

COMPREHENSIVE CHEMICAL KINETICS

EDITED BY

C.H.BAMFORD M.A., Sc.D., F.R.S. and C.F.H.TIPPER Ph.D., D.Sc.

VOLUME 5

DECOMPOSITION AND ISOMERIZATION OF ORGANIC COMPOUNDS

ELSEVIER PUBLISHING COMPANY

AMSTERDAM LONDON NEW YORK

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EDITED BY

C. H. BAMFORD

M.A., Ph.D., Sc.D. (Cantab.), F.R.I.C., F.R.S.
*Campbell-Brown Professor of Industrial Chemistry,
University of Liverpool*

AND

C. F. H. TIPPER

Ph.D. (Bristol), D.Sc. (Edinburgh)
*Senior Lecturer in Physical Chemistry,
University of Liverpool*

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DECOMPOSITION AND ISOMERISATION OF
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ELSEVIER PUBLISHING COMPANY

AMSTERDAM - LONDON - NEW YORK

1972

ELSEVIER PUBLISHING COMPANY
335 JAN VAN GALENSTRAAT
P.O. BOX 211, AMSTERDAM, THE NETHERLANDS

AMERICAN ELSEVIER PUBLISHING COMPANY, INC.
52 VANDERBILT AVENUE
NEW YORK, NEW YORK 10017

LIBRARY OF CONGRESS CARD NUMBER 76-151731
ISBN 0-444-40861

WITH 35 ILLUSTRATIONS AND 228 TABLES

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Contributors to Volume 5

- T. BÉRCES Gas Kinetics Research Group of the
Hungarian Academy of Sciences,
Szeged, Hungary
- H. E. GUNNING Department of Chemistry,
University of Alberta,
Edmonton, Canada
- K. J. LAIDLER Department of Chemistry,
University of Ottawa,
Ottawa, Canada
- L. F. LOUCKS University of Prince Edward Island,
Charlottetown, P.E.I., Canada
- J. W. LOWN Department of Chemistry,
University of Alberta,
Edmonton, Canada
- H. E. O'NEAL Department of Chemistry,
San Diego State College,
California, U.S.A.
- W. H. RICHARDSON Department of Chemistry,
San Diego State College,
California, U.S.A.
- O. P. STRAUZ Department of Chemistry,
University of Alberta,
Edmonton, Canada
- E. S. SWINBOURNE The New South Wales Institute of Technology,
Broadway, N.S.W.,
Australia

Preface

The rates of chemical processes and their variation with conditions have been studied for many years, usually for the purpose of determining reaction mechanisms. Thus, the subject of chemical kinetics is a very extensive and important part of chemistry as a whole, and has acquired an enormous literature. Despite the number of books and reviews, in many cases it is by no means easy to find the required information on specific reactions or types of reaction or on more general topics in the field. It is the purpose of this series to provide a background reference work, which will enable such information to be obtained either directly, or from the original papers or reviews quoted.

The aim is to cover, in a reasonably critical way, the practice and theory of kinetics and the kinetics of inorganic and organic reactions in gaseous and condensed phases and at interfaces (excluding biochemical and electrochemical kinetics, however, unless very relevant) in more or less detail. The series will be divided into sections covering a relatively wide field; a section will consist of one or more volumes, each containing a number of articles written by experts in the various topics. Mechanisms will be thoroughly discussed and relevant non-kinetic data will be mentioned in this context. The methods of approach to the various topics will, of necessity, vary somewhat depending on the subject and the author(s) concerned.

It is obviously impossible to classify chemical reactions in a completely logical manner, and the editors have in general based their classification on types of chemical element, compound or reaction rather than on mechanisms, since views on the latter are subject to change. Some duplication is inevitable, but it is felt that this can be a help rather than a hindrance.

Section 2 deals with reactions involving only one molecular reactant, *i.e.* decompositions, isomerisations and associated physical processes. Where appropriate, results from studies of such reactions in the gas phase and condensed phases and induced photochemically and by high energy radiation, as well as thermally, are considered. The effects of additives, *e.g.* inert gases, free radical scavengers, and of surfaces are, of course, included for many systems, but fully heterogeneous reactions, decompositions of solids such as salts or decomposition flames are discussed in later sections. Rate parameters of elementary processes involved, as well as of overall reactions, are given if available.

The decompositions and isomerizations of organic compounds are discussed in this volume, aliphatic, homocyclic, aromatic and heterocyclic being considered together, where appropriate, under the general headings of (1) hydrocarbons (2) halogen compounds of all types (3) aldehydes and ketones (4) other com-

pounds of carbon, hydrogen and oxygen (alcohols, ethers, acids, esters, peroxides, etc.) (5) nitrogen compounds and (6) sulphur compounds.

The Editors express their sincere appreciation for the continued advice and support given by the members of the Advisory Board.

Liverpool
August, 1971

C. H. BAMFORD
C. F. H. TIPPER

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The Decomposition and Isomerization of Hydrocarbons

K. J. LAIDLER AND L. F. LOUCKS

1. Introduction

Substances can be made to decompose (*i.e.* to break down into smaller molecular fragments) by the action of heat and of radiation. Decomposition brought about by the action of heat alone is known as thermal decomposition, or *pyrolysis*. Processes directly induced by radiation are conveniently classified as *photolyses* or *radiolyses*. The former are those reactions in which the radiation is of such a type that it does not give rise to a substantial number of ions in the reaction system; visible light, and ultraviolet light of not too short wavelength, are of this character. Radiolyses are reactions brought about by radiations which produce ions in the reaction system; these are the higher energy radiations such as X-rays and γ -rays (which are non-particle radiations) and beams of particles like α - and β -rays.

Decomposition can also be brought about by radiations in an indirect way, the radiation being absorbed by a sensitizer which in turn induces reaction in another substance. One can therefore speak of *photosensitized* and *radiosensitized decompositions*; little systematic work has been done on the latter.

Much of this chapter is concerned with the thermal, photolytic, photosensitized and radiolytic decompositions of pure organic hydrocarbons. Since the action of heat on cyclic hydrocarbons usually leads to reactions that occur by simpler mechanisms than is the case with the other hydrocarbons, these reactions are considered first (Section 2). This section deals with isomerizations as well as decompositions. Section 3 is concerned with *cis-trans* isomerizations, in which there is twisting about a double bond. The decompositions of non-cyclic hydrocarbons are dealt with in Sections 4–7, and a final section (8) treats the effects of additives, such as inhibitors, on the various decompositions and isomerizations.

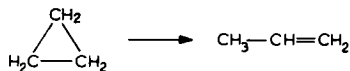
The organization of the four sections on decompositions is that we will consider the four modes of decomposition separately, giving a number of examples in each section. An alternative procedure would have been to consider the hydrocarbons separately, dealing in each case with the four modes of decomposition. The latter procedure has certain advantages, but we decided that on the whole the first would suit our purposes somewhat better. However, to help the reader who may be interested in comparing the various modes of decomposition of a given hydrocarbon we have prepared Table 1, which indicates the page on which each topic is dealt with.

TABLE I
HYDROCARBON REACTIONS

<i>Hydrocarbon</i>	<i>Mode of reaction</i>				
	<i>Pyrolysis</i>	<i>Isomerization</i>	<i>Photolysis</i>	<i>Photo-sensitization</i>	<i>Radiolysis</i>
Paraffins					
Methane	35		57	100	110
Ethane	40		61	100	112
Propane	44		66	101	114
Butanes	47		69	101	116
Pentanes	50		74		116
Higher alkanes	50				116
Olefins					
Ethylene	52		77	103	117
Propene	55		81	105	119
Butenes			83		120
Higher olefins			86	105	119
Acetylenes					
Acetylene	56		86	105	120
Propyne			88		121
Other acetylenes					121
Cyclic hydrocarbons					
Cyclopropanes		3	93	102	
Cycloalkanes		17	94		
Higher cyclic paraffins		22	95		123
Cycloalkenes		22	98		
Aromatic hydrocarbons			89	106	121

2. Reactions of cyclic hydrocarbons

During the past few years a very considerable amount of work has been done on the decompositions and isomerizations of cyclic compounds. Perhaps the most important reason for the recent interest in these reactions of cyclic hydrocarbons is that a number of them occur in a reasonably simple manner, so that they are particularly suitable for the evaluation of theories of unimolecular reactions. The simplest of these processes is the conversion of cyclopropane into propene



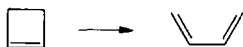
This reaction almost certainly occurs in an elementary manner, and it therefore represents one of the simplest of all unimolecular reactions. As will be discussed later, it has been carefully studied over a wide range of temperatures and pressures, and has played an important part in the testing of the theories of unimolecular reactions.

The reactions that occur when cyclic hydrocarbons are heated are of various types, and may be classified as follows.

(i) Structural isomerizations, which are of two kinds:

(a) Breaking of a carbon-carbon bond with the migration of a hydrogen atom; an example is the conversion of cyclopropane into propene (see above).

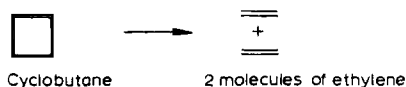
(b) Breaking of a carbon-carbon bond with bond reorganization; an example is the conversion of cyclobutene into butadiene, *viz.*



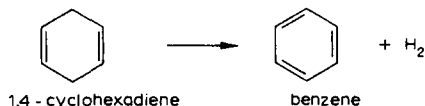
(ii) Geometrical isomerizations, involving the rearrangement of substituents (or D or T atoms) with respect to the plane of the ring; for example, *cis*-1,2-dimethylcyclopropane is converted into the *trans* form



(iii) Dissociation, with the breaking of carbon-carbon bonds, for example



(iv) Hydrogen eliminations, for example



In this section the reactions will be grouped not in terms of the above classification, but from the point of view of the structures of the parent compounds.

2.1 CYCLOPROPANE

The thermal isomerization of cyclopropane into propene has been very extensively investigated from the experimental point of view, and a considerable amount of work has been done to apply the various theories of unimolecular reactions. The reaction rate is not influenced by the surface or by inhibitors such as nitric oxide or propene; the process therefore appears to be a homogeneous unimolecular reaction. The main experimental results are summarized in Table 2. In this and