of ethylene. The order of the total reaction rate was about two and the activation energy was 40 kcal/mole.

5. From thermodynamic and kinetic data it was shown that the most likely initiation step is the bimolecular reaction of ethylene to form an ethyl and a vinyl radical.

6. A radical polymerization mechanism was proposed for the pyrolysis of ethylene. The chain propagation reactions included the addition of small radicals to ethylene and the decomposition of large radicals to form products. Hydrogen abstraction from ethylene was also important. Polymerization occurred by two parallel chain reactions, one carried by saturated radicals and the other carried by unsaturated radicals. Large unsaturated radicals decomposed to form olefins and smaller radicals. Large saturated radicals decomposed to form saturated hydrocarbons and smaller unsaturated radicals. The unsaturated radicals may also decompose to form a diolefin and a smaller saturated radical. This results in the interchange of the two radical chains.

7. The induction periods for the formation of the major products were explained by the secondary dissociation of the olefin products, particularly butene-1.

8. A steady-state treatment was applied to the proposed mechanism and the rate equations of the five major products were derived accordingly.

9. From the experimental rates of formation of ethane, the rate constant for the hydrogen-abstraction of the ethyl radical from ethylene was estimated as

$$k = 3 \times 10^{11} e^{-13400/RT} \text{cc mole}^{-1}\text{sec}^{-1}$$

10. From the experimental rates of formation of butadiene, the rate constant for the decomposition of the butenyl radical to form butadiene and a hydrogen atom was estimated as

$$k = 6 \times 10^{14} e^{-35000/RT} \mathrm{sec}^{-1}$$

11. The pyrolysis of ethylene was not significantly affected by the presence of excess carbon dioxide or small quantities of oxygen. In the presence of ethane the rate of formation of saturated hydrocarbons increased but the rate of formation of unsaturated hydrocarbons was not changed. From the results obtained from experiments using a packed reaction vessel it was concluded that the reactions occurring in the pyrolysis are mostly homogeneous.