

ADVANCES IN CATALYSIS

AND RELATED SUBJECTS

VOLUME 18

EDITED BY

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Exponentials

A Preface

The flux of scientific papers must somehow relate to

$$dN/dt = \varepsilon n \quad (1)$$

where n = number of investigators, ν = rate of information bits produced per investigator, and ε = number of papers written per number of information bits. This applies to papers generally, as well as to those in any given segment of science, including ours.

There are many busy investigators. There is a population explosion. We are told that the scientific age is upon us, that science itself is playing an ever-more important role in our activities. The fraction of individuals involved in science is on the upswing. Therefore, the number of scientific workers is growing even more rapidly, probably like $\partial n/\partial t = k_1 n$. With technology advancing, the rate of production of data per researcher is itself climbing. Only a while ago, it took some of us 10 days to analyze the product from a single catalytic experiment. Now, with the gas chromatograph, we do it in 10 minutes, faster by a factor greater than 10^3 . Similarly, we sometimes wrestled with an equation for several months; now a useful solution often can pour out of a computer after a few days, minutes, or even seconds.

Information is self-catalyzing; it increases our capability to develop information, $\partial \nu/\partial t = k_2 \nu$. The rate constant k_2 is clearly impressive in magnitude! Thus both n and ν are exponentials, and the rate law for the production of papers (1) assumes the menacing form

$$dN/dt \sim \varepsilon \exp(k_1 + k_2)t$$

Unfortunately, there is little hope for substantial growth in our reading speed. It is pretty constant, $(dN/dt)_0$. Therefore, the fraction of written material with which we can keep up is threatening to decay exponentially, as

$$f = (dN/dt)_0 / (dN/dt) \approx (1/\varepsilon) \exp[-(k_1 + k_2)t]$$

Editors have no good way (nor moral right) to influence the reproductive rate constants k_1 and k_2 . Alas, the scientist must consciously or subconsciously operate on ε ! Just how great the pressures are follows from the fact that, to keep f manageably constant, *we must keep* $(1/\varepsilon)$

growing exponentially. It becomes the symbol of effectiveness for practical information transfer. We learn to lump many bits of information into a summary concept; we accept—when necessary—new language to express new summary concepts; we become increasingly selective in choosing to report only the most relevant information. We learn to control the urge to write about all that we know or have so elegantly done, and to tune our selectivity more narrowly to *the needs of the reader.*

To maximize $(1/\epsilon)$ becomes a modern need that invites conscious effort from all of us who write, issue, or edit papers, reports, reviews, etc. We believe it to be a major goal for a publication such as ours: to *integrate* information effectively and with mature criticality; to present that which *orients* and *instructs* concerning the state of the current boundary of knowledge, and which thereby *may significantly influence the propagative chain process of evolving our science.*

For elementary statistical reasons, a simple volume of the *Advances*, containing four topics such as this one, will not exemplify the total scope intended for this medium. Yet it will give a small sample with diversity.

We seem to recall that one of our catalytic colleagues on a discussion panel (R. L. Burwell, Jr., at the 57th Meeting of the A.I.Ch.E., Boston, 1964) challenged the catalytic investigator who believes he should study a very "simple" system (hydrogen-deuterium exchange, CO oxidation, etc.), with the proposition that good chemical understanding could be derived from observing the transformations of complex molecules. G. N. Schrauzer's study of bicyclo-[2,2,1]-heptadiene (2,5-norbornadiene for short), its interaction with catalysts, and its diverse reaction paths to products is a fine example to support that thesis.

In its manifold ventures, chemistry wears many characteristic dresses. Complexity is but one. Variety is another. P. B. Venuto and P. S. Landis survey many classic organic reactions in the presence of a modern class of catalysts: acidic solids derived from crystalline aluminosilicates.

Another characteristic dress is molecular-structural detail. A. W. Weitkamp, in his study of the hydrogenation of polycyclic aromatic molecules, provides us with an excellent demonstration of the role of the "finer" points of stereochemical architecture and conformational adaptability. Incidentally, his introductory sentence ("Perhydro derivatives of monomethyl- and dimethylnaphthalenes should be among the very best candidates for components of . . . fuels for aviation turbine engines") provides an interesting illustration for the strong motivating role of the industrial community in the expansion of catalytic research.

In an earlier contribution (Volume 13 of the *Advances*), R. Coekelbergs, A. Crucq, and A. Frennet wrote on "Radiation Catalysis." In that case, emphasis was on the irradiated system: reactants plus catalyst. In this volume, Ellison H. Taylor reviews the field of radiation-induced changes in electronic, chemical, and physical structure in solids and the resulting effects on their catalytic properties. The focal point in each case is different, yet taken together, they may challenge some readers to explore phenomenological overlaps.

PAUL B. WEISZ

January, 1968

Contents of Previous Volumes

Volume 1

The Heterogeneity of Catalyst Surfaces
for Chemisorption

HUGH S. TAYLOR.

Alkylation of Isoparaffins

V. N. IPATIEFF AND LOUIS SCHMERLING.

Surface Area Measurements. A New Tool
for Studying Contact Catalysts

P. H. EMMETT.

The Geometrical Factor in Catalysis

R. H. GRIFFITH.

The Fischer-Tropsch and Related Processes
for Synthesis of Hydrocarbons by
Hydrogenation of Carbon Monoxide

H. H. STORCH.

The Catalytic Activation of Hydrogen

D. D. ELEY.

Isomerization of Alkanes

HERMAN PINES.

The Application of X-Ray Diffraction to
the Study of Solid Catalysts

M. H. JELLINEK AND I. FANKUCHEN.

Volume 2

The Fundamental Principles of Catalytic
Activity

FREDERICK SEITZ.

The Mechanism of the Polymerization of
Alkenes

LOUIS SCHMERLING AND V. N. IPATIEFF.

Early Studies of Multicomponent Catalysts

ALWIN MITTASCH.

Catalytic Phenomena Related to Photographic
Development

T. H. JAMES.

Catalysis and the Adsorption of Hydrogen
on Metal Catalysts

OTTO BEECK.

Hydrogen Fluoride Catalysis

J. H. SIMONS.

Entropy of Adsorption

CHARLES KEMBALL.

About the Mechanism of Contact Catalysis

GEORGE-MARIA SCHWAB.

Volume 3

Balandin's Contribution to Heterogeneous
Catalysis

B. M. W. TRAPNELL.

Magnetism and the Structure of Catalytically
Active Solids

P. W. SELWOOD.

Catalytic Oxidation of Acetylene in Air for
Oxygen Manufacture

J. HENRY RUSHTON AND K. A. KRIEGER.

The Poisoning of Metallic Catalysts

E. B. MAXTED.

Catalytic Cracking of Pure Hydrocarbons
VLADIMIR HAENSEL.

Chemical Characteristics and Structure
of Cracking Catalysts

A. G. OBLAD, T. H. MILLIKEN, Jr., AND
G. A. MILLS.

Reaction Rates and Selectivity in Catalyst
Pores

AHLBORN WHEELER.

Nickel Sulfide Catalysts

WILLIAM J. KIRKPATRICK.

Volume 4

Chemical Concepts of Catalytic Cracking
R. C. HANSFORD.

Decomposition of Hydrogen Peroxide by
Catalysts in Homogeneous Aqueous
Solution

J. H. BAXENDALE.

Structure and Sintering Properties of
Cracking Catalysts and Related Materials

HERMAN E. RIES, Jr.

Acid-Base Catalysis and Molecular Structure

R. P. BELL.

Theory of Physical Adsorption

TERRELL L. HILL.

The Role of Surface Heterogeneity in Adsorption

GEORGE D. HALSEY.

Twenty-Five Years of Synthesis of Gasoline by Catalytic Conversion of Carbon Monoxide and Hydrogen

HELMUT PICHLER.

The Free Radical Mechanism in the Reactions of Hydrogen Peroxide

JOSEPH WEISS.

The Specific Reactions of Iron in Some Hemoproteins

PHILIP GEORGE.

Volume 5

Latest Developments in Ammonia Synthesis

ANDERS NIELSEN.

Surface Studies with the Vacuum Microbalance: Instrumentation and Low-Temperature Applications

T. N. RHODIN, Jr.

Surface Studies with the Vacuum Microbalance: High-Temperature Reactions

EARL A. GULBRANSEN.

The Heterogeneous Oxidation of Carbon Monoxide

MORRIS KATZ.

Contributions of Russian Scientists to Catalysis

J. G. TOLPIN, G. S. JOHN, AND E. FIELD.

The Elucidation of Reaction Mechanisms by the Method of Intermediates in Quasi-Stationary Concentrations

J. A. CHRISTIANSEN.

Iron Nitrides as Fischer-Tropsch Catalysts

ROBERT B. ANDERSON.

Hydrogenation of Organic Compounds with Synthesis Gas

MILTON ORCHIN.

The Uses of Raney Nickel

EUGENE LIEBER AND FRED L. MORRITZ.

Volume 6

Catalysis and Reaction Kinetics at Liquid Interfaces

J. T. DAVIES

Some General Aspects of Chemisorption and Catalysis

TAKAO KWAN

Noble Metal—Synthetic Polymer Catalysts and Studies on the Mechanism of Their Action

WILLIAM P. DUNWORTH AND F. F. NORD.

Interpretation of Measurements in Experimental Catalysis

P. B. WEISZ AND C. D. PRATER.

Commercial Isomerization

B. L. EVERING.

Acidic and Basic Catalysis

MARTIN KILPATRICK.

Industrial Catalytic Cracking

RODNEY V. SHANKLAND.

Volume 7

The Electronic Factor in Heterogeneous Catalysis

M. McD. BAKER AND G. I. JENKINS.

Chemisorption and Catalysis on Oxide Semiconductors

G. PARRAVANO AND M. BOUDART.

The Compensation Effect in Heterogeneous Catalysis

E. CREMER.

Field Emission Microscopy and Some Applications to Catalysis and Chemisorption

ROBERT GOMER.

Adsorption on Metal Surfaces and Its Bearing on Catalysis

JOSEPH A. BECKER.

The Application of the Theory of Semiconductors to Problems of Heterogeneous Catalysis

K. HAUFFE.

Surface Barrier Effects in Adsorption, Illustrated by Zinc Oxide

S. ROY MORRISON.

Electronic Interaction between Metallic Catalysts and Chemisorbed Molecules

R. SUHRMANN.

Volume 8

- Current Problems of Heterogeneous Catalysis
J. ARVID HEDVALL.
- Adsorption Phenomena
J. H. DE BOER.
- Activation of Molecular Hydrogen by Homogeneous Catalysts
S. W. WELLER AND G. A. MILLS.
- Catalytic Syntheses of Ketones
V. I. KOMAREWSKY AND J. R. COLEY.
- Polymerization of Olefins from Cracked Gases
EDWIN K. JONES.
- Coal-Hydrogenation Vapor-Phase Catalysts
E. E. DONATH.
- The Kinetics of the Cracking of Cumene by Silica-Alumina Catalysts
CHARLES D. PRATER AND RUDOLPH M. LAGO.

Volume 9

- Proceedings of the International Congress on Catalysis, Philadelphia, Pennsylvania, 1956

Volume 10

- The Infrared Spectra of Adsorbed Molecules
R. P. EISCHENS AND W. A. PLISKIN.
- The Influence of Crystal Face in Catalysis
ALLAN T. GWATHMEY AND ROBERT E. CUNNINGHAM.
- The Nature of Active Centers and the Kinetics of Catalytic Dehydrogenation
A. A. BALANDIN.
- The Structure of the Active Surface of Cholinesterases and the Mechanism of Their Catalytic Action in Ester Hydrolysis
F. BERGMANN.
- Commercial Alkylation of Paraffins and Aromatics
EDWIN K. JONES
- The Reactivity of Oxide Surfaces
E. R. S. WINTER.
- The Structure and Activity of Metal-on-Silica Catalysts
G. C. A. SCHUIT AND L. L. VAN REIJEN.

Volume 11

- The Kinetics of the Stereospecific Polymerization of α -Olefins
G. NATTA AND I. PASQUON.
- Surface Potentials and Adsorption Process on Metals
R. V. CULVER AND F. C. TOMPKINS.
- Gas Reactions of Carbon
P. L. WALKER, JR., FRANK RUSINKO, JR., AND L. G. AUSTIN.
- The Catalytic Exchange of Hydrocarbons with Deuterium
C. KEMBALL.
- Immersional Heats and the Nature of Solid Surfaces
J. J. CHESSICK AND A. C. ZETTMLOYER.
- The Catalytic Activation of Hydrogen in Homogeneous, Heterogeneous, and Biological Systems
J. HALPERN.

Volume 12

- The Wave Mechanics of the Surface Bond in Chemisorption
T. B. GRIMLEY.
- Magnetic Resonance Techniques in Catalytic Research
D. E. O'REILLY.
- Base-Catalyzed Reactions of Hydrocarbons
HERMAN PINES AND LUKE A. SCHAAP.
- The Use of X-Ray K-Absorption Edges in the Study of Catalytically Active Solids
ROBERTS A. VAN NORDSTRAND.
- The Electron Theory of Catalysis on Semiconductors
TH. WOLKENSTEIN.
- Molecular Specificity in Physical Adsorption
D. J. C. YATES.

Volume 13

- Chemisorption and Catalysis on Metallic Oxides
F. S. STONE.
- Radiation Catalysis
R. COEKELBERGS, A. CRUCQ, AND A. FRENNETT.

Polyfunctional Heterogeneous Catalysis

PAUL B. WEISZ.

A New Electron Diffraction Technique,
Potentially Applicable to Research in
Catalysis

L. H. GERMER.

The Structure and Analysis of Complex
Reaction Systems

JAMES WEI AND CHARLES D. PRATER.

Catalytic Effects in Isocyanate Reactions

A FARKAS AND G. A. MILLS.

Volume 14

Quantum Conversion in Chloroplasts

MELVIN CALVIN.

The Catalytic Decomposition of Formic
AcidP. MARS, J. J. F. SCHOLTEN, AND
P. ZWIETERING.Application of Spectrophotometry to the
Study of Catalytic Systems

H. P. LEFTIN AND M. C. HOBSON, Jr.

Hydrogenation of Pyridines and Quino-
lines

MORRIS FREIFELDER.

Modern Methods in Surface Kinetics: Flash
Desorption, Field Emission Microscopy,
and Ultrahigh Vacuum Techniques

GERT EHRLICH.

Catalytic Oxidation of Hydrocarbons

L. YA. MARGOLIS.

Volume 15

The Atomization of Diatomic Molecules by
Metals

D. BRENNAN.

The Clean Single-Crystal-Surface Ap-
proach to Surface Reactions

H. E. FARNSWORTH.

Adsorption Measurements during Surface
Catalysis

KENZI TAMARU.

The Mechanism of the Hydrogenation of
Unsaturated Hydrocarbons on Transi-
tion Metal Catalysts

G. C. BOND AND P. B. WELLS.

Electronic Spectroscopy of Adsorbed Gas
Molecules

A. TERLINEN.

The Catalysis of Isotopic Exchange in
Molecular Oxygen

G. K. BORESKOV.

Volume 16

The Homogeneous Catalytic Isomerization
of Olefins by Transition Metal Complexes

MILTON ORCHIN.

The Mechanism of Dehydration of Alco-
hols over Alumina Catalysts

HERMAN PINES AND JOOST MANASSEN.

 π Complex Adsorption in Hydrogen Ex-
change on Group VIII Transition Metal
CatalystsJ. L. GARNETT AND W. A. SOLLICH-
BAUMGARTNER.Stereochemistry and the Mechanism of
Hydrogenation of Unsaturated Hydro-
carbons

SAMUEL SIEGEL.

Chemical Identification of Surface Groups

H. P. BOEHM.

Volume 17

On the Theory of Heterogeneous Catalysis

JURO HORIUTI AND TAKASHI NAKAMURA.

Linear Correlations of Substrate Reac-
tivity in Heterogeneous Catalytic Reac-
tions

M. KRAUS.

Application of a Temperature-Programmed
Desorption Technique to Catalyst
Studies

R. J. CVETANOVIC AND Y. AMENOMIYA

Catalytic Oxidation of Olefins

HERVEY H. VOGEL AND CHARLES R.
ADAMS.The Physical-Chemical Properties of
Chromia-Alumina CatalystsCHARLES P. POOLE, Jr., AND D. S.
MACIVER.Catalytic Activity and Acidic Property of
Solid Metal SulfatesKOZO TANABE AND TSUNEICHI TAKE-
SHITA.

Electrocatalysis

S. SRINIVASEN, H. WROBLOWA, AND
J. O'M. BOCKRIS

Contents

CONTRIBUTORS	v
PREFACE	vii
CONTENTS OF PREVIOUS VOLUMES	xiii

Stereochemistry and Mechanism of Hydrogenation of Naphthalenes on Transition Metal Catalysts and Conformational Analysis of the Products

A. W. WEITKAMP

I. Introduction	2
II. Conformational Analysis	8
III. Experimental	19
IV. Mechanism of Hydrogenation of Naphthalene	21
V. Hydrogenation of Monomethylnaphthalenes	45
VI. Hydrogenation of Dimethylnaphthalenes	64
VII. Equilibria and Conformational Analysis of the Octahydronaphthalenes	101
VIII. Conclusions	106
References	107

The Effects of Ionizing Radiation on Solid Catalysts

ELLISON H. TAYLOR

I. Introduction	111
II. The Irradiation Technique in Catalysis	115
III. Effects of Radiation on Catalytic and Chemisorptive Properties....	130
IV. Nonspecific Effects of Radiation	179
V. Miscellaneous Topics	195
VI. Conclusions	214
Appendix I: Elementary Considerations on Dosimetry	219
Appendix II: Effects of Radiation on Catalytic and Chemisorptive Properties of Solids	219
References	248

Organic Catalysis over Crystalline Aluminosilicates

P. B. VENUTO AND P. S. LANDIS

I. Introduction and Scope	259
II. Relation between Catalyst Structure and Catalytic Activity	261
III. Organic Reactions Catalyzed by Crystalline Aluminosilicates	305
References	366

**On Transition Metal-Catalyzed Reactions of
Norbornadiene and the Concept of
 π Complex Multicenter Processes**

G. N. SCHRAUZER

I. Introduction	373
II. Properties of Norbornadiene	374
III. Some Reactions	375
IV. Catalysis of Norbornadiene Cycloaddition Reactions	377
V. Catalytic Carbonylation	380
VI. Catalytic Dimerization	381
VII. Binuclear Catalysis: The Stereospecific Synthesis of Binor-S.	387
VIII. Catalytic Reaction of $\text{Zn} [\text{Co}(\text{CO})_4]_2$ with Acetylene	393
IX. Catalytic Trimerization	394
X. Summary and Conclusions	394
References	395
 AUTHOR INDEX	 397
 SUBJECT INDEX	 411

Stereochemistry and Mechanism of Hydrogenation of Naphthalenes on Transition Metal Catalysts and Conformational Analysis of the Products

A. W. WEITKAMP

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I. Introduction	2
A. Hydroaromatics as High-Energy Fuels	2
B. Literature	4
C. Course of Hydrogenation	6
II. Conformational Analysis	8
A. Theory	8
B. Conformational Analysis of Cyclohexanes	9
C. Conformational Analysis of Decahydronaphthalenes	17
III. Experimental	19
A. Materials	20
B. Apparatus and Methods	20
IV. Mechanism of Hydrogenation of Naphthalene	21
A. Role of Tetrahydronaphthalene	21
B. Formation of Isomeric Decahydronaphthalenes	23
C. Olefin Intermediates	30
V. Hydrogenation of Monomethylnaphthalenes	45
A. Monomethyltetrahydronaphthalenes	46
B. Steric Effects	48
C. Methyldecahydronaphthalenes	49
D. Conformational Analysis	55
VI. Hydrogenation of Dimethylnaphthalenes	64
A. Dimethyltetrahydronaphthalenes	66
B. Dimethyldihydronaphthalenes	69
C. Dimethyldecahydronaphthalenes	72
D. Identification of Dimethyldecahydronaphthalenes	81
VII. Equilibria and Conformational Analysis of the Octahydronaphthalenes	102
A. Experimental	102
B. Conformational Analysis	103
VIII. Conclusions	107
References	108

1. Introduction

A. HYDROAROMATICS AS HIGH-ENERGY FUELS

Perhydro derivatives of monomethyl- and dimethylnaphthalenes should be among the very best candidates for components of high-energy, high-stability, low-volatility fuels for aviation turbine engines. A survey report published in 1960 (1), covering some 6000 compounds of diverse types, consistently pointed to the fully saturated polycyclic hydrocarbons as having favorably high densities, boiling points, and heats of combustion, as well as good burning characteristics. Not only do the perhydronaphthalenes fit into this group but also they are potentially available, via hydrogenation of methylnaphthalenes, in large quantities and at low enough cost to share significantly in what has been described as a billion dollar annual market (2).

Prior to 1960 the only perhydronaphthalenes for which physical properties were available were the *cis* and *trans* isomers of decalin.* Soon thereafter, our investigation of the hydrogenation of the two monomethylnaphthalenes led to the isolation, identification, and measurement of the physical properties of all eight of the resulting isomeric monomethyldecalins (3). The 68 dimethyldcalins, obtainable by hydrogenation of the 10 dimethylnaphthalenes, will be described in this contribution

Accurate calorimetric determination of the heats of combustion of *cis*-decalin and *trans*-decalin was reported by Speros and Rossini (4) in 1960. While these unsubstituted decalins would not possess the low volatilities desired in safety fuels, their other properties will serve to

	Heat of combustion ^a			
	kcal/mole (4)	Btu/gal	Btu/lb	Density
<i>cis</i> -Decalin	1502.92 ± 0.22	137,500	20,000	0.8963
<i>trans</i> -Decalin	1500.23 ± 0.22	133,300	19,950	0.8699
Kerosene	—	120,000	19,300	0.81

^a The heat of combustion expressed in British thermal units does not include the heat of condensation of the steam.

illustrate the potential advantage of naphthenes over the usual paraffinic kerosene-type fuels as well as the range of quality that can be expected within the naphthene class by enhancement of favorable structures.

* The term "decalin" as used here is synonymous with "decahydronaphthalene."

Most of the energy of combustion comes from the conversion of the carbon and hydrogen of the fuel to carbon dioxide and water; a minor part arises from strains that are built into the structure of the molecule itself. Accordingly, comparison of the heats of combustion on a weight basis shows only a small advantage for the naphthenes. However, the density of *cis*-decalin is more than 10% higher than that of kerosene and about 3% higher than that of *trans*-decalin. There is a significant advantage in heat of combustion on a volume basis that can be exploited for greater range or greater payload. The preferred naphthenic "super" fuels would be those with maximum contents of high-energy isomers, as exemplified by *cis*-decalin.

The 3 kcal/mole by which the heat of combustion of *cis*-decalin exceeds that of *trans*-decalin reflects energy required to isomerize the relatively unstrained *trans* isomer to the more compact *cis* configuration. Comprising, as it does, only 0.2% of the total combustion energy, this small increment is of no great significance; its importance derives almost entirely from the higher density that accompanies the intramolecular crowding that is its source.

Naphthalene and its methyl derivatives traditionally have been obtained from coal tar but petroleum is an expanding source. By 1963 petroleum-based naphthalene capacity reached about 600 million pounds and for the first time exceeded the 500 million available from coal tar (5).

While oxidation to phthalic anhydride remains the most important reaction of naphthalene, its alkyl derivatives are less desirable for oxidation and are potential raw materials for hydrogenation to high-energy fuels. Excellent jet fuels can be made by the hydrogenation of coal, coal tar, and the aromatic residues from the processing of petroleum (6). However, these materials contain heterocyclic derivatives of sulfur, nitrogen, and oxygen that poison transition metal catalysts. They can be hydrogenated under drastic conditions (420–430° and 200–250 atm hydrogen pressure) with poison-resistant catalysts such as the sulfides of tungsten and molybdenum. Maximum volumetric energy values are not realized because the drastic conditions accelerate formation of the less desirable, but thermodynamically more stable, *trans* isomers.

A large and growing source of naphthalenes is the high-boiling by-product from the reforming processes that are used for the manufacture of high-octane motor fuels, and especially the unleaded fuels. These