Chapter 5

The Oxidation of Organic Compounds by Non-metallic Anions

O. J. BUIST

1. Kinetics of oxidations by periodate

1.1 INTRODUCTION

Periodate is well known as a specific oxidant in organic chemistry, and it has been used extensively in structural studies of carbohydrates (see reviews by Jackson1, Bobbitt2, and Dryhurst3), its particular value is that under suitable conditions of pH and temperature its action is largely restricted to the oxidation of certain types of compounds (those classified under (a) below). For example, 1,2-diols and 1,2-diketones are readily oxidised, whereas most alcohols, aldehydes, and ketones are resistant. However, the action of periodate is not nearly so specific as was thought at one time, and there is a wide range of compounds which it is capable of oxidising (Sklarz*). Periodate oxidations of organic compounds may be classified as follows: (a) oxidations accompanied by carbon-carbon bond fission (at a suitable pH most of these proceed rapidly at room temperature or below), (b) other types of oxidations proceeding at a measurable rate at room temperature, and (c) exidations whose rate is only appreciable at higher temperatures, or in the presence of ultraviolet radiation. Oxidations of type (a) are often referred to as "Malapradian" after the discoverer of the fission of 1,2-diols by periodate (Malaprade⁶, 1928). Other compounds whose oxidations are of this type are 1,2-diketones, 1,2-hydroxyketones, 1,2-aminoalcohols, 1,2-diamines, ahydroxy acids, and z-keto acids. Most kinetic studies of periodate oxidations have concerned the reaction with 1.2-diols, but some work on other exidations of type (a) has been reported, and will be reviewed in sections 1.4 and 1.5. The very few kinetic studies of exidations of type (b) will be reviewed in sections 1.6 and 1.7. No kinetic studies of type (c) oxidations have been reported. Bunton 5 has reviewed the mechanisms of periodate oxidations.

In most of its reactions periodate is a two-electron oxidant, and it is reduced to iodate. Periodate oxidations are normally carried out in aqueous solution, but organic or mixed aqueous—organic solvents can be used (Qureshi and Sklarz⁷) and in section 1.8 the very limited amount of kinetic data available for mixed solvents is reviewed.

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Pharmaceutical Organic Chemistry, Vol 1 Mr. Rohit Manglik,2024-05-24 This volume covers the fundamentals of organic chemistry with a focus on pharmaceutical applications including structure properties and reactions of organic compounds relevant to drug development Organic Chemistry, Volume One Frank C. Whitmore,2011-12-14 A rich source of chemical facts theories and processes this two volume series treats the entire subject of organic chemistry It has served for decades as a reference for chemists in industry and education as well as a classroom text for students with a year or more of experience in organic chemistry Volume One provides thorough coverage of aliphatic compounds devoting 500 pages to the physical properties and various methods of synthetic preparation of hydrocarbons halides alcohols ethers carbohydrates proteins ketones amines monobasic acids and many other related compounds The second part of this volume discusses alicyclic compounds with reactions isomers and processes given for terpenes cyclopropane derivatives carotenoids and the cholane series Methods of synthetic preparation receive a critical analysis and many biochemical compounds are described

Advanced Techniques of Analytical Chemistry: Volume 1 Harish Kumar, 2022-02-25 Advanced Techniques of Analytical Chemistry explains analytical chemistry in an accessible manner for students The book provides basic and practical knowledge that helps the learner to understand the methods used in conducting experiments Readers will understand the key concepts of qualitative and quantitative analysis through easy to read chapters written for chemistry students Volume 1 covers the topic of volumetric analysis in detail Topic wise chapters introduce the reader to volumetric titrations and then explain the range of titration techniques which include agueous acid base titration non agueous titration redox titration complexometric titration and some miscellaneous methods like diazotisation titration Kjeldahl s method and the oxygen flask combustion method The combination of basic and advanced methods makes this an ideal textbook for chemistry students at graduate and undergraduate levels as well as an ideal handbook for the laboratory instructor A Textbook of Organic **Chemistry Vol-1** Dr. Akshay Kumar Shukla, Dr. Alka Tangri, Dr. Anjali Shukla, 2020-06-22 Knowledge of organic chemistry continues to move ahead in the many fronts This Competitor's Organic Chemistry has been thoroughly covering the subject to reflect this growth Competitor's Organic Chemistry has been divided in three volumes I II and III for the study of organic chemistry to the students of B Sc I II and III respectively These books have been written according to UGC curriculum and cover full syllabus The series of books are basically designed for the study of organic chemistry of graduate level students but these books will also be helpful and useful for many competitive examinations. The books describe the basic and fundamental concepts basic structures reactions and mechanisms of organic chemistry. An effort has also been made to guide the students for reaction based numerical problems of organic chemistry. The readers will observe that this text contains much and sufficient material and it goes more deeply into the subject It is our request that readers will provide their valuable feedback about books Metal-Catalyzed Oxidations of Organic Compounds Roger Sheldon, 2012-12-02 Metal Catalyzed Oxidations of

Organic Compounds Mechanistic Principles and Synthetic focuses on the oxidative transformations of functional groups This book explores oxidation as being extensively used in the laboratory synthesis of fine organic chemicals and in the manufacture of large volume petrochemicals Organized into two parts encompassing 13 chapters this book starts with an overview of the mechanistic principles of oxidation reduction in biochemical organic and inorganic systems This text then proceeds with a discussion of the use of molecular oxygen hydrogen peroxide and alkyl hydroperoxides as primary oxidants Other chapters explore stoichiometric oxidations with metal oxidants which include permanganate and chromic acid This book discusses as well the synthetic applications of catalytic oxidations as well as the technology of petrochemical oxidation The final chapter deals with the autoxidations of sulfur phosphorus and nitrogen compounds This book is intended for chemists involved in organic synthesis catalysis and organometallic chemistry both in academic institutions and in industrial laboratories S. Chand's Applied Chemistry Volume - 1 (For 1st Semester of Mumbai University) Dara S.S. & Shete S.D., 2022 S Chand s Applied Chemistry A Textbook of Organic Chemistry - Volume 1 Mandeep Dalal,2019-01-01 An advanced level textbook of organic chemistry for the graduate B Sc and postgraduate M Sc students of Indian and foreign universities This book is a part of the four volume series entitled A Textbook of Organic Chemistry Volume I II III IV CONTENTS Chapter 1 Nature of Bonding in Organic molecules Delocalized chemical bonding Conjugation Cross conjugation Resonance Hyperconjugation Tautomerism Aromaticity in benzenoid and nonbenzenoid compounds Alternant and non alternant hydrocarbons Huckel's rule Energy level of p molecular orbitals Annulenes Antiaromaticity Homo aromaticity PMO approach Bonds weaker than covalent Addition compounds crown ether complexes and cryptands inclusion compounds cyclodextrins Catenanes and rotaxanes Chapter 2 Stereochemistry Chirality Elements of symmetry Molecules with more than one chiral centre diastereomerism Determination of relative and absolute configuration octant rule excluded with special reference to lactic acid alanine Methods of resolution Optical purity Prochirality Enantiotopic and diastereotopic atoms groups and faces Asymmetric synthesis Cram s Rule and its modifications Prelog s rule Conformational analysis of cycloalkanes upto six membered rings Decalins Conformations of sugars Optical activity in absence of chiral carbon biphenyls allenes and spiranes Chirality due to helical shape Geometrical isomerism in alkenes and oximes Methods of determining the configuration Chapter 3 Reaction Mechanism Structure and Reactivity Types of mechanisms Types of reactions Thermodynamic and kinetic requirements Kinetic and thermodynamic control Hammond's postulate Curtin Hammett principle Potential energy diagrams Transition states and intermediates Methods of determining mechanisms Isotope effects Hard and soft acids and bases Generation structure stability and reactivity of carbocations carbanions free radicals carbenes and nitrenes Effect of structure on reactivity The Hammett equation and linear free energy relationship Substituent and reaction constants Taft equation Chapter 4 Carbohydrates Types of naturally occurring sugars Deoxy sugars Amino sugars Branch chain sugars General methods of determination of structure and ring size of sugars with particular

reference to maltose lactose sucrose starch and cellulose Chapter 5 Natural and Synthetic Dyes Various classes of synthetic dyes including heterocyclic dyes Interaction between dyes and fibers Structure elucidation of indigo and Alizarin Chapter 6 Aliphatic Nucleophilic Substitution The SN2 SN1 mixed SN1 and SN2 SNi SN1 SN2 SNi and SET mechanisms The neighbouring group mechanisms Neighbouring group participation by p and s bonds Anchimeric assistance Classical and nonclassical carbocations Phenonium ions Common carbocation rearrangements Applications of NMR spectroscopy in the detection of carbocations Reactivity effects of substrate structure attacking nucleophile leaving group and reaction medium Ambident nucleophiles and regioselectivity Phase transfer catalysis Chapter 7 Aliphatic Electrophilic Substitution Bimolecular mechanisms SE2 and SEi The SE1 mechanism Electrophilic substitution accompained by double bond shifts Effect of substrates leaving group and the solvent polarity on the reactivity Chapter 8 Aromatic Electrophilic Substitution The arenium ion mechanism Orientation and reactivity Energy profile diagrams The ortho para ratio ipso attack Orientation in other ring systems Quantitative treatment of reactivity in substrates and electrophiles Diazonium coupling Vilsmeir reaction Gattermann Koch reaction Chapter 9 Aromatic Nucleophilic Substitution The ArSN1 ArSN2 benzyne and SRN1 mechanisms Reactivity effect of substrate structure leaving group and attacking nucleophile The von Richter Sommelet Hauser and Smiles rearrangements Chapter 10 Elimination Reactions The E2 E1 and E1cB mechanisms Orientation of the double bond Reactivity effects of substrate structures attacking base the leaving group and the medium Mechanism and orientation in pyrolytic elimination Chapter 11 Addition to Carbon Multiple Bonds Mechanistic and stereochemical aspects of addition reactions involving electrophiles nucleophiles and free radicals Regio and chemoselectivity orientation and reactivity Addition to cyclopropane ring Hydrogenation of double and triple bonds Hydrogenation of aromatic rings Hydroboration Michael reaction Sharpless asymmetric epoxidation Chapter 12 Addition to Carbon Hetero Multiple Bonds Mechanism of metal hydride reduction of saturated and unsaturated carbonyl compounds acids esters and nitriles Addition of Grignard reagents organozinc and organolithium reagents to carbonyl and unsaturated carbonyl compounds Wittig reaction Mechanism of condensation reactions involving enolates Aldol Knoevenagel Claisen Mannich Benzoin Perkin and Stobbe reactions Hydrolysis of esters and amides Ammonolysis of esters March's Advanced Organic Chemistry Michael B. Smith, 2020-02-19 The completely revised and updated definitive resource for students and professionals in organic chemistry The revised and updated 8th edition of March's Advanced Organic Chemistry Reactions Mechanisms and Structure explains the theories of organic chemistry with examples and reactions This book is the most comprehensive resource about organic chemistry available Readers are guided on the planning and execution of multi step synthetic reactions with detailed descriptions of all the reactions The opening chapters of March's Advanced Organic Chemistry 8th Edition deal with the structure of organic compounds and discuss important organic chemistry bonds fundamental principles of conformation and stereochemistry of organic molecules and reactive intermediates in organic chemistry Further coverage concerns general

principles of mechanism in organic chemistry including acids and bases photochemistry sonochemistry and microwave irradiation The relationship between structure and reactivity is also covered The final chapters cover the nature and scope of organic reactions and their mechanisms This edition Provides revised examples and citations that reflect advances in areas of organic chemistry published between 2011 and 2017 Includes appendices on the literature of organic chemistry and the classification of reactions according to the compounds prepared Instructs the reader on preparing and conducting multi step synthetic reactions and provides complete descriptions of each reaction The 8th edition of March s Advanced Organic Chemistry proves once again that it is a must have desktop reference and textbook for every student and professional working in organic chemistry or related fields Winner of the Textbook Acadmic Authors Association 2021 McGuffey Longevity The Elements of Qualitative Chemical Analysis, vol. 1 Julius Stieglitz, 2020-08-13 Reproduction of the original The Elements of Qualitative Chemical Analysis vol 1 by Julius Stieglitz Green Chemistry, its Role in Achieving Sustainable Development Goals, Volume 1 Sanjay K. Sharma, 2023-10-03 Green Chemistry practices and principals can play an important role in achieving the United Nations UN special development goals The expert contributors here have selected key goals and reviewed the implementation of green chemistry for these goals As described by the UN it is crucial to harmonize three core elements economic growth social inclusion and environmental protection. The sustainable development goals embrace the sustainability mindset and this will lead to greater productivity and a greener environment For sustainable development to be achieved these elements are interconnected and all are crucial for the well being of individuals and societies Features The chapters explore sustainable development through green engineering Demonstrates the progress made in the search for processes that use fewer toxic chemicals and produce less waste while using less energy Highlights the importance of chemistry to everyday life and demonstrates the benefits the exploitation of green chemistry can have for society The pollution of water is of the utmost concern globally and bioremediation has a strong role to play in ensuring adequate supplies of high quality water These unique volumes address the vast interest in green chemistry and clean processes which has grown significantly in recent years The Chemistry of the Actinide and Transactinide Elements (Set Vol.1-6) L.R. Morss, Norman M. Edelstein, Jean Fuger, 2010-10-21 The fourth edition of The Chemistry of the Actinide and Transactinide Elements comprises all chapters in volumes 1 through 5 of the third edition published in 2006 plus a new volume 6 To remain consistent with the plan of the first edition to provide a comprehensive and uniform treatment of the chemistry of the actinide and transactinide elements for both the nuclear technologist and the inorganic and physical chemist and to be consistent with the maturity of the field the fourth edition is organized in three parts. The first group of chapters follows the format of the first and second editions with chapters on individual elements or groups of elements that describe and interpret their chemical properties A chapter on the chemical properties of the transactinide elements follows The second group chapters 15 26 summarizes and correlates physical and chemical properties that are in general unique to the

actinide elements because most of these elements contain partially filled shells of 5f electrons whether present as isolated atoms or ions as metals as compounds or as ions in solution The third group chapters 27 39 focuses on specialized topics that encompass contemporary fields related to actinides in the environment in the human body and in storage or wastes Two appendices at the end of volume 5 tabulate important nuclear properties of all actinide and transactinide isotopes Volume 6 Chapters 32 through 39 consists of new chapters that focus on actinide species in the environment actinide waste forms nuclear fuels analytical chemistry of plutonium actinide chalcogenide and hydrothermal synthesis of actinide compounds The subject and author indices and list of contributors encompass all six volumes

Energy Research Abstracts,1995**

Organic Electrochemistry, Fourth Edition, Ole Hammerich, Henning Lund, 2000-12-14 A presentation of developments in the electrochemistry of C60 and related compounds electroenzymatic synthesis conducting polymers and electrochemical partial fluorination It contains accounts of carbonyl compounds anodic oxidation of oxygen containing compounds electrosynthesis of bioactive materials electrolyte reductive coupling and more Chemistry Vol.-1 YCT Expert Team, 2022 23 NTA NEET JEE MAIN Chemistry Vol 1 Chapter wise Solved Papers Organic and Bio-molecular Chemistry -Volume I Francesco Nicotra, 2009-04-14 Organic And Bio Molecular Chemistry is the component of Encyclopedia of Chemical Sciences Engineering and Technology Resources in the global Encyclopedia of Life Support Systems EOLSS which is an integrated compendium of twenty one Encyclopedias The Theme on Organic And Bio Molecular Chemistry in the Encyclopedia of Chemical Sciences Engineering and Technology Resources deal with the discipline that studies the molecules of life which are made by carbon atoms and includes also all the synthetic compounds the skeletons of which contain carbon atoms The first chapter describes in general terms for not expert readers what Organic and Bio molecular chemistry is the nature and behavior of organic compounds in living organisms the importance of organic compounds in the market and in our every day life The subsequent chapters are organized in order to provide the reader with information on the structure reactivity analysis and different applications of Organic Compounds These two volumes are aimed at the following five major target audiences University and College students Educators Professional practitioners Research personnel and Policy analysts managers and decision makers and NGOs The Chemistry of Peroxides, Volume 3 ,2015-04-20 The understanding of functional groups is key for the understanding of all organic chemistry. In the tradition of the Patai Series each volume treats all aspects of functional groups Each volume contains chapters on the theoretical and physicochemical foundations on analytical aspects on reaction mechanisms on applications in synthesis Depending on the functional group there are additional chapters on industrial use on medical use and on human and environmental toxicity issues The last volume in the series on the topic Peroxides Vol 2 was published in 2006 In the eight years since then a lot of developments have taken place especially in the areas of synthesis analysis and a better theoretical understanding of the reaction mechanism all of which are covered here As with all new volumes the chapters are first published online in Patai s

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Transactions of the Electrochemical Society Electrochemical Society,1920 Organic Chemistry of Sulfur S.

Oae,2012-12-06 In recent years organic sulfur chemistry has been growing at an even faster pace than the very rapid development in other fields of chemistry This phenomenal growth is undoubtedly a reflection of industrial and public demands not only was sulfur recently in overall surplus for the first time in the history of the chemical industry but it has now become a prin cipal environmental hazard in the form of sulfur dioxide sulfuric acid and hydrogen sulfide Another reason discernible in the last fifteen years has been the desire on the part of individual chemists and all types of research managers to move away from the established chemistry of carbon into the less well understood and sometimes virgin chemistries of the other elements which form covalent bonds As a result of this movement the last decade has seen the development of sulfur chemistry into a well organized and now much better understood branch of organic chemistry Enough of the detail has become clear to see mechanistic interrelationships between previously unconnected reactions and with this clarification the whole subject has in tum become systema tized and subdivided The divalent sulfur chemistry of thiols monosulfides disulfides and polysulfides is a large area in itself much of it devoted to oxidation reduction and the breakage and formation of sulfur sulfur bonds although interesting discoveries are now being made about the reac tivity of certain sulfur carbon bonds Of course this area has its own mas sive biochemical branch involving enzymes and proteins

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Table of Contents Oxidation Of Organic Compounds Volume 1

- 1. Understanding the eBook Oxidation Of Organic Compounds Volume 1
 - The Rise of Digital Reading Oxidation Of Organic Compounds Volume 1
 - Advantages of eBooks Over Traditional Books
- 2. Identifying Oxidation Of Organic Compounds Volume 1
 - Exploring Different Genres
 - o Considering Fiction vs. Non-Fiction
 - Determining Your Reading Goals
- 3. Choosing the Right eBook Platform
 - Popular eBook Platforms
 - Features to Look for in an Oxidation Of Organic Compounds Volume 1
 - User-Friendly Interface
- 4. Exploring eBook Recommendations from Oxidation Of Organic Compounds Volume 1
 - Personalized Recommendations
 - o Oxidation Of Organic Compounds Volume 1 User Reviews and Ratings

- Oxidation Of Organic Compounds Volume 1 and Bestseller Lists
- 5. Accessing Oxidation Of Organic Compounds Volume 1 Free and Paid eBooks
 - o Oxidation Of Organic Compounds Volume 1 Public Domain eBooks
 - Oxidation Of Organic Compounds Volume 1 eBook Subscription Services
 - o Oxidation Of Organic Compounds Volume 1 Budget-Friendly Options
- 6. Navigating Oxidation Of Organic Compounds Volume 1 eBook Formats
 - o ePub, PDF, MOBI, and More
 - o Oxidation Of Organic Compounds Volume 1 Compatibility with Devices
 - Oxidation Of Organic Compounds Volume 1 Enhanced eBook Features
- 7. Enhancing Your Reading Experience
 - Adjustable Fonts and Text Sizes of Oxidation Of Organic Compounds Volume 1
 - Highlighting and Note-Taking Oxidation Of Organic Compounds Volume 1
 - Interactive Elements Oxidation Of Organic Compounds Volume 1
- 8. Staying Engaged with Oxidation Of Organic Compounds Volume 1
 - Joining Online Reading Communities
 - Participating in Virtual Book Clubs
 - Following Authors and Publishers Oxidation Of Organic Compounds Volume 1
- 9. Balancing eBooks and Physical Books Oxidation Of Organic Compounds Volume 1
 - Benefits of a Digital Library
 - Creating a Diverse Reading Collection Oxidation Of Organic Compounds Volume 1
- 10. Overcoming Reading Challenges
 - Dealing with Digital Eye Strain
 - Minimizing Distractions
 - Managing Screen Time
- 11. Cultivating a Reading Routine Oxidation Of Organic Compounds Volume 1
 - Setting Reading Goals Oxidation Of Organic Compounds Volume 1
 - Carving Out Dedicated Reading Time
- 12. Sourcing Reliable Information of Oxidation Of Organic Compounds Volume 1
 - Fact-Checking eBook Content of Oxidation Of Organic Compounds Volume 1
 - Distinguishing Credible Sources

- 13. Promoting Lifelong Learning
 - Utilizing eBooks for Skill Development
 - Exploring Educational eBooks
- 14. Embracing eBook Trends
 - Integration of Multimedia Elements
 - Interactive and Gamified eBooks

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