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KINETICS OF THE BIMOLECULAR INITIATION PROCESS IN THE THERMAL REACTIONS OF ETHYLENE

by

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A thesis submitted in partial fulfillment

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TO

MY SON, ÇAĞRI

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

The effect of the additions of small amounts of 1-butene, neopentane and ethane on the thermal reactions of ethylene has been studied in a static-system over the temperature range 699 to 819 K. The pressure of ethylene has covered the range from 75 to 400 torr. The measurement of the initial rate of formation of the main products methane, ethane, propylene, 1-butene and in some cases, butadiene has been made by gas chromatographic analysis. From the results of the pyrolysis of ethylene in the presence and absence of the additive it has been concluded that the only effect of the additive has been the addition of a new initiation process to the radical chain reactions of ethylene.

It has been shown that in the reactions of ethylene alone the main initiation process is

$$2C_2H_4 \rightarrow C_2H_5 + C_2H_3 \qquad (1)$$

while in the presence of the additive, RH, an additional initiation process occurs.

$$RH \rightarrow R_1 + R_2 \qquad (a)$$

where R_1 and R_2 are radicals. The ratio of the initial rates of formation of the products in the presence and absence of the additive is then given as follows.

$$\frac{(V_0)_a}{V_0} = [1 + \frac{(R_i)_a}{R_i}]^{1/2}$$

where V_0 and $(V_0)_a$ refer to the initial rate of product formation in the absence and presence of the additive respectively, and R_i and $(R_i)_a$ refer to the rates of initiation by the pure substance and by the additive, respectively. Since $R_i = k_1[C_2H_4]^2$ and $(R_i)_a = k_a[RH]$, the ratio of rate constants k_a/k_1 may be obtained from the measurements and since the value of k_a for each additive is known, values for k_1 were obtained from each set of additions.

The average value of the rate constant for the bi-molecular initiation reaction of ethylene has been obtained by combining the results of the three additives with an analysis of the experimental uncertainties in each system. This value of k_1 is given below.

$$\text{Log } k_1(\text{L mol}^{-1} \text{ s}^{-1}) = (11.27 \pm 0.6) - \frac{(64200 \pm 2000)}{2.3\ RT}$$

The value of the frequency factor has been shown to be consistent with the calculated value. Using the value of the activation energy obtained for reaction (1) from the present research, the heat of formation of the vinyl radical has been calculated as 63.4±2 kcal mol^{-1}. This measurement leads to a value of 103 kcal mol^{-1} for the bond dissociation energy of the C-H bond in ethylene.

From the results of the pyrolysis of ethylene alone, the orders and the activation energies for the initial formation of the major products have been obtained. These observations have been discussed in terms of a radical chain mechanism for the thermal reactions of ethylene.

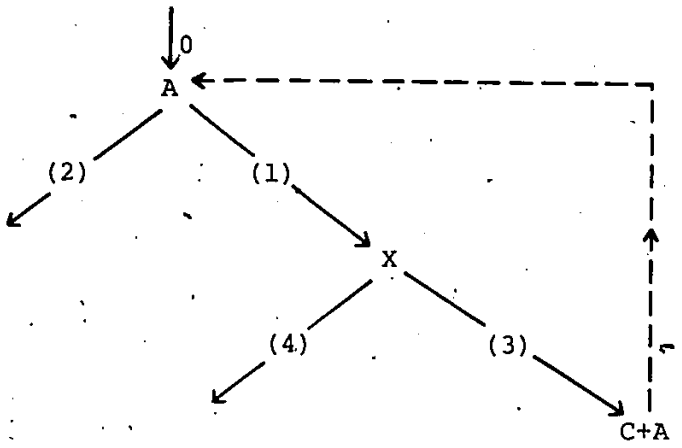
CHAPTER I

INTRODUCTION

From the viewpoint of chemical kinetics, chemical reactions may be broadly subdivided into simple and complex reactions. Simple reactions are those which take place in one step, the equation for the reaction being identical with the stoichiometric equation and the rate of reaction being expressed by the law of mass action. The mechanism of these reactions can be established easily. In gas phase reactions, however, the proportion of these single elementary reactions is very small. The vast majority of gas phase reactions occur by complex mechanisms, that is, they take place in a number of well-defined steps, each of which is an elementary reaction. A complex reaction yields intermediates that are more reactive than the initial reactants. These intermediates might be atoms, free radicals or unstable molecules. A complex reaction can often be identified experimentally by having a complex rate equation, or a rate equation that does not correspond to the stoichiometry.

1. Chain Reactions

In general, two types of complex reactions may be distinguished: chain and non-chain reactions. The scheme of a chain reaction is illustrated below.



Path 0 is the activation process leading to the formation of the active species A. This active species may react either along path (1), which leads to the formation of the intermediate X, or by path (2), which leads to deactivation. The intermediate X may then react either by path (3), to yield the reaction product C together with the active species A, or by path (4), which leads to the process resulting in the disappearance of X. This active species A produced from X can further react along the reaction paths (1)-(4) and hence the reaction is continuously repeated until the sequence is interrupted through disappearance of the active center. Reactions of such a type are termed "chain reactions". In non-chain complex reactions, regeneration of the active species does not occur. Chain reactions can be either of the kind described above, where the concentration of active centers stays constant, called linear-chain reactions, or branched-

chain reactions, where there is an increase in the number of active centers.

Many important reactions occur by chain mechanisms, for example, thermal decompositions of organic compounds, oxidation of many compounds by molecular oxygen, chlorination and bromination of unsaturated hydrocarbons and many polymerization reactions.

Chain reactions were discovered by Bodenstein[1] in 1913. After observing very high quantum yields of some photochemical reactions, he suggested that a chemical reaction, particularly, one initiated by light, may proceed by a chain process. In 1918, Nernst[2] proposed a mechanism for the reaction between chlorine and hydrogen. Later in 1919, Christiansen[3a], Herzfeld[3b], and Polanyi[3c], applied the steady-state treatment of intermediates for the first time to the reaction between bromine and hydrogen. The theory of branched-chain reactions was formulated by Semenov[4] in 1927. In 1934, the decomposition of organic compounds was examined by Rice and Herzfeld[5] and they showed that free radicals play an important role in their mechanisms. The rules suggested by Rice and Herzfeld and their application to the pyrolysis of many compounds form the basis for the mechanistic discussion of these chain reactions. They proposed specific free radical mechanisms, and showed how complex mechanisms can lead to simple overall kinetics.

In general, chain processes in the decomposition of organic molecules consist of three types of elementary reactions.

i) Initiation Reactions:

These reactions are the initial split of the organic molecule into radicals. Initiation is usually unimolecular for the decomposition of a large molecule and thus gives first-order kinetics for this step at high pressures, and second-order kinetics at low pressures.

ii) Propagation Reactions:

These reactions are either the reaction of a radical with the parent molecule to give another radical and a small saturated molecule, or the dissociation of the radical to give an unsaturated molecule and a radical.

iii) Termination Reactions:

These reactions remove the radicals from the system. They occur by either association of radicals, where the two radicals combine to give one stable molecule, or, disproportionation of radicals, where a hydrogen atom is transferred from one radical to another thus forming one saturated and one unsaturated molecule.

The overall order of the reaction is determined by which type of radicals combine in the termination reactions. This problem was carefully examined by Goldfinger, Letort and Niclause[6] by considering the role of the radical in the propagation reactions. They defined two kinds of radicals.

i) β Radicals:

radicals which are involved in second-order propagation reactions.

ii) μ Radicals:

radicals which are involved in first-order propagation reactions.

The method of participation of β and μ radicals in the termination steps of a reaction mechanism determines the overall order of the reaction. Thus, they concluded that, if the initiation reaction is unimolecular, and the termination reaction occurs without the presence of third bodies, the overall order for ββ termination is 3/2, for βμ termination it is 1, and for μμ termination it is 1/2. If the initiation is bimolecular, the orders are higher by one-half and if the third body is present in the termination reactions, the overall orders are reduced by one-half. Table 1 summarizes these results.

Table 1

OVERALL ORDERS OF REACTION FOR VARIOUS TYPES OF INITIATION AND TERMINATION STEPS

First-Order Initiation		Second-Order Initiation		
Simple Termination	Third-Body Termination	Simple Termination	Third-Body Termination	Overall Order
		ββ		2
ββ		βμ	ββM	3/2
βμ	ββM	μμ	βμM	1
μμ	βμM		μμM	1/2
	μμM			0

The arrows point to the possible change at low pressures.

The use of this table greatly simplifies the problem of elucidating the mechanism for a specific pyrolysis reaction. Nevertheless, there are many factors that should be taken into account in specifying the initiation and termination processes. For the initiation reactions, nature of the organic compound and the temperature and pressure of the pyrolysis are important. For termination reactions, the relative concentrations of β and μ radicals, relative complexities of these radicals and the presence or absence of third bodies should also be considered.

2. Pyrolysis of Hydrocarbons

The thermal decomposition of hydrocarbons has been of great interest to chemists for almost one hundred years and a very considerable amount of experimental study has been performed in this area. Pyrolyses of cyclic compounds usually occur by molecular processes and yield one or two products. Most of the straight and branched-chain hydrocarbons on the other hand, pyrolyze by free radical mechanisms and give several products. Specific chain mechanisms are needed for the understanding of the decomposition of these compounds.

Thermal reactions of hydrocarbons are very important in industrial processes. Catalytic and homogenous hydrocracking are used extensively commercially in petroleum refining to produce high quality gasoline, jet fuel and lubricants. During petroleum refining, many aromatics and other chemicals are produced. Therefore, there is a great need to obtain a better understanding of the chemistry of pyrolysis. Thermal reactions also play a very important role in polymerization reactions. Ethylene is an important starting material in polymerization processes. Since ethylene is produced mainly by pyrolysis of hydrocarbons, thermal reactions of hydrocarbons should be very well understood. In the past, light paraffins, especially ethane and propane were the major feedstocks used for the

production of ethylene. Limited availability of these light paraffins has necessitated consideration of and increased use of heavier petroleum-based stocks including naphtas, gas oils and even crude oil. With increased use of heavy feedstocks, more propylene, dienes and aromatics are also being produced by pyrolysis. Yet, the understanding of the chemistry of pyrolysis, especially of heavier hydrocarbons, is relatively limited.

There are many differences in the thermal reactions of alkanes, alkenes and alkynes. The pyrolysis of alkenes follow quite a different pattern than that of alkanes. The stability and chemical reactivity of alkenes are greatly influenced by the presence of the double bond and their thermal reactions present many problems not encountered with the alkanes. In olefinic compounds, both polymerization and decomposition may occur. Initiation of polymerization by the radicals produced in the decomposition reactions, secondary decomposition of polymers, and complex isomerization processes are among the many reactions occurring during the pyrolysis of alkenes. Therefore, thermal reactions result in the formation of high molecular weight compounds for alkenes, whereas alkanes usually undergo cracking to smaller compounds by the breakdown of bonds. The mechanism of the pyrolysis of alkynes is even more complex than that of alkenes, due mainly to highly reactive products which make

the measurements very difficult and also due to variable effects of heterogenous reactions.

In this thesis, attention will be focused on ethylene, which, as the simplest alkene, provides a model for understanding the processes occurring in alkene pyrolysis.

3. Studies of the Ethylene Pyrolysis

Studies on the thermal reactions of ethylene started as early as 1886[7a-d]. In 1931, Pease[8] measured the rate of polymerization of ethylene at 2.5,5 and 10 atmospheres from 623 to 773 K. The reaction was found to be second-order with an activation energy of 35 kcal mol^{-1}* which is abnormally low for a hydrocarbon decomposition. Storch[9] suggested 42 kcal mol^{-1} for the activation energy of ethylene polymerization in the temperature range 623-673 K. The primary product was indicated as butene. The effect of small additions of nitric oxide on the polymerization reactions of ethylene was examined by Burnham and Pease[10]. The observed inhibition of the rate was interpreted as indicating a chain mechanism involving free radicals. In support, Douglas, Rabinovitch and Looney[11], in their study of the geometrical isomerization of cis-ethylene-d_2, observed the formation of appreciable amounts

* Throughout the thesis the unit kcal is used since most of the data in literature are in this unit. It can be converted into kJ by multiplying by 4.184.

of d_1- and d_3-ethylenes as well as deuteropropylenes and deuterobutenes. On the other hand, Silcocks[12] did not observe any effect of nitric oxide on the polymerization processes and suggested that these reactions occur by molecular mechanisms. Products methane, propylene and a polymer were supposed to be formed from 1-butene, either by decomposition of the latter or from its reaction with ethylene, 1-butene being itself formed by the bimolecular reaction of ethylene. In 1958, Dahlgren and Douglas[13] followed the course of ethylene pyrolysis by mass spectrometric analysis and showed that butene, butadiene, propylene and ethane were primary products. The addition of nitric oxide reduced the amounts of all primary products implying that free radical processes were involved in forming these substances. Second-order rate constants for overall ethylene removal led to an activation energy of 41.1 kcal mol^{-1}. Taniewski[14] studied the relative rates of decomposition and polymerization of ethylene at 803, 873 and 903 K. On the basis of chromatographic analysis of the reaction products both in the presence and absence of nitric oxide, it was concluded that the ethane was formed mainly from the secondary decomposition of polymers. The activation energies for decomposition and polymerization were reported as 53.4 and 43.3 kcal mol^{-1}, respectively.

In these early works, because an induction period was observed, primary and secondary products were not always distinguished. The relative importance of molecular and radical processes was also uncertain. In this respect, the investigations of Halstead and Quinn[15] and Boyd, Wu and Back[16] have provided a general framework for the mechanism of simultaneous polymerization and decomposition of ethylene between 750-900 K, although their results first appeared to be conflicting[17,18]. Halstead and Quinn have studied the pyrolysis of ethylene in the temperature range 798-923 K with reactant pressures between 10-270 torr. The major products were butadiene, hydrogen, ethane, propylene, 1-butene and methane. From the percentage composition of these products with time they have decided that hydrogen, ethane, 1-butene and butadiene were primary in character, 1-butene and butadiene being consumed by secondary processes. All products showed self-acceleration and no changes in total pressure were observed. These observations contradicted the suggestion that there was a molecular precursor of polymeric nature which then underwent a cracking to form the observed products[19]. Halstead and Quinn[15] concluded that the pyrolysis of ethylene was a degenerately branched-chain reaction with 1-butene as the chain branching agent. They suggested that the only important chain initiation was the decomposition of 1-butene to give methyl and allyl radicals without specifying the mechanism for the formation of 1-butene.

$$1 - C_4H_8 \rightarrow CH_3 + C_3H_5$$

Ethyl and vinyl radicals were the main chain propagating radicals and addition, decomposition and abstraction reactions of the radicals present in the system were able to account quantitatively for the time dependence of the yield of the major products.

Boyd, Wu and Back[16] made measurements at lower temperatures (773-873 K) and higher pressures (150-600 torr). The main products were ethane and a polymer, containing eight or more carbon atoms. The formation of these primary products did not show an induction period. All the other main products, propylene, butene, butadiene, a second polymer and the minor products, methane, unsaturated C_5 and C_6 and benzene showed an induction period. Minor product butane did not show an induction period. The order with respect to ethylene of ethane, propylene and butene was close to two. The activation energy for the formation of these products was about 40 kcal mol^{-1}. They have interpreted their results in terms of a free radical chain polymerization, initiated by the interaction of two ethylene molecules to form a vinyl and an ethyl radical. It was suggested that this polymerization yields products ethane and a polymer, all the other products being formed from the thermal breakdown of the polymer.

The relation between the two studies[15,16] was clarified by considering the effect of temperature and pressure on the reaction. Simon and Back[17] suggested that at low temperatures and high pressures, polymerization was favored and the high molecular weight unsaturated compounds were the major source of secondary initiation. At high temperatures and low pressures, the molecular weight of the polymer would decrease and dissociation of 1-butene would probably be the main initiation process. Apparently, the mechanisms given by these two groups are essentially similar. One or the other predominates under certain conditions of temperature and pressure.

In 1979, Back and Martin[20] examined the thermal reactions of ethylene at 773 K in the presence and absence of small quantities of oxygen, and proposed a more detailed mechanism. Ethylene pressures were between 100 and 400 torr. The main products were propylene, ethane, 1-butene, methane, butadiene, 1-pentene and cyclopentene. The results were essentially in agreement with the mechanism suggested earlier[16]. The main initiation step was the bimolecular reaction of ethylene:

$$C_2H_4 + C_2H_4 \rightarrow C_2H_5 + C_2H_3$$

The termination reaction was either the association or disproportionation reaction of two ethyl radicals:

$$C_2H_5 + C_2H_5 \rightarrow C_4H_{10} \text{ or } C_2H_4 + C_2H_6$$

The chain propagation reactions consisted of two parallel and interacting sets involving reactions of the ethyl and vinyl radicals. In the reactions of C_6-alkyl radicals, 1,5- and 1,4-hydrogen migrations were suggested. If the activation energy of 1,4-migration is 3 or 4 kcal mol^{-1} higher than that for the 1,5-migration, 1,5-migration will be predominant at low temperatures. But at 773 K, the rate of 1,4-migration becomes 1/10 of the rate of 1,5-migration. Since these migrations can explain the formation of all the light primary products, a simplified mechanism can be written for reactions of the ethyl and vinyl radicals.

Considering only the ethyl radical,

$$C_2H_5 + C_2H_4 \rightarrow C_2H_6 + C_2H_3$$

$$\rightarrow C_4H_9$$

$$C_4H_9 + C_2H_4 \rightarrow n\text{-}C_6H_{13}$$

$$n\text{-}C_6H_{13} \rightarrow 2\text{-}C_6H_{13}$$

$$2\text{-}C_6H_{13} \rightarrow C_3H_6 + n\text{-}C_3H_7$$

$$n\text{-}C_3H_7 + C_2H_4 \rightarrow n\text{-}C_5H_{11}$$

$$n\text{-}C_5H_{11} \rightarrow 2\text{-}C_5H_{11}$$

$$2\text{-}C_5H_{11} \rightarrow C_3H_6 + C_2H_5$$

$$n\text{-}C_6H_{13} \rightarrow 3\text{-}C_6H_{13}$$

$$3\text{-}C_6H_{13} \rightarrow 1\text{-}C_4H_8 + C_2H_5$$

$$3\text{-}C_6H_{13} \rightarrow 1\text{-}C_5H_{10} + CH_3$$

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

$$CH_3 + C_2H_4 \rightleftharpoons C_3H_7$$

The relative yield of 1,5- and 1,4-hydrogen migration was observed experimentally by the yields of propylene and 1-butene which were the major products of decomposition of 2-hexyl and 3-hexyl radicals, respectively. The yield of propylene was between 5 and 10 times larger than the yield of 1-butene. Reactions of the vinyl radical on the other hand, produce unsaturated radicals which may decompose more slowly and hence lead to polymerization.

Since the 1960s, there have been several experimental studies of the ethylene pyrolysis made using the shock tube technique[21-28].

The temperature range was about 973-2273 K, and the kinetics were again complex but quite different from those

at lower temperatures. There was general agreement that ethylene decomposes primarily to acetylene and hydrogen at these temperatures and the reaction was first-order with respect to ethylene concentration. The measured activation energies covered a considerable range, 40-74 kcal mol^{-1}. Just, Roth and Damm[25] used the technique of atomic resonance absorption spectroscopy to investigate the generation of hydrogen atoms at 1700-2200 K. They suggested that ethylene decomposes simultaneously via the two reactions:

$$C_2H_4 + M \rightarrow C_2H_3 + H + M \qquad \text{(i)}$$

$$C_2H_4 + M \rightarrow C_2H_2 + H_2 + M \qquad \text{(ii)}$$

and that the initial reactions were followed by the reactions of C_2H_3 and H.

$$C_2H_3 + M \rightarrow C_2H_2 + H + M$$

$$H + C_2H_4 \rightarrow C_2H_3 + H_2$$

$$H + C_2H_3 \rightarrow C_2H_2 + H_2$$

The rate constants for reactions (i) and (ii) were reported as:

$$k_i \ (cm^3\ mol^{-1}\ s^{-1}) = (3.8 \pm 1.3)10^{17} \exp(-\ 98{,}200 \pm 900/RT)$$

$$k_{ii} (cm^3\ mol^{-1}\ s^{-1}) = (2.6 \pm 0.5)10^{17} \exp(-\ 79{,}300 \pm 500/RT)$$

Recently, Tanzawa[26] studied the thermal decomposition of ethylene between 2000-2500 K using the laser schlieren technique. For reactions (i) and (ii), the following rate constants were determined:

$$k_i \ (cm^3\ mol^{-1}\ s^{-1}) = 3.1 \times 10^{17} \exp(-95700/RT)$$

$$k_{ii} (cm^3\ mol^{-1}\ s^{-1}) = 3.0 \times 10^{17} \exp(-81300/RT)$$

Through computer modelling, it was found that both reactions (i) and (ii) were necessary in the mechanism to explain the observed density gradient profiles. The values of the rate constants k_i and k_{ii} obtained by Tanzawa[26] and Just et al[25] are in very good agreement and suggest that the unimolecular decomposition of ethylene at high temperatures occurs by two competing channels, that is, reactions (i) and (ii). Decomposition of ethylene into acetylene and hydrogen by a molecular process dominates at early stages of the reaction, before the chain mechanism initiated by the formation of the vinyl radical and hydrogen atom, reaction (i), takes over. Butadiene was also found as an important product at these temperatures together with acetylene and hydrogen[26].

4. Object of the Present Investigation

The rates of the pyrolysis reactions can be determined from the propagation processes, when the chains are long. A rate expression must include the concentration of any one of the radical chain carriers which is fixed by the rates of the initiation and termination processes. Therefore, identification of the initiation and termination processes has great importance in kinetic investigations. The termination reaction in a complex chain is mostly between the radicals present in largest concentrations and can be chosen from the estimates of the chain steps.

The initiation step of the pyrolysis of most hydrocarbons is unimolecular[29]. Since the unimolecular dissociations of the reactants into radical fragments have generally high frequency factors, $10^{16\pm1}$ s^{-1}, the possibility of occurrence of bimolecular reactions, which have lower frequency factors, about $10^{9\pm1}$ L mol^{-1} s^{-1}, is quite small[30]. An example will show the importance of activation energy for these processes:

$$A \xrightarrow{k_u} \text{two radicals}$$

$$A + A \xrightarrow{k_b} \text{two radicals}$$

Here A is the reactant which gives two radicals either by a unimolecular dissociation, with rate constant k_u, or by a bimolecular reaction, with rate constant k_b. The ratio of the two rates is

$$\frac{R_u}{R_b} = \frac{k_u[A]}{k_b[A]^2} \approx \frac{10^{16\pm1 - E_u/2.3\ RT}}{10^{9\pm1 - E_b/2.3\ RT}[A]}$$

At 800 K with 100 torr reactant pressure, this ratio may be written:

$$\frac{R_u}{R_b} \approx 10^{9.7\pm2 - (E_u - E_b)/2.3\ RT}$$

Therefore, the unimolecular and bimolecular reaction rates are competitive only when $E_u - E_b = (9.7 \pm 2)4.57\ T$. This difference in the activation energy is 36 ± 7 kcal mol^{-1}. At these temperatures and higher, unimolecular initiation steps are therefore usually favored.

There are, however, a few unsaturated molecules such as ethylene[16], acetylene[31] and benzene[32] whose dissociation into radical fragments is very difficult because of their strong chemical bonds. Bimolecular initiation steps for these compounds may have much lower activation energies than the simple unimolecular bond fissions. Experimental observations of low activation energies and high orders of

the rates of decompositions of these molecules make this suggestion quite reasonable.

In the case of ethylene, the following initiation reaction has been proposed.

$$C_2H_4 + C_2H_4 \rightarrow C_2H_5 + C_2H_3 \qquad (1)$$

and the subsequent reactions of the ethyl and vinyl radicals have been shown to lead to the formation of the main products[20]. Although the reaction (1) has been shown to be consistent with the kinetics of the reaction, no direct experimental measurement of this rate constant has been reported.

In the present investigation, a method is described to examine the kinetics of the initiation process in the ethylene pyrolysis, and to provide a measurement of the rate constant for this process.

The activation energy and frequency factor for reaction (1) may be calculated from thermochemical data. But not all the thermochemical data for reaction (1) is perfectly established. As will be discussed later, the greatest uncertainty comes from the value of the heat of formation of the vinyl radical. The results of the present study will constitute a kinetic measurement from which the heat of formation of the vinyl radical may be obtained. The present results therefore lead to important and fundamental thermochemical data.

5. Heats of Formation of Radicals

Heats of formation of radicals are defined as equal to the enthalpies of the formation reactions when product radicals and reactant elements are in their standard states of 1 atmosphere of ideal gas. As an example, the heat of formation of the methyl radical, P = 1 atm at 298 K, is given by[33]:

$$34.3 \text{ kcal} + \text{C(graphite)} + \frac{3}{2} H_2(\text{gas}) \rightarrow CH_3(\text{gas})$$

$$\Delta H_r^o = \Delta H_f^o\ (CH_3) = 34.3 \text{ kcal mol}^{-1}$$

where ΔH_r^o and ΔH_f^o refer to the enthalpy of the reaction and the heat of formation, respectively.

In the case where the reaction involves the breaking of a single bond,

$$R - X \rightleftharpoons R + X$$

the bond dissociation energy, BDE(R-X), is defined as the enthalpy change of the reaction, reactant and products being in their standard states of ideal gas at 1 atm and 298 K.

$$\text{BDE(R-X)} = \Delta H_r^o = \Delta H_f^o(R) + \Delta H_f^o(X) - \Delta H_f^o(R\text{-}X)$$

This equation is very useful in relating bond dissociation energies to heats of formation of reactants and products.

Heats of formation and bond dissociation energies are very important in quantitative understanding of the mechanisms of chemical reactions. But yet, accurate data for heats of formation of radicals are not always available because the measurements involving radicals are generally difficult.

The methods of measuring the heat of formation of radicals include a variety of experimental techniques[34]. These are kinetic methods, electron-impact studies, the use of Polanyi relations, chemical activation studies and equilibrium studies. The most important methods are kinetic studies and electron-impact studies.

Electron-impact studies are numerous and a large number of values has been obtained from these techniques. In principle, heats of formation of radicals and bond dissociation energies in molecules are determined from the energetics of ion formation induced in molecules and radicals by their interaction with high energy ionizing particles, for example, electrons and photons. The important equations are:

$$e + AB \rightarrow A^+ + B + 2e \qquad \Delta H^0_{(2)} = AP(A^+)/AB \qquad (2)$$

$$e + A \rightarrow A^+ + 2e \qquad \Delta H^\circ_{(3)} = IP(A^+)/A \qquad (3)$$

The appearance potential of A^+ from AB, $AP(A^+)/AB$, is defined as the minimum energy necessary to dissociate the

ground-state molecule AB into the positive ion A^+ and the radical B, both in their ground electronic states. The minimum energy required to remove an electron from the highest energy molecular orbital of the radical A is the first ionization potential of the A radical, $IP(A^+)/A$. The bond dissociation energy of the A-B bond in the AB molecule is the difference in enthalpies of reactions (2) and (3)

$$BDE(A-B) = AP(A^+)/AB - IP(A^+)/A$$

Basically, experimental AP and IP measurements are made with a mass spectrometer on gaseous samples at very low pressures. There are some problems however, such as the production of ions and radicals with excess kinetic energy[35]. Solutions to these problems include the use of monoenergetic electron beam techniques[36,37] and the retarding potential difference method[38,39].

Kinetic methods provide the most reliable data for the determination of heats of formation of radicals. The two main techniques in this area are:

i) Pyrolytic reactions

ii) Metathetical reactions

In pyrolysis systems, single bond-fission reactions are mostly studied.

$$R - R' \underset{r}{\overset{f}{\rightleftharpoons}} R + R' \qquad (4)$$

The enthalpy change for this reaction is related to the activation energies of the forward, E_f, and reverse reactions, E_r, by the equation

$$\Delta H^{\circ}_{(4)} = (E_f - E_r) + RT$$

In metathetical reactions, atom metatheses systems are of primary interest:

$$X + RY \underset{r}{\overset{f}{\rightleftharpoons}} XY + R \qquad (5)$$

The enthalpy change for this reaction is again defined as the difference between forward and reverse activation energies

$$\Delta H^{\circ}_{(5)} = E_f - E_r$$

In order to obtain $\Delta H^{\circ}_{(4)}$ and $\Delta H^{\circ}_{(5)}$, the forward and reverse activation energies for processes (4) and (5) should be determined. When the reaction enthalpies are established, temperature correction to 298 K should be made by using the following equation:

$$\Delta H^{\circ}_{T} = \Delta H^{\circ}_{298} + \int_{298}^{T} \Delta C^{\circ}_{P}\, dT \qquad (6)$$

where ΔH^{o}_{T} and ΔH^{o}_{298} are the enthalpy change of the reaction at temperature T and at T = 298 K, respectively. ΔC^{o}_{p} is the heat capacity change of the reaction which is generally a function of temperature. Then, heats of formation of radicals can be calculated from Hess' Law:

$$\Delta H^{o}_{r} = \sum_{\text{products}} \Delta H^{o}_{f} - \sum_{\text{reactants}} \Delta H^{o}_{f}$$

In the case of reaction (4), the correction for ΔH^{o}_{T}, equation (6), usually offsets the term ΔnRT, when $\Delta n = +1$, and the enthalpy change is usually expressed simply as

$$\Delta H^{o}_{(4)} = E_{f} - E_{r}$$

In such reactions, equation (4), the enthalpy change of the reaction, $\Delta H^{o}_{(4)}$, is given directly by E_{f}, because the reverse reaction of equation (4), which is a radical-radical recombination reaction, is assumed to have an activation energy of zero[40-42]. Therefore, experimental systems are designed to study the kinetics of reactions which yield absolute values for the rate constants and activation energies of dissociation reactions. Much of the information from pyrolytic reactions has been derived from flow experiments by the application of toluene-carrier or aniline-carrier techniques[43,44]. As long as the mechanism of the reaction is well-established, these methods lead to reliable data for heats of formation of radicals.

Another experimental approach to the study of pyrolysis reactions is the single-pulse shock-tube comparative rate technique (SPST-CR) developed by Tsang[45,46]. This technique involves decomposing dilute mixtures of two compounds at very low concentrations in the presence of an argon-toluene gas mixture by the same reflected shock wave. One of the compounds, with previously established kinetics, serves as a standard for the decomposition of the second. SPST-CR technique appears to give quite reliable results.

Atom metatheses reactions have been very successfully studied by iodination and bromination systems. For instance, in iodination experiments, the rates of reactions, such as the following

$$I + RI \rightleftharpoons I_2 + R$$

$$I + RH \rightleftharpoons HI + R$$

have been measured in a variety of systems giving values for the activation energies for these reactions. Assuming values for the activation energies of the reverse processes, the enthalpies of such reactions were determined. Thus, bond dissociation energies and heats of formation of radicals were obtained[33,47,48].

6. Description of the Method

Niclause, Martin, Baronnet and Scacchi[49] have thoroughly analyzed the effect of small quantities of additives on the pyrolysis of an organic substance which decomposes by a free-radical chain mechanism.

At small extents of reaction, an organic substance "μH" undergoes the following free radical chain processes:

Initiation $\mu H \rightarrow$ free radicals (7)

$\mu \rightarrow m + \beta$ (8)

Propagation { $\beta + \mu H \rightarrow \beta H + \mu$ (9)

$\beta + \beta \rightarrow$ (10)

Termination { $\beta + \mu \rightarrow$ } Products (11)

$\mu + \mu \rightarrow$ (12)

where radical "μ" represents the free radical chain carrier that is involved in first-order chain propagation reactions, and radical or atom "β" represents the chain carrier that is involved in second-order chain propagation reactions. "m" and "βH" show the major primary products.

In the presence of an additive "YH" with a mobile hydrogen atom, new reaction steps should be added to the chain reactions of μH, described above, depending on the effect of the additive on the pyrolysis of μH. The additive may affect the reaction by adding new initiation processes, or new propagation processes, or new termination processes. If the additive adds new initiation steps, it leads to the acceleration of the rate. When new termination processes occur in the presence of an additive, an inhibition of the rate is observed. The effect of the additive on the propagation steps can be either accelerating or inhibiting. The cases where the additive affects the propagation and termination reactions have been extensively studied[49,50-53].

For the special case where the only effect of additive YH is on the initiation steps, the initiation reaction by the additive should be added to the initiation of μH.

$$YH \rightarrow \text{free radicals.} \qquad \text{(a)}$$

Thus, the rate of initiation is increased relative to the rate of initiation of μH alone. Radicals μ and β from the pyrolysis of μH do not react with YH, and therefore, the mechanism of the pyrolysis of μH is unchanged in the presence of YH. The effect of YH is an acceleration of the rate.

Then, the general mechanism of the pyrolysis of μH in the presence of YH can be represented through reactions (7)-(12) including (a).

In the case when k_9 is rate controlling, the initial rate of decomposition of μH alone is:

$$(V_0)_{\mu H} = \frac{k_9 (v_i)_{\mu H}^{1/2}}{k_{10}^{1/2}} [\mu H]_0$$

where the rate of initiation is $(v_i)_{\mu H} = k_7 [\mu H]_0$.

In the presence of YH, the initial rate of decomposition of the mixture is:

$$(V_0)_{\mu H, YH} = \frac{k_9 (v_i)_{\mu H, YH}^{1/2}}{k_{10}^{1/2}} [\mu H]_0$$

and now the total rate of initiation is obtained by including the rate of initiation by YH:

$$(v_i)_{\mu H, YH} = k_7 [\mu H]_0 + k_a [YH]_0$$

The ratio of the initial rates of reaction in the presence and absence of YH is:

$$\frac{(V_0)_{\mu H, YH}}{(V_0)_{\mu H}} = \frac{(v_i)^{1/2}_{\mu H, YH}}{(v_i)^{1/2}_{\mu H}}$$

$$= \frac{(k_7[\mu H]_0 + k_a[YH]_0)^{1/2}}{(k_7[\mu H]_0)^{1/2}}$$

$$= (1 + \frac{k_a[YH]_0}{k_7[\mu H]_0})^{1/2}$$

Or,

$$\frac{(V_0)_a}{V_0} = [1 + \frac{(R_i)_a}{R_i}]^{1/2} \qquad (13)$$

where, $(V_0)_a$ and V_0 refer to the initial rate of product formation in the presence and absence of an additive, respectively, and $(R_i)_a$ and R_i refer to the rate of initiation by the additive and by the pure substance, respectively.

Following the earlier suggestion that the initiation step in the pyrolysis of ethylene is reaction (1),

$$2C_2H_4 \rightarrow C_2H_5 + C_2H_3. \qquad (1)$$

the rate of initiation of the ethylene is

$$R_i = k_1[C_2H_4]^2$$

Then, equation (13) may be written as

$$\frac{(V_0)_a}{V_0} = \left(1 + \frac{k_a[YH]_0}{k_1[C_2H_4]^2}\right)^{1/2} \qquad (14)$$

for the pyrolysis of ethylene in the presence of an additive, where k_1 and k_a refer to the initiation rate constants for ethylene and the additive, respectively.

Consequently, if the rate of initiation of the additive, which in general is its rate of dissociation into radicals, is known, the rate of initiation in the absence of an additive may be obtained from measurements of the rate of product formation in the presence and absence of the additive.

For the application of equation (14), the additive should have certain characteristics. It should not enter into the propagation reactions of the chain mechanism of the ethylene decomposition. The additive will therefore be present in relatively small quantities. These amounts, however, must be sufficient to produce a measurable increase in the overall rate, or in other words, to add appreciably to the initiation rate. The radicals produced by this additive may or may not be the same radicals that the parent compound gives in its initiation step. It is also evident that its rate of dissociation should be well established.

In the present study, the additives used were 1-butene, neopentane and ethane. The results obtained from each additive will be described separately and further discussion will be given in Chapter V.

CHAPTER II

EXPERIMENTAL

1. Apparatus

The pyrolysis was performed in a conventional static system. The main features of the apparatus are shown schematically in Figure 1a. The entire system could be evacuated to 10^{-5} torr by means of a mercury diffusion pump (MDP) in series with a Duo-Seal rotary pump (RP). All stopcocks were greased with Apiezon-N grease except in those leading to reaction vessel, mixture flasks and sampling system, in which silicone grease was used.

The electrically heated cylindrical furnace was about 50 cm long and 30 cm in diameter. The resistance wires were wound around a ceramic core in three separate sections. Power input to each section was varied to obtain a constant temperature gradient along the furnace. This gradient was no more than about $1^{o}C$ along the length of the reaction vessel. The filling material of furnace was vermiculite inside the cement part. The inner resistor was connected to a Thermoelectric thermoregulator, which controlled the furnace temperature to within $\pm 1^{o}C$. The thermocouple in the reaction vessel was calibrated against the ice point and boiling point of water. Temperature of the furnace was

Figure 1a - Schematic Diagram of the Apparatus
Figure 1b - Schematic Diagram of the Reaction Vessel and the Furnace

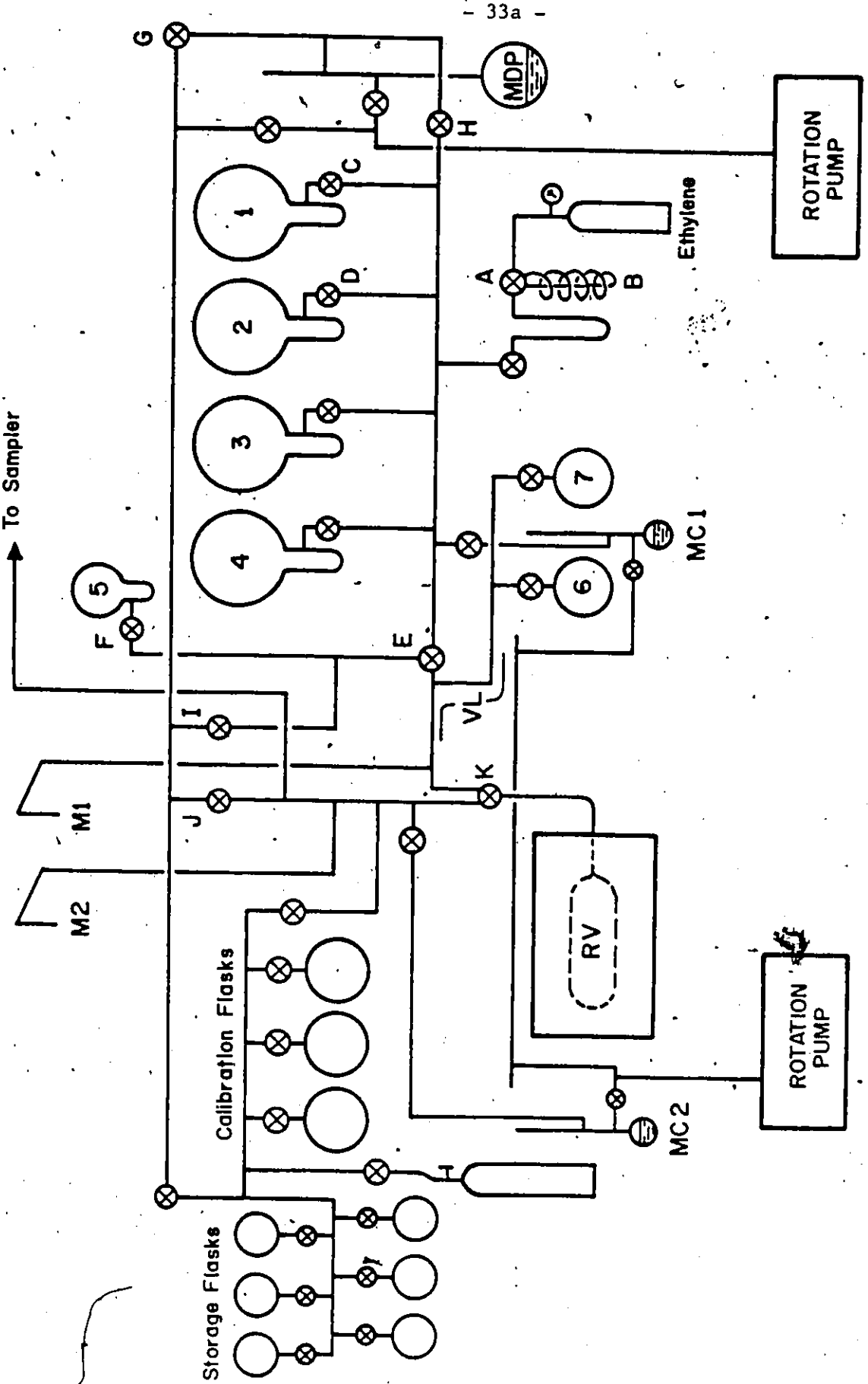

G
MDP
H
ROTATION PUMP
C
1
D
2
A
B
Ethylene
3
7
4
MC1
6
5
F
E
To Sampler
VL
I
M1
K
J
M2
RV
Calibration Flasks
ROTATION PUMP
MC2
L
Storage Flasks

Figure 1a.

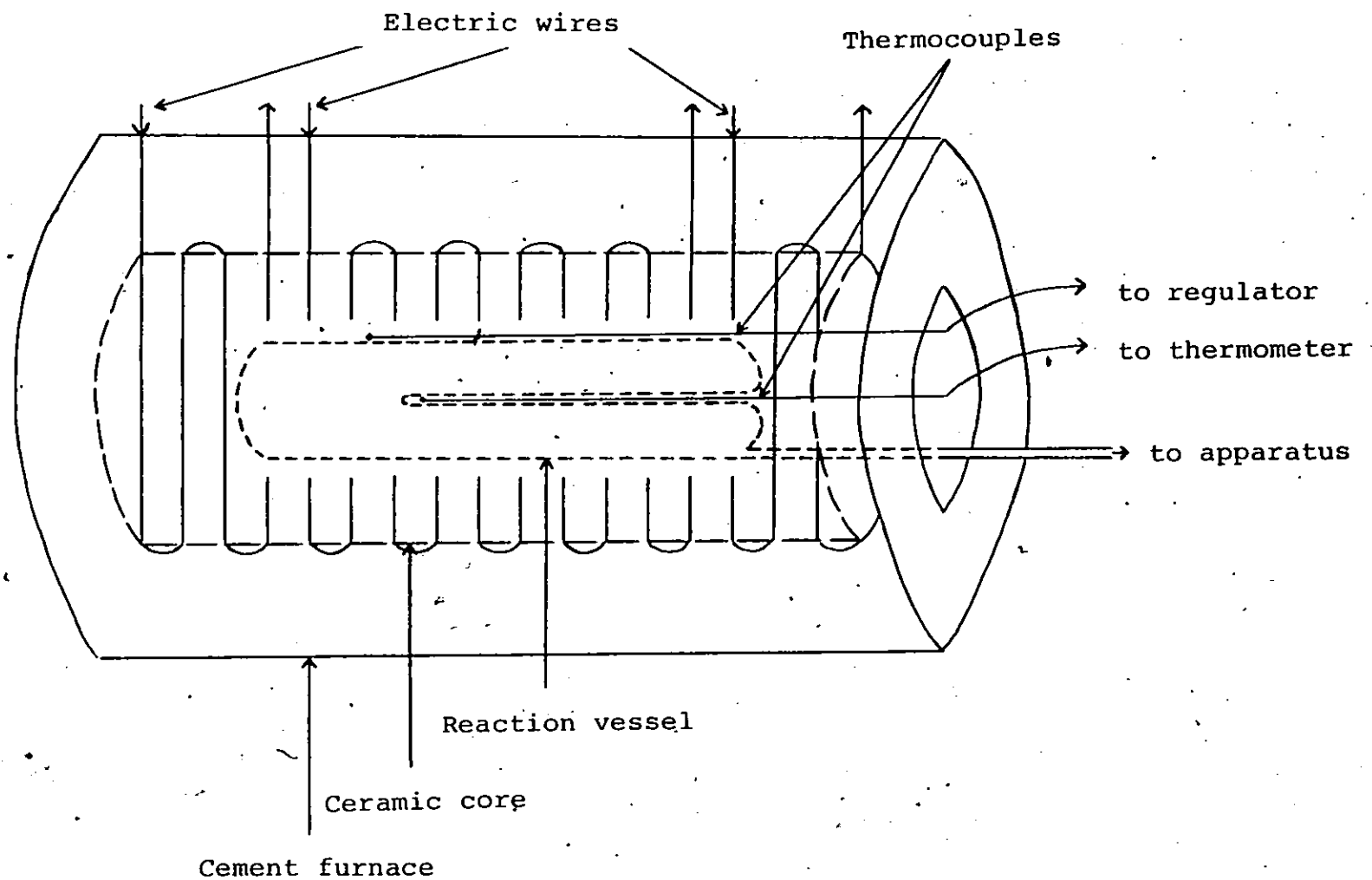

Electric wires
Thermocouples
to regulator
to thermometer
to apparatus
Reaction vessel
Ceramic core
Cement furnace

Figure 1b.

measured with a Digital Heat Prober Thermometer, Wahl Thermocouple Model 1370. Temperature range of the thermometer was 0-1370°C. Measurement accuracy was ± 1°C, with a thermocouple type K.

For the pyrolysis of ethylene in the presence of ethane and neopentane, a quartz cylinder with 210 ml volume and surface to volume ratio of 1.1 cm^{-1} was used. In the experiments, where 1-butene was the additive, the reaction vessel was a pyrex cylinder, 208 ml, with a surface to volume ratio of 1.1 cm^{-1}. Surface effect studies were made by using a similar pyrex vessel packed with 30 pyrex tubes giving a surface/volume ratio of 8 cm^{-1}. The thermocouple was inserted in an inner finger along the axis of the reaction vessel. The reaction vessel was placed horizontally inside the furnace and sealed to the 3-way stopcock (K) (Fig. 1b).

The pressure measurements were made with two McLeod Gauges, Mc(1) and Mc(2) with ranges from 10^{-5} to 1 and 2 torr, respectively. Product analysis was made using a glass sampler system directly connected to the gas chromatograph from the reaction vessel. The analytical part of the apparatus is shown in Figure 2 and will be described later.

2. Materials

Research grade ethylene, labelled 99.98% pure, was obtained from Matheson Canada, Limited. Analysis revealed

about 6.4×10^{-4}% ethane and 3×10^{-3}% acetylene. When necessary, ethylene was purified in a purification apparatus, assembled next to the pyrolysis apparatus. In this system, ethylene at atmospheric pressure was introduced into a 100 ml sampler, made from 0.6 cm diameter copper tubing; by a 4-way metal valve, then was passed through a column (1 m x 1.2 cm) filled with silica gel and maintained at 25°C. Detection of hydrocarbons was made by a thermal conductivity detector. After the ethane had been eluted, the helium flow was deviated to the trap (B) through stopcock (A) where the purified ethylene was trapped and subsequently transferred directly to the storage flask.

Research grade 1-butene (99.9%), ethane (99.96%) and neopentane (99.87%) were also obtained from Matheson Canada, Limited. Impurities detected in 1-butene were cis- and trans-2-butene. The main impurities in ethane and neopentane were methane and propylene, respectively. Since only small quantities of the additives were used, the amounts of impurity in these compounds did not affect the measurement of the yields of the reaction products, and therefore no purification was made. Matheson research grade ethane, propylene, 1-butene, cis-2-butene and butadiene were used for calibrations, and all gases were distilled and degassed from bulb to bulb before use.

3. Experimental Procedure

The apparatus was always kept at 10^{-5} torr pressure. Before the experiments, ethylene was introduced into the system through inlet (A) and stored in 5 L-bulbs (1) and (2) (Figure 1). Then, it was condensed in 1 L-bulb (5) using liquid nitrogen and the system was evacuated for half an hour while the stopcocks (C), (D) and (F) were open. Stopcocks (G), (H) and (I) were closed and by removing liquid nitrogen from bulb (5), all ethylene was degassed. This time, ethylene was condensed in bulb (1) and the system was evacuated for another half an hour and then it was degassed again. This procedure was repeated for four times and thus the ethylene gas was stored in bulbs (1) and (2). The 5 L-bulbs (3) and (4) were also used for the same purpose, when necessary.

The additive gas, either 1-butene, ethane or neopentane was stored in one of 0.5 L-storage bulbs and condensed and degassed several times before use. Mixtures were prepared in 3 L-flasks (6) and (7) with an inner cold finger and minimum connecting tubing. Calculated amount of additive was introduced into the mixing flask and then diluted by adding a high pressure of ethylene. Complete mixing of the gases was achieved by condensing on the cold finger and then warming rapidly. It was also found that complete mixing was achieved by allowing the mixture to stand overnight. The

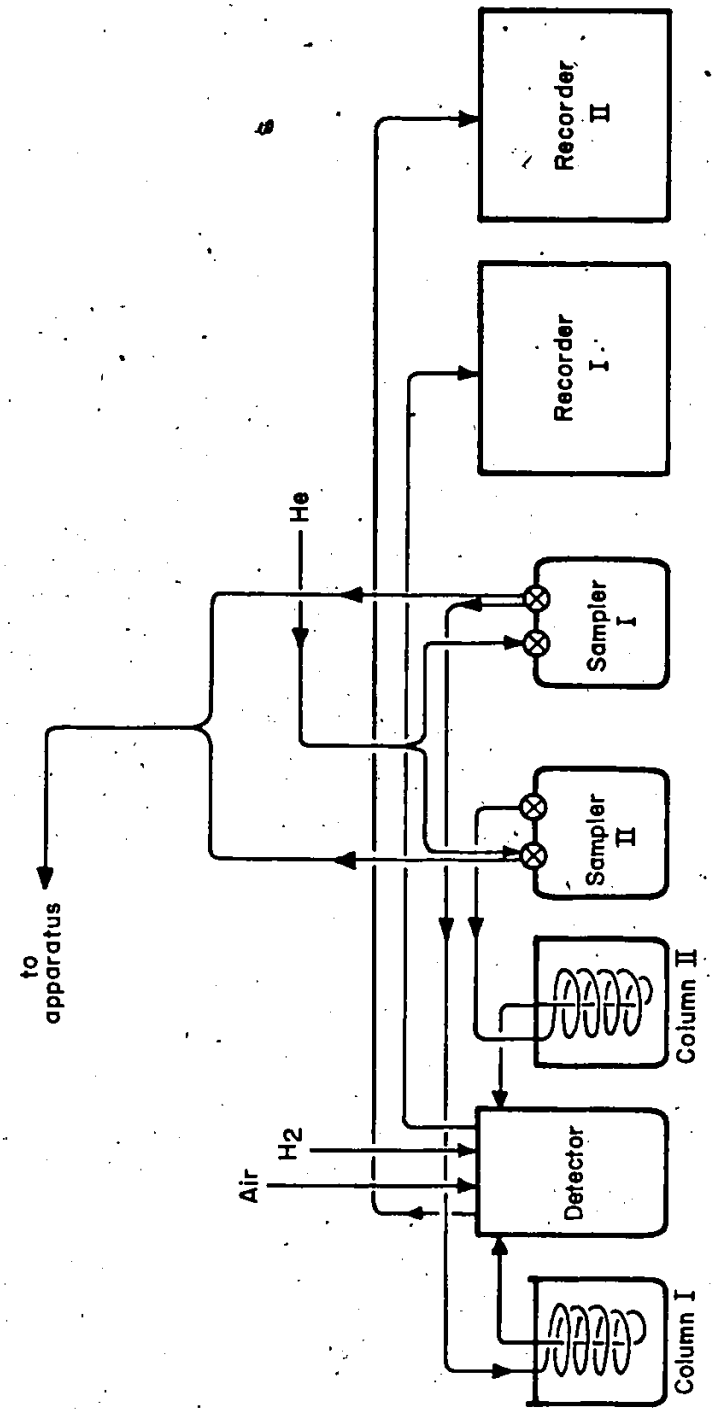
exact ratio of additive to ethylene was then obtained by analysis before the pyrolysis reactions. Analyses of the prepared mixtures at different times were always in agreement.

To obtain initial rates, pyrolysis reactions were performed at different reaction times. The reaction mixture was first expanded carefully into the vacuum line — VL — until a desired pressure was attained which was measured on the U-tube mercury manometer M(1). Then, it was introduced into the reaction vessel (RV) through 3-way stopcock (K). At the end of the reaction, the reaction mixture was expanded into the glass sampler system through the stopcock (K). The pressure of the mixture after the pyrolysis was measured on the manometer M(2). Following the closing of the stopcock (J), the products of the reaction were analyzed by gas chromatography.

4. Analytical System

The products were analyzed with a Hewlett-Packard Model 5710 A Gas Chromatograph, equipped with a dual-flame ionization detector. For the analyses of low and high molecular weight products, two different columns and two recorders were used simultaneously. Figure 2 shows the analytical system schematically. The carrier gas was helium and the flow rate of 60 ml/min was maintained constant with

Figure 2 - Sampling System for Gas Chromatography Analysis


Recorder II
Recorder I
He
Sampler I
Sampler II
to apparatus
Column II
H2
Air
Detector
Column I

an Edwards pressure regulator. Air and hydrogen flow rates were 240 and 60 ml/min, respectively. Purification of helium, air and hydrogen gases from small amounts of water vapor and oxygen was achieved by using molecular sieve filters.

For the ethylene+1-butene pyrolysis product analysis, two different Durapak columns were used. Methane, ethane, propylene and 1-butene were analyzed on (Phenylisocyanate/ Poracil C) column, 4.2 m x 0.6 cm at 30°C. For butadiene, (n-octane/Poracil C) column, 4 m x 0.6 cm at 50°C was used. For the systems ethylene+ethane and ethylene+neopentane, the analysis of methane, ethane, propylene, 1-butene and neopentane were made on (Phenylisocyanate/Poracil C) column, 4.5 m x 0.6 cm, at 20°C. Butadiene, where followed, was analyzed on squalane + adiponitrile column, (2 m + 8 m), at 10°C.

Calibration mixtures were prepared by introducing small pressures of gases, measured by McLeod gauge, into a 250 ml-flask and then transferring some of it into a 3 L-calibration flask and diluting it by air. Calibration graphs were obtained by plotting the length (or the area for higher products) of the peak versus the pressure of gas in the sampler. Calibration factors were calculated from the slopes of these lines. As an example, these factors that are calculated for the ethylene+neopentane studies are given below:

Product	Calibration Factor x 10^{-4}
Methane	6.78 cm /torr
Ethane	9.25 cm_2/torr
Propylene	1.60 cm^2/torr
1-Butene	2.06 cm^2/torr
Butadiene	1.90 cm^2/torr
Neopentane	2.68 cm^2/torr

These calibration factors have approximately 2% uncertainty. Sensitivity of the analysis system was quite good. For instance, a 1 cm peak on 1 x 1 scale would represent 1 x 10^{-5} torr of ethane in the sampler and 3 x 10^{-5} torr ethane in the reaction vessel.

5. Method for the Determination of Initial Rates

In kinetic experiments, initial rates of reactions are usually measured by one of three methods:

(a) directly from the slope of yield-time plots,

(b) by extrapolation of the rate as a function of time where the intercept at zero time is the initial rate,

(c) by fitting the data to polynomial curves and calculating the rate at zero time.

In this research, initial rates were determined directly from the yield-time curves. This method seemed to be most reliable for several reasons. First of all, the initial linear part of the yield-time curves were quite well defined except at the highest temperatures and pressures.

Because the experiments were performed at very short reaction times, it was possible to obtain enough data to define this linear part before the onset of secondary reactions. The extrapolation method may be applied when it is known that the yield is a quadratic function of the time,

$$y = at + bt^2$$

and hence

$$y/t = a + bt$$

where a is the initial rate. In the present experiments, this relation was not sufficiently well-defined to provide an improvement over method (a). In fact, plots of this relationship appeared not to be linear. For comparison purposes, however, most of the results were analyzed by this method and the initial rates were found to be lower by about 10% from those obtained by method (a). The ratios of the initial rates, however, in the presence and absence of the additive were not significantly altered. The method of initial rate determinations from a polynomial function necessitates very well defined yield-time curves for the product formation covering a wide time range. The present measurements emphasized yields of products at short reaction times. When all these effects were considered, it was decided that direct measurement of initial rates from the yield-time plots gave the most reliable ratio of initial rates.

CHAPTER III

ADDITIONS OF 1-BUTENE

The initial rates of formation of the major products methane, ethane and propylene have been measured at six temperatures in the presence and absence of additive 1-butene. Initial pressures of ethylene were between 75 and 400 torr. At each pressure, about four or five mixtures of 1-butene and ethylene were studied, ranging in composition from 0.07 to 0.9% 1-butene. Reaction temperatures were 699, 721, 732, 748, 763 and 773 K. Before the mixture experiments, pyrolyses of ethylene alone were performed at all pressures and temperatures. Discussion of the ethylene pyrolysis alone will be given in Chapter VI. The pyrolysis of ethylene at these temperatures shows marked self-acceleration due predominantly to the formation of 1-butene in the products[20] and it was necessary to measure yields at very short reaction times. The determination of the initial rates of products was most difficult at high temperatures and high pressures due to the onset of autocatalysis.

The pyrolysis of ethylene in the presence of small amounts of 1-butene led to yield-time plots for all the measured products similar to those from the ethylene pyrolysis alone. As the reaction temperature was increased, the effect of 1-butene on the initial rates of product

formation also increased. This effect was more noticeable at low pressures of ethylene compared to higher pressures.

It was estimated that for most of the initial rates, the uncertainty was between 5-10%. A detailed discussion of the errors involved in the present experiments will be deferred to Chapter V. Individual error limits are therefore not included in the tables of initial rates which follow.

Except for plots given as examples in this chapter, all data from the study of the ethylene + 1-butene system is illustrated in Appendix A.

1. Pyrolysis of 1-Butene

The earliest of the investigations concerned with the pyrolysis of 1-butene was by Wheeler and Wood[54]. They studied the decomposition of 1-butene by a flow technique in the temperature range 873-973 K and suggested a molecular mechanism for the formation of the main products methane, propylene, ethylene and ethane. Later Molera and Stubbs[19], Danby, Spall, Stubbs and Hinshelwood[55] also concluded that the 1-butene decomposition proceeds primarily by molecular mechanisms. However, Sehon and Swzarc[56], Lossing, Ingold and Henderson[57] and Bryce and Kebarle[58] proposed free radical chain mechanisms for this decomposition. The initiation step was the dissociation of 1-butene into methyl and allyl radicals. Recent studies on the pyrolysis

of 1-butene[59-61] also favour a radical chain mechanism with a first-order dependence of products on 1-butene pressure.

Powers and Corcoran[61] investigated the decomposition of 1-butene in the temperature range 803-878 K by a flow technique. The overall activation energy was found to be 76 kcal mol^{-1}. Applying computer modelling to the system, they estimated individual rate constants for several elementary steps.

The principle initiation step of the 1-butene pyrolysis is the dissociation of 1-butene into methyl and allyl radicals.

$$1 - C_4H_8 \rightarrow CH_3 + C_3H_5$$

The propagation steps include reactions such as the hydrogen-atom abstraction of the methyl, allyl and ethyl radicals from 1-butene, the hydrogen-atom addition to 1-butene, the decomposition of 2-butenyl and 1 and 2-butyl radicals. Important reaction products are methane, ethane, propylene, cis- and trans-2 butenes and butadiene. The main termination reactions are the recombination of 2-butenyl radicals and cross-combinations of methyl and 2-butenyl radicals.

Arrhenius parameters for the rate constant of the initiation step of 1-butene pyrolysis are given in Table 2.

Table 2

ARRHENIUS PARAMETERS OF THE RATE CONSTANT FOR THE INITIATION STEP OF 1-BUTENE PYROLYSIS

log A/s^{-1}	$E/kcal\ mol^{-1}$	Reference
16.0	74.5	61
16.3	71.5	60
16.0	73.3	44

The two other possible initiation steps for 1-butene decomposition,

$$\text{1-butene} \rightarrow \text{2-butenyl} + H.$$

$$\text{1-butene} \rightarrow \text{vinyl} + \text{ethyl}$$

have higher activation energies, 87 and 94 kcal mol^{-1}, respectively, and therefore they are much less important at temperatures of these experiments than the dissociation of 1-butene into methyl and allyl radicals.

In the calculations of the present study, the value of the rate constant for the initiation step of the 1-butene pyrolysis is taken from Powers and Corcoran[61] because their work appeared to involve the most recent and extensive research on 1-butene. Also, the activation energy, 74.5 kcal mol^{-1}, correlates well with the heats of formation of methyl[73,74], 35.1, and allyl[75-77], 39.1 kcal mol^{-1}. The values of the Arrhenius parameters suggested by other

workers however, are not much different than those of Powers and Corcoran, as shown in Table 2. But yet, due to the complexity of reactions occurring in the pyrolysis of 1-butene, more research is necessary for a complete understanding of the kinetics of the 1-butene decomposition. Nevertheless, the use of 1-butene as the first additive served to show that the kinetic method used in the present study was applicable to the determination of the initiation rate constant in the pyrolysis of ethylene.

2. Product Formation

i) Methane

An example of a yield-time plot for methane is given in Figure 3. At lower temperatures, the linear portion of the yield-time curves was well identified. In the presence of 1-butene, the rate of formation of methane was significantly increased. In Table 3, the initial rates of methane formation in the presence and absence of 1-butene at all temperatures are presented together with the ratios of these rates. The yields of methane were somewhat scattered probably because a small "residual" peak of methane appeared in blank experiments. Correction for this "impurity" was attempted but led to some scatter in yield-time plots.

Figure 3 - Yield-time Plot for the Formation of Methane at 721 K

○ 299.9 torr C_2H_4
● 301.0 torr C_2H_4 + 0.31 torr 1-C_4H_8
△ 299.7 torr C_2H_4 + 0.67 torr 1-C_4H_8
▲ 299.7 torr C_2H_4 + 1.66 torr 1-C_4H_8

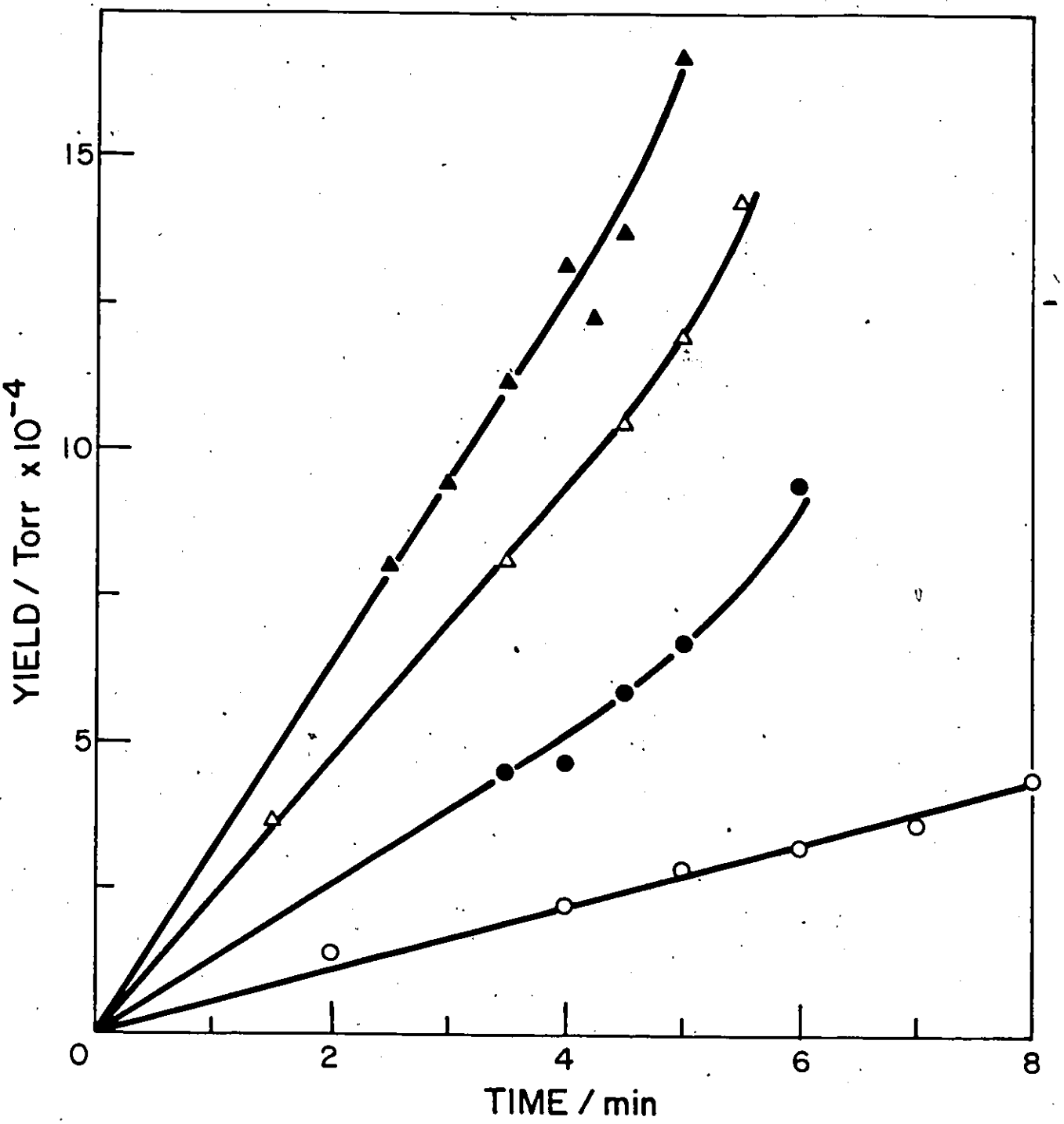

YIELD / Torr x 10⁻⁴
15
10
5
0
2
4
6
8
TIME / min

Table 3

EFFECT OF 1-BUTENE ON THE INITIAL RATES OF METHANE FORMATION

T/K	$[C_2H_4]$/torr	$[1\text{-}C_4H_8]$/torr	Initial rate of formation/torr s^{-1}	$(V_0)_B/(V_0)$
699	199.9	0	1.94×10^{-7}	
	199.5	0.20	5.67×10^{-7}	2.92
	200.1	0.52	7.50×10^{-7}	3.87
	200.2	1.34	1.12×10^{-6}	5.77
	300.7	0	3.00×10^{-7}	
	300.5	0.50	8.33×10^{-7}	2.78
	300.1	0.78	1.23×10^{-6}	4.10
	300.1	2.01	2.00×10^{-6}	6.67
	400.0	0	4.00×10^{-7}	
	400.0	0.40	1.27×10^{-6}	3.18
	400.1	1.04	1.67×10^{-6}	4.18
	400.0	2.68	2.03×10^{-6}	5.08
721	100.3	0	2.60×10^{-7}	
	100.2	0.10	5.06×10^{-7}	1.95
	99.8	0.22	1.44×10^{-6}	5.54
	99.8	0.55	1.99×10^{-6}	7.65
	200.0	0	5.00×10^{-7}	
	200.8	0.21	1.11×10^{-6}	2.22
	200.0	0.45	2.25×10^{-6}	4.50
	200.0	1.11	3.43×10^{-6}	6.86
	299.9	0	9.17×10^{-7}	
	301.0	0.31	2.17×10^{-6}	2.37
	299.7	0.67	3.89×10^{-6}	4.24
	299.7	1.66	5.22×10^{-6}	5.69
732	100.0	0	2.19×10^{-7}	
	100.7	0.10	1.00×10^{-6}	4.57
	100.0	0.35	1.92×10^{-6}	8.75
	200.0	0	6.76×10^{-7}	
	200.0	0.20	2.50×10^{-6}	3.70
	200.0	0.69	3.83×10^{-6}	5.67
	300.0	0	1.23×10^{-6}	
	300.0	1.04	6.00×10^{-6}	4.88

T/K	$[C_2H_4]$/torr	$[1\text{-}C_4H_8]$/torr	Initial rate of formation/torr s^{-1}	$(V_0)_B/(V_0)$
748	99.7	0	4.00×10^{-7}	
	99.4	0.09	2.73×10^{-6}	6.83
	100.1	0.40	3.64×10^{-6}	9.10
	99.8	0.73	5.17×10^{-6}	12.9
	199.3	0	1.22×10^{-6}	
	199.3	0.18	5.42×10^{-6}	4.44
	200.0	0.81	9.17×10^{-6}	7.52
	199.0	1.45	1.22×10^{-5}	10.0
	299.6	0	2.50×10^{-6}	
	300.2	0.28	8.75×10^{-6}	3.50
	300.0	1.21	1.46×10^{-5}	5.84
	299.2	2.18	2.08×10^{-5}	8.32
763	100.0	0	8.33×10^{-7}	
	100.3	0.20	-	-
	100.2	0.35	6.92×10^{-6}	8.31
	100.0	0.51	1.01×10^{-5}	12.1
	200.1	0	2.33×10^{-6}	
	199.6	0.41	1.23×10^{-5}	5.28
	200.1	0.69	1.37×10^{-5}	5.88
	200.0	1.03	1.83×10^{-5}	7.85
	300.4	0	8.33×10^{-6}	
	300.2	1.54	4.03×10^{-5}	4.84
773	75.0	0	5.67×10^{-7}	
	75.0	0.11	4.05×10^{-6}	7.14
	74.2	0.38	7.75×10^{-6}	13.7
	74.1	0.63	1.04×10^{-5}	18.3
	74.5	2.80	3.47×10^{-5}	61.2
	100.6	0	8.33×10^{-7}	
	100.0	0.07	4.92×10^{-6}	5.91
	101.9	0.17	6.50×10^{-6}	7.80
	100.1	0.42	1.04×10^{-5}	12.5
	100.3	0.85	1.25×10^{-5}	15.0
	99.7	3.75	2.08×10^{-5}	25.0
	205.0	0	2.71×10^{-6}	
	208.6	0.05	8.33×10^{-6}	3.07
	206.3	0.11	1.15×10^{-5}	4.24
	205.8	0.37	1.40×10^{-5}	5.17
	208.9	0.65	2.08×10^{-5}	7.68

T/K	$[C_2H_4]$/torr	$[1\text{-}C_4H_8]$/torr	Initial rate of formation/torr s^{-1}	$(V_0)_B/(V_0)$
	304.0	0	6.67×10^{-6}	
	305.0	0.74	3.06×10^{-5}	4.59
	305.1	1.54	4.78×10^{-5}	7.17
	302.5	2.57	6.67×10^{-5}	10.0
	306.0	11.5	2.00×10^{-4}	30.0

In this table, $(V_0)_B$ and (V_0) refer to the initial rate of product formation from the ethylene pyrolysis in the presence and absence of 1-butene, respectively.

The problem was later solved by improved procedures in the experimental techniques, which removed this "residual" methane. At some low pressure experiments, namely 75 torr pyrolyses at temperatures 721, 748 and 763 K, the initial rates of methane formation could not be determined accurately and hence these data were not included in Table 3. The reason for that was mainly the large uncertainty in the very small yields of methane at this total pressure, especially in the pyrolysis of ethylene alone.

ii) Ethane

A typical yield-time plot for the formation of ethane in the absence and presence of 1-butene is given in Figure 4. The initial rates of ethane formation from the ethylene and mixture pyrolyses are presented in Table 4. Because the yields of products were measured at very low conversions, the presence of a small impurity of ethane in the ethylene caused some difficulties in the measurement of the initial rate. If the yield of ethane was corrected for the ethane impurity, based on the analysis made before each set of the experiments, a large scatter in the data was obtained. A better representation of the data was achieved by plotting the uncorrected yields for the reaction of both ethylene and ethylene+1-butene mixtures. The amount of impurity was found by extrapolating the yield-time curves to zero time.

Figure 4 - Yield-time Plot for the Formation of Ethane at 748 K

○ 299.6 torr C_2H_4
● 300.2 torr C_2H_4 + 0.28 torr 1-C_4H_8
△ 300.0 torr C_2H_4 + 1.21 torr 1-C_4H_8
▲ 299.2 torr C_2H_4 + 2.18 torr 1-C_4H_8

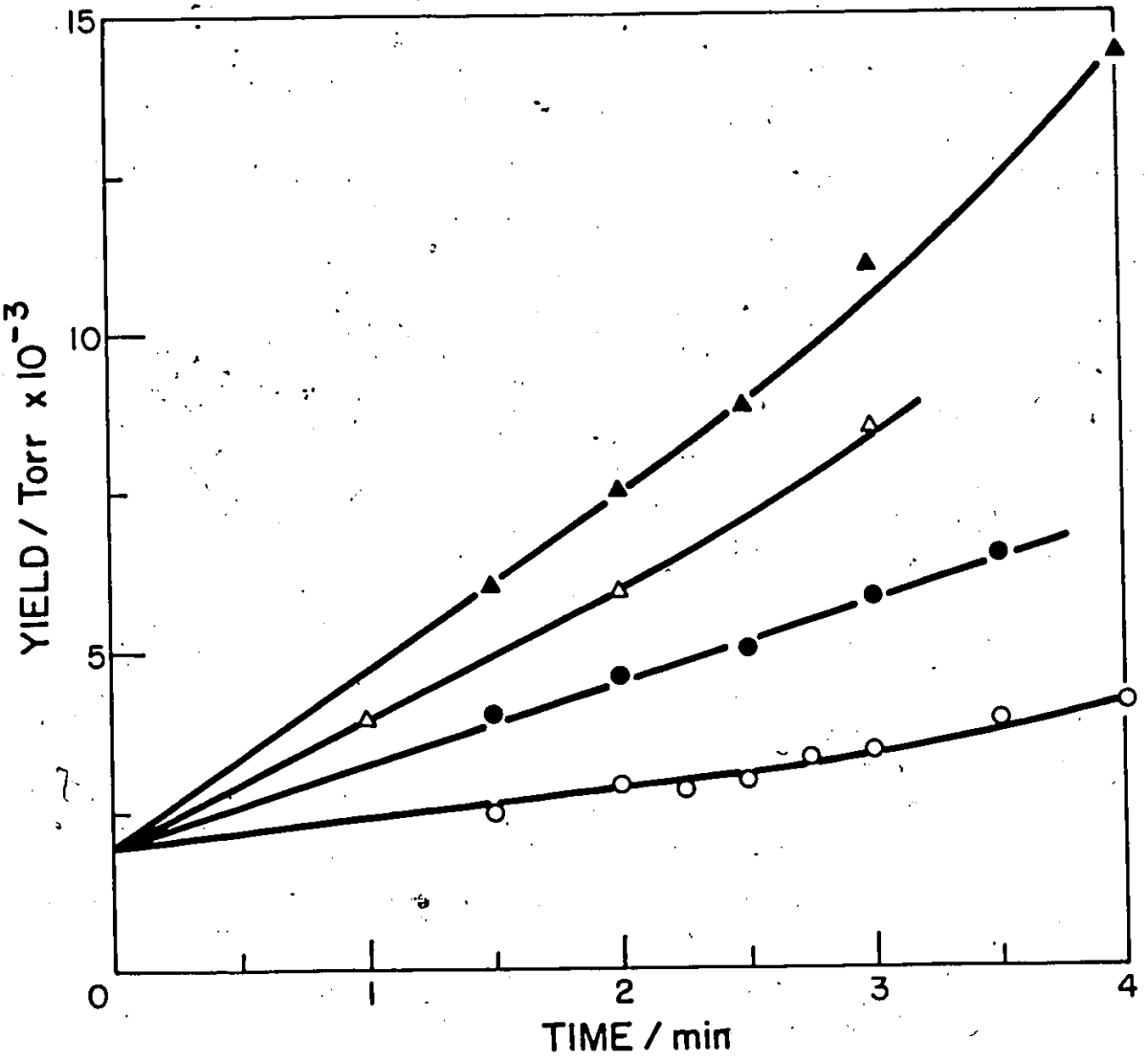

15
10
5
0
1
2
3
4
YIELD / Torr x 10^-3
TIME / min

Table 4

EFFECT OF 1-BUTENE ON THE INITIAL RATES OF ETHANE FORMATION

T/K	$[C_2H_4]$/torr	$[1\text{-}C_4H_8]$/torr	Initial rate of formation/torr s^{-1}	$(V_0)_B/(V_0)$
699	199.9	0	5.00×10^{-7}	
	199.5	0.20	1.47×10^{-6}	2.94
	200.1	0.52	2.27×10^{-6}	4.54
	200.2	1.34	3.33×10^{-6}	6.66
	300.7	0	1.25×10^{-6}	
	300.5	0.50	3.61×10^{-6}	2.89
	300.1	0.78	4.43×10^{-6}	3.54
	300.1	2.01	6.15×10^{-6}	4.92
	400.0	0	1.96×10^{-6}	
	400.0	0.40	4.72×10^{-6}	2.41
	400.1	1.04	5.75×10^{-6}	2.93
	400.0	2.68	8.33×10^{-6}	4.25
721	74.8	0	1.43×10^{-7}	
	74.9	0.08	6.33×10^{-7}	4.43
	74.6	0.17	9.21×10^{-7}	6.44
	74.5	0.41	1.42×10^{-6}	9.93
	100.3	0	2.50×10^{-7}	
	100.2	0.10	1.17×10^{-6}	4.68
	99.8	0.22	1.49×10^{-6}	5.96
	99.8	0.55	2.44×10^{-6}	9.76
	200.0	0	9.67×10^{-7}	
	200.8	0.21	3.10×10^{-6}	3.21
	200.0	0.45	4.00×10^{-6}	4.14
	200.0	1.11	6.67×10^{-6}	6.90
	299.9	0	1.94×10^{-6}	
	301.0	0.31	5.33×10^{-6}	2.75
	299.7	0.67	7.25×10^{-6}	3.74
	299.7	1.66	1.08×10^{-5}	5.57
732	100.0	0	3.63×10^{-7}	
	100.7	0.10	1.79×10^{-6}	4.93
	100.0	0.35	3.33×10^{-6}	9.17
	200.0	0	1.45×10^{-6}	
	200.0	0.20	4.58×10^{-6}	3.17
	200.0	0.69	8.96×10^{-6}	6.20

T/K	$[C_2H_4]$/torr	$[1\text{-}C_4H_8]$/torr	Initial rate of formation/torr s^{-1}	$(V_0)_B/(V_0)$
	300.0	0	3.67×10^{-6}	
	300.0	1.04	1.79×10^{-5}	4.88
748	74.0	0	3.67×10^{-7}	
	74.5	0.07	2.55×10^{-6}	6.95
	73.8	0.30	4.23×10^{-6}	11.5
	74.3	0.54	5.67×10^{-6}	15.5
	99.7	0	6.11×10^{-7}	
	99.4	0.09	3.94×10^{-6}	6.45
	100.1	0.40	6.00×10^{-6}	9.82
	99.8	0.73	7.89×10^{-6}	12.9
	199.3	0	2.37×10^{-6}	
	199.3	0.18	9.08×10^{-5}	3.83
	200.0	0.81	1.54×10^{-5}	6.50
	199.0	1.45	2.09×10^{-5}	8.82
	299.6	0	5.89×10^{-6}	
	300.2	0.28	2.14×10^{-5}	3.63
	300.0	1.21	3.31×10^{-5}	5.62
	299.2	2.18	4.59×10^{-5}	7.79
763	74.3	0	6.42×10^{-7}	
	74.7	0.15	5.99×10^{-6}	9.33
	75.1	0.26	8.20×10^{-6}	12.8
	100.0	0	1.33×10^{-6}	
	100.3	0.20	1.02×10^{-5}	7.67
	100.2	0.35	1.35×10^{-5}	10.2
	100.0	0.51	1.69×10^{-5}	12.7
	200.1	0	5.55×10^{-6}	
	199.6	0.41	2.96×10^{-5}	5.33
	200.1	0.69	3.96×10^{-5}	7.14
	200.0	1.03	4.54×10^{-5}	8.18
	300.4	0	1.83×10^{-5}	
	300.2	1.54	8.88×10^{-5}	4.85
773	75.0	0	8.33×10^{-7}	
	75.0	0.11	7.50×10^{-6}	9.00
	74.2	0.38	1.33×10^{-5}	16.0
	74.1	0.63	1.91×10^{-5}	23.0
	74.5	2.80	4.13×10^{-5}	50.0

T/K	$[C_2H_4]$/torr	$[1\text{-}C_4H_8]$/torr	Initial rate of formation/torr s^{-1}	$(V_0)_B/(V_0)$
	100.6	0	2.22×10^{-6}	
	100.0	0.07	1.00×10^{-5}	4.50
	101.9	0.17	1.48×10^{-5}	6.67
	100.1	0.42	2.33×10^{-5}	10.5
	100.3	0.85	3.08×10^{-5}	13.9
	99.7	3.75	7.17×10^{-5}	32.3
	205.0	0	7.67×10^{-6}	
	208.6	0.05	1.61×10^{-5}	2.10
	206.3	0.11	2.40×10^{-5}	3.13
	205.8	0.37	3.22×10^{-5}	4.20
	208.9	0.65	4.07×10^{-5}	5.31
	304.0	0	1.72×10^{-5}	
	305.0	0.74	6.73×10^{-5}	3.91
	305.1	1.54	1.06×10^{-4}	6.16
	302.5	2.57	1.65×10^{-4}	9.59
	306.0	11.5	3.76×10^{-4}	21.9

In all cases, the amount of ethane impurity was the same from ethylene and from the mixtures. This procedure was shown to be reasonable by comparison of the rate of formation of ethane from the purified ethylene. The rate from the pyrolysis of purified ethylene was almost the same as the rate from the unpurified ethylene pyrolysis. This observation showed also that this amount of ethane impurity was not interfering with the rate of formation of the product ethane. The results of the purified ethylene pyrolysis will be discussed in the following section and examples of yield-time plots of purified and unpurified ethylene will be given.

iii) Propylene

There was no propylene impurity in either ethylene or 1-butene and hence the yield-time plots, as in Figure 5, are shown without any correction. The only difficulty with the determination of the initial rates of formation of propylene was the rapid increase in rate due to secondary reactions. This was most serious at high temperatures and high pressures. Nevertheless, the direct measurement of initial rates from the yield-time plots was judged the most reasonable for this product also. The initial rates of propylene formation in the presence and absence of 1-butene are given in Table 5. Also presented are the ratios of the initial rates.

Figure 5 - Yield-time Plot for the Formation of Propylene at 699 K

○ 400.0 torr C_2H_4
● 400.0 torr C_2H_4 + 0.40 torr 1-C_4H_8
△ 400.1 torr C_2H_4 + 1.04 torr 1-C_4H_8
▲ 400.0 torr C_2H_4 + 2.68 torr 1-C_4H_8

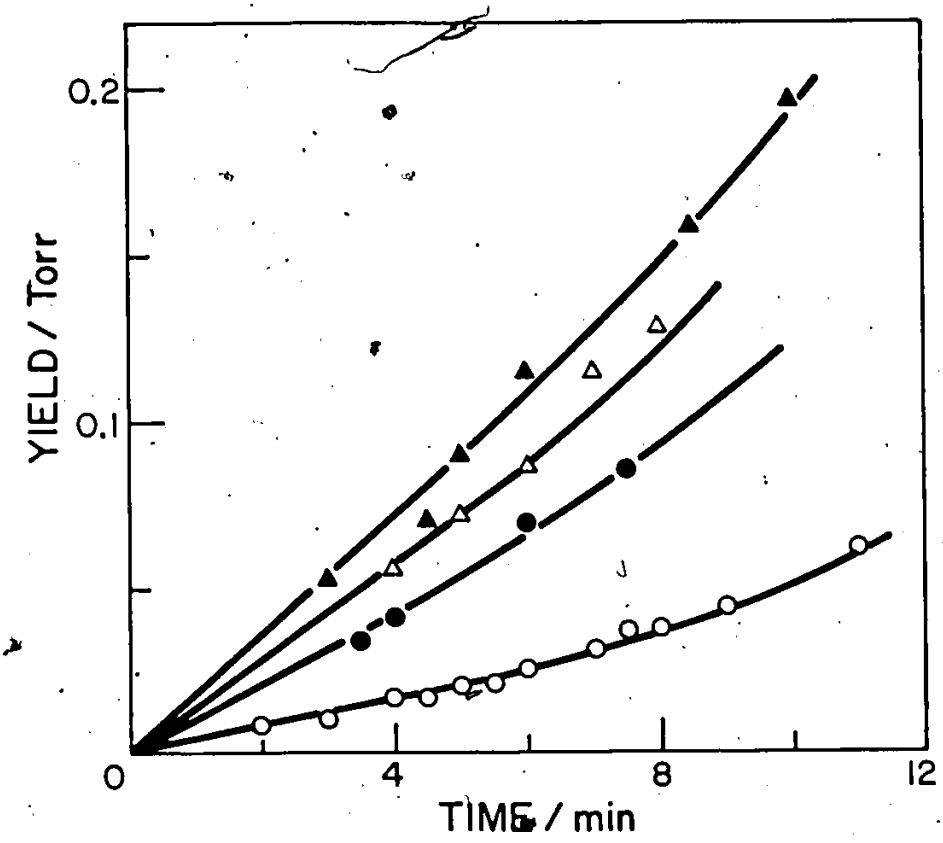

0.2
0.1
YIELD / Torr
0
4
8
12
TIME / min

Table 5

EFFECT OF 1-BUTENE ON THE INITIAL RATES OF PROPYLENE FORMATION

T/K	$[C_2H_4]$/torr	$[1\text{-}C_4H_8]$/torr	Initial rate of formation/torr s^{-1}	$(V_0)_B/(V_0)$
699	199.9	0	1.33×10^{-5}	
	199.5	0.20	3.61×10^{-5}	2.71
	200.1	0.52	5.55×10^{-5}	4.17
	200.2	1.34	7.31×10^{-5}	5.50
	300.7	0	3.13×10^{-5}	
	300.5	0.50	8.67×10^{-4}	2.77
	300.1	0.78	1.09×10^{-4}	3.49
	300.1	2.01	1.64×10^{-4}	5.24
	400.0	0	6.67×10^{-5}	
	400.0	0.40	1.58×10^{-4}	2.37
	400.1	1.04	2.33×10^{-4}	3.49
	400.0	2.68	2.88×10^{-4}	4.32
721	74.8	0	1.92×10^{-6}	
	74.9	0.08	6.67×10^{-5}	3.47
	74.6	0.17	1.01×10^{-5}	5.26
	74.5	0.41	1.28×10^{-5}	6.67
	100.3	0	3.00×10^{-6}	
	100.2	0.10	1.36×10^{-5}	4.53
	99.8	0.22	1.62×10^{-5}	5.40
	99.8	0.55	2.08×10^{-5}	6.93
	200.0	0	1.75×10^{-5}	
	200.8	0.21	6.31×10^{-5}	3.61
	200.0	0.45	7.71×10^{-5}	4.41
	200.0	1.11	9.79×10^{-5}	5.59
	299.9	0	6.25×10^{-5}	
	301.0	0.31	1.60×10^{-4}	2.56
	299.7	0.67	2.05×10^{-4}	3.28
	299.7	1.66	2.46×10^{-4}	3.94
732	100.0	0	3.33×10^{-6}	
	100.7	0.10	1.66×10^{-5}	4.98
	100.0	0.35	2.81×10^{-5}	8.44

T/K	$[C_2H_4]$/torr	$[1\text{-}C_4H_8]$/torr	Initial rate of formation/torr s^{-1}	$(V_0)_B/(V_0)$
	200.0	0	2.09×10^{-5}	
	200.0	0.20	8.33×10^{-5}	3.99
	200.0	0.69	1.36×10^{-4}	6.51
	300.0	0	6.61×10^{-5}	
	300.0	1.04	3.17×10^{-4}	4.80
748	74.0	0	2.78×10^{-6}	
	74.5	0.07	1.17×10^{-5}	4.21
	73.8	0.30	2.00×10^{-5}	7.19
	74.3	0.54	2.42×10^{-5}	8.71
	99.7	0	4.17×10^{-6}	
	99.4	0.09	2.25×10^{-5}	5.40
	100.1	0.40	4.00×10^{-5}	9.59
	99.8	0.73	4.33×10^{-5}	10.4
	199.3	0	2.50×10^{-5}	
	199.3	0.18	9.42×10^{-5}	3.77
	200.0	0.81	1.75×10^{-4}	7.00
	199.0	1.45	1.94×10^{-4}	7.80
	299.6	0	7.96×10^{-5}	
	300.2	0.28	2.58×10^{-4}	3.24
	300.0	1.21	4.08×10^{-4}	5.13
	299.2	2.18	5.42×10^{-4}	6.81
763	100.0	0	6.08×10^{-6}	
	100.3	0.20	4.00×10^{-5}	6.58
	100.2	0.35	5.50×10^{-5}	9.05
	100.0	0.51	6.00×10^{-5}	9.87
	200.1	0	4.17×10^{-5}	
	199.6	0.41	2.15×10^{-4}	5.16
	200.1	0.69	2.53×10^{-4}	6.07
	200.0	1.03	3.00×10^{-4}	7.19
	300.4	0	1.00×10^{-4}	
	300.2	1.54	7.08×10^{-4}	7.08
773	75.0	0	4.72×10^{-6}	
	75.0	0.11	3.40×10^{-5}	7.20
	74.2	0.38	5.40×10^{-5}	11.4
	74.1	0.63	6.60×10^{-5}	14.0
	74.5	2.80	4.60×10^{-4}	97.5

T/K	$[C_2H_4]$/torr	$[1\text{-}C_4H_8]$/torr	Initial rate of formation/torr s^{-1}	$(V_0)_B/(V_0)$
	100.6	0	7.50×10^{-6}	
	100.0	0.07	4.33×10^{-5}	5.77
	101.9	0.17	5.58×10^{-5}	7.44
	100.1	0.42	8.08×10^{-5}	10.8
	100.3	0.85	1.21×10^{-4}	16.1
	99.7	3.75	6.17×10^{-4}	82.2
	205.0	0	6.55×10^{-5}	
	208.6	0.05	1.33×10^{-4}	2.03
	206.3	0.11	1.50×10^{-4}	2.29
	205.8	0.37	1.67×10^{-4}	2.55
	208.9	0.65	2.67×10^{-4}	4.08
	304.0	0	1.00×10^{-4}	
	305.0	0.74	4.67×10^{-4}	4.67
	305.1	1.54	7.00×10^{-4}	7.00
	302.5	2.57	9.42×10^{-4}	9.42
	306.0	11.5	2.10×10^{-3}	21.0

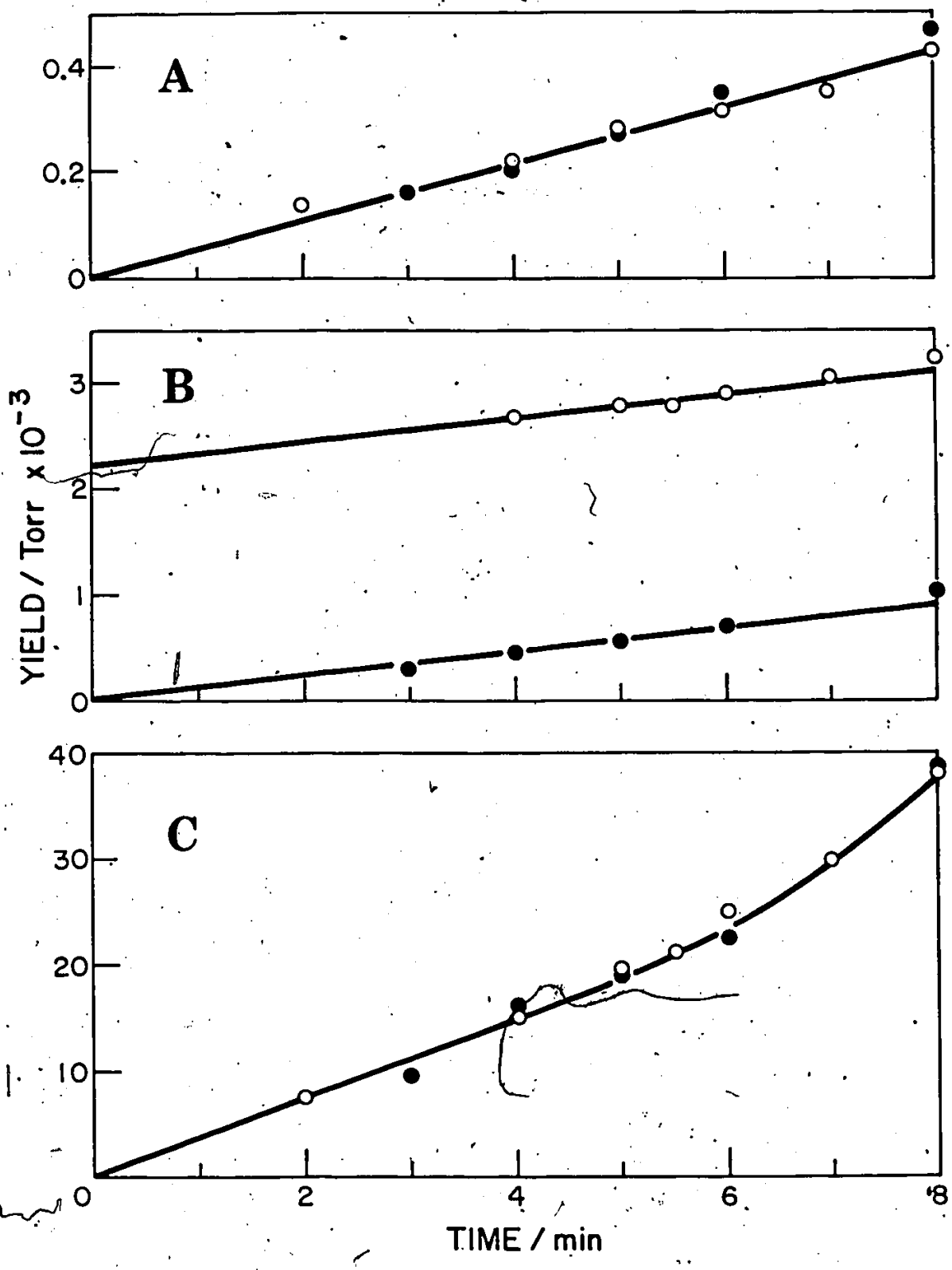
3. Pyrolysis of Purified Ethylene

In the procedure of obtaining the ratio of the initial rates of product formation in the presence and absence of 1-butene, the value of the initial rate from the ethylene pyrolysis alone, V_0, has a great importance. Because the ratio of initial rates, $(V_0)_B/V_0$, is squared in order to obtain the ratio of rate constants k_B/k_1, described later, the result is very sensitive to the measurements of the initial rates of products in the ethylene pyrolysis alone.

The effect of the ethane impurity in ethylene, ranging from 6.0×10^{-4}% to 6.4×10^{-4}%, was tested by pyrolysis experiments with purified ethylene. Figure 6 is an example that shows the yield-time plots for methane, ethane and propylene from the pyrolysis of 300 torr ethylene at 721 K with and without purification. The results of pyrolysis of purified ethylene at 75, 100 and 200 torr pressure at this temperature will be presented in Appendix A. It is clear that there is no difference between the initial rates of product formation from purified and unpurified ethylene reactions, and these results show that the measurements using the Research Grade ethylene are reliable. Because such large amounts of ethylene were needed for the experiments and many weeks would have been required for purification,

Figure 6 - Effect of Purification of Ethylene on the Yield-Time Plots for Methane, Ethane and Propylene, Respectively, at 721 K

● 299.6 torr purified ethylene
○ 299.9 torr unpurified ethylene


A
B
C
0.4
0.2
0
3
2
1
0
40
30
20
10
0
2
4
6
8
YIELD / Torr x 10⁻³
TIME / min

most of the pyrolysis experiments in the presence and absence of 1-butene have been performed without purification of the ethylene.

4. Additions of Propylene and Cis-2-Butene

In order to test whether 1-butene affected the propagation reactions of the ethylene pyrolysis, some experiments have been performed by adding separately propylene and cis-2-butene.

The effect of the additive on the propagation reactions occurs by the generation of the main radical through another set of reactions. A new radical is produced by the reaction of the main radical with the additive and then the abstraction reaction of this new radical with the reactant regenerates the main radical. Hence in such propagation reactions, both the reactant and the additive react with the main radical. In the case where the reaction of the main radical with the additive is faster than the reaction of it with the parent reactant, an acceleration of the rate is observed. If the reactivity of the new radical toward the reactant is less than that of the main radical, inhibition may occur. Examples of each type were given by Niclause et al.[72] in their discussion of the effect of various additives on alkane pyrolyses.

In the pyrolyses of ethylene, the ethyl radical probably has the highest steady-state concentration[20]. When 1-butene is an additive in the system, the reactions of the ethyl radical with 1-butene can be written as:

$$C_2H_5 + 1\text{-}C_4H_8 \rightarrow C_2H_6 + C_4H_7 \quad (15)$$

$$\rightarrow 3\text{-}C_6H_{13} \quad (16)$$

$$\rightarrow \text{3-methyl pentyl} \quad (17)$$

The abstraction reaction (15) gives ethane and butenyl radical. The addition reaction (16) produces 3-hexyl radical but this reaction is expected to reverse easily since the lowest energy path in this case would be the reverse of the addition reaction. Reaction (17) leads to the formation of a branched molecule. Branched products did not appear under the present conditions, and it may be concluded that the only important propagation reaction of 1-butene would be the abstraction reaction (15). The butenyl radical, although not the same isomer as the one formed by addition of vinyl to ethylene[20], will enter the chain propagation steps of the unsaturated radicals and lead to the formation of products more unsaturated than ethylene. Thus, if reaction (15) occurs, some of the ethyl radical will be converted to the butenyl radical. This can affect the rate

of the reaction in two ways. Since the abstraction of a hydrogen atom from 1-butene is easier than the abstraction from ethylene, an acceleration of the rate might be observed. Another possibility is the inhibition of the rate because the butenyl radical is less reactive than the ethyl radical. Because an exact analysis of this system is difficult, in this study, the importance of reaction (15) was tested experimentally by using propylene and cis-2-butene as additives.*

These two compounds were chosen because their effect on the propagation reactions were expected to be similar to that of 1-butene, since each of them has a labile hydrogen atom. On the other hand, as a result of their high bond dissociation energy, the unimolecular dissociation of both propylene and cis-2-butene is much slower than that of 1-butene. Decomposition of propylene may follow the following two reactions[62,63]:

$$C_3H_6 \rightarrow CH_3 + C_2H_3 \qquad (18)$$

$$C_3H_6 \rightarrow C_3H_5 + H \qquad (19)$$

The possibility of bimolecular initiation[64-66]

$$2C_3H_6 \rightarrow C_3H_5 + C_3H_7$$

* In this section, the initial rate of product formation in the presence of additives propylene and cis-2-butene will be referred to as $(V_o)_p$ and $(V_o)_c$, respectively.

may be ruled out under the present experimental conditions, since very small amounts of propylene were used. At high temperatures, reaction (18) is the initiation step whereas, at lower temperatures, dissociation occurs by reaction (19)[67-69]. The initiation step of cis-2-butene thermal reaction is essentially unimolecular[70,71].

$$cis\text{-}2\text{-}C_4H_8 \rightarrow C_4H_7 + H \qquad (20)$$

Bond dissociation energies for the C-H bond in propylene and cis-2-butene are 85 and 95 kcal mol^{-1}, respectively[43]. These values are much higher than the bond dissociation energy[30], 74.5 kcal mol^{-1}, for the split of CH_3 from 1-butene molecule in its initiation step. Therefore, propylene and cis-2-butene were expected not to affect the initiation processes, but might react with the main radical in the system and hence enter into the propagation reactions.

Propylene additions were made at 773 K and at 100 torr ethylene pressure. Five additions were made with the amount of propylene ranging from 0.46 to 4.78%. The initial rates of ethane and the increase in rates in the presence of propylene are shown in Table 6. Very little increase in the rate of formation of methane was observed and it was estimated that $(V_0)_p/(V_o)$ was about 1.5 with 4.78% propylene.

Additions of cis-2-butene in the range 0.16-0.60% were made at temperatures 763 and 725.5 K. Ethane, methane and propylene were measured but again the increase in methane

Table 6

EFFECT OF PROPYLENE ON THE INITIAL RATES OF FORMATION OF ETHANE AT 773 K

(V_0 for 100 torr C_2H_4 = 2.22 x 10^{-6} torr s^{-1})

	Ethane	
%C_3H_6 in C_2H_4	$(V_0)_p$/torr s^{-1}	$(V_0)_p/(V_0)$
0.46	2.5 x 10^{-6}	1.1
0.86	3.4 x 10^{-6}	1.5
1.91	3.7 x 10^{-6}	1.7
2.85	4.0 x 10^{-6}	1.8
4.78	5.8 x 10^{-6}	2.6

was too small for accurate measurement. The results of cis-butene-2 additions are presented in Table 7. As an example, the yield-time plots for the formation of propylene at 763 K are given in Figure 7 including the three pressures studied at this temperature.

It is seen from Tables 6 and 7 that the effect of additions of propylene or cis-2-butene on the initial rates is much less than that of 1-butene. For example, at 763 K with about 0.2% cis-2-butene, the rate of formation of ethane was increased by 58%, whereas with the same ratio of 1-butene under the same conditions, the rate of formation of ethane was increased by a factor of 6.7. Also, at 773 K, the addition of about 0.86% propylene caused only 53% increase in the rate of formation of ethane while this increase was 12.9 times with the same percentage of 1-butene addition,

Table 7

EFFECT OF CIS-2-BUTENE ON THE INITIAL RATES OF FORMATION OF ETHANE AND PROPYLENE

			Ethane			Propylene		
T/K	$[C_2H_4]$/torr	$[2\text{-}C_4H_8]$/%	V_0/torr s^{-1}	$(V_0)_c$/torr s^{-1}	$(V_0)_c/(V_0)$	V_0/torr s^{-1}	$(V_0)_c$/torr s^{-1}	$(V_0)_c/(V_0)$
763	100.0	0.23	1.33×10^{-6}	2.1×10^{-6}	1.6	4.39×10^{-6}	6.6×10^{-6}	1.5
	100.0	0.60	1.33×10^{-6}	2.3×10^{-6}	1.7	4.39×10^{-6}	7.7×10^{-6}	1.7
	200.1	0.23	5.55×10^{-6}	7.9×10^{-6}	1.4	2.70×10^{-5}	3.8×10^{-5}	1.4
	200.1	0.60	5.55×10^{-6}	8.7×10^{-6}	1.6	2.70×10^{-5}	4.6×10^{-5}	1.7
	300.4	0.23	1.39×10^{-5}	1.7×10^{-5}	1.2	1.02×10^{-4}	1.2×10^{-4}	1.2
	300.4	0.60	1.39×10^{-5}	2.2×10^{-5}	1.6	1.02×10^{-4}	1.4×10^{-4}	1.4
725.5	200.2	0.16	3.04×10^{-6}	3.0×10^{-6}	1.0	3.04×10^{-5}	3.3×10^{-5}	1.1
	200.2	0.51	3.04×10^{-6}	3.6×10^{-6}	1.2	3.04×10^{-5}	3.6×10^{-5}	1.2
	200.2	1.00	3.04×10^{-6}	4.6×10^{-6}	1.5	3.04×10^{-5}	4.0×10^{-5}	1.3
	200.2	1.64	3.04×10^{-6}	6.5×10^{-6}	2.1	3.04×10^{-5}	4.5×10^{-5}	1.5

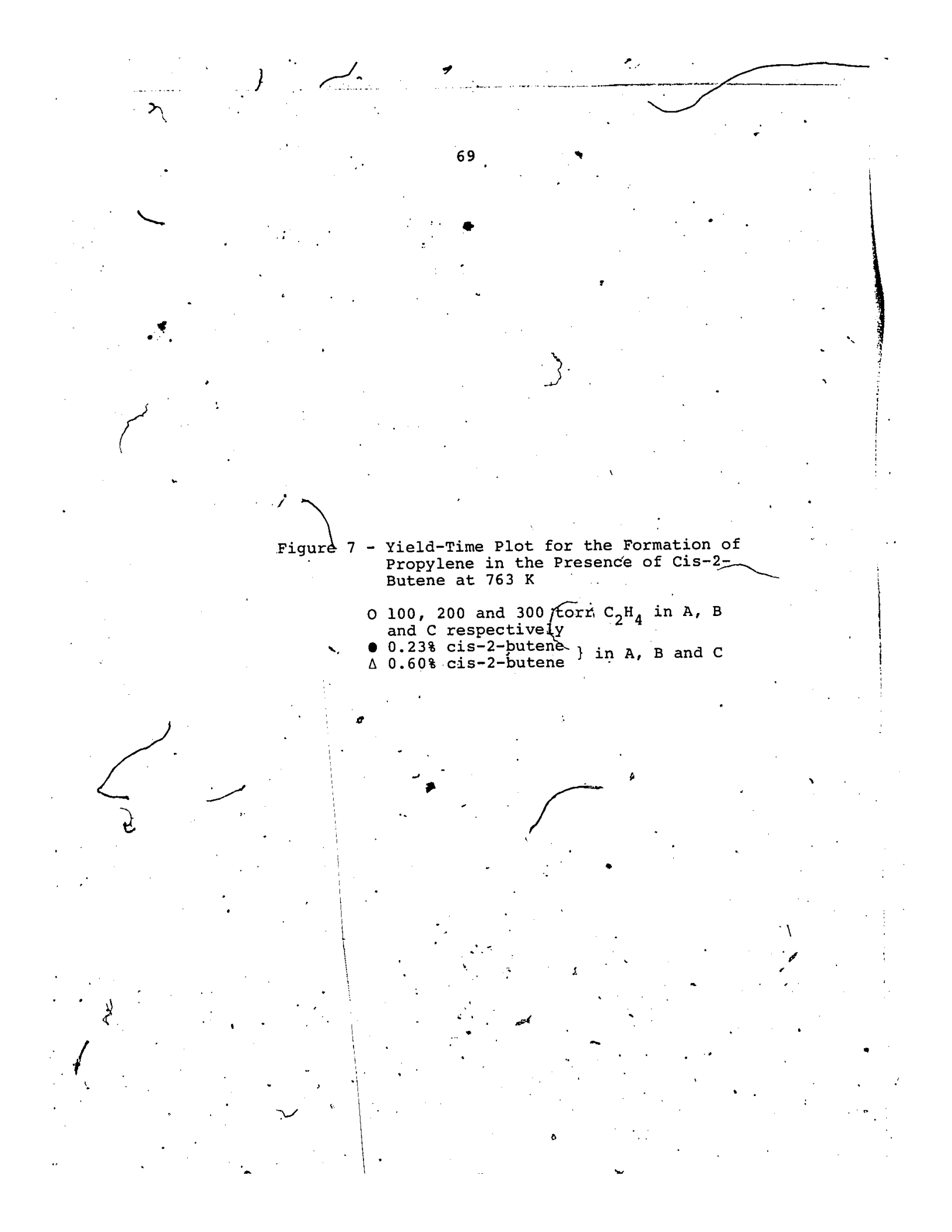
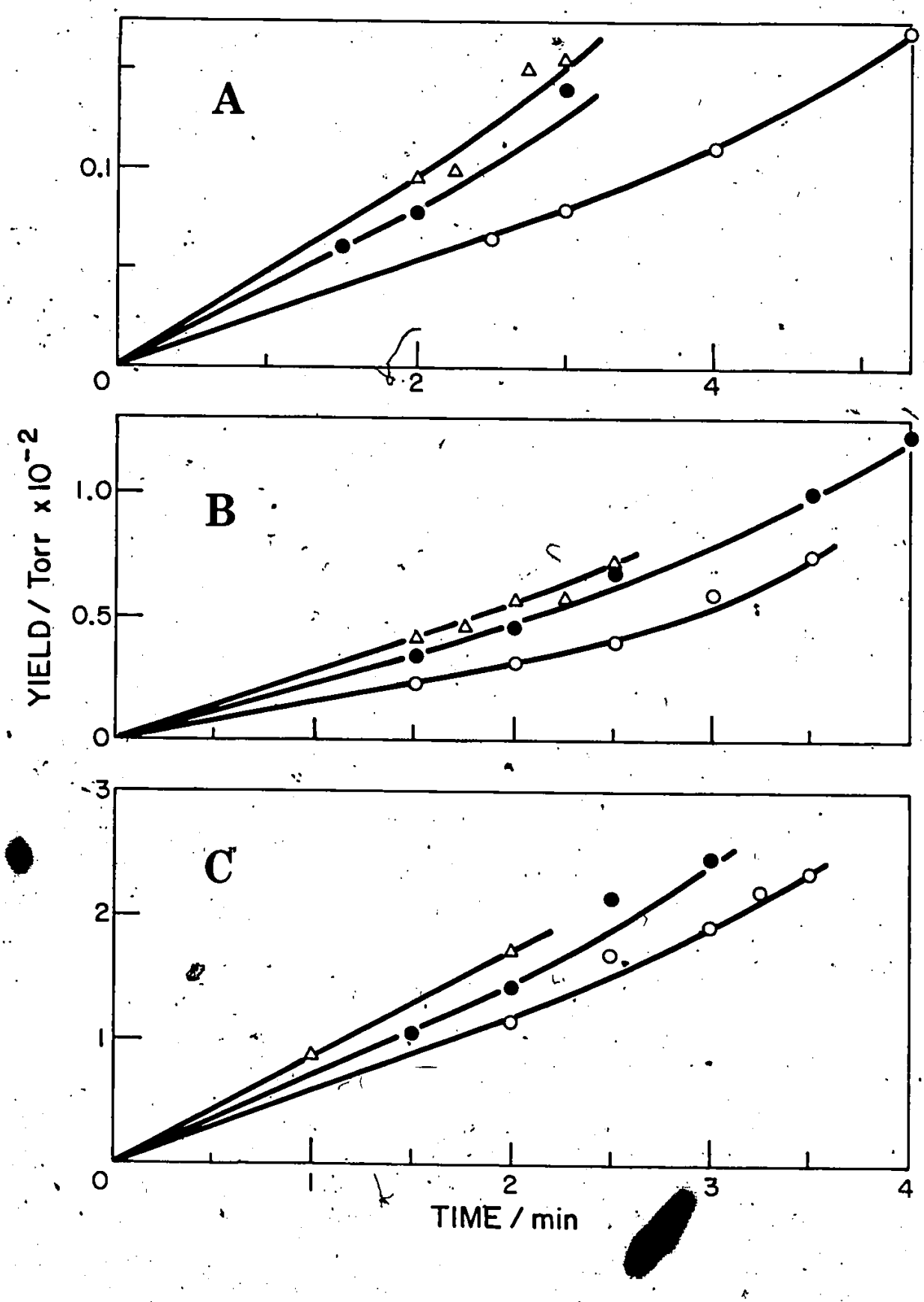


Figure 7 - Yield-Time Plot for the Formation of Propylene in the Presence of Cis-2-Butene at 763 K

O 100, 200 and 300 torr C_2H_4 in A, B and C respectively
● 0.23% cis-2-butene } in A, B and C
Δ 0.60% cis-2-butene


A
B
C
0.1
0
2
4
1.0
0.5
3
2
1
0
1
2
3
4
YIELD / Torr x 10⁻²
TIME / min

again under the same conditions. Therefore, the effects of cis-2-butene and propylene are insignificant compared to the effect of similar additions of 1-butene. It can be estimated that even with mixtures of 0.5% 1-butene, the error introduced into quantity $[(V_0)_B/V_0]^2-1$ by occurrence of reaction (15) will not be more than 1%. Therefore, for the additions of 1-butene up to 0.5%, the effect of 1-butene on propagation reactions can be accepted as negligible and hence, the assumption that 1-butene affects only the initiation processes of the ethylene pyrolysis is justified.

The question of the effect of 1-butene on the propagation processes was also examined by the nature and distribution of the reaction products. The participation of 1-butene in the propagation reactions would be expected to lead to branched hydrocarbon products and these were not observed as mentioned before. The ratios of products are given in Table 8. These results show that addition of 1-butene has almost no effect on the product distribution and provide further evidence that the effect of 1-butene is only the addition of a new initiation process. Therefore, the general equation for the ratio of rates in the presence and absence of 1-butene may be written in the simplified form of equation (14).

Table 8

EFFECT OF 1-BUTENE ON THE DISTRIBUTION OF PRODUCTS

T/K	$[C_2H_4]$/torr	$[1\text{-}C_4H_8]/[C_2H_4]$ (x10^2)	$R_{CH_4}/R_{C_3H_6}$	$R_{C_2H_6}/R_{C_3H_6}$
699	199.9	0	0.015	0.038
	199.5	0.10	0.016	0.041
	200.1	0.26	0.014	0.041
	200.2	0.67	0.015	0.046
	300.7	0	0.0096	0.040
	300.5	0.10	0.0096	0.042
	300.1	0.26	0.011	0.041
	300.1	0.67	0.012	0.038
	400.0	0	0.0060	0.029
	400.0	0.10	0.0080	0.030
	400.1	0.26	0.0072	0.025
	400.0	0.67	0.0070	0.029
721	74.8	0	–	0.075
	74.9	0.10	–	0.095
	74.6	0.22	–	0.091
	74.5	0.55	–	0.11
	100.3	0	0.087	0.083
	100.2	0.10	0.037	0.086
	99.8	0.22	0.088	0.092
	99.8	0.55	0.096	0.12
	200.0	0	0.029	0.055
	200.8	0.10	0.018	0.049
	200.0	0.22	0.029	0.052
	200.0	0.55	0.035	0.068
	299.9	0	0.015	0.031
	301.0	0.10	0.014	0.033
	299.7	0.22	0.019	0.036
	299.7	0.55	0.021	0.044
732	100.0	0	0.066	0.11
	100.7	0.10	0.060	0.11
	100.0	0.35	0.068	0.12
	200.0	0	0.032	0.069
	200.0	0.10	0.030	0.055
	200.0	0.35	0.028	0.066

T/K	$[C_2H_4]$/torr	$[1\text{-}C_4H_8]/[C_2H_4]$ ($\times 10^2$)	$R_{CH_4}/R_{C_3H_6}$	$R_{C_2H_6}/R_{C_3H_6}$
	300.0	0	0.019	0.056
	300.0	0.35	0.019	0.056
748	74.0	0	-	0.06
	74.5	0.09	-	0.22
	73.8	0.41	-	0.21
	74.3	0.73	-	0.23
	99.7	0	0.096	0.15
	99.4	0.09	0.12	0.18
	100.1	0.40	0.09	0.15
	99.8	0.73	0.12	0.18
	199.3	0	0.049	0.095
	199.3	0.09	0.058	0.096
	200.0	0.40	0.052	0.088
	199.0	0.73	0.063	0.11
	299.6	0	0.031	0.074
	300.2	0.09	0.034	0.083
	300.0	0.40	0.036	0.081
	299.2	0.73	0.038	0.085
763	100.0	0	0.14	0.22
	100.3	0.20	-	0.26
	100.2	0.35	0.13	0.25
	100.0	0.51	0.17	0.28
	200.1	0	0.056	0.13
	199.6	0.20	0.057	0.14
	200.1	0.35	0.054	0.16
	200.0	0.52	0.061	0.15
	300.4	0	0.08	0.18
	300.2	0.51	0.06	0.13
773	75.0	0	0.12	0.18
	75.0	0.15	0.12	0.22
	74.2	0.52	0.14	0.25
	74.1	0.85	0.16	0.29
	100.6	0	0.11	0.29
	100.0	0.07	0.11	0.23
	101.9	0.17	0.12	0.27
	100.1	0.42	0.13	0.29
	100.3	0.85	0.10	0.26

T/K	$[C_2H_4]$/torr	$[1\text{-}C_4H_8]/[C_2H_4]$ ($\times 10^2$)	$R_{CH_4}/R_{C_3H_6}$	$R_{C_2H_6}/R_{C_3H_6}$
	205.0	0	0.041	0.12
	208.6	0.02	0.063	0.12
	206.3	0.05	0.077	0.16
	205.8	0.18	0.084	0.19
	208.9	0.31	0.078	0.15
	304.0	0	0.067	0.17
	305.0	0.24	0.066	0.14
	305.1	0.50	0.068	0.15
	302.5	0.85	0.071	0.18
	306.0	3.76	0.095	0.18

5. Kinetics of the Initiation Steps in the Presence of 1-Butene

The initiation processes of the ethylene pyrolysis in the presence of 1-butene will include, besides the bimolecular initiation of ethylene, the unimolecular dissociation and the bimolecular reaction of 1-butene with ethylene.

$$C_2H_4 + C_2H_4 \rightarrow C_2H_5 + C_2H_3 \qquad (1)$$

$$1\text{-}C_4H_8 \rightarrow CH_3 + C_3H_5 \qquad (B)$$

$$1\text{-}C_4H_8 + C_2H_4 \rightarrow C_4H_7 + C_2H_5 \qquad (B')$$

The rates of the processes (B) and (B') are:

$$R_B = k_B[1\text{-}C_4H_8] \text{ and } R_{B'} = k_{B'}[1\text{-}C_4H_8][C_2H_4]$$

where k_B and $k_{B'}$ refer to the rate constants of the processes (B) and (B') respectively.

Case i:

If reactions (1) and (B) are the only important initiation processes, equation (14) becomes:

$$\frac{(V_0)_B}{(V_0)} = \left(1 + \frac{k_B[1\text{-}C_4H_8]}{k_1[C_2H_4]^2}\right)^{1/2} \qquad (21)$$

Case ii:

If only reactions (1) and (B') occur, then

$$\frac{(V_0)_B}{(V_0)} = \left(1 + \frac{k_{B'}[1\text{-}C_4H_8]}{k_1\,[C_2H_4]}\right)^{1/2} \qquad (22)$$

Tests of these equations showed that, under all conditions of temperature and pressure, equation (21) was a more satisfactory representation of the data. Figures 8 and 9 present the results for ethane at 721 K by these two equations. This example shows that, equation (22) gives $k_{B'}/k_1$ values which are dependent on total ethylene pressure, whereas equation (21) gives almost the same value of k_1 at all pressures of ethylene. Since at any temperature, the value of $(V_0)_B/V_0$ should not depend on the total pressure, but only on the ratio of 1-butene to ethylene, equation (21) gives the best interpretation of the mechanism and was used to obtain the experimental value of k_1.

The conclusion that the reaction (B') is unimportant compared to the reaction (B) is also confirmed by the results of propylene and cis-2-butene additions, since the rate of reaction (B') would be expected to be the same with either 1-butene or 2-butene as reactant and similar with propylene as reactant, whereas, as mentioned previously, the unimolecular dissociation of cis-2-butene or propylene is much slower than

Figure 8 - Plot of $[(V_0)_B/V_0]^2-1$ Versus $[1-C_4H_8]/[C_2H_4]^2$ for Ethane at 721 K

X 100 torr C_2H_4

● 200 torr C_2H_4

◇ 300 torr C_2H_4

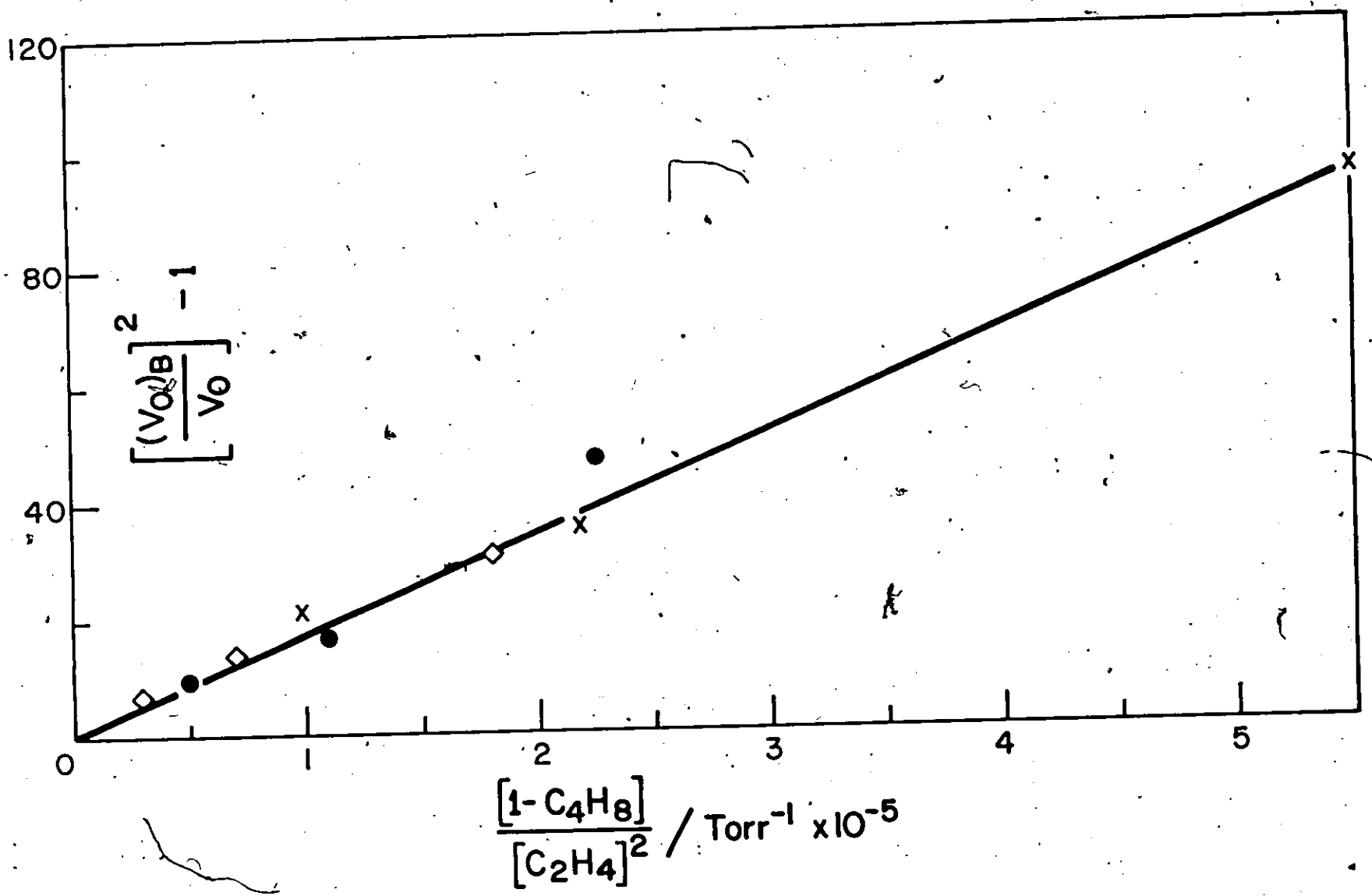
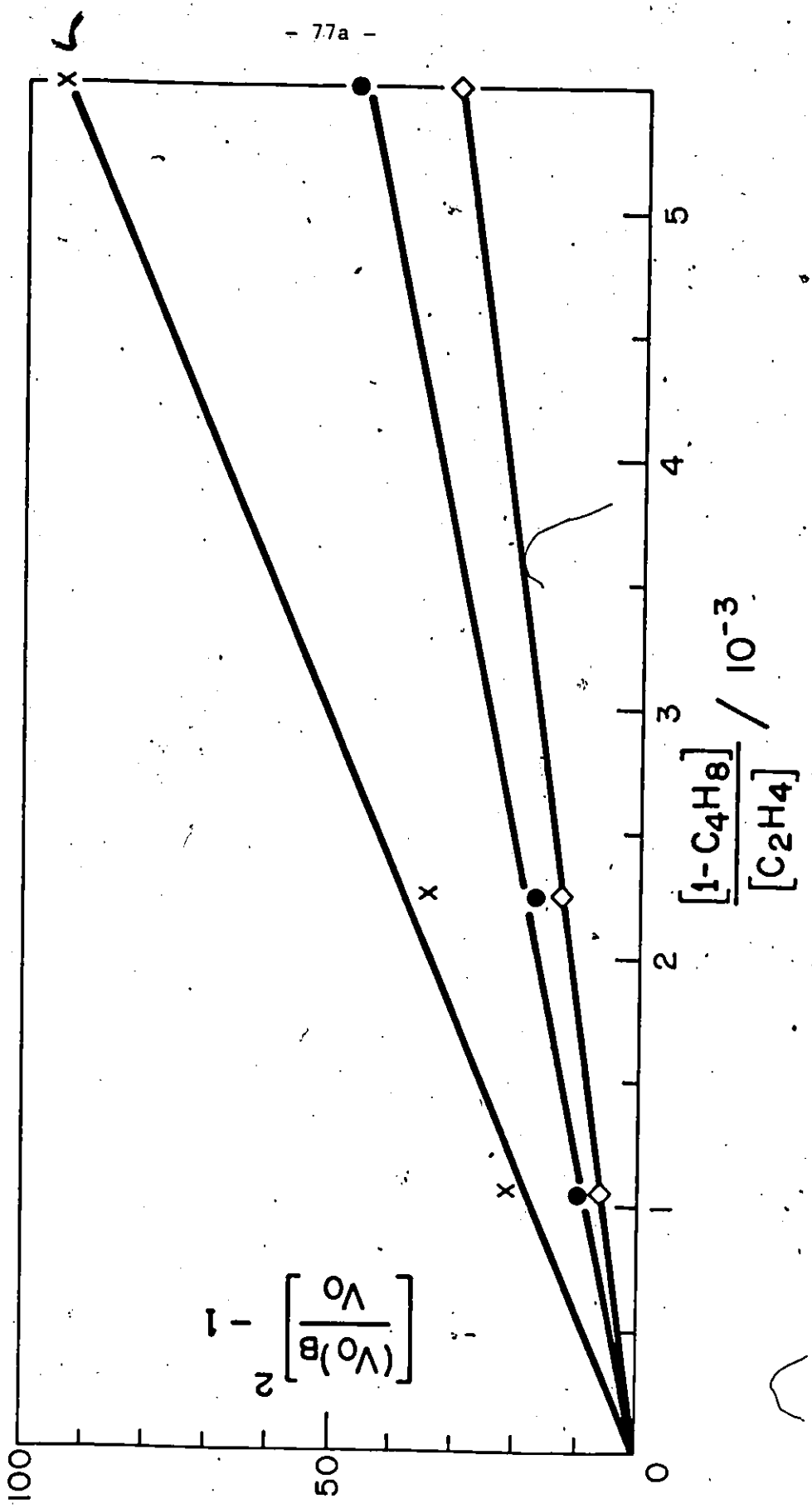

120
80
40
0
1
2
3
4
5
$\left[\frac{(V_0)_B}{V_0}\right]^2 - 1$
$\frac{[1\text{-}C_4H_8]}{[C_2H_4]^2}$ / Torr^{-1} x10^{-5}

Figure 9 - Plot of $[(V_0)_B/V_0]^2-1$ Versus $[1\text{-}C_4H_8]/[C_2H_4]$ for Ethane at 721 K

X 100 torr C_2H_4
● 200 torr C_2H_4
◇ 300 torr C_2H_4


100
50
0
$\left[\frac{(V_0)_B}{V_0}\right]^2 - 1$
0
1
2
3
4
5
$\frac{[1\text{-}C_4H_8]}{[C_2H_4]} / 10^{-3}$

that of 1-butene.

Therefore, the procedure for the interpretation of the kinetic data was first to obtain the initial rates of product formation in the presence and absence of 1-butene, then by using equation (21), to find the ratio of k_B to k_1 at various temperatures and from the Arrhenius plot, to obtain the expression for the ratio of k_B to k_1.

6. Determination of the Initiation Rate Constant, k_1

Figures 10, 11 and 12 show the plots of $[(V_0)_B/V_0]^2-1$ versus $[1\text{-}C_4H_8]/[C_2H_4]^2$ for methane, ethane and propylene. These plots correspond to the yield-time plots given in Figures 3, 4 and 5 for these products including all the other pressures studied at those temperatures.

The slopes of these plots give the ratio of rate constants k_B/k_1. In the following table (Table 9), the values of k_B/k_1 obtained from such graphs are given at each temperature studied. These were calculated by the least squares method.

Table 9

RATIOS OF THE INITIATION RATE CONSTANTS IN THE PRESENCE OF 1-BUTENE

	k_B/k_1/mol L^{-1}		
T/K	Methane	Ethane	Propylene
699	27.67	28.84	27.54
721	35.14	36.31	38.90
732	44.67	47.86	47.32
748	53.89	51.29	47.29
763	52.75	60.26	49.43
773	59.33	58.88	60.26

Figure 10 - Plot of $[(V_0)_B/V_0]^2-1$ Versus $[1\text{-}C_4H_8]/[C_2H_4]^2$ for Methane at 721 K

X 100 torr C_2H_4
▲ 200 torr C_2H_4
◇ 300 torr C_2H_4

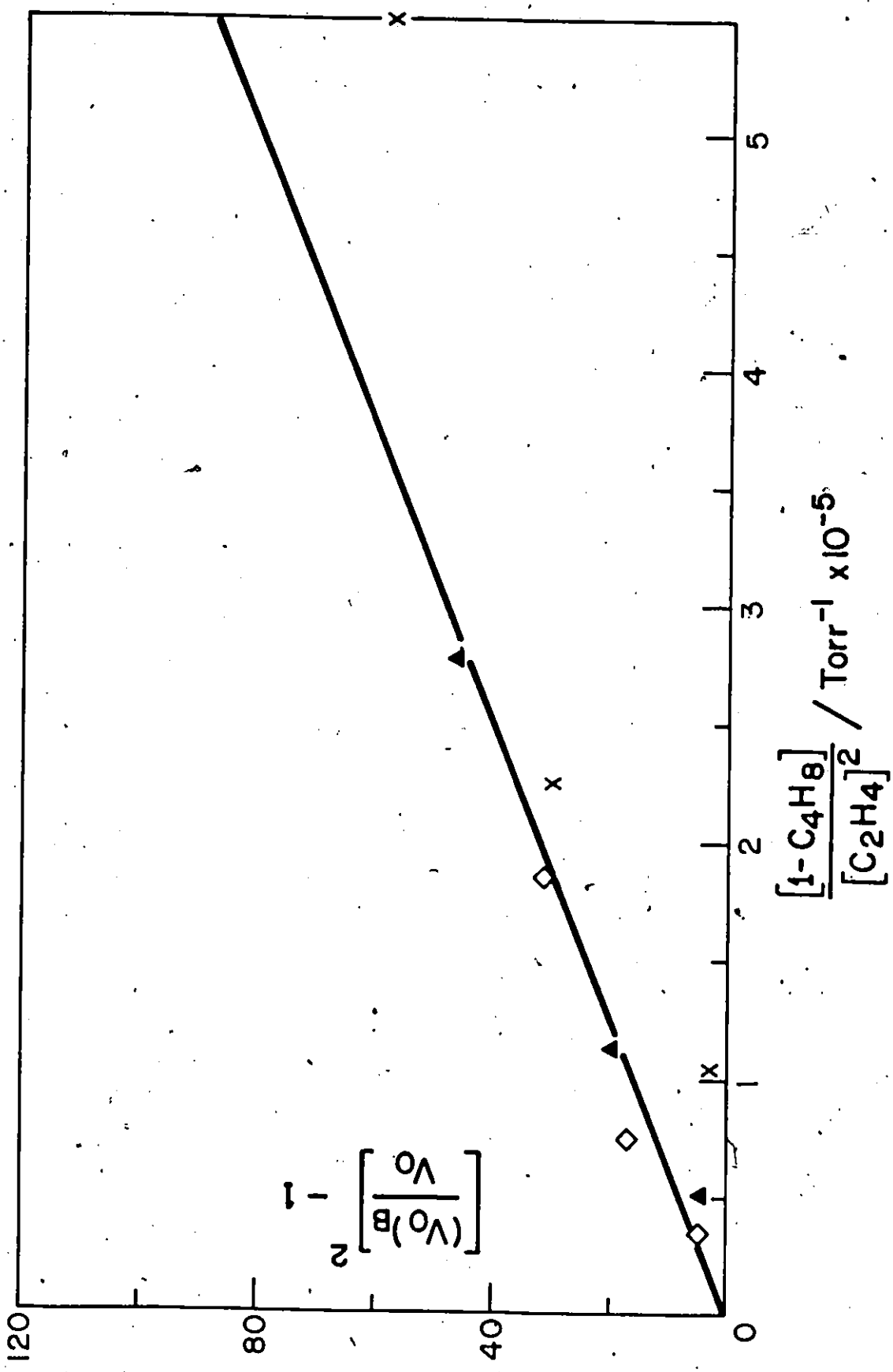

$\left[\frac{(V_O)_B}{V_O}\right]^2 - 1$
0
40
80
120
1
2
3
4
5
$\frac{[1\text{-}C_4H_8]}{[C_2H_4]^2}$ / Torr^{-1} x10^{-5}

Figure 11 - Plot of $[(V_0)_B/V_0]^2-1$ Versus $[1\text{-}C_4H_8]/[C_2H_4]^2$ for Ethane at 748 K

O 75 torr C_2H_4
X 100 torr C_2H_4
● 200 torr C_2H_4
◇ 300 torr C_2H_4
■ 200 torr C_2H_4 in packed vessel

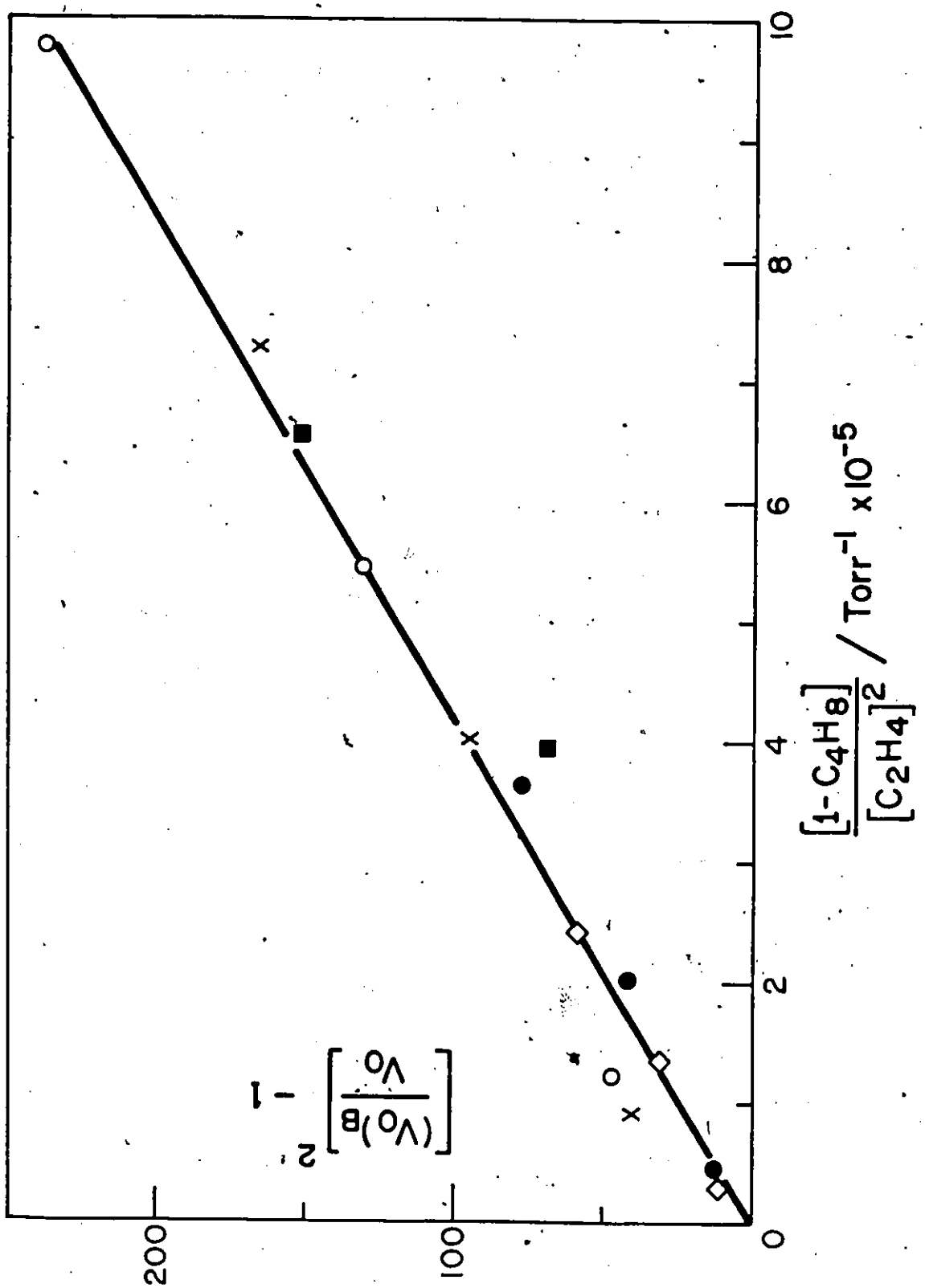
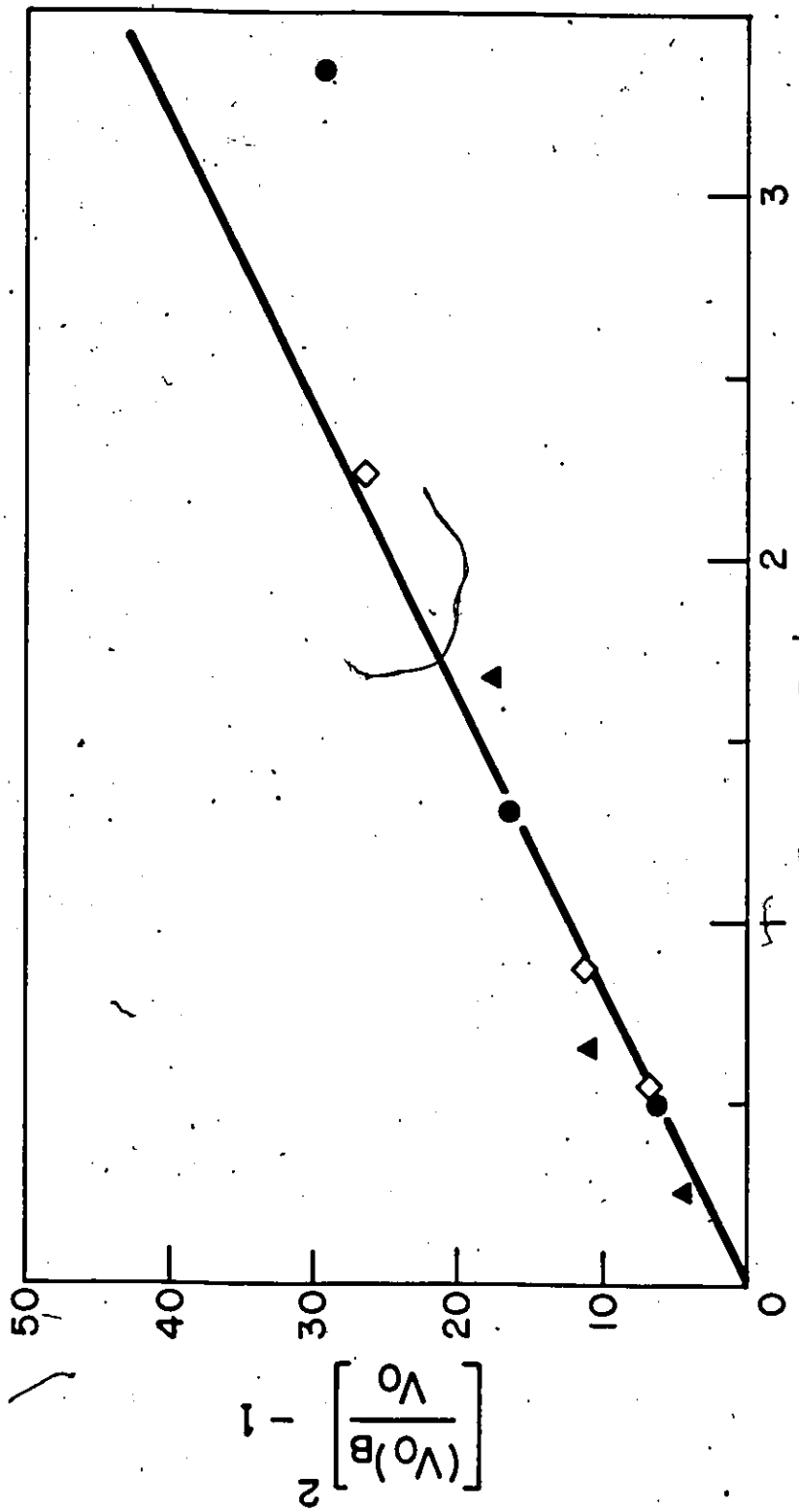

$\left[\frac{(V_0)_B}{V_0}\right]^2 - 1$
200
100
0
0
2
4
6
8
10
$\frac{[1-C_4H_8]}{[C_2H_4]^2}$ / Torr^{-1} x10^{-5}

Figure 12 - Plot of $[(V_0)_B/V_0]^2-1$ Versus $[1\text{-}C_4H_8]/[C_2H_4]^2$ for Propylene at 699 K

● 200 torr C_2H_4

◇ 300 torr C_2H_4

▲ 400 torr C_2H_4


$\left[\frac{(V_0)_B}{V_0}\right]^2 - 1$
0
10
20
30
40
50
1
2
3
4
$\frac{[1\text{-}C_4H_8]}{[C_2H_4]^2}$ / Torr^{-1} x10^{-5}

The Arrhenius plots obtained from these ratios for each product are shown in Figures 13, 14 and 15. From these plots, the following expressions were derived for k_B/k_1 by the least squares method:

$$\text{Log}\,\frac{k_B}{k_1}\,(\text{mol L}^{-1}) = 4.93 - \frac{11100}{2.3RT} \qquad \text{(Methane)} \quad (23)$$

$$\text{Log}\,\frac{k_B}{k_1}\,(\text{mol L}^{-1}) = 4.93 - \frac{11000}{2.3RT} \qquad \text{(Ethane)} \quad (24)$$

$$\text{Log}\,\frac{k_B}{k_1}\,(\text{mol L}^{-1}) = 4.57 - \frac{9900}{2.3RT} \qquad \text{(Propylene)} \quad (25)$$

Assuming the following expression for k_B[61],

$$\text{Log}\,k_B(s^{-1}) = 16 - \frac{74500}{2.3\,RT} \qquad (26)$$

the rate constant of initiation of the ethylene pyrolysis, k_1, can be calculated as:

$$\text{Log}\,k_1(\text{L mol}^{-1}\,s^{-1}) = 11.07 - \frac{63400}{2.3RT} \qquad \text{(Methane)}$$

$$\text{Log}\,k_1(\text{L mol}^{-1}\,s^{-1}) = 11.07 - \frac{63500}{2.3RT} \qquad \text{(Ethane)}$$

$$\text{Log}\,k_1(\text{L mol}^{-1}\,s^{-1}) = 11.43 - \frac{64600}{2.3RT} \qquad \text{(Propylene)}$$

The final values of the Arrhenius parameters of k_1 were obtained by averaging those of the three products.

Figure 13 - Arrhenius Plot for Methane

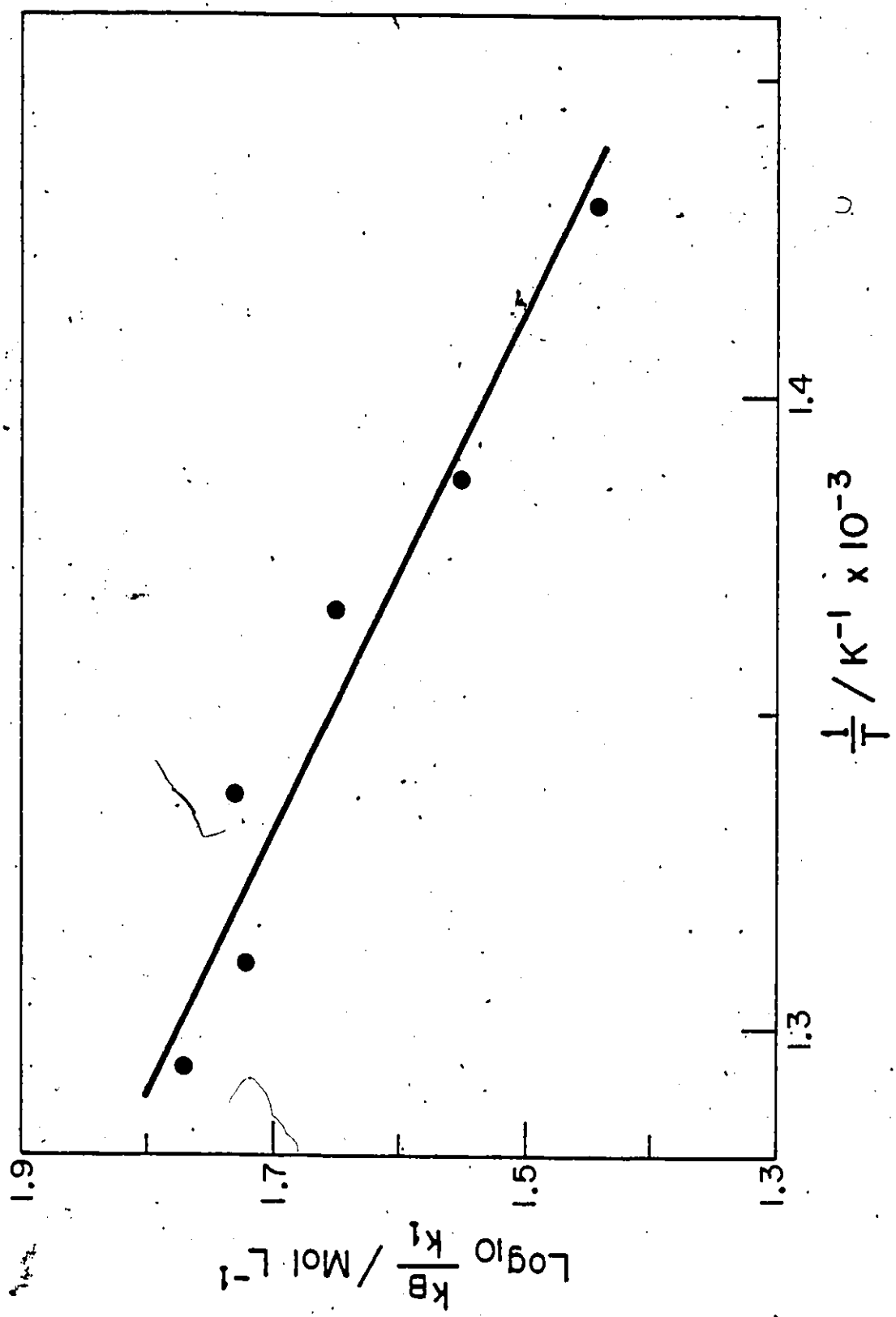
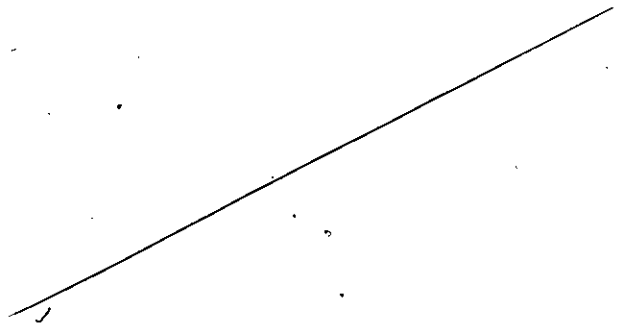

1.9
1.7
1.5
1.3
$\log_{10} \frac{k_B}{k_1}$ / Mol L^{-1}
1.3
1.4
$\frac{1}{T}$ / K^{-1} x 10^{-3}

Figure 14 - Arrhenius Plot for Ethane



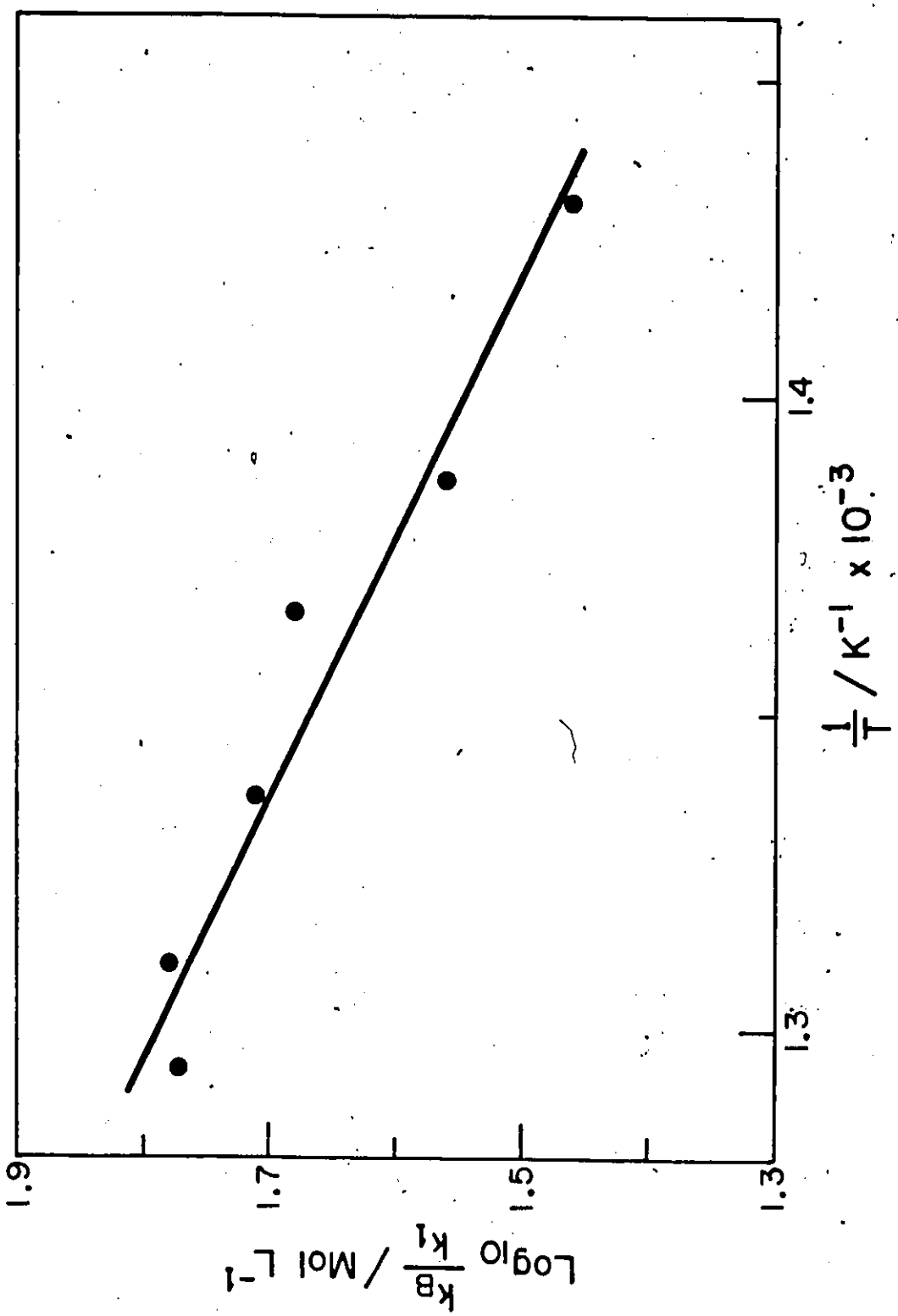
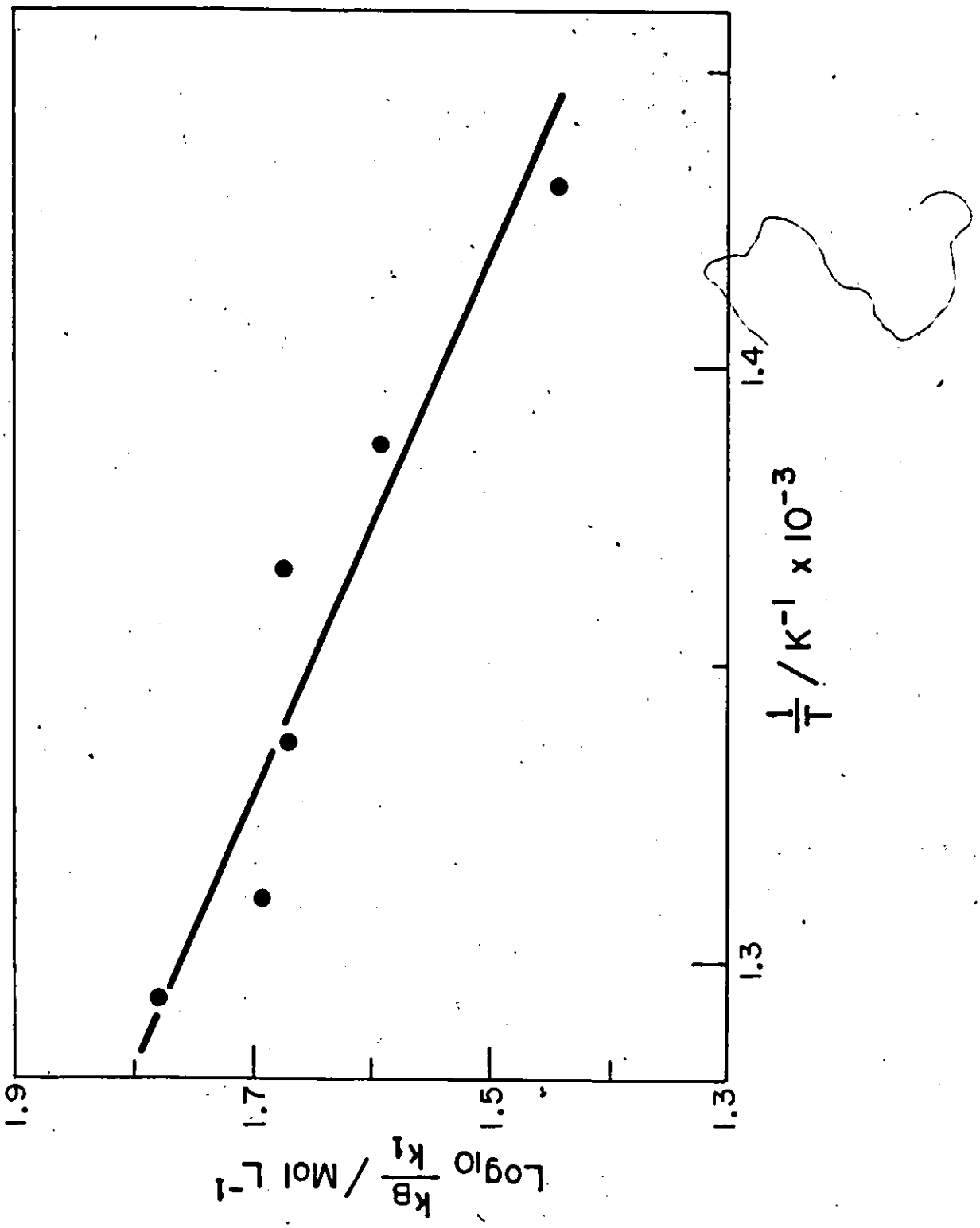

1.9
1.7
1.5
1.3
$\log_{10} \frac{k_B}{k_1}$ / Mol L^{-1}
1.3
1.4
$\frac{1}{T}$ / K^{-1} x 10^{-3}

Figure 15 - Arrhenius Plot for Propylene


$\log_{10} \frac{k_B}{k_1}$ / Mol L^{-1}
1.9
1.7
1.5
1.3
$\frac{1}{T}$ / K^{-1} x 10^{-3}
1.4
1.3

The average rate constant expression is given as follows:

$$\text{Log } k_1 (\text{L mol}^{-1} \text{ s}^{-1}) = 11.19 - \frac{63800}{2.3RT} \qquad (27)$$

This expression for the rate constant of the initiation step of the ethylene pyrolysis will be referred to later in Chapter V for the general discussion of the value of k_1.

7. Reactions in the Packed Vessel

The importance of heterogenous processes in the presence and absence of 1-butene were examined by using a pyrex vessel, packed with pyrex tubes giving a surface-to-volume ratio of 8 cm^{-1}. Products methane and ethane were measured at 749 and 725.5 K at various ethylene and 1-butene pressures. The data from the packed vessel reactions at 749 K are included in Figure 11, the plot of $[(V_0)_B/V_0]^2-1$ versus $[1\text{-}C_4H_8]/[C_2H_4]^2$ for ethane at 748, together with data from the unpacked vessel pyrolyses. In Table 10, the initial rates are presented.

The initial rates of formation of methane and ethane in the packed vessel were very close to those in the unpacked vessel at similar temperatures. These results are in agreement with observations reported earlier[20]. Additions of 1-butene in the packed vessel gave approximately the same increases in the rates as in unpacked vessel. Therefore, it seems that heterogeneous processes are not important in these systems and it was concluded that the reactions in ethylene+1-butene pyrolysis occur homogenously under these conditions.

Table 10

INITIAL RATES OF PRODUCT FORMATION IN THE PACKED VESSEL

T/K	$[C_2H_4]$/torr	$[1\text{-}C_4H_8]$/torr	Initial rate of formation/torr s^{-1}	
			Methane	Ethane
749	200.0	0	1.00×10^{-6}	1.90×10^{-6}
	200.0	1.58	9.50×10^{-6}	1.58×10^{-5}
	200.0	2.62	1.17×10^{-5}	2.34×10^{-5}
725.5	200.0	0	5.75×10^{-7}	1.12×10^{-6}
	200.0	0.39	2.55×10^{-6}	4.40×10^{-6}
	200.0	0.70	2.90×10^{-6}	5.60×10^{-6}
	200.0	1.33	4.00×10^{-6}	7.30×10^{-6}
	300.2	0	1.10×10^{-6}	2.15×10^{-6}
	300.2	1.08	4.65×10^{-6}	8.55×10^{-6}
	300.3	2.16	6.00×10^{-6}	1.25×10^{-5}
	300.0	5.27	1.04×10^{-5}	2.43×10^{-5}

CHAPTER IV

A. ADDITIONS OF NEOPENTANE

The pyrolyses of the mixtures of ethylene and neopentane have been performed in the temperature range 748-819 K. Most of the time, three or four mixtures with constant ethylene pressure and changing neopentane concentrations were studied. At 756 K and 803 K, however, pyrolysis of mixtures were made at two different pressures of ethylene in order to test the order of the initiation process. Methane, ethane, propylene, 1-butene and butadiene were the products analyzed. The concentration of neopentane was in the range 0.3 to 9.5%.

1. Pyrolysis of Neopentane

The pyrolysis of neopentane has been extensively studied over a wide temperature range. These studies include static systems[78-83], flow systems[84-86] and shock-tube experiments[87-89].

The mechanism of the pyrolysis of neopentane is fairly well established. At temperatures in the neighbourhood of 800 K, decomposition occurs by a radical chain mechanism. The early stages of the reaction have been shown to occur by the following processes:

$$\text{neo-}C_5H_{12} \rightarrow CH_3 + (CH_3)_3C \qquad (N)$$

$$(CH_3)_3C \rightarrow (CH_3)_2CCH_2 + H$$

$$H + \text{neo-}C_5H_{12} \rightarrow H_2 + (CH_3)_3CCH_2$$

$$(CH_3)_3CCH_2 \rightarrow (CH_3)_2CCH_2 + CH_3$$

$$CH_3 + \text{neo-}C_5H_{12} \rightarrow CH_4 + (CH_3)_3CCH_2$$

$$2CH_3 \rightarrow C_2H_6$$

The major primary products are methane and isobutene. Small amounts of minor products include hydrogen, ethane, isobutane, ethylene, propylene, propane, 2-methyl-1-butene and 2-methyl-2-butene. The overall order of the decomposition is 3/2 with an overall activation energy 50-58 kcal mol^{-1}. The pyrolysis of neopentane is self-inhibited by the isobutene formed, which is discussed in detail by Baronnet et al.[81]. Surface effects have been investigated by several workers[83,81,86] and no change in the formation of major or minor products was observed when coated surfaces or packed vessels were used. Recently, Pacey and Wimalasena[85,86] have studied the rate of the establishment of the steady state concentration of radicals in neopentane pyrolysis and determined independent rate constants for several

elementary reactions. The value of the initiation rate constant was determined as 1.7×10^{-5} s^{-1} at 823 K.

Available literature data for the frequency factor and activation energy of the rate constant for the initiation process in neopentane pyrolysis are presented in Table 11.

Table 11

ARRHENIUS PARAMETERS OF THE RATE CONSTANT FOR THE INITIATION STEP OF THE NEOPENTANE PYROLYSIS

Log A/s^{-1}	$E/kcal\ mol^{-1}$	Temperature range/K	Reference
16.1	78.2	1070-1240	87
18.1 ± 0.6	85.9 ± 2.2	713- 823	83
16.8	82.0	723- 803	81
17.7 ± 0.3	85.2 ± 1.4	793- 953	84
16.1 ± 1.0	78.9 ± 3.6	756- 845	79
16.5	80.4	1030-1300	88
17.3	80.8	1000	89

Although the reported Arrhenius parameters for this unimolecular bond fission reaction (N) are not always in agreement, the actual values of the rate constant are very close to each other in the temperature range of this study. For example, at 800 K, the value of k_N ranges only in between 2.34×10^{-6} s^{-1} and 3.98×10^{-6} s^{-1} from references 73, 71, 74, 69 and 78. Arrhenius parameters taken from Tsang[87] and Baldwin[89] lead to k_N values slightly out of this range, 5.13×10^{-6} and 1.58×10^{-5} s^{-1}, respectively.

In this study, the rate constant expression for the initiation step of the neopentane pyrolysis was chosen from Baronnet et al.[81] because their experimental conditions seemed very similar to the present ones. The pyrolysis of neopentane has been studied by means of a static apparatus, between 723-803 K. The Arrhenius parameters they have obtained for the initiation rate constant are almost the average of the other values suggested in approximately the same temperatue range. The reported values of the heat of formation of t-butyl radicals cover a wide range[90-96], 6.7 to 12.9 kcal mol^{-1}. There is good agreement between the activation energy suggested by Baronnet et al. for the rate constant of the initiation of neopentane and the currently accepted value of the heat of formation of the t-butyl radicals, 8.4 kcal mol^{-1}. For these reasons, their expression was judged to represent the dissociation rate constant of neopentane the best.

2. Kinetics of the Reactions in the Ethylene+Neopentane System

In the pyrolysis of ethylene containing small amounts of neopentane, it is important to understand whether neopentane has any effect on the propagation reactions. If neopentane enters into the propagation reactions of ethylene, it reacts with the free radicals present in the system.

Thus, the abstraction reactions of the radicals with neopentane would be added to the propagation processes of the ethylene pyrolysis and would be expected to increase the initial rates of formation of saturated products with respect to unsaturated ones. Also, the decomposition of tertiary butyl and neopentyl radicals would lead to the formation of isobutene. Another possible reaction is the addition of the neopentyl radical to ethylene which would lead to branched products containing seven carbon atoms.

In the case where neopentane does not enter into the propagation processes of ethylene, but affects only the initiation steps, then additions of neopentane would increase the initial rates of formation of all products leaving the ratios of products unchanged. Isobutene and other branched hydrocarbons would not be observed because the free radicals produced in the initiation step by the dissociation of neopentane are soon converted to the radicals involved in the chain propagation reactions of ethylene.

Therefore, in order to test whether the neopentane was interfering with the propagation steps of ethylene, the ratios of the initial rates of the products in the ethylene pyrolysis were compared in the absence and presence of neopentane at all concentrations studied. Table 12 presents the ratios of the initial rates of methane, propylene,

Table 12

RATIOS OF THE INITIAL RATES OF PRODUCTS

T/K	$[C_2H_4]$/torr	$[neo\text{-}C_5H_{12}]$/%	$\frac{R_{CH_3}}{R_{C_2H_6}}$	$\frac{R_{C_3H_6}}{R_{C_2H_6}}$	$\frac{R_{1\text{-}C_4H_8}}{R_{C_2H_6}}$	$\frac{R_{C_4H_6}}{R_{C_2H_6}}$
748	201.6	0	0.68	11.3	2.17	
	201.6	0.40	0.66	11.5	2.32	
	201.4	2.10	0.62	10.6	1.94	
756	104.1	0	0.50	4.75		
	104.0	0.31	0.43	4.76		
	103.6	0.67	0.48	5.13		
	104.0	2.10	0.51	5.68		
	104.3	5.54	0.61	5.42		
	302.1	0	0.34	10.2		
	303.0	0.31	0.34	9.07		
	301.9	0.67	0.39	10.9		
	302.0	2.10	0.38	9.54		
	302.0	5.54	0.46	8.57		
766	104.4	0	0.65	3.19		
	103.4	0.40	0.62	3.33		
	103.8	1.70	0.67	3.60		
777	204.0	0	0.35	4.54	1.06	
	204.4	0.54	0.35	4.66	1.00	
	204.7	2.21	0.39	5.17	1.18	
	204.3	4.27	0.53	4.64	0.96	
	204.0	9.45	0.64	3.49	0.74	
803	105.3	0	0.32	1.38	0.83	0.36
	105.5	0.27	0.31	1.72	0.90	0.29
	106.0	0.92	0.36	1.89	0.98	0.47
	106.5	4.27	0.45	1.46	0.71	0.37
	206.2	0	0.41	3.05	0.83	0.38
	205.1	0.27	0.43	3.24	0.97	0.34
	205.5	0.92	0.37	2.63	0.72	0.28
	205.7	4.27	0.46	2.76	0.67	0.32
819	106.5	0	0.39	1.30	0.75	0.48
	106.0	0.92	0.38	1.58	0.79	0.51
	106.0	1.71	0.40	1.52	0.76	0.44
	106.0	2.68	0.46	1.58	0.79	0.53
	106.4	4.71	0.50	1.39	0.63	0.47

1-butene and butadiene with respect to ethane. In the ethylene+neopentane mixtures containing less than about 4% neopentane, there is practically no change in the ratios of these products. For mixtures with more than about 4% neopentane these ratios change and larger increases were observed in the formation of methane and ethane when compared to propylene and 1-butene. This aspect of the results will be discussed in Section 6. With the present analysis system, it was not possible to separate 1-butene and isobutene. But even at the highest concentration of neopentane, no indication of a change was observed in the shape of the 1-butene peak nor were abnormally large amounts of 1-butene measured. It seems likely that isobutene is not an important product. This would be the case if the neopentyl radical reacted largely by addition to ethylene rather than by dissociation. Other branched products were also not observed. The very long analysis time required for the observation of these products was a limitation in their detection. A few analyses were performed to search for these products but none were found. It was concluded that the constant ratios of products was sufficient indication that the sole effect of neopentane up to a concentration of about 4% was the addition of a new initiation step to the chain mechanism of the ethylene pyrolysis.

The ratio of the initial rates of products in the presence and absence of neopentane can hence be obtained by using the equation (14).

Neopentane may increase the rate of initiation by the following reactions:

$$\text{neo-}C_5H_{12} \rightarrow CH_3 + (CH_3)_3C \qquad (N)$$

$$\text{neo-}C_5H_{12} + C_2H_4 \rightarrow C_2H_5 + \text{neo-}C_5H_{11} \qquad (N')$$

Again, two cases should be taken into account:

Case i

When only the reactions (1) and (N) are the important initiation reactions, the ratio of the initial rates is:

$$\frac{(V_0)_N}{V_0} = \left(1 + \frac{k_N[\text{neo-}C_5H_{12}]}{k_1[C_2H_4]^2}\right)^{1/2} \qquad (28)$$

Case ii

when reaction (N') is predominant over reaction (N) thus making the reactions (1) and (N') the only important initiation processes, the ratio becomes

$$\frac{(V_0)_N}{V_0} = \left(1 + \frac{k_{N'}[\text{neo-}C_5H_{12}]}{k_1[C_2H_4]}\right)^{1/2} \qquad (29)$$

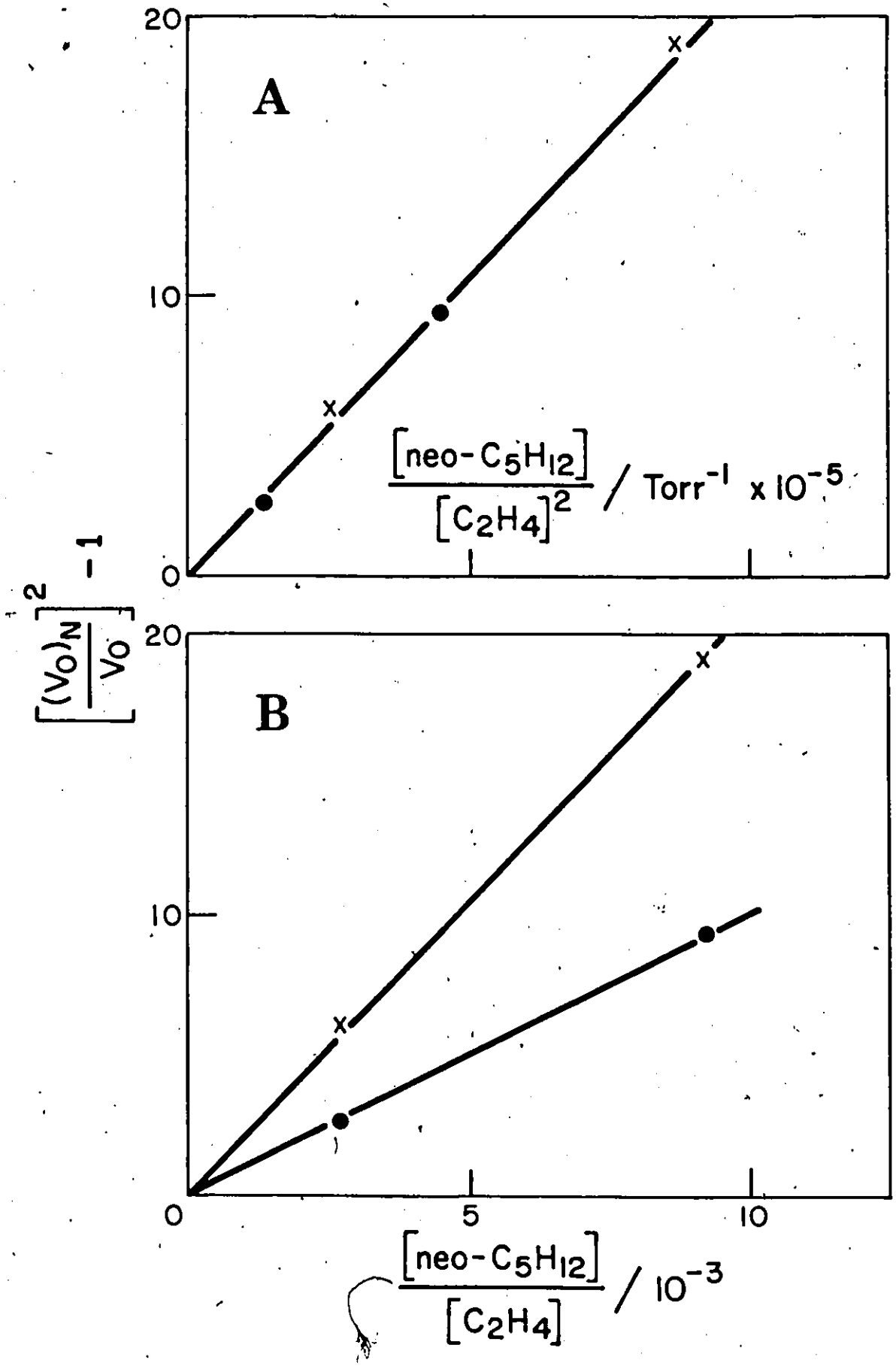
In equations (28) and (29), $(V_0)_N$ refers to the initial rate of formation of a product in the presence of neopentane and k_N and $k_{N'}$ refer to the rate constant for reactions (N) and (N'), respectively.

As an example of the results, plots of these two equations for the product methane at 803 K are given in Figure 16. Equation (29) leads to a pressure-dependent rate constant, whereas equation (28) yields almost the same ratio of rate constants for the two pressures studied. Other products gave similar plots. Therefore, the only important initiation process added by the presence of neopentane is reaction (N) and the kinetic equation for its effect is equation (28).

Effect of surface on the pyrolysis of the mixtures of ethylene and neopentane was not studied in the present work. As discussed in Chapter III.7, no effect on the ethylene pyrolysis alone was observed by changing the surface-to-volume ratio of the reaction vessel. Also, it has been well established that the surface reactions did not occur in the pyrolysis of neopentane[81,83,86]. Therefore, it was assumed that surface reactions are not important in the pyrolyses of mixtures of these two compounds and reactions occur homogeneously. Hence no further studies of this aspect was thought to be necessary.

Figure 16 - Plots of A: $[(V_0)_N/V_0]^2-1$ Versus $[neo\text{-}C_5H_{12}]/[C_2H_4]^2$ and
B: $[(V_0)_N/V_0]^2-1$ Versus $[neo\text{-}C_5H_{12}]/[C_2H_4]$
for methane at 803 K

X 100 torr C_2H_4
● 200 torr C_2H_4


A
B
20
10
0
5
10
x
$\left[\frac{(V_0)_N}{V_0}\right]^2 - 1$
$\frac{[neo\text{-}C_5H_{12}]}{[C_2H_4]^2}$ / Torr^{-1} x 10^{-5}
$\frac{[neo\text{-}C_5H_{12}]}{[C_2H_4]}$ / 10^{-3}

3. Product Formation

In this section, the results obtained from each product will be presented separately. The data from 803 K will be used in examples for all products. The rest of the data from the study of the ethylene+neopentane system will be illustrated in Appendix B.

i) Methane

The yield-time plots at 803 K in the presence and absence of neopentane are given in Figure 17. Due to the improved experimental techniques, scatter in the data was less than that of the ethylene+1-butene studies. The corresponding plot of $[(V_0)_N/V_0]^2-1$ versus $[neo\text{-}C_5H_{12}]/[C_2H_4]^2$ at 803 K is shown in Figure 16. With 4.27% neopentane, the value of $[(V_0)_N/V_0]^2-1$ is abnormally high and is not shown in the graph. This amount of neopentane therefore, not only increases the rate of initiation but also enters into the propagation processes and produces more methane as will be discussed later in this chapter. In Table 13, the initial rates of formation of methane in the presence and absence of neopentane at six temperatures studied are presented. Also shown in this table is the effect of neopentane on the initial rates, as $(V_0)_N/V_0$. These ratios are smaller than the ratios of initial rates

Figure 17 - Yield-Time Plots for Methane at 803 K

A. O 105.3 torr C_2H_4
● 105.5 torr C_2H_4 + 0.27 torr neo-C_5H_{12}
Δ 106.0 torr C_2H_4 + 0.92 torr neo-C_5H_{12}
▲ 106.5 torr C_2H_4 + 4.27 torr neo-C_5H_{12}

B. O 206.2 torr C_2H_4
● 205.1 torr C_2H_4 + 0.27 torr neo-C_5H_{12}
Δ 205.5 torr C_2H_4 + 0.92 torr neo-C_5H_{12}
▲ 205.7 torr C_2H_4 + 4.27 torr neo-C_5H_{12}

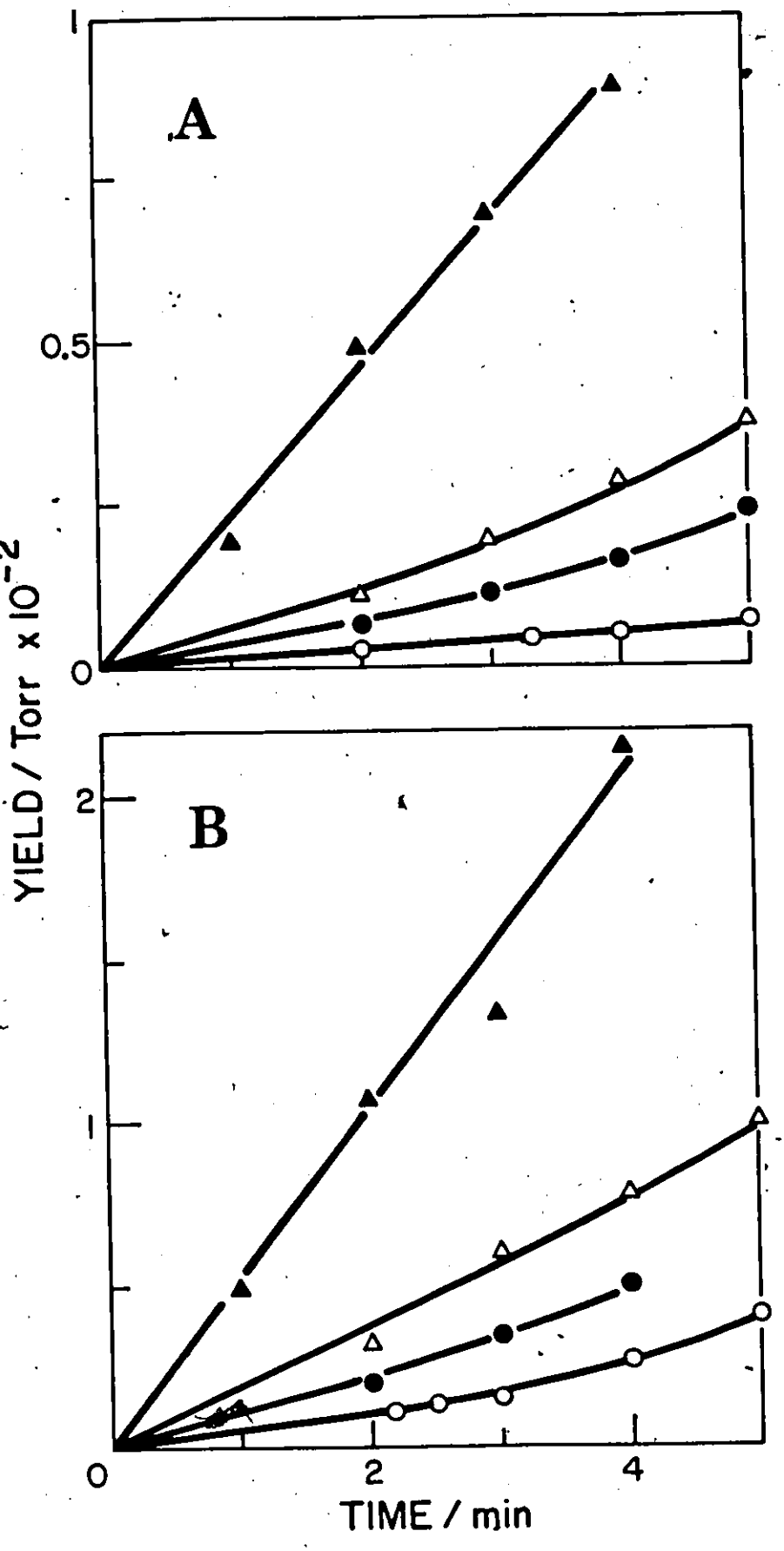

A
B
1
0.5
0
2
1
0
2
4
YIELD / Torr x 10⁻²
TIME / min

Table 13

EFFECT OF NEOPENTANE ON THE INITIAL RATE OF FORMATION OF METHANE

T/K	$[C_2H_4]$/torr	$[C_5H_{12}]$/%	Initial rate of formation/torr s^{-1}	$(V_0)_N/(V_0)$
748	201.6	0	1.31×10^{-6}	
	201.6	0.40	2.27×10^{-6}	1.73
	201.4	2.10	4.40×10^{-6}	3.36
756	104.1	0	4.89×10^{-7}	
	104.0	0.31	1.00×10^{-6}	2.04
	103.6	0.67	1.33×10^{-6}	2.72
	104.0	2.10	2.62×10^{-6}	5.36
	104.3	5.54	5.25×10^{-6}	10.7
	302.12	0	2.92×10^{-6}	
	303.0	0.31	4.44×10^{-6}	1.52
	301.9	0.67	5.83×10^{-6}	2.00
	302.0	2.10	1.00×10^{-5}	3.42
	302.0	5.54	2.00×10^{-5}	6.85
766	104.4	0	6.33×10^{-7}	
	103.4	0.40	1.56×10^{-6}	2.46
	103.8	1.70	3.17×10^{-6}	5.01
777	204.0	0	2.74×10^{-6}	
	204.4	0.54	6.83×10^{-6}	2.49
	204.7	2.21	1.17×10^{-5}	4.27
	204.3	4.27	2.47×10^{-5}	9.01
	204.0	9.45	5.50×10^{-5}	20.1
803	105.3	0	1.92×10^{-6}	
	105.5	0.27	5.08×10^{-6}	2.65
	106.0	0.92	8.58×10^{-6}	4.47
	106.5	4.27	3.08×10^{-5}	16.0
	206.2	0	8.33×10^{-6}	
	205.1	0.27	1.58×10^{-5}	1.90
	205.5	0.92	2.67×10^{-5}	3.21
	205.7	4.27	8.33×10^{-5}	10.0
819	106.5	0	3.65×10^{-6}	
	106.0	0.92	2.00×10^{-5}	5.48
	106.0	1.71	2.63×10^{-5}	7.21
	106.0	2.68	3.50×10^{-5}	9.59
	106.4	4.71	6.33×10^{-5}	17.3

in the presence of 1-butene as expected from the activation energies of these two additives. From the plots of $[(V_0)_N/V_0]^2-1$ versus $[neo\text{-}C_5H_{12}]/[C_2H_4]^2$ at each temperature, the ratios of the rate constants k_N/k_1 were calculated. These are presented in Table 14. In this table, results from other products are also given and will be referred to when necessary.

Table 14

RATIOS OF THE INITIATION RATE CONSTANTS IN THE PRESENCE OF NEOPENTANE

	$\frac{k_N}{k_1}$/mol·L^{-1}			
T/K	Methane	Ethane	Propylene	1-Butene
748	2.12	2.55	2.26	2.05
756	2.71	2.76	2.52	-
766	3.06	2.93	3.75	-
777	3.31	3.22	3.51	2.90
803	4.34	5.15	4.85	4.89
819	6.78	5.44	7.93	6.13

In the calculation of the slopes by the least-squares method, the data after about 4% neopentane additions were not included because very large increases of methane formation by the addition of such pressures of neopentane indicated a change in the mechanism of the ethylene pyrolysis, as mentioned before.

The Arrhenius plot obtained from the measurements of methane is shown in Figure 18. Then, the Arrhenius expression for k_N/k_1 from this graph is obtained by the least squares method:

$$\text{Log}\,\frac{k_N}{k_1}\,(\text{mol L}^{-1}) = 5.42 - \frac{17300}{2.3RT} \qquad (30)$$

ii) Ethane

The initial rates of formation of ethane were obtained by the same procedure described in the case of ethylene+1-butene mixture pyrolysis. The increases in the initial rates of ethane formation by the additions of neopentane more than about 4% were again larger than those of propylene and 1-butene. Figure 19 shows the yield-time plots for ethane formation at 803 K. At this temperature, the ratio k_N/k_1 was calculated from the plot of $[(V_0)_N/V_0]^2-1$ versus $[\text{neo-}C_5H_{12}]/[C_2H_4]^2$ shown in Figure 20.A. The effect of neopentane on the initial rate of formation of ethane is presented in Table 15 at all temperatures. Ratios of initiation rate constants k_N/k_1 and the corresponding Arrhenius plot are given in Table 14 and Figure 21, respectively. Then, the Arrhenius expression obtained for the ratio of rate constants k_N/k_1 is:

$$\text{Log}\,\frac{k_N}{k_1}\,(\text{mol L}^{-1}) = 4.52 - \frac{14200}{2.3RT} \qquad (31)$$

Figure 18 - Arrhenius Plot for Methane

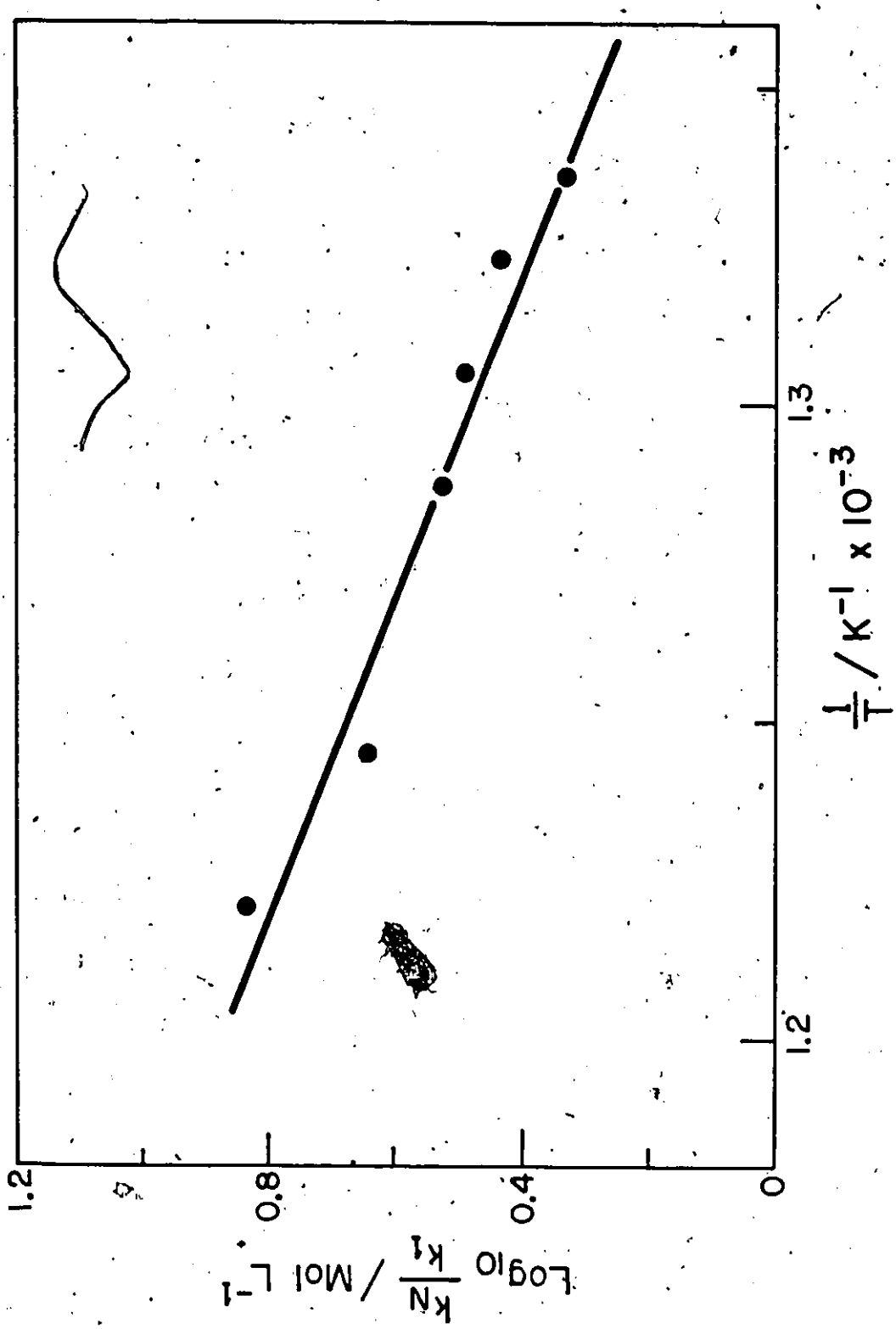
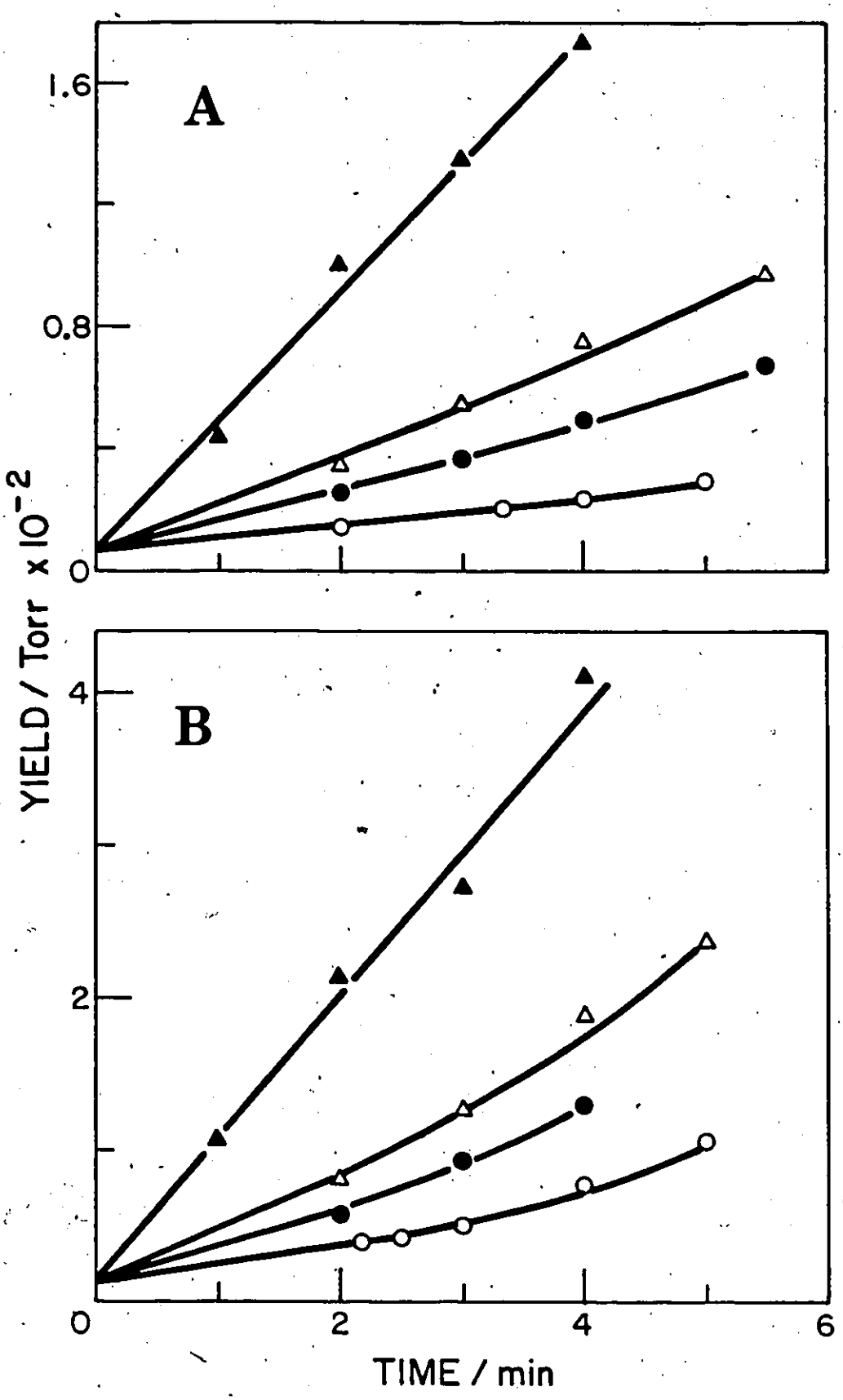

1.2
0.8
0.4
0
$\log_{10} \frac{k_N}{k_1}$ / Mol L^{-1}
1.2
1.3
$\frac{1}{T}$ / K^{-1} x 10^{-3}

Figure 19 - Yield-Time Plots for Ethane at 803 K

A. ○ 105.3 torr C_2H_4
● 105.5 torr C_2H_4 + 0.27 torr neo-C_5H_{12}
△ 106.0 torr C_2H_4 + 0.92 torr neo-C_5H_{12}
▲ 106.5 torr C_2H_4 + 4.27 torr neo-C_5H_{12}

B. ○ 206.2 torr C_2H_4
● 205.1 torr C_2H_4 + 0.27 torr neo-C_5H_{12}
△ 205.5 torr C_2H_4 + 0.92 torr neo-C_5H_{12}
▲ 205.7 torr C_2H_4 + 4.27 torr neo-C_5H_{12}


A
B
1.6
0.8
0
4
2
0
2
4
6
YIELD / Torr x 10⁻²
TIME / min

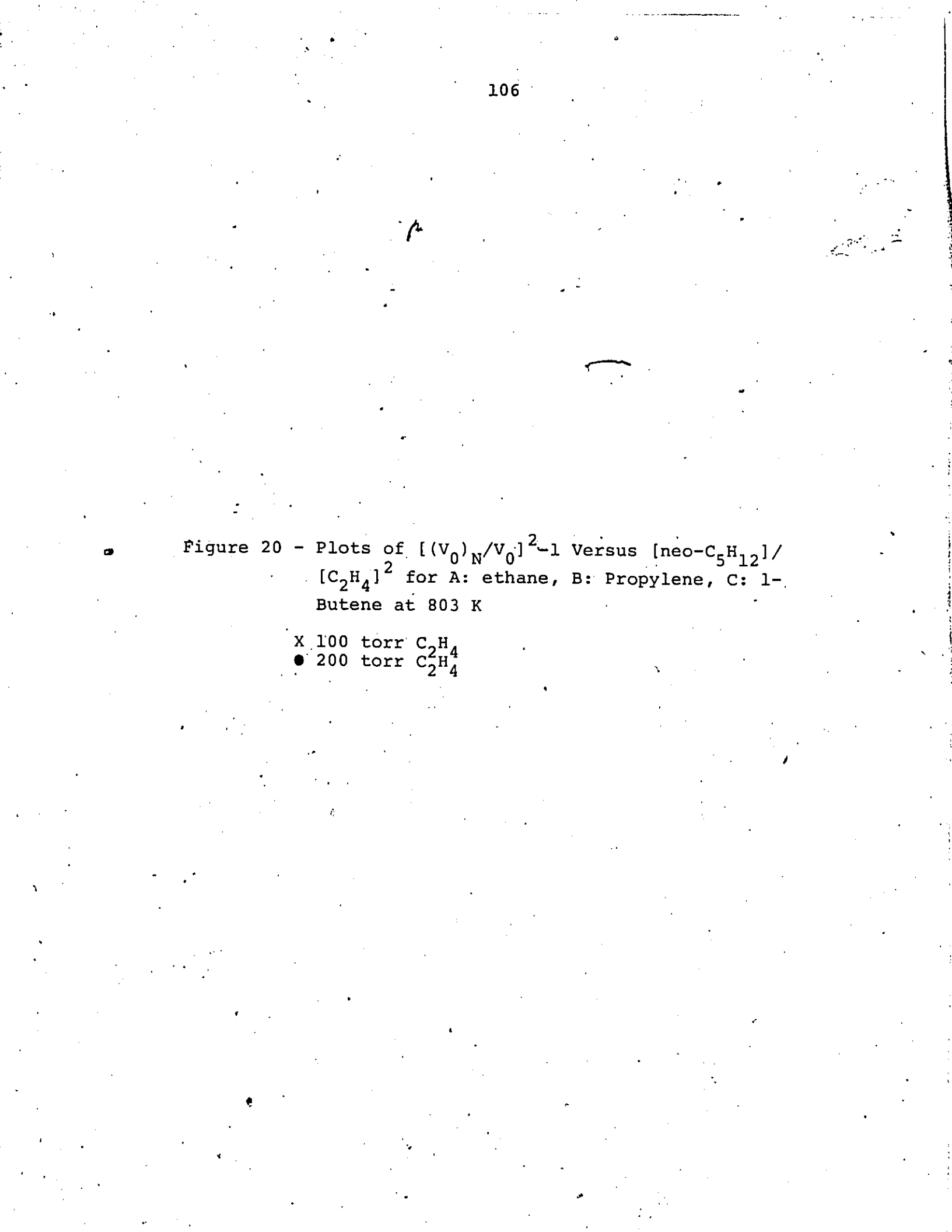


Figure 20 - Plots of $[(V_0)_N/V_0]^2-1$ Versus $[neo\text{-}C_5H_{12}]/[C_2H_4]^2$ for A: ethane, B: Propylene, C: 1-Butene at 803 K

X 100 torr C_2H_4
● 200 torr C_2H_4

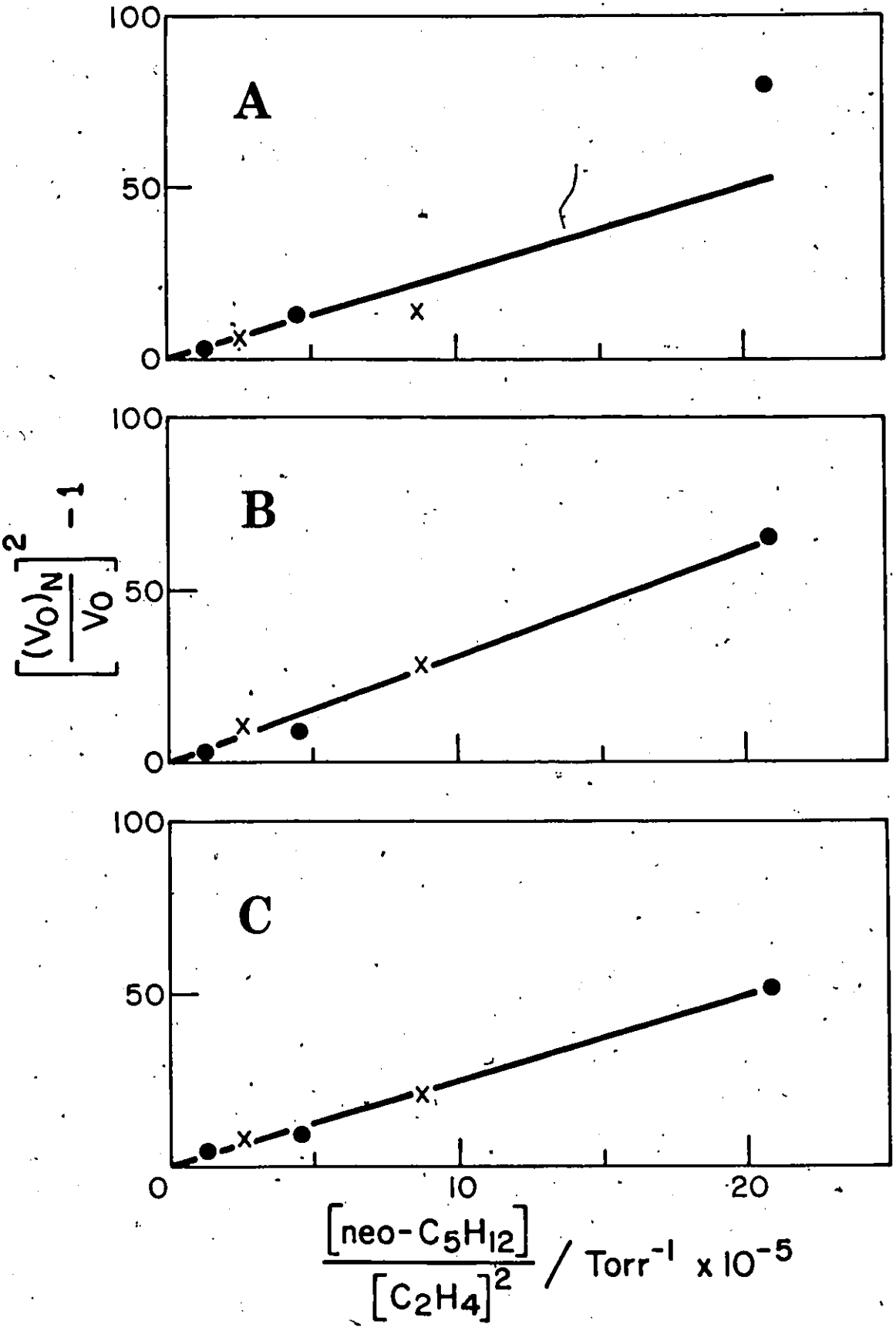
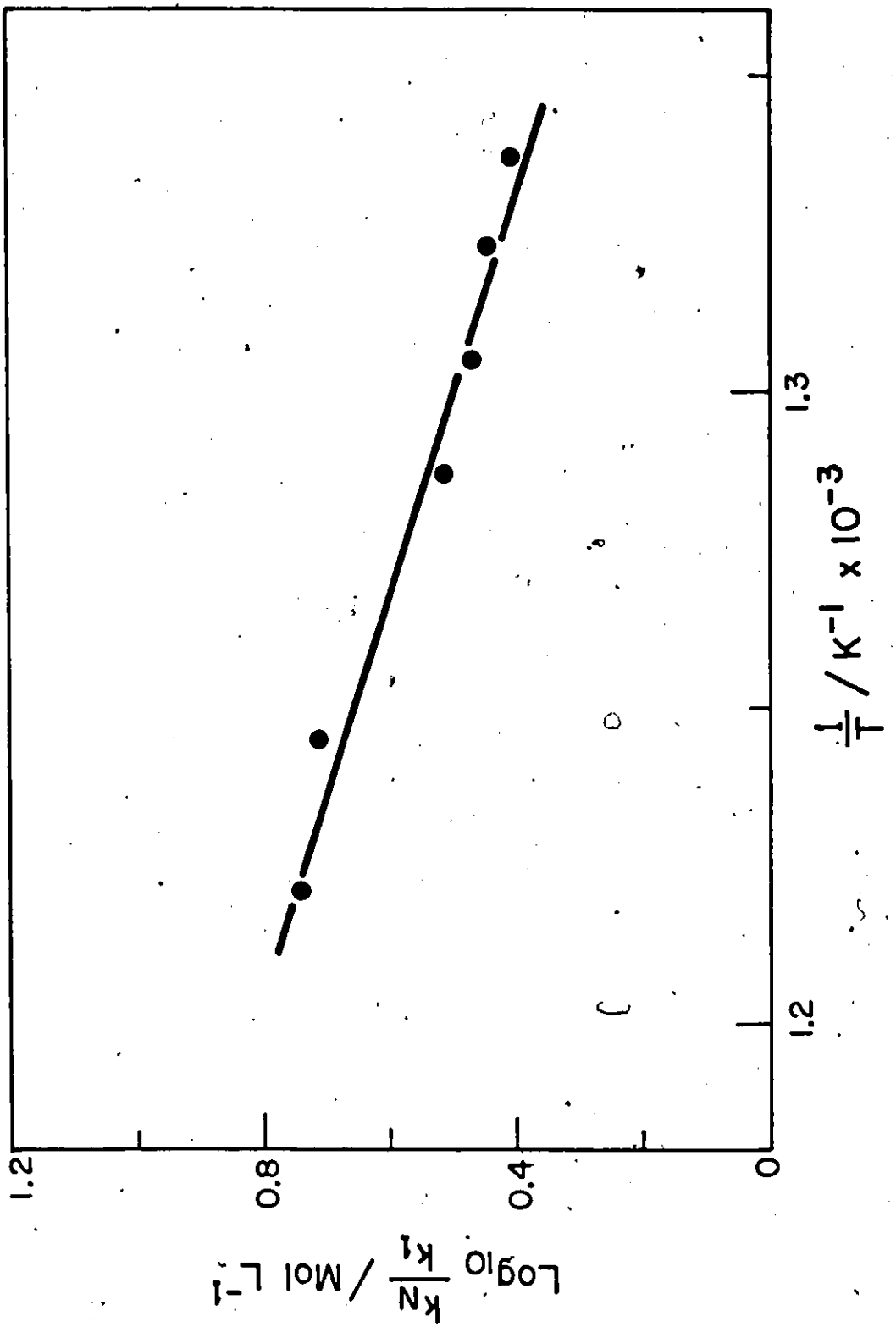

A
B
C
100
50
0
10
20
$\left[\frac{(V_0)_N}{V_0}\right]^2 - 1$
$\frac{[neo\text{-}C_5H_{12}]}{[C_2H_4]^2}$ / $Torr^{-1}$ x 10^{-5}

Table 15

EFFECT OF NEOPENTANE ON THE INITIAL RATES OF FORMATION OF ETHANE

T/K	$[C_2H_4]$/torr	neo-C_5H_{12}]/%	Initial rate of formation/torr s^{-1}	$(V_0)_N/(V_0)$
748	201.6	0	1.92×10^{-6}	
	201.6	0.40	3.42×10^{-6}	1.78
	201.4	2.10	7.06×10^{-6}	3.68
756	104.1	0	9.75×10^{-7}	
	104.0	0.31	2.33×10^{-6}	2.39
	103.6	0.67	2.77×10^{-6}	2.84
	104.0	2.10	5.14×10^{-6}	5.27
	104.3	5.54	8.62×10^{-6}	8.84
	302.1	0	8.51×10^{-6}	
	303.0	0.31	1.29×10^{-5}	1.52
	301.9	0.67	1.50×10^{-5}	1.76
	302.0	2.10	2.62×10^{-5}	3.07
	302.0	5.54	4.33×10^{-5}	5.08
766	104.4	0	9.67×10^{-7}	
	103.4	0.40	2.50×10^{-6}	2.58
	103.8	1.70	4.72×10^{-6}	4.88
777	204.0	0	7.89×10^{-6}	
	204.4	0.54	1.93×10^{-5}	2.45
	204.7	2.21	3.02×10^{-5}	3.83
	204.3	4.27	4.68×10^{-5}	5.93
	204.0	9.45	8.60×10^{-5}	10.9
803	105.3	0	6.05×10^{-6}	
	105.5	0.27	1.63×10^{-5}	2.69
	106.0	0.92	2.38×10^{-5}	3.93
	106.5	4.27	6.85×10^{-5}	11.3
	206.2	0	2.02×10^{-5}	
	205.1	0.27	3.70×10^{-5}	1.83
	205.5	0.92	7.31×10^{-5}	3.62
	205.7	4.27	1.81×10^{-4}	8.96
819	106.5	0	9.33×10^{-6}	
	106.0	0.92	5.27×10^{-5}	5.65
	106.0	1.71	6.60×10^{-5}	7.07
	106.0	2.68	7.60×10^{-5}	8.15
	106.4	4.71	1.26×10^{-4}	13.5

Figure 21 - Arrhenius Plot for Ethane


1.2
0.8
0.4
0
$\log_{10} \frac{k_N}{k_1}$ / Mol L^{-1}
1.2
1.3
$\frac{1}{T}$ / K^{-1} x 10^{-3}

iii) Propylene

Examples for the yield-time plots of propylene are given in Figure 22. Corresponding plot of $[(V_0)_N/V_0]^2-1$ versus $[neo\text{-}C_5H_{12}]/[C_2H_4]^2$ at 803 K including the results of 100 and 200 torr mixture pyrolyses is shown in Figure 20.B. In Table 16, initial rates of formation of propylene are presented in the presence and absence of neopentane. Also, the ratio of rates $(V_0)_N/V_0$ are tabulated at all temperatures and pressures. At high concentrations of neopentane (about 4%), propylene did not show any abnormal increase in its initial rate of formation but in fact its rate was slightly less than expected from the relation expressed as equation (21). The ratios of initiation rate constants k_N/k_1 are calculated from the slopes of the plots such as illustrated in Figure 20.B and given in Table 14. Finally, the frequency factor and activation energy for the ratio of the initiation rate constants are obtained from the Arrhenius plot for propylene, Figure 23, as the following:

$$\text{Log}\frac{k_N}{k_1}\,(\text{mol L}^{-1}) = 6.02 - \frac{19300}{2.3RT} \qquad (32)$$

iv) 1-Butene

The product 1-butene was measured at all temperatures studied except at 756 and 766 K. At these temperatures only

Figure 22 - Yield-Time Plots for Propylene at 803 K

A. O 105.3 torr C_2H_4
● 105.5 torr C_2H_4 + 0.27 torr neo-C_5H_{12}
Δ 106.0 torr C_2H_4 + 0.92 torr neo-C_5H_{12}
▲ 106.5 torr C_2H_4 + 4.27 torr neo-C_5H_{12}

O 206.2 torr C_2H_4
● 205.1 torr C_2H_4 + 0.27 torr neo-C_5H_{12}
Δ 205.5 torr C_2H_4 + 0.92 torr neo-C_5H_{12}
▲ 205.7 torr C_2H_4 + 4.27 torr neo-C_5H_{12}

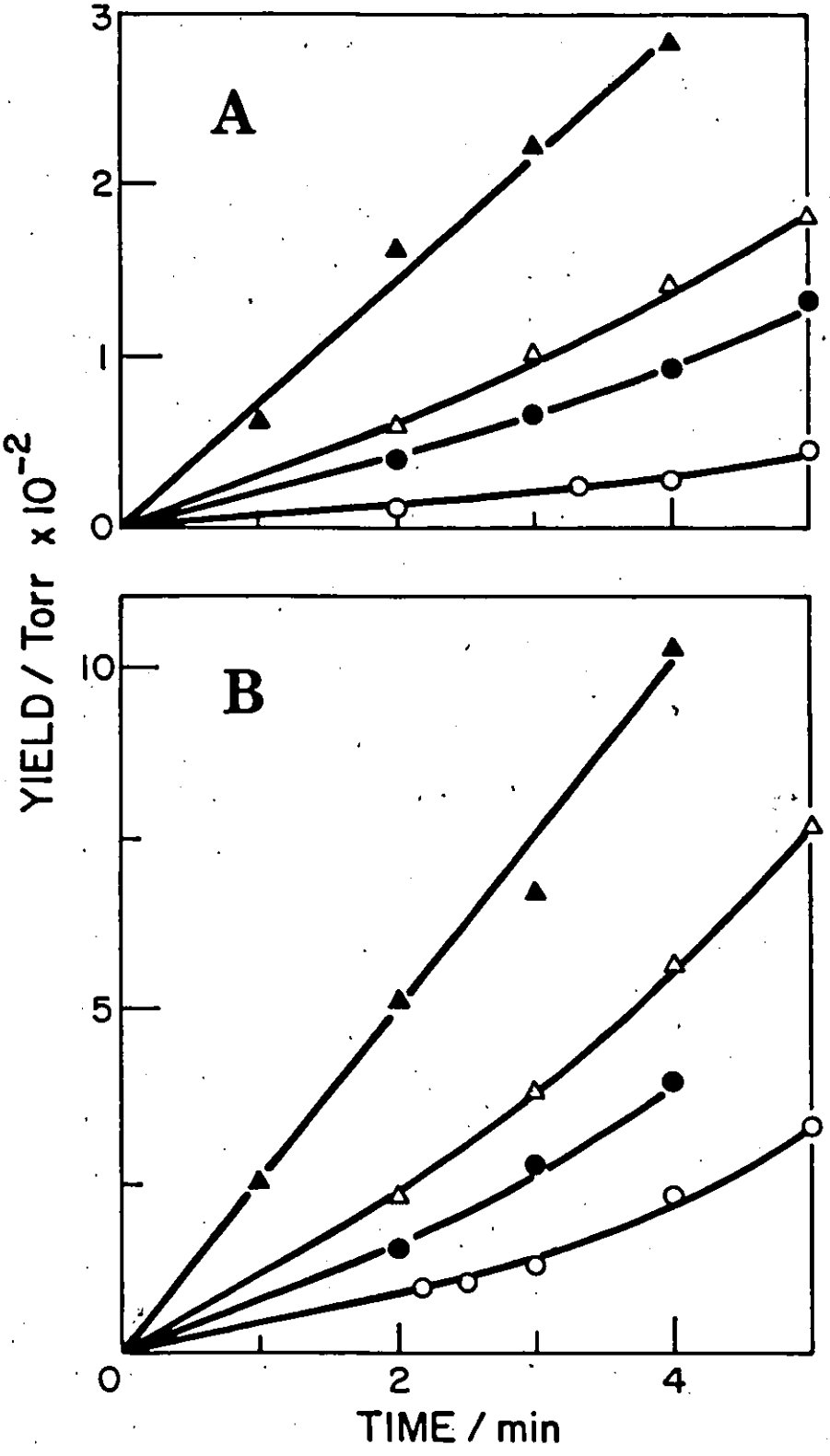
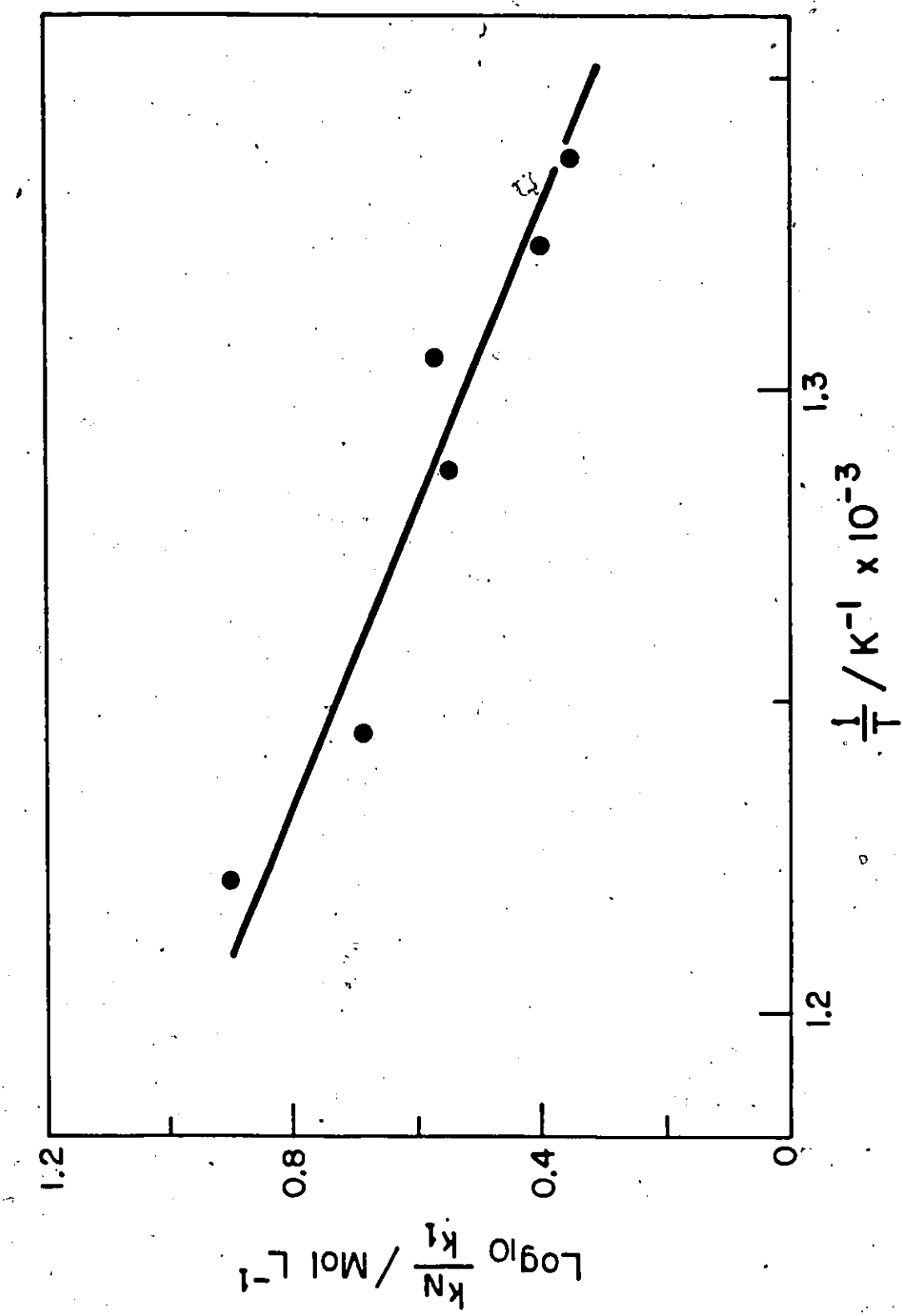

A
B
YIELD / Torr x 10^{-2}
TIME / min
0
1
2
3
5
10
0
2
4

Table 16

EFFECT OF NEOPENTANE ON THE INITIAL RATES OF FORMATION OF PROPYLENE

T/K	$[C_2H_4]$/torr	$[neo\text{-}C_5H_{12}]$/%	Initial rate of formation/torr s^{-1}	$(V_0)_N/(V_0)$
748	201.6	0	2.17×10^{-5}	
	201.6	0.40	3.92×10^{-5}	1.81
	201.4	2.10	7.50×10^{-5}	3.46
756	104.1	0	4.63×10^{-6}	
	104.0	0.31	1.11×10^{-5}	2.40
	103.6	0.67	1.42×10^{-5}	3.07
	104.0	2.10	2.92×10^{-5}	6.31
	104.3	5.54	4.67×10^{-5}	10.1
	302.1	0	8.71×10^{-5}	
	303.0	0.31	1.17×10^{-4}	1.34
	301.9	0.67	1.63×10^{-4}	1.87
	302.0	2.10	2.50×10^{-4}	2.87
	302.0	5.54	3.71×10^{-4}	4.26
766	104.4	0	3.08×10^{-6}	
	103.4	0.40	8.33×10^{-6}	2.70
	103.8	1.70	1.70×10^{-5}	5.52
777	204.0	0	3.58×10^{-5}	
	204.4	0.54	9.00×10^{-5}	2.51
	204.7	2.21	1.56×10^{-4}	4.36
	204.3	4.27	2.17×10^{-4}	6.06
	204.0	9.45	3.00×10^{-4}	8.38
803	105.3	0	8.33×10^{-6}	
	105.5	0.27	2.80×10^{-5}	3.36
	106.0	0.92	4.50×10^{-5}	5.40
	106.5	4.27	1.00×10^{-4}	12.0
	206.2	0	6.17×10^{-5}	
	205.1	0.27	1.20×10^{-4}	1.94
	205.5	0.92	1.92×10^{-4}	3.11
	205.7	4.27	5.00×10^{-4}	8.10
819	106.5	0	1.21×10^{-5}	
	106.0	0.92	8.33×10^{-5}	6.88
	106.0	1.71	1.00×10^{-4}	8.26
	106.0	2.68	1.20×10^{-4}	9.92
	106.4	4.71	1.75×10^{-4}	14.5

Figure 23 - Arrhenius Plot for Propylene


1.2
0.8
0.4
0
$\log_{10} \frac{k_N}{k_1}$ / Mol L^{-1}
1.2
1.3
$\frac{1}{T}$ / K^{-1} x 10^{-3}

methane, ethane and propylene were measured. Examples for the yield-time plots and the corresponding plot of $[(V_0)_N/V_0]^2-1$ versus $[neo\text{-}C_5H_{12}]/[C_2H_4]^2$ at 803 K are shown in Figures 24 and 20.C, respectively. At this high temperature, occurrence of the secondary reactions in the ethylene pyrolysis makes the determination of the initial rates of products rather difficult. However, yield-time plots given in Appendix B show that, at lower temperatures than this, much better identification of the initial rates is possible for all products. Experimental initial rate data are given in Table 17. The increases observed in the initial rates of 1-butene formation in the presence of neopentane are comparable to other products. In mixtures containing more than 4% neopentane, 1-butene gave similar results to that of propylene. The ratios of k_N/k_1 at four temperatures are presented in Table 14. The Arrhenius plot of this data is given in Figure 25. Then, the expression for k_N/k_1 is calculated as:

$$\text{Log}\ \frac{k_N}{k_1}\ (\text{mol}\ L^{-1}) = 5.90 - \frac{19200}{2.3RT} \qquad (33)$$

v) Butadiene

The product butadiene was measured at the two highest temperatures, 803 and 819 K. At other temperatures the data was too scattered for a good measurement of the initial

Figure 24 - Yield-Time Plots for 1-Butene at 803 K

A. ○ 105.3 torr C_2H_4
● 105.5 torr C_2H_4 + 0.27 torr neo-C_5H_{12}
Δ 106.0 torr C_2H_4 + 0.92 torr neo-C_5H_{12}
▲ 106.5 torr C_2H_4 + 4.27 torr neo-C_5H_{12}

B. ○ 206.2 torr C_2H_4
● 205.1 torr C_2H_4 + 0.27 torr neo-C_5H_{12}
Δ 205.5 torr C_2H_4 + 0.92 torr neo-C_5H_{12}
▲ 205.7 torr C_2H_4 + 4.27 torr neo-C_5H_{12}

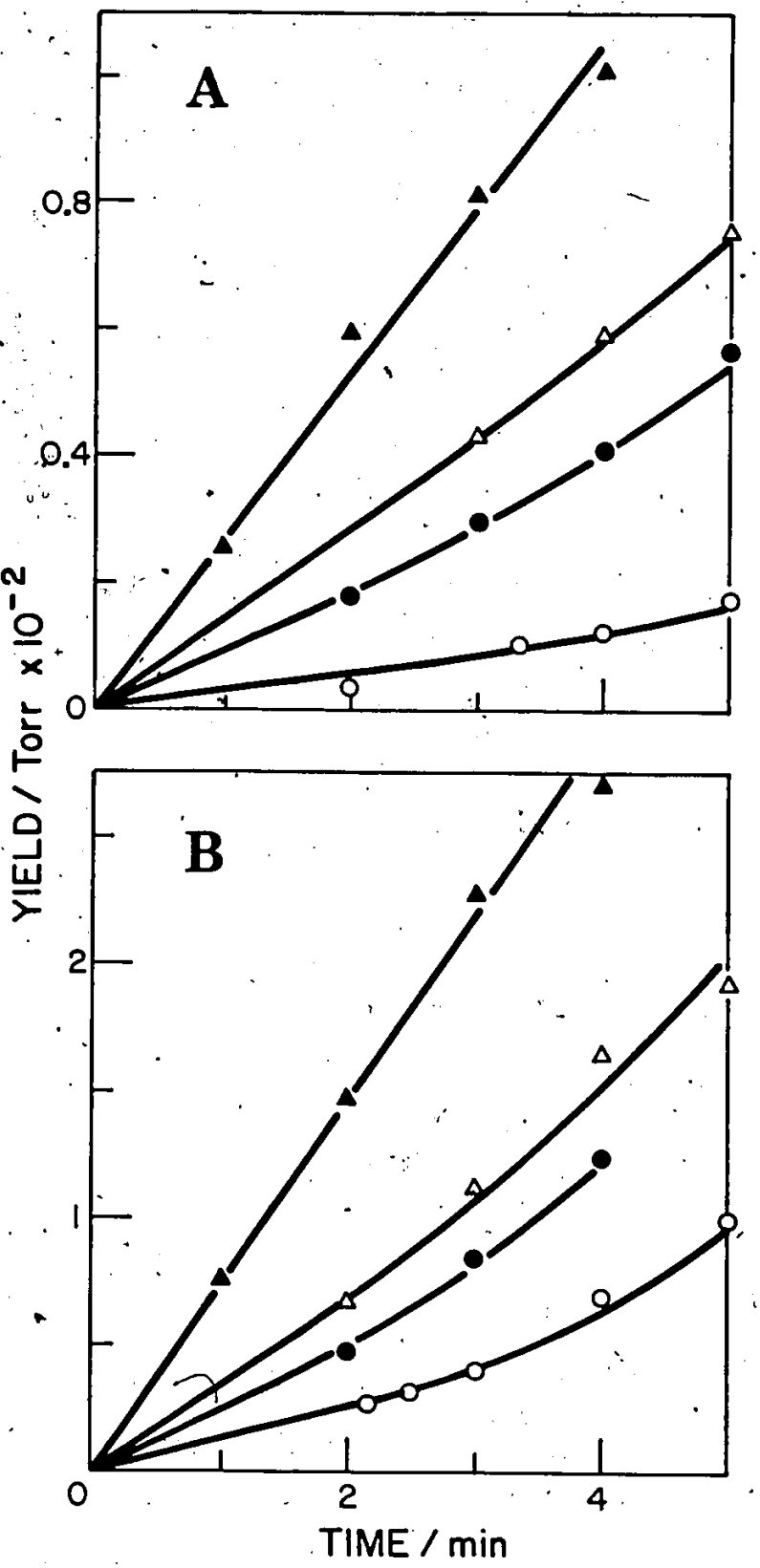
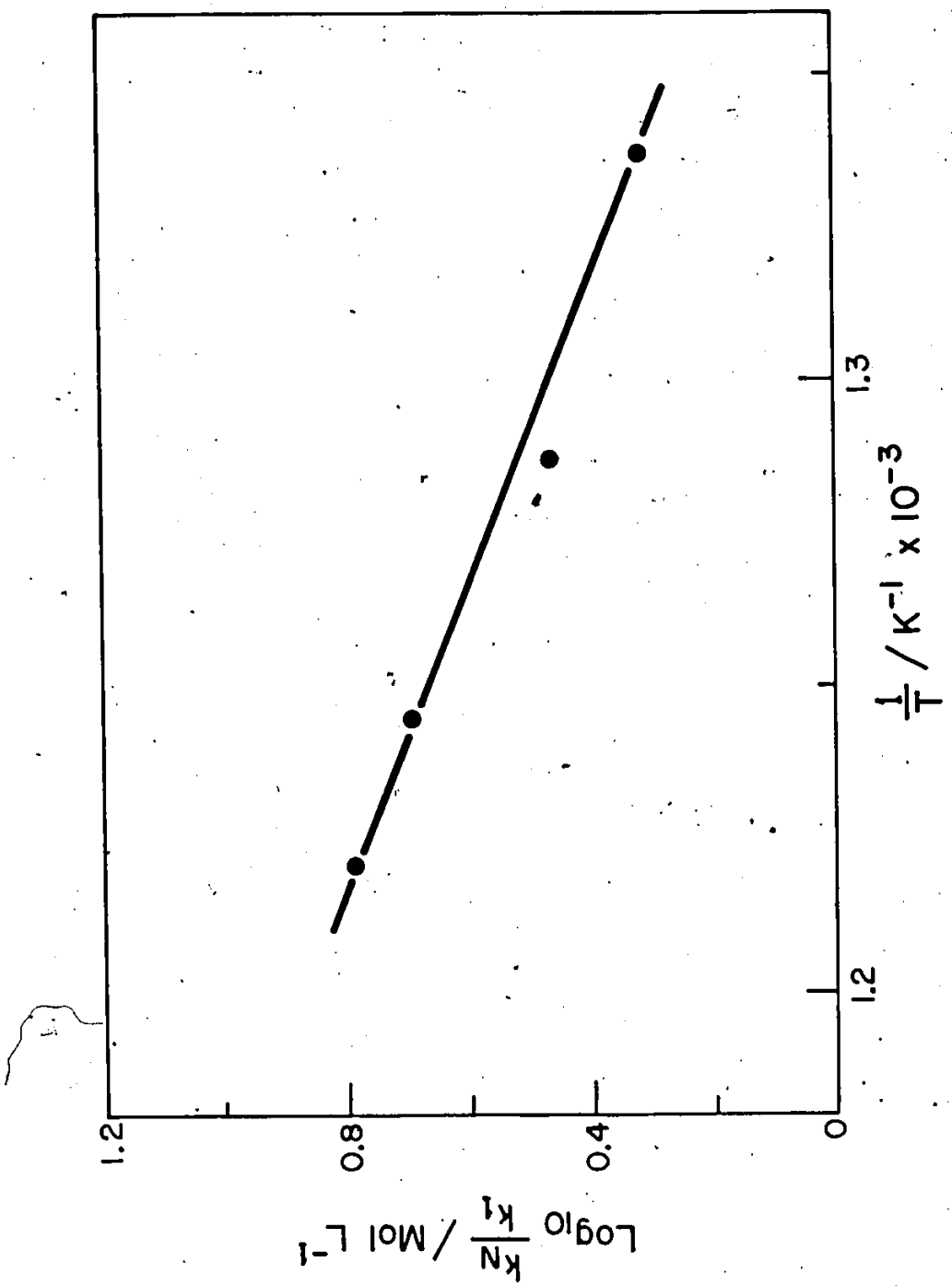

A
B
0.8
0.4
0
2
1
0
2
4
YIELD / Torr x 10⁻²
TIME / min

Table 17

EFFECT OF NEOPENTANE ON THE INITIAL RATES OF FORMATION OF 1-BUTENE

T/K	$[C_2H_4]$/torr	$[neo\text{-}C_5H_{12}]$/%	Initial rate of formation/torr s^{-1}	$(V_0)_N/(V_0)$
748	201.6	0	4.16×10^{-6}	
	201.6	0.40	7.94×10^{-6}	1.91
	201.4	2.10	1.37×10^{-5}	3.29
777	204.0	0	8.33×10^{-6}	
	204.4	0.54	1.94×10^{-5}	2.32
	204.7	2.21	3.56×10^{-5}	4.27
	204.3	4.27	4.50×10^{-5}	5.40
	204.0	9.25	6.35×10^{-5}	7.62
803	105.3	0	5.00×10^{-6}	
	105.5	0.27	1.47×10^{-5}	2.94
	106.0	0.92	2.34×10^{-5}	4.68
	106.5	4.27	4.83×10^{-5}	9.66
	206.2	0	1.67×10^{-5}	
	205.1	0.27	3.58×10^{-5}	2.14
	205.5	0.92	5.25×10^{-5}	3.14
	205.7	4.27	1.21×10^{-4}	7.25
819	106.5	0	7.00×10^{-6}	
	106.0	0.92	4.17×10^{-5}	5.96
	106.0	1.71	5.00×10^{-5}	7.14
	106.0	2.68	6.00×10^{-5}	8.57
	106.4	4.71	8.00×10^{-5}	11.4

Figure 25 - Arrhenius Plot for 1-Butene


1.2
0.8
0.4
0
$\log_{10} \frac{k_N}{k_1}$ / Mol L^{-1}
1.2
1.3
$\frac{1}{T}$ / K^{-1} x 10^{-3}

rate. The values of initial rates in the presence and absence of neopentane are given in Table 18. Yield-time plots at 803 and 819 K are presented in Appendix B. From this data, the ratios of the initiation rate constants k_N/k_1 are calculated as below:

T/K	$\frac{k_N}{k_1}$/mol L^{-1}
803	4.93
819	5.87

These two ratios are not enough to obtain an expression for k_N/k_1 by the use of an Arrhenius plot, but they are comparable to the results obtained from other products at 803 and 819 K.

Table 18

EFFECT OF NEOPENTANE ON THE INITIAL RATES OF FORMATION OF BUTADIENE

T/K	$[C_2H_4]$/torr	$[neo\text{-}C_5H_{12}]$/%	Initial rate of formation/torr s^{-1}	$(V_0)_N/(V_0)$
803	105.3	0	2.17×10^{-6}	
	105.5	0.27	4.75×10^{-6}	2.19
	106.0	0.92	1.11×10^{-5}	5.12
	106.5	4.27	2.55×10^{-5}	11.8
	206.2	0	7.66×10^{-6}	
	205.1	0.27	1.25×10^{-5}	1.63
	205.5	0.92	2.05×10^{-5}	2.68
	205.7	4.27	5.83×10^{-5}	7.61
819	106.5	0	4.50×10^{-6}	
	106.0	0.92	2.67×10^{-5}	5.93
	106.0	1.71	2.92×10^{-5}	6.49
	106.0	2.68	4.00×10^{-5}	8.89
	106.4	4.71	5.92×10^{-5}	13.2

4. Pyrolysis of Purified Ethylene

Purified ethylene pyrolyses were performed at three temperatures, 748, 766 and 793 K. At 748 K, the ethylene pressure was 200 torr while at 766 and 793 K, 100 torr ethylene was studied. Also, a mixture containing 1% neopentane was prepared using purified ethylene and its pyrolysis was examined at these temperatures. Products methane, ethane, propylene and 1-butene were analyzed. The initial rates of formation of these products from pyrolyses of the purified ethylene in the presence and absence of neopentane are presented in Table 19. These results may be compared with results of pyrolyses of the unpurified ethylene at 766 and 748 K. Pyrolysis of the unpurified ethylene was not studied at 793 K.

At 748 and 766 K, the purification of ethylene caused almost no change in the initial rates of formation of these products. This result is illustrated in the yield-time plots of methane, ethane and propylene in Figure 26. The yields of methane and propylene are the same within experimental error at each reaction time. The difference in the yields of ethane corresponds to the presence of the ethane impurity. Also shown in Figure 26 is the effect of 1% neopentane addition on the initial rate of formation of products. Because it gives only one value for ratios of the initial rates, the best way of observing its effect is

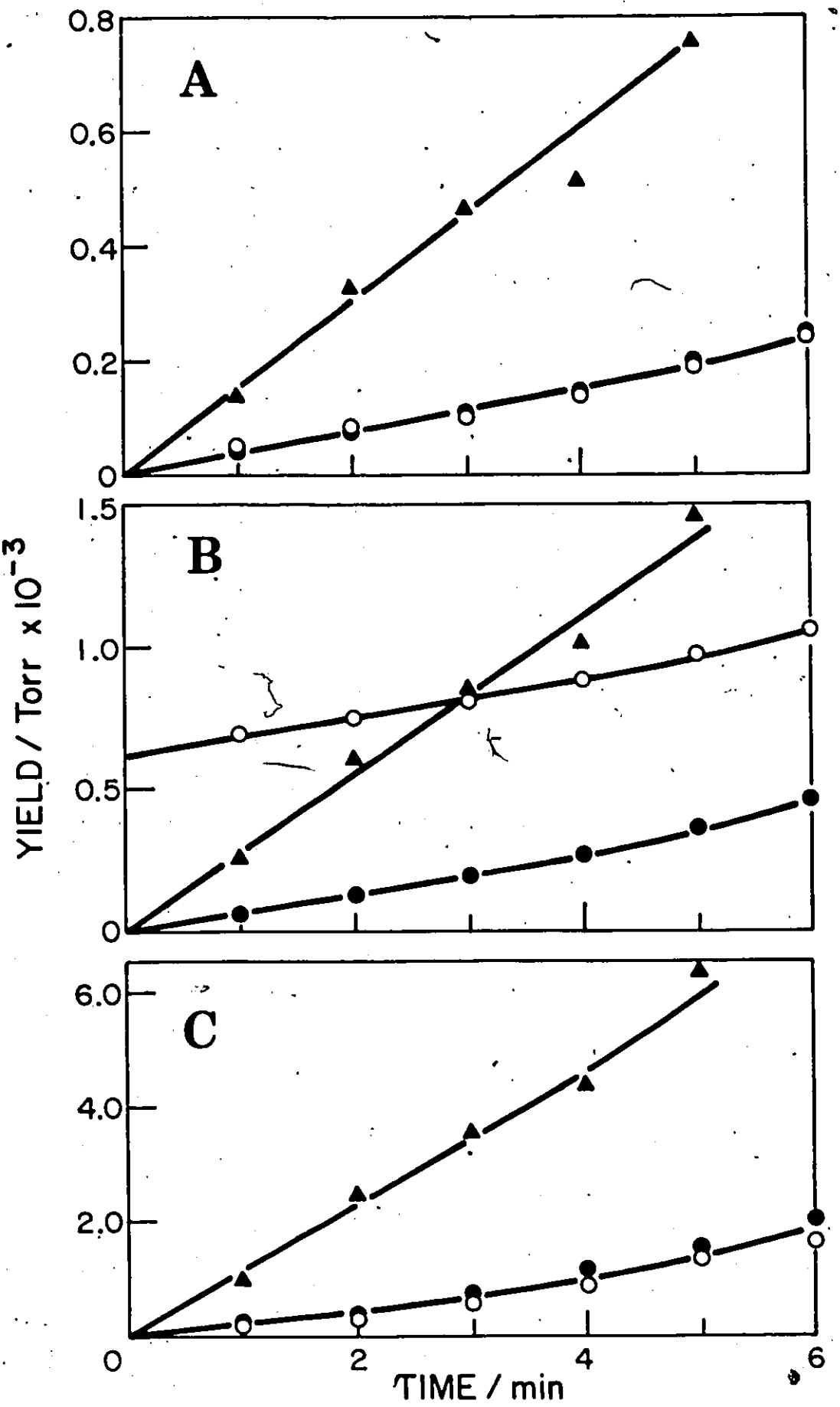
Table 19

INITIAL RATES OF THE FORMATION OF PRODUCTS FROM PYROLYSES OF THE PURIFIED ETHYLENE

			Methane		Ethane		Propylene		1-Butene	
T/K	$[C_2H_4]$/torr	$[neo\text{-}C_5H_{12}]$/%	Initial rate of formation/ torr s^{-1}	$(V_0)_N/V_0$	Initial rate of formation/ torr s^{-1}	$(V_0)_N/V_0$	Initial rate of formation/ torr s^{-1}	$(V_0)_N/V_0$	Initial rate of formation/ torr s^{-1}	$(V_0)_N/V_0$
748	201.8	0	9.83×10^{-7}		1.75×10^{-6}		2.17×10^{-5}		-	
	201.6	1.0	2.50×10^{-6}	2.54	4.41×10^{-6}	2.52	5.00×10^{-5}	2.30	-	-
766	104.3	0	6.33×10^{-7}		1.09×10^{-6}		3.33×10^{-6}		-	
	104.4	1.0	2.46×10^{-6}	3.89	4.40×10^{-6}	4.04	1.50×10^{-5}	4.50	-	-
793	105.4	0	1.23×10^{-6}		2.96×10^{-6}		6.94×10^{-6}		3.33×10^{-6}	
	105.5	1.0	6.50×10^{-6}	5.28	1.50×10^{-5}	5.07	3.75×10^{-5}	5.40	1.46×10^{-5}	4.38

Figure 26 - Yield-Time Plots for A: Methane, B: Ethane and C: Propylene from Purified Ethylene at 766 K

● 104.3 torr purified ethylene
▲ 104.4 torr purified ethylene + 1.04% neo-C_5H_{12}
O 104.4 torr unpurified ethylene


A
B
C
YIELD / Torr x 10^{-3}
TIME / min
0.8
0.6
0.4
0.2
0
1.5
1.0
0.5
0
6.0
4.0
2.0
0
2
4
6

the use of this data in plots of $[(V_0)_N/V_0]^2-1$ versus $[neo\text{-}C_5H_{12}]/[C_2H_4]^2$ obtained from the unpurified ethylene mixture pyrolysis. Figure 27 shows these plots for methane, ethane and propylene at 766 K, including the data from both purified and unpurified ethylene experiments. The first and third points on these graphs are the results of the unpurified ethylene mixtures containing 0.4 and 1.7% neopentane, respectively. The results at 748 K are shown in similar plots in Appendix B. It is seen from these graphs that there is no difference between the ratio of rate constants obtained from purified or unpurified ethylene reactions.

The experiments made with the purified ethylene therefore give results identical with those obtained using research grade ethylene without purification. They also illustrate the consistency of the kinetic method and the accuracy of the technique used for the determination of the initial rates of product formations.

5. Determination of the Initiation Rate Constant, k_1

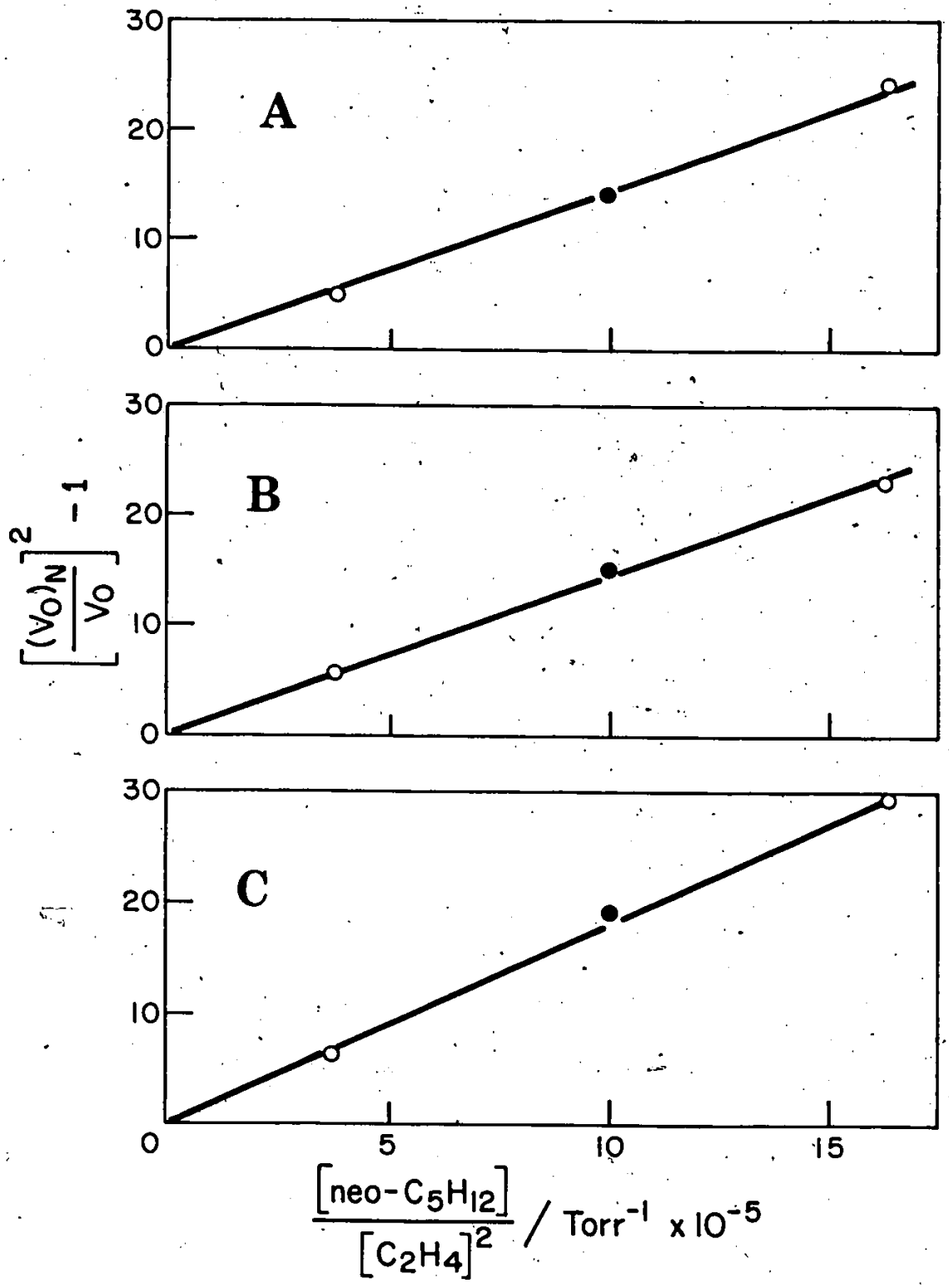
The Arrhenius parameters for the ratio of initiation rate constants k_N/k_1 were obtained from the formation of each product and were reported in Section 3. The rate constant for the initiation step of the neopentane pyrolysis[81] is given below.

$$\text{Log } k_N(s^{-1}) = 16.8 - \frac{82000}{2.3RT} \qquad (34)$$

Figure 27 - Plots of $[(V_0)_N/V_0]^2-1$ Versus $[neo\text{-}C_5H_{12}]/[C_2H_4]^2$, for A: Methane, B: Ethane and C: Propylene at 766 K

● 100 torr purified C_2H_4

o 100 torr unpurified C_2H_4


A
B
C
30
20
10
0
5
10
15
$\left[\frac{(V_0)_N}{V_0}\right]^2 - 1$
$\frac{[neo\text{-}C_5H_{12}]}{[C_2H_4]^2}$ / Torr^{-1} x 10^{-5}

When this value is combined with equations (30), (31), (32) and (33), which are the expressions for the ratio of rate constants k_N/k_1 obtained from each product, the following expressions are calculated for the bimolecular initiation rate constant of ethylene:

$$\text{Log } k_1(\text{L mol}^{-1}\ \text{s}^{-1}) = 11.38 - \frac{64700}{2.3RT} \qquad \text{(Methane)}$$

$$\text{Log } k_1(\text{L mol}^{-1}\ \text{s}^{-1}) = 12.28 - \frac{67800}{2.3RT} \qquad \text{(Ethane)}$$

$$\text{Log } k_1(\text{L mol}^{-1}\ \text{s}^{-1}) = 10.78 - \frac{62700}{2.3RT} \qquad \text{(Propylene)}$$

$$\text{Log } k_1(\text{L mol}^{-1}\ \text{s}^{-1}) = 10.90 - \frac{62800}{2.3RT} \qquad \text{(1-Butene)}$$

The average rate constant is obtained as described earlier, by averaging the Arrhenius parameters obtained from each product, and is given below. The error limits are the calculated standard deviations.

$$\text{Log } k_1(\text{L mol}^{-1}\ \text{s}^{-1}) = 11.34 - \frac{64500}{2.3RT} \qquad (35)$$

The values of the Arrhenius parameters of this rate constant will be discussed later, in Chapter V, together with results from other mixture experiments.

6. Measurements with Mixtures of Neopentane > 4%

In the pyrolysis of mixtures containing more than 4% neopentane the constant ratios of products observed at lower concentrations of neopentane were no longer maintained. Yields of methane and ethane were enhanced relative to those of propylene and 1-butene. In other words, saturated products became relatively more important while unsaturated products propylene and 1-butene became less important. The change in the ratios of products suggests that neopentane may have entered into the propagation reactions of the ethylene pyrolysis. Methane and ethane are the main products that form by abstraction reactions in the pyrolysis of ethylene, whereas propylene and 1-butene formation result mostly from addition and decomposition processes.

In this case, the increase in the formation of methane and ethane may be attributed to the reactions of methyl and ethyl radicals with neopentane, in competition with reactions with ethylene. The formation of products methane and ethane may come from two reactions:

$$CH_3 + C_2H_4 \rightarrow CH_4 + C_2H_3 \qquad (36)$$

and

$$CH_3 + \text{neo-}C_5H_{12} \rightarrow CH_4 + CH_2C(CH_3)_3 \qquad (37)$$

$$C_2H_5 + C_2H_4 \rightarrow C_2H_6 + C_2H_3 \qquad (38)$$

and $$C_2H_5 + \text{neo-}C_5H_{12} \rightarrow C_2H_6 + CH_2C(CH_3)_3 \qquad (39)$$

As the methyl and ethyl radicals react with neopentane, the portion of these radicals that undergo addition reactions with ethylene, and then eventually produce propylene and 1-butene, decreases correspondingly. Hence, the observed decreases in the formation of these two products are not unexpected.

If only methane is considered, because the treatment is similar for ethane, the initial rate of formation of this product in the absence of neopentane can be written as:

$$R^{o}_{CH_4} = k_{36}[CH_3]^{o}[C_2H_4] \qquad (40)$$

In the presence of neopentane, more than about 4%, the rate expression should also include the reaction (37):

$$R^{N}_{CH_4} = k_{36}[CH_3]^{N}[C_2H_4] + k_{37}[CH_3]^{N}[\text{neo-}C_5H_{12}] \qquad (41)$$

Here $R^{o}_{CH_4}$, $R^{N}_{CH_4}$ refer to the rate of formation and $[CH_3]^{o}$, $[CH_3]^{N}$ refer to the concentration of methyl radicals in the absence and presence of neopentane, respectively.

If R_i and $(R_i)_N$ present the rate of initiation of ethylene and neopentane shown below,

$$2C_2H_4 \rightarrow C_2H_5 + C_2H_3 \qquad (1)$$

$$\text{neo-}C_5H_{12} \rightarrow CH_3 + C(CH_3)_3 \qquad (N)$$

and k_t is the termination rate constant, the total radical concentration is $(R_i/k_t)^{1/2}$ in ethylene alone, and $[(R_i + (R_i)_N)/k_t]^{1/2}$ in the presence of neopentane. The concentration of methyl radicals in ethylene alone may be written as a fraction, f, of the total radical concentration.

$$[CH_3]^O = f(R_i/k_t)^{1/2} \qquad (42)$$

In the presence of neopentane, the total radical concentration is increased and the concentration of methyl radicals may be similarly expressed:

$$[CH_3]^N = f'\left[\frac{R_i + (R_i)_N}{k_t}\right]^{1/2} \qquad (43)$$

This expression assumed that the rate constants for any new propagation reactions are not significantly different in the new system and the main termination reaction is not changed. The ratio of rates from equations (40) and (41) is

$$\frac{R^N_{CH_4}}{R^O_{CH_4}} = \frac{[CH_3]^N}{[CH_3]^O}\left\{1 + \frac{k_{37}}{k_{36}}\frac{[\text{neo-}C_5H_{12}]}{[C_2H_4]}\right\} \qquad (44)$$

From (42) and (43), the ratio of concentration of CH_3 may be written as:

$$\frac{[CH_3]^N}{[CH_3]^o} \doteq \frac{f'}{f} \left[\frac{R_i + (R_i)_N}{R_i}\right]^{1/2}$$

$$\doteq \frac{f'}{f} \left[1 + \frac{(R_i)_N}{R_i}\right]^{1/2}$$

Then, equation (44) may be expressed as following:

$$\frac{R^N_{CH_4}}{R^o_{CH_4}} = \frac{f'}{f} \left[1 + \frac{(R_i)_N}{R_i}\right]^{1/2} \left[1 + \frac{k_{37}}{k_{36}} \frac{[\text{neo-}C_5H_{12}]}{[C_2H_4]}\right] \quad (45)$$

Since $\left[1 + \frac{(R_i)_N}{R_i}\right]^{1/2} = \frac{(V_0)_N}{V_0}$ under conditions where the only effect of neopentane is the addition of a new initiation step,

$$\frac{R^N_{CH_4}}{R^o_{CH_4}} = \frac{f'}{f} \left[\frac{(V_0)_N}{V_0}\right] \left[1 + \frac{k_{37}}{k_{36}} \frac{[\text{neo-}C_5H_{12}]}{[C_2H_4]}\right] \quad (46)$$

If it is further assumed that, f and f' are, to a first approximation, the same fraction, then,

$$\frac{R^N_{CH_4}}{R^o_{CH_4}} = \frac{(V_0)_N}{V_0} \left[1 + \frac{k_{37}}{k_{36}} \frac{[\text{neo-}C_5H_{12}]}{[C_2H_4]}\right] \quad (47)$$

The assumptions involved in the derivation of this expression will not be seriously in error if the concentration of neopentane is not too high. The results used to test equation (47) were obtained with mixtures in the range 4-9% neopentane.

The rate of formation of ethane in the presence and absence of neopentane may be expressed by a similar equation, involving the ratio of rate constants k_{39}/k_{38} for the analogous abstraction reactions of the ethyl radical, equations (39) and (38).

The value of $(V_0)_N/V_0$ for each product was taken from measurements of the product itself and was obtained by extrapolation of the initial slope of plots such as illustrated in Figure 19 to the appropriate ratio of neopentane to ethylene. Table 20 presents the values of the ratios of rate constants k_{37}/k_{36} and k_{39}/k_{38} for methane and ethane, respectively.

Because of the limited number of experiments on mixtures containing larger pressures of neopentane, these values are not sufficient to allow a direct determination of an Arrhenius expression for the ratio of rate constants k_{37}/k_{36} and k_{39}/k_{38}. A qualitative explanation for the ratio of these rate constants can be given in the following way. The rate constant expressions for reactions (36) and (37) are

Table 20

RATIOS OF RATE CONSTANTS
IN THE PRESENCE OF NEOPENTANE > 4%

T/K	$[C_2H_4]$/torr	$[neo\text{-}C_5H_{12}]$/%	Methane k_{37}/k_{36}	Ethane k_{39}/k_{37}	k_{37}/k_{36} (calculated) ΔE/kcal mol^{-1} 2	3	4	6
756	104.3	5.54	5.25	1.08	3.80	7.41	14.5	55.0
	302.0	5.54	6.92	0.36				
777	204.3	4.27	12.6	-	3.63	6.92	13.5	49.0
	204.0	9.45	14.1	-				
803	106.5	4.27	16.6	2.51	3.55	6.61	12.3	43.7
	205.7	4.27	11.0	4.90				
819	106.4	4.71	8.51	4.27	3.39	6.31	11.8	39.8

$$\text{Log } k_{36} = \text{Log } A_{36} - \frac{E_{36}}{2.3RT}$$

$$\text{Log } k_{37} = \text{Log } A_{37} - \frac{E_{37}}{2.3RT}$$

Then, the ratio of these rate constants may be expressed as:

$$\text{Log } \frac{k_{37}}{k_{36}} = \text{Log } \frac{A_{37}}{A_{36}} - \frac{(E_{37}-E_{36})}{2.3RT} \qquad (48)$$

The abstraction reaction of methyl radicals with neopentane has been studied by several workers and the rate constant of this reaction in a large temperature range is now known[80,84,86,88,97]. In general, the frequency factor for reactions of methyl radicals with organic molecules are all very similar and have values close to $10^{8.5}$ [98-102]. Therefore, assuming equal values of the frequency factors in equation (48), the ratio of rate constants k_{37}/k_{36} will depend primarily on the difference of activation energies, $E_{37}-E_{36}$. Results of the present experiments show that (Table 20), the difference in activation energies of reactions (37) and (36), $E_{37}-E_{36}$, is between 3 and 4 kcal mol^{-1}. The ratio k_{39}/k_{38} for the ethyl radical would be expected to be similar to that for the methyl radical. It should be noted that if f' > f, as might be expected, a lower value of

k_{37}/k_{36} would be obtained, indicating a smaller difference between the activation energies. The difference in activation energy of reactions (37) and (36) will be closely related to the difference in C-H bond dissociation energy between ethylene and neopentane since the same radical, methyl, reacts with these two compounds forming the same product, methane, in each case. The value of $E_{37}-E_{36}$ indicates that there is only 3-4 kcal mol^{-1} difference between the C-H bond dissociation energies of ethylene and neopentane.* A value for BDE in (C_5H_{11}-H) of 99.3 ± 1 kcal mol^{-1} was reported for neopentane[43]. The results of this study therefore suggest qualitatively that the C-H bond dissociation energy in ethylene is not more than a few kcal mol^{-1} larger than that of in neopentane, and is in agreement with the value of about 103 kcal mol^{-1} obtained from the present research.

B. ADDITIONS OF ETHANE

Pyrolysis of ethylene in the presence of small quantities of ethane was made at four temperatures. The pressure of ethane used in these experiments was somewhat higher than the other additives. In most cases, the ratio of ethane was 2.85% but at 777 K, an additional mixture of 7.65% ethane was studied.

* The reverse reactions are assumed to have identical activation energies.

1. Pyrolysis of Ethane

Pyrolysis of ethane has been studied extensively and the mechanism of its decomposition is now well understood. The reaction was shown to occur almost entirely by a free-radical mechanism[103]. Thermal decomposition of ethane starts with the unimolecular dissociation of ethane

$$C_2H_6 \rightarrow CH_3 + CH_3 \qquad (E)$$

This initiation process is followed by the reaction of methyl radical with ethane

$$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$$

This is the only reaction leading to formation of methane, therefore, it is directly related to the initiation process. Lin and Back[104,105] studied the kinetics of methane formation over a range of pressure and temperature and showed that the first-order rate constant for the initiation reaction is pressure-dependent. This was also observed by Trenwith[106] and later confirmed by Clark and Quinn[107]. The chain-propagating steps are:

$$C_2H_5 \rightarrow C_2H_4 + H$$

$$H + C_2H_6 \rightarrow H_2 + C_2H_5$$

Since the ethyl radical has the highest concentration, the chain terminating step is

$$2C_2H_5 \rightarrow C_4H_{10} \text{ and } C_2H_6 + C_2H_4$$

The studies of the effect of surface[104,110] led to the conclusion that the initiation step is largely homogeneous. Pratt and Rogers[111] examined the dissociation of ethane in a wall-less reactor and obtained results that agreed with the reaction mechanism and rate constants suggested from studies in conventional reactors. The thermal dissociation of ethane has recently been re-examined by Trenwith[109] and the initiation rate constant was determined from rates of methane formation. Table 21 presents the Arrhenius parameters for the rate constant of initiation reaction obtained by several workers.

Table 21

ARRHENIUS PARAMETERS OF THE RATE CONSTANT FOR THE INITIATION STEP IN THE PYROLYSIS OF ETHANE

Log A/s^{-1}	$E/kcal\ mol^{-1}$	Temperature range/K	Reference
16.00 ±0.066	86.00 ±0.37	823- 893	104
16.130±0.082	86.735±0.313	778- 878	107
16.90	89.500	1000-1500	108
16.72 ±0.17	88.850±0.68	840- 913	109

In the following calculations, the rate constant used for the initiation step of the ethane pyrolysis is the

value recommended by Trenwith[109]. The result of his work is consistent with current thermochemical data for reaction (E) and there is also satisfactory agreement between experimentally determined rate constants for the recombination of methyl radicals[112,113] and calculated values obtained using the Arrhenius equation determined by Trenwith for the initiation step of the ethane pyrolysis.

2. Determination of the Initiation Rate Constant, k_1

The initial rates of formation of three products, methane, propylene and 1-butene were measured in the presence and absence of ethane. By analogy with the ethylene-neopentane system, it was assumed that with the concentration of ethane used in the experiments, 2.85%, abstraction reactions from ethane would not be important, and the only effect of the ethane was the addition of a new initiation process. Also by comparison with the previous systems, it was concluded that the unimolecular dissociation of ethane should be the only important additional initiation process:

$$C_2H_6 \rightarrow 2CH_3 \qquad (E)$$

the ratio of rates in the presence and absence of ethane could therefore be represented by the following equation:

$$\frac{(V_o)_E}{V_0} = \left(1 + \frac{k_E[C_2H_6]}{k_1[C_2H_4]^2}\right)^{1/2} \qquad (49)$$

where $(V_0)_E$ refers to the initial rate of product formation in the presence of the additive ethane, k_E presents the rate constant for the initiation step of the pyrolysis of ethane.

The initial rates of product formation in the presence and absence of ethane are presented in Table 22. As a result of the high activation energy for the dissociation of ethane, the increase observed in the rate of product formation was very small. The ratio of rate constants k_E/k_1 was calculated from equation (49). Since the presence of 7.65% ethane would probably affect the propagation reactions, its results were not included in the calculation of k_E/k_1. Arrhenius plots of k_E/k_1 obtained from ratios of formation of methane, propylene and 1-butene are shown in Figure 28. From these data, the following expressions were obtained for the ratio of rate constants k_E/k_1:

$$\text{Log}\ \frac{k_E}{k_1}\ (\text{mol L}^{-1}) = 7.00 - \frac{28500}{2.3RT} \qquad \text{(Methane) (50)}$$

$$\text{Log}\ \frac{k_E}{k_1}\ (\text{mol L}^{-1}) = 4.26 - \frac{18700}{2.3RT} \qquad \text{(Propylene) (51)}$$

$$\text{log}\ \frac{k_E}{k_1}\ (\text{mol L}^{-1}) = 5.46 - \frac{22800}{2.3RT} \qquad \text{(1-Butene) (52)}$$

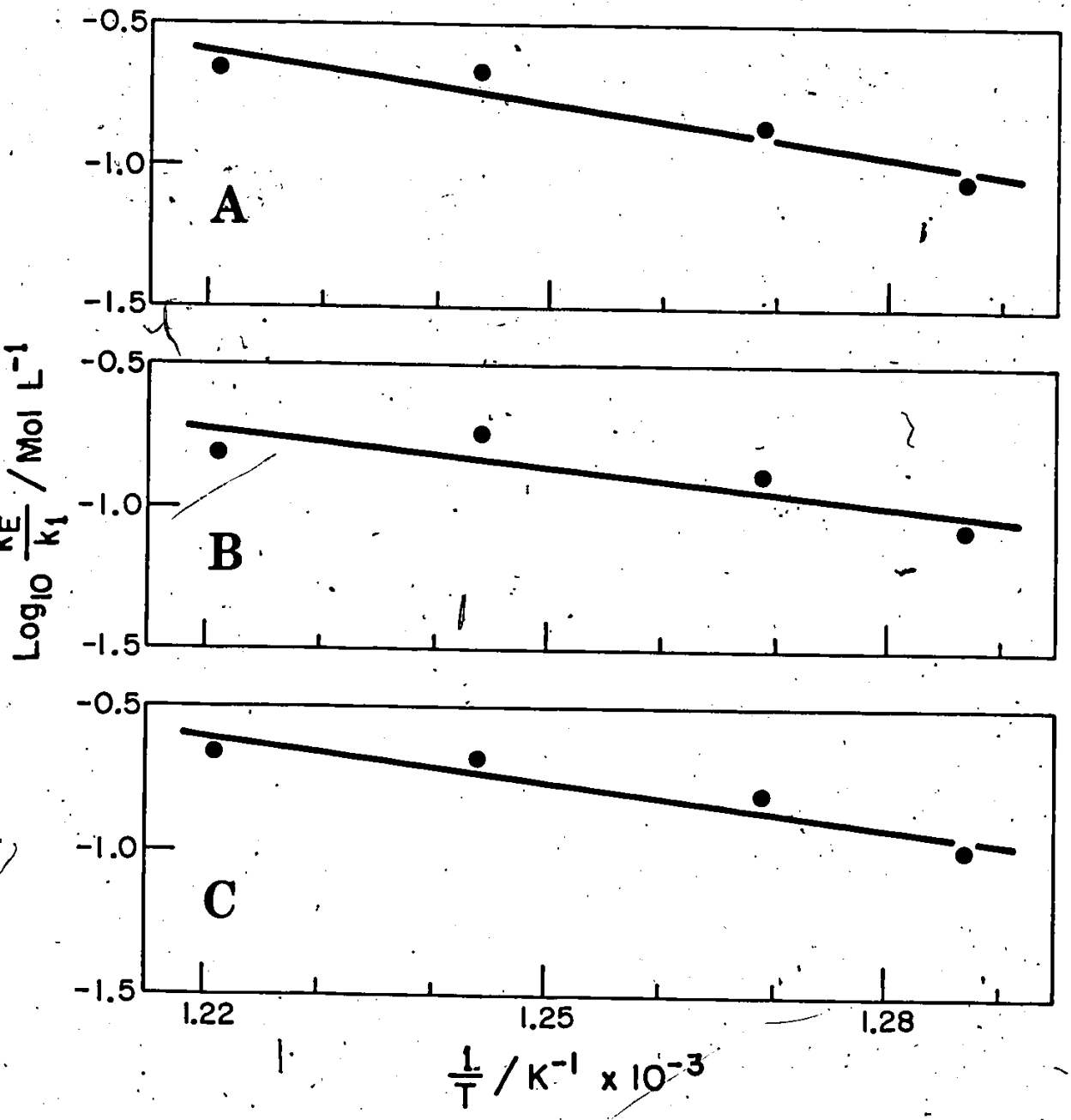
Then, using the rate constant expression obtained by Trenwith[109] for the dissociation of ethane

Table 22

EFFECT OF ETHANE ON THE INITIAL RATES OF FORMATION OF PRODUCTS

T/K	$[C_2H_4]$/torr	$[C_2H_6]$/%	Initial rate of formation/torr s^{-1}	$(V_0)_E/V_0$	$\frac{k_E}{k_1}$/mol L^{-1}
777			METHANE		
	204.3	0	3.96×10^{-6}		
	204.1	2.85	5.00×10^{-6}	1.26	0.087
	204.3	7.65	1.00×10^{-5}	2.53	
			PROPYLENE		
	204.3	0	3.17×10^{-5}		
	204.1	2.85	3.96×10^{-5}	1.25	0.083
	204.3	7.65	5.00×10^{-5}	1.58	
			1-BUTENE		
	204.3	0	9.50×10^{-6}		
	204.1	2.85	1.23×10^{-5}	1.29	0.098
	204.3	7.65	1.64×10^{-5}	1.73	
788			METHANE		
	105.5	0	1.54×10^{-6}		
	105.4	2.85	2.58×10^{-6}	1.68	0.136
			PROPYLENE		
	105.5	0	5.33×10^{-6}		
	105.4	2.85	8.75×10^{-6}	1.64	0.129
			1-BUTENE		
	105.5	0	2.30×10^{-6}		
	105.4	2.85	4.03×10^{-6}	1.75	0.156
804			METHANE		
	106.0	0	2.33×10^{-6}		
	106.1	2.85	4.58×10^{-6}	1.97	0.212
			PROPYLENE		
	106.0	0	5.83×10^{-6}		
	106.1	2.85	1.08×10^{-5}	1.85	0.180
			1-BUTENE		
	106.0	0	3.67×10^{-6}		
	106.0	2.85	7.17×10^{-6}	1.95	0.208
819			METHANE		
	106.5	0	3.33×10^{-6}		
	106.6	2.85	6.67×10^{-6}	2.00	0.221
			PROPYLENE		
	106.5	0	6.66×10^{-6}		
	106.0	2.85	1.17×10^{-5}	1.76	0.153
			1-BUTENE		
	106.5	0	3.77×10^{-6}		
	106.0	2.85	7.50×10^{-6}	1.99	0.217

Figure 28 - Arrhenius Plots for A: Methane, B: Propylene, C: 1-Butene


-0.5
-1.0
-1.5
A
B
C
$\log_{10} \frac{k_E}{k_1}$ / Mol L^{-1}
1.22
1.25
1.28
$\frac{1}{T}$ / K^{-1} x 10^{-3}

$$\text{Log } k_E(s^{-1}) = (16.72 \pm 0.17) - \frac{(88850 \pm 680)}{2.3\ RT} \qquad (53)$$

the Arrhenius expressions for the rate constant of the initiation step of ethylene are calculated as:

$$\text{Log } k_1(L\ mol^{-1}\ s^{-1}) = 9.72 - \frac{60400}{2.3RT} \qquad \text{(Methane)}$$

$$\text{Log } k_1(L\ mol^{-1}\ s^{-1}) = 12.46 - \frac{70200}{2.3RT} \qquad \text{(Propylene)}$$

$$\text{Log } k_1(L\ mol^{-1}\ s^{-1}) = 11.26 - \frac{66100}{2.3RT} \qquad \text{(1-Butene)}$$

The average rate constant is obtained by averaging the Arrhenius parameters obtained from the three products, as shown below:

$$\text{Log } k_1(L\ mol^{-1}\ s^{-1}) = 11.15 - \frac{65600}{2.3RT} \qquad (54)$$

This expression has a larger uncertainty than the other rate constants obtained in this work from the 1-butene and neopentane additions, because the scatter in the data is larger. This is mostly due to the limited number of experiments and to the small increase in rate observed. In order to observe an increase in the initial rates of the products it was necessary to prepare the mixture using a larger concentration of ethane, 2.85%. On the other hand,

it was judged by analogy with neopentane that at concentrations greater than about 4%, ethane would probably enter into propagation reactions. The useful range for ethane additions was therefore limited. Thus, it cannot be given the same weight as the values obtained from the other additives. Nevertheless, it provides useful confirmation of the other values reported in this research.

It should be pointed out that in tables of Chapters III and IV where the yields of products are listed, the pressures of ethylene quoted represent the total pressures of the respective mixtures. In the experiments with the addition of 1-butene it was reasonable not to make any corrections for the pressures of 1-butene present because these amounts were too small to cause any change in the values of the ratio k_B/k_1. In the case of the additives neopentane and ethane, neglect of this correction introduces an error in the value of k_a/k_1 of not more than 5% for most of the measurements and between 5 and 10% only in a few cases. The extent of the correction depends on the pressures of additive used at each temperature and the order of the rate of formation of a product. This uncertainty in k_a/k_1 causes almost no change in the value of the activation energy obtained from the mixture experiments and increases the value of the frequency factor by a maximum of 10%. It will be seen in the following chapter that this error is not important in the final expression derived for k_1. This correction is also not very significant in the values reported in Table 20 for the ratios of the rate constants from the results of the additions of higher pressures of neopentane because these ratios are calculated by subtraction of two values of $(V_o)_a/V_o$ obtained at the same % mixture of neopentane and the conclusion of Section IV-6 is therefore not affected.

CHAPTER V

EVALUATION OF THE RESULTS

1. Arrhenius Parameters for the Initiation Rate Constant of the Ethylene Pyrolysis

So far, the results of the ethylene pyrolysis experiments in the presence and absence of an additive have been presented. For convenience, the Arrhenius expressions obtained from the ethylene+1-butene, ethylene+neopentane and ethylene+ethane studies for the initiation process of the ethylene pyrolysis are given below:

$$\text{Log } k_1(\text{L mol}^{-1}\text{s}^{-1}) = 11.19 - \frac{63800}{2.3RT} \quad \text{from } C_2H_4+1\text{-}C_4H_8 \tag{27}$$

$$\text{Log } k_1(\text{L mol}^{-1}\text{s}^{-1}) = 11.34 - \frac{64500}{2.3RT} \quad \text{from } C_2H_4+\text{neo-}C_5H_{12} \tag{35}$$

$$\text{Log } k_1(\text{L mol}^{-1}\text{s}^{-1}) = 11.15 - \frac{65600}{2.3RT} \quad \text{from } C_2H_4+C_2H_6 \tag{54}$$

These values were calculated by averaging the results obtained from all the products in a particular pyrolysis system.

A statistical treatment of the random errors does not include all the errors in the present type of measurements. Systematic errors are usually very important in kinetic measurements. Some of these sources of errors will be discussed in the following paragraphs.

In each pyrolysis system, there are two main sources of error involved in obtaining the value for k_1. The first

includes all the errors of measurement in the present experiments and the other includes the errors in the rate constant for dissociation of the additive. Estimation of the limits of the latter errors is difficult and involves a study of the methods used in measurement and comparison of the various values reported. Discussions of the choice of rate constants for the dissociation of each additive were given before in related sections. After the discussion of the experimental errors in the present investigation, some approximate error limits will be suggested for the Arrhenius parameters of k_1 which will include all possible errors in its determination.

The experimental errors in the determination of the initial rates originate directly from the yield-time measurements. This may differ a little from product to product but in general, the error in the initial rate determinations was about 10%. This number may be slightly larger at the highest and lowest temperatures, because the linear portion of the yield-time curves are shorter at high temperatures due to the early start of secondary reactions, and the yields of products are too small and difficult to measure at the lowest temperatures. In these cases, up to 20% error may sometimes occur. The presence of an additive does not particularly change these error limits, except at lower temperatures, it may reduce the error in initial rate determinations by increasing the yields of products. Since

the initial rate ratios, $(V_0)_a/V_0$, are squared for the determination of the ratio of rate constants, the error is correspondingly increased by this procedure. However, this difficulty is overcome by introducing a large number of data to the plots of $[(V_0)_{additive}/V_0]^2-1$ versus $[additive]/[C_2H_4]^2$. Therefore, although each datum point was possibly including more than 10% error, the final average error in the value of the ratio of rate constants was not that high. In most cases, the error in each value of k_a/k_1 was about 5% or less.

Since for each ethylene+additive system, a value for k_1 was obtained from each product analyzed, the advantage of averaging these values is quite important. Also, the fact that these averaged rate constants were determined by using three different additives makes the final rate constant expression for the initiation step of the pyrolysis of ethylene, which will be given below, even more reliable.

When all the errors discussed in this section are considered, the following Arrhenius expression is suggested for the rate constant of the initiation step in the pyrolysis of ethylene:

$$\text{Log } k_1(\text{L mol}^{-1}\text{s}^{-1}) = (11.27 \pm 0.6) - \frac{(64200 \pm 2000)}{2.3\ RT} \qquad (55)$$

The standard deviation in the activation energy obtained by averaging the activation energies presented in equations (27), (35) and (54) is slightly smaller than the

error shown in equation (55). It is felt that this error represents a reasonable estimate of the overall accuracy of the result.

Since the results from C_2H_4+1-C_4H_8 and C_2H_4+neo-C_5H_{12} systems had less uncertainty than that of C_2H_4+C_2H_6 system because of the reasons discussed in Chapter IV.B, more weight was given to the rate constants obtained from the former systems. Hence, the activation energy in equation (55) was obtained by averaging the activation energies of the rate constant expressions (27) and (35). The error limits were assigned such that they would cover easily the value of the activation energy from the expression (54). Error limits for the average frequency factor were calculated from the range of the activation energy when the assigned error limits were taken into consideration.

A value may be calculated for the frequency factor of the initiation of the ethylene pyrolysis

$$2C_2H_4 \rightarrow C_2H_5 + C_2H_3 \qquad (1)$$

from the entropy change of the reaction,

$$\text{Log}\ \frac{A_1}{A_{-1}} = \frac{\Delta S^\circ}{2.3R} \qquad (56)$$

assuming a value for the frequency factor for the reverse reaction, which is the disproportionation of the vinyl and ethyl radicals. A value of 0.03 has been reported for the ratio of rate constants of disproportionation to combination, k_d/k_c, for ethyl+vinyl radicals[114]. Almost all other disproportionation/combination ratios involving the transfer of a hydrogen atom from the ethyl radical are larger[115] and it is probable that the ratio for ethyl+vinyl is greater than 0.03. The accepted value of k_d/k_c for ethyl+ethyl combination is 0.14[100]. In general, the ratio of k_d/k_c involving the ethyl radical in combination with saturated radicals is larger than in combination with unsaturated radicals. The number of data for k_d/k_c is very limited for the reactions involving the vinyl radicals. For vinyl+vinyl reaction, the reported values of k_d/k_c are 1.1[116] and 0.02[117]. A value of 0.5 was calculated from the data of LeRoy and Tickner[118]. The range of uncertainty is too large to be able to reach a conclusion about the behaviour of the vinyl radical. Therefore, for the reaction of the ethyl+vinyl radicals, it seems reasonable to choose $k_d/k_c = 0.1$.

Since the rate constant for combination of an ethyl and vinyl radical is probably similar to the rate constant for combination of two ethyl radicals, 1×10^{10} L mol^{-1} s^{-1} [119,120], the value of k_{-1} can be calculated from

equation (56) assuming that the frequency factor for reverse of reaction (1) is equal to k_d. Necessary data for standard entropy for reaction (1) is given in Table 23.

Table 23

THERMOCHEMICAL DATA FOR REACTION (1)*

	S^o_{300}/cal mol^{-1} K^{-1}	C_p^o/cal mol^{-1} K^{-1}	
		300K	800K
C_2H_4	52.4	10.3	20.0
C_2H_3	56.3	9.7	16.8
C_2H_5	59.0	11.1	22.2

* Values taken from References 30 and 33.

The value of ΔS^o for reaction (1) at 298 K is 10.5. Because most of the studies for the determination of k_d/k_c are made at low temperatures no temperature correction was made to ΔS^o (298 K).

Taking the values $k_d/k_c = 0.1$ and $k_c = 1 \times 10^{10}$ L mol^{-1} s^{-1}, the value of log A was calculated as 11.3 from the equation (56). This value is in excellent agreement with the frequency factor obtained from the present study for reaction (1). James and Troughton[114]'s value for k_d/k_c, 0.03, is probably not very accurate due to the limited number of experimental data. However, even if k_d/k_c is taken as 0.03, the value of log A_1 does not change drastically and 10.8 is obtained in this case. This number is probably within the error limits of these calculations.

2. Mechanism of the Initiation Process

It has been well established that the initiation step of the ethylene pyrolysis is bimolecular. The rate constant which has been measured in the present study refers to a bimolecular reaction of ethylene without specifying the products of the reaction, except that radicals are produced. Reaction (1) designates the simplest course of such a reaction.

$$2C_2H_4 \rightarrow C_2H_5 + C_2H_3 \qquad (1)$$

and the measured activation energy and frequency factor are in good agreement with the thermochemical data of the species involved. Other mechanisms should, however, be considered.

Experimental observations of the low activation energy and high orders of the rates of formation of products during the pyrolysis of ethylene at about 800 K exclude the possibility of unimolecular initiation processes. Unimolecular dissociation reactions (57) and (58)

$$C_2H_4 \rightarrow C_2H_3 + H \qquad (57)$$

$$C_2H_4 \rightarrow C_2H_2 + H_2 \qquad (58)$$

were observed to occur in the high temperature pyrolysis of ethylene at about 1200 K, with activation energies of 98.2 and 79.3 kcal mol^{-1}, respectively[25]. Decomposition of ethylene to acetylene and hydrogen by a molecular process, reaction (58), does not occur at low temperatures because the formation of products suggest that radical reactions are involved at these temperatures. Formation of two methylene radicals

$$C_2H_4 \rightarrow 2CH_2 \qquad (59)$$

is very unlikely since it involves the breakage of the ethylene double bond. The endothermicity of reaction (59) is calculated as 173.5 kcal mol^{-1} by taking 93 kcal mol^{-1} for the heat of formation of the methylene radical[121,122].

Bimolecular initiation of ethylene may occur by several reactions. Formation of ethane and acetylene by a molecular process

$$2C_2H_4 \rightarrow C_2H_6 + C_2H_2 \qquad (60)$$

is rejected because it does not produce radicals. Experiments with mixtures of deuterated and normal ethylene[16] helped to rule out the possibility of this reaction. Reaction (61) leading to the formation of 1-butene through an intermediate

$$2C_2H_4 \rightarrow C_4H_8^* \rightarrow 1\text{-}C_4H_8 \qquad (61)$$

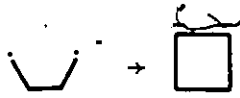
is also a molecular process. The formation of 1-butene and its subsequent decomposition into radicals was suggested by Halstead and Quinn[15] as the primary initiation leading to the formation of all the other products. However, Simon and Back[17] concluded that this behaviour of 1-butene was important only at higher temperatures and low pressures. In fact, whether the reaction (61) is the main initiation process is very difficult to resolve since very small amounts of 1-butene could initiate the formation of radicals in the system. In the present experiments, two observations indicate that this mechanism is not important at temperatures below 820 K and pressures above 100 torr. It was observed that 1-butene is not the only primary product of the pyrolysis of ethylene. Examples of the yield-time plots given in Chapters III and IV show that methane, ethane and propylene are also primary in character. Furthermore, the experiments performed in the ethylene+1-butene system in the present study lead to the understanding of the exact quantity of 1-butene required to increase the rate of initiation. It can be shown that the amount of 1-butene formed in the initial stages is not sufficient to account for the formation of the other products. By reference to Tables 3, 4 and 5 in Chapter III, that show the increase in

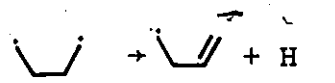
the initial rates of formation of the products methane, ethane and propylene in the pyrolysis of ethylene by the presence of small amounts of 1-butene, the yield of 1-butene necessary to cause a measurable increase in the formation of the products can be deduced. For instance at 748 K and 200 torr ethylene pressure, the condition $[(V_0)_N/V_0] = 1$ will be obtained only if the amount of 1-butene is about 0.02 torr or more. The yield of product 1-butene therefore should be more than this quantity in order to cause any increase in the initial rates of the product formation. However, experimental data under the same conditions show that the yields of 1-butene are much smaller than 0.02 torr (Appendix B). The rates of all the products were measured long before the product 1-butene had attained this value. Even at a higher reaction temperature, 773 K, the formation of all the products were observed much before the amount of 1-butene required to cause any increase in the initial rate, was formed. Therefore, it can be concluded that the dissociation of 1-butene into radicals cannot be the main initiation process and the formation of all the products occurs through another primary initiation reaction.

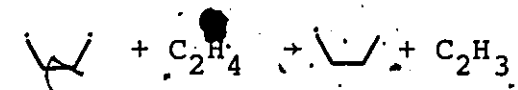
Another possible bimolecular reaction of ethylene is the formation of the tetramethylene diradical.

$2C_2H_4 \rightleftharpoons$  (62), (-62)

Tetramethylene has a very short life time and it can either decompose to give two ethylene molecules, reaction (-62), or react by unimolecular or bimolecular processes.

 (63)

 (64)

 (65)

Reaction (63) does not produce radicals and therefore only reactions (64) and (65) lead to initiation of radical chain processes. The importance of reactions (64) and (65) relative to the bimolecular reaction of ethylene to give an ethyl and vinyl radical

$$2C_2H_4 \rightarrow C_2H_5 + C_2H_3 \qquad (1)$$

can be tested by comparing the rates of these reactions under the same conditions. In order to do these calculations, an estimate of the concentration of tetramethylene diradicals is required together with the values of the rate constants for reactions (62)-(65) and (1). Assuming a steady-state concentration of diradicals the following expression is obtained.

$$[\square] = \frac{k_{62}[C_2H_4]^2}{k_{-62} + k_{63} + k_{64} + k_{65}[C_2H_4]} \qquad (66)$$

The Arrhenius parameters for reactions of four-membered ring compounds were discussed by O'Neal and Benson[123]. From their values, the rate constant for the ring closing of the diradical can be estimated as

$$\text{Log } k_{63}(s^{-1}) = 12. - \frac{5000}{2.3RT} \qquad (67)$$

The reverse of reaction (62) was suggested to have Arrhenius parameters similar to those of reaction (63). Estimated rate constants for reactions (64) and (65) were taken from Benson and Haugen[23].

$$\text{Log } k_{64}(s^{-1}) = 14 - \frac{38300}{2.3RT} \qquad (68)$$

$$\text{Log } k_{65}(\text{L mol}^{-1}\ s^{-1}) = 8.8 - \frac{7800}{2.3RT} \qquad (69)$$

The rate constant for the formation of diradicals, reaction (62), can be estimated in the following way. The formation of cyclobutane from ethylene has been studied by Quick, Knecht and Back[124]

$$2C_2H_4 \rightarrow \square \qquad (62')$$

and the value of the rate constant for this reaction was reported as

$$\text{Log } k_{62}\text{, (L mol}^{-1}\text{ s}^{-1}\text{)} = 7.84 - \frac{43800}{2.3RT}. \qquad (70)$$

The activation energy for the formation of the diradical by reaction (62) can be estimated as 38.8 kcal mol^{-1} by combining the values of the activation energies in equations (70) and (67). This value would not change much if it were calculated by using the estimated value of the heat of formation of the diradical, 61.6 kcal mol^{-1} [23]. The frequency factor for the rate constant of reaction (62) can be calculated from the relation

$$\text{Log } \frac{A_{62}}{A_{-62}} = \frac{\Delta S_c^o}{2.3R} \qquad (71)$$

ΔS_c^o can be obtained from thermochemical data using the values estimated by Benson and Haugen. For the diradical, $S^o(1400\text{ K}) = 135$ cal mol^{-1} K^{-1}, $C_p^o(1400\text{ K}) = 53.4$ and $C_p^o(300\text{ K}) = 22.4$ cal mol^{-1} K^{-1}. The standard entropy for the diradical at 300 K was calculated as 76.7 cal mol^{-1} K^{-1}. Taking $S^o(300\text{ K}) = 52.4$ cal mol^{-1} K^{-1} for C_2H_4, ΔS_p^o for reaction (62) is -28.1 cal mol^{-1} K^{-1}. Then, ΔS_c^o was calculated from the following relation

$$\Delta S_c^o = \Delta S_p^o - R\Delta n - \Delta nR\ 2.3\ \text{Log}(0.082\ T)$$

$$\Delta S_c^o = -19.8 \text{ cal } mol^{-1}\ K^{-1}$$

In the above treatment, ΔS_c^o and ΔS_p^o are the entropy changes at standard states expressed in concentration and pressure units, respectively.

From equation (71), taking Log $A_{-62}(s^{-1})$ as 12, the value of Log A_{62} was determined as 7.7 L mol^{-1} s^{-1}. Considering the error in the estimated thermochemical data and assuming that A_{62} should be slightly larger than A_{62}', a value of 8 L mol^{-1} s^{-1} seems a better estimate for Log A_{62}. Hence,

$$\text{Log } k_{62}(\text{L mol}^{-1}\ \text{s}^{-1}) = 8.0 - \frac{38800}{2.3RT} \qquad (72)$$

Having the expressions for all the necessary rate constants, the concentration of diradicals can now be calculated from equation (66). At 773 K and 100 torr initial ethylene pressure, the value of [⌒] is 5.9 x 10^{-20} mol L^{-1}. The rate expressions and the calculated values of the rates of reactions (62)-(65) using the above value of [⌒] and equations (72) and (67)-(69) are presented in Table 24. The rate constant for reaction (1) is the value determined from the present research using equation (55) under the same conditions.

Table 24 shows that the rate of formation of the tetramethylene diradicals by reaction (62) is about 10^4 times faster than the rate of formation of the ethyl and and vinyl radicals by reaction (1). However, the rate of formation of cyclobutane by reaction (63) is 10^8 and 10^7 times faster than the unimolecular and bimolecular reactions of the diradicals, reactions (64) and (65), respectively.

Table 24

COMPARISON OF RATES FOR DETERMINATION OF THE MECHANISM OF THE INITIATION PROCESS

Reaction No.	Rate Expression	Rate/mol L^{-1} s^{-1}
62	$k_{62}[C_2H_4]^2$	4.5×10^{-9}
63 ≈ - 62	$k_{63}[\diagdown\!\diagup\cdot]$	2.3×10^{-9}
64	$k_{64}[\diagdown\!\diagup\cdot]$	8.5×10^{-17}
65	$k_{65}[\diagdown\!\diagup\cdot][C_2H_4]$	4.8×10^{-16}
1	$k_1[C_2H_4]^2$	5.4×10^{-13}

Hence although the diradicals from faster than the ethyl and vinyl radicals, almost all of these diradicals form either cyclobutane or undergo reverse dissociation by reaction (-62). Only a very small fraction leads to the formation of radicals by reactions (64) and (65). Comparison of the rates of reactions (64) and (65) with that of reaction (1) show that the rate of formation of the ethyl and vinyl radicals is 10^4 and 10^3 times faster than the formation of radicals by the reactions of the tetramethylene diradical. Calculations of the rates of reactions (1) and (65) at the lowest and highest temperatures studied in the present experiments indicate that the rate of reaction (1) is still 220 times faster than the rate of reaction (65) at 699 K. This ratio increases to 2800 at 819 K.

Therefore, even at the lowest temperature of the present study, the chain initiation through the formation of an intermediate diradical is not important. In the thermal reactions of ethylene, the most probable initiation reaction is the bimolecular reaction of ethylene to give ethyl and vinyl radicals. The mechanism of this reaction is probably a simple hydrogen transfer reaction, similar to head-to-tail association mechanism[125], which is postulated for the disproportionation reactions of radicals.

3. Heat of Formation of the Vinyl Radical

For the initiation process of the ethylene pyrolysis,

$$2C_2H_4 \rightarrow C_2H_5 + C_2H_3 \qquad (1)$$

the change in the enthalpy of the reaction is given as the following:

$$\Delta H_1^\circ = \Delta H_f^\circ(C_2H_5) + \Delta H_f^\circ(C_2H_3) - 2\Delta H_f^\circ(C_2H_4) \qquad (73)$$

The overall change in enthalpy is the difference between the enthalpy of activation for the forward and reverse reactions.

$$\Delta H_1^\circ = \Delta H_f^{\neq} - \Delta H_r^{\neq}$$

The relation between the enthalpy of activation, $\Delta H^{\neq}$, and the internal energy of activation, $\Delta E^{\neq}$, which is the increase in energy in passing from the initial state to the activated state, is

$$\Delta H^{\neq} = \Delta E^{\neq} + P\Delta V^{\neq}$$

where $\Delta V^{\neq}$ is the increase in volume in going from the initial state to the activated state. For gas reactions, $P\Delta V^{\neq}$ is generally expressed as

$$P\Delta V^{\neq} = \Delta n^{\neq} RT$$

where $\Delta n^{\neq}$ is the increase in the number of moles when the activated complex is formed from the reactants. In reaction (1), for example, two molecules of ethylene form one molecule in the activated state, so $\Delta n^{\neq}$ is equal to -1 for the forward process. Because the same change occurs in the number of moles for the reverse process, these $P\Delta V$ terms cancel and the enthalpy change for reaction (1) can be written as the difference between the forward and reverse internal energies of activation:

$$\Delta H_1^{\circ} = \Delta E_f^{\neq} - \Delta E_r^{\neq} \qquad (74)$$

The relationship between the experimental activation energy, E_A, and the internal energy of activation has been discussed by Pacey[126]. Starting from the thermodynamic formulation

of the activated complex theory[127,128],

$$k = \frac{k_B T \kappa}{h} e^{\Delta S^{\neq}/R} e^{-\Delta E^{\neq}/RT} e^{-\delta} \left(\frac{1 \text{ mole}}{L}\right)^{(1-m)} \qquad (75)$$

and using the definition for the Arrhenius or experimental activation energy,

$$E_A = - R \frac{d\ln k}{d(1/T)} \qquad (76)$$

the simplified relationship was obtained as in the equation below:

$$E_A = \Delta E^{\neq} + RT \qquad (77)$$

In equation (75), k_B is the Boltzmann constant, h the Planck constant, T the absolute temperature, R the gas constant, $\Delta S^{\neq}$ the entropy of activation with a standard state of 1 mol L^{-1}. δ represents $\Delta n^{\neq}$ and m shows the molecularity of the reaction. The transmission coefficient, κ, is often omitted.

When the expression of $\Delta E^{\neq}$ from equation (77) is used in equation (74), the term RT disappears and the overall change in enthalpy becomes equal to the difference in experimental activation energy between forward and reverse reactions.

$$\Delta H_1^o = (E_A)_f - (E_A)_r$$

The activation energy for the reverse of reaction (1) is assumed to be zero. It is generally assumed that in a radical disproportionation reaction, particularly for small radicals, there is no energy barrier for interaction and the reaction rate is thus determined only by the value of the frequency factor. When $(E_A)_r$ is taken as zero,

$$\Delta H_1^\circ = (E_A)_f$$

Therefore, the heat of formation of the vinyl radical may be obtained from the measured activation energy for reaction (1), 64.2 kcal mol^{-1}, together with values of $\Delta H_f^\circ(C_2H_4)$ and $\Delta H_f^\circ(C_2H_5)$. The heat of formation of ethylene is 12.5 kcal mol^{-1}. Values of ΔH_f° for the ethyl radical at 298 K are summarized in Table 25.

Table 25

HEAT OF FORMATION OF THE ETHYL RADICAL

Reference	$\Delta H_f^\circ(C_2H_5)$, kcal mol^{-1}	Method of Measurement
129, 130	26.0	Bromination of ethane
131	25.3 ± 1.2	Inverse iodination of EtI
132	26.2	Thermal decomposition of the ethyl radical
91	26.3	Calculation by an electrostatic model
133	28.0 ± 1	Radical buffer system

In his book, Benson[30] suggests 26 ± 1 kcal mol^{-1} for the heat of formation of the ethyl radical. Most of the data in Table 25 agree well with this estimation. The only high value comes from the results of a radical buffer system reported by Castelhano et al[133]. However, their technique, which involved the measurements of the equilibrium constants for the reactions of different radicals with MeI by EPR led to a high value also for ΔH_f^o of tertiary butyl radical. Until more confirmation is obtained, the value for the heat of formation of the ethyl radical is taken as 26 kcal mol^{-1} in the present study. Also a recent work on the pyrolysis of propane[134] supports this choice. The rate constant for the initiation process of propane, shown below, has been well established by several studies.

$$C_3H_8 \rightarrow CH_3 + C_2H_5$$

Juste et al.[134] report 84.9 kcal mol^{-1} for the activation energy of this reaction. For the above reaction, by taking the values $\Delta H_f^o(C_3H_8)$ = - 24.8 kcal mol^{-1}, $\Delta H_f^o(CH_3)$ = 35.1 kcal mol^{-1}, $\Delta H_f^o(C_2H_5)$ is obtained as 26.1 kcal mol^{-1}. If $\Delta H_f^o(C_2H_5)$ were 28 kcal mol^{-1} as suggested by Castelhano et al.[133], the activation energy for dissociation of propane would be 87.9 kcal mol^{-1}, which is higher than the currently accepted value.

Then, the value for the heat of formation of the vinyl radical can be calculated from equation (73) after the correction of ΔH_1^o to 298 K using equation (6). From Table 23, the heat capacity change for reaction (1) is -0.4 cal mol^{-1} K^{-1}. Then, ΔH_1^o at 298 K is calculated as 64.4 kcal mol^{-1}. Using equation (73),

$$64.4 = \Delta H_f^o(C_2H_3) + 26 - 25 .$$

$$\Delta H_f^o(C_2H_3) = 63.4 \text{ kcal mol}^{-1}$$

From the value of heat of formation of the vinyl radical and using the known values for heats of formation of H and C_2H_4, the bond dissociation energy for the C-H bond in ethylene can be determined from the reaction:

$$C_2H_4 \rightarrow C_2H_3 + H$$

Taking the values, $\Delta H_f^o(C_2H_4)$ = 12.5 kcal mol^{-1} and $\Delta H_f^o(H)$ = 52.1 kcal mol^{-1},

$$BDE(C_2H_3\text{-}H) = 63.4 + 52.1 - 12.5 = 103.0 \text{ kcal mol}^{-1}$$

Hence, the BDE for $(C_2H_3\text{-}H)$ is obtained as 103 kcal mol^{-1} from the present research.

Values of $\Delta H_f^o(C_2H_3)$ and the $BDE(C_2H_3\text{-}H)$ reported above contain the uncertainty of ± 2 kcal mol^{-1} as indicated in equation (55).

For the purpose of comparison, the available data for the heat of formation of the vinyl radical at 298 K are summarized in Table 26.

Table 26

HEAT OF FORMATION OF THE VINYL RADICAL

Reference	$\Delta H_f^o(C_2H_3)$ kcal mol^{-1}	Method of Measurement
135	65 ± 3	Electron-impact study
136	63 ± 3	Pyrolysis of divinyl mercury
68	61 ± 2	Shock-tube pyrolysis of propylene
47	≥68	Inverse iodination of vinyl iodide
137	59.6	Electron-impact study
138	71.5 ± 2.2	Ion cyclotron resonance technique
139	63	Energy-partitioning study
140	64	Electron-impact study
This work	63.4 ± 2	Kinetics of the pyrolysis of ethylene

In 1960, Harrison and Lossing[135] determined the heat of formation of the vinyl radical as 65 ± 3 kcal mol^{-1} from electron-impact studies. They produced the vinyl radical from the pyrolysis of methyl vinyl mercury and determined its ionization potential directly using a mass

spectrometer. Trotman-Dickenson and Verbeke[136] suggested 63 kcal mol^{-1} from the kinetic studies of the dissociation of divinyl mercury by the toluene-carrier technique and assigned an uncertainty of 3 kcal mol^{-1}. Later, a shock-tube study of the pyrolysis of propylene led Chappel and Shaw[68] to suggest 61 ± 2 kcal mol^{-1} for the heat of formation of the vinyl radical. From unpublished results on the reaction of HI with vinyl iodide, Golden and Benson[47] deduced that the heat of formation of the vinyl radical must be greater or equal to 68 kcal mol^{-1}. However, they also noted that complications in the kinetics were observed in their system. In 1971 Lossing[137] reported a value of 59.6 kcal mol^{-1} from mass spectrometric studies of the vinyl radical obtained from the pyrolysis of divinyl sulfone. Ionization potentials of the radicals were measured using an energy-resolved electron beam. A recent work by DeFrees et al.[138] on the studies of ion-molecule reactions using the ion cyclotron double resonance spectroscopy indicate a high value of 71.5 ± 2.2 kcal mol^{-1}, which yields 111 kcal mol^{-1} for the C-H bond dissociation energy in ethylene. This high value for $D(C_2H_3\text{-}H)$ appears to be incompatible with results of measurements of the energy-partitioning in the reaction of F atoms with ethylene[139].

$$F + C_2H_4 \rightarrow HF^{\neq} + C_2H_3 \qquad (78)$$

Analysis of the rotational distribution of the energy in the various vibrational levels of the newly-formed HF molecule were interpreted to indicate that the exothermicity of reaction (78) was 32 kcal $mole^{-1}$ and therefore, the BDE in C_2H_3-H was 103 kcal mol^{-1}, giving a value for $\Delta H_f^o(C_2H_3)$ as 63 kcal mol^{-1}. Recent studies of appearance potentials for some fragmentation reactions, for example,

$$e^- + CH_3COOC_2H_5 \rightarrow H\text{-}C(OH^+)(OH) + C_2H_3 + 2e^-$$

which give directly a value for the heat of formation of the vinyl radical, have given values of $\Delta H_f^o(C_2H_3)$ = 64 kcal mol^{-1} [140]. It seems therefore, that the only published studies which indicate a value for $\Delta H_f^o(C_2H_3)$ greater than about 65 kcal mol^{-1} are the measurements using the ion-cyclotron resonance technique.

4. Evaluation of the Method

The kinetic method applied in the present study, which is based on the analysis of the effect of small quantities of additives on the rate of the initiation step of the pyrolysis of ethylene has led to reasonable values for the Arrhenius parameters of reaction (1). The calculated value of the heat of formation of the vinyl radical is in good agreement with other studies.

In some chain reaction mechanisms, the initiation step leads to the formation of a product which is not produced by any subsequent reactions in the system and the rate of formation of this product may be equated to the rate of the initiation step. An example for this is the pyrolysis of ethane, whose rate of the initiation step can be determined by the rate of formation of the product, methane. In some other cases however, such as the chain reactions occurring during the pyrolysis of ethylene, the initiation step does not lead to the formation of a specific product and there is no direct and simple means of identifying the initiation step and measuring its rate constant. In such reactions, the method described in this study can be very helpful. Some necessary precautions that should be taken into account are that the initial rates of the products should be measurable, the only effect of the additive should be to add a new initiation process and the rate constant of the dissociation step of the additive should be well determined. As the number of additives is increased, the accuracy of the initiation rate constant in question may be improved. As mentioned earlier, the experimental errors come directly from the determination of the initial rates. Therefore, the experimental conditions such as the temperature control and sensitivity of the analytical systems are very important. The only disadvantage of the method

seems to be the use of other literature values for the initiation rate constants of additives. But this should not be a problem as long as the additives are chosen carefully. The method is very promising and may be applied to other chain reactions in which the rate constant of the initiation step cannot be easily measured by other techniques.

CHAPTER VI

PYROLYSIS OF ETHYLENE

Pyrolysis of ethylene has been performed at all temperatures and pressures where the pyrolysis of the mixtures of ethylene+additive was studied. The two exceptions were at 732 K and 756 K for 300 torr ethylene pressure. At these temperatures the initial rates of the products were calculated from their Arrhenius plots of V_0. Studies of the ethylene pyrolysis therefore cover the temperature range 699-819 K with a pressure range of 75-400 torr.

In the experiments where 1-butene was used as the additive, the product 1-butene could not be followed during the pyrolysis of the mixture. For this reason, 1-butene analysis was not attempted from the pyrolysis of ethylene alone. The same applies for the product ethane when the additive in the mixtures was ethane. Hence the number of products analyzed from the pyrolysis of ethylene alone was the same as for the pyrolysis of the ethylene+additive mixtures. The maximum percent conversions of ethylene were 2×10^{-2}% at 699 K and 1×10^{-3}% at 773 K at the highest reaction pressure and longest reaction time. The total ethylene conversion was obtained from the summation of all the measured reaction products. The initial rates

were measured within a much smaller range of percentage conversion. The conversion of ethylene within which the initial rates were measured was 7×10^{-3}% at 699 K and 8×10^{-3}% at 773 K, both at the highest pressures.

Except the ones that are given as examples in Chapters III and IV, the yield-time plots of the products at all temperatures and pressures from the pyrolysis of ethylene alone are given in Appendices A and B together with the corresponding plots of the mixture pyrolysis. For all products, first a linear increase of yield with respect to reaction time was observed, then the yields increased curving upwards. This behaviour indicates the formation of these products by secondary reactions. The linear stage of the reaction was shortest at the highest temperatures and pressures. Generally this portion was shorter for propylene than the other products showing the early start of self-acceleration for this product. The discussion of the mechanism will be confined to the primary reactions occurring during the linear region of the yield-time curves.

1. Orders and Activation Energies for the Formation of Products

From the plots of the logarithm of the initial rate against the logarithm of the initial pressures, the order

for the initial rate of formation of each product with respect to ethylene was obtained. These order plots are shown in Figures 29-31. The order for methane increased from 1.1 at 699 K to 2.2 at 803 K. Ethane has an order of 2.0 at all temperatures. The order for propylene is 2.7 at all temperatures except the lowest temperature, 699 K, where it is 2.3. At 75 torr ethylene pressure, propylene has lower orders at all temperatures. The orders for 1-butene and butadiene were determined at 803 K, as 1.8 and 1.9 respectively.

From plots of the logarithm of the initial rate against the reciprocal of the absolute temperature at a constant pressure of ethylene, the activation energy for the initial rate of formation of each product was obtained. These plots are shown in Figures 32 to 34. These data are the results of the ethylene pyrolysis experiments that were performed over the whole course of this study. Consistency of the results is reasonable considering the different experimental conditions, such as different reaction vessels and furnace, used during the complete study. It should be noted that in the experiments with additives, because the ratio of rates was measured, consistency within a set of experiments was more important than exact agreement of the initial rates from the pyrolysis of ethylene alone.

Figure 29 - Order Plots for Methane from the Pyrolysis of Ethylene

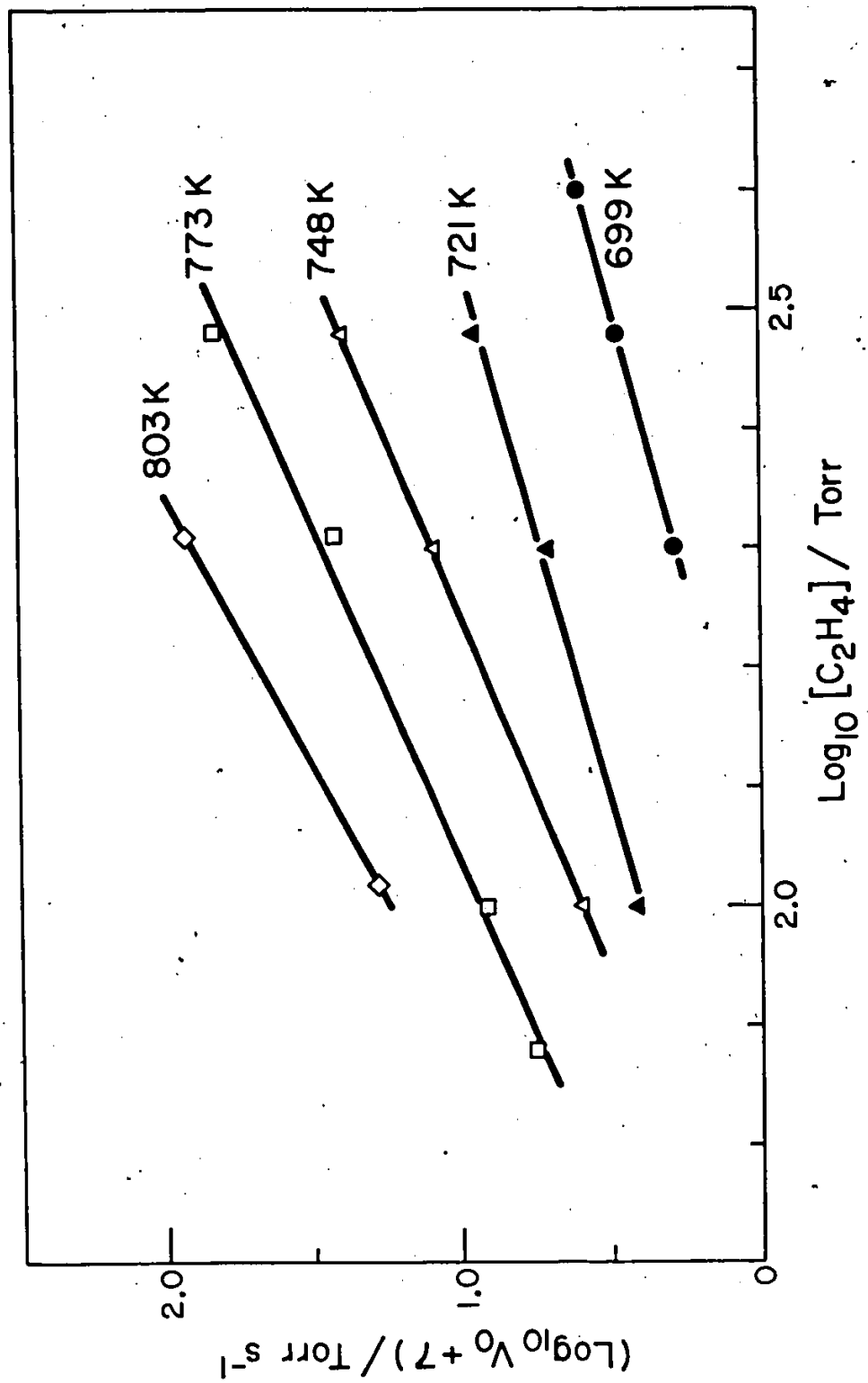

803 K
773 K
748 K
721 K
699 K
2.0
2.5
$\log_{10}[C_2H_4]$ / Torr
0
1.0
2.0
$(\log_{10} V_0 + 7)$ / Torr s^{-1}

Figure 30 - Order Plots for Ethane from the Pyrolysis of Ethylene

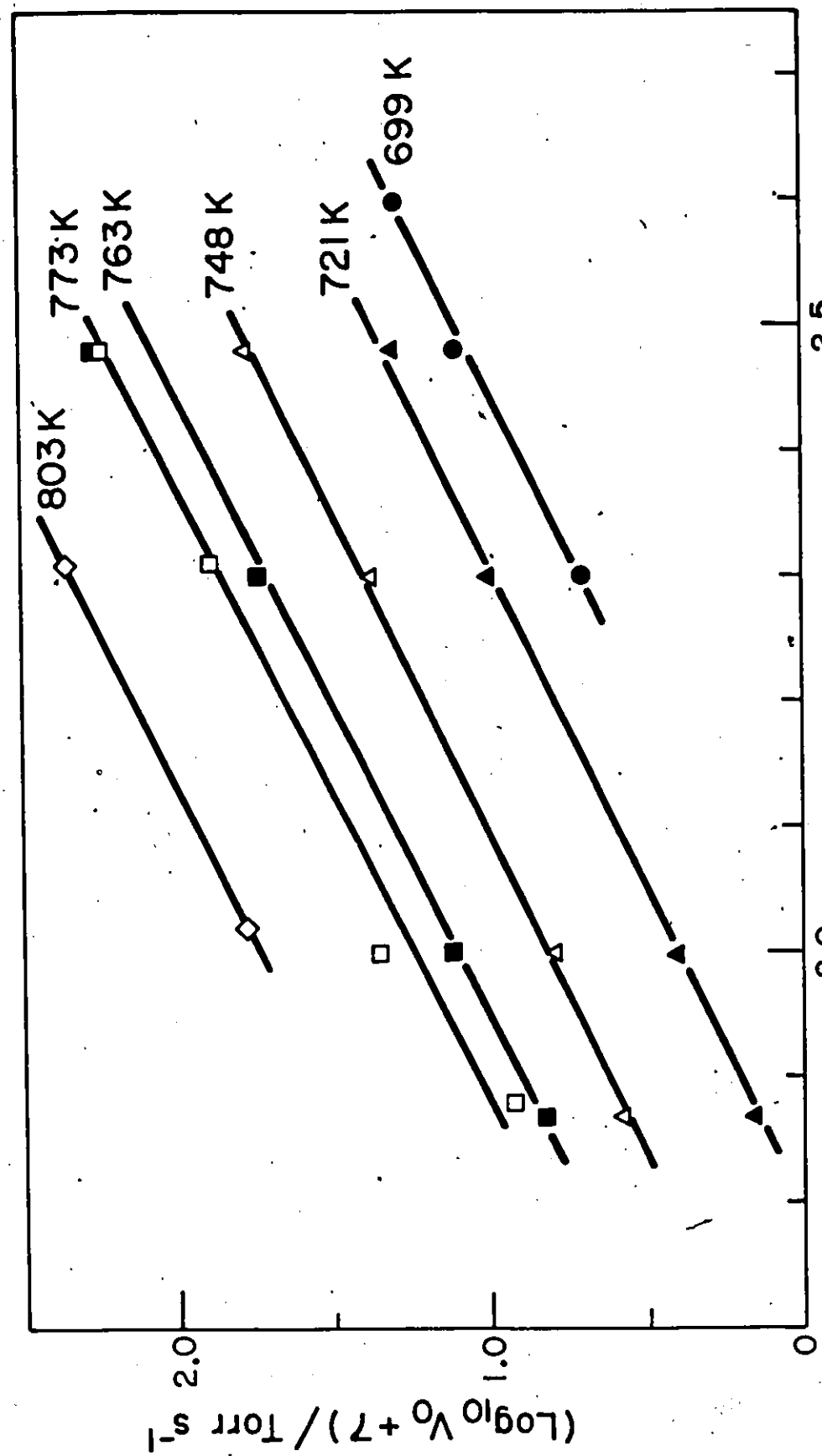

803K
773K
763K
748K
721K
699K
2.5
2.0
$\log_{10}[C_2H_4]$ / Torr
0
1.0
2.0
$(\log_{10} V_0 + 7)$ / Torr s^{-1}

Figure 31 - Order Plots for Propylene from the Pyrolysis of Ethylene

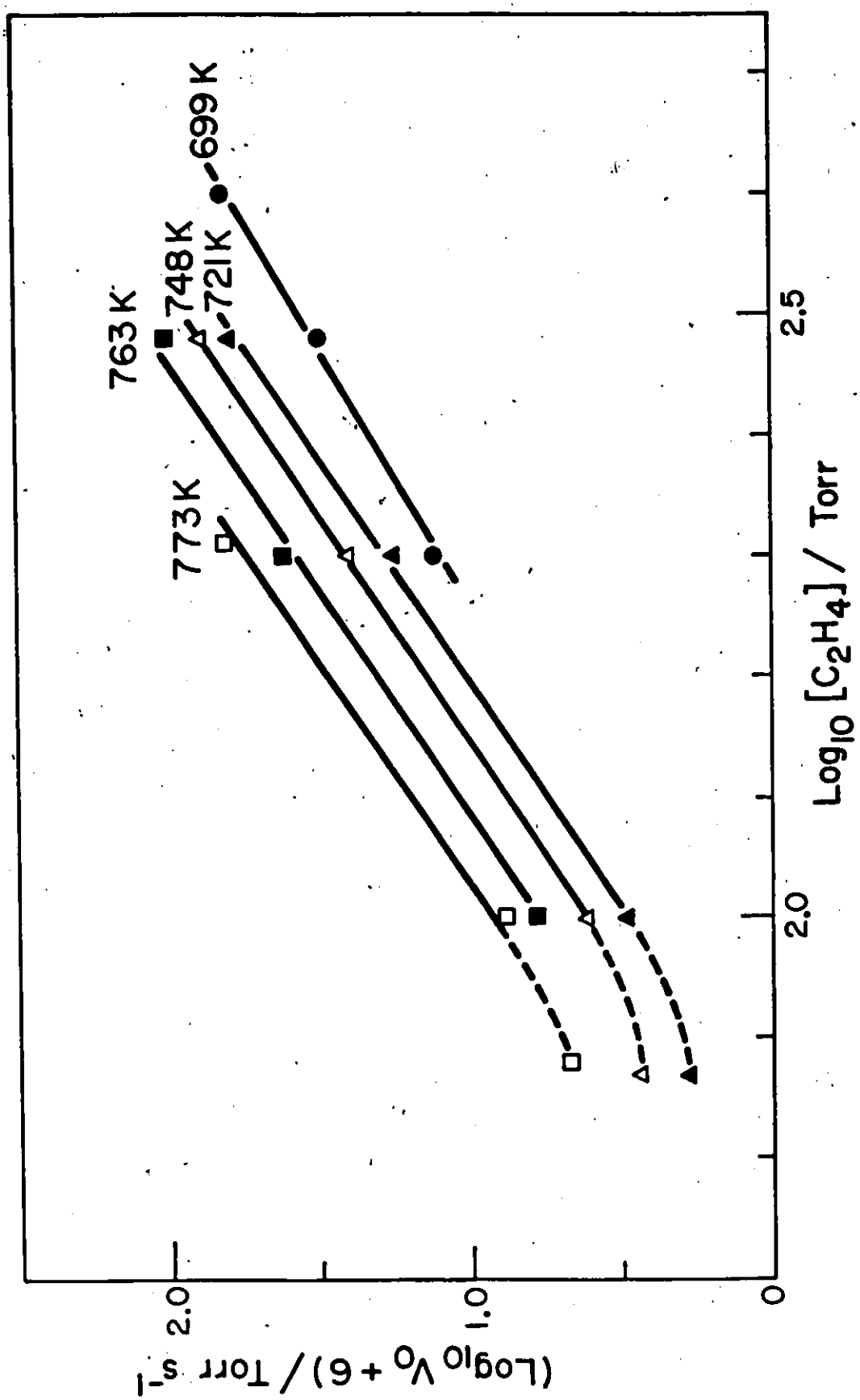
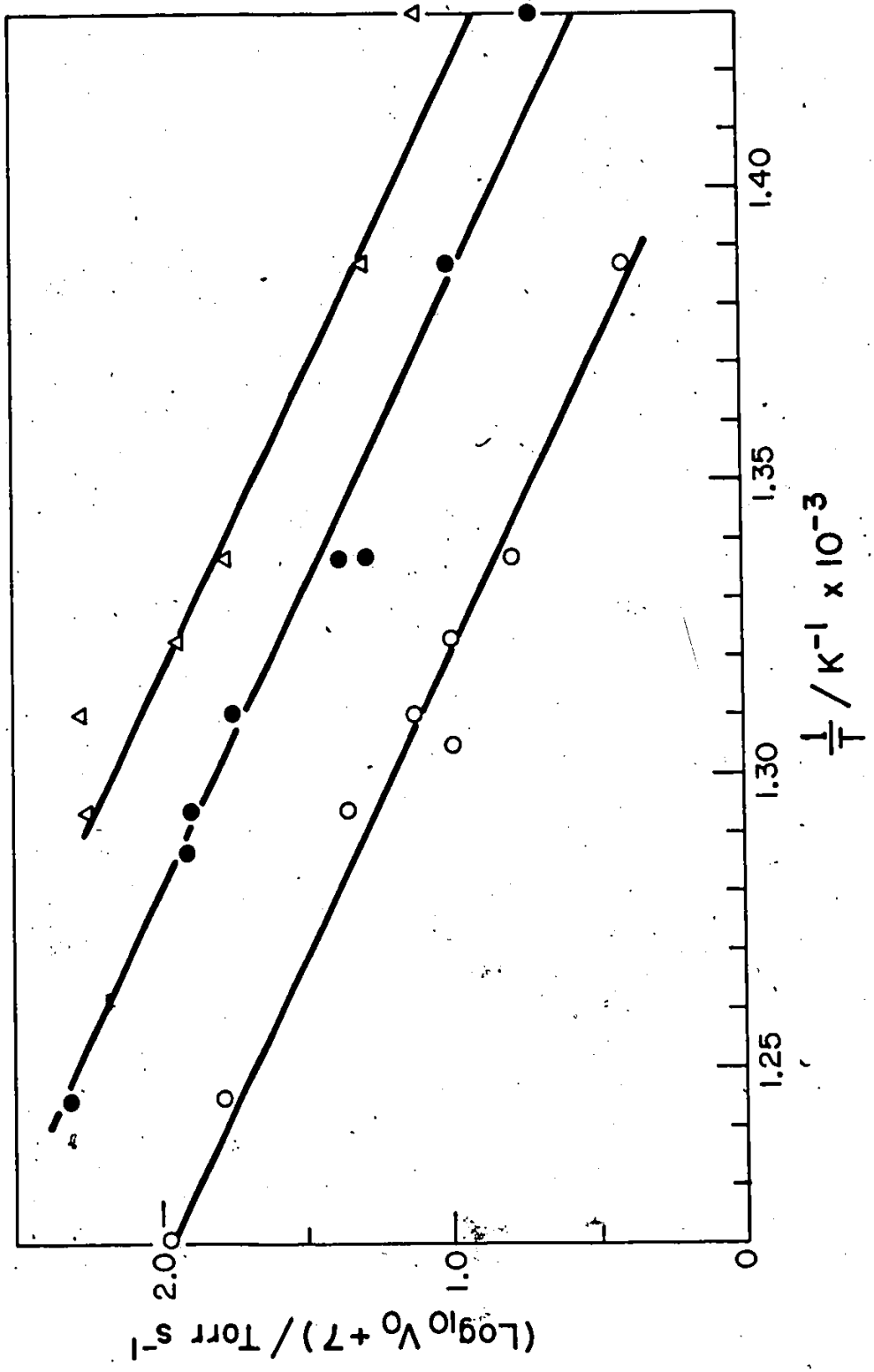

699 K
748K
721K
763 K
773K
2.5
2.0
0
1.0
2.0
$Log_{10}[C_2H_4]$ / Torr
$(Log_{10} V_o + 6)$ / Torr s^{-1}

Figure 32 - Arrhenius Plots for Methane from the Pyrolysis of Ethylene

O 100 torr C_2H_4
● 200 torr C_2H_4
Δ 300 torr C_2H_4


(Log10 V0 +7) / Torr s-1
2.0
1.0
0
1.25
1.30
1.35
1.40
1/T / K-1 x 10-3

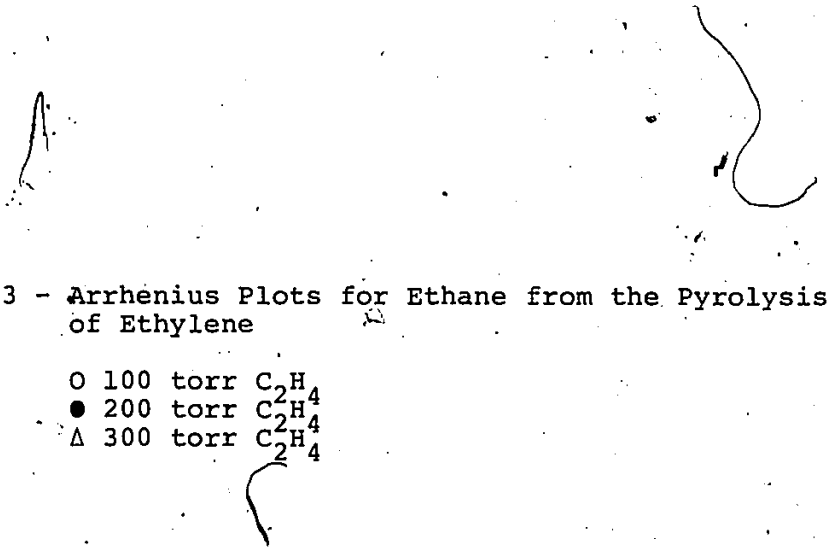


Figure 33 - Arrhenius Plots for Ethane from the Pyrolysis of Ethylene

O 100 torr C_2H_4
● 200 torr C_2H_4
Δ 300 torr C_2H_4

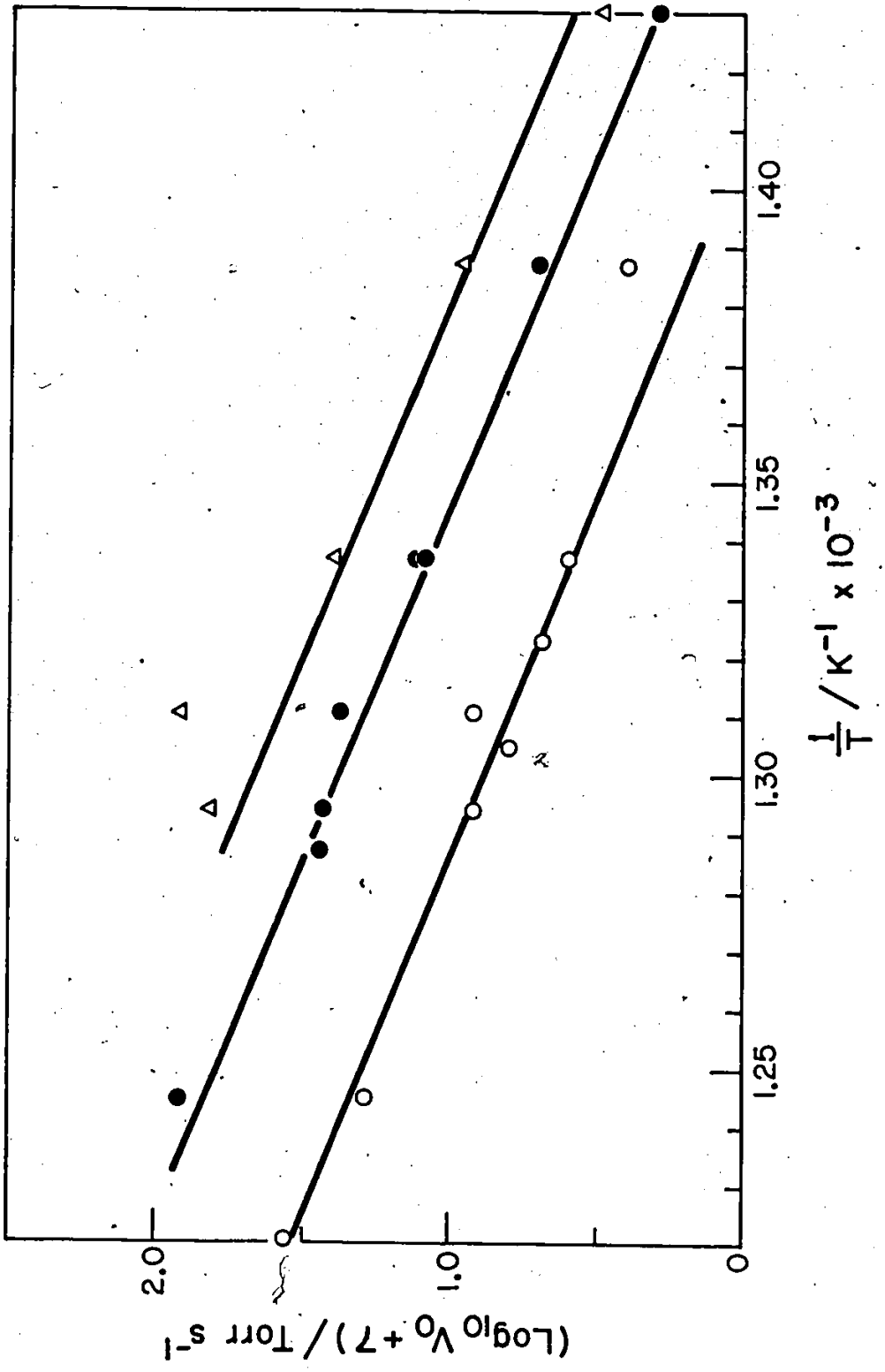
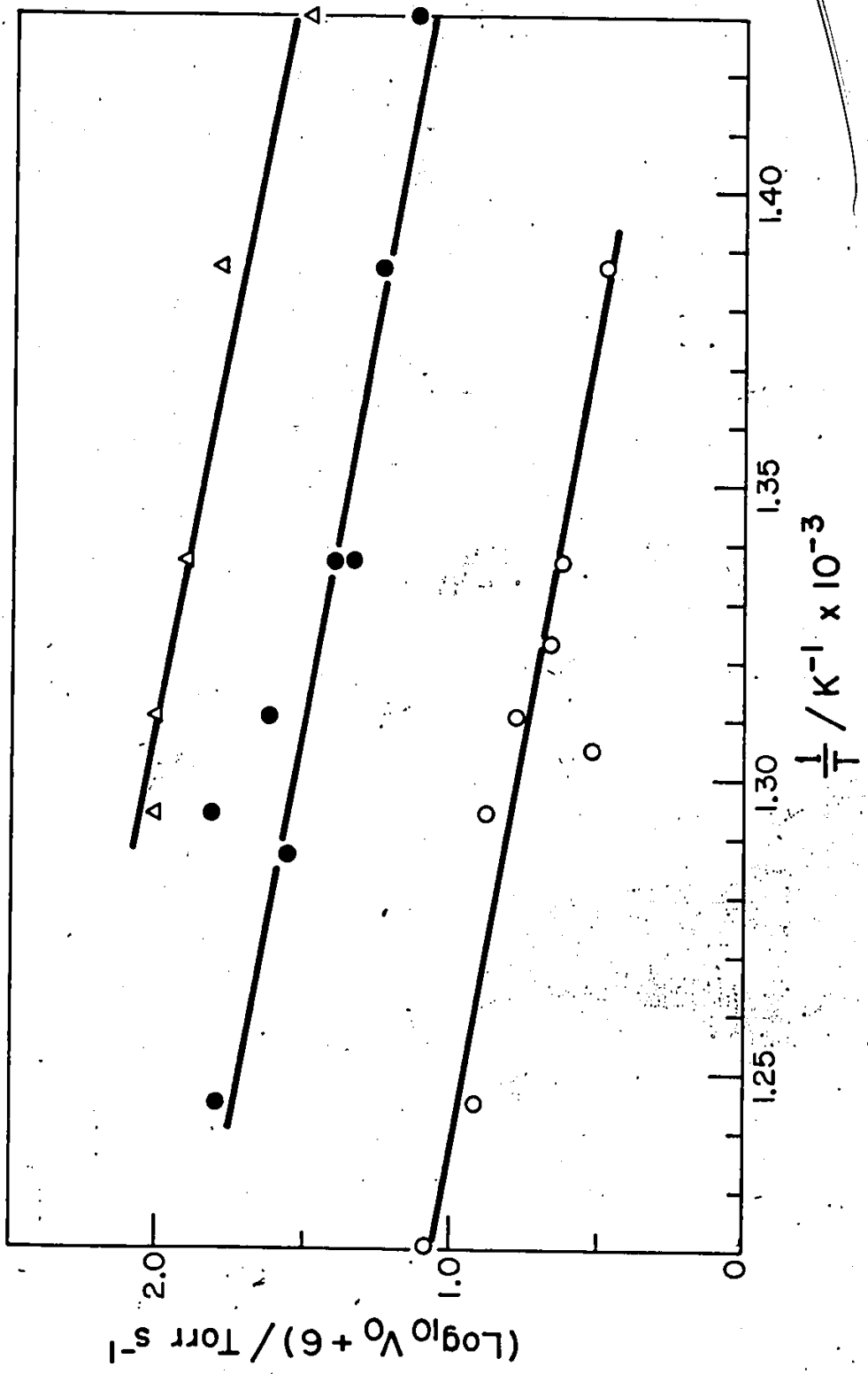

(Log10 V0 +7) / Torr s-1
2.0
1.0
0
1.25
1.30
1.35
1.40
1/T / K-1 x 10-3

Figure 34 - Arrhenius Plots for Propylene from the Pyrolysis of Ethylene

O 100 torr C_2H_4
● 200 torr C_2H_4
Δ 300 torr C_2H_4


(Log10 V0 + 6) / Torr s-1
2.0
1.0
0
1.25
1.30
1.35
1.40
1/T / K-1 x 10-3

The reaction orders and activation energies for each product are summarized in Table 27. The error limits quoted for activation energies in this table are the estimated values considering the scatter of data. Likewise, the errors in the calculation of orders were estimated as 10%.

Table 27

SUMMARY OF ORDERS (WITH RESPECT TO ETHYLENE) AND ACTIVATION ENERGIES FOR THE INITIAL FORMATION OF PRODUCTS

Product	Temperature range/K	E/kcal mol^{-1}
Methane	699-819	38 ± 2
Ethane	699-819	43 ± 2
Propylene	699-819	16 ± 2
1-Butene	748-819	30 ± .3
Butadiene	803-819	57 ± .3

	Order with respect to C_2H_4					
Product	699 K	721 K	748 K	763 K	773 K	803 K
Methane	1.1	1.1	1.6	1.8	1.8	2.2
Ethane	2.0	2.0	2.0	2.0	2.0	2.0
Propylene	2.3	2.7	2.7	2.7	2.7	-
1-Butene	-	-	-	-	-	1.8
Butadiene	-	-	-	-	-	1.9

The activation energies and orders determined in this research are in substantial agreement with earlier results[16,20]. The activation energies of propylene and butadiene however, are smaller than the values reported before.

The distribution of products in the initial stages of the pyrolysis of ethylene was well determined in the temperature range 699 to 819 K. Propylene was the largest product. At low temperatures, propylene was about 20 times larger than ethane but as the temperature was increased the relative yield of ethane was also increased. At the highest temperatures, propylene was larger than ethane only by about 1.3 times. Yields of 1-butene were about 2 times larger than ethane at 748 K. At higher temperatures than this, ethane was almost equal to or slightly larger than 1-butene. The production of methane and butadiene were less than the other products. At the two highest temperatures, where it was measured, butadiene was approximately equal to methane. The yield of ethane was about twice as that of methane and this ratio was slightly increased with increasing temperature.

2. Mechanism of the Pyrolysis of Ethylene

The results obtained during this study largely substantiate the mechanism of the thermal reactions of ethylene around 773 K proposed earlier[20]. The analysis of the mechanism would be very complex if all the possible reactions were included. The formation of methane, ethane, propylene and 1-butene however, may be discussed using a simplified mechanism. This mechanism was suggested by Back and Martin[20]

and is given, with minor modifications, in the following page. It can be summarized as follows.

The main initiation process under the present conditions is the bimolecular reaction of ethylene to produce ethyl and vinyl radicals. Radicals produced in the system react by the following propagation processes.

- Addition to ethylene and reverse decomposition
- Hydrogen abstraction from ethylene
- For C_5 and C_6 radicals, isomerization followed by decomposition to an alkene and an alkyl radical.

In this set of propagation reactions, the ethyl radical has probably the highest steady-state concentration. Therefore the termination reaction is predominantly the combination or disproportionation reactions of the ethyl radical.

In the mechanism presented here only reactions of the ethyl radical, and other saturated radicals, methyl, n-propyl, n-butyl, n-pentyl and n-hexyl radicals are considered. Abstraction, addition, decomposition and isomerization reactions of these radicals lead to the formation of the observed products. Methane and ethane are formed by the hydrogen abstraction reactions of the methyl and ethyl radicals, respectively, from ethylene. Propylene and 1-butene are produced by the decomposition

$$2C_2H_4 \rightarrow C_2H_5 + C_2H_3 \qquad (1)$$

$$C_2H_5 + C_2H_4 \rightarrow C_2H_6 + C_2H_3 \qquad (79)$$

$$C_2H_5 + C_2H_4 \rightleftharpoons n\text{-}C_4H_9 \qquad (80), (-80)$$

$$n\text{-}C_4H_9 + C_2H_4 \rightleftharpoons n\text{-}C_6H_{13} \qquad (81), (-81)$$

$$n\text{-}C_6H_{13} + C_2H_4 \rightarrow n\text{-}C_8H_{17} \qquad (82)$$

$$n\text{-}C_6H_{13} \rightarrow 2\text{-}C_6H_{13} \qquad (83)$$

$$2\text{-}C_6H_{13} \rightarrow C_3H_6 + n\text{-}C_3H_7 \qquad (84)$$

$$n\text{-}C_6H_{13} \rightarrow 3\text{-}C_6H_{13} \qquad (85)$$

$$3\text{-}C_6H_{13} \rightarrow 1\text{-}C_4H_8 + C_2H_5 \qquad (86)$$

$$3\text{-}C_6H_{13} \rightarrow 1\text{-}C_5H_{10} + CH_3 \qquad (87)$$

$$CH_3 + C_2H_4 \rightarrow CH_4 + C_2H_3 \qquad (88)$$

$$CH_3 + C_2H_4 \rightleftharpoons n\text{-}C_3H_7 \qquad (89), (-89)$$

$$n\text{-}C_3H_7 + C_2H_4 \rightleftharpoons n\text{-}C_5H_{11} \qquad (90), (-90)$$

$$n\text{-}C_5H_{11} \rightarrow 2\text{-}C_5H_{11} \qquad (91)$$

$$2\text{-}C_5H_{11} \rightarrow C_3H_6 + C_2H_5 \qquad (92)$$

$$n\text{-}C_5H_{11} + C_2H_4 \rightarrow n\text{-}C_7H_{15} \qquad (93)$$

$$2C_2H_5 \rightarrow C_4H_{10} \qquad (t)$$

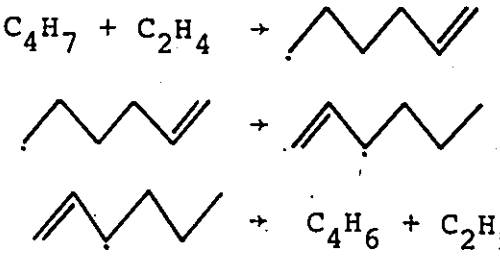
$$\text{or} \rightarrow C_2H_4 + C_2H_6$$

of larger radicals after isomerization. The n-hexyl radical is the first radical in the polymerization process to undergo isomerization and it has been suggested that the relative importance of 1,5- and 1,4-hydrogen migration of this radical determines the yields of propylene and 1-butene. Although the 1,5-hydrogen migration is the most facile isomerization for n-hexyl radicals, at high temperatures 1,4-hydrogen migration also becomes important. The present results show that at 803 K, the initial rate of formation of 1-butene, which is the product of 1,4-isomerization of n-hexyl radicals, is 0.6 of the initial rate of formation of propylene, which is the product of 1,5-isomerization of n-hexyl radicals, when the ethylene pressure is 100 torr. This suggests that the rates of 1,5- and 1,4-isomerization processes become almost comparable at these temperatures.

The main omission in the mechanism outlined here for the pyrolysis of ethylene however, is the set of reactions involving the vinyl radical. Because of the lack of detailed knowledge of the corresponding reactions of unsaturated radicals it was not judged useful to outline a mechanism comparable to that for the saturated radicals. The most important product which is probably formed through reactions of the vinyl radical is butadiene. The following reactions are suggested to account for the formation of this product.

$$C_2H_3 + C_2H_4 \rightarrow C_4H_7$$

$$C_4H_7 + C_2H_4 \rightarrow$$



$$\rightarrow C_4H_6 + C_2H_5$$

On the other hand, since propylene, ethane, 1-butene and methane constitute more than about 90% of all the products in the initial stages of the thermal reactions of ethylene and their mechanism of formation may be explained through reactions of the saturated radicals, the set of propagation reactions involving the vinyl radical probably favour polymerization reactions with consequent formation of higher molecular weight products.

3. Analysis of the Mechanism of the Formation of Products

Except for the product ethane, the analysis of this mechanism with regard to the kinetics of the formation of the main products has not previously been discussed in detail. In the following sections, the rates of formation of the main products ethane, methane and propylene will be discussed in this respect and the experimental orders and activation energies of these products will be compared with those predicted from the mechanism. The data for 1-butene and butadiene are not sufficient for a good test of

the mechanism. The principle criterion in the analysis of the mechanism is the importance of the decomposition process for the radicals relative to the addition to ethylene. It is assumed that decomposition becomes progressively more important as the number of carbon atoms in the radical increases. Application of this assumption to the mechanism and its effect on the orders of the rates of formation of the products will be examined.

i. Ethane

In this mechanism, ethane is formed by the hydrogen abstraction of the ethyl radical from ethylene. The rate of formation of ethane is

$$\frac{d[C_2H_6]}{dt} = k_{79}\ [C_2H_5][C_2H_4] \tag{94}$$

Assuming that the main termination process involves ethyl radicals, the concentration of the ethyl radicals may be obtained from the rates of the initiation and termination reactions.

$$[C_2H_5] = (k_1/2k_t)^{1/2}[C_2H_4] \tag{95}$$

Then, equation (94) is rearranged as the following

$$\frac{d[C_2H_6]}{dt} = k_{79}\ \left(\frac{k_1}{2k_t}\right)^{1/2}\ [C_2H_4]^2 \tag{96}$$

From this equation, the rate of ethane production is second order with respect to ethylene. This order was observed for ethane under all experimental conditions (Table 27). Therefore, the agreement of the experimental results with the suggested mechanism is excellent for ethane.

The activation energy for the formation of ethane can be estimated from equation (96). Taking E_1 = 64.2 kcal mol^{-1} from the present study and assuming E_t = 0 and E_{79} = 10 kcal mol^{-1} [115], the activation energy required for the formation of ethane is

$$E_{C_2H_6} = 10 + \frac{1}{2}(64.2 - 0) = 42.1 \text{ kcal mol}^{-1} \qquad (97)$$

This value is close to the activation energy determined for ethane experimentally, 43 ± 2 kcal mol^{-1}.

ii. Methane and Propylene

The production of methane occurs by the hydrogen abstraction of the methyl radical from ethylene. Hence the rate of formation of methane is

$$\frac{d[CH_4]}{dt} = k_{88}\,[CH_3][C_2H_4] \qquad (98)$$

The rate of formation of propylene on the other hand is expressed in terms of 2-hexyl and 2-pentyl radicals

$$\frac{d[C_3H_6]}{dt} = k_{84}\ [2\text{-}C_6H_{13}] + k_{92}\ [2\text{-}C_5H_{11}] \qquad (99)$$
$$\qquad\qquad\qquad\qquad\quad A \qquad\qquad\qquad B$$

since these are the two sources of propylene formation. These terms will be referred to as A and B.

Assuming steady-state conditions, concentrations of the methyl, 2-hexyl and 2-pentyl radicals can be expressed as the following

$$[CH_3] = \frac{k_{87}[3\text{-}C_6H_{13}] + k_{-89}[n\text{-}C_3H_7]}{k_{88}[C_2H_4] + k_{89}[C_2H_4]} \qquad (100)$$

$$[2\text{-}C_6H_{13}] = \left(\frac{k_{83}}{k_{84}}\right)\ [n\text{-}C_6H_{13}] \qquad (101)$$

$$[2\text{-}C_5H_{11}] = \left(\frac{k_{91}}{k_{92}}\right)\ [n\text{-}C_5H_{11}] \qquad (102)$$

In order to obtain the concentrations of methyl, 2-hexyl and 2-pentyl radicals in terms of only the ethyl radical and ethylene, the steady-state concentration of all the other radicals that are involved in equations (100)-(102) should also be determined. The following expressions are obtained for n-propyl, n-butyl, n-pentyl and 3- and n-hexyl radicals.

$$[n\text{-}C_3H_7] = \frac{k_{89}[CH_3][C_2H_4] + k_{-90}[n\text{-}C_5H_{11}] + k_{84}[2\text{-}C_6H_{13}]}{k_{-89} + k_{90}\ [C_2H_4]} \qquad (103)$$

$$[n\text{-}C_4H_9] = \frac{k_{80}[C_2H_5][C_2H_4] + k_{-81}[n\text{-}C_6H_{13}]}{k_{-80} + k_{81}[C_2H_4]} \quad (104)$$

$$[n\text{-}C_5H_{11}] = \frac{k_{90}\ [n\text{-}C_3H_7][C_2H_4]}{k_{-90} + k_{91} + k_{93}[C_2H_4]} \quad (105)$$

$$[3\text{-}C_6H_{13}] = \left(\frac{k_{85}}{k_{86} + k_{87}}\right)\ [n\text{-}C_6H_{13}] \quad (106)$$

$$[n\text{-}C_6H_{13}] = \frac{k_{81}[n\text{-}C_4H_9]\quad [C_2H_4]}{k_{-81} + k_{83} + k_{85} + k_{82}[C_2H_4]} \quad (107)$$

From the analysis of these equations, the steady-state concentration of the n-hexyl radical is obtained as:

$$[n\text{-}C_6H_{13}] = \frac{\dfrac{k_{80}k_{81}[C_2H_5][C_2H_4]^2}{k_{-80} + k_{81}[C_2H_4]}}{k_{-81} + k_{83} + k_{85} + k_{82}[C_2H_4] - \dfrac{k_{-81}\ k_{81}[C_2H_4]}{k_{-80} + k_{81}[C_2H_4]}} \quad (108)$$

Taking

$$\alpha = \frac{k_{80}k_{81}[C_2H_5][C_2H_4]^2}{k_{-80} + k_{81}[C_2H_4]} = \frac{k_{80}k_{81}\left(\frac{k_1}{2k_t}\right)^{1/2}[C_2H_4]^3}{k_{-80} + k_{81}[C_2H_4]} \quad (109)$$

$$\beta = k_{-81} + k_{83} + k_{85} + k_{82}[C_2H_4] - \frac{k_{-81}\ k_{81}[C_2H_4]}{k_{-80} + k_{81}[C_2H_4]} \quad (110)$$

the concentration of n-hexyl radicals is equivalent to α/β. The methyl radical concentration is dependent on both the 3-hexyl and n-propyl radical concentrations. Defining γ

$$\gamma = k_{-89} + k_{90}[C_2H_4] - \frac{k_{-90}k_{90}[C_2H_4]}{k_{-90} + k_{91} + k_{93}[C_2H_4]} \quad (111)$$

and using equation (106) for the dependence of the concentration of 3-hexyl on that of n-hexyl, the steady-state concentration of the methyl radical which is now expressed only in terms of the ethylene concentration is obtained.

$$[CH_3] = \frac{\frac{k_{85}k_{87}}{k_{86}+k_{87}}\frac{\alpha}{\beta} + \frac{k_{83}k_{-89}\alpha}{\beta\gamma}}{k_{88}[C_2H_4] + k_{89}[C_2H_4] - \frac{k_{-89}k_{89}[C_2H_4]}{\gamma}} \quad (112)$$

Combining this equation with equation (98), the rate of formation of methane can be written as in equation (113), which is dependent only on the concentration of ethylene.

$$\frac{d[CH_4]}{dt} = \frac{\frac{k_{85}k_{87}k_{88}}{k_{86}+k_{87}}\frac{\alpha}{\beta}[C_2H_4] + \frac{k_{83}k_{-89}k_{88}}{\beta\gamma}[C_2H_4]}{k_{88}[C_2H_4] + k_{89}[C_2H_4] - \frac{k_{-89}k_{89}[C_2H_4]}{\gamma}} \quad (113)$$

The order of the rate of methane formation with respect to ethylene concentration will hence be one degree higher than the order of the rate of formation of the methyl radical.

To obtain the rate expression for propylene in terms of ethylene, the dependence of the concentrations of 2-hexyl and 2-pentyl radicals on ethylene concentration should be defined. From equations (101) and (108) the steady-state concentration of 2-hexyl radical is

$$[2\text{-}C_6H_{13}] = \frac{(\frac{k_{83}}{k_{84}})\ \frac{k_{80}k_{81}[C_2H_5][C_2H_4]^2}{k_{-80}+k_{81}[C_2H_4]}}{k_{-81}+k_{83}+k_{85}+k_{82}[C_2H_4] - \frac{k_{-81}\ k_{81}[C_2H_4]}{k_{-80}+k_{81}[C_2H_4]}} \qquad (114)$$

The steady-state concentration of 2-pentyl radical is dependent on the concentration of n-propyl radical which in turn is expressed in terms of the concentrations of methyl and 2-hexyl radicals. Hence

$$[2\text{-}C_5H_{11}] = (\frac{k_{91}}{k_{92}})\ (\frac{k_{90}[C_2H_4)}{k_{-90}+k_{91}+k_{93}[C_2H_4]})$$

$$(\frac{k_{89}[CH_3][C_2H_4] + k_{84}[2\text{-}C_6H_{13}]}{k_{-89}+k_{90}[C_2H_4] - \frac{k_{-90}k_{90}[C_2H_4]}{k_{-90}+k_{91}+k_{93}[C_2H_4]}}) \qquad (115)$$

Using the values of α, β and γ in equations (114) and (115), the two terms in the rate equation of propylene can now be rewritten.

Term A

$$k_{84}[2\text{-}C_6H_{13}] = k_{83}\frac{\alpha}{\beta} \tag{116}$$

Term B

$$k_{92}[2\text{-}C_5H_{11}] = \frac{k_{90}k_{91}[C_2H_4]}{k_{-90}+k_{91}+k_{93}[C_2H_4]}\left[\frac{k_{89}[C_2H_4]}{\gamma}\right. \tag{117}$$

$$\left.\frac{\frac{k_{85}\,k_{87}}{k_{86}+k_{87}}\frac{\alpha}{\beta} + k_{83}k_{-89}\frac{\alpha}{\beta\gamma}}{k_{88}[C_2H_4] + k_{89}[C_2H_4] - \frac{k_{-89}k_{89}[C_2H_4]}{\gamma}}) + k_{83}\frac{\alpha}{\beta\gamma}\right]$$

Determination of the order of the rate of propylene formation on ethylene will be made using the equations (116) and (117). For methane, reference will be made to equation (113).

Several possibilities may be examined. In the case where it is assumed that the decomposition reactions of all the radicals are much faster than their addition reactions,

For α in equation (109), $k_{-80} >> k_{81}[C_2H_4]$ and this leads to an order of 3.

For β in equation (110), $k_{-80} >> k_{81}[C_2H_4]$ and

$$(k_{-81}+k_{83}+k_{85}) >> (k_{82} - \frac{k_{-81}k_{81}}{k_{-80}})[C_2H_4]$$

and there is no dependence on ethylene concentration.

For γ in equation (111), $k_{-90}+k_{91} >> k_{93}[C_2H_4]$ and

$$k_{-89} >> (k_{90} - \frac{k_{-90}\, k_{90}}{k_{-90}+k_{91}})[C_2H_4]$$

and again no dependence on ethylene concentration. Then, from equation (113), the order of the rate of formation of methane will be 3. The order of rate of propylene formation will be 3 from term A, equation (116), and 4 from term B. These orders are higher than the experimentally observed orders for methane and propylene.

The assumption concerning the importance of the decomposition of the radicals is, of course, not valid for the methyl and ethyl radicals and the decomposition reactions of these radicals were not included in the mechanism. It may now be suggested that the decomposition of the n-propyl radical is also slower than its addition to ethylene, but the original assumption holds for the n-butyl and higher radicals. The validity of this will be discussed later.

With these assumptions, terms α and β have again orders of 3 and zero, respectively. But the term γ changes its order to 1 because of the conditions $k_{93}[C_2H_4] << k_{-90} + k_{91}$ and $[k_{90} - (k_{-90}k_{90})/(k_{-90} + k_{91})][C_2H_4] >> k_{-89}$. Then, the rate of methane formation will have an order of 3 from the term including the 3-hexyl radical or 2 from the

term including the n-propyl radical. The rate of propylene production is, on the other hand, third order because of term A. The first part of term B will have the same order as in methane formation, i.e., between 3 and 2. The second part in term B will have an order of 3 because of the 2-hexyl radical.

Thus the effect of the assumption concerning the n-propyl radical is to lower the order of the rate of formation of methane to 2, provided the main source of the methyl radical is the n-propyl radical. The order of the rate of formation of propylene will remain as 3 if the main source is the decomposition of the 2-hexyl radical. The observed order for propylene was, however, somewhat less than 3 while the order for methane formation was also less than 2. Nevertheless this explanation appears promising because experimentally the order of the rate of formation of methane was consistently about one less than the order for propylene.

One further modification can be suggested to explain the experimental orders of methane and propylene. If the rate of decomposition of the radicals becomes progressively more important relative to addition as the size of the radical is increased, it is reasonable to suggest that for the n-butyl radical the rates of the decomposition and addition reactions may be comparable. If the rate of addition

of n-butyl radical to ethylene is comparable to the rate of its decomposition, i.e., the reaction (-80) is not much faster than reaction (81), it will have the effect of lowering to a certain extent the order of 3 obtained from the term α. This will lower the orders of the rates of formation of both methane and propylene in the same way and hence give intermediate orders, lower than 2 for methane and lower than 3 for propylene, but different by one. This situation is very close to the experimental results.

This interpretation of the reaction leads to the conclusion that for the formation of methane the term

$$\frac{\frac{k_{83}k_{-89}k_{88}\ \alpha\ [C_2H_4]}{\beta\gamma}}{k_{88}[C_2H_4] + k_{89}[C_2H_4] - \frac{k_{-89}k_{89}[C_2H_4]}{\gamma}} \qquad (118)$$

is more important. For the formation of propylene, decomposition of the 2-hexyl radical is the predominant reaction while the decomposition of the n-propyl radical is the main source of methyl radicals. Although it was assumed that the n-propyl radical addition was faster than decomposition, the decomposition reaction (-89) cannot be completely neglected, since this is the source of methyl radicals. It was observed however that the formation of methane was small compared to the formation of larger products.

The assumption made in this analysis may now be examined in more detail. The relative magnitude of the rates of decomposition and addition processes for n-propyl and n-butyl radicals may be estimated. Taking the values Log A = 7.89 L mol^{-1} s^{-1} and E = 7.4 kcal mol^{-1} for the addition reaction[115] and Log A = 13.8 s^{-1} and E = 32.7 kcal mol^{-1} for the decomposition reaction[100] of the n-propyl radical, at 800 K and 100 torr ethylene pressure the ratio of rates of decomposition to addition for n-propyl radical is calculated as about 40. In the case of n-butyl radical, taking Log A = 7.6 L mol^{-1} s^{-1} and E = 7.3 kcal mol^{-1} for addition[115] and Log A = 13.6 s^{-1} and E = 28.7 kcal mol^{-1} for decomposition reaction[100], the rate of decomposition is 700 times faster than the rate of addition. In the experimental determination of the rate constants, the frequency factors contain the largest uncertainty. If the frequency factors of these n-propyl and n-butyl radicals were ten times less for decomposition reactions and ten times more for addition reactions, for n-propyl radicals the rate of addition reaction would be slightly larger than the rate of decomposition reaction, while almost comparable rates are obtained for the addition and decomposition reactions of n-butyl radicals. The assumptions made to account for the orders are therefore probably reasonable within the uncertainty in the values for the decomposition

and addition reactions of these radicals.

The activation energy required for the formation of methane and propylene can be estimated from the derived rate equations. For propylene, it can be obtained from the term A in equation (116) together with equations (109) and (110).

$$E_{C_3H_6} = E_{80} + E_{81} + \frac{1}{2} E_1 - E_{-80} \qquad (119)$$

The activation energy for reaction (83) which is the important process in term β is not included in equation (119) because it is cancelled by the activation energy of the same reaction already present in term A. Taking the values $E_{80} = 6.9$, $E_{81} = 7.3$, $E_{-80} = 28.7$[115,100] and $E = 64.2$ kcal mol^{-1}, the activation energy necessary for the production of propylene is estimated as 17.6 kcal mol^{-1}. Experimental activation energy is 16 ± 2 kcal mol^{-1} which is in good agreement with the calculated value. Propylene is the most important product and its activation energy has the lowest value. These results show the importance of the isomerization processes of n-hexyl radical in the pyrolysis of ethylene.

For methane, the activation energy can be estimated from equation (118), which is the second term in equation (113), and equations (109)-(111). Equation (118) includes the term A from the rate expression of propylene. Therefore,

$$E_{CH_4} = E_{C_3H_6} + E_{-89} + E_{88} - E_{90} - E_{89} \qquad (120)$$

From the term γ, the activation energy of the reaction (90) is included in accordance with the assumptions applied in the analysis of the mechanism. The addition of methyl radicals to ethylene is the most important process in the denominator of the expression (118), and therefore the activation energy of this reaction, E_{89}, is included in equation (120). Taking the estimated value of the activation energy of propylene, 17.6 kcal mol^{-1}, as calculated above and E_{-89} = 31.4, E_{88} = 10, E_{90} = 9 and E_{89} = 8 kcal mol^{-1} 115,100, the activation energy necessary for the formation of methane is calculated as 41.6 kcal mol^{-1}. The experimental activation energy is 38 ± 2 kcal mol^{-1}, close to the estimated value.

From the above detailed discussions, it can be concluded that the main features of the mechanism of the thermal reactions of ethylene at temperatures lower than 820 K are consistent with most of the experimental observations obtained in this study. The main assumption in the analysis of the mechanism was the change in behaviour of the radicals with respect to decomposition and addition reactions with increasing number of carbon atoms. It was assumed that the addition reaction of n-propyl radical was faster than its decomposition, as is the case for the

methyl and ethyl radicals. The n-butyl radical was assumed to have an intermediate behaviour, with the rate of addition to ethylene comparable to the rate of decomposition. The n-pentyl and n-hexyl radicals on the other hand, were assumed to undergo mostly decomposition and isomerization reactions.

APPENDIX A

EXPERIMENTAL DATA FOR THE MIXTURES OF ETHYLENE AND 1-BUTENE

In this appendix the experimental data from the additions of 1-butene are presented in yield-time plots for the products methane, ethane and propylene.

Figures 1, 2 and 3 - Yield-Time Plots at 699 K for Methane, Ethane and Propylene, Respectively

A. O 199.9 torr C_2H_4
● 199.5 torr C_2H_4 + 0.20 torr 1-C_4H_8
Δ 200.1 torr C_2H_4 + 0.52 torr 1-C_4H_8
▲ 200.2 torr C_2H_4 + 1.34 torr 1-C_4H_8

B. O 300.7 torr C_2H_4
● 300.5 torr C_2H_4 + 0.50 torr 1-C_4H_8
Δ 300.1 torr C_2H_4 + 0.78 torr 1-C_4H_8
▲ 300.1 torr C_2H_4 + 2.01 torr 1-C_4H_8

C. O 400.0 torr C_2H_4
● 400.0 torr C_2H_4 + 0.40 torr 1-C_4H_8
Δ 400.1 torr C_2H_4 + 1.04 torr 1-C_4H_8
▲ 400.0 torr C_2H_4 + 2.68 torr 1-C_4H_8

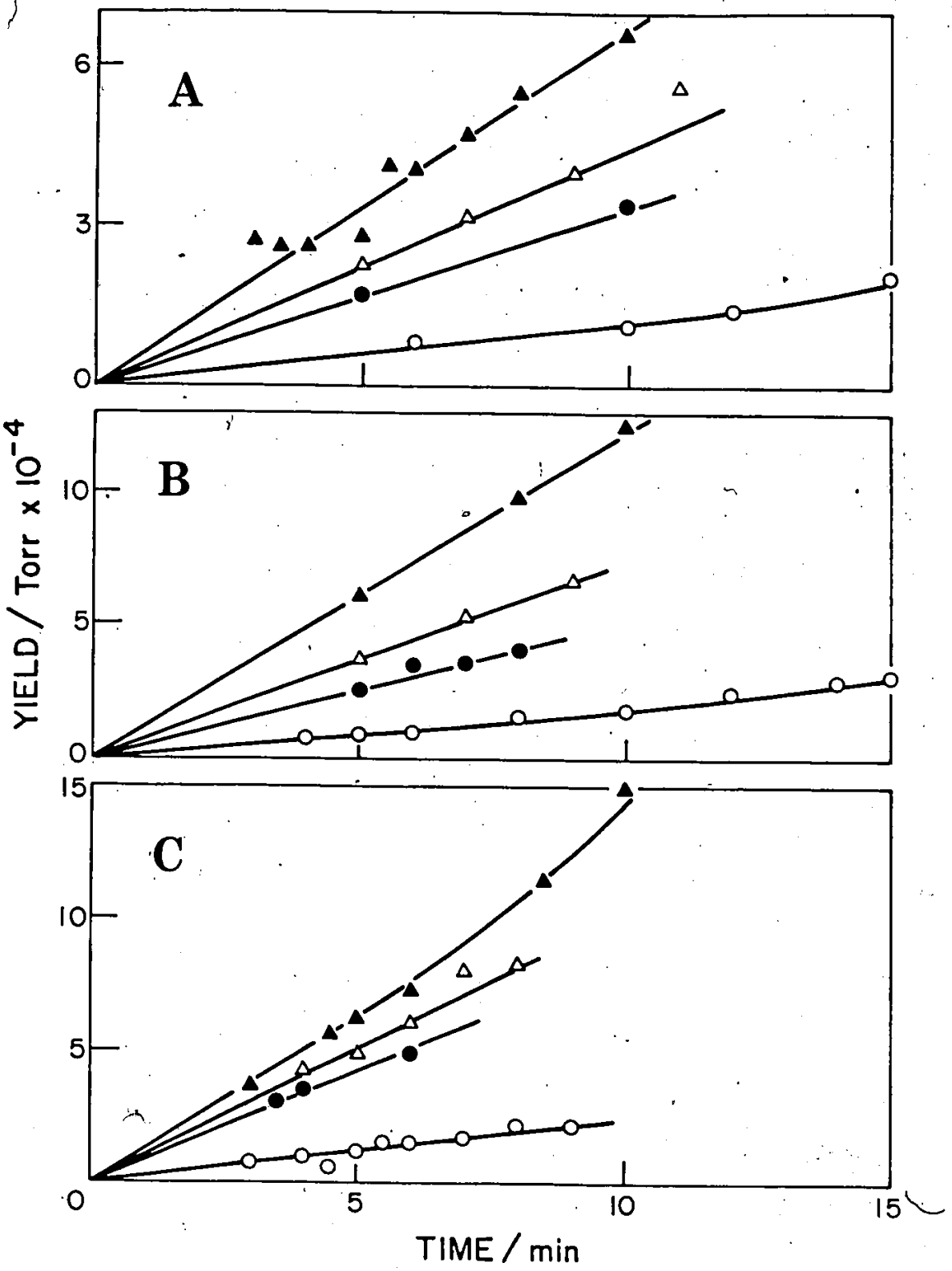


Fig. 1

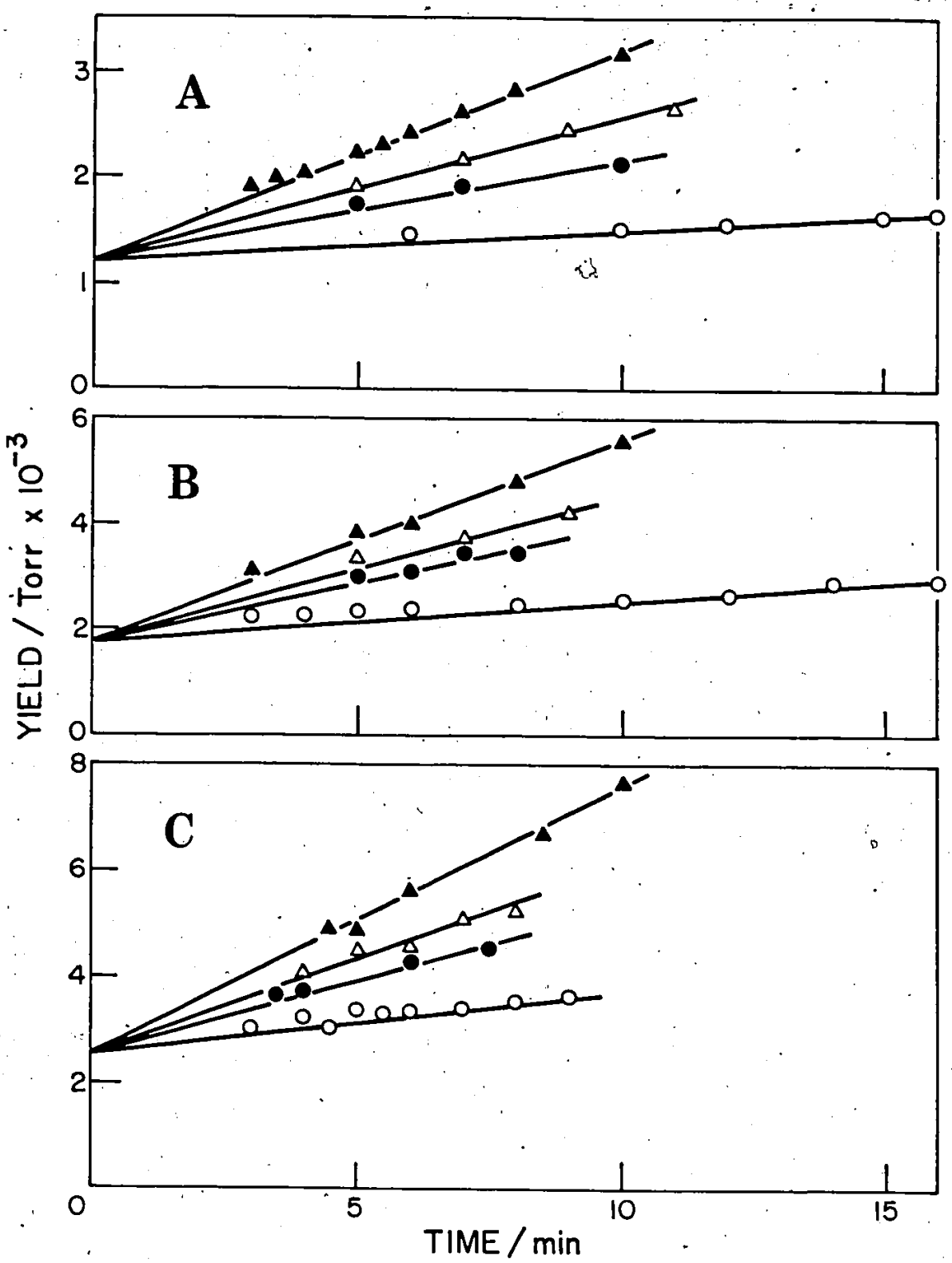


Fig. 2

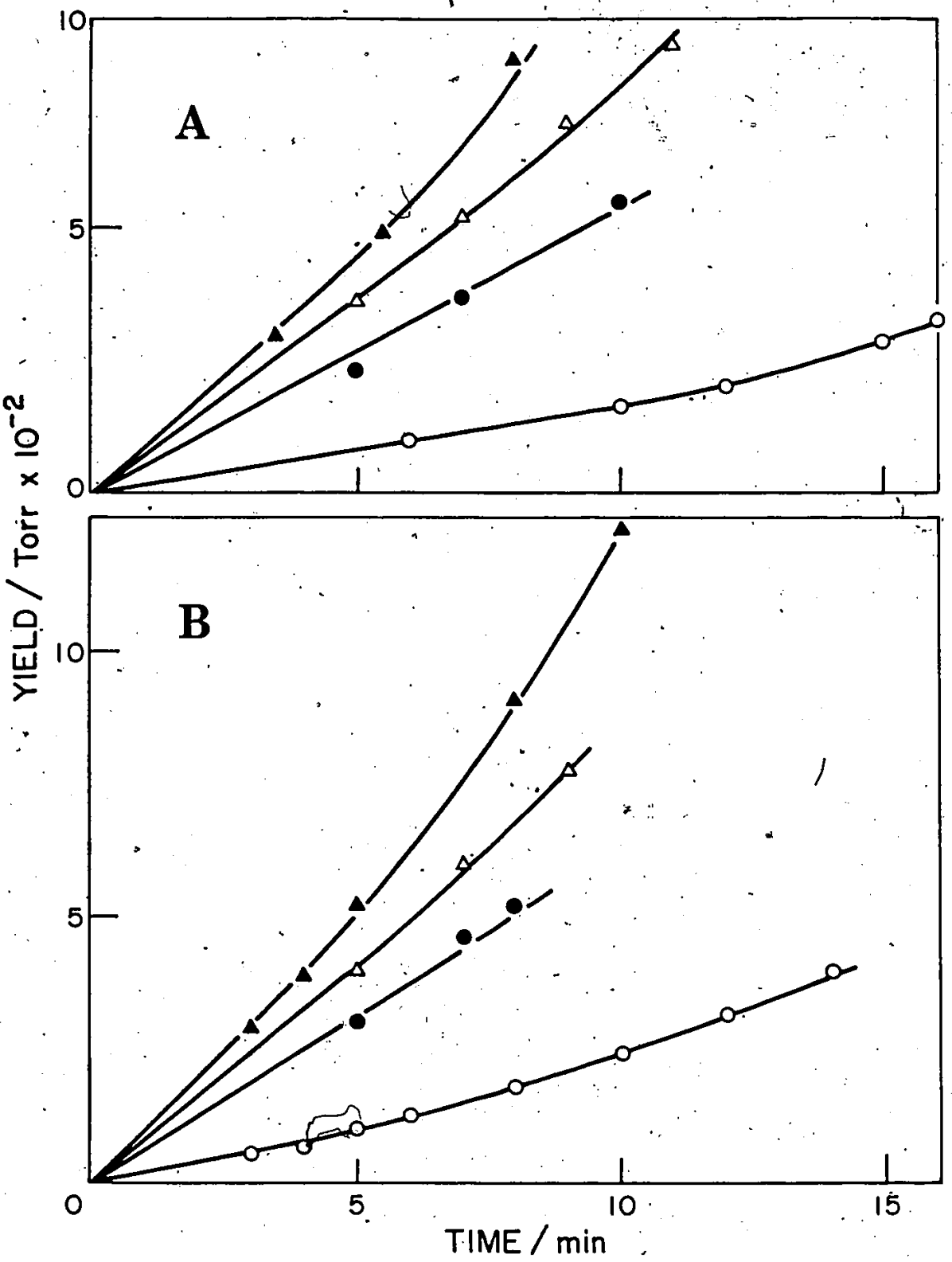


Fig. 3

Figures 4, 5 and 6 - Yield-Time Plots at 721 K for Methane, Ethane and Propylene, Respectively

A. O 74.8 torr C_2H_4

● 74.9 torr purified C_2H_4

▲ 74.9 torr C_2H_4 + 0.08 torr 1-C_4H_8
Δ 74.6 torr C_2H_4 + 0.17 torr 1-C_4H_8
■ 74.5 torr C_2H_4 + 0.41 torr 1-C_4H_8

B. O 100.3 torr C_2H_4

● 99.0 torr purified C_2H_4

▲ 100.2 torr C_2H_4 + 0.10 torr 1-C_4H_8
Δ 99.8 torr C_2H_4 + 0.22 torr 1-C_4H_8
■ 99.8 torr C_2H_4 + 0.55 torr 1-C_4H_8

C. O 200.0 torr C_2H_4

● 200.0 torr purified C_2H_4

▲ 200.8 torr C_2H_4 + 0.21 torr 1-C_4H_8
Δ 200.0 torr C_2H_4 + 0.45 torr 1-C_4H_8
■ 200.0 torr C_2H_4 + 1.11 torr 1-C_4H_8

D. O 299.9 torr C_2H_4

● 299.6 torr purified C_2H_4

▲ 301.0 torr C_2H_4 + 0.31 torr 1-C_4H_8
Δ 299.7 torr C_2H_4 + 0.67 torr 1-C_4H_8
■ 299.7 torr C_2H_4 + 1.66 torr 1-C_4H_8

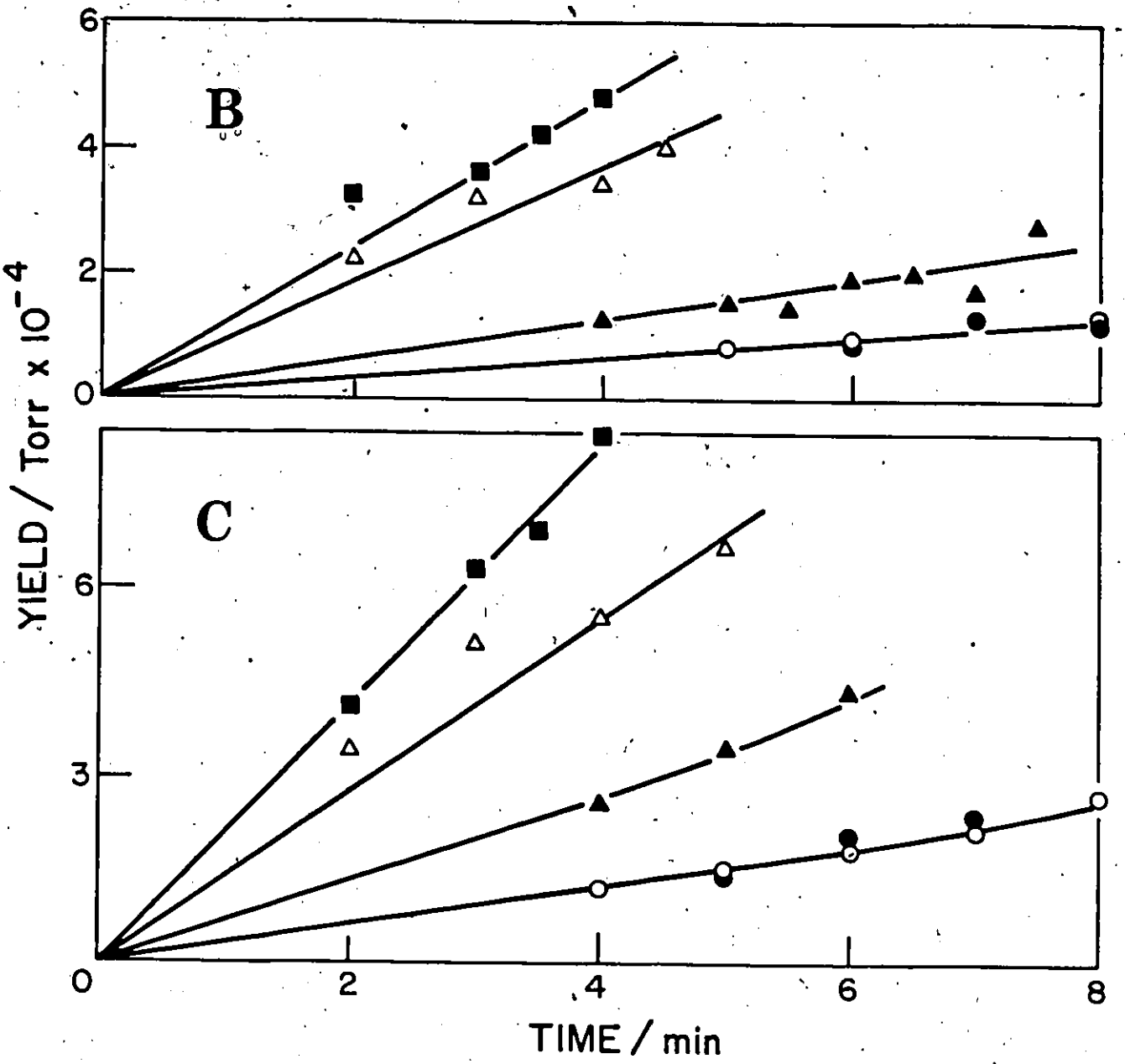


Fig. 4

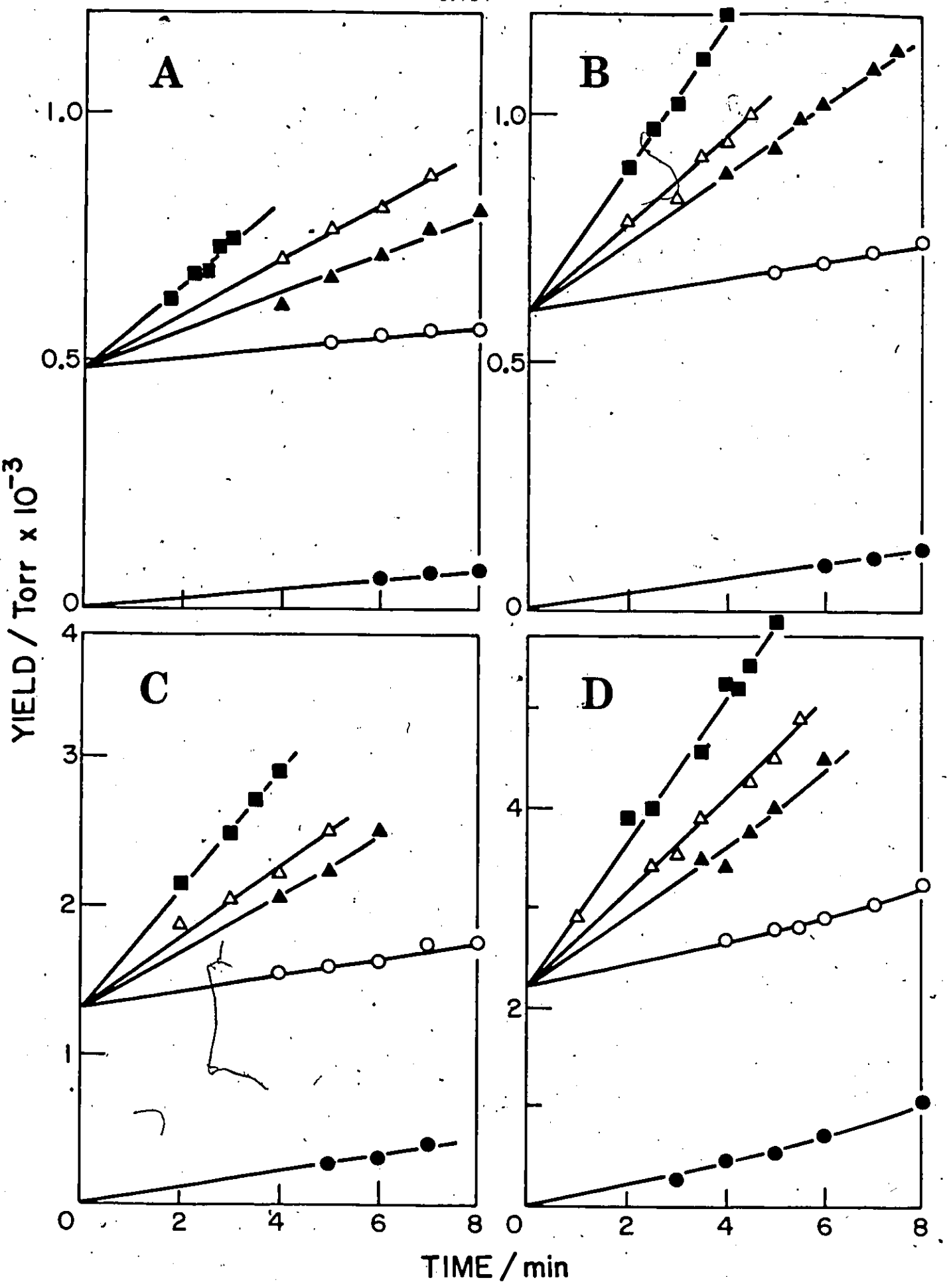


Fig. 5

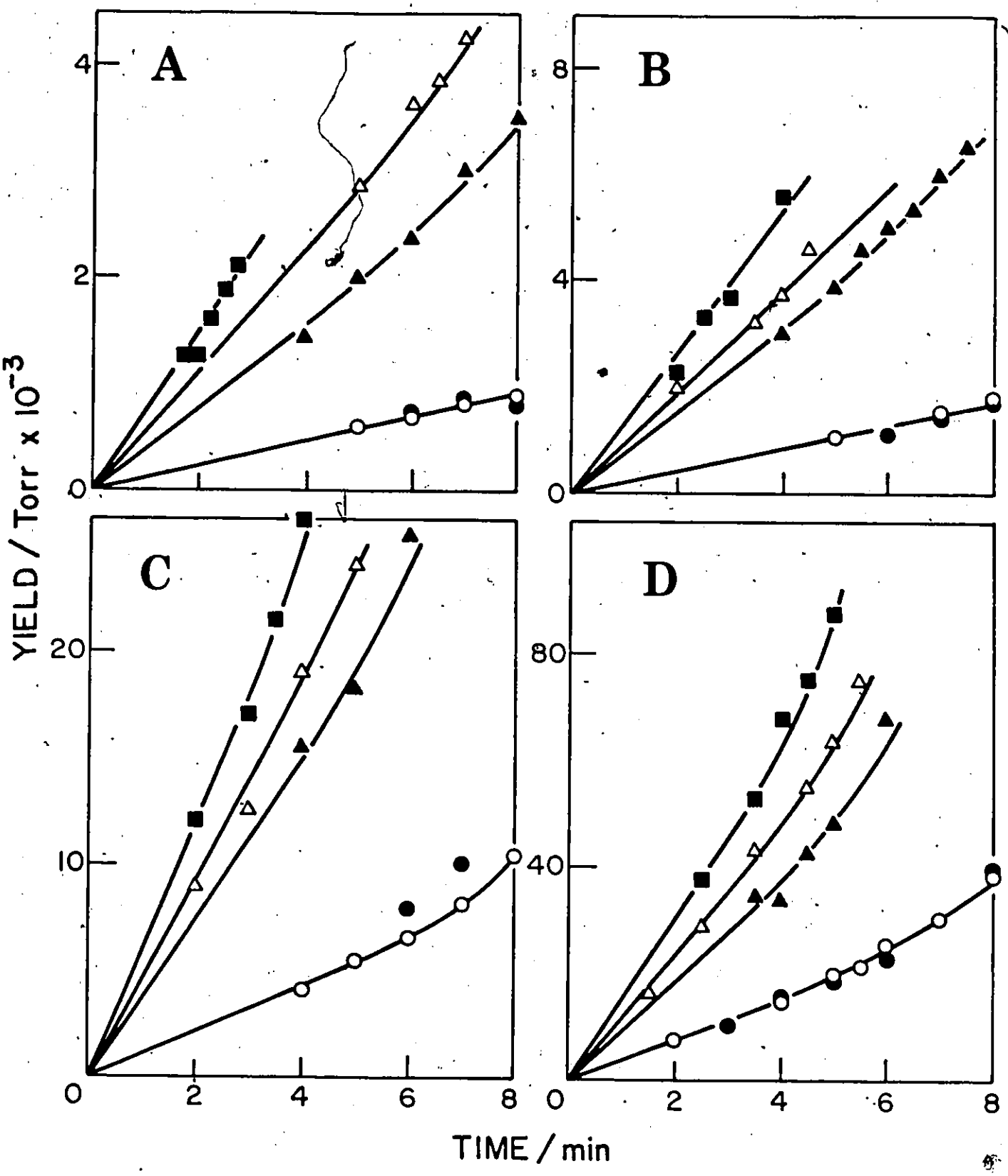


Fig. 6

Figures 7, 8 and 9 - Yield-Time Plots at 732 K for Methane, Ethane and Propylene, Respectively

A. ● 100.7 torr C_2H_4 + 0.10 torr 1-C_4H_8
   Δ 100.0 torr C_2H_4 + 0.35 torr 1-C_4H_8

B. ● 200.0 torr C_2H_4 + 0.20 torr 1-C_4H_8
   Δ 200.0 torr C_2H_4 + 0.69 torr 1-C_4H_8

C. ● 300.0 torr C_2H_4 + 1.04 torr 1-C_4H_8

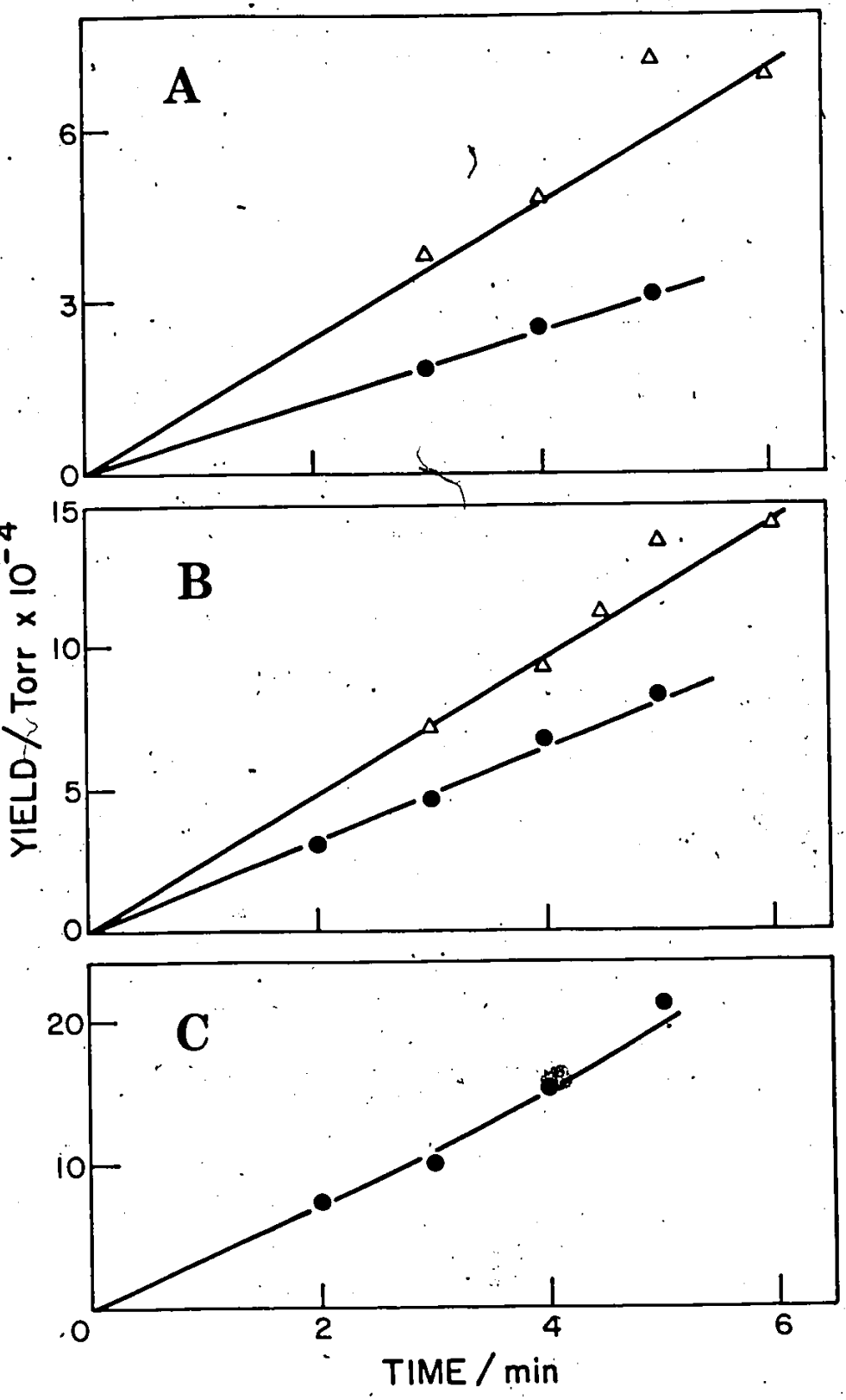


Fig. 7

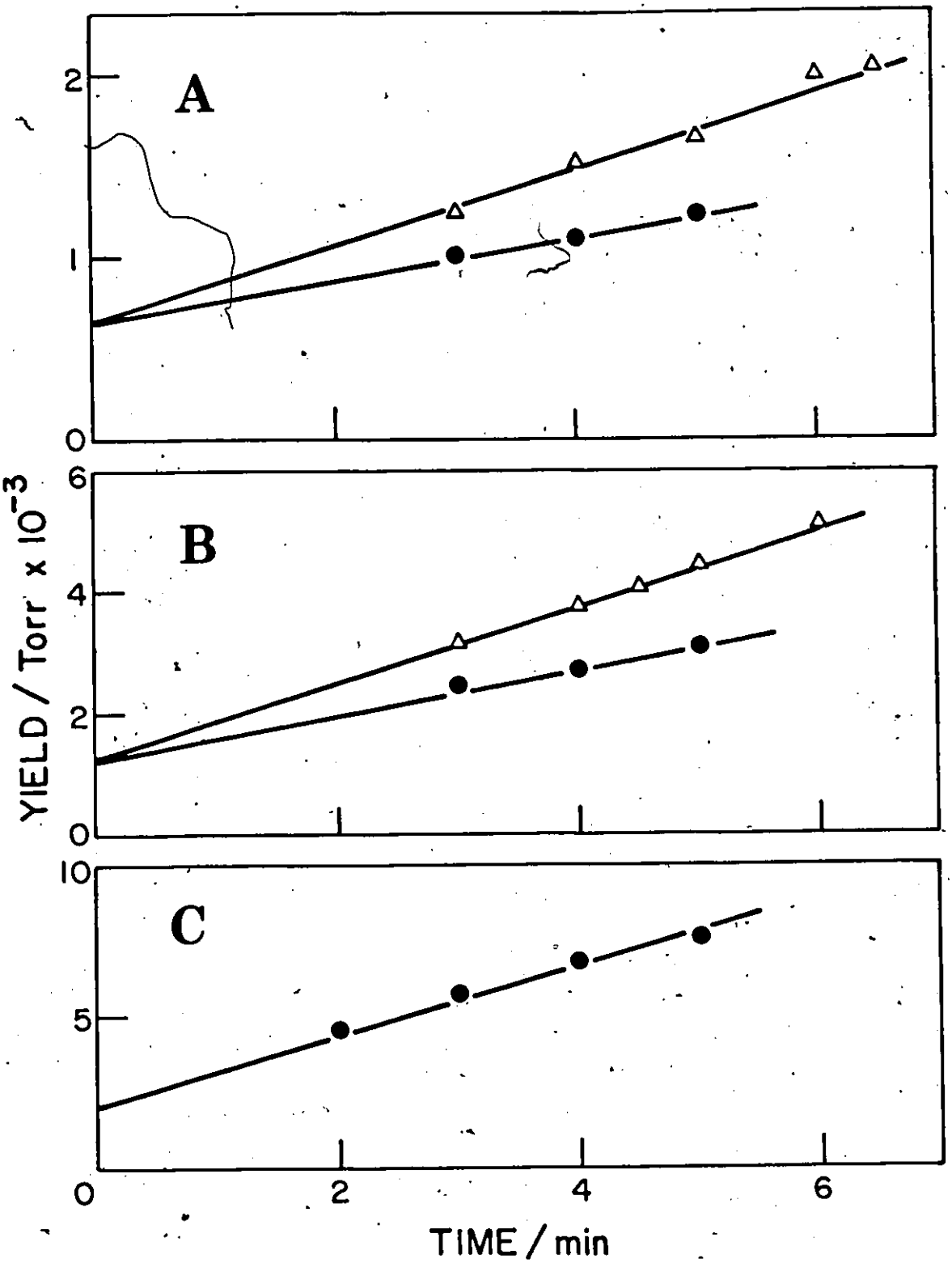


Fig. 8

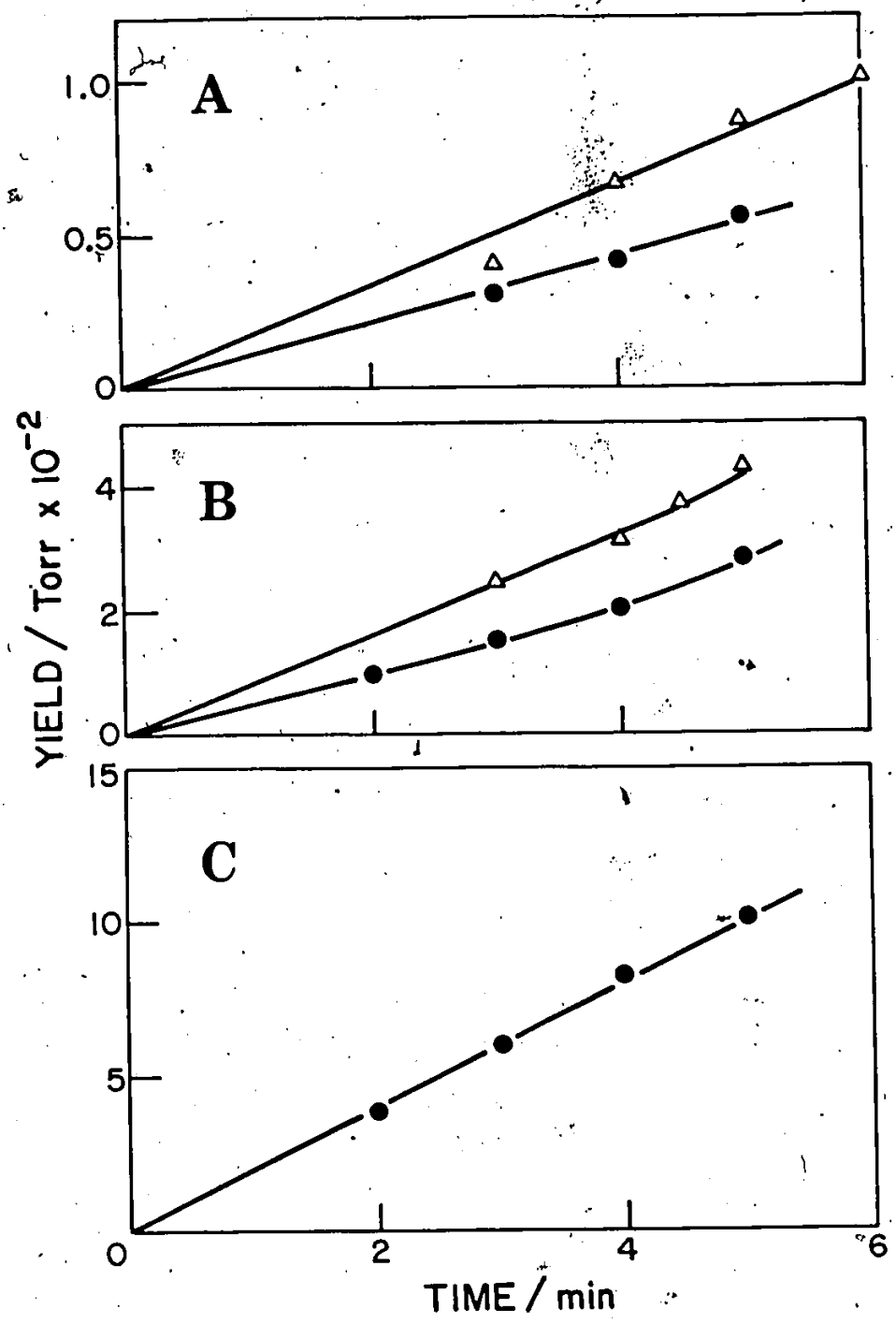


Fig. 9

Figures 10, 11 and 12 - Yield-Time Plots at 748 K for Methane, Ethane and Propylene, Respectively

A. O 74.0 torr C_2H_4
● 74.5 torr C_2H_4 + 0.07 torr 1-C_4H_8
Δ 73.8 torr C_2H_4 + 0.30 torr 1-C_4H_8
▲ 74.3 torr C_2H_4 + 0.54 torr 1-C_4H_8

B. O 99.7 torr C_2H_4
● 99.4 torr C_2H_4 + 0.09 torr 1-C_4H_8
Δ 100.1 torr C_2H_4 + 0.40 torr 1-C_4H_8
▲ 99.8 torr C_2H_4 + 0,73 torr 1-C_4H_8

C. O 199.3 torr C_2H_4
● 199.3 torr C_2H_4 + 0.18 torr 1-C_4H_8
Δ 200.0 torr C_2H_4 + 0.81 torr 1-C_4H_8
▲ 199.0 torr C_2H_4 + 1.45 torr 1-C_4H_8

D. O 299.6 torr C_2H_4
● 300.2 torr C_2H_4 + 0.28 torr 1-C_4H_8
Δ 300.0 torr C_2H_4 + 1.21 torr 1-C_4H_8
▲ 299.2 torr C_2H_4 + 2.18 torr 1-C_4H_8

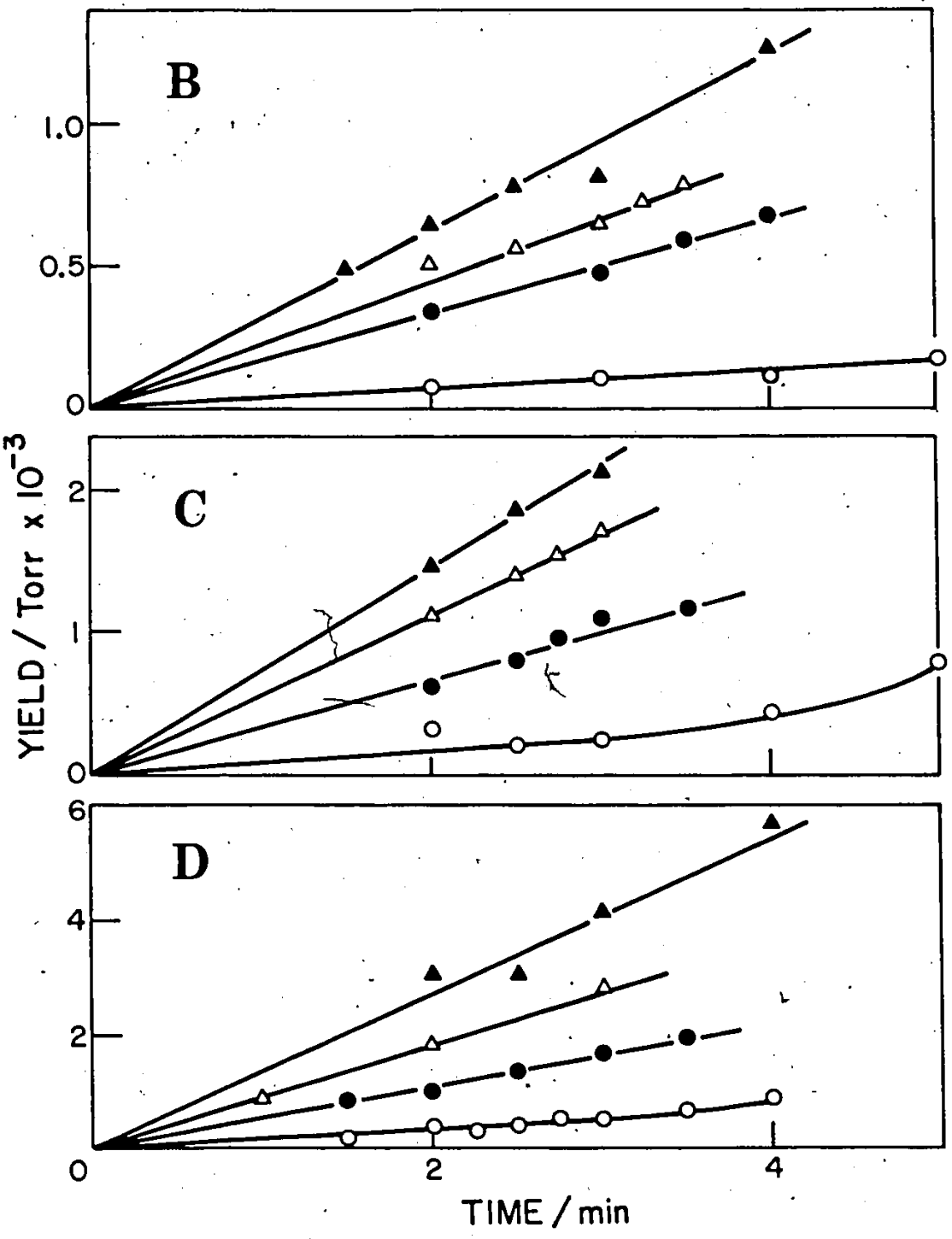


Fig. 10

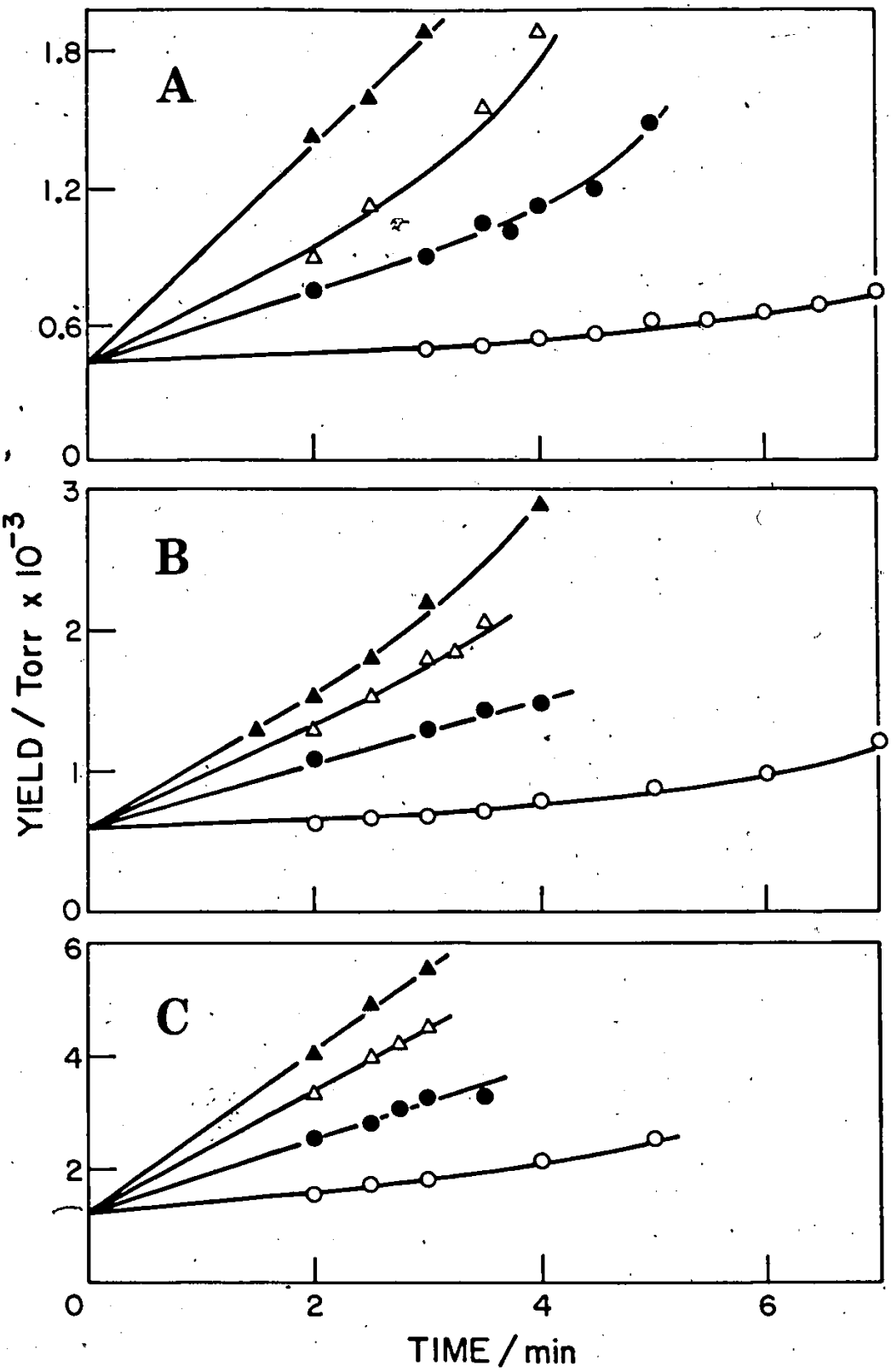


Fig. 11

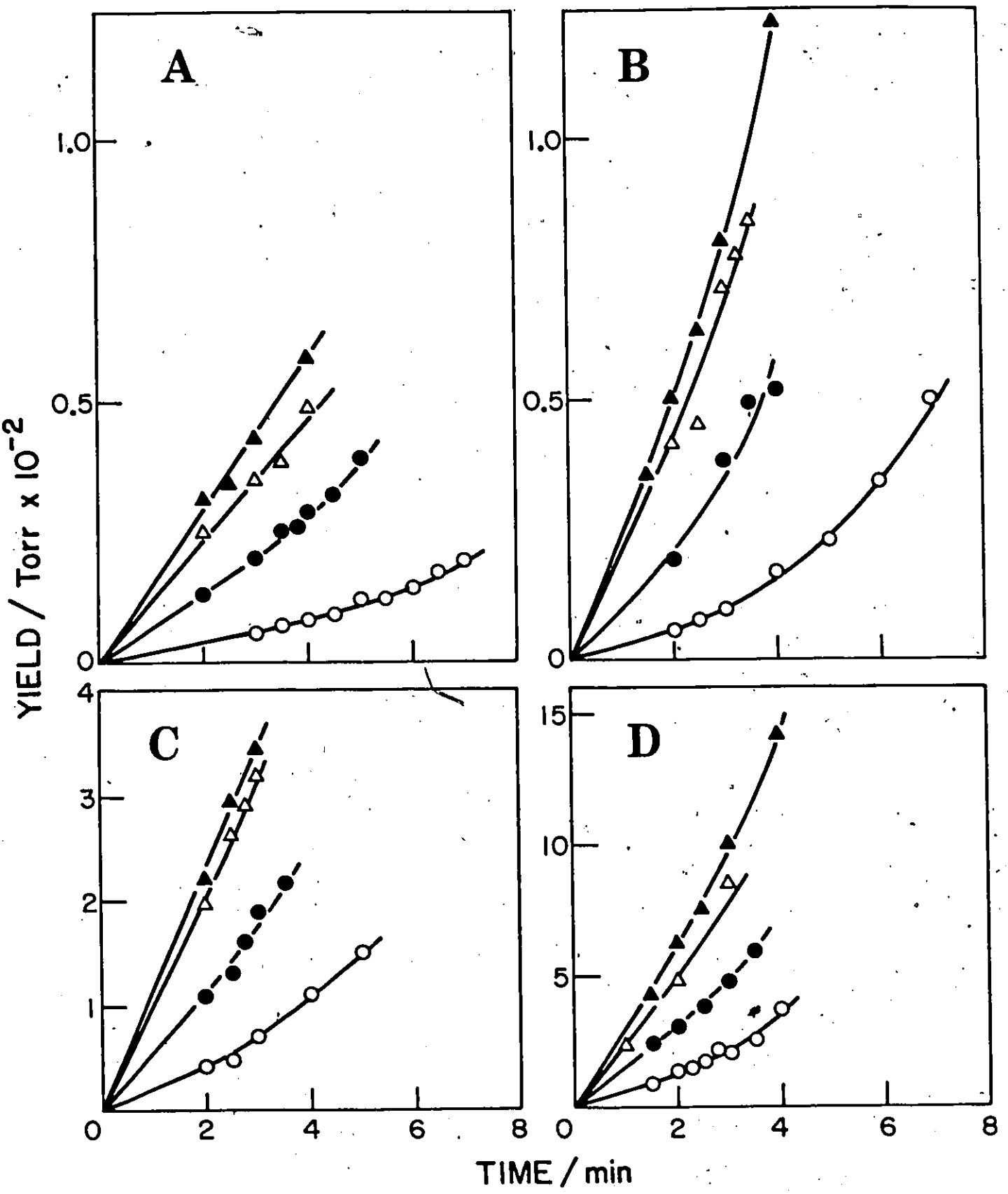


Fig. 12

Figures 13, 14 and 15 - Yield-Time Plots at 763 K for Methane, Ethane and Propylene, Respectively

A. O 74.3 torr C_2H_4
● 74.7 torr C_2H_4 + 0.15 torr 1-C_4H_8
Δ 75.1 torr C_2H_4 + 0.26 torr 1-C_4H_8

B. O 100.0 torr C_2H_4
● 100.3 torr C_2H_4 + 0.20 torr 1-C_4H_8
Δ 100.2 torr C_2H_4 + 0.35 torr 1-C_4H_8
▲ 100.0 torr C_2H_4 + 0.51 torr 1-C_4H_8

C. O 200.1 torr C_2H_4
● 199.6 torr C_2H_4 + 0.41 torr 1-C_4H_8
Δ 200.1 torr C_2H_4 + 0.69 torr 1-C_4H_8
▲ 200.0 torr C_2H_4 + 1.03 torr 1-C_4H_8

D. O 300.4 torr C_2H_4
● 300.2 torr C_2H_4 + 1.54 torr 1-C_4H_8

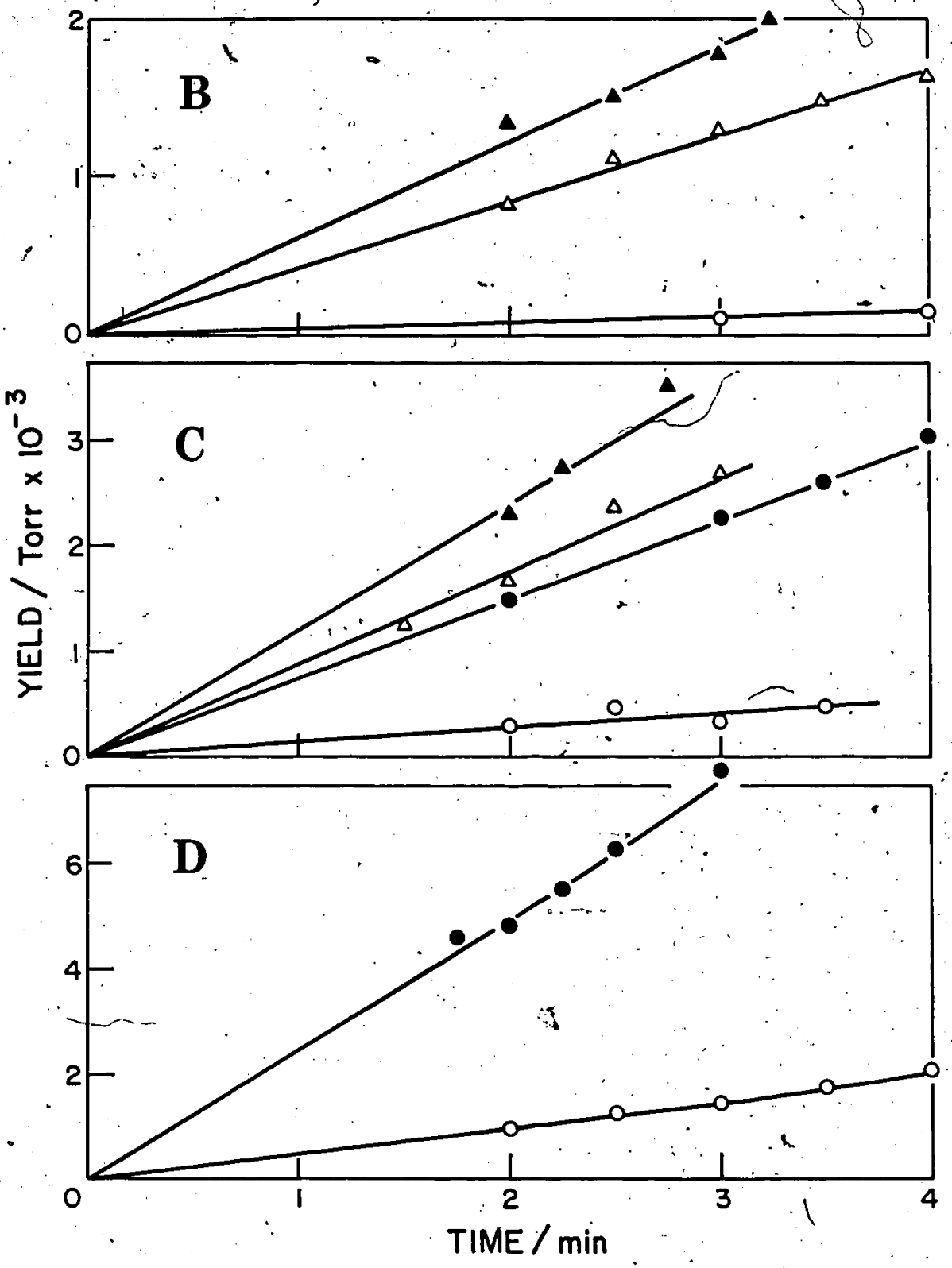


Fig. 13

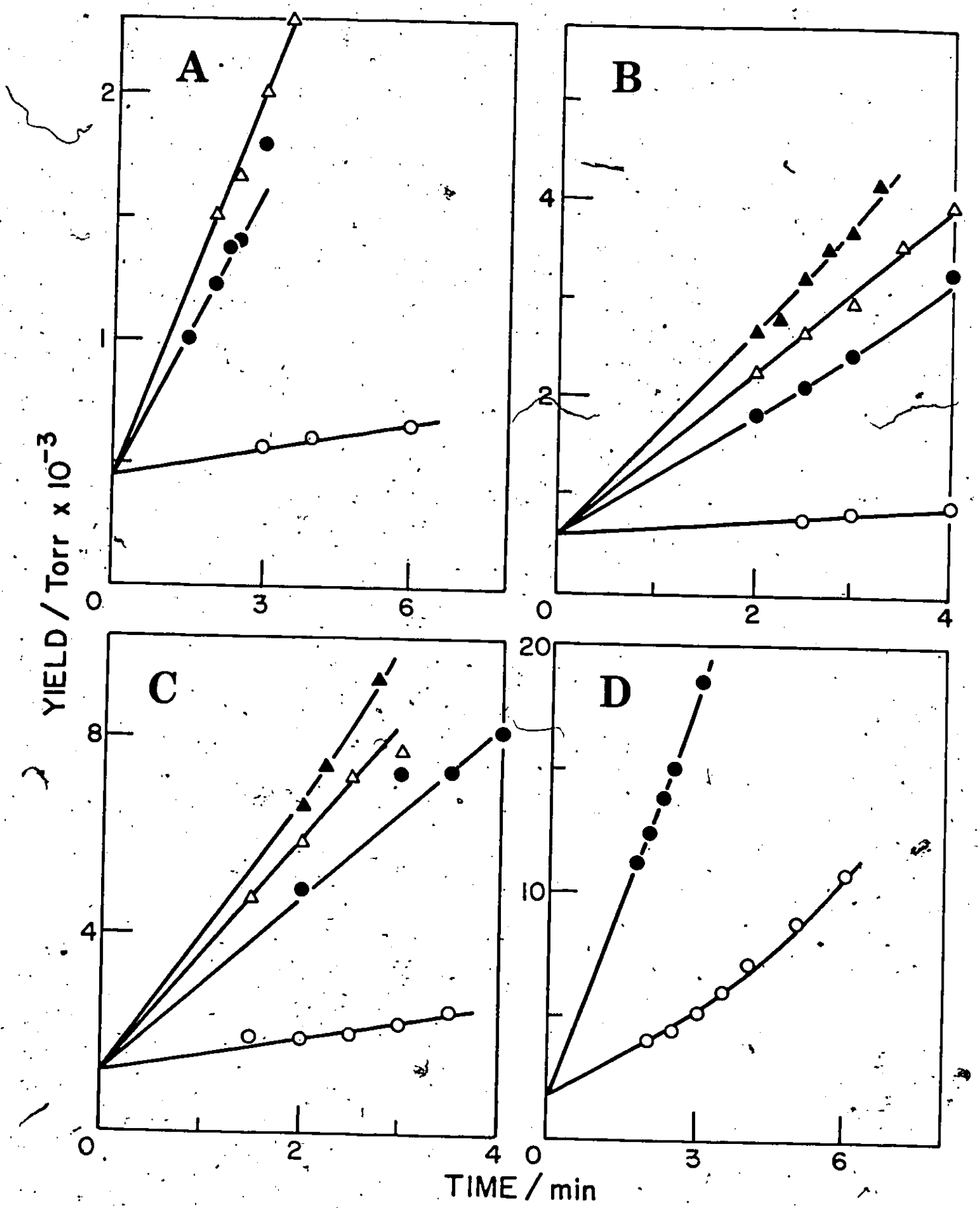


Fig. 14

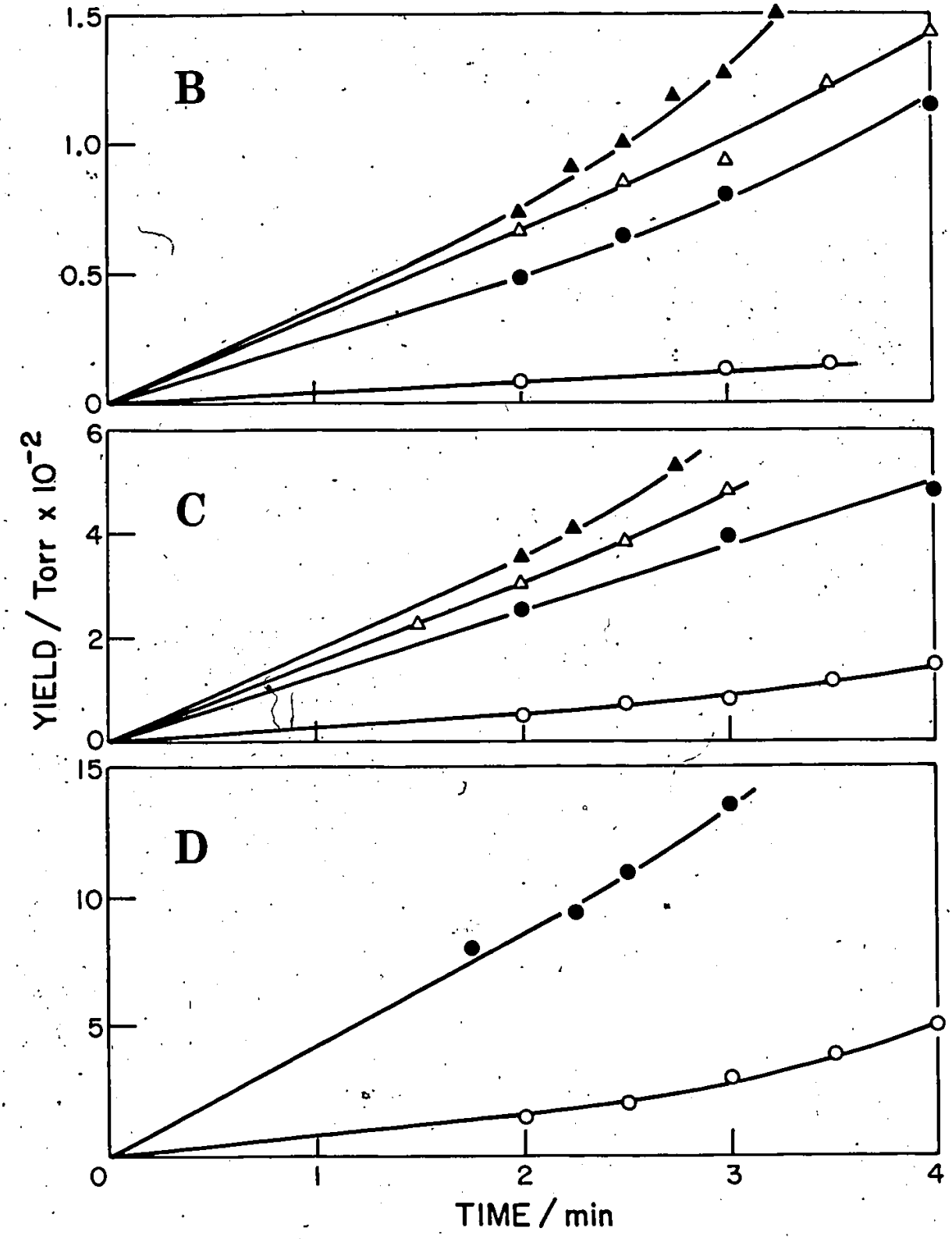


Fig. 15

Figures 16, 17 and 18 - Yield-Time Plots at 773 K for Methane, Ethane and Propylene, Respectively

A. ○ 75.0 torr C_2H_4
● 75.0 torr C_2H_4 + 0.11 torr 1-C_4H_8
△ 74.2 torr C_2H_4 + 0.38 torr 1-C_4H_8
▲ 74.1 torr C_2H_4 + 0.63 torr 1-C_4H_8
□ 74.5 torr C_2H_4 + 2.80 torr 1-C_4H_8

B. ○ 100.6 torr C_2H_4
● 100.0 torr C_2H_4 + 0.07 torr 1-C_4H_8
△ 101.9 torr C_2H_4 + 0.17 torr 1-C_4H_8
▲ 100.1 torr C_2H_4 + 0.42 torr 1-C_4H_8
□ 100.3 torr C_2H_4 + 0.85 torr 1-C_4H_8
■ 99.7 torr C_2H_4 + 3.75 torr 1-C_4H_8

C. ○ 205.0 torr C_2H_4
● 208.6 torr C_2H_4 + 0.05 torr 1-C_4H_8
△ 206.3 torr C_2H_4 + 0.11 torr 1-C_4H_8
▲ 205.8 torr C_2H_4 + 0.37 torr 1-C_4H_8
□ 208.9 torr C_2H_4 + 0.65 torr 1-C_4H_8

D. ○ 304.0 torr C_2H_4
● 305.0 torr C_2H_4 + 0.74 torr 1-C_4H_8
△ 305.1 torr C_2H_4 + 1.54 torr 1-C_4H_8
▲ 302.5 torr C_2H_4 + 2.57 torr 1-C_4H_8
□ 306.0 torr C_2H_4 + 11.5 torr 1-C_4H_8

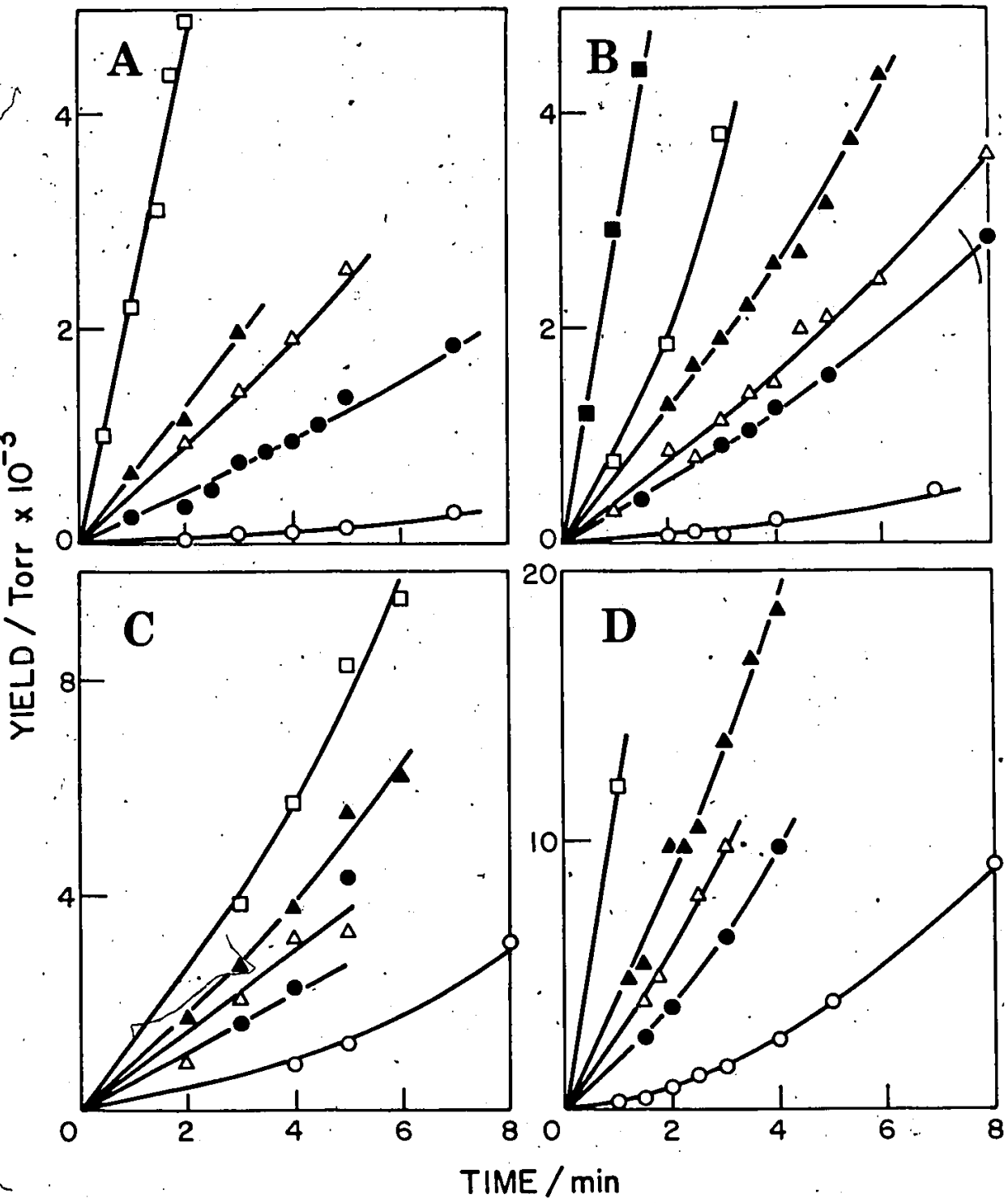


Fig: 16

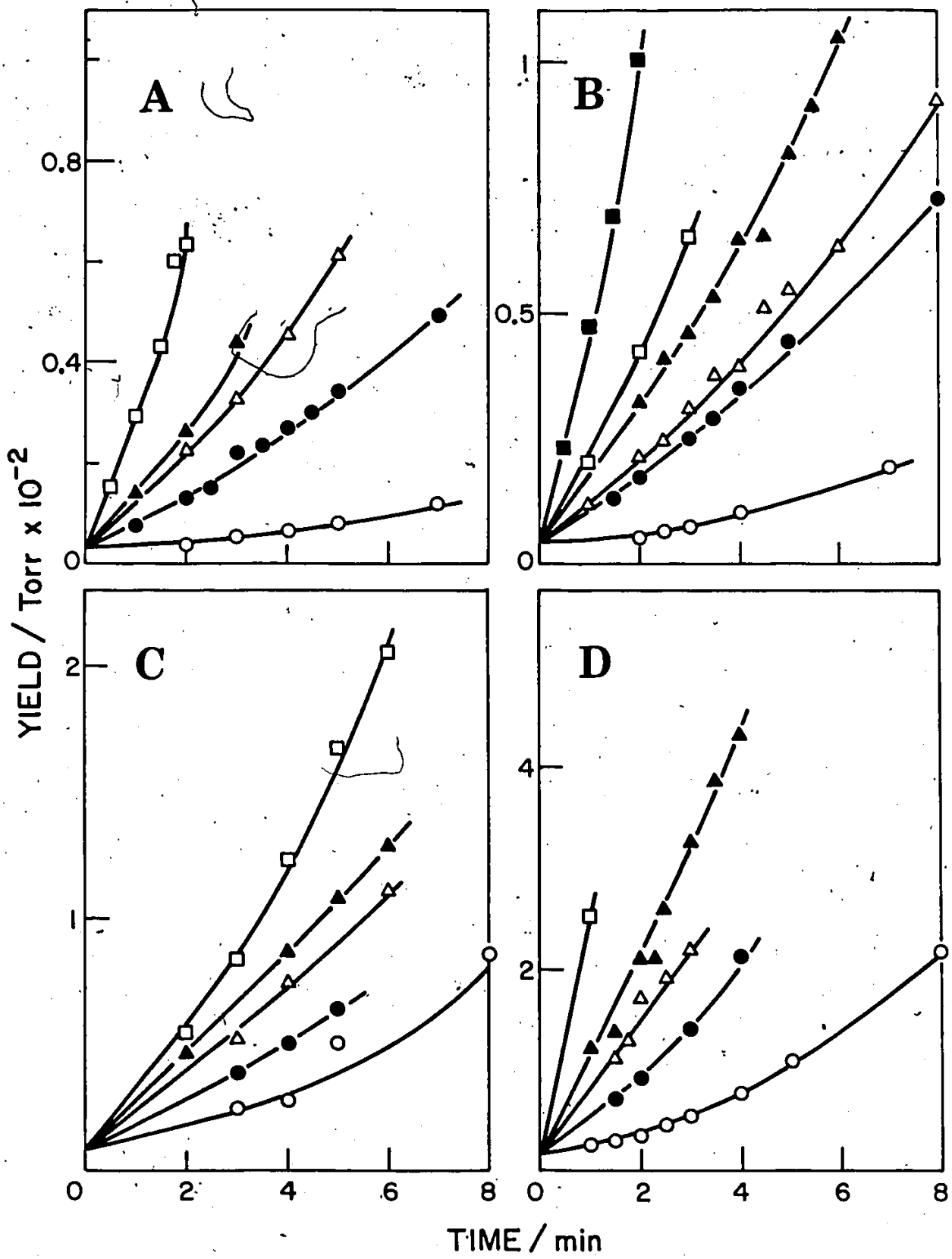


Fig. 17

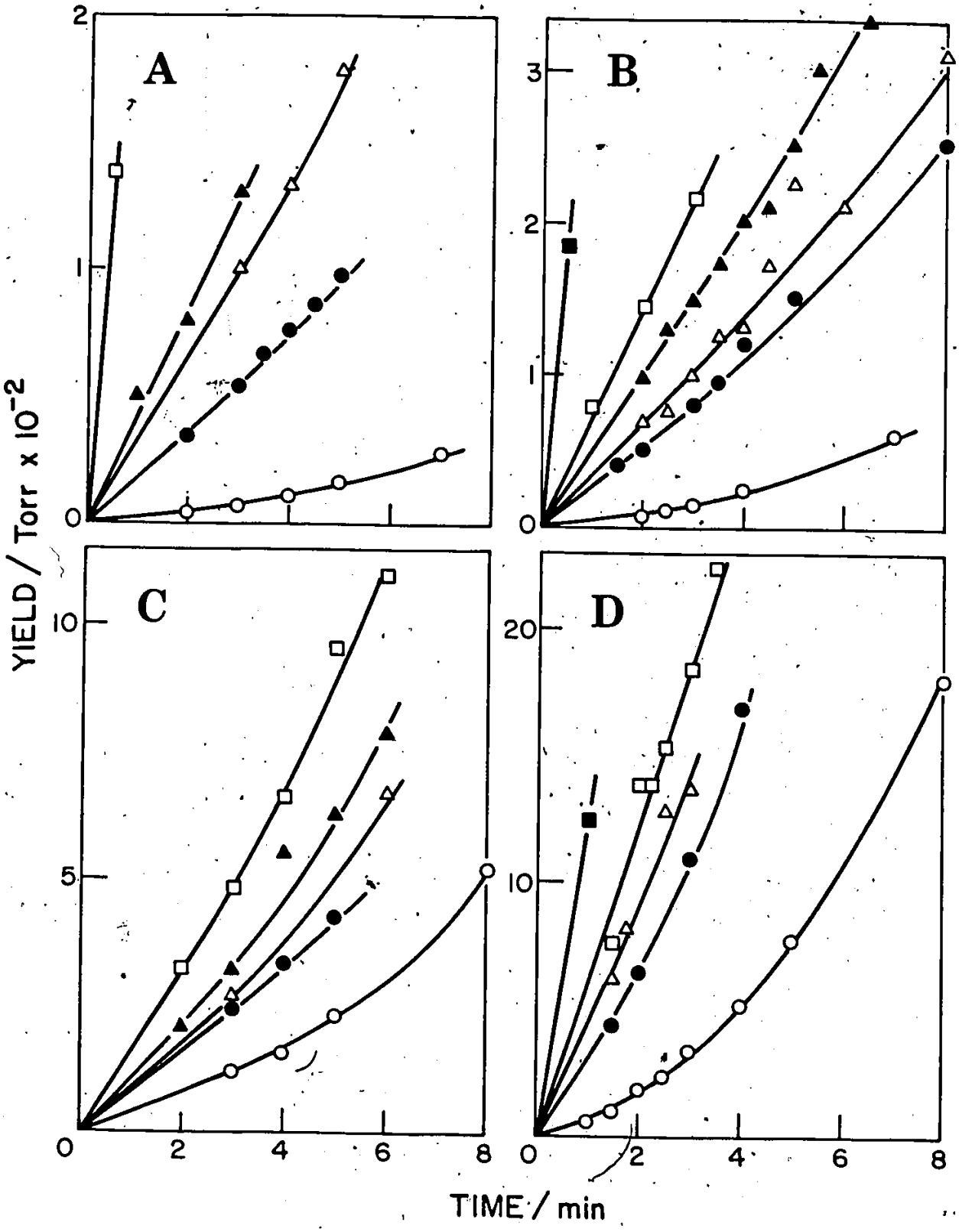


Fig. 18

APPENDIX B

EXPERIMENTAL DATA FOR THE MIXTURES OF ETHYLENE WITH NEOPENTANE AND ETHANE

In this appendix the data from the additions of neopentane are presented in yield-time plots for each product. The additions of ethane, on the other hand caused very small increases in the initial rates and the presentation of these data on similar yield-time plots would not be sufficient. Therefore, the experimental data from the ethylene+ethane system are given in Table 1.

Figures 1, 2 and 3 - Yield-Time Plots for Methane, Ethane and Propylene, Respectively.

A. 748 K ○ 201.6 torr C_2H_4
● 201.6 torr C_2H_4 + 0.40% neo-C_5H_{12}
△ 201.4 torr C_2H_4 + 2.10% neo-C_5H_{12}

B. 756 K ○ 104.1 torr C_2H_4
● 104.0 torr C_2H_4 + 0.31% neo-C_5H_{12}
△ 103.6 torr C_2H_4 + 0.67% neo-C_5H_{12}
▲ 104.0 torr C_2H_4 + 2.10% neo-C_5H_{12}
□ 104.6 torr C_2H_4 + 5.54% neo-C_5H_{12}

C. 756 K ○ 302.1 torr C_2H_4
● 303.0 torr C_2H_4 + 0.31% neo-C_5H_{12}
△ 301.9 torr C_2H_4 + 0.67% neo-C_5H_{12}
▲ 302.0 torr C_2H_4 + 2.10% neo-C_5H_{12}
□ 302.0 torr C_2H_4 + 5.54% neo-C_5H_{12}

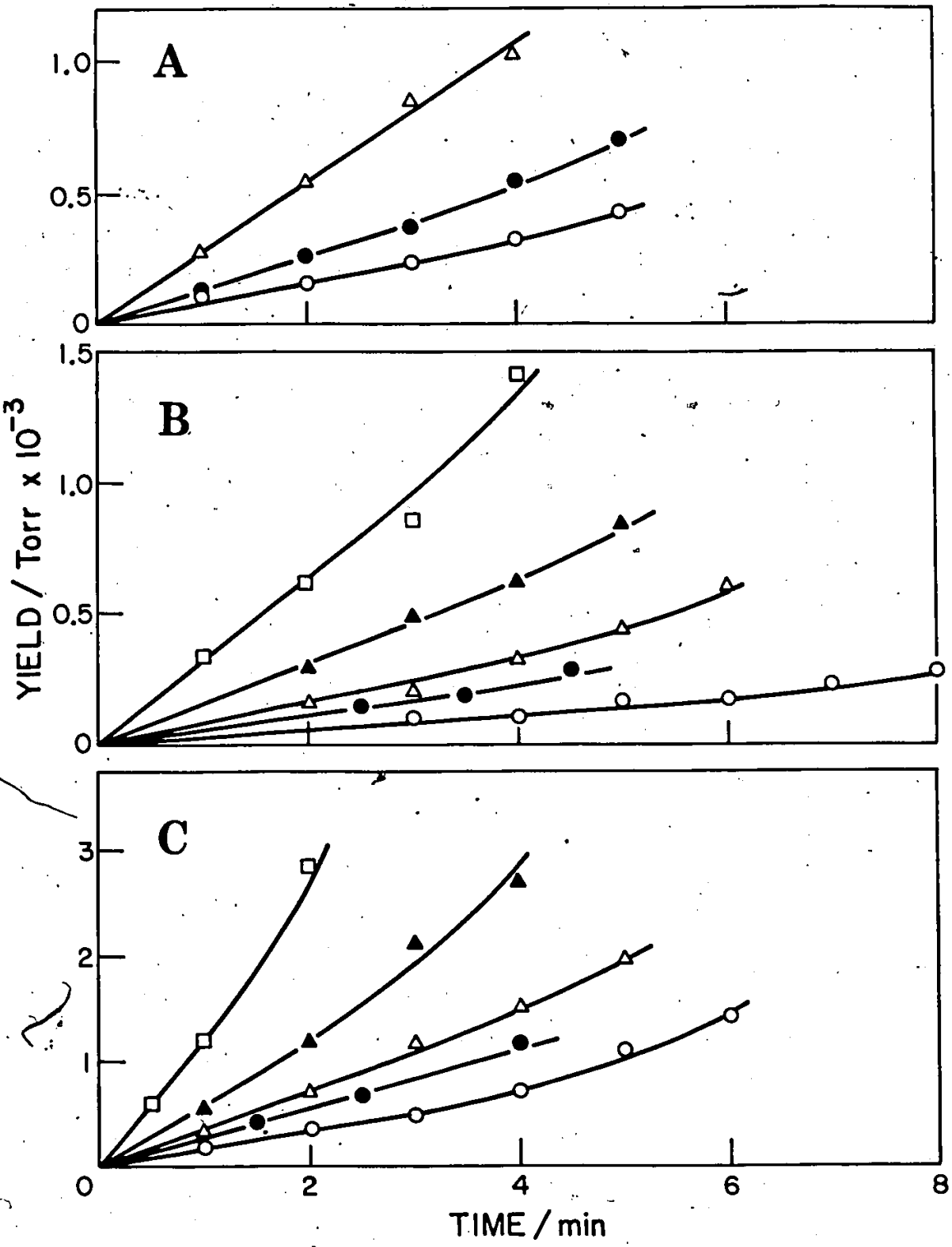


Fig. 1

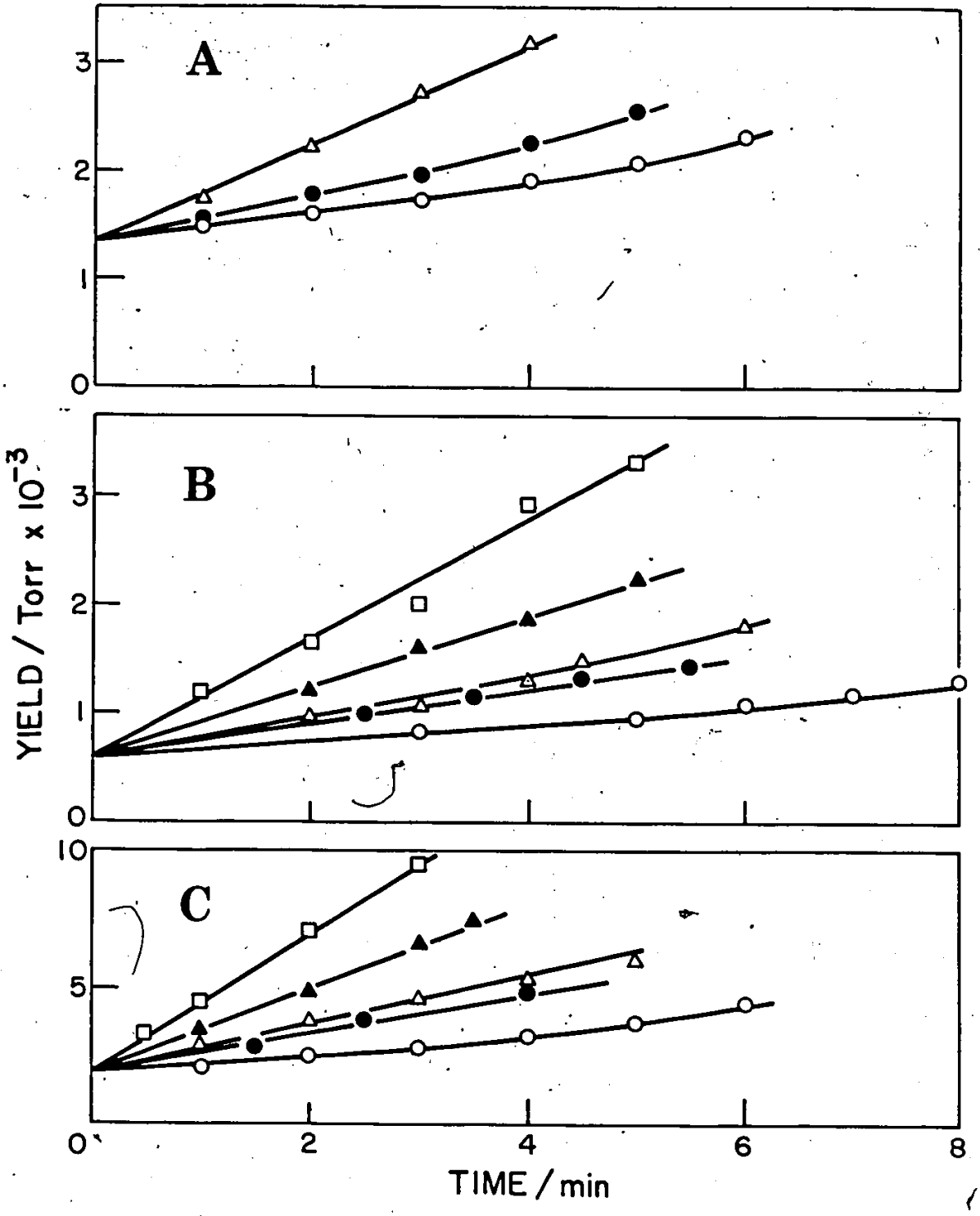


Fig. 2

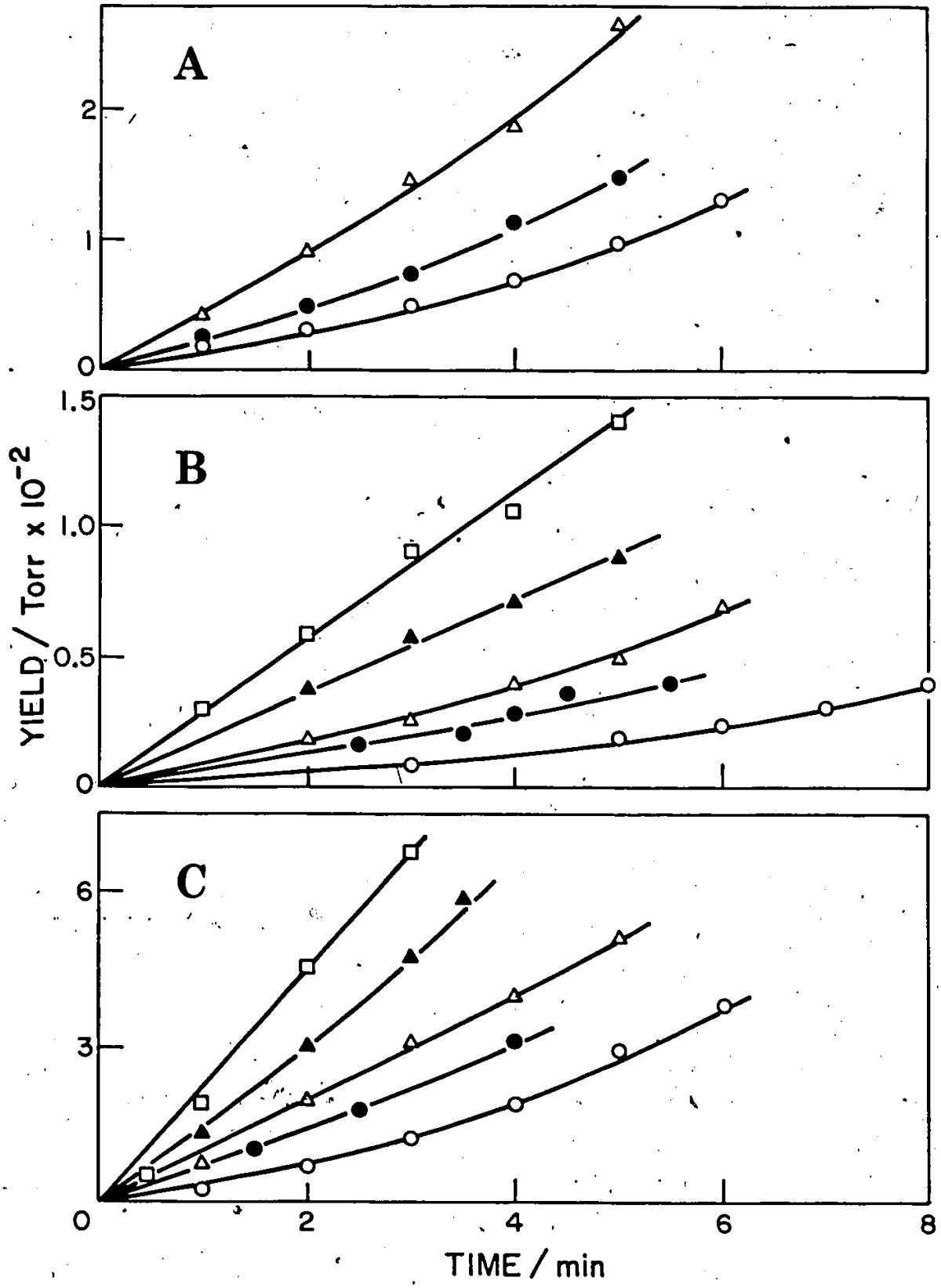


Fig. 3

Figures 4, 5, and 6 - Yield-Time Plots for Methane, Ethane and Propylene, Respectively

A. 766 K ○ 104.0 torr C_2H_4
● 103.4 torr C_2H_4 + 0.40% neo-C_5H_{12}
Δ 103.8 torr C_2H_4 + 1.70% neo-C_5H_{12}

B. 777 K ○ 204.0 torr C_2H_4
● 204.4 torr C_2H_4 + 0.54% neo-C_5H_{12}
Δ 204.7 torr C_2H_4 + 2.21% neo-C_5H_{12}
▲ 204.3 torr C_2H_4 + 4.27% neo-C_5H_{12}
□ 204.0 torr C_2H_4 + 9.45% neo-C_5H_{12}

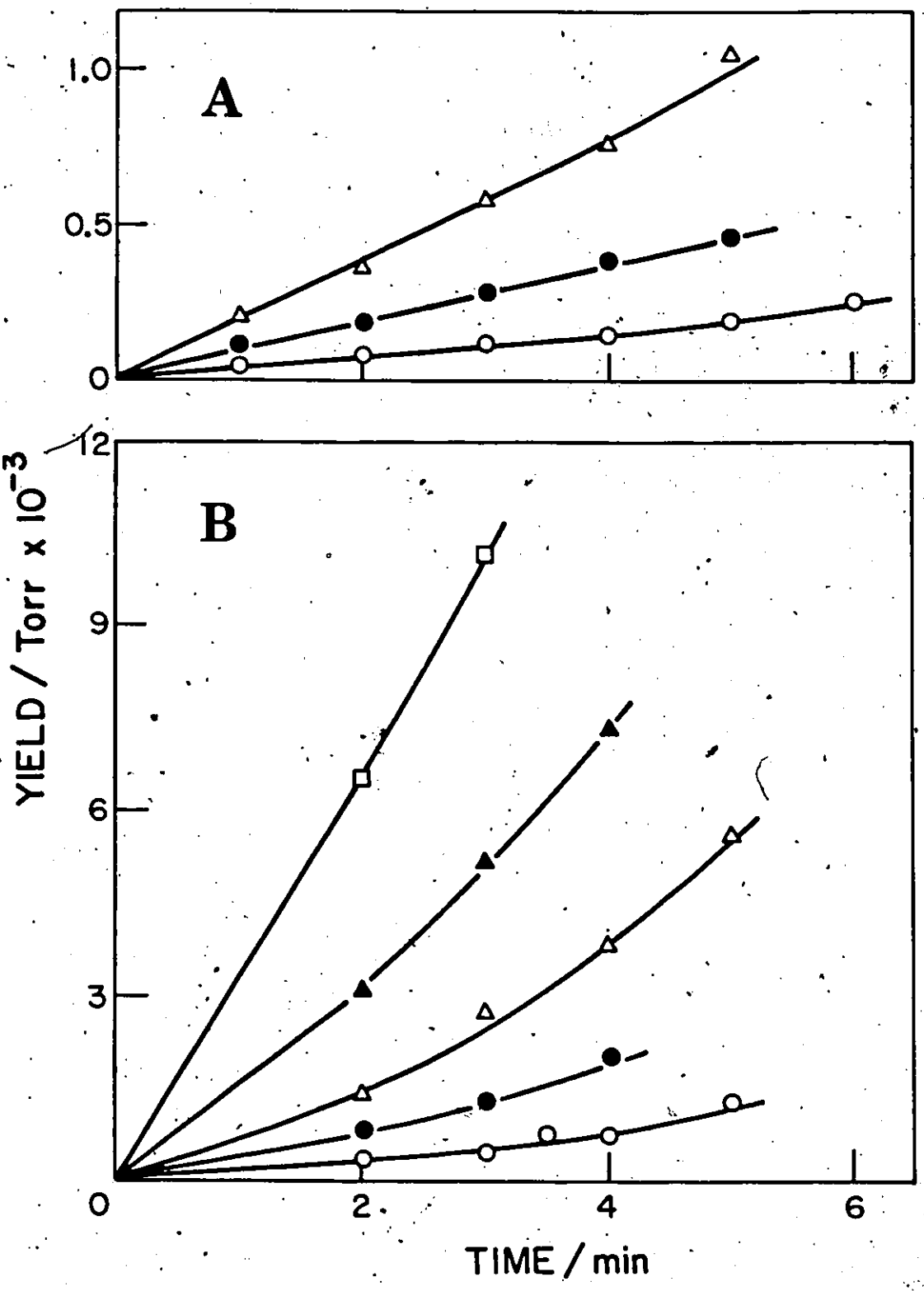


Fig. 4

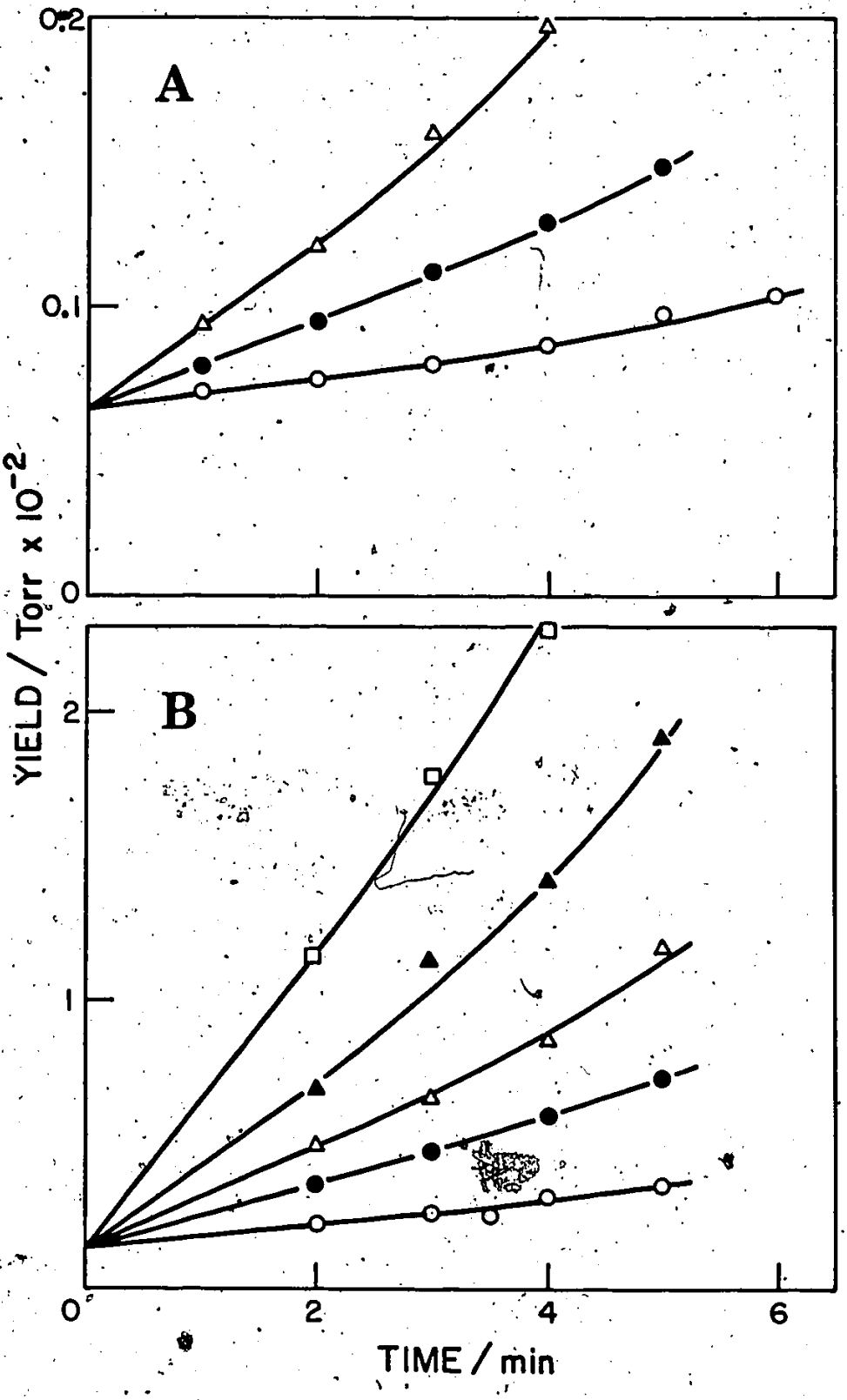


Fig. 5

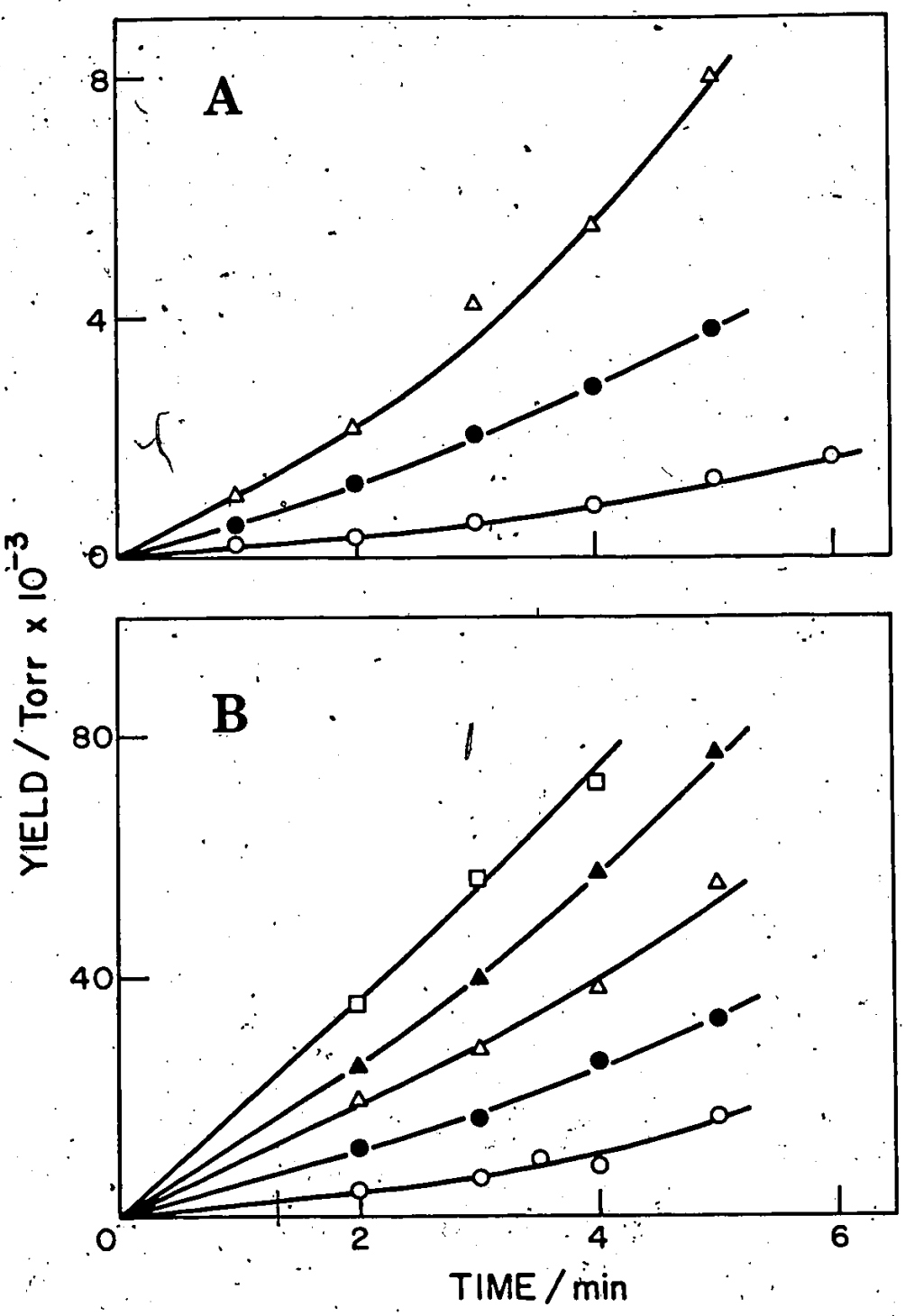
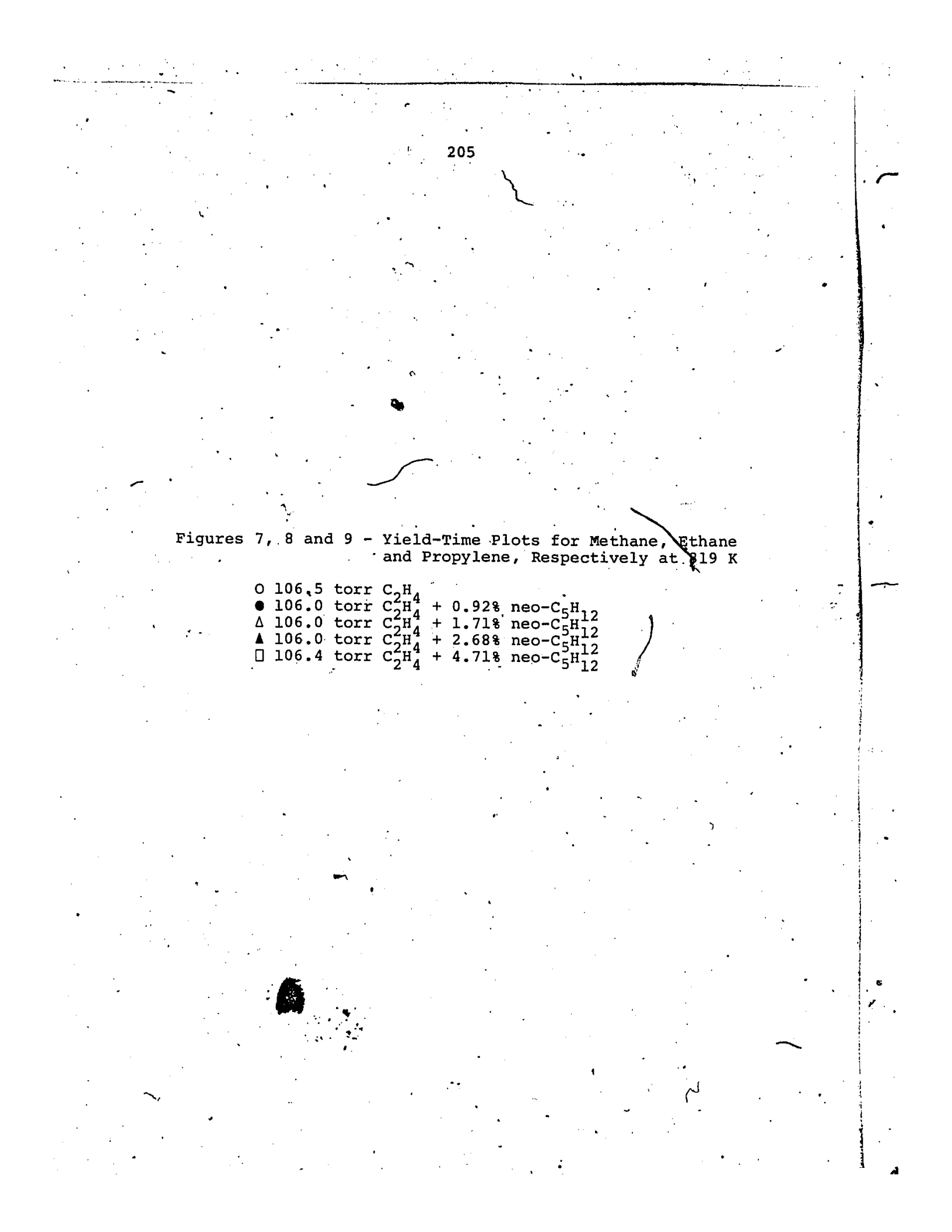


Fig. 6



Figures 7, 8 and 9 - Yield-Time Plots for Methane, Ethane and Propylene, Respectively at 819 K

○ 106.5 torr C_2H_4
● 106.0 torr C_2H_4 + 0.92% neo-C_5H_{12}
△ 106.0 torr C_2H_4 + 1.71% neo-C_5H_{12}
▲ 106.0 torr C_2H_4 + 2.68% neo-C_5H_{12}
□ 106.4 torr C_2H_4 + 4.71% neo-C_5H_{12}

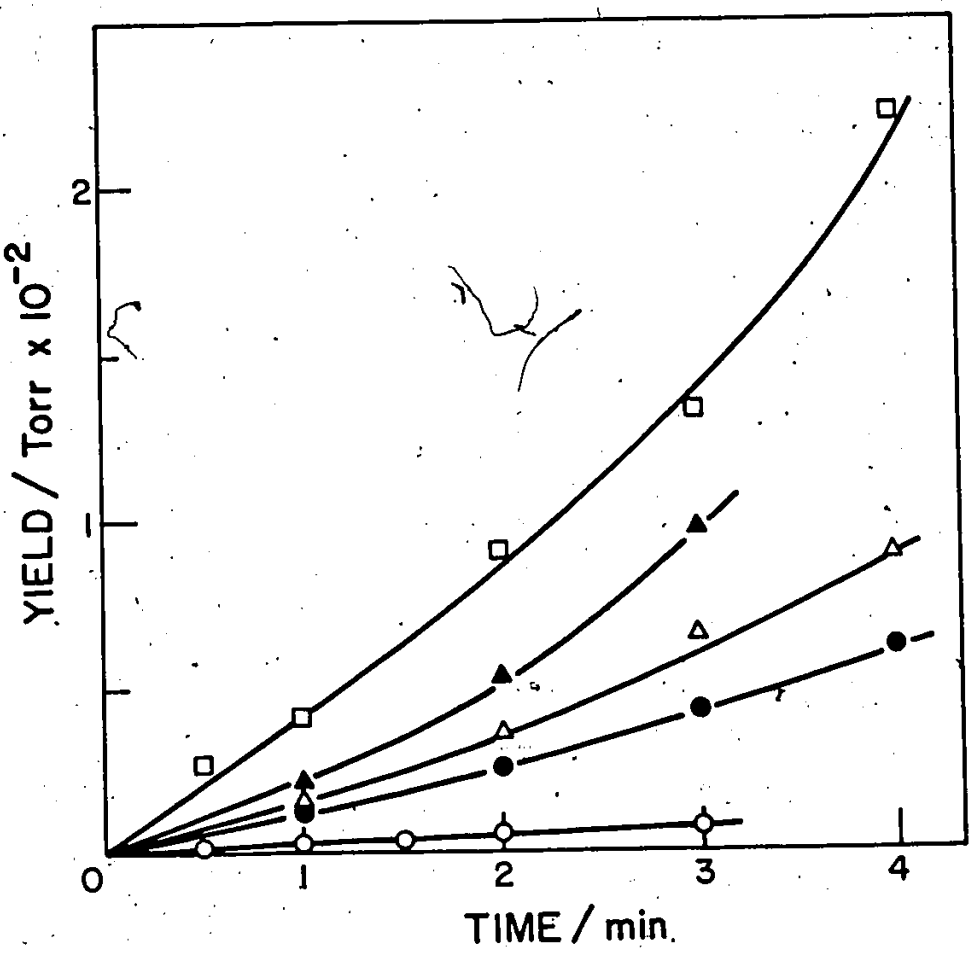


Fig. 7

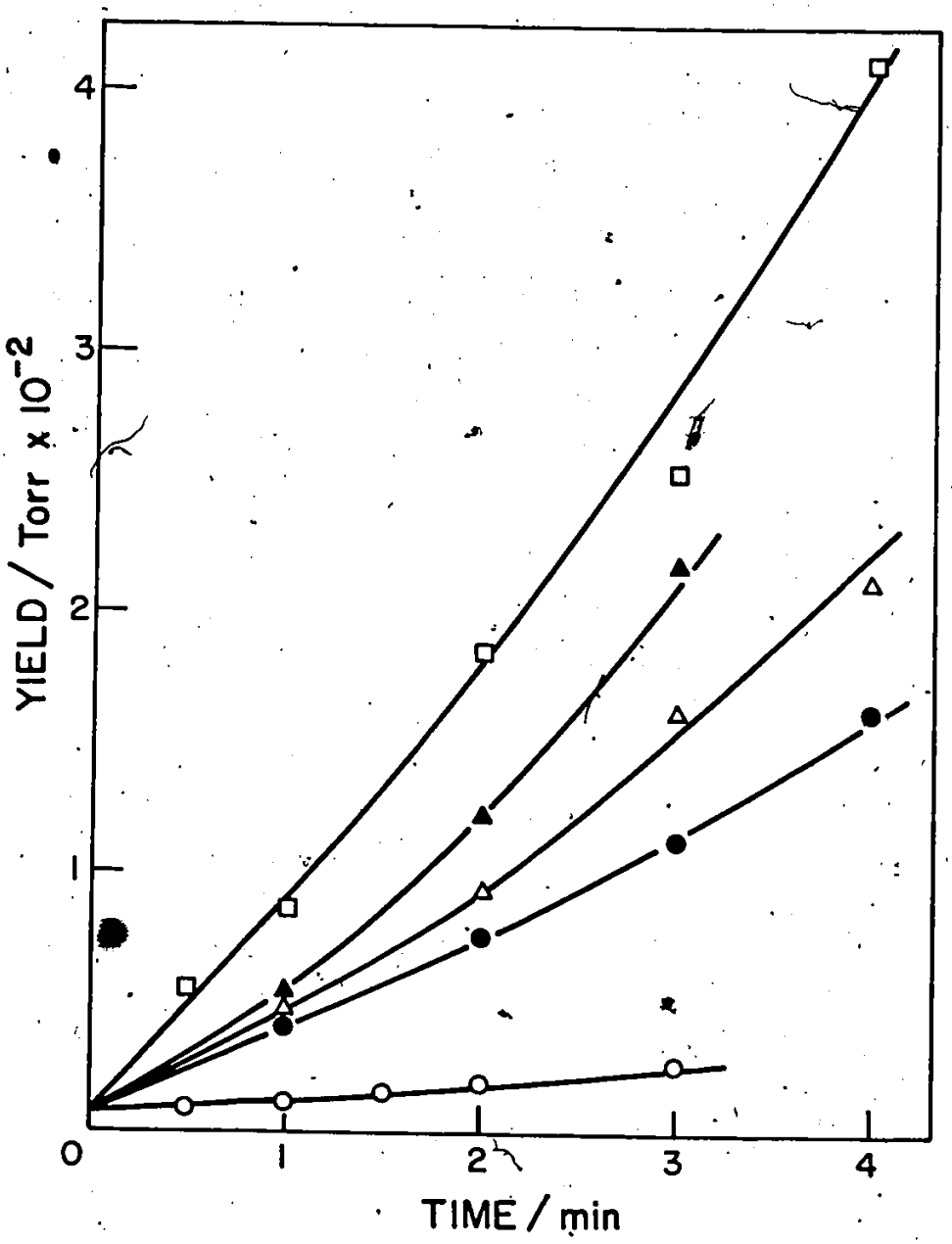


Fig. 8

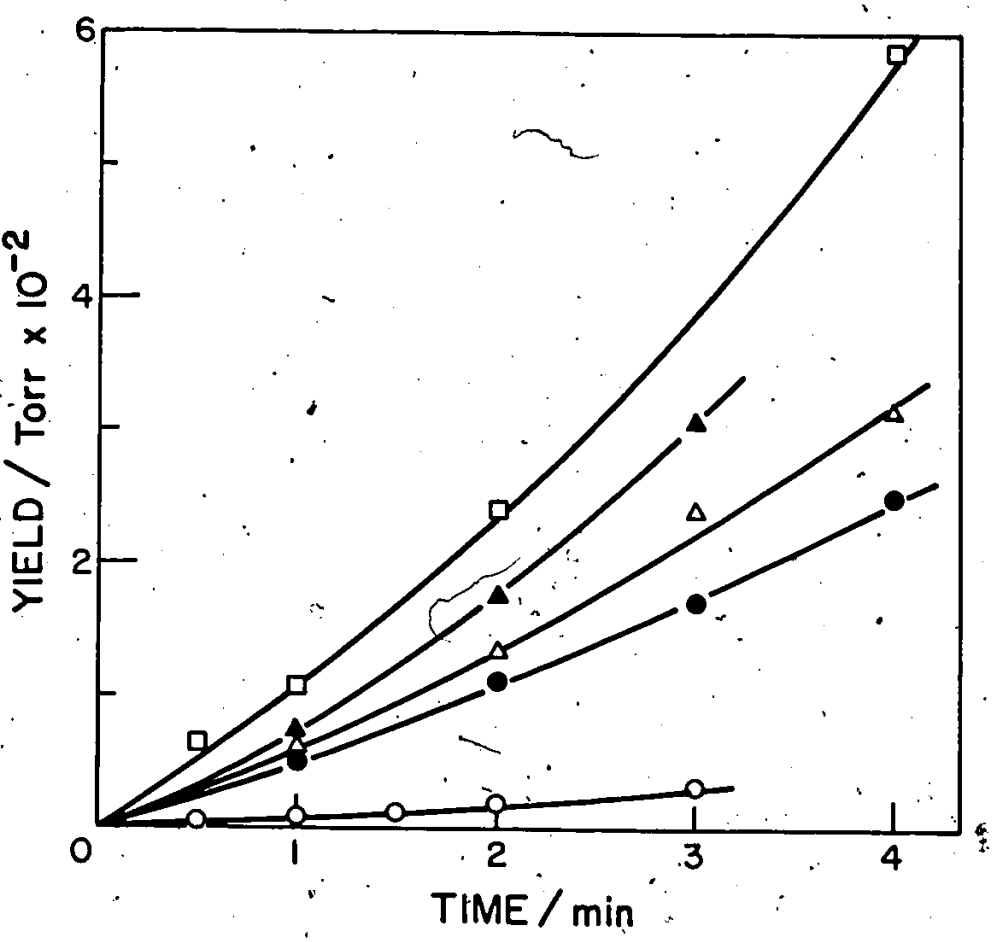


Fig. 9

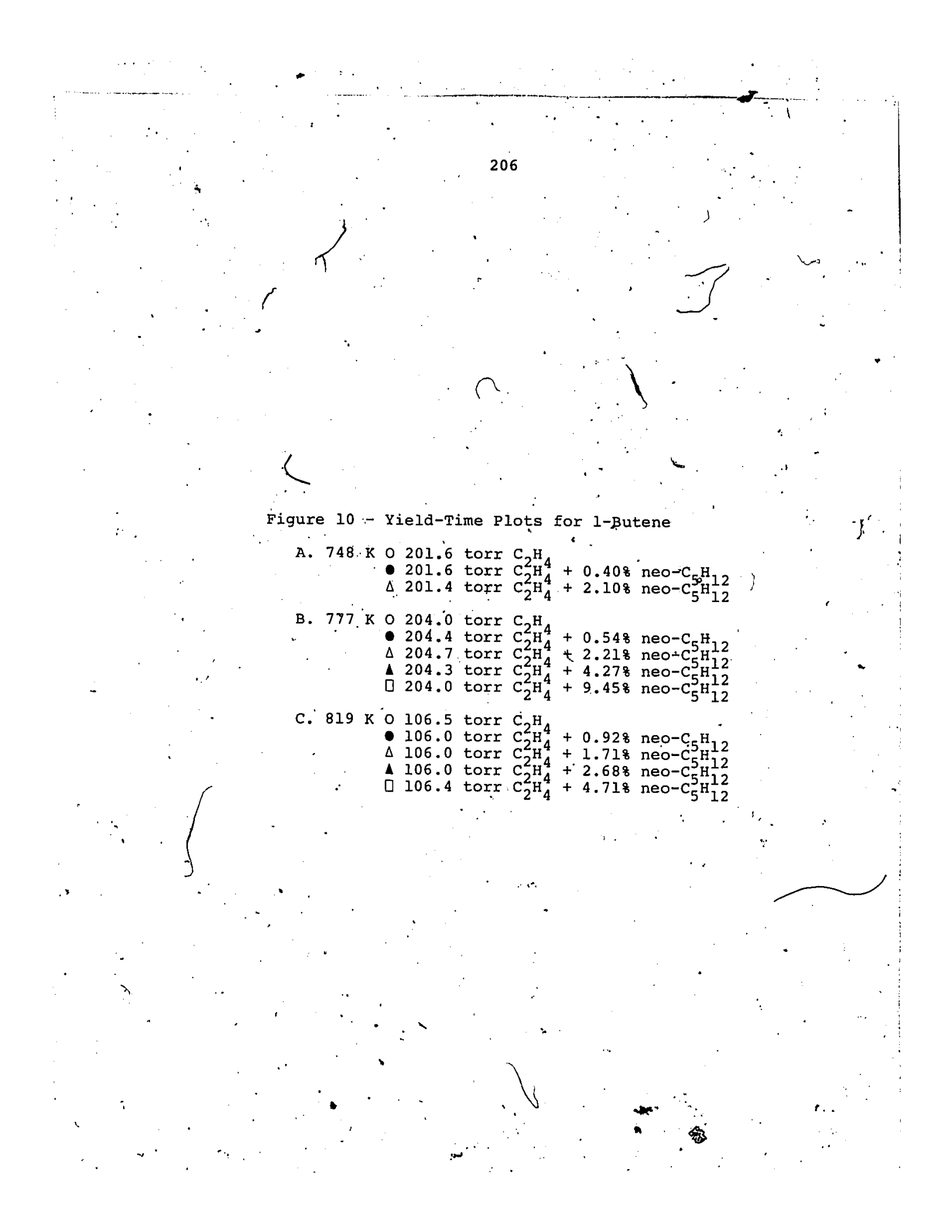


Figure 10 – Yield-Time Plots for 1-Butene

A. 748 K ○ 201.6 torr C_2H_4
● 201.6 torr C_2H_4 + 0.40% neo-C_5H_{12}
△ 201.4 torr C_2H_4 + 2.10% neo-C_5H_{12}

B. 777 K ○ 204.0 torr C_2H_4
● 204.4 torr C_2H_4 + 0.54% neo-C_5H_{12}
△ 204.7 torr C_2H_4 + 2.21% neo-C_5H_{12}
▲ 204.3 torr C_2H_4 + 4.27% neo-C_5H_{12}
□ 204.0 torr C_2H_4 + 9.45% neo-C_5H_{12}

C. 819 K ○ 106.5 torr C_2H_4
● 106.0 torr C_2H_4 + 0.92% neo-C_5H_{12}
△ 106.0 torr C_2H_4 + 1.71% neo-C_5H_{12}
▲ 106.0 torr C_2H_4 + 2.68% neo-C_5H_{12}
□ 106.4 torr C_2H_4 + 4.71% neo-C_5H_{12}

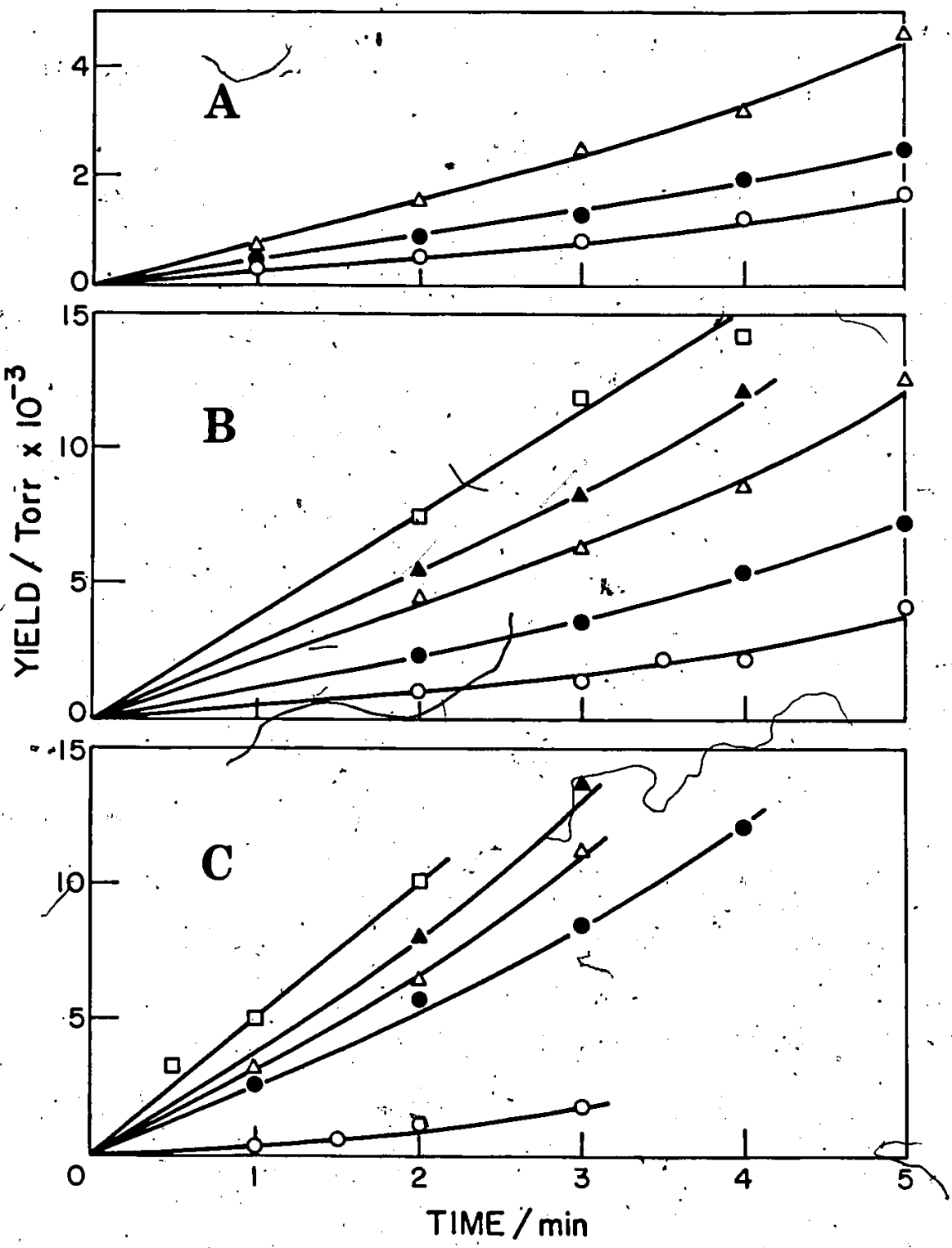


Fig. 10

Figure 11 - Yield-Time Plots for Butadiene

A. 803 K ○ 105.3 torr C_2H_4
● 105.5 torr C_2H_4 + 0.27% neo-C_5H_{12}
△ 106.0 torr C_2H_4 + 0.92% neo-C_5H_{12}
▲ 106.5 torr C_2H_4 + 4.27% neo-C_5H_{12}

B. 803 K ⊙ 206.2 torr C_2H_4
● 205.1 torr C_2H_4 + 0.27% neo-C_5H_{12}
△ 205.5 torr C_2H_4 + 0.29% neo-C_5H_{12}
▲ 205.7 torr C_2H_4 + 4.27% neo-C_5H_{12}

C. 819 K ○ 106.5 torr C_2H_4
● 106.0 torr C_2H_4 + 0.92% neo-C_5H_{12}
△ 106.0 torr C_2H_4 + 1.71% neo-C_5H_{12}
▲ 106.0 torr C_2H_4 + 2.68% neo-C_5H_{12}
□ 106.4 torr C_2H_4 + 4.71% neo-C_5H_{12}

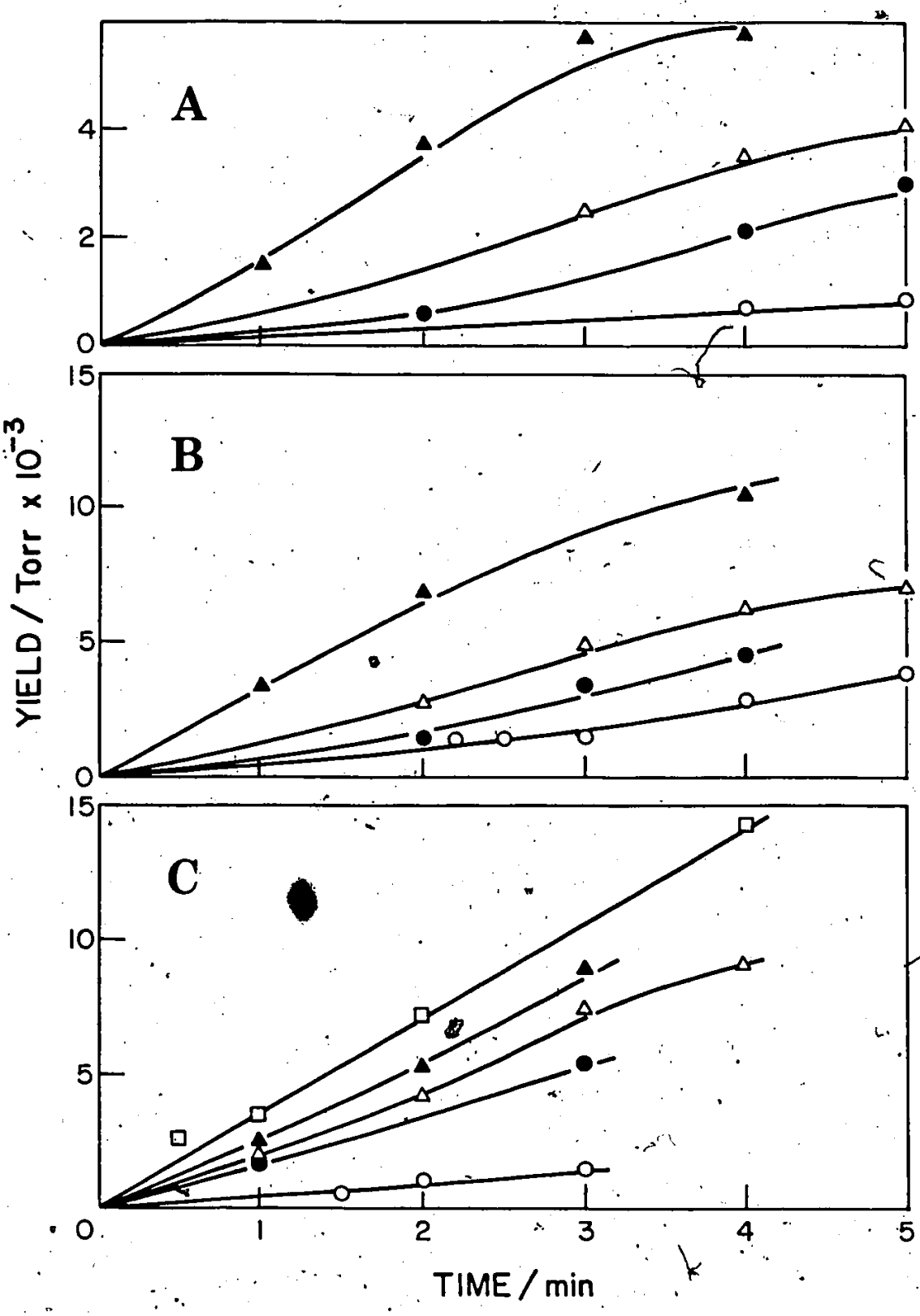


Fig. 11

Figure 12 - Yield-Time Plots for the Formation of Products from Purified Ethylene Pyrolysis

A, B & C - Methane, Ethane and Propylene, Respectively at 748 K

o 201.8 torr purified C_2H_4
● 201.6 torr purified C_2H_4 + 1.0% neo-C_5H_{12}

D,E,F & G - Methane, Ethane, Propylene and 1-Butene, Respectively at 793 K

o 105.4 torr purified C_2H_4
● 105.5 torr purified C_2H_4 + 1.0% neo-C_5H_{12}

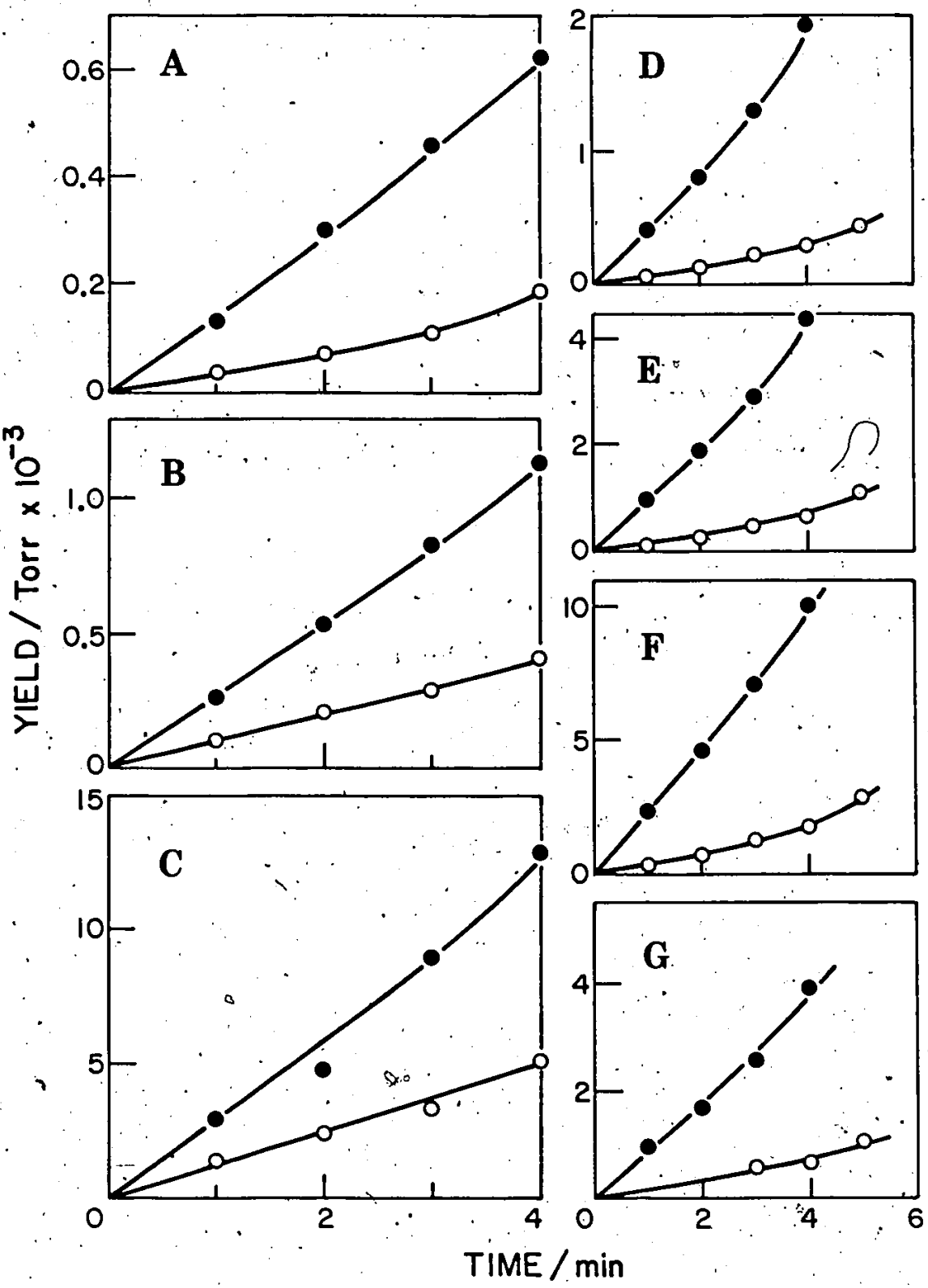


Fig. 12

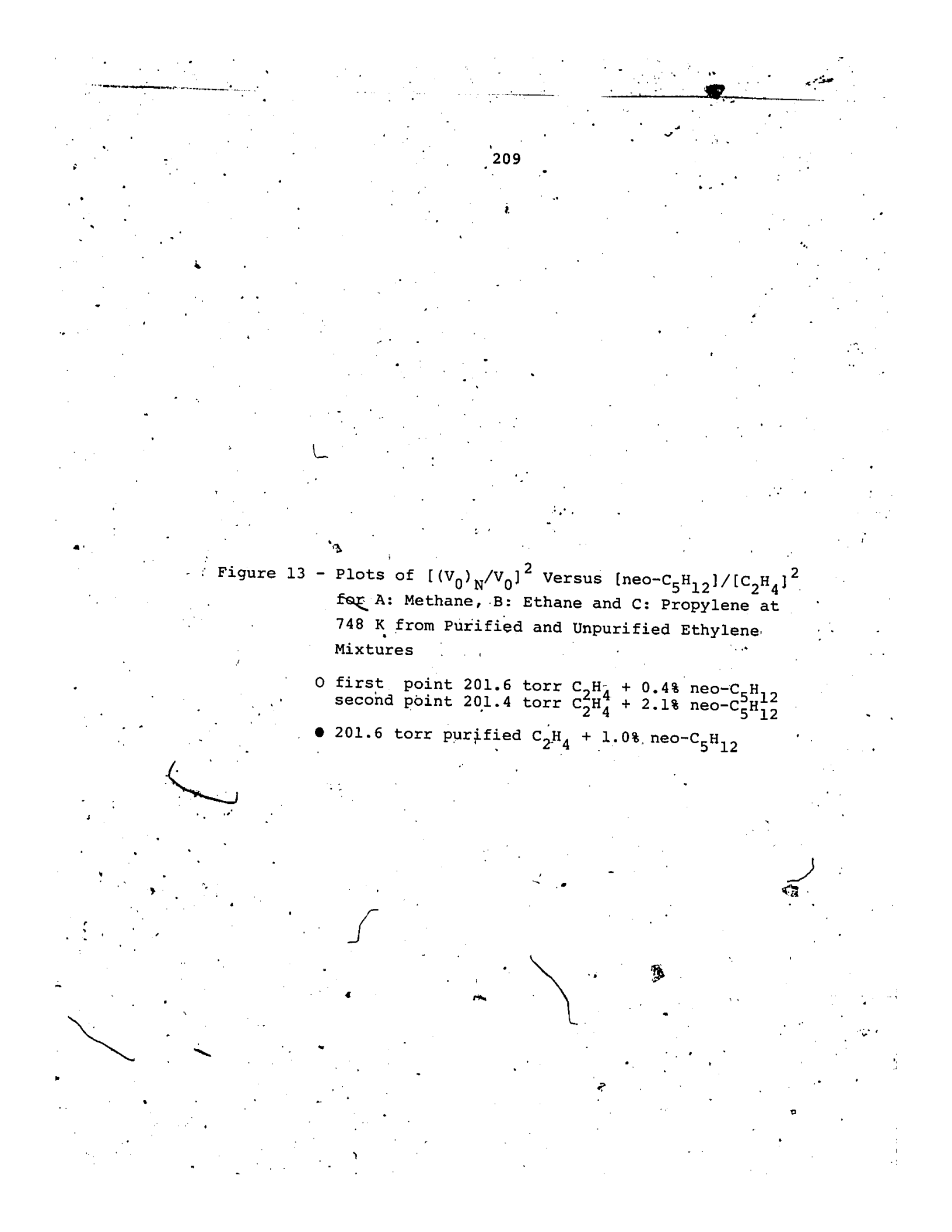


Figure 13 - Plots of $[(V_0)_N/V_0]^2$ Versus $[neo\text{-}C_5H_{12}]/[C_2H_4]^2$ for A: Methane, B: Ethane and C: Propylene at 748 K from Purified and Unpurified Ethylene Mixtures

O first point 201.6 torr C_2H_4 + 0.4% $neo\text{-}C_5H_{12}$
second point 201.4 torr C_2H_4 + 2.1% $neo\text{-}C_5H_{12}$

● 201.6 torr purified C_2H_4 + 1.0% $neo\text{-}C_5H_{12}$

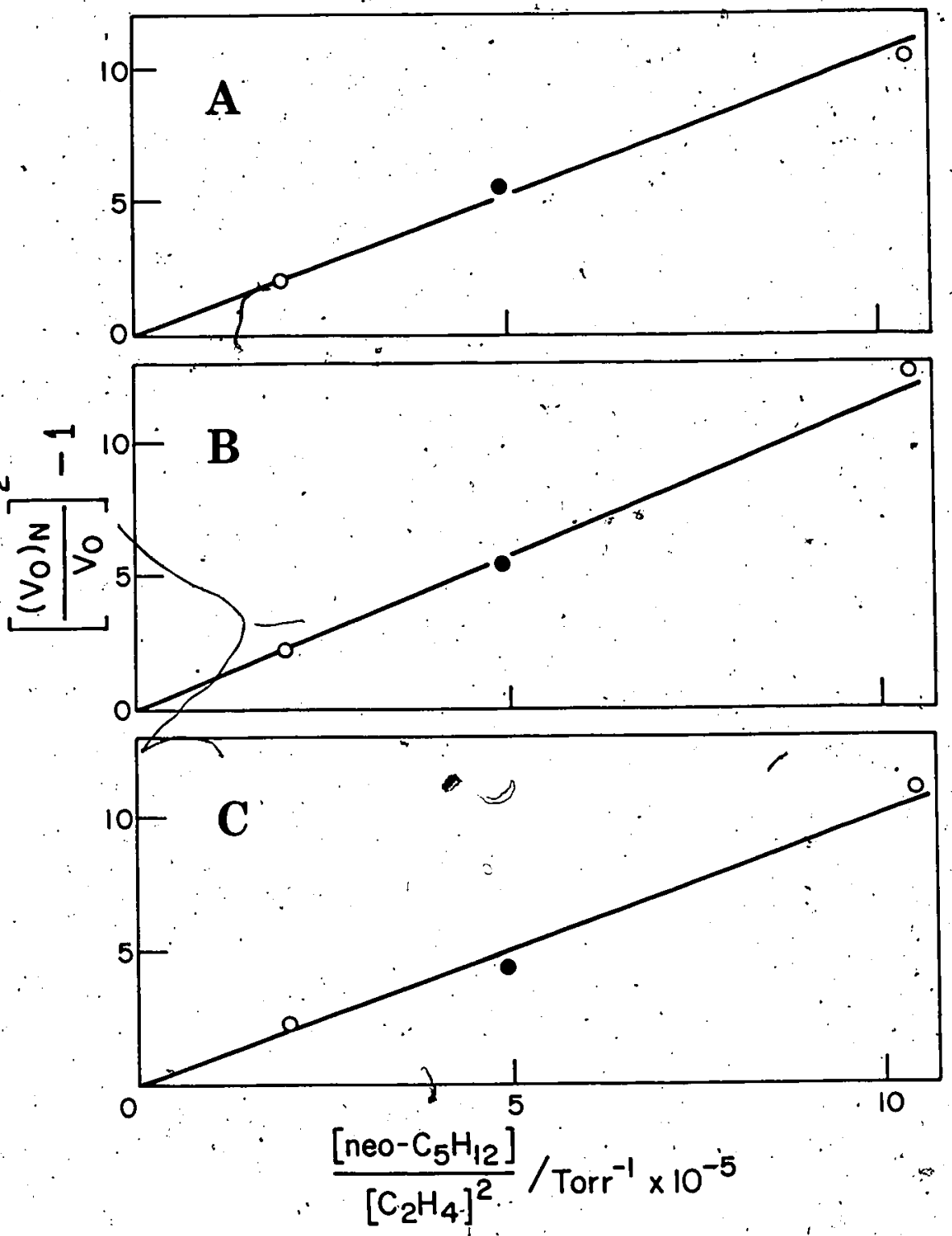

A
B
C
10
5
0
$\left[\frac{(V_0)_N}{V_0}\right]^2 - 1$
$\frac{[neo\text{-}C_5H_{12}]}{[C_2H_4]^2}$ / Torr^{-1} x 10^{-5}

Fig. 13

Table 1

YIELD-TIME DATA FOR THE C_2H_4+C_2H_6 SYSTEM

T/K	Reactant(s)	Reaction time/min	Yield/torr Methane	Propylene	1-Butene
777	204.3 torr C_2H_4	3.5	8.63×10^{-4}	8.50×10^{-3}	2.47×10^{-3}
		4	9.50×10^{-4}	1.10×10^{-2}	3.00×10^{-3}
		5	1.16×10^{-3}	1.45×10^{-2}	3.45×10^{-3}
		6	1.46×10^{-3}	1.85×10^{-2}	3.90×10^{-3}
		7	2.09×10^{-3}	2.60×10^{-2}	5.67×10^{-3}
		8	3.06×10^{-3}	4.05×10^{-2}	8.82×10^{-3}
	204.1 torr C_2H_4	3	8.80×10^{-4}	7.64×10^{-3}	1.84×10^{-3}
		4	1.47×10^{-3}	1.18×10^{-2}	3.00×10^{-3}
	+2.85% C_2H_6	5	1.69×10^{-3}	1.81×10^{-2}	4.12×10^{-3}
		6	2.19×10^{-3}	2.17×10^{-2}	4.77×10^{-3}
	204.3 torr C_2H_4	2	1.16×10^{-3}	5.83×10^{-3}	-
		2.5	1.85×10^{-3}	1.19×10^{-2}	2.40×10^{-3}
	+7.65% C_2H_6	3.5	2.33×10^{-3}	1.40×10^{-2}	3.47×10^{-3}
		6	4.28×10^{-3}	3.05×10^{-2}	7.12×10^{-3}
788	105.5 torr C_2H_4	2	1.84×10^{-4}	8.17×10^{-4}	2.84×10^{-4}
		3	2.70×10^{-4}	1.54×10^{-3}	6.47×10^{-4}
		4	4.14×10^{-4}	2.48×10^{-3}	9.47×10^{-4}
		5	5.98×10^{-4}	3.53×10^{-3}	1.46×10^{-3}
		6	7.82×10^{-4}	5.01×10^{-3}	1.80×10^{-3}
	105.4 torr C_2H_4	1	1.92×10^{-4}	4.80×10^{-4}	-
		2	3.08×10^{-4}	1.05×10^{-3}	3.46×10^{-4}
	+2.85% C_2H_6	3	4.66×10^{-4}	1.86×10^{-3}	6.13×10^{-4}
		4	6.97×10^{-4}	3.44×10^{-3}	1.23×10^{-3}
		5	8.40×10^{-4}	4.21×10^{-3}	1.48×10^{-3}
804	106.0 torr C_2H_4	0.5	4.70×10^{-5}	1.77×10^{-4}	1.19×10^{-4}
		1	1.39×10^{-4}	5.03×10^{-4}	2.19×10^{-4}
		2	3.01×10^{-3}	-	6.37×10^{-4}
		2.3	3.31×10^{-3}	1.42×10^{-3}	-
		3	4.97×10^{-3}	2.72×10^{-3}	1.34×10^{-3}
		4	6.27×10^{-3}	3.85×10^{-3}	1.47×10^{-3}
	106.1 torr C_2H_4	0.5	1.37×10^{-4}	2.66×10^{-4}	1.91×10^{-4}
		1	2.69×10^{-4}	6.64×10^{-4}	-
	+2.85% C_2H_4	2	5.68×10^{-4}	2.07×10^{-3}	9.72×10^{-4}
		3	8.24×10^{-4}	3.43×10^{-3}	1.72×10^{-3}
819	106.5 torr C_2H_4	0.5	1.08×10^{-4}	2.27×10^{-4}	-
		1	1.74×10^{-4}	4.87×10^{-4}	2.79×10^{-4}
		1.5	3.04×10^{-4}	1.14×10^{-3}	6.24×10^{-4}
		2	4.41×10^{-4}	1.88×10^{-3}	1.15×10^{-3}
		3	6.65×10^{-4}	3.18×10^{-3}	1.80×10^{-3}
	106.6 torr C_2H_4	0.5	1.99×10^{-4}	4.50×10^{-4}	2.46×10^{-4}
		1	4.00×10^{-4}	1.08×10^{-3}	4.60×10^{-4}
	+2.85% C_2H_4	1.5	4.92×10^{-4}	1.55×10^{-3}	8.70×10^{-4}
		2	8.55×10^{-4}	2.78×10^{-3}	1.54×10^{-3}
		3	1.28×10^{-3}	5.13×10^{-3}	2.91×10^{-3}

CLAIMS TO ORIGINAL RESEARCH

1. A kinetic method was developed for the measurement of the rate constant of the initiation process for a chain reaction mechanism. The method was based on the analysis of the effect of small quantities of additives on the reaction mechanism of the parent hydrocarbon.

2. This method was applied to the pyrolysis of ethylene in a static system using the additives 1-butene, neopentane and ethane in the temperature range 699 to 819 K with ethylene pressures 75 to 400 torr.

3. From the kinetics of the reaction in the presence and absence of the additives it was shown that the sole effect of the additives was the introduction of new initiation processes. The initiation process of the thermal reactions of ethylene alone was identified as a second-order reaction and was found to be homogeneous.

4. The rate constant of the initiation process of the pyrolysis of ethylene was measured as

$$\text{Log } k_1(\text{L mol}^{-1}\ \text{s}^{-1}) = (11.27 \pm 0.6) - \frac{(64200 \pm 2000)}{2.3RT}$$

5. Based on the measured frequency factor and the activation energy, the initiation process was further identified as the bimolecular reaction of ethylene to produce ethyl and vinyl radicals.

$$2C_2H_4 \rightarrow C_2H_5 + C_2H_3$$

6. From the measured activation energy, the value of the heat of formation of the vinyl radical was obtained as 63.4 ± 2 kcal mol^{-1}.

7. Using this value, the bond dissociation energy for the C-H bond in ethylene was calculated as 103 ± 2 kcal mol^{-1}. It was suggested that the C-H bond dissociation energy in neopentane could be only 3-4 kcal mol^{-I} less than that of ethylene.

8. The mechanism of the chain processes in the thermal decomposition of ethylene was discussed and shown to be consistent with the observed orders and activation energies of the rates of formation of the major products.

REFERENCES

1. M. Bodenstein, Z. Physik. Chem., 85, 329 (1913).

2. W. Nernst, Z. Electrochem., 24, 335 (1918).

3. a) J.A. Christiansen, Kgl. Danske Videnskab. Selskab Mat.-Fys. Medd., 1, 14 (1919); b) K.F. Herzfeld, Z. Electrochem., 25, 301 (1919); Ann. Physik., 59, 635 (1919); c) M. Polanyi, Z. Electrochem., 26, 50 (1920).

4. N. Semenov, Chemical Kinetics and Chain Reactions, Clarendon Press, Oxford, (1935).

5. F.O. Rice and K.F. Herzfeld, J. Am. Chem. Soc., 56, 284 (1934).

6. P. Goldfinger, M. Letort and M. Niclause, Contribution a l'étude de la structure moleculaire, Victor Henri Commemorative Volume, p. 283, Desoer, Liège (1948).

7. a) D.T. Day, Am. Chem. J., 8, 153 (1886); b) W.A. Bone and H.F. Coward, J. Chem. Soc., 93, 1197 (1908); c) E.N. Hague and R.V. Wheeler, J. Chem. Soc., 378 (1929); d) R.N. Pease, J. Am. Chem. Soc., 52, 1158 (1930).

8. R.N. Pease, J. Am. Chem. Soc., 53, 613 (1931).

9. H.H. Storch, J. Am. Chem. Soc., 56, 374 (1934).

10. H.D. Burnham and R.N. Pease, J. Am. Chem. Soc., 64, 1404 (1942).

11. J.E. Douglas, B.S. Rabinovitch and F.S. Looney, J. Chem. Phys., 23, 315 (1955).

12. C.G. Silcocks, Proc. Roy. Soc. London, Ser. A, 233, 465 (1956).

13. G. Dahlgren, Jr., and J.E. Douglas, J. Am. Chem. Soc., 80, 5108 (1958).

14. M. Taniewski, Proc. Roy. Soc. London, Ser. A, 265, 519 (1962).

15. M.P. Halstead and C.P. Quinn, Trans. Far. Soc., 64, 103 (1968).

16. M.L. Boyd, T.M. Wu and M.H. Back, Can. J. Chem., 46, 2415 (1968).

17. M. Simon and M.H. Back, Can. J. Chem., 47, 251 (1969).

18. M.H. Back, National Bureau of Standards Special Publication 357, 17 (1972).

19. M.J. Molera and F.J. Stubbs, J. Chem. Soc., 381 (1952).

20. M.H. Back and R. Martin, Int. J. Chem. Kinet., 11, 757 (1979).

21. G.B. Skinner and E.M. Sokoloski, J. Phys. Chem., 64, 1028 (1960).

22. I.D. Gay, R.D. Kern, G.B. Kistiakowski and H. Niki, J. Chem. Phys., 45, 2371 (1966).

23. S.W. Benson and G.R. Haugen, J. Phys. Chem., 71, 1735.(1967).

24. G.B. Skinner, R.C. Sweet and S.K. Davis, J. Phys. Chem., 75, 1 (1971).

25. T.H. Just, P. Roth and R. Damm, Proceedings of 16th International Symposium on Combustion, 16, 961 (1976).

26. T. Tanzawa and W.C. Gardiner, Jr., Comb. and Flame, 39, 241 (1980).

27. R.B. Cundall, D.E. Fussey, A.J. Harrison and D. Lampard, J. Chem. Soc. Far. Trans. I, 74, 1403 (1978).

28. T. Koike and K. Morinaga, Bull. Chem. Soc. Jpn., 54, 530 (1981).

29. K.J. Laidler and L.F. Loucks, Comp. Chem. Kinet., 5, 1 (1971).

30. S.W. Benson, Thermochemical Kinetics, Second Ed., Wiley, New York (1976).

31. M.H. Back, Can. J. Chem., 49, 2199 (1971).

32. R. Louw and H.J. Lucas, Rec. Trav. Chim. Pays-Bas, 92, 55 (1973).

33. H.E. O'Neal and S.W. Benson, "Thermochemistry of Free Radicals" in Free Radicals, Ed. J.K. Kochi, V:2, p. 275, Wiley, New York (1973).

34. S.W. Benson, J. Chem. Ed., 502 (1965).

35. F. Elder, C.F. Giese, B. Steiner and M.G. Ingham, J. Chem. Phys., 36, 3292 (1962).

36. P. Marmet and L. Kerwin, Can. J. Phys., 38, 787 (1960).

37. P. Marmet and J.D. Morrison, J. Chem. Phys., 36, 1238 (1962).

38. R.E. Fox, W.M. Hickman, T. Kjildaas and D.J. Grove, Phys. Rev., 84, 859 (1951).

39. R.E. Fox, W.M. Hickman, T. Kjildaas and D.J. Grove, Rev. Sci. Instrum., 12, 1101 (1955).

40. J.A. Kerr and A.F. Trotman-Dickenson, Progr. Reaction Kinetics, 1, 113 (1961).

41. E.L. Metcalfe, J. Chem. Soc., 3560 (1963).

42. E.L. Metcalfe and A.F. Trotman-Dickenson, J. Chem. Soc., 4620 (1962).

43. J.A. Kerr, Chem. Rev., 66, 465 (1966).

44. S.W. Benson and H.E. O'Neal, Kinetic Data on Gas Phase Unimolecular Reactions, NSRDS-NBS21, U.S. Government Printing Office, Washington, D.C., (1970).

45. W. Tsang, J. Chem. Phys., 42, 1805 (1964).

46. W. Tsang, Int. J. Chem. Kinet., 10, 821 (1978).

47. D.M. Golden and S.W. Benson, Chem. Rev., 69, 125 (1969).

48. S.W. Benson, "The Thermochemistry and Kinetics of Gas Phase Reactions" in Frontiers of Free Radical Chemistry, Ed. W.A. Pryor, p. 1, Academic Press, New York (1980).

49. M. Niclause, R. Martin, F. Baronnet and G. Scacchi, Rev. Inst. Fr. Pétrole, 21, 1724 (1966).

50. J. Müller, F. Baronnet and M. Niclause, C.R. Acad. Sc., 274C, 1772 (1972).

51. G. Scacchi, F. Baronnet, R. Martin and M. Niclause, J. Chim. Phys., 65, 1671 (1968).

52. J. Muller, F. Baronnet, G. Scacchi and M. Niclause, C.R. Acad. Sc., 272C, 271 (1971).

53. Y. Gousty and R. Martin, Reac. Kin. and Cat. Lett., 1, 189 (1974).

54. R.V. Wheeler and W.L. Wood, J. Chem. Soc., 1819 (1930).

55. C.J. Danby, B.C. Spall, F.J. Stubbs and C. Hinshelwood, Proc. Roy. Soc. London, Ser. A, 228, 448 (1955).

56. A.H. Sehon and M. Szwarc, Proc. Roy. Soc. London, Ser. A, 202, 263 (1950).

57. F.P. Lossing, K.V. Ingold and I.H.S. Henderson, J. Chem. Phys., 22, 621 (1954).

58. W.A. Bryce and P. Kebarle, Trans. Far. Soc., 54, 1660 (1958).

59. H. Mellottee and R. Delbourgo, Bull. Soc. Chim., 10, 3473 (1970).

60. A.B. Trenwith, J. Chem. Soc. Far. Trans. I, 69, 1737 (1973).

61. D.R. Powers and W.H. Corcoran, Industrial and Laboratory Pyrolyses, ACS Sym. Ser. 32, p. 117, ACS, Washington, D.C., (1976).

62. K.J. Laidler and B.W. Wojciechowski, Proc. Roy. Soc. London, Ser. A, 259, 257 (1960).

63. A.S. Kallend, J.H. Purnell and B.C. Shurlock, Proc. Roy. Soc. London, Ser. A, 300, 120 (1967).

64. M. Simon and M.H. Back, Can. J. Chem., 48, 317 (1970).

65. M. Simon and M.H. Back, Can. J. Chem., 51, 2934 (1973).

66. M.H. Back, Int. J. Chem. Kinet., 2, 409 (1970).

67. T. Yano, Int. J. Chem. Kinet., 9, 725 (1977).

68. G.A. Chappel and H. Shaw, J. Phys. Chem., 72, 4672 (1968).

69. R.B. Cundall, D.W. Fussey, A.J. Harrison and D. Lampard, J. Chem. Soc. Far. Trans. I, 75, 1390 (1979).

70. C. Richard and R. Martin, J. Chim. Phys., 73, 745 (1976).

71. C. Richard, A. Boiveaut and R. Martin, Int. J. Chem. Kinet., 12, 921 (1980).

72. M. Niclause, F. Baronnet, G. Scacchi, J. Muller and J.Y. Jezequel, Industrial and Laboratory Pyrolyses, ACS Sym. Ser. 32, p. 17, ACS, Washington, D.C., (1976).

73. S.W. Benson, Int. J. Chem. Kinet., 11, 147 (1979).

74. S.P. Heneghan, P.A. Knoot and S.W. Benson, Int. J. Chem. Kinet., 13, 677 (1981).

75. M. Rossi and D.M. Golden, J. Am. Chem. Soc., 101, 1230 (1979).

76. M. Rossi, K.D. King and D.M. Golden, J. Am. Chem. Soc., 101, 1223 (1979).

77. W. Tsang, J. Chem. Phys., 46, 2817 (1967).

78. J. Muller, F. Baronnet, G. Scacchi, M. Dzierzynski and M. Niclause, Int. J. Chem. Kinet., 9, 425 (1977).

79. R.M. Marshall, H. Purnell and P.D. Storey, J. Chem. Soc. Far. Trans. I, 72, 85 (1976).

80. E. Furimsky and K.J. Laidler, Can. J. Chem., 50, 1115 (1972).

81. F. Baronnet, M. Dzierzynski, G.M. Come, R. Martin and M. Niclause, Int. J. Chem. Kinet., 3, 197 (1971).

82. F. Baronnet, M. Dzierzynski, R. Martin and M. Niclause, C.R. Acad. Sc. Paris, t. 267, 937 (1968).

83. M.P. Halstead, R.S. Konar, D.A. Leathard, R.M. Marshall and J.H. Purnell, Proc. Roy. Soc. London, Ser. A, 310, 525 (1969).

84. P.D. Pacey, Can. J. Chem., 51, 2415 (1973).

85. P.D. Pacey and J.H. Wimalasena, Chem. Phys. Lett., 53, 593 (1978).

86. P.D. Pacey and J.H. Wimalasena, J. Phys. Chem., 84, 2221 (1980).

87. W. Tsang, J. Chem. Phys., 44, 4283 (1966).

88. J.N. Bradley and K.O. West, J. Chem. Soc. Far. Trans. I, 78, 8 (1976).

89. A.C. Baldwin, K.E. Lewis and D.M. Golden, Int. J. Chem. Kinet., 11, 529 (1979).

90. G.M. Atri, R.R. Baldwin, G.A. Evans and R.W. Walker, J. Chem. Soc. Far. Trans. I, 74, 366 (1978).

91. M. Luria and S.W. Benson, J.Am. Chem. Soc., 97, 3342 (1975).

92. K.Y. Choo, P.C. Beadle, L.W. Piskiewicz and D.M. Golden, Int. J. Chem. Kinet., 8, 45 (1976).

93. F.A. Houle and J.L. Beauchamp, J. Am. Chem. Soc., 100, 3290 (1978).

94. M. Rossi and D.M. Golden, Int. J. Chem. Kinet., 11, 969 (1979).

95. H. Teranishi and S.W. Benson, J. Am. Chem. Soc., 85, 2887 (1963).

96. D.A. Parkes and C.P. Quinn, J. Chem. Soc. Far. Trans. I, 72, 1952 (1976).

97. R.E. Berkley, I. Safarik, H.E. Gunning and O.P. Strausz, J. Phys. Chem., 77, 1734 (1973).

98. A.F. Trotman-Dickenson and E.W.R. Steacie, J. Chem. Phys., 19, 169 (1951).

99. J.H. Purnell, "Homogeneous Alkane Cracking" in Frontiers of Free Radical Chemistry, Ed. W.A. Pryor, p. 93, Academic Press, New York, (1980).

100. J.A. Kerr, "Rate Processes in the Gas Phase" in Free Radicals, Ed. J.K. Kochi, V. 1, p. 1, Wiley, New York, (1973).

101. P.D. Pacey and J.H. Purnell, J. Chem. Soc. Far. Trans. I, 68, 1462 (1972).

102. T.C. Clark, T.P.J. Izod and G.B. Kistiakowski, J. Chem. Phys., 54, 1295 (1971).

103. F.O. Rice and R.E. Varnerin, J. Am. Chem. Soc., 76, 324 (1954).

104. M.C. Lin and M.H. Back, Can. J. Chem., 44, 505 (1966).

105. M.C. Lin and M.H. Back, Can. J. Chem., 44, 2357 (1966).

106. A.B. Trenwith, Trans. Far. Soc., 62, 1538 (1966).

107. J.A. Clark and C.P. Quinn, J. Chem. Soc. Far. Trans. I, 72, 706 (1976).

108. A. Burcat, G.B. Skinner, R.W. Crossley and K. Scheller, Int. J. Chem. Kinet., 5, 345 (1973).

109. A.B. Trenwith, J. Chem. Soc. Far. Trans. I, 75, 614 (1979).

110. M.C. Lin and M.H. Back, Can. J. Chem., 45, 3165 (1967).

111. G. Pratt and D. Rogers, J. Chem. Soc. Far. Trans. I, 75, 1089 (1979).

112. R.W. Walker, in Gas Kinetics and Energy Transfer, Ed. P.G. Ashmore and R.J. Donovan, Spec. Per. Rep., The Chem. Soc., London, V. 2 (1976).

113. K. Glanzer, M. Quack and J. Troe, 16th Int. Sym. Comb., The Comb. Inst., (1976).

114. D.G.L. James and G.E. Troughton, Trans. Far. Soc., 62, 145 (1966).

115. Handbook of Bimolecular and Termolecular Gas Reactions, Edts. J.A. Kerr and S.J. Moss, V. I and II, CRS Press, Inc., (1981).

116. N.A. Weir, J. Chem. Soc., 6870 (1965).

117. A.G. Sherwood and H.E. Gunning, J. Phys. Chem., 69, 2323 (1965).

118. D.J. LeRoy and A.W. Tickner, J. Chem. Phys., 19, 1247 (1951).

119. D.M. Golden, K.Y. Choo, M.J. Perona and L.W. Piszkiewicz, Int. J. Chem. Kinet., 8, 381 (1976).

120. H. Adachi, N. Basco and D.G.L. James, Int. J. Chem. Kinet., 11, 995 (1979).

121. P. Warneck, Z. Naturforsch Teil.A, 26, 2047 (1971).

122. W.A. Chupkaand and C. Lifshitz, J. Chem. Phys., 48, 1109 (1968).

123. H.E. O'Neal and S.W. Benson, J. Phys. Chem., 72, 1866 (1968).

124. L.M. Quick, D.A. Knecht and M.H. Back, Int. J. Chem. Kinet., 4, 61 (1972).

125. S.W. Benson, Adv. Photochem., 2, 1 (1964).

126. P.D. Pacey, J. Chem. Ed., 58, 612 (1981).

127. P.J. Robinson, J. Chem. Ed., 55, 509 (1978).

128. D.M. Golden, J. Chem. Ed., 48, 235 (1971).

129. G.C. Fettis, J.H. Knox and A.F. Trotman-Dickenson, J. Chem. Soc., 4177 (1960).

130. G.C. Fettis and A.F. Trotman-Dickenson, J. Chem. Soc., 3037 (1961).

131. D.B. Hartley and S.W. Benson, J. Chem. Phys., 39, 132 (1963).

132. L.F. Loucks and K.J. Laidler, Can. J. Chem., 45, 2795 (1967).

133. A.L. Castelhano, P.R. Marriott and D. Griller, J. Am. Chem. Soc., in press.

134. C. Juste, G. Scacchi and M. Niclause, Int. J. Chem. Kinet., 13, 855 (1981).

135. A.G. Harrison and F.P. Lossing, J. Am. Chem. Soc., 82, 519 (1960).

136. A.F. Trotman-Dickenson and G.J.O. Verbeke, J. Chem. Soc., 2580 (1961).

137. F.P. Lossing, Can. J. Chem., 49, 357 (1971).

138. D.J. DeFrees, R.T. McIver, Jr., and W.J. Hehre, J. Am. Chem. Soc., 102, 3334 (1980).

139. D.J. Donaldson, D.G. Watson and J.J. Sloan, Chem. Phys., in press.

140. F.P. Lossing, private communication.