THE DECOMPOSITION OF BUTYL ACETATES
OVER CHARCOAL CATALYST

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by

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A Thesis
Submitted to the School of Graduate Studies
in Partial Fulfilment of the Requirements
for the Degree
Doctor of Philosophy

McMaster University
December, 1970

DOCTOR OF PHILOSOPHY (1971)
(Chemical Engineering)

McMASTER UNIVERSITY
Hamilton, Ontario

TITLE: The Decomposition of Butyl Acetates Over Charcoal Catalyst

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SUPERVISOR: Professor R. B. Anderson

NUMBER OF PAGES: xii, 179

SCOPE AND CONTENTS:

This thesis presents an experimental study of the decomposition of the four isomers of butyl acetate over charcoal catalyst in a fixed bed reactor. The research attempts to determine the kinetics and mechanism of butyl acetate decomposition over a high surface area, non-selective catalyst, and to compare the catalyzed reactions of butyl acetates with their gas-phase reactions. When interpreting the experimental kinetic data it is hypothesized that each of the butyl acetates follows the same mechanism when reacting on charcoal. The best theoretical equation for expressing the rate of butyl acetate reaction was selected from the Langmuir-Hinshelwood equations.

ACKNOWLEDGEMENTS

The author would like to acknowledge his gratitude to those people who contributed special assistance to this work.

I would like to thank Dr. W. W. Smeltzer of the Metallurgy Department, Dr. J. Warkentin of the Chemistry Department, and Dr. A. E. Hamielec and Dr. C. M. Crowe of the Chemical Engineering Department for their helpful discussions during the course of this work.

I am especially grateful to Dr. Robert B. Anderson, my research supervisor, for his guidance and for his patience.

Finally, I would like to thank my wife, Helen, for her assistance and constant encouragement.

Financial Acknowledgement:

The author is pleased to acknowledge scholarship funds from the National Research Council of Canada, Apparatus and operating expenses were obtained from a grant from the Petroleum Research Fund, administered by the Americah Chemical Society.

P. J. Pettit

Hamilton, December, 1970

P. J. Pettit

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CHAPTER 1

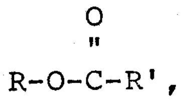
INTRODUCTION

This chapter provides basic information about the reagents, the catalyst, and the approach used in this study.

1.1 INTRODUCTION TO THE REACTION

1.1.1 The Reagents and Products

The structures of the four isomers of butyl acetate, iso, normal, secondary, and tertiary-butyl acetate, are given in Figure (1-1), which shows the structural formula for each isomer as well as a detailed schematic of the sec-butyl acetate structure. Butyl acetates are organic esters since they have the general structure



$$R{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R',$$

where R and R' represent organic molecular groups. In butyl acetates the butyl carbon atom which is attached to the acetyl group is called the α-carbon atom, and carbon atoms neighbouring the α-carbon are known as β-carbons. Hydrogen atoms attached to α or β-carbon atoms are called, respectively, α or β-hydrogens. Examples of α and β atoms are shown in the sec-butyl acetate schematic in Figure (1-1).

In the gas phase, a butyl acetate molecule can undergo an intramolecular elimination reaction in which the ester

FIGURE (1-1) STRUCTURES OF BUTYL ACETATES, BUTENES, AND ACETIC ACID

$CH_3CO_2CH_2CH(CH_3)_2$

ISO-BUTYL ACETATE

$CH_3CO_2(CH_2)_2C_2H_5$

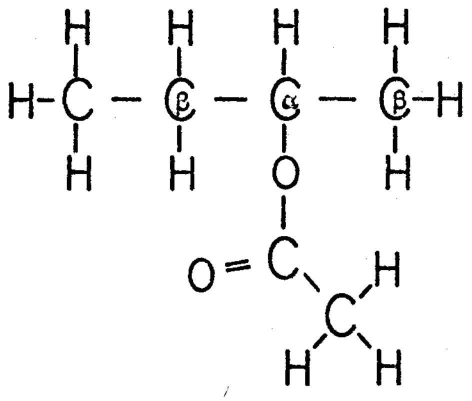
N-BUTYL ACETATE

$CH_3CO_2CH(CH_3)C_2H_5$

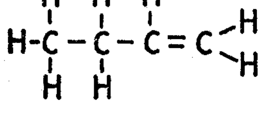
SEC-BUTYL ACETATE

$CH_3CO_2C(CH_3)_3$

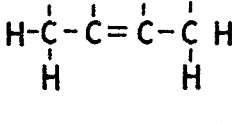
TERT-BUTYL ACETATE



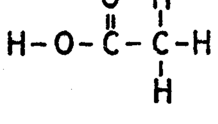
SEC-BUTYL ACETATE



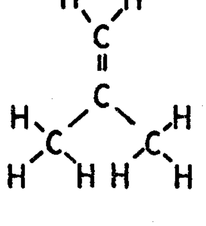
I-BUTENE



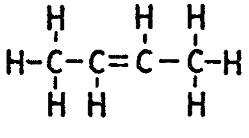
CIS-2-BUTENE



ACETIC ACID



ISO-BUTENE



TRANS-2-BUTENE

decomposes to acetic acid and butene. During such a reaction the butyl group loses both the acetate part and a β-hydrogen atom. Different butenes can result from the reaction, depending on the butyl acetate isomer which decomposes. For example, the reaction of sec-butyl acetate can produce all three straight chain butene isomers. The four isomers of butene are depicted in Figure (1-1).

1.1.2 Charcoal

Charcoal is a microcrystalline or amorphous form of carbon which is porous and has a high surface area. Some charcoals made by charring and steam activating coconut shells have a rather narrow micropore size distribution(1), with an average pore diameter of about 20 Å, sufficiently large to accommodate butyl acetate molecules. Coconut shell charcoals have surface areas ranging from about 1000 to 1600 m^2/gram, and these large surfaces readily adsorb most molecules(2,3). Charcoal is an active, non-selective catalyst for hydrocarbon cracking(4,19). Charcoal may also facilitate the decomposition of butyl acetates; adsorption of an ester by the charcoal may concentrate the reactant and/or may orient the adsorbed molecules in some way which is advantageous for their reaction; or, adsorption of the ester by the charcoal may otherwise facilitate the reaction.

1.1.3 Purposes

This research attempts to determine the interaction between charcoal and reactant in the heterogeneous decomposition of butyl acetates. The isomers of butyl acetate are convenient organic molecules to use as indicators of the catalyst-reactant interaction; the type of reaction these esters undergo is limited, at least in the gas phase, and yet, the isomers of butyl acetate are sufficiently complex that rates and products of their heterogeneous decomposition may give clues to the reaction mechanism. For example, sec-butyl acetate has two different β-carbon atoms, and the butenes produced from this isomer may reveal valuable clues about the reaction mechanism. Charcoal is a highly porous, non-selective cracking catalyst for hydrocarbons. It is possible that a direct comparison can be made between the catalyzed butyl acetate reactions and the simple, first order gas-phase reactions of the esters. The knowledge gained from studying the butyl acetate-charcoal system can possibly be applied elsewhere.

1.2 THE APPROACH TO THE PROBLEM

The problem involves studying the rate and products of the decomposition of each of the four butyl acetates over charcoal catalyst. The study should determine the kinetics of the reactions, namely the "best" rate equation and the "best" values of the rate constants, activation energies, and adsorption constants. Comparison of the kinetics and products of the catalyzed and gas-phase decompositions of butyl acetates may provide clues to the function of charcoal catalyst. The heterogeneous reactions should be studied over "pure" charcoal in an integral or fixed bed reactor. Integral reactors are simple to construct and use, and the mathematics for handling integral data are fairly well established. Diffusional effects on the catalyzed reaction must be either accounted for mathematically or eliminated by using suitable reactant flows and catalyst particle size. Suitable rate equations and the best values of constants in such equations should be determined by statistical methods.

1.3 THE LITERATURE REVIEW

A search of the Chemical Abstracts revealed no reports of research on the decomposition of butyl acetates over charcoal catalyst. A review was made of theories and published experimental results relative to this thesis. The topics of the literature review are conveniently divided into three classes: (a) the decomposition of butyl acetates and other esters in the gas phase, (b) carbon as a catalyst, and (c) other topics related to the research, such as experimental techniques. Each of these subjects is discussed separately below.

1.3.1 Decomposition of Esters

The gas-phase reactions of esters have been the subject of a considerable amount of research, and the pyrolysis of butyl acetates has been studied to a moderate extent(5-11). Butyl acetates decompose thermally to butenes and acetic acid following first order kinetics(6,7), and have activation energies in the range of 40 to 42 kcal/mole and pre-exponential factors of about 10^{12} sec.$^{-1}$(14). Entropies of activation of butyl acetates are negative(14), indicating that the reacting molecules are constrained in the activated state. In general, the rates of reaction of esters increase considerably as the number of alkyl groups attached to the α-carbon atoms becomes higher, but the effect on the rate is small when the β-carbon is alkylated(7). The structure of the acid part of the ester molecule also has some influence on the reaction rate(12,13).

The elimination reaction of butyl acetates are "clean", producing principally acetic acid and butenes; however, for the thermal decomposition of iso-butyl acetates at temperatures above 500°C, Hurd and Blunck(8) obtained small amounts of methane and carbon monoxide in addition to butene and acetic acid. When any butyl acetate decomposes thermally, the butenes produced are approximately those which could be expected if, during reaction, β-hydrogen atoms are eliminated at random; for example, for the pyrolysis of sec-butyl acetate(7,9-11) the ratio of the 2-butenes to 1-butene produced was about 0.75, compared to the ratio of 2/3 = .67 calculated on the basis of the number of β-hydrogens available for reaction. The ratio of cis/trans-2-butene is approximately 1/2.

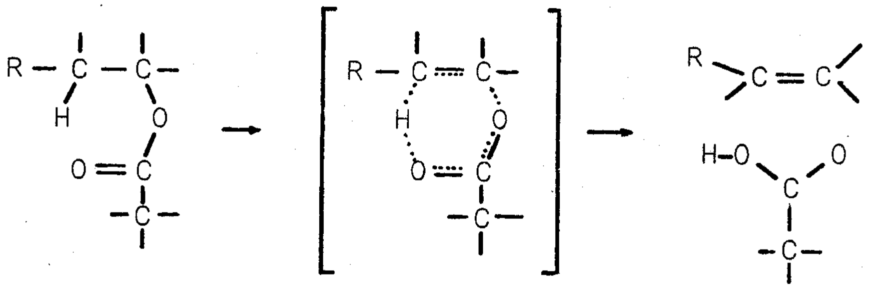
Various mechanisms have been proposed for the intramolecular elimination reactions of butyl acetates. In 1938 Hurd and Blunck(8) postulated that the reaction involves intramolecular rearrangement to form a cyclic, six-membered, covalent bonded, activated complex which then decomposes by concerted rupture of the α-C-O and β-C-H bonds. This mechanism is depicted in Figure (1-2). The concerted reaction scheme is compatible with the observed order of reaction, negative entropy of activation, and products formed when butyl acetates decompose. By calculating the entropy decrease resulting from cyclic transition states, O'Neal and Benson(14) were able to predict with remarkable success the gas-phase Arrhenius A factors for several ester decompositions. Some claims have been made,however, that the concerted mechanism does not provide a satisfactory explanation of the significance of the structure of the acid group or the effect of substituents on the β-carbon atom. Maccoll(49) suggested that the unimolecular elimination reactions of esters proceed by an ionic mechanism as shown in Figure (1-2-b), and Scheer et al.(7) proposed the revised ionic scheme depicted in Figure (1-2-c). Each of these postulated mechanisms for ester decomposition involves the notion of a cyclic intermediate.

1.3.2 Catalysis by Charcoal

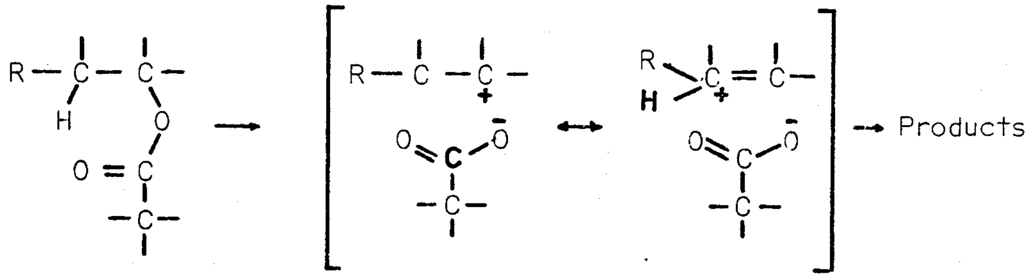
Charcoal catalysts are known to catalyze a wide variety of chemical reactions including oxidation-reduction, polymeri-

Figure (I-2)

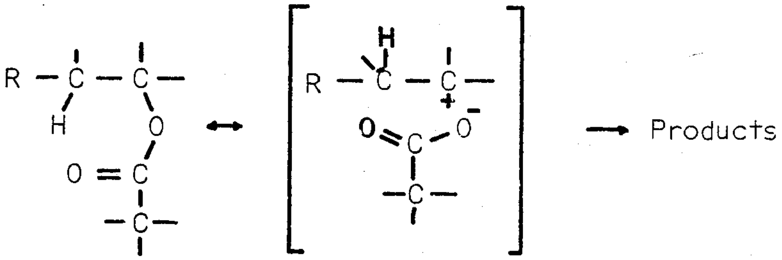
Some Mechanisms Proposed for the Butyl Acetate Decomposition



a, Concerted Mechanism



b, Simple Ionic Mechanism



c, Revised Ionic Mechanism

zation, and hydrocarbon cracking reactions. Nevertheless, catalysis by charcoal and other forms of carbon has not been studied thoroughly, and the reason is probably that better catalysts than carbon exist for most reactions. Some theoreticians have attributed the activity of carbon in diverse reactions to the simultaneous existence of a variety of surface oxide groups, some of which are weak acids and others weak bases. For charcoal, the numbers of acidic and basic surface oxide groups, as well as the concentration of free radicals, depend on the entire history of the catalyst(17).

Unfortunately, only a few studies have successfully revealed the chemical nature of reaction mechanisms on carbon catalysts. For example, Turkevich and LaRoche(18) used electron spin resonance spectroscopy to show that the rate of the ortho-para hydrogen reaction on charcoal was proportional to the concentration of free radicals in the catalyst. In 1949 Voge et. al.(19) reported that charcoal is an active catalyst for hydrocarbon cracking. For example, cetane ($C_{16}H_{34}$) decomposes over charcoal at a rate "at least 50 times the thermal rate"(19) and produces a rather even distribution of saturated, straight-chain cracked products from C_1 to C_{15}. In comparison, C_1, C_2 and C_3 hydrocarbons are the preferential products from the thermal decomposition of cetane, which proceeds by a free-radical chain mechanism(20). Voge et. al. postulated that the cracking of hydrocarbons over charcoal also involves a free-radical intermediate, but that chemisorbed hydrogen interrupts the life of the radical and results in preferential cracking of high molecular weight alkanes.

1.3.3 Topics Related to the Research

Some information was gathered about methods and theories which could be useful in obtaining experimental data or analyzing results. For example, it was found that several researchers(21,22,23) have determined the heats of adsorption of some gases on solids by using gas-solid chromatography. This method of determining heat of adsorption can sometimes be applied to reactant-catalyst systems(24).

Several mathematical methods have been suggested for analyzing kinetic data when catalyst deactivation occurs. Many of these methods propose referring catalytic activities to some standard: unfouled or unpoisoned catalyst, for example. For catalysts which deactivate by fouling, Froment and Bischoff(25,26) have been able to predict the time dependence of conversion for some fairly complex reaction mechanisms.

CHAPTER 2

THE APPARATUS AND REAGENTS

2.1 APPARATUS

A flow diagram of the apparatus used for studying butyl acetate decomposition is shown in Figure (2-1). The reactor consisted of a 1.35 cm. ID 18-8 stainless steel tube heated by a coaxial aluminum cylinder of three-inch outside diameter which was wound with resistance wire. The 1.35 cm. tube could be used as a reactor, or a 1.0 cm. ID tube, fitted coaxially with the larger tube, could serve the purpose. At high temperatures it was necessary to use a 1.0 cm. ID glass tube to eliminate wall effects exhibited by stainless steel. The furnace and reactor were supported by a horizontal shaft which allowed the assembly to be inverted for inserting the catalyst. Nitrogen or helium was fed to the reactor through a flexible tube so that the reactor could be purged in any position.

Inside the reactor a three-inch preheating zone was filled with 1/8 inch Pyrex beads supported above the catalyst by either a stainless steel screen or a wad of quartz fibers. The catalyst bed was also supported by screen or fibers and could be varied in depth from 1 to 10 cm. The fittings at the top and bottom of the reactor allowed a stainless steel

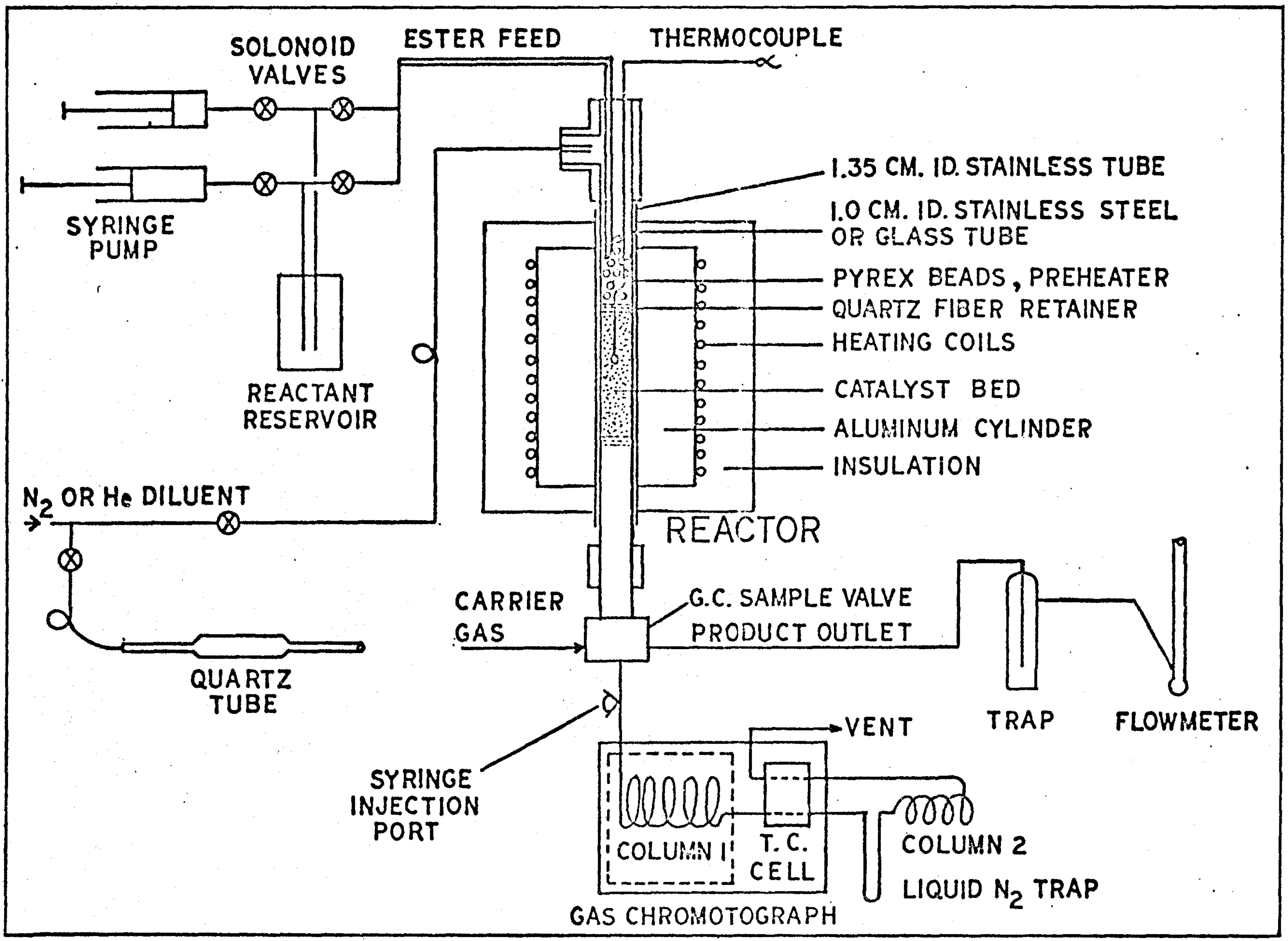


Figure (2-1) A schematic of the apparatus used for studying the decomposition of butyl acetates over charcoal.

sheathed thermocouple to be placed in the catalyst bed and moved vertically along the axis of the reactor. This thermocouple was used to measure the temperature of reaction. For the sec-butyl acetate experiments, the temperature of the reactor was controlled by using an on-off controller which shunted part of the heater current through an isolated resistor. The temperature varied by about 2°C from top to bottom of the catalyst bed during reaction, and the temperature level, say 350°C, could be maintained to within ± 1.5°C by the on-off controller. For experiments on the other three esters the reactor temperature was controlled by supplying regulated voltage to the heating element of the furnace. A Watford Controll Instruments Limited A/C Voltage Stabiliser, model SF-3-L-R, was used to eliminate variations in the 117V line voltage. The output from this regulator was fed through two voltage dividers in series, the first being used to set a nominal output between 0 and 117V, while the second could be used to make small fractional changes in the voltage supplied to the reactor heater. By using regulated voltage and making small corrections from time to time (with the second voltage divider), the reactor temperature could be maintained to within 0.2°C at any given position in the reactor.

For most experiments, liquid ester was fed to the reactor by a Harvard Continuous Automatic Infusion/Withdrawal Pump, model 600-950. The commercial pump was modified to actuate stainless steel solenoid valves as shown in Figure (2-1). These valves were used only in the case of sec-butyl acetate and were bypassed by the other ester feeds. The reason for by passing the valves will be explained later. The hypodermic syringes used in the Harvard pump were highest quality Yale syringes with ground glass bores and matching pistons. Tertiary-butyl acetate was fed at high rates to the reactor by using a Sage Instrument Syringe Pump, model 355, equipped with Hamilton gas-tight syringes.

The reaction products were analyzed by a modified Aerograph 90-P3 Gas Chromatograph* equipped with a thermal conductivity detector. The modifications rerouted the carrier gas and enabled the use of two chromatographic columns in series as shown in Figure (2-1). The first column separated those components of the sample which have high boiling points and are normally liquids, while the second column separated the low boiling point components. The columns used were different for the different butyl acetates; these will be described in the appropriate chapters. Samples of reactor product were taken close to the reactor outlet with an in-line Aerograph Six-Way Gas Valve*. The sample valve and the short conduit connecting it to the reactor were heated and lagged to maintain the reactor effluent in the gaseous state until it had

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*Varian Aerograph, Walnut Creek, California.

passed through the valve.

A Texas Instrument Servoriter II (Recorder) with Disc Integrator was used for measuring the response from the thermal conductivity detector of the gas chromatograph.

A Burrell high temperature electric furnace, model H-1-9 (tubular), was used for heating the catalyst to 930°C prior to use.

2.2 THE REAGENTS

The charcoal which was used for catalyst was PCB coconut Shell Charcoal, kindly furnished by the Pittsburgh Activated Carbon Company. The catalyst was prepared by treating the charcoal as follows: Impurities were removed from the charcoal by three 24 hour acid treatments: first with 50% HCl, second 50% HNO_3, and third with 30% HF. After each acid treatment the charcoal was washed for several hours in flowing distilled water. The de-ashed charcoal was then dried in air at 250°C, crushed in a mortar and pestle, and sieved. The acid washed charcoal had an ash content less than 0.1%, compared with about 4% for the untreated charcoal. After being crushed and sieved, the charcoal was again washed to remove charcoal dust which adhered electrostatically to the sieved particles. The charcoal to be cleaned of dust was placed in a tall graduated cylinder and washed with distilled water which flowed from a jet directed toward the bottom of the cylinder and located about two thirds of the way down the inside wall. The turbulent action of the water agitated the charcoal particles, and the overflow of water from the cylinder carried off the dust. The charcoal was dried in air at 250°C and stored in capped bottles until use. Two batches of charcoal catalyst (called Batch 1 and Batch 2) were prepared according to the above procedure.

Reagent grade sec-butyl acetate containing traces only of n-butyl acetate and n-butanol was purchased from British Drug Houses Limited and was used as obtained. The other three butyl acetates were purchased as reagent grade from Eastman Organic Chemicals Distillation Products Industries. Each ester contained traces of the butanol isomer corresponding to the ester isomer. To insure that the reagents stored in the reactant reservoir did not accumulate moisture from the atmosphere, about 200 grams of dried 4A molecular sieves were placed in the reservoir. Some of the properties of butyl acetates are given in the following table

Table (2-1) Some Properties of Butyl Acetates

Isomer	Boiling (1) Point °C	Critical Properties Temp. °C	Critical Properties P. Atm.	Vaporization (1) Heat ΔH_v kcal/mole
iso-	118	561.5 (2)	38.29 (2)	9.14
n-	125	570.8 (3)	-	8.58
sec-	112	-	-	-
tert-	95-6	540.2 (3)	40.62 (3)	9.13

(1) Perry, R.H., Chilton, C.H., and Kirkpatrick, S.D., "Chemical Engineers' Handbook", McGraw-Hill (1963)

(continued next page)

(2) Kobe, K. A., and Linn, R. E., Chem. Rev. 52, 117 (1953)

(3) Gambill, E. A., Chem. Eng., June 15, 1959, p. 182.

Certified pure nitrogen and reagent grade helium were obtained from Canadian Liquid Air Limited, and reagent grade butenes were purchased from Matheson of Canada Limited. Nitrogen and helium used in the reactor were purified by passing them through a charcoal trap at -196°C.

CHAPTER 3

RELATED EXPERIMENTS

This chapter describes the procedures and results of some experiments made to determine physical and chemical characteristics of materials and reagents used for the catalysis experiments.

3.1 ADSORPTION AND SURFACE AREA STUDIES

Two types of adsorption experiments were performed: In the first type a conventional glass volumetric apparatus was used to measure nitrogen adsorption isotherms on charcoal catalyst. Some of the samples tested were: (a) fresh Batch 1 catalyst which had been heated in nitrogen at 930°C for 20 minutes, (b) catalyst used for n-butyl acetate decomposition, and (c) fresh Batch 2 catalyst which had been heated in nitrogen at 930°C for 20 minutes. The nitrogen adsorption isotherms at -195°C obtained for these samples are shown in Figure (3-1) and are all of type I(27). For unused catalyst the surface area calculated by the "point B" method(28) was 1490 m^2/gram, and the pore volume was 0.56 cc/gram. If a cylindrical pore structure is assumed, the average pore diameter calculated is about 15 Å. Using charcoal as a catalyst for n-butyl acetate decomposition reduces the surface area. The adsorption isotherms for used catalyst will be discussed in

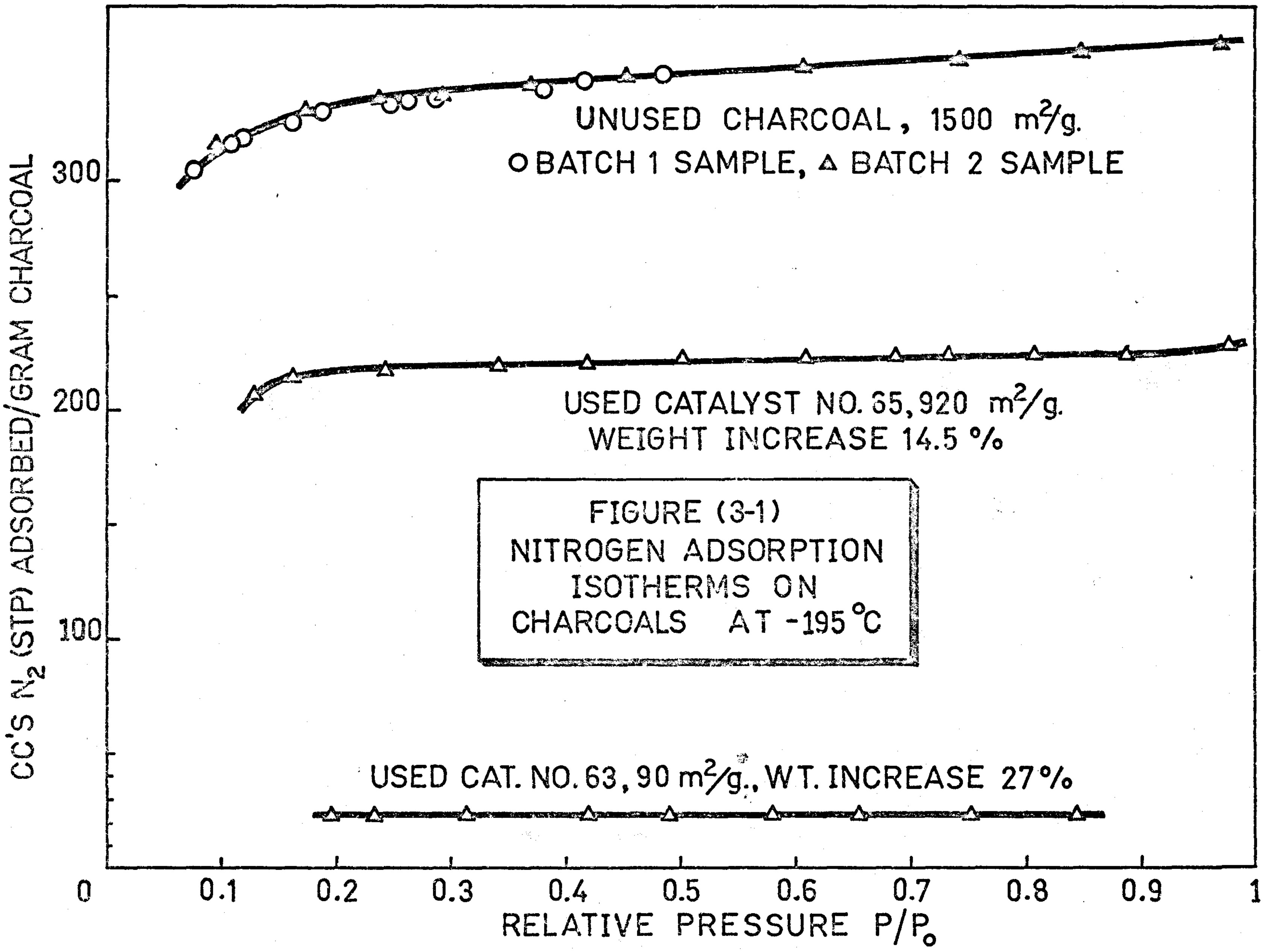

FIGURE (3-1)
NITROGEN ADSORPTION
ISOTHERMS ON
CHARCOALS AT -195 °C

Section 4.4, Catalyst Fouling.

Two experiments were made to assess the effects of butanes on charcoal. In each experiment an isomer of butene was passed over a bed of about 3 grams of fresh catalyst at 418°C. The butene isomers which were used were cis-2-butene and 1-butene, and these were passed through the catalyst at a rate of 2.0 cc(STP) per sec. for a period of seven hours. The charcoal which was used was prepared by heating in helium at 930°C for 20 minutes. The catalyst beds were comprised of three adjacent sections of charcoal partitioned by quartz fiber. During each experiment the reactor products were frequently sampled and analyzed with the gas chromatograph. When the 7 hour period for an experiment was over, the butene flow was discontinued and the reactor was purged with helium for about half an hour at 419°C. The three sections of the catalyst bed were then removed from the reactor and weighed individually to determine the change in weight incurred by each section. Nitrogen adsorption isotherms were determined on samples from each bed section.

When 1-butene was passed over the charcoal, the reactor products were an equilibrium mixture of 1- and 2-butenes for approximately the first three hours of the experiment; thereafter, an increasing excess of 1-butene was found in the mixture of butenes. Cis-2-butene produced an equilibrium mixture of straight-chain butenes for about the first 2 hours, after which the degree of isomerization of the feed decreased. Other experimental results are shown in Table (3-1). The butenes fouled the catalyst and decreased the surface area. The surface areas shown in Table (3-1) were calculated by the "point B" method(28) and are based on the weight of unfouled charcoal in the samples from the beds. The nitrogen adsorption isotherms at -195°C for the fouled samples had the same shape as the adsorption isotherm for unused charcoal shown in Figure (3-1), which indicates that butenes destroy surface area non-selectively; large pores as well as small pores are eliminated. The pore volumes of fouled and fresh charcoal were compared from the adsorption isotherms, and it was found that the decrease in pore volume caused by the fouling was greater than

Table (3-1) The Effect of Butenes on Charcoal

Butene isomer	Bed section	Initial cat. wt. grams	% change in wt.	Area after use m^2/g.
Cis-2-	inlet	1.1418	+14.5	900
"	middle	1.4877	+23.5	-
"	outlet	0.5332	+23.8	500
1-	inlet	0.9257	+23.0	900
"	middle	1.6265	+26.5	-
"	outlet	0.4478	+28.7	-
		Fresh, preheated charcoal		1500

the decrease which could be expected if the deposited material was randomly distributed on the charcoal. Such data suggest that the fouling material blocks the openings to pores.

The second type of adsorption experiment involved passing pulses of esters and their decomposition products over a chromatographic column of charcoal. A suitable length of 1/4 inch copper tubing was filled with 4.075 grams of powdered, de-ashed charcoal and installed in the oven of the chromatograph, replacing column 1 shown in Figure (2-1). For all tests helium carrier-gas was used at a flow rate of 48 cc/minute, as measured at the chromatograph outlet. The temperature of the oven was set at the desired level and the charcoal column was conditioned by injecting a few cc's of sec-butyl acetate into the syringe port. After the ester and products passed from the column, pulses of sec-butyl acetate, acetic acid and butenes were separately injected onto the charcoal column and their retention times after the air peak were measured. This procedure was repeated for several column temperatures between 230° and 400°C. The quantities of the samples injected were constant for each species and were as follows: 10 μl liquid sec-butyl acetate, 3 μl liquid acetic acid, and 200 μl of 1-butene at room conditions. The results of these experiments are shown in Figure (3-2), where the retention time is the time lapse between the appearance of the air peak and the time of maximum response from the species considered. Retention times for acetic acid and butenes could

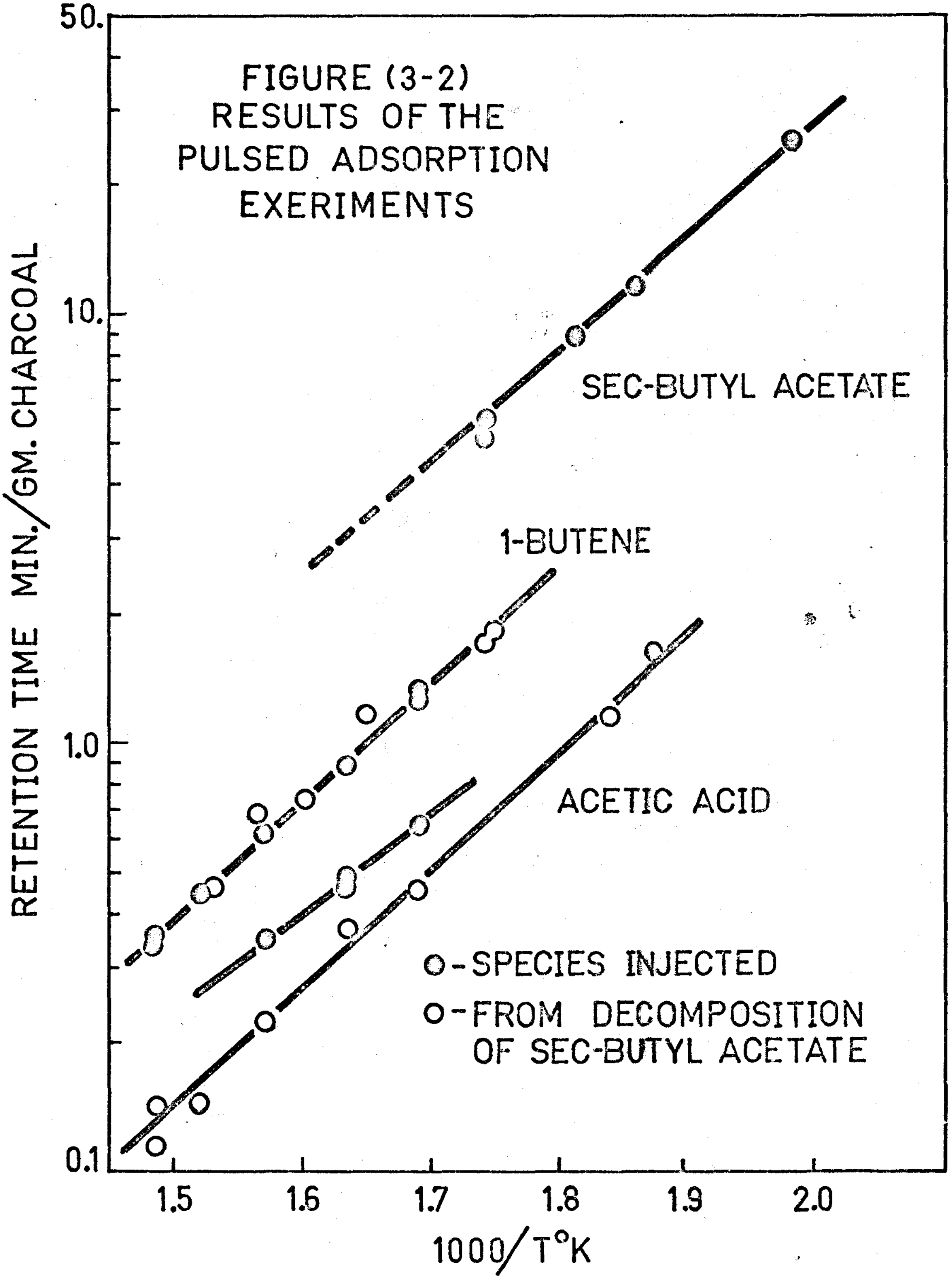

FIGURE (3-2)
RESULTS OF THE
PULSED ADSORPTION
EXERIMENTS

be obtained either by injecting samples of the pure species into the syringe port, or by injecting butyl acetate and measuring the retention times of the products. These two methods gave similar retention times for butenes but not for acetic acid. The butene peaks were Gaussian shaped, and the sec-butyl acetate elutions were similar, despite over-lapping of the responses from the ester decomposition products. For acetic acid the peaks were skewed and had a long tail. Most of the organic effluents from the charcoal column could be collected in the liquid nitrogen trap located between chromatograph columns 1 and 2 (see Figure (2-1)). The contents of the trap could be analyzed by using chromatograph column number 2; the condensed species in the trap were vaporized into the carrier stream by removing the trap from the liquid nitrogen and thrusting it into hot water. The butene pulses emerging from the charcoal column were found to be equilibrium mixtures of 1 and 2-butenes. Also, carbon dioxide was identified as a product of acetic acid decomposition on charcoal.

The retention time of an adsorbate passing through a column of adsorbent gives a measure of the magnitude of the adsorption rate constant relative to the desorption rate constant(21,30). From Figure (3-2) it is apparent that charcoal adsorbs sec-butyl acetate more strongly than its decomposition products in the temperature range investigated. This result suggests that the butyl acetate is the principal adsorbate on the charcoal and the ester term would probably be the most important concentration term in the denominator of a Langmuir-Hinshelwood(31,32) rate equation for ester decomposition. The heat of adsorption of sec-butyl acetate on charcoal calculated(21,23) from the slope of the ester plot in Figure (3-2) was 11.4 kcal/mole.

3.2 CATALYST EXAMINATIONS

3.2.1 Examinations by microscope

The coconut shell charcoal was examined with an optical microscope and also with a scanning electron microscope. For optical microscopy the samples were first heated in helium at 930°C and then mounted in Bakelite and polished. Photomicrographs of some of these samples are shown in Figure (3-3). For electron microscopy, preheated charcoal particles were mounted on brass studs and covered with a thin film of evaporated aluminum to insure that the samples would conduct electricity. Scanning electron micrographs are shown in Figure (3-4).

Figure (3-3-a) shows a group of typical porous catalyst particles containing large numbers of macropores which appear as black holes in the figure. The electron micrographs also show that the charcoal had large pores. In some charcoal particles the holes were of considerable depth, as could be determined by using the optical microscope at high magnification where the depth of focus is short. The depth of a hole could

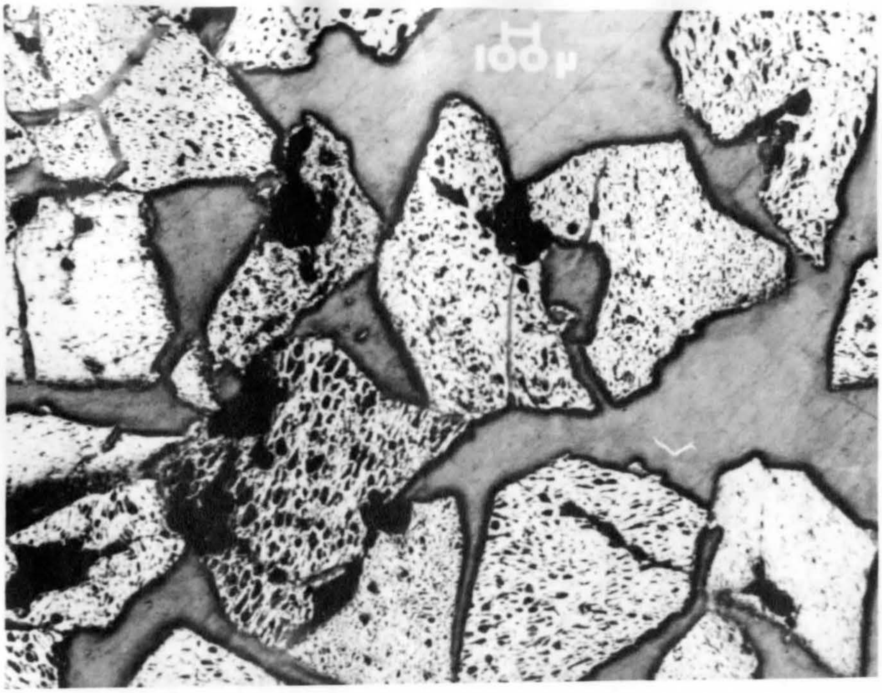

Figure (3-3-a) A photomicrograph of unused 30-40 mesh Batch 2 charcoal catalyst, 40x.

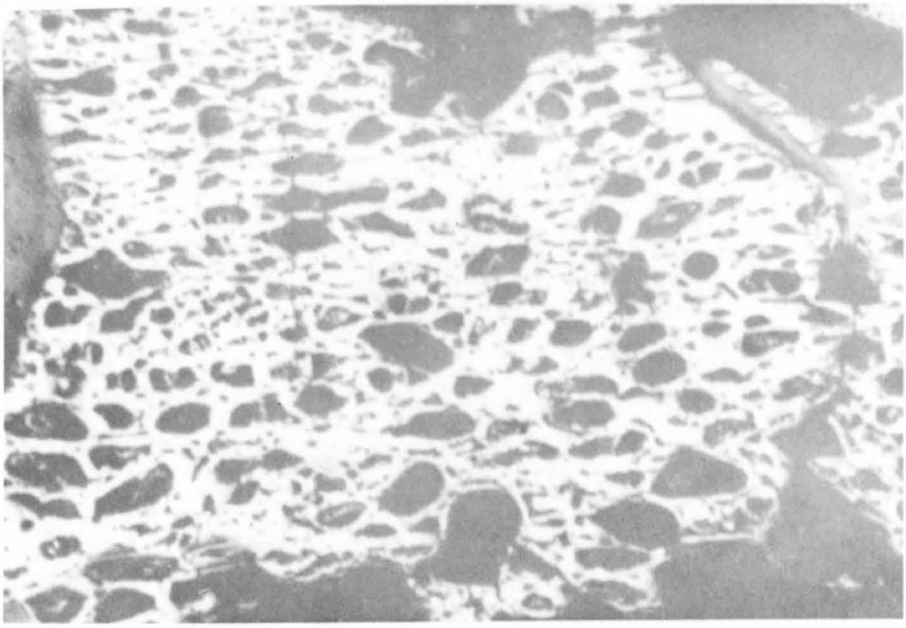

Figure (3-3-b) A photomicrograph of unused Batch 2 charcoal, 250x.

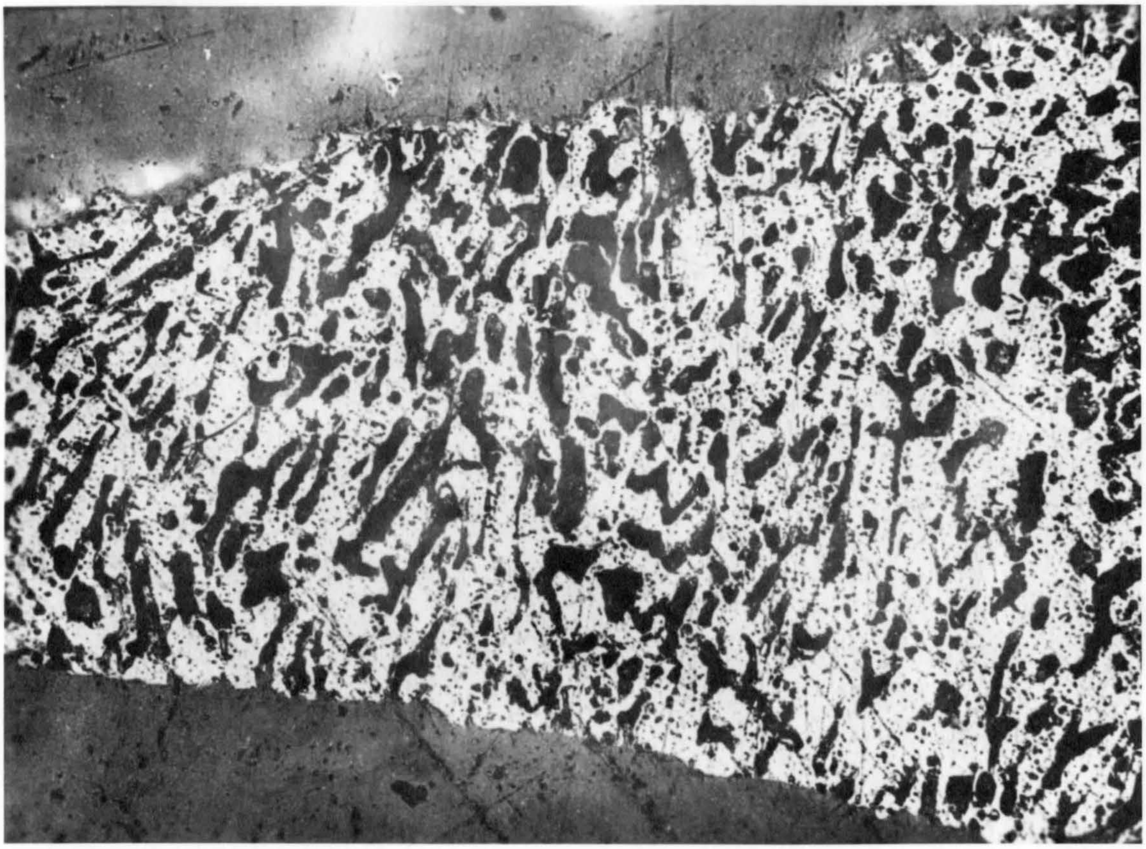

Figure (3-3-c)

A photomicrograph of unused Batch 2 charcoal, 200x.

Figure (3-4-a) A scanning electron micrograph of unused Batch 2 charcoal, 1000x.

Figure (3-4-b) A scanning electron micrograph of used Batch 2 charcoal, 1000x.

be estimated by first focusing the microscope on the perimeter of the pore and then focusing down into the hole. Often the holes appeared in the shapes of circles or ellipses as shown in Figure (3-3-b). These facts suggest that the macropores may be roughly circular in cross section and extend for long distances in a preferred direction through the charcoal particles. Figure (3-3-c) shows a particle having long channels which possibly were exposed by polishing the sample parallel to the direction of the pores. Some of these macropores appear to extend through the particle.

From measurements made on Figure (3-3-a), the average macropore cross section was calculated to be about 0.004 cm. in diameter. The macropores certainly account for only a small fraction of the total surface area of charcoal (1500 m^2/gram); therefore, the region of the charcoal between the macropores must be microporous. An estimate was made of the largest region of charcoal not accessible by macropores. The largest circle that could be drawn over a non-macroporous area in Figure (3-3-a) had a radius of 0.0025 cm., or the radius of a 500 mesh particle. In comparison, the particle sizes of catalysts used in the decomposition experiments ranged from 20 mesh to 80 mesh.

3.2.2 Spectroscopic Examination of the Charcoal

Some charcoals contain free radicals which enhance their catalytic activity. Turkevich and Laroche(18) reported catalysis of the ortho-parahydrogen reaction by sugar charcoal containing around 10^{20} spins/gram·gauss, as determined by electron spin resonance spectroscopy (ESR). To estimate the free radical content of coconut shell charcoal, ESR measurements were made on preheated, unused charcoal, and also on samples of used catalyst. Two instruments were used for the spectroscopy: (1) a Japan Electron Optics Laboratory Company model 3BS-X instrument having a sensitivity of 10^{11} spins/gauss, and (2) a Varian K_a band ESR instrument capable of detecting a minimum of around 5×10^9 spins/gauss. Prior to ESR measurements, samples were evacuated to remove adsorbed gases, such as molecular oxygen, which might occupy unpaired electrons in the charcoal(33,34). Measurements were made at room temperature on samples which were first evacuated and then treated as follows: (a) no treatment (b) exposed to carbon dioxide (c) exposed to nitrogen and heated to 300°C and (d) exposed to air. No free radicals were observed in any of the charcoal samples. Possibly, any free radicals that might have been present in the charcoal prior to pretreatment were destroyed when the catalyst was heated to 930°C. Turkevich and Laroche(18) found that the free radical concentration was small in sugar charcoals heated above 900°C.

3.3 EXAMINATION OF COCONUT SHELL

The shell of a coconut was examined visually and found to consist of brittle material, approximately 1/8 inch thick, pervaded by a network of fibers. These fibers resembled plant roots and consisted of main trunks branching into decreasingly smaller fibers which appeared to be hollow and ran roughly parallel to the surface of the shell. The fibers were found at all depths within the shell, crossing and inter-weaving and giving the appearance that the shell was made up of matted fibers bonded together by the brittle material.

Pieces of the broken shell were bathed overnight in a concentrated sodium hydroxide solution and then dried. This treatment shrank or decomposed the fibers and left long channels running through the brittle material.

A char produced form the coconut shell by heating it at 930°C in helium appeared similar to the charcoal used for catalyst. Sections of the coconut shell were cut to expose roughly circular ends of truncated fibers. The char resulting from heating these specimens had holes visible in the places previously occupied by fibers.

CHAPTER 4

NORMAL-BUTYL ACETATE

4.1 EXPERIMENTAL PROCEDURE

The apparatus depicted in Figure (2-1) was used for experiments with n-butyl acetate. Some experiments were made in the stainless steel reactor, but the kinetic data from these tests were discarded since it was found that at around 400°C the stainless steel was active in decomposing the ester to carbon. Nevertheless, the preliminary experiments with the stainless steel reactor facilitated product identification since the selectivities for some of the minor products were increased in this reactor. For the kinetic study of the n-butyl acetate decomposition, a 1.0 cm. ID Pyrex tube was used as the reactor.

Catalyst preparation for the kinetic experiments was as follows: Prior to use, a sample of charcoal was placed in a quartz tube and heated at 930°C in a stream of helium for 30 minutes. The hot catalyst was then transferred to a bottle, capped airtight, and left to stand until cool, after which it was weighed and then returned to the quartz tube. The charcoal was again heated in helium for 15 minutes at 930°C and then transferred to the reactor without contacting the atmosphere. The transfer was accomplished by inserting the helium-purged quartz tube into the reactor and inverting the assembly so that the catalyst poured into the bed position. The quartz tube was removed, and the inverted reactor was tapped sharply a few times to settle the bed. The charcoal was maintained in position by inserting a wad of quartz fibers into the reactor before re-inverting it to the normal position. A flow of helium was maintained through the reactor, via the feed port, during this procedure and was continued until the time when the catalyst was used.

All experiments were made at a total pressure of one atmosphere using Batch 2 Catalyst. The decomposition reaction was investigated at 365° and 385°C using pure ester feed. Preliminary experiments showed that the catalyst lost activity during the reaction; therefore, the method used in obtaining experimental data was as follows: A given amount of charcoal was put into the reactor, the helium purge was stopped, and then ester was fed over the catalyst at a constant rate for several hours. During this period of time the conversion of ester, x, was measured as a function of the "process time", the time which had elapsed since the beginning of the reaction. The start of the reaction, or zero process time, was indicated by a transient reaction-temperature disturbance which occurred shortly after the ester was admitted to the reactor. When n-butyl acetate contacted the charcoal the temperature of the catalyst bed immediately increased by at least 15°C. After peaking, the reactor temperature decreased approximately exponentially with time and returned in about ten minutes to the value which had existed before admitting the reactant. The temperature increase may have been caused by the heat released when the ester or products adsorbed on "clean" charcoal. Zero process time was defined as the time when the reactor thermocouple first recorded the temperature rise. When the experiment was finished the charcoal was removed from the reactor, weighed, and then set aside for future examination. At each reactor temperature this procedure was repeated a number of times using fresh charcoal samples of different weight, W (grams). For any given temperature the feed rate of ester, F, was kept constant at 0.960 grams of n-butyl acetate per hour; thus the space time, $\tau = W/F$, was proportional to the catalyst weight.

The catalyst particle size was 48-65 mesh in all experiments except for W/F = 2.29 hours at 365°C, at which conditions an experiment was made with 30-35 mesh charcoal to compare the results with data obtained using the smaller particle size.

The exit stream from the reactor was analyzed by gas chromatography. Two columns in series were used as shown in Figure (2-1). For preliminary experiments the reactor products were separated and identified by using 1/4 inch × 4 feet of 50-80 mesh Poropak P* as column 1, while column 2 was 1/4 inch

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*Dow Chemical Company, Freeport, Texas.

× 36 feet of propylene carbonate on 80-100 mesh Chromosorb W. The second column was used at room temperature to separate the gaseous reaction products, and column 1 was temperature programmed from 110° to 245°C to separate products having high boiling points. The temperature increases were begun 3 minutes after sampling and required approximately 3 minutes to reach 245°C. After the last liquid product eluted from column 1 the temperature was returned to 110°C over a 15 minute period. The Poropak P column gave excellent separation of products, but the analysis time with this column was long; therefore, for routine experiments 1/4 inch × 4 feet of FFAP** on 40-60 mesh Teflon was used as column 1. Temperature programming of this column was similar to that for the Poropak P column. Appendix A describes the calibration of the response of the gas chromatograph thermal conductivity detector to different chemical species.

The conversion of butyl acetate and the selectivities were determined from the results of the chromatographic analysis. For the n-butyl acetate reaction, which was found from preliminary experiments to have a complicated stoichiometry, an equation for conversion was derived as follows:

[**] Varian Aerograph, Walnut Creek, California.

Assume that at steady state the reaction occurs as shown in the schematic

$$E + I \rightarrow \boxed{\text{Reactor}} \rightarrow U + B + A + M + I$$

where each symbol designates the weight rate at which a particular species enters or leaves the reactor. For example, E is the weight of ester entering the reactor per unit time. The species referred to by the other symbols are: U = unreacted butyl acetate, B = butene products, A = acetic acid product, M = miscellaneous (secondary, side) products, and I = an inert species diluting the feed. By definition, the conversion of the ester is

$$x = \frac{\text{change in moles of ester}}{\text{total moles of ester entering the reactor}} = \frac{E-U}{E} . \qquad (4\text{-}1)$$

Now, the weight fraction of butyl acetate in the product is

$$V = \frac{U}{U + B + A + M + I} ;$$

but,

$$E = U + B + A + M .$$

Therefore,

$$U = V(E + I) . \qquad (4\text{-}2)$$

Substituting (4-2) into (4-1) gives

$$x = \frac{E - U}{E} = \frac{E - (E + I)\cdot V}{E} ,$$

or,

$$x = 1 - (1 + \frac{I}{E})\cdot V. \qquad (4\text{-}3)$$

In the kinetic experiments, the conversion of n-butyl acetate was calculated by using the chromatograph to determine the weight fraction of ester in the products and then by applying Equation (4-3). This method of calculating conversion is shown to be valid by the material balance calculation in Appendix V.

The selectivity of the n-butyl acetate reaction was calculated as follows: The selectivity for product B is defined as

$$S_b = \frac{B/M_b}{x \cdot E/M_e} = \frac{B \cdot M_e}{x \cdot (U+B+A+M) \cdot M_b} \qquad (4\text{-}4)$$

$$\frac{\text{moles B}}{\text{mole ester (decomposed)}} ,$$

where M_b is the molecular weight of product B expressed in the same units as the weight B, and M_e is the molecular weight of the ester. Program 1 in Appendix E shows a computer program which uses Equations (4-3) and (4-4) to calculate x and S from raw data.

4.2 RESULTS OF THE NORMAL-BUTYL ACETATE EXPERIMENTS

This section presents the experimental data and gives a brief summary of the conclusions readily made from the experiments. Detailed interpretations of the data will be presented in later sections.

The principal products from n-butyl acetate decomposition at 365°-386°C were acetic acid and 1-butene, but relatively large amounts of methane, water, and 2-butenes also appeared in the reaction products. Some of the products which occurred in small amounts (called "minor" products below) were: methanol, propane, carbon dioxide and isobutane. During the reaction the activity of the charcoal decreased, and the selectivities for the principal products, acetic acid and 1-butene, increased. The weights of the catalysts were found to increase by about 15-20% when used for periods of 24 to 75 hours.

Experimental results are given in the following figures and tables. Figures (4-1) and (4-2) show the conversion as a function of the process time; the data are fitted with least squares straight lines. Figures (4-3) and (4-4) illustrate some typical selectivity data.

4.3 ANALYSIS OF THE NORMAL-BUTYL ACETATE DATA

The analysis of the experimental data was, in general, in two parts: Analysis of the kinetics and the study of the selectivities. The conclusions which are obvious from the data will first be discussed, and then results of detailed analyses will be presented.

The procedure used to obtain kinetic information from the experimental data was as follows: In Figures (4-1) and (4-3) the conversion appears to decrease linearly with process time for all experimental conditions. No departure from this

TABLE (4-1)
RESULTS OF THE N-BUTYL ACETATE EXPERIMENTS
CONVERSION AND SELECTIVITIES FOR MAJOR PRODUCTS

TEMPERATURE = 365.00 C , W/F= 3.5870 HR

			SELECTIVITY				
RUN	X	PROCESS TIME,HR	ACETIC ACID	1- BUTENE	TRANS- BUTENE	CIS-2- BUTENE	TOTAL BUTENES
967	.4977	.250	.7388	.4738	.1858	.0993	.7590
968	.4487	.840	.7926	.4875	.1394	.0842	.7111
969	.5492	1.500	.8040	.5169	.1405	.0937	.7512
970	.5331	2.000	.7920	.5543	.1294	.0848	.7685
971	.6664	2.840	.7666	.4923	.1557	.1052	.7532
972	.5368	3.750	.7969	.5758	.1307	.0896	.7961
973	.5116	4.500	.8009	.6083	.1252	.0811	.8147
974	.4749	6.840	.8093	.6404	.1120	.0762	.8285
975	.4971	8.080	.8127	.6287	.1136	.0756	.8180
976	.5127	11.750	.8195	.6193	.1099	.0736	.8028
977	.4874	12.280	.8038	.6417	.1179	.0868	.8463
978	.4610	19.250	.8209	.6492	.1084	.0720	.8295
979	.4228	24.750	.8176	.6698	.1030	.0657	.8385
980	.4396	25.420	.8026	.6760	.1098	.0729	.8587
981	.4599	26.170	.7991	.6495	.1038	.0688	.8220
982	.4330	27.520	.7689	.7037	.1170	.0703	.8910
983	.4266	28.080	.8348	.6502	.0926	.0617	.8045
984	.4206	28.750	.8304	.6670	.0952	.0570	.8192
985	.4023	29.750	.8329	.6504	.0908	.0605	.8016
986	.4194	30.580	.8449	.6569	.0900	.0603	.8072
987	.4299	36.000	.8251	.6476	.0924	.0621	.8021
988	.4226	36.670	.8317	.6779	.1002	.0628	.8409
989	.4231	37.180	.8288	.6745	.0986	.0675	.8406
990	.4210	42.750	.8245	.6715	.0984	.0680	.8379
991	.4004	43.280	.8604	.6581	.0937	.0586	.8104
992	.3918	47.750	.8367	.6681	.0977	.0636	.8294
993	.3724	48.750	.8161	.6942	.1027	.0653	.8622
994	.3679	49.280	.8598	.6695	.0831	.0623	.8149
995	.3763	50.250	.8541	.6723	.0967	.0587	.8276
996	.3407	54.000	.8655	.6762	.0837	.0578	.8177
997	.2834	72.950	.8367	.7061	.0996	.0511	.8569
998	.2842	73.500	.8657	.6906	.0776	.0511	.8193

TABLE (4-1) (CONTINUED)

TEMPERATURE = 365.00 C , W/F= 2.2908 HR

			SELECTIVITY				
RUN	X	PROCESS TIME,HR	ACETIC ACID	1- BUTENE	TRANS- BUTENE	CIS-2- BUTENE	TOTAL BUTENES
1000	.3746	3.170	.7982	.6513	.1142	.0739	.8395
1001	.3668	3.680	.8395	.6467	.0946	.0646	.8060
1002	.3616	4.250	.8341	.6662	.0913	.0633	.8207
1003	.3576	4.750	.8256	.6915	.0930	.0582	.8427
1004	.3822	10.130	.8266	.6861	.0972	.0636	.8469
1005	.3532	10.670	.8570	.6965	.0838	.0497	.8300
1006	.3511	11.170	.8551	.6976	.0789	.0463	.8229
1007	.3311	21.580	.8370	.7355	.0799	.0460	.8614
1008	.3388	23.750	.8361	.7195	.0972	.0560	.8726
1009	.3403	24.250	.8406	.7350	.0786	.0511	.8647
1010	.3306	24.750	.8421	.7034	.0760	.0462	.8257
1011	.3362	25.670	.8699	.7151	.0692	.0488	.8330
1012	.3216	31.750	.8644	.7265	.0730	.0422	.8417
1013	.3252	32.250	.8632	.7255	.0777	.0515	.8546
1014	.3275	32.750	.8511	.7434	.0731	.0476	.8642
1015	.2992	44.500	.8474	.7562	.0765	.0425	.8752
1016	.2957	45.020	.8496	.7419	.0745	.0438	.8602
1017	.2997	45.670	.8528	.7466	.0772	.0456	.8694

TEMPERATURE = 365.00 C , W/F= 4.6727 HR

			SELECTIVITY				
RUN	X	PROCESS TIME,HR	ACETIC ACID	1- BUTENE	TRANS- BUTENE	CIS-2- BUTENE	TOTAL BUTENES
1141	.6375	1.500	.7895	.4426	.1666	.1046	.7137
1142	.6382	2.000	.8019	.4411	.1550	.1030	.6991
1143	.6142	3.000	.7855	.4946	.1484	.1004	.7434
1144	.6019	3.500	.8128	.4945	.1389	.0882	.7216
1145	.6104	4.000	.8081	.5019	.1386	.0939	.7344
1146	.5914	5.000	.7947	.5330	.1494	.0924	.7748
1147	.5844	6.000	.7940	.5541	.1307	.1087	.7936
1148	.5638	7.000	.8421	.5510	.1267	.0796	.7574
1149	.5646	7.500	.8251	.5517	.1252	.0886	.7656
1151	.5814	10.500	.8379	.5564	.1212	.0813	.7589
1152	.5070	24.000	.8502	.6118	.1138	.0743	.7999
1153	.4950	24.500	.8154	.6291	.1124	.0754	.8169
1154	.5056	25.000	.8527	.6047	.1103	.0718	.7868
1155	.4964	25.500	.8623	.6071	.1055	.0666	.7792
1156	.5103	26.500	.8667	.6013	.1033	.0684	.7730
1157	.5059	27.000	.8631	.6018	.1031	.0739	.7788
1158	.4762	35.000	.8333	.6491	.1030	.0716	.8237
1159	.4809	35.500	.8522	.6176	.1047	.0704	.7926

TABLE (4-1) (CONTINUED)

TEMPERATURE = 385.00 C , W/F= 1.2940 HR

			SELECTIVITY				
RUN	X	PROCESS TIME,HR	ACETIC ACID	1-BUTENE	TRANS-BUTENE	CIS-2-BUTENE	TOTAL BUTENES
1054	.4971	2.000	.8125	.6620	.1051	.0589	.8260
1055	.4882	3.000	.8503	.6475	.0943	.0603	.8021
1056	.5190	3.500	.8738	.6385	.0918	.0620	.7923
1057	.5184	4.000	.8965	.6530	.0980	.0607	.8117
1058	.4974	5.000	.8738	.6496	.0814	.0574	.7884
1059	.4581	8.330	.8636	.6948	.0805	.0505	.8257
1060	.4752	9.000	.8462	.6933	.0810	.0567	.8309
1061	.3762	24.000	.8770	.7282	.0766	.0422	.8470
1062	.3620	24.500	.9053	.7083	.0707	.0437	.8227
1063	.3713	25.000	.8700	.7327	.0739	.0429	.8494
1064	.3507	26.000	.8792	.7352	.0794	.0469	.8615
1065	.3532	27.000	.8953	.7306	.0684	.0464	.8454
1066	.3566	28.000	.8856	.7340	.0716	.0425	.8481
1067	.3379	32.250	.8486	.7772	.0780	.0413	.8966
1068	.3318	33.000	.8619	.7555	.0637	.0435	.8627
1069	.3592	33.500	.8041	.7966	.0708	.0437	.9111

TEMPERATURE = 385.00 C , W/F= 2.3007 HR

			SELECTIVITY				
RUN	X	PROCESS TIME,HR	ACETIC ACID	1-BUTENE	TRANS-BUTENE	CIS-2-BUTENE	TOTAL BUTENES
1074	.7188	3.500	.7972	.5427	.1376	.0934	.7736
1075	.7068	4.000	.8179	.5411	.1280	.0922	.7614
1076	.6962	4.500	.8245	.5474	.1261	.0873	.7607
1077	.6881	5.000	.8269	.5636	.1259	.0852	.7747
1078	.6651	6.000	.8401	.5723	.1179	.0817	.7719
1079	.6548	6.500	.8439	.5830	.1159	.0793	.7782
1080	.6361	7.000	.8238	.6045	.1116	.0785	.7946
1081	.6414	8.000	.8509	.5832	.1139	.0783	.7754
1082	.4763	25.000	.8586	.6623	.1021	.0624	.8268
1083	.5292	25.500	.8846	.6239	.0877	.0733	.7849
1084	.5063	26.000	.8816	.6310	.0958	.0604	.7872
1085	.4864	27.000	.8455	.6552	.1000	.0651	.8203
1086	.4910	27.500	.8747	.6455	.0948	.0634	.8037
1087	.5023	28.000	.8844	.6261	.0966	.0646	.7873
1088	.4595	29.250	.8679	.6520	.0954	.0598	.8072

TABLE (4-1) (CONTINUED)

TEMPERATURE = 365.00 C , W/F= 1.2912 HR

			SELECTIVITY				
RUN	X	PROCESS TIME,HR	ACETIC ACID	1-BUTENE	TRANS-BUTENE	CIS-2-BUTENE	TOTAL BUTENES
1019	.2284	2.500	.8657	.7331	.0431	.0252	.8015
1019	.2035	4.750	.8452	.7468	.0661	.0369	.8499
1020	.2035	5.250	.8561	.7420	.0604	.0423	.8447
1021	.1735	5.750	.8634	.7601	.0577	.0310	.8488
1022	.2104	13.500	.8590	.7753	.0595	.0351	.8700
1023	.2310	14.000	.8563	.7613	.0586	.0368	.8567
1024	.2192	14.500	.8779	.7632	.0609	.0323	.8564
1025	.2167	15.000	.8802	.7599	.0548	.0309	.8456
1026	.2019	17.750	.8734	.7691	.0518	.0355	.8564
1027	.2031	18.250	.8806	.7782	.0506	.0335	.8624
1028	.2066	18.750	.8567	.7857	.0598	.0389	.8844
1029	.2172	22.500	.8469	.7938	.0509	.0362	.8809
1030	.2213	23.000	.8177	.8266	.0493	.0360	.9120
1031	.2050	23.500	.8602	.7885	.0532	.0294	.8711
1032	.1979	24.000	.8768	.7723	.0480	.0299	.8503
1033	.2140	29.000	.8666	.7817	.0568	.0324	.8709
1034	.2134	29.500	.8382	.8109	.0540	.0367	.9016
1035	.2039	30.000	.8589	.8116	.0518	.0326	.8960
1036	.1866	41.750	.8237	.8532	.0520	.0262	.9314
1037	.1861	42.250	.8819	.7912	.0483	.0302	.8696
1038	.1819	42.750	.9049	.7789	.0536	.0268	.8593
1039	.1783	43.500	.9098	.7695	.0690	.0285	.8670
1040	.1767	44.000	.8957	.7899	.0417	.0340	.8655

TEMPERATURE = 385.00 C , W/F= 2.2935 HR

			SELECTIVITY				
RUN	X	PROCESS TIME,HR	ACETIC ACID	1-BUTENE	TRANS-BUTENE	CIS-2-BUTENE	TOTAL BUTENES
1041	.6835	4.000	.6555	.5052	.1419	.0879	.7350
1042	.6805	5.000	.7661	.4977	.1240	.0758	.6976
1043	.6673	5.500	.7469	.5202	.1212	.0733	.7147
1044	.6594	6.000	.7468	.5391	.1159	.0751	.7302
1045	.6386	7.330	.7459	.5485	.1113	.0697	.7295
1046	.6333	13.830	.7368	.5527	.1183	.0735	.7445
1047	.6249	14.330	.7591	.5555	.1160	.0715	.7430
1048	.7141	26.000	.7259	.6017	.1263	.0732	.8012
1049	.5371	26.500	.7449	.5931	.1268	.0761	.7960
1050	.4661	32.500	.7519	.6292	.1083	.0656	.8030
1051	.4689	33.000	.7365	.6193	.1100	.0645	.7938
1052	.3566	51.000	.7261	.6701	.1137	.0631	.8470
1053	.3563	51.500	.7484	.6746	.1179	.0643	.8568

TABLE (4-1) (CONTINUED)

TEMPERATURE = 385.00 C , W/F= .6376 HR

			SELECTIVITY				
RUN	X	PROCESS TIME,HR	ACETIC ACID	1-BUTENE	TRANS-BUTENE	CIS-2-BUTENE	TOTAL BUTENES
1090	.3840	2.500	.8552	.6955	.0682	.0447	.8084
1091	.3759	3.000	.8648	.7078	.0657	.0444	.8178
1092	.3944	3.500	.8546	.6942	.0702	.0486	.8130
1093	.3524	4.500	.8516	.7317	.0679	.0394	.8390
1094	.3344	5.000	.8757	.7340	.0582	.0344	.8266
1095	.3423	5.500	.8665	.7363	.0605	.0361	.8329
1096	.3202	8.000	.8618	.7585	.0548	.0345	.8477
1097	.3263	8.500	.8811	.7491	.0533	.0347	.8370
1098	.3237	9.000	.8759	.7519	.0541	.0350	.8410
1099	.3155	11.500	.8546	.7771	.0592	.0341	.8705
1100	.3226	12.000	.8771	.7637	.0522	.0346	.8505
1101	.2728	24.000	.8726	.8011	.0605	.0298	.8914
1102	.2870	24.500	.8918	.7756	.0514	.0310	.8579
1103	.2812	25.000	.9122	.7526	.0522	.0354	.8401
1104	.2825	26.000	.8890	.7844	.0521	.0351	.8717

TABLE (4-2)
RESULTS OF THE N-BUTYL ACETATE EXPERIMENTS
CONVERSION AND SELECTIVITIES FOR MINOR PRODUCTS

TEMPERATURE = 365.00 C W/F= 3.5870 HR

			SELECTIVITY						
RUN	X	TIME	ACETONE	CH4OH	WATER	CO+ CH4	PROPANE	CO2	ISOBUTANE
967	.4977	.25	.007	.026	.317	.546	.008	.047	.010
968	.4487	.84	.007	.019	.245	.786	.015	.039	.006
969	.5492	1.50	.008	.020	.238	.641	.017	.036	.008
970	.5331	2.00	.010	.022	.218	.693	.017	.036	.007
971	.6664	2.84	.010	.015	.238	.712	.020	.039	.009
972	.5368	3.75	.009	.022	.193	.637	.015	.038	.008
973	.5116	4.50	.010	.021	.186	.609	.014	.036	.006
974	.4749	6.84	.010	.020	.164	.576	.014	.039	.007
975	.4971	8.08	.012	.021	.175	.582	.014	.042	.007
976	.5127	11.75	.015	.024	.191	.574	.015	.042	.005
977	.4874	12.28	.014	.022	.178	.510	.013	.043	.007
978	.4610	19.25	.013	.023	.165	.569	.014	.038	.006
979	.4228	24.75	.019	.028	.167	.501	.012	.045	.008
980	.4396	25.42	.018	.026	.135	.536	.012	.045	.006
981	.4599	26.17	.017	.025	.164	.624	.015	.049	.006
982	.4330	27.52	.018	.024	.163	.515	.013	.043	.006
983	.4266	28.08	.018	.027	.154	.588	.014	.041	.006
984	.4206	28.75	.017	.026	.147	.558	.014	.044	.005
985	.4023	29.75	.017	.026	.152	.621	.013	.043	.006
986	.4194	30.58	.017	.025	.161	.531	.013	.044	.008
987	.4299	36.00	.016	.025	.155	.627	.013	.044	.009
988	.4226	36.67	.018	.027	.146	.468	.013	.045	.007
989	.4231	37.18	.016	.025	.146	.507	.014	.040	.005
990	.4210	42.75	.015	.024	.159	.513	.013	.044	.005
991	.4004	43.28	.016	.020	.146	.523	.012	.041	.005
992	.3918	47.75	.016	.026	.146	.508	.015	.045	.005
993	.3724	48.75	.016	.027	.138	.502	.012	.040	.004
994	.3679	49.28	.017	.025	.146	.490	.012	.043	.006
995	.3763	50.25	.016	.025	.147	.470	.013	.043	.005
996	.3407	54.00	.018	.028	.143	.460	.011	.042	.006
997	.2834	72.95	.017	.027	.131	.457	.013	.046	.005
998	.2842	73.50	.017	.028	.146	.485	.009	.039	.004

TABLE (4-2) (CONTINUED)

TEMPERATURE = 365.00 C W/F= 2.2908 HR

			SELECTIVITY						
RUN	X	TIME	ACETONE	CH4OH	WATER	CO+ CH4	PROPANE	CO2	ISOBUTANE
1000	.3746	3.17	.013	.032	.197	.540	.009	.037	.006
1001	.3668	3.68	.015	.034	.168	.543	.010	.037	.006
1002	.3616	4.25	.015	.029	.169	.524	.010	.039	.006
1003	.3576	4.75	.014	.028	.156	.507	.009	.038	.007
1004	.3822	10.13	.017	.029	.171	.483	.010	.039	.005
1005	.3532	10.67	.014	.028	.135	.493	.010	.039	.004
1006	.3511	11.17	.017	.032	.143	.487	.010	.039	.006
1007	.3311	21.58	.013	.030	.171	.441	.009	.038	.005
1008	.3388	23.75	.016	.029	.136	.446	.007	.038	.005
1009	.3403	24.25	.017	.029	.121	.454	.009	.039	.005
1010	.3306	24.75	.017	.032	.137	.573	.011	.037	.004
1011	.3362	25.67	.018	.031	.122	.443	.010	.041	.005
1012	.3216	31.75	.016	.031	.134	.428	.010	.040	.006
1013	.3252	32.25	.014	.030	.128	.419	.009	.036	.005
1014	.3275	32.75	.013	.028	.121	.435	.010	.040	.004
1015	.2992	44.50	.015	.029	.123	.408	.010	.038	.005
1016	.2957	45.02	.018	.030	.103	.463	.010	.040	.005
1017	.2997	45.67	.013	.028	.112	.439	.009	.038	.004

TEMPERATURE = 365.00 C W/F= 4.6727 HR

			SELECTIVITY						
RUN	X	TIME	ACETONE	CH4OH	WATER	CO+ CH4	PROPANE	CO2	ISOBUTANE
1141	.6375	1.50	.007	.023	.294	.673	.021	.034	.006
1142	.6382	2.00	.008	.023	.266	.737	.021	.034	.009
1143	.6142	3.00	.011	.021	.263	.697	.018	.036	.013
1144	.6019	3.50	.011	.024	.227	.751	.018	.033	.009
1145	.6104	4.00	.009	.023	.237	.704	.019	.038	.009
1146	.5914	5.00	.012	.026	.218	.665	.017	.036	.009
1147	.5844	6.00	.012	.026	.208	.637	.017	.032	.007
1148	.5638	7.00	.010	.025	.193	.630	.016	.037	.007
1149	.5646	7.50	.010	.026	.200	.660	.016	.036	.007
1151	.5814	10.50	.013	.027	.184	.645	.017	.035	.009
1152	.5070	24.00	.012	.023	.178	.527	.015	.038	.005
1153	.4950	24.50	.012	.026	.171	.573	.016	.038	.008
1154	.5056	25.00	.012	.025	.166	.571	.015	.036	.007
1155	.4964	25.50	.012	.024	.166	.561	.015	.039	.006
1156	.5103	26.50	.012	.025	.170	.564	.014	.037	.008
1157	.5059	27.00	.012	.024	.163	.563	.015	.036	.007
1158	.4762	35.00	.012	.023	.159	.517	.014	.040	.008
1159	.4809	35.50	.012	.023	.162	.557	.015	.039	.009

TABLE (4-2) (CONTINUED)

TEMPERATURE = 385.00 C W/F= 1.2940 HR

			SELECTIVITY						
RUN	X	TIME	ACE- TONE	CH4OH	WATER	CO+ CH4	PRO- PANE	CO2	ISO- BUTANE
1054	.4971	2.00	.012	.028	.170	.565	.015	.042	.007
1055	.4882	3.00	.011	.024	.177	.547	.013	.039	.007
1056	.5190	3.50	.012	.024	.168	.498	.014	.039	.005
1057	.5184	4.00	.011	.024	.164	.550	.014	.042	.007
1058	.4974	5.00	.012	.024	.158	.540	.012	.039	.007
1059	.4581	8.33	.011	.026	.160	.461	.011	.041	.006
1060	.4752	9.00	.012	.023	.162	.516	.011	.040	.006
1061	.3762	24.00	.012	.024	.127	.411	.011	.040	.005
1062	.3620	24.50	.013	.025	.113	.392	.011	.042	.005
1063	.3713	25.00	.011	.024	.118	.446	.012	.037	.005
1064	.3507	26.00	.013	.026	.114	.393	.009	.034	.004
1065	.3532	27.00	.010	.023	.112	.398	.008	.036	.003
1066	.3566	28.00	.010	.024	.116	.401	.011	.035	.004
1067	.3379	32.25	.010	.025	.118	.374	.009	.039	.004
1068	.3318	33.00	.010	.025	.122	.445	.008	.037	.004
1069	.3592	33.50	.012	.026	.115	.469	.009	.042	.004

TEMPERATURE = 385.00 C W/F= 2.3007 HR

			SELECTIVITY						
RUN	X	TIME	ACE- TONE	CH4OH	WATER	CO+ CH4	PRO- PANE	CO2	ISO- BUTANE
1074	.7188	3.50	.009	.018	.221	.667	.017	.046	.009
1075	.7068	4.00	.009	.019	.196	.651	.019	.050	.009
1076	.6962	4.50	.009	.018	.191	.667	.017	.047	.009
1077	.6881	5.00	.009	.018	.188	.623	.016	.047	.008
1078	.6651	6.00	.011	.019	.179	.614	.016	.043	.008
1079	.6548	6.50	.009	.018	.175	.594	.017	.045	.008
1080	.6361	7.00	.012	.021	.161	.608	.016	.047	.008
1081	.6414	8.00	.012	.020	.184	.577	.015	.042	.007
1082	.4763	25.00	.011	.022	.149	.456	.014	.044	.007
1083	.5292	25.50	.012	.020	.143	.489	.016	.046	.006
1084	.5063	26.00	.011	.020	.140	.517	.016	.044	.007
1085	.4864	27.00	.010	.021	.143	.505	.016	.046	.007
1086	.4910	27.50	.012	.021	.138	.488	.015	.044	.006
1087	.5023	28.00	.011	.020	.130	.491	.015	.048	.007
1088	.4595	29.25	.012	.022	.144	.488	.015	.044	.007

TABLE (4-2) (CONTINUED)

TEMPERATURE = 365.00 C W/F= 1.2912 HR

			SELECTIVITY						
RUN	X	TIME	ACETONE	CH4OH	WATER	CO+ CH4	PROPANE	CO2	ISOBUTANE
1018	.2284	2.50	.016	.035	.174	.455	.007	.040	.005
1019	.2035	4.75	.022	.043	.119	.445	.007	.040	.005
1020	.2035	5.25	.022	.039	.114	.447	.006	.040	.005
1021	.1735	5.75	.025	.043	.108	.397	.005	.041	.005
1022	.2104	13.50	.018	.035	.112	.407	.004	.039	.004
1023	.2310	14.00	.019	.036	.131	.415	.007	.037	.005
1024	.2192	14.50	.015	.031	.110	.396	.007	.037	.004
1025	.2167	15.00	.019	.038	.101	.402	.007	.037	.005
1026	.2019	17.75	.020	.038	.114	.371	.006	.038	.005
1027	.2031	18.25	.020	.037	.088	.362	.005	.039	.004
1028	.2066	18.75	.019	.034	.096	.388	.007	.035	.004
1029	.2172	22.50	.017	.036	.106	.420	.006	.037	.004
1030	.2213	23.00	.018	.035	.103	.404	.008	.039	.005
1031	.2050	23.50	.018	.035	.099	.392	.008	.042	.006
1032	.1979	24.00	.021	.039	.110	.397	.007	.037	.004
1033	.2140	29.00	.018	.033	.125	.367	.007	.038	.005
1034	.2134	29.50	.019	.037	.083	.378	.008	.043	.005
1035	.2039	30.00	.017	.034	.066	.374	.009	.038	.004
1036	.1866	41.75	.012	.033	.102	.344	.008	.042	.006
1037	.1861	42.25	.018	.034	.090	.349	.006	.036	.004
1038	.1819	42.75	.017	.034	.092	.319	.006	.036	.004
1039	.1783	43.50	.014	.035	.078	.319	.006	.035	.003
1040	.1767	44.00	.018	.035	.069	.342	.007	.038	.005

TEMPERATURE = 385.00 C W/F= 2.2935 HR

			SELECTIVITY						
RUN	X	TIME	ACETONE	CH4OH	WATER	CO+ CH4	PROPANE	CO2	ISOBUTANE
1041	.6835	4.00	.031	.024	.321	.956	.034	.070	.011
1042	.6805	5.00	.031	.024	.280	.735	.030	.082	.012
1043	.6673	5.50	.032	.025	.262	.792	.028	.076	.012
1044	.6594	6.00	.031	.021	.284	.744	.026	.077	.011
1045	.6386	7.33	.034	.024	.274	.722	.026	.083	.011
1046	.6333	13.83	.039	.019	.260	.736	.024	.086	.011
1047	.6249	14.33	.039	.021	.249	.681	.025	.084	.010
1048	.7141	26.00	.045	.021	.235	.619	.022	.094	.008
1049	.5371	26.50	.042	.021	.220	.604	.023	.099	.007
1050	.4661	32.50	.046	.021	.237	.525	.022	.095	.007
1051	.4689	33.00	.045	.022	.206	.680	.022	.092	.007
1052	.3566	51.00	.044	.027	.211	.550	.020	.088	.006
1053	.3563	51.50	.042	.026	.164	.531	.016	.084	.005

TABLE (4-2) (CONTINUED)

TEMPERATURE = 385.00 C W/F= .6376 HR

			SELECTIVITY						
RUN	X	TIME	ACETONE	CH4OH	WATER	CO+ CH4	PROPANE	CO2	ISOBUTANE
1090	.3840	2.50	.011	.028	.159	.567	.012	.037	.006
1091	.3759	3.00	.011	.029	.150	.520	.011	.037	.006
1092	.3944	3.50	.010	.027	.159	.531	.012	.042	.011
1093	.3524	4.50	.012	.028	.151	.499	.010	.037	.008
1094	.3344	5.00	.013	.028	.142	.495	.008	.035	.006
1095	.3423	5.50	.013	.030	.123	.486	.010	.044	.008
1096	.3202	8.00	.013	.028	.130	.466	.009	.039	.008
1097	.3263	8.50	.011	.027	.122	.464	.010	.039	.006
1098	.3237	9.00	.013	.031	.118	.461	.009	.040	.006
1099	.3155	11.50	.012	.027	.123	.444	.008	.040	.007
1100	.3226	12.00	.012	.029	.119	.422	.010	.039	.008
1101	.2728	24.00	.012	.026	.135	.308	.010	.040	.004
1102	.2870	24.50	.010	.024	.106	.386	.010	.037	.008
1103	.2812	25.00	.012	.025	.099	.388	.010	.036	.006
1104	.2825	26.00	.008	.023	.099	.394	.007	.034	.006

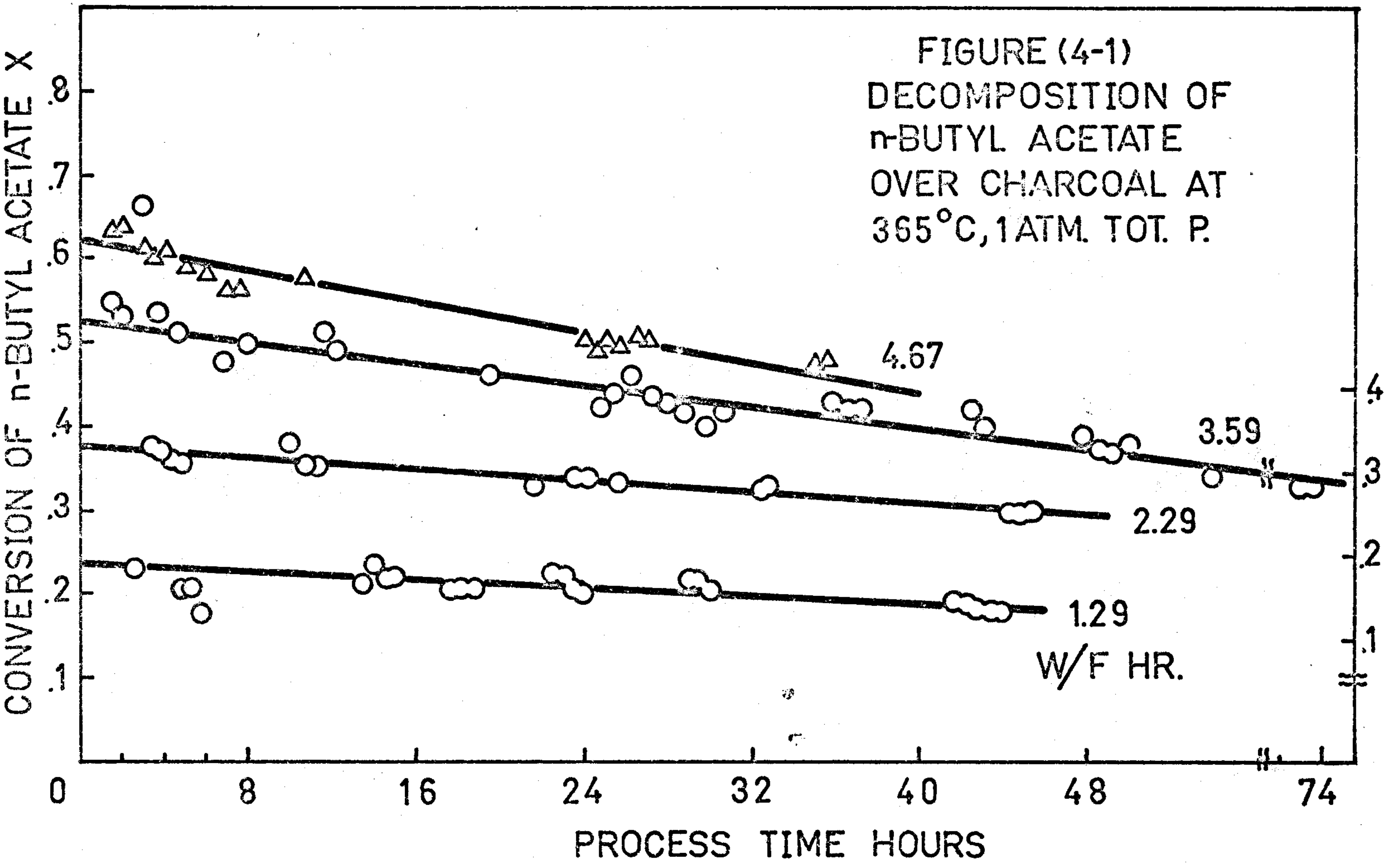

FIGURE (4-1)
DECOMPOSITION OF
n-BUTYL ACETATE
OVER CHARCOAL AT
365°C, 1ATM. TOT. P.

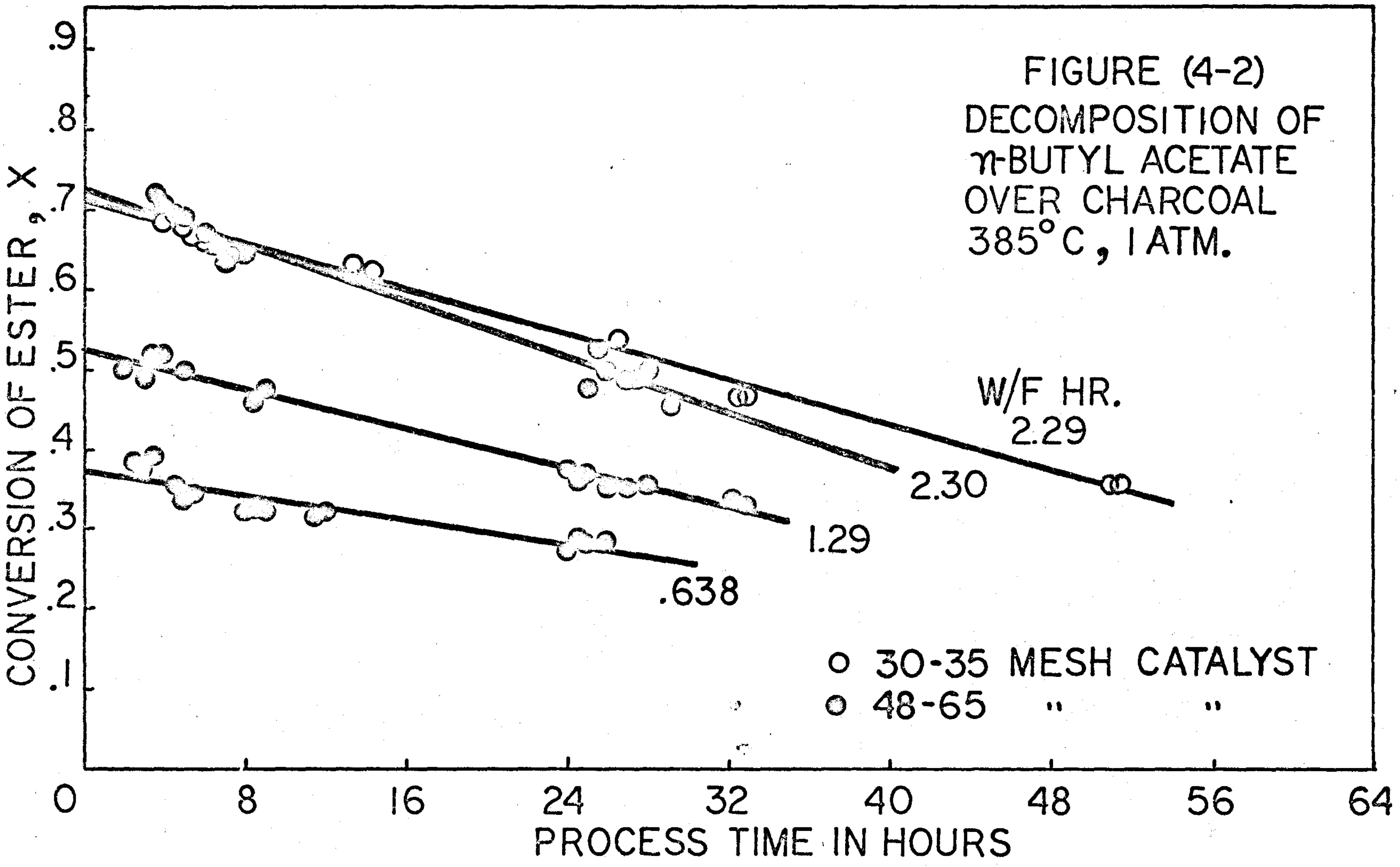

FIGURE (4-2)
DECOMPOSITION OF
n-BUTYL ACETATE
OVER CHARCOAL
385°C, 1 ATM.

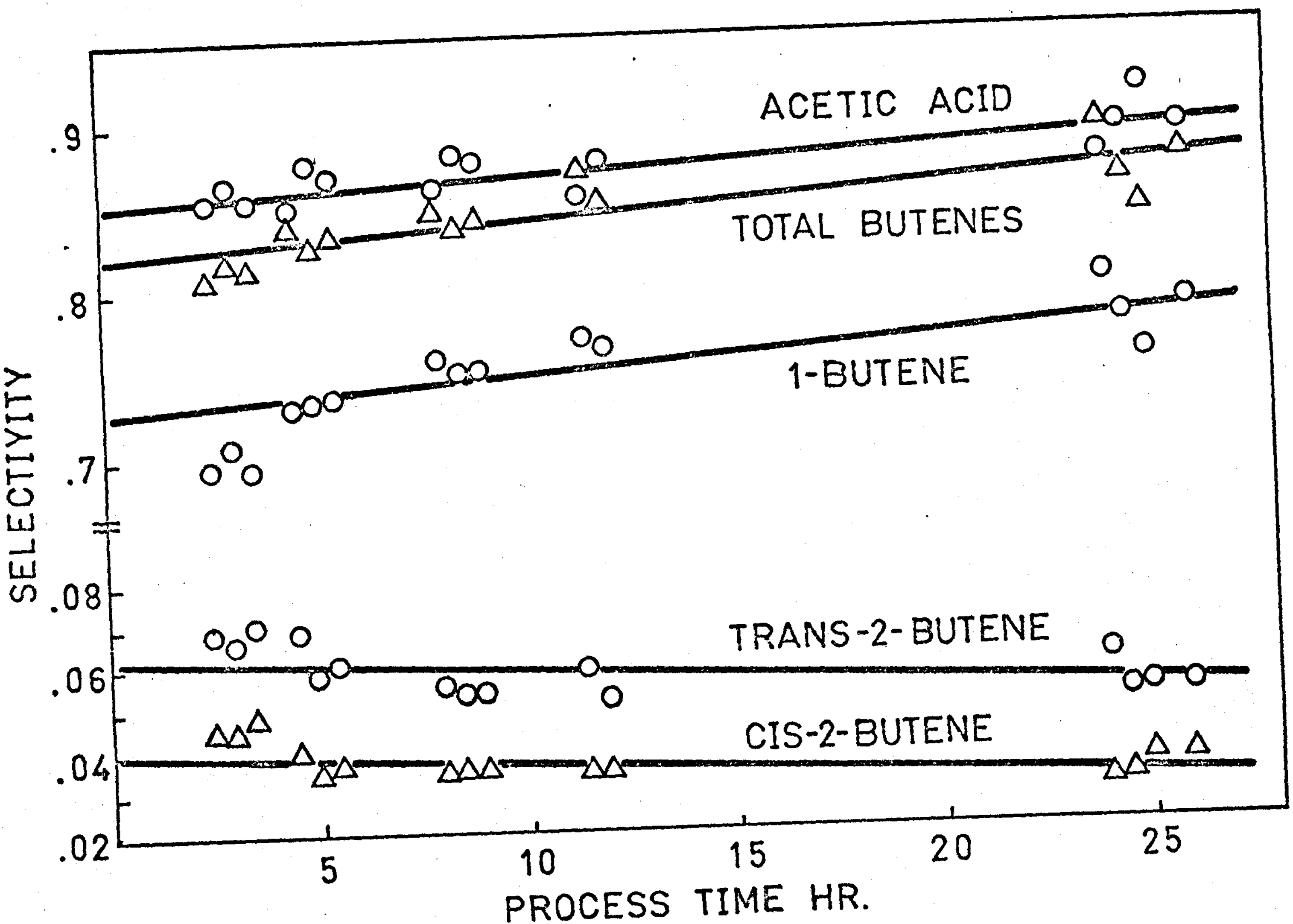

Figure (4-3) Selectivity data for n-butyl acetate decomposition over charcoal at 385°C and W/F = 0.638 hours.

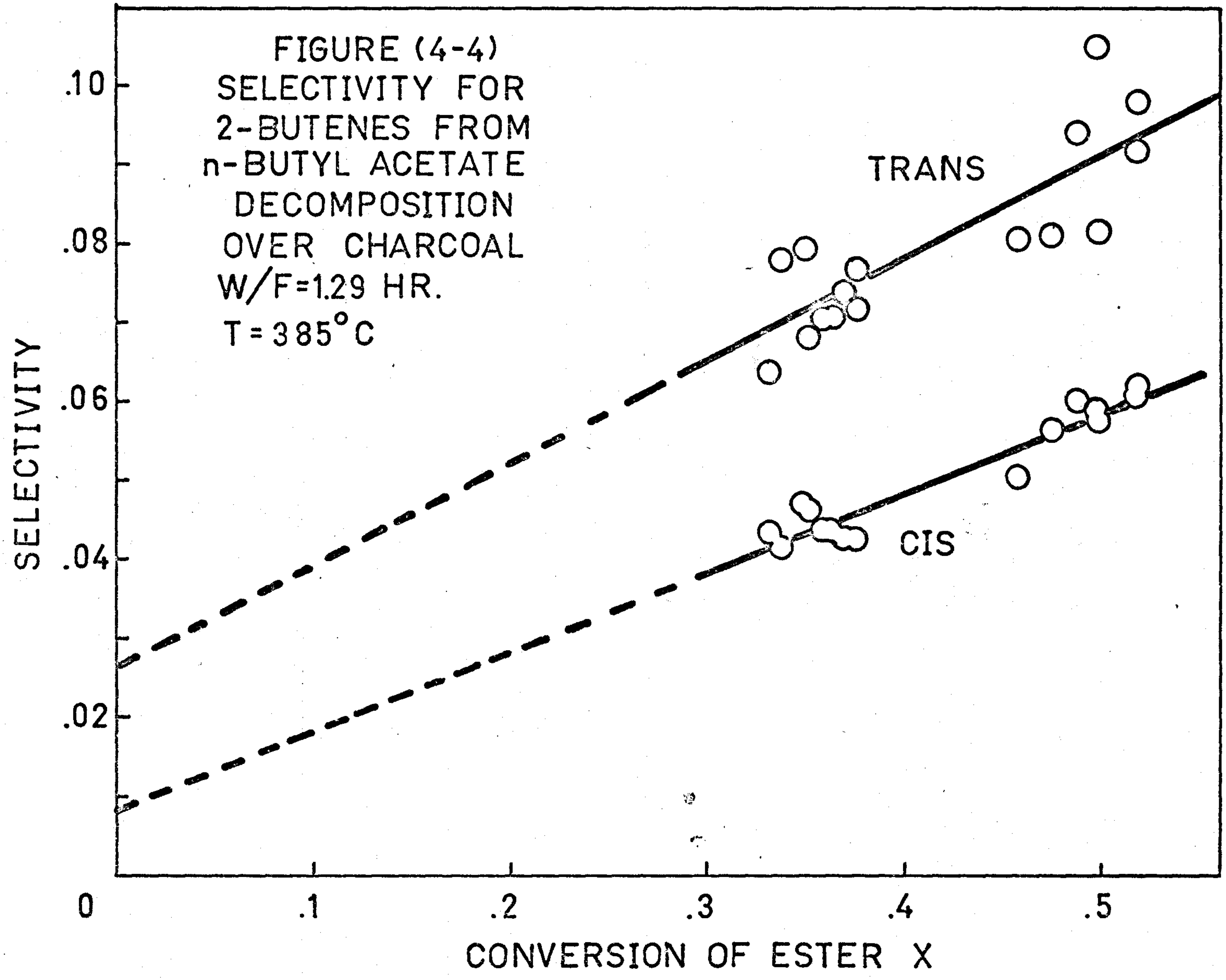

FIGURE (4-4)
SELECTIVITY FOR
2-BUTENES FROM
n-BUTYL ACETATE
DECOMPOSITION
OVER CHARCOAL
W/F=1.29 HR.
T=385°C

apparent linear decay was observed even for a process time of 73 hours as shown by Figure (4-1). To derive kinetic data, i.e., conversions at different space times, the conversion versus process time data were fitted with least squares straight lines. These lines were then extrapolated to zero process time to calculate x on unfouled charcoal. The kinetic data derived in this manner are shown in Figure (4-5). Calculating conversions at zero process time insures that an important requirement for the kinetic data is fulfilled: the data all refer to catalyst having the same specific activity. In this case the specific activity of the catalyst depends on the extent of fouling; hence, it was assumed that at zero process time the charcoal was not fouled and that the amount of active catalyst is equal to the weight of charcoal put into the reactor.

The selectivity data from the n-butyl acetate experiments were treated in much the same way as the conversion data: The selectivities for the major products were fitted with least squares straight lines which were extrapolated to zero process time to calculate selectivities on unfouled charcoal. Examples of some typical selectivity data with fitted lines appear in Figures (4-3) and (4-4). To determine how the products changed with the extent of reaction, selectivities at zero process time were plotted against conversion at zero process time as shown in Figure (4-6). The selectivity plots show that,

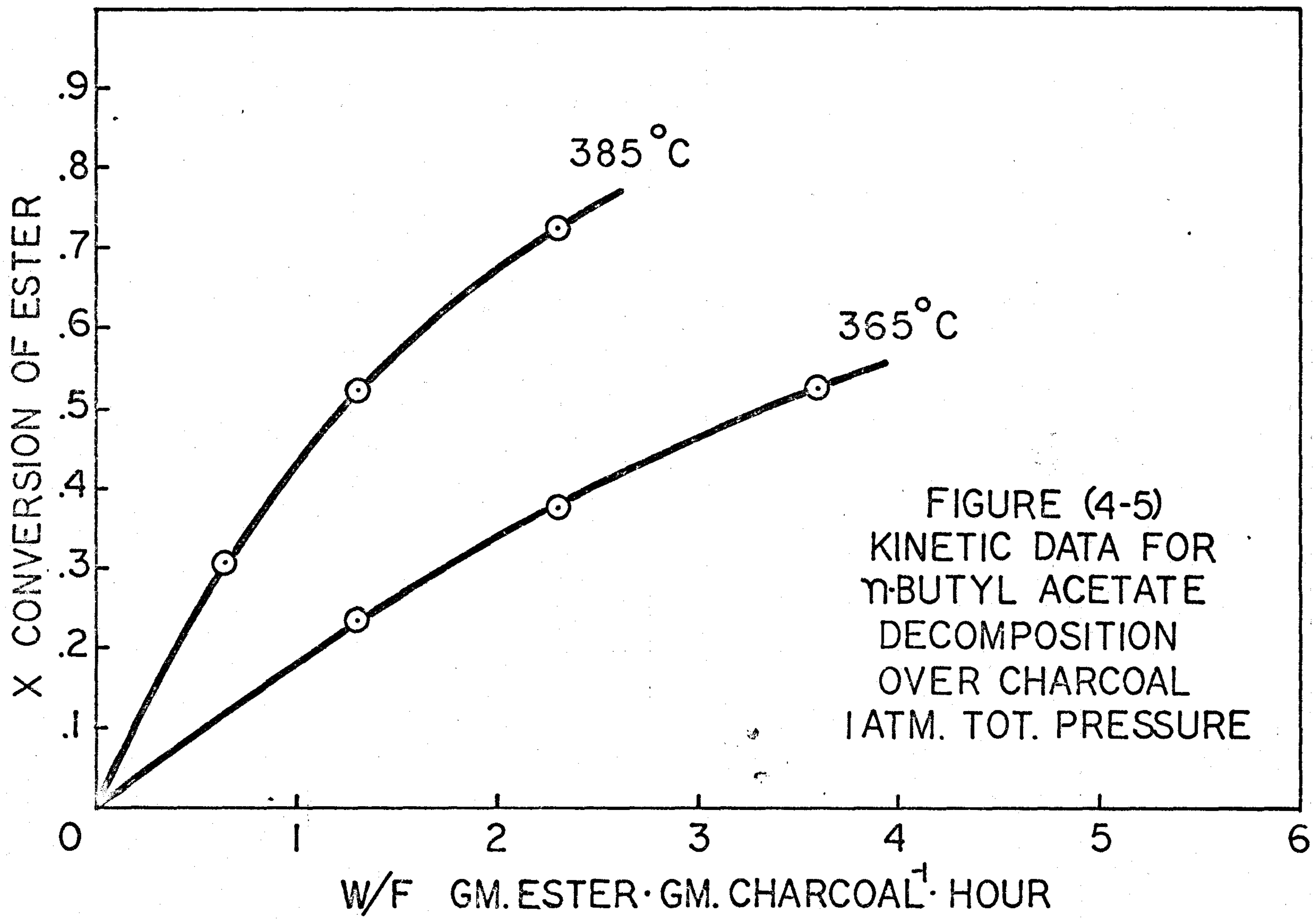

FIGURE (4-5)
KINETIC DATA FOR
n-BUTYL ACETATE
DECOMPOSITION
OVER CHARCOAL
1 ATM. TOT. PRESSURE

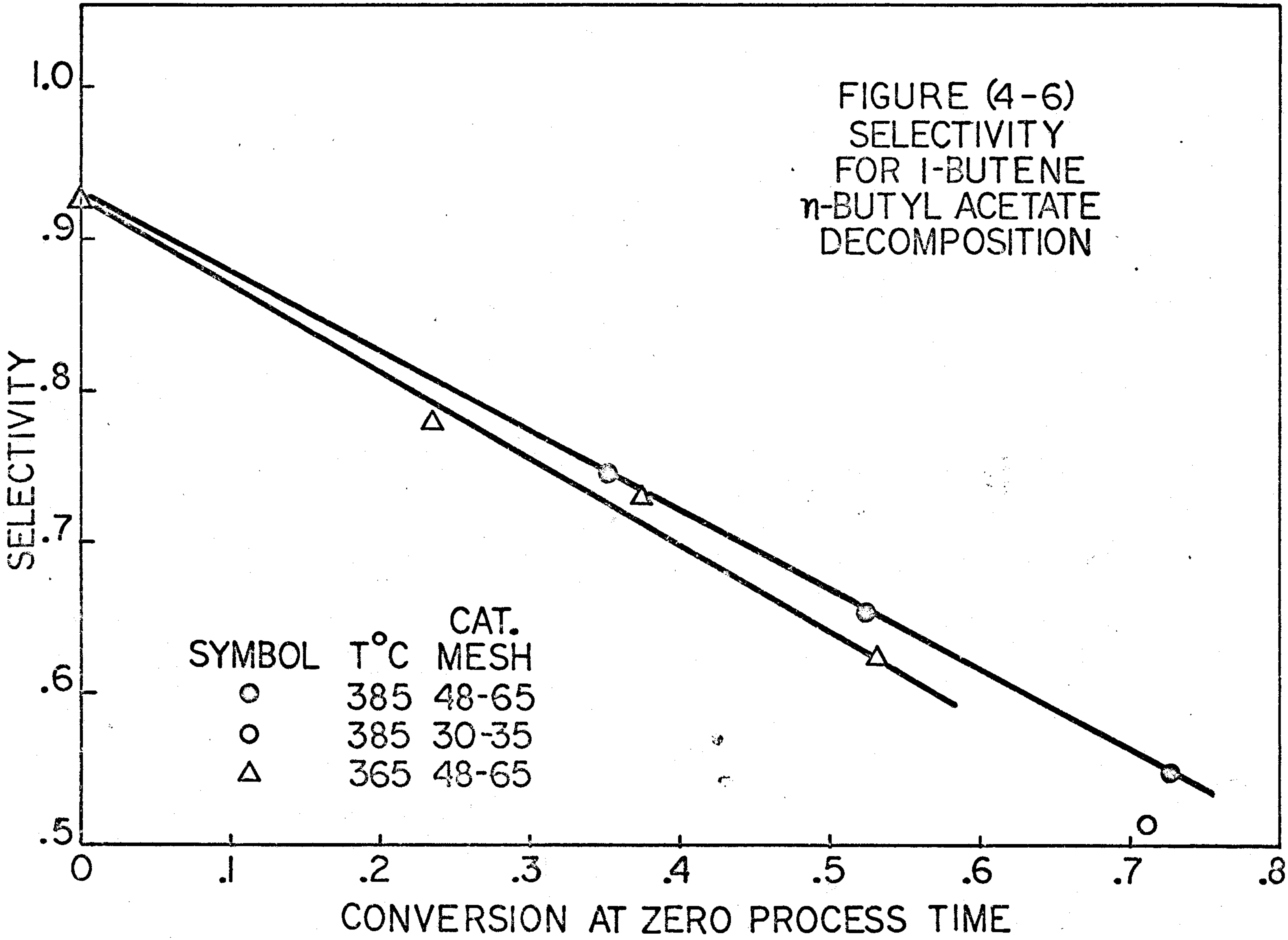

FIGURE (4-6)
SELECTIVITY
FOR 1-BUTENE
n-BUTYL ACETATE
DECOMPOSITION

of the olefins produced, 1-butene predominates, and unlike the gas phase decomposition of n-butyl acetate(7,9), some cis and trans-2-butenes are formed. A similar conclusion about the initial selectivity for 1-butene can be made from Figure (4-7), which is a plot of the experimental data showing the selectivity for 1-butene as a function of the conversion of ester. As the conversion of ester increases the fraction of 2-butenes to 1-butene increases, with trans, the more stable(35) 2-butene, being produced in greater quantities than cis-2-butene. Experimental evidence suggests that most of the conclusions made about initial butene selectivities from Figures (4-4) and (4-7) are valid. The datum at zero conversion shown in Figure (4-6) was determined experimentally at 365°C.

The first step in the kinetic analysis was to examine the data in Figure (4-5). Few facts about the reaction kinetics are obvious from the figure, except that the rate of reaction increases with temperature. Any mechanism which might be proposed to explain the reaction kinetics must be consistent with the data in Figure (4-5).

One of the primary objects of the research is to determine what role the charcoal surface plays in the ester decomposition reaction. Bearing in mind the limitations of Langmuir surface coverage expressions(36,37) and the other assumptions made in this analysis, important information about the role of the charcoal surface can perhaps be deduced

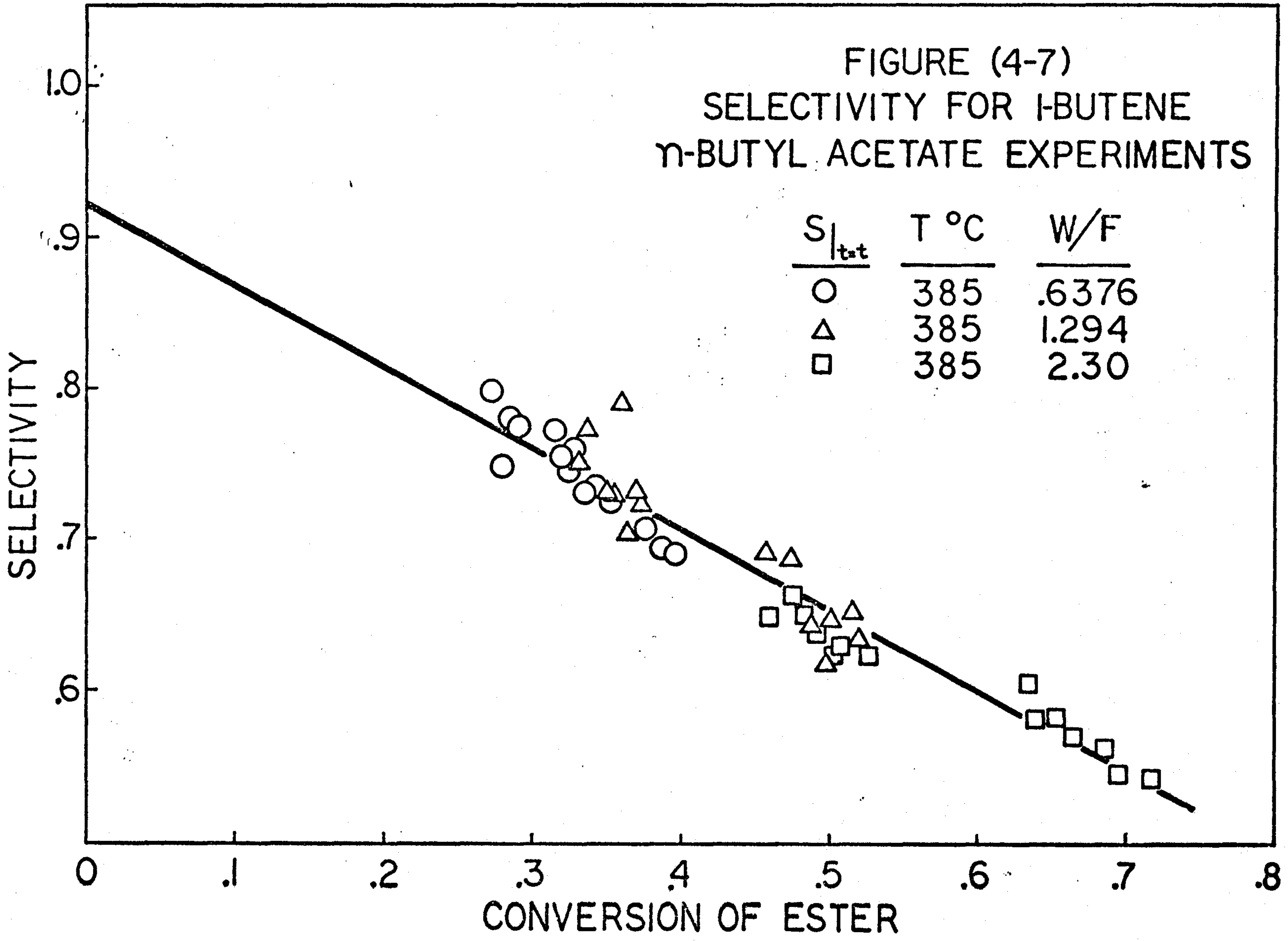

FIGURE (4-7)
SELECTIVITY FOR 1-BUTENE
n-BUTYL ACETATE EXPERIMENTS

if a suitable rate expression for the data in Figure (4-5) can be found. Determining which type of rate equation a reaction follows may establish the slowest step in the adsorption-reaction-desorption sequence through which reacting molecules pass. When mass transfer of reactants in the gas phase is not an important factor, the rate controlling step is a reaction involving a surface adsorption site. The most satisfactory method of determining the rate expression for the overall reaction is the trial-and-error procedure of proposing rate equations and testing them with experimental data. Speculating about the reaction system of interest here, it is reasonable to expect that the overall reaction rate of esters over charcoal might be controlled by desorption of products, since charcoal adsorbs most organic vapors very strongly(2,3); or, from what is known of charcoal as a catalyst(4,18), one might expect the rate of the surface reaction to be the controlling step.

For a preliminary mathematical analysis of the kinetics, the data in Figure (4-5) were fitted with an empirical equation which expressed the rate of reaction as a simple power function of the ester concentration. The equation used was

$$\text{rate} = r = \frac{dx}{d(W/F)} = kP_{e_o}(1 - x)^n \qquad (4\text{-}5)$$

where P_{e_o} is the partial pressure of ester entering the reactor

(P_{e_o} = 1 atm. for all n-butyl acetate experiments), k is an empirical rate constant having units of grams of ester per gram of charcoal per hour, and n is a constant representing the order of the reaction. The values of k and n at 365° and 385°C were calculated using minimum residual sums of squares of deviations (RSS_{min}) as a criterion for the "best" fit, as shown in Program 2 of Appendix E. The results of the fittings were as follows: At 385°C, k = 0.586, n = 1.07, and RSS = 0.0000007; and at 365° C, k = 0.196, n = 0.84, and RSS = 0.00017. These figures show that the empirical rate constant increases as expected with temperature, and that the empirical order of reaction increases to around unity as temperature changes from 365° to 385°C.

The method of Hinshelwood(31) was used for developing rate expressions from theory to describe the kinetics of catalyzed butyl acetate decomposition. This method assumes various rate limiting steps for the reaction and calculates the resulting rate equation; it is assumed that surface coverage of the catalyst can be expressed by the Langmuir adsorption isotherm(38). Rate equations derived in this manner are known as Langmuir-Hinshelwood equations(31,32). The theoretical rate expressions which were considered in this study are shown in Table (4-3). Three assumptions were made in applying the Langmuir-Hinshelwood equations to the butyl acetate reactions: (a) the reaction kinetics are not complicated by resistance to diffusional mass transfer, as suggested by the kinetic data in Figure (4-2), as well as the data which will be presented in later chapters, (b) the adsorption constants K_a and K_b in the rate equations are negligible based on the results of the pulse adsorption studies presented in Chapter 3, (c) each isomer of butyl acetate decomposes on charcoal by the same reaction mechanism. Each of these assumptions simplifies the analyses of the kinetic data. For example, assumption (c) implies that n-butyl acetate decomposition will follow zero order kinetics at low temperatures and low conversions, as does sec-butyl acetate.

Each of the theoretical rate equations in Table (4-3) was tested for its ability to reproduce the kinetic data for the butyl acetate reactions. The methods used for selecting the best rate equation were approximately the same for each type of butyl acetate. These methods will be described in general in the following paragraphs, and the results of applying the methods to the n-butyl acetate data will be presented.

A trial-and-error method was used to eliminate rate equations which were not satisfactory. First, each rate equation was examined to determine if its form is consistent with the observed data; for example, the butyl acetate reactions become zero order at low temperatures and low conversions as mentioned above. Of the Langmuir-Hinshelwood rate equations shown in Table (4-3), only two expressions could possibly be zero order in ester over a wide range of conversions. These

TABLE (4-3)

Kinetic Equations

Mechanism Controlling Rate of Reaction	Rate equation $r = dx/d(W/F)$ (Differential Form)	Linear form of integrated rate equation, $(W/F) = \underline{\theta}\ \underline{X}$		Notes and Explanations
		$\underline{\theta}$	$\underline{X}$	
Rate of Surface Reaction on Adjacent Sites $E\cdot\square+\square\rightarrow B\cdot\square+A\cdot\square$	$r = \frac{kLK_e(P_e-P_aP_b/K)}{(1+K_eP_e+K_bP_b+K_aP_a)^2}$	$\frac{m^2+N^2}{2kLK_e}$	$\ln\frac{(1+x)}{(1-x)}$	Species Representations: E=Ester B=Butene A=Acetic Aci □=Empty Catalyst Site L=Saturation Concentration of active catalyst site grams of ester/gram of catalyst Definitions: K_e=Adsorptio constant for ester on charcoal,atm^{-1} k=reaction rate constant $time^{-1}$. P_e=partial pressure of ester, atm^{-1} K=equilibriu constant for reaction: $K = \frac{P_aP_b}{P_e}$ $M = (1-K_e)$ $N=(K_b+K_a-K_e)$
		$-\frac{MN}{kLK_e}$	$\ln(1-x^2)$	
		$-\frac{N^2}{kLK_e}$	x	
Rate of surface reaction on individual sites $E\cdot\square\rightarrow B\cdot\square + A$	$r = \frac{kLK_e(P_e-P_aP_b/K)}{1+K_eP_e+K_bP_b}$	$-\frac{(L-K_e+K_b)}{kLK_e}$	x	
		$-\frac{(2=K_b)}{kLK_e}$	$\ln(1-x)$	
Rate of adsorption on surface $E+\square\rightarrow E\cdot\square$	$r = \frac{kL(P_e-P_aP_b/K)}{1+\frac{K_e}{K}P_bP_a+K_bP_b+K_aP_a}$	$-\frac{(1+K_e+K_b+K_a)}{kLK_e}$	x	
		$-\frac{(2+K_b+K_a)}{kL}$	$\ln(1-x)$	
		$\frac{K_e}{2kL}$	$\ln(\frac{1-x}{1+x})$	
Rate of Desorption of Product $B\cdot\square\rightarrow B+\square$	$r = \frac{kLK(P_e/P_a-P_e/K)}{1+K_eP_e+K_bK\frac{P_e}{P_a}+K_aP_a}$	$-\frac{(1-K_e-KK_b+K_a)}{kLK}$	x	
		$\frac{(1+K_e)}{2kLK}$	$\ln(1-x^2)$	
		$\frac{(1-K_e+K_a)}{2kLK}$	$\ln\frac{(1-x)}{(1-x)}$	
Pseudohomogeneous Reaction	$r = k(1-x)^n$ $n = 1$	$\frac{2}{k}$	$\ln\frac{1}{1-x}$	
		-1	x	

are the equations for desorption control and for rate control by surface reaction on a single site.

In order to determine which of the two remaining expressions most likely represents the actual reaction scheme the following method was used: The equations for differential reaction rate were integrated and arranged in the linear form

$$\tau = \theta_1 \cdot X_1 + \theta_2 \cdot X_2 + \theta_3 \cdot X_3 + \ldots + \theta_n \cdot X_n \qquad (4\text{-}6)$$

or

$$\tau = \underline{\theta} \cdot \underline{X}$$

where the θ_i coefficients are combinations of the adsorption, kinetic, and equilibrium constants in the original rate equation*, and the X_i variables are functions of conversion only. Linear forms of the integrated rate equations are shown in Table (4-3). An "objective-function", $|Z|$, for each rate expression can be set up by rearranging Equation (4-5) to give

$$z = \tau - (\theta_1 \cdot X_1 + \theta_2 \cdot X_2 + \ldots)$$

$$z = \tau - \underline{\theta} \cdot \underline{X} \; . \qquad (4\text{-}6)$$

Appendix D shows the derivation of the objective functions for the single-site surface reaction rate equation and for the desorption-control rate equation.

The objective function is the key equation in a trial-and-

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*For convenience the group of constants in any rate equation will be given the symbol $\underline{C}$.

error search for the "best" value of $\underline{C}$; it forms the link between assumed values of $\underline{\theta}$ and the value of some criterion used for judging how acceptable $\underline{\theta}$ is. In this analysis the criterion used was minimum residual sum of squares between the observed x at some τ and values of x calculated using Equation (4-6). For any τ and for an assumed $\underline{\theta}$ there is a unique value of x for which z will become zero; this is the calculated x. The rate expression for which the minimum RSS results can be assumed to be the mostly like rate equation, provided all of the components of $\underline{C}$ calculated by the search have physically reasonable values.

Two mathematical techniques were used in the search for best C coefficients: The first, shown in Program 2, was a grid search used to find an approximate value of $\underline{C}$. Next, the Rosenbrock Search Technique(39) was applied to refine the initial coefficient estimates and calculate $\underline{C}$ to high precision. The Rosenbrock method is shown in Program 3 in Appendix E. The results of the search for the coefficients of the desorption expression and the single - site equation are presented in Table (4-4). Both of the rate expressions fit the data quite well, and the calculated values of the coefficients are physically reasonable at both temperatures. The RSS values for both cases were around 10^{-6}, which suggests that the single-site mechanism expresses the rate limiting step of the reaction somewhat better than the desorption mechanism does; the desorption

TABLE (4-4)

Values of Rate Equation Coefficients and RSS

Rate Controlling Mechanism	C	Grid Search Values 365°	Grid Search Values 385°	Grid Search RSS	Rosenbrock Search Values 365°	Rosenbrock Search Values 385°	Rosenbrock Search RSS
Desorption of B controlling; $r=\frac{k_bLK\ P_e/P_a}{1+K_eP_e+K_bK_e\ P_e/P_a}$	k_bLK	1.	1.	0.00017 at 365°	0.243	0.532	5.44×10^{-6} at 365°
	K_e	13.	6.		0.481	.0407	
	K_bK	4.	1.	0.0003 at 385°	1.15	0.898	3.29×10^{-7} at 385°
Surface Reaction, 1 site; $r = \frac{kLK_eP_e}{1+K_eP_e}$	kL	0.396	1.35	7.9×10^{-6} at 365°	0.39	1.34	7.5×10^{-6} at 365°
	K_e	1.08	0.78	3.9×10^{-7} at 385°C	1.10	0.79	3.6×10^{-7} at 385°

equation contains three parameters, and if the data correlations were empirical only, would be expected to result in a smaller RSS than the surface reaction equation containing only two parameters. Thus, the surface reaction mechanism might be favored since it is the simplest of the two expressions and reproduces the n-butyl acetate data reasonably. Evidence is given in later chapters to show that the desorption equation is unsatisfactory for other esters.

A necessary part of the kinetic analysis is determining the ranges of reasonable values of coefficients, or the confidence limits of the coefficients. For a Langmuir-Hinshelwood rate expression, finding coefficient limits is not straightforward, since the integrated equation cannot be arranged to give x explicitly. The customary calculation of confidence limits using the Student's t Test is not possible. Instead, to estimate how reasonable some set of coefficients $\underline{C}$ might be, one can evaluate what is known as the "likelihood function"(40, 41) at the particular set of coefficients. The value of the likelihood function depends on the parameters and also on experimental error; it is given by

$$L(\underline{C},\sigma) = \frac{1}{\sigma^n (2\pi)^{n/2}} \cdot \exp\{\frac{-1}{2\sigma^2} \sum_i^n [x_i - f(\underline{C},\tau_i)]^2\} \quad (4\text{-}7)$$

where n is the number of experimental observations

x_i is the ith observation of the dependent variable

τ_i is the ith value of the independent variable f is an equation with k parameters correlating x and τ and is derived from the rate equation

σ is the variance, $\sigma^2 = \mathrm{RSS(minimum)}/(n-k)$.

The maximum of the likelihood function occurs at that value of $\underset{\sim}{C}$ which results in minimum RSS, that is, the best $\underset{\sim}{C}$. For any other value of $\underset{\sim}{C}$ the likelihood will be smaller. Confidence limits of parameters can be found by calculating the ratio

$$\lambda = \frac{L(\sigma, \underset{\sim}{C}_{\text{assumed}})}{L(\sigma, \underset{\sim}{C}_{\text{best}})} . \tag{4-8}$$

A set of coefficients $\underset{\sim}{C}$ can be defined as being "unreasonable" if the value of λ calculated using $\underset{\sim}{C}_{\text{assumed}}$ is less than some criterion, say $\lambda_{min} = 0.1$. Program 4 in Appendix E shows the calculation of λ values for a grid of assumed values of kL and K_e for the surface reaction rate equation. This program uses Program 3,b to solve the problem of the integrated equation implicit in x.

For the n-butyl acetate data the acceptable values of K_e and kL were found to lie along a very narrow, almost linear ridge. This was true at both 365° and 385°C. Contours of equal λ values will not be illustrated here since their determination is time consuming and unnecessary. (See Figure (5-3) for similar contours for sec-butyl acetate coefficients.) The ranges of acceptable values of coefficients for the surface reaction rate equation are given in Table (4-5).

TABLE (4-5)

Values of the Kinetic and Adsorption Coefficients for the Rate Equation $r = kLK_eP_e/1+K_eP_e$ Fitted to n-Butyl Acetate Data

Coefficient	Temp °C	"Best" Value	Confidents Limits $\lambda = 0.1$		$\lambda = 0.01$	
			Min.	Max.	Min.	Max.
$k \cdot L \frac{\text{gram ester}}{\text{gram cat.} \cdot \text{hr.}}$	365	0.391	0.355	0.439	.355	.460
$k \cdot L \frac{\text{gram ester}}{\text{gram cat.} \cdot \text{hr.}}$	385	1.340	1.315	1.365	1.298	1.375
K_e atm^{-1}	365	1.100	0.915	1.290	0.840	1.34
K_e atm^{-1}	385	0.790	0.760	0.810	0.760	0.824

TABLE (4-6)

Values of the Temperature Independent Coefficients for Expression $kL = k_oL\ e^{-(E/RT)*}$ and $K_e = K_{e_o}\ e^{-(H/RT)**}$

Coefficient	"Best" Value	$\lambda = 0.1$ (99.9%) Min.	Max.	$\lambda = 0.01$ Min.	Min.
$\log k_oL \frac{\text{g ester}}{\text{g cat.} \cdot \text{hr.}}$	17.17	15.79	18.80	14.72	18.91
E* kcal/mole	51.33	47.19	56.23	43.30	56.54
$\log K_{e_o}$ atm^{-1}	-4.68	-1.73	-7.22	-0.34	-7.73
H** kcal/mole	-13.80	-5.09	-22.09	-0.81	-23.68

*E = The Arrhenius activation energy

**H = The heat of adsorption of n-butyl acetate on the catalyst

The Arrhenius activation energy, E, and its confidence limits were found by applying the Arrhenius equation $kL = k_oL \cdot \exp(-E/RT)$ to the data in Table (4-5); for example, a maximum E likely to be found with the data at $\lambda = 0.1$ was calculated by simultaneously solving the Arrhenius equation for $kL_{(max)} = 1.365$ at 385°C and $kL_{(min)} = 0.355$ at 365° C. The heat of adsorption of the ester on charcoal, H, was calculated in a similar manner by expressing the adsorption constant as $K_e = K_{e_o} \cdot \exp(-H/RT)$. Values of pre-exponential factors, activation energies, and heats of adsorption are shown in Table (4-6). As a comparison, reported values of the activation energy for the pyrolysis of n-butyl acetate range from 44.5 to 49.3 kcal/mole(7), and the latent heat of vaporization-condensation of n-butyl acetate is 8.58 kcal/mole(42).

Although the confidence limits of the exponential and pre-exponential factors were calculated from data at confidence levels of $\lambda = 0.01$ and $\lambda = 0.1$, these confidence levels do not actually apply to the limits found for E,H, etc. The limits of the factors shown in Table (4-6) are overestimated for the levels $\lambda = 0.1$ and $\lambda = 0.01$. There is a small likelihood (relatively 0.1) of finding a value of kL so high as 1.365 at 385° or so low as 0.355 at 365°C. The likelihood of the simultaneous occurrence of these extreme values of $k \cdot L$ is even smaller. There is no simple relationship between the likelihood ratio and the percentile confidence level calculated from the Student's t Test, but the confidence limits of E, H, etc. found from data at $\lambda = 0.1$ have a percentile confidence level of at least 99.9%(41,43).

4.4 CATALYST FOULING

After each experiment the catalyst was removed from the reactor and weighed to determine the weight that it gained during its use. The weight increases were about 15 to 20% for most catalysts. The used catalysts had the same appearance as fresh charcoal, and microscopic examination revealed nothing about the physical nature of the fouling material except that it appeared to be randomly deposited on the catalyst as shown by Figure (4-4-b). After weighing used Catalyst no. 64 the charcoal was heated in helium for ten minutes. (Catalyst no. 64 was the charcoal which was used at a temperature of 365°C and W/F = 3.59 hours.) The heating produced no weight loss, indicating that some non-volatile fouling material caused the weight increase. This catalyst was then returned to the reactor and additional measurements of the conversion were made at the same space time of 3.59 hr. as had been used prior to removing the catalyst from the reactor. The values of conversion measured during the second use of Catalyst no. 64 were the same as the values which could have been expected had the initial experiment not been interrupted.

A nitrogen adsorption isotherm was measured at -195°C on a sample of Catalyst no. 63 removed from the outlet of the catalyst bed. The results of this isotherm appear in Figure (3-1) and show that the sample had suffered a severe loss of surface area equivalent to about a twenty-fold decrease from the surface area of unused charcoal. Figure (3-1) also shows the nitrogen adsorption isotherm for a sample of used Catalyst no. 65, selected to represent an "average" sample from the bed. As shown in the figure the surface area that was measured was intermediate between those areas found for Catalyst no. 65 and unused charcoal. The weight increases given in Figure (3-1) pertain to the overall catalyst bed and may not apply to the particular samples of the beds which were used for isotherm measurements.

The surface area measurements suggest that a part of the catalyst fouling is caused by the products, since the outlet of the catalyst bed incurs the greatest surface area loss. These findings agree with the results of experiments made by passing butenes over charcoal (see Section 3.1). The plots in Figures (4-1) and (4-2) give additional evidence that products contribute to fouling, since the slopes show that the rate of fouling is proportional to the conversion. The dependence of the fouling rate on the initial conversion follows, in general, the behavior predicted by Froment and Bischoff (25,26) for exponential activity decrease caused by products fouling the catalyst.

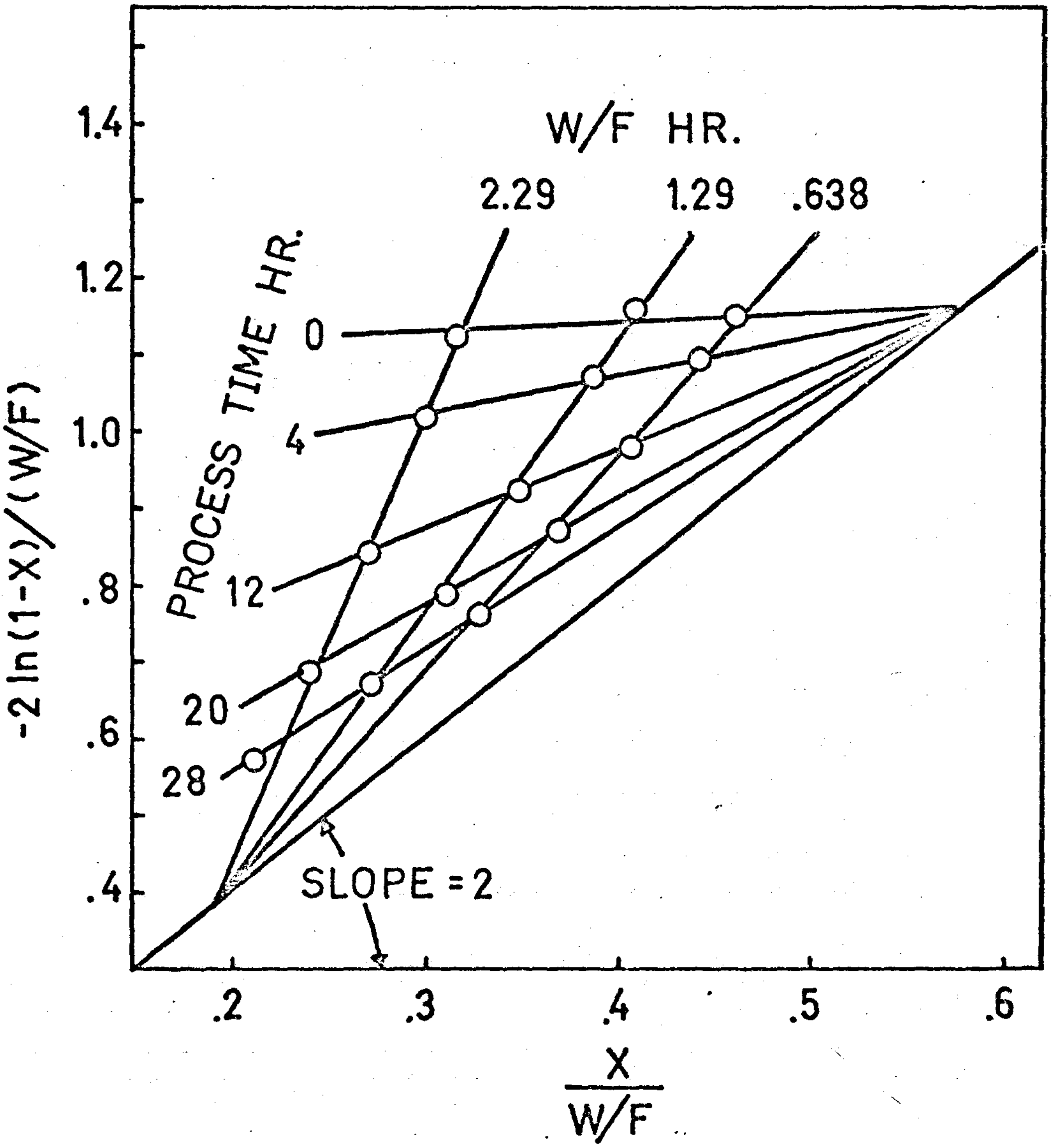
At relative pressures above 0.3, the adsorption isotherms for used catalysts (Figure (3-1)) have somewhat smaller slopes than the isotherm for fresh charcoal, which indicates that the n-butyl acetate reaction causes the selective destruction of the large pores of the catalyst. The reaction apparently results in a different type of area destruction than that caused by butenes alone, which eliminate surface area non-selectively. Attempts were made to correlate losses in activity with either the total amounts of reactant or product passed over the catalyst; however, no correlations could be found.

An interesting correlation between space time, process time, and conversion was found for the decomposition of n-butyl acetate over fouled charcoal. This correlation resulted from attempts to determine graphically the values of K_e and kL for the integrated surface reaction rate equation. One of the linear forms of the integrated rate equation which can be plotted to find the coefficients is

$$-\ 2 \cdot \frac{\ln(1-x)}{(W/F)} = (1-K_e)\ \frac{x}{(W/F)} + kL \cdot K_e \ . \qquad (4\text{-}9)$$

Plots of this equation using conversions calculated at zero process time yield approximately the same values of kL and K_e as were found from the search methods described in Section 4.3. Plots of equation (4-9) using conversions calculated at other process times yield the results shown in Figure (4-8).

Figure (4-8) A plot of
$-2\ln(1-x)/(W/F) = x(1-K_e)/(W/F) + K_e kL$
for n-butyl acetate decomposition
over charcoal at 385° C.



CHAPTER 5

SECONDARY-BUTYL ACETATE

5.1 EXPERIMENTAL PROCEDURE

Two sets of experiments were made with sec-butyl acetate: The first series was made between 303° and 393°C using Batch 1 catalyst in the 1.35 cm. ID stainless steel reactor, and the second set of experiments was made between 195.9° and 350° C with Batch 2 catalyst and a 1.0 cm. ID Pyrex reactor. Samples of charcoal from the different batches were used at 350°C to determine the reproducibility of catalyst preparation. It was necessary to know the relative activity of the two batches since most sec-butyl acetate experiments were made using Batch 1 catalyst, while the decompositions of the other three esters were studied with Batch 2 charcoal. (The catalyst was reproducible).

Prior to use, Batch 1 catalyst was heated to 930°C in nitrogen for 20 minutes, and Batch 2 catalyst was pretreated similarly using helium. The catalysts were loaded into the reactor by the procedure described in Section 4.1, except that Batch 1 charcoal was weighed after exposure to air. All experiments were made at a total pressure of 1 atmosphere. Pure sec-butyl acetate was used at all temperatures, and, in addition, at 350°C experiments were made using ester which was diluted to an initial partial pressure, P_{e_o}, of about 0.3 atm. Nitrogen was used to dilute the sec-butyl acetate reacted over Batch 1 catalyst, and ester diluted with acetic acid was used with Batch 2 charcoal to obtain kinetic data at $P_{e_o} = 0.3$ atm.

In preliminary experiments, 30-35 mesh charcoal which was used as a catalyst at 350°C in a stainless steel reactor showed no loss in activity after about 9 hours of continuous use at a conversion of about 0.7. Kinetic data were therefore obtained by measuring the conversions which resulted when sec-butyl acetate was fed at different rates over fixed amounts of catalyst. That is, since the catalyst activity was constant, x could be measured directly at various values of space time, $\tau = W/F$.

The reaction was started by feeding a mixture of nitrogen and sec-butyl acetate to the reactor. The nitrogen acted as a carrier gas and transported ester through the catalyst bed so that "bare" charcoal at the bed outlet might not be exposed only to high concentrations of products during the initial period of the reaction. After about a half hour the nitrogen carrier flow was discontinued and ester was left to feed to the reactor. When steady conditions had established, usually in about another half hour, the products were sampled and analyzed. The feed rate of ester was then changed to obtain data at another space velocity. For the nitrogen dilution experiments, the flow of gas through the reactor was set with a needle valve before butyl acetate was admitted. The gaseous diluent rate was adjusted to approximately 2.5 times the molar flow rate of the reactant and was measured by a soap-film flowmeter at the end of the flow system. For ester diluted with acetic acid the feed rates were calibrated by weighing the quantities of mixture delivered by the syringe pump in measured time intervals.

The actual time that any particular catalyst was used for obtaining kinetic data was less than 10 hours, and during the period of use checks were frequently made to determine if the catalytic activity had decreased. Catalysts were weighed after removing them from the reactor.

The GC analysis of the reactor products was made using 1/4 inch × 5 feet of Silicone Ge SF-96* on 40-60 mesh Chromosorb P at 120°C as Column 1 (see Figure (2-1)), while Column 2 was 1/4 inch × 25 feet of propylene carbonate on 80-100 mesh Chromosorb W at 25° C. The conversion of sec-butyl acetate was calculated by using Equation (4-3) and the selectivities were calculated using Equation (4-4).

5.2 RESULTS OF THE SECONDARY-BUTYL ACETATE EXPERIMENTS

Acetic acid and butenes were the principal products from sec-butyl acetate decomposition over charcoal, but the

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*Varian Aerograph, Walnut Creek, California.

reaction also produced small amounts of methane, carbon dioxide, carbon monoxide, and n-butane. The butenes were produced in about the same ratio as in the gas-phase reaction of sec-butyl acetate: the ratio of 1-butene to 2-butenes was about 3:2. The activity of the catalyst did not decrease during the kinetic experiments with sec-butyl acetate.

The results of the experiments are presented in Table (5-1). Figure (5-1) summarizes most of the kinetic data in a plot of the conversion of ester as a function of space time. The details of the experimental conditions are included in Table (5-1).

Exploratory experiments made with sec-butyl acetate showed that the catalytic activity was independent of the time that the charcoal was heated in helium at 930°C. In other preliminary experiments, air was passed through the catalyst bed at 350°C for about 15 minutes. This treatment did not change the activity of the catalyst. The gas-phase decomposition of sec-butyl acetate in the reactor was negligible at the ester feed rates used in the kinetic experiments.

The kinetic data were reproducible with different samples of catalyst as Figure (5-1) illustrates. Although no changes in the catalytic activity were observed during the kinetic experiments, a sharp drop in the activity occurred with a catalyst which was used overnight at 375°C. These

TABLE (5-1)
KINETIC AND SELECTIVITY DATA FOR SEC-BUTYL ACETATE DECOMPOSITION OVER CHARCOAL

TEMPERATURE OF REACTION = 393 **C**, BATCH 1 30-35 MESH CATALYST
STAINLESS STEEL REACTOR, PURE ESTER FEED

Hr.		SELECTIVITY						
SPACE TIME	X	ACETIC ACID	CO+ CH4	CO2	N- BUTANE	1- BUTENE	TRANS- BUTENE	CIS-2- BUTENE
.0779	.9336	.798	.025	.009	.0320	.5986	.3208	.2485
.0309	.4918	.964	.010	.005	.0195	.5388	.2740	.1977
.1581	.9905	.847	.049	.014	.0244	.5733	.3171	.2224
.0636	.5094	.968	.011	.007	.0163	.5749	.2690	.1649

TEMPERATURE OF REACTION= 375 **C**, BATCH 1 30-35 MESH CATALYST
STAINLESS STEEL REACTOR, PURE ESTER FEED

Hr.		SELECTIVITY						
SPACE TIME	X	ACETIC ACID	CO+ CH4	CO2	N- BUTANE	1- BUTENE	TRANS- BUTENE	CIS-2- BUTENE
.1861	.9394	.824	.044	.009	.0262	.5812	.3322	.2267
.1861	.9360	.896	.036	.007	.0228	.5607	.3037	.2066
.2518	.9734	.854	.055	.013	.0258	.5699	.3172	.2143
.2518	.9453	.911	.042	.010	.0219	.5550	.2986	.1977
.1251	.7359	.924	.022	.008	.0183	.5600	.2915	.1977
.1251	.7274	.930	.021	.009	.0180	.5637	.2876	.1914
.0944	.5202	.965	.014	.008	.0175	.5602	.2692	.1797
.0944	.5466	.968	.013	.007	.0162	.5519	.2729	.1836
.3878	.9928	.849	.060	.015	.0261	.5741	.3247	.2044
.3878	.9938	.900	.058	.014	.0237	.5543	.3014	.1976
.2298	.9346	.915	.027	.009	.0184	.5695	.2945	.1923
.0600	.3201	.955	.010	.006	.0163	.5830	.2582	.1819
.0600	.3420	1.010	.011	.006	.0151	.5556	.2423	.1676

TEMPERATURE OF REACTION = 350 **C**, BATCH 2 30-35 MESH CATALYST
GLASS REACTOR, INITIAL ESTER P=1ATM.

Hr.		SELECTIVITY						
SPACE TIME	X	ACETIC ACID	CO+ CH4	CO2	N- BUTANE	1- BUTENE	TRANS- BUTENE	CIS-2- BUTENE
.5430	.9056	.919	.058	.013	.0939	.5147	.2576	.1878
.5430	.9025	.917	.045	.014	.0753	.5320	.2583	.1955
.5430	.9044	.919	.060	.013	.0821	.5308	.2531	.1886
.2651	.5996	.909	.035	.015	.0621	.5583	.2619	.1896
.2651	.6633	.916	.041	.014	.0601	.5571	.2558	.1903
.2651	.6132	.933	.036	.015	.0573	.5480	.2538	.1876
.3312	.7288	.932	.034	.017	.0610	.5432	.2532	.1889
.3312	.7182	.928	.043	.023	.0572	.5405	.2572	.1888
.3312	.7033	.931	.044	.020	.0579	.5525	.2501	.1821

TABLE (5-1) (CONTINUED)

TEMPERATURE OF REACTION = 350C,BATCH 1 20-30 MESH CATALYST
STAINLESS STEEL REACTOR, INITIAL ESTER P = 1 ATM.

		SELECTIVITY						
SPACE TIME	X	ACETIC ACID	CO+ CH4	CO2	N- BUTANE	1- BUTENE	TRANS- BUTENE	CIS-2- BUTENE
.4994	.9418	.889	.029	.019	.0243	.5586	.3081	.2027
.4994	.9429	.922	.027	.021	.0233	.5332	.3008	.2011
.2416	.5857	.951	.024	.014	.0199	.5496	.2772	.1868
.2416	.6165	.978	.022	.014	.0182	.5361	.2696	.1812
.1200	.2987	.961	.018	.014	.0203	.5629	.2482	.1933
.1200	.3224	1.026	.015	.012	.0178	.5279	.2379	.1742
.3720	.7345	.894	.029	.013	.1153	.5905	.3845	0.0000
.3720	.7896	.918	.031	.012	.0197	.5719	.2856	.1901
.1786	.4377	.919	.020	.010	.0186	.5963	.2714	.1853
.1786	.4578	.951	.019	.009	.0181	.5747	.2681	.1779
.0906	.9509	.922	.074	.019	.0275	.5254	.2948	.1961
.0906	.9934	.902	.053	.020	.0263	.5466	.2998	.1983

TEMPERATURE OF REACTION = 303C,BATCH 1 30-35 MESH CATALYST
STAINLESS STEEL REACTOR, PURE ESTER FEED

		SELECTIVITY						
SPACE TIME	X	ACETIC ACID	CO+ CH4	CO2	N- BUTANE	1- BUTENE	TRANS- BUTENE	CIS-2- BUTENE
2.3104	.7139	.928	.012	.004	.0303	.5294	.2725	.2373
2.3104	.6498	.856	.014	.004	.0316	.5545	.3287	.2304
1.0988	.3498	.941	.013	.006	.0250	.5257	.2920	.2113
1.0988	.3611	.966	.013	.010	.0245	.5087	.2826	.2078
5.5875	1.0000	.859	.043	.006	.0509	.4945	.3426	.2429
5.5875	.9967	.825	.047	.008	.0504	.4976	.3640	.2526
.4367	.1192	.999	.011	.008	.0282	.4632	.2628	.2363
.4367	.1367	.986	.010	.011	.0220	.4680	.2645	.2483
.4367	.1488	1.049	.014	.008	.0229	.4568	.2583	.1983
.2062	.0624	.827	.042	.015	.0286	.5252	.2988	.3066
.2062	.0487	.869	.041	.030	.0221	.5214	.2908	.2689
5.7506	.9610	.893	.044	.007	.0412	.4973	.3283	.2274
2.4019	.5898	.918	.025	.006	.0277	.5221	.3082	.2165
2.4019	.6092	.945	.025	.005	.0252	.5129	.2986	.2097
.8639	.2701	1.023	.021	.007	.0204	.4991	.2467	.1967
.8639	.2354	.937	.019	.010	.0226	.5539	.2645	.2121

TABLE (5-1) (CONTINUED)

TEMPERATURE OF REACTION = 350 C,30-35 MESH BATCH 2 CATALYST
GLASS REACTOR, ACETIC ACID DILUENT, P = 0.30 ATM.

SPACE TIME	X	ESTER PRES.	SELECTIVITY		
			1-BUTENE	TRANS-BUTENE	CIS-2-BUTENE
.2711	.3729	.30	.5587	.2589	.1824
.2711	.3585	.30	.5605	.2520	.1876
.2711	.3929	.30	.5551	.2534	.1915
.2711	.3636	.30	.5537	.2548	.1915
.4150	.5706	.30	.5600	.2546	.1854
.4150	.5587	.30	.5551	.2584	.1865
.4150	.6336	.30	.5493	.2589	.1917
.4150	.5543	.30	.5592	.2548	.1860
.6610	.7250	.30	.5544	.2605	.1851
.6610	.7510	.30	.5706	.2491	.1803
.6610	.7257	.30	.5552	.2569	.1879
.6610	.7257	.30	.5552	.2569	.1879

TEMPERATURE OF REACTION = 350 C,30-35 MESH BATCH 1 CATALYST
STAINLESS STEEL REACTOR, NITROGEN DILUENT, P = 0.29 ATM.

SPACE TIME	X	ESTER PRES.	SELECTIVITY		
			1-BUTENE	TRANS-BUTENE	CIS-2-BUTENE
.3463	.4519	.30	.4901	.3303	.1797
.3463	.4235	.30	.5221	.2879	.1900
.3463	.4737	.295	.5409	.2817	.1774
.1662	.2013	.29	.5174	.2908	.1918
.1662	.2660	.31	.5387	.2873	.1740
.5796	.6553	.30	.5462	.2753	.1786
.5796	.6621	.31	.5478	.2765	.1757
.2052	.2862	.28	.5444	.2722	.1834
.2052	.3133	.28	.5479	.2701	.1820
.4156	.5681	.266	.5392	.2869	.1739
.4156	.5661	.27	.5410	.2859	.1730
.8499	.8206	.26	.5395	.2792	.1813
.8499	.8097	.34	.5423	.2774	.1802
2.1989	.9991	.24	.5002	.2979	.2019
2.1989	.9998	.24	.5045	.2965	.1990
.1117	.1682	.28	.5250	.2747	.2003

TABLE (5-1) (CONTINUED)

TEMPERATURE OF REACTION= 350 C,BATCH 1 30-35 MESH CATALYST
STAINLESS STEEL REACTOR, INITIAL ESTER P = 1 ATM.

		SELECTIVITY						
SPACE TIME	X	ACETIC ACID	CO+ CH4	CO2	N- BUTANE	1- BUTENE	TRANS- BUTENE	CIS-2- BUTENE
.8499	.9817	.851	.059	.012	.0379	.5688	.3299	.1935
.4156	.8552	.912	.037	.010	.0263	.5369	.3026	.2075
.4156	.7985	.877	.028	.010	.0244	.5676	.3110	.2115
.2052	.5047	.906	.021	.008	.0211	.5581	.2900	.2179
.2052	.5168	.886	.021	.010	.0206	.5788	.3019	.2060
1.2187	1.0000	.830	.085	.024	.0412	.5300	.3363	.2267
.5796	.9155	.899	.045	.016	.0225	.5597	.2999	.1984
.5796	.8428	.905	.042	.012	.0211	.5481	.3194	.1901
.1088	.2985	.913	.012	.008	.0191	.5937	.2705	.1998
.1088	.2934	1.088	.010	.006	.0158	.4909	.2207	.1699
.3463	.6553	.887	.021	.009	.0195	.5872	.2983	.2016
.3463	.6901	.900	.025	.007	.0181	.5796	.2978	.1968
.1662	.3995	.917	.014	.008	.0174	.5902	.2826	.1877
.0843	.2001	.962	.007	.009	.0114	.5703	.2512	.1983

LOW TEMPERATURE EXPERIMENTS, BATCH 2 30-35 MESH CATALYST

			SELECTIVITY		
SPACE TIME	X	TEMP. C	1- BUTENE	TRANS- BUTENE	CIS-2- BUTENE
2.2700	.000485	195.9	-	-	-
2.2700	.000520	195.9	-	-	-
2.2700	.000461	195.9	-	-	-
2.2700	.000488	195.9	-	-	-
2.2700	0.00371	217.8	.2190	.3700	.4110
2.2700	0.00310	217.8	.2460	.3610	.3930
2.2700	0.00387	217.8	.2200	.3390	.4410
2.2700	0.00410	217.8	.2500	.3750	.3750
2.2700	0.00358	217.8	.2140	.4710	.3140
2.2700	0.00450	217.8	.2000	.4000	.4000
2.2700	0.00356	217.8	.2270	.3790	.3940
2.2700	0.0271	247.8	.3520	.3310	.3180
2.2700	0.0261	247.8	.3580	.3400	.3020
2.2700	0.0265	247.8	.3400	.3320	.3280
2.2700	0.0226	247.8	.3380	.3560	.3510

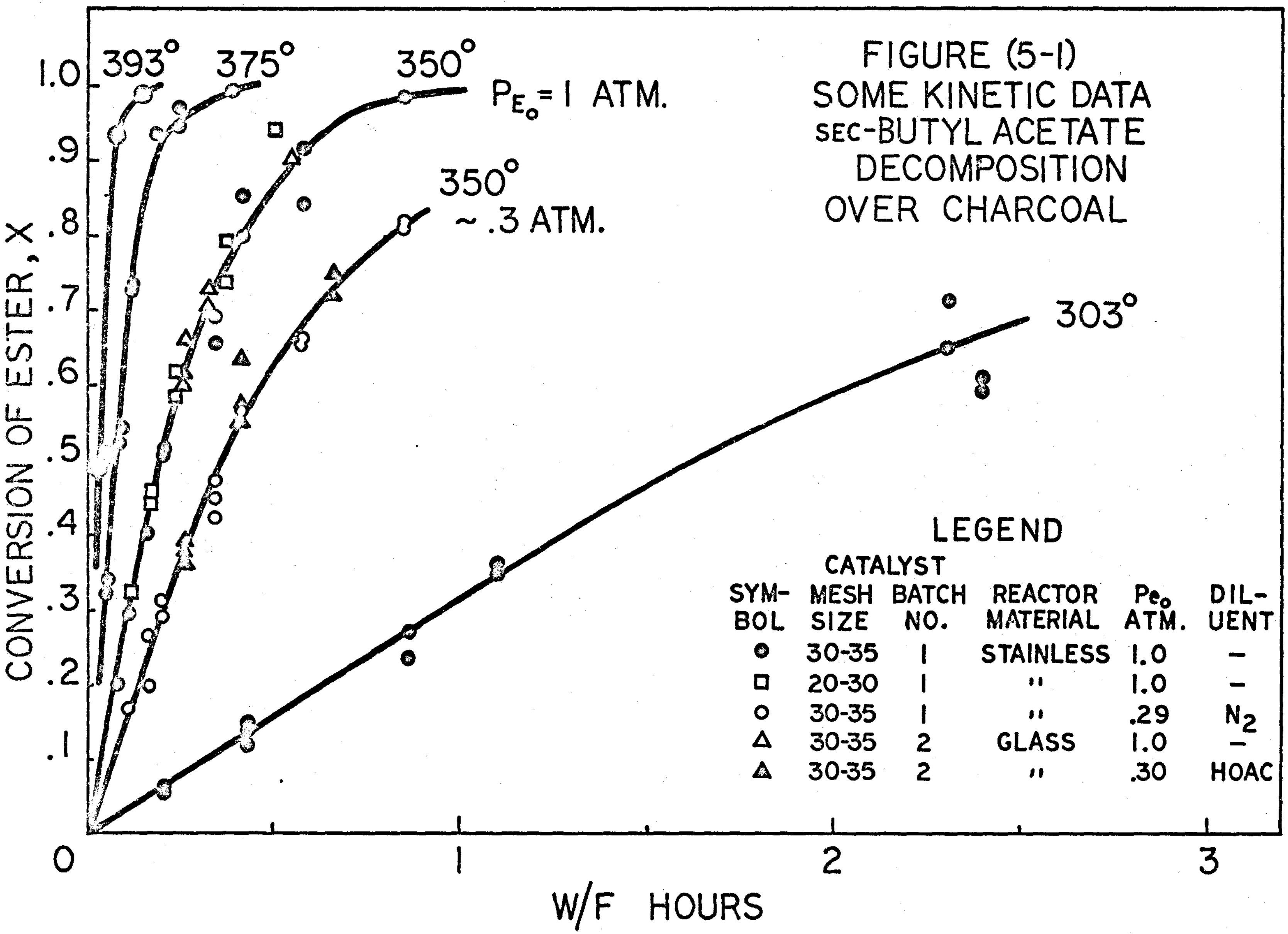

FIGURE (5-1)
SOME KINETIC DATA
SEC-BUTYL ACETATE
DECOMPOSITION
OVER CHARCOAL

data are not presented. All catalysts gained weight during the experiments, but the increases were only about 4% of the original catalyst weight.

5.3 ANALYSIS OF THE SECONDARY BUTYL ACETATE DATA

The methods of data analysis described for n-butyl acetate were also applied to the sec-butyl acetate data. From the kinetic data shown in Figure (5-1) it appears that the reaction is nearly zero order in ester at low conversion and may approach zero order as the temperature decreases, but the reaction is obviously not zero order at high conversions and high temperatures. The dilution experiments at 350°C show that the rate of reaction decreases with decreasing reactant pressure; however, the change in the rate is not directly proportional to the pressure change. The reaction goes to completion on charcoal.

Diffusion of reactant in the catalyst pores apparently does not strongly limit the rate of reaction, since there was no difference in the reaction rate when the different catalyst particle sizes were used. At the same reaction temperature the different particle sizes used should have resulted in an average rate difference of about 17%(44) if diffusion in the catalyst pores strongly limited the rate of reaction. Comparing the results from the glass and the stainless steel reactors shows that the walls of the stainless steel reactor did not catalyze the decomposition of sec-butyl acetate to an appreciable extent.

At any given reaction conditions the selectivities for the butenes were independent of the conversion of ester for x less than about 0.9. The nearly constant selectivities are shown in Table (5-1), but are better illustrated by Figure (5-2), in which the productivity, G, is plotted as a function of the conversion. The productivity for a species is defined as the number of moles of the species produced per mole of ester fed to the reactor. The productivity for species B is calculated by the equation

$$G_b = S_b \cdot x \,, \qquad (5\text{-}1)$$

where S_b is the selectivity for species B defined by Equation (4-4), and x is the fractional conversion of the reactant. The productivity is used here since it is somewhat less sensitive to experimental error than is the selectivity. Figure (5-2) shows that the selectivities for the butenes, the slopes of the plots, increase slightly at high conversion. On the other hand, selectivity for acetic acid decreases at high conversion, possibly because some of the acid decomposes to methane and carbon dioxide. A summary of the selectivity data is given in Table (5-2) along with data for the thermal decomposition and equilibrium butene ratios. The products from the heterogeneous reaction are nearly the same as from the gas reaction(7,9), and the butenes are not formed in the

Figure (5-2) Product distribution for the decomposition of sec-butyl acetate over charcoal at 375°C.

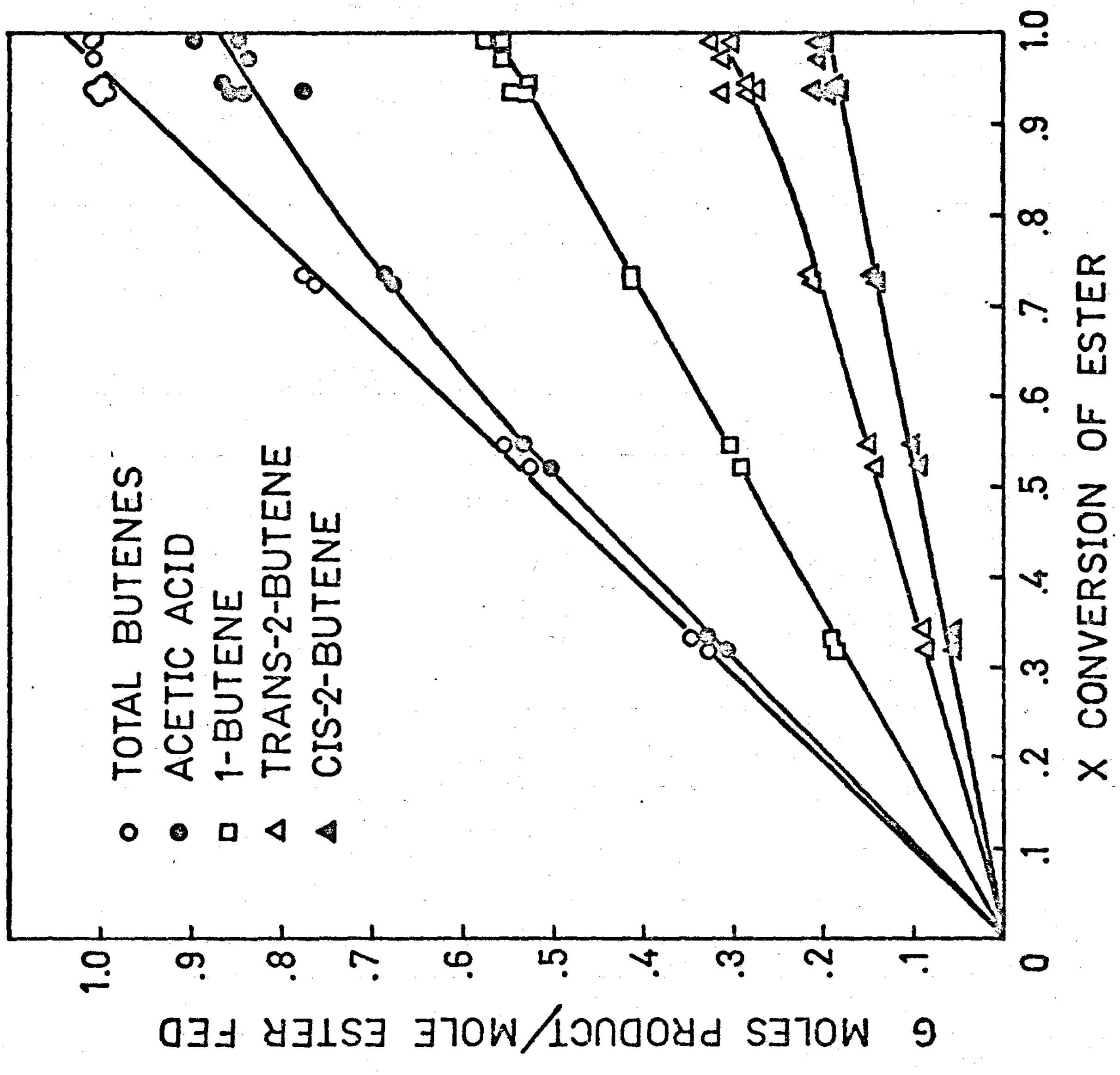

TABLE (5-2)

Selectivities for Butenes Expressed as Percentages of the Total Butenes

Butene Isomer	Reaction over charcoal						Gas-Phase Reaction(1) at 450°C	Equilibrium(2) Mix at 350°C	Expected from βH's
	217.8°	247.8°	303°	350°	375°	393°			
1-	20.7	34.3	49.2	54.5	53.8	53.1	62.0	22.5	60
Trans-2	32.8	33.6	28.4	27.1	27.7	27.5	24.0	43.2	40
Cis-2	37.5	32.1	22.4	18.4	18.5	19.4	13.8	34.3	
$\frac{\text{Cis}}{\text{Trans}}$	1.14	.95	.79	.68	.67	.70	.57	.76	-

(1) Emovan, E. V., and Maccoll, A., J. Chem. Soc., 335 (1962)

(2) Maccoll, A., and Ross, R.A., J. Am. Chem. Soc., 87 1169 (1965)

equilibrium ratio. The fraction of 1-butene produced increases with temperature and approaches the value of 60% expected from statistical elimination of the β-hydrogens.

The sec-butyl acetate kinetic data were treated by the method described in Section 4.3 in an attempt to find the best rate equation. Two rate schemes were considered: desorption control and surface reaction control. Two variations of the surface reaction rate equation were considered: the first equation was the simple surface rate expression containing one adsorption term and was based on the assumption that the ester is the sole adsorbate on the catalyst. The second variation of the surface rate equation contained a term (in the denominator) to account for the possible adsorption of acetic acid and butenes on the catalyst. Some of the criteria used in selecting the best rate equation were obtained from mathematical analysis of the kinetic data. These criteria were: (a) the ability of the rate equation to express the observed data as reflected in RSS, and (b) the values of the coefficients of the rate equations. For the most part, the coefficients and RSS values were found by using Program 3 which incorporates the Rosenbrock Search(39). The analysis of the kinetic data was done in two parts: (1) the data taken at each experimental temperature were analyzed separately to determine the coefficients and the values of RSS at each of the seven experimental temperatures, and (2) the coefficients were calculated using all of the kinetic data (at once) in Program 3 incorporating either equations (D-4) and (D-5) or (D-10) and (D-11) with all of the coefficients in the equations expressed in the Arrhenius form. Results of the two parts of the analysis are shown in Tables (5-3) and (5-4). For given temperatures above 300°C, the values of coefficients for the two rate equations were calculated by the Rosenbrock Search, and the rate constants for the surface reaction at 247.8° and below were calculated by assuming that the reaction was zero order in ester. That is, at low temperatures when K_eP_e becomes large compared to 1, the charcoal surface is substantially covered with the reactant and the "single-site" surface reaction rate equation becomes

$$dx/d\tau = kLK_eP_e/(1+K_eP_e) = kL \; . \qquad (5\text{-}2)$$

The confidence limits for the coefficients at given temperatures above 300°C were calculated using the Likelihood theory discussed in Section 4.3 and summarized in Equations (4-7) and (4-3). Program 4 calculated the confidence limits for fixed temperatures above 300°C. This program simultaneously searched between minimum and maximum values of each of the coefficients and calculated the value of Equation (4-8), the likelihood ratio, at each of several hundred combinations of the coefficients. By using this method,

TABLE (5-3)

Values of Best Rate Equation Coefficients and RSS for Separate Analysis of Data at Each Temperature

Rate Controlling Mechanism T°C	Desorption of B				Surface Reaction		
	$k_B LK$	K_e	$K_B K$	RSS	kL	K_e	RSS
393.	-	-	-	-	21.16	2.74	0.065
375.	-	-	-	-	7.24	7.58	0.0082
350 (1 atm.)	4.99	-2.34	2.04	0.022	3.66	3.75	0.0236
350 (.29 atm.)	2.29	-0.0089	1.27	0.007	3.18	3.62	0.007
303	-	-	-	-	0.392	5.06	0.0165
247.8	-	-	-	-	0.0113	-	-
217.8	-	-	-	-	0.0011	-	-
195.9	-	-	-	-	0.000215	-	-

TABLE (5-4)

Values of the Best Coefficients of the Rate Equations and the Confidence Limits at $\lambda = 0.1$ for Composite Analysis of All Data

Mechanism	term	Base 10 pre-exponential factor			Exponential factor kcal/mole		
		minimum	best	maximum	minimum	best	maximum
Desorption of B controls	k_bLK	11.5	11.65	11.7	29.5	30.03	30.5
	K_e	-1.92	-2.08	-2.21	-9.27	-9.36	-9.42
	K_bK	-2.84	-2.96	-3.08	-6.22	-6.28	-6.34
	RSS =	0.279					
Surface reaction control	kL	12.20	12.25	12.30	33.40	33.47	33.60
	K_e	-1.56	-1.64	-1.70	-6.48	-6.60	-6.75
	RSS =	0.126					
Surface reaction control with additional term	kL		12.25			33.46	
	K_e		-1.64			-6.60	
	K_b		-3.71			+0.31	
	RSS =	0.126					

a realistic estimate could be made of the bounds of the confidence limits. For example, Figure (5-3) shows an "area" of confidence which was found when likely values of kL and K_e for the surface reaction mechanism are plotted on perpendicular axes. Figure (5-3) will be discussed in more detail below. Estimates of the confidence limits of kL at temperatures below 300°C were made by calculating the rates of reaction at two standard deviations away from the mean rate at any given temperature. Two standard deviations is approximately the 95% confidence level and corresponds roughly to the limits calculated when the value of λ is fixed at 0.1 in Equation (4-8). Table (5-5) shows the confidence limits for the coefficients found from separately analyzing the data at each experimental temperature. For part (2) of the analysis using all of the kinetic data at once, the confidence limits for the coefficients were found by perturbing one of the coefficients at a time while the others were fixed at their best values. The results of estimating the confidence limits using Likelihood theory are shown in Table (5-4).

The calculated coefficients appear reasonable for the most part, except that the best coefficients at 350°C for the desorption equation are physically unreasonable ($\hat{\underline{C}}$ at 0.29 atm. $\neq \hat{\underline{C}}$ at 1 atm., and K_e at 1 atm. is negative); however, Table (5-5) shows that the confidence limits of the

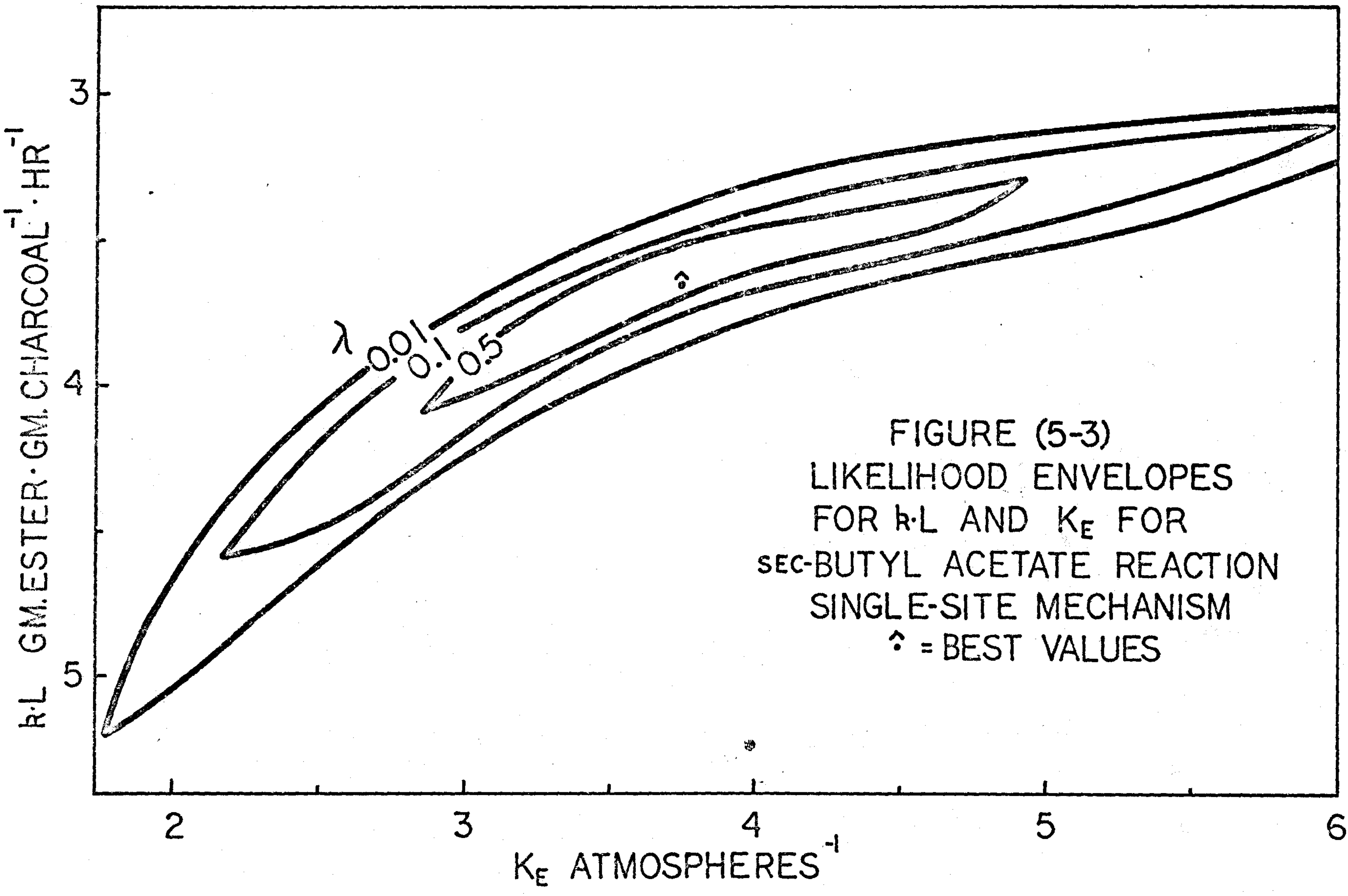

FIGURE (5-3)
LIKELIHOOD ENVELOPES
FOR k·L AND K_E FOR
SEC-BUTYL ACETATE REACTION
SINGLE-SITE MECHANISM
$\hat{\cdot}$ = BEST VALUES

TABLE (5-5)

Coefficient Limits

			kL		K_e	
Mechanism	T°C	λ	Minimum	Maximum	Minimum	Maximum
Surface Reaction	393	0.1	7.4*	125*	0.1*	5.2*
	375	0.1	6.3	9.00	3.65	12.5
	375	0.2	6.7	8.70	4.10	10.0
	375	0.3	6.9	8.51	4.36	9.3
	350**	0.01	-	5.25	1.78	-
	350	0.1	3.10	4.55	2.23	6.00
	350	0.2	3.17	4.36	2.41	5.80
	303	0.01	-	0.600	1.63	-
	303	0.1	0.300	0.556	2.12	-
	303	0.2	0.305	0.505	2.40	16.
	303	0.3	0.319	0.490	2.60	14.20
	247.8	$\sim$0.1	0.0073	0.0153	-	-
	217.8	$\sim$0.1	.0011	.0023	-	-
	195.9	$\sim$0.1	.00019	.00024	-	-
Desorption of B	350**	0.1	-	-	-6.	+1.3
	350	0.3	-	-	-	+0.1

*Approximate value, actual value indeterminable due to computational difficulties

**Initial reactor pressure = 1 atm.

coefficients at 350°C include physically possible values. Figure (5-3) illustrates the shapes of some confidence contours calculated from the data at 350°C at 1 atmosphere initial reactant pressure. These shapes are typical of the contours found for the coefficients of the surface region rate equation at other given temperatures. Figure (5-3) suggests that in part (2) of the data analysis the confidence limits are underestimated and that wider limits might be found if all of the coefficients were perturbed simultaneously.

Nearly equal RSS values result when the sec-butyl acetate kinetic data are fitted with any of the rate expressions which were considered. From Tables (5-3) and (5-4) it appears that the simple surface reaction rate equation reproduces the data as well as the surface reaction rate equation which includes a term to account for the adsorption of acetic acid and butenes. For the composite data analysis (analysis part(2) using all data at once) the RSS value for the desorption control rate equation is a little more than twice the RSS value for the surface rate equation. This small difference in RSS values for the two mechanisms is not sufficient evidence to discount the desorption scheme, nor do the values of the coefficients for the rate equations shown in Tables (5-3) and (5-4) offer any evidence for rejecting either mechanism. Nevertheless, the simple surface reaction rate equation will be considered to be the "best rate equation" since it is the simplest equation and it expresses the data at least as well as any of the other theoretical-based rate equations which were considered.

For the "best rate equation" the confidence limits for the rate coefficients, k^L, at the seven experimental temperatures are shown in the Arrhenius plot in Figure (5-4). The limits of kL are wide at 303° and 393°C, compared to the limits at 350° and 375°C. The extreme cases in the higher temperature experiments reflect the influence of ths RSS on the magnitude of λ, or on the change in λ when $\underline{C}$ changes. From equations (4-7) and (4-8) it can be shown that λ is proportional to $\exp-\{[(n-k)/2][RSS/RSS_{min.}]\}$; that is, the ratio of RSS at $\underline{C}$ to the minimum RSS influences λ. The confidence limits at 393°C are wide since there are few data to contribute to changes in RSS, and values of kL between about 7 and 125 grams of ester/gram of catalyst per hour result in values of RSS near the minimum. At 303°C the confidence limits are wide because the kinetic data are scattered as Figure (5-1) shows, and the minimum RSS is relatively large compared to zero.

It is interesting to compare the temperature independent coefficients calculated in the analysis of the composite data (part (2)) with similar coefficients calculated from the data in Table (5-5). Assuming that the sur-

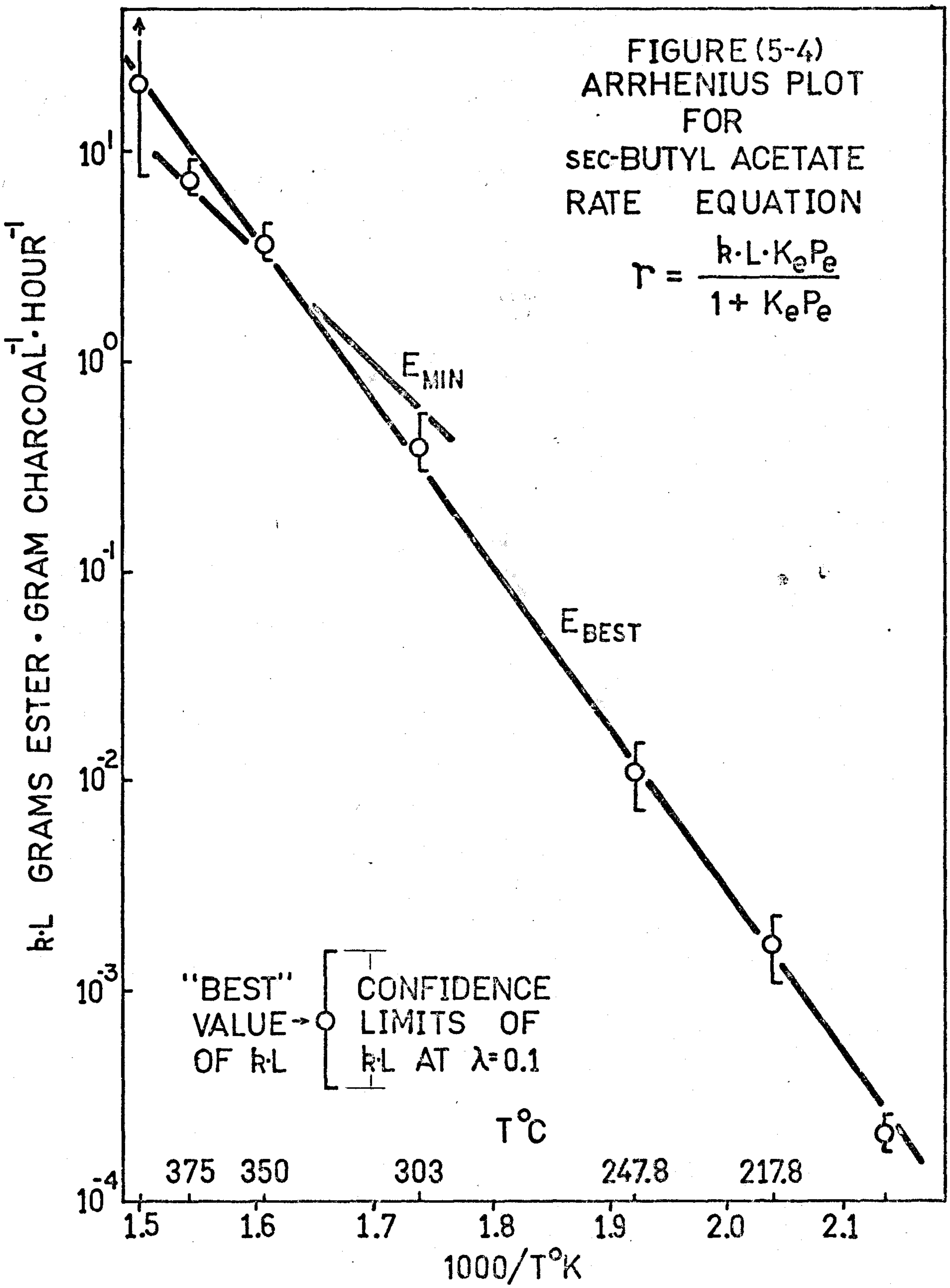

FIGURE (5-4)
ARRHENIUS PLOT
FOR
SEC-BUTYL ACETATE
RATE EQUATION

$$r = \frac{k \cdot L \cdot K_e P_e}{1 + K_e P_e}$$

face reaction controls the rate of ester decomposition, the data in Table (5-5) can be used to calculate the Arrhenius activation energy, E, the pre-exponential factor k_oL, and other coefficients by using the traditional method of finding the slope of the Arrhenius plot. The Arrhenius plot in Figure(5-4) appears to be linear over the range of temperatures studied, and for sec-butyl acetate decomposition over charcoal, the "best" energy of activation E = 35.3 kcal/mole, as calculated form the least sqaures fit of the best values of kL at the seven experimental temperatures by the equation

$$\ln(kL) = \ln(k_oL) - E/RT . \qquad (5-2)$$

Confidence limits of E were estimated by fitting Equation (5-2) to those extreme values of kL at $\lambda = 0.1$ which gave the maximum and minimum slopes to the Arrhenius plot. The results were: $32.81 \leq E \leq 36.20$ k/cal/mole. The limits for the activation energy are obviously overestimated when calculated using only the values of kL at the confidence level $\lambda = 0.1$, since the probability of extreme values of kL being found at each of the seven experimental temperatures would be about $(0.1)^7$. Nevertheless, the confidence limits calculated in this manner are remarkably narrow. From analysis of the composite data $33.4 \leq E \leq 33.6$ kcal/mole. Arrhenius activation energies between 46.0 and 48.4 kcal/mole have been reported(5,7) for the gas-phase decomposition of sec-butyl acetate.

The heat of adsorption of the ester on charcoal, H, is difficult to estimate from the Arrhenius-type plot in Figure (5-5). It appears that there is no correlation between the adsorption constant K_e and the temperature. This faulty indication is possible due to the fact that the surface reaction rate equation contains K_e in the form $K_eP_e/(1+K_eP_e)$, which is somewhat insensitive to the value of K_e. The Arrhenius-type plot does not give a satisfactory estimate of the heat of adsorption of ester in this case. The value of the heat of adsorption of sec-butyl acetate on charcoal which was found from the pulse studies was 11.4 kcal/mole (see Section 3.1). The heat of liquefaction-vaporization of sec-butyl acetate is around 9. kcal/mole(42).

If one considers only the best values of kL at temperatures of 195.9° to 375°C, it appears that the slope of the Arrhenius plot increases at high temperatures; however, use of the data in this manner is misleading, and when the ranges of reasonable values of kL are considered it is not possible to deny that the Arrhenius plot is linear. The linearity of the plot suggests that diffusion of the reactant in the catalyst pores does not limit the rate of reaction. If diffusion did limit the rate, the activation energy would have decreased at high temperatures. From the confidence limits of kL calculated at $\lambda = 0.1$, the minimum possible E = 23.0 kcal/mole between 303° and 375°C; this value of E is very close to the minimum value of E possible at $\lambda = 0.1$ between 217.8° and 247.8°C, as Figure (5-4) illustrates.

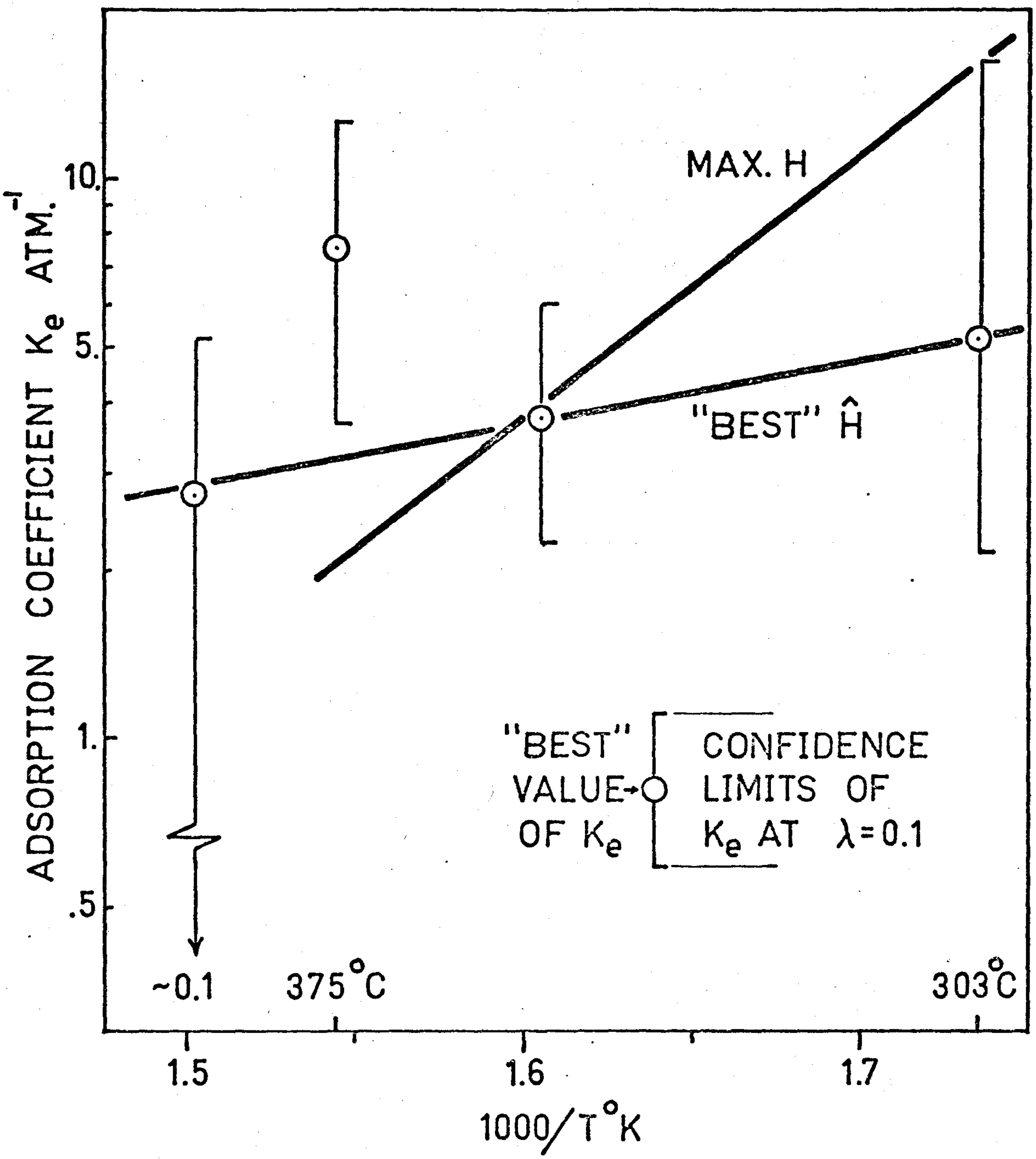

Figure (5-5) The adsorption coefficient K_e for sec-butyl acetate calculated from the surface reaction rate equation (D-1).

CHAPTER 6

TERTIARY-BUTYL ACETATE

6.1 EXPERIMENTAL PROCEDURE

Experiments with tert-butyl acetate were made at 1 atmosphere total pressure and at several temperatures between 151.3° and 288.0°C using Batch 2 catalyst and a 1.0 cm.ID stainless steel reactor. The catalyst was heated to 930°C in helium for 1 hour before use and then charged into the reactor without contacting the air by the procedure described in Section 4.1. Various particle sizes of catalyst ranging from 28 to 80 mesh were used for the tert-butyl acetate experiments. Experiments were made at several temperatures using pure ester feed and also using diluted feed. The diluents helium, nitrogen, acetic acid, cis-2-butene, and toluene were used to determine how the reaction rate was influenced by initial ester pressure and by the products. The procedure used for diluting the ester are described in Section 5.1. Details of the experimental conditions are presented with the kinetic data.

Kinetic data were obtained by a procedure similar to the one described for sec-butyl acetate in Section 5.1. After starting an experiment or changing the feed rate, the reaction was allowed to run for about three hours to attain steady conditions before kinetic data were taken. Catalysts were used for a maximum time of about 30 hours before being discarded.

In preliminary experiments with tert-butyl acetate, the reactor products were separated and identified by gas chromatography using the following columns (see Figure (2-1)): Column 1 was 1/4 thick × 4 feet of 7% FFAP* on 40-60 mesh Teflon, and its temperature was programmed between 90° and 140°C, and Column 2 was 1/4 inch × 25 feet of 18% propylene carbonate on 80-100 mesh Chromosorb W at room temperature.

For routine analysis of the reaction products from pure ester feed, the FFAP (number 1) column was used alone at 90°C, since this separated the hydrocarbon products from the unreacted ester. Column 2 was replaced by an empty capillary tube which served to increase the pressure in column 1 and broaden the single, composite response peak of the hydrocarbons, thus facilitating analysis. In the routine analysis the products were assumed to be pure isobutene. For experiments with ester diluted by nitrogen, helium or cis-2-butene, analysis of the reactor products was made by using the FFAP column at 90°C and the propylene carbonate column at 25°C. Conversion of tert-butyl acetate was calculated by using the equation

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*Varian Aerograph, Walnut Creek, California.

$$x = \frac{\text{moles of isobutene in product}}{\text{moles of isobutene + tert-butyl acetate}} \ . \qquad (6\text{-}1)$$

Equation (6-1) results from assuming that the ester decomposes cleanly to isobutene and acetic acid and that the butene undergoes no subsequent reactions.

6.2 RESULTS OF TERTIARY-BUTYL ACETATE EXPERIMENTS

Tertiary-butyl acetate decomposed rather cleanly to acetic acid and iso-butene, with small amounts of secondary products being formed. A detailed GC analysis of the products from a preliminary experiment made at 287°C showed that the mole fractions of products were as follows: acetic acid, 0.477; isobutene, 0.446; isobutane, 0.0174: methane, 0.0512; isobutanol, 0.0096, and only a trace of carbon dioxide. The conversion for this experiment calculated from Equation (6-1) is 0.955, assuming that the isobutane results from the hydrogenation of isobutene. If the GC responses for methane and carbon monoxide were also added to the isobutene response, as was done in the routine analyses, the conversion calculated would be 0.957. These data show that no appreciable error is introduced by using the routine analysis and measuring the composite of the gaseous products. The catalyst in the preliminary experiment showed no change in activity during 24 hours of continuous use at 287°C at a conversion of x = 0.96. Pyrolysis of tert-butyl acetate at 287°C was found to be negligible at the same feed rate as in the preliminary experiment when the catalyst was replaced by small glass beads.

In other exploratory experiments it was found that the catalytic activity for the tert-butyl acetate decomposition depended on the length of time that the charcoal was heated in helium at 930°C. The activity appeared to increase with the heating time and attain a reproducible activity at some time between 30 and 60 minutes. The catalysts used in the tert-butyl acetate experiments were heated in helium at 930°C for 60 minutes.

Table (6-1) shows the experimental conditions and the kinetic data in detail, and Figure (6-1) summarizes these data in a plot of the average conversion as a function of the space time for most of the experimental conditions.

6.3 ANALYSIS OF THE TERT-BUTYL ACETATE DATA

The straight lines in Figure (6-1) show that the decomposition of tert-butyl acetate was zero order in ester at x less than about 0.95 when the feed consisted of pure ester or ester diluted with helium, nitrogen,or acetic acid to as low as $P_{e_o} = 0.5$ atmospheres. The observed zero order could result if the rate of reaction is controlled by a surface reaction and the active catalyst sites are saturated at a low ester pressure. This condition is represented in the rate equation (see Equation (D-1)) by the terms K_bP_b and K_aP_a having small values, while the product K_eP_e for ester is so large that the rate equation becomes

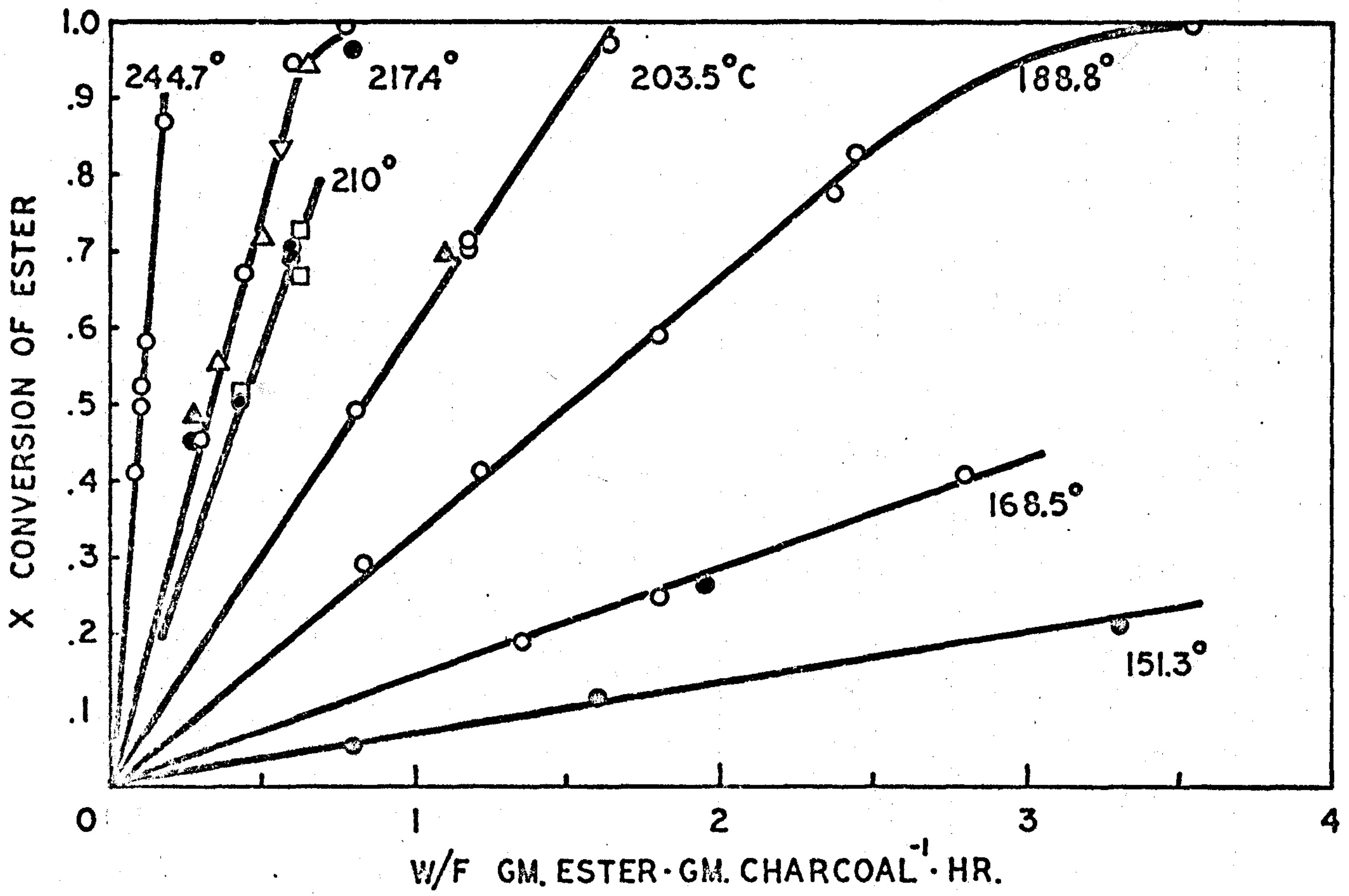

Figure (6-1) Kinetic data for tert-butyl acetate decomposition over charcoal. □, P_{e_o} = 1 atm., 48-65 mesh cat.; ●, P_{e_o} = 1 atm., 32-35 mesh cat; ○, P_{e_o} = 1 atm., 65-80 mesh cat.; △, P_{e_o} = 0.5 atm., acetic acid diluent, 65-80 mesh cat.; ▽, P_{e_o} = 0.5 atm., helium diluent, 65-80 mesh cat.; ▲, P_{e_o} = 0.1 atm., acetic acid diluent, 65-80 mesh cat.

$$r = kLK_eP_e/(1 + K_eP_e + K_bP_b) \approx kL.$$

On the other hand, the desorption mechanism might apply, and the coefficients in the rate equation (Equation (D-6)) might have values which render the reaction zero order under a wide variety of conditions: for example, $k_bLKP_e/P_a \approx K_bKP_e/P_a$. The data at 217.4°C clearly show the dilution of the feed with acetic acid does not decrease that reaction rate; therefore, the rate is not controlled by the desorption of acetic acid; furthermore, the term K_aP_a is probably negligibly small.

For x > 0.95 at 188.8°C and 217.4°C, the order of reaction increases as could occur if the rate of reaction was controlled by either a surface reaction mechanism or by the desorption of products. For example, if the surface reaction scheme applied, the rate of reaction on the surface would decrease when the gas phase concentration of reactant drops to a pressure where the majority of active sites on the catalyst are no longer covered with ester. For conversions of 0.95 and 0.98 the partial pressures of ester are, respectively, 0.0256 and 0.0101 atmospheres when pure ester is fed to the reactor. If the desorption of product B controls the rate of reaction, the decrease in the rate observed at high conversion (x = 0.95 to 0.98) could only be due to the negative term $-k_bLP_e/(1+K_bKP_e/P_a)$ in Equation (D-6). For x = 0.98 the value of the reverse term in Equation (D-6) is only 0.00024 times the value of the forward term, assuming that the constant K has the value of 10^5 calculated by Fugassi$^{(6)}$. This small value of the reverse term could not account for the deviations from zero order observed at high conversions; therefore, the desorption mechanism is unsatisfactory for expressing the data, at least at the conditions considered.

Tert-butyl acetate diluted with cis-2-butene to $P_{e_o} = 0.5$ atmospheres reacted at a slower rate than did pure ester at the same temperature (205.3°C). These data suggest that isobutene is responsible for the decrease in reaction rate observed at high conversion. Considering the available data, the most satisfactory rate expression for tert-butyl acetate decomposition over charcoal is the equation for surface reaction rate controlling (Equation (D-6)) containing a term K_bP_b for surface coverage by isobutene; the term K_bP_b becomes important at a butene pressure of about 0.5 atmospheres when the total reaction pressure is 1 atmosphere.

Ester which was diluted with acetic acid decomposed at a slightly faster rate than did pure ester at 195.5° and 217.4-218.5°C. These observations are not explained by the Langmuir-Hinshelwood rate equations. Possibly, acetic acid in high concentrations acts as a catalyst for the ester decomposition in the presence of the charcoal.

The data in Table (6-1) demonstrates that neither diffusion in the catalyst pores nor diffusion in the bulk phase limit the rate of reaction. The rates of decomposition at about 288°C on 28-32 mesh and 48-65 mesh charcoal particles are, respectively, 24.80 and 23.00 grams of tert-butyl acetate reacted per hour per gram of charcoal. If diffusion in the catalyst pores was strongly inhibited, the ratio of rates for the different particle sizes would have been at least 5/3(44), considering that the minimum particle size at 28-32 mesh is 0.500 mm., and the maximum particle size for 48-65 mesh is 0.297 mm. At 288°C the decomposition of tert-butyl is faster than the maximum rates of reaction encountered for the other butyl acetates. Since pore diffusion is potentially more important at higher reaction rates(44), the data for tert-butyl acetate suggests that pore diffusion is not important for the other esters.

The data at 223°C given on page 118 in Table (6-1) show that the reaction rate is not limited by diffusion of ester from the bulk phase to the catalyst surface. At W/F = 0.652 hours and 0.259 hours, the weight of catalyst used was 2.4402 grams, while for W/F = 0.456 hours and 0.937 hours, the weight of catalyst was 1.7236 grams. The 35% change in catalyst bed length produced no difference in the reaction rates. For these two catalysts the limits of the reaction rates calculated from the equation $r = x/(W/F)$ are: for 2.4402 grams of catalyst, $0.934 \leq r \leq 1.165$; for 1.7236 grams of catalyst, $0.980 \leq r \leq 1.041$, where the rate is expressed in grams of ester decomposed per hour per gram of charcoal.

The rate of reaction for any temperature was found by calculating the slope of the least squares straight line fitted to the x vs τ data at the temperature. The straight lines shown in Figure (6-1) are examples of the least squares lines. Assuming that the decomposition of tert-butyl acetate follows the surface reaction mechanism, the value of the reaction rate at any temperature is equal to kL. The Arrhenius plot in Figure (6-2) shows the values of rate or kL calculated from the least squares fittings (not forced to pass through the origin).

The activation energy and pre-exponential factor for the tert-butyl acetate reaction were calculated by two different methods: (1) the slope of the Arrhenius plot in Figure (6-2) was found by least squares fitting the best values of kL to the equation $\ln(kL) = \ln(k_oL) - E/RT$, (2) Program 2 incorporating the Rosenbrock Search was used to search on "raw" data for the best values of E and k_oL. To conserve computation time, the large number of kinetic data shown in Table (6-1) were summarized; the "raw" data were the averages of the measured conversions at each experimentally fixed temperature and space time. From the slope of the Arrhenius plot, the results were $\hat{E} = 21.55$ kcal/mole, and $\log \hat{k_oL} = 9.74$ grams of ester per gram of charcoal per hour. Data analysis (2) gave the results: $\hat{E} = 21.74$ kcal/mole, and $\log \hat{k_oL} = 9.84$ grams of ester per gram of charcoal per hour.

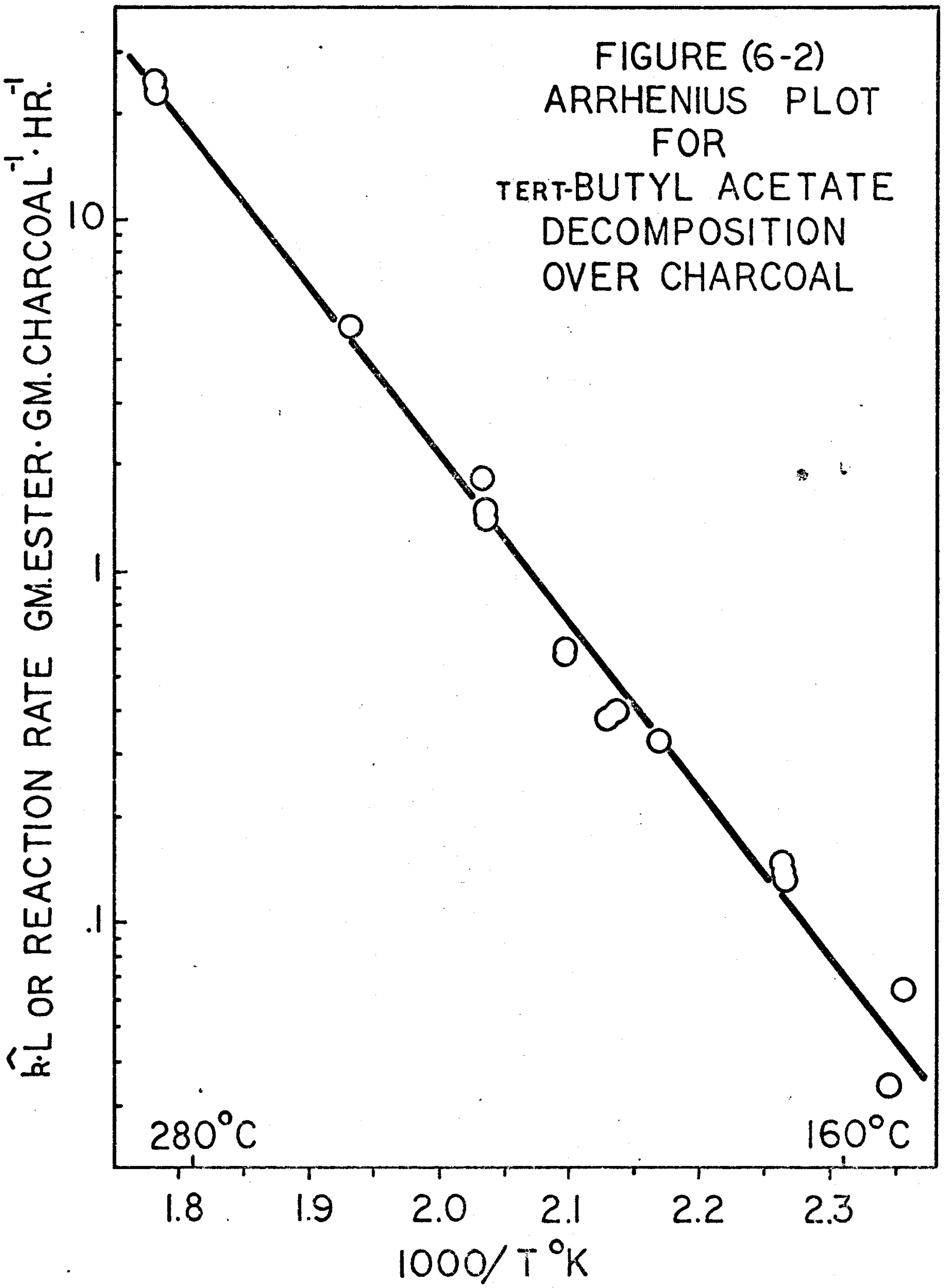

FIGURE (6-2)
ARRHENIUS PLOT
FOR
TERT-BUTYL ACETATE
DECOMPOSITION
OVER CHARCOAL

The confidence limits of the coefficients were calculated by using Program 4 which determined likelihood ratios (Equation (4-8)). Each of 400 combinations of E and k•L were tested by the program as the two coefficients were changed by 20 increments each between some arbitrarily chosen minima and maxima which encompassed the best values of the coefficients. This method gave a realistic estimate of the confidence limits, since the coefficients were changed simultaneously. At the $\lambda = 0.1$ confidence level the results were $20.80 \leq E \leq 22.64$ kcal/mole, and $9.42 \leq k_oL \leq 10.24$ grams of ester per gram of charcoal per hour.

TABLE (6-1)
KINETIC DATA FOR THE DECOMPOSITION OF TERT-BUTYL ACETATE OVER CHARCOAL

T °C	CATALYST MESH SIZE	P_{ec} ATM.	DILUENT	W/F HR.	X
288.5	28-32	1.00	-	0.03889	.979
288.5	28-32	1.00	-	0.03889	.951
288.5	28-32	1.00	-	0.03889	.955
288.0	48-65	0.99	TOLUENE	0.03212	.740
288.0	48-65	0.99	TOLUENE	0.03212	.738
288.0	48-65	1.00	-	0.03212	.808
288.0	48-65	1.00	-	0.03212	.812
288.0	48-65	1.00	-	0.03212	.800
288.0	48-65	1.00	-	0.03212	.798
288.0	48-65	1.00	-	0.03700	.842
288.0	48-65	1.00	-	0.03700	.834
288.0	48-65	1.00	-	0.01842	.475
288.0	48-65	1.00	-	0.01842	.456
288.0	48-65	1.00	-	0.01842	.458
288.0	48-65	1.00	-	0.01842	.434
288.0	48-65	1.00	-	0.01842	.440
244.7	48-65	1.00	-	0.0840	.421
244.7	48-65	1.00	-	0.0840	.402
244.7	48-65	1.00	-	0.0840	.436
244.7	48-65	1.00	-	0.0840	.412
244.7	48-65	1.00	-	0.0840	.404
244.7	48-65	1.00	-	0.1072	.492
244.7	48-65	1.00	-	0.1072	.485
244.7	48-65	1.00	-	0.1072	.529
244.7	48-65	1.00	-	0.1072	.553
244.7	48-65	1.00	-	0.1072	.544
244.7	48-65	1.00	-	0.1072	.500
244.7	48-65	1.00	-	0.1072	.542
244.7	48-65	1.00	-	0.1751	.890
244.7	48-65	1.00	-	0.1751	.836
244.7	48-65	1.00	-	0.1751	.855
244.7	48-65	1.00	-	0.1751	.890
244.7	48-65	1.00	-	0.1072	.508
244.7	48-65	1.00	-	0.1072	.489
244.7	48-65	1.00	-	0.1072	.488
244.7	48-65	1.00	-	0.1296	.538
244.7	48-65	1.00	-	0.1296	.613
244.7	48-65	1.00	-	0.1296	.602
244.7	48-65	1.00	-	0.1296	.627
244.7	48-65	1.00	-	0.1296	.594
218.5	32-35	0.10	CH3COOH	0.2724	.493
218.5	32-35	0.10	CH3COOH	0.2724	.492
218.5	32-35	0.10	CH3COOH	0.2724	.499
218.5	32-35	0.10	CH3COOH	0.2724	.495
195.5	32-35	0.10	CH3COOH	1.090	.706
195.5	32-35	0.10	CH3COOH	1.090	.730

TABLE (6-1) (CONTINUED)

T °C	CATALYST MESH SIZE	P_{e_o} ATM.	DILUENT	W/F HR.	X
195.5	32-35	0.10	CH3COOH	1.090	.720
195.5	32-35	0.10	CH3COOH	1.090	.722
195.5	32-35	0.10	CH3COOH	1.090	.702
153.5	32-35	1.00	-	2.2694	.0793
153.5	32-35	1.00	-	2.2694	.0802
153.5	32-35	1.00	-	2.2694	.0780
153.5	32-35	1.00	-	2.2694	.0813
153.5	32-35	1.00	-	2.2694	.0774
153.5	32-35	1.00	-	2.2694	.0783
153.5	32-35	1.00	-	2.2694	.0801
153.5	32-35	1.00	-	2.2694	.0762
203.5	32-80	1.00	-	1.105	.644
203.5	32-80	1.00	-	1.105	.641
203.5	32-80	1.00	-	1.105	.631
203.5	32-80	1.00	-	1.105	.665
203.5	32-80	1.00	-	1.105	.656
202.2	32-80	1.00	-	1.105	.541
202.2	32-80	1.00	-	1.105	.572
202.2	32-80	1.00	-	1.105	.556
202.2	32-80	1.00	-	1.105	.561
202.2	32-80	1.00	-	1.105	.584
205.3	32-80	0.50	CIS	1.105	.498
205.3	32-80	0.50	CIS	1.105	.489
205.3	32-80	0.50	CIS	1.105	.492
205.3	32-80	0.50	CIS	1.105	.502
196.2	32-35	1.00	-	1.6140	.582
196.2	32-35	1.00	-	1.6140	.604
196.2	32-35	1.00	-	1.6140	.595
196.2	32-35	1.00	-	1.6140	.627
196.2	32-35	1.00	-	1.6140	.615
196.2	32-35	1.00	-	1.6140	.608
196.2	32-35	1.00	-	1.6140	.608
217.4	35-48	0.50	H	0.570	.835
217.4	35-48	0.50	H	0.570	.839
217.4	35-48	0.50	N_2	0.2751	.392
217.4	35-48	0.50	N_2	0.2751	.389
217.4	35-48	0.50	N_2	0.2751	.392
217.4	35-48	0.50	N_2	0.2751	.396
217.4	35-48	0.50	N_2	0.2751	.390
217.4	35-48	0.50	N_2	0.2751	.387
217.4	35-48	1.00	-	0.6930	.968
217.4	35-48	1.00	-	0.6930	.954
217.4	35-48	1.00	-	0.6930	.960
217.4	35-48	1.00	-	0.2751	.473
217.4	35-48	1.00	-	0.2751	.464
217.4	35-48	1.00	-	0.2751	.464
217.4	35-48	1.00	-	0.2751	.434
217.4	35-48	1.00	-	0.2751	.463
217.4	35-48	1.00	-	0.2751	.411

TABLE (6-1) (CONTINUED)

T °C	MESH SIZE	P_{e_o} ATM.	DILUENT	W/F HR.	X
217.4	35-48	0.50	CH3COOH	0.3589	.561
217.4	35-48	0.50	CH3COOH	0.3589	.558
217.4	35-48	0.50	CH3COOH	0.3589	.555
217.4	35-48	0.50	CH3COOH	0.3589	.510
217.4	35-48	0.50	CH3COOH	0.3589	.537
217.4	35-48	0.50	CH3COOH	0.3589	.548
217.4	35-48	0.50	CH3COOH	0.3589	.545
217.4	35-48	0.50	CH3COOH	0.4408	.712
217.4	35-48	0.50	CH3COOH	0.4408	.706
217.4	35-48	0.50	CH3COOH	0.4408	.703
217.4	35-48	0.50	CH3COOH	0.4408	.721
217.4	35-48	0.50	CH3COOH	0.4408	.733
217.4	35-48	0.50	CH3COOH	0.4408	.756
217.4	35-48	0.50	CH3COOH	0.4408	.717
217.4	35-48	0.50	CH3COOH	0.4408	.739
217.4	35-48	0.50	CH3COOH	0.4408	.727
217.4	35-48	0.50	CH3COOH	0.6339	.937
217.4	35-48	0.50	CH3COOH	0.6339	.949
217.4	35-48	0.50	CH3COOH	0.6339	.949
217.4	35-48	0.50	CH3COOH	0.6339	.951
217.4	35-48	0.50	CH3COOH	0.6339	.936
217.4	65-80	1.00	-	0.7741	.993
217.4	65-80	1.00	-	0.7741	.994
217.4	65-80	1.00	-	0.7741	.987
217.4	65-80	1.00	-	0.7741	.996
217.4	65-80	1.00	-	0.7741	.989
217.4	65-80	1.00	-	0.4437	.679
217.4	65-80	1.00	-	0.4437	.660
217.4	65-80	1.00	-	0.4437	.675
217.4	65-80	1.00	-	0.4437	.671
217.4	65-80	1.00	-	0.4437	.672
217.4	65-80	1.00	-	0.4437	.662
217.4	65-80	1.00	-	0.3085	.448
217.4	65-80	1.00	-	0.3085	.448
217.4	65-80	1.00	-	0.3085	.452
217.4	65-80	1.00	-	0.3085	.451
217.4	65-80	1.00	-	0.3085	.457
217.4	65-80	1.00	-	0.3085	.457
217.4	65-80	1.00	-	0.3085	.465
217.4	65-80	1.00	-	0.3085	.440
217.4	65-80	1.00	-	0.5954	.945
217.4	65-80	1.00	-	0.5954	.946
217.4	65-80	1.00	-	0.5954	.949
217.4	65-80	1.00	-	0.5954	.947
217.4	65-80	1.00	-	0.5954	.947
217.4	65-80	1.00	-	0.5954	.950
217.4	65-80	1.00	-	0.5954	.951
203.5	65-80	1.00	-	1.175	.704

TABLE (6-1) (CONTINUED)

T °C	MESH SIZE	P_{eo} ATM.	DILUENT	W/F HR.	X
203.5	65-80	1.00	-	1.175	.715
203.5	65-80	1.00	-	1.175	.700
203.5	65-80	1.00	-	1.175	.709
203.5	65-80	1.00	-	1.175	.703
203.5	65-80	1.00	-	1.175	.699
203.5	65-80	1.00	-	1.6478	.968
203.5	65-80	1.00	-	1.6478	.968
203.5	65-80	1.00	-	1.6478	.974
203.5	65-80	1.00	-	0.8119	.486
203.5	65-80	1.00	-	0.8119	.491
203.5	65-80	1.00	-	0.8119	.482
203.5	65-80	1.00	-	0.8119	.494
203.5	65-80	1.00	-	0.8119	.505
203.5	65-80	1.00	-	0.8119	.511
203.5	65-80	1.00	-	0.8119	.481
203.5	65-80	1.00	-	1.179	.709
203.5	65-80	1.00	-	1.179	.709
203.5	65-80	1.00	-	1.179	.711
203.5	65-80	1.00	-	1.179	.711
203.5	65-80	1.00	-	1.179	.712
203.5	65-80	1.00	-	1.179	.713
203.5	65-80	1.00	-	1.179	.706
194.8	65-80	1.0	-	1.162	.469
194.8	65-80	1.0	-	1.162	.457
194.8	65-80	1.0	-	1.162	.463
194.8	65-80	1.0	-	1.162	.455
194.8	65-80	1.0	-	1.162	.474
188.8	65-80	1.00	-	2.3839	.763
188.8	65-80	1.00	-	2.3839	.767
188.8	65-80	1.00	-	2.3839	.774
188.8	65-80	1.00	-	2.3839	.779
188.8	65-80	1.00	-	2.3839	.779
188.8	65-80	1.00	-	2.3839	.772
188.8	65-80	1.00	-	2.3839	.781
188.8	65-80	1.00	-	2.3839	.781
188.8	65-80	1.00	-	2.3839	.753
188.8	65-80	1.00	-	2.3839	.766
188.8	65-80	1.00	-	2.3839	.771
188.8	65-80	1.00	-	2.3839	.756
188.8	65-80	1.00	-	2.3839	.757
188.8	65-80	1.00	-	3.505	.995
187.8	65-80	1.00	-	1.805	.586
187.8	65-80	1.00	-	1.805	.586
187.8	65-80	1.00	-	1.805	.606
187.8	65-80	1.00	-	1.805	.597
187.8	65-80	1.00	-	1.805	.597
187.8	65-80	1.00	-	1.805	.602
187.8	65-80	1.00	-	1.805	.576
187.8	65-80	1.00	-	1.805	.582

TABLE (6-1) (CONTINUED)

T °C	MESH SIZE	Pe$_o$ ATM.	DILUENT	W/F HR.	X
187.8	65-80	1.00	-	1.805	.581
187.8	65-80	1.00	-	1.805	.589
187.8	65-80	1.00	-	1.805	.621
187.8	65-80	1.00	-	1.805	.551
187.8	65-80	1.00	-	1.805	.586
187.8	65-80	1.00	-	0.8373	.312
187.8	65-80	1.00	-	0.8373	.312
187.8	65-80	1.00	-	0.8373	.319
187.8	65-80	1.00	-	0.8373	.319
187.8	65-80	1.00	-	0.8373	.318
187.8	65-80	1.00	-	0.8373	.309
187.8	65-80	1.00	-	0.8373	.309
187.8	65-80	1.00	-	0.8373	.314
187.8	65-80	1.00	-	0.8373	.319
187.8	65-80	1.00	-	0.8373	.307
187.8	65-80	1.00	-	3.553	.997
187.8	65-80	1.00	-	2.4584	.835
187.8	65-80	1.00	-	2.4584	.828
187.8	65-80	1.00	-	2.4584	.828
187.8	65-80	1.00	-	2.4584	.831
187.8	65-80	1.00	-	2.4584	.831
187.8	65-80	1.00	-	2.4584	.829
187.8	65-80	1.00	-	2.4584	.822
187.8	65-80	1.00	-	1.2155	.434
187.8	65-80	1.00	-	1.2155	.428
187.8	65-80	1.00	-	1.2155	.416
168.8	48-65	1.00	-	1.3593	.219
168.8	48-65	1.00	-	1.3593	.217
168.8	48-65	1.00	-	1.3593	.218
168.8	48-65	1.00	-	1.3593	.21
168.8	48-65	1.00	-	1.3593	.216
168.8	48-65	1.00	-	1.3593	.225
168.8	48-65	1.00	-	2.8090	.399
168.8	48-65	1.00	-	2.8090	.410
168.8	48-65	1.00	-	2.8090	.410
168.8	48-65	1.00	-	2.8090	.413
168.8	48-65	1.00	-	2.8090	.415
168.8	48-65	1.00	-	2.8090	.408
168.5	65-80	1.00	-	1.8055	.248
168.5	65-80	1.00	-	1.8055	.252
168.5	65-80	1.00	-	1.8055	.250
168.5	65-80	1.00	-	1.8055	.246
168.5	65-80	1.00	-	1.8055	.256
168.5	65-80	1.00	-	1.8055	.253

TABLE (6-1) (CONTINUED)

T °C	MESH SIZE	Pe_o ATM.	DILUENT	W/F HR.	X
168.5	32-35	1.00	-	1.9448	.244
168.5	32-35	1.00	-	1.9448	.216
168.5	32-35	1.00	-	1.9448	.254
168.5	32-35	1.00	-	1.9448	.266
168.5	32-35	1.00	-	1.9448	.264
168.5	32-35	1.00	-	1.9448	.253
168.5	32-35	1.00	-	1.9448	.255
151.3	32-35	1.00	-	3.3079	.212
151.3	32-35	1.00	-	3.3079	.207
151.3	32-35	1.00	-	3.3079	.224
151.3	32-35	1.00	-	3.3079	.215
151.3	32-35	1.00	-	3.3079	.217
151.3	32-35	1.00	-	3.3079	.210
151.3	32-35	1.00	-	1.6006	.114
151.3	32-35	1.00	-	1.6006	.127
151.3	32-35	1.00	-	1.6006	.127
151.3	32-35	1.00	-	1.6006	.124
151.3	32-35	1.00	-	1.6006	.096
151.3	32-35	1.00	-	1.6006	.134
151.3	32-35	1.00	-	1.6006	.133
151.3	32-35	1.00	-	1.6006	.116
151.3	32-35	1.00	-	1.6006	.102
151.3	32-35	1.00	-	1.6006	.118
151.3	32-35	1.00	-	1.6006	.119
151.3	32-35	1.00	-	1.6006	.103
151.3	32-35	1.00	-	1.6006	.113
151.3	32-35	1.00	-	1.6006	.128
210.0	32-35	1.00	-	0.595	.705
210.0	32-35	1.00	-	0.595	.703
210.0	32-35	1.00	-	0.595	.691
210.0	32-35	1.00	-	0.595	.701
210.0	32-35	1.00	-	0.595	.702
210.0	32-35	1.00	-	0.733	.911
210.0	32-35	1.00	-	0.733	.908
210.0	32-35	1.00	-	0.733	.913
210.0	48-65	1.00	-	0.425	.506
210.0	48-65	1.00	-	0.425	.528
210.0	48-65	1.00	-	0.425	.514
210.0	48-65	1.00	-	0.425	.517
210.0	48-65	1.00	-	0.425	.517
210.0	48-65	1.00	-	0.615	.674
210.0	48-65	1.00	-	0.615	.709
210.0	48-65	1.00	-	0.615	.731
210.0	48-65	1.00	-	0.615	.661
210.0	48-65	1.00	-	0.615	.759
210.0	48-65	1.00	-	0.615	.710
210.0	48-65	1.00	-	0.615	.719
210.0	48-65	1.00	-	0.336	.366

TABLE (6-1) (CONTINUED)

T °C	MESH SIZE	P_{eo} ATM.	DILUENT	W/F HR.	X
210.0	48-65	1.00	-	0.336	.354
210.0	48-65	1.00	-	0.336	.360
210.0	48-65	1.00	-	0.336	.359
210.0	48-65	1.00	-	0.336	.362
210.0	48-65	1.00	-	0.336	.362
210.0	48-65	1.00	-	0.668	.719
222.5	48-65	1.00	-	0.584	.936
222.5	48-65	1.00	-	0.584	.929
222.5	48-65	1.00	-	0.584	.926
222.5	48-65	1.00	-	0.234	.506
222.5	48-65	1.00	-	0.234	.506
222.5	48-65	1.00	-	0.234	.533
222.5	48-65	1.00	-	0.234	.488
222.5	48-65	1.00	-	0.234	.530
222.5	48-65	1.00	-	0.234	.508
223.0	48-65	1.00	-	0.324	.519
223.0	48-65	1.00	-	0.324	.503
223.0	48-65	1.00	-	0.324	.488
223.0	48-65	1.00	-	0.324	.509
223.0	48-65	1.00	-	0.324	.502
223.0	48-65	1.00	-	0.324	.496
223.0	48-65	1.00	-	0.324	.505
223.0	48-65	1.00	-	0.469	.665
223.0	48-65	1.00	-	0.469	.665
223.0	48-65	1.00	-	0.469	.671
223.0	48-65	1.00	-	0.469	.674
223.0	48-65	1.00	-	0.469	.661
223.0	48-65	1.00	-	0.469	.644
223.0	48-65	1.00	-	0.438	.717
223.0	48-65	1.00	-	0.438	.700
223.0	48-65	1.00	-	0.438	.693
223.0	48-65	1.00	-	0.438	.708
223.0	48-65	1.00	-	0.438	.721
223.0	48-65	1.00	-	0.438	.684
223.0	48-65	1.00	-	0.438	.690
223.0	48-65	1.00	-	0.438	.691

TABLE (6-1) (CONTINUED)

T C	MESH SIZE	P_{c_o} ATM.	DILUENT	W/F HR.	X
223.0	48-65	1.00	-	0.652	.656
223.0	48-65	1.00	-	0.652	.652
223.0	48-65	1.00	-	0.652	.672
223.0	48-65	1.00	-	0.652	.672
223.0	48-65	1.00	-	0.652	.677
223.0	48-65	1.00	-	0.652	.673
223.0	48-65	1.00	-	0.652	.663
223.0	48-65	1.00	-	0.2592	.285
223.0	48-65	1.00	-	0.2592	.265
223.0	48-65	1.00	-	0.2592	.242
223.0	48-65	1.00	-	0.2592	.297
223.0	48-65	1.00	-	0.2592	.293
223.0	48-65	1.00	-	0.2592	.302
223.0	48-65	1.00	-	0.456	.455
223.0	48-65	1.00	-	0.456	.455
223.0	48-65	1.00	-	0.456	.466
223.0	48-65	1.00	-	0.456	.447
223.0	48-65	1.00	-	0.456	.447
223.0	48-65	1.00	-	0.456	.454
223.0	48-65	1.00	-	0.456	.475
223.0	48-65	1.00	-	0.456	.458
223.0	48-65	1.00	-	0.456	.456
223.0	48-65	1.00	-	0.937	.930
223.0	48-65	1.00	-	0.937	.942
223.0	48-65	1.00	-	0.937	.928
223.0	48-65	1.00	-	0.937	.927
223.0	48-65	1.00	-	0.937	.938
223.0	48-65	1.00	-	0.937	.936

CHAPTER 7

ISO-BUTYL ACETATE

7.1 EXPERIMENTAL PROCEDURE

The iso-butyl acetate experiments were made with pure ester at 394° and 419°C and 1 atmosphere pressure. The catalyst was 32-35 mesh Batch 2 charcoal, and the reactor was a 1.0 cm. ID Pyrex tube. The charcoal was pretreated before use by heating it to 930°C in helium for 30 minutes. Catalysts were weighed and then charged into the reactor without contacing air by the procedures described in Section 4.1.

Kinetic data were obtained by a procedure similar to the one for n-butyl acetate described in Section 4.1. For each experiment pure ester was fed to the catalyst at a constant rate for a long period of time. During the period the conversion of ester was measured as a function of the process time. Chromatographic analysis of the reactor products was the same as described in Section 4.1 for n-butyl acetate, except that Column 1 (FFAP) was temperature programmed starting at a base temperature of 140°C (rather than 110°C). The conversion of iso-butyl acetate was calculated by using Equation (4-3), and selectivities were calculated from Equation (4-4).

7.2 RESULTS OF THE ISO-BUTYL ACETATE EXPERIMENTS

Iso-butyl acetate decomposed primarily to acetic acid and isobutene, but considerable fractions of carbon dioxide, methane and other hydrocarbons were found in the products. The activities of the catalysts decreased more or less linearly with process time, similar to the n-butyl acetate results, and the weights of the catalysts increased by about 12% during the experiments. The results of the experiments are presented in Tables (7-1) and (7-2). The conversion is plotted as a function of the process time in Figures (7-1) and (7-2), and a plot of the selectivities for a typical experiment appears in Figure (7-3).

Exploratory experiments were made to determine the reproducibility of the catalyst preparation and the extent of the thermal decomposition of the ester. A catalyst preheated in helium at 930°C for 1 hour gave the same results as charcoal preheated for 30 minutes. These results, shown in Figure (7-2), suggest that the initial activities of the catalysts were the same for all of the iso-butyl acetate experiments. When the catalyst bed was replaced by a bed of small glass beads, pyrolysis of iso-butyl acetate at 419°C was found to be negligible at the reactant feed rate used for the kinetic experiments.

TABLE (7-1)
RESULTS OF ISO-BUTYL ACETATE EXPERIMENTS
CONVERSION AND SELECTIVITIES FOR MAJOR PRODUCTS

0 TEMPERATURE OF REACTION = 394.0°C., W/F = 1.1572 HR.

		SELECTIVITY					
PROCESS TIME,HR	X	ACETIC ACID	CO+ CH4	1- BUTENE	ISO- BUTENE	TRANS- BUTENE	CIS-2- BUTENE
6.750	.3102	.7810	.5440	.0068	.6895	.0050	.0075
7.250	.3147	.8189	.5200	.0106	.6720	.0094	.0059
7.750	.3171	.8443	.4997	.0071	.6748	.0049	.0048
8.250	.3238	.8216	.5216	.0098	.6803	.0056	.0055
16.830	.2909	.9085	.4661	.0061	.6370	.0058	.0057
17.250	.2819	.9097	.4416	.0089	.6433	.0068	.0067
17.670	.2659	.8858	.4579	.0068	.6701	.0078	.0067
18.000	.2523	.9165	.4814	.0125	.6166	.0105	.0090
18.330	.2617	.8752	.4616	.0115	.6818	.0066	.0051

0 TEMPERATURE OF REACTION = 394.0°C., W/F = 1.4190 HR.

		SELECTIVITY					
PROCESS TIME,HR	X	ACETIC ACID	CO+ CH4	1- BUTENE	ISO- BUTENE	TRANS- BUTENE	CIS-2- BUTENE
1.000	.4137	.8165	.6251	.0054	.5800	.0051	.0056
2.500	.4101	.7900	.5999	.0089	.6391	.0101	.0041
3.000	.4226	.8344	.5625	.0062	.6163	.0053	.0055
4.000	.4012	.7983	.5850	.0087	.6550	.0100	.0065
4.500	.3956	.8390	.5416	.0080	.6396	.0060	.0042
5.000	.4056	.8626	.5297	.0076	.6279	.0066	.0031
6.000	.3910	.8308	.5456	.0080	.6513	.0066	.0064
8.000	.3479	.7821	.5825	.0075	.7017	.0053	.0037
8.500	.3998	.8212	.6325	.0056	.6178	.0050	.0046
9.000	.3660	.8360	.5335	.0087	.6617	.0079	.0051
9.500	.3551	.8467	.5292	.0088	.6610	.0063	.0055
16.500	.3341	.8439	.5015	.0066	.6831	.0056	.0048
16.920	.3247	.8553	.5111	.0075	.7059	.0075	.0046
17.330	.3293	.8297	.4984	.0068	.6872	.0050	.0056
18.500	.3204	.8320	.5125	.0062	.6923	.0030	.0029
19.000	.3141	.8595	.4754	.0093	.6759	.0052	.0050

TEMPERATURE OF REACTION = 419.5°C., W/F = 1.2899 HR.
CATALYST HEATED AT 930 C FOR 1 HOUR PRIOR TO USE

		SELECTIVITY					
PROCESS TIME,HR	X	ACETIC ACID	CO+ CH4	1- BUTENE	ISO- BUTENE	TRANS- BUTENE	CIS-2- BUTENE
2.000	.7160	.6666	.6498	.0058	.6463	.0097	.0036
4.000	.6525	.7262	.5802	.0059	.6676	.0059	.0068
6.000	.6042	.7311	.5559	.0069	.6833	.0062	.0053

TABLE (7-1) (CONTINUED)

TEMPERATURE OF REACTION = 394.0°C., W/F = 2.1054 HR.

PROCESS TIME,HR	X	SELECTIVITY ACETIC ACID	CO+ CH4	1- BUTENE	ISO- BUTENE	TRANS- BUTENE	CIS-2- BUTENE
2.000	.5179	.8168	.5978	.0062	.5766	.0082	.0050
2.500	.5288	.7847	.6318	.0066	.6007	.0076	.0062
3.000	.5191	.8070	.5986	.0055	.6013	.0073	.0051
3.500	.3729	.7937	.5944	.0099	.6421	.0085	.0076
4.000	.5004	.7691	.6037	.0091	.6357	.0087	.0080
4.330	.5009	.7911	.5909	.0084	.6208	.0080	.0073
4.670	.4961	.7808	.5854	.0106	.6341	.0076	.0069
5.000	.4911	.7763	.5721	.0103	.6403	.0103	.0074
5.330	.4870	.7831	.5807	.0093	.6407	.0064	.0054
5.670	.4737	.7989	.5753	.0099	.6405	.0056	.0054
6.000	.4749	.7813	.5729	.0095	.6540	.0088	.0055

TEMPERATURE OF REACTION = 419.5°C., W/F = 1.3002 HR.

PROCESS TIME,HR	X	SELECTIVITY ACETIC ACID	CO+ CH4	1- BUTENE	ISO- BUTENE	TRANS- BUTENE	CIS-2- BUTENE
2.000	.7040	.6653	.6532	.0062	.6449	.0083	.0048
2.500	.6889	.6612	.6464	.0058	.6677	.0076	.0044
3.000	.6914	.6816	.6137	.0067	.6530	.0099	.0043
3.500	.7045	.6854	.6229	.0062	.6466	.0049	.0048
4.000	.6598	.7248	.5818	.0063	.6658	.0075	.0049
4.500	.6450	.7219	.5792	.0069	.6677	.0081	.0049
5.000	.6281	.7315	.5558	.0069	.6791	.0056	.0030
5.500	.6162	.7356	.5628	.0049	.6869	.0052	.0035
6.000	.6043	.7287	.5579	.0060	.6866	.0073	.0046
6.500	.5781	.7369	.5411	.0073	.6935	.0075	.0026
7.000	.5777	.7554	.5347	.0082	.6809	.0062	.0051
7.500	.5668	.7275	.5480	.0056	.7006	.0053	.0037

TABLE (7-1) (CONTINUED)

0 TEMPERATURE OF REACTION = 419.5°C., W/F = 1.0117 HR.

		SELECTIVITY					
PROCESS TIME,HR	X	ACETIC ACID	CO+ CH4	1- BUTENE	ISO- BUTENE	TRANS- BUTENE	CIS-2- BUTENE
1.500	.6521	.6973	.6091	.0061	.6487	.0073	.0062
2.000	.6282	.7333	.5708	.0084	.6703	.0090	.0058
2.500	.6247	.7057	.5756	.0054	.7056	.0077	.0045
3.000	.6067	.7229	.5689	.0059	.6874	.0098	.0050
3.500	.5924	.7064	.5659	.0050	.7205	.0080	.0052
4.000	.5829	.7674	.5013	.0061	.7005	.0089	.0041
4.500	.5716	.7595	.5109	.0055	.7110	.0053	.0052
5.000	.5572	.7602	.5084	.0066	.6977	.0053	.0036
5.500	.5442	.7453	.5051	.0056	.7096	.0091	.0063
6.000	.5305	.7523	.5164	.0063	.7116	.0060	.0027
6.500	.5248	.7791	.4928	.0068	.7049	.0070	.0032
7.000	.5060	.7521	.5022	.0065	.7256	.0068	.0022
7.500	.5012	.7615	.5067	.0059	.7135	.0045	.0033

TEMPERATURE OF REACTION = 419.5°C., W/F = .5607 HR.

		SELECTIVITY					
PROCESS TIME,HR	X	ACETIC ACID	CO+ CH4	1- BUTENE	ISO- BUTENE	TRANS- BUTENE	CIS-2- BUTENE
3.500	.4497	.8056	.4582	.0045	.7335	.0061	.0042
4.000	.4374	.7808	.4606	.0065	.7431	.0087	.0061
4.500	.4259	.7825	.4439	.0060	.7535	.0083	.0050
5.000	.4148	.7762	.4460	.0062	.7594	.0066	.0051
5.500	.4128	.7977	.4209	.0047	.7472	.0089	.0044

TABLE (7-2)
RESULTS OF ISO-BUTYL ACETATE EXPERIMENTS
CONVERSION AND SELECTIVITIES FOR MINOR PRODUCTS

0 TEMPERATURE OF REACTION = 394.0 °C., W/F = 1.1572 HR.

PROCESS TIME,HR	X	SELECTIVITY IBA*	ETHANE	PRO- PANE	CO2	ISO- BUTANE	N- BUTANE
6.750	.3102	.0600	.0096	.0191	.0952	.0736	.0058
7.250	.3147	.0484	.0062	.0157	.0995	.0722	.0056
7.750	.3171	.0434	.0063	.0147	.1031	.0681	.0034
8.250	.3238	.0509	.0062	.0127	.0994	.0628	.0075
16.830	.2909	.0423	.0065	.0107	.0950	.0621	.0054
17.250	.2819	.0492	.0067	.0089	.0940	.0529	.0080
17.670	.2659	.0469	.0129	.0085	.1015	.0447	.0026
18.000	.2523	.0405	.0076	.0102	.1031	.0490	.0046
18.330	.2617	.0417	.0058	.0080	.0931	.0527	.0074

0 TEMPERATURE OF REACTION = 394.0 °C., W/F = 1.4190 HR.

PROCESS TIME,HR	X	SELECTIVITY IBA	ETHANE	PRO- PANE	CO2	ISO- BUTANE	N- BUTANE
1.000	.4137	.0283	.0107	.0222	.0821	.1525	.0064
2.500	.4101	.0375	.0108	.0178	.0896	.1161	.0045
3.000	.4226	.0338	.0181	.0227	.0874	.1161	.0034
4.000	.4012	.0317	.0111	.0187	.0996	.0966	.0040
4.500	.3956	.0361	.0050	.0191	.0905	.1005	.0050
5.000	.4056	.0320	.0115	.0176	.0944	.0943	.0047
6.000	.3910	.0404	.0110	.0164	.0918	.0889	.0017
8.000	.3479	.0360	.0101	.0144	.0939	.0816	.0030
8.500	.3998	.0342	.0073	.0167	.1098	.0893	.0030
9.000	.3660	.0352	.0092	.0135	.0983	.0822	.0028
9.500	.3551	.0405	.0088	.0138	.0901	.0745	.0028
16.500	.3341	.0357	.0058	.0151	.0947	.0739	.0049
16.920	.3247	.0293	.0096	.0160	.1004	.0361	.0029
17.330	.3293	.0389	.0089	.0136	.1032	.0741	.0057
18.500	.3204	.0328	.0093	.0146	.0966	.0769	.0056
19.000	.3141	.0425	.0061	.0115	.0912	.0725	.0040

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* IBA = ISO-BUTYRALDEHYDE

TABLE (7-2) (CONTINUED)

TEMPERATURE OF REACTION = 394.0 °C., W/F = 2.1054 HR.

PROCESS TIME,HR	X	SELECTIVITY IBA	ETHANE	PRO-PANE	CO2	ISO-BUTANE	N-BUTANE
2.000	.5179	.0279	.0128	.0222	.0932	.1570	.0056
2.500	.5288	.0343	.0126	.0231	.0803	.1531	.0035
3.000	.5191	.0319	.0139	.0205	.0878	.1447	.0052
3.500	.3729	.0355	.0163	.0171	.0953	.1048	.0049
4.000	.5004	.0370	.0145	.0156	.0924	.1339	.0054
4.330	.5009	.0273	.0134	.0210	.1018	.1366	.0040
4.670	.4961	.0315	.0136	.0235	.1023	.1285	.0035
5.000	.4911	.0351	.0100	.0206	.1081	.1266	.0030
5.330	.4870	.0357	.0175	.0188	.1027	.1220	.0036
5.670	.4737	.0360	.0177	.0171	.0963	.1142	.0036
6.000	.4749	.0366	.0156	.0200	.0992	.1132	.0042

TEMPERATURE OF REACTION = 419.5°C., W/F = 1.3002 HR.

PROCESS TIME,HR	X	SELECTIVITY IBA	ETHANE	PRO-PANE	CO2	ISO-BUTANE	N-BUTANE
2.000	.7040	.0334	.0123	.0238	.1348	.1751	.0123
2.500	.6889	.0274	.0135	.0218	.1411	.1673	.0106
3.000	.6914	.0269	.0123	.0271	.1521	.1638	.0089
3.500	.7045	.0302	.0140	.0238	.1509	.1644	.0094
4.000	.6598	.0305	.0108	.0183	.1325	.1447	.0065
4.500	.6450	.0283	.0126	.0198	.1386	.1413	.0071
5.000	.6281	.0294	.0127	.0173	.1430	.1316	.0086
5.500	.6162	.0280	.0086	.0202	.1351	.1293	.0052
6.000	.6043	.0309	.0130	.0197	.1381	.1240	.0083
6.500	.5781	.0353	.0133	.0181	.1330	.1215	.0037
7.000	.5777	.0326	.0130	.0183	.1332	.1183	.0042
7.500	.5668	.0345	.0089	.0175	.1371	.1206	.0075

TEMPERATURE OF REACTION = 419.5 °C., W/F = 1.2899 HR.
CATALYST HEATED AT 930 C FOR 1 HOUR PRIOR TO USE

PROCESS TIME,HR	X	SELECTIVITY IBA	ETHANE	PRO-PANE	CO2	ISO-BUTANE	N-BUTANE
2.000	.7160	.0329	.0126	.0228	.1352	.1774	.0119
4.000	.6525	.0312	.0101	.0199	.1336	.1464	.0066
6.000	.6042	.0294	.0145	.0206	.1399	.1255	.0062

TABLE (7-2) (CONTINUED)

TEMPERATURE OF REACTION = 419.5°C., W/F = .5607 HR.

		SELECTIVITY					
PROCESS TIME,HR	X	IBA	ETHANE	PRO-PANE	CO2	ISO-BUTANE	N-BUTANE
3.500	.4497	.0330	.0162	.0103	.1022	.0850	.0036
4.000	.4374	.0360	.0176	.0122	.1125	.0801	.0037
4.500	.4259	.0348	.0149	.0125	.1109	.0814	.0045
5.000	.4148	.0334	.0186	.0103	.1150	.0816	.0039
5.500	.4128	.0326	.0160	.0125	.1199	.0795	.0045

TEMPERATURE OF REACTION = 419.5°C., W/F = 1.0117 HR.

		SELECTIVITY					
PROCESS TIME,HR	X	IBA	ETHANE	PRO-PANE	CO2	ISO-BUTANE	N-BUTANE
1.500	.6521	.0330	.0194	.0216	.1351	.1602	.0097
2.000	.6282	.0296	.0182	.0169	.1198	.1418	.0050
2.500	.6247	.0244	.0231	.0188	.1272	.1372	.0041
3.000	.6067	.0306	.0129	.0162	.1358	.1291	.0051
3.500	.5924	.0326	.0115	.0146	.1283	.1237	.0048
4.000	.5829	.0312	.0105	.0151	.1179	.1196	.0052
4.500	.5716	.0359	.0132	.0172	.1120	.1137	.0032
5.000	.5572	.0358	.0263	.0165	.1211	.1128	.0047
5.500	.5442	.0384	.0152	.0176	.1286	.1098	.0038
6.000	.5305	.0352	.0182	.0178	.1235	.1067	.0044
6.500	.5248	.0387	.0108	.0113	.1247	.0972	.0054
7.000	.5060	.0325	.0141	.0177	.1246	.1032	.0056
7.500	.5012	.0353	.0187	.0147	.1291	.1000	.0034

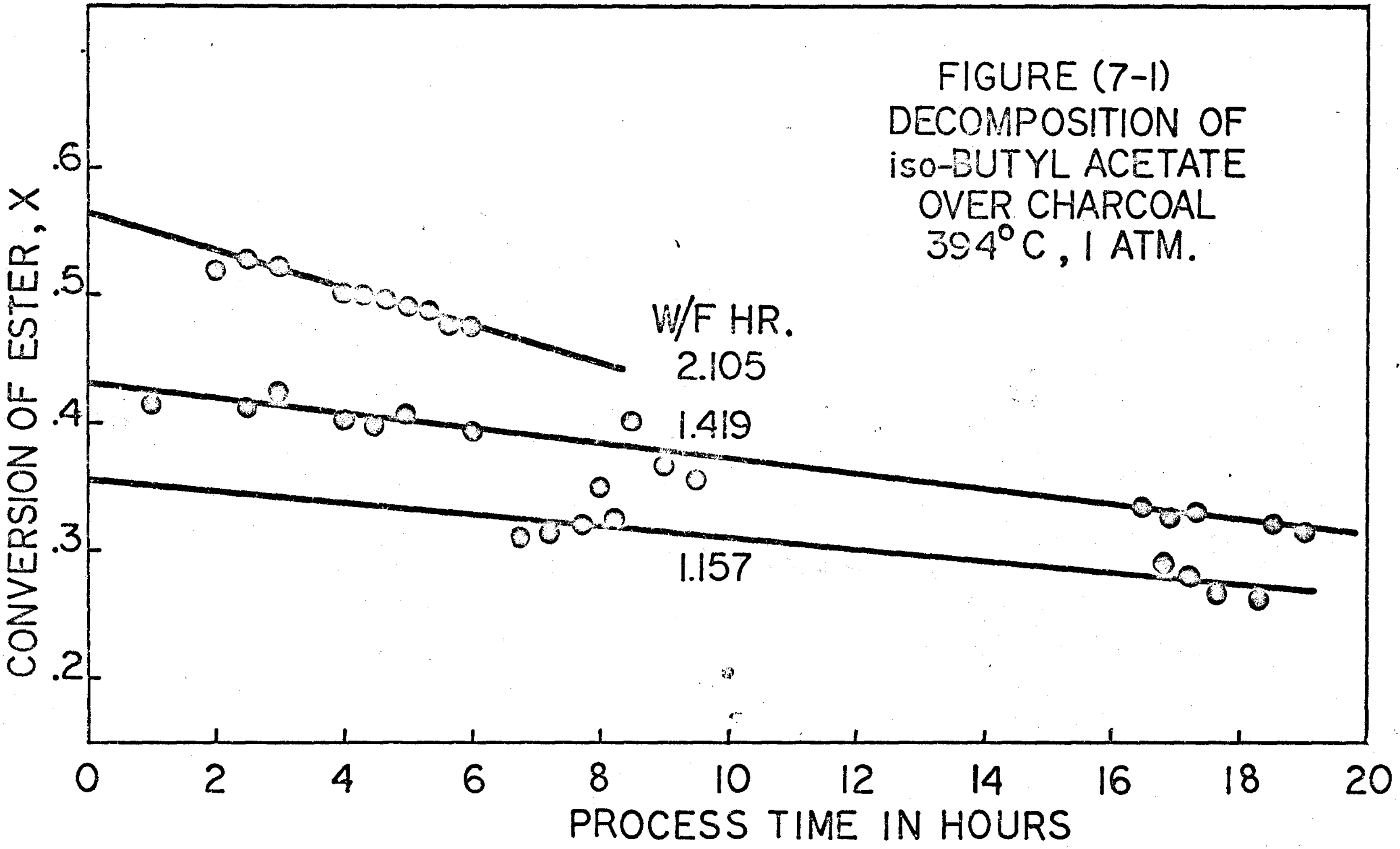


FIGURE (7-1)
DECOMPOSITION OF
iso-BUTYL ACETATE
OVER CHARCOAL
394° C, 1 ATM.

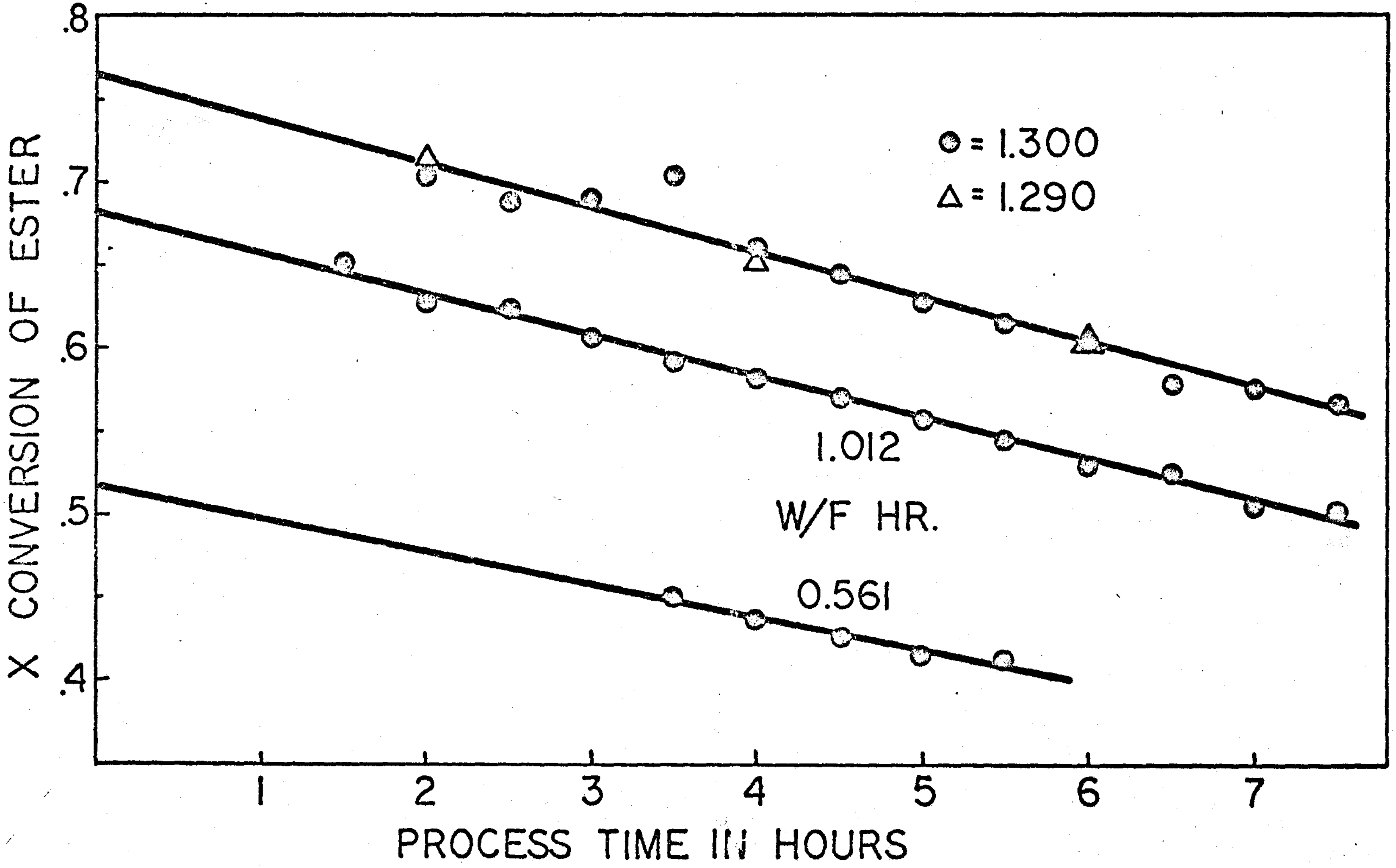


Figure (7-2) Decomposition of iso-butyl acetate over charcoal at 419.5° C, 1 atm. total pressure.

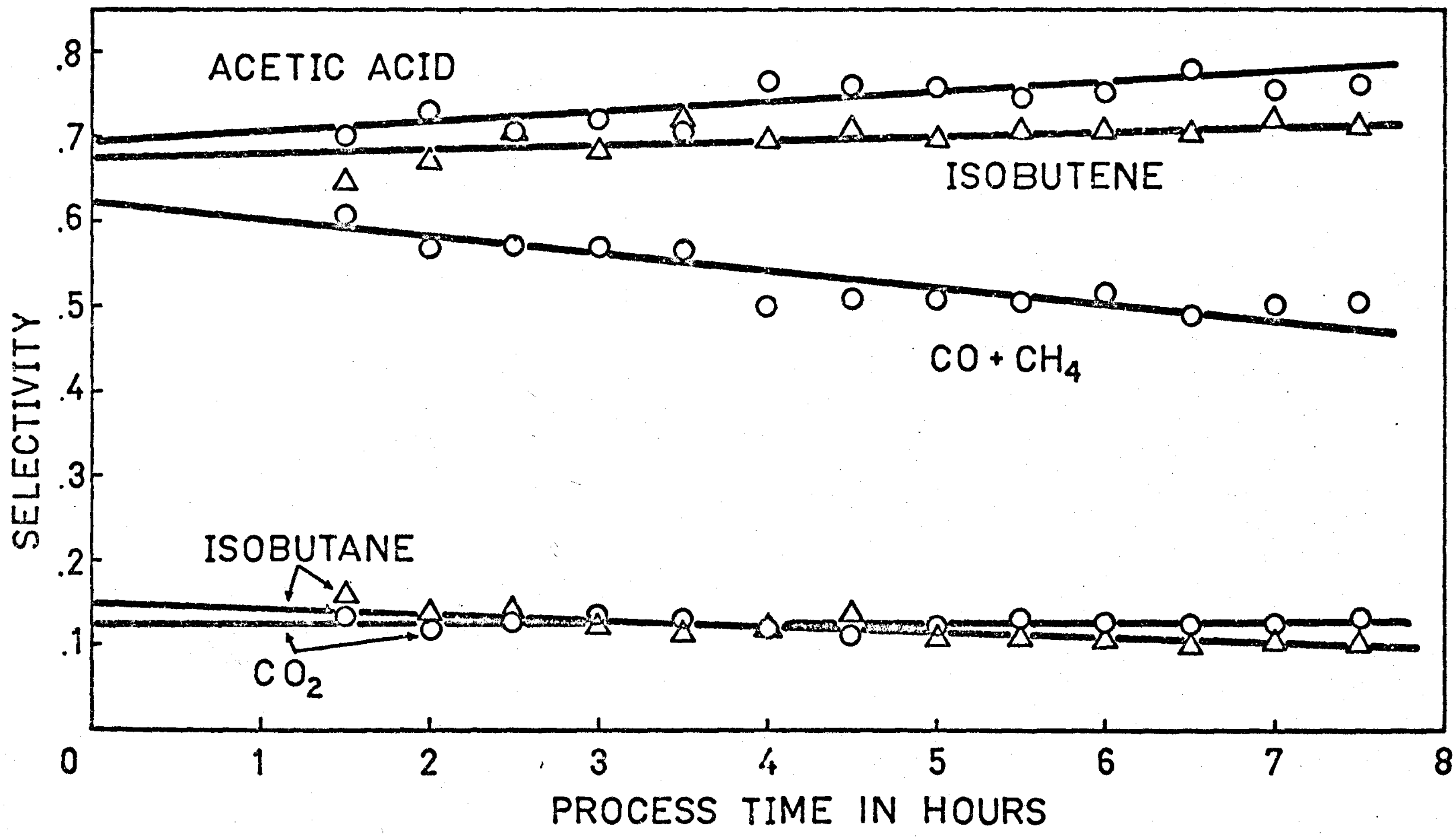
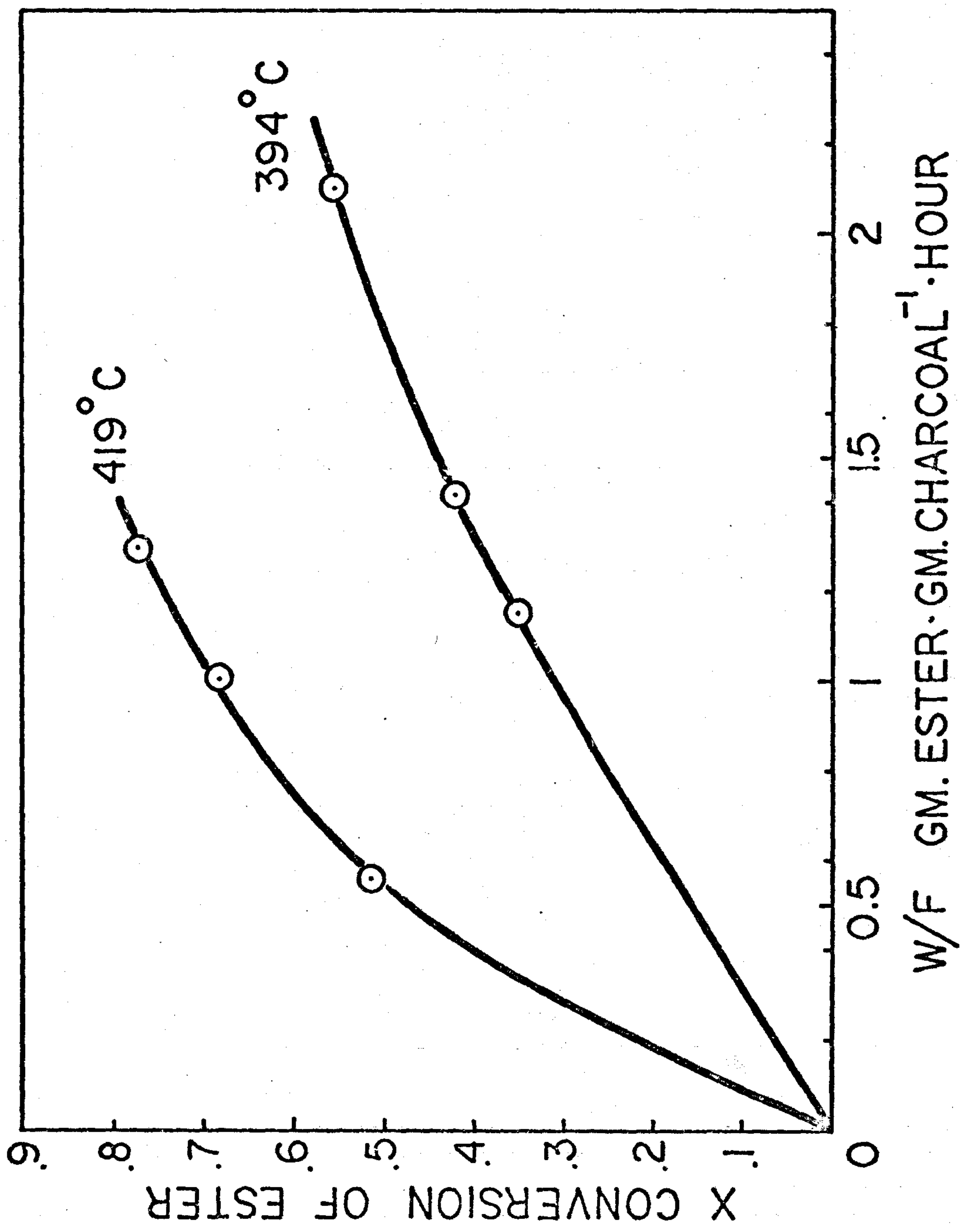


Figure (7-3) Product distribution for the decomposition of isobutyl acetate over charcoal at 419.5°C and W/F = 1.012 hours.

Figure (7-4) Kinetic data for iso-butyl acetate decomposition over charcoal, 1 atm. total pressure.



7.3 ANALYSIS OF THE ISO-BUTYL ACETATE DATA

Kinetic data were derived from the experimental data by fitting least squares straight lines to the conversion versus process time data. The straight lines for each space time (W/F) were extrapolated to zero process time to calculate x for unfouled catalyst. The least squares lines are shown in Figures (7-1) and (7-2), and the kinetic data derived form the figures appears in Figure (7-4).

It was assumed that the surface reaction equation (Equation (D-1)) with coefficient kL and K_e describes the kinetics of the iso-butyl acetate reaction. The best values of the coefficients were calculated from the data in Figure (7-4) by using the Rosenbrock Search in Program 3. The results were:

$$kL = 10^{17.16} \exp(-51.74/RT) \frac{\text{grams of ester}}{\text{grams of charcoal}\cdot\text{hour}} ,$$

and

$$K_e = 10^{-3.50} \exp(+9.33/RT) \text{ atmospheres}^{-1}.$$

CHAPTER 8

DISCUSSION

The purpose of this chapter is to consider some of the results of the research and to make appropriate conclusions about the role of the charcoal catalyst and the "paths" of the ester reactions. The conclusions,made in the light of rates of reaction, surface coverage, and selectivities, determine in part the extent to which the objectives of the research are fulfilled.

The results of the data analyses in Chapters 4 through 7 suggest that butyl acetates may decompose on charcoal by a mechanism which is similar to the gas-phase reaction scheme. Butyl acetates appear to decompose on charcoal by first order surface reactions; that is, for each ester the rate of the heterogeneous reaction can be expressed as the product of a kinetic coefficient and the concentration of the reactant on the charcoal surface, which is qualitatively similar to the observed(6,7) unimolecular thermal decompositions of the esters. Similarities also exist between the products of the catalyzed and gas-phase reactions as discussed in Chapters 4 through 7. The decomposition of butyl acetates over charcoal may proceed via a cyclic, six membered, intramolecular complex.

Table (8-1) compares the best values of some kinetic and adsorption coefficients for the reactions of butyl acetates in the gas-phase and on charcoal. For the gas-phase reactions some average values(14) are given for the Arrhenius activation energies and A factors. For the catalyzed reactions the activation energies are summarized from Chapters 6-9, and the pre-exponential factors were determined by dividing the values of $\hat{k_o L}$ by L = 0.45 grams of ester per gram of charcoal*. The values of entropy of activation, $\Delta S^{\ddagger}$, given in Table (8-1) were calculated for the arbitrary temperature of 300°C by using the equation(45)

$$k_o = \frac{e\underline{k}T}{\underline{h}} \cdot \exp(\Delta S^{\ddagger}/R) \quad , \qquad (8\text{-}1)$$

where e is the base of the natural logarithm, $\underline{k}$ is the Boltzmann constant, and $\underline{h}$ is Planck's constant. For convenience in most of the following discussion, only the best values of the coefficients will be considered. The confidence limits for the coefficients calculated in Chapters 4 through 7 show that there are significant differences between the coefficients for the different esters except for the iso- and n-isomers.

The activation energies for the surface reactions

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[*] See Appendix C for the calculation of L.

TABLE (8-1)

Best Values of Kinetic and Adsorption Coefficients and Entropies of Activation for Butyl Acetate Reactions

$$r_{gas} = k_o \exp(-E/RT) \cdot C$$

$$r_{cat.} = k_o L \exp(-E/RT) [(K_{e_o} \exp(-H/RT) \cdot P_e)/(1+K_{e_o} \exp(-H/RT) \cdot P_{e_o})]$$

	Arrhenius E kcal/mole		Pre-exponential Factors, sec^{-1}		$\Delta S^{\ddagger}$, 300°C cal/mole.°K		Adsorption Coeff.	
Ester isomer	Cata-lyzed	Gas$^{(1)}$ Phase	Cata-lyzed $\log k_0$	Gas$^{(1)}$ Phase $\log k^{(1)}$	Cata-lyzed	Gas Phase	Pre-Exp. atm^{-1} $\log K_{e_o}$	Heat $\frac{kcal}{mole}$ $\hat{H}$
Iso	51.7	47.3	13.95	11.9	+2.15	-7.13	-3.50	-9.33
Normal	51.3	46.0	13.95	13.1	+2.15	-6.0	-4.63	-13.80
Sec	33.5	45.2	9.14	12.4	-20.7	-5.0	-1.64	-6.60
Tert	21.7	40.0	6.03	12.2	-31.5	-1.8	-	-

(1) Benson, S.W., and O'Neal, H.E., J. Phys. Chem., 71, 2903 (1967) The values of E and A derived in this reference represent reasonable averages of experimental E and A values.

of normal and iso-butyl acetates are indistinguishable from the Arrhenius E values for the corresponding gas-phase decompositions if the confidence limits of $\hat{E}$ are considered. For both classes of reaction the activation energies change in the order n>sec>tert; however, the differences in E are larger for the catalyzed reactions. From Table (8-1) it appears that the quantitative differences between the reaction kinetics for the homogeneous and heterogeneous reactions are perhaps more striking than are the similarities. For the homogeneous reaction, E changes by a maximum of about 6 kcal/mole from the normal to the tertiary-ester, and for the heterogeneous reactions, the activation energy changes by a minimum of about 20 kcal/mole between the n- and the tert-isomers. The reaction of the tert-ester on the surface is energetically much more favorable than by the gas-phase reaction. The values of the pre-exponential factors for the surface reactions change in the direction n>sec>tert, which is opposite to the observed direction of change for the thermal reactions. Also, $\widehat{k_o L}$ changes by a factor of about $10^{-7.3}$ between normal and tertiary-butyl acetates, but k_o changes by only about 10^{+1}. Apparently, comparatively more n-butyl acetate molecules than tert-ester molecules are adsorbed by the catalyst in some conformation which is favorable for reaction.

In the heterogeneous decomposition, the presence of the charcoal surface might afford different and more rapid reaction paths than the homogeneous decomposition of the ester; or, the reaction mechanism might remain essentially the same on the surface as it is in the gas phase, but the heterogeneous reaction might be modified by the adsorption of reactants, activated complex, and products. The present discussion considers the second possibility: all of the esters may react according to the same type of mechanism but the energy changes occuring during the reactions may be different for the different molecules. A possible reaction scheme and its potential energy diagram are depicted in Figure (8-1). The dotted curve in the potential energy diagram represents the variation of potential energy in the decomposition coordinate for the homogeneous reaction, and the full line represents the energy changes during the course of the heterogeneous reaction. E_g and E_s are the activation energies of the gas-phase and surface reactions, respectively, and H and H* are the heats of adsorption of the ester and of the activated complex. The reaction scheme shown in Figure (8-1) can result in a rate equation of the form $r = kL\theta$, which agrees with the experimental data. The value of E_s for any ester decomposition depends on both H and H*. Since the heats of vaporization-condensation of the different butyl acetates are nearly the same(42,47), and Table (8-1) does not show large differences in the values of $\hat{H}$, it can be assumed that the heats of adsorption of the different

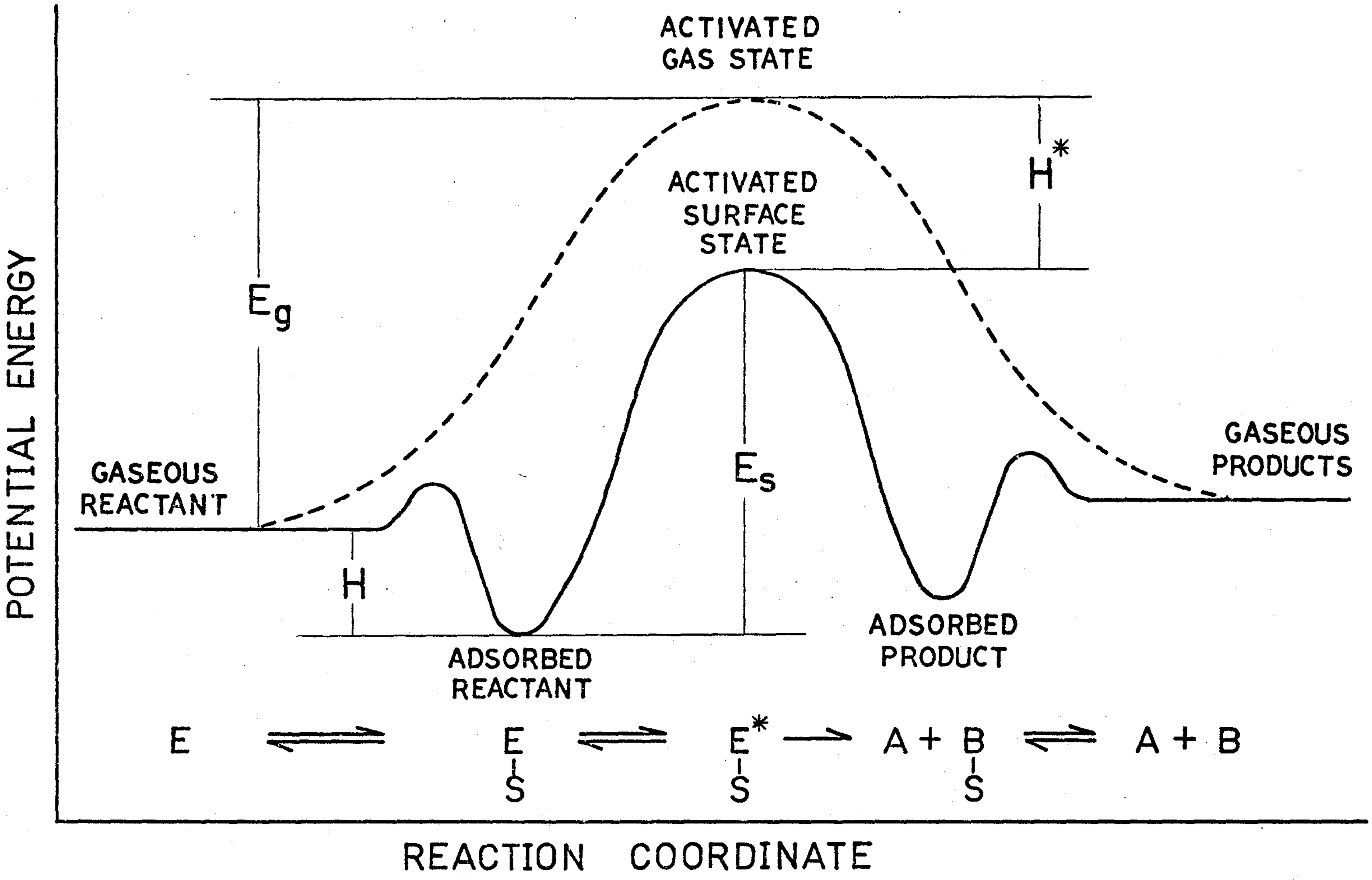

Figure (8-1) Heterogeneous reaction scheme and potential energy curves for the same reaction as a homogeneous and heterogeneous process.

ester isomers on charcoal are about equal, with, say, an average of about -10 kcal/mole. Thus, E_s depends primarily on the value of H*. For the decomposition of n-butyl acetate with $\hat{E}_s = 51.3$ and $E_g = 46.0$ kcal/mole, the value of H* would be -4.7 kcal/mole. This value is calculated from Equation (8-2), a simple energy balance on Figure (8-1), where H and H* are the heats taken up by the adsorbing species.

$$E_g - H = E_s - H^* \tag{8-2}$$

From the value of the pre-exponential factor, log $\hat{k}_o L$ = 13.60 grams of n-butyl acetate per gram of catalyst per sec, it appears that the catalyst has little effect on the transition state of n-butyl acetate. The entropy of activation calculated from $\hat{k}_o$ by using equation (8-1) is $\Delta S^{\ddagger}_{(300°C)} \approx 0$ cal/°K·mole, which means that there is little change in the degree of restriction of the n-butyl acetate molecule as it moves from the adsorbed state to the activated state along the reaction coordinate. Apparently, the heterogeneous and homogeneous n-butyl acetate reactions have many similarities.

At the other extreme, the kinetic coefficients for the catalyzed decomposition of tert-butyl acetate differ markedly from E and k_o for the thermal reaction. The differences may be due to a more pronounced effect of the charcoal on the tert-butyl acetate activated complex. For example, the value of 28.3 kcal/mole was found for the heat of adsorption of the tert-ester activated complex on charcoal by using data from Table (8-1) in Equation (8-2). This value is (statistically) significantly greater than the heat of adsorption of the n-butyl acetate complex and probably accounts for the difference in activation energies between n- and tert-ester reactions. In comparison to the n-complex, the tert-complex is much more highly restricted, as suggested by the value of $\Delta S^{\ddagger}_{(300°C)}$ = -31.5 cal/°K· mole for tert-butyl acetate. The difference in $\Delta S^{\ddagger}$ between the n- and tert-butyl acetate complexes is close to the value of $\Delta S^{\ddagger}_{(300°K)}$ = 37.6 cal/mole·°K calculated by Eyring et.al.(46) for the adsorption of gaseous molecules to form a mobile layer. This closeness of calculated and experimental $\Delta S^{\ddagger}$ values suggests that the difference between the n- and tert-activated complexes resembles the difference between gaseous and adsorbed molecules.

Differences in kinetic and adsorption coefficients result ultimately in differences in reaction rates. In the following discussion the heterogeneous rates of reaction of the different esters are compared to each other and to their gas-phase decomposition rates. Various criteria have been used for comparing kinetics(32,48); for example, it can be stated that at 385°C n-butyl acetate reacts 47 times faster in a charcoal filled reactor than it would in the same empty reactor. Such comparisons have some use, but can be misleading if variables such as catalyst and gas-phase concentration differences are not considered in their proper perspective. There is probably no single satisfactory method of comparing the rates in question here, particularly over a range of temperature , since the temperature dependence of the kinetic coefficients and surface coverages complicate the problem. Perhaps the most informative approach would be to compare rates of decomposition under approximately equal reaction conditions; for example, to compare the (measured) heterogeneous reaction rates on a catalyst, $\hat{r}_o$, with the rates that would be expected if the charcoal merely concentrated the ester by adsorption, and the ester decomposed according to gas-phase kinetics. The latter rate, the "pseudo-gas-phase" rate, r_{pg}, can be calculated if the amount of ester adsorbed on the charcoal is known. Appendix C gives details of the calculations of r_o and r_{pg}. The amount of an ester adsorbed on the catalyst at given conditions was found by using the method of Grant and Manes$^{(50)}$ to determine the isotherm for physical adsorption of the ester on charcoal. Then, r_{pg} was found by multiplying the concentration of ester by the value of the gas-phase rate constant at the appropriate conditions.

For a given temperature the simplest measure of the rate of the heterogeneous reaction is the initial rate, the rate at x = 0, expressed by

$$\hat{r}_o = \rho_c \cdot \hat{k}_o \cdot L \cdot \hat{K}_e / (M_e \cdot (1 + \hat{K}_e)) \qquad (8\text{-}3)$$

Equation (8-3) is essentially the same as Equation (D-1), except that ρ_c, the bulk density of the charcoal catalyst, and M_e, the molecular weight of the ester, have been included in Equation (8-3) for adjustment of the units. Figure (8-2) shows plots of $\hat{r}_o$, the "best" heterogeneous rate, and of r_{pg}, the "pseudo-gas-phase" rate, for each of the four butyl acetates. For convenience, temperatures of 300 and 400°C were arbitrarily chosen for references. By using Figure (8-2), a direct comparison can be made of the initial heterogeneous reaction rate and the pseudo-homogeneous rate. However, it must be emphasized that in Figure (8-2) r_{pg} does not represent the actual rate of the homogeneous reaction; the rates at which the butyl acetates would decompose in an empty reactor at 1 atmosphere pressure and 300° to 400°C are about 50 times lower than the values of r_{pg} shown in Figure (8-2).

At any given temperature shown in Figure (8-2) the initial heterogeneous rates for the different esters can be compared since the surface coverages by the different esters are all approximately equal, as shown by the adsorption isotherms in Figure (C-1).

From Figure (8-2) it appears that the charcoal does something other than merely concentrate the esters. Charcoal lowers the activation energy for the reactions of sec- and

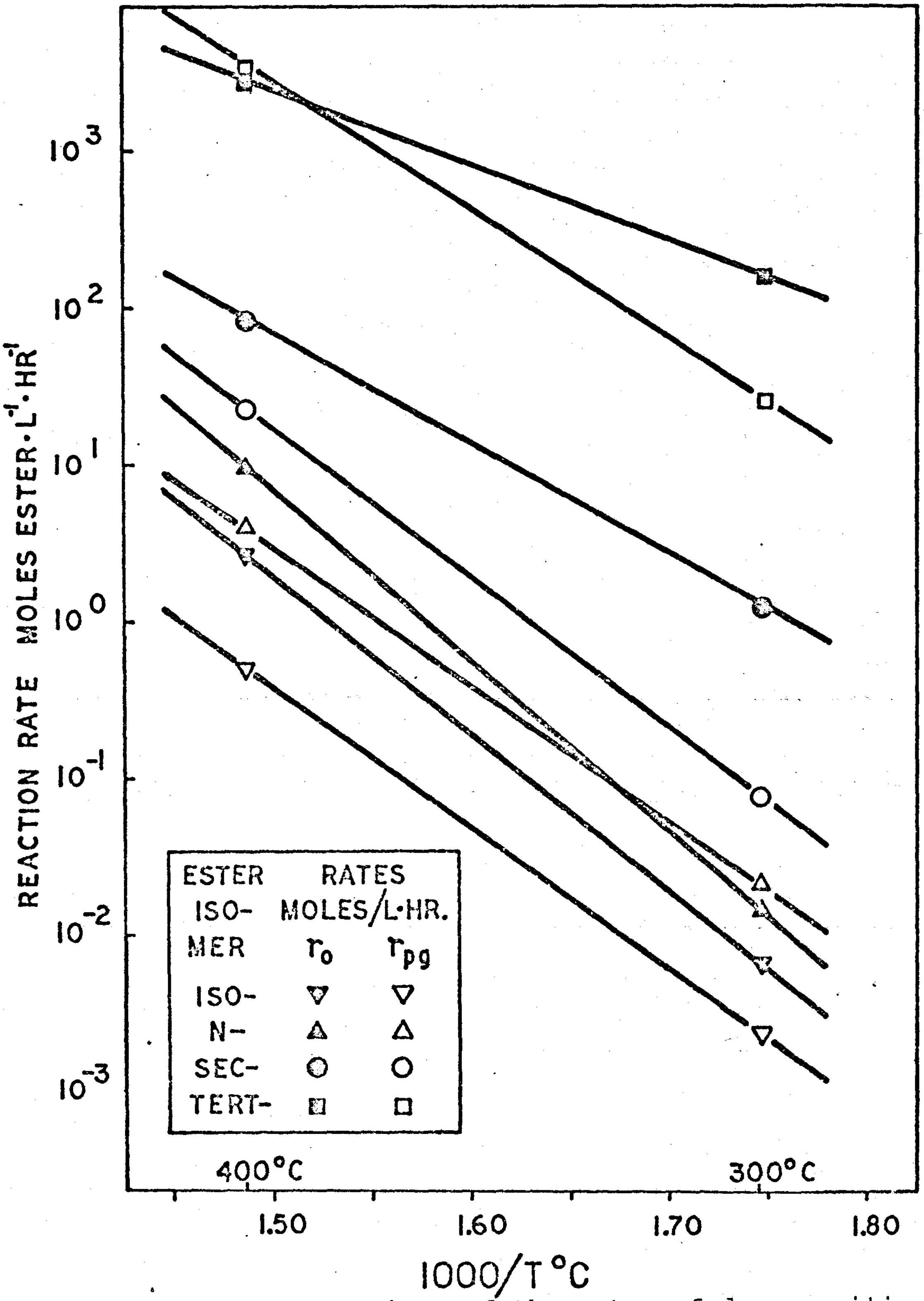

Figure (8-2) A comparison of the rates of decomposition of butyl acetates over charcoal at P_e = 1 atm., r_o, with the 'pseudo gas-phase" reaction rates, r_{pg}.

tert-butyl acetates, and the rates at which these two esters decompose on charcoal at 300°C are faster than their pseudo-gas-phase reaction rates at that temperature. The different activation energies for the catalyzed reactions of the different esters may provide clues about the mechanisms of the reactions or about the activation steps; however, the reason for the differences in the activation energies is not clear. It is possible that, contrary to what was assumed at the beginning of this chapter, the charcoal provides entirely different reaction paths for the different esters.

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APPENDIX A

CALIBRATION OF THE GAS CHROMATOGRAPH DETECTOR

The detector of the gas chromatograph (GC) used for the chemical analysis of the reaction products was a thermal conductivity cell. The cell comprises a resistance bridge through which the current can be balanced when carrier gas alone passes through the cell. When some chemical species having a thermal conductivity different from that of the carrier gas passes through the detector, an imbalance of voltage across the bridge results. This voltage imbalance, known as the response of the detector, is usually directly proportional(1) to the quantity of the species causing the imbalance. Calibration of the response of the detector to different chemical species was made by one of two methods: (a) injecting known quantities of the species into the GC and measuring the responses directly, or (b) mixing the species with a standard and measuring the relative response of the species to that of the standard. In general, the responses of gases were measured by method (a), and the responses of liquids were measured by method (b).

Samples of gases were taken with a constant volume gas sampling valve, and the quantities of gas in the samples could be changed by varying the pressure of the gas in the valve. For each gas the responses observed were plotted as a function of the amounts injected, and the data were fitted with the least squares straight line.

When the response to a liquid species was to be calibrated, the liquid was mixed in known proportions with benzene. Samples of such mixtures produced two peaks when injected into the GC. The relative response for a liquid was calculated by using the equation

$$R_1 = \frac{A_1}{A_2} \cdot \frac{W_2}{W_1} \cdot \frac{M_1}{M_2} \cdot R_2 \qquad \text{(A-1)}$$

where R is the response of one mole of species divided by the response of one mole of the standard (benzene), A is the area of a peak measured on the recorder, W is the weight in grams of a species in the mixture with the standard, M is the molecular weight of a species in grams, subscript 1 refers to the species being calibrated, and subscript 2 refers to the standard species.

It can be seen that the quantity of any species measured by the GC is inversely proportional to its relative response defined by Equation (A-1). The relative response of benzene was arbitrarily chosen to be 100 area units per mole, the same standard used by Messner et. al.(1). When calibrating any given liquid, two or more mixtures of the species with benzene were made at widely separated molar ratios to insure that the response was not concentration dependent.

Consistency between the calibrations made by methods (a) and (b) is demonstrated by the agreement between columns 3 and 4 in Table (A-1). The responses of some of the products of reaction which occurred in small quantities were not calibrated, and published calibrations were used(1).

TABLE (A-1)

G C DETECTOR CALIBRATIONS

Species	Calibration Results		Published[(1)] Relative Response
	Slope*	Relative Response**	
Cis-2-butene	0.307	87.	87
Trans-2-butene	0.311	86.	85
1-Butene	0.344	78.	81
Nitrogen	0.617	43.	42
Methane	0.776	34.5	36
Carbon Dioxide	0.552	48.5	48
n-Butane	0.318	85.	85
n-Butyl acetate	-	-	135
Sec-butyl acetate	-	132.	-
Tert-butyl acetate	-	130.	-
Iso-butyl acetate	-	65.5	-
Acetic Acid	-	65.5	-

[*] From plot of MV response vs approx. no. moles calculated from pressure of sample in torr.

[**] Response relative to the same base used in reference (1), and calculated here by letting the measured slope of 0.307 for cis-2-butene be proportional to 1/87, the reference (1) value.

(1) Messner, A.E., Rosie, D.M., and Argabright, P.A., Annal. Chem., 31(2), 230 (1959).

APPENDIX B

A MATERIAL BALANCE CALCULATION

B.1 INTRODUCTION

A material balance shows only that there is consistency within the calculations, and cannot distinguish between fortuitous cancelling of errors and accurate quantitative determination of products. Only the material balance for n-butyl acetate is presented here; balances for the other esters were obtained. The maximum imbalance was found for sec-butyl acetate where the calculated weight of products was 4% less than the measured input of ester.

B.2 PROCEDURE

The material balance experiment for n-butyl acetate was made for a duration of 135 minutes at a temperature of 347.5°C and a conversion of approximately 0.7. Ester was fed to the reactor at the rate of 0.0217 grams/min., and after the reaction had reached quasi-steady conditions the rates of gaseous and liquid products were measured. The liquid products were caught in a trap at room temperature and weighed at the end of the experiment, and the rate of the gaseous products escaping the trap was measured with a soap film flowmeter. When the 135 minute period was approximately half over, the reaction products were sampled and analyzed with the gas chromatograph.

B.3 RESULTS OF THE MATERIAL BALANCE EXPERIMENT

For six measurements of the gaseous product rate at 25°C the results were: 4.00, 3.80, 3.92, 3.78, 3.66 and 3.24 cc/min.

The average gaseous product rate = 3.82 cc/min.

The weight of liquid collected in 135 min., = 1.923 grams.

Table (B-1) shows the results of the GC analysis of the products.

B.4 CALCULATIONS

The average molar rate of the gaseous products according to the Ideal Gas Law was

$$\frac{3.82}{22{,}400\ \frac{273.2 + 25.0}{273.2}} = 1.56 \times 10^{-4} \text{ moles/min.}$$

The weight rates of gaseous products based on the average molar rate are:

Butenes:	$1.56\times10^{-4}\cdot56.1\cdot0.5402$	=	0.004730 g/min.
Butanes:	$1.56\times10^{-4}\cdot0.0955\cdot58.12$	=	0.000866
CO_2+Propane:	$1.56\times10^{-4}\cdot0.045\cdot44.$	=	0.000309
Methane:	$1.56\times10^{-4}\cdot16.04\cdot0.3303$	=	0.000826
Total:			0.006731 g/min.

In 135 minutes the weight of gaseous products was

$$\text{Weight} = (0.006731)\cdot(135.) = 0.910 \text{ grams.}$$

TABLE (B-1)

Product Analysis

Species	Mole Number*	Gas Product Mole Fraction
cis-2-butene	0.1204	0.0810
trans-butene	0.1788	0.1200
1-butene	0.5050	0.3392
n-butane	0.1330	0.0894
isobutane	0.0090	0.0061
propane+CO_2	0.0669	0.0450
ethane	negligible	
CO + CH_4	0.4750	0.3303
n-butyl acetate	0.5480	
butanol	0.0366	
acetic acid	1.1000	
water	0.452	

---

[*] The number of moles of each species relative to an arbitrary base (see Program 1, Appendix E, relative no. moles = (peak area)·(attenuation)/relative response of detector to species).

The rate of liquid products can be calculated in the same manner to compare with the measured rate. The calculated rate for butenes is used as a reference here. The weight rates of liquids are:

Ester: $0.5402\,\frac{0.5480}{0.8042}\cdot 116.16\cdot 1.56\times10^{-4} = 0.00668$ g/min

Butanol: $0.5402\,\frac{0.0366}{0.8042}\cdot 74.12\cdot 1.56\times10^{-4} = 0.00028$

Acetic Acid : $0.5402\,\frac{1.100}{0.8042}\cdot 60.05\cdot 1.56\times10^{-4} = 0.00693$

Water: $0.5402\,\frac{0.452}{0.8042}\cdot 18.0\cdot 1.56\times10^{-4} = 0.00085$.

The calculated total weight rate of liquid = 0.01474 g/min. In 135 minutes the weight of liquid products was

Weight = 135•0.01474 = 1.990 grams liquid.

The material balance is as follows:

The measured liquid rate = 1.923 grams in 135 min.
The calculated gas rate = $\underline{0.910}$
The total material out = 2.833 grams in 135 min. ;

or,

The calculated liquid rate = 1.990 g
The calculated gas rate = $\underline{0.910}$
The total material out = 2.900 grams in 135 min.

The weight of material entering the reactor in 135 minutes was

Weight input = 135•0.0217 = 2.930 grams

The material imbalance is

$$\frac{2.93 - 2.90}{2.93} \cdot 100 = -1\% \;;$$

or

$$\frac{2.93 - 2.833}{2.93} \cdot 100 = -3\%.$$

The variation in the ester feed rate found from the calibration of the syringe pump was

$$\frac{0.02182 - 0.02171}{0.0217} \approx 0.5\%.$$

The rate of ester disappearance was

$$(0.0217-0.00668)/116.16 = 1.29\times10^{-4} \text{ moles/min.}$$

The rate of acetic acid production was

$$0.00693/60.05 = 1.154 \text{ moles/min.}$$

The difference may be due to acetic acid decomposing to minor products.

The percentage of butanol in the product was

$$0.00028\cdot100/(0.0217-0.006680) \approx 2\%.$$

This amount is negligible when the conversion is calculated from the weight percent of ester in the product.

B.5 THE EQUATION FOR ESTER CONVERSION

The conversion of n-butyl acetate based on the measured ester input and on the calculated ester output is

$$x = \frac{\text{change in weight}}{\text{weight input}} = \frac{0.0217-0.00668}{0.0217} = 0.692.$$

If the conversion is calculated on the basis of the amount of four-carbon species produced, the result is

$$x = \frac{\text{moles of butenes, butanes and butanol}}{\text{moles of butenes, butanes, butanol and ester}}$$

$$= \frac{.1204+.1788+.5050+.1330+.0090+.0366}{.1204+.1788+.5050+.1330+.0090+.0366+.05480}$$

$$= 0.642.$$

The conversion based on the calculated weight fraction of ester in the product is

$$x = 1.0 - \text{wt. fraction of ester in product}$$

$$= 1.0 - \frac{(0.00668)\cdot 135}{2.900} = 0.690.$$

The last method of calculating the conversion appears to give the best approximation for x.

APPENDIX C

CALCULATION OF COMPARATIVE RATES OF REACTION

The purpose of this appendix is to present the methods and assumptions used in calculating the rates of the butyl acetate reactions. The gas-phase and the catalyzed rates of reaction of the different esters are compared with each other. The rates of butyl acetate reactions will be calculated in units of moles per liter per hour for convenience of comparison.

C.1 THE HETEROGENEOUS RATE

For a catalyzed reaction the initial reaction rate (x = 0) at a given temperature can be expressed in convenient units by using the equation

$$\hat{r}_o = \rho_c \, \hat{k}_o \cdot L \cdot \hat{K}_e / (M_e \, (1 + \hat{K}_e)) \qquad \text{(C-1)}$$

where $\hat{k}_o L$ and $\hat{K}_e$ are the best kinetic and adsorption coefficients at the temperature; M_e is 116.16 grams/mole, the molecular weight of butyl acetate; and ρ_c is the bulk density of the charcoal catalyst. The values of ρ_c were not very different for the different catalyst particle sizes used in the experiments; thus, for all of the calculations of the initial heterogeneous rate, the value of the catalyst density which was used was $\rho_c = 0.53$ grams of charcoal per cc, the value measured for 48-65 mesh charcoal particles.

C.2 "PSEUDO GAS-PHASE" RATES

The "pseudo gas-phase" rate, r_{pg}, is defined as the rate at which butyl acetate adsorbed on the surface of charcoal would react if it obeyed the equations for gas-phase kinetics, namely the rate $r = kC^1$, where k is the gas-phase kinetic coefficient at the temperature of interest, and C is the concentration of the reactant in moles per liter. It is assumed for these calculations that the function of the charcoal is only to concentrate the reactant. The "pseudo gas-phase" rate can be calculated if the concentration of the ester in the catalyst bed is known. Determining the concentration of the reactant per unit volume of catalyst requires finding the saturation amount on the catalyst and also the fractional saturation. The saturation of the catalyst by the reactant can be assumed to occur at either complete surface coverage or at complete pore filling. For the calculations which follow, it is assumed that saturation occurs at complete surface coverage and that the concentration of the reactant on the charcoal can be expressed as the product of the fractional surface coverage, θ, and the saturation concentration. By using the data of Grant and Manes (2), the fractional surface coverage can be estimated. Figure (C-1) shows calculated adsorption isotherms for butyl acetate on charcoal catalyst. The saturation value of adsorbed liquid, 56 cc/100 grams of charcoal, was calculated

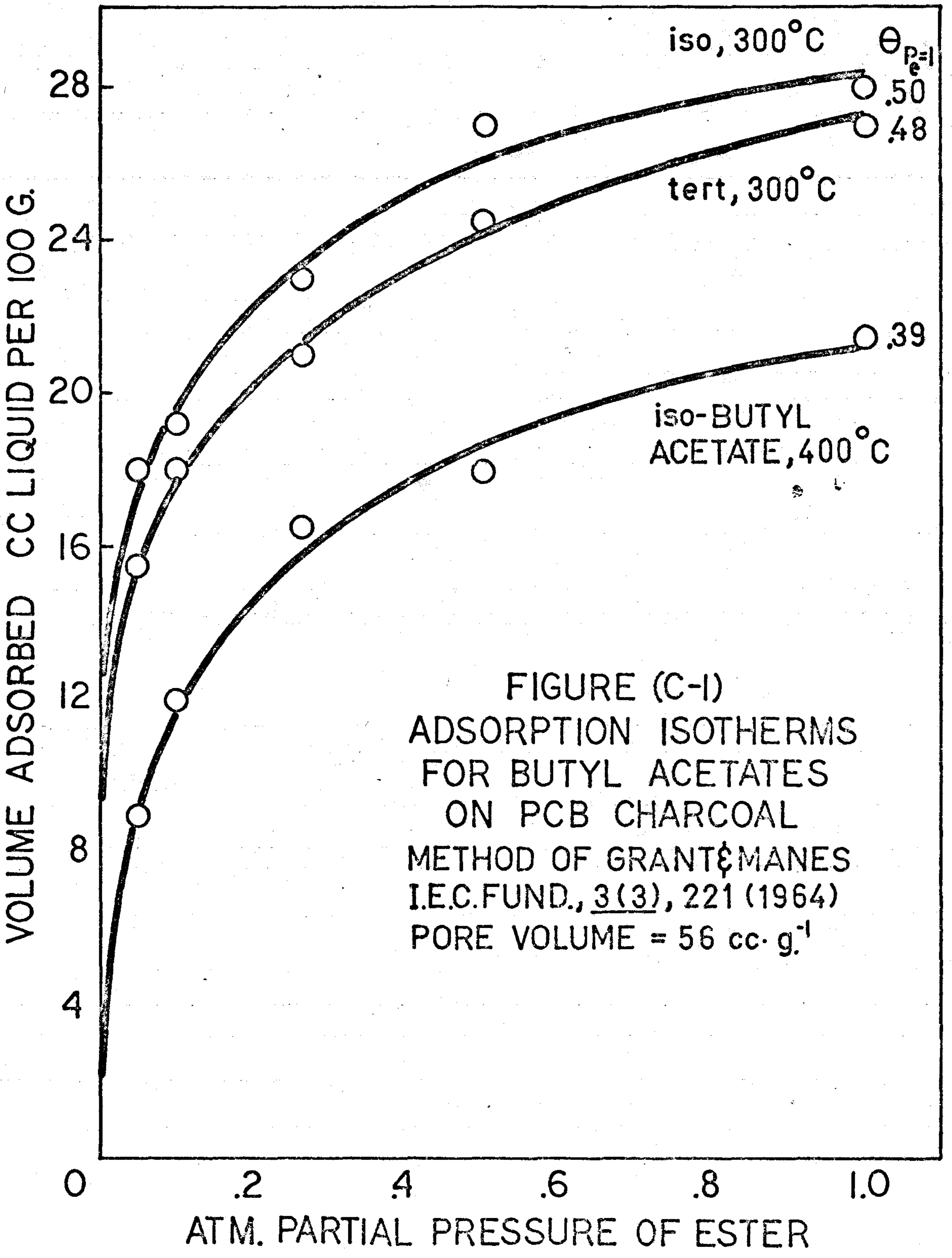


FIGURE (C-1)
ADSORPTION ISOTHERMS
FOR BUTYL ACETATES
ON PCB CHARCOAL
METHOD OF GRANT & MANES
I.E.C. FUND., <u>3(3)</u>, 221 (1964)
PORE VOLUME = 56 cc·g.$^{-1}$

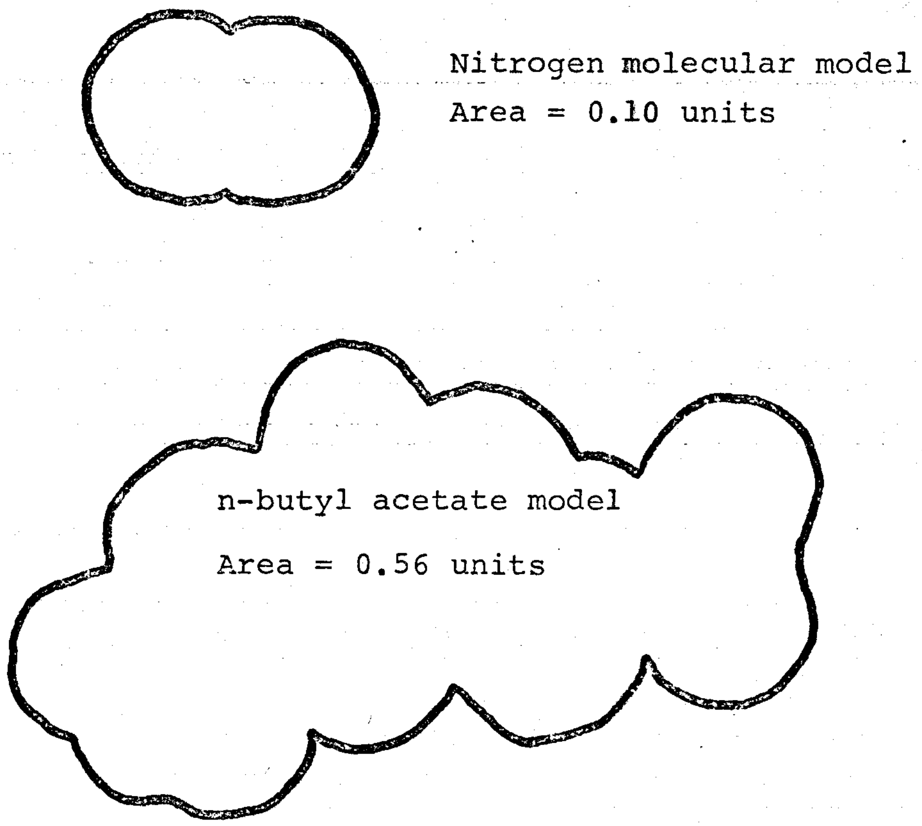
from the nitrogen adsorption isotherms shown in Figure (3-1). The fraction of the available charcoal surface which is covered with ester, θ, can be found at any condition by dividing the volume of ester adsorbed by 56 cc/100 g. For example, at 400°C and 1 atm. of iso-butyl acetate over charcoal,we find that $\theta = 21.2/56 = 0.39$. The surface area available for the adsorption of butyl acetate on charcoal is assumed to be 1490 m^2/gram, the surface area of virgin charcoal determined from nitrogen adsorption isotherms.

The saturation concentration of ester on the catalyst can be found if the surface area occupied by an adsorbed reactant molecule is known. The surface area occupied by an adsorbed butyl acetate molecule was estimated by comparing the projected areas of nitrogen and butyl acetate molecular models. For example, Figure (C-2) shows the calculation of the area covered by one n-butyl acetate molecule. The molecular models were of the Fisher-Hirschfelder-Taylor type* and their projected areas were measured with a planimeter. The surface area occuped by n-, sec-, and iso-butyl acetate molecules are about 91 $\mathring{A}^2$, and the projected area of a tert-butyl ester molecule is approximately 70 $\mathring{A}^2$. The

---

*Fisher Scientific Company Catalog No. 12-821, references and details are given in the Catalog.

Figure (C-2) Projected areas of molecular models on a plane surface



Adsorbed N_2 molecule occupies 16.2 $\mathring{A}^2$ of surface area(3); therefore, area occupied by adsorbed n-butyl acetate is

$$16.2 \times \frac{0.56}{0.10} = 90.8\ \mathring{A}^2$$

saturation concentration of n-butyl acetate per unit volume of catalyst, a "pseudo-concentration", is then

$$C_p' = \frac{1490\ \text{m}^2/\text{g.} \times 0.53\ \text{g.cat./cc} \times 10^3\ \text{cc/l}}{91 \times 10^{-20}\ \text{m}^2/\text{molecule} \times 6.023 \times 10^{23}\ \text{molecules/mole}}$$

$$= 1.44\ \text{moles n-butyl acetate/liter.}$$

For any fractional surface coverage, the "pseudo-concentration" is

$$C_p = \theta \cdot C_p'.$$

A sample calculation of the pseudo gas-phase rate of reaction is shown below for sec-butyl acetate at 300°C and 1 atmosphere of reactant pressure.

The gas-phase rate coefficient is$^{(4)}$

$$k = 10^{12.4} \cdot \exp(-45.2/R \cdot T) \cdot 1/\text{sec.} \cdot 3600\ \text{sec./hr.}$$

$$= 5.57 \times 10^{-2}\ \text{hr.}^{-1}.$$

From Figure (E-1) the fractional surface coverage by the reactant at 300°C is approximately

$$\theta = 27.5/56 = 0.491.$$

The pseudo-concentration of reactant is

$$C_p = C_p' \cdot \theta = 1.44 \times 0.491 = 0.706\ \text{moles/liter.}$$

The pseudo gas-phase reaction rate is then,

$$r_{pg} = k \cdot C_p = 4.47 \times 10^{-2} \times 0.706$$

$$= 3.94 \times 10^{-2}\ \text{moles sec-butyl acetate/l} \cdot \text{hr.}$$

APPENDIX D

DERIVATION OF EQUATIONS

D.1 THE EQUATION FOR RATE CONTROL BY A SURFACE REACTION ON A SINGLE SITE

The Langmuir-Hinshelwood$^{(5)}$ rate equation for the mechanism is

$$\text{rate} = r = \frac{k_s L K_e (P_e - P_a P_b/K)}{1+K_e P_e + K_b P_b + K_i P_i} \quad . \qquad \text{(D-1)}$$

The symbols in this equation are defined in Table (4-3).

The partial pressures of species e, a, and b can be related to the ester conversion through

$$P_e = \frac{(1-x)P_T}{(G+x)} \text{ and } P_a = P_b = \frac{x}{(G+x)} P_T,$$

where P_T = the total pressure of the reaction in atmospheres, and G = (1 + moles of inert diluent I/mole ester fed to reactor). Substituting for the pressures in Equation (D-1), and assuming that K is very large$^{(7)}$, K_i is negligible, and P_T = 1 atmosphere results in the following equation:

$$r = \frac{k_s L K_e \frac{1-x}{G+x}}{1 + K_e \frac{1-x}{G+x} + K_b \frac{x}{G+x}}$$

By definition, the differential rate of reaction is dx/dτ; when dx/dτ is substituted into Equation (d-2) and the equation is rearranged, we have

$$d\tau = \frac{G+x+K_e-K_e x+K_b}{k_s L K_e (1-x)}\, dx,$$

and

$$\tau = \frac{(K_e-1-K_b)}{k_sLK_e}\int\frac{xdx}{(x-1)} - \frac{(G+K_e)}{k_sLK_e}\int\frac{dx}{(x-1)} \, .$$

Integrating this equation and simplifying the results gives

$$\tau = \frac{(K_e-1-K_b)}{k_sLK_e}\,x - \frac{(G+1-K_b)}{k_sLK_e}\ln(1-x) \, . \qquad \text{(D-3)}$$

An "objective function" to relate assumed values of coefficients K_e, kL, etc. to the residual sums of squares is derived from equation (D-3) as follows:

$$Z = \tau \; \frac{(K_e-1-K_b)}{k_sLK_e}\,x + \frac{(G+1-K_b)}{k_sLK_e}\ln(1-x) \qquad \text{(D-4)}$$

The rate of change of the objective function with respect to a change in x is

$$\text{Slope} = -\frac{(K_e-1-K_b)}{k_sLK_e} - \frac{(G+1-K_b)}{k_sLK_e}\,\frac{1}{(1-x)} \, . \qquad \text{(D-5)}$$

An example of the use of Equations (D-4) and (D-5) is shown in Program 3.

D.2 THE EQUATION FOR RATE CONTROL BY DESORPTION OF PRODUCT B FROM INDIVIDUAL SITES

The Langmuir-Hinshelwood$^{(5)}$ rate equation for the mechanism is

$$\text{rate} = r = \frac{k_bLK(P_e/P_a-P_o/K)}{1+K_eP_e+KK_bP_e/P_a+K_aP_a+K_iP_i} \qquad \text{(D-6)}$$

The symbols in (D-6) are defined in Table (4-3).

To derive an "objective function" from Equation (D-6) the following assumptions were made: total pressure, P_T, is 1 atmosphere, G = (1+moles of inert I/mole ester fed to the reactor), $K >> 1$, $K_I << 1$, $P_e = P_T(1-x)/(G+x)$, $P_a = P_b = P_T x/(G+x)$, and $r = dx/d\tau$. Using these assumptions, Equation (D-6) can be written

$$\frac{dx}{d\tau} = \frac{k_b LK \frac{1-x}{x}}{1+K_e \frac{1-x}{G+x} - KK_b \frac{1-x}{x} + K_a \frac{x}{G+x}} \tag{D-7}$$

Rearranging equation (D-7) gives

$$d\tau = [\frac{x}{(1-x)} + \frac{K_e x}{(G+x)} + K_b K + \frac{K_a x^2}{(G+x)}] \frac{dx}{k_b LK} .$$

When this equation is integrated and rearranged the result is

$$\tau = (\frac{K_e+KK_b-K_a-1}{k_b LK})x + (\frac{K_a-1}{k_b LK})\ln(1-x) +$$

$$+ (K_a-K_e) \frac{G}{k_b LK} \ln(G+x) + \frac{GK_a}{k_b LK(1-G)} \ln(\frac{1-x}{G+x}) \tag{D-8}$$

If K_a is negligibly small Equation (D-8) reduces to

$$\tau = (\frac{K_e+K_b K-1}{k_b LK})x - \frac{\ln(1-x)}{k_b LK} - \frac{K_e G}{k_b LK} \ln(G+x) \tag{D-9}$$

The "objective function" for the desorption control mechanism is

$$Z = \tau_{observed} - [\text{RHS of (D-8) or (D-9)}]. \tag{D-10}$$

For calculating x by the Newton-Raphson method$^{(6)}$ the rate of change of Z with respect to the calculated x must be used.

APPENDIX E

COMPUTER PROGRAMS

PROGRAM 1 A PROGRAM TO CALCULATE CONVERSION,X, AND SELECTIVITY ,S, FOR THE N-BUTYL ACETATE REACTION

```
C
C
      DIMENSION WP(20), WT(20), SF(20)
      N = 200.
      NN = 0
      PJ = 0.0
   10 READ (5,6) TRIAL,CATCHG,W,TEMP,FEED,TIME
    6 FORMAT (4F12.4,F14.5,F10.5)
      READ (5,5) H1,H2,H3,H4,H5,H7,H9,H12,H13,H14,H15,H16,H18
C     H = PEAK AREA, A = ATTENUATION
      READ (5,5) A1,A2,A3,A4,A5,A7,A9,A12,A13,A14,A15,A16,A18
    5 FORMAT (13F6.2)
      NN = NN+1
      DO 15 I=1,20
      WT(I) = 0.0
      WP(I) = 0.0
      SF(I) = 0.0
   15 CONTINUE
      WT(1)= H1*A1*526.638/(86.0*64.0)*5.808      (acetone)
      WT(2)= H2*A2*8.229/72.*4.607                (ethanol)
      WT(3)= H3*A3*526.632/(21.0*64.0)*1.8        (water)
      WT(4)= H4*A4*8.229/135.0*11.616             (n-butyl acetate)
      WT(5)= H5*A5*526.638/(65.5*64.0)*6.005      (acetic acid,HOAc)
      WT(7)= H7*A7*8.229/40.0*2.801
      WT(9)= H9*A9*8.229/65.0*4.409               (propane)
      WT(12)= H12*A12*8.229/48.0*4.401            (CO2)
      WT(13)= H13*A13*8.229/82.0*5.812            (isobutane)
      WT(14)=H14*A14*8.229/85.0*5.812             (n-butane)
      WT(15)= H15*A15*8.229/81.0*5.610            (l-butene)
      WT(16)= H16*A16*8.229/85.0*5.610            (trans-2-butene)
      WT(18)= H18*A18*8.229/87.0*5.610            (cis-2-butene)
      TOTLWT = 0.0
      DO 17 I = 1,18
      TOTLWT = TOTLWT + WT(I)
   17 CONTINUE
      C = 0.002927
      WTH2O = C*TOTLWT
      WT(3) = WT(3) - WTH2O
      IF (WT(3)) 18,19,19
   18 WTH2O = WT(3)
      WT(3) = 0.0
   19 TOTLWT = TOTLWT - WTH2O
      DO 20 I = 1,18
      WP(I) = WT(I)/TOTLWT
```

```
      PROGRAM 1 (CONTINUED)

   20 CONTINUE
C
C     SF MEANS SELECTIVITY FACTOR
C
      SF(1) = WP(1)*11.616/5.808
      SF(2) = WP(2)*11.616/4.607
      SF(3) = WP(3)*11.616/1.8
      SF(5) = WP(5)*11.616/6.005
      SF(7) = WP(7)*11.616/1.604
      SF(9) = WP(9)*11.616/4.409
      SF(12) = WP(12)*11.616/4.401
      SF(13) = WP(13)*11.616/5.812
      SF(14) = 11.616*WP(14)/5.812
      SF(15) = WP(15)*11.616/5.61
      SF(16) = WP(16)*11.616/5.61
      SF(18) = WP(18)*11.616/5.61
      SF(20) = (WP(15)+WP(16)+WP(18))*11.616/5.61
      CONVER = 1.0-WP(4)
      F = FEED*60.0
      T = W/F
C
C     TO CONVERT SF TO  MOLES PROD/MOLE ESTER DECOMPOSED
C
      DO 21 J=1,20
      SF(J) = SF(J)/CONVER
   21 CONTINUE
      IF (T.EQ. PJ) GO TO 23
      WRITE (6,22) TEMP, T
   22 FORMAT (1H0,12X,13HTEMPERATURE =,F7.2,4H C ,2X,
     14HW/F=,F7.4,3H HR/)
      PJ = T
      WRITE (6,95)
   95 FORMAT (24X,7HPROCESS,1X,6HACETIC,3X,2H1-,
     13X,6HTRANS-,1X,6HCIS-2-,
     12X,5HTOTAL)
      WRITE (6,97)
   97 FORMAT (13X,3HRUN,4X,1HX,3X,7HTIME,HR,2X,4HACID,
     A2X,6HBUTENE,1X,6HBUTENE,1X,6HBUTENE,1X,7HBUTENES)
   23 WRITE (6,98) TRIAL, CONVER, TIME, SF(5),
      SF(15), SF(16), SF(18), SF(20)
   98 FORMAT (10X,F6.0,F7.4,F7.3,5F7.4)
      IF (NN .LT.N) GO TO 10
      STOP
      END
```

PROGRAM 2 A THREE DIMENSIONAL GRID SEARCH

```
      DIMENSION X(20),T(20),XX(20),B(20),XB(20)
      READ (5,1) NS
      DO 50 NI=1,NS
      READ (5,1) S,TEMP,ND
    1 FORMAT (I5,F10.4,I5)
      READ (5,3) (X(I),T(I), I=1,ND)
    3 FORMAT (2F10.4)
      WRITE (6,9) S, TEMP
    9 FORMAT (1H1,9X,8HSPECIES=,I3,13HBUTYL ACETATE/
     1 10X,16HTEMP OF REACTION,F8.2,11H  DEGREES C///
     2 10X,39HTHE DATA AND THE CORRESPONDING BEST FIT/
     3 10X,41HVALUES OF X FOR THE MODEL SHOWN BELOW ARE//
     4 17X,1HX,8X,3HW/F,5X,6HBEST X)
      TSS = 0.0
      DO 14 NT = 1,ND
   14 TSS = TSS + X(NT)*X(NT)
      READ (5,2) CL,CH,AL,AH,DL,DH
    2 FORMAT (6F10.4)
      C2= 100.
C     SET THE STEP SIZE BY THE RANGE DIVISOR SS
      SS = 10.
      DC = (CH-CL)/SS
      DA = (AH-AL)/SS
      DD = (DH-DL)/SS
C     SET VALUES OF PARAMETERS, FIND THE VALUES OF X THAT
C     SHOULD BE OBSERVED AT THE SPACE TIMES USED
      D = DL
   33 C = CL
    4 A = AL
    5 CONTINUE
      DO 10  II = 1,ND
      C1 = 100.
      W = 0.0
C     TO FIND X APPROXIMATELY
      DW = 0.01
      DO 6 J = 1,99
      Z = 0.0
      W = W + DW
C       C = KLK,    A = KE         D = KB
      Z = T(II) + ((1.-A-D)*W/C)-((((1.+A)/(2.*C))*
     1ALOG(1.-(W*W)))-(((1.-A)/(2.*C))*ALOG((1.-W)/(1.+W)))
      CRIT1 = ABS(Z)
      IF (CRIT1 .GT. C1) GO TO 6
      C1 = ABS (Z)
      WBEST = W
    6 CONTINUE
      Y = WBEST
    7 CONTINUE
```

PROGRAM 2 (CONTINUED)

```
C     TO FIND A MORE PRECISE VALUE OF X
C     USING THE NEWTON-RAPHSON METHOD
C     DESORPTION CONTROL MODEL
      IF (Y .GE. 1.00) GO TO 12
      IF (Y .LE. 0.0) GO TO 12
      Z = T(II) + ((1.-A-D)*W/C)-(((1.+A)/(2.*C))*
     1ALOG(1.-(W*W)))-(((1.-A)/(2.*C))*ALOG((1.-W)/(1.+W)))
      SLOPE = -(1.-A-D)/C-(Y*(1.+A))/(C*(1.-
     A  (Y*Y))) + (A-1.)/(C*(1.-(Y*Y)))
      YNEW = Y - Z/SLOPE
      CRIT = ABS(YNEW-Y)
      IF (CRIT .LT. 0 000001) GO TO 8
      Y = YNEW
      GO TO 7
    8 CONTINUE
      XX(II) = YNEW
   10 CONTINUE
      BS = 0.0
      DO 11 IJ = 1,ND
      B(IJ) = X(IJ) - XX(IJ)
   11 BS = BS + B(IJ)*B(IJ)
      IF (BS.LT.C2) GO TO 13
   12 A = A+DA
      IF (A .LT. AH) GO TO 5
      C = C+DC
      IF(C.LT.CH) GO TO 4
      D = D+DD
      IF(D.GT.DH) GO TO 40
      GO TO 33
C     SAVE THE BEST VALUES OF K, A AND X AS CALCULATED
C     FROM LOWEST RESIDUAL SUM OF SQUARES
   13 C2 = BS
      R = C2/TSS
      CBEST = C
      ABEST = A
      DBEST = D
      DO 15 K = 1,ND
   15 XB(K) = XX(K)
      GO TO 12
   40 WRITE (6,20) (X(I),T(I),XB(I),I = 1,ND)
   20 FORMAT (10X,3F10.4)
      WRITE (6,21) CL,CH,AL,AH,DL,DH,CBEST,ABEST,DBEST
   21 FORMAT (1H0,9X,32HFOR THE DESORPTION CONTROL MODEL/
     110X,26HSEARCHED IN THE RANGE KLK=,F6.3,3H TO,F8.3/
     232X,2HA=,F6.3,3H TO,F8.3/
     331X,3HKB=,F6.3,3H TO,F8.3//
     410X,4HKLK=,F12.6,5X,2HA=,F12.6,5X,3HKB=,F12.6)
      WRITE(6,22) TSS,C2,R
   22 FORMAT (10X,49HTHE TOTAL SUM OF SQUARES OF THE X OBSERVATIONS IS,F
     A12.8/
     1 10X,44HTHE RESIDUAL SUM OF SQUARES AFTER FITTING IS,F12.8/
     2 10X,46HRESIDUAL SUM OF SQUARES/TOTAL SUM OF SQUARES =,F12.8)
   50 CONTINUE
      STOP
      END
```

PROGRAM 3 A PROGRAM TO SEARCH FOR THE BEST VALUES OF COEFFICIENTS FOR THE RATE EQUATIONS

PROGRAM 3,A THE MAIN PROGRAM.

```
    COMMON AKE(10), D(20), V(10,10), BL(20,20)
    COMMON AJ(20), E(20), AL(20,20), AFK(20),ALPHA
    COMMON BLEN(20), EPS(10),BETA, NSTEP, SUMN
    COMMON NS,ND,X(80), S(80), T(80),KM,XX(80), B(80)
    COMMON MAXK, MKAT,MCYC
    READ (5,1) NS
    DO 50 NI = 1,NS
    READ(5,1) L,ND
  1 FORMAT (2I5)
    READ(5,3) (X(I),S(I),T(I),I = 1,ND)
  3 FORMAT (3F10.4)
    READ (5,500) KM,MCYC,NSTEP,MAXK, MKAT
    READ(5,501) (AKE(I),I = 1,KM)
501 FORMAT (10F10.4)
500 FORMAT (5I5)
    READ (5,501) (EPS(I),I=1,KM)
    READ (5,501) ALPHA,BETA
    DO 502 I = 1,KM
    DO 502 J = 1,KM
    V(I,J) = 0.0
502 CONTINUE
    DO 503 I = 1,KM
    V(I,I) = 1.0
503 CONTINUE
    WRITE(6,4) L
  4 FORMAT (1H1,9X,8HSPECIES=,I3,14H BUTYL ACETATE//
   110X,10HINPUT DATA/17X,1HX,8X,3HW/F,5X,4HTEMP)
    WRITE (6,5) (X(I),S(I),T(I),I = 1,ND)
  5 FORMAT (10X,2F10.4F13.4)
    CALL SEARCH
 50 CONTINUE
    STOP
    END
```

PROGRAM 3,B A PROGRAM WHICH USES THE OBJECTIVE
FUNCTION TO LINK THE OBSERVED AND CALCULATED
VALUES OF X

```
      SUBROUTINE OBJECT
      COMMON AKE(10), D(20), V(10,10), BL(20,20)
      COMMON AJ(20), E(20), AL(20,20), AFK(20),ALPHA
      COMMON BLEN(20), EPS(10),BETA, NSTEP, SUMN
      COMMON NS,ND,X(80), S(80), T(80),KM,XX(80), B(80)
      COMMON MAXK, MKAT,MCYC
      NT = 1
      NT = NT+1
C     NT IS THE NUMBER OF TIMES OBJECT HAS BEEN CALLED
      WBEST = 0.0
      DO 10 II = 1,ND
      WNEW = 0.0
      C1 = 100.
      W = 0.0
      DW = 0.1
C     TO FIND X APPROXIMATELY
      DO 6 J = 1,9
      Z = 0.0
      W = W + DW
C
C
C     AKE(1) = K0, AKE(2) = E, AKE(3)=KE0, AKE(4)=H
      RVALU = 0.001987
      Z = S(II) - ((((10.**AKE(3))*EXP(-AKE(4)/(RVALU*T(II)))-1.)*W)-
     1   (2.*ALOG(1.-W)))/
     2  (((10.**AKE(3))*EXP(-AKE(4)/(RVALU*T(II))))*((10.**AKE(1))*EXP(-
     3  AKE(2)/(RVALU*T(II)))))
      CRIT1 = ABS(Z)
      IF (CRIT1 .GT. C1) GO TO 6
      C1 = ABS (Z)
      WBEST = W
    6 CONTINUE
      W = WBEST
      IC = 1
    7 CONTINUE
C     TO FIND A MORE PRECISE VALUE OF X
C     ****************************************************************
C
C     TO PROTECT AGAINST A NEG ARGUMENT IN ALOG
C     SET X JUST INSIDE THE CONSTRAINT
      IF (W.LT.1.0) GO TO 12
      W = 0.9999
   12 IF(W.GE. 0.0) GO TO 13
      W = 0.001
```

```
      PROGRAM 3,B (CONTINUED)

   13 Z = S(II) - ((((10.**AKE(3))*EXP(-AKE(4)/(RVALU*T(II)))-1.)*W)-
     1   (2.*ALOG(1.-W)))/
     2  (((10.**AKE(3))*EXP(-AKE(4)/(RVALU*T(II))))*((10.**AKE(1))*EXP(-
     3  AKE(2)/(RVALU*T(II)))))
      SLOPE =-(((10.**AKE(3))*EXP(-AKE(4)/(RVALU*T(II)))-1.)+2./(1.-W))/
     1  (((10.**AKE(3))*EXP(-AKE(4)/(RVALU*T(II))))*((10.**AKE(1))*EXP(-
     2  AKE(2)/(RVALU*T(II)))))
      WNEW = W-Z/SLOPE
      CRIT = ABS(WNEW-W)
      IC = IC + 1
      IF (IC.LT. 12) GO TO 15
C     NF IS AN INDICATOR WHICH IS 0 IF THIS PACKETT IS NOT CALLED
C     IF THIS PACKETT IS CALLED AT ALL DURING THE CALCULATION NF = 1
      NF = 1
      WNEW = 1.0
      GO TO 8
C     THE FOLLOWING PROTECTIVE PACKETT CAN BE USED AS AN
C     ALTERNATE TO SETTING Y=1.0
C     *****************************************************************
C     IF (IC.LT. 14) GO TO 15
C     WRITE (6,14) NT,II,Z,SLOPE,WNEW,CRIT
C  14 FORMAT (10X,39HNEWTON RAPHSON SEARCH DOES NOT CONVERGE/
C    110X,16HWORKING DATA ARE,2I10,4F15.7)
C     STOP
C     *****************************************************************
   15 IF(CRIT .LT. 0.00001) GO TO 8
      W = WNEW
      GO TO 7
C     *****************************************************************
    8 CONTINUE
C     IF THE NEWTON RAPHSON PACKETT IS OMITTED USE THE FOLLOWING CARD
C     WNEW = WBEST
      XX(II) = WNEW
   10 CONTINUE
      BS = 0.0
      DO 11 IJ = 1,ND
      B(IJ) = X(IJ) - XX(IJ)
   11 BS = BS + B(IJ)*B(IJ)
      SUMN = BS
      RETURN
      END
```

PROGRAM 3,C THE ROSENBROCK SEARCH PROGRAM (8)

```
      SUBROUTINE SEARCH
      COMMON AKE(10), D(20), V(10,10), BL(20,20)
      COMMON AJ(20), E(20), AL(20,20), AFK(20),ALPHA
      COMMON BLEN(20), EPS(10),BETA, NSTEP, SUMN
      COMMON NS,ND,X(80), S(80), T(80),KM,XX(80), B(80)
      COMMON MAXK, MKAT,MCYC
C     OPTIMIZATION BY ROSENBROCK METHOD
C   AJ= INDICATORS
C   AFK= OPTIMIZED VALUES FOR VARIABLES
C   AKE = VARIBLES
C   ALPHA =SCALE FACTOR FOR STEP SIZE  WHEN STEP IS SUCCESSFUL
C   BETA =SCALE FACTOR FOR STEP SIZE WHEN STEP IS UNSUCCESSFUL
C   E = TEMPORARY STORAGE FOR STEP SIZE
C   EPS =STEP SIZE
C   KAT = NO OF TIMES OBJECT BEING CALLED
C   KK1  =NO OF STAGES
C   KM = NO OF VARIBLES
C   MCYC = NO OF SUCCESSIVE FAILURES ENCOUNTERED IN ALL DIRECTIONS
C   NSTEP =1, USE INITIAL STEP SIZE FOR EVERY NEW STAGE
C   NSTEP =2, USE STEP SIZE OF KTH STAGE FOR (K+1)TH STAGE
C   OBJECT = SUBROUTINE FOR OBJECTIVE FUNCTION SUMN
C   SUMO = STORAGE FOR MINIMUM SUMN
C   V =ORTHOGONAL UNIT VECTORS
C   V IS A UNIT MATRIX INITIALLY
C   THE PROGRAMME TERMINATES AFTER  MAXK STAGES
C           OR AFTER  OBJECT BEING CALLED MKAT TIMES
C           OR AFTER MCYC SUCCESSIVE FAILURES BEINNG ENCOUNTERED
C    BEFORE TERMINATION
C   MAX NUMBER OF VARIBLES =20  ( LIMITED BY DIMENSION)
C
C
C   READ IN DATA
C
      KAT =1
      CALL OBJECT
      SUMO =SUMN
      DO 812 K=1,KM
      AFK(K) =AKE(K)
  812 CONTINUE
      KK1=1
      IF (NSTEP .EQ.1) GO TO 1000
      DO 350 I=1,KM
      E(I)  =EPS(I)
  350 CONTINUE
 1000 DO 250 I=1,KM
      AJ(I) =2.0
      IF (NSTEP .NE.1) GO TO 250
      E(I) =EPS(I)
  250 D(I) =0.0
```

PROGRAM 3,C (CONTINUED)

```
      III=0
  397 III=III+1
  258 I=1
  259 DO 251 J=1,KM
  251 AKE(J) =AKE(J) +E(I) *V(I,J)
      CALL OBJECT
C   ******************************************************************
C    PRINT HERE IF DESIRED NO OF TIMES OBJECTIVE FUNCTION BEING CALLED
C      (KAT), OBJECTIVE FUNCTION(SUMN), VARIBLES(AKE(I))
C   ******************************************************************
      KAT =KAT +1
      IF (KAT .EQ. MKAT ) GO TO 1002
      IF (SUMN .LE. SUMO ) GO TO 253
      DO 254 J=1,KM
  254 AKE(J) =AKE(J) -E(I) *V(I,J)
      E(I) =-BETA*E(I)
      IF (AJ(I) .LT. 1.5) AJ(I) =0.0
      GO TO 255
  253 D(I) =D(I) +E(I)
      E(I) =ALPHA *E(I)
      SUMO =SUMN
      DO 813 K=1,KM
  813  AFK(K) =AKE(K)
      IF (AJ(I) .GT. 1.5) AJ(I) =1.0
  255 DO 256 J=1,KM
      IF (AJ(J) .GT. 0.5) GO TO 299
  256 CONTINUE
      GO TO 257
  299 IF (I.EQ. KM) GO TO 399
      I=I+1
      GO TO 259
  399 DO 398 J=1,KM
      IF (AJ(J) . LT.2. ) GO TO 258
  398 CONTINUE
      IF (III.LT. MCYC ) GO TO 397
      GO TO 1001
  257 CONTINUE
      DO 290 I=1,KM
      DO 290 J=1,KM
  290 AL(I,J) =0.0
C
C    ORTHOGONALIZATION
C
      WRITE (6,280 ) KK1
      WRITE (6,281) SUMO,(AKE(I) ,I=1,KM)
      DO 260 I=1,KM
      KL=I
      DO 260 J=1,KM
      DO 261 K=KL,KM
  261 AL(I,J) =D(K) *V(K,J) +AL(I,J)
  260 BL (1,J)= AL(1,J)
      BLEN(1)=0.0
```

PROGRAM 3,C (CONTINUED)

```
      DO 351 K=1,KM
      BLEN(1)= BLEN(1) +BL(1,K)*BL(1,K)
  351 CONTINUE
      BLEN(1) =SQRT(BLEN(1))
      DO 352 J=1,KM
      V(1,J) =BL(1,J) /BLEN(1)
  352 CONTINUE
      DO 263 I=2,KM
      II=I-1
      DO 263 J=1,KM
      SUMAVV=0.0
      DO 264 KK=1,II
      SUMAV =0.0
      DO 262 K=1,KM
  262 SUMAV=SUMAV + AL(I,K)*V(KK,K)
  264 SUMAVV =SUMAV*V(KK,J) +SUMAVV
  263 BL(I,J) =AL(I,J) -SUMAVV
      DO 266 I=2, KM
      BLEN(I) =0.0
      DO 267 K=1,KM
  267 BLEN(I) =BLEN(I) +BL(I,K) *BL(I,K)
      BLEN(I) = SQRT(BLEN(I) )
      DO 266 J=1, KM
  266 V(I,J) =BL(I,J) / BLEN(I)
      KK1 =KK1+1
      IF (KK1.EQ.MAXK ) GO TO 1001
      GO TO 1000
 1002 WRITE (6,910 ) KAT
 1001 WRITE (6, 1003) KK1, KAT ,III
      WRITE (6, 1004) SUMO
      WRITE (6, 1006) (AFK(I),I=1, KM)
      WRITE (6, 294)
      WRITE(6,815) (( V (I,J) ,J=1,KM),I=1,KM)
C
C
  280 FORMAT(//3X, 12HNO OF STAGE=, 3X, I5/)
  281 FORMAT (10X,  18HSUMO AND VARIABLES,3X, 7E12.4/)
  294 FORMAT(/3X, 23HORTHOGONAL UNIT VECTORS/)
  815 FORMAT (3X,9E12.4/)
C
  910 FORMAT(//3X,25HPROGRAM HAS CALLED OBJECT,2X,I5, 2X,
     1 25HTIMES WITHOUT CONVERGANCE/)
 1003 FORMAT(/3X, 13HNO OF STAGES=,I5, 3X, 23HAND OBJECT BEING CALLED,
     1 I5, 3X, 5HTIMES,3X,26HNO OF SUCCESSIVE FAILURES=,I5/)
 1004 FORMAT(/3X, 7HOBJECT=, E15.5/)
 1006 FORMAT(/3X, 16HTHE VARIBLES ARE, 7E12.5/)
      RETURN
      END
```

```
      PROGRAM 4  A PROGRAM TO FIND THE RATIO OF THE
      LIKELIHOOD FUNCTION FOR ANY VALUES OF COEFFICIENTS
      TO THE LIKELIHOOD FUNCTION FOR THE BEST VALUES
      OF THE COEFFICIENTS.

      COMMON X(100), T(100),K, A, ND, G(20),F(20),XX(100), B(100),SUMN
      COMMON S(100),E,H
      COMMON NT,NF
      REAL K,KL,KH,M,JM1,IM1,IJM1
C     PROGRAM TO FIND THE RATIO OF LIKELIHOOD FUNCTION FOR ANY K AND KE
C     TO THE LIKELIHOOD FUNCTION FOR BEST VALUES OF K AND KE
C     E=ESTER SPECIES
C
      R = THE RESIDUAL SUM OF SQUARES BETWEEN THE OBSERVED
      X VALUES AND THOSE VALUES OF X CALCULATED USING
      THE BEST  VALUES OF THE COEFFICIENTS IN THE MODEL.
C     BK = BEST VALUE OF KINETIC CONSTANT
C     BA = BEST VALUE OF ADSORPTION CONSTANT
C
      NT = 0
      READ (5,1) NS
      DO 100 NI = 1,NS
      READ (5,1)  E,ND
    1 FORMAT (2I5)
      READ (5,2) (X(I),S(I),T(I),I=1,ND)
    2 FORMAT (3F10.4)
      READ (5,44) BK,BE,BA,BH,R
   44 FORMAT (4F10.4,F20.14)
      READ (5,3) KL,KH,EL,EH,AL,AH,HL,HH
    3 FORMAT (8F10.4)
      WRITE (6,4) E
    4 FORMAT (1H1,9X,7HSPECIES,I5,14H BUTYL ACETATE/)
      WRITE (6,5)
    5 FORMAT (10X,12HTHE DATA ARE/28X,1HX,9X,3HW/F/)
      WRITE (6,17) (X(I), S(I), T(I), I=1,ND)
   17 FORMAT (20X,3F12.5)
      K = BK
      E = BE
      A = BA
      H = BH
C     LIKELIHOOD FOR THE BEST ESTIMATES OF K AND KE
      M = ND-4
      CALL OBJECT
      SOS = SUMN
      S2 = SOS/M
      V = EXP(-SOS/(2.*S2))
      WRITE (6,45) SOS
   45 FORMAT (1H0,9X,4HRSS=,F12.7/)
      WRITE (6,15)
   15 FORMAT (1H0,4X,40HTABLES OF RATIOS OF LIKELIHOOD FUNCTIONS/
     1  5X,35HVARIABLE IN FIRST COLUMN IS CHANGED/
     2  5X,48HWHILE OTHERS ARE KEPT EQUAL TO THEIR BEST VALUES//)
      DO 20 IJ = 1,20
      IJM1 = (IJ-1)
```

PROGRAM 4 (CONTINUED)

```
 20 G(IJ) = KL+((KH-KL)*IJM1)/20.
    WRITE (6,30) (G(IJ),IJ=1,20)
 30 FORMAT (1H0,4X,1HK,7X,20F6.3)
    DO 40 I = 1,20
    IM1 = (I-1)
    K = KL+((KH-KL)*IM1)/20.
    CALL OBJECT
 40 F(I) = EXP(-SUMN/(2.*S2))/V
    WRITE (6,50) (F(I),I = 1,20)
    K = BK
    DO 21 IJ = 1,20
    IJM1 = (IJ-1)
 21 G(IJ) = EL+((EH-EL)*IJM1)/20.
    WRITE (6,31) (G(IJ), IJ=1,20)
 31 FORMAT (1H0,4X,1HE,7X,20F6.3)
    DO 41 I = 1,20
    IM1 = (I-1)
    E = EL+((EH-EL)*IM1)/20.
    CALL OBJECT
 41 F(I) = EXP(-SUMN/(2.*S2))/V
    WRITE (6,50) (F(I),I = 1,20)
    E = BE
    DO 22 IJ = 1,20
    IJM1 = (IJ-1)
 22 G(IJ) = AL+((AH-AL)*IJM1)/20.
    WRITE (6,32) (G(IJ), IJ=1,20)
 32 FORMAT (1H0,4X,1HA,7X,20F6.3)
    DO 42 I = 1,20
    IM1 = (I-1)
    A = AL+ ((AH-AL)*IM1)/20.
    CALL OBJECT
 42 F(I) = EXP(-SUMN/(2.*S2))/V
    WRITE (6,50) (F(I),I = 1,20)
    A = BA
    DO 23 IJ = 1,20
    IJM1 = (IJ-1)
 23 G(IJ) = HL+((HH-HL)*IJM1)/20.
    WRITE (6,33) (G(IJ), IJ=1,20)
 33 FORMAT (1H0,4X,1HH,7X,20F6.3)
    DO 43 I = 1,20
    IM1 = (I-1)
    H = HL+((HH-HL)*IM1)/20.
    CALL OBJECT
 43 F(I) = EXP(-SUMN/(2.*S2))/V
    WRITE (6,50) (F(I),I = 1,20)
 50 FORMAT (13X,20F6.4)
100 CONTINUE
    STOP
    END
```

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