Chem Soc Rev

Chemical Society Reviews
www.rsc.org/chemsocrev

RSC Publishing is a not-for-profit publisher and a division of the Royal Society of Chemistry. Any surplus made is used to support charitable activities aimed at advancing the chemical sciences. Full details are available from www.rsc.org

IN THIS ISSUE

ISSN 0306-0012 CODEN CSRVBR 37(3) 433–612 (2008)

Cover
See Alessandra Roncaglioni and Emilio Benfenati, page 441.
New computer programs offer a palette of tools to investigate chemicals interfering with the endocrine and reproductive system.
Image reproduced by permission of Alessandra Roncaglioni and Emilio Benfenati from *Chem. Soc. Rev.*, 2008, **37**, 441.

Inside cover
See Luiz C. Dias and Andrea M. Aguilar, page 451.
This cover pictures simple structures which can be prepared from aldol reactions of boron enolates generated from methyl ketones. The boron enolate and the aldol adducts derived from it appear as a very reactive nucleus with electrons in rings around it.
Image reproduced by permission of Luiz C. Dias and Andrea M. Aguilar from *Chem. Soc. Rev.*, 2008, **37**, 451.

CHEMICAL SCIENCE

C17

Drawing together the research highlights and news from all RSC publications, *Chemical Science* provides a ‘snapshot’ of the latest developments across the chemical sciences showcasing newsworthy articles, as well as the most significant scientific advances.

Chemical Science
March 2008/Volume 5/Issue 3
www.rsc.org/chemicalscience

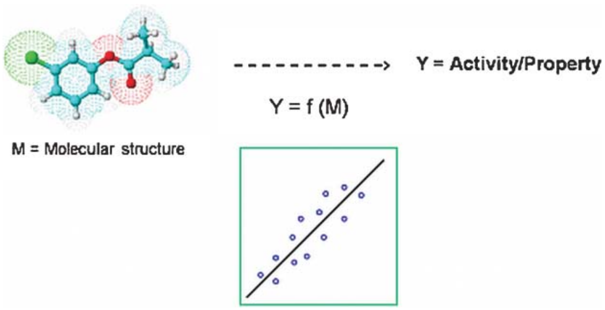
TUTORIAL REVIEWS

441

In silico-aided prediction of biological properties of chemicals: oestrogen receptor-mediated effects

Alessandra Roncaglioni and Emilio Benfenati*

In silico methods are challenging for their possible use as quick alternative methods, avoiding animal use and huge costs.



Chem Soc Rev

Chemical Society Reviews

www.rsc.org/chemsocrev

Chemical Society Reviews publishes accessible, succinct and reader-friendly articles on topics of current interest in the chemical sciences. The promotion of international and multidisciplinary awareness and cooperation is particularly encouraged. Chemical Society Reviews publishes two article types: tutorial reviews, which present an accessible introduction to the topic, and critical reviews, which provide a deeper evaluation of the current literature.

EDITORIAL BOARD

ADVISORY BOARD

INFORMATION FOR AUTHORS

The Editorial Board commissions articles that encourage international, interdisciplinary progress in chemical research. The Board welcomes proposals for new tutorial reviews or critical reviews and the appropriate synopsis pro forma should be requested from the Editorial Office (csr@rsc.org). Full details of how to submit material for publication in Chemical Society Reviews are given in the Instructions for Authors (available from http://www.rsc.org/authors). Submissions should be sent *via* ReSourCe: http//www.rsc.org/resource

Authors may reproduce/republish portions of their published contribution without seeking permission from the RSC, provided that any such republication is accompanied by an acknowledgement in the form: (Original Citation) – Reproduced by permission of The Royal Society of Chemistry.

∞ The paper used in this publication meets the requirements of ANSI/NISO Z39.48–1992 (Permanence of Paper).

Royal Society of Chemistry: Registered Charity No. 207890.

EDITORIAL STAFF

Chemical Society Reviews (print: ISSN 0306-0012; electronic: ISSN 1460-4744) is published 12 times a year by the Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge, UK CB4 0WF.

All orders, with cheques made payable to the Royal Society of Chemistry, should be sent to RSC Distribution Services, c/o Portland Customer Services, Commerce Way, Colchester, Essex, UK CO2 8HP. Tel +44 (0) 1206 226050; Email sales@rscdistribution.org

2008 Annual (print + electronic) subscription price: £514; US$995. 2008 Annual (electronic) subscription price: £463; US$896. Customers in Canada will be subject to a surcharge to cover GST. Customers in the EU subscribing to the electronic version only will be charged VAT.

If you take an institutional subscription to any RSC journal you are entitled to free, site-wide web access to that journal. You can arrange access via Internet Protocol (IP) address at www.rsc.org/ip. Customers should make payments by cheque in sterling payable on a UK clearing bank or in US dollars payable on a US clearing bank. Periodicals postage paid at Rahway, NJ, USA and at additional mailing offices. Airfreight and mailing in the USA by Mercury Airfreight International Ltd., 365 Blair Road, Avenel, NJ 07001, USA.

US Postmaster: send address changes to: Chemical Society Reviews, c/o Mercury Airfreight International Ltd., 365 Blair Road, Avenel, NJ 07001. All dispatches outside the UK by Consolidated Airfreight.

PRINTED IN THE UK

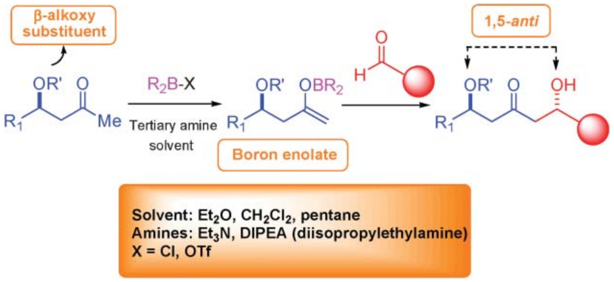
TUTORIAL REVIEWS

451

1,5-Asymmetric induction in boron-mediated aldol reactions of β-oxygenated methyl ketones

Luiz C. Dias* and Andrea M. Aguilar

Recent advances in the 1,5-asymmetric induction in boron-mediated aldol reactions of β-oxygenated methyl ketones are reviewed, demonstrating the diversity of this reaction towards synthetically useful intermediates.



470

Catalytic methods for the destruction of chemical warfare agents under ambient conditions

Bryan M. Smith

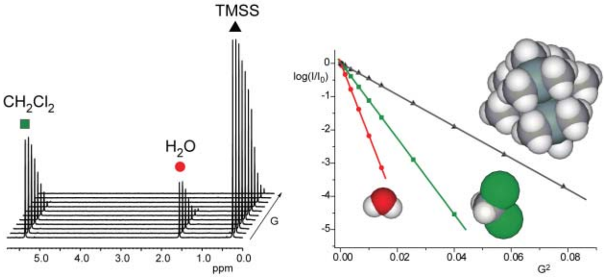
This review surveys recent advances into a wide variety of catalysts for converting chemical warfare agents into relatively benign products.

479

Determining accurate molecular sizes in solution through NMR diffusion spectroscopy

Alceo Macchioni,* Gianluca Ciancaleoni, Cristiano Zuccaccia and Daniele Zuccaccia

A "recipe" on how diffusion NMR data should be treated in order to obtain accurate molecular sizes.

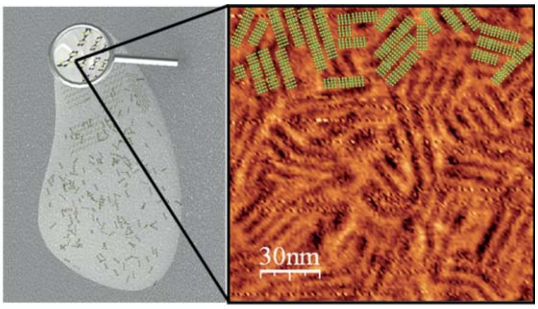


490

Assembly of functional molecular nanostructures on surfaces

Elba Gomar-Nadal,* Josep Puigmartí-Luis and David B. Amabilino

Arranging molecules precisely at surfaces through supramolecular chemistry will prove an important milestone on the road to molecular electronic devices.



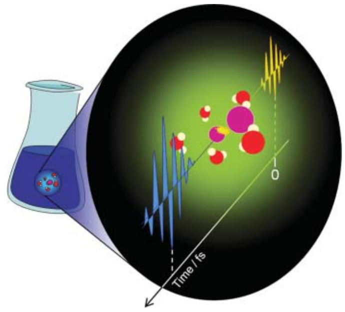
TUTORIAL REVIEWS

505

Femtosecond spectroscopy of cluster anions: insights into condensed-phase phenomena from the gas-phase

Jan R. R. Verlet

Clusters present a middle-ground between the gas- and condensed-phase. This *tutorial review* considers recent femtosecond experiments on cluster anions and shows how these can provide detailed insights into ultrafast dynamics of condensed phase systems.

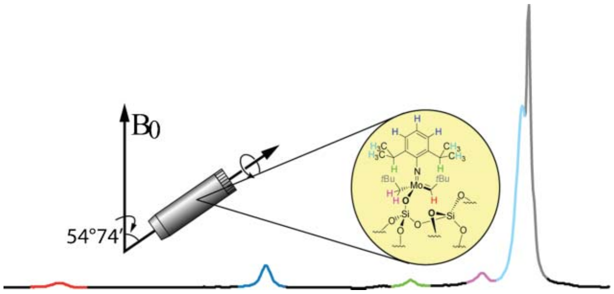


518

High resolution solid state NMR spectroscopy in surface organometallic chemistry: access to molecular understanding of active sites of well-defined heterogeneous catalysts

Frédéric Blanc, Christophe Copéret,* Anne Lesage and Lyndon Emsley*

This review will discuss some recent advances in solid state NMR focusing on their application to the understanding of surface species and active sites in heterogeneous catalysis at a molecular level.



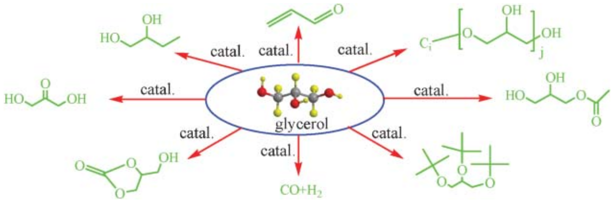
CRITICAL REVIEWS

527

Chemoselective catalytic conversion of glycerol as a biorenewable source to valuable commodity chemicals

Chun-Hui (Clayton) Zhou,* Jorge N. Beltramini, Yong-Xian Fan and G. Q. (Max) Lu*

Chemoselective catalytic conversion has shown great promise for many valuable commodity chemicals from glycerol as a biorenewable source.

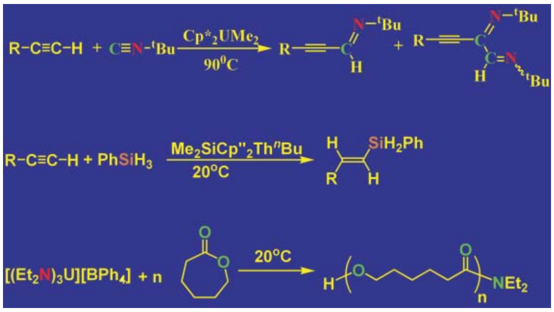


550

Recent advances in organothorium and organouranium catalysis

Tamer Andrea and Moris S. Eisen*

The unique reactivity of organoactinides in various catalytic processes stimulates the design of new complexes for highly demanding chemical transformations.



FREE E-MAIL ALERTS AND RSS FEEDS

Contents lists in advance of publication are available on the web *via* www.rsc.org/csr – or take advantage of our free e-mail alerting service (www.rsc.org/ej_alert) to receive notification each time a new list becomes available.

Try our RSS feeds for up-to-the-minute news of the latest research. By setting up RSS feeds, preferably using feed reader software, you can be alerted to the latest Advance Articles published on the RSC web site. Visit www.rsc.org/publishing/technology/rss.asp for details.

ADVANCE ARTICLES AND ELECTRONIC JOURNAL

Free site-wide access to Advance Articles and electronic form of this journal is provided with a full-rate institutional subscription. See www.rsc.org/ejs for more information.

* Indicates the author for correspondence: see article for details.

Electronic supplementary information (ESI) is available *via* the online article (see http://www.rsc.org/esi for general information about ESI).

March 2008 / Volume 5 / Issue 3 / ISSN 1478-6524 / CSHCBM / www.rsc.org/chemicalscience

Chemical Science

A fruit lactone has been found to have all the qualities of a good biofuel

A fruity alternative to fossil fuels

LES CHATFIELD

γ-valerolactone is an attractive alternative to ethanol

A naturally occurring fruit lactone could prove useful as a new type of biofuel, say Hungarian scientists.

Istvan Horvath and colleagues at Eotvos University in Budapest have found that γ-valerolactone has 'all the qualities of a good biofuel,' including being easy and safe to store and transport.

Horvath said 'of course the quantity of γ-valerolactone found in fruits is very, very small and we would not want to use a food resource as a fuel, instead we plan to convert carbohydrates obtained from agricultural residues, wood and wood wastes directly to γ-valerolactone.'

The team tested the lactone and ethanol as 10% additive:90% gasoline mixtures and found that as fuel additives their properties were very similar. However, what makes γ-valerolactone an attractive alternative to ethanol is that it is produced by a less energy demanding process, because (unlike ethanol) it can be removed by distillation. Additionally, 'its lower vapour pressure may also mean improved fuel performance', said Horvath. The lower vapour pressure means emissions of volatile organic compounds are minimised, he said. Corrosion and instability which can be a problem during storage and transportation of fuels are also avoided.

Robert Crabtree from the Centre for Green Chemistry and Green Engineering at Yale University, US, explained that it is difficult, but critically important, to find sustainable biofuels. 'Horvath has taken the first step by showing that γ-valerolactone has many of the right properties. The challenge now is to find a synthetic route that can be run economically at the scale required and which does not compete with food resources.'

Horvath has ambitious plans to improve the yields of γ-valerolactone obtained from biomass and to develop novel chemistries to enable it to be used as a feedstock for carbon-based chemicals.

Janet Crombie

Reference

I T Horvath *et al*, *Green Chem.* 2008, **10**, 238 (DOI:10.1039/b712863k)

In this issue

Artificial cells mimic ion transport
Capsule allows specific cations to pass through its surface

Something 'fishy' in the air
Humans and flatulent cows have been blamed for global warming, but plankton may also be guilty

Instant insight: Speeding up cocaine
Chang-Guo Zhan introduces the use of computational designs to develop therapeutics for treating cocaine overdoses

Interview: Model behaviour
Stephen Klippenstein tells Hilary Crichton how theoretical chemistry can help solve global warming

A snapshot of the latest developments from across the chemical sciences

Research highlights

Capsule allows specific cations to pass through its surface

Artificial cells mimic ion transport

An inorganic capsule that could be used to study cell functions has been developed by a team of German and US scientists.

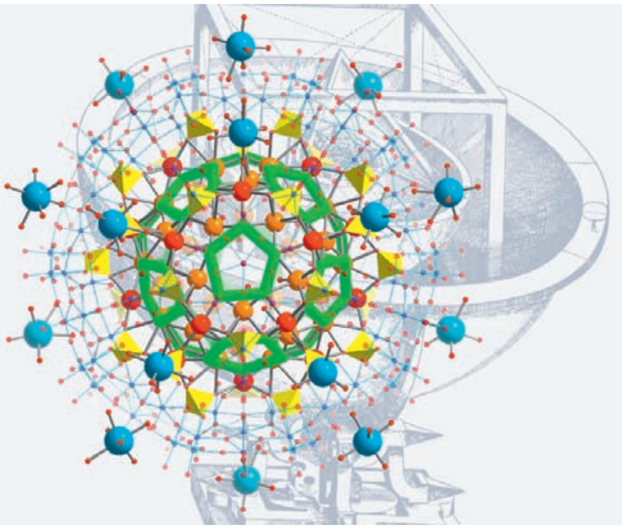
Achim Müller, University of Bielefeld, Germany, and colleagues have made a capsule that allows specific cations to pass through its surface, akin to selective ion transport through pores in cell membranes.

The metal-oxide based capsule, called a keplerate, has a similar structure to a football and has a negatively charged core. Its key function is an ability to distinguish between different cations in solution explained Müller. ‘Al^{3+} ions should have a high affinity for the capsule and its negatively charged cavity, but because these ions have strong interactions with water molecules they form complexes too large to enter, meaning Al^{3+} can only be found on the capsule surface or in solution. However, a cation such as Na+ with only weak interactions with water molecules can be found inside the cavity, even though it is less positively charged and larger,’ he continued.

The capsules can be used as artificial cell models because they are structurally well defined and have a large inner cavity. They can be used to model selective cation uptake in cells and to better understand biological transport through membranes. They can also be used to separate ions on a cellular scale. Future work could include doing coordination chemistry inside the capsules, on the surface and in the pores to adapt the model for different biological systems to be studied, said Müller.

The interesting thing is that these capsules are intrinsically very highly charged yet appear to be able to distinguish between different cations, said Lee Cronin an expert in nanoscale science from the University of Glasgow, UK. ‘This is similar to ion gating found in biology and hence these models could have a great deal of potential as nanocell models, ion storage models and even in the construction of nanoscale molecular machines with valves that can be opened or shut according to the ion size and charge,’ he said.

Michele Zgraggen



The capsule is named after Johannes Kepler - the first person to explain planetary motion

Reference

A Merca *et al*, *Chem. Commun.*, 2008, 948 (DOI:10.1039/b718260k)

Organocatalysts based on natural enzymes increase reaction rate 3.7 million-fold

Triple action catalysts

Trifunctional organocatalysts that closely mimic natural enzymes can significantly increase reaction rates, say chemists in Japan.

Tadashi Ema, Takashi Sakai and co-workers at Okayama University in Japan have made highly active organocatalysts by combining the reactivity of three separate organic components. Mimicking the catalytic triad structure found inside many enzyme active sites, the three components work cooperatively, accelerating a test reaction 3.7 million-fold.

Ema’s catalysts were inspired by lipase, an enzyme known to work through a catalytic triad. ‘With precise information about the structures and reaction mechanism of lipases, we decided to test our abilities to mimic the active site,’ said Ema. The resulting trifunctional organocatalyst has a nucleophilic OH group, a pyridine moiety, and either a urea or thiourea group.

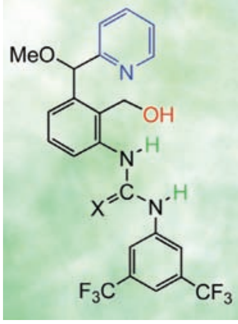
Ema tested his catalysts using the transesterification reaction, a synthetic transformation often applied to organic molecules to switch one ester side chain for another. The catalyst’s hydroxyl group, boosted in reactivity by the adjacent pyridine, initiates the reaction by attacking the ester group in vinyl trifluoroacetate – and the urea group stabilises the resulting intermediate through hydrogen bonding.

Adding the catalyst increased the rate of reaction up to 3.7 million times, depending on the exact substrate used. For comparison, Ema also made three bifunctional control catalysts each missing a different one of the three components – and found all three to be essentially inactive.

‘The observed rate accelerations are impressive,’ said Ben List, who develops organocatalysts at the Max-Planck Institute in Mülheim an der Ruhr, Germany. ‘The authors have elegantly combined previously developed organocatalysis motifs to make a highly active and promising new organocatalyst type. Designing an asymmetric version is clearly the next logical step, which I look forward to.’

Ema agrees that, along with further tuning the catalyst structure to boost reactivity levels even closer to those of enzymes, the next target will be to develop the catalyst for asymmetric synthesis.

James Mitchell Crow



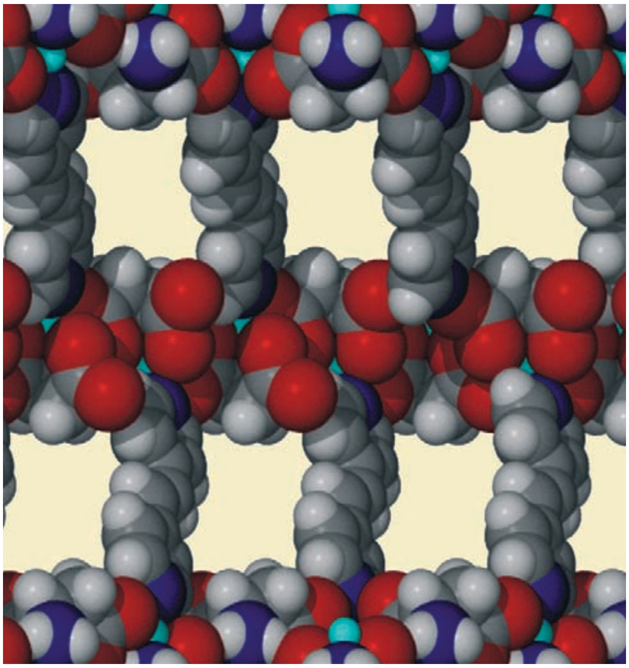
The organocatalyst has three reactive sites

Reference

T Ema *et al*, *Chem. Commun.*, 2008, 957 (DOI: 10.1039/b718763g)

Crystalline solids with chiral pores trigger stereoselective reactions

Catalytic cavities



The chiral catalyst is made using the amino acid aspartate

Chiral porous solids converted into catalysts could provide a versatile new way to trigger reactions, say chemists in the UK.

University of Liverpool chemists, Matthew Rosseinsky and co-workers, have developed a method to install catalytic activity within the pores of crystalline solids called metal organic frameworks (MOFs). Rosseinsky made a copper-aspartate based MOF, where the inherent chirality of aspartate (an amino acid) ensures a chiral environment within the solid's pores. To convert the MOF into a chiral catalyst, Rosseinsky treated it with acid, protonating the aspartate to give a catalytically active form.

'We have been working for several years on the development of chiral crystalline porous solids,' said Rosseinsky. 'Amino acids are attractive chiral components as they are cheap and have a variety of functional groups.'

The reaction used by the Liverpool group to test their catalyst was opening an epoxide with methanol. The chiral nature of the catalytic pores meant the product was formed with a modest enantiomeric excess – one of two possible mirror-image products was formed in slight preference over the other.

'This is a very nice piece of work,' commented Randall Snurr, who reserches MOFs at Northwestern University, Evanston, US. 'On paper, you can imagine a variety of ways to combine chirality and catalysis in MOFs. But in practice very few groups have achieved it.'

'MOF catalysis has the potential to marry up the best features of homogeneous and heterogeneous catalysts – a solid catalyst that is easy to recover, with well defined, identical catalytic sites,' added Snurr.

In fact, the catalytic groups in the copper-aspartate based MOF are only stable within its pores, and the homogenous phase equivalents cannot be isolated, said Rosseinsky.

'This work is about proof of principle,' added Rosseinsky. 'Making the catalytic site in a solid that cannot be made in a homogeneous catalyst. We'll need other examples of chiral porous solids, probably based on amino acids or oligopeptides, to generate sites that have better enantioselectivity. The synthetic possibilities in porous amino acid based materials are extremely broad – we will explore routes to larger pore and multiple metal systems, for example.'

James Mitchell Crow

Reference

M J Ingleson *et al*, *Chem. Commun.*, 2008, DOI: 10.1039/b718443c

Microcontainers cast like chocolate figures could prove useful for drug delivery

Repulsive containers

Microcontainers made from amino acids and polymers have potential uses in the controlled release of drugs, say German scientists.

Markus Antonietti and colleagues from the Max Planck Institute of Colloids and Interfaces, Potsdam-Golm, have made microcontainers with hollow centres from alternating layers of a positively charged amino acid-based compound and a negatively charged polymer. Attractions between the opposite charges hold the layers together.

Increasing the amount of carbon dioxide in the environment around the microcontainer causes the positively charged amino groups to reversibly switch to negatively charged carbamates. The carbamates and negatively charged polymer then repel each other causing the structure to open up.

The mild conditions needed for the switching means the microcontainers could be used to deliver medical drugs to specific locations in the body, said Antonietti. He hopes that when a microcontainer carrying a drug is administered to oxygen starved tissues - with raised levels of carbon dioxide - the container will open releasing the drug it is carrying.

These microcontainers are made by layering a compound with 11 positively charged amino groups - based on the natural amino acid lysine - and a water-soluble polymer on to a silicon dioxide template. Removal of the template leaves a hollow container. Antonietti describes this as like casting a chocolate figure.

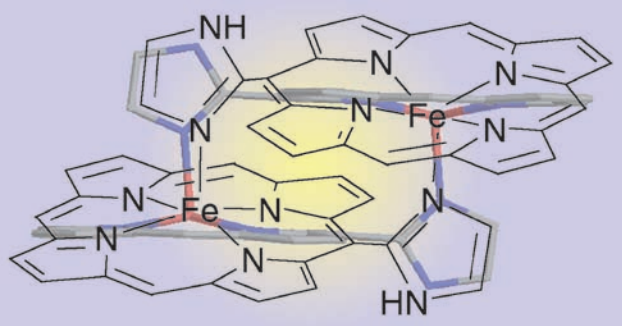
Nicola Tirelli, chair in polymers and biomaterials at the University of Manchester, UK, said that 'there is little doubt that this method can be utilised in a vast range of biomedical applications, and possibly also in bioreactor technology'.

Nicola Burton

Reference

L Hartmann *et al*, *Soft Matter*, 2008, **4**, 535 (DOI: 10.1039/b713660a)

Ironing out fuel cells



An iron complex may offer an alternative to expensive Pt catalysts in fuel cells

A simple iron complex could pave the way for new oxygen reduction catalysts with potential uses in low-temperature fuel cells, say US scientists.

The complex made by Roman Boulatov's team, at the University of Illinois at Urbana-Champaign, may offer an alternative to expensive platinum catalysts currently used for reducing molecular oxygen – the energy-releasing conversion of oxygen into water in fuel cells.

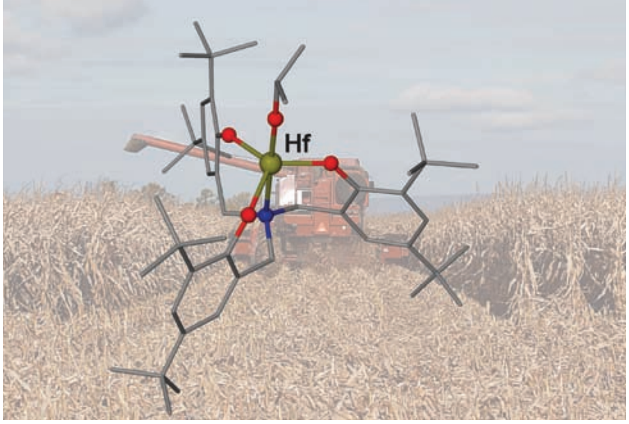
Boulatov's catalyst is a heme, an iron complex of a porphyrin, attached to a single imidazole ligand. Imidazole turns heme into a good catalyst, Boulatov explained. This complex can be made in a few short steps, exists as a stable dimer and has 'reactivity comparable to its more complex and expensive cousins', he said.

To develop these complexes into oxygen reduction catalysts, knowledge of how the enzyme cytochrome oxidase uses the heme group to reduce oxygen will be exploited, explained Boulatov. The realistic, yet challenging, goal is to use the catalysts in low-temperature fuel cells, he said. 'Porphyrin chemistry offers many opportunities to fine-tune metalloporphyrin catalysts.' *Jon Silversides*

Reference

Q.-Z. Yang *et al*, *Chem. Commun.*, 2008, 963 (DOI: 10.1039/b717858a)

Taking the initiative



Zr and Hf based initiators provide a greener route to polylactide

A new breed of initiators that aid the formation of biodegradable polymers without the need for solvents has been developed. UK researchers claim the advantages of these are faster production rates and more control of the polymer properties.

Matthew Davidson at the University of Bath and colleagues have produced zirconium and hafnium alkoxide based initiators for polylactide production. Significantly unlike earlier tin-based initiators they don't only perform well in dilute conditions. They work in solvent-free melt conditions, and also promote stereoselective polymers. This is advantageous as tuning the stereochemistry allows the polymer properties to be controlled.

Polylactide has applications ranging from packaging, to sutures and implants, and is biodegradable and derived from renewable resources such as corn starch – making it an attractive alternative to petrochemical based polymers. A desire to protect the environement and use more benign Group 4 metals was the motivation behind this work.

A leading specialist in polymerisation catalysis, Malcolm Chisholm from Ohio State University, Columbus, US, said 'melt polymerisation is of industrial interest and stereoselective polymerisation is even more interesting. Currently no other catalysts do this in the melt'.

Davidson plans to develop more benign metal based initiators for other biodegradable polymers. To do this 'a greater mechanistic understanding of the origin of stereocontrol in these systems is needed in order to design catalysts with the desired selectivity', he said. He suggested collaborations with computational chemists and detailed kinetic studies are needed next. *Michael Brown*

Reference

A J Chmura *et al*, *Chem. Commun.*, 2008, DOI:10.1039/ b718678a

Something 'fishy' in the air

Humans and flatulent cows have been blamed for global warming, but plankton may also be guilty. Now, German researchers have quantified the small, yet significant amounts of volatile organic contaminants (VOCs) – for example isoprene, dimethyl sulfide and halogenated compounds – emitted by various species of plankton into the atmosphere.

Aurélie Colomb from the Max-Planck Institute for Chemistry, Mainz, and co-workers looked at VOC emissions from five species of marine plankton using the technique head-space gas chromatography/ mass spectrometry. Colomb found that different species emitted different amounts of pollutants, and that some pollutants were emitted only by certain species. She also provided the first evidence of natural sources for pollutants such as chlorobenzene and dichlorobenzene, previously thought to be entirely human in origin.

'The potential climate impacts of various trace organic gases have been established, and the terrestrial inputs are well studied, but little is known about which of these can be emitted from plankton,' said Noureddine Yassaa, one of Colomb's co-workers. The emissions from plankton may influence global warming and the greenhouse effect in both negative and positive ways. The halogenated compounds are well known to cause the destruction of high atmosphere ozone, while isoprene oxidation produces aerosols which reflect some radiation away from the Earth.

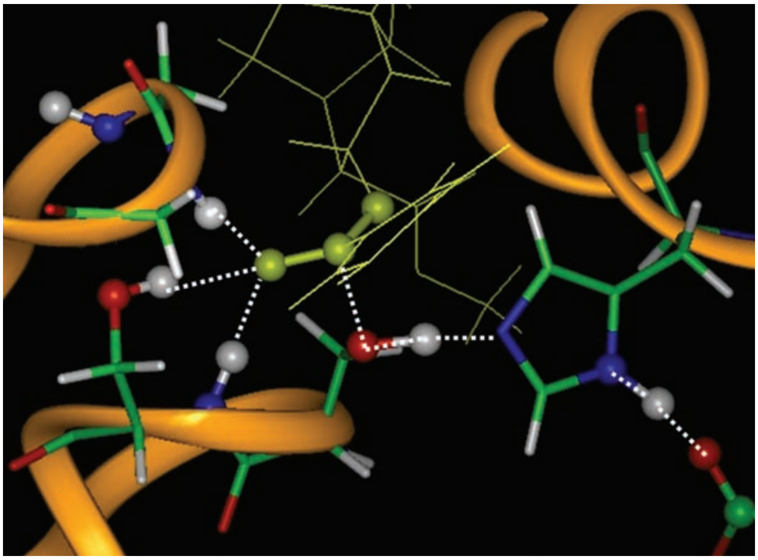
Next Colomb plans to investigate the effects of temperature, pH, and growth stage of the plankton on the emission rates. 'Experiments with mixed species will also be necessary, since emissions from one species may be consumed by another,' explained Yassaa. 'It's important to realise that climate change may also change emission levels, since it may affect the distribution and relative amounts of these plankton in the environment.'
Stephen Davey

Reference

A Colomb *et al*, *J. Environ. Monit.*, 2008, DOI:10.1039/b715312k

Speeding up cocaine

Chang-Guo Zhan from the University of Kentucky, Lexington, US, introduces the use of computational designs to develop promising therapeutics for treating cocaine addiction and overdoses



Simulated rate-determining transition state of a high-activity mutant of human butyrylcholinesterase against cocaine

Cocaine addiction and overdoses are major medical and public health problems that continue to defy treatment. The medical and social consequences of cocaine use - such as violent crime, loss in individual productivity, illness, and death - means the development of an effective pharmacological treatment has become a high priority. Cocaine anti-addiction strategies generally use the classical approach of developing small molecules that interact with one or more neuronal binding sites, with the goal of blocking or counteracting the drug's neuropharmacological actions. Despite decades of effort these approaches have not yet proved successful.

The inherent difficulties in antagonising a neuronal binding site blocker like cocaine has led to the development of a pharmacokinetic approach that acts directly on the drug to alter its distribution or increase the speed it leaves the body. This could be achieved using a molecule, such as an anti-cocaine antibody, which binds tightly to cocaine preventing it crossing the blood-brain barrier. Alternatively an enzyme that both binds to cocaine and accelerates its metabolism in the body could be used. These enzymes are designed not to cross the blood-brain barrier, meaning they would have no direct pharmacodynamic action. Ideally this would be a potent enzyme that transforms cocaine into biologically inactive metabolites.

A major cocaine-metabolising pathway in primates is hydrolysis catalysed by a plasma enzyme called butyrylcholinesterase (BChE). The metabolites of this pathway are all biologically inactive, meaning that amplifying this pathway could be a good way to speed up cocaine metabolism in users. However, the catalytic activity of this plasma enzyme is low, taking 45 to 90 minutes for cocaine to be broken down. This is too long, as it takes only a few minutes for cocaine to travel the central nervous system. A higher activity BChE that works faster is therefore needed.

To achieve this, an enzyme with the desirable catalytic activity needs to be rationally designed. Rational design is very challenging for this type of system where the chemical reaction step is rate-determining, as traditional computational design based on modeling the enzyme-substrate complex can not be used. Without decreasing the activation free energy for the rate-determining step, an enzymatic reaction cannot go faster, no matter how good the enzyme-substrate binding is.

To design the perfect enzyme for this purpose, the mechanism the enzyme uses to metabolise cocaine needs to be understood. Once the rate-determining transition state is known, a mutation can be designed with a more stable transition state structure and thus lower activation free energy.

Using state-of-the-art computational studies, encouraging progress has now been made in understanding the cocaine-metabolism mechanism. The rational design of high-activity mutants of human BChE has also been started using computational designs based on structure and mechanism. In particular, the development of a novel computational design strategy based on transition-state modeling and simulation has led to the discovery of high-activity mutants of human BChE.

High-activity mutants of enzymes or catalytic antibodies for other therapeutic purposes could also be designed using these rational computer design methods.

Read Chang-Guo Zhan's perspective on 'Structure-and-mechanism-based design and discovery of therapeutics for cocaine overdose and addiction' in issue 5, 2008 of Organic & Biomolecular Chemistry

Reference

F Zheng and C-G Zhan, *Org. Biomol. Chem.*, 2008, **6**, 836 (DOI: 10.1039/b716268e)

Bruker **BioSpin**

CryoProbe™

Just one NMR sample per hour?

Or sixteen?

The Bruker CryoProbe™ cools the NMR coils and preamplifiers to improve sensitivity by a factor of 4 and throughput by a factor of 16!

Only From Bruker...

- Over 600 cryoprobes installed in laboratories worldwide, including over 400 inverse triple resonance ^{1}H (^{13}C, ^{15}N) z-gradient Cryoprobes, used extensively for protein studies
- Sensitivity-optimised Cryoprobes for a range of nuclei (^{1}H, ^{19}F, ^{3}H, ^{13}C, ^{2}H, ^{15}N, ^{31}P, etc.)
- Available for a range of tube diameter sizes and types including 1.7mm (for small quantities), 5mm (for standard-sized samples), 10mm (for polymer applications), and shaped tubes (for high dielectric samples)
- Convertible to flow cell applications such as LC-NMR, and use with liquid handling robots
- Winner of four R&D Awards

Contact us for more details: 075 – 6285251 bruker@bruker.nl www.bruker-biospin.com

think forward

NMR Solutions

Model behaviour

Stephen Klippenstein tells Hilary Crichton how theoretical chemistry can help solve global warming

Stephen Klippenstein

Stephen Klippenstein is a senior theoretical chemist at Argonne National Laboratory, US. He is primarily interested in the dynamics of reactions important in combustion, atmospheric and interstellar chemistry.

What inspired you to become a scientist?

My parents, especially my mother, were always strong proponents of education. Aside from that, I always enjoyed learning things and was always intrigued by science. Hearing and learning about how our natural world functions was always a great joy.

What drew you to theoretical chemistry and gas phase chemical dynamics in particular?

I majored in both chemistry and mathematics for my undergraduate degree at the University of British Columbia. I enjoyed the fundamental side of mathematics as well as the applied side of chemistry. Theoretical chemistry seemed like a perfect combination of these. I was particularly drawn to gas phase dynamics as it was an area where there was an interaction between theory and experiment; one could make quantitative predictions and directly compare with detailed experiments. I was intrigued by the increasingly detailed gas phase dynamics experiments that arose from the laser age.

What projects are you working on at the moment?

We are studying the kinetics of a variety of reactions of importance in combustion, atmospheric and interstellar chemistry. Within combustion chemistry, we are interested in three key topics: soot formation; low temperature oxidation chemistry; and NO_x abatement strategies. Our studies of oxidation chemistry are designed to contribute to our understanding and development of novel engine designs, such as the homogeneous charge compression ignition engine, and of the implementation of novel fuels, such as alcohols, esters, and cyclic hydrocarbons.

Your work can be applied to help solve problems such as global warming and ozone depletion. Can you explain how?

Much of the applied work in these areas centres round the development of global chemical models, which typically include hundreds to thousands of chemical reactions. The usefulness of these models depends on the accuracy of their predictions, which in turn hinges on the accuracy of the underlying rate coefficients. The sensitivity analyses of the global modellers suggest the importance of certain key chemical reactions. Our theoretical analyses of these key reactions help to reduce the uncertainties in their rate coefficients, and thus in the overall predictions of the models. This naturally increases their utility in the search for solutions to our energy problems.

How important do you think it is to promote chemists and the positive aspects of chemical research when environmental issues are reported in the media?

I think that's very important. The focus of the media on the contribution of chemical pollution to our environmental issues is understandable. Many of the issues are important and need to be emphasised. At the same time, it is unfortunate that the more positive aspects of chemical research are seldom commented on by the media. Our knowledge of the global warming problem and our 'solution' of the ozone problem are essentially triumphs of chemical research.

What do you find to be the most rewarding aspect of your career?

I really enjoy solving problems. To me it is a lot like playing video games – you set out with an idea in mind and you just keep working at it until you get an answer. When I get there, I feel like when I've won the game!

I am always happy when I find that one of my predictions is in good agreement with experiment. It is especially fun when the initial results are in discord, and we are able to sort out the reasons for the discrepancies.

It is also enjoyable to meet up with various long term collaborators and colleagues at scientific meetings.

What advice would you give to young researchers embarking on an academic career?

Work hard, don't give up, be patient and careful. Start by choosing one thing to become a recognised expert at. As much as possible, develop a synergy between theory and experiment, and don't be afraid to collaborate with other experts who could provide the missing link for your studies.

Essential elements

ChemComm makes an impact

The first in a series of *ChemComm* International Symposia was held, with great success, in China in December. The meeting, on Polymers and Polymer Science, featured a mix of speakers from the UK, the Netherlands, the US and China and was held in three different venues: The Institute of Chemistry of the Chinese Academy of Sciences, Beijing; Fudan University, Shanghai; and Sun Yat-Sen University, Guangzhou.

ChemComm editor Sarah Thomas explained the aim of the symposium: 'The purpose of this event was to bring together scientists in a stimulating and friendly environment that will foster collaborations between the researchers and the universities involved. This was successfully achieved with the first symposium, which was met with an overwhelmingly positive response from all who took part.'

ChemComm editorial board member, and speaker at the symposium, David Haddleton was extremely impressed by the event and what it represents for advancing the chemical sciences. 'The RSC is right to focus efforts on China,' he said, 'my impression is that the Chinese are on the whole very receptive of the UK and the RSC.'

ChemComm is the flagship journal of the RSC, publishing some of the most significant work in the chemical sciences. A long and successful history has seen the journal adapt and evolve to meet the changing publishing environment. Today the journal is the fastest at publishing general chemistry communications.

Building on the success of the first symposium, two more *ChemComm* international symposia are planned over the next 18 months, both likely to be held in Asia.

Watch out for details of these events and other exciting ChemComm developments at www.rsc.org/chemcomm

Journal free for all

RSC Publishing is using a new approach to provide access to *Energy & Environmental Science*, the new journal scheduled for launch in summer 2008.

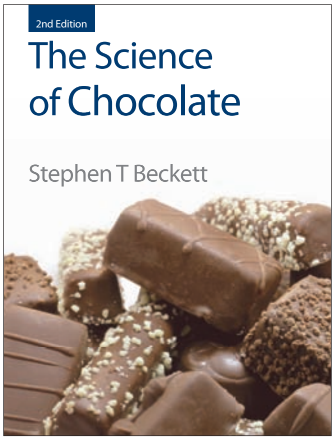
All online content will be available for free during 2008 and 2009. Access, which will be managed by institution and IP address, will be provided following a simple registration process. In addition, the current issue of the journal will be freely available to everyone online, without the need for any registration.

The new approach is in response to feedback from scientists, librarians and other information specialists. The free access will help both scientists and librarians/information specialists to fully evaluate the new journal, before they consider taking out a license or a subscription in 2010.

'We're delighted to launch this new journal in response to feedback from the community,' commented John Haynes, RSC Publishing's editorial director. 'Authors will also benefit from publishing in the journal because the access model is designed to maximise ease of use and global visibility.'

To register for free access at your institution, please complete the online form at www.rsc.org/ees_registration

Hot off the press



First published in 2000 *The Science of Chocolate* has become an international best seller! Widely used in industry and academia throughout the world, *The Science of Chocolate* has even been translated into Spanish and Japanese.

February 2008 sees the arrival of the highly anticipated 2nd edition. Readers will be pleased to hear the 2nd edition has been fully revised and updated: describing the complete chocolate making process from the growing of beans to the sale in the shops. New chapters cover topics such as nutrition, including why chocolate is good for you; how to stop it melting in hot countries; and possible methods of putting bubbles inside a chocolate bar.

A perfect book for chocolate enthusiasts and scientists alike! *For more information visit www.rsc.org/books*

Chemical Science (ISSN: 1478-6524) is published monthly by the Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge UK CB24 0WF. It is distributed free with *Chemical Communications*, *Dalton Transactions*, *Organic & Biomolecular Chemistry*, *Journal of Materials Chemistry*, *Physical Chemistry Chemical Physics*, *Chemical Society Reviews*, *New Journal of Chemistry*, and *Journal of Environmental Monitoring*. *Chemical Science* can also be purchased separately. 2008 annual subscription rate: £199; US $396. All orders accompanied by payment should be sent to Sales and Customer Services, RSC (address above). Tel +44 (0) 1223 432360, Fax +44 (0) 1223 426017. Email: sales@rsc.org

Editor: Nina Notman

Associate editors: Neil Withers, Celia Clarke

Interviews editor: Joanne Thomson

Web editors: Edward Morgan, Tina Morrell, James Hodge

Essential elements: Daniel Bradnam, Rebecca Jeeves and Valerie Simpson

Publishing assistant: Ruth Bircham

Publisher: Janet Dean

Royal Society of Chemistry: Registered Charity No. 207890.

RSC Publishing