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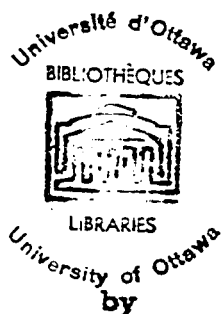
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PYROLYSIS OF ETHANE



Ming-Chang Lin

A thesis submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
in the
Department of Chemistry
University of Ottawa
Ottawa, Canada

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To
MY PARENT

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ABSTRACT

Ethane has been pyrolyzed at temperatures ranging from 530 to 726°C. From the rate of production of methane, the initial split of ethane into methyl radicals was found to be pressure-dependent below 200 mm. The activation energy of this step obtained from high-pressure first-order rate constants was 36.0 kcal mole⁻¹. This led to a dissociation energy of the C-C bond, $D(\text{CH}_3\text{-CH}_3)$, of 85.0 kcal mole⁻¹, assuming the activation energy for the combination of methyl radicals was to be zero.

The order of the decomposition determined from hydrogen production was found to change smoothly from 0.94 at 500 mm. to 1.20 at 50 mm, approaching 1.5 at lower pressures. The activation energy obtained from first-order rate constants based on the hydrogen production was 77.6 kcal mole⁻¹.

The kinetics of butane production showed that the main terminating step was the combination of ethyl radicals. Under the conditions of the present experiments, the decomposition of the ethyl radical was found to be pressure-dependent. Using Powell's method of extrapolation, the limiting rate constants at high and low pressures were obtained and the corresponding activation energies were determined to be 38.0 and 32.4 kcal mole⁻¹, respectively. The pressure sensitivity of both initiation and propagation reactions accounts for the observed order of the decomposition.

A 15-fold increase in surface/volume ratio reduced the rates of both hydrogen and butane production, whereas that of methane formation remained essentially the same.

In the temperature range 640-725°C, the pressure dependence of the unimolecular decomposition of the ethane molecule was studied at pressures from 1 to 200 mm. The fall-off of the first order rate constants could be described roughly by HRR theory with 13 effective oscillators. Powell's extrapolation led to an activation energy of 72.5 kcal mole⁻¹ for the second order decomposition.

Equations were proposed to describe quantitatively the production of hydrogen, methane and butane to conversion as high as 50%. Small amounts of ethylene inhibited the decomposition, but increased the rates of methane, butane, butene-1 and butadiene formation. The activation energy of butene-1 formation was 40 ± 4 kcal/mole and probably was produced by decomposition of the n-butyl radical. At the higher temperatures butadiene and acetylene were the main secondary products. The most probable precursor for both products is the C₂H₃ radical formed by the abstraction of hydrogen from ethylene.

On the basis of the mechanism of the ethane decomposition, a free radical chain mechanism for the reverse reaction, C₂H₄ + H₂ → C₂H₆ was proposed, according to which the chain was initiated by the disproportionation of two ethylene molecules to form ethyl and vinyl radicals and terminated by the combination of ethyl radicals. This mechanism led to an activation energy of 44.5 kcal mole⁻¹, which agrees with the experimental value of 44.8 kcal mole⁻¹.

PART I

KINETICS AND MECHANISM OF PRIMARY
AND SECONDARY REACTIONS

CHAPTER 1

INTRODUCTION

I. Object of the present investigation:

The mechanism of the pyrolysis of ethane has long been a subject of discussion and controversy. Only in recent years has there been general agreement that decomposition proceeds essentially by a free radical chain process. Earlier work, largely done in static systems by manometric methods, indicated first-order kinetics. A study of pressure change alone is not sufficient to elucidate the complete mechanism, however, unless the kinetics of the elementary reactions are all well-known. Controversies arose partly because of insufficient experimental data.

The problem of the ethane decomposition hinges on whether the initial unimolecular decomposition of ethane into methyl radicals is first-order, second-order or in an intermediate region. To answer this question the products produced from both initiation and termination steps were analysed under different conditions of pressure and temperature.

This thesis is divided into two parts. The first part of the thesis deals mainly with the mechanisms of primary and secondary reactions and the second part discusses the unimolecular decompositions of ethane and the ethyl radical. The theories of unimolecular reactions are briefly reviewed and the structures of the activated complexes associated with these two reactions have been considered in terms of the symmetries of the activated complexes.

II. Historical review

(1). Evidence for the occurrence of radicals:

There is a great deal of evidence that free radicals are formed in the thermal decomposition of ethane. Using the Paneth technique (1), Rice and Dooley (2) found that lead mirrors were removed by the products of ethane decomposition at 850 to 950°C. Using a mass spectrometer Eltenton (3) detected methyl and ethyl radicals at 900-1070°C and at pressures from 10^{-2} to 120 mm. Similar results were reported by Lossing and coworkers (4) at 1100°C.

Wall and Moore (5) studied the decomposition of C_2H_6 and C_2D_6 mixtures in the presence and absence of nitric oxide at 610°C. They found HD, CH_3D , CD_3H , CH_2D_2 , C_2H_5D and C_2D_5H among the products. The work of Rice and Varnerin (6) was more conclusive. They investigated the normal and inhibited decomposition of C_2D_6 in the presence of CH_4 . The CH_3D/CH_4 ratio was found to be proportional to the amount of C_2D_6 decomposed. The same relationship held for HD and C_2H_5D . All these findings strongly support the presence of radicals in the pyrolysis of ethane.

(2). Kinetics of the Reaction:

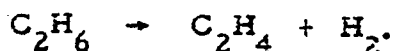
Early work on the decomposition of ethane by Pease (7) and by Frey and Smith (8) indicated that the reaction led predominantly to ethylene and hydrogen, and that it was probably homogeneous and of the first order.

The first quantitative investigation was done by Marek and McCluer (9) in 1931 using a flow system. They concluded that the reaction was of the first order. Recalculation of their results by Paul and Marek (10)

led to the first order rate constants

$$k_{\text{over-all}}^{\infty} = 1.1 \times 10^{16} e^{-77,700/RT} \text{ sec}^{-1}$$

for the over-all reaction,



This value disagreed markedly with that of Sachsse (11), who carried out a more thorough study by a static method. The high-pressure first-order rate constants obtained by extrapolation were represented by

$$k_{\text{over-all}}^{\infty} = 1.3 \times 10^{14} e^{-69,800/RT} \text{ sec}^{-1}.$$

He also found a small amount of condensable products when ethylene and hydrogen were added to the system. This finding was further confirmed by Storch and Kassel (12). The extrapolated rate constants, $k_{\text{over-all}}^{\infty}$, were of doubtful meaning, however, as the rate constant of an over-all reaction usually involves several rate constants of individual steps any one of which may be pressure-dependent. If such is the case the ordinary Lindemann extrapolation is no longer valid.

In 1939, Kuchler and Theile (13) investigated the reaction in the presence of inert gases. They found that the addition of inert gases enhanced the rate of over-all decomposition. From their results on ethane alone they obtained the following expression for the high-pressure rate constants,

$$k_{\text{over-all}}^{\infty} = 5.2 \times 10^{15} e^{-76,400/RT} \text{ sec}^{-1}.$$

This disagreed keenly with that of Sachsse in activation energy, although the absolute values of the rate constants were similar. This

high value of the activation energy, however, agrees with that of Marek and McCluer.

The reaction was reinvestigated by Steacie and Shane (14) using a static method. The rates were obtained either by measuring initial rates of pressure change or by correcting for the back reaction, $C_2H_4 + H_2 \rightarrow C_2H_6$. A 15-liter quartz vessel was used in order to minimize surface effects and to ensure a sufficient quantity of products for measurements at the initial stage of decomposition. Products other than ethylene and hydrogen accounted for about 5-10% of the total yield. Methane appeared to be about 2~5% of ethylene. Their high-pressure rate constants were given by

$$k_{\text{over-all}}^{\infty} = 1.0 \times 10^{14} e^{-69,700/RT} \text{ sec}^{-1},$$

in excellent agreement with that of Sachsse.

In view of the uncertainties in the kinetics and mechanism of the reaction, Laidler and Wojciechowski (15) re-examined the problem in both theoretical and experimental aspects. Using a spiral gauge and automatic recording system, they were able to determine initial rates of decomposition. The reaction was found to be accurately of the first-order in the high pressure and low temperature regions. At lower pressures and higher temperatures, the order of the reaction increased to 3/2. The rate was decreased slightly by an increase in surface/volume ratio, while the order and activation energy were increased. From the effect of the addition of hydrogen and ethylene, they proposed a mechanism which was able to predict the rate of decomposition at any instant of reaction. The first order rate constants they obtained were given by

$$k_{\text{over-all}}^{\infty} = 1.07 \times 10^{15} e^{-73,100/RT} \text{ sec}^{-1}.$$

The absolute values of the rate constants agreed fairly well with those of Sachse, of Kuchler and Theile and of Steacie and Shane. The activation energy, $73.1 \text{ kcal mole}^{-1}$, which is about the average of previous results, agrees quite reasonably with the value $74.6 \text{ kcal mole}^{-1}$ calculated according to the Kuchler-Theile mechanism and the theoretical treatment of Gill and Laidler (16).

All the results aforementioned were obtained from the measurement of pressure changes. None of them dealt with the formation of minor products quantitatively. The first attempt to do this was made by Leigh, Szwarc and Bigeleisen (17). They used a tracer technique in a flow system at $766\text{-}836^{\circ}\text{C}$, using toluene as a carrier gas with total pressure of about 15 mm Hg. Their preliminary measurements of methane production led to an activation energy of $85 - 89 \text{ kcal mole}^{-1}$ for the initial split of ethane. The order of this reaction with respect to ethane was close to one.

Recently, Davis and Williamson (18) studied the reaction laying special emphasis on the measurement of minor products in the range of temperature $675\text{-}775^{\circ}\text{C}$ using a flow system. Methane was formed probably by a first-order reaction with the extrapolated rate constants given by

$$k_1 = 1.95 \times 10^{16} e^{-86,000/RT} \text{ sec}^{-1}.$$

An increase in the total pressure of the reaction mixture enhanced slightly the rate of methane production and increased markedly that of hydrogen formation. The formation of methane was not inhibited by propylene and was considered to measure the

primary rupture of the carbon-carbon bond in ethane to form methyl radicals. From their butane measurement, they concluded that the combination of ethyl radicals was a major chain-ending step.

These findings were further confirmed by Quinn (19). He applied the same technique as that of Laidler and Wojciechowski to determine the initial over-all rate of decomposition and at the same time measured methane production by gas chromatography. The order of the over-all reaction was found to be 1.10 and that of methane production exactly one at 564°C and at pressures varying from 60 to 200 mm Hg. The activation energy of the over-all decomposition was $78.2 \pm 3 \text{ kcal mole}^{-1}$, which is slightly higher than previous values. The first-order rate constants associated with methane formation were given by

$$k_1 = 2.81 \times 10^{17} e^{-91,700/RT} \text{ sec}^{-1}.$$

This activation energy disagrees sharply with that of Davis and Williamson.

Gordon (20), on the other hand, reported a much lower value for the activation energy of the initiation reaction. Using a mass spectrometer, he found that both methane and hydrogen production were first-order reactions. At higher temperatures and lower pressures, the transition of the order of hydrogen production from 1 to 3/2 was also observed. The first-order rate constants of hydrogen and methane production were represented, respectively, by

$$k_{\text{over-all}} = 3.2 \times 10^{16} e^{-81,000/RT} \text{ sec}^{-1}$$

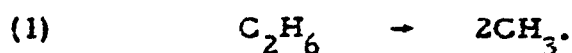
and

$$k_1 = 4.0 \times 10^{14} e^{-81,000/RT} \text{ sec}^{-1}.$$

The activation energy, 81.0 kcal mole⁻¹ is probably too high for the over-all decomposition, and perhaps too low for the initiation reaction.

(3). Mechanism of decomposition:

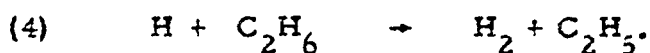
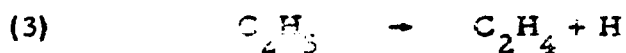
On the evidence of the occurrence of radicals in the ethane system observed by Rice and Dooley, Rice and Herzfeld (21) in 1934 postulated a chain mechanism to explain the first-order kinetics for the over-all reaction, $\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$. The reaction was considered to be initiated by a first-order unimolecular dissociation of ethane:



This was followed by the abstraction of a hydrogen atom from the parent molecule, which was present in comparatively large amount.



The ethyl radical was assumed to decompose unimolecularly and propagate the chain:



To explain the first-order over-all kinetics, the termination step was postulated as:



Steady-state treatment of the proposed mechanism leads to

$$-\frac{d[C_2H_6]}{dt} = \left(\frac{k_1 k_3 k_4}{k_6} \right)^{1/2} [C_2H_6] \quad [1]$$

This is in agreement with the experimental results in so far as the order of the reaction is concerned. However, with recent values for the rates of the individual steps in the mechanism, the concentration of the ethyl radicals is much greater than that of hydrogen atoms (22); accordingly, the reaction



should be more important. This, however, leads to 1/2 order kinetics if reaction (1) is in its first-order region.

In an attempt to overcome this difficulty inherited from the Rice-Herzfeld mechanism and to explain the acceleration effect of inert gases on the rate of decomposition, Klichler and Theile (13) proposed that the initial split of ethane into methyl radicals was a second-order reaction. The first-order over-all kinetics could then be accounted for with the combination of ethyl radicals as the chain-ending step. The chain-propagating processes were, considered to be the same. Steady-state treatment of reactions (1) to (5) leads to

$$-\frac{d[C_2H_6]}{dt} = k_3 \left(\frac{k_1}{k_5} \right)^{1/2} [C_2H_6]^{1/2} \quad [2]$$

According to their assumption that reaction (1) was a second-order

reaction, then

$$k_1 = k_1^0 [C_2H_6] \quad [3]$$

where k_1^0 is the low-pressure second-order rate constant of reaction (1). Combining equations [2] and [3],

$$-\frac{d[C_2H_6]}{dt} = k_3 \left(\frac{k_1^0}{k_5} \right)^{1/2} [C_2H_6]. \quad [4]$$

which is also consistent with the experimental findings.

This point of view was strongly supported by Laidler and Wojciechowski (15). Using the results of Dodd and Steacie (23) and the work by Gill and Laidler (16), they concluded that reaction (1) would be second-order at 180 or even as high as 1800 mm Hg at 600°C. The transition of the order of over-all decomposition from 1 to 3/2, was explained by assuming the occurrence of reaction (6) as a main termination step at higher temperatures and lower pressures. Using the data then available, they showed that such a transition would occur when

$$[C_2H_6] = 88 e^{-32,700/RT} \text{ mole cc}^{-1} \quad [5]$$

At 600°C, this corresponded to a pressure of 30 mm Hg, which was, in fact, in good agreement with the experimental value of 60 mm Hg.

This mechanism, however, was first questioned by Davis and Williamson (18) in 1959, on the grounds that the rate of methane production is approximately of the first order. They suggested that the pressure sensitivity of reaction (1) and reaction (3) could

combine to give first-order kinetics.

This suggestion was made more specific by Quinn (19). He proposed that the initiation was exactly first order and that the unimolecular decomposition of the ethyl radical was in its fall-off region. This had been suggested by the results from the butane decomposition (24). To explain the over-all kinetics, he assumed that k_3 was proportional to $P^{0.55}$. This is, nevertheless, an over-simplified mechanism.

Recent work of Gordon (20) supported qualitatively the mechanism proposed by Davis and Williamson and Quinn. In addition to the occurrence of reaction (5), the quenching of hydrogen atoms on surface was considered as an important chain-terminating step.

CHAPTER 2

EXPERIMENTAL AND RESULTS

I. Apparatus:

The experiments were carried out in a conventional static system, which is drawn schematically in Figure 1. Silicone grease was used for all stop-cocks. The entire system could be evacuated to less than 10^{-4} mm Hg by means of a mercury diffusion pump D_1 , which was in series with a liquid nitrogen trap T_3 and a single stage Welch rotary pump P_1 . A single manifold connected all parts of the apparatus. A 511.5 c. c. spherical quartz reaction vessel was enclosed in an electrically heated steel cylinder about 2 cm thick and 26 cm high.

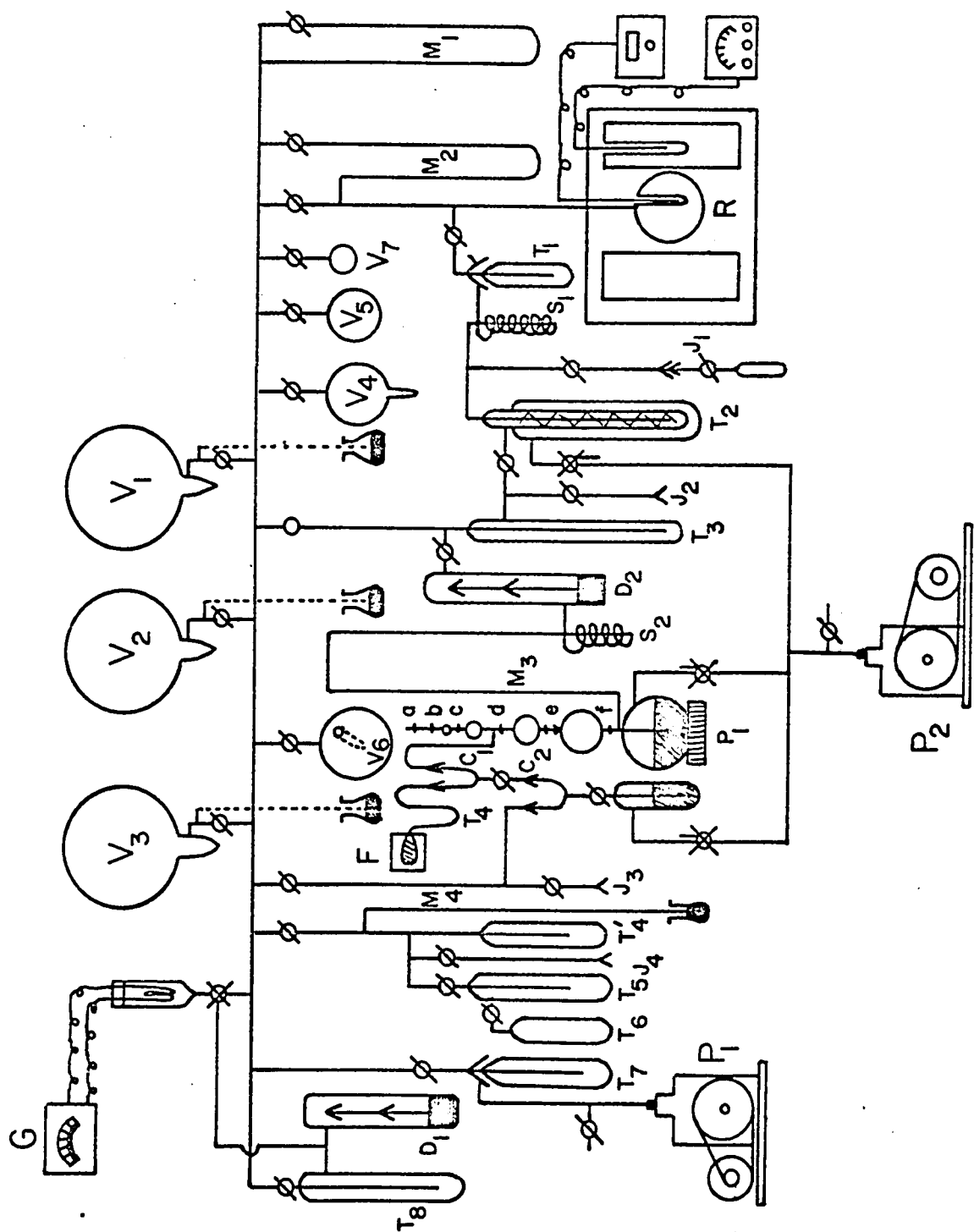
Temperatures were measured by means of an alumel-chromel thermocouple connected with a potentiometer, which was accurate to 0.25°C in the range of temperature studied. The thermocouple was calibrated against the ice point, boiling point of water and melting point of lead (327.4°C). No deviation was observed. A temperature gradient along the thermocouple well of the reaction vessel was not detected. The temperature of the reaction vessel was controlled to within 0.25°C when it was evacuated, but the recorded temperatures for runs were precise only within 0.5°C .

Before being used, the vessel was treated with hot concentrated nitric acid and washed several times with distilled water.

The pressure of the system was measured by Pirani Gauge G, which had been standardized roughly against the McLeod

Figure 1.

Schematic diagram of the apparatus.



Gauge. A LeRoy still T_2 (25) was used to separate the C_4 fraction from the large amount of reactant, ethane. A Toepler pump connected to a calibrated grease-free gas burette was applied to collect and measure the non-condensable products, hydrogen and methane. A mercury diffusion pump D_2 was used to assist the collection. A copper oxide furnace F, in series with a U-trap T_4 , a mercury cut-off C_1 and a gas burette, was operated at 280°C to separate hydrogen from methane.

For the study of surface effects a 500 cc. quartz bulb was packed with fire-polished silica tubing. The surface/volume ratio increased from 0.6 to 9.4 cm^{-1} . Before being used, the vessel was treated with concentrated nitric acid for more than 24 hours and finally washed several times with distilled water.

II. Experimental procedure:

(1). Preparation of gases:

Gases used were research grade chemicals obtained from Phillips Petroleum Company. An appropriate amount of gas was introduced through joint J_4 and condensed into trap T_6 at -196°C . The inlet pressure was measured by manometer M_4 , which served also as a safety escape. After complete condensation, the stop-cock attached to J_4 was closed, and the liquid nitrogen bath in T_6 was replaced by melting isopentane at -160°C for the degassing of C_2H_6 and C_2H_4 or by melting n-propanol at -120°C for CO_2 . Liquid nitrogen baths were used simultaneously in T_4' and T_5 . The whole series of traps were subject to evacuation during distillation. When the gas in T_6 was completely distilled, the liquid nitrogen bath in T_6 was again replaced by the bath at -160°C or -120°C . The procedure

the
might be repeated after all of/gas was transferred into T_4' by condensing it back to T_6 . Traps of the style of T_5 were found to be more efficient for degassing than traps such as T_6 . Only the middle three fourths of purified gas in T_4' was finally collected in the storage bulbs V_1 , V_2 and V_3 . The series of traps T_1 , T_2 (LeRoy still) and T_3 could also be used to purify gases by using the LeRoy still to provide a temperature of about -160°C . No impurity was detected in V.P.C. tests using ^ahundred micromoles of purified gases.

(2) Procedure for experiments

Before each experiment the system was evacuated to a pressure lower than 10^{-4} mm Hg. The initial pressure of reactant was adjusted by two calibrated bulbs V_4 (1105.3 c.c.) and V_5 (166.35 c.c.). Pressure readings could be taken from both manometers M_1 and M_2 . In order to minimize dead space, M_2 was made of 3 mm capillary tubing. Dead space of the reaction vessel was not more than 7 c.c., which caused less than 3% error even if maximum diffusion were assumed. No effect was observed when the dead space was reduced to less than 3 c.c. by removing manometer M_2 .

Mixing of gases was accomplished in the 2164 c.c. volume V_6 which possessed a cooling well inside the bulb as deep as the radius. The mixing time was always longer than one hour.

In high-temperature and low-pressure experiments, initial pressures of ethane, $P_{\text{C}_2\text{H}_6}^0$, in the range of $20 > P_{\text{C}_2\text{H}_6}^0 > 5$ mm Hg were determined from a calibration curve, which was obtained at each temperature by expanding different amounts of CO_2 in V_5 into the manifold and reaction vessel. CO_2 was used instead of ethane because of its stability.

For $P_{C_2H_6}^0 < 5$ mm Hg, pressures were calculated from the ideal gas equation by expanding a known amount of ethane in V_7 (12.767 c. c.) into the reaction vessel and manifold. In this case, P_{V_7} was greater than 5 mm Hg for $P_{C_2H_6}^0$ as low as 1 mm Hg.

(3). Analyses of Products:

Hydrogen and methane:

The conversion of most experiments was kept lower than 3% to avoid secondary reactions. In some experiments, for which secondary reactions were considered, conversion was as high as 50%.

Reactions were quenched by expanding the contents of the reaction vessel into the train of analysis traps. The spiral trap S_1 , cooled in liquid nitrogen, prevented small amounts of butane from being carried over through the LeRoy still, T_2 , by large amounts of hot reactant and non-condensable products. Traps S_1 , T_2 , T_3 and S_2 were kept at -196°C . Trap T_1 was filled with ascarite and kept at 150°C to remove CO_2 when the inert gas effect was studied.

Non-condensable products were collected with the Toepler pump assisted by the mercury diffusion pump D_2 . The completion of collection was indicated by constant pressure in the gas burette. This gave the total concentration of hydrogen and methane. The stop-cock of the reaction vessel was then closed and the liquid nitrogen bath on S_1 removed.

Hydrogen and methane were separated by combusting the former in CuO furnace F operated at 280°C . Methane is essentially stable under this condition. Water formed from the combustion was

condensed into the U-trap T_4 at -196°C . During combustion, the mercury in the Toepler pump was raised to d-level, and lowered every now and then to aid mixing and at the same time to collect more methane from the LeRoy still. Methane is known to be soluble in solid or liquid ethane. The extra amount of methane thus collected was too little to affect the total hydrogen and methane reading already taken, since the total amount of methane from the decomposition is only about 2% that of hydrogen. Combustion and distillation thus proceeded concurrently.

Owing to incessant toeplering during distillation, small amounts of ethylene and ethane were collected in trap S_2 as well as T_4 . To remove this error from the methane reading, the following procedure was applied. With the valve at e closed, mercury was lowered to the reservoir. The purpose was to saturate the whole Toepler pump with ethylene and ethane from both T_4 and S_2 traps while retaining methane above the valve. After saturation, (~ 10 min.), mercury was raised to f and the valve e opened. Methane now expanded into the whole Toepler pump. Mercury cut-off C_1 was closed and the pressure reading was then taken. Calibration showed that the amount of methane so measured was 96.92% of total concentration, i. e., there was always 3.08% of methane left in the furnace. The calibrated volumes were as follows: $V_a = 0.0333$, $V_b = 0.286$, $V_c = 1.200$, $V_d = 8.365$, $V_e = 21.460$ c. c. The ratio of the volume of the side arm attached to C_1 to the volume above the joint of the side arm was 0.2601: 0.7399. The concentration of ethylene and ethane which saturated the whole Toepler pump was 0.3886/RT moles: The completion of hydrogen combustion was ascertained by successive constant readings.

Butane and other condensable products

Before distillation, the outer jacket of the LeRoy still was evacuated for one minute through rotary pump P_2 . Temperatures inside the still were measured at three different positions with copper-constantan thermocouples. The temperature difference between top and bottom thermocouples was about 3°C . Distillation was carried out at -160°C according to the bottom thermocouple. Butane and other residues were condensed into a sample tube at -196°C attached to ground joint J_1 . Distillation losses were corrected by blank tests. Fortunately, this correction was necessary only for higher ethane concentrations where the yield of butane was large. The correction was never higher than 10%.

Butane was analyzed on a Model 154 Perkin Elmer Vapor Fractometer using a 12-foot column of 30% by weight of 2,5-hexanedione on 60/80 mesh Firebrick operated at 0°C . The detector was maintained at 30°C . Since peaks were essentially symmetrical and retention times fairly constant, peak heights were used instead of areas. The accuracy of the butane calibration was about $\pm 3\%$. Concentrations of butadiene and butene-1 were obtained by a retention time correction, while that of acetylene was obtained by both retention time and thermal conductivity corrections.

III. Results:

(1). The products of reaction:

The results may be presented with reference to two temperature regions. More than one hundred runs were made in each region. In the first region, from 550 to 620°C , initial pressures varied from 40 to 600 mm Hg. The over-all kinetics of decomposition

was the main concern. In the second region, 640-726°C, a study of the pressure effect on the initial split of ethane was the principal purpose. The pressure varied from 1 to 200 mm Hg. Methane was the product of primary interest, but in some runs secondary products such as butene-1, butadiene and acetylene were also measured.

Comprehensive analytical studies showed that the only products at the initial stage of decomposition were hydrogen, methane, ethylene and butane. Methane and butane were only 2% that of hydrogen or ethylene. As the reaction time increased, propylene, butene-1 and butadiene were also detected and measured. At very high temperatures, large amounts of acetylene were found. Traces of cis- and trans-butene-2 appeared in almost equal amounts. All products were confirmed by the method of retention time coincidence on one or two columns.

(2). The production of hydrogen:

It is well known that hydrogen and ethylene are the major products from the ethane pyrolysis. They are produced at the same rate up to very high conversions (19). Only hydrogen was measured in the present study and was used as a measure of the rate of decomposition. A typical hydrogen production plot is shown in Figure 2, in which conversions were less than 3%. The rate of production decreased from a finite initial value as reaction progressed. A more detailed discussion on the rate of hydrogen formation as a function of time will be considered in chapter 4.

The initial rate, $R_{H_2}^0$ was obtained by extrapolating the integrated rate $R_{H_2} = (H_2)/t$ vs time plot to zero contact time. This procedure was found to be more accurate than taking the slope at zero time from yield-time plots. Double logarithmic plot of $R_{H_2}^0$

Figure 2.

Typical hydrogen yield-time plots at 585°C.

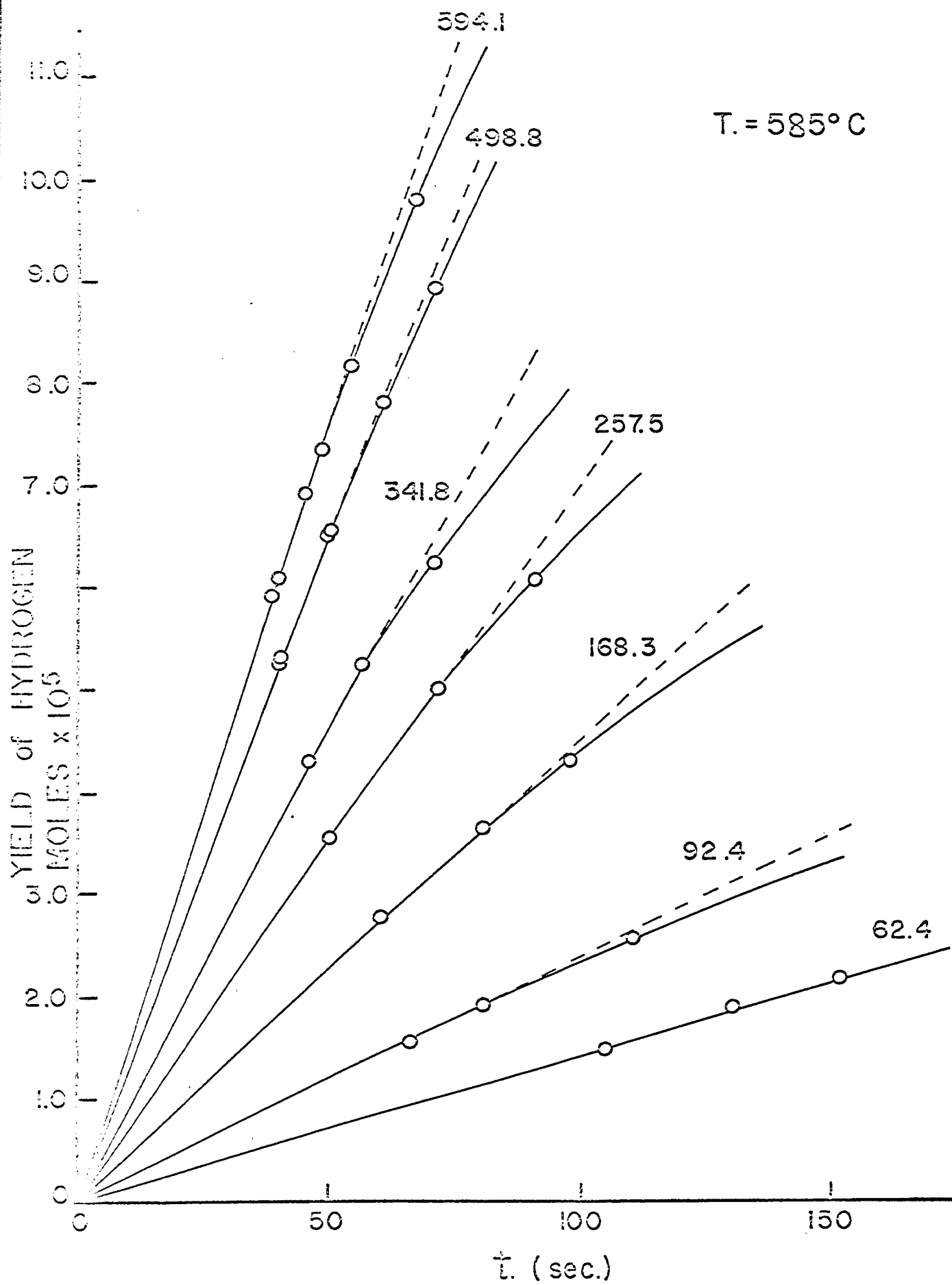


Figure 3.

Order plots for hydrogen production at low temperatures.

Data obtained from the packed vessel ($S/V = 9.4$) are given by +
and those from the unpacked one ($S/V = 0.60$) by o.

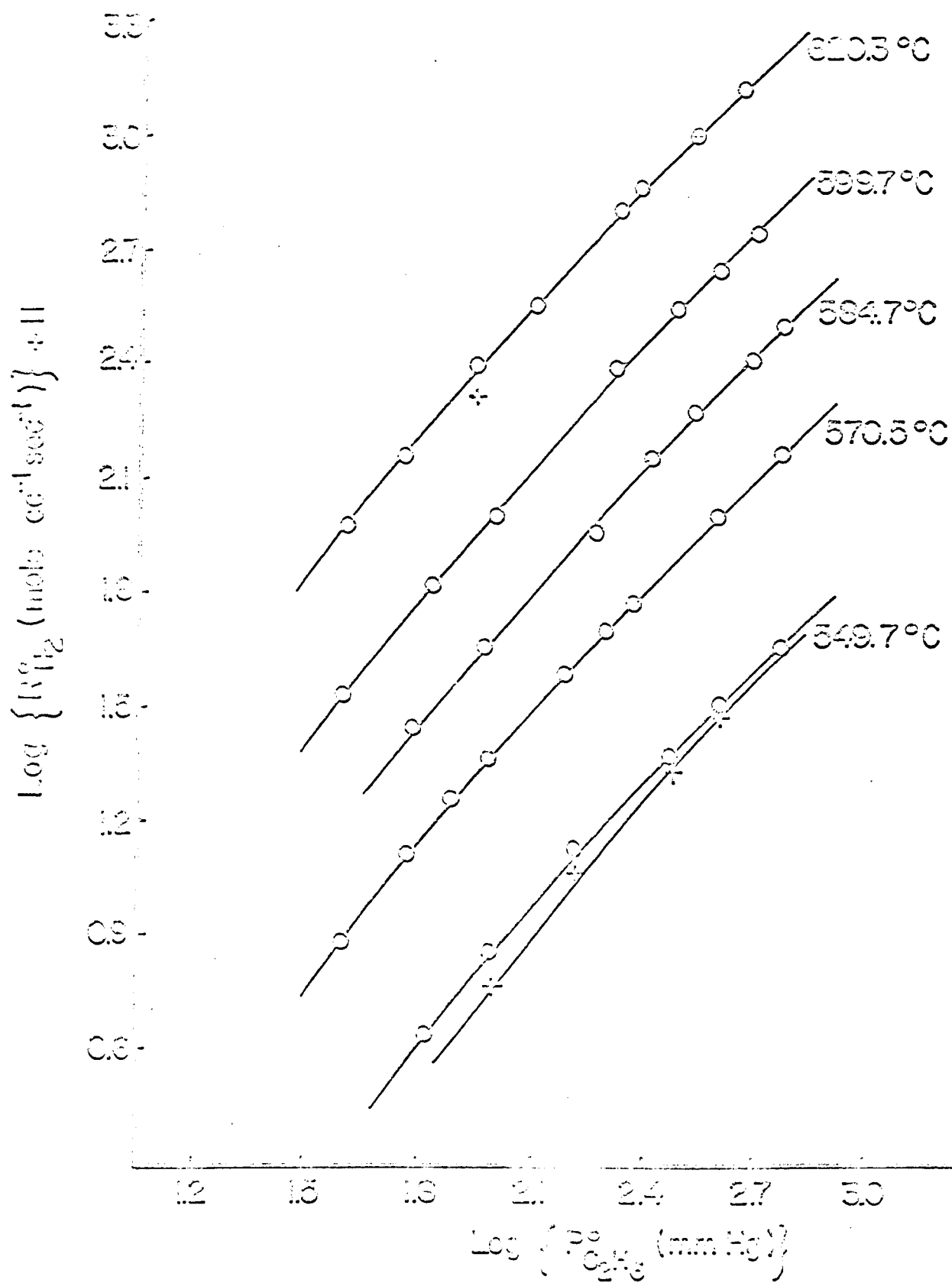


Table 1

First-order rate coefficients of hydrogen, methane and butane production as a function of temperature and pressure in the packed and unpacked vessels.*

$t^{\circ}\text{C}$	$P^{\circ}_{\text{C}_2\text{H}_6}$ (mm Hg)	$k_{\text{H}_2} \times 10^5$	$k_1 \times 10^7$	$k'_1 \times 10^7$	k_1/k'_1
549.7	592.3	3.94	1.43	1.06	1.35
	401.5	4.17(3.76)	1.44	0.902(0.77)	1.59(1.9)
	299.7	4.06(3.72)	1.41	0.921(0.65)	1.53(2.2)
	164.7	4.24(3.52)	1.34	0.854(0.53)	1.57(2.5)
	97.4	3.76(3.16)	1.28	0.743(0.47)	1.72(2.7)
	67.3	3.32	1.15	0.758	1.55
570.5	590.5	13.1	5.48	3.28	1.67
	400.0	13.5	5.19	3.34	1.55
	236.0	13.4	5.12	2.96	1.73
	199.7	13.5	5.13	3.19	1.61
	153.4	13.4	4.92	3.02	1.62
	96.0	12.6	4.63	2.57	1.80
	78.3	12.3	4.50	2.68	1.68
	59.4	11.9	3.96	2.43	1.63
	40.1	10.0	-	-	-
584.7	594.1	28.6	12.7	8.80	1.44
	498.8	29.2	12.7	8.81	1.44
	341.8	30.1	12.5	8.78	1.46
	257.5	30.2	12.3	8.41	1.46
	168.2	30.2	12.5	8.27	1.51
	92.4	26.5	11.4	7.70	1.48
	62.4	24.2	10.4	6.41	1.63
599.7	500.6	60.3	29.5	20.4	1.40
	402.1	61.3	29.3	20.2	1.40
	298.9	65.4	29.6	19.8	1.49
	203.1	67.8	29.1	18.3	1.59
	99.9	60.0	26.7	15.7	1.69
	68.4	52.9	24.6	14.0	1.76
	41.0	46.6	22.4	10.4	2.15
620.3	448.3	170	88.8	75.3	1.18
	335.6	171(171)	89.7	72.7(60.7)	1.23(1.5)
	236.1	176	89.9	69.1	1.27
	209.8	172	84.3	70.1	1.20
	124.5	175	83.9	56.8	1.47
	87.6	159(135)	78.2	54.7(39.8)	1.43(2.0)
	57.9	156	73.1	45.1	1.63
	40.7	131	66.5	37.8	1.76

Note:* (1). The results from packed vessel are given in parentheses.

(2). $k_{\text{H}_2} = R^{\circ}_{\text{H}_2} / [\text{C}_2\text{H}_6]$, $k_1 = R^{\circ}_{\text{CH}_4} / 2 [\text{C}_2\text{H}_6]$ and $k'_1 = R^{\circ}_{\text{C}_4\text{H}_{10}} / [\text{C}_2\text{H}_6]$

(3). All rate coefficients are in sec^{-1} .

Figure 4.

Order plots for hydrogen production at high temperatures.

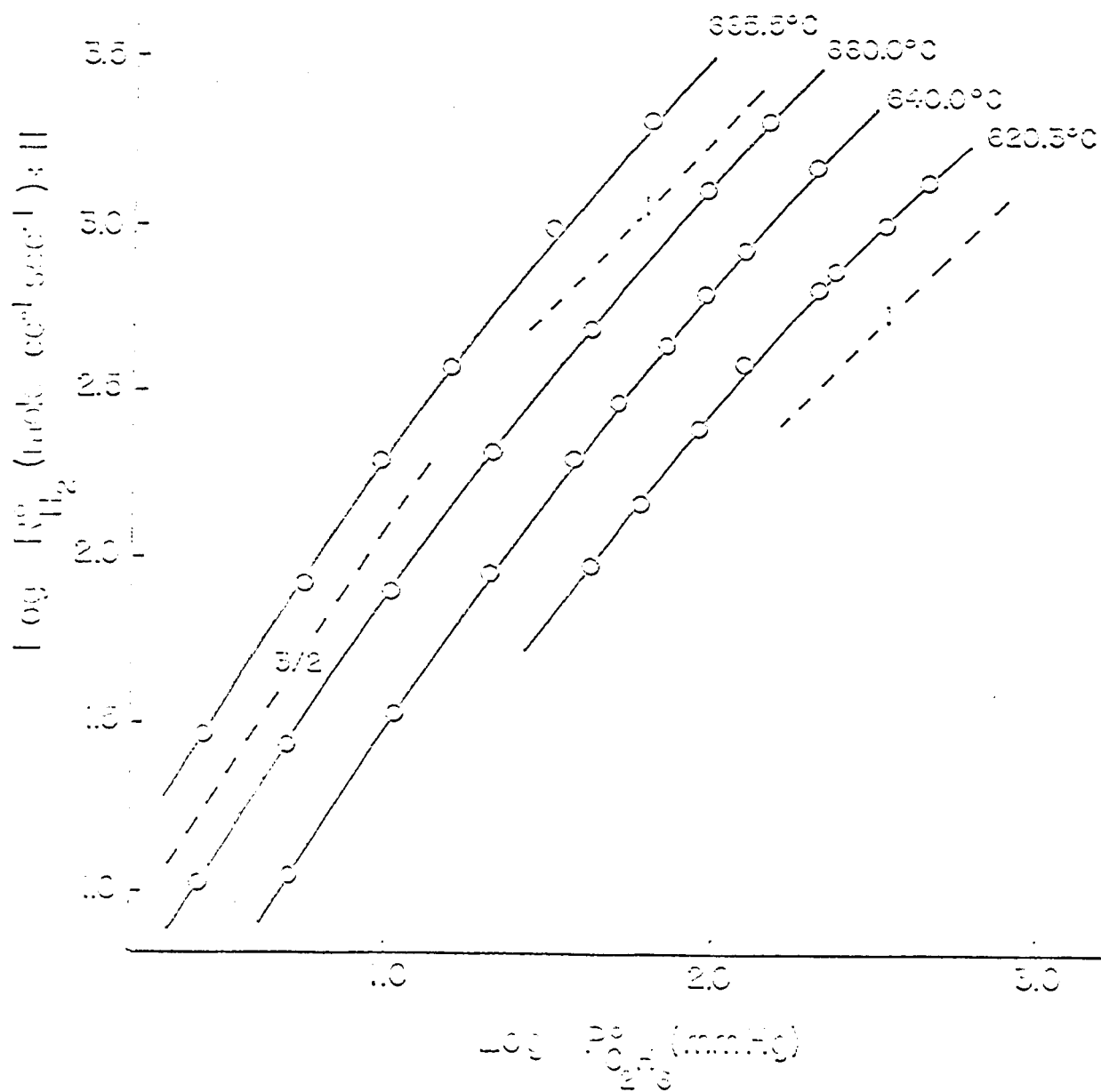
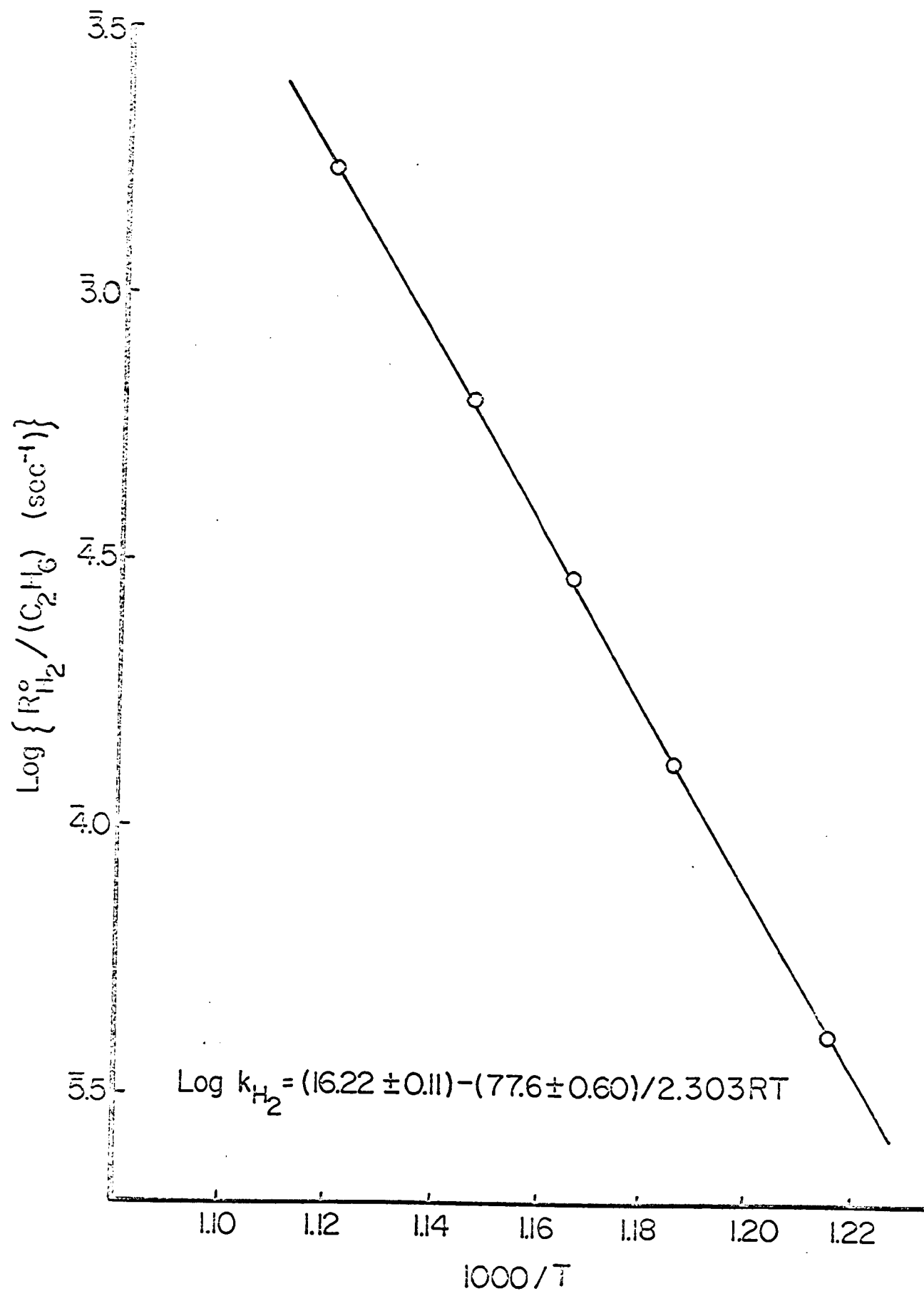


Figure 5.

Arrhenius plot for the first-order rate constant of over-all reaction.



against initial ethane pressure, $P_{C_2H_6}^0$ at lower temperatures is shown in Figure 3. The order changes continuously from 0.94 at 500 mm to 1.20 at 50 mm for all temperatures. This continuous change of order can be seen more clearly from Table 1, in which the first order rate coefficients of hydrogen formation, $k_{H_2} = R_{H_2}^0/[C_2H_6]$ are listed as a function of temperature and pressure. The over-all order is one at pressures between 150 and 400 mm Hg. Figure 4 shows the order of hydrogen production at higher temperatures. Clearly the order of the over-all reaction changes smoothly from approximately one at high pressure to 1.5 below about 50 mm Hg of ethane.

The Arrhenius plot of the average values of the first-order rate constants given in Table 1 in the range of pressure 150-400 mm Hg is shown in Figure 5. Least-squares treatment of the data leads to

$$\log k_{H_2} (\text{sec}^{-1}) = (16.22 \pm 0.11) - \frac{77,600 \pm 600}{2.303 RT} \quad [6]$$

(3). The production of methane:

A typical plot of yield against time at 584.7°C is shown in Figure 6. At high pressures the rate increases rapidly from the initial finite value as the reaction proceeds. This indicates that methane is generated by both primary and secondary reactions. The initial rate of methane production was obtained from the extrapolation of the rate vs. t^2 plot or other equivalent methods discussed in chapter 4. The order plot of the initial rate of methane production, $R_{CH_4}^0$ in the first region of temperatures is presented in Figure 7. The order is exactly one above 200 mm Hg, and increases slowly as pressure decreases. The first order rate coefficients, $k_1 = R_{CH_4}^0/2[C_2H_6]$

-28-

Figure 6.

Typical methane yield-time plots at 585°C.

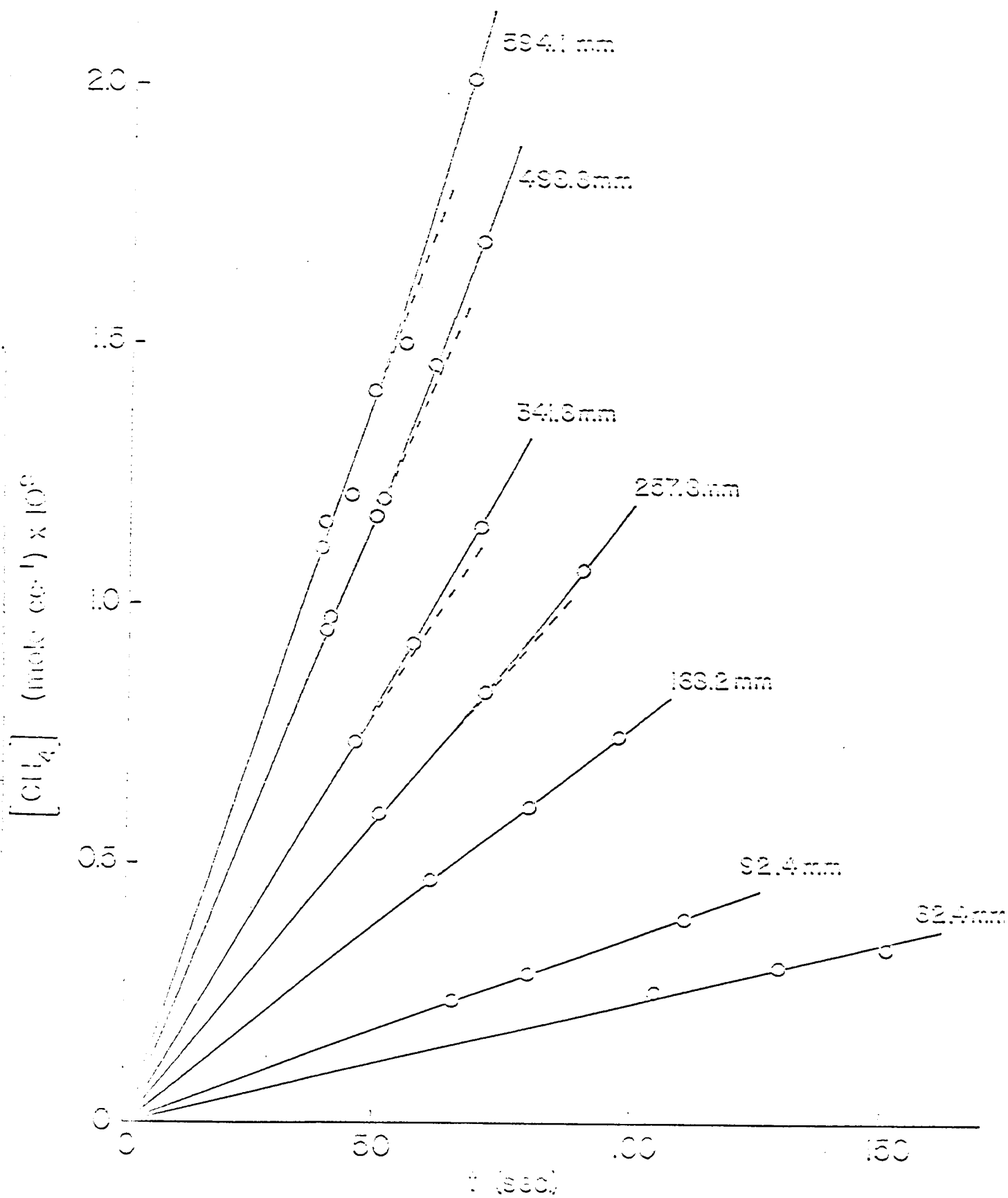


Figure 7.

Order plots for methane production at low temperatures.

Data obtained from the packed vessel ($S/V = 9.4$) are given by +
and those from the unpacked one ($S/V = 0.60$) by o.

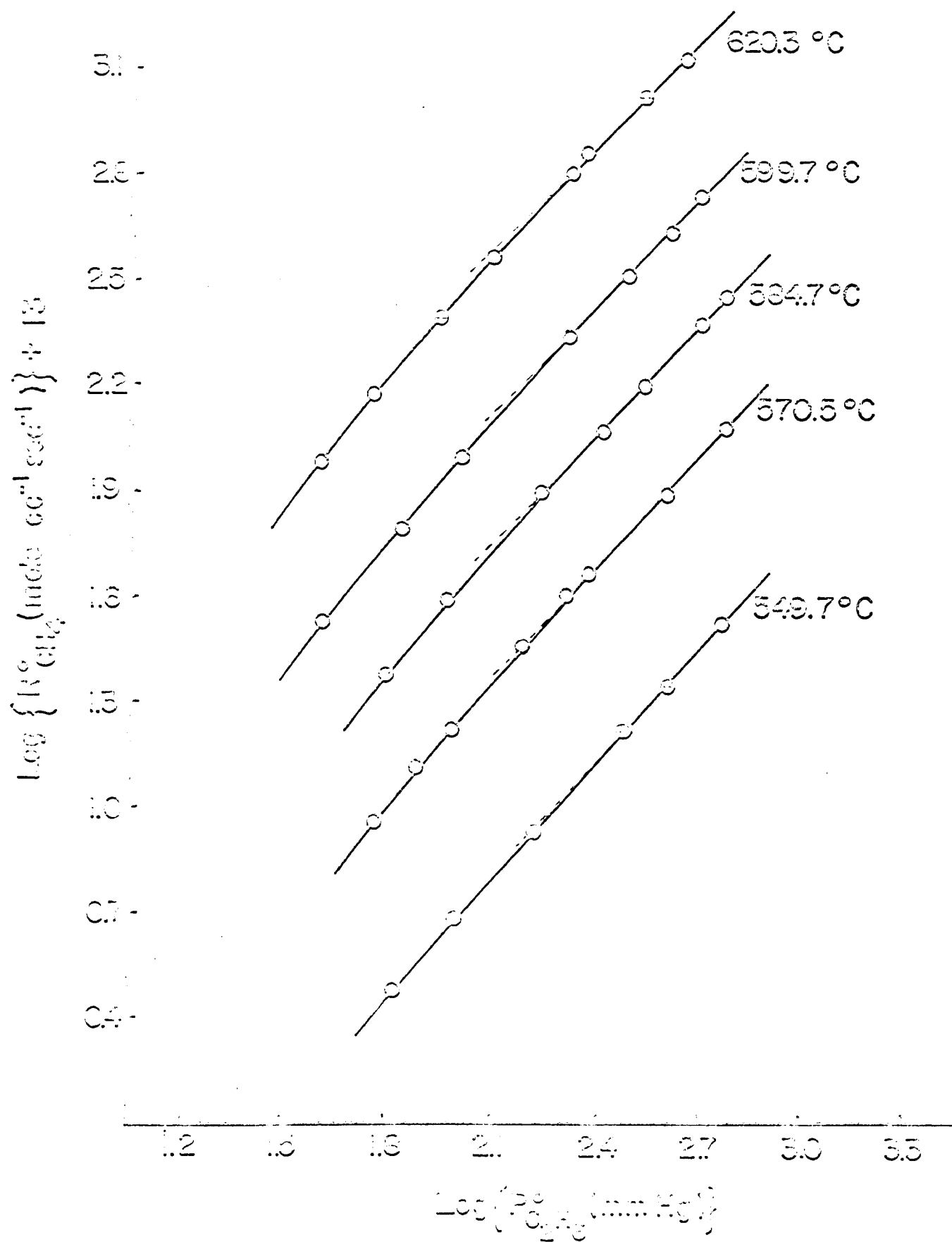


Figure 8.

Arrhenius plot for the first-order rate constant k_1^∞ .

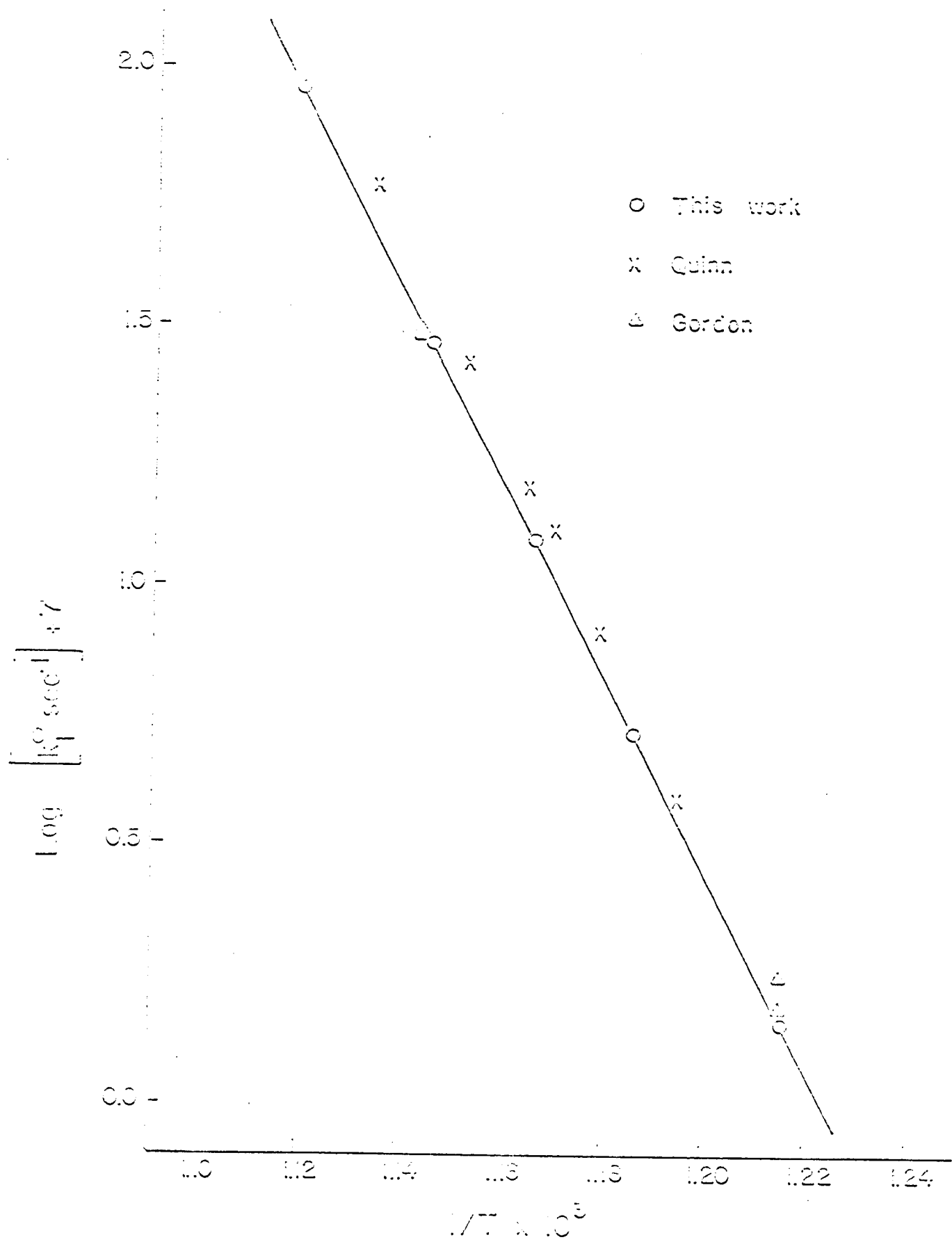
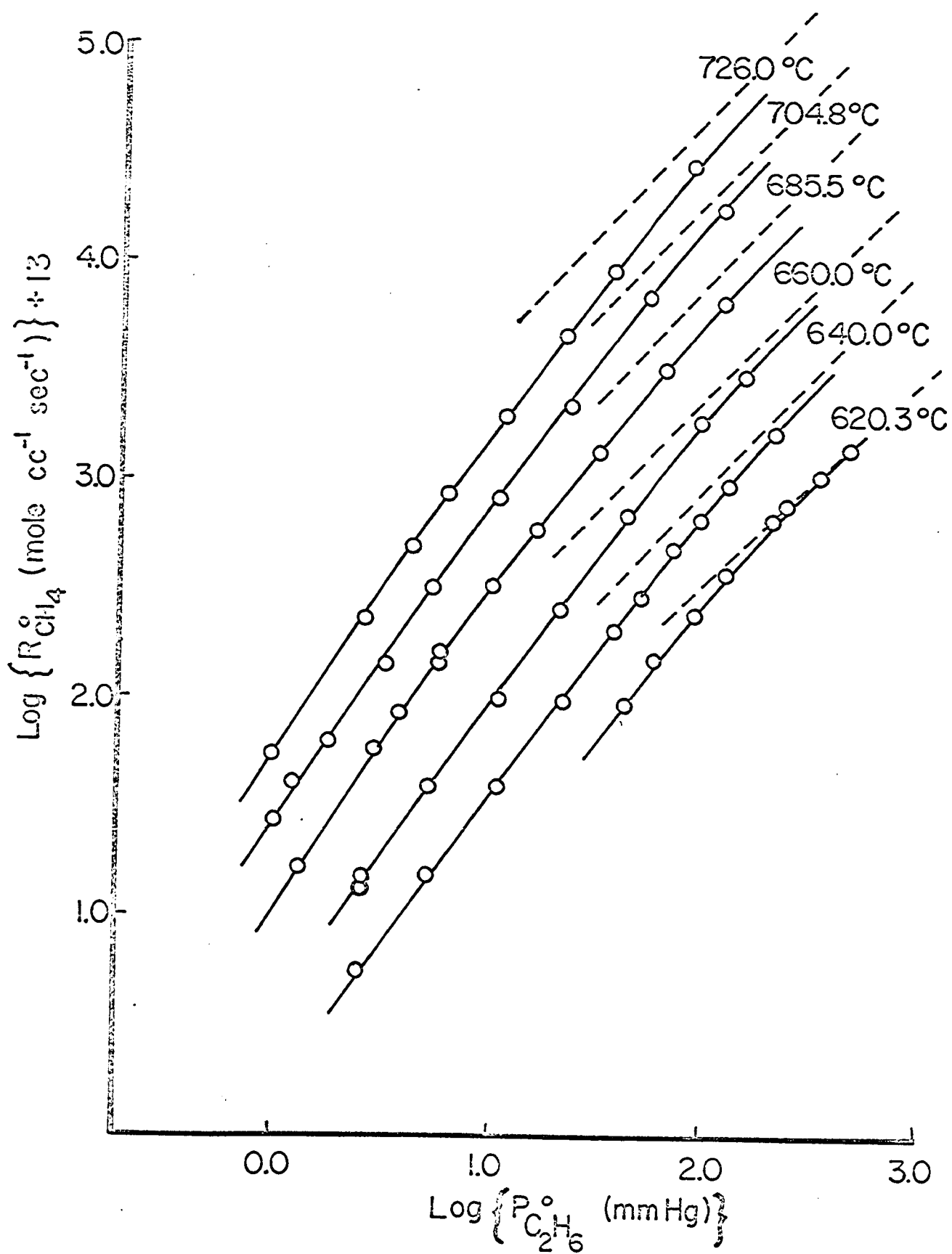


Figure 9.

Order plots for methane production at high temperatures.



are listed in Table 1. The Arrhenius plot of the first order rate constants, k_1^∞ 's in the high-pressure region is shown in Figure 8, in which the results of Quinn and Gordon are plotted together for comparison. Least-squares analysis of the data leads to

$$\log k_1^\infty (\text{sec}^{-1}) = (16.00 \pm 0.066) - \frac{86,000 \pm 370}{2.303 RT} \quad [7]$$

In order to examine more closely the effect of pressure on k_1 , the initial rate of methane production was measured in the second region of temperature, 640-726°C at pressure from 1 to 200 mm Hg. Initial rates were obtained by extrapolation. A double logarithmic plot of $R_{\text{CH}_4}^\circ$ against $P_{\text{C}_2\text{H}_6}^\circ$ is shown in Figure 9. The dotted lines, which were computed from the following equation:

$$\begin{aligned} R_{\text{CH}_4}^\circ &= 2k_1^\infty [\text{C}_2\text{H}_6] \\ &= 2 \times 1.00 \times 10^{16} e^{-86,000/RT} [\text{C}_2\text{H}_6], \end{aligned} \quad [8]$$

indicate the position of first-order rates of methane production in infinite pressure region at each temperature studied. The comparison of the fall-off of k_1 with various theories of unimolecular reaction will be given in chapter 7.

(4). The production of butane:

Typical yield-time plots of butane production at 584.7°C are shown in Figure 10. Initial rates of butane production, $R_{\text{C}_4\text{H}_{10}}^\circ$ were obtained by extrapolation of the rate-time plot. The detailed discussion of secondary butane reactions is given in chapter 4. The order plot of $R_{\text{C}_4\text{H}_{10}}^\circ$ is presented in Figure 11.

Figure 10.

Typical butane yield-time plots at 585°C.

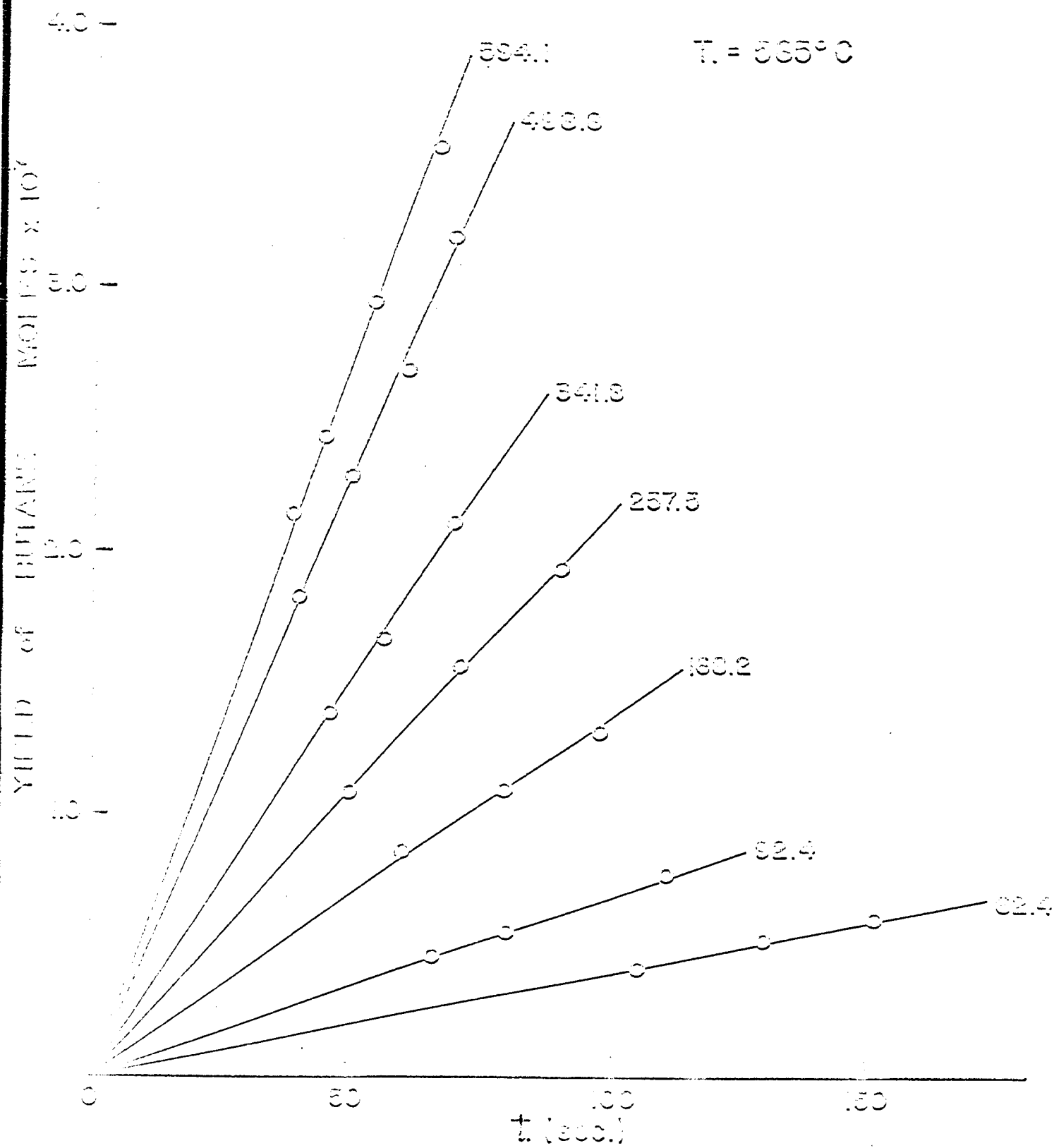


Figure 11.

Order plots for butane production.

Data obtained from the packed vessel ($S/V = 9.4$) are given by +
and those from the unpacked one ($S/V = 9.60$) by O.

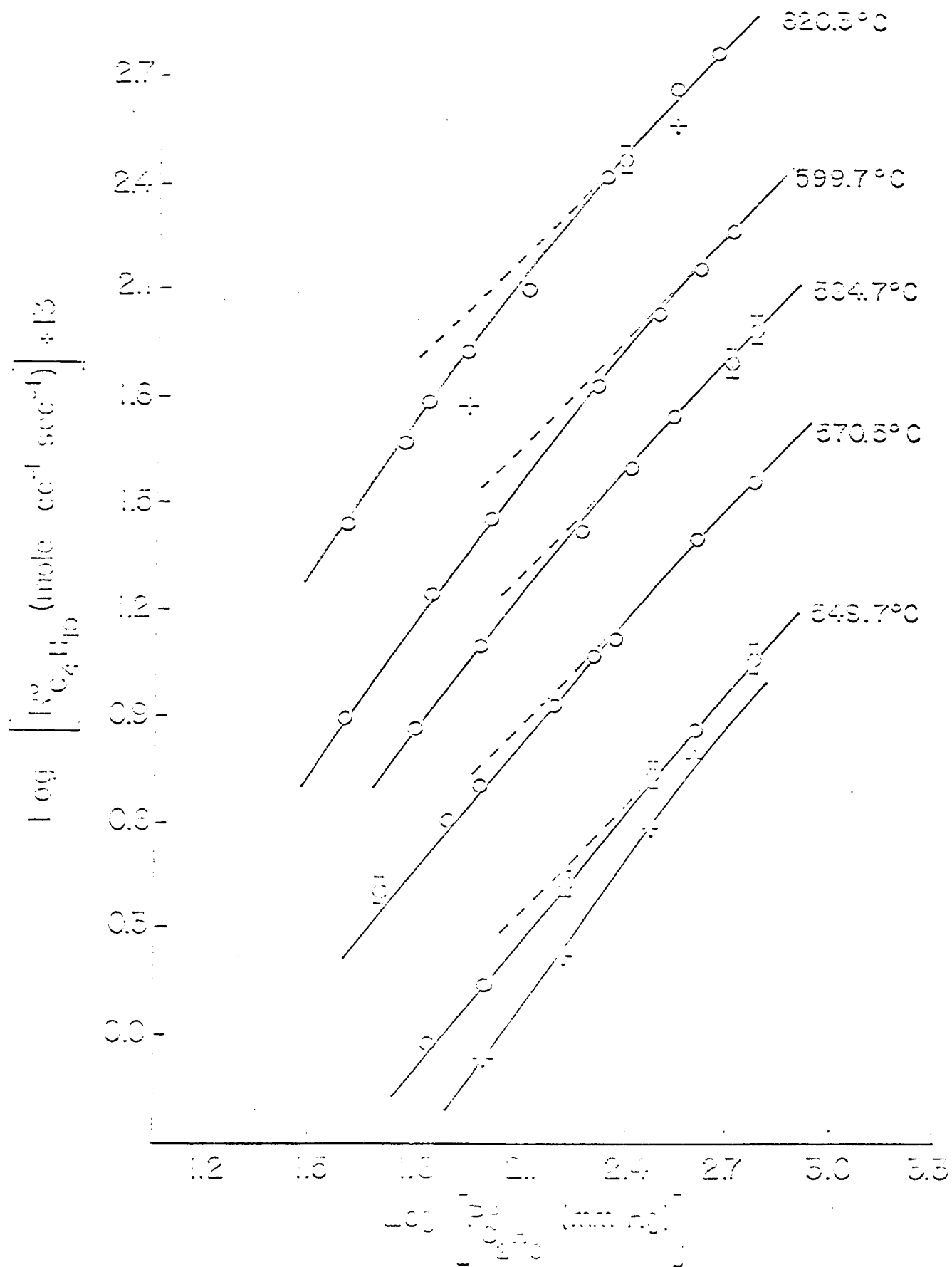
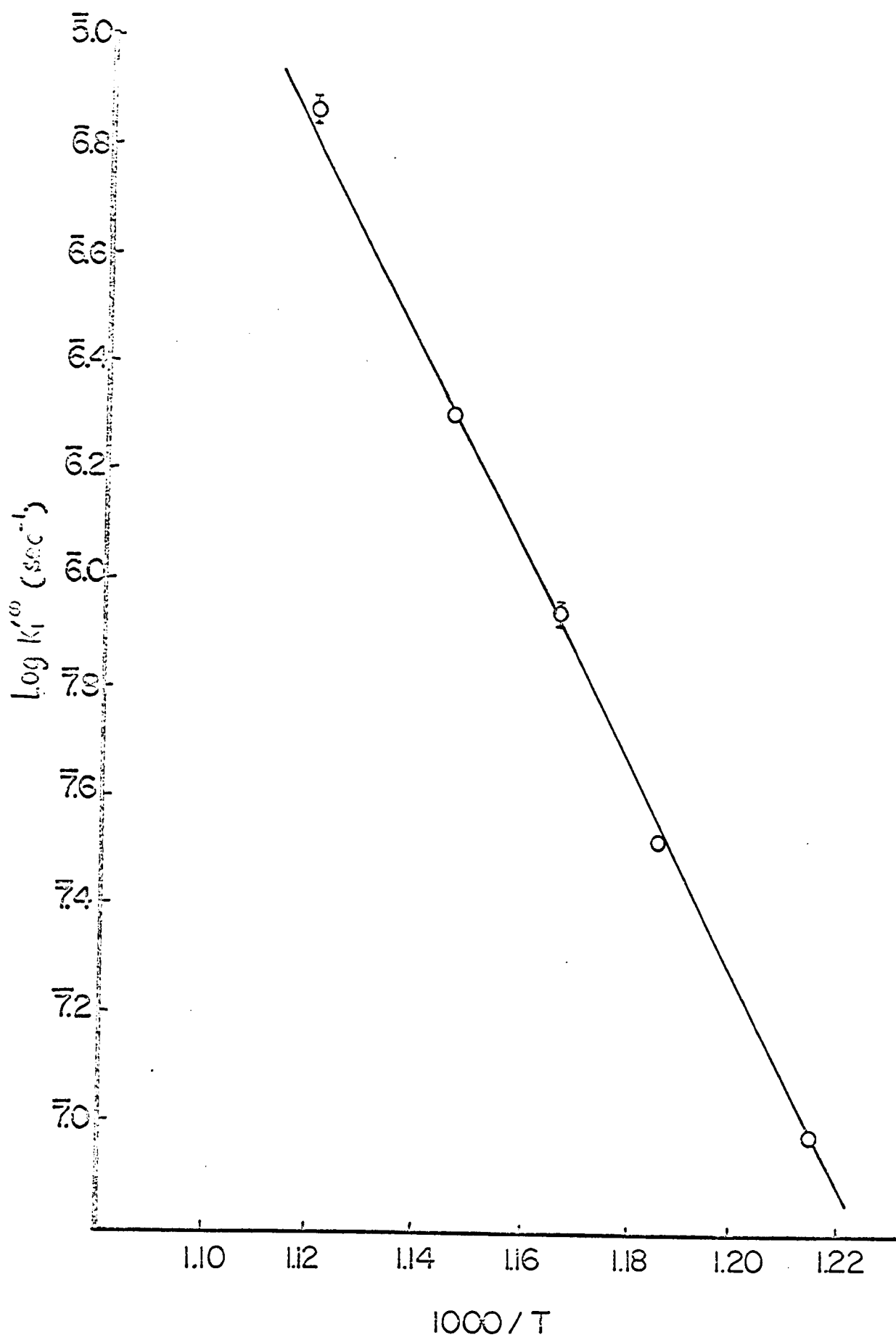


Figure 12.

Arrhenius plot for the first-order rate constant k_1^{∞} .



As with methane, the order of butane production at pressures above 200 mm is exactly one within experimental error. First-order rate coefficients, $k_1' = R_{C_4H_{10}}^0 / [C_2H_6]$ at different temperatures and pressures^{are} given in Table 1.^{4,10} The average of the values in the high-pressure region, are plotted in Figure 12. Least-squares treatment of the data gives

$$\log k_1'^{\infty} (\text{sec}^{-1}) = 16.82 - 89,800/2.303 RT \quad [9]$$

The activation energy, 89.8 kcal mole⁻¹ with a probable error of about ± 1.5 kcal mole⁻¹ is higher than that of methane production by 3.8 kcal mole⁻¹.

(5). Productions of butene-1, butadiene-1,3 and acetylene:

At lower temperatures, butene-1 and butadiene appeared only at high conversions. Butene-1 was always formed earlier than butadiene. At high temperatures, butadiene and acetylene became important products, while butene-1 disappeared at high conversions. The results obtained from experiments in the temperature range 640-726°C are given in Table 2. Typical yield-time plots at four temperatures between 570.5 and 704.6°C are shown in Figures 13 and 14. The discussion on the mechanism of the formation of these products will be presented in chapter 4.

(6). Inert gas effect:

The effect of inert gas on the rates of hydrogen, methane and butane formation was examined by mixing various amounts of CO₂ with 100 mm of ethane at 585.2°C. The results are shown in Figures 15 and 16. The rate of hydrogen production increased by 15%

Table 2

The productions of butene-1, butadiene and acetylene at high temperatures

Temperature (°C)	Pressure (mm Hg)	Reaction time (sec)	$[C_4H_8] \times 10^{10}$ (mole/cc)	$[C_4H_6] \times 10^{10}$ (mole/cc)	$[C_2H_2] \times 10^{10}$ (mole/cc)
640.0	204.6	15.0	1.9	0.65	*(1)
		18.1	2.4	0.98	*
		25.1	4.1	2.4	*
		42.0	7.2	7.2	*
	123.3	18.1	0.93	0.33	*
		35.1	2.6	2.5	*
		55.2	4.3	6.9	*
	91.2	15.1	0.45	-(2)	*
		25.0	1.0	0.66	*
		40.0	1.8	2.2	*
		40.1	1.8	2.2	*
		99.9	4.5	13.9	*
660.0	144.5	21.9	3.3	6.5	*
		30.2	4.6	12.7	*
		46.0	6.8	25.6	*
	91.2	21.8	1.6	4.3	*
		30.0	2.2	7.6	*
		45.0	2.9	15.5	*
		58.1	3.7	23.1	*
	41.0	24.3	0.46	1.1	-
		35.4	0.68	2.9	0.17
		55.0	0.91	6.3	0.53
		83.9	1.26	13.0	1.51
	20.5	25.3	-	-	-
		45.3	0.20	0.42	-
		70.3	0.27	1.8	0.28
		120.0	0.41	11.7	0.87
	10.7	25.5	-	-	-
		45.2	-	0.34	-
		79.6	0.12	1.9	0.14
		125.0	0.07	4.8	0.35

Table 2 (cont'd)

685.5	30.7	22.2	0.57	5.7	0.89	
		35.1	0.64	15.5	1.7	
		50.0	0.95	19.2	3.1	
		15.6	21.9	-	2.3	0.24
		35.0	-	5.4	0.63	
		50.0	-	10.5	1.5	
		70.1	-	14.1	2.2	
		9.7	30.2	-	1.8	0.13
		59.9	-	6.1	0.87	
704.6	21.5	20.9	0.30	9.2	1.2	
		34.9	0.44	13.0	3.0	
		49.9	0.36	22.2	4.7	
		70.1	0.30	25.7	7.2	
	5.3	24.7	-	1.0	0.35	
		39.9	-	3.2	0.49	
		51.6	-	4.4	0.64	
		74.9	-	6.8	1.5	
726.0	10.8	25.0	-	11.9	3.5	
		35.2	-	15.0	5.7	
		50.0	-	17.5	6.8	
		70.0	-	18.3	8.7	
	5.7	30.8	-	6.8	1.9	
		45.0	-	8.2	3.1	

Note: (1). "*" denotes "not measured"

(2). "-" denotes "trace quantity"

Figure 13.

Typical yield-time plots for butane, butene-1
and butadiene production at 570 and 640°C.

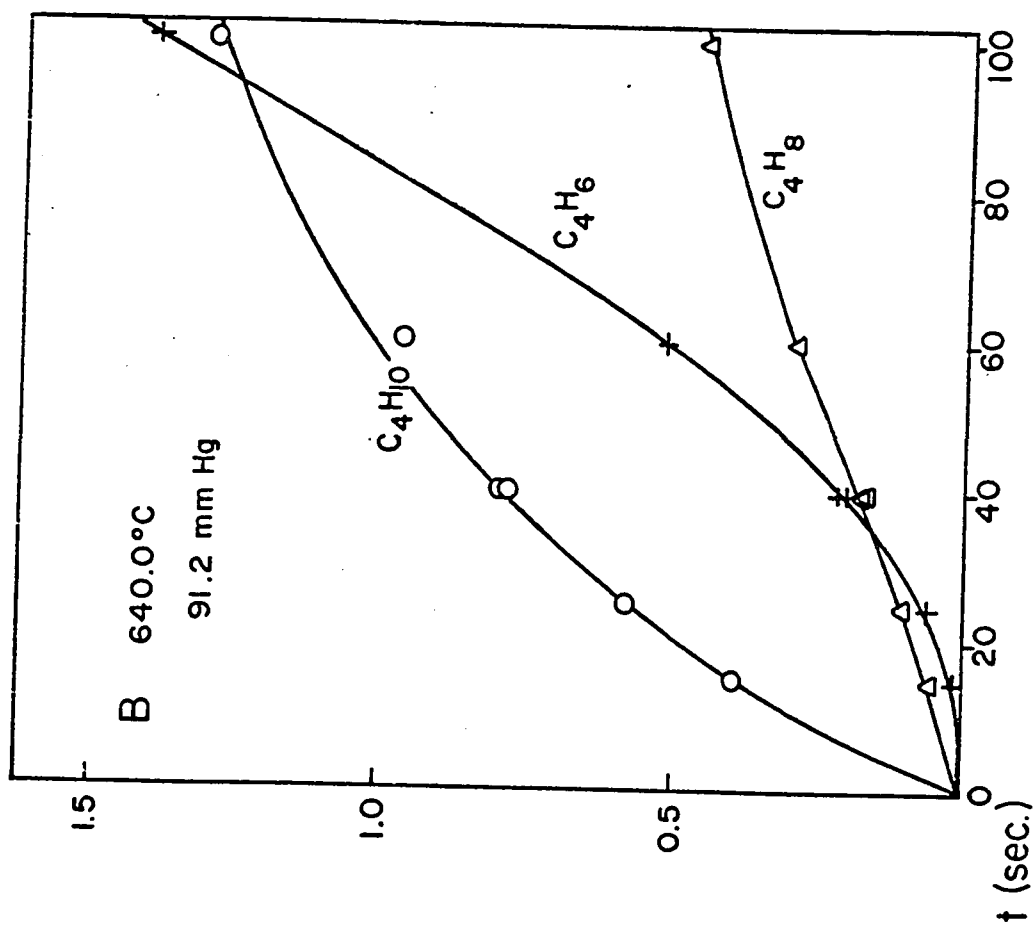
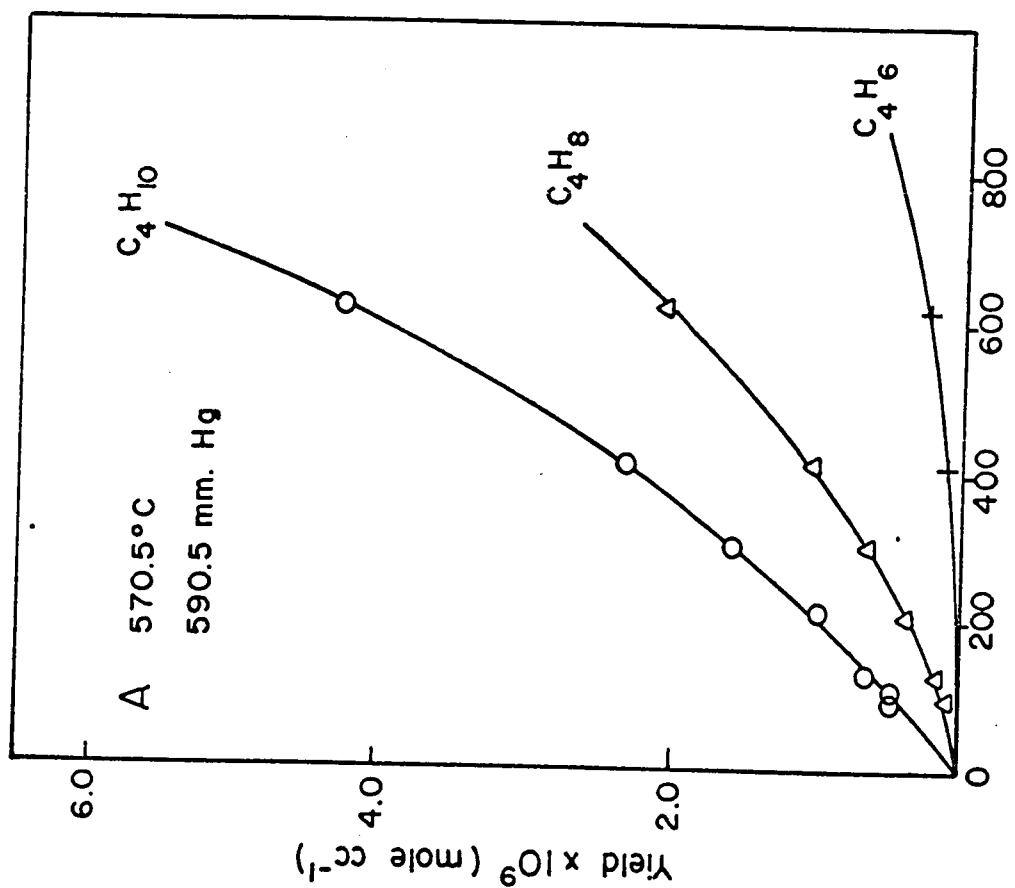


Figure 14.

Typical yield-time plots for butane, butene-1
butadiene and acetylene production at 660 and 705°C.

Butane is given by O, Butene-1 by .
butadiene by + and acetylene by X.

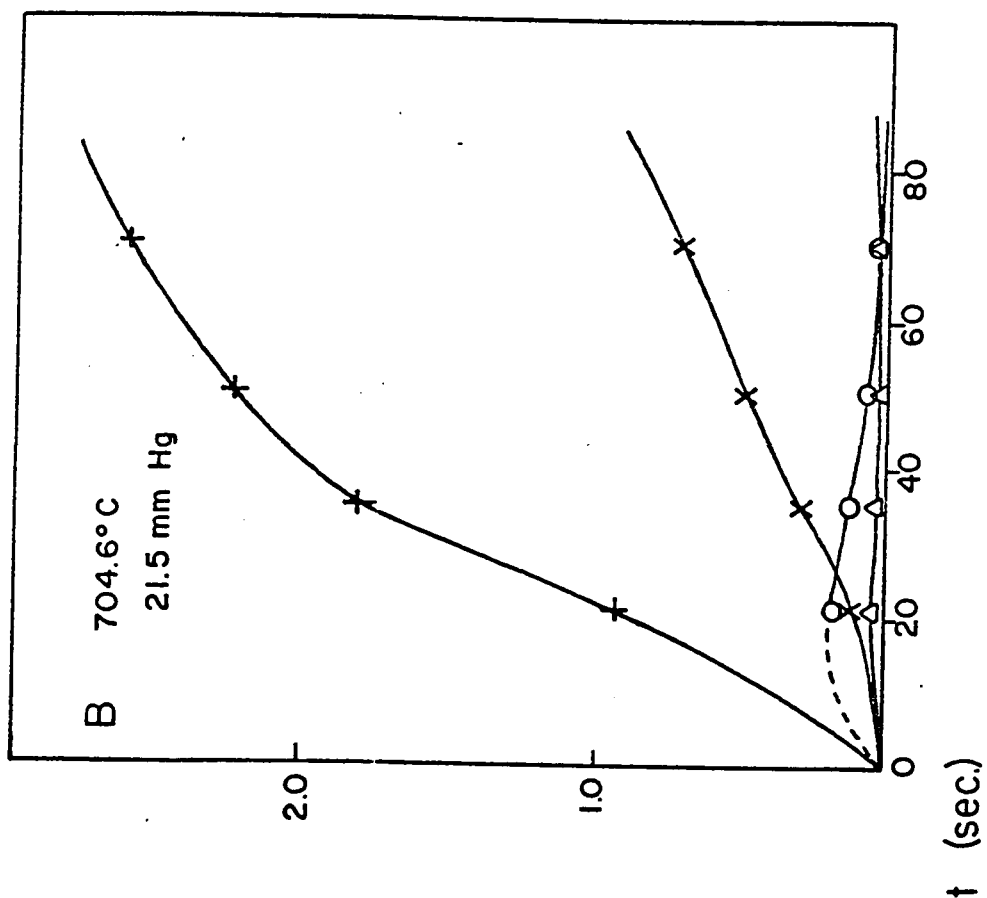
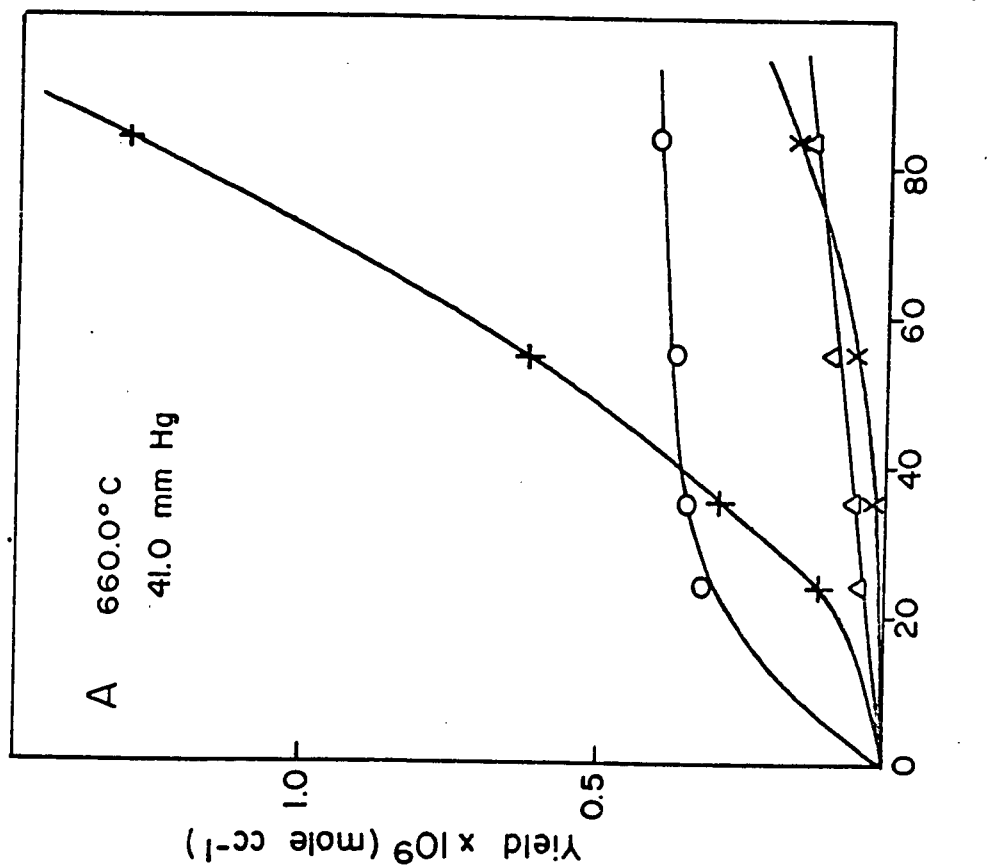


Figure 15.

Inert gas effect on hydrogen production.

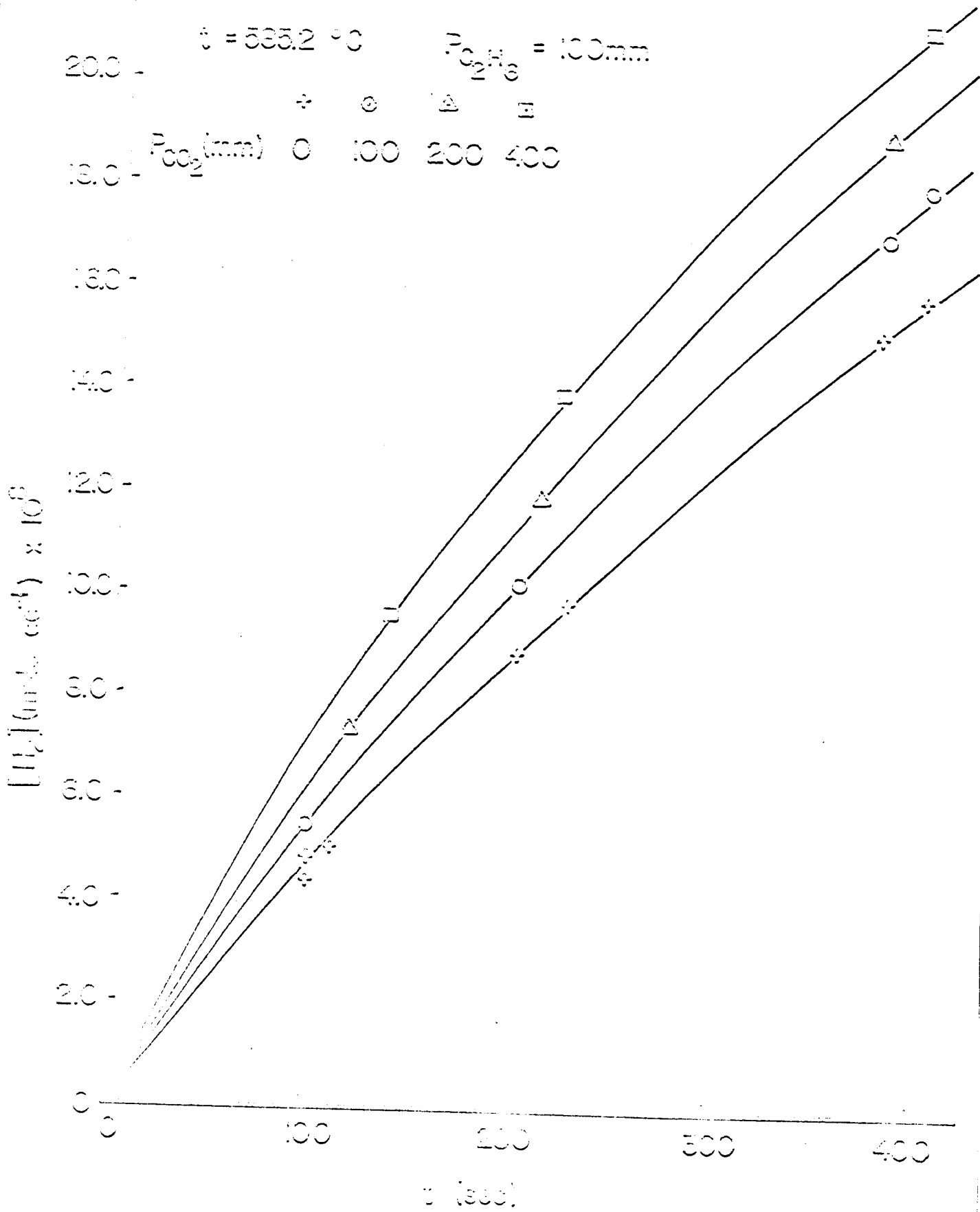


Figure 16.

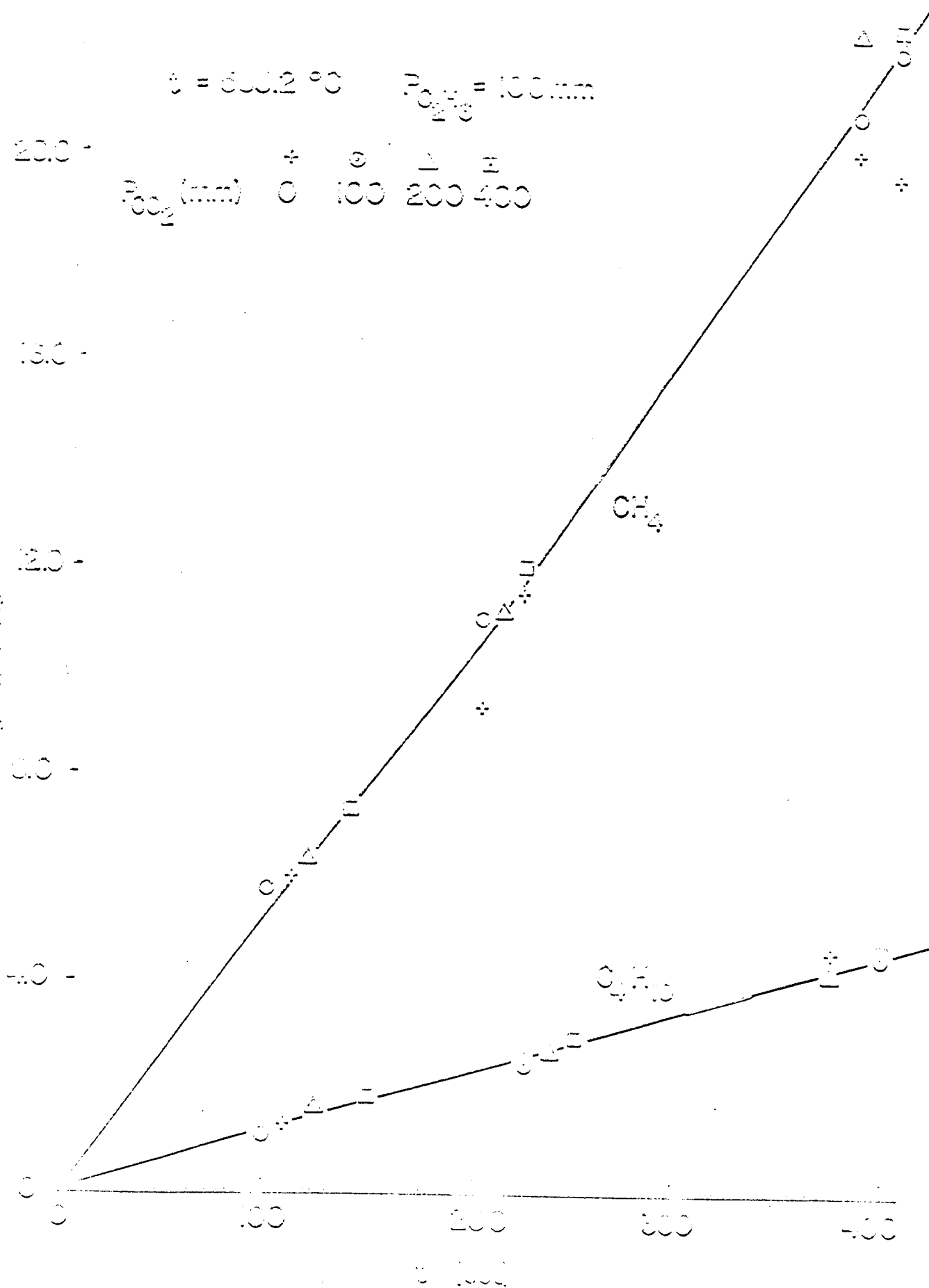
Inert gas effect on methane and butane productions.

$t = 600.2^\circ\text{C}$

$P_{\text{O}_2/\text{H}_2} = 100 \text{ mm}$

$P_{\text{CO}_2} \text{ (mm)}$ $\circ$ $\oplus$ $\triangle$ $\square$
 0 100 200 400

$[\text{CH}_4] + [\text{C}_2\text{H}_6] + [\text{C}_3\text{H}_8] \times 10^3$



when the total pressure was doubled, whereas the rates of methane and butane formation were hardly affected.

For the sake of convenience, the results of the effect of inert gas on k_1 in low-pressure region will be presented in chapter 7.

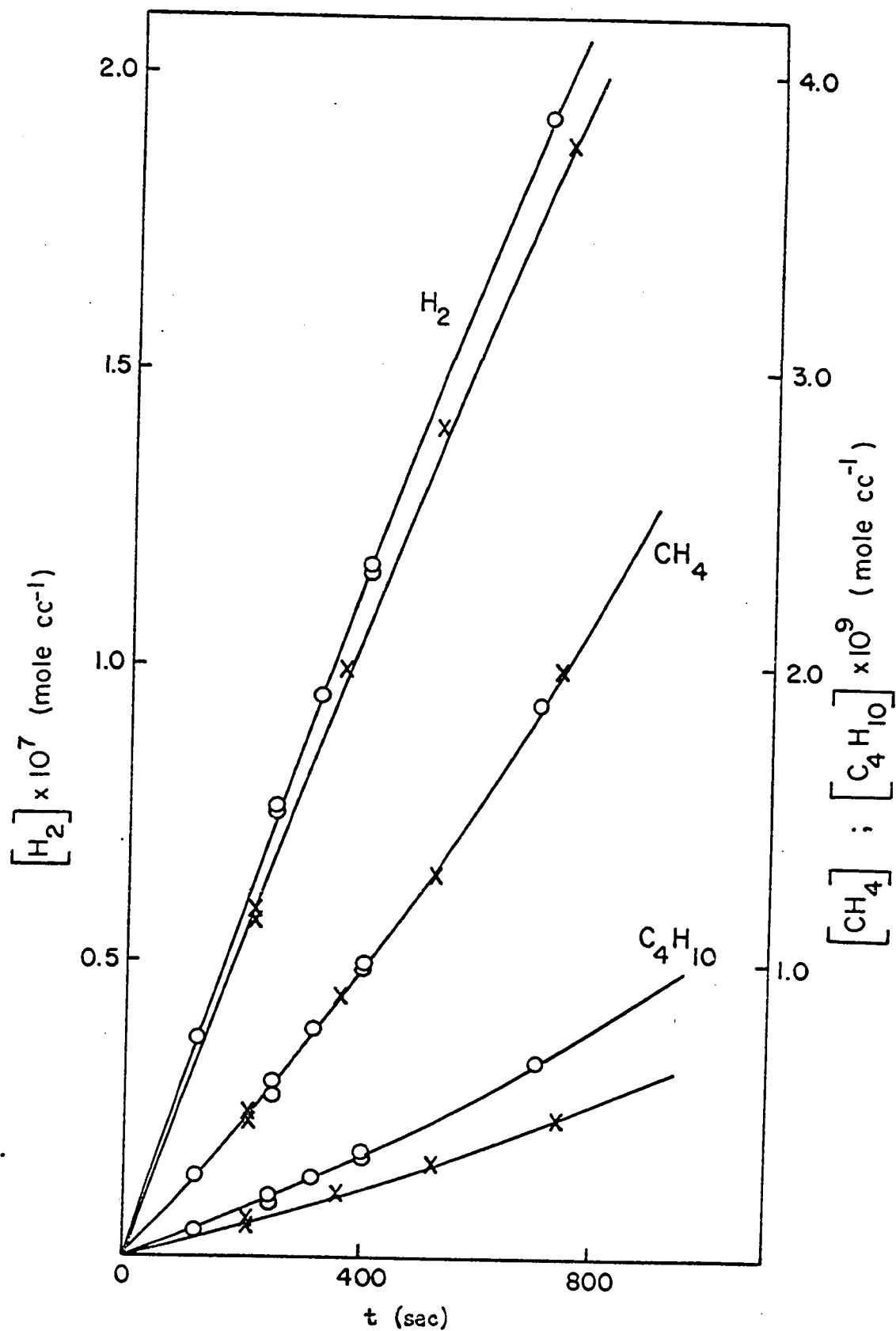
(7). Surface effect:

The effect of surface/volume ratio on the rates of hydrogen, methane and butane production was studied by increasing the S/V ratio by a factor of 15. Experiments were done at 500 and 620°C. The effect was found to be more pronounced at the low temperature and low pressures. Typical results are presented in Figure 17, and the extrapolated initial rates of hydrogen, methane and butane production at two temperatures and various pressures are plotted in Figures 3, 7 and 11, respectively. The rates of both hydrogen and butane production were markedly reduced, whereas that of methane formation remained essentially the same. The first order rate coefficients of hydrogen and butane production in the packed vessel are given in Table 1.

Figure 17.

Typical yield-time plots for hydrogen, methane and butane production at 550°C in the packed and unpacked vessels.

Results obtained from 401.5 mm ethane at 550°C.
X denotes the result obtained from the packed vessel and O denotes that from the unpacked one.



CHAPTER 3

KINETICS AND MECHANISMS OF PRIMARY REACTIONS

A primary reaction is the reaction which occurs with a non-vanishing rate at zero reaction time. If there is no complication which may affect this particular reaction, it will proceed indefinitely with the same rate. In a free radical chain system, however, complications arise from the interactions of radicals with the products of primary reactions. There are usually two different ways to avoid this sort of complication. One can either shorten the reaction time or evaluate a function which describes quantitatively the formation of a primary product as the reaction progresses. The former method is limited by the amount of product to be measured. The latter is, however, more laborious. The detailed discussion of this matter will be presented in the next chapter.

The object of the present chapter is to consider a mechanism which can account for the primary reactions in the pyrolysis of ethane from which hydrogen, methane and butane are produced. For the sake of convenience, the subsequent discussion will be based on a complete general scheme shown as follows:

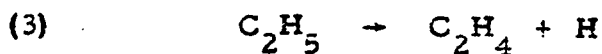
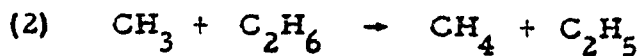
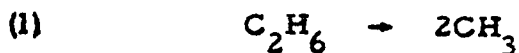
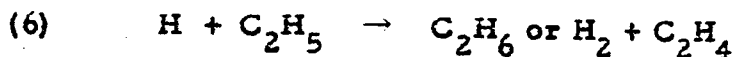
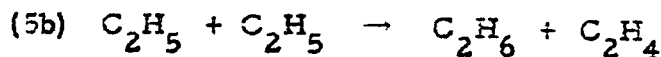
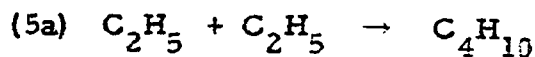
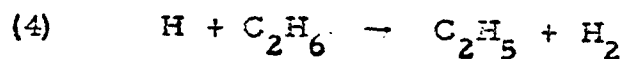


Table 3

Kinetic parameters for elementary reactions

<u>Reactions</u>	<u>Frequency Factor</u> (sec ⁻¹ or cc mole ⁻¹ sec ⁻¹)	<u>Activation Energy</u> (kcal mole ⁻¹)	<u>References</u>
$\text{C}_2\text{H}_6 \xrightarrow{k_1^\infty} 2\text{CH}_3$	1.00×10^{16}	86.0	This work (chapter 2)
$\text{C}_2\text{H}_6 + \text{M} \xrightarrow{k_1^0} 2\text{CH}_3 + \text{M}$	1.8×10^{21}	72.5	This work (chapter 7)
$\text{CH}_3 + \text{C}_2\text{H}_6 \xrightarrow{k_2} \text{CH}_4 + \text{C}_2\text{H}_5$	2.0×10^{11}	10.4	Trotman-Dickenson et al. (26)
$\text{C}_2\text{H}_5 \xrightarrow{k_3^\infty} \text{C}_2\text{H}_4 + \text{H}$	3.8×10^{13}	38.0	This work (chapter 6)
$\text{C}_2\text{H}_5 + \text{M} \xrightarrow{k_3^0} \text{C}_2\text{H}_4 + \text{H} + \text{M}$	3.0×10^{14}	39.5	Bywater and Steacie (27)
$\text{H} + \text{C}_2\text{H}_6 \xrightarrow{k_4} \text{H}_2 + \text{C}_2\text{H}_5$	1.3×10^{18}	32.4	This work (chapter 6)
$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5 \xrightarrow{k_{5a}} \text{C}_4\text{H}_{10}$	3.4×10^{12}	6.8	Berlie and LeRoy (28)
$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5 \xrightarrow{k_{5b}} \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$	1.29×10^{14}	9.7	Baldwin and Melvin (29)
$\text{H} + \text{C}_2\text{H}_5 \xrightarrow{k_6} \text{C}_2\text{H}_6$	2.0×10^{13}	0	Shepp and Kutschke (30)
$\text{CH}_3 + \text{C}_2\text{H}_5 \xrightarrow{k_7} \text{C}_3\text{H}_8$	$A_{5b}/A_{5a}=0.15$	0	Kerr and Trotman-Dickenson (31)
	1.6×10^{13}	0	Ivin and Steacie (32)
	4.2×10^{13}	0	Calculated (this chapter)



The Arrhenius parameters for these individual reactions are given in Table 3.

1. The chain-initiating reaction and the initial split of ethane:

The C-H split of ethane has never been considered as an important chain-initiating step because the dissociation energy $D(\text{C}_2\text{H}_5 - \text{H})$ is known to be about 12 kcal higher than $D(\text{CH}_3 - \text{CH}_3)$. Thus, at 900°K, the probability of C-C split is about 10^{+4} times larger than that of C-H split, if the frequency factors are assumed to be the same.

The unimolecular decomposition of ethane by the breaking of the C-C bond may result either in two methyl radicals or in a methane molecule and a methylene radical. Energetically, one cannot choose between the two. The latter was proposed by Danby et al. (33) in order to explain the fact that the rate of methane production was not completely inhibited by nitric oxide. It was thought to occur simultaneously with reaction (1). The occurrence of CH_2D_2 in the work of Wall and Moore (5) has been quoted as strong evidence for the presence of CH_2 or CD_2 radicals in the

$C_2H_6 + C_2D_6$ system (34). However, CH_2D_2 was not detected in a similar but more conclusive work by Rice and Varnerin (6). There is also no evidence for the occurrence of CH_2 radicals in the work of Eltenton (3) and of Lossing et al. (4). As discussed in the next chapter, there are several reactions which may produce methane, especially in such high-conversion experiments as those of Wall and Moore.

In the presence of a large amount of ethane CH_2 radicals may form propane by an insertion reaction. The excited propane so formed would be expected to have a half-life intermediate between the excited ethane and butane produced by the insertion of CH_2 radicals into methane and propane respectively (35, 36) and would thus not be completely stabilized even at the highest pressures used in the present experiments. Decomposition would probably yield methyl and ethyl radicals. The effect of stabilization of the excited propane would be to reduce the rate of initiation and hence increase the ratio of methane to butane beyond that expected from the mechanism proposed. Moreover, this ratio would increase as the total pressure increased. This effect was not observed and it may be concluded that the break-down of ethane to give methane and a methylene radical is not an important initiation step.

The rate of methane production would be reduced considerably if methyl radicals were quenched by reaction (7). The extent of reaction (7) can be measured by the ratio:

$$\frac{R_7}{R_2} = \frac{k_7 [C_2H_5]}{k_2 [C_2H_6]} \quad [10]$$

Combining this equation with the rate equation for butane production:

$$R_{C_4H_{10}}^o = k_{5a} [C_2H_5]^2 \quad [11]$$

we have

$$\frac{R_7}{R_2} = \frac{k_7 R_{C_4H_{10}}^o \frac{1}{2}}{k_2 k_{5a}^{\frac{1}{2}} [C_2H_6]} \quad [12]$$

k_7 can be obtained by the relation (37):

$$k_7 = 2.0 (k_{-1} k_{5a})^{1/2} = 4.2 \times 10^{13} \text{ cc mole}^{-1} \text{ sec}^{-1},$$

where $k_{-1} = 2.2 \times 10^{13} \text{ cc mole}^{-1} \text{ sec}^{-1}$. Using the values of $R_{C_4H_{10}}^o$ given in Figure 12, for 100 mm Hg of ethane, $R_7/R_2 = 5.0 \times 10^{-3}$ at 550°C and 2.8×10^{-2} at 620°C . Obviously, reaction (7) is of negligible importance under present conditions. It may, however, become important at very high temperature and low pressures.

Neglecting the termination reaction involving methyl radicals, the steady-state assumption for methyl radical leads to

$$\left(\frac{d[CH_4]}{dt} \right)_{t=0} = R_{CH_4}^o = 2k_1 [C_2H_6] \quad [13]$$

The initial rate of methane production is therefore a measure of the

initial split of ethane. This reaction is essentially homogeneous, since an increase in S/V ratio by a factor of 15 did not affect the rate of methane production as shown in Figures 7 and 17. The order of methane production was exactly one at pressures greater than about 200 mm of ethane as shown in Figure 7 and Table 1. The pressure dependence of k_1 will be discussed in detail in chapter 7.

The first-order rate constants given in equation [7] can be rewritten as

$$k_1^\infty = 1.00 \times 10^{16} e^{-86,000/RT} \text{ sec}^{-1} \quad [14]$$

which is in excellent agreement with that of Davis and Williamson:

$$k_1^\infty = 1.95 \times 10^{16} e^{-86,000/RT} \text{ sec}^{-1},$$

although their data were rather scattered and uncertain. The activation energy differs from those of Gordon and Quinn by $\pm 5 \text{ kcal mole}^{-1}$, although the absolute values of the rate constants are fairly consistent. Another estimate of k_1 by Leigh, Szwarc and Bigeleisen (17) was about a factor of ten lower than the present results. In view of the pressure dependence of this reaction, the difference may be related to the low total pressure ($\sim 15 \text{ mm Hg}$) employed. Their activation energy $85\text{-}89 \text{ kcal mole}^{-1}$ is, however, consistent with the present value.

According to absolute rate theory (38), the bond dissociation energy D , of a molecule which dissociates unimolecularly into radicals, is related to the experimental activation energy, E_{exp} , by the equation

$$E_{\text{exp}} = D + N \left(\sum_{i=1}^{3n-7} \frac{h\nu_i^\ddagger}{e^{h\nu_i^\ddagger/kT} - 1} - \sum_{i=1}^{3n-6} \frac{h\nu_i}{e^{h\nu_i/kT} - 1} + kT \right) \quad [15]$$

if the association of radicals is assumed, as usual, to occur with zero activation energy. $\nu_i^\ddagger$ and ν_i are the frequencies of the i th mode of vibration for the activated complex and the reactant molecule, respectively, N is Avogadro's number, k , the Boltzmann constant, h , Planck's constant and n , the number of atoms in the molecule.

If $h\nu/kT \gg 1$, where ν stands for both $\nu_i^\ddagger$ and ν_i , equation [15] reduces to:

$$E_{\text{exp}} = D + RT, \quad [16]$$

whereas, when $h\nu/kT \ll 1$,

$$E_{\text{exp}} = D. \quad [17]$$

The experimental activation energy must therefore lie within two extreme values

$$D + RT > E_{\text{exp}} > D \quad [18]$$

In the case of ethane, the C-H stretch, 2960 cm^{-1} and C-H deformation, 1436 cm^{-1} for the reactant molecule may not differ significantly from those of the activated complex, and the very high frequency factor associated with its decomposition is thought to be due to the softening of the torsional, rocking and bending motions (39, 40). Thus equation [15] reduces to

$$E_1 = D(\text{CH}_3 - \text{CH}_3) + N \left(\sum_{i=1}^5 \frac{h\nu_i^\ddagger}{e^{h\nu_i^\ddagger/kT} - 1} - \sum_{i=1}^6 \frac{h\nu_i}{e^{h\nu_i/kT} - 1} + kT \right) \quad [19]$$

Since the frequencies of C-C stretch and other deformation vibrations lie within $1000 - 300 \text{ cm}^{-1}$, in the temperature range $550 - 620^\circ \text{C}$ $h\nu/kT$

is about of the order of 1. Hence, according to equation [18], we may conclude that

$$\begin{aligned} D(\text{CH}_3-\text{CH}_3) &= E_1 - \frac{1}{2} RT \pm 0.5 \\ &= 85.0 \pm 0.5 \text{ kcal mole}^{-1}. \end{aligned}$$

This value leads to

$$\Delta H_f(\text{CH}_3)_{0^\circ\text{K}} = 34.2 \text{ kcal mole}^{-1}$$

and

$$D(\text{CH}_3-\text{H}) = 101.8 \text{ kcal mole}^{-1},$$

which is in excellent agreement with the value:

$$D(\text{CH}_3-\text{H}) = 101 \pm 1 \text{ kcal mole}^{-1}$$

obtained by Kistiakowsky et al. from the photobromination of methane (41).

II. The chain-terminating reaction and the formation of butane:

The importance of butane measurement lies in its possibility to decide the main termination step out of the three most probable reactions:



and



Reaction (7) has already been shown to be of negligible importance.

Similarly, the relative rate of reaction (6) can be estimated as follows:

$$\frac{R_6}{R_{5a}} = \frac{k_6 [H]}{k_{5a} [C_2H_5]}$$

or

$$\frac{R_6}{R_5} = \frac{[H]}{1.15 [C_2H_5]} \quad [20]$$

since $k_{5a} \doteq k_6$ and $k_{5b}/k_{5a} = 0.15$ as given in Table 3. The rate of hydrogen production can be expressed as:

$$R_{H_2}^o = k_4 [H] [C_2H_6] = k_3 [C_2H_5] \quad [21]$$

This equation is valid, inasmuch as the chain-length, which is defined as $R_{H_2}^o / R_{CH_4}^o$, is always greater than 100 over the range of temperature and pressure studied.

Combining equation [11], [20] and [21], we get

$$\frac{R_6}{R_{5a}} = \frac{k_{5a}^{1/2} R_{H_2}^o}{1.15 k_4 R_{C_4H_{10}}^o^{1/2} [C_2H_6]} \quad [22]$$

Using Berlle and LeRoy's value for k_4 , and $R_{H_2}^o$ and $R_{C_4H_{10}}^o$ from Figures 3 and 11, respectively, for 100 mm of ethane, $R_6/R_5 = 7.0 \times 10^{-3}$ at 550°C and 3.0×10^{-2} at 620°C . This ratio will be lower if the other value for k_4 given in Table 3 is used. Reaction (6) is thus seen to be too slow to compete with reaction (5) under the present conditions.

The kinetics of butane production follows a similar pattern to that of methane. The order of its formation is exactly one above about 200 mm of ethane as shown in Figure 11 and Table 1. As the pressure is lowered the rate of butane production falls slightly faster than that of methane formation. The Arrhenius equation of the first order rate constants given in equation [9] can be written as

$$k_1^{\infty} = 6.6 \times 10^{16} e^{-89,000/RT} \text{ sec}^{-1}. \quad [23]$$

Both activation energy and frequency factor are higher than those of k_1^{∞} from methane formation.

If reaction (5) is the main termination step, the following relation should be observed:

$$\frac{R_{\text{CH}_4}^0}{2R_{\text{C}_4\text{H}_{10}}^0} = \frac{k_1}{k_1'} = 1.15 \quad [24]$$

assuming $k_{5b}/k_{5a} = 0.15$ and independent of temperature and pressure. The results given in Table 1, however, indicate higher values. In the high-pressure first-order region, the ratio was higher than 1.15 by ~ 30% at low temperatures and by ~ 5% at 620°C. This discrepancy is not due to a temperature coefficient of the k_{5b}/k_{5a} ratio (30), since the ratio k_1/k_1' decreased as the temperature increased. k_1/k_1' also varied with pressure as well as the S/V ratio (Table 1).

At constant temperature and S/V ratio, it increased as the ethane pressure decreased. A 15-fold increase in S/V ratio increased k_1/k_1' by a factor of about 1.5. In the packed vessel k_1/k_1' decreased considerably with increasing temperature. All these findings indicate that chain-carriers may be quenched on the surface. A more detailed discussion on the possible mechanism which might occur on the surface will be presented in section V.

The k_1/k_1' ratio in the high-pressure first-order region can be calculated from equations [14] and [23]:

$$\frac{k_1^{\infty}}{k_1'^{\infty}} = \frac{1.00 \times 10^{16} e^{-86,000/RT}}{6.6 \times 10^{16} e^{-89,800/RT}} \quad [25]$$

or

$$\frac{k_1'^{\infty}}{k_1^{\infty}} = 6.6 e^{-3,800/RT} \quad [26]$$

III. The chain-propagating steps and the decomposition of ethyl radicals:

It is generally agreed that the chain-propagating processes in the decomposition of ethane are



Figure 18.

Double-logarithmic plots of $R_{H_2}^{\circ} / R_{C_4H_{10}}^{\circ} \frac{1}{2}$ vs. $P_{C_2H_6}^{\circ}$.

Data obtained from the packed vessel are given by +
and those from the unpacked one by O.

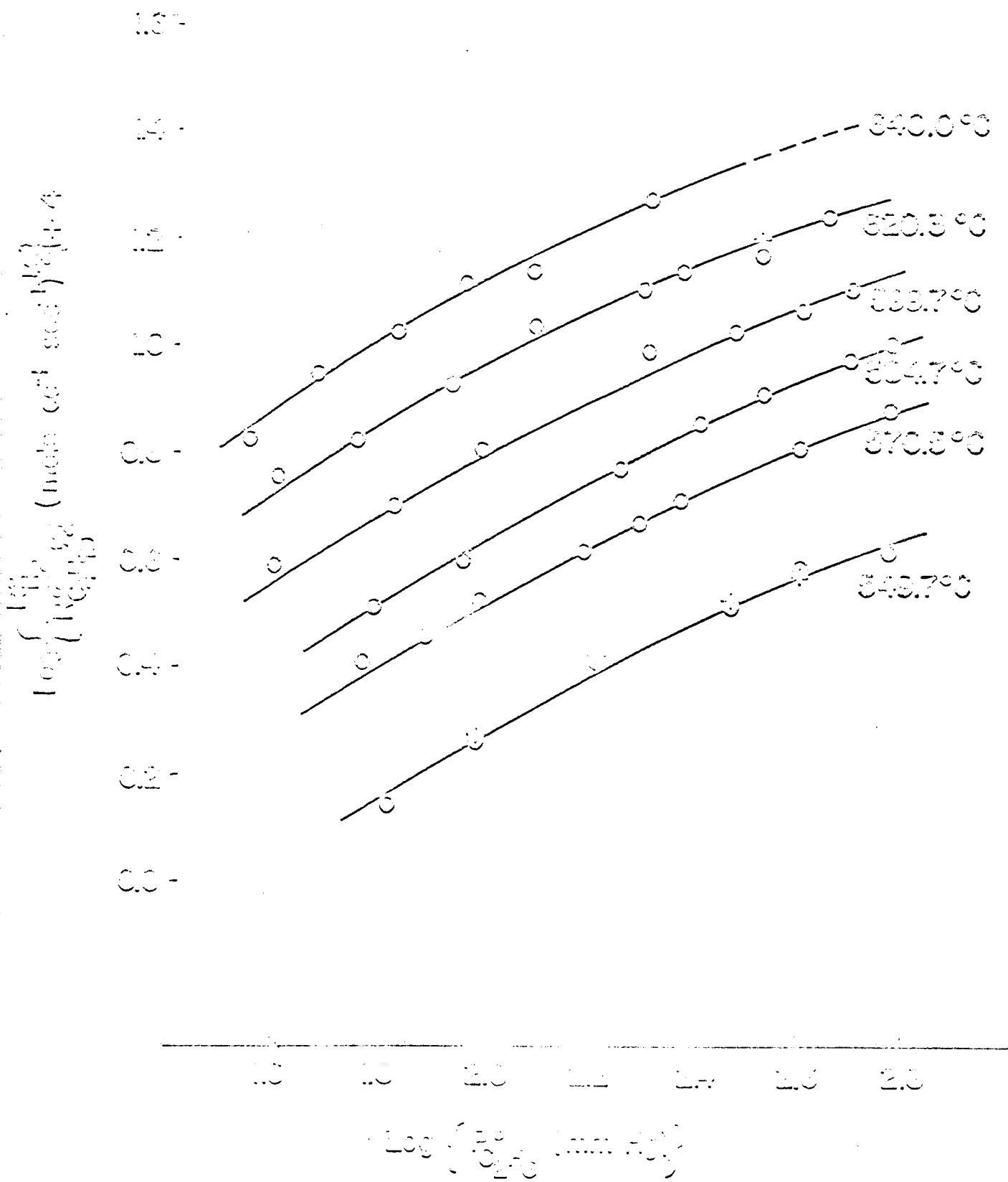
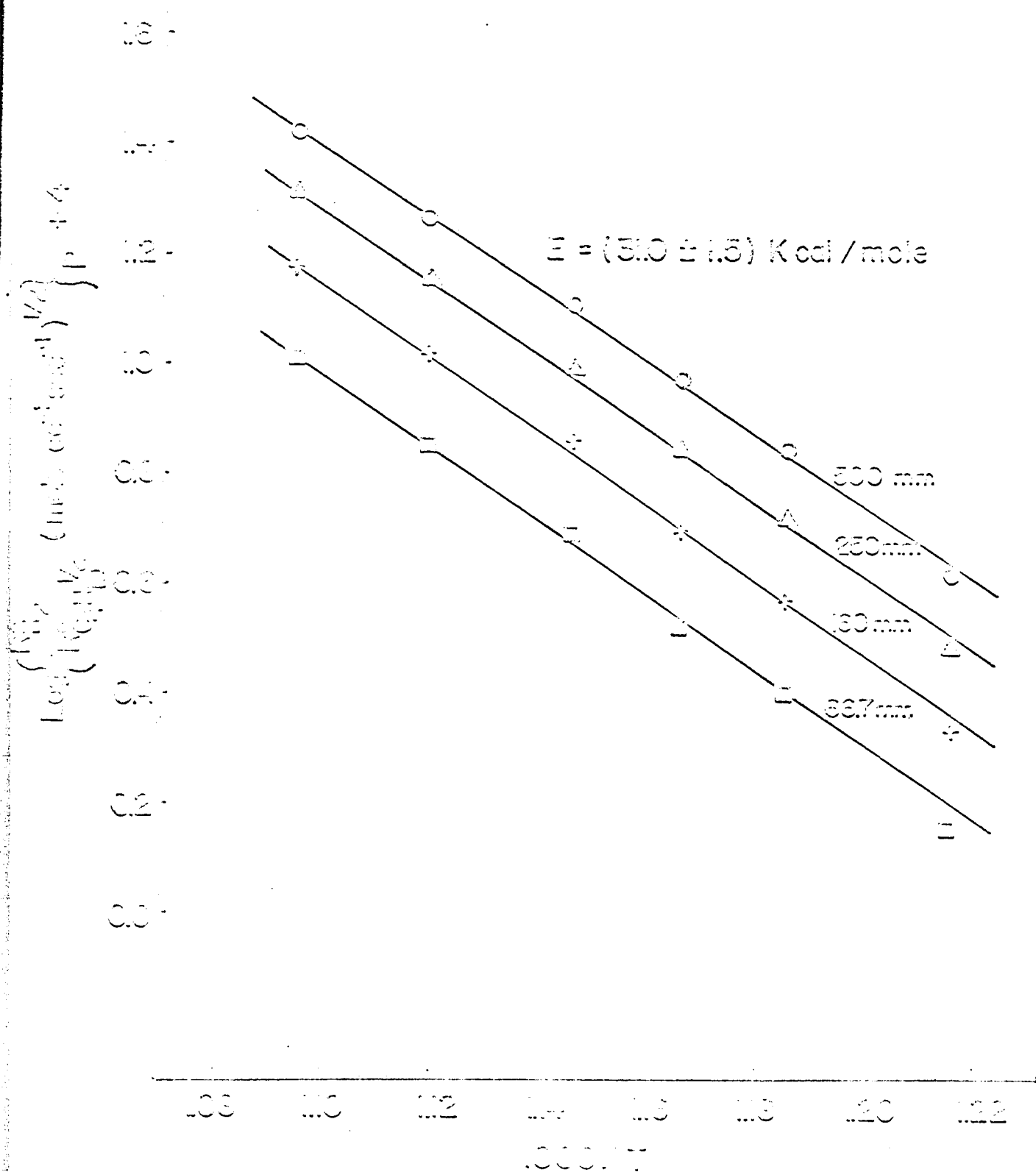


Figure 19.

Plots of $\log R_{H_2}^{\circ} / R_{C_4H_{10}}^{\circ} \frac{1}{2}$ vs. $\frac{1}{T}$ at various pressures.



In both the Rice-Herzfeld and the K  chler-Theile mechanisms, reaction (3) was implicitly assumed to be independent of pressure.

The rates of production of hydrogen and butane provide a measure of k_3 . From equations [11] and [21]

$$\frac{R_{H_2}^o}{R_{C_4H_{10}}^o}^{1/2} = \frac{k_3}{k_{5a}}^{1/2} \quad [27]$$

This equation is valid provided

$$k_3 [C_2H_5] - k_4 [H] [C_2H_6] = 0$$

and butane is produced only by reaction (5).

Double-logarithmic plots of $R_{H_2}^o / R_{C_4H_{10}}^o$ against initial ethane pressure are shown in Figure 18, in which the results obtained from the unpacked and packed vessels are presented together. The $R_{H_2}^o / R_{C_4H_{10}}^o$ ratios are essentially independent of S/V ratio within experimental error. This indicates that the processes giving hydrogen and butane are predominantly homogeneous. The slopes of the curves for all temperatures vary from ~ 0.4 at high pressures to ~ 0.6 at low pressures. If k_{5a} is assumed to be independent of pressure, as it might reasonably be, the pressure dependence of $R_{H_2}^o / R_{C_4H_{10}}^o$ must be due to reaction (3). Further evidence for the pressure dependence of k_3 was indicated by the experiments in which various amounts of CO_2 were added. As shown in Figures 15 and 16, the rates of both methane and butane production were hardly affected by the increase in total pressure, whereas the rate of hydrogen production

was increased by 15% when the total was doubled.

The activation energy of the ethyl radical decomposition in the fall-off region can be obtained by plotting the logarithm of $R_{H_2}^o / R_{C_4H_{10}}^o$ ^{1/2} at constant pressure against $1/T$. The results given in Figure 19 lead to an activation energy of $31.0 \text{ kcal mole}^{-1}$ with an error of about $\pm 1.5 \text{ kcal}$ for all pressures specified. This value corresponds to $31.0 + RT \doteq 32.7 \text{ kcal mole}^{-1}$ in the temperature range $550-620^\circ\text{C}$, if constant concentration instead of pressure is used. This value is in excellent agreement with the value $32.6 \pm 2 \text{ kcal mole}^{-1}$ obtained by Purnell and Quinn in the range temperature $420-530^\circ\text{C}$ if an activation energy of $10.4 \text{ kcal mole}^{-1}$ (42) is taken for the abstraction of a hydrogen atom from butane by the ethyl radical instead of $15.2 \text{ kcal mole}^{-1}$ as used by these authors. As expected, this value is significantly lower than $39.5 \text{ kcal mole}^{-1}$ (27) or $38.0 \pm 2 \text{ kcal mole}^{-1}$ (chapter 6) for the first order decomposition. A more detailed discussion on this decomposition will be presented in chapter 6.

IV. Over-all kinetics of decomposition:

Applying the steady-state treatment to reaction (1) to (5) leads to the following radical concentrations:

$$[CH_3] = 2k_1/k_2 \quad [28]$$

$$[C_2H_5] = \left(\frac{k_1}{k_5} \right)^{1/2} [C_2H_6]^{1/2} \quad [29]$$

and

$$[H] = \frac{k_3}{k_4} \left(\frac{k_1}{k_5} \right)^{1/2} \frac{1}{[C_2H_6]^{1/2}} \quad [30]$$

where

$$k_5 = k_{5a} + k_{5b}$$

The rate equations for methane, hydrogen and butane at the initial stage of decomposition are:

$$R_{CH_4}^o = \left(\frac{d [CH_4]}{dt} \right)_{t=0} = 2k_1 [C_2H_6] \quad [13]$$

$$R_{H_2}^o = \left(\frac{d [H_2]}{dt} \right)_{t=0} = k_3 \left(\frac{k_1}{k_5} \right)^{1/2} [C_2H_6]^{1/2} \quad [31]$$

and

$$R_{C_4H_{10}}^o = \left(\frac{d [C_4H_{10}]}{dt} \right)_{t=0} = k_{5a} \left(\frac{k_1}{k_5} \right) [C_2H_6] \quad [32]$$

On the basis of these equations and the data given in Table 3 and chapter 2, the steady-state concentrations of hydrogen atoms, methyl and ethyl radicals at various pressures were evaluated at 550.7 and 640.0°C and are given in Table 4.

Table 4

The concentrations of radicals as a function of temperature and pressure.

Radical Conc. (mole/cc)	550.7°C		640.0°C	
	500 mm	100 mm	205 mm	36 mm
[CH ₃]	8.1x10 ⁻¹⁶	7.3x10 ⁻¹⁶	7.2x10 ⁻¹⁴	5.2x10 ⁻¹⁴
[C ₂ H ₅]	2.2x10 ⁻¹³	8.6x10 ⁻¹⁴	1.8x10 ⁻¹²	6.5x10 ⁻¹³
[H]	7.7x10 ⁻¹⁶	6.9x10 ⁻¹⁶	5.3x10 ⁻¹⁴	3.8x10 ⁻¹⁴

The order of over-all decomposition was found to vary from 0.94 at 500 mm to 1.20 at 50 mm. No sharp transition in order was observed at 640°C or higher temperatures, as shown in Figure 4, although the over-all order approached 1.5 in the region of a few cm of

pressure. According to equation [31], the order of the over-all reaction can be calculated from the orders of reaction (1) and reaction (3), assuming k_5 is independent of pressure. At very high pressure, where the decomposition of the ethyl radical is first-order, the over-all order will be 1/2, while at very low pressures, it may become 2. The occurrence of reactions (6) and (7) at very high temperatures and very low pressures might, of course, bring about further complications.

The self-consistency of the over-all order with the orders of the individual reactions is shown in Table 5. The order of the over-all reaction was one in the region of pressure 150-400mm Hg.

Table 5

The order of over-all reaction at different temperatures and pressures.

t °C	P mm Hg	Order with respect to ethane			
		k_1	k_3	over-all	
				calc.	obs.
570.5	500	0	0.44	0.94	0.935
	200	0.11	0.47	1.02	1.00
	50	0.20	0.56	1.16	1.17
548.7	400	0	0.45	0.95	0.966
	100	0.18	0.53	1.10	1.12
620.3	500	0	0.38	0.88	0.940
	200	0.11	0.44	1.00	1.01
	50	0.21	0.59	1.20	1.20

The first-order rate constants given by equation [6] can be rewritten as

$$k_{H_2} = 1.65 \times 10^{16} e^{-77,600/RT} \text{ sec}^{-1}$$

[33]

which is in excellent agreement with the results obtained by Marek and McCluer and other authors as given in Table 6.

Table 6

Comparison of the Arrhenius parameters of the first-order rate constants for over-all reaction.

Temperature range (°C)	Frequency factor (sec ⁻¹)	Activation Energy (kcal mole ⁻¹)	References
600-700	1.1×10^{16}	77.7	Marek and McCluer (10)
585 - 637	1.3×10^{14}	69.8	Sachsse (11)
551 - 665	5.2×10^{15}	76.4	Kuchler and Theille (13)
565 - 640	1.0×10^{14}	69.7	Steacie and Shane (14)
550 - 630	1.07×10^{15}	73.1	Laidler and Wojciechowski (15)
564 - 608	1.6×10^{16}	78.2	Quinn (19)
475 - 600	3.2×10^{16}	81.0	Gordon (20)
550 - 620	1.65×10^{16}	77.6	This work

According to equation [31], the over-all activation energy can be evaluated from

$$E_{\text{over-all}} = E_3 + \frac{1}{2} E_1 \quad [34]$$

assuming $E_5 = 0$. Using $E_3 = 32.7$ and $E_1 = 86.0 \text{ kcal mole}^{-1}$, we have

$$\begin{aligned} E_{\text{over-all}} &= 32.7 + 43.0 \\ &= 75.7 \text{ kcal mole}^{-1}. \end{aligned}$$

Exact agreement can be obtained by using $E_1' = 89.8 \text{ kcal mole}^{-1}$ from the butane production:

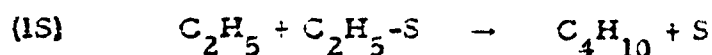
$$\begin{aligned} E_{\text{over-all}} &= 32.7 + \frac{1}{2} \times 89.8 \\ &= 77.6 \text{ kcal mole}^{-1} \end{aligned}$$

This difference in activation energy, $1.9 \text{ kcal mole}^{-1}$ may be due to a surface effect as discussed in section II. Since both the ethyl radical decomposition and the initial split of ethane are independent of S/V ratio, the calculated activation energy, $75.7 \text{ kcal mole}^{-1}$, may correspond to the homogeneous over-all decomposition.

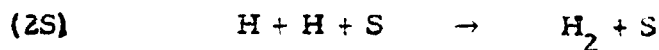
V. Surface effect:

As mentioned before, an increase in S/V ratio from 0.6 to 9.4 reduced significantly the rates of hydrogen and butane production, whereas that of methane formation remained the same. At 550°C , for 100 mm of ethane, $R_{\text{H}_2}^0$ decreased by 17% and $R_{\text{C}_4\text{H}_{10}}^0$ by 41%. Higher ethane pressures reduced this effect. The orders of hydrogen and butane production in the packed vessel were therefore higher than those in the unpacked one.

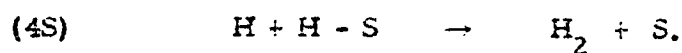
Since butane formation was reduced significantly, the production of butane through a heterogeneous process such as



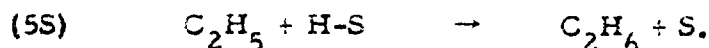
is probably not important. The recombination of hydrogen atoms on the surface



has been proposed by Laidler and Wojciechowski (15). In view of the very short life of the excited H_2^* ($\sim 10^{-14}$ sec) formed by the homogeneous combination of H atoms, reaction (2S) could only proceed by the following successive reactions:



Termination may also occur by



If the rate constants of reactions (4S) and (5S) do not differ significantly, reaction (5S) would be more important than (4S), since the concentration of ethyl radicals is much higher than that of hydrogen atoms. Reaction (5S) is analogous to the termination reaction:



in the nitric oxide inhibited decomposition of ethane (43).

The following reaction



might also provide H-S. The relative rates of reaction (3S) and (6S) may be estimated as follows:

$$\begin{aligned} \frac{R_{3S}}{R_{6S}} &= \frac{k_{3S} [\text{H}] [\text{S}]}{k_{6S} [\text{C}_2\text{H}_5] [\text{S}]} \\ &= \frac{[\text{H}]}{[\text{C}_2\text{H}_5]} \frac{P_{\text{H}} Z_{\text{H}} e^{-E_{3S}/RT}}{P_{\text{C}_2\text{H}_5} Z_{\text{C}_2\text{H}_5} e^{-E_{6S}/RT}} \end{aligned} \quad [35]$$

where P is the steric factor and Z the collision number. If it is assumed that $P_{\text{H}} = P_{\text{C}_2\text{H}_5}$ and $E_{3S} = 0$, equation [35] becomes

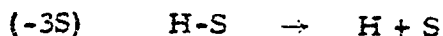
$$\frac{R_{3S}}{R_{6S}} = \frac{[\text{H}]}{[\text{C}_2\text{H}_5]} \left(\frac{M_{\text{C}_2\text{H}_5}}{M_{\text{H}}} \right)^{1/2} e^{E_{6S}/RT} \quad [36]$$

At 550°C , $[\text{H}]/[\text{C}_2\text{H}_5] = 8.0 \times 10^{-3}$ for 100 mm of ethane. If we assume that $E_{6S} = 10\text{-}20 \text{ kcal mole}^{-1}$, the relative rate becomes

$$\frac{R_{3S}}{R_{6S}} = 15 \sim 1500.$$

Thus if $E_{3S} > 10 \text{ kcal mole}^{-1}$, reaction (3S) would be more important than reaction (6S).

At higher temperatures the desorption reaction:



may become important and the concentration of H-S would therefore be reduced. This may explain the fact that the surface effect is less significant at high temperatures.

Incorporating reactions (3S), (-3S) and (5S) in the reaction scheme, we have

$$R_{H_2}^o = k_3 \left(\frac{k_1}{k_5 + X} \right)^{1/2} [C_2H_6]^{1/2} \quad [37]$$

and

$$\begin{aligned} R_{C_4H_{10}}^o &= k_{5a} \left(\frac{k_1}{k_5 + X} \right)^{1/2} [C_2H_6] \\ &\equiv k_1' [C_2H_6] \end{aligned} \quad [38]$$

where

$$X = \frac{k_{3S} k_{5S} [S]}{k_{-3S} + k_{5S} \left(\frac{k_1}{k_5} \right)^{1/2} [C_2H_6]^{1/2}} \frac{k_3}{k_4 [C_2H_6]} \quad [39]$$

is the term allowing for a surface combination reaction, and

$$k_1' \equiv k_{5a} \left(\frac{k_1}{k_5 + X} \right)$$

or

$$k'_1/k_1 = \frac{k_{5a}}{k_5 + X} \quad [40a]$$

Combination of equations [26] and [40a] in the high-pressure first-order region gives

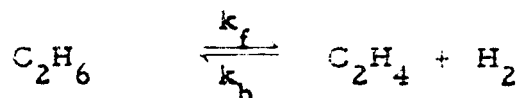
$$\frac{k_{5a}}{k_5 + X} = 6.6 e^{-3,800/RT} \quad [41]$$

The activation energy $3.8 \text{ kcal mole}^{-1}$ may be ascribed to the temperature-dependence of the quantity X , which decreases with increasing temperature because both terms in the denominator increase with temperature.

Equation [39] also predicts the value of X to be augmented by increasing the S/V ratio or lowering the pressure. The mechanism is thus consistent with the facts that the surface effect tends to vanish at high temperature, that the methane/butane ratio increases with decreasing pressure and that the orders of hydrogen and butane production are higher in the packed vessel.

VI. The equilibrium $C_2H_6 \rightleftharpoons C_2H_4 + H_2$ and the kinetics and mechanism of the reverse reaction:

The purpose of this section is to calculate the equilibrium constants for the over-all reaction,



from the known value of k_f obtained from present work,

$$k_f = k_{H_2} = 1.65 \times 10^{16} e^{-77,600/RT} \text{ sec}^{-1}$$

and the existing data for k_b , the rate constant of the backward reaction, and to propose a mechanism to account for the kinetics of the backward reaction.

Very little work has been done on the reverse reaction. The results of Pease (44) seem by far the most detailed. Using a static system with a 500 ml. vessel, he followed both the total pressure change and the rate of production of ethane. The decreases in pressure of both hydrogen and ethylene were equal to the ethane produced in experiments with 3:1 hydrogen-ethylene mixtures. Hydrogen was used in large excess in order to avoid the polymerization of ethylene. Some dependence on S/V ratio was also observed. In the range of temperatures 475-550°C, fairly good values of k_b were obtained by following the time course of the reaction using the second order rate equation:

$$k_b = \frac{1}{t([H_2]_0 - [C_2H_4]_0)} \ln \frac{[H_2]_0([C_2H_4]_0 - x)}{[C_2H_4]_0([H_2]_0 - x)} \quad [42]$$

where $[C_2H_4]_0$ and $[H_2]_0$ are the initial concentrations of ethylene and hydrogen, respectively, and x, the amount of reactant disappeared at time t. The rate constants thus obtained were given by

$$k_b = 7.60 \times 10^8 e^{-43,200/RT} \text{ atm}^{-1} \text{ sec}^{-1} \quad [43]$$

The equilibrium constant, $K = k_f/k_b$, calculated from the experimental values for k_f and k_b are given in Table 7 under the heading "obs." The observed values are about a factor of 2 higher than those calculated from thermodynamic data (45).

Table 7

The equilibrium constants of the reaction $C_2H_6 \rightleftharpoons C_2H_4 + H_2$

T°K	ΔS° (Gibbs mole ⁻¹) [*]	ΔH° (kcal mole ⁻¹)	K (atm)	
			calc	obs.
700	31.92	34.12	1.11×10^{-4}	3.9×10^{-4}
800	32.15	34.29	4.38×10^{-3}	8.5×10^{-3}
900	32.30	34.42	5.02×10^{-2}	9.4×10^{-2}
1000	32.37	34.49	3.39×10^{-1}	6.6×10^{-1}

* Standard state: 1 atm of ideal gas.

In order to calculate the heat of reaction directly from the rate constants k_f and k_b , the Arrhenius equation:

$$k_i = A_i e^{-E_i/RT}$$

should be transformed into:

$$k_i = \frac{kT}{h} e^{\Delta S_i^\ddagger/R} e^{-\Delta H_i^\ddagger/RT} \quad [44]$$

For the forward reaction, the change in heat capacity accompanying the formation of the activated complex is negligible. The heat of activation can be obtained either from the relationship (38)

$$\Delta H_i^\ddagger = E_{\text{exp}} - RT + \Delta n_i^\ddagger (RT) \quad [45]$$

where $\Delta n_i^\ddagger$ is the increase in the number of molecules from reactant to activated complex, or from the slope of the $\log(k_f/T)$ vs. $1/T$ plot; the result is

$$\Delta H_f^\ddagger = \Delta H_{fo}^\ddagger = 75.5 \text{ kcal mole}^{-1}.$$

Since two rotational and three translational degrees of freedom disappear when hydrogen and ethylene are converted into the activated complex, $(\Delta C_p^\ddagger)_b$ is about $-7R/2$ if the contribution of each degree of freedom is taken as equal to the classical value of $\frac{1}{2}R$ and the contribution due to vibrational degree of freedom is neglected. Then

$$\begin{aligned}\Delta H_b^\ddagger &= \Delta H_{bo}^\ddagger + T(\Delta C_p^\ddagger)_b \\ &= \Delta H_{bo}^\ddagger - \frac{7}{2} RT.\end{aligned}\quad [46]$$

The entropy of activation for the backward reaction, at constant pressure, can be expressed as

$$\begin{aligned}\Delta S_b^\ddagger &= (\Delta S_b^\ddagger)_{T_o} + (\Delta C_p^\ddagger)_b \ln \frac{T}{T_o} \\ &= (\Delta S_b^\ddagger)_{T_o} - \frac{7}{2} R \ln \frac{T}{T_o}\end{aligned}\quad [47]$$

where T_o is the reference temperature. Inserting equations [46] and [47] in [44], taking logarithms and differentiating gives

$$\frac{d \ln k_b}{dT} = \frac{\Delta H_{bo}^\ddagger - \frac{5}{2} RT}{RT}$$

or

$$\frac{d \ln k_b T^{5/2}}{d(1/T)} = - \frac{\Delta H_{bo}^\ddagger}{R} \quad [48]$$

$\Delta H_{bo}^\ddagger$ can be obtained by plotting the experimental values of $\ln k_b T^{5/2}$ against $1/T$; in this way Pease's results lead to $\Delta H_{bo}^\ddagger = 48.3 \pm 2 \text{ kcal mole}^{-1}$.

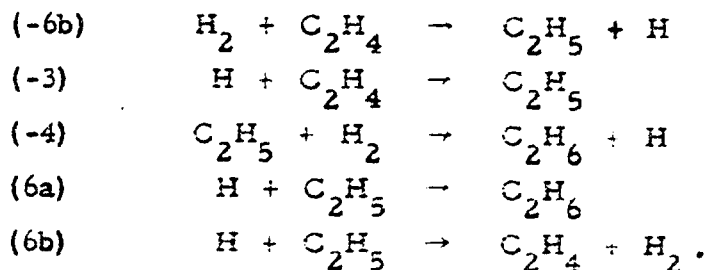
$\Delta H_b^\ddagger$ at any temperature can be calculated from equation [46] and the heat of reaction ΔH° from the following equation,

$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\ddagger - \Delta H_b^\ddagger \\ &= 27.2 + \frac{7}{2} RT.\end{aligned}\quad [49]$$

At 700°K, $\Delta H^\circ = 32.1 \text{ kcal mole}^{-1}$ and at 1000°K, $\Delta H^\circ = 34.2 \text{ kcal mole}^{-1}$ with an error of about 3 kcal mole⁻¹. This agrees reasonably well with thermodynamic values and the experimental value of 33.6 kcal mole⁻¹ obtained by Kistiakowsky and Nickle (46) over the range of temperature 25-415°C.

The occurrence of radicals in the hydrogen-ethylene system has been reported by several authors. The reaction was found to be inhibited by NO, and in the fully inhibited region, the heat of reaction was found to be 33.6 kcal mole⁻¹ in the temperature range 610-660°C (47), which is again in agreement with the values calculated above. Varnerin and Dooling studied the reaction of D₂ with C₂H₄ (48). In the region of temperature 550-660°C, they found that a large amount of C₂H₃D was formed and among various ethane products, C₂H₅D and C₂H₄D₂ were the major ones.

Rice and Herzfeld (21) proposed a mechanism similar to that of the ethane decomposition to explain the over-all second order kinetics, viz.,



Steady-state treatment of this scheme leads to

$$\frac{d[C_2H_6]}{dt} = \left(\frac{k_{-6}k_{-3}k_{-4}}{k_{6a} + k_{6b}} \right)^{1/2} [C_2H_4][H_2] \quad [50]$$

which is consistent with the observed order of the reaction. However, there are several reasons to doubt this mechanism.

(1) As shown before, the decomposition of the ethyl radical under similar conditions is pressure-dependent with an order of about 1.5. This indicates that the reverse reaction (-3) must also be pressure-dependent. This requires that the over-all order of the reverse reaction be about 2.3, which is incompatible with the experimental results.

(2) As in the ethane decomposition reaction (6) is probably too slow to compete with reaction (5). The relative rate of these two reactions can be estimated from equation [20]. If the chain-length of the backward reaction were long, then

$$\frac{[H]}{[C_2H_5]} = \frac{k_{-4}[H_2]}{k_{-3}[C_2H_4]} \quad [51]$$

Combination of equation [51] and [20] gives

$$\frac{R_6}{R_5} = \frac{k_{-4}[H_2]}{1.15 k_{-3}[C_2H_4]} \quad [52]$$

k_{-4} and k_{-3} can be calculated respectively from the corresponding forward rate constants and the equilibrium constants. At $900^\circ K$, $K_3 = 6.2 \times 10^{-9}$ mole cc⁻¹, $K_4 = 1.4 \times 10^3$ (49), $k_4 = 7.6 \times 10^{10}$ cc mole⁻¹ sec⁻¹ (28) and from Figure 19, $k_3 = 1.1 \times 10^4$ sec⁻¹ for 500 mm of total pressure; equation [52] then gives

$$\frac{R_6}{R_5} = 2.6 \times 10^{-5} \frac{[H_2]}{[C_2H_4]} \quad [53]$$

For 3:1 hydrogen-ethylene mixture, equation [53] leads to a value of $R_6/R_5 = 7.8 \times 10^{-5}$ which strongly favors reaction (5).

(3) The over-all activation energy predicted by the Rice-Herzfeld mechanism is

$$E_b = \frac{1}{2}(E_{-6b} + E_{-3} + E_{-4} - E_6) \quad [54]$$

Using $E_{-3} = 2.0$ (49), $E_{-6b} = 66.5$, and $E_{-4} = 12.5$ kcal mole⁻¹ (calculated from $D(C_2H_5 - H) = 97.5$ (50), $D(H - H) = 103.2$ kcal mole⁻¹ and assuming $E_6 = 0$)

$$E_b = 41 \text{ kcal mole}^{-1},$$

which is lower than the experimental value $43.2 + RT = 44.8$ kcal mole⁻¹ over the range of temperature 475-550°C, when k_b is expressed in concentration units. An even lower value will be obtained if one used the experimental activation energy for E_3 which was found to be equal to 32.7 kcal mole⁻¹ in the fall-off region over the range of temperature 420 to 620°C. Combining this value with the heat of reaction (3), 38.6 kcal mole⁻¹ (49), one obtains

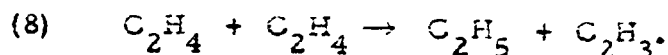
$$\begin{aligned} E_{-3} &= 32.7 - 38.6 \\ &= -5.9 \text{ kcal mole}^{-1}. \end{aligned}$$

This value would further reduce the over-all activation energy to 36.5 kcal mole⁻¹, which is much lower than the experimental value.

If reaction (5) is introduced as a termination step instead of reaction (6), the previous scheme gives:

$$\frac{d[C_2H_6]}{dt} = k_{-4} \left(\frac{k_{-6b}}{k_5} \right)^{1/2} [C_2H_4]^{1/2} [H_2]^{3/2} \quad [55]$$

which is inconsistent with the experimental results. This difficulty, however, could be overcome by introducing the molecular disproportionation of ethylene as an initiating step, viz.,



The C_2H_3 and C_2H_5 radicals thus formed could react with hydrogen molecules to initiate the chain.

A scheme including reactions (8), (-3), (-4) and (5) leads to a rate equation:

$$\frac{d[C_2H_6]}{dt} = k_{-4} \left(\frac{k_8}{k_5} \right)^{1/2} [C_2H_4] [H_2] \quad [56]$$

which is able to account for the order of the reaction and does not involve the pressure dependence of reaction (-3).

The over-all activation energy cannot be evaluated without knowing the heat of formation of the vinyl radical. Estimates of the dissociation energy of the C-H bond in ethylene have spread over a wide range from 122 to 92 kcal mole⁻¹. Laidler deduced a value of 99.9-102.8 kcal mole⁻¹ from the photosensitized decomposition of ethylene (51). Recent work of Harrison and Lossing (52) from electron impact studies of the vinyl radical produced by the decomposition of methyl vinyl mercury leads to a value of 103 ± 3 kcal mole⁻¹ (53), which

is in agreement with Laidler's value. Using $D(C_2H_3 - H) = 103 \pm 3$ kcal mole⁻¹, E_8 is found to be 64.0 ± 3 kcal mole⁻¹, if E_{-8} is assumed to be zero. The activation energy predicted by equation [56] is

$$\begin{aligned} E_b &= E_{-4} + \frac{1}{2}(E_8 - E_5) \\ &= 12.5 + \frac{1}{2}(64.0 - 0) \\ &= 44.5 \text{ kcal mole}^{-1}, \end{aligned}$$

which is in excellent agreement with the experimental value, 44.8 kcal mole⁻¹.

The backward reaction was also found to be sensitive to the S/V ratio, as mentioned before. In view of the related mechanisms of the forward and backward reactions, the heterogeneous reactions proposed for the former might be applicable to the latter.

Neglecting the surface effect on both forward and backward reactions or assuming the effect on both reactions to be the same, then at equilibrium, equations [31] and [56] lead to

$$\begin{aligned} K &= \frac{[C_2H_4][H_2]}{[C_2H_6]} \\ &= \frac{k_3'}{k_{-4}} \left(\frac{k_1}{k_2} \right)^{1/2} \end{aligned} \quad [57]$$

where

$$k_3' = k_3/[C_2H_6]^{1/2}.$$

The heat of reaction is therefore given by

$$\Delta H^\circ = \Delta H_3^\ddagger - \Delta H_{-4}^\ddagger + \frac{1}{2}(\Delta H_1^\ddagger - \Delta H_8^\ddagger). \quad [58]$$

Applying equation [45] to equation [58] produces:

$$\begin{aligned}\Delta H^{\circ} &= E_3 - E_{-4} + \frac{1}{2}(E_1 - E_8) + \frac{3}{2} RT \\ &= 31.2 + \frac{3}{2} RT\end{aligned}\quad [59]$$

At 700 and 1000°K, equation [59] gives, respectively,

$$\Delta H^{\circ}_{700^{\circ}\text{K}} = 33.3 \text{ kcal mole}^{-1}$$

and

$$\Delta H^{\circ}_{1000^{\circ}\text{K}} = 34.2 \text{ kcal mole}^{-1},$$

which agree closely with previous calculations from equation [49] at the same temperatures and also with the thermodynamic values given in Table 7.

The over-all reaction reaches equilibrium when the rates of the propagation reactions for both the forward and the reverse reactions are equal, viz., $k_3 [C_2H_5] = k_{-3} [H][C_2H_4]$ and $k_4 [H][C_2H_6] = k_{-4} [H_2][C_2H_5]$. These two equations lead to equilibrium constant, $K = [H_2][C_2H_4] / [C_2H_6] = k_3 k_4 / k_{-3} k_{-4}$. Comparing this expression with that given by equation (57), one gets $k_1 = \frac{k_8}{[C_2H_6]} \left(\frac{k_4}{k_{-3}} \right)^2$. It is, however, difficult to understand why the rate constant for the initial C-C split of ethane is dependent on the other rate constants when the over-all reaction is at equilibrium. The correctness of equation (57) is, therefore, doubtful.

CHAPTER 4

KINETICS AND MECHANISMS OF SECONDARY REACTIONS

The object of the present chapter is to describe the methods used to distinguish the secondary reactions from the primary ones and to evaluate the mechanisms for those secondary reactions which initially proceed with vanishing rates.

Ethylene is known to be more reactive than ethane, because it possesses a double bond. The activation energies for the addition of small species such as hydrogen atoms, methyl radicals and ethyl radicals to double bonds range from 2-10 kcal mole⁻¹. To study the effect of ethylene on the rates of formation of those primary products discussed in the last chapter, various amounts of ethylene were mixed with 147.7 mm of ethane at 570°C. The results, shown in Figure 20, were obtained with constant reaction time (100 sec). The rate of hydrogen production decreased linearly at first and then proceeded with a smaller but constant rate. The rate of methane production increased more rapidly than that of butane, which is seen to depend almost linearly on the amount of ethylene added. Butene-1 and butadiene, which disappeared at zero ethylene concentration, are obviously produced from the interaction of radicals in the system with the ethylene introduced. Detailed mechanisms and the derivation of the rate equation for each product will be discussed in the subsequent sections.

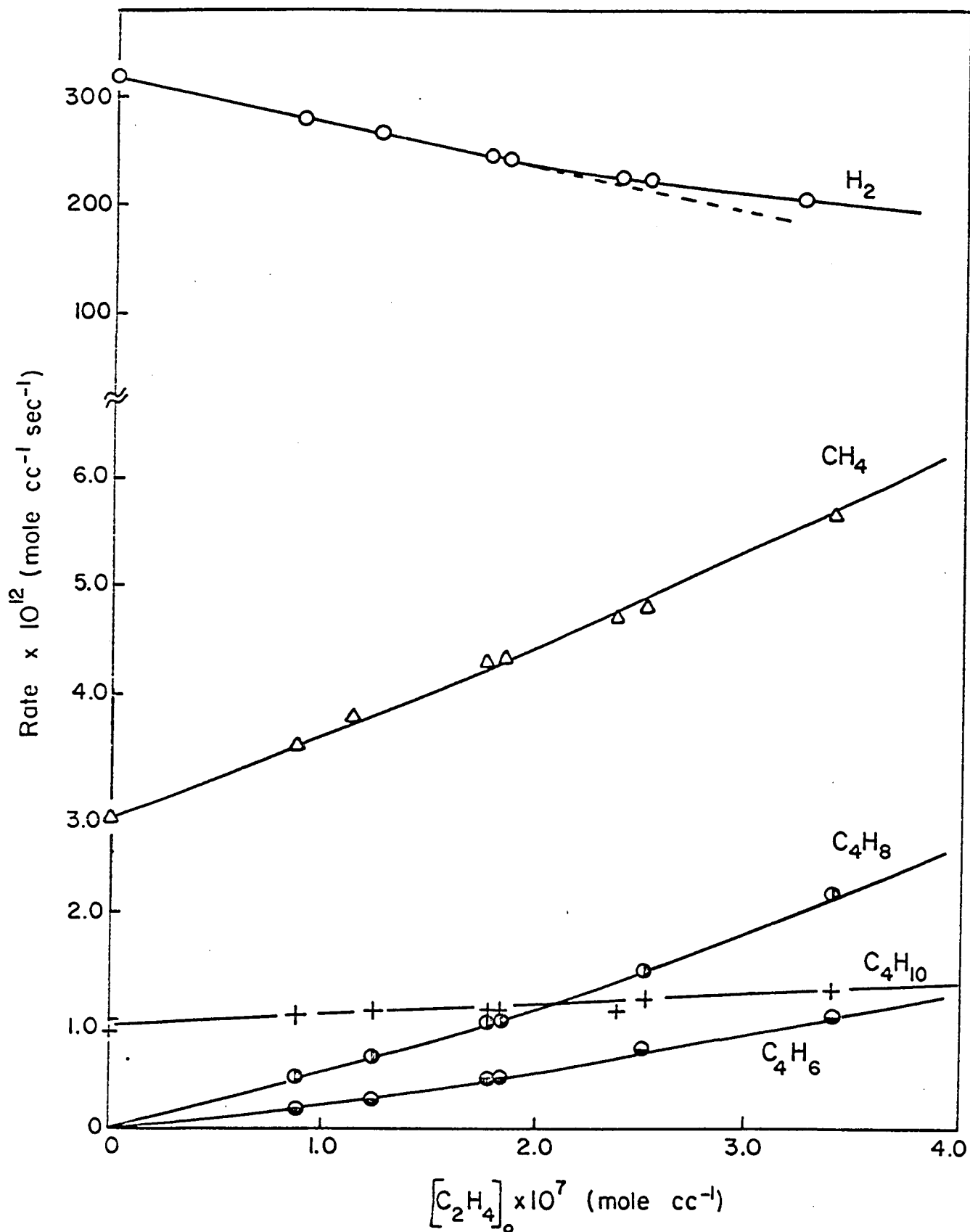
1. Inhibition of the over-all reaction by product:

The decrease in the initial rate of over-all decomposition caused by the introduction of a small amount of ethylene is probably

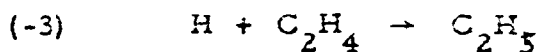
Figure 20.

The effect of ethylene on the rates of production of hydrogen,
methane, butane, butene-1 and butadiene.

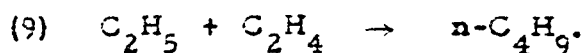
Data obtained from 147.5 mm ethane + C_2H_4 at $570.5^\circ C$.



due to the reduction of the steady-state concentrations of hydrogen atoms and ethyl radicals. Ethylene may react with a hydrogen atom via reaction (-3):

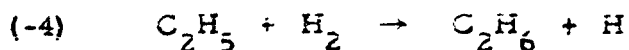


or with an ethyl radical,



The $\text{n-C}_4\text{H}_9$ radical thus produced may undergo the reverse reaction react with ethane to form butane, produce butene-1 by C-H split, or undergo further addition to give secondary methane as discussed later. However, these secondary products by no means account for the loss of hydrogen production, since the decrease in the latter was about 50 times more than the increase in the formation of methane, butane and butene-1 in the earlier stages of reaction as shown in Figure 20.

The abstraction of hydrogen atoms from H_2 by ethyl radicals,



may also reduce the rate of decomposition. The steady-state assumption for hydrogen atoms in a scheme including reactions (1)-(5), (-3) and (-4) leads to

$$\begin{aligned} \frac{d[\text{H}_2]}{dt} &= k_4 [\text{H}] [\text{C}_2\text{H}_6] - k_{-4} [\text{C}_2\text{H}_5] [\text{H}_2] \\ &= k_3 [\text{C}_2\text{H}_5] - k_{-3} [\text{H}] [\text{C}_2\text{H}_4] . \end{aligned} \quad [60]$$

Equation [60] explains the fact that addition of small amounts of ethylene reduced linearly the rate of hydrogen production. Theoretically, continuous addition of ethylene should reduce the rate of over-all decomposition to zero when reaction (3) reaches equilibrium, i. e.,

$$k_3 [C_2H_5] = k_{-3} [H] [C_2H_4].$$

In fact, Frost (54) found that the addition of a certain amount of ethylene did not inhibit the rate of decomposition; Dintses (55, 56), on the other hand, found a slight acceleration when ethylene was added. These paradoxical results could be explained if the effect of ethylene on initiation is taken into consideration. As shown in Figure 20, ethylene accelerates sharply the rate of methane production; the inhibition of the rate of chain propagation reactions by a certain amount of ethylene may be balanced by the acceleration in initiation. Beyond this point, further addition of ethylene would accelerate the over-all decomposition, since the rate of initiation at ordinary pressures, as shown in section II, is proportional to $[C_2H_4]^2$, whereas, according to equation [60], that of inhibition is proportional to $[C_2H_4]$.

In pure ethane the differential equation [60] can be easily solved by assuming that $[C_2H_4] = [H_2]$ and that $[C_2H_5]$ and $[H]$ are independent of reaction time in the early stage of decomposition. Thus letting $k_3 [C_2H_5] = a$, and $k_{-3} [H] = b$, equation [60] becomes

$$\frac{d [H_2]}{dt} = a - b [H_2] \quad [61]$$

Integrating from $t = 0$ to $t = t$, we have

$$[H_2] = \frac{a}{b} (1 - e^{-bt}) \quad [62]$$

e^{-bt} can be expanded into a power series:

$$e^{-bt} = 1 - bt + \frac{(bt)^2}{2!} - \frac{(bt)^3}{3!} + \dots \quad [63]$$

When reaction time is short or $bt \ll 1$, equation [63] reduces to

$$e^{-bt} = 1 - bt + \frac{b^2 t^2}{2} \quad [64]$$

Substituting equation [64] in [62] and dividing the resulting equation by t , we find

$$\frac{[H_2]}{t} = R_{H_2} = a - \frac{ab}{2} t \quad [65]$$

This equation predicts a linear relationship in a plot of R_{H_2} vs. t at early stages of decomposition, as shown in Figure 21. The shapes of these curves are the same as those shown in Figure 20. The intercept of this plot at zero time gives

$$a = k_3 [C_2H_5] = \left(\frac{d[H_2]}{dt} \right)_{t=0} = R_{H_2}^0$$

and the slope of the linear portion equals $ab/2$. Combination of intercept and slope leads to

$$b = 2 \times \text{slope}/a \quad [66]$$

$$= k_{-3} [H] \quad [66a]$$

Inserting the values of a and b thus obtained in equation [62], we get a function which can describe the production of hydrogen at any instant of reaction so long as a and b or, what is equivalent, $[C_2H_5]$ and $[H]$, are independent of time. The results presented in Figure 22 show good agreement of the calculated curves with the experimental points

Figure 21.

Typical rate-time plots for hydrogen production.

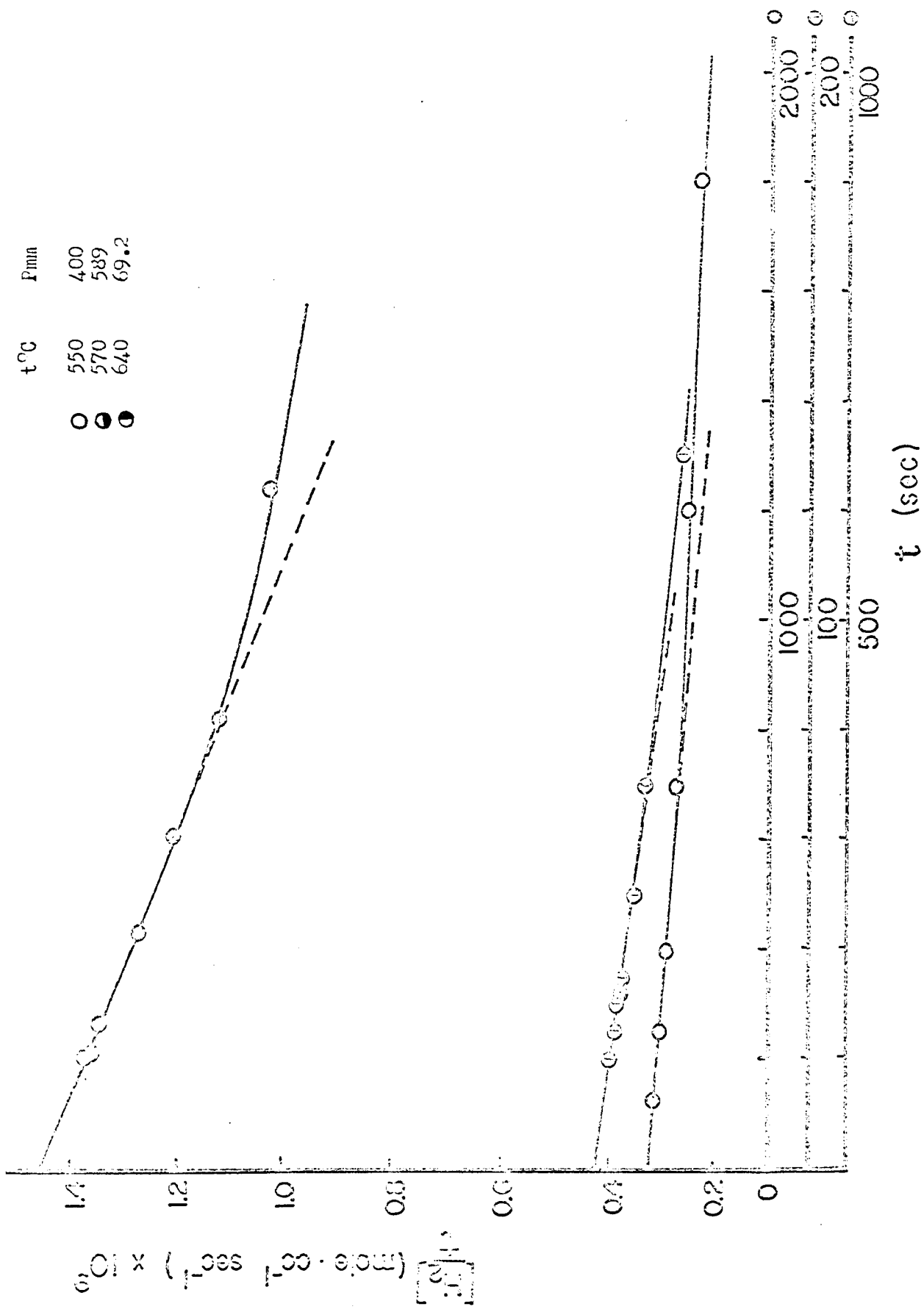
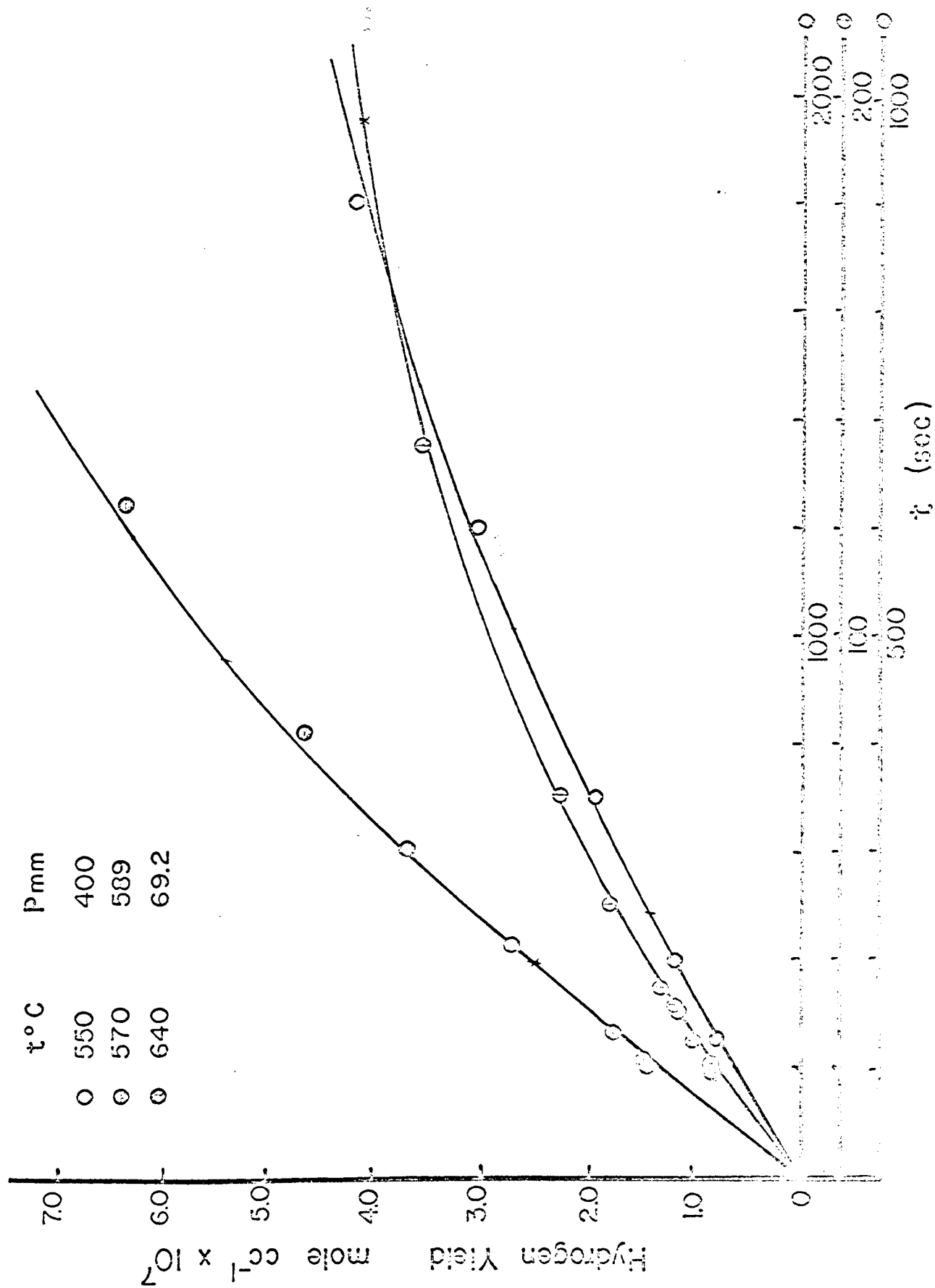


Figure 22.

Comparison of the calculated yield-time curves with the experimental results for hydrogen production.

Solid curves calculated from equation [62].



up to a conversion as high as 33%.

According to the definition of a and b, we have

$$\text{slope} = \frac{ab}{2} = \frac{1}{2} k_3 k_{-3} [C_2H_5][H] . \quad [67]$$

Inserting the steady-state concentrations of hydrogen atoms and ethyl radicals:

$$[H] = \frac{k_3}{k_4} \left(\frac{k_1}{k_5} \right)^{1/2} \frac{1}{[C_2H_6]^{1/2}}$$

and

$$[C_2H_5] = \left(\frac{k_1}{k_5} \right)^{1/2} [C_2H_6]^{1/2}$$

in equation [67], we have

$$\frac{ab}{2} = \frac{k_1 (k_3)^2 k_{-3}}{2 k_4 k_5}$$

or

$$\frac{ab}{2} = \frac{k_1 (k_3)^3}{2 K_3 k_4 k_5} , \quad [68]$$

where $K_3 = k_3/k_{-3}$ is the equilibrium constant of reaction (3).

Since k_3 is pressure-dependent the quantity $ab/2$ must be sharply dependent on pressure as indicated in Figure 23, where $\log ab/2$ is plotted against $\log P_{C_2H_6}^0$ at various temperatures. All values of $ab/2$ were obtained by least squares method. The order of $ab/2$ at $570^\circ C$ and 400 mm of ethane was found to be 1.32, which is in agreement with the value $3 \times 0.45 = 1.35$ obtained from Figure 18. This pressure-dependence of $ab/2$ is further evidence of the effect of pressure on k_3 .

Figure 23.

Double-logarithmic plots of $\frac{ab}{2}$ vs. $P_{C_2H_6}^o$.

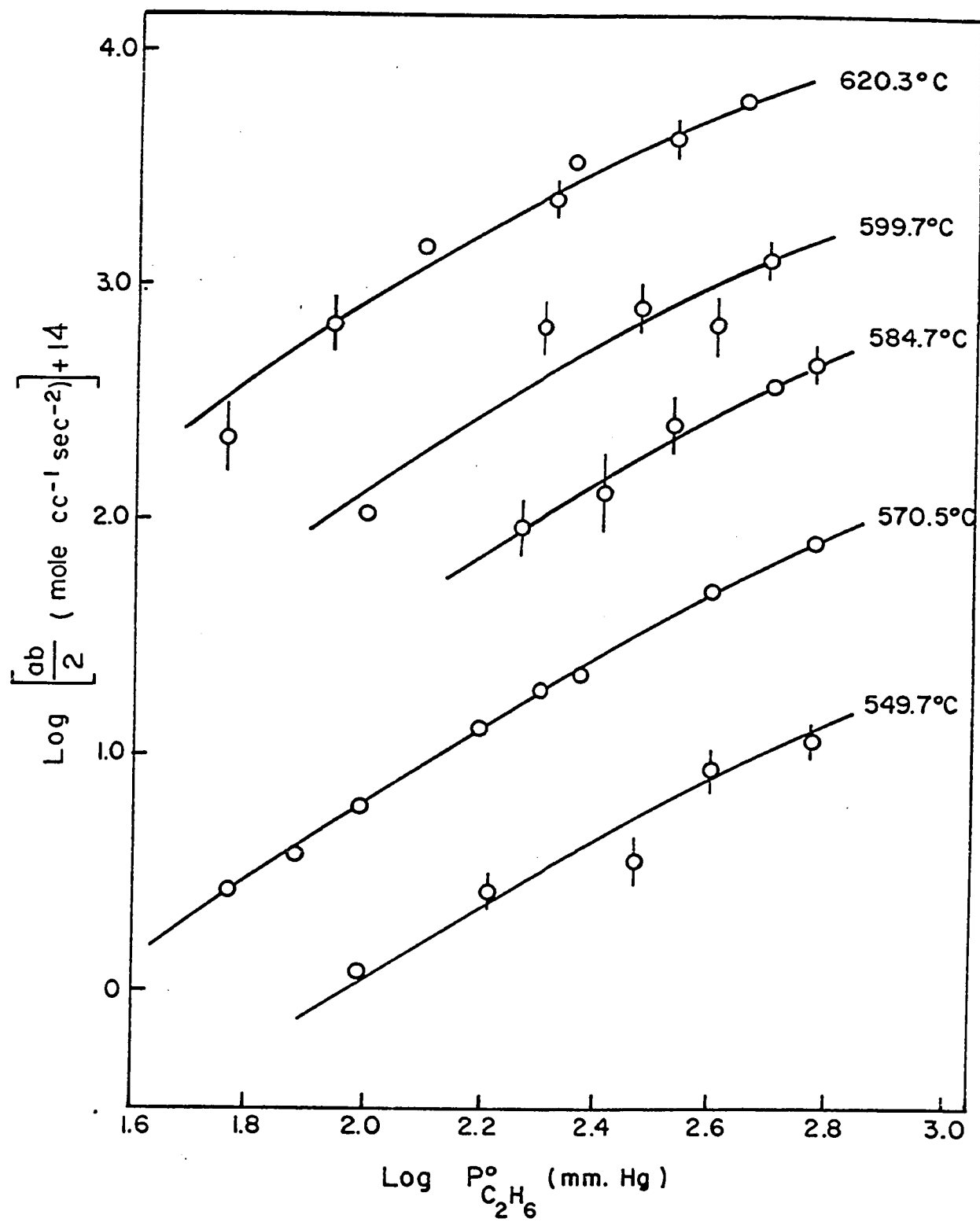
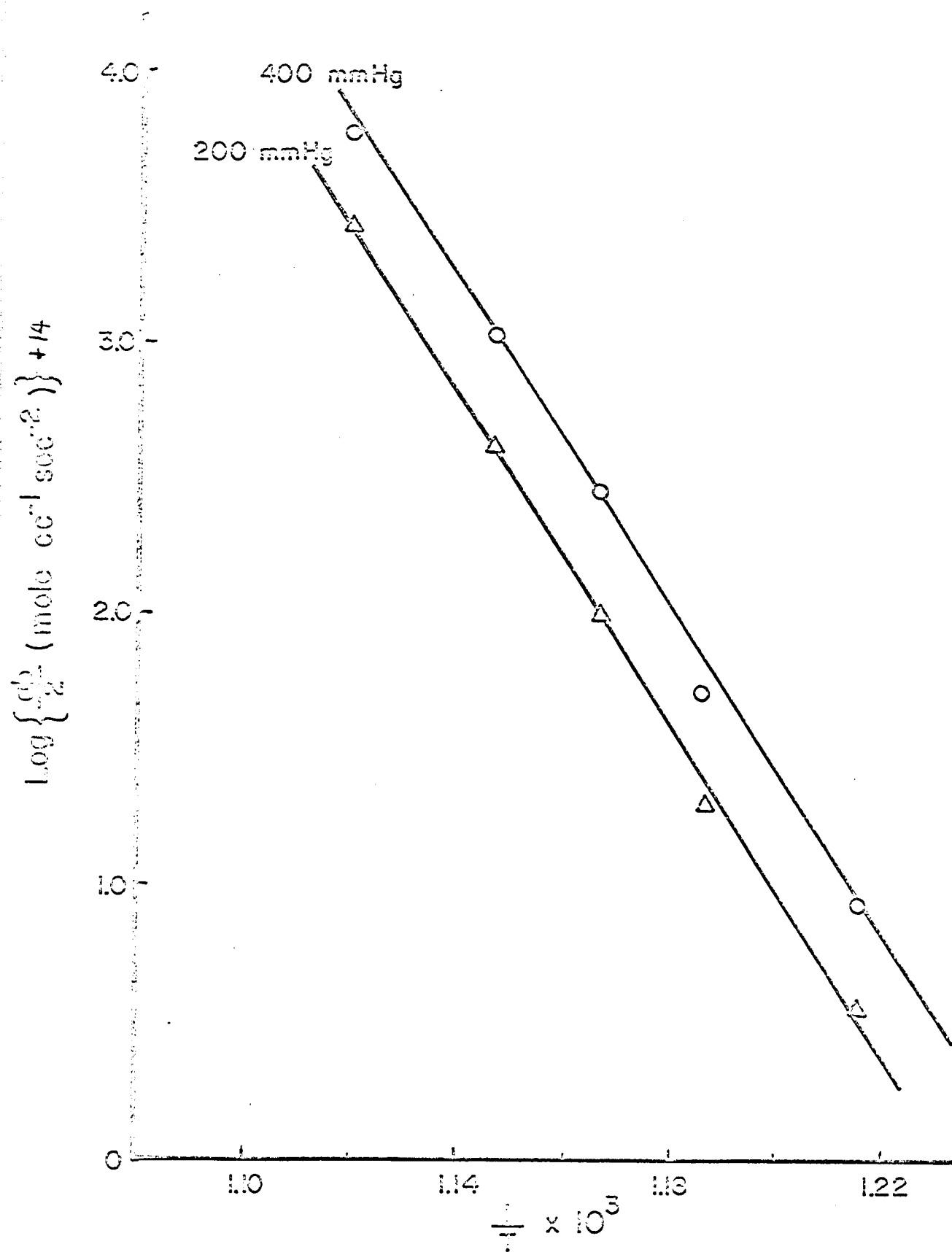


Figure 24.

Plots of $\log \frac{ab}{2}$ vs. $\frac{1}{T}$ for different pressures.



According to equation [68], the temperature coefficient of $ab/2$ can be calculated by

$$E_{ab/2} = E_1 + 3E_3 - \Delta H_3^0 - E_4 - E_5. \quad [69]$$

Substituting the values of $E_1 = 86.0$, $E_3 = 32.7$, $E_4 = 6.8$, $E_5 = 0$ and $\Delta H_3^0 = 38.6 \text{ kcal mole}^{-1}$ in equation [69] gives

$$E_{ab/2} = 138.7 \text{ kcal mole}^{-1},$$

which is in excellent agreement with the experimental value $137.5 + RT = 139 \text{ kcal mole}^{-1}$ obtained from Figure 24. $E_{ab/2}$ at 400 and 290 mm of ethane has the same value; this reflects the fact that E_3 is independent of pressure in this region of pressure as mentioned before.

II. Secondary methane production:

Two different processes were found to be responsible for the secondary production of methane. In the first process, which occurs at higher pressures, the rate of methane production can be described by

$$\frac{[CH_4]}{t} = R_{CH_4} = c + d \overline{[C_2H_4]}^2 : \quad [70]$$

whereas, in the second process, which becomes predominant at lower pressures, the rate of methane production is given by

$$R_{CH_4} = c + d' \overline{[C_2H_4]} , \quad [71]$$

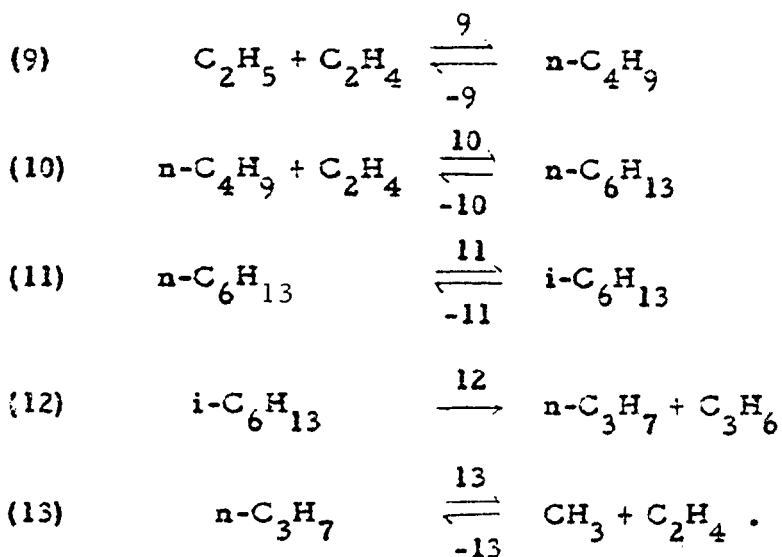
where $c = R_{CH_4}^0$, the initial rate of methane production; d and d' , the proportionality constants, are functions of temperature and pressure,

$$\overline{[C_2H_4]^2} = \frac{1}{t} \int_0^t [C_2H_4]^2 dt \quad [72]$$

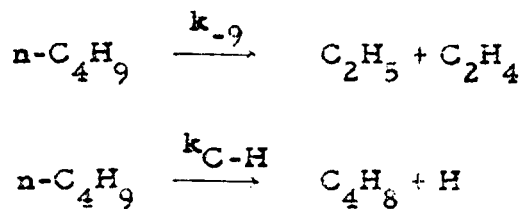
and

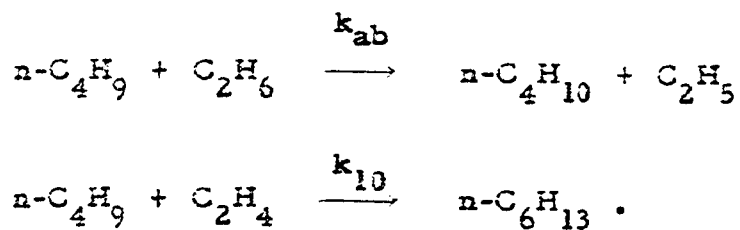
$$\overline{[C_2H_4]} = \frac{1}{t} \int_0^t [C_2H_4] dt. \quad [73]$$

The first process described by equation [70] was first observed by Quinn (57) who proposed the following mechanism to explain this relationship:



The possible reactions of the alkyl radicals in the system can be illustrated by taking the $n-C_4H_9$ radical as an example:





The relative rates of these reactions can be estimated by assuming:

$$k_{-9} = 10^{13} e^{-23,000/RT} \text{ sec}^{-1} \quad (58),$$

$$k_{\text{C-H}} = 10^{14} e^{-40,000/RT} \text{ sec}^{-1} \quad (58),$$

$$k_{ab} = 10^{12} e^{-15,000/RT} \text{ cc mole}^{-1} \text{ sec}^{-1} \quad (59),$$

and

$$k_{10} = 5 \times 10^{10} e^{-5,300/RT} \text{ cc mole}^{-1} \text{ sec}^{-1} \quad (60).$$

At 550°C, with 600 mm of ethane and 100 mm of ethylene, we find

$$k_{-9} = 6 \times 10^6,$$

$$k_{\text{C-H}} = 2 \times 10^3,$$

$$k_{ab} [\text{C}_2\text{H}_6] = 1 \times 10^2$$

and

$$k_{10} [\text{C}_2\text{H}_4] = 5 \times 10^3 \text{ sec}^{-1}.$$

Therefore, reaction (9) is, in effect, at equilibrium.

Reactions (12) and (13) were proposed to reconcile the facts that no C_5 products were detected and that the amounts of propylene and secondary methane were almost equal. Because of the limitation of the present measurements, we were not able to confirm this point. Propylene and secondary methane might not result from $n-C_4H_9$ radicals at these pressures, since this would imply that the rate of production of secondary methane should be proportional to $[C_2H_4]$.

Steady-state treatment of the scheme including reactions (1) to (5) and (9) to (13), leads to

$$\begin{aligned} R_{CH_4} &= k_2 [CH_3] [C_2H_6] \\ &= 2k_1 [C_2H_6] + k_{13} [n-C_3H_7] - k_{-13} [CH_3] [C_2H_4] \\ &= 2k_1 [C_2H_6] + k_{12} [i-C_6H_{13}] . \end{aligned} \quad [74]$$

A simple expression for the concentration of $i-C_6H_{13}$ radicals cannot be obtained without further assumptions; to do this, Quinn assumed that $k_{-11} \gg k_{12}$. The activation energy for reaction (-11), a strainless intramolecular H atom abstraction, is probably the same as ordinary H atom abstraction from hydrocarbons by alkyl radicals (~ 15 kcal mole⁻¹). The activation energy of reaction (12) is probably within the range of 25 ± 5 kcal mole⁻¹. Thus, if $A_{12}/A_{-11} > 10^3$, Quinn's assumption would be applicable, so that we have

$$\begin{aligned} [i-C_6H_{13}] &= K_{11} [n-C_6H_{13}] \\ &= K_{10} K_{11} [n-C_4H_9] [C_2H_4] \\ &= K_9 K_{10} K_{11} [C_2H_5] [C_2H_4]^2 . \end{aligned} \quad [75]$$

Substituting equation [75] in equation [74] produces

$$\frac{d[\text{CH}_4]}{dt} = 2k_1 [\text{C}_2\text{H}_6] + k_{12} K_9 K_{10} K_{11} [\text{C}_2\text{H}_5] [\text{C}_2\text{H}_4]^2. \quad [76]$$

Comparison of equation [76] with equation [70] gives

$$\begin{aligned} c &= R_{\text{CH}_4}^0 = 2k_1 [\text{C}_2\text{H}_6] \\ \text{and} \quad d &= k_{12} K_9 K_{10} K_{11} [\text{C}_2\text{H}_5]. \end{aligned} \quad [77]$$

At constant temperature and pressure, in the early stage of the decomposition, equation [76] can be integrated as

$$[\text{CH}_4] = \int_0^t d[\text{CH}_4] = ct + d \int_0^t [\text{C}_2\text{H}_4]^2 dt. \quad [78]$$

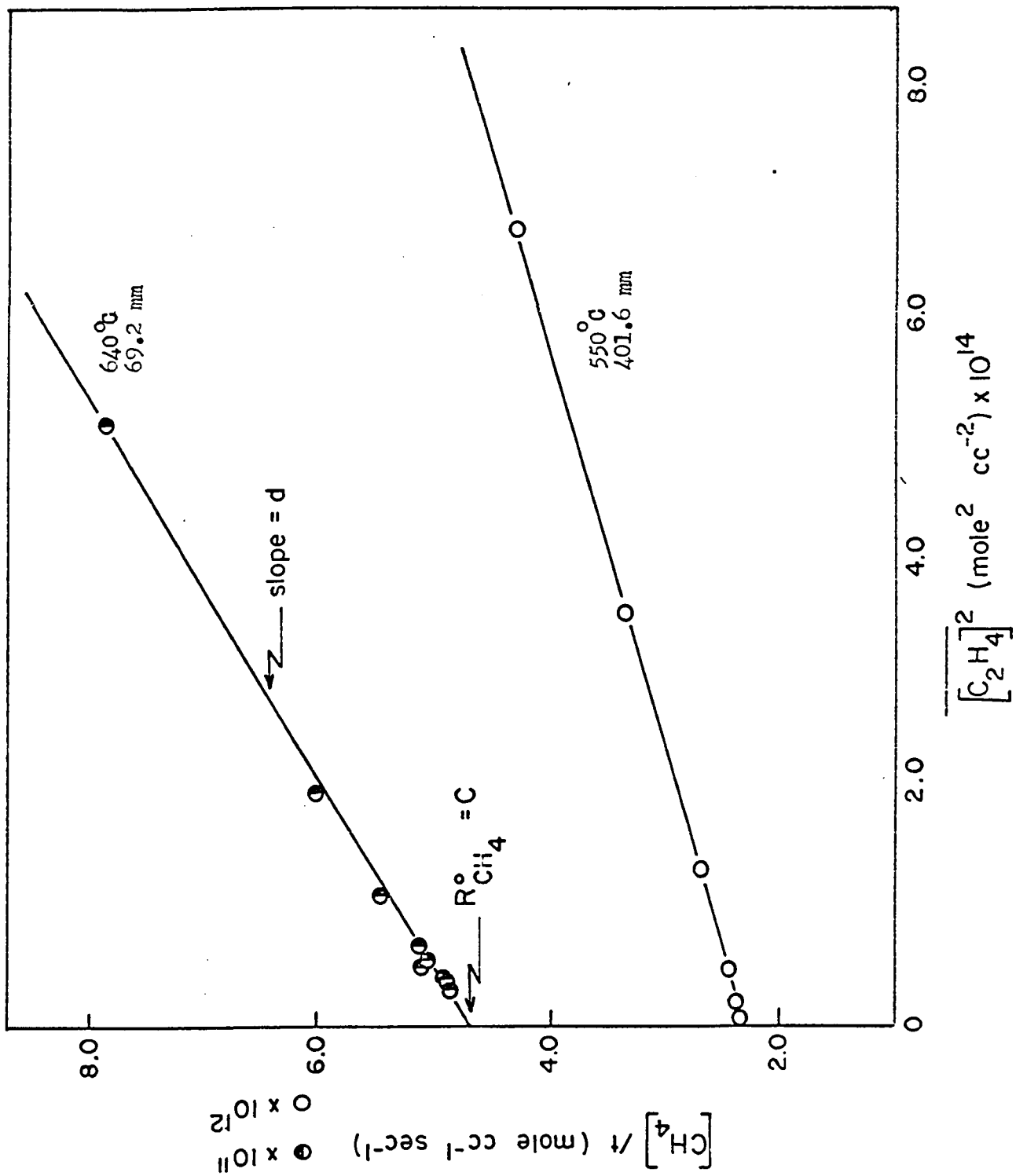
with the assumption that ethane concentration remains unchanged. If the conversion is very high, the consumption of ethane should be taken into account: then

$$c = 2k_1 [\text{C}_2\text{H}_6]_0 e^{-k_{\text{H}_2} t}. \quad [79]$$

The integral $\int_0^t [\text{C}_2\text{H}_4]^2 dt$ can be evaluated either by a graphical method or by the integration of the analytical function. Both methods were used; the first method was originally used by Quinn. The graphical integration was done with a planimeter. Typical results are shown in Figure 25, in which the integrated rate, $[\text{CH}_4]/t$, is plotted against $[\text{C}_2\text{H}_4]^2$. From the intercept we have c , the initial rate of methane production, and from the slope, d .

Figure 25.

Typical R_{CH_4} vs. $\overline{[C_2H_4]^2}$ plots.



The alternative is to utilize equation [62], i.e.,

$$[C_2H_4] = [H_2] = \frac{a}{b} (1 - e^{-bt}).$$

Substituting this equation in equation [78], we have

$$[CH_4] = ct + d \int_0^t \frac{a}{b} (1 - e^{-bt})^2 dt \quad [80]$$

After integration, equation [80] reduces to

$$[CH_4] = ct + \frac{a^2 d}{b^3} [bt - (1 - e^{-bt}) - \frac{1}{2}(1 - e^{-bt})^2] \quad [81]$$

or

$$\frac{[CH_4]}{t} = R_{CH_4} = c + \frac{a^2 d}{b^3} \frac{1}{t} [bt - (1 - e^{-bt}) - \frac{1}{2}(1 - e^{-bt})^2] \quad [82]$$

$$= c + \frac{a^2 d}{b^3} f(t), \quad [82a]$$

where

$$f(t) = \frac{1}{t} [bt - (1 - e^{-bt}) - \frac{1}{2}(1 - e^{-bt})^2] \quad [83]$$

Applying the value of b obtained from the hydrogen production calculated from equation [66], $f(t)$ can be evaluated at any time t . Typical plots of R_{CH_4} vs. $f(t)$ are shown in Figure 26.

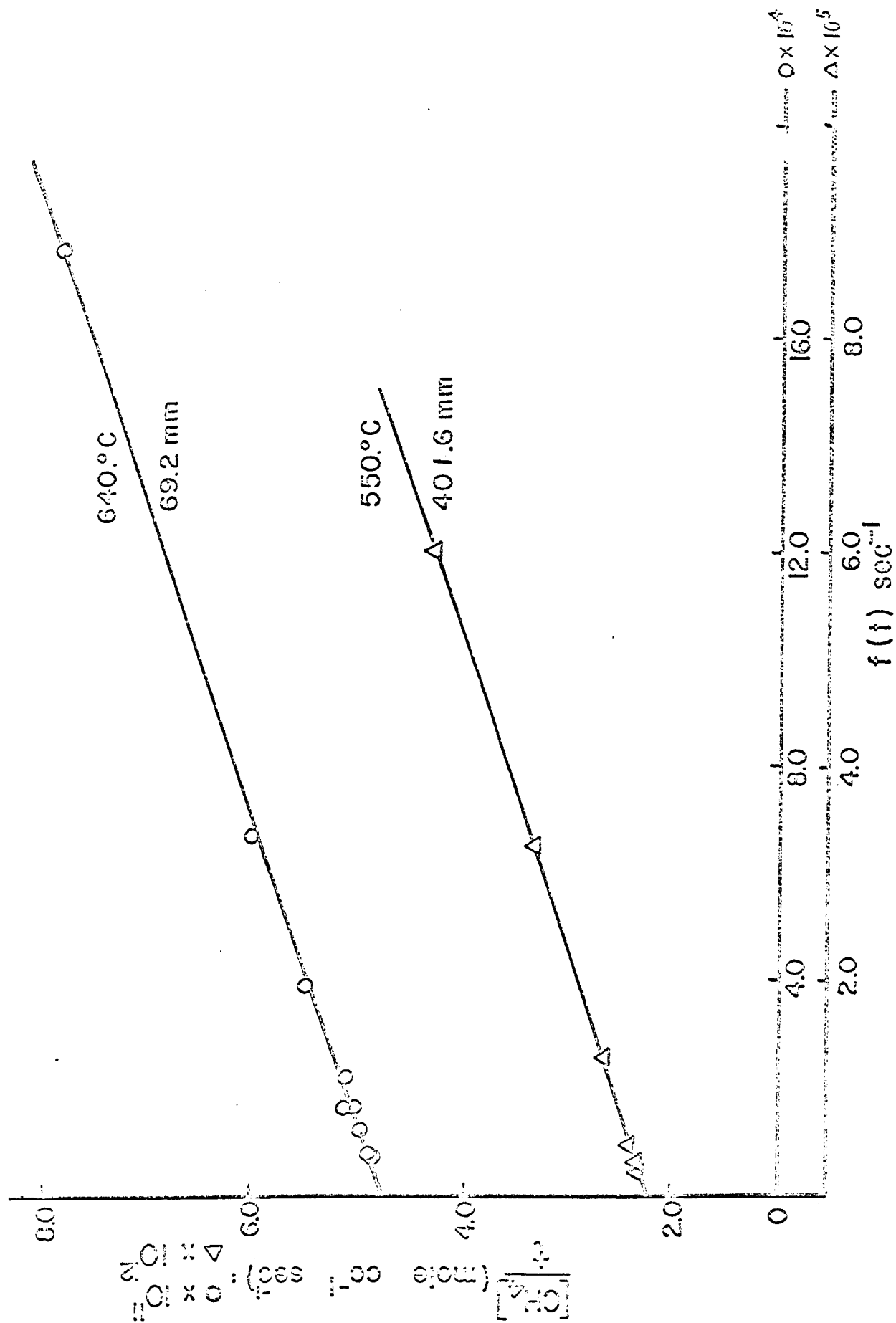
When t is small, $f(t)$ reduces to

$$f(t) = \frac{b^3 t^2}{3}. \quad [84]$$

Inserting equation [84] in equation [82a] gives

Figure 26.

Typical R_{CH_4} vs. $f(t)$ plots.



$$\frac{[\text{CH}_4]}{t} = c + \frac{a^2 d}{3} t^2. \quad [55]$$

Figure 27 shows the plots of both $[\text{CH}_4]/t$ vs. t^2 and $[\text{CH}_4]/t$ vs. t . Since most runs in the temperature range 550-620°C were limited to low conversions, the initial rates of methane production were extrapolated from the plots of R_{CH_4} vs. t^2 . The initial rates obtained from the three different methods agree excellently, whereas the values of d are only consistent within ~10%. The values of d obtained from equation [52a] may be subject to larger errors because of the accumulated errors involved in the factor a^2/b^3 .

Using values of d obtained from plots of R_{CH_4} vs. $[\text{C}_2\text{H}_6]^2$, at any instant of reaction can be calculated from equation [51]; the calculated curves are compared with the experimental points in Figure 28.

According to Quinn's mechanism, d is defined by

$$d = k_{12} K_9 K_{10} K_{11} [\text{C}_2\text{H}_6].$$

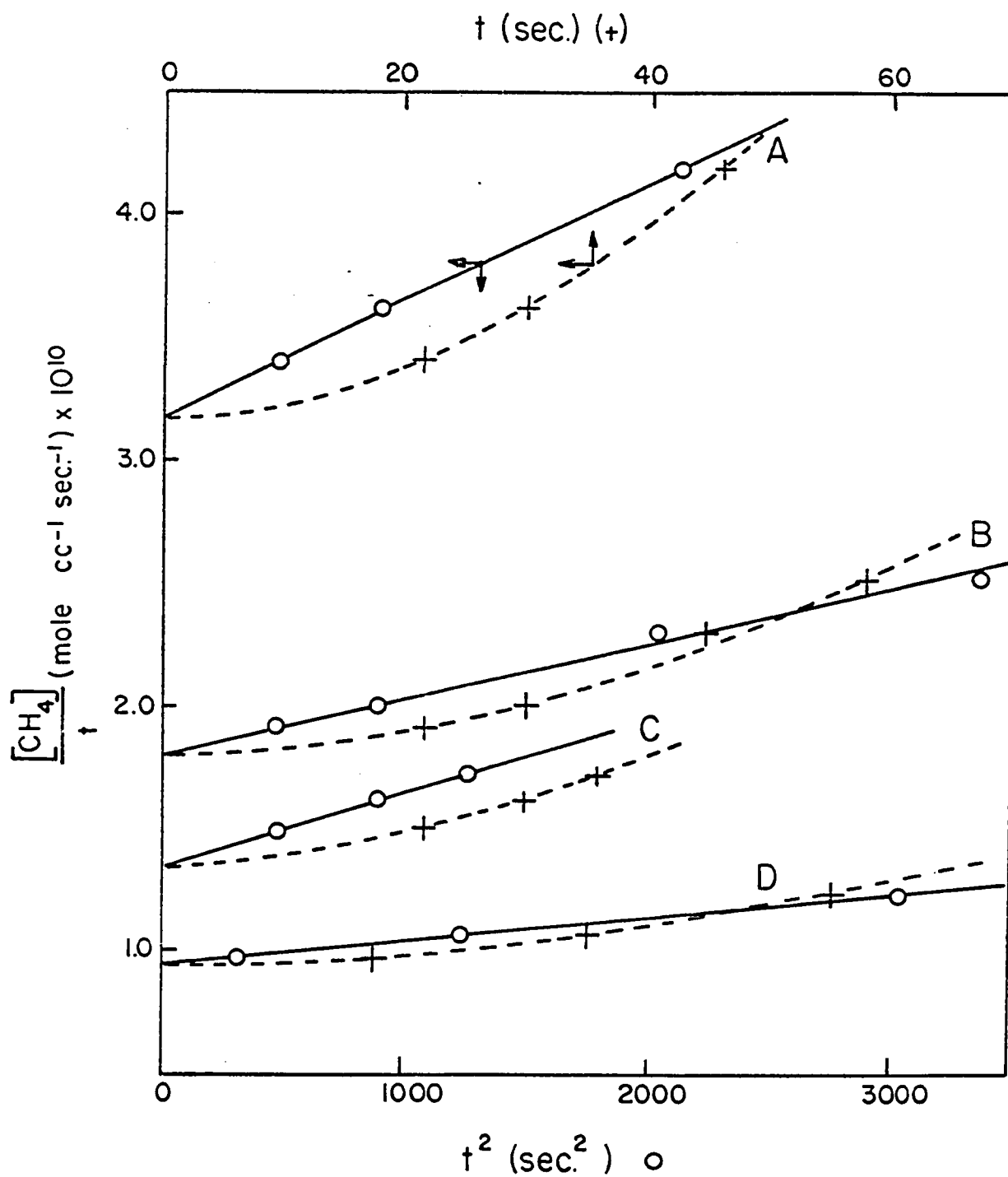
or

$$d = k_{12} K_9 K_{10} K_{11} \left(\frac{k_1}{k_5} \right)^{1/2} [\text{C}_2\text{H}_6]^{1/2}. \quad [56]$$

A double logarithmic plot of d against initial ethane concentration is shown in Figure 29, in which Quinn's results are also plotted for comparison. At high pressures, the order is fairly close to 1/2 as predicted by equation [56]; at low pressures, however, it decreases from 1/2 to a negative value with decreasing pressure. Quinn's results also show a similar tendency. This phenomenon probably indicates that the second process may occur concurrently at low pressures. Thus combining equations [70] and [71], the rate of methane production

Figure 27.

Typical R_{CH_4} vs. t^2 and R_{CH_4} vs. t plots.

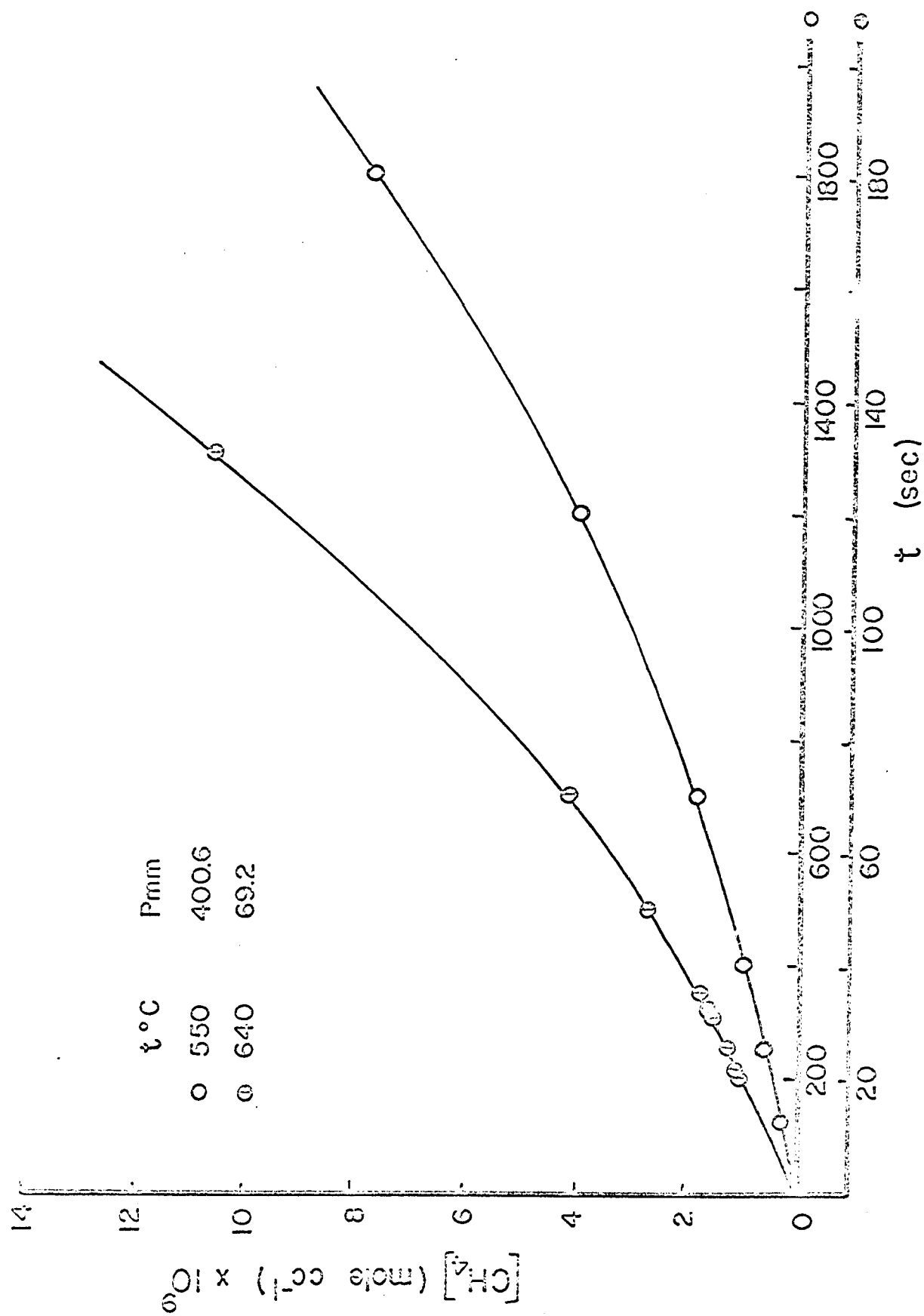


	t °C	P mm Hg
A	660.0	145.2
B	660.0	91.1
C	620.3	448.3
D	640.0	123.3

Figure 28.

Comparison of the calculated yield-time curves
with experimental results for methane production.

Solid curves calculated from equation (31) .



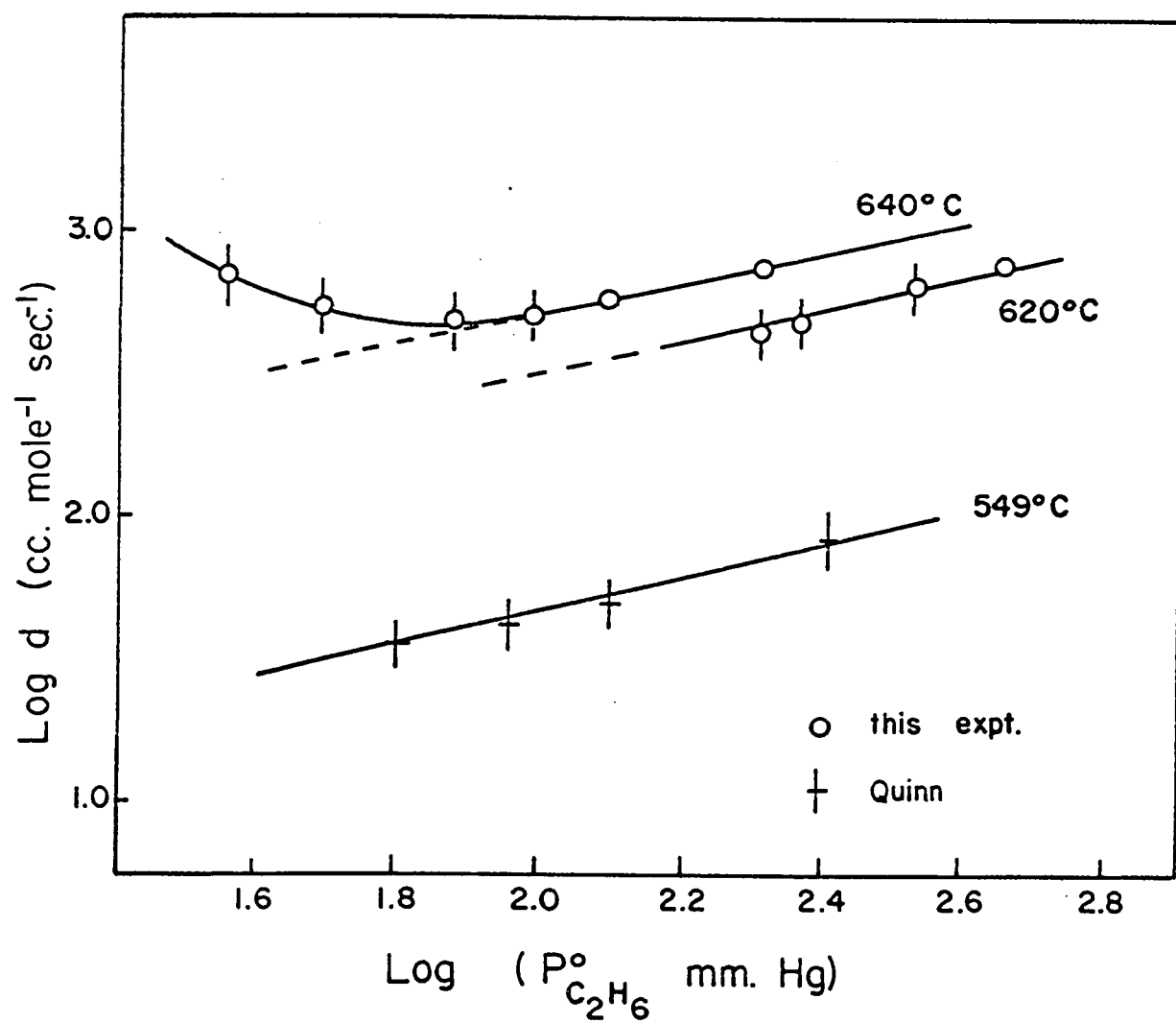


Figure 29.

Double-logarithmic plots of d vs. $P^{\circ}_{C_2H_6}$.

in this intermediate region becomes

$$R_{CH_4} = c + d' \overline{[C_2H_4]} + d \overline{[C_2H_4]}^2 \quad [87]$$

Hence, in the plot of R_{CH_4} vs. $\overline{[C_2H_4]}^2$,

$$\text{slope} = d + d' \frac{\overline{[C_2H_4]}}{\overline{[C_2H_4]}^2} \quad [88]$$

Equation [88] explains why the apparent value of d increased with decreasing pressure.

Using the values of d at high pressures, at 640 and 620°C, the temperature coefficient of the quantity

$$k_{12} K_9 K_{10} K_{11} \left(\frac{k_1}{k_5} \right)^{1/2} = d/[C_2H_6]^{1/2} \quad [89]$$

can be calculated from the Arrhenius equation:

$$\log \left(\frac{d}{[C_2H_6]^{1/2}} \right)_1 - \log \left(\frac{d}{[C_2H_6]^{1/2}} \right)_2 = - \frac{E_d}{4.58} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad [90]$$

Inserting the values:

$$\left(\frac{d}{[C_2H_6]^{1/2}} \right)_{640^\circ C} = 3.9 \times 10^5 \text{ (cc mole}^{-1}\text{)}^{3/2} \text{ sec}^{-1}$$

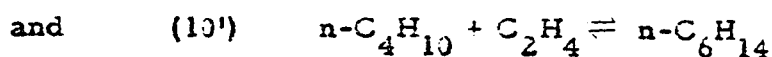
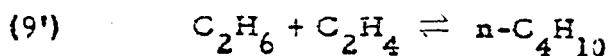
and

$$\left(\frac{d}{[C_2H_6]^{1/2}} \right)_{620^\circ C} = 2.8 \times 10^5 \text{ (cc mole}^{-1}\text{)}^{3/2} \text{ sec}^{-1}$$

in equation [90] gives

$$E_d = 27 \text{ kcal mole}^{-1}.$$

If the heats of reaction for reactions (9) and (10) are taken, respectively, to be the same as those of the reactions



$$\text{then } \Delta H_9^{\circ} = \Delta H_{10}^{\circ} = -22 \text{ kcal mole}^{-1}.$$

Assuming $K_{11} = 1$, $\Delta H_{11}^{\circ} = 0$ and $E_5 = 0$, we have

$$E_d = 27 = E_{12} + 2\Delta H_9^{\circ} + \frac{1}{2} E_1$$

$$= E_{12} - 2 \times 22 + \frac{1}{2} \times 86.0$$

$$\therefore E_{12} = 26 \text{ kcal mole}^{-1}.$$

Substituting the values of E_{12} , ΔH_9° , ΔH_{10}° , and the values (at 640°C)

$$\Delta S_9^{\circ} = \Delta S_9^{\circ} = -10.0, \quad \Delta S_{10}^{\circ} = \Delta S_{10}^{\circ} = -10.6 \text{ gibbs mole}^{-1} \text{ (standard state:}$$

1 mole cc^{-1}), $k_1 = 2.30 \times 10^{-5} \text{ sec}^{-1}$ and $k_5 = 2.30 \times 10^{13} \text{ cc mole}^{-1} \text{ sec}^{-1}$, in equation [89], the frequency factor for reaction (12) is found

to be

$$A_{12} = 3.2 \times 10^{13} \text{ sec}^{-1}.$$

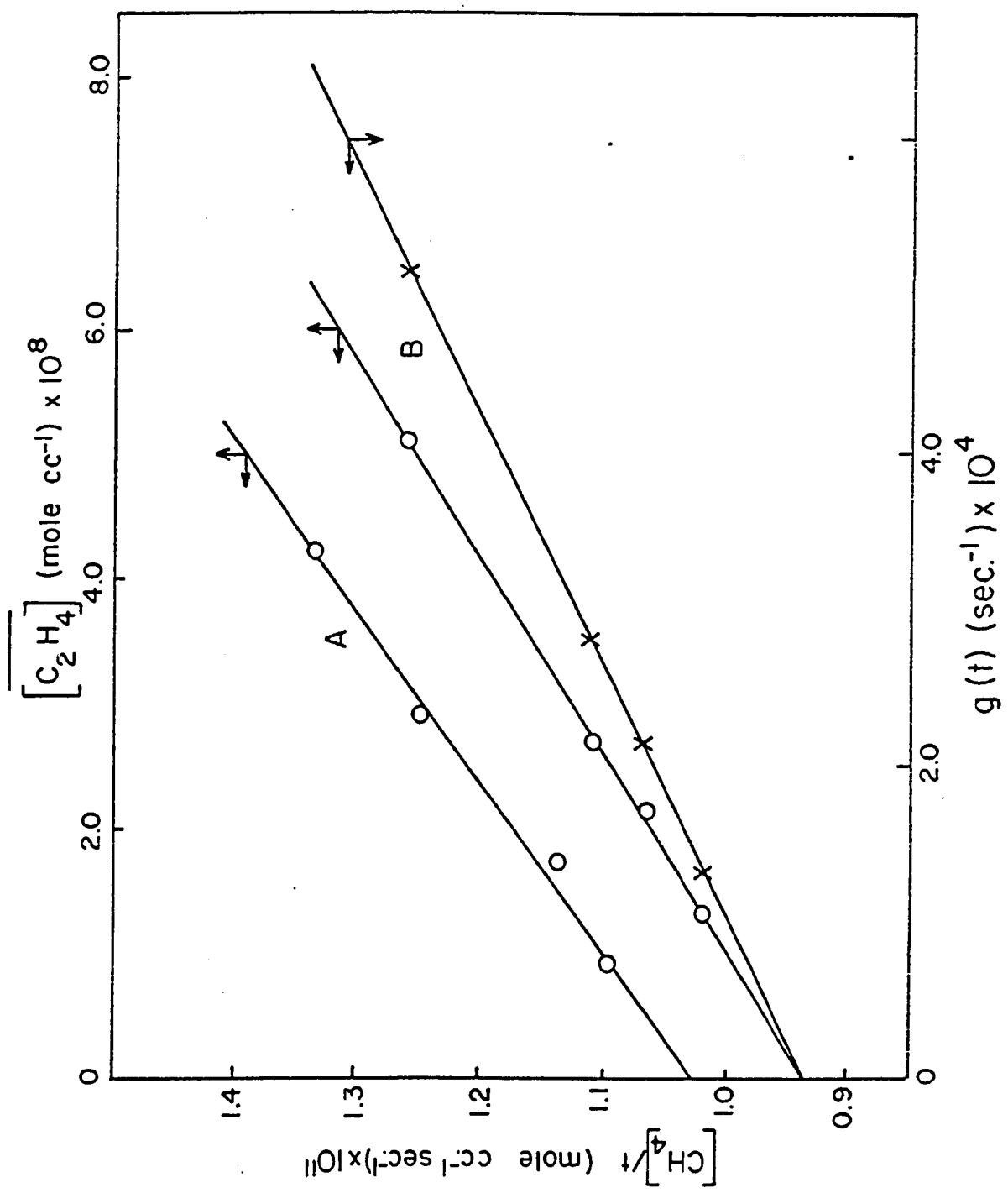
At high temperatures and low pressures, the rate of methane production is linear with $[C_2H_4]$ as shown in Figure 30.

This implies that

Figure 30.

Typical R_{CH_4} vs. $\overline{[C_2H_4]}$ and R_{CH_4} vs. $g(t)$ plots

A. 660°C , 10.7 mm; B. 640°C , 20.7 mm.



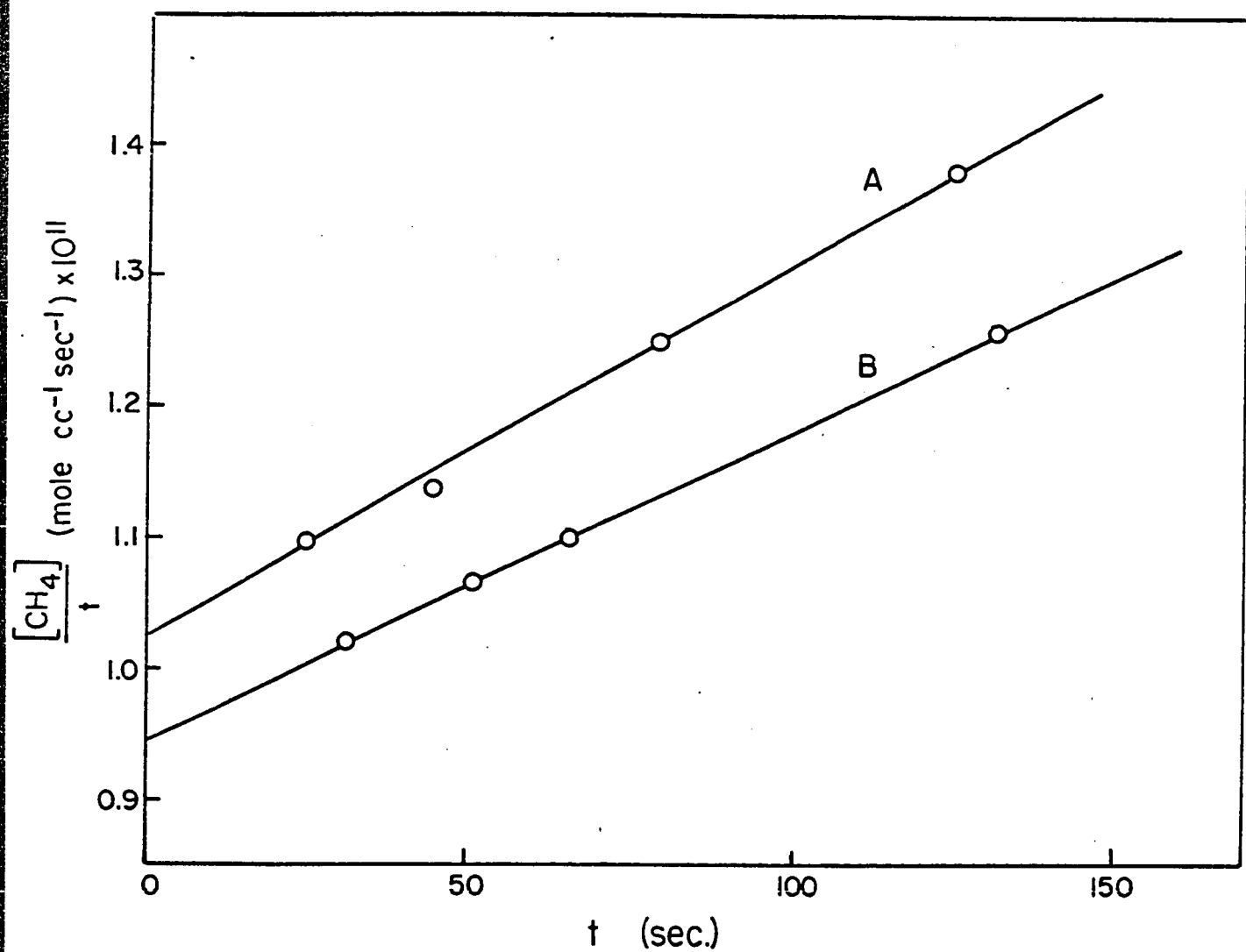


Figure 31.

Plots of R_{CH_4} vs. t at low pressures.

A, 660°C, 10.7 mm; B, 640°C, 20.7 mm

$$\frac{d[\text{CH}_4]}{dt} = d + d' [\text{C}_2\text{H}_4] . \quad [91]$$

On integration, equation [91] becomes:

$$\frac{[\text{CH}_4]}{t} = c + d' \frac{1}{t} \int_0^t [\text{C}_2\text{H}_4] dt \quad [92]$$

$$= c + d' \overline{[\text{C}_2\text{H}_4]} . \quad [92a]$$

The values of $\overline{[\text{C}_2\text{H}_4]}$ used in Figure 30 were obtained by graphical integration of the instantaneous $[\text{H}_2]$ with a planimeter. Using equation [62], one obtains the integrated rate:

$$\frac{[\text{CH}_4]}{t} = c + \frac{ad'}{b^2} \frac{1}{t} (bt + e^{-bt} - 1) \quad [93]$$

$$= c + \frac{ad'}{b^2} g(t) , \quad [93a]$$

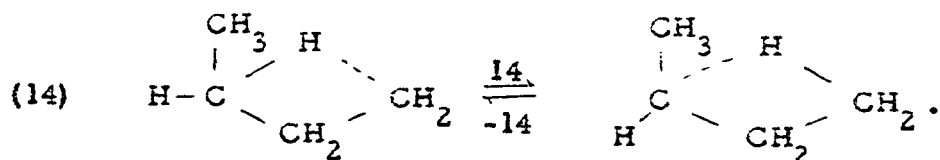
where $g(t) = \frac{1}{t} (bt + e^{-bt} - 1) . \quad [94]$

A typical plot of R_{CH_4} vs. $g(t)$ is also shown in Figure 30. Both methods gave exactly the same value of c . When the reaction time is short, equation [93] reduces to:

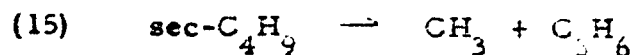
$$\frac{[\text{CH}_4]}{t} = c + \frac{ad'}{2} t . \quad [95]$$

Plots of R_{CH_4} vs. t are shown in Figure 31. Values of d' obtained from the three different methods are in good agreement.

The meaning of d' is worth some speculation. Previous results at high pressures seem consistent with the fact that the isomerization of $n\text{-C}_4\text{H}_9$ to $\text{sec-C}_4\text{H}_9$ might be rather slow compared with the addition of $n\text{-C}_4\text{H}_9$ to ethylene. However, as the pressure is lowered, isomerization will become faster relative to addition. The isomerization may proceed as



The heat of reaction (14) is probably about $-2 \text{ kcal mole}^{-1}$, the difference between secondary and primary C-H bond energies. Because of the high activation energy for isomerization (61), $\text{sec-C}_4\text{H}_9$ may decompose into CH_3 and C_3H_6 ,



E_{15} is about $23 \text{ kcal mole}^{-1}$ (58).

Steady-state treatment of reactions (1)-(5), (9), (14) and (15), leads to

$$\frac{d[\text{CH}_4]}{dt} = 2k_1[\text{C}_2\text{H}_6] + k_{14}K_9[\text{C}_2\text{H}_5][\text{C}_2\text{H}_4]. \quad [96]$$

if it is assumed that

$$k_{15} \gg k_{-14} \quad \text{and} \quad k_{14} \ll k_{-9}$$

Comparing equation [91] with [96] gives

$$c = 2k_1[\text{C}_2\text{H}_6]$$

and

$$d' = k_{14}K_9[\text{C}_2\text{H}_5]. \quad [97]$$

Inserting the steady-state concentration of C_2H_5 radicals,

$$d' = k_{14} K_9 \left(\frac{k_1}{k_5} \right)^{1/2} [C_2H_6]^{1/2} \quad [98]$$

The present results are not sufficient to verify this relationship. The temperature coefficient of the quantity

$$\frac{d'}{\left(\frac{k_1}{k_5} \right)^{1/2} [C_2H_6]^{1/2}} = k_{14} K_9 \quad [99]$$

may, however, be estimated from the two available points. Using $k_5 = 2.3 \times 10^{13} \text{ cc mole}^{-1} \text{ sec}^{-1}$ and the data listed below,

$t^\circ C$	P mm Hg	$d'(\text{sec}^{-1})$	$k_1(\text{sec}^{-1})$	$d' \left(\frac{k_1}{k_5} \right)^{1/2} [C_2H_6]^{1/2}$
640	20.7	5.51×10^{-5}	1.30×10^{-5}	1.21×10^8
660	10.6	7.20×10^{-5}	2.77×10^{-5}	1.50×10^8

we have for the temperature coefficient of the quantity $d' \left(\frac{k_1}{k_5} \right)^{1/2} [C_2H_6]^{1/2}$,

$$E_{d'} = E_{14} + \Delta H_9^0 = 19 \text{ kcal mole}^{-1}.$$

If again, the equilibrium constant for reaction (9) is assumed to be the same as that of reaction (9'), then

$$\Delta H_9^0 = -22 \text{ kcal mole}^{-1},$$

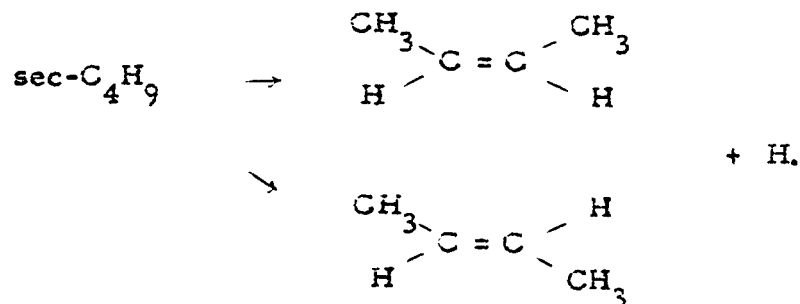
$$\therefore E_{14} = 19 + 22 = 41 \text{ kcal mole}^{-1},$$

which is the activation energy for the isomerization of $n-C_4H_9$ to $sec-C_4H_9$. Inserting the values of E_{14} , ΔH_9^0 and ΔS_9^0 at $640^\circ C$ in

equation [99], we obtain

$$A_{14} = 5.2 \times 10^{14} \text{ sec}^{-1}.$$

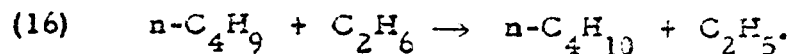
The existence of $\text{sec-C}_4\text{H}_9$ radicals in the system also explains the appearance of small amounts of cis- and trans-butene-2 at high conversions; they might be produced from a C-H split:



III. Secondary reactions involving butane:

Typical rate-time plots of butane production are shown in Figure 32. Apparently, the modes of butane production are more complicated than those of hydrogen and methane formation. At low temperatures, the rates of butane production increased rapidly at high pressures, whereas at temperatures higher than 600°C , the rates decreased as the reactions proceeded.

Since the introduction of ethylene at 570°C enhanced linearly the rate of butane production (Figure 20), the increase in $R_{\text{C}_4\text{H}_{10}}$ should probably be ascribed to the increase in the concentration of $\text{n-C}_4\text{H}_9$ radicals. A $\text{n-C}_4\text{H}_9$ radical may abstract a hydrogen atom from ethane to form butane:



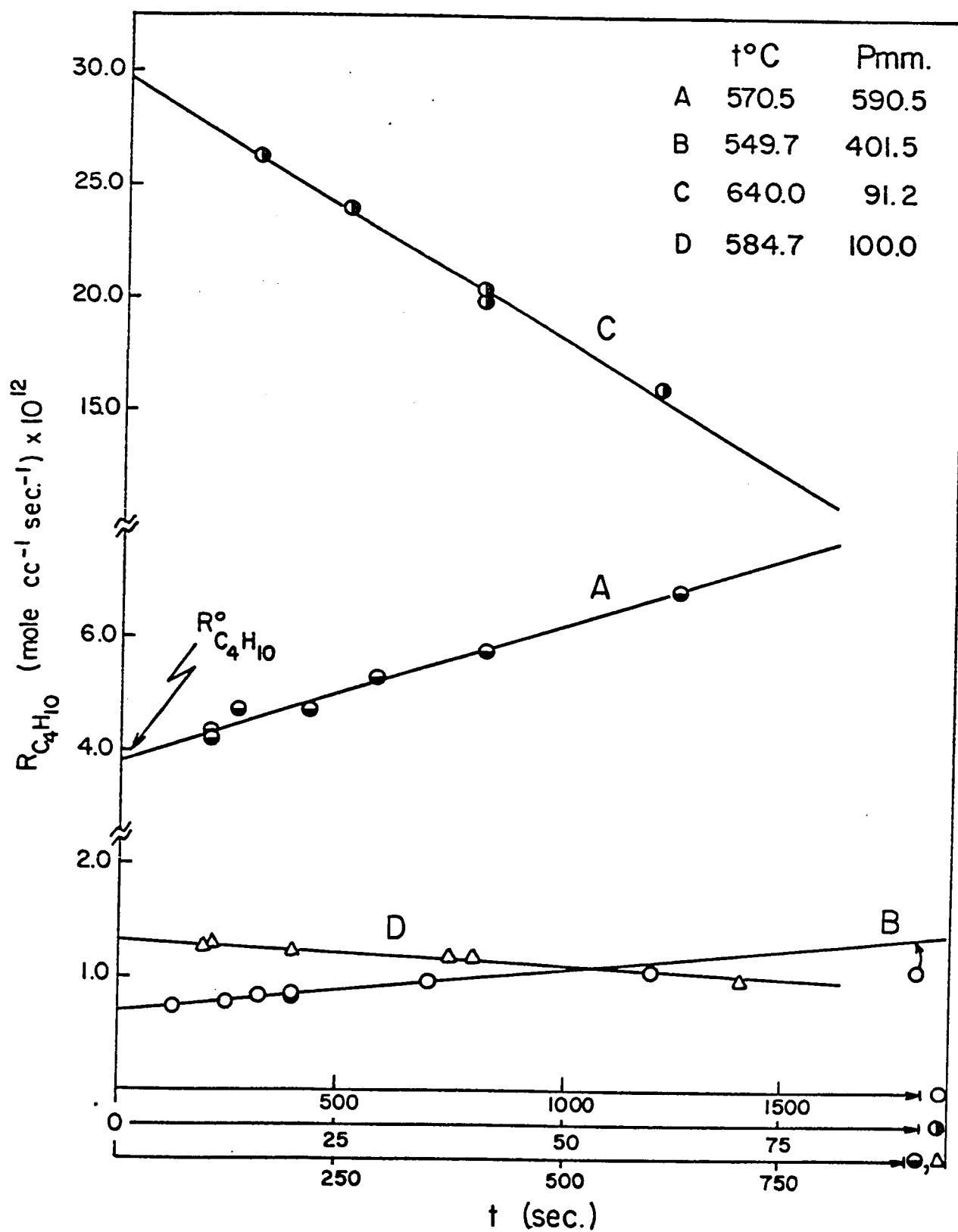
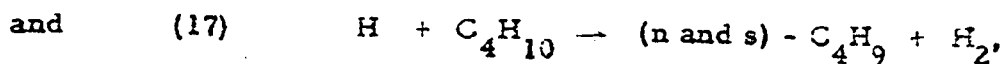


Figure 32.

Typical $R_{C_4H_{10}}$ vs. t plots.

The decrease in the rate of butane production was likely due to the attack by ethyl radicals or hydrogen atoms via the reactions;



or to the unimolecular decomposition of butane,



Including all these possible reactions, the rate of butane production becomes:

$$\begin{aligned} \frac{d[\text{C}_4\text{H}_{10}]}{dt} = & k_{5a}[\text{C}_2\text{H}_5]^2 + k_{16}[\text{n-C}_4\text{H}_9][\text{C}_2\text{H}_6] - (k_{-16}[\text{C}_2\text{H}_5] \\ & + k_{17}[\text{H}] + k_{-5})[\text{C}_4\text{H}_{10}]. \end{aligned} \quad [100]$$

For simplicity, let

$$k_{5a}[\text{C}_2\text{H}_5]^2 = R_{\text{C}_4\text{H}_{10}}^0 = g \quad [101]$$

$$\begin{aligned} k_{16}[\text{n-C}_4\text{H}_9] &= k_{16} K_9[\text{C}_2\text{H}_5][\text{C}_2\text{H}_4] \\ &= h[\text{C}_2\text{H}_4] \\ &= h \frac{a}{b} (1 - e^{-bt}) \end{aligned} \quad [102]$$

and $k_{-16}[\text{C}_2\text{H}_5] + k_{17}[\text{H}] + k_{-5a} = j. \quad [103]$

Inserting equations [101], [102] and [103] in the differential equation [100] produces

$$\frac{d[\text{C}_4\text{H}_{10}]}{dt} = g + h \frac{a}{b} (1 - e^{-bt}) - j[\text{C}_4\text{H}_{10}]. \quad [104]$$

After integration, we have

$$[C_4H_{10}] = \frac{gb + ha}{bj} (1 - e^{-jt}) + \frac{ha}{b(b-j)} (e^{-bt} - e^{-jt}). \quad [105]$$

When reaction time is short or $bt \ll 1$, $jt \ll 1$; equation [105] reduces to

$$[C_4H_{10}] = gt + \frac{ha - gj}{2} t^2 \quad [106]$$

$$\text{or} \quad \frac{[C_4H_{10}]}{t} = R_{C_4H_{10}} = g + \frac{ha - gj}{2} t \quad [107]$$

$$= g + st, \quad [107a]$$

$$\text{where} \quad s = \frac{ha - gj}{2} \quad [108]$$

When $s > 0$ or $ha > gj$, the rate of butane production increases linearly with time, whereas if $s < 0$ or $ha < gj$, the rate decreases linearly as reaction progresses. Thus equation [107] is able to explain all the cases presented in Figure 32.

At 640°C , the rates of butane production at all pressures studied decreased sharply and linearly with time. The results are given in Figure 33. Interestingly, the slope, s , of the straight line at each pressure divided by the corresponding intercept, g , obtained from the least squares method, gives fairly constant values, given in Table 8.

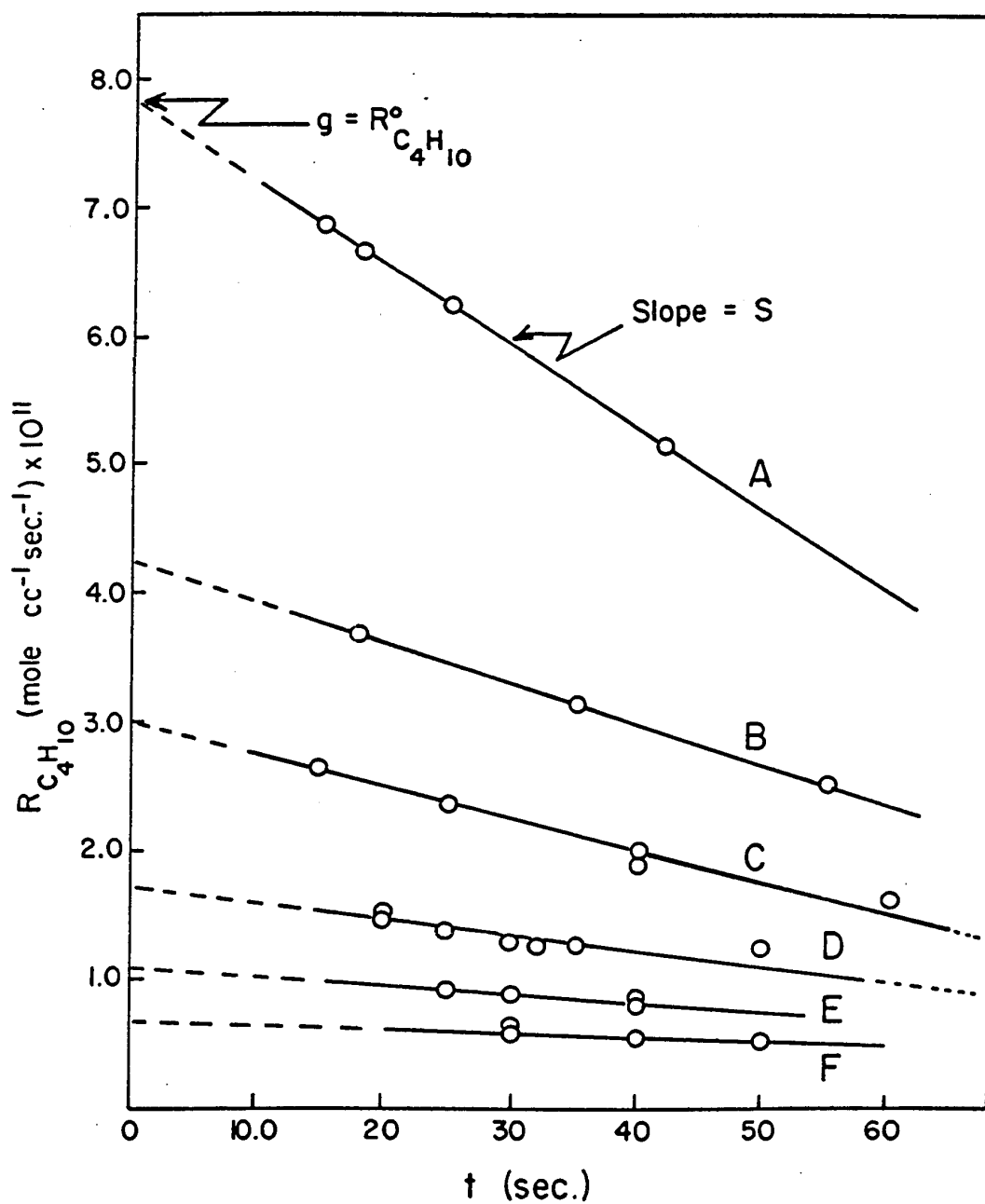


Figure 33.

$R_{C_4H_{10}}$ vs. t plots at $640^{\circ}C$.

A. 204.6 mm; B. 123.3 mm; C. 91.2 mm; D. 69.2 mm;
E. 48.6 mm and F. 36.2 mm.

Table 8

2s/g at 640° C

P mm Hg	2s/g x 10 ² sec ⁻¹
204.6	1.61 ± 0.06
123.8	1.44 ± 0.04
91.2	1.55 ± 0.09
69.2	1.60 ± 0.10
48.6	1.53 ± 0.05
36.2	1.43 ± 0.10
average	1.53 ± 0.10

According to equation [108] and the definitions of h, a, g and j, we have

$$\begin{aligned} \frac{2s}{g} &= \frac{ha - gj}{g} \\ &= \frac{k_3 k_{16}}{k_{5a}} K_9 [C_2H_6] - (k_{-16} [C_2H_5] + k_{17} [H] + k_{-5a}) \end{aligned} \quad [109]$$

In this equation, all terms except k_{-5a} are functions of pressure. In order to explain the fact that at 640° C, the rate of butane production decreased linearly with time for all pressures, and that 2s/g was constant within experimental error over the range of pressure studied, we might conclude that at this temperature

$$gj \gg ha$$

and

$$j = k_{-5a}.$$

According to this conclusion, $2s/g = j = k_{-5a} = (1.53 \pm 0.10) \times 10^{-2} \text{ sec}^{-1}$ is the rate constant of the unimolecular decomposition of butane at 640°C , which agrees reasonably with the values, 0.7×10^{-2} and 3.1×10^{-2} , calculated from $k_{-5a} = 1.0 \times 10^{17} e^{-80,000/RT}$ (62) and $3.77 \times 10^{18} e^{-86,300/RT} \text{ sec}^{-1}$ (24), respectively. Combining $k_{-5a} = (1.53 \pm 0.10) \times 10^{-2} \text{ sec}^{-1}$ at 640°C with $E_{-5a} = 80.0 \text{ kcal mole}^{-1}$, we have

$$k_{-5a} = (2.2 \pm 0.1) \times 10^{17} e^{-80,000/RT} \text{ sec}^{-1} \quad [110]$$

Assuming $k_3 = k'_3 [\text{C}_2\text{H}_6]^{1/2}$, where k'_3 is assumed to be constant for a first approximation, equation [109] reduces to

$$\frac{2s}{g} = \frac{k'_3 k_{16} K_9}{k_{5a}} [\text{C}_2\text{H}_6]^{3/2} - (k_{-16} [\text{C}_2\text{H}_5] + k_{17} [\text{H}] + k_{-5a}) \quad [111]$$

This equation predicts a linear relationship between $2s/g$ and $[\text{C}_2\text{H}_6]^{3/2}$, if $k_{-16} [\text{C}_2\text{H}_5] + k_{17} [\text{H}] \ll k_{-5a}$. Results at 570°C are shown in Figure 34, where the intercept $j = 3.8 \times 10^{-4} \text{ sec}^{-1}$, matches closely the rate constant

$$k_{-5a} = 3.9 \times 10^{-4} \text{ sec}^{-1}$$

calculated from equation [110] at 570°C . Evidently, this indicates that $k_{-5a} \gg k_{16} [\text{C}_2\text{H}_5] + k_{17} [\text{H}]$ even at temperature as low as 570°C . Thus we conclude that the decrease in the rate of butane production over the range of temperature and pressure studied is probably due to the unimolecular decomposition of butane.

The relation between the rate of butane production at low temperatures and high pressures, and the average ethylene

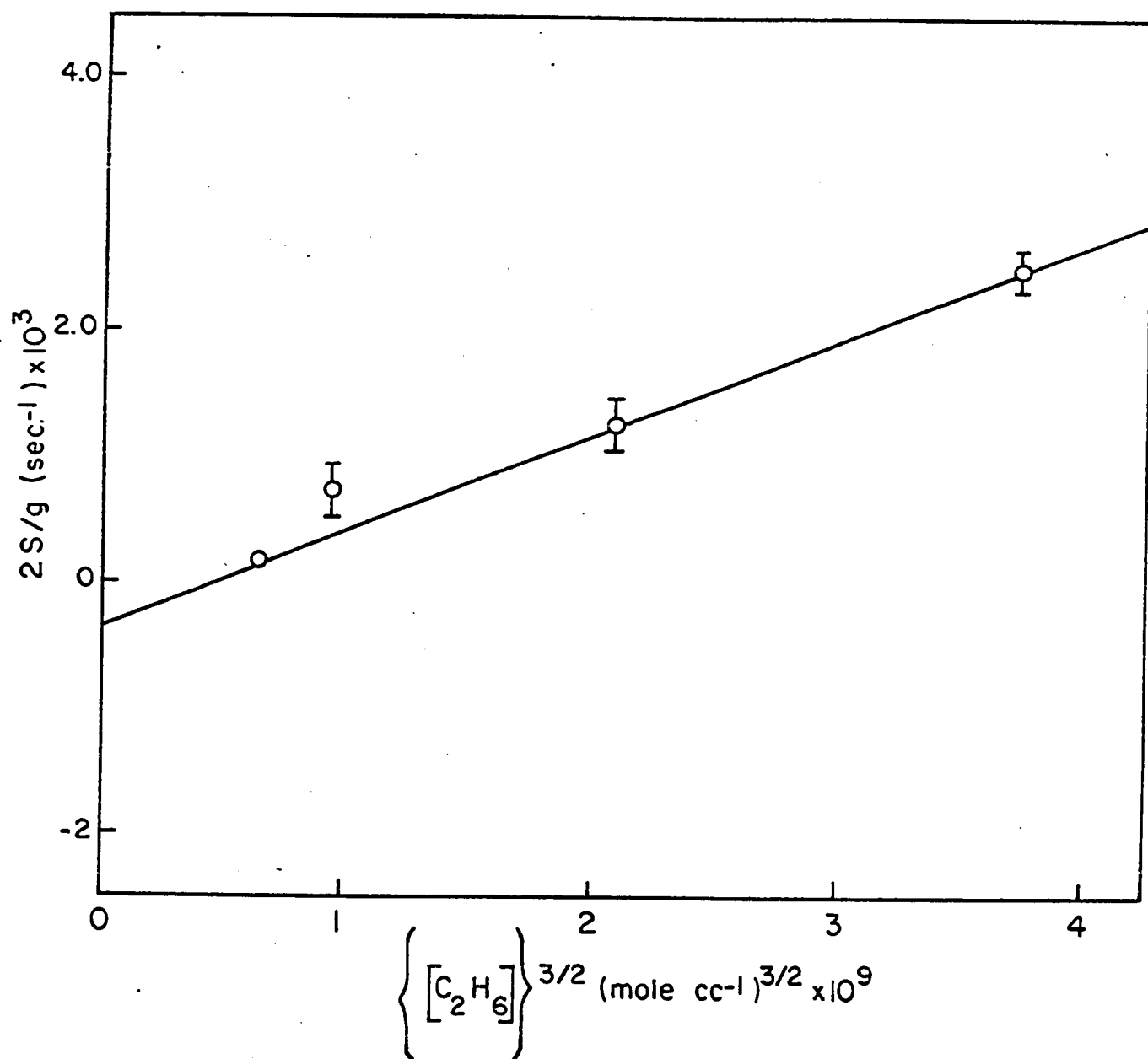


Figure 34.

$2s/g$ vs. $[C_2H_6]^{3/2}$ plot at $570^\circ C$.

concentration, $[C_2H_4]$, can be deduced directly from equation [105]; at low temperatures, when $jt = k_{-5a} t \ll 1$, equation [105] reduces to

$$\begin{aligned} \frac{[C_4H_{10}]}{t} &= g + \frac{hb}{b-j} \cdot \frac{1}{b} \left(a - \frac{[H_2]}{t} \right) \\ &= g + \frac{hb}{b-j} [C_2H_4] \end{aligned} \quad [112]$$

$$= g + h [C_2H_4], \text{ if } b \gg j. \quad [112a]$$

Plots of $R_{C_4H_{10}}$ vs. $[C_2H_4]$ are shown in Figure 35, on which the results given in Figure 20 are plotted again for comparison.

The values of h , which is the quantity related to the abstraction of hydrogen atoms from ethane by $n-C_4H_9$ radicals, can be evaluated from the slope, s , of the plot of $R_{C_4H_{10}}$ vs. t , or directly from the slope of the plot of $R_{C_4H_{10}}$ vs. $[C_2H_4]$. The first method gave slightly higher values than the latter, as one might expect, since equation [112a] is derived by assuming that butane decomposition is negligible. Using the first method,

$$s = \frac{ha - gj}{2}$$

we have $h = (2s + gj)/a. \quad [113]$

By definition,

$$\begin{aligned} h &= k_{16} K_9 [C_2H_5] [C_2H_6] \\ &= k_{16} K_9 \frac{R_{C_4H_{10}}^{1/2}}{k_{5a}^{1/2}} [C_2H_6] \\ &= k_{16} K_9 \left(\frac{g}{k_{5a}} \right)^{1/2} [C_2H_6] \end{aligned}$$

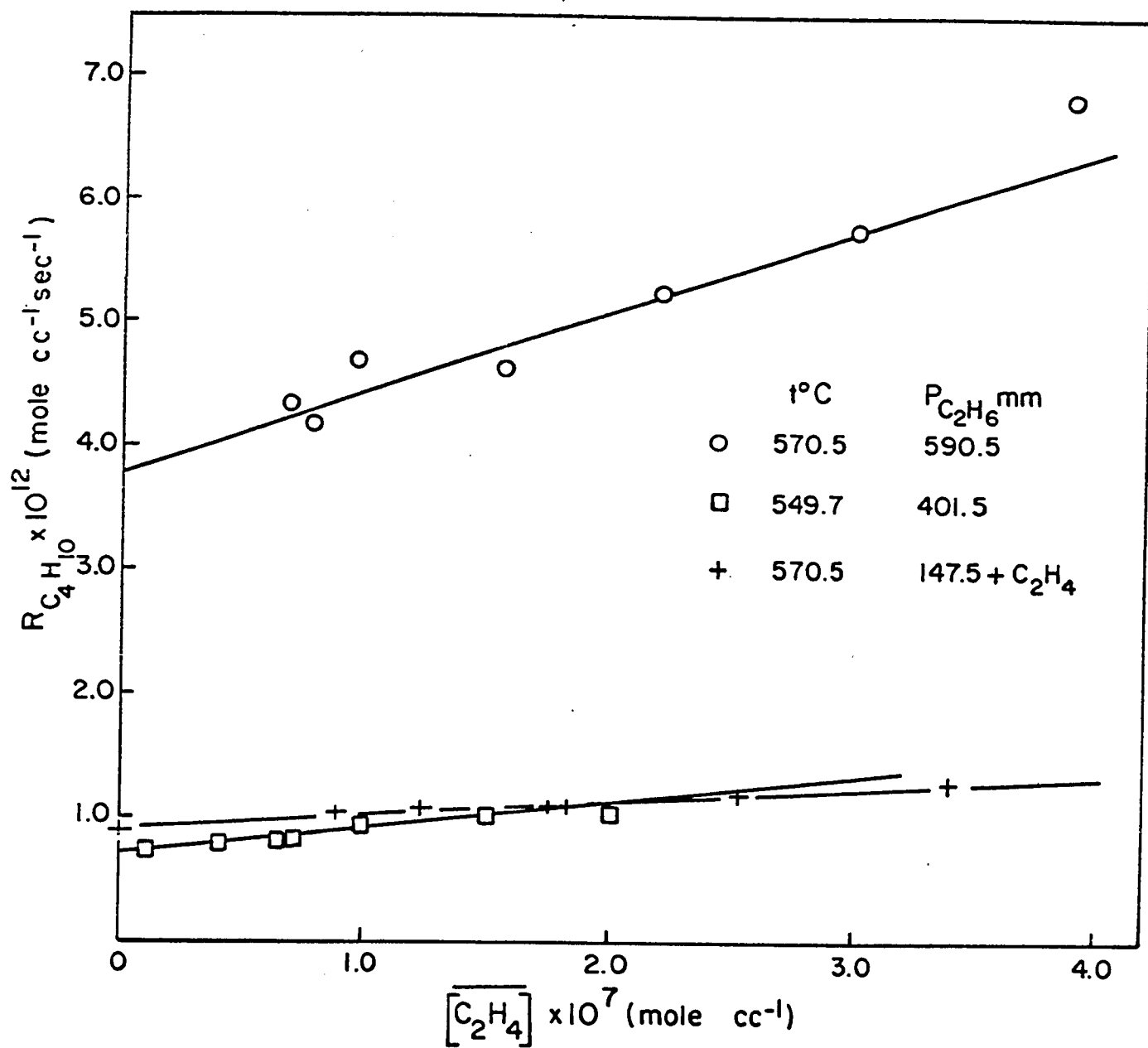


Figure 35.

$R_{\text{C}_4\text{H}_{10}}$ vs. $[\text{C}_2\text{H}_4]$ plots at low temperatures.

$$\frac{h}{g^{1/2} [C_2H_6]} = \frac{k_{16} K_9}{k_{5a}^{1/2}} \quad [114]$$

Combination of equation [113] and [114] produces

$$\frac{k_{16} K_9}{k_{5a}^{1/2}} = \frac{2s + gj}{a g^{1/2} [C_2H_6]} \quad [115]$$

Therefore, from the intercept, g , and the slope, s , of a plot of $R_{C_4H_{10}}$ vs. t , and the initial rate of hydrogen production, a , one can estimate the rate constant of reaction (16). Table 9 shows the values of $K_9 k_{16} / k_{5a}^{1/2}$ obtained from the available data at three temperatures. The values of g , s and a were all determined by least squares. The Arrhenius plot of the quantity $k_{16} K_9 / k_{5a}^{1/2}$ leads to an activation energy of

Table 9

$K_9 k_{16} / k_{5a}^{1/2}$ at low temperatures				
$t^\circ C$	P mm Hg	$g(\text{mole cc}^{-1} \text{sec}^{-1})$	$s(\text{mole cc}^{-1} \text{sec}^{-1})$	$K_9 k_{16} / k_{5a}^{1/2} \times 10^{-5}$ (cc mole ⁻¹) ^{3/2} sec ^{-1/2}
549.7	401.5	7.02×10^{-13}	3.49×10^{-16}	3.7 ± 0.3
570.5	590.5	3.70×10^{-12}	4.98×10^{-15}	3.6 ± 0.1
	400.0	2.61×10^{-12}	1.50×10^{-15}	3.4 ± 0.7
584.7	100.0	1.32×10^{-12}	-3.34×10^{-16}	3.1 ± 0.8

about $-7 \pm 4 \text{ kcal mole}^{-1}$. Assuming $E_{5a} = 0$ and $\Delta H_9^0 = \Delta H_9^{0'} = -22 \text{ kcal mole}^{-1}$, we have

$$E_{16} = -(7 \pm 4) + 22 = 15 \pm 4 \text{ kcal mole}^{-1},$$

which agrees with the calculated value, $15.2 \text{ kcal mole}^{-1}$ (59). The frequency factor of reaction (16) can be estimated by

$$A_{16} = \frac{k_{5a}^{1/2}}{K_9} \frac{2s + gj}{ag^{1/2} [C_2H_6]} e^{E_{16}/RT} \quad [116]$$

according to equation [115]. At 550°C ,

$$\frac{2s + gj}{ag^{1/2} [C_2H_6]} = \frac{K_9 k_{16}}{k_{5a}^{1/2}} = 3.7 \times 10^5 (\text{cc mole}^{-1})^{3/2} \text{ sec}^{-1/2}$$

and from Table 9, $K_9 = e^{-10.4} e^{22,000/RT} \text{ cc mole}^{-1}$ (standard state: 1 mole/cc), $E_{16} = 15.2 \text{ kcal mole}^{-1}$ and $k_{5a} = 2.0 \times 10^{13} \text{ cc mole}^{-1} \text{ sec}^{-1}$; inserting these values in equation [116] gives

$$A_{16} = 4.6 \times 10^{11} \text{ cc mole}^{-1} \text{ sec}^{-1},$$

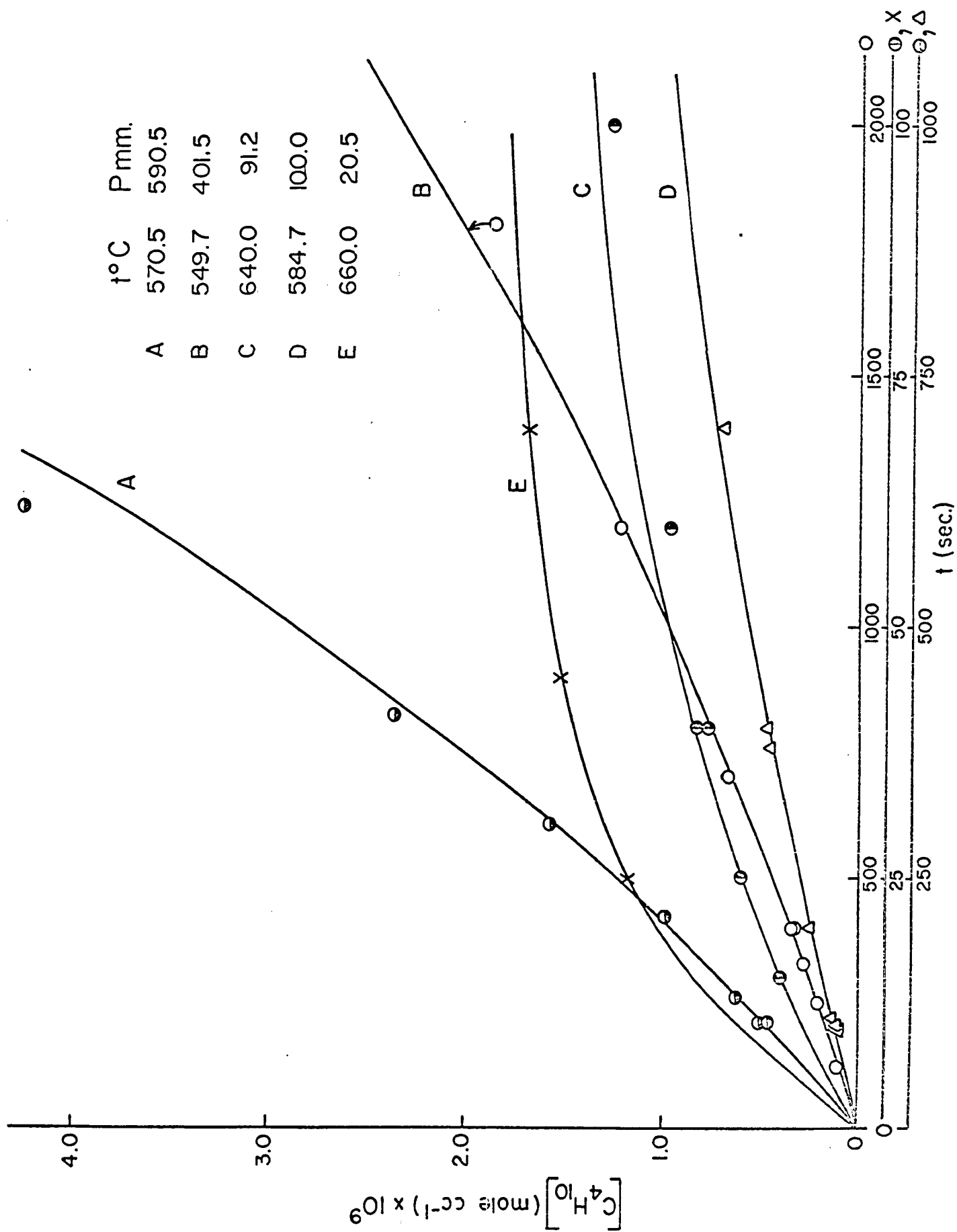
which is to be compared with the values of $A_{-16} = 5.9 \times 10^{11}$ (24) or $7.7 \times 10^{11} \text{ cc mole}^{-1} \text{ sec}^{-1}$ (42).

The production of butane at any instant of reaction can be calculated from the general equation [105]. Using $j = k_{-5a} = 2.2 \times 10^{17} e^{-80,000/RT} \text{ sec}^{-1}$, a and b from hydrogen production, and g , the initial rate of butane production, and h , calculated from equation [113], the yield-time curves for various temperatures and pressures were evaluated and compared with experimental points as shown in Figure 36.

Figure 36.

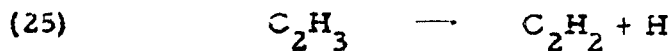
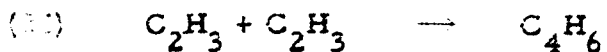
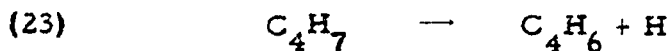
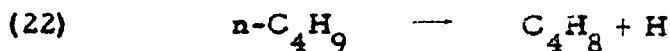
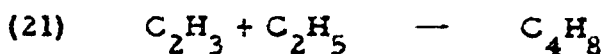
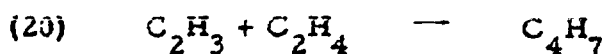
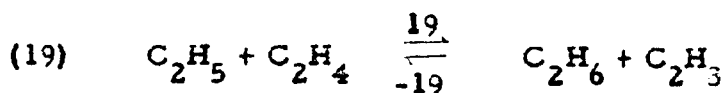
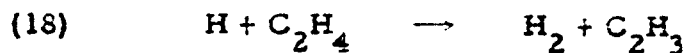
Comparison of the calculated yield-time curves
with experimental results for butane production.

Solid curves calculated from equation (105).



IV. The production of butene-1, butadiene and acetylene:

The addition of ethylene to ethane increased markedly the production of butene-1 and butadiene as shown in Figure 20. In the decomposition of ethane alone, these products appeared only at high conversions, and butene-1 always appeared earlier. At high temperatures, the production of acetylene and butadiene became more important. The results obtained from the experiments of temperatures higher than 640°C are presented in Table 2. Butene-1 disappeared at high conversions at those temperatures. Since these unsaturated products are very reactive at high temperatures, especially in the presence of radicals, their rates of disappearance become appreciable at an early stage of the decomposition. It is therefore difficult to draw definite, quantitative conclusions about their origins, particularly those of butadiene and acetylene. The following mechanism is proposed to account for their formations:



Steady-state treatment of this scheme leads to

$$[C_2H_3] = \frac{(k_{18} [H] + k_{19} [C_2H_5]) [C_2H_4]}{k_{-19} [C_2H_6] + k_{20} [C_2H_4] + k_{21} [C_2H_5] + k_{25}} \quad [117]$$

$$[C_4H_7] = \frac{k_{20}}{k_{23}} [C_2H_3] [C_2H_4] \quad [118]$$

$$\frac{d [C_4H_3]}{dt} = k_{22} [n-C_4H_9] + k_{21} [C_2H_3] [C_2H_5] \quad [119]$$

$$\frac{d [C_4H_6]}{dt} = k_{20} [C_2H_3] [C_2H_4] + k_{24} [C_2H_3]^2 \quad [120]$$

and

$$\frac{d [C_2H_2]}{dt} = k_{25} [C_2H_3] \quad [121]$$

Substituting the steady-state concentrations of $n-C_4H_9$ and C_2H_3 radicals in equation [119], the rate equation for butene-1 formation becomes

$$\frac{d [C_4H_8]}{dt} = k_{22} K_9 [C_2H_5] [C_2H_4] + \frac{k_{21} (k_{18} [H] + k_{19} [C_2H_5]) [C_2H_4]}{k_{-19} [C_2H_6] + k_{20} [C_2H_4] + k_{21} [C_2H_5] + k_{25}} \quad [122]$$

$$= (n + p) [C_2H_4] \quad [122a]$$

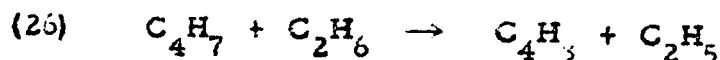
where

$$n = k_{22} K_9 [C_2H_5] \quad [123]$$

and

$$p = \frac{k_{21} (k_{18} [H] + k_{19} [C_2H_5])}{k_{-19} [C_2H_6] + k_{20} [C_2H_4] + k_{21} [C_2H_5] + k_{25}} \quad [124]$$

Equation [122] predicts a linear relationship between $R_{C_4H_5}$ and $[C_2H_4]$, if $n \gg p$ or $k_{20} [C_2H_4]$ is small comparing with other terms in the denominator of p . Typical plots of $R_{C_4H_5}$ vs. $[C_2H_4]$ are shown in Figure 37. A linear relationship holds only at earlier stages of the reaction. The decrease in rate at high conversion might be due either to the decomposition of butene-1 or to the effect of the term $k_{20} [C_2H_4]$ in p , if p is comparable with n . Because of the decrease in $R_{C_4H_5}$ at higher conversions, a possible reaction:



has been omitted from the previous scheme, since this reaction predicts that $R_{C_4H_5}$ must increase rapidly with increasing $[C_2H_4]$. However, the increase in $R_{C_4H_5}$ in experiments with added ethylene as shown in Figure 20 might indicate the occurrence of reaction (26).

The initial slopes of plots of $R_{C_4H_5}$ vs. $[C_2H_4]$ at 550-620°C are given in Table 10. At temperatures higher than 640°C, $R_{C_4H_5}$ decreases rapidly as the reaction proceeds as shown in Figure 14. According to equation [122], the initial slope equals:

$$\begin{aligned} \lim_{[C_2H_4] \rightarrow 0} \frac{R_{C_4H_5}}{[C_2H_4]} &= \left(\frac{R_{C_4H_5}}{[C_2H_4]} \right)_0 \\ &= n + p_0 \end{aligned}$$

Table 13

$\left(\frac{R_{C_4H_8}}{[C_2H_4]} \right)_o / R_{C_4H_{10}}^o$ ^{1/2} as a function of temperature and pressure.

t °C	P mm Hg	$\left(\frac{R_{C_4H_8}}{[C_2H_4]} \right)_o \times 10^6 \text{ (sec}^{-1}\text{)}$	$\left(\frac{R_{C_4H_8}}{[C_2H_4]} \right)_o / R_{C_4H_{10}}^o$ ^{1/2} (cc mole ⁻¹ sec ⁻¹) ^{1/2}
549.7	401.6	3.7	4.4 $\pm$ 0.3
550.7	590.5	10.0	5.2 $\pm$ 0.5
	402.0	8.3	5.1 $\pm$ 0.3
	199.0	5.4	4.9 $\pm$ 0.5
	96.3	3.5	5.2 $\pm$ 0.3
584.7	341.8	1.6	6.9 $\pm$ 0.3
	168.1	1.1	7.1 $\pm$ 0.2
599.7	402.1	3.2	8.4 $\pm$ 0.6
	298.9	2.7	3.3 $\pm$ 0.3
	203.1	2.4	9.2 $\pm$ 0.7
	99.9	0.90	5.3 $\pm$ 1.5
620.3	335.1	7.2	10.4 $\pm$ 0.3
	209.8	5.5	10.7 $\pm$ 0.3

where

$$P_o = \frac{k_{21} (k_{18} [H] + k_{19} [C_2H_5])}{k_{-19} [C_2H_6] + k_{21} [C_2H_5] + k_{25}} \quad [125]$$

As shown in Table 10, the ratio

$$\left(\frac{R_{C_4H_8}}{[C_2H_4]} \right)_o / R_{C_4H_{10}}^o \text{ }^{1/2} = n / R_{C_4H_{10}}^o \text{ }^{1/2} + P_o / R_{C_4H_{10}}^o \text{ }^{1/2} \quad [126]$$

at constant temperature, is independent of pressure within the error.

Combination of equation [123], [125] and [126] gives rise to

$$\left(\frac{R_{C_4H_8}}{[C_2H_4]} \right)_0 / R_{C_4H_{10}}^{1/2} = \frac{k_{22} K_9}{k_{5a}^{1/2}} + \frac{k_{21} (k_{18}[H] + k_{19}[C_2H_5])}{k_{5a}^{1/2} (k_{-19}[C_2H_6] + k_{21}[C_2H_5] + k_{25}[C_2H_5])} \quad [127]$$

The first term of the right-hand side of equation [127] is probably pressure-independent. The second term, however, might be dependent on pressure as shown in the following calculations, assuming

$$k_{-19} = k_2 = 2.0 \times 10^{11} e^{-10,400/RT} \text{ cc mole}^{-1} \text{ sec}^{-1},$$

$$k_{21} = k_{-1} = 2.2 \times 10^{13} \text{ cc mole}^{-1} \text{ sec}^{-1}$$

$$\text{and } k_{25} = 10^{13} e^{-42,000/RT} \text{ sec}^{-1},$$

where $E_{25} = 42 \text{ kcal mole}^{-1}$ was evaluated from $D(C_2H_3-H) = 103 \text{ kcal mole}^{-1}$ and $E_{-25} = 2 \text{ kcal mole}^{-1}$ (59). At 620°C , for 200 mm Hg of ethane, we find

$$k_{-19} [C_2H_6] = 2 \times 10^3,$$

$$k_{21} [C_2H_5] = 24$$

$$\text{and } k_{25} = 5 \times 10^2 \text{ sec}^{-1};$$

so that if the above assumptions were correct, the ratio $p_0 / R_{C_4H_{10}}^{1/2}$ would, under present conditions, be pressure-dependent because of the predominance of $k_{-19} [C_2H_6]$. Thus we conclude that

$$n \gg P_0$$

and that

$$\begin{aligned} \left(\frac{R_{C_4H_8}}{[C_2H_4]} \right)^{1/2} / R_{C_4H_{10}}^0 &= \frac{n}{R_{C_2H_{10}}^0{}^{1/2}} \\ &= \frac{k_{22} K_9}{k_{5a}{}^{1/2}} \end{aligned} \quad [128]$$

The Arrhenius plot of the average values of $(k_{22} K_9 / k_{5a}{}^{1/2})$ given in Table 10 is shown in Figure 38, from which an activation energy of 18 ± 4 kcal mole⁻¹ was obtained. Assuming $\Delta H_9^0 = -22$ kcal mole⁻¹ and $E_{5a} = 0$, we have

$$\begin{aligned} E_n &= 18 \pm 4 = E_{22} + \Delta H_9^0 \\ &= E_{22} - 22 \end{aligned}$$

$$\therefore E_{22} = 40 \pm 4 \text{ kcal mole}^{-1},$$

which agrees excellently with the reported value of 40 kcal mole⁻¹ (58). Using $\Delta S_9^0 = \Delta S_9^{\circ 1} = -10.4$ gibbs at 550°C, the frequency factor of reaction (22) is estimated to be

$$A_{22} = 10^{14.3 \pm 1.0} \text{ sec}^{-1}.$$

Figure 37.

Typical $R_{C_4H_8}$ vs. $\overline{[C_2H_4]}$ plots at $570^\circ C$.

A. 590.5 mm; B. 96.3 mm. (The scales 10 times expanded).

Figure 39.

Typical $R_{C_4H_6}$ vs. $\overline{[C_2H_4]}^2$ plot.

Figure 37

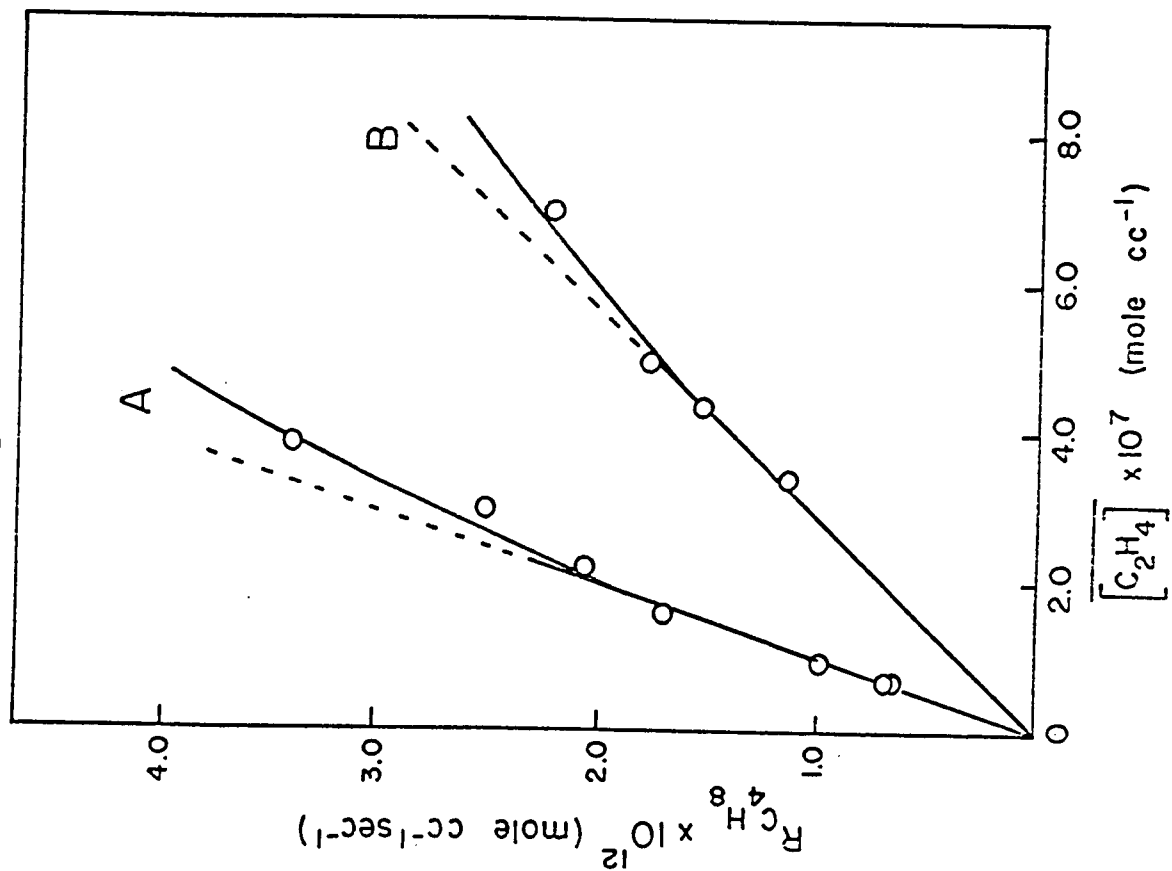
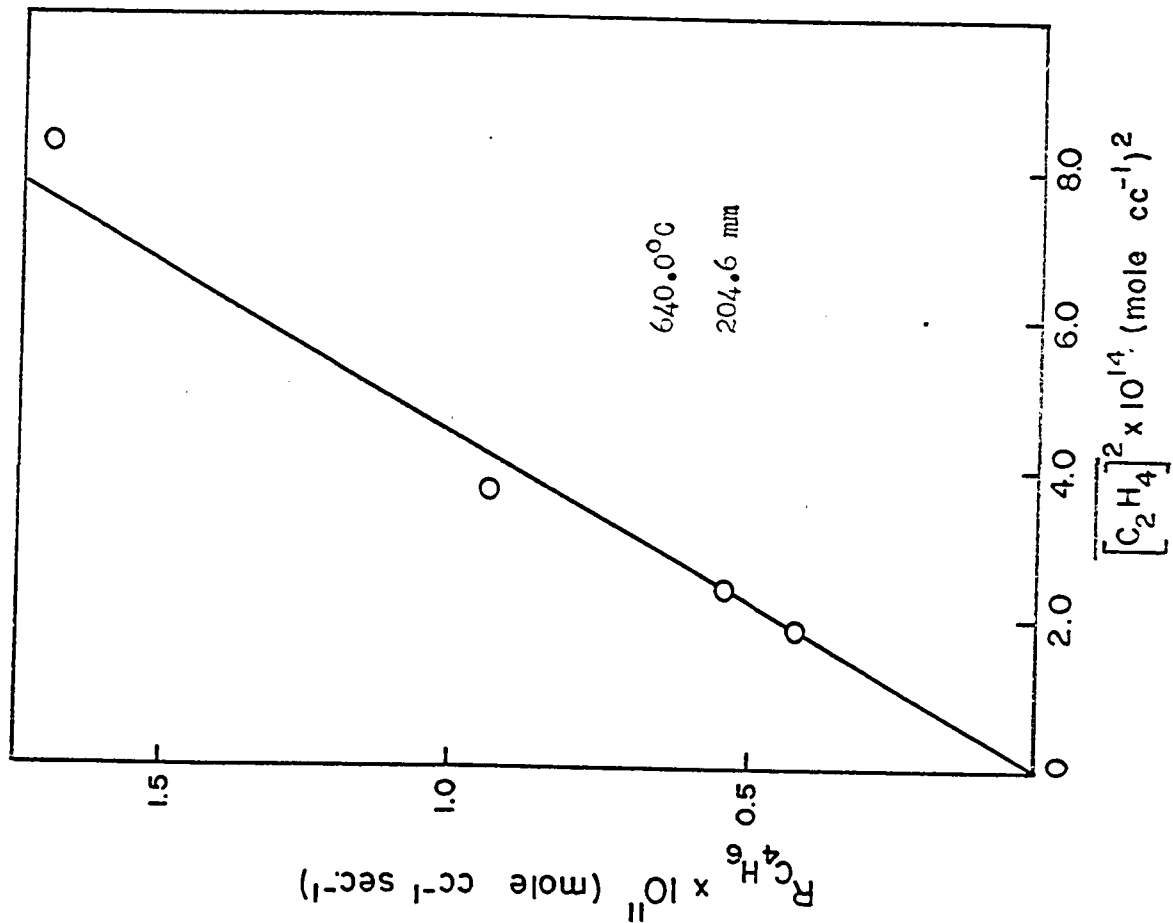


Figure 39



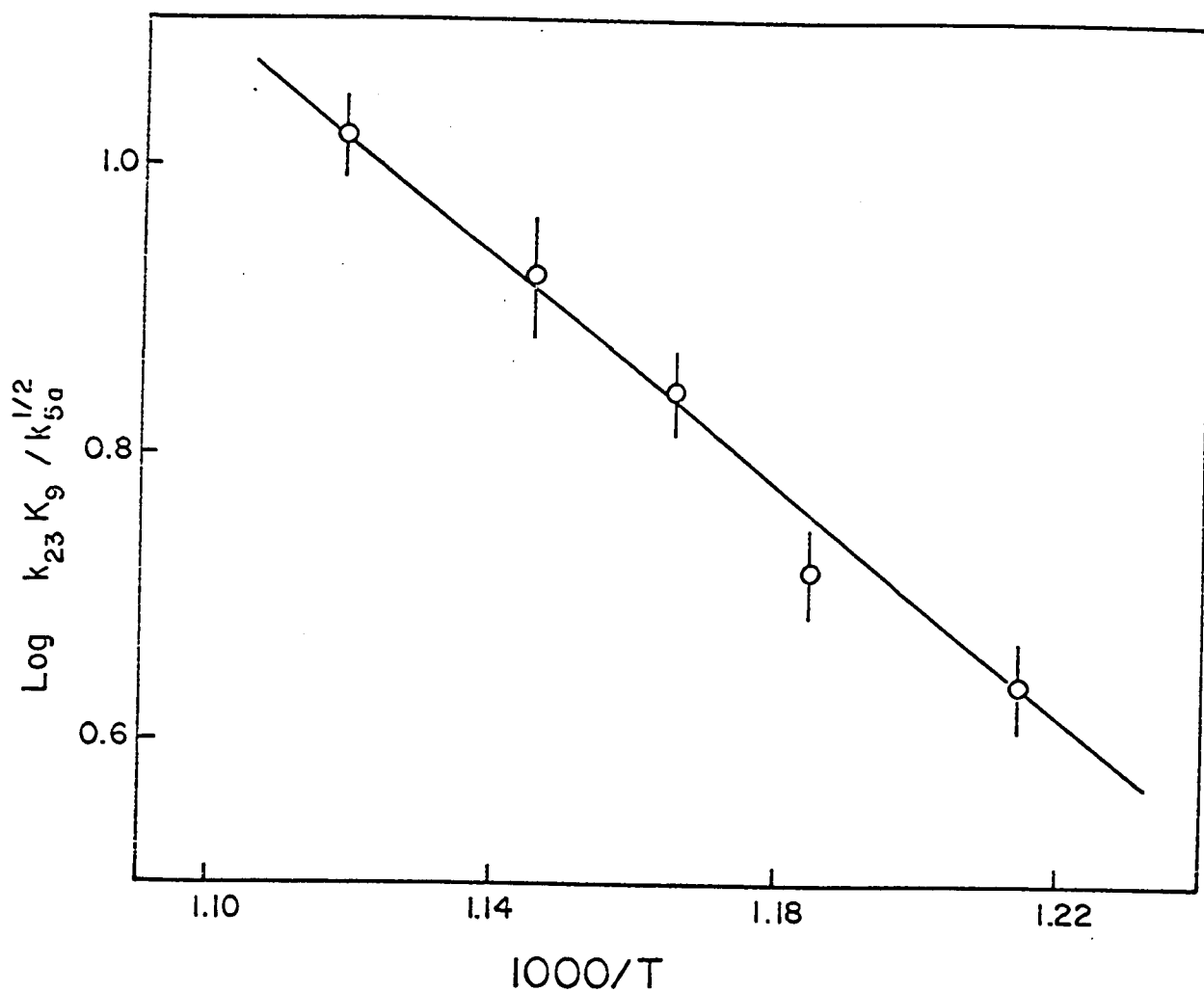
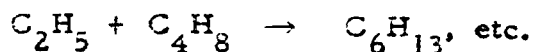


Figure 38.

Plot of $\log k_{23}K_9/k_{5a}^{1/2}$ vs. $1/T$.

$$\frac{k_{23}K_9}{k_{5a}^{1/2}} = \left(\frac{R_{C_4H_8}}{[C_2H_4]} \right)_o / R_{C_4H_{10}}^{o \frac{1}{2}}$$

In view of these reasonable results, we may conclude that the reaction (22) is probably more important than reaction (21). The decrease in $R_{C_4H_8}$ at higher conversions is probably due to the unimolecular decomposition of C_4H_8 . The C_3-C_4 bond in butene-1 is known to be much weaker than an ordinary C-C bond in a saturated hydrocarbon because of the resonance stabilization of the resulting allyl radicals. Other radical interactions such as



might also consume butene.

Equation [120] predicts that the rate of butadiene production should be approximately proportional to $[C_2H_4]^2$. This relationship was actually found at $640^\circ C$ as shown in Figure 39. The slopes of these plots for three pressures at $640^\circ C$ are presented in Table 11.

Table 11

$R_{C_4H_6} / [C_2H_4]^2 \text{ at } 640^\circ C$	
P mm Hg	$R_{C_4H_6} / [C_2H_4]^2 \times 10^{-2} \text{ (cc mole}^{-1} \text{ sec}^{-1})$
204.6	2.2 ± 0.3
123.4	3.1 ± 0.3
91.2	3.6 ± 0.2

They are roughly proportional to $[C_2H_4]^{-0.7}$.

Since the rate of butadiene production at temperatures higher than 640°C decreases rapidly, the linear relationship between $R_{\text{C}_4\text{H}_6}$ and $[\text{C}_2\text{H}_4]^2$ no longer holds. It is thus not possible to draw definite conclusion about the origin of C_4H_6 from the results in Table 11.

For similar reasons it is not possible to decide the mechanism of acetylene formation.

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PART II

UNIMOLECULAR DECOMPOSITIONS OF ETHYL RADICAL AND ETHANE

CHAPTER 5

THEORIES OF UNIMOLECULAR REACTIONS

The molecularity of an elementary reaction is defined as the number of molecules involved in the activated complex. A unimolecular reaction is a reaction with an activated complex consisting of only one reactant molecule. Decomposition, isomerization and inversion may clearly be of this type. The order of a unimolecular reaction may become greater than one and as high as two in certain region of pressures. However, a bimolecular reaction is usually second order and a termolecular reaction third order.

In order for a unimolecular reaction to take place, the molecule should first of all possess sufficient energy, i. e., the activation energy. If the molecules do not obtain this energy by absorption of radiation the source of activation can only be molecular collisions. This, however, seemed inconsistent with the first-order kinetics observed over a wide range of pressures, since the collision frequency depends on the square of the number of molecules in unit volume of a single reactant.

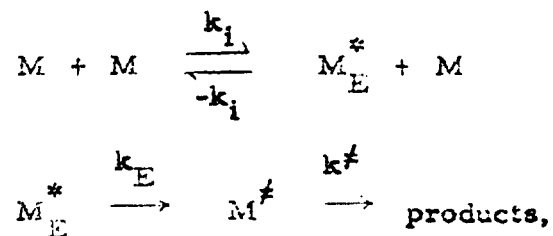
This puzzle was first solved by Lindemann (63). It was suggested that after a reacting molecule acquires its activation energy as the result of collision, there is a definite time lag before it reacts. If the average time interval between activation and reaction is large in comparison with the interval between successive collisions, the process is kinetically of the first order in spite of the fact that two molecules are involved in the collision. On the other hand, if the

time lag is relatively small, one may observe second-order kinetics.

Later modifications of this idea by Hinshelwood (64), Rice and Ramsperger (65) and Kassel (66) on the one hand, and by Slater (67) on the other, permitted it to be applied quantitatively to a number of reactions. Recent work of Marcus (68, 69, 70), by incorporating the transition-state theory of unimolecular reaction in HKRR theory, showed satisfactory agreement of the theory with the available data on unimolecular reactions (70, 71).

1. Formulations of the theories of unimolecular reactions:

All modern theories of unimolecular reactions are derived from the following mechanism based on Lindemann's idea:



where M is the reacting molecule, M_E^* , the energized molecule which possesses energy equal to or greater than the minimum energy, E^* , and $M^\ddagger$, the activated complex.

A steady-state assumption for M_E^* and $M^\ddagger$ leads to

$$-\frac{d[M]}{dt} = \frac{k_1 k_E [M]^2}{k_{-1} [M] + k_E} \quad [129]$$

$$= k_E^1 [M] , \quad [129a]$$

where

$$k_E^1 = \frac{k_i k_E [M]}{k_{-i} [M] + k_E} \quad [130]$$

is the first-order rate-coefficient for the reaction of molecules with energy E . The first-order rate-coefficient of the reaction for molecules possessing energy between E and $E + dE$ is therefore given by

$$\begin{aligned} dk_E^1 &= \frac{k_E [M] dk_i}{k_{-i} [M] + k_E} \\ \text{or } dk_E^1 &= \frac{K_E k_E dE}{1 + \frac{k_E}{Z [M]}}, \end{aligned} \quad [131]$$

where $K_E dE = \frac{dk_i}{k_{-i}}$ is the equilibrium fraction of the molecules which possess energy between E and $E + dE$, and $k_{-i} = Z$ is the collision number. Integration of equation [131] with respect to energy from E^* to ∞ gives:

$$k^i = \int_{E^*}^{\infty} \frac{K_E k_E dE}{1 + \frac{k_E}{Z [M]}}. \quad [132]$$

Equation [132] is the general expression of the first order rate-coefficient of a unimolecular reaction. When the pressure is sufficiently high, or $k_E/Z [M] \ll 1$, equation [132] reduces to

$$k^1 = k^\infty = \int_{E^*}^{\infty} K_E k_E dE \quad [133]$$

and if the pressure is low or $k_E/Z [M] \gg 1$, equation [132] becomes

$$k^1 = \int_{E^*}^{\infty} Z [M] K_E dE \quad [134]$$

$$= k^0 [M] , \quad [134a]$$

where

$$k^0 = Z \int_{E^*}^{\infty} K_E dE \quad [135]$$

is the second-order rate constant.

The differences between the various theories lie mainly in the differences in the assumptions about the modes of intramolecular energy transfer, Lindemann assumed

$$k_i = Z e^{-E/kT} \quad [136]$$

or

$$\frac{k_i}{k_{-i}} = e^{-E/kT} \quad [137]$$

hence

$$K_E = \frac{e^{-E/kT}}{kT} , \quad [138]$$

which is actually, as shown later, the special case of the Hinshelwood theory with $s = 1$. The second assumption was that all energized molecules with $E > E^*$ reacted with the same rate regardless of their energies, i.e., $k_E = \text{constant}$.

The first assumption leads the Lindemann theory to predict higher values of $[M]_{1/2}$ than are observed, where $[M]_{1/2}$ is the concentration of reactant at which $k^1 = k^0/2$; the second assumption that $k_E = \text{constant}$

leads to a linear relationship between $1/k^1$ and $1/[M]$, which does not hold for polyatomic molecules.

Hinshelwood's theory may be regarded as the first major development of Lindemann's idea, stressing the role of the complexity of the molecule. According to this theory, it is proposed that the energy that a molecule possesses may be distributed freely among its total number of degrees of vibrational freedom, but that the molecule is capable of reacting only when the requisite energy E^* , or greater, is confined to specified degrees of freedom. The energized molecules, however, are still assumed to react with equal rates irrespective of their energies. These two assumptions lead to

$$K_{\infty} = \left(\frac{E}{kT} \right)^{s-1} \frac{1}{(s-1)!} \frac{e^{-E/kT}}{kT} \quad [139]$$

and

$$k_E = \text{constant} = A. \quad [140]$$

Substituting equations [139] and [140] in [133] and [135], respectively, gives

$$k^{\infty} = A \sum_{r=1}^{s-1} \frac{1}{r!} \left(\frac{E^*}{kT} \right)^r e^{-E^*/kT} \quad [141]$$

and

$$k^0 = Z \sum_{r=1}^{s-1} \frac{1}{r!} \left(\frac{E^*}{kT} \right)^r e^{-E^*/kT} \quad [142]$$

If $E^*/kT \gg 1$, both equations [141] and [142] reduce to

$$k^{\infty} = A \left(\frac{E^*}{kT} \right)^{s-1} \frac{1}{(s-1)!} e^{-E^*/kT} \quad [143]$$

and

$$k^0 = Z \left(\frac{E^*}{kT} \right)^{s-1} \frac{1}{(s-1)!} e^{-E^*/kT} \quad [144]$$

Although Hinshelwood's modifications bring about much larger values for k^0 and thus smaller values of $[M]_{1/2}$, there are still certain difficulties. (1) The objection to the Lindemann theory that $k_E = \text{constant}$ still remains. (2) The high-pressure rate-constant given by equation [143] predicts strong temperature dependence in the pre-exponential factor. However, this temperature dependence has not been observed. (3) There is no a priori knowledge of the values of s or its relationship with total number of degrees of freedom of vibration.

Rice and Ramsperger, and Kassel, overcame the first two difficulties inherited from the Hinshelwood theory by considering the molecule as a system of loosely coupled harmonic oscillators of equal frequency. Energy can freely flow among these oscillators. Reaction takes place when the minimum amount of energy E^* , or greater, concentrates in one of s oscillators. Statistical treatment of this assumption gives (66):

$$k_E = k^{\ddagger} \left(\frac{E - E^*}{E} \right)^{s-1} \quad [145]$$

Inserting equations [139] and [145] in [132] produces

$$k^1 = \frac{k^{\ddagger} e^{-E^*/kT}}{(s-1)!} \int_0^{\infty} \frac{x^{s-1} e^{-x} dx}{1 + \frac{k^{\ddagger}}{Z[M]} \left(\frac{x}{x+b} \right)^{s-1}} \quad [146]$$

where

$$x = \frac{E - E^*}{kT}$$

$$b = E^*/kT.$$

At high and low pressure limits, equation [146] reduces, respectively, to

$$k^\infty = k^\ddagger e^{-E^*/kT} \quad [147]$$

and

$$k^0 = Z \left(\frac{E^*}{kT} \right)^{s-1} \frac{1}{(s-1)!} e^{-E^*/kT}, \quad [144]$$

if $E^* \gg kT$.

Experimentally, one can obtain both E^* and $k^\ddagger$ directly from high-pressure first-order rate constants. Inserting these values in equation [146] one may obtain a family of curves with different values of s in plots of $\log k^1$ vs. $\log [M]$. Comparing these curves with experimental points, the best-fitted one gives the value of s . Experimentally, it was always found that

$$\frac{2}{3}n \geq s \geq \frac{1}{2}n$$

for relatively complex molecules (72), where n is the total number of vibrational degrees of freedom. No interpretation of this relation, however, has ever been offered.

Laidler and Wojciechowski (73) concluded from their detailed analyses of a number of reactions that s is usually close to the number of totally symmetrical modes of vibration of the activated complex, and accordingly that only the totally symmetrical vibrations are responsible for intramolecular energy transfer.

The classical formulation of Slater's theory (67) is based on a model which consists of classical harmonic oscillators. The molecule is described in terms of independent internal coordinates which relate to the displacement of interatomic distances or angles from their equilibrium values, with reaction taking place when a specified coordinate attains a critical distance or angle. In this theory, energy does not flow from one oscillator to another, and the energies and phases of different vibrational modes change only upon collision. The statistical expression of the equilibrium fraction of energized molecules which possess total energies between E and $E + dE$ is given by

$$K_E dE = \frac{e^{-E/kT}}{(kT)^n} dE_1 dE_2 \dots dE_n \quad [148]$$

where n is the number of oscillators and E is the total energy, i. e.,

$$E = \sum_{r=1}^n E_r \quad [149]$$

The specific dissociation probability is given by

$$k_E = \frac{\left(\sum_{r=1}^n a_r \sqrt{E_r - q_0} \right)^{\frac{1}{2}(n-1)}}{(2\pi)^{\frac{1}{2}(n-1)} \Gamma\left(\frac{1}{2}n + \frac{1}{2}\right)} \left(\frac{\sum_{r=1}^n a_r \nu_r^2 \sqrt{E_r}}{\prod_{r=1}^n a_r \nu_r \sqrt{E_r}} \right)^{\frac{1}{2}(n-1)} \quad [150]$$

where a_r is the amplitude factor, E_r , the energy, ν_r , the frequency of vibration associated with r th oscillator, $\Gamma\left(\frac{1}{2}n + \frac{1}{2}\right)$ is the gamma function of $\left(\frac{1}{2}n + \frac{1}{2}\right)$ and q_0 , the critical value of q , which characterizes

the internal motion of the molecule leading to its unimolecular reaction and may be expressed as

$$q = \sum_{r=1}^n a_r \sqrt{E_r} \cos 2\pi(\sqrt{E_r}t + \phi_r). \quad [151]$$

The reaction occurs only when $k_E \geq 0$ or

$$\sum_{r=1}^n a_r \sqrt{E_r} \geq q_0 \quad [152]$$

or

$$\sum_{r=1}^n a_r \sqrt{E_r} \geq \left(E^* \sum_{r=1}^n a_r^2 \right)^{1/2}. \quad [152a]$$

where E^* is the minimum energy related to q_0 by

$$E^* = q_0^2 / \sum_{r=1}^n a_r^2. \quad [153]$$

Substituting equations [149] and [150] in [133] and [135], and integrating under the condition given by equation [152] produce, respectively,

$$k^\infty = \overline{V} e^{-E^*/kT} \quad [154]$$

and

$$k^0 = Z \left(\frac{E^*}{kT} \right)^{\frac{1}{2}(n-1)} \prod_{r=1}^n \mu_r e^{-E^*/kT}, \quad [155]$$

where

$$\bar{\nu} = \frac{\prod_{r=1}^n \nu_r}{\prod_{r=1}^{n-1} \nu_r} \quad [156]$$

and μ_r is the normalized amplitude factor defined by

$$\mu_r = a_r / \left(\sum_{r=1}^n a_r^2 \right)^{\frac{1}{2}}. \quad [157]$$

The general equation obtained from equation [132] is given by

$$k^1 = \frac{\bar{\nu} e^{-E^*/kT}}{\Gamma(\frac{1}{2}n + \frac{1}{2})} \int_0^{\infty} \frac{x^{\frac{1}{2}(n-1)} e^{-x} dx}{1 + x^{\frac{1}{2}(n-1)} e^{-1}} \quad [158]$$

where

$$x = \frac{E - E^*}{kT}$$

$$\theta = \frac{Z(M)}{\bar{\nu}} \left(\frac{E^*}{kT} 4\pi \right)^{\frac{1}{2}(n-1)} \Gamma(\frac{1}{2}n + \frac{1}{2}) \prod_{r=1}^n \mu_r. \quad [159]$$

This theory has been applied successfully to the isomerization of cyclopropane to propylene, in which the decline of the unimolecular rate is in excellent agreement with experimental results (67, 74). However, Gill and Laidler (17), and Laidler and Wojciechowski (73), have shown that in some instances when the number of the vibrational modes of the reactant is small, the second-order rate constants predicted by Slater theory are too low.

The main weakness of the Slater theory is that it does not allow for energy flow. The HKRR assumption of flow between all oscillators

seems to go too far in one direction, and Slater's assumption too far in the other; the truth may in general lie between the HKRR and the Slater theories (75).

Marcus and Rice have recently developed a quantum mechanical transition-state formulation of the HKRR theory, that includes both quantum and anharmonic effects. They categorized the activated complex as "loose", "semirigid" and "rigid" according to the magnitude of the entropy of activation. The energy has been divided as "fixed" and "nonfixed". "Nonfixed" energy refers to that which is exclusive of the external translational energy, the ground-state vibrational energy, and the rotational energy of those rotations which do not effectively contribute to the reaction; such rotations are called "adiabatic" rotations. In the case of the activated complex, the potential energy of the newly broken bond is also excluded. All the vibrational degrees of freedom are considered as active. According to this theory we have

$$K_E = \frac{N(E) e^{-E/kT}}{P_2} \quad [160]$$

and

$$k_E = \alpha \frac{P_1^\ddagger P_R^\ddagger \sum_{E_v^\ddagger \ll E^\ddagger} \left(\frac{E^\ddagger - E_v^\ddagger}{kT} \right)^{\frac{r}{2}} P(E_v^\ddagger)}{P_1 \Gamma(1 + \frac{r}{2}) h N(E^\ddagger + E^\ddagger)} \quad [161]$$

where $N(E)$ = the number of energy states per unit energy of the degrees of freedom which participate in intramolecular energy transfer.

- P_1 and $P_1^\ddagger$ = partition functions of adiabatic rotations of M and $M^\ddagger$, respectively.
- $P_R^\ddagger$ = partition function of active rotations of $M^\ddagger$.
- r = the number of active rotation of $M^\ddagger$.
- P_2 = partition function of all active degrees of freedom of M.
- Γ = gamma function.
- $P(E_v^\ddagger)$ = vibrational degeneracy at the vibrational energy $E_v^\ddagger$.
- $E^\ddagger$ = nonfixed energy of $M^\ddagger$.
- α = number of equivalent optical or geometrical isomers for which the activated complex may exist; α may be replaced by a more general quantity $l^\ddagger$ introduced by Bishop and Laidler (76).

Substituting equations [160] and [161] in equations [133] and [135], gives, respectively

$$k^\infty = \alpha \frac{kT}{h} \frac{P_1^\ddagger P_2^\ddagger}{P_1 P_2} e^{-E^*/kT} \quad [162]$$

$$\text{and } k^o = \frac{Z e^{-E^*/kT}}{P_2} \int_0^\infty N(E^* + E^\ddagger) e^{-E^\ddagger/kT} dE^\ddagger \quad [163]$$

where

$$P_2^\ddagger = P_R^\ddagger \sum_{E_v^\ddagger=0}^{\infty} P(E_v^\ddagger) e^{-E^\ddagger/kT}$$

is the partition of all active modes of $M^\ddagger$. k^∞ is equivalent to the expression of Eyring's theory (38). No simple expression of k° is obtained. From equation [132], the general first-order rate coefficient is given by

$$k^1 = \frac{\propto P_1^\ddagger P_R^\ddagger e^{-E^*/kT}}{P_1 P_2 h \Gamma(\frac{r}{2} + 1)} \int_0^\infty \frac{\sum_{E_v^\ddagger \leq E^\ddagger} \left(\frac{E^\ddagger - E_v^\ddagger}{kT} \right)^{\frac{r}{2}} P(E_v^\ddagger) e^{-E^\ddagger/kT} dE^\ddagger}{1 + \frac{k_E}{Z [M]}} \quad [164]$$

where k_E is given by equation [161].

This revised HKRR theory has been applied successfully to both equilibrium and nonequilibrium systems (70, 71, 77, 78).

II. The frequency factor of unimolecular reaction in the high-pressure region:

According to absolute rate theory (76), the entropy of activation is related to the high-pressure frequency factor by the relation,

$$\Delta S^\ddagger = R \left(\ln \frac{A^\infty h}{\kappa kT l^\ddagger} - 1 \right) \quad [165]$$

where $\Delta S^\ddagger$ is the entropy of activation without including the symmetry contributions for both M and $M^\ddagger$, κ the transmission coefficient, and $l^\ddagger$, the statistical factor which is equal to the number of possible ways the activated complex can be formed. The

transmission coefficient lies between 1 and 0, and for most reactions $\kappa = 1$ (38). Since $kT/h \sim 10^{13} \text{ sec}^{-1}$ at ordinary temperatures, the reactions with $A^\infty \sim 10^{13} \text{ sec}^{-1}$ therefore have small $\Delta S^\ddagger$. An A-factor of $\sim 10^{13} \text{ sec}^{-1}$ is usually referred to as a "normal frequency factor", whereas those higher than 10^{13} sec^{-1} by several powers of ten such as $A_1^\infty = 1.0 \times 10^{16} \text{ sec}^{-1}$ for ethane decomposition or $A_{-5a} = 2.2 \times 10^{17} \text{ sec}^{-1}$ for butane decomposition, are called "abnormally high frequency factors". The decomposition of N_2O or CH_3CO is known to occur with a very low frequency factor. These low values have been ascribed to the fact that these reactions have low transmission coefficients because of the changes in multiplicities (33).

The distribution of the magnitudes of A-factors for unimolecular reactions is presented in Table 12, which is obtained from the data given in the recent review of Benson and DeMore (79). These 125 reactions appeared in the interval 1 January 1962 to 15 October 1964 (also including our present results for C_2H_6 and C_2H_5 decompositions). The range of each value of $\log A^\infty$ covers ± 0.25 logarithm units.

Table 12

The distribution of high-pressure frequency factors for unimolecular decompositions.

$\log A^\infty$	No. of occurrence	$\log A^\infty$	No. of occurrence
17.5	2	13.5	20
17.0	4	13.0	14
16.5	1	12.5	6
16.0	6	12.0	4
15.5	6	11.5	4
15.0	10	11.0	3
14.5	22	10.5	1
14.0	22		

According to these statistics, about 70% of reactions possess A-factors in the range of $10^{12.5} \sim 10^{14.5} \text{ sec}^{-1}$.

According to the HKRR theory, A^∞ is equal to the rate constant $k^\ddagger$. The physical significance of $k^\ddagger$ is not clear. Kassel refers to it as a "proportionality constant" (66). Slater (67) pictures it as playing the same role in relation to the internal energy exchange as the effective collision frequency, $Z [M]$, plays in the over-all energy changes. He defines $k^\ddagger$ by saying that $k^\ddagger \Delta t$ is the probability that in time Δt there is an internal energy change in the critical oscillators. According to this picture, $k^\ddagger$ must be of the order of the vibration frequency, $\sim 10^{13} \text{ sec}^{-1}$.

According to equation [145], $k_E \rightarrow k^\ddagger$ when $E \rightarrow \infty$. This indicates that when an energized molecule possesses an infinite amount of energy, it decomposes within one vibration; $k^\ddagger$ is thus the rate constant corresponding to the free passage of the system over the energy barrier. This must be equivalent to the universal frequency kT/h according to absolute rate theory (38); $k^\ddagger$ is therefore equal to $\sim 10^{13} \text{ sec}^{-1}$. This is consistent with Slater's explanation. This, however, implies that $k^\ddagger$ is independent of $\Delta S^\ddagger$ and, therefore, the HKRR theory is not applicable to reactions with high or low frequency factors.

Rosenstock et al. (80) showed that the application of HKRR's assumption that the molecule and the activated complex are loosely coupled harmonic oscillators, to the equation,

$$k_E = \frac{k}{h} \int_0^{E-E^*} \frac{P^\ddagger(E, E^*, E_t)}{P(E)} dE_t \quad [166]$$

leads to

$$k_E = \kappa \frac{\prod_{j=1}^s \nu_j}{\prod_{i=1}^{s-1} \nu_i^*} \left(\frac{E - E^*}{E} \right)^{s-1}, \quad [167]$$

where $\rho(E)dE$ is the number of states of the system having energy between E and $E + dE$ and $\rho^{\ddagger}(E, E^*, E_t) dE dE_t$ is the number of states of the system in the activated complex configuration with potential energy and translation energy between E_t and $E_t + dE_t$ in the reaction coordinate, and total energy between E and $E + dE$. Comparison of equation [145] and [167] gives

$$k^{\ddagger} = \kappa \frac{\prod_{j=1}^s \nu_j}{\prod_{i=1}^{s-1} \nu_i^*}. \quad [168]$$

A similar expression can also be obtained by comparing k^{∞} of HKRR (equation [147]) with that of Slater (equation [154]) or of Eyring and Marcus (equation [162]) if one neglects rotational contributions and employs the classical partition function for vibrational degrees of freedom. Equation [168] is able to account for both high and low frequency factors by virtue of the values of ν_i^* 's and κ . However, this is in contradiction to the previous conclusion that $k^{\ddagger} \sim kT/h$. This contradiction is actually the outcome of the crude assumptions of the HKRR and Slater theories. By incorporating $\Delta S^{\ddagger}$ of the absolute rate theory in the HKRR theory, Marcus and Rice overcame this difficulty.

III. The activation energy of unimolecular reactions:

According to both HKRR and Slater theories, the experimental activation energy of a unimolecular reaction should be a

function of pressure. Both theories predict that the activation energy in the high-pressure region is $NE^* = E^\infty$. The activation energy in the second-order region can be obtained by HKRR theory from equation [144] and by Slater's theory from equation [155]. Taking logarithms and differentiating with respect to T, we have, according to HKRR theory

$$E^\circ = E^\infty - (s - \frac{3}{2}) RT \quad , \quad [164]$$

and Slater theory;

$$E^\circ = E^\infty - (\frac{1}{2}n - 1) RT \quad [170]$$

if Z is expressed in concentration units. E° for both theories will be reduced by RT if Z is in pressure units.

In the intermediate region, the activation energy has been evaluated as a function of pressure by Steel (81) according to the HKRR theory:

$$E_P = E^\infty - (s - \frac{1}{2}) RT \frac{d \ln I}{d \ln P} \quad [171]$$

where I is the Kassel's integral given in equation [146]. Since I is independent of pressure in the first-order region, and is proportional to pressure in the second-order region, equation [171] therefore leads to the correct limiting values. Applications of this equation to the decomposition of N_2O_5 and $CH_3N_2CH_3$ have been fairly successful (81). The Marcus theory has also been used by Rabinovitch and Schneider (82) to evaluate E_P .

IV. Powell's method of extrapolation:

Since ^{the} Lindemann-Hinshelwood extrapolation for k^∞ and k^0 from the data in the intermediate region of pressure dependence is not valid for complex molecules, Powell in 1959 (83) derived a function which may be applied to molecules of high complexity, viz.,

$$\frac{k^1}{k^\infty} = \int_0^\infty \frac{e^{-x} dx}{s'^1/x^{s'} + 1/m} \quad [172]$$

where

$$m = (k^1/k^\infty)/(k^1/k^0 [M]) \quad [173]$$

$$x = \frac{E - E^*}{kT}$$

s' = a theoretical parameter.

In the case of $s' = 0$, equation [172] gives

$$\frac{1}{k^1} = \frac{1}{k^\infty} + \frac{1}{k^0 [M]} \quad [174]$$

which is Hinshelwood's first theory.

In Powell's paper, a table of k^1/k^∞ and $k^1/k^0 [M]$ as functions of s' and $1/m$ is given for $s' = 1$ to 3. To extrapolate k^∞ and k^0 from the data in the fall-off region, a double-logarithmic plot of k^1 vs. $k^1/[M]$ is matched against a family of theoretical curves with different s' values in the plot of $\log k^1/k^\infty$ vs. $\log k^1/k^0 [M]$. From the differences between the values at any chosen point on the experimental curve and the values of the best matched theoretical curve for the corresponding coordinates, one obtains k^∞ and k^0 , i.e.,

$$(\log k^1)_{\text{exp}} - (\log k^1/k^\infty)_{\text{th}} = \log k^\infty \quad [175]$$

$$(\log k^1/[M])_{\text{exp}} - (\log k^1/[M]k^0)_{\text{th}} = \log k^0. \quad [176]$$

This method was found to be quite satisfactory, as will be shown in the next chapter.

According to Powell, the parameter s' is one less than s in HKRR theory. However, practically, s' is found to be as low as half the value of s . This is probably due to the following reason.

Substituting equation [173] in [172] and rearranging, we have

$$\frac{k^1}{k^\infty} = \int_0^\infty \frac{\left(\frac{E}{kT}\right)^{s'} \frac{1}{s'!} \left(\frac{E-E^*}{E}\right)^{s'} e^{-(E-E^*)/kT} \frac{dE}{kT}}{1 + \frac{k^\ddagger}{Z[M]} \left(\frac{E-E^*}{E^*}\right)^{s'}} \quad [177]$$

which is to be compared with the usual integral obtained from equation [148]:

$$\frac{k^1}{k^\infty} = \int_0^\infty \frac{\left(\frac{E}{kT}\right)^{s-1} \frac{1}{(s-1)!} \left(\frac{E-E^*}{E}\right)^{s-1} e^{-(E-E^*)/kT} \frac{dE}{kT}}{1 + \frac{k^\ddagger}{Z[M]} \left(\frac{E-E^*}{E}\right)^{s-1}}. \quad [178]$$

The main difference lies in the second term of the denominators in both integrands, viz.,

$$E_P = \left(\frac{E-E^*}{E^*}\right)^{s'} \quad [179]$$

and

$$B_K = \left(\frac{E - E^*}{E} \right)^{s-1} \quad [180]$$

B_P and B_K possess different limiting values at $E = \infty$ and $E = 0$, i.e., when

$$E = \infty: B_P = \infty, \text{ whereas } B_K = 1$$

$$E = 0: B_P = \pm 1, \text{ whereas } B_K = \pm \infty.$$

Therefore, the comparison of s' and s is probably meaningless.

CHAPTER 6

DECOMPOSITION OF ETHYL RADICALS

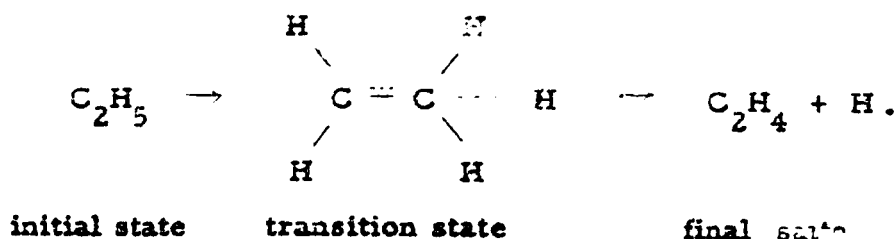
I. Historical review:

The decomposition of the ethyl radical,



was first proposed by Rice and Herzfeld (21) as an essential step in the pyrolysis of ethane. In order to explain the over-all activation energy of the ethane decomposition, Rice (84) assigned a value of 49 kcal mole⁻¹ to E_3 , the activation energy of reaction (3).

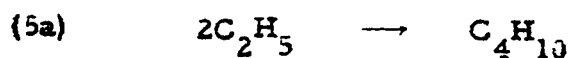
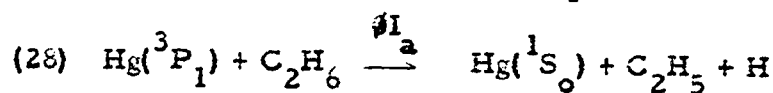
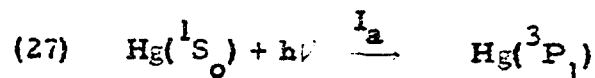
Bawn (85) estimated E_3 by using potential energy surfaces and obtained a value of 48-50 kcal mole⁻¹. The reaction coordinate was chosen as the extension of the C-H bond:



All these estimates are only of qualitative significance.

The first direct measurement of the reaction was that of Bywater and Steacie (27). They carried out the mercury photo-sensitized decomposition of ethane at 9 temperatures ranging from 27 to 500°C using 400 mm of ethane. At temperatures higher than 400°C, the rate of hydrogen production increased sharply with increasing temperature. They ascribed this increase to the occurrence of reaction (3), which gave rise to reaction chains. The mechanism

of this sensitized decomposition is:



Steady-state assumption for this scheme leads to

$$R_{\text{H}_2} = \phi_{I_a} + \frac{k_3}{k_{5a}^{1/2}} (\phi_{I_a})^{1/2} \quad [181]$$

$$\text{or} \quad k_3 = (R_{\text{H}_2} - \phi_{I_a}) k_{5a}^{1/2} / (\phi_{I_a})^{1/2} \quad [181a]$$

where ϕ_{I_a} is the rate of initiation. At high temperatures it can be evaluated by extrapolating from the low temperature experiments, from which they obtained $E_{\phi_{I_a}} = 1.0 \text{ kcal mole}^{-1}$. Assuming $E_{5a} = 0$, E_3 was found to be $39.5 \text{ kcal mole}^{-1}$. The rate constant for the reaction was given by:

$$k_3 = 3.0 \times 10^{14} e^{-39,500/RT} \text{ sec}^{-1} \quad [182]$$

Recently, Kerr and Trotman-Dickenson (86) studied the photolysis of propionaldehyde. To avoid any pressure effect in this reaction, the pressure of aldehyde was kept constant at ~ 45 mm Hg. Above 350°C , they found a sharp increase in the rate of ethylene formation. At temperatures between 360 and 505°C , the following equation,

$$k_3 = k_{5a}^{1/2} \frac{R_{C_2H_4} - 0.150 R_{C_4H_{10}}}{R_{C_4H_{10}}^{1/2}}, \quad [183]$$

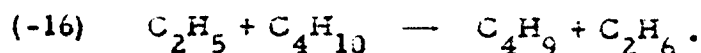
$$\text{leads to } k_3 = 1.5 \times 10^{12} e^{-32,000/RT} \text{ sec}^{-1}, \quad [184]$$

if $k_{5a} = 2.0 \times 10^{13} \text{ cc mole}^{-1} \text{ sec}^{-1}$ is used instead of $10^{14} \text{ cc mole}^{-1} \text{ sec}^{-1}$ as used by these authors. The term, $0.150 R_{C_4H_{10}}$, is the rate of ethylene formation through disproportionation of ethyl radicals. The activation energy of $32.0 \text{ kcal mole}^{-1}$ is in excellent agreement with our value $32.7 \text{ kcal mole}^{-1}$ (chapter 3), for the decomposition in the fall-off region. They explained this low activation energy as being due to the over-estimation of $R_{C_4H_{10}}$ at high temperatures because of corrections. In view of the low pressure they employed, this low activation energy may probably be ascribed to the fact that the first-order rate constant is in its pressure-dependent region.

The pressure-dependence of this reaction was first reported in the work of Purnell and Quinn (24) on the thermal decomposition of butane, mentioned in chapter 3. k_3 was measured by the following equation:

$$k_3 = \frac{1}{2} k_{-16} (r - 1) [C_4H_{10}] \quad [185]$$

where $r = R_{C_2H_4} / R_{C_2H_6}$, and k_{-16} is the rate constant of reaction (-16):



Since $(r - 1) [C_4H_{10}]$ decreased with decreasing pressure, they concluded that k_3 must be in its fall-off region. At temperatures $420\text{--}530^\circ\text{C}$ and pressures 25-150 mm, an activation energy of

$32.6 \pm 2.0 \text{ kcal mole}^{-1}$ was obtained, if $E_{-16} = 10.4 \text{ kcal mole}^{-1}$ was used (32). This is consistent with that of Kerr and Trotman-Dickenson and with the present result.

II. Powell's extrapolation for k_3^∞ and k_3^0 :

Powell's method described in the last chapter was applied to extrapolate k_3^∞ and k_3^0 from the data given in Table 1 and in Figure 18. The parameter $s' = 3$ gives the best fit. Arrhenius plots of k_3^∞ and k_3^0 thus obtained are presented in Figure 40, from which we obtained:

$$k_3^\infty = 3.8 \times 10^{13} e^{-33,000/RT} \text{ sec}^{-1} \quad [186]$$

and

$$k_3^0 = 1.8 \times 10^{18} e^{-32,400/RT} \text{ cc mole}^{-1} \text{ sec}^{-1} \quad [187]$$

The errors in the activation energies are about $\pm 2 \text{ kcal mole}^{-1}$. A double-logarithmic plot of k_3/k_3^∞ vs. $k_3/k_3^0 [M]$ is shown in Figure 41, in which the experimental results are compared with the theoretical curve with $s' = 3$.

The high-pressure rate constant k_3^∞ given by equation [186] is in fair agreement with that of Bywater and Steacie given by equation [182], as well as that of Benson (49) calculated from the results of Melville and Robb on the reverse reaction (57):

$$k_3 = 2.4 \times 10^{13} e^{-40,000/RT} \text{ sec}^{-1}. \quad [188]$$

The high-pressure frequency factor, A_3^∞ , can be estimated by the absolute rate theory (76), if the entropy of activation for the reaction, $\Delta S_3^\ddagger$ is assumed to be negligible, viz.,

Figure 40.

Arrhenius plots of k_3^{∞} and k_3^0 .

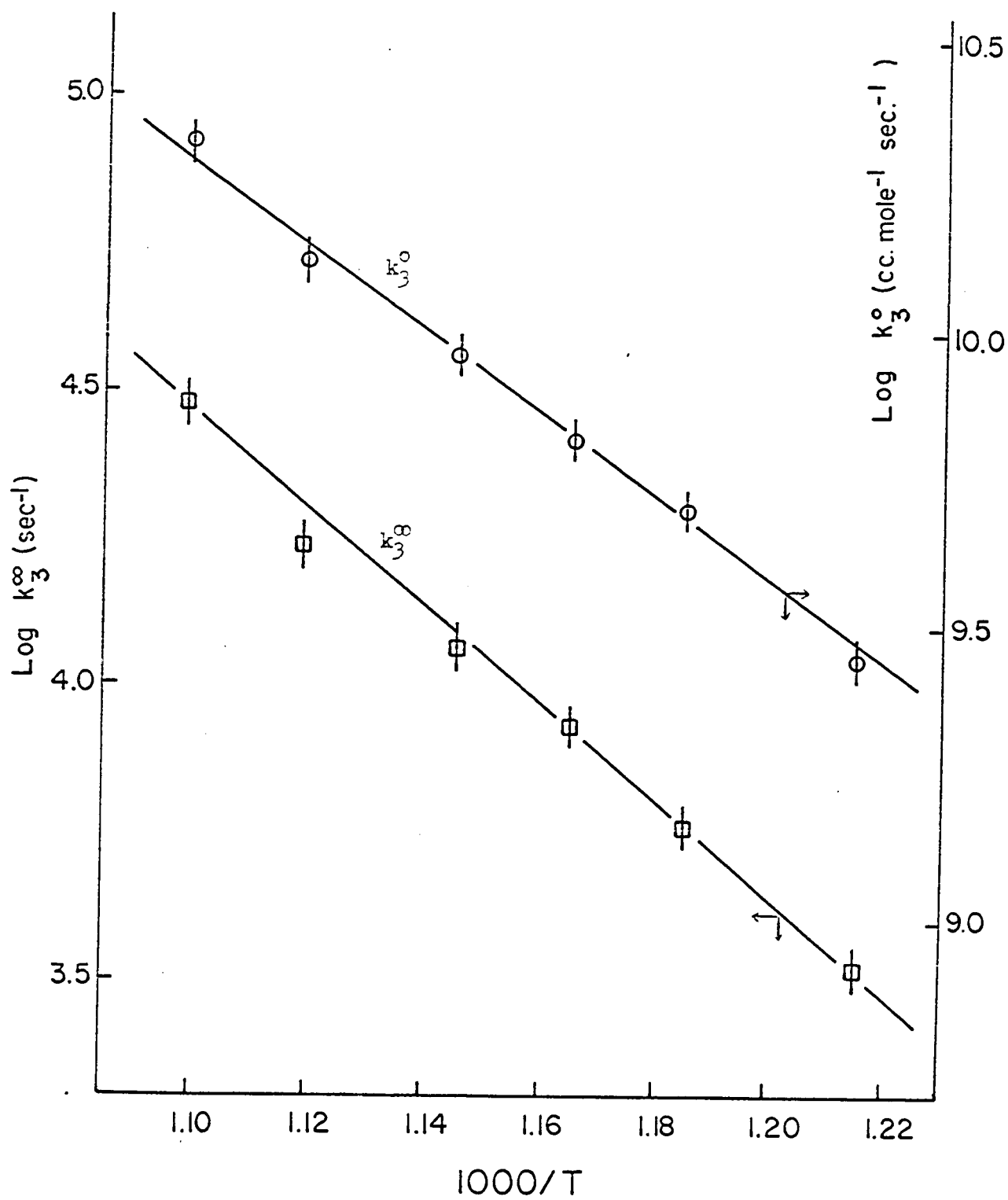
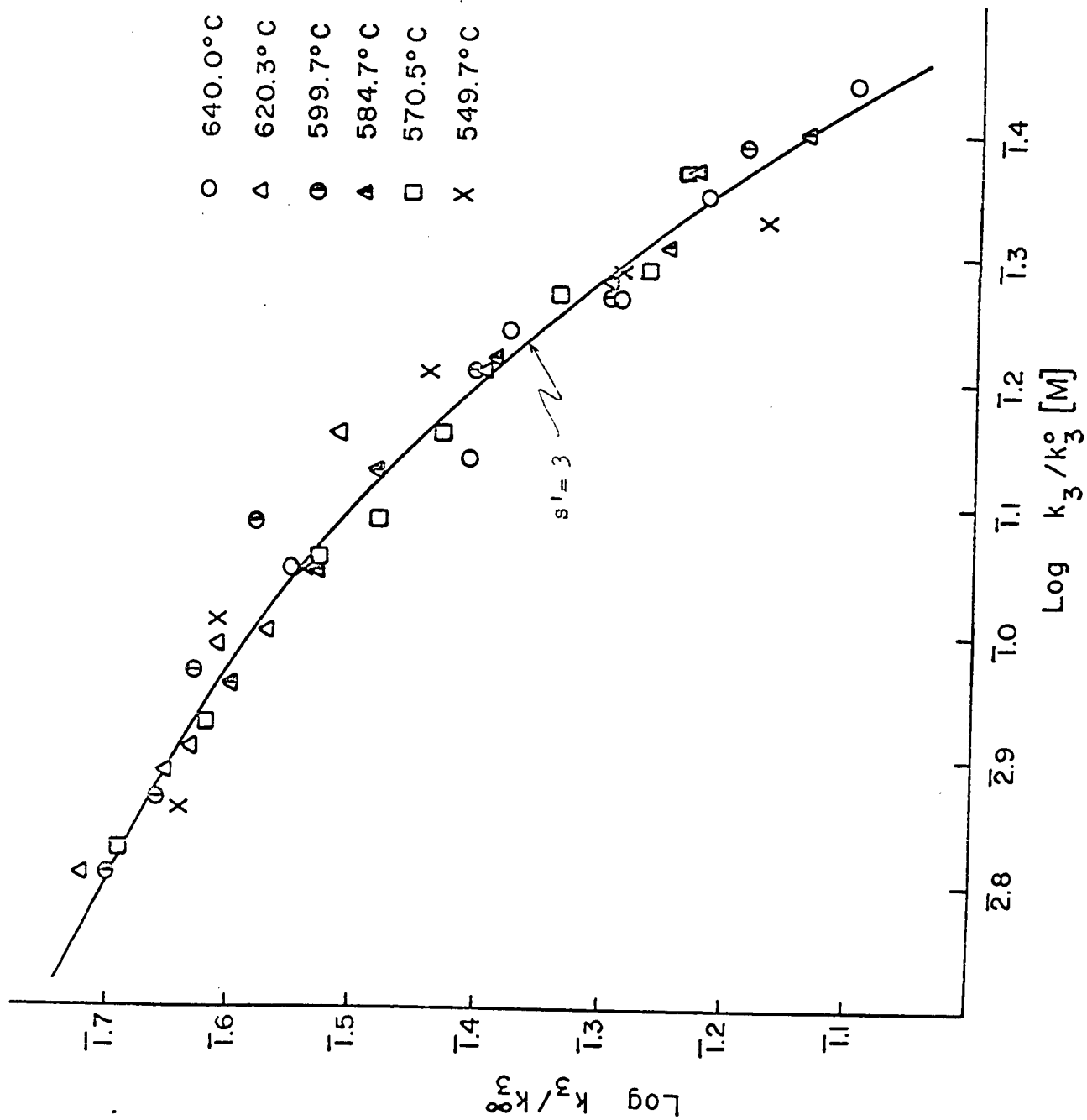


Figure 41.

Double-logarithmic plot of k_3/k_3^∞ vs. k_3/k_3^0 [M].



$$A_3^\infty = \kappa_3 l_3^\ddagger ekT/h, \quad [189]$$

where κ_3 is the transmission coefficient and $l_3^\ddagger$, the statistical factor, which is equal to 3 for this reaction, since there are three H atoms available in CH_3 -group. At 600°C , equation [189] leads to

$$A_3^\infty = 1.5 \times 10^{14} \text{ sec}^{-1},$$

if κ_3 is assumed to be unity. This is in agreement with the experimental values: $2.4 \times 10^{13} \sim 3.0 \times 10^{14} \text{ sec}^{-1}$.

Since the range of pressure studied is not wide enough to allow detailed comparison with HKRR or other theories, the effective number of modes of vibration can only be estimated by equation [169]. At 600°C , using $E_3^\infty = 39.5$ and $E_3^0 = 32.4 \text{ kcal mole}^{-1}$, we get

$$s = 5.6.$$

Assuming $\sigma = 3.3 \text{ \AA}$, at 600°C , equation [144] leads to

$$k_3^0(s=5) = 1.0 \times 10^{17} e^{-33,900/RT} \quad [190]$$

$$k_3^0(s=6) = 1.4 \times 10^{17} e^{-31,800/RT} \quad [191]$$

and

$$k_3^0(s=7) = 1.2 \times 10^{17} e^{-30,000/RT} \text{ cc mole}^{-1} \text{ sec}^{-1}. \quad [192]$$

$s=6$ gives better Arrhenius parameters, although the calculated frequency factor is about a factor of ten lower than the extrapolated value given in equation [187]. The result is, nevertheless, consistent with that of Purnell and Quinn, who found that $s=7$ fitted reasonably

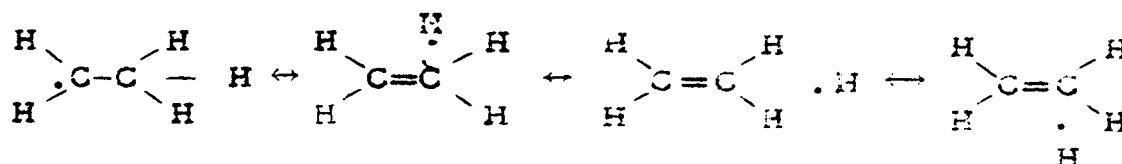
with their results if the limiting-pressure rate constant for the reaction was assumed to be

$$k_3^\infty = 10^{13} e^{-40,000/RT} \text{ sec}^{-1}$$

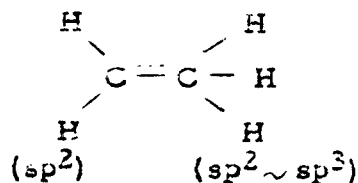
and the mean collision diameter, $\sigma = 3.35 \text{ \AA}$.

III. The activated complex:

According to Ewart (87), hyperfine interaction occurs in the ethyl radical. This interaction can be expressed in terms of the following resonance structures:

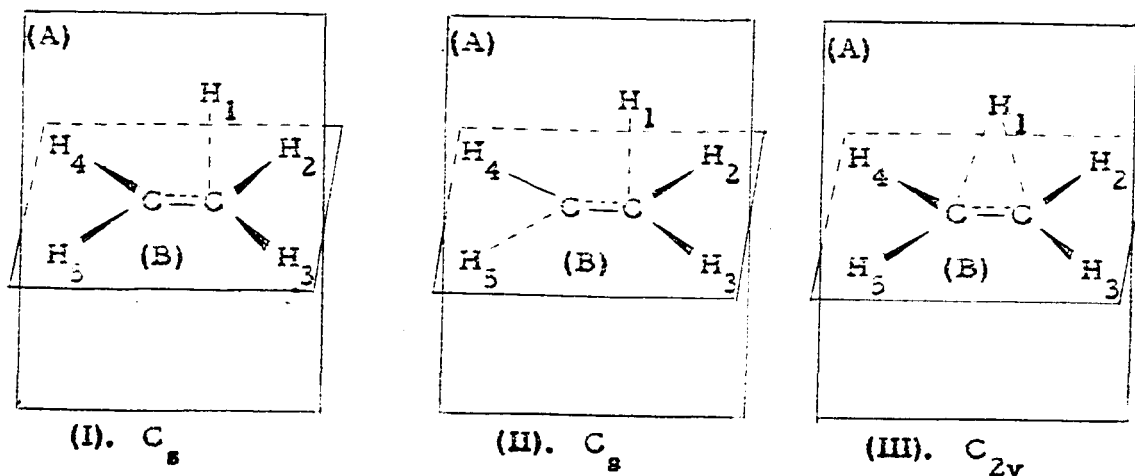


The mesomeric structure of the C_2H_5 radical may actually be



Since the formation of a π -bond releases $\sim 60 \text{ kcal mole}^{-1}$ of energy (89), the decomposition of the C_2H_5 radical with an activation energy of $\sim 38 \text{ kcal mole}^{-1}$ indicates that the reaction takes place after the formation of the π -bond.

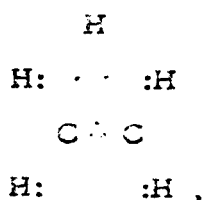
The activated complex for ethyl radical decomposition might belong to one of the following three possible structures:



In structure (I), four hydrogen atoms H_2 , H_3 , H_4 and H_5 are assumed to be coplanar with the C-C bond in plane B and the leaving H_1 atom in plane A, which passes through the C-C bond and is perpendicular to B. The point group of structure (I) is C_s . There are 9 totally symmetric modes of vibration associated with this structure (90).

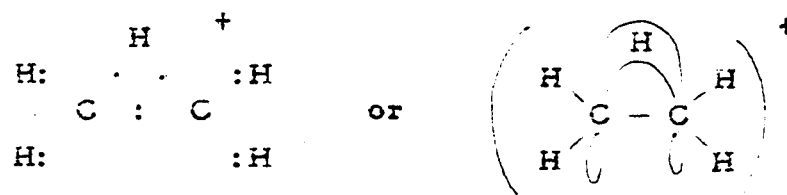
In structure (II), H_2 and H_3 are assumed to be coplanar with the C-C bond, while H_1 , H_4 and H_5 are in plane A; again $A \perp B$. This structure is also of the C_s group, which possesses 10 totally symmetrical modes of vibration (90). The structure (III) is similar to that of ethylene oxide (C_2H_4O), possessing 5 totally symmetrical modes of vibration (90).

According to Laidler and Wojciechowski (73), the effective modes of vibration, s , for structures (i), (II) and (III) will be equal to 9, 10 and 5, respectively. The experimental result, $s = 6$, favors structure (III). The electron distribution for this structure might be



which is actually analogous to the structure of the π -complex,

$C_2H_5^+$ (91):



Recent work of Abell and Piette (92) provides perhaps the strongest evidence for the formation of π -complex between olefins, e.g., butene-2, and bromine atoms. They succeeded in stabilizing the intermediate and examining its electron-spin resonance spectrum. The identity of 6 hydrogen atoms indicated the symmetry expected in a π -complex.

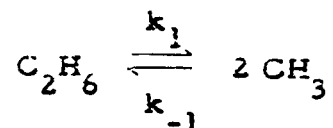
CHAPTER 7

UNIMOLECULAR DECOMPOSITION OF ETHANE

The present chapter includes the calculation of equilibrium constants for reaction (1), the comparison of the values for k_1 observed at higher temperatures and lower pressures with both HKRR and Marcus theories, and finally, a discussion of the proposed structures of the activated complex for ethane decomposition.

I. The equilibrium $C_2H_6 \rightleftharpoons 2CH_3$:

The equilibrium constant of the reactions



can be calculated directly from standard entropy and enthalpy changes according to the equation:

$$K_1 = \frac{k_1}{k_{-1}} = e^{\frac{\Delta S_1^0}{R}} e^{-\frac{\Delta H_1^0}{RT}} \quad [193]$$

Recently Purnell and Quinn (93) have made the detailed calculations of the standard entropies of methyl, ethyl and propyl radicals over the temperature range 200-1000°K. Using their data for the methyl radical, and those for C_2H_6 from elsewhere (45), values of ΔS_1^0 were evaluated and are given in Table 13. ΔH_1^0 is calculated from the following equation:

$$\Delta H_1^{\circ} = \Delta H_1^{\ddagger} - \Delta H_{-1}^{\ddagger} \quad [194]$$

$$= E_1 - E_{-1} + RT \quad [194a]$$

or $\Delta H_1^{\circ} = 85.0 + \frac{3}{2} RT, \quad [195]$

assuming $E_{-1} = 0$

and $E_1 = 85.0 + \frac{1}{2} RT$

Table 13

The equilibrium constant K_1^*

$T^{\circ}K$	$S_{C_2H_6}^{\circ}$ (Gibbs)	$S_{CH_3}^{\circ}$ (Gibbs)	ΔS_1° (Gibbs)	ΔH_1° (kcal/mole)	K_1 (atm)
298.16	54.85	46.43	38.01	85.9	1.8×10^{-55}
500	62.79	51.71	40.63	86.5	1.3×10^{-29}
700	69.93	55.69	41.45	87.1	6.9×10^{-19}
900	76.39	58.99	41.59	87.7	6.2×10^{-13}

* note: standard state: 1 atm of ideal gas.

The rate constant of the reverse reaction in the high-pressure region, k_{-1}^{∞} , can be estimated from the known value of K_1^{∞} , and the equilibrium constant given in Table 13, by

$$k_{-1}^{\infty} = k_1^{\infty} K_1^{-1} = 1.00 \times 10^{16} e^{-86,000/RT} K_1^{-1} \quad [196]$$

$$= 1.00 \times 10^{16} e^{-\Delta S_1^{\circ}/R} \quad [196a]$$

At 900°K, equation [195] leads to

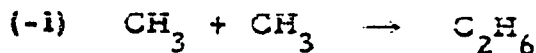
$$k_{-1}^{\infty} = 1.63 \times 10^{12} \text{ cc mole}^{-1} \text{ sec}^{-1},$$

which is about a factor of 3 lower than the accepted value, 2.2×10^{13} cc mole⁻¹ sec⁻¹ (94, 95).

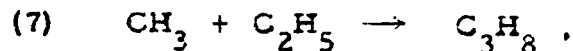
II. Decomposition of ethane in the pressure-dependent region:

The results obtained at high temperatures and low pressures are presented in Figure 9, and the first-order rate coefficients, $k_1 = R_{\text{CH}_4}^{\circ} / 2[\text{C}_2\text{H}_6]$ is given in Table 14. The order of methane formation was about 1.1 at 200 mm and increased to 1.5 at 1 mm. This increase in the order of methane production is ascribed to the pressure-dependence of k_1 . The effect of inert gas on k_1 shown in Figure 42 indicates more clearly the pressure-dependence of the ethane decomposition. In this series of experiments, 3.8 mm of ethane was mixed with various amounts of CO₂ at 685.5°C.

If the termination reactions,



and



were significant at low pressures, the addition of CO₂ would not increase k_1 to its value at an equivalent pressure of pure ethane. In other words, $k_1^{P(3.8 + \text{CO}_2)}$ would be smaller than $k_1^{P_{\text{C}_2\text{H}_6}}$ when $P_{\text{C}_2\text{H}_6} = P(3.8 + \text{CO}_2)$. This can be shown as follows:

$$\frac{R_{-1}}{R_2} = \frac{k_{-1} [\text{CH}_3]}{k_2 [\text{C}_2\text{H}_6]}$$

[197]

Table 14

The first-order rate coefficient, k_1 for unimolecular decomposition
of ethane at high temperatures (640-726°C).

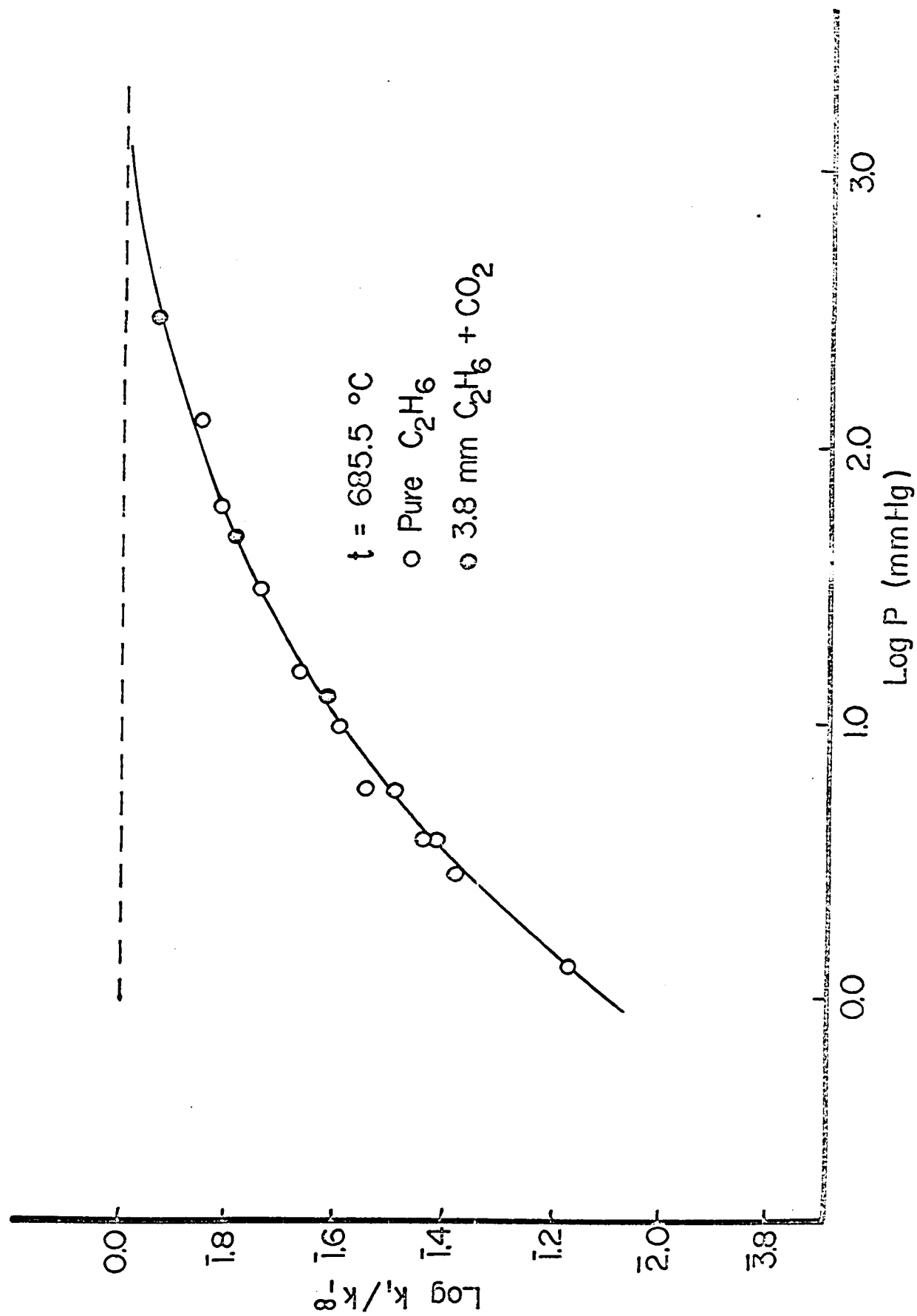
$t^{\circ}\text{C}$	P mm	$R_{\text{CH}_4}^{\circ}$ (mole $\text{cc}^{-1} \text{sec}^{-1}$) $\times 10^{11}$	$k_1(\text{sec}^{-1}) \times 10^5$
640.0	204.6	16.6	2.30
	123.3	9.55	2.21
	91.2	6.60	2.06
	69.2	4.75	1.95
	48.6	2.95	1.73
	36.2	2.10	1.65
	20.7	0.945	1.30
	10.6	0.397	1.07
	5.01	0.150	0.853
	2.55	0.0558	0.623
660.0	145.2	31.2	6.26
	91.1	18.2	5.81
	41.1	6.80	4.81
	20.6	2.56	3.62
	10.7	1.02	2.77
	5.07	0.386	2.22
	2.62	0.139	1.54
	2.62	0.150	1.66
685.5	291.4*	2.73	21.4
	114.6	66.0	17.7
	60.8	33.0	16.2
	47.4*	1.93	15.2
	30.7	13.9	13.5
	15.6	5.96	11.4
	12.4*	1.30	10.3
	9.69	3.20	9.87
	5.62	1.64	8.78
	5.62	1.45	7.72
	3.85	0.920	7.15
	3.77	0.870	6.90
	2.84	0.571	6.02
	1.32	0.164	3.71

704.8	113.0	171	48.6
	50.7	69.2	41.6
	21.5	21.5	30.5
	10.4	8.11	23.7
	5.29	3.15	18.1
	3.18	1.44	13.8
	1.78	0.637	10.9
	1.24	0.405	9.96
	1.03	0.278	8.22
726.0	81.8	282	107
	35.0	90.5	80.6
	20.8	46.0	68.9
	10.8	19.5	56.3
	5.70	8.80	48.1
	4.16	5.03	37.6
	2.61	2.29	27.8
	0.97	0.54	17.2

note: * Total pressure of 3.77 mm ethane + CO₂.

Figure 42.

The inert gas effect on k_1 .



$$\text{and} \quad \frac{R_7}{R_2} = \frac{k_7 [C_2H_5]}{k_2 [C_2H_6]} \quad [10]$$

The substitution of the steady-state concentrations of CH_3 and C_2H_5 in equations [197] and [10] leads to

$$\frac{R_{-1}}{R_2} = \frac{2k_i^2}{K_1 k_2^2 [C_2H_6]} \propto k_1^2 \quad [198]$$

and

$$\frac{R_7}{R_2} = \frac{k_7 \left(\frac{k_1}{k_5} \right)^{1/2}}{k_2 [C_2H_6]^{1/2}} \propto k_1^{1/2} \quad [199]$$

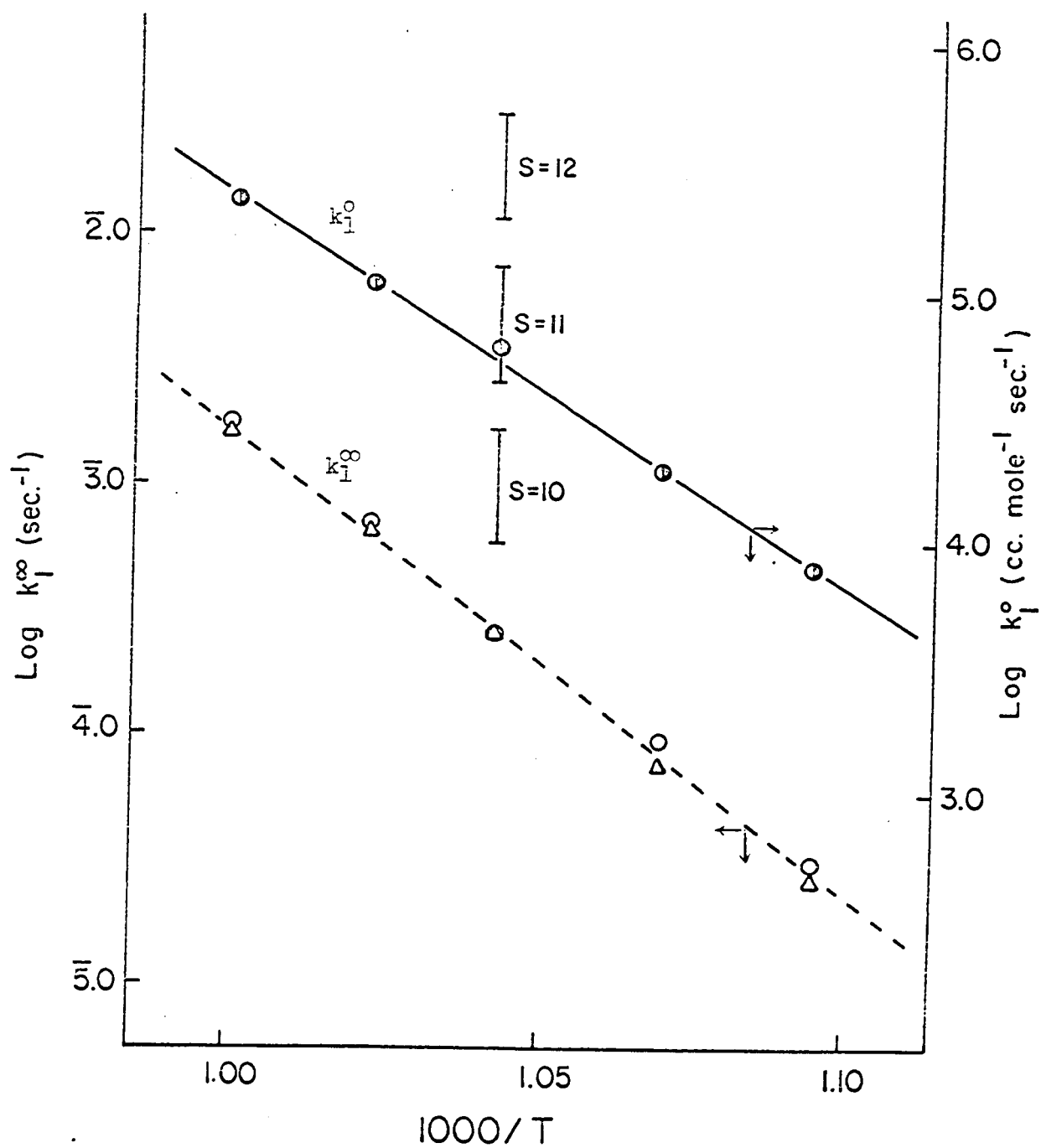
R_{-1} and R_7 would therefore be enhanced at the expense of methane formation by introducing CO_2 if reactions (-1) and (7) were important. The results given in Figure 42 show that these two termination reactions were probably not significant even at pressures as low as 3.8 mm of ethane.

In order to determine k_1^0 and k_1^∞ from these data in the pressure-dependent region, Powell's method of extrapolation was applied. The Arrhenius plots of the extrapolated first-order and second-order rate constants are shown in Figure 43. For k_1^∞ , the results obtained from Lindemann-Hinshelwood extrapolation are also presented on the same graph for comparison. ^{The} Lindemann-Hinshelwood extrapolation is applicable to this case because the extrapolation is short; k_1 in the neighborhood of 150 mm is nearly in the first-order region. Both extrapolations lead to satisfactory agreement with the

Figure 43.

Arrhenius plots of k_1^∞ and k_1^0 .

Dotted line calculated from $k_1^\infty = 1.00 \times 10^{16} e^{-86,000/RT} \text{ sec}^{-1}$.



Δ ----- From Lindemann extrapolation

$\circ, \bullet$ --- From Powell extrapolation

values calculated from the expression,

$$k_1^\infty = 1.00 \times 10^{16} e^{-86,000/RT},$$

obtained at lower temperatures. The Arrhenius plot of the second-order rate constants gives rise to

$$k_1^0 = 1.82 \times 10^{21} e^{-72,500 \pm 2,000/RT} \text{ cc mole}^{-1} \text{ sec}^{-1}, \quad [200]$$

which coincides with the value of k_1^0 calculated from equation [201],

$$k_1^0 = Z \left(\frac{E_1^\infty}{RT} \right)^{s-1} \frac{1}{(s-1)!} e^{-E_1^\infty/RT}, \quad [201]$$

with $\sigma = 3.3 \text{ \AA}$ and $s = 11$.

The double-logarithmic plot of k_1/k_1^∞ vs. $k_1/k_1^0 [M]$ is shown in Figure 44, in which the experimental points are compared with the theoretical Powell curve with $z' = 6$.

Using $\sigma = 3.3 \text{ \AA}$, $A_1^\infty = 1.00 \times 10^{16} \text{ sec}^{-1}$, and $E_1^\infty = 86.0 \text{ kcal mole}^{-1}$, Kassel curves were evaluated using an IBM-650 computer, and compared with the experimental data in Table 14. The results are presented in Figure 45. The theoretical curves with $s = 13$ fit roughly with the experimental points at high temperatures. On the same graph, Dexter and Trenwith's (96) results at 567°C are also presented for comparison. Their k_1^∞ is slightly lower than our value at the same temperature. The Kassel curve with $s = 13$ is seen to be reasonably parallel with their points except those at the lowest pressure, although the values of which they reported were as high as 15 or 16.

The difference between $s = 11$ obtained from equation [201] and $s = 13$ from the direct comparison of Kassel curves with k_1 might

Figure 44.

Double-logarithmic plot of k_1/k_1^∞ vs. $k_1/k_1^0 [M]$.

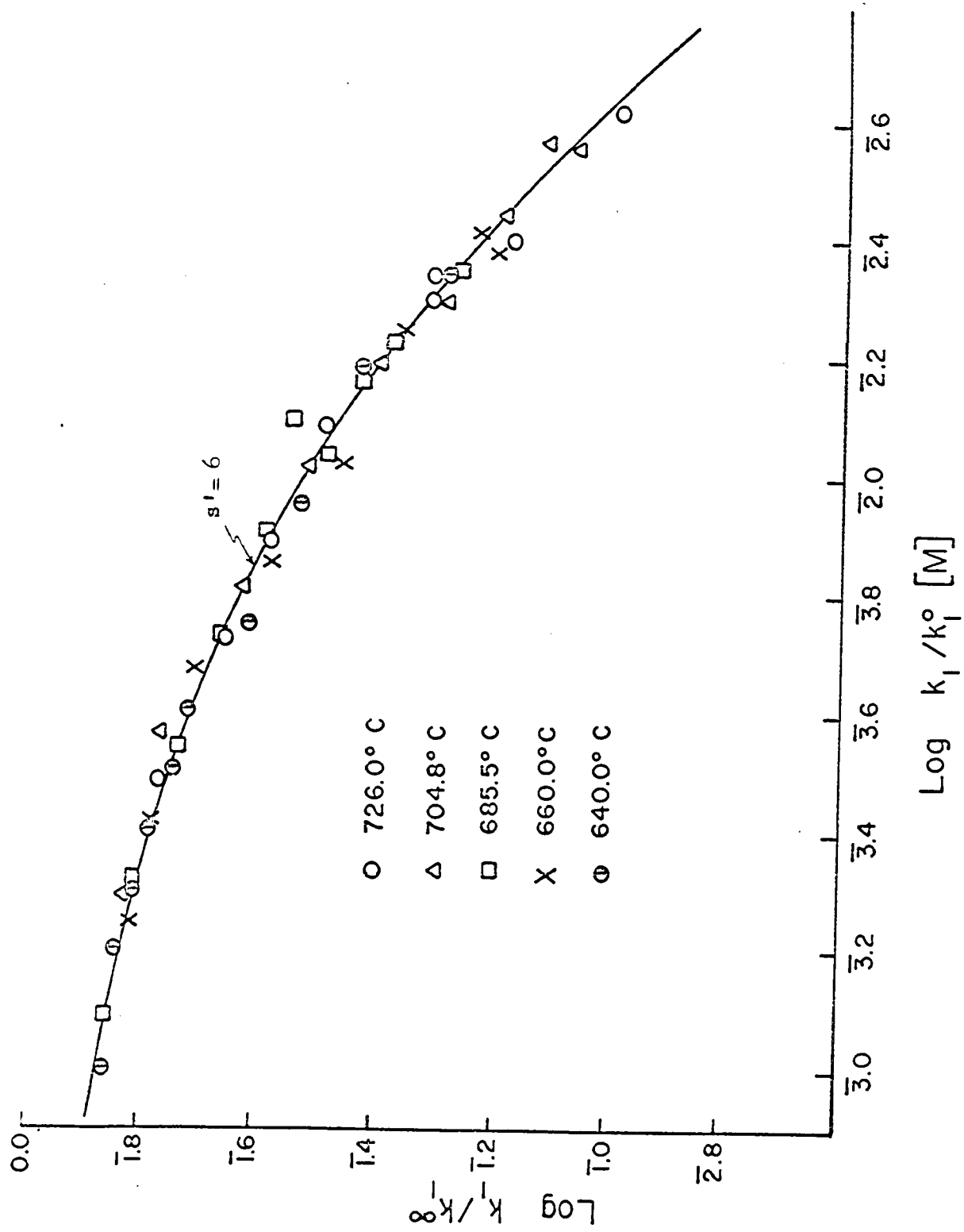


Figure 45.

Comparison of the experimental results with
HKRR theory for ethane decomposition.

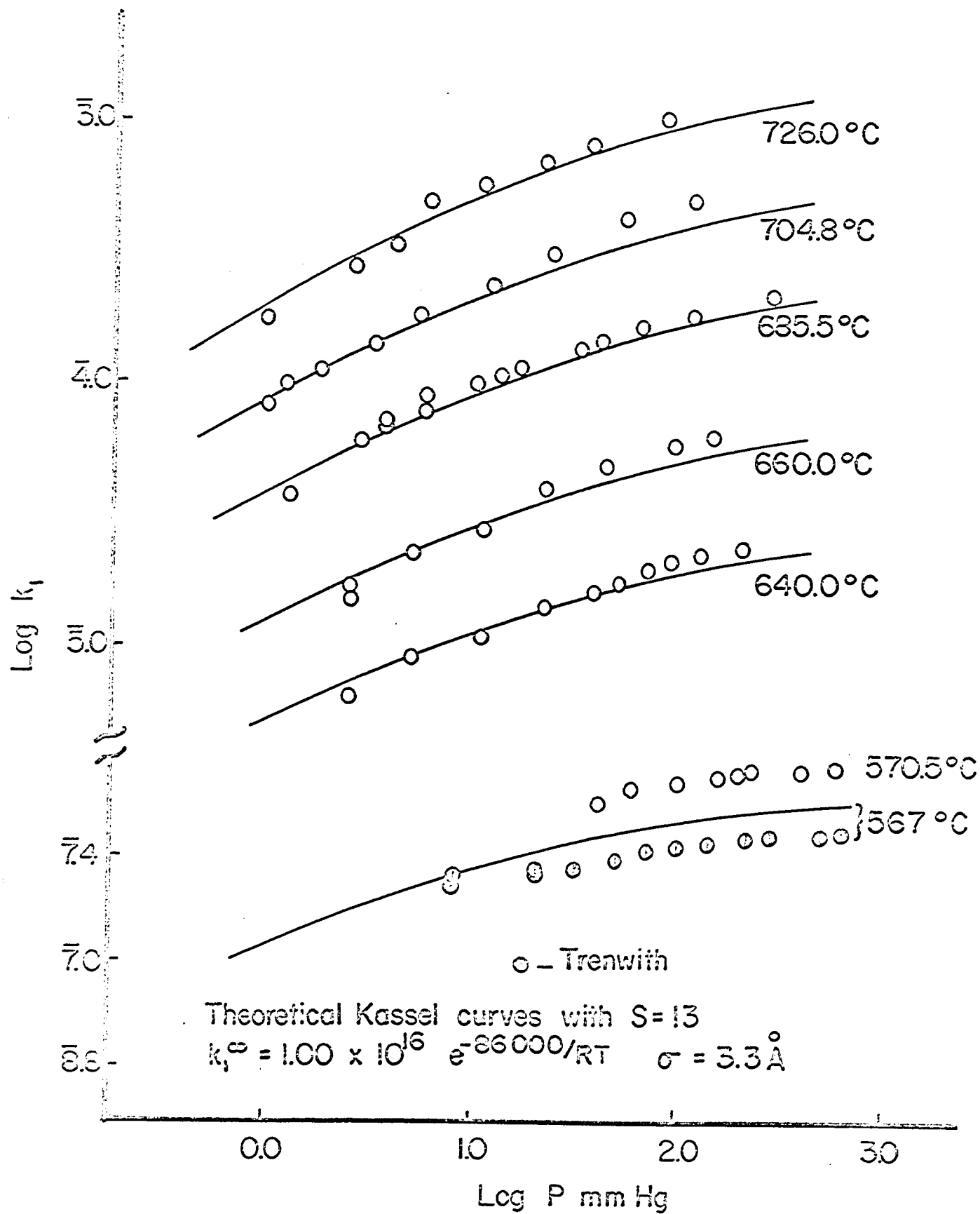
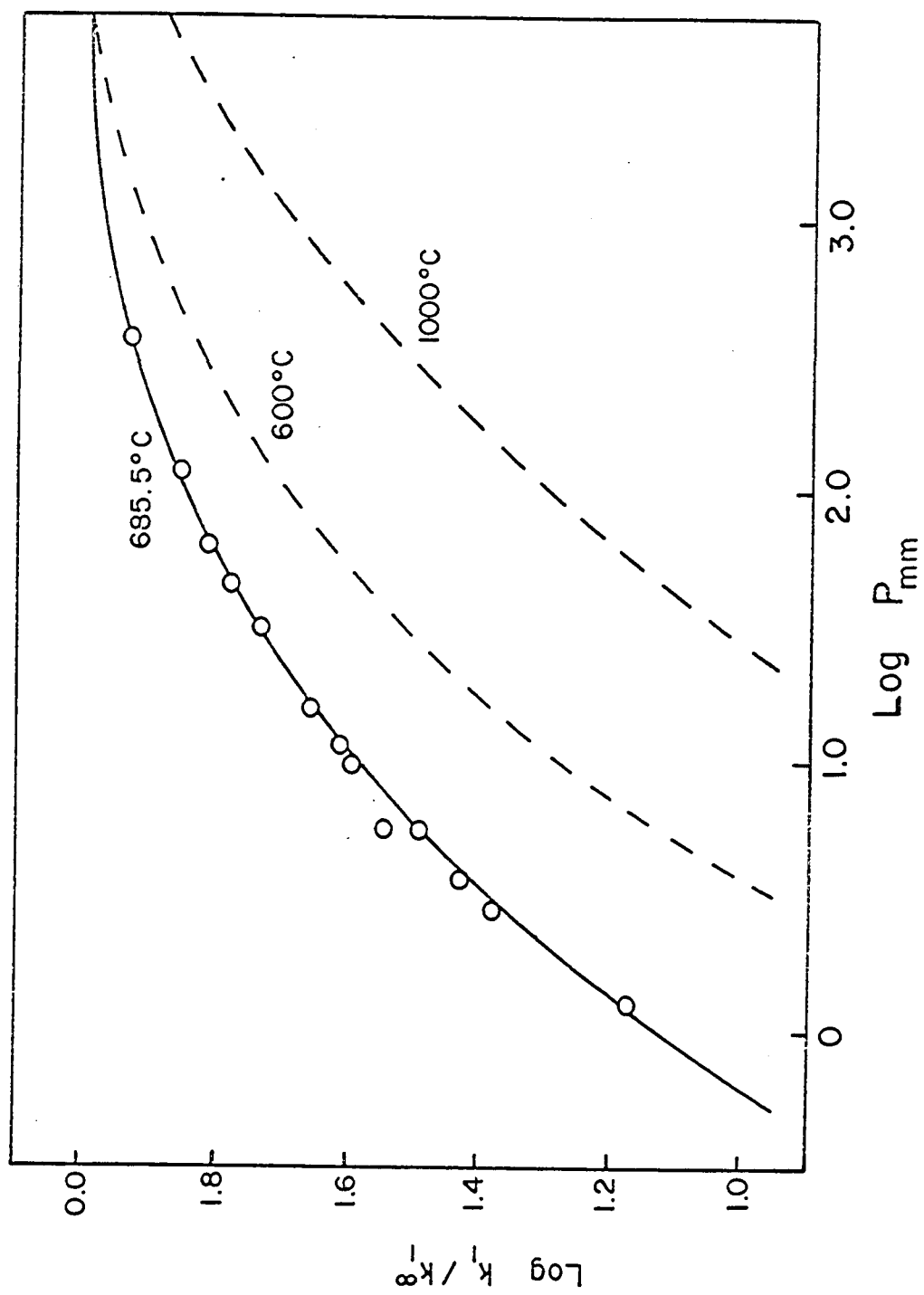


Figure 46.

Comparison of the experimental results with
Marcus theory for ethane decomposition.

Dotted lines are those of Rabinovitch and Setser
evaluated according to Marcus theory.



be due to the crudeness of HKRR theory, which is known to be inapplicable to reactions with high-frequency factors, as discussed in chapter 5.

Recently Rabinovitch and Setser (71) evaluated the theoretical curves of $\log k_1/k_1^\infty$ vs. $\log P$ at 600 and 1000°C according to the Marcus theory. They considered the activated complex to be completely loose. The detail of the model of this "loose" complex is discussed in the next section. Assuming $E_1^\infty = 85.3 \text{ kcal mole}^{-1}$, they obtained,

$$k_1^\infty(600^\circ\text{C}) = 1.0 \times 10^{17} e^{-85,300/RT} \quad [202]$$

and $k_1^\infty(1000^\circ\text{C}) = 1.3 \times 10^{17} e^{-85,300/RT} \quad [203]$

Combining these two equations with [164], they obtained two fall-off curves for those two temperatures as shown in Figure 46. The present results at 685.5°C are also included in the same graph. The calculated value of k_1/k_1^∞ decreases much faster than the observed one. This may be due to the rather high frequency factors they employed.

The activation energy in the pressure-dependent region can be obtained by plotting $\log k_1$ vs. $1/T$ for each concentration of ethane. The results are given in Table 15, in which the activation energies evaluated from Kassel curves with $s = 13$ by the same method are also given. The observed values may be subject to an error of $\pm 1 \text{ kcal mole}^{-1}$.

Table 15

E_1 in the pressure-dependent region

P mm Hg	E_1 (kcal/mole)	
	obs.	calc. (HKRR)
0	72.5	-
2.0	82.4	79.9
6.3	83.5	81.0
20.0	84.3	83.2
63.0	84.6	83.9
100.0	84.9	84.4
200.0	85.4	84.4
∞	86.0	(86.0)

III. The structure of the activated complex and the theoretical evaluation of the high-pressure frequency factor:

In order to account for the high frequency factors associated with both the ethane decomposition and the combination of methyl radicals, the "loose" activated complex of Gorin (47) has been postulated by a number of authors (70, 71, 77, 98, 99, 100). According to this model the separation of the centers of the radicals in the activated state is so large that the vibrational and rotational degrees of freedom may be assumed to be the same as in the free radicals themselves. The radicals attract each other at large distances chiefly by means of polarization forces, and this is opposed by the centrifugal force of the rotation of the two radicals about the center of mass of the complex. The superposition of these two forces gives rise to a slight energy barrier, the top of which corresponds to the activated complex. The detailed treatment of this model has been given by

Glasstone et al. (38). Using the data then available for the polarizability and ionization potential of the methyl radicals, at 873°K they obtained

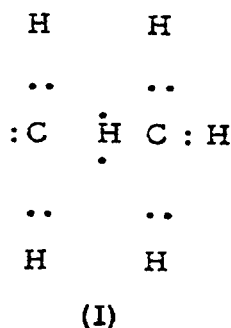
$$k_{-1}^{\infty} = 1.2 \times 10^{13} \kappa_1 \text{ cc mole}^{-1} \text{ sec}^{-1}.$$

Recalculating of this quantity of 400°K using recent data, Ree et al. obtained (100):

$$k_{-1}^{\infty} = 4.8 \times 10^{13} \kappa_1 \text{ cc mole}^{-1} \text{ sec}^{-1},$$

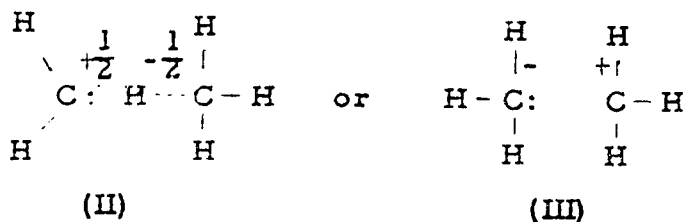
which corresponds to $\Delta S_1^{\ddagger} = 18.6$ gibbs(standard state: 1 mole cc⁻¹), the present results give a value of $\Delta S_1^{\ddagger} = 12.2$ gibbs.

Recently O.K. Rice (98) suggested a model of three-center bonds which might be formed on any hydrogen atom, giving a structure such as



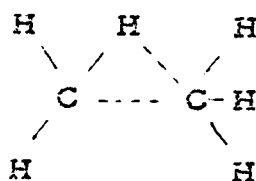
which would have some stability. Such a structure would be expected to have considerably loosened bending vibrations.

Benson (101) modified this model by proposing partial ionic bonding



It was suggested that the high frequency factor of both the forward and backward reactions was due to the rocking motions of these complexes. Since two methyl radicals have equal electronegativity, the formation of the ionic complex might require a higher energy than the ordinary homolytic one.

In order to explain the 9 effective modes of vibration estimated by Gill and Laidler (17) from Dodd and Steacie's results for the combination methyl radicals, Laidler and Wojciechowski (73) proposed an activated complex of " C_s " symmetry,



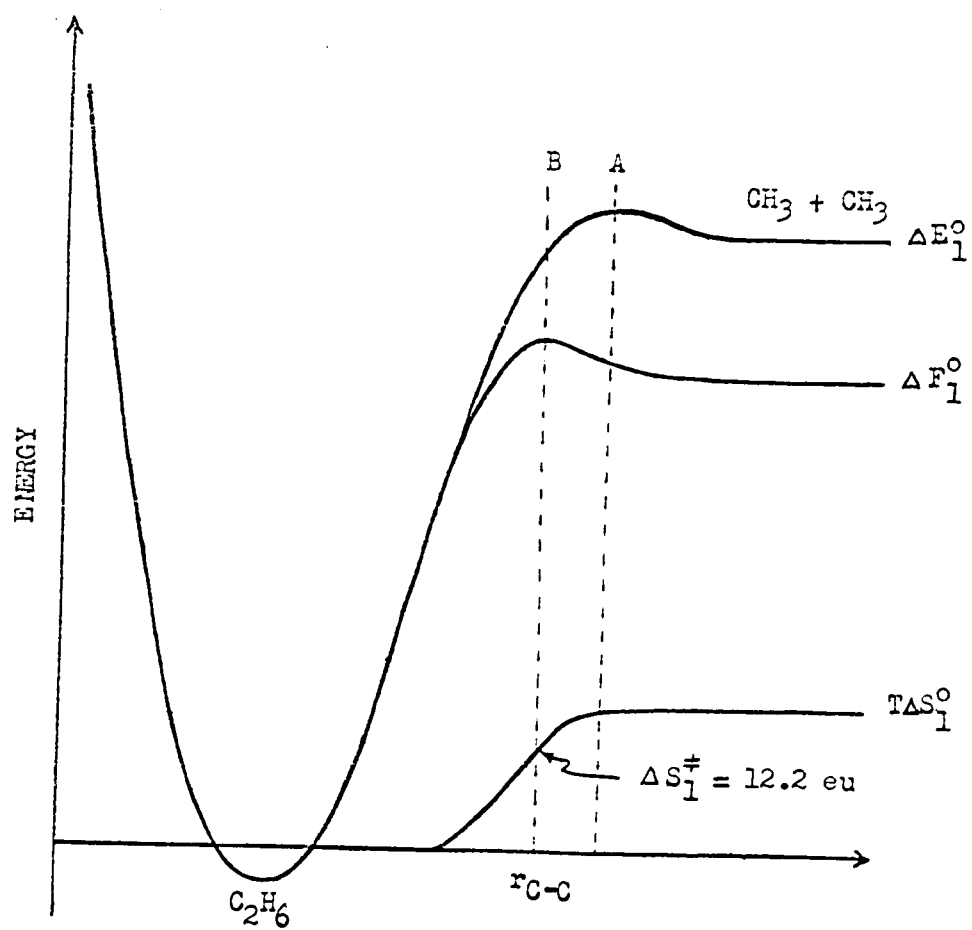
(IV)

This complex possesses 11 totally symmetric modes of vibration, which agrees with the value of $s = 11$ or 13 observed experimentally. The high frequency factor of the reaction was accounted for by the softened torsional, rocking and bending motions without considering the free rotations of the methyl radicals (39). The difference between complex (IV) and Corin's or Rice's "loose" complex can be seen in a schematic energy diagram shown in Figure 47. The activated state of the completely "loose" complex may have the configuration corresponding to the dotted line A. As mentioned previously, the activated complex occurs at the maximum of the potential energy curve. $\Delta S_1^\ddagger$ associated with this complex is 18.6 gibbs which is approximately the entropy of reaction, ΔS_1^0 . Owing to the disappearance of free

Figure 47.

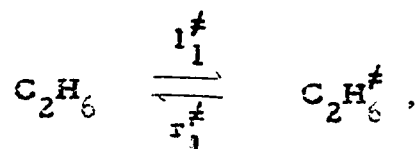
Hypothetical energy curves for ethane decomposition.

Line A corresponds to the configuration of Gorin's "loose" complex and Line B, that of Laidler-Wojciechowski's three-centered complex.



rotations, the complex (IV) may possess smaller entropy, and thus a lower value of $\Delta S_1^\ddagger$; experimentally we found $\Delta S_1^\ddagger = 12.2$ gibbs, which might be associated with this structure. Complex (IV) might therefore be the true activated complex in terms of $\Delta F_1^\ddagger$, the quantity that actually determines the rate of the reaction (102).

The pre-exponential factor of the high-pressure high-order rate constant for the ethane decomposition,



can be estimated from absolute rate theory according to the following equation,

$$A_1^\infty = \kappa_1 l_1^\ddagger \frac{ekT}{h} \frac{F_{\text{rot}}^\ddagger F_{\text{vib}}^\ddagger F_{\text{int}}^\ddagger}{F_{\text{rot}} F_{\text{vib}}}, \quad [204]$$

where $F^\ddagger$ and F stand for the partition functions of the activated complex and the reacting molecule, respectively. To evaluate A_1^∞ , one has to assign the vibrational frequencies and the C-C distance for the activated complex. κ_1 is usually taken to be unity and $l_1^\ddagger$ is always unity regardless of the model of the activated complex. Although the estimation of these quantities is only qualitative, it provides some ideas about the structure of the complex. In the following sections the frequency factor is calculated for three types of activated complex - rigid, semirigid and loose. Rabinovitch and Setser's data given in Table 16 were used for all calculations (71).

Table 16

Vibrational frequencies and moments of inertia of ethane and the activated complexes.

	Molecule	Activated Complex			
		Rigid	Semirigid(a)	Semirigid(b)	Loose
Frequency(cm^{-1})	2960(6)	2960(6)	2960(6)	2960(6)	3023(6)
	1436(6)	1436(6)	1436(6)	1436(6)	1420(4)
	1190(2)	1190(2)	595(2)	238(2)	950(2)
	993(1)				
	822(2)	822(2)	410(2)	164(2)	Free rotors (5)
	350(1)	350(1)	Free rotor(1)	Free rotor(1)	
$r_{\text{C-C}}^{\text{O}}$ (Å)	1.543	1.7	2.7	2.7	4.5
moment of Inertia $\times 10^{40}$ (g-cm^2)					
I_z	10.8	10.8	10.8	10.8	11.7
I_x, I_y	42.2	50.7	103.3	103.3	258.6
I_r	-	-	2.7	2.7	2.92

1. Rigid complex:

The activated complex has the structure of the ethane molecule with the C-C bond length increased by $\sim 10\%$ and one of the vibrational degrees of freedom transformed into a fourth translational degree of freedom which leads to the decomposition. There is no internal rotation because of its rigidity. According to this model, equation [204] reduces to

$$A_1^{\infty}(\text{rigid}) = \frac{ekT}{h} \left(\frac{I_x^{\neq} I_y^{\neq} I_z^{\neq}}{I_x I_y I_z} \right)^{1/2} (1 - e^{-h\nu/kT}) \quad [205]$$

where ν is the frequency of C-C stretch of the ethane molecule, and I represents a moment of inertia. Substituting the data given in Table 16, gives at 900°K

$$A_1^\infty (\text{rigid}) = 4.87 \times 10^{13} \text{ sec}^{-1},$$

which is much lower than the experimental value.

2. Semirigid complex:

The deformation vibrations such as bending and rocking of the activated complex are assumed to be "softened" on account of the elongation of the C-C bond. In the first semirigid complex (a), these frequencies are assumed to be reduced by 50%, whereas in the second semirigid complex (b), these frequencies are decreased by 30%. Because of the extension of the C-C bond, the internal rotational barrier disappears completely; two methyl groups can therefore rotate freely about the C-C axis. The partition function of the internal rotation is given by (103):

$$F_{\text{int}} = \frac{(8\pi^3 I_r kT)^{1/2}}{nh} \quad [206]$$

$$= 2.7935 \frac{(I_r T 10^{33})^{1/2}}{n} \quad [206a]$$

where $n = 3$, the number of indistinguishable positions, and I_r is the reduced moment of inertia of methyl groups rotating about the figure axis. For this model, we have

$$A_1^\infty (\text{semirigid}) = \frac{ekT}{h} \left(\frac{I_x^\# I_y^\# I_z^\#}{I_x I_y I_z} \right)^{1/2} F_{\text{int}}^\# \frac{\prod_{i=1}^{16} (1 - e^{-h\nu_i^\# / kT})^{-1}}{\prod_{i=1}^{18} (1 - e^{-h\nu_i / kT})^{-1}} \quad [207]$$

Applying the data given in Table 16, at 900°K we have

$$A_1^\infty (\text{semirigid a}) = 8.84 \times 10^{14},$$

and $A_1^\infty (\text{semirigid b}) = 1.36 \times 10^{16} \text{ sec}^{-1}.$

3. Loose complex:

This model is slightly different from that of Gorin for the association of methyl radicals. The over-all rotations are assumed to be adiabatic, and five rotations (four methyl tumblings and one internal rotation) and 12 vibrations of two methyl radicals are active. According to this model, equation [204] becomes

$$A_1^\infty(\text{loose}) = \frac{ekT}{h} \left(\frac{I_x^\# I_y^\# I_z^\#}{I_x I_y I_z} \right)^{1/2} F_{\text{int}}^\# f_{\text{rot}}^\# \frac{\frac{12}{11} (1 - e^{-h\nu_i^\#/kT})^{-1}}{\frac{18}{11} (1 - e^{-h\nu_i/kT})^{-1}} \quad [208]$$

where

$$f_{\text{rot}}^\# = \left(\frac{8\pi^2 I_{\text{CH}_3} kT}{h^2} \right)^2 \quad [209]$$

represents the rotational partition function of two methyl radicals in the activated complex; I_{CH_3} is the moment of inertia of the methyl radical about its own axis, which also has a value of $2.92 \times 10^{-40} \text{ g-cm}^2$ (71).

Applying the data given in Table 16 at 900°K , we find

$$A_1^\infty(\text{loose}) = 1.11 \times 10^{18} \text{ sec}^{-1},$$

which is about a factor of 100 higher than the experimental value.

Using the same data Rabinovitch and Setser obtained a value of

$$A_1^\infty(\text{loose}) = 1.0 \times 10^{17} \text{ sec}^{-1}$$

This deviation is probably due to the ratio of symmetry numbers

$$\frac{\sigma_{\text{C}_2\text{H}_6}}{\sigma^\#} = \frac{\sigma_{\text{C}_2\text{H}_6}}{\sigma_{\text{CH}_3}^2 \sigma_{\text{C}_2\text{H}_6}^\#} = \frac{6}{6 \times 6 \times 2} = \frac{1}{12},$$

where $\sigma_{C_2H_6}$, σ_{CH_3} and $\sigma_{C_2H_5^\ddagger}$ are the symmetry numbers of ethane, methyl, and the activated complex as a whole, respectively. In the present calculation, the ratio $1/12$ has been replaced by $1_1^\ddagger = 1$.

These calculations show that the high frequency factor of a unimolecular reaction can be explained by assuming the softening of the vibrational frequencies as proposed by Steel and Laidler (39) without introducing free rotations of the separating groups. However, the question arises as to whether those vibrational degrees of freedom can still exist even if the frequencies associated with them are reduced to only 20% of their original values.

CLAIMS TO ORIGINAL RESEARCH

The pyrolysis of ethane was reinvestigated at 10 temperatures ranging from 550 to 720°C and pressures between 1 and 600 mm. The kinetics of the formation of hydrogen, methane, butane and butene-1 have been studied in full detail.

1. The initial split of ethane was found to be first-order above 200 mm. The C-C bond dissociation energy, $D(\text{CH}_3 - \text{CH}_3) = 85.0 \text{ kcal mole}^{-1}$, was determined directly from the kinetics of methane production in the high-pressure region.
2. The comparison of the experimental results for the unimolecular decomposition of ethane in the pressure-dependent region with HKRR theory led to a value of $s = 11$ or 13 for the effective number of oscillators.
3. The decomposition of the ethyl radical was measured^{from} the formation of hydrogen and butane; the pressure-dependence of this reaction was confirmed. A three-centered activated complex was proposed to account for the effective number of oscillators, $s = 6$, obtained from the present study.
4. The application of Powell's method of extrapolation led to activation energies of 72.5 and 32.4 kcal mole⁻¹ for the decomposition of ethane and the ethyl radical, respectively, in the second-order region.
5. The unimolecular decompositions of both ethane and^{the} ethyl radical were found to be independent of surface/volume ratio. The surface effect on the over-all reaction was shown to be associated with the chain-termination step.

6. Various methods were used to extrapolate to obtain the initial rates of primary reactions. Mechanisms of secondary reactions involving hydrogen, methane, butane and butene-1 were proposed to account for their formation at high conversions.
7. The Rice-Herzfeld mechanism of the hydrogen-ethylene reaction was found to be inapplicable. A new mechanism, which accounted satisfactorily for both the over-all order and the activation energy of the reaction, was proposed.

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