

Thermal Hydrocarbon Chemistry

Alex G. Oblad, Hubert G. Davis,
and R. Tracy Eddinger



ADVANCES IN CHEMISTRY SERIES

183

Thermal Hydrocarbon Chemistry

Alex G. Oblad, EDITOR

University of Utah

Hubert G. Davis, EDITOR

Union Carbide Corporation

R. Tracy Eddinger, EDITOR

Cogas Development Company

Based on a symposium
jointly sponsored by
the ACS Divisions of
Petroleum Chemistry and
Fuel Chemistry at the
175th National Meeting of the
American Chemical Society,
Anaheim, California,
March 15–16, 1978.

ADVANCES IN CHEMISTRY SERIES

183

AMERICAN CHEMICAL SOCIETY
WASHINGTON, D. C. 1979



Library of Congress CIP Data

Thermal hydrocarbon chemistry.
(Advances in chemistry series; 183 ISSN 0065-2393)

Includes bibliographies and index.

1. Hydrocarbons—Congresses. 2. Pyrolysis—Congresses.

I. Oblad, Alex Golden, 1909— . II. Davis, Hugh G., 1915— . III. Eddinger, R. Tracy, 1922— . IV. American Chemical Society. Division of Petroleum Chemistry. V. American Chemical Society. Division of Fuel Chemistry. VI. American Chemical Society. VII. Series.

QD1.A355 no. 183 [QD305.H5] 540'.8s [661'.81]
ISBN 0-8412-0468-3 ADCSAJ 183 1-364-1979
79-22817

Copyright © 1979

American Chemical Society

All Rights Reserved. The appearance of the code at the bottom of the first page of each article in this volume indicates the copyright owner's consent that reprographic copies of the article may be made for personal or internal use or for the personal or internal use of specific clients. This consent is given on the condition, however, that the copier pay the stated per copy fee through the Copyright Clearance Center, Inc. for copying beyond that permitted by Sections 107 or 108 of the U.S. Copyright Law. This consent does not extend to copying or transmission by any means—graphic or electronic—for any other purpose, such as for general distribution, for advertising or promotional purposes, for creating new collective works, for resale, or for information storage and retrieval systems.

The citation of trade names and/or names of manufacturers in this publication is not to be construed as an endorsement or as approval by ACS of the commercial products or services referenced herein; nor should the mere reference herein to any drawing, specification, chemical process, or other data be regarded as a license or as a conveyance of any right or permission, to the holder, reader, or any other person or corporation, to manufacture, reproduce, use, or sell any patented invention or copyrighted work that may in any way be related thereto.

PRINTED IN THE UNITED STATES OF AMERICA

Thermal Hydrocarbon Chemistry

Advances in Chemistry Series

M. Joan Comstock, *Series Editor*

Advisory Board

Kenneth B. Bischoff

Donald G. Crosby

Robert E. Feeney

Jeremiah P. Freeman

E. Desmond Goddard

Jack Halpern

Robert A. Hofstadter

James D. Idol, Jr.

James P. Lodge

John L. Margrave

Leon Petrakis

F. Sherwood Rowland

Alan C. Sartorelli

Raymond B. Seymour

Aaron Wold

Gunter Zweig

FOREWORD

ADVANCES IN CHEMISTRY SERIES was founded in 1949 by the American Chemical Society as an outlet for symposia and collections of data in special areas of topical interest that could not be accommodated in the Society's journals. It provides a medium for symposia that would otherwise be fragmented, their papers distributed among several journals or not published at all. Papers are reviewed critically according to ACS editorial standards and receive the careful attention and processing characteristic of ACS publications. Volumes in the ADVANCES IN CHEMISTRY SERIES maintain the integrity of the symposia on which they are based; however, verbatim reproductions of previously published papers are not accepted. Papers may include reports of research as well as reviews since symposia may embrace both types of presentation.

PREFACE

Thermal reactions of hydrocarbons have been of great interest to chemists even before the petroleum industry began. Thermal cracking and reforming processes primarily for gasoline production dominated the industry through World War II, but have been replaced by catalytic processes in the ensuing years with the dominance of high octane gasoline and the high compression engine. The industry of producing chemicals from petroleum began when chemists in the 1920's produced alcohols from the ethylene and propylene formed in thermal cracking. From this start, thermal processes for making the main chemical building blocks: ethene, propene, butenes, butadiene, and aromatics (epbba) have grown in importance. Now a vast industry exists in many parts of the world based upon olefins and aromatics produced by thermal reactions of hydrocarbons. An array of other products, such as cokes and carbons, pitches and asphalts, are available as commercial items and all are produced by thermal means. Thermal reactions will play an important role in the production of hydrocarbons from shale, tar sands, coal, and lignite.

Interest in the chemistry of thermal reactions of hydrocarbons has persisted. The size of the U.S. manufacturing industry in chemicals from petroleum and the dollar volume of the products are enormous. It has recently been reported that the petrochemical output comprised nearly 23% of all manufacturing sales in the U.S. in 1976 and required over 16% of the total capital investment for that year. The Division of Petroleum Chemistry of the American Chemical Society, in its programs, has continued over the years to bring advances in this field to the attention of chemists, chemical engineers, and others interested in petroleum processing. This book contains papers from two division programs held at Anaheim, California in March, 1978: "Thermal Hydrocarbon Chemistry" and "Recent Advances in the Production and Utilization of Light Olefins."

Previous "Advances in Chemistry Series" have dealt with aspects of thermal hydrocarbon chemistry. Volume 97, "Refining Petroleum for Chemicals," edited by Leo J. Spillane was published in 1970. Symposium Series 32, "Industrial and Laboratory Pyrolyses," edited by Lyle F. Albright and Billy L. Crynes, was published in 1976.

The chapters in this volume are grouped in several sequences as follows: Chapters 1-6 relate to epbba production directly. Specific subjects covered are pyrolysis of alpha-olefins, butenes, paraffins, unsubsti-

tuted mono-, di-, and tricycloalkanes, virgin and hydrogenated gas oils, and feedstocks from processed shale oils.

Chapters 7-9 deal with the process aspects of pyrolysis to produce epbba. The first discusses the use of aerospace technology to simulate an unconventional process. The second discusses the results of recent attempts to develop computer models for large scale pyrolysis of hydrocarbons and the third discusses recent process and furnace design advances.

Chapters 10-12 cover important aspects of coke formation in metal tubular reactors during pyrolysis of hydrocarbons. Chapters 13 and 14 are concerned with coal and lignite pyrolysis. Chapters 15 and 16 deal with pitch formation from, respectively, heavy petroleum fraction and tar sand bitumen. Chapters 17 and 18 cover studies on the mechanisms of thermal alkylation and hydropyrolysis. Chapters 19 and 20 on oil shale deal with the properties of oil shale and shale oil as developed by techniques of microwave heating and thermal analysis.

This volume, although it covers a wide range of subjects in the general area of thermal hydrocarbon chemistry, contains the latest information on subject areas important to the petrochemical industry and to the science of pyrolysis. It is hoped that it will be a useful addition to this important area of science and technology. We want to thank all those who helped in arranging these symposia, and participated in them. Particular thanks go to J. W. Bunger for his help.

University of Utah
Salt Lake City, Utah

ALEX G. OBLAD

Union Carbide Corp.
South Charleston, West Virginia

HUGH G. DAVIS

Cogas Development Co.
Princeton, New Jersey
April 24, 1979

R. TRACY EDDINGER

CONTENTS

Preface	ix
1. Pyrolysis of Alpha-Olefins—A Mechanistic Study	1
C. Rebick	
2. Steam Pyrolysis of Normal Butenes	21
H. P. Leftin	
3. Product Inhibition in the Pyrolysis of Paraffinic Hydrocarbons	41
H. G. Davis and K. D. Williamson	
4. Pyrolysis of Unsubstituted Mono-, Di-, and Tricycloalkanes	67
P. S. Virk, A. Korosi, and H. N. Woebecke	
5. Pyrolysis of Virgin and Hydrogenated Gas Oils	77
P. S. Virk, A. Korosi, and H. N. Woebecke	
6. Feedstocks from Paraho Shale Oil	91
C. G. Rudershausen and J. B. Thompson	
7. Development of Scaling Methods for a Crude Oil Cracking Reactor by Using Short Duration Test Techniques	107
J. D. Kearns, D. Milks, and G. R. Kamm	
8. Computer Modeling of Hydrocarbon Pyrolysis for Olefins Production	129
L. L. Ross and W. R. Shu	
9. Improvements in Cracking Technology and Furnace Design	153
B. Lohr and W. Schwab	
10. Types of Coke Formed During the Pyrolysis of Light Hydrocarbons	175
L. F. Albright, C. F. McConnell, and K. Welther	
11. Production of Coke and Other Pyrolysis Products from Acetylene, Butadiene, and Benzene in Various Tubular Reactors	193
L. F. Albright and Y.-H. C. Yu	
12. Deposition and Gasification of Coke During Ethane Pyrolysis	205
L. F. Albright and C. F. McConnell	
13. Mild Hydrocarbonization of Western Coal	225
H. D. Cochran, Jr. and J. M. Holmes	
14. A Comparison of the Rapid Pyrolysis of a Lignite and a Bituminous Coal	239
E. M. Suuberg, W. A. Peters, and J. B. Howard	
15. Thermogravimetric Studies on Catalytic and Noncatalytic Pyrolysis of Pitch Derived from Hydrocracked Athabasca Bitumen	259
M. V. C. Sekhar and M. Ternan	

16. Production of Electrode Binder Pitch from Petroleum-Based Materials	273
E. C. Pease and A. Logan	
17. Modification of Thermal Alkylation with HCl	289
R. K. Lyon and J. E. Mitchell	
18. Hydropyrolysis of Model Compounds	297
J. Shabati, R. Ramakrishnan, and A. G. Oblad	
19. Retorting Oil Shale by Microwave Power	329
E. T. Wall, R. Damrauer, W. Lutz, R. Bies, and M. Cranney	
20. A Comparison Between the Properties of Devonian Shale and Green River Oil Shale via Thermal Analysis	343
C. S. Wen and T. F. Yen	
Index	353

Pyrolysis of Alpha-Olefins—A Mechanistic Study

CHARLES REBICK

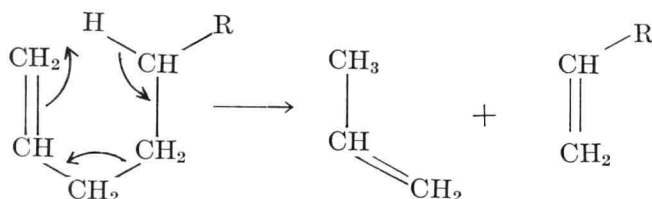
Exxon Research and Engineering Company, P.O. Box 45, Linden, NJ 07036

The products from the pyrolyses of four higher alpha-olefins have been accounted for by an empirical model involving three competing decomposition pathways: a molecular decomposition involving a six-membered ring transition state (which yields both propylene and an alpha-olefin with three less carbon atoms than the reactant) and two free radical chain pathways. One free radical channel involves hydrogen abstraction from, the second radical addition to the reactant olefin. The relative contributions of these three paths have been estimated from experimental data from the laboratory pyrolysis of higher alpha-olefins. The pyrolyses were carried out at low conversions in a quartz flow reactor at 475°–550°C.

The expansion of the petrochemical industry and the accompanying increase in the demand for ethylene, propylene, and butadiene has resulted in renewed interest and research into the pyrolytic reactions of hydrocarbons. Much of this activity has involved paraffin pyrolysis for two reasons: saturates make up most of any steam cracker feed and since the pioneering work of Rice 40 years ago, the basic features of paraffin cracking mechanisms have been known (1). The emergence of gas chromatography as a major analytical tool in the past 15 years has made it possible to confirm the basic utility of Rice's hypotheses (*see*, for example, Ref. 2).

By contrast, few studies have been made of the pyrolysis of alpha-olefins. The large number of apparent primary reaction products and the complexity of the mechanism as well as the absence of olefins in cracking feedstocks all have inhibited research. Yet, it is well known that alpha-

olefins are major primary products of paraffin cracking, and secondary reactions of alkenes must be important in moderate-to-high severity steam cracking to ethylene and in thermal cracking processes such as coking and visbreaking. Most of the prior olefin studies have involved propylene or butene cracking since these are the major primary olefinic products besides ethylene from gaseous and naphtha feedstocks (3, 4). However, longer chain olefins play an important role in the cracking of gas oils, residual stocks, and whole crudes. Previous studies of higher alpha-olefins have included octadecene (5), heptene, dodecene, and tetradecene (6), and various isomers of tetradecene (7). These compounds crack to form shorter alpha-olefins, diolefins, methane, ethane, and hydrogen. Also, all of these researchers reported a surprisingly high yield of $C_{n-3}H_{2n-6}$ from the cracking of C_nH_{2n} . A concerted molecular mechanism was proposed by Miller (5) to account for this product:



This retro-ene reaction is accepted as the primary mode of ester decomposition. For olefins, it has been investigated both directly (8) and via the reverse reaction, the ene reaction (9). The best estimates for 1-hexene and 1-heptene are that the reaction proceeds with an activation energy of about 54 kcal/mol and a preexponential factor of 10^{12} sec^{-1} .

It has been assumed that the remaining products are formed by some sort of free radical chain mechanism, but no generalized mechanism like that of Rice's for paraffin pyrolysis has been proposed. Tanaka et al. have been able to simulate product distributions for shorter olefins—up to hexene (10). We shall describe a model for higher alpha-olefin pyrolysis and use it to account for the products from the cracking of several olefins.

Experimental

All experiments were carried out in a simple flow system. A schematic diagram of the apparatus is shown in Figure 1. The quartz reactor (10 mm i.d.) was heated in a three-zone electric furnace which gave a flat ($\pm 2^\circ\text{C}$) temperature profile over about 45 cm. Reactor temperatures were measured by a thermocouple which could be moved in a sheath attached to the outside of the reactor. Initially, the sheath was placed inside the reactor, but the inside temperatures agreed so closely with the reactor wall temperatures that the inner thermocouple was removed to minimize catalytic effects.

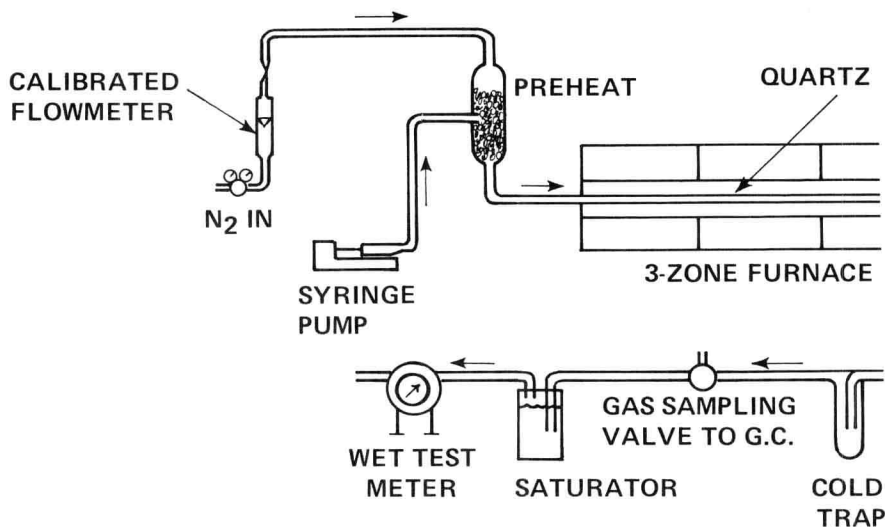


Figure 1. Diagram of flow apparatus

N_2 diluent was metered into the system through a calibrated flowmeter. Olefins were fed by a syringe pump to a preheater where they were vaporized and mixed with the diluent gas. The mixture flowed through the reactor tube, and unreacted hydrocarbon and liquid products condensed in two traps, one at room temperature and one at approximately -50°C . Gaseous products were sampled on-line and were analyzed by using gas chromatography. Total gas flow was measured by using a wet test meter. At the conclusion of an experiment, the liquid products were collected and analyzed by using gas chromatography. Initial product identification was made with gas chromatography-mass spectroscopy. The gas chromatography and programming rates used are summarized on Table I. Commercially available α -olefins were used

Table I. Gas Chromatographic Analysis

Analysis	Column	Detector	Temperature Program
H_2	molecular sieve 5A 6 ft \times 1/8 in.	thermal conductivity	100°C isothermal
C_1 – C_5 hydrocarbons	0.19% pieric acid on 80/100 mesh carbopack C 3 m \times 1/8 in.	flame ionization	4 min at 30°C 30° – 100°C @ $4^\circ/\text{min}$
Hydrocarbon liquids	20% SP2100 on 80/100 mesh chromosorb W AW-DMCS 10 ft \times 1/8 in.	flame ionization	4 min at 60°C 60° – 300°C @ $4^\circ/\text{min}$

without further purification. Four olefins were studied: 1-nonene, 1-dodecene, 1-tetradecene, and 1-hexadecene. Gas chromatographic analysis showed the purity of all reagents to be at least 99%.

Results

Typical product distributions for the four olefins studied are shown in Table II. The major products are ethylene, propylene, methane, and ethane. Lesser amounts of higher alpha-olefin products also are observed. In these respects the product distribution from the cracking of an alpha-olefin resembles that of the corresponding *n*-paraffin. However, there are several differences between olefin and paraffin cracking. The first is the presence of butadiene and smaller amounts of higher diolefins (mostly alpha-omega dienes) and cyclic olefins as primary products of olefin cracking. These products are not primary cracking products of paraffins. A second difference is the surprisingly large yield of $C_{n-3}H_{2n-6}$ from the cracking of C_nH_{2n} . This effect is most visible if we compare the olefin product yields from the cracking of an alpha-olefin and the corresponding paraffin. Figure 2 does this for hexadecene and hexadecane. The fluctuations in product olefin levels with carbon number are real and reproducible, reflecting mechanistic features and not experimental scatter. Figure 3 indicates this by comparing olefin product yields from the different compounds pyrolyzed.

Another difference between olefin and paraffin pyrolysis is the reaction order. Typically, higher *n*-paraffins crack according to first-order kinetics. Alpha-olefin pyrolysis is somewhat higher order. Figure 4 is a log-log plot of average dodecene cracking rate vs. average $C_{12}C_{24}$ pressure at 525°C. The decomposition is 1.33 order in dodecene. Table III gives the reaction orders (in $C_{12}H_{24}$) for the formation of individual products. Reaction order measurements for C_4 – C_6 products have been omitted because of small partial-pressure-dependent errors in the detection of these products, which make order measurements impossible. Note that ethylene, propylene, and nonene formation are of significantly lower order than those of the other products. Reasons for this will be discussed in the next section.

The rates of alpha-olefin decomposition measured in our laboratory are only slightly higher than those for corresponding paraffins. For example, at 500°C, hydrocarbon partial pressure of 0.18 atm, and approximately 20 seconds residence time, 6.2% hexadecene is cracked compared with 4.5% hexadecane. Figure 5 shows average rate constants for alpha-olefin cracking plotted vs. the size of the olefin being cracked, indicating only a slight increase in cracking rate with increasing molecular weight.

Table II. Product Distributions from Alpha-Olefin Pyrolysis

		<i>Reactant</i>			
		<i>C</i> ₉ <i>H</i> ₁₈	<i>C</i> ₁₂ <i>H</i> ₂₄	<i>C</i> ₁₄ <i>H</i> ₂₈	<i>C</i> ₁₆ <i>H</i> ₃₂
Temperature (°C)		500	500	500	500
Initial hydrocarbon partial pressure (atm)		0.26	0.22	0.19	0.18
Space time (sec)		18.0	9.7	19.8	9.2
Conversion (wt %)		6.4	2.8	5.8	3.1
Products (mol/100 mol cracked)					
	H ₂	1.9	—	—	—
	CH ₄	23.6	27.8	27.7	28.2
	C ₂ H ₄	53.8	63.1	60.9	60.4
	C ₂ H ₆	14.5	19.8	19.7	18.6
	C ₃ H ₆	46.0	49.7	47.0	46.2
	C ₃ H ₈	2.9	3.7	3.5	3.7
	1-C ₄ H ₈	12.3	16.4	15.4	16.3
	1,3-C ₄ H ₆	8.6	9.3	7.6	8.7
	C ₅ H ₁₀	13.3	15.4	8.3	11.9
	C ₅ H ₈	8.1	1.7	2.2	1.1
	C ₆ H ₁₂	22.4	11.3	12.1	13.3
C ₆ H ₁₀	{ C ₆ = =	5.6	1.2	1.3	1.2
	{ MCP = + CH = ^a	5.3	3.8	4.3	3.9
	C ₇ H ₁₄	5.8	6.7	12.3	9.6
	C ₇ H ₁₂	6.4	3.3	4.9	3.0
	C ₈ H ₁₆	5.8	8.5	9.0	8.0
	C ₈ H ₁₄	4.3	3.1	0.7	2.7
	C ₉ H ₁₈	—	20.8	6.3	11.6
	C ₉ H ₁₆	—	1.5	1.7	1.9
	C ₁₀ H ₂₀	—	4.4	9.3	10.2
	C ₁₀ H ₁₈	—	0.9	1.3	1.3
	C ₁₁ H ₂₂ ^b	—	2.7	24.3	4.9
	C ₁₂ H ₂₄	—	—	4.7	8.0
	C ₁₃ H ₂₆	—	—	2.5	24.6
	C ₁₄ H ₂₈	—	—	—	3.5
	C ₁₅ H ₃₀	—	—	—	1.5

^a Methylcyclopentene and cyclohexene.^b C₁₁⁺ diolefins were not separated from C₁₁⁺ olefins.

An Arrhenius plot of log rate constant vs. reciprocal temperature (Figure 6) indicates an activation energy of 61.9 ± 1.3 kcal/mol for dodecene cracking. This is similar to the activation energies measured for *n*-paraffin cracking and is somewhat higher than previously measured values for alpha-olefins (6).

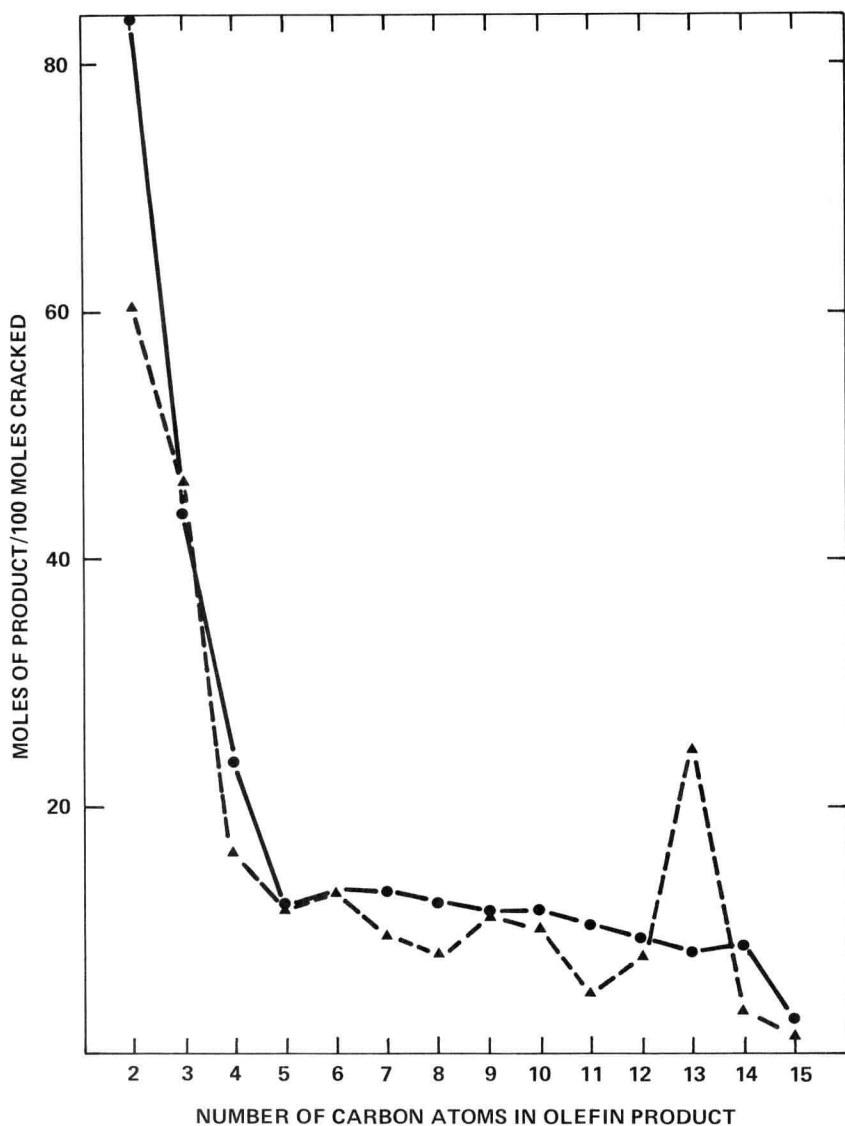


Figure 2. A comparison of the yields of alpha-olefin products from the pyrolysis of hexadecane and hexadecene at 500°C. (●) From $C_{16}H_{34}$, (▲) from $C_{16}H_{32}$.

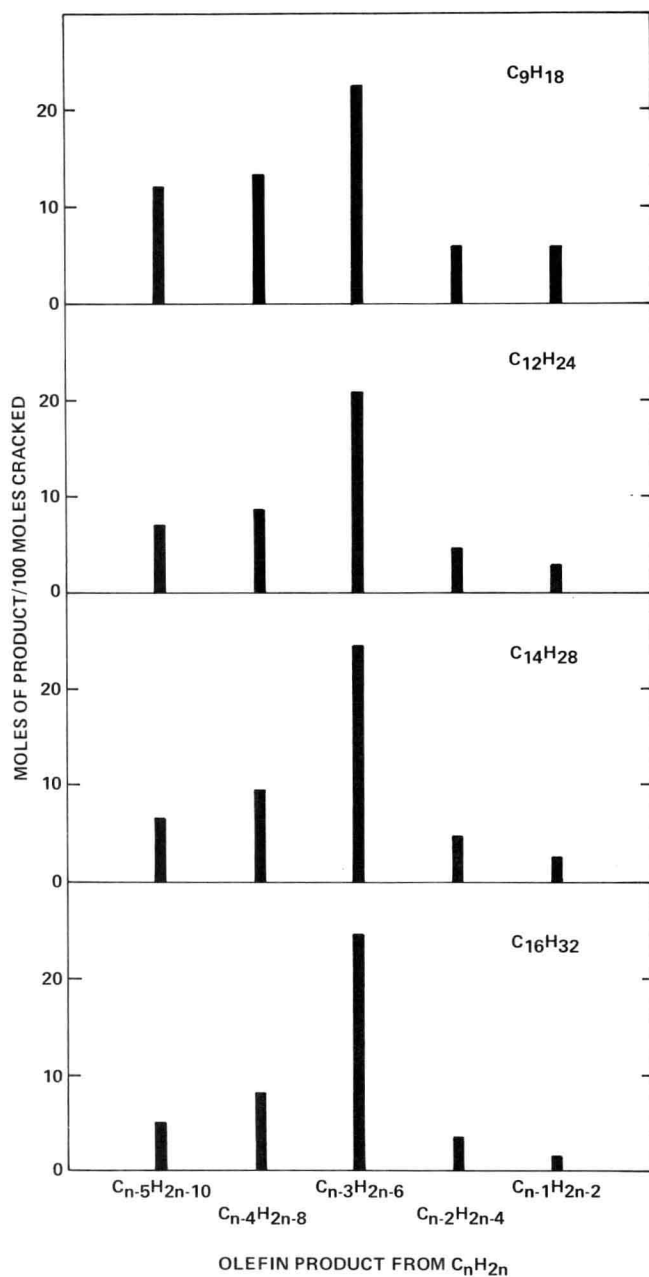


Figure 3. A comparison of the α -olefin product yields from the pyrolysis of four higher α -olefins at 500°C