Chemical Society Reviews

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Radical Interpret Fe

Fe^{ll} + HD₂ Fe^{ll} + H₂O₂

Various iron-catalysed procedures for the functionalisation of saturated hydrocarbons have been designated 'Gif' reactions. These were originally conceived as biomimetic models for non-haem oxidase systems, and a mechanism in which high-valent iron-oxo species interact with the hydrocarbon has been adduced in support of this analogy. This review examines the evidence against an alternative free-radical mechanism. It concludes that plausible radical schemes are available for the interpretation of most, if not all, of the Gif data, but that more information is required before any unambiguous mechanistic interpretation can be justified.

On the Mechanism of Gif Reactions By Derek H. R. Barton (pp. 237-239)

A Radical Reappraisal of Gif Reactions By M. John Perkins (pp. 229-236)

Gif chemistry converts saturated hydrocarbons selectively into ketones. On a limited conversion of up to about 25%, the yield is quantitative. Two manifolds can be distinguished: Fe^{III} - Fe^{V} and Fe^{II} - Fe^{IV} . The first manifold, with a few exceptions, does not involve radical chemistry. The second always affords carbon radicals. However, for both manifolds, the K.I.E. is identical at about 2.1 and the selectivity for secondary positions is the same. The activation process, in both cases, requires the presence of an appropriate carboxylate ligand and affords a species which reacts faster with saturated hydrocarbons than with substrates which are traditionally more easily oxidized.



Application of Fluorescence Microscopy to a Study of Chemical Problems By R. S. Davidson (pp. 241-253)

The review outlines the photophysical properties that a compound should possess if it is to be of value as a reagent for fluorescence microscopy. Applications of fluorescence microscopy and related techniques to the study of the uptake of dyes by fibres, the photodegradation of dyes and polymers (e.g. wool and lignin) and for determining the softening temperatures of polymers are described.

Assembly and Encapsulation with Self-complementary Molecules By Julius Rebek, Jr. (pp. 255-264)

Molecular assemblies provide a means of evaluating intermolecular forces and chemical information involved in recognition processes. Self-complementary molecules are especially useful in this regard, and here are described synthetic structures inspired by sports equipment. These molecules dimerize through hydrogen bonding to generate pseudo-spherical capsules. Their assembled states are capable of reversible encapsulation of smaller molecules of complementary size and shape. The unusual thermodynamic parameters observed for the encapsulation process suggest a host-hostage relationship. The capsules show promise as reaction chambers.

New Approaches to Chemical Patterns By Barry R. Johnson and Stephen K. Scott (pp. 265–273)

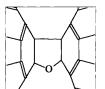
Approximately 40 years ago, Alan Turing predicted that the coupling of diffusion to complex chemical kinetics could give rise to the spontaneous development of chemical patterns. Several challenges have stood in the way of the experimental realisation of this prediction, but these have recently been overcome. Several new experimental configurations for studying the progress of reactions in space and time are now available to the chemist.

INGOLD LECTURE: Reactive Intermediates: Carboxylic Acid Enols and Other Unstable Species By A. J. Kresge (pp. 275-280)

Newly developed flash photolytic methods for generating the unstable enol isomers of simple aldehydes and ketones, under conditions where they can be observed directly and accurate new information about their chemistry can be obtained, are extended to the considerably less stable and much shorter-lived enols of selected carboxylic acids and their functional derivatives.

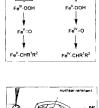
Photoelectron Spectroscopy in a New Light: Zero Kinetic Energy (ZEKE) Photoelectron Spectroscopy with Coherent Vacuum Ultraviolet Light By John W. Hepburn (pp. 281–287)

The combination of coherent vacuum ultraviolet light sources with zero kinetic energy photoelectron spectroscopy (ZEKE-PES) is discussed in this review. The generation of coherent light with photon energies up to 19 eV is described, followed by a general description of ZEKE-PES. These general remarks are followed by some specific examples, which illustrate some unusual features of ZEKE-PES.



The Changing Face of Arene Oxide-Oxepine Chemistry By Derek R. Boyd and Narain D. Sharma (pp. 289–296)

Improved methods of arene oxide synthesis by direct oxidation of arenes, and by multistep conversion of vicinal cis-diol and halohydrin precursors, provide entry to a new range of heterocyclic arene oxides (benzofuran, benzothiophene, indole, quinoline, isoquinoline, acridine). Factors which determine both the rate of interconversion and the equilibrium ratio of arene oxide-oxepine tautomers have been elucidated. Recognition that enzymemediated epoxidation can occur on arene oxide, oxepine, phenol and trans-diol, metabolites of arenes has led to renewed interest in the biological effects of these novel epoxide metabolites.



Fe^{ll} + H₂O₂











Articles that will appear in forthcoming issues include

Designing New Lattice Inclusion Hosts Roger Bishop

Potential Energy Surface Crossings in Organic Photochemistry Fernando Bernadi, Michael Robb and Massimo Olivucci

Specificity and Versatility in Erythromycin Biosynthesis Rembert Pieper, Camilla Kao, Chaitan Khosla, Guanglin Luo and David E. Cane

Glutamate and 2-Methyleneglutarate Mutase: From Microbial Curiosities to Paradigms for Coenzymes B₁₂-dependent Enzymes Wolfgang Buckel and Bernard T. Golding

Nitrous Acid and Nitrile in the Atmosphere Gerhard Lammel and J. Neil Cape

Environmentally Friendly Catalytic Methods James H. Clark and Duncan J. Macquarrie

'Covalent' Effects in 'Ionic' Systems Paul A. Madden and Mark Wilson

Non-porphyrin Photosensitisers in Biomedicine Mark Wainwright

Scanning Transitiometry Stanislaw L. Randzio

Inhibitors of Glycosphingolipid Biosynthesis Thomas Kolter and Konrad Sandhoff

The Chemistry of the Semiconductor Industry Sean O'Brien

An Odyssey from Stoichiometric Carbotitanation of Alkynes to Zirconium-catalysed Enantioselective Carboalumination of Alkenes Ei-ichi Negishi and Denis Y. Kondakov

Photo- and Redox-active [2]Rotaxanes and [2]Catenanes Andrew C. Benniston