

# Refining Petroleum for Chemicals

ADVANCES IN CHEMISTRY SERIES

97

# Refining Petroleum for Chemicals

Advances in Chemistry Series

Robert F. Gould, Editor

A symposium co-sponsored by  
the Division of Petroleum  
Chemistry and the Division  
of Industrial and Engineering  
Chemistry at the 158th Meeting  
of the American Chemical  
Society, New York, N.Y.,  
Sept. 10-12, 1969.

**L. J. Spillane and H. P. Leftin,**  
*Symposium Co-chairmen*

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AMERICAN CHEMICAL SOCIETY  
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# Advances in Chemistry Series

Robert F. Gould, *Editor*

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**AMERICAN CHEMICAL SOCIETY PUBLICATIONS**

Advances in Chemistry Series

Robert E. Gould, Editor

## 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 refereed critically according to ACS editorial standards and receive the careful attention and processing characteristic of ACS publications. Papers published in ADVANCES IN CHEMISTRY SERIES are original contributions not published elsewhere in whole or major part and include reports of research as well as reviews since symposia may embrace both types of presentation.





## PREFACE

This volume reviews the processing by which liquid petroleum may be converted to a maximum yield of chemicals, not fuels. Petroleum is considered to include natural gasoline, condensate, crude oil, or fractions of these materials obtained by physical methods. Excluded are liquefied petroleum gas (LPG), ethane, and natural gas. Processing is restricted for the most part to production of the first materials saleable as chemicals. In these contexts an alternate name for the symposium might well be the Technology of the Petrochemical Refinery.

A considerable volume of literature has been published on the production of petrochemicals and even a few prophetic papers on the petrochemical refinery (1, 3, 4, 5). To date, however, the petrochemical refinery concept has been used in two slightly differing contexts: one wherein the plant output (using crude oil as feed) is exclusively chemicals (4); the other wherein the production of petrochemicals is integrated into an existing fuels refinery (1, 5). The former has been reduced successfully to practice on a commercial scale only in one acknowledged instance (6), and this operation has been restricted to condensate as feedstock. The second context does not differ much from present petrochemical operations of oil companies except in degree. From a technological viewpoint the former, operating on heavy crude oil, would represent perfection of the petrochemical refinery concept and would demand the most of new technology. Hence, in the present symposium the chemistry and new processing techniques will be directed exclusively to the production of chemicals, not fuels.

Whether or not the production of chemicals from crude oil can be independent of the production of fuels has still not been determined. It will indeed be a new industry, but its future depends largely on the development of new technology. Technology employed so far, however, has largely been an adaptation of processes designed for ethylene production from gaseous hydrocarbons or for maximum gasoline production by petroleum refining.

Since the introduction of hydrodealkylation processes some 11 years ago (2), the pace has quickened in the development of processes specifically designed to manufacture chemicals from liquid petroleum feedstocks. This volume is designed to unify and stimulate further development of new concepts, ultimately leading to establishment of the

petrochemical refinery as an independent and economically viable enterprise.

Any refinery is based upon taking a crude mixture of raw materials and producing a spectrum of desired products. It differs from a chemical plant primarily in that several products are desired—i.e., the coproduct concept. In common with the fuels refinery, the technology of the petrochemical refinery is influenced by four fundamental considerations:

- (a) Selection of raw material
- (b) Definition of product mix
- (c) Selection of basic processes
- (d) Integration of processes and products

All but the last, which depends so much on individual circumstances, are discussed to some degree in this book. Emphasis is on basic processing, the main point of impact for chemical science.

With crude oil as feed the production of chemicals by known methods rests upon four types of processing:

- (1) Thermal pyrolytic cracking
- (2) Catalytic reforming
- (3) Catalytic or thermal hydrocracking
- (4) Separation and purification

The papers in this volume have been organized around four main topics which combine both the broad considerations of the petrochemical refinery and the specific types of processing:

- (1) Review of the basic chemical reactions employed in the present-day petrochemical refinery.
- (2) Description of new chemical developments in dehydrogenation and cracking reactions.
- (3) Discussion of the products and economics of the petrochemical refinery.
- (4) Presentation of typical new processing concepts—chemical as well as physical—applicable to the petrochemical refinery of the future.

Although the papers in this volume do not represent an exhaustive review of the petrochemical refinery concept, they do offer for the first time a "status report" on the general subject. Former publications have directed themselves to some specific phase, usually economic or engineering, with little attention directed to their interface with chemistry and process development. Hopefully, the papers presented here will offer a starting point for continuing development of a fascinating and most important subject on an integrated basis.

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Recent work on elementary steps of importance in hydrocarbon pyrolysis are described and summarized from a quantitative and predictive point of view. This includes the thermal H atom transfer reactions, addition of radicals to unsaturates, and carbon reactions responsible for chain propagation, as well as the initiation and termination steps. The large activation energies for the cleavage of C-C bonds (about 300 kJ/mol) and the low energies of other important steps are described. The importance of these reactions for molecular reactions of unimolecular decomposition are discussed, in particular Cope rearrangements and 1,5-H shift reactions. Some anomalies with shock tube data are described briefly as are the kinetic properties of small radicals. Some difficulties of kinetic modeling are discussed along with the importance of determination of bimolecular rate constants from Arrhenius behavior at high temperatures.

From a molecular, or a technological, or an economic point of view, the analysis of hydrocarbons must rank as one of the most important chemical processes of our 20th century. Research activity on the pyrolysis of hydrocarbons has mirrored this intense interest since the early part of the century. These studies have yielded a number of simple conclusions. One is that pyrolytic systems are an extremely complex assembly of chemical reactions taking place mainly through the action of a relatively small number of very active free radicals.

The kinetic understanding of the role played by free radical processes stems from two historic papers by R. O. Colclough (15, 16) outlining plausible chain sequences to explain both the products and kinetics of pyrolysis



# CONTENTS

Preface .....	vii
1. Some Recent Developments in the Gas-Phase Pyrolysis of Hydrocarbons .....	1
Sidney W. Benson, Stanford Research Institute, Menlo Park, Calif.	
2. The Chemistry of Aromatics Production via Catalytic Reforming ..	20
E. L. Pollitzer, J. C. Hayes, and Vladimir Haensel, Universal Oil Products Co., Des Plaines, Ill.	
3. Chemistry of Hydrocracking .....	38
G. E. Langlois and R. F. Sullivan, Chevron Research Co., Richmond, Calif.	
4. Secondary Reactions of Olefins in Pyrolysis of Petroleum Hydrocarbons .....	68
Tomoya Sakai, Kazuhiko Soma, Yoichi Sasaki, Hiroo Tominaga, and Taiseki Kunugi, University of Tokyo, Tokyo, Japan	
5. Rate Modeling for the Butane-Butenes System .....	92
John Happel, Miguel A. Hnatow, and Reiji Mezaki, New York University, Bronx, N. Y.	
6. Some Problems of the Cracking Mechanism of Hydrocarbons ....	110
R. S. Magaril, Tyumen Industrial Institute, Tyumen, U.S.S.R.	
7. The Chemical Refinery in Perspective .....	123
Matthew F. Stewart and James T. Jensen, Arthur D. Little, Inc., Cambridge, Mass.	
8. Product Optimization in the Petrochemical Refinery .....	137
Harry M. Walker, Monsanto Co., Alvin, Tex.	
9. The Manufacture of Propylene .....	153
Alvin H. Weiss, Worcester Polytechnic Institute, Worcester, Mass.	
10. Kinetics of the Demethylation of Methylcyclohexane .....	179
M. M. Johnson and H. J. Hepp, Phillips Petroleum Co., Bartlesville, Okla.	
11. Catalytic Dehydrogenation of Higher Normal Paraffins to Linear Olefins .....	193
James F. Roth, Joseph B. Abell, Loyd W. Fannin, and Andrew R. Schaefer, Monsanto Co., St. Louis, Mo.	

12. The Octafining Process for Isomerization of $C_8$ Aromatics Containing Ethylbenzene .....	204
H. F. Uhlig and W. C. Pfefferle, Engelhard Minerals and Chemicals Corp., Newark, N. J.	
13. Process Evaluation of Improved Solvents for Butadiene Recovery ..	215
G. D. Davis, E. C. Makin, Jr., and C. H. Middlebrooks, Monsanto Co., St. Louis, Mo.	
14. Tetraethylene Glycol—A Superior Solvent for Aromatics Extraction	228
G. S. Somekh and B. O. Friedlander, Union Carbide Corp., Tarrytown, N. Y.	
15. A New Solvent for Aromatics Separation .....	242
Julian Feldman, U. S. Industrial Chemicals Co., Cincinnati, Ohio	
16. Carbon Black from Petroleum Oil .....	264
T. A. Ruble, Continental Carbon Co., Houston, Tex.	
17. Petrochemical Feedstocks from Residuals .....	271
A. R. Johnson, S. Alpert, and L. M. Lehman, Hydrocarbon Research, Inc., New York, N. Y.	
Index .....	289

# Some Recent Developments in the Gas-Phase Pyrolysis of Hydrocarbons

SIDNEY W. BENSON

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*Recent work on elementary steps of importance in hydrocarbon pyrolysis are described and summarized from a quantitative and predictive point of view. This includes the normal H atom metathesis reactions, addition of radicals to unsaturates, and fission reactions responsible for chain propagation, as well as the initiation and termination steps. The large negative activation energies characteristic of kinetic chain lengths put an upper limit of about 1000°K on the temperature at which propagation steps are important. Arrhenius parameters for molecular reactions of unsaturated hydrocarbons are discussed, in particular Cope rearrangements and 1,5-H shift reactions. Some anomalies from shock tube data are described briefly as are the kinetic properties of small biradicals. Some difficulties of kinetic modeling are discussed along with the importance of deviations of unimolecular rate constants from Arrhenius behavior at high temperatures.*

From a scientific, or a technological, or an economic point of view, the pyrolysis of hydrocarbons must rank as one of the most important chemical processes of our 20th century. Research activity on the pyrolysis of hydrocarbons has mirrored this intense interest since the early part of the century. These studies have yielded a number of simple conclusions. One is that pyrolytic systems are an extremely complex assembly of chemical reactions taking place mainly through the aegis of a relatively small number of very active free radicals.

The kinetic understanding of the role played by free radical processes stems from two historic papers by F. O. Rice (52, 53) outlining plausible chain sequences to account both for the products of pyrolysis

and the over-all concentration dependence of the rate. Although all the important chain steps and the cogent thermochemical arguments for their importance were made in these two papers by Rice, it has become common practice to refer to the Rice-Herzfeld mechanism of chain pyrolysis on the basis of a third paper (54). This third paper differs from the earlier ones only in extending the Rice scheme to include acetone and acetaldehyde and also in assigning A-factors and activation energies to all of the individual chain steps in an effort to reproduce the over-all kinetic parameters.

Two important elementary step reactions were described in these radical chains of Rice. One was the ubiquity of the metathetical reaction of H atom abstraction by free radicals from hydrocarbons. The second was the rapid unimolecular decomposition of free radicals into olefins and secondary atoms or radicals, as a chain step competitive with metathesis.

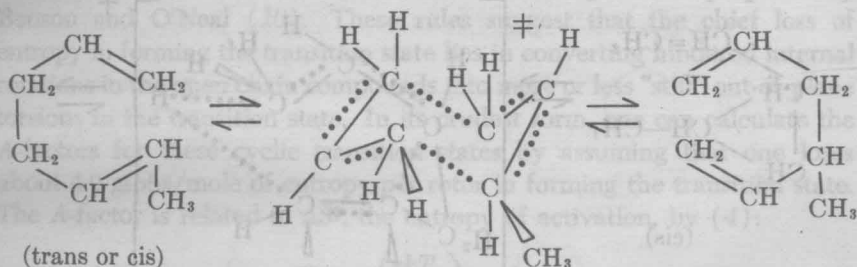
A few years later, a third type of reaction was added to the scheme, the isomerization of large radicals by internal abstraction of H atoms (9). This was shown (41) to account satisfactorily for the product distribution arising from the pyrolysis of long chain hydrocarbons (*e.g.*,  $n\text{-C}_{16}\text{H}_{34}$ ). Very little has happened in the approximately 25 years since the last of these contributions to alter our conceptual understanding of the kinetics of hydrocarbon pyrolysis. Instead, the very extensive research done since then has generally been devoted to determining the quantitative kinetic parameters associated with the elementary step reactions of the pyrolysis chain. Much of this work has been summarized in some recent books (62) and reviews (26, 51).

One new field related to hydrocarbon pyrolysis of small ring compounds (3- and 4-membered rings) has been developed in the past decade, and that is the subject of biradicals. These are discussed briefly. In the present article, I consider in some detail the present status of our experimental and theoretical understanding of these step reactions and how they relate to the very practical problems of kinetic modeling of pyrolysis systems.

### **Molecular Reactions of Hydrocarbons**

One of the early controversies in the field of pyrolysis revolved about the question of the importance of concerted, molecular elimination reactions of hydrocarbons to give olefins and alkanes as products. Numerous experiments (51) have given a decisive answer to this problem in favor of the completely radical mechanism for alkane pyrolysis. At the same time, ironically, very clear cut evidence has been elicited to show that both mono- and polyolefins can react quite readily in concerted, molecu-

lar processes to form isomeric products or fission products (26). These usually involve the formation of a cyclic transition state with a six-membered ring. The Cope rearrangement provides one of the oldest examples (25) of such an isomerization:



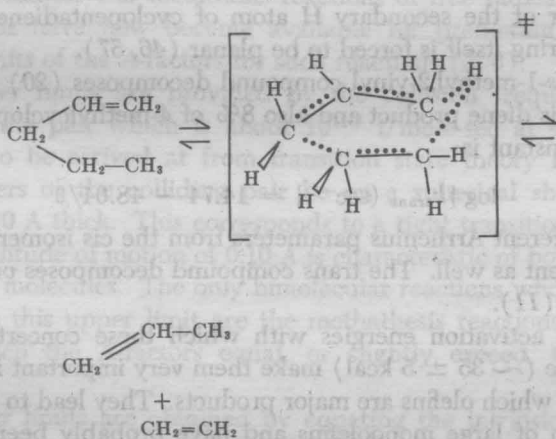
$$\log [k_{\text{cis}}(\text{sec}^{-1})] = 10.66 - 36.72/\theta$$

$$\log [k_{\text{trans}}(\text{sec}^{-1})] = 10.39 - 35.36/\theta$$

where  $\theta = 2.303 RT$  in units of kcal/mole.

In the illustration shown, the transition state involves a six-membered ring, and it is presumed on structural grounds that it has the thermodynamically favored conformation of the chair form of cyclohexane. Since it also has a mobile  $\pi$ -electron system, it seems reasonable to picture it as two allylic radicals interacting with each other *via* their terminal (carbon atoms 1 and 3)  $\pi$ -electrons. For such a structure, the cis diolefin will have its bulky methyl group in the structurally unfavorable quasi-axial position. The higher activation energy of 1.36 kcal/mole observed for the reaction of the cis isomer supports such a structure.

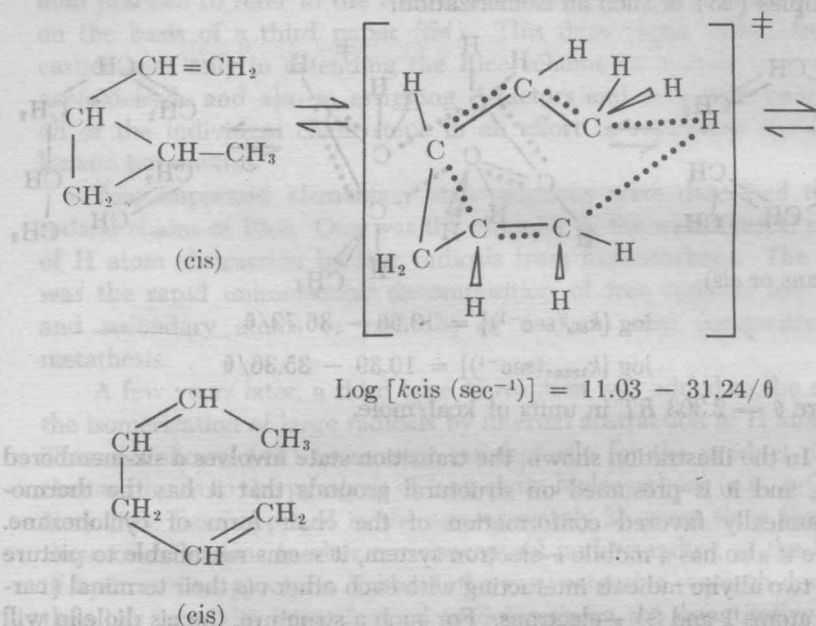
The "ene" reaction, or more prosaically, the 1,5-H shift reaction, provides another more recent example of a molecular reaction:



Such reactions were initially studied for the vinyl ethyl ethers (14, 70).



A second example of this is provided by the pyrolysis of *cis*-1-methyl-2-vinylcyclopropane, which decomposes at about 120°C lower than its *trans* isomer to give *cis*-hexa-1,4-diene (17, 18, 58):



For both examples of 1,5-H shifts, the transition state is probably best regarded as involving a puckered five-membered ring of carbon atoms with the transferring H atom out of the plane. In one of the simplest examples of the 1,5-H shift reaction, however, namely the suprafacial transfer of the secondary H atom of cyclopentadiene around the C-5 ring, the ring itself is forced to be planar (46, 57).

The *trans*-1-methyl-2-vinyl compound decomposes (20) to give 92% of the same *cis* diene product and also 8% of 4-methylcyclopentene. The diene rate constant is:

$$\log [k_{\text{trans}} (\text{sec}^{-1})] = 14.74 - 48.64/\theta$$

with very different Arrhenius parameters from the *cis* isomer. The mechanism is different as well. The *trans* compound decomposes *via* a biradical intermediate (11).

The low activation energies with which these concerted reactions can take place ( $\sim 35 \pm 5$  kcal) make them very important in all pyrolysis systems in which olefins are major products. They lead to an enhanced fragmentation of large monoolefins and have probably been responsible for much misidentification of cracking rate parameters.

While it is not possible to make *a priori* estimates of the activation energies of these reactions, such estimates can be made from values observed in homologous compounds. The A-factors for concerted processes can be estimated on the basis of some simple rules proposed by Benson and O'Neal (10). These rules suggest that the chief loss of entropy in forming the transition state lies in converting hindered internal rotations in the open chain compounds into more or less "stiff" out-of-plane torsions in the transition state. In its crudest form, one can calculate the A-factors for these cyclic transition states by assuming that one loses about 4.0 gibbs/mole of entropy per rotor in forming the transition state. The A-factor is related to  $\Delta S^\ddagger$ , the entropy of activation, by (4):

$$A = \left( \frac{ekT_m}{h} \right) e^{\Delta S^\ddagger/R}$$

where  $T_m$  is the mean temperature of the range used. At 600°K the factor  $ekT_m/h = 10^{13.55} \text{ sec}^{-1}$ .

Table I lists a few representative examples of estimated A-factors for some hydrocarbon reactions proceeding through six-membered ring, cyclic transition states. We see that although the simple rotor rule is fairly effective in estimating A-factors, it generally errs on the high side. The more complex analysis (10) which takes into account all the changes in frequencies in going to the cyclic complex does a somewhat better job of estimating the A-factors.

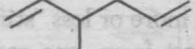


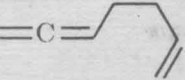
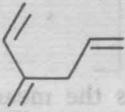

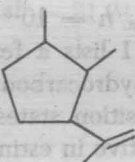
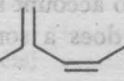
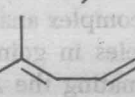
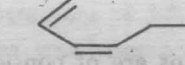
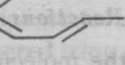


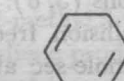


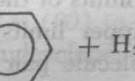
### Metathesis Reactions

While the molecular reactions of olefins are of considerable importance, free radical reactions are still the major route for pyrolysis of both alkenes and alkanes. For metathesis reactions of free radical with molecules, methods have now become available for predicting both lower and upper limits of the A-factors for such reactions (3, 6).

The upper limits are provided by the collision frequency of the radical-molecule pair which is about  $10^{11.3}$  l/mole-sec at 400°K. This result can also be arrived at from transition state theory by assuming that the centers of the colliding pair lie on a spherical shell 3.5 Å in radius and 0.10 Å thick. This corresponds to a tight transition state since the small amplitude of motion of 0.10 Å is characteristic of bond vibration amplitudes in molecules. The only bimolecular reactions whose A-factors come close to this upper limit are the methathesis reactions of I atoms (27) for which the A-factors equal, or slightly exceed, the collision frequency.

The lower limits are obtained by equating the intrinsic entropy of the transition state to a molecule of similar structure and molecular weight. Thus, for the reaction  $\text{H} + \text{C}_2\text{H}_6 \rightleftharpoons \text{C}_2\text{H}_5 + \text{H}_2$ , we can assume

**Table I. Measured Arrhenius Parameters and Estimated A-Factors  
Ring Cyclic**

Reactant	Product
a $\text{CD}_2=\text{CHCH}_2\text{CH}_2\text{CH}=\text{CD}_2$	$\text{CH}_2=\text{CHCD}_2\text{CD}_2\text{CH}=\text{CH}_2$
b 	1, 5-heptadiene (cis + trans)
c 	
d 	
e 	
f 	
g 	
h 	
i 	
ii 	 + $\text{H}_2$

that the transition state has an intrinsic entropy in excess of  $\text{C}_2\text{H}_6$ . By intrinsic entropy is meant the entropy of the species corrected for symmetry, optical isomerism, and electron spin (4).

Thus, at  $400^\circ\text{K}$

$$\begin{aligned}
 \Delta S^\ddagger_{400} &= S^\ddagger_{400}(\text{C}_2\text{H}_6 \dots \text{H}) - S^\circ_{400}(\text{C}_2\text{H}_6) - S^\circ_{400}(\text{H}) \\
 &\geq R \ln 2 + R \ln 6 - S^\circ_{400}(\text{H}) \\
 &\geq 1.4 + 3.6 - 28.9 = -23.9 \text{ gibbs/mole}
 \end{aligned}$$

# for Unimolecular Reactions Proceeding through Six-Membered Transition States

$E_{obs},$ kcal/mole	$\text{Log } [A(\text{sec}^{-1})],$ observed	$\text{Log } [A(\text{sec}^{-1})],$ estimated <sup>a</sup>	Ref.
35.5	11.1	11.1 (10.9)	63
35.0	10.85	11.3 (10.9)	25
29.9	11.85	11.5 (11.7)	42
28.47	9.97	10.8 (11.2)	23
35.2	9.06	9.6 (9.9)	31
32.76	11.24	11.1 (12.3)	19
32.5	11.8	11.9 (12.1)	24
31.2	11.03	11.1 (12.3)	17, 18, 58
43.8	12.36	12.4 (—)	13, 21
42.7	12.02		

<sup>a</sup> Values in parentheses are obtained by making proper corrections for symmetry (reaction path degeneracy) and subtracting from  $S^\ddagger$ , 4.0 gibbs/mole for every rotor involved.

On correcting to moles/liter standard states, this leads to an A-factor for the metathesis:

$$A = \frac{ekT_m}{h} e^{\Delta S^\ddagger/R} \geq 10^{13.4 - 3.2} = 10^{10.2} \text{ l/mole-sec}$$

The reported "best" value is  $10^{11.0}$  l/mole-sec (4).