Reporting from Tokyo

The first international symposium on Green and Sustainable Chemistry (GSC) was held in Tokyo in March 2003. I was one of some 700 people who attended this high-level event and I am delighted to report that it was a great success in terms of the programme which was stimulating and wide-reaching, the level of participation which included leading figures from academia, government and industry, and in terms of the organisation which was first class throughout. A number of the most significant papers at the Symposium will be published in this journal and we are already processing the first of these for publication in future issues.

I was very pleased to hear some inspiring papers from ‘captains of industry’ at the Tokyo meeting. There were excellent presentations from senior representatives of many companies from around the world including BASF, Rohm & Haas, Pfizer, Sumitomo, Nippon paint, Fuji and BP.

The session on ‘Implementation of GSC by Industry’ added to the impressive industrial contribution to this symposium.

There were many other notable highlights in Tokyo. The 2nd GSC Awards ceremony was held at the magnificent Chinzan-so and was open to all of the Symposium delegates. Representatives from Japanese Ministries attended the event which rewarded examples of excellence in green chemistry from researchers and from industry. One guest of honour deserves special mention—the Nobel Laureate Professor Noyori (see Profile in this issue)—who gave an excellent talk which showed real warmth for the implementation of green chemistry.

The real commitment to introducing green chemistry into the education process in Japan was highlighted by a special evening session on ‘Education and Enlightenment for GSC’ which was open to non-registrants. The session was designed to demonstrate the importance of education in promoting GSC and related experiences in teaching the next generation. There were presentations from Japan, Korea, the USA and the UK which covered school level and University education as well as public awareness. It is pleasing to see two articles in the front section of this issue of *Green Chemistry* which describe efforts to incorporate the principles of green chemistry into undergraduate chemistry practical classes. That one of them is from a developing country helps illustrate the international importance of the green chemistry educational movement.

Improving the public awareness of science and the public appreciation of the importance of chemistry in particular are also fundamentally vital areas if we are to improve the poor image that we have among the general public. I was very pleased to be involved in the organisation of a ‘first-of-a-kind’ event ‘Green Chemistry and the Consumer’ held recently in London. The workshop was organised by the Green Chemistry Network and generously sponsored by Marks and Spencer PLC. Delegates from many of the leading retail companies covering food, clothes, electronics and other consumer goods came together with representatives of the chemical industry and experts in renewable resources so as to provide a complete life cycle perspective. Representatives from government, academia, the media and pressure groups completed the audience. Retailers are in a powerful position with the potential to influence suppliers and encourage the implementation of greener processes and the availability of more sustainable and less hazardous products. One of the most lively debating topics at the workshop was on chemical testing and product toxicity issues. Whatever one’s views on the new European REACH and other systems designed to massively increase the requirements for testing the safety of chemical products, this is a sign of our times. It is very important that, like other aspects of green and sustainable chemistry, toxicity and environmental impact are also covered in the education process (see *Green Chemistry*, 2003, G13). I would be delighted to hear from any readers of examples of student courses where these topics are currently addressed.

James Clark, York, May 2003

DOI: 10.1039/b305227n

Ryoji Noyori

A research profile of Professor Noyori from Nagoya University in Japan, who shared the 2001 Nobel Prize in Chemistry with William Knowles and Barry Sharpless "for their work on chirally catalysed reactions".

Timeline

1961: Kyoto University, Bachelor, with Professor K. Sisido
1963: Kyoto University, Master, with Professor K. Sisido
1963: Kyoto University, Instructor with Professor H. Nozaki
1967: Kyoto University, Ph.D. (Dr. of Eng.), with Professor H. Nozaki
1968: Nagoya University, Associate Professor
1969–1970: Harvard University, Postdoctoral Fellow with Professor E. J. Corey
1972 to present: Nagoya University, Professor
1979–1991: Nagoya University, Director of Chemical Instrument Center
1991–1996: Research Development Corporation of Japan, Director of ERATO Noyori Molecular Catalysis Project
1992–1996: Ministry of Education, Science and Culture, Science Advisor
1993–1996: Kyushu University, Adjunct Professor
1996–2003: Ministry of Education, Science and Culture, Member of Scientific Council
1997–1999: Nagoya University, Dean of Graduate School of Science
1997–1999: The Society of Synthetic Organic Chemistry, Japan, President
2000 to present: Nagoya University, Director of Research Center of Materials Science
2001 to present: The Japan Society for the Promotion of Science, Science Advisor
2002–2003: The Chemical Society of Japan, President
2002 to present: Nagoya University, Director of Institute for Advanced Research
2002 to present: Meijo University, Guest Professor

Awards

Major Awards: Chemical Society of Japan Award (1985); Asahi Prize (1992); Tetrahedron Prize (1993); Japan Academy Prize (1995); Arthur C. Cope Award (1997); Person of Cultural Merit (1998); King Faisal International Prize (1999); The Order of Culture (2000); Wolf Prize in Chemistry (2001); Roger Adams Award (2001); Nobel Prize in Chemistry (2001).

Honorary Degrees: Technische Universität München (1995); University of Rennes (2000); University of Bologna (2002); University of Alicante (2003); Uppsala University (2003); University of Ottawa (2003); University of Chicago (2003).

Honorary Professorships: Shanghai Institute of Organic Chemistry (2001); Hong Kong Polytechnic University (2002); South China University of Technology (2002).

Academies: Pontifical Academy of Sciences (2002); Japan Academy (2002); National Academy of Sciences, Washington, DC (2003).

Honorary Memberships: American Association for the Advancement of Science (1996); Chemical Society of Japan (1998); Royal Society of Chemistry, London (2000); American Academy of Arts and Sciences (2001); European Academy of Sciences and Arts, Vienna–Salzburg (2001); Society of Synthetic Organic Chemistry, Japan (2002); Pharmaceutical Society of Japan (2002); Kinki Chemical Society (2002); European Academy of Sciences, Brussels (2002).

Ryoji Noyori was born on September 3, 1938, in Kobe, Japan. He now lives in Nisshin City, a suburb of Nagoya, with his wife, Hiroko, and their older son, Eiji, who is working as a staff writer for a newspaper company. Their younger son, Koji, studies painting at an art university in Tokyo. Currently, Noyori conducts research and teaches at Nagoya University, but he is deeply involved in public and administrative works in Tokyo. He very frequently travels back and forth between Nagoya and Tokyo and also gives many lectures worldwide. The official duties and administrative responsibilities associated with being a senior scholar currently demand much of his time, which is otherwise dedicated to advancing the field of synthetic chemistry.

Research

Chemistry is not merely a science of making observations in order to better understand Nature. It is creative and productive. We chemists are proud of our ability to create high values from almost nothing on the basis of accumulated scientific knowledge. Our field of study has greatly enhanced the quality of life worldwide by providing an impressive range of useful man-made substances and materials. In order to realize the

DOI: 10.1039/b305339n

> "We chemists are proud of our ability to create high values from almost nothing on the basis of accumulated scientific knowledge"

sustainable development of the global society in this new millennium, advanced chemical processes must be economical, safe, environmentally benign, and resource- and energy-saving. Thus new catalytic systems effecting 'perfect chemical reactions' will be in increased demand; such reactions would give only the desired products, with 100% selectivity and 100% yield, and without unwanted waste products. Every reaction of a multi-step synthesis should proceed with a high atom-economy, and the overall synthesis needs to be accomplished with a low E (ecological) factor. Long before Green Chemistry received proper appreciation, the Noyori research group had already consistently focused on molecular catalysis and, consequently, contributed in many ways to the progress of modern chemistry directed toward this goal.

Hydrogenation is a core technology in the field of chemical synthesis. When it gives the desired selectivity, this catalytic approach is much more beneficial than conventional stoichiometric metal hydride chemistry. For quite some time, we have engaged in the development of efficient asymmetric hydrogenation, where the designing of efficient chiral catalysts and the selection of suitable reaction conditions are the key issues. In 1980, we devised a new atropisomeric chiral diphosphine referred to as BINAP. In particular, our discovery of BINAP–Ru(II) complex catalysts led to the asymmetric hydrogenation of functionalized olefins and ketones of high generality. Furthermore, our invention of the catalysts of the type $RuCl_2$(diphosphine)(1,2-diamine) provided a major breakthrough in stereoselective organic synthesis. This method enabled the asymmetric hydrogenation of a wide range of aromatic, hetero-aromatic, and olefinic ketones. This reaction is very rapid, productive, and stereoselective, and it provides the most practical means of converting simple ketones to desired chiral secondary alcohols. Furthermore, we invented a range of η^6-arene–Ru(II) catalysts modified with a chiral β-amino alcohol or a 1,2-diamine derivative that enabled the asymmetric transfer hydrogenation of ketones and imines using 2-propanol or formic acid as hydrogen donors. These processes have been applied in the synthesis of numerous chiral compounds including terpenes, vitamins, β-lactam antibiotics, α- and β-amino acids, alkaloids, prostaglandins, and other compounds of biological interest. Further technical refinements have led to the large-scale industrial production of the synthetic intermediates of antibiotic carbapenems and an antibacterial quinolone, among other pharmaceuticals. The efficiency of the asymmetric catalysts discovered by the Noyori group rivals or, in certain cases, exceeds that of enzymes.

The BINAP–Rh(I) complexes were found to catalyze asymmetric isomerization of allylic amines to enamines of high enantiomeric purity. The reaction using geranyldiethylamine, giving (*R*)-citronellal diethylenamine, currently plays a key role in the industrial production of (−)-menthol and other optically active terpenes, producing a total of 2000 tons per year. This process was accomplished at Takasago International Co. together with the research groups of S. Otsuka and H. Takaya.

Recent progress in asymmetric synthesis has revolutionized the approach to chemical synthesis. Efficient asymmetric catalysis now generally utilizes chiral organometallic molecular catalysts that consist of a metallic element and a beneficially shaped chiral organic ligand(s). This widely practised catalytic principle dates back to our discovery in 1966 of the asymmetric cyclopropanation of styrene with diazoacetates in the presence of a small amount of a chiral Schiff base–Cu complex, although only a low level of enantioselectivity was achieved with that earlier catalyst.

Organic reactions are performed largely in liquid organic solvents. For both scientific and environmental reasons, the development of new reaction media is now becoming extremely important. We demonstrated for the first time the remarkable utility of supercritical CO_2 as a 'green' medium for homogeneous catalysis by accomplishing the hydrogenation of supercritical CO_2 catalyzed by $RuH_2[P(CH_3)_3]_4$ or $RuCl_2[P(CH_3)_3]_4$. Hydrogenation in the presence of triethylamine occurs very rapidly, whereas the addition of methanol results in thermal esterification, producing methyl formate in a high yield. Hydrogenation in the presence of dimethylamine, giving DMF, proceeds with unprecedented efficiency. This finding has served as the basis for further studies investigating the utility of supercritical fluids in other catalytic reactions.

Although oxidation is a fundamental means of converting petroleum-based materials to useful chemicals with a higher oxidation state, this remains an extremely problematic process from an environmental point of view. Many textbook oxidation methods are unacceptable for practical synthesis. H_2O_2, viewed as an adduct of an O atom and an H_2O molecule, is a 'green' and relatively cheap [<0.7 US dollar kg^{-1} (100% H_2O_2)] oxidant that is attractive for liquid-phase reactions. Recently, we found that, when coupled with a tungstate complex and a quaternary ammonium hydrogensulfate as an acidic phase-transfer catalyst, aqueous H_2O_2 oxidizes alcohols, olefins, and sulfides under organic solvent- and halide-free conditions in an economically, technically, and environmentally satisfying manner. The turnover numbers of the biphasic oxidation of secondary alcohols to ketones were two orders of magnitude higher than any previously reported. With this approach, straight-chain primary alcohols can be directly oxidized to carboxylic acids. In addition, this method allows the epoxidation of various olefins, including terminal olefins which are otherwise cumbersome substrates to epoxidize. We now strongly recommend that the current practices using toxic stoichiometric oxidants be replaced by these more efficient catalytic processes. The H_2O_2 oxidation method was successfully applied to achieve the direct conversion of cyclohexene to analytically pure, colorless adipic acid. The current industrial production of adipic acid employs the nitric acid oxidation of cyclohexanol or a cyclohexanol–cyclohexanone mixture. In contrast, this newly developed 'green route' avoids the emission of N_2O, which is a known contributor to global warming and ozone depletion.

Our endeavors are not limited to Green Chemistry. Other major accomplishments in the field of asymmetric synthesis have included the invention of a chirally modified lithium aluminium hydride reagent and its application to prostaglandin synthesis; the establishment of a three-component asymmetric synthesis of prostaglandins; the discovery of a highly enantioselective addition of dialkylzincs to aldehydes catalyzed by chiral amino alcohols and the elucidation of the molecular mechanism of the chirality amplification (non-linear effects); and the demonstration of the general utility of dynamic kinetic resolution in asymmetric catalysis. The iron carbonyl–polybromo ketone reaction, discovered during my early days in Nagoya, enabled the construction of five- and seven-membered carbocycles in a [3 + 2] and [3 + 4] manner, respectively. My research group exercised initiative in the catalytic use of organosilicon compounds for organic synthesis. In addition, we explored a series of synthetic methodologies using organocopper, -tin, and -zinc reagents for selective carbon–carbon bond forming reactions. The combined use of these reactions with our asymmetric reduction of ketones has resulted in the long-sought convergent synthesis of prostaglandins. We also achieved the first truly efficient synthesis of solid-anchored DNA oligomers using organopalladium chemistry. Overall, the applications of our original and versatile approaches have allowed us and many other scientists to achieve the truly efficient synthesis of numerous organic molecules of theoretical and practical importance.

Conclusion

Chemical synthesis is crucial for the future of mankind because this significant realm provides a logical and technical basis for the natural sciences and technologies. Thus, chemists have an immense responsibility to solve a wide range of current, or even unforeseen, social and global problems associated with health, synthetic materials, food, energy, the environment, and many other aspects of life. Theoretically, we can synthesize an infinite variety of compounds in any quantity. However, the practical synthesis is currently limited to the production of substances in small volumes and to those with a very high value. Synthetic efficiency is in reality limited only by scientific principles and the boundary conditions of our planet, rather than by economical and biological factors. Chemists are thus encouraged to develop truly efficient processes at all costs, and the key phrase in this context should be ‘Practical Elegance’. Without Green Chemistry, chemical manufacturing will be unable to survive into the 22nd century. However, these are not matters of clear-cut scientific or technical expertise, but rather these issues are serious, complex social issues. In addition to our efforts as scientists, public understanding and agreement, as well as worldwide cooperation, are crucial for the realization of sustainable societies. Most importantly, such endeavors not only protect our environment but also greatly contribute to an improvement in the quality of life for future generations. If we can dream today, we can live tomorrow.

> “Without Green Chemistry, chemical manufacturing will be unable to survive into the 22nd century”

Makoto Misono

A research profile of a leading Japanese green chemist

Personal summary

Makoto Misono was born on 1 March 1939 in Kagoshima (Kyushu Island), Japan. At the age of seven, after a few years in Taiwan and Yamaguchi, he moved to Tokyo. Since then he has lived in Tokyo, except for 28 months in the USA. Married in 1970 to Yoshiko, he has two daughters.

Career

Misono graduated from the Department of Applied Chemistry, University of Tokyo, in 1961 with a Bachelor's degree and obtained his Master's degree (1963) and Doctorate (1966) in engineering from the same university. He started his academic carrier as a research associate of the university in 1966 and was promoted stepwise to a full professor in catalytic chemistry in 1983. In 1999, he retired with an Emeritus professorship and became a professor at the Department of Environmental & Chemical Engineering at Kogakuin University (located in Shinjuku, the busiest district of Tokyo). He was elected a member of the Science Council of Japan in 2000 and recently was elected the President of the Chemical Society of Japan for 2004.

From 1967 to 1969, Misono stayed in the USA as a postdoc, one year at University of California, Santa Barbara (with Professor P. W. Selwood) and another year at the Mellon Institute, Pittsburgh (with Dr. W. Keith Hall). In addition, he spent two months in 1996 as an Ipatieff Lecturer at Northwestern University, USA, and a month as a Professor Emeritus at Litoral University, Argentina.

From 1995–1998 Misono ran a project on catalysts of unique reaction fields (environmental and microporous catalysts) which was funded (0.7 billion ¥) by the Ministry of Education. He is now (2002–2007) a project director of the nano-structured environmental catalyst program within the 3 billion ¥ Governmental Nanotechnology initiative.

Research

Makoto Misono started his research in 1960 in the field of heterogeneous catalysis. The study of engineering sciences (or design-oriented sciences) has been a research focus throughout his career, but his research interests have changed somewhat to reflect the rapid growth and subsequent decline of heavy industries in Japan. First he worked on catalysts for the petrochemical industry and, after several oil crises, on more fundamental studies, as well as environment- and energy-related catalysts, as described below. He is no longer directly involved in experimental research, but is involved mainly in environment-related issues such as green/sustainable chemistry, clean fuels, alternative energies, and automobile emission control in both academic and government circles.

Misono's earliest research was on solid acid catalysts to find correlations between catalytic performance and the acidity of catalysts. His first paper was about *in situ* measurement of the acidity of silica–alumina and was presented at the Third International Congress on Catalysis (3 ICC) at Amsterdam in 1964. The strong dependency of catalytic activity on acid strength was demonstrated. Then he attempted to elucidate the relationships between acid strength and catalytic performance. He found good correlations for catalytic activity (oligomerization of propene), and selectivity (isomerization of butenes). He also proposed parameters for soft and hard acids and bases, referring to several data books. This time-consuming work broadened his view of chemistry. His major background is physical chemistry for industry, so the underlying principle was to find general rules for catalyst design, in particular, to establish the following three relationships (eqn. 1):

$$\text{Catalytic performance} \Leftrightarrow \text{Chemical and physical properties}$$
$$\Leftrightarrow \text{Composition and structure} \Leftrightarrow \text{Method of syntheses} \qquad (1)$$

In this period, the first relationship of eqn. 1 was focused as directed by his supervisor. Later, stress was also placed on the second and third relationships, noting the variety and diversity of chemistry.

Misono's studies during his postdoc were also on heterogeneous catalysis, but with different aims. In a small laboratory at Santa Barbara, USA, he discovered the effect of a magnetic field on *o*- to *p*-conversion of hydrogen. Under an extrinsic magnetic field, the reaction over ruby powder or chromia was accelerated or suppressed significantly depending on

DOI: 10.1039/b305229j

the temperature and the magnitude of the magnetic field. This phenomenon was not expected from the conventional theory and was hence called, for a while, the 'Misono–Selwood effect.' The effect was suggested to be the origin of the ability of migratory birds to find their direction (Selwood, *Nature*, 1970).

In Pittsburgh, reduction and oxidation of copper in hydroxyapatite was studied in an orthodox way. Reduction by hydrogen took place for diluted copper as follows: atomic Cu(2+) → atomic Cu(+) → Cu(0) cluster, and, upon re-oxidation, Cu(0) → Cu(2+) oxide → atomic Cu(2+). Cu(+) was most active for H_2–D_2 isotopic equilibration.

Misono learned some valuable things in the USA:

- the presence and influence of a different culture in both daily life and the way in which research is conducted
- the importance of stoichiometry in chemistry
- the vital importance of originality in research

After he returned to Tokyo, Misono slowly restored the importance of research, at a time when student movements in the late 1960s were still active. He found distinct relationships between acid–base properties and the selectivity and stereochemistry for dehydrohalogenation of haloalkanes and became productive in the publication arena. Rational interpretation for the above relationships was given based on the detailed mechanism elucidated by tracer studies and quantum chemical calculations.

At that time, the chemical industry suffered from pollution problems, and chemical technology was criticized by the public. As he was conscious of these issues, Misono thought that new approaches and new catalytic technology were needed and hence started two research projects on mixed oxides.

From the beginning, he placed a strong emphasis on catalyst structure and preparation, *i.e.* the second and third relationships in eqn. 1, in order to form the scientific basis for industrial catalysts. He set up several criteria to choose appropriate catalyst materials to study:

- the structure of catalysts must be well characterized, at least for the solid bulk
- the composition and hence the chemical properties must vary across a wide range by substitution of constituent elements, maintaining the bulk structure
- the catalytic performance must not be far from the level required for commercialization

According to these criteria, crystalline mixed oxides such as heteropoly compounds (or polyoxometalates), perovskites, V–P–O, and a few more compounds have been chosen since the mid-1970s. The study started with the elucidation of bulk structure, in particular, with the confirmation of molecularity of solid heteropoly compounds, followed by the measurement of chemical properties and catalytic performance. Many unexpected phenomena that convinced him of the wonder and depth of chemistry came across in this period. The findings of hierarchical structure and the three types of catalysis for solid heteropoly compounds, he believes, have provided the sound basis of catalyst design of heteropoly compounds at the molecular level (*Chem. Commun.*, 2001, 1141). The presence of bulk-type catalysis (*e.g.*, 'pseudoliquid' behavior) is very unexpected, and the idea solved several puzzles present at that time in the literature. These achievements were presented as a plenary lecture at the 10th International Chamber of Commerce (ICC) World Congress in Budapest in 1992. Several large-scale chemical processes were industrialized in Japan utilizing heteropoly compounds, although Misono's contribution was only to basic understanding. Most of these processes are very green (Misono *et al.*, *Pure Appl. Chem.*, 2000).

The second subject, *i.e.* environmental catalysis, was chosen to publicize the usefulness of catalysts to the general public. A perovskite catalyst was commercialized for the suppression of smoke and cooking smells in kitchens; 50,000 of these catalytic devices were sold annually in the 1980s. Recently, a motor company successfully applied Pd-perovskite catalysts to control automobile emissions.

Professor Misono received awards from the Chemical Society of Japan in 2001 and 1987, the Catalysis Society of Japan (CSJ) in 1994, and the Petroleum Institute of Japan in 1996 for these studies.

His research efforts in the last two decades have essentially followed the same direction with respect to Green Chemistry (GC). Environmentally friendly catalytic processes have long been the common concern of chemical engineers in Japan and in this area Japan made remarkable achievements in the 1970s and 1980s (Misono and Nojiri, *Appl. Catal.*, 1990 and 1993). In 1990, he founded the Environmental Catalyst Forum in Japan and, with the help of colleagues, has organized international and national forums many times. He led the committee for environment and safety, CSJ, from 1999–2003. Based on these activities, he became one of the founders of the GC Forum, CSJ (1999) and the GSC Network (2000).

Conclusion

The roles for catalytic science and technology obviously continue to expand. The difficulty is that the catalytic performance characteristics now needed have become too tough to achieve by current catalytic science and technology. New catalytic technology is urgently needed. The design of catalysts at the atomic level, which can integrate multi-functions, is probably the goal. If enzymes were tolerant and active enough, they would be the ideal catalysts. However, this is not yet true and progress in synthetic catalysts is still rather slow. Therefore the new technology goals are still distant.

There are two possible approaches to overcome the current difficulties. One is a steady but very slow approach, which constructs catalyst building blocks step by step on a purely scientific basis. Another is the engineering approach, which establishes key technologies for catalyst design. For example, elucidation of the catalytic chemistry of noble metals supported on oxide in an oxidizing atmosphere is undoubtedly the key to the development of efficient environmental catalysts; little reliable information on this has been gained in the last decade.

As for GC, the top priority targets must be identified taking into account economy and contemporary technology, and the benefits of GC must be assessed in a transparent manner, that is visible to the community. Sound metrics which promote innovative R&D will help in this regard. GC sometimes promotes an image of chemistry that is 'less negative'. It is very desirable, if not essential, to erase this image, for example, by ensuring that green chemistry is synonymous with innovative chemistry.

Bert Holland

Ian Brindle from Brock University, Canada, writes an obituary of a man who made many contributions to green chemistry, especially in the area of biotransformations

Professor Herbert Leslie Holland FRSC(UK), MCIC, Professor of Chemistry at Brock University, Canada, passed away peacefully, surrounded by his family, on the 7th of April after a courageous battle with cancer. Bert was always a soft-spoken colleague, whose teaching was greatly appreciated by many generations of students. Bert was born in Bolton, UK, and attended Canon Slade School. Subsequently, he took a degree in Chemistry at Cambridge, followed by an MSc at Warwick University and a PhD at Queen's University in Belfast, where he worked with the eminent Professor Henbest. He spent the years between 1972 and 1976 at McMaster, Ontario, Canada, as a post-doctoral fellow and later as a teaching fellow, working with Professor Dave MacLean.

Bert was an eclectic researcher and he wholeheartedly immersed himself in the new area of biotransformations, an area in which he made major contributions to the understanding and exploitation of microbial systems and enzymes for chemical transformations. He was the author of over 120 papers and communications, more than 30 reviews and book chapters, and two books on biotransformations. Bert's interests in biotransformations led him naturally to the area of green chemistry where he made substantial contributions at a Gordon Conference, where he chaired a session in the conference that was organized by another Brock Alumnus, Professor James Clark of York University, UK. He is remembered by a colleague from the White House Office of Science & Technology, Dr. Paul Anastas, who writes: 'Bert Holland brought perspective, thoughtfulness and creativity to all of his work and this was especially true of his work in green chemistry. While Bert will certainly be missed his contributions will long be appreciated and built upon.'

Bert and I were born in the same town and we shared many conversations about the oddities of Lancashire dialect. There are Lancashire words that I will no longer be able to use, since Bert is no longer around to nod and say 'Aye'. An avid train enthusiast, Bert also wrote books on steam trains and one of his last books was "Plodder Lane for Farnworth"; a small monograph that describes the railway line that ran through the small station that was virtually at the end of the street on which Bert lived as a child.

Bert's wife Fran was his companion on the many trips that they took to conferences, she also looked after the students in the research labs and helped students with techniques in the lab and she assisted scores of Bert's students through the travails of research work and thesis production. Bert's legacy of students, who can be found across the world, will be deeply saddened by his loss. Bert leaves his wife Frances, and sons Giles and Colin.

Ian D. Brindle is Dean, Faculty of Mathematics and Science and Professor of Chemistry at Brock University, St. Catharines, Ontario L2S 3A1, Canada (e-mail: ibrindle@brocku.ca)

Postscript: James Clark, Scientific Editor of *Green Chemistry*, adds: 'I knew Bert from when he was a young academic at Brock to when he became an internationally leading scientist for his excellent work on biotransformation. I always enjoyed his company – he was a skilled chemist with a real belief in green chemistry. His contributions to meetings I organised were always intelligent and positive. Bert was a modest man and someone who found time for people. As my colleague Helen Coombs said when I told her of Bert's death 'He was always so pleasant'. Bert was a gentleman and a scholar. We will miss him very much.'

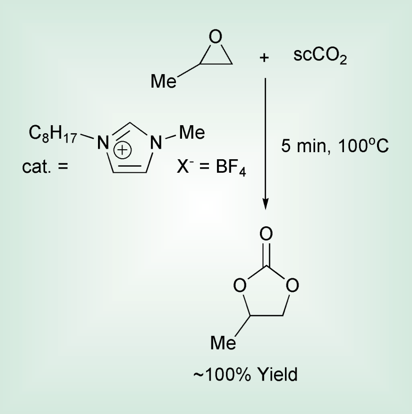
DOI: 10.1039/b305228c

Highlights

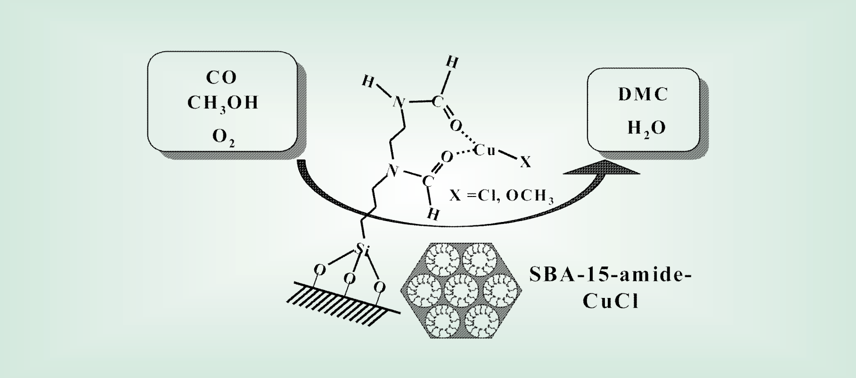
Duncan Macquarrie reviews some of the recent literature in green chemistry

Carbonylations

Formation of propylene carbonate from propylene oxide and CO_2 is an active theme as it produces the important cyclic carbonates without using phosgene. Hajime Kawanami, Yutaka Ikushima and colleagues from the National Institute of Advanced Industrial Science and Technology, and CREST in Japan have now provided a very efficient synthesis of this product using a combination of ionic liquids and supercritical CO_2 (*Chem. Commun*., 2003, 896). The ionic liquid functions as a reaction medium and as an acid–base catalyst for the reaction. With the correct ionic liquid and the right conditions, the reaction can proceed to completion in under 5 minutes, compared to the 6 hours or more required in systems not involving the ionic liquid, but with other acid–base catalysts. A series of other cyclic carbonates were also produced in good yields.

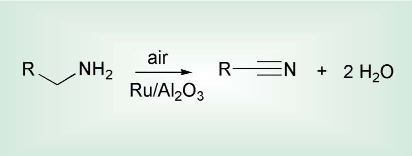


A related area is the carbonylation of methanol to dimethyl carbonate (below). This has been investigated by Yong Cao, Kang-Nian Fan and their colleagues from Fudan University in China. They found that a mesoporous silica (SBA-15) could be functionalised with a diamide ligand capable of coordinating CuCl (*Chem. Commun*., 2003, 908). This species was able to catalyse the oxidative carbonylation of methanol in excellent yields and selectivities.



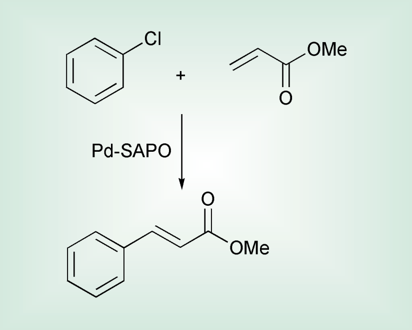
Oxidations

The oxidation of amines to nitriles or (in the case of secondary amines) to imines is a transformation normally carried out by stoichiometric quantities of high oxidation state metals. Now Kazuya Yamaguchi and Noritaka Mizuno of the University of Tokyo, Japan, have shown that these transformations can be carried out using only air and a supported Ru catalyst (*Angew. Chem., Int. Ed*., 2003, **42**, 1480). They have shown that a Ru/Al_2O_3 catalyst will readily convert primary amines to nitriles and secondary amines to nitriles in a few hours at 100 °C in benzotrifluoride. Conversions are essentially quantitative and selectivity generally is excellent. No loss of Ru was found and reuse was possible with no reduction in performance. Other Ru catalysts were much less active. Mechanistic details are discussed.



Heck reactions

A contribution to the development of the Heck reaction has come from the group led by Paul Ratnaswamy at the National Chemistry Laboratory in Pune in India. They have developed a phosphine-free heterogeneous catalyst which is capable of converting aryl chlorides in good yields (*Tetrahedron Lett*., 2003, **44**, 3649).



Their catalyst system is based on the SAPO support, which is a silica–alumina–phosphate system. These catalysts (with a 3% Pd loading) are excellent in the reactions of bromo- and iodo-arenes, as expected, but are also capable of 70% conversions of chloroarenes in reasonable times. The absence of phosphines is a big advantage, and is unusual that such systems can convert C–Cl systems effectively. Another interesting feature is that Pd is lost into solution during the reaction, but is not present at the end of the reaction; the authors attribute this to the redeposition onto the support, which can be reused.

Nylon production

The battle to clean up nylon production has produced a fascinating paper from the group led by Sir John Meurig Thomas at the Royal Institution and the University of Cambridge (*Angew. Chem., Int. Ed*., 2003, **42**, 1520). They have shown that a titanium-substituted aluminium phosphate (TAPO) catalyst can selectively oxidise cyclohexene to adipic acid using hydrogen peroxide as oxidant under solvent-free conditions. Selectivity increases with time, and conversions are quantitative. A considerable amount of mechanistic information is also uncovered

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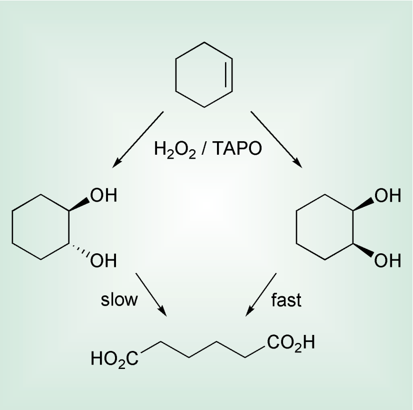
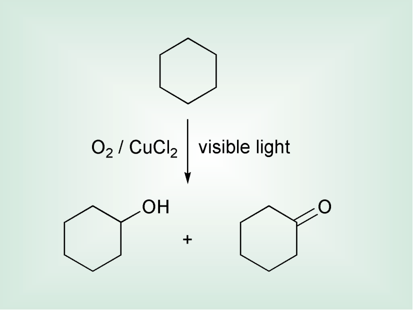


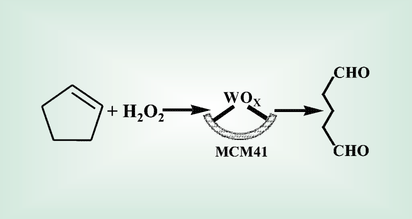
– a key observation is that the reaction proceeds *via* the 1,2-diol, but that the *cis*-diol oxidises further much more readily than the *trans*. The latter is formed by ring-opening of the epoxide, but the former is derived from a radical mechanism.

A further paper devoted to oxidation of hydrocarbons (and also with potential application to nylon) comes from Ken Tanaki's group at Hiroshima University, Japan (*Bull. Chem. Soc*. Japan, 2003, **76**, 393). While there are several papers discussing the oxidation of cyclohexane using metal compounds and UV light, this group has shown that visible light is also very effective for this transformation. Copper or iron chloride and oxygen in acetonitrile give, upon irradiation with visible light, over 50% conversion of the alkane to the alcohol and ketone. A mixture of these two compounds is currently oxidised to give adipic acid.



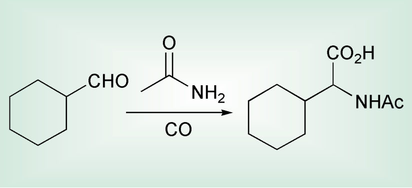
W-MCM-41 catalyst

The conversion of cyclopentene to glutaraldehyde using a W-MCM-41 material and hydrogen peroxide has been shown to be effective (*Chem. Commun*., 2003, 892). Wei-Lin Dai and his co-workers from Fudan University and Shanghai Normal University in China have developed a modified route to the W-MCM-41, which involves the use of ethyl acetate rather than HCl in the synthesis gel. They claim that this gives a cleaner process and a material with better structural order. Furthermore, they show that the material is a very active catalyst for the hydrogen peroxide oxidation of cyclopentene, being much more active than other W-silica systems. Interestingly, in other systems, hydroxylation is the main reaction, whereas here cleavage to the dialdehyde is preferred. Reuse is also demonstrated, and leaching could not be detected.



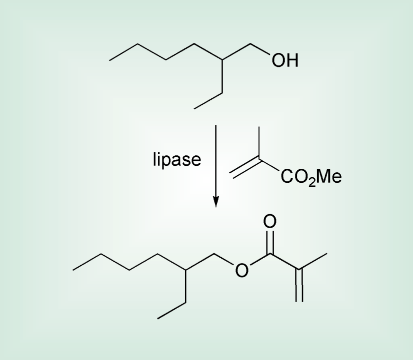
Amidocarbonylation

Amidocarbonylation is the coupling of CO, an amide and an aldehyde to give N-acyl aminoacids in one step. Co and Pd catalysts have been described recently, but the Pt–phosphine system which is the subject of a paper by Shu Kobayashi and his group at the University of Tokyo appears to have some advantages over these earlier catalysts (*Chem. Lett*., 2003, 160). They found that the Pt–phosphine systems were active in the reaction, leading to good yields of the desired product under a CO pressure of 60 atm. The potential advantage of the current system is that enantioselective reactions seem to be possible. The difficulty so far has been the ability of the catalyst to racemise the product rapidly, meaning that, even if the formation of product is enantioselective, this will be lost readily. The Pt systems do racemise the product, but considerably more slowly than the Pd systems.



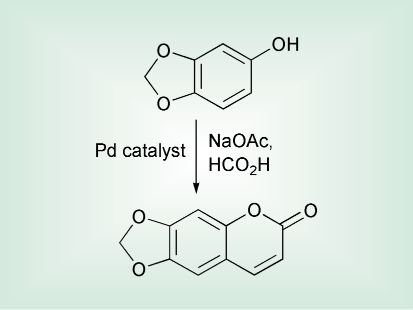
Ionic liquids

The use of ionic liquids as solvents for enzyme-catalysed transformations has been established. Now a paper by Alan Russel and his group at the University of Pittsburgh, USA, has shed light on the requirements of the ionic liquid (*J. Am. Chem. Soc*., 2003, **125**, 4125). They studied the transesterification of various esters with lipases in a series of ionic liquids and compared them to organic solvents. While the best ionic liquids supported higher rates (×1.5) than in hexane and led to greater enzyme stability, hydrophilic ionic liquids were poor matrices for the reaction, with little or no activity evident in any case.



Addition reactions

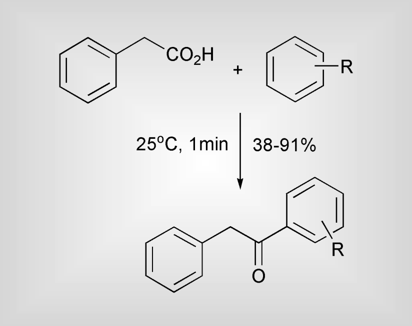
The conversion of phenols to coumarins using propargyl esters is a novel and efficient addition reaction, which has just been published by Barry Trost and his group at Stanford University, USA (*J. Am. Chem. Soc*., 2003, **125**, 4518). They have shown that Pd catalysis can induce *ortho* functionalisation of an intermediate Pd-phenolate, followed by ring-closure to give the coumarin. The reaction requires formic acid and a small amount of sodium acetate. Many examples are given, indicating the generality of the system, and yields range from good to excellent. Mechanistic details are also discussed.



Acylating aromatics

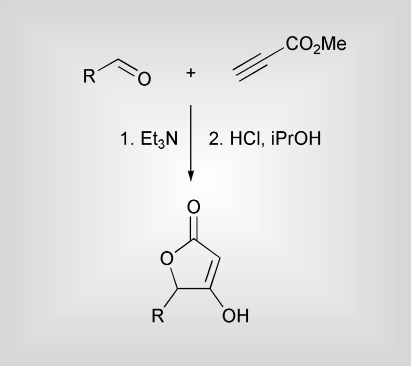
Acylation of aromatics using Friedel–Crafts methodology is an important but polluting method, with considerable quantities of aluminium chloride typically being irretrievably used in reactions. Many alternatives have been sought, but most fall short of the desired efficiency. Koteswar RaoYeleswarapu and colleagues from Dr Reddy's Laboratories

Ltd in Hyderabad, India, have now shown that a combination of phosphoric acid and trifluoroacetic anhydride is a remarkably effective way of acylating aromatics (including non-activated arenes such as toluene) at room temperature and extremely short reaction times (*Tetrahedron*, 2003, **59**, 3283). This combination of reagents is thought to give a phosphoric–trifluoroacetic anhydride type species which is capable of producing high yields of ketone when arylacetic acids are reacted with aromatics. Yields of up to 91% are possible with activated aromatics, but even unactivated systems can give 38–40% yields within 1 minute.



Tetronic acids

The tetronic acid structure is a biologically significant one, as it includes vitamin C as one of its examples. An elegant and simple domino sequence has just been published by a group led by Fernando Garcia-Tellado at the University de la Laguna in Tenerife (*J. Org. Chem.*, 2003, **68**, 3363). They simply took methyl propiolate and an aldehyde and reacted them together in the presence of triethylamine to form an intermediate which was then converted to the final product by the addition of hydrochloric acid and isopropanol. This gives an overall addition of the two components, with the loss of methanol and the addition of water, making the overall process simple and clean; yields are good for a series of aldehydes.



Reviews

Rik Tykwinski of the University of Alberta, Canada, has produced a short highlights article relating to the Sonagashira coupling of alkynes to aryl halides and triflates. This reaction type is catalysed by Pd and Cu, and the article brings together some of the most recent advances, many of which broaden the scope of the method (*Angew. Chem. Int. Ed.*, 2003, **42**, 1566).

A second Pd-catalysed reaction type is the subject of a review. Darcy Culkin and John Hartwig of Yale University, USA, review the Pd-catalysed arylation of carbonyl compounds and nitriles (*Acc. Chem. Res.*, 2003, **36**, 234), covering both synthetic and mechanistic aspects.

Hydroformylation is often covered in our Highlights section, and a review covering the synthetic aspects of stereoselective hydroformylation may be of interest in this regard. Bernhard Brett of Albert Ludwigs University in Freiburg, Germany, discusses the control of stereoselectivity in this important reaction type (*Acc. Chem. Res.*, 2003, **36**, 264).

Some highly selective hydrogenation catalysts based on bimetallic nanoparticles within silica mesopores are the subject of a review by Sir John Meurig Thomas and colleagues at the Royal Institution and Cambridge University (*Acc. Chem. Res.*, 2003, **36**, 20).

The Baylis–Hillman reaction is a versatile route to highly functional intermediates. It has been reviewed by Deevi Basavaiah and colleagues from the University of Hyderabad, India, (*Chem. Rev.*, 2003, **103**, 811).

Teaching green chemistry: from lemons to lemonade bottles

Stewart Tavener, Jeff Hardy, Nick Hart and Andy Goddard from the Clean Technology Centre at the University of York, UK, describe their experiences in trying to design challenging but realistic green chemistry experiments for advanced undergraduate and Masters level chemistry students

Introduction

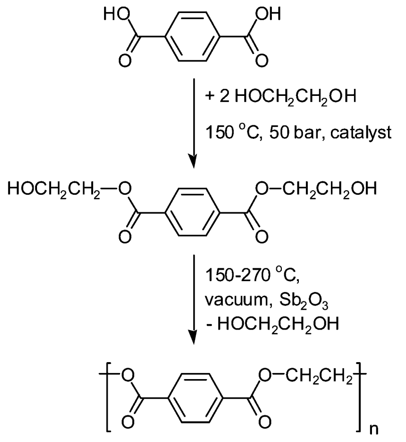
In the spring term of 2000, we started to run green chemistry mini-projects as an optional part of the undergraduate courses at the Department of Chemistry, University of York. The projects were run over a period of six weeks, with a total of six days laboratory time allocated during that period. The projects were intended to cover key areas of green chemistry, including clean synthesis, life cycle analysis, atom efficiency, and the use of renewable feedstocks. An additional aim was to broaden the students' view of chemistry by encouraging them to estimate the total resources required for a particular process. We would like to share some of our experiences from the first year of these projects.

To encourage independent learning, the students were involved in the selection of their own project. Rather than studying a single reaction in isolation and judging its success on the basis of 'percent yield' alone, the students were asked to consider a product and to work backwards. They were each asked to select an everyday product that could be found in a supermarket or high street store, and to think about the chemicals that went into the manufacture of that product. We then met to discuss their suggestions and make a final choice for study.

The suggestions at this stage included a nylon rucksack, plastic drink bottles (PET) and washing-up liquid (detergents and surfactants). We were looking for something that contained enough chemistry to keep five students busy for six days in the laboratory, and any of these suggestions would have fitted the bill. We could have studied the manufacture of nylon polymers and the synthesis of the monomers (including adipic acid) necessary for its production; or we might have investigated the synthesis of non-ionic surfactants and their fate in the environment. Instead, the students voted to investigate all aspects of the manufacture of polyethylene terephthalate fizzy drinks bottles, including the polymerisation itself, and manufacture of the monomers. They were asked to keep track of everything they used during their lab work, measuring volumes of aqueous and organic solvent use, water usage for cooling, and the electricity consumption alongside the familiar % yield calculations. They were also asked to calculate 'mass' and 'atom' efficiencies (see box below for an example), and to consider whether less harmful solvents or renewable feedstocks could be used at any stage.

The chemistry

PET is formed by reaction of ethylene glycol with either terephthalic acid (Scheme 1), or with dimethyl terephthalate via transesterification. These



Scheme 1

Sample measurements and calculations for the conversion of limonene to p-cymene using N-lithioethylenediamine

% Yield

Limonene used = 13.6 g = 0.100 mol
p-cymene produced = 12.7 g = 0.095 mol
∴ yield = 95%

Reagents used

Lithium metal	4.12 g
Ethylene diamine	84.5 g
Limonene	13.6 g
Diethyl ether	35.2 g
water (quenching)	300 g

Total mass of reagents 437 g (not including cooling water)
∴ mass yield = 12.7/437 = 2.9%

Other resources

water (cooling): 32.6 kg   electricity: 1 kW hr (approximate)

Table 1 Atom efficiencies

Element	Number in reagents	Number in product	Theoretical efficiency (%)	Actual efficiency[a] (%)
Li	1	0	0	0
N	2	0	0	0
C	12	10	83	79
H	22	14	64	60

[a] Calculated from (yield) × (theoretical efficiency).

DOI: 10.1039/b305233h

reactions proceed at high pressures and temperatures, which we were unable to replicate safely with equipment available to us in a teaching laboratory environment. These steps are very efficient anyway, particularly if the ethylene glycol produced in the second step can be reused. Instead, attention was turned to the monomers.

The monomers: ethylene glycol and terephthalic acid

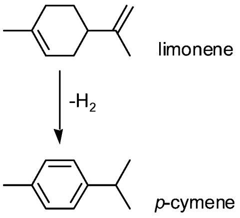
Ethylene glycol is generally produced by catalytic hydration of ethylene oxide, which, in turn, is manufactured by catalytic epoxidation of ethene. Because of the high toxicity of ethylene oxide, and the need for high temperatures and pressures, manufacture of ethylene oxide was not considered a suitable practical for undergraduates. We could have studied a model alkene epoxidation, for example cyclohexene using a supported reagent catalyst, but instead we focused on manufacture of the other half of the PET jigsaw, terephthalic acid.

Terephthalic acid

Terephthalic acid is generally produced *via* oxidation of *p*-xylene in the liquid phase using a Mn or Co salt catalyst at relatively high temperatures (140–200 °C). A co-catalyst or promoter (bromide) is often used, and a co-oxidant such as acetaldehyde is frequently employed to ensure oxidation of both methyl groups. Some attempts were made to recreate these conditions on a lab scale, and to measure the waste produced. This reaction appeared to be a likely candidate for a green study. The students recognised *p*-xylene as a non-renewable feedstock, and wondered if there might be a better route starting with a renewable.

An alternative route to terephthalic acid?

Limonene is a cyclic terpene and is found as a major constituent of citrus peel oils, of which about 50,000 tonnes are produced annually. It is generally considered safe and is sometimes used as a solvent substitute for xylenes. Importantly, it may be converted to p-cymene (Scheme 2), which provides a renewable method of synthesising aromatics. This was investigated further.



Scheme 2

The production of *p*-cymene from limonene was initially achieved by a literature method involving lithium metal in ethylenediamine. Whilst very effective (95% yield), this required stoichiometric amounts of the lithium reagent, and so a catalytic method was sought. Having identified this as a dehydrogenation and aromatisation reaction, the students suggested that some kind of hydrogenation catalyst should, in the absence of additional hydrogen, also be capable of catalysing dehydrogenations. Palladium on charcoal sprang to mind, and this was applied to a liquid phase reaction of limonene. The reaction gave complete conversion of the limonene, but only about 50% selectivity to *p*-cymene [subsequent projects have already seen this figure improve to about 70%]. It is potentially a very green way of preparing an aromatic from a renewable feedstock.

Oxidation of p-cymene

This was a greater challenge. We found that *p*-cymene could be oxidised to terephthalic acid successfully using stoichiometric CrO_3 as an oxidising agent—hardly a green method! The search for a catalytic method, perhaps using a supported reagent oxidation catalyst and air or hydrogen peroxide as the oxidant, would have been the next sensible step. Frustratingly, our allocated lab time had run out and we had to stop here. If a suitable catalytic oxidation method could be found, then limonene really could give a green route from lemons to lemonade bottles.

Outcomes

The decision to give the students free choice over the topic had the advantage that they felt ownership of the project and displayed a genuine enthusiasm for it. However, this left us, the 'learning facilitators' feeling somewhat under-prepared as we didn't know what the students would be doing until a week before laboratory work commenced. In subsequent years we gave the students a list of perhaps four or five projects from which to choose, although this perhaps sacrificed some of the spontaneity and enthusiasm witnessed during that first year. One of the most exciting aspects of running the project was seeing the students discover solutions to problems that we had not thought of ourselves—indeed it was as much of a learning experience for us as it was for them (see box below).

Postscript

The mini-projects have since been superseded by a full MRes postgraduate course in Clean Chemical Technology course. Building upon the experience gained during the mini-projects, a practical experiment was developed for the MRes students, based on examining all steps of transforming limonene to terephthalic acid. The practical is carried out over two days and the students are

A student's perspective

The project was our first experience of carrying out genuine research, as opposed to the following of a pre-defined laboratory script during our university studies. Although it was initially a daunting task to attempt to locate reports on relevant subjects, the guidance given made this a very useful and confidence-building exercise. From knowing nothing about how to research previous work done on a subject, we became confident in using both library and internet resources in order to develop a starting point for the laboratory work.

It was especially exciting to be able to integrate a number of principles forming the basis of green chemistry – namely the use of heterogeneous catalysis in organic synthesis, the development of a process originating from a widely available natural and renewable product (limonene), and working to minimise both the amount of waste produced and the energy used throughout the stages of the reaction.

The exercise was not only beneficial in teaching how to approach novel research, it also taught us important principles in designing a process from a green chemistry prospective. The project was one of the deciding factors in my decision to continue my studies at PhD level in the Department of Green Chemistry at the University of York.

Nick Hart

split into small teams (2–3 students) to examine separate steps in the process. The stages examined in the practical are as follows:

(1) Extraction of limonene from citrus fruit *via* cold pressing, steam distillation and solvent extraction methods.

(2) Transformation of limonene to *p*-cymene *via* catalytic dehydrogenation (both in a batch reactor and in a continuous flow reactor), oxidative dehydrogenation and stoichiometric dehydrogenation (using *N*-lithioethylenediamine).

(3) Oxidation of *p*-cymene to terephthalic acid (to date only stoichiometric CrO_3 has been examined, but other oxidation methods will be examined next time around).

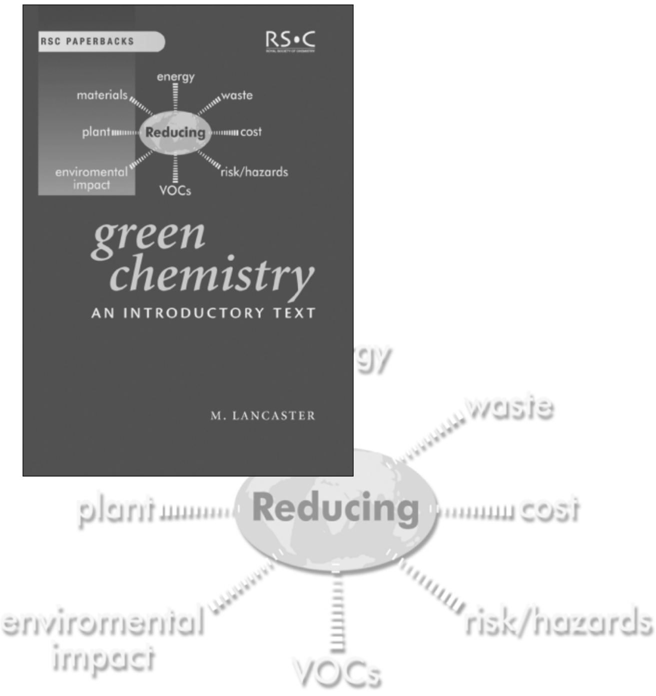
In all steps the students are asked to measure all inputs (including energy) and measure (or estimate) all outputs (including chemicals required in neutralisation *etc*.). The results from all the steps are then pooled in a common table from which the students metadoxically decide upon which route has the lowest environmental impact. The students also are required to comment upon the suitability of each method for scale-up for industrial production. This often results in some excellent discussion.

The practical has been running for two years now, and each year more experimental routes are added. We are currently setting up a suite of clean technology reactors for teaching and other purposes, so in next year's experiment the students will hopefully have the opportunity to examine supercritical CO_2 as a solvent for extracting limonene from citrus fruit peel.

Acknowledgement

We thank the University of York Teaching Innovation Fund for support of this work.

For further information contact Dr Stewart Tavener (sjt4@york.ac.uk).



Towards an environmentally friendly chemistry laboratory: managing expired chemicals

Teaching laboratories present on a small scale many of the environmental problems facing larger commercial facilities. Teaching good practice to the chemists of the future is of vital importance to the successful implementation of the principles of green chemistry in industrial practice so devising new ways of both dealing with laboratory waste and using more environmentally friendly chemicals to teach chemistry are very important goods. Here, Ahmad Houri and Hania Wehbe from the Lebanese American University in Beirut† discuss these issues in the context of teaching chemistry in a developing country. A detailed experimental procedure is provided for utilising an expired chemical in an undergraduate chemistry practical

In our never-ending endeavor to protect our environment while at the same time performing the necessary tasks of our daily life we aim to fulfil the 'act locally think globally' slogan. Currently, Lebanon just like many third world countries has no existing system for hazardous waste disposal. This lack of control results in heavy pollution of streams, rivers and seas by chemicals from all sorts of sources. Some of these pollution sources are the chemistry laboratories at educational institutions that tend to generate toxic chemicals.

For several years now, many attempts at the collection and proper disposal of these chemicals have been undertaken. Without the support and implementation of strict laws, or the presence of clear financial returns these efforts have not materialized. Proper disposal tends to cost a lot of money and effort due to the lack of the basic hazardous waste disposal facilities. A different attitude had to be undertaken and a conscious decision was made to cut down on the pollutants from the source. This meant that we had to rethink our experiments so that they can provide the same educational learning experience but with the use of non-hazardous chemicals that could be disposed of in the sink with minimal health and environmental adverse effects.

Part of this shift was done through the adoption of modern chemistry laboratory texts that in general have followed this trend. For example, the concept of steam distillation used to be illustrated by the use of bromobenzene and separation of benzene and xylene.[1] These compounds are either carcinogenic, irritants or have foul smells. The same concept is now being illustrated within the context of extraction of aromatic constituents of clove oil.[2] This is a much better illustration that is directly related to students' lives especially when other spices are used such as cinnamon and cumin. In addition to the friendlier smells in the lab, minimal amounts of toxic chemicals are generated (the extraction solvent).

With the implementation of these more benign experiments, we opted to tackle two other aspects of chemical disposal:

- What should we do with 'bad' and old chemicals?
- How can we actually take a positive attitude towards cleaning up the environment from wastes that would otherwise find their way to the freshwater supplies or the sea?

This paper aims at providing creative alternatives for the cost efficient and environmentally friendly disposal of an old stock chemical. The second aspect will be tackled in a future paper.

The problem

Chemicals in the stockroom have a tendency to be lost in the back of shelves or pushed back by new materials; accordingly, one tends to find many bottles with chemicals that are no longer useful for their originally intended purpose. One example of such a case is magnesium powder or filings. This reagent is usually purchased to perform Grignard reactions in the organic chemistry lab. Unfortunately, it is usually kept in metallic containers which, under the hot and humid summer conditions dominant in the eastern Mediterranean, tend to rust relatively quickly. Oxygen starts making its way through the closed containers (even those that were never opened), and the magnesium gets partially oxidized and turns gray. Once partial oxidation occurs, the magnesium can no longer be used for the Grignard reaction. The presence of several hundred grams of this material provided us with a motivation to make the most out of the money we have already paid, and to minimize damage to the environment. We set out to devise an experiment to use this material.

The solution

The realization that the contaminated Mg essentially contains only MgO made it

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DOI: 10.1039/b305234f

possible to design an experiment in the introductory chemistry lab utilizing this obtained Mg–MgO mixture. The basic idea of the experiment is teaching students how to measure the molecular weight of magnesium by measuring the amount of hydrogen generated when magnesium is treated with hydrochloric acid. This experiment is well known and widely used. Many other metals may be used.[3–6] This technique is then used to determine the composition of a Mg–MgO mixture which is essentially our oxidized magnesium. The reaction generally proceeded smoothly and students obtained reasonable results. Improper sealing of the setup results in smaller hydrogen volumes and accordingly higher molecular weights for Mg and smaller Mg percentages in the Mg–MgO mixture. Rubber stoppers should be used and not corks to avoid hydrogen losses. The detailed procedure and some thought provoking questions directed to students are outlined below for easy reference. The procedures indicated may be conducted in duplicate to insure more reliable data sets.

The experiment

Atomic weight determination of magnesium and determination of % composition of an unknown Mg–MgO mixture.

Objective

- To determine the atomic weight of Mg by H_2 gas generation.
- To apply the ideal gas equation $PV = nRT$ in calculating the yield of the reaction.
- To calculate the percentage composition of an unknown mixture of MgO and Mg.

Glassware needed and the setup

- One large test tube (size: 90 mL).
- A one-hole rubber stopper (regular cork is not good enough, it will leak).
- A bent glass tubing (S-shaped, pre-made).
- A 500 mL graduated cylinder.
- A 2000 mL beaker.

Procedure

Part A

Prepare the setup by filling the 500 mL graduated cylinder completely with water. Wrap the top of the graduated cylinder with parafilm trying to avoid spilling water. Place 1000 mL of water into the 2000 mL beaker and then place the graduated cylinder upside down in the beaker and clamp it so that the water covers at least 5 cm of the cylinder. Remove the parafilm from the cylinder carefully. Does the water spill out of the cylinder? Why? Now carefully place one tip of the bent tubing inside the hole of the cork (insert the tubing in a circular motion while using grease, DO NOT USE EXCESSIVE FORCE as it may result in injury). Place the other tip inside the graduated cylinder. Measure the volume of air that might have leaked into the graduated cylinder during these manipulations.

Place 15 mL of 3 M HCl in the test tube and place it in an ice bath. (Why?) Then accurately weigh about 400 mg of Mg powder. What is your limiting reagent? Drop the Mg rapidly into the test tube containing HCl and close it with the rubber stopper immediately. Make sure all the magnesium is in the solution and none is sticking to the sides. Wait till the reaction goes to completion as indicated by the disappearance of the solid metallic particles or as indicated by the lack of H_2 gas formation. Remove the ice bath and wait for five extra minutes. Measure the volume of gas generated by subtracting the graduated cylinder reading now from the reading recorded earlier due to air leakage.

- Record atmospheric pressure in atmospheres.
- Record the water temperature in °C, convert to K.
- Calculate the number of moles of H_2 gas formed using the ideal gas equation ($PV = nRT$; $R = 0.082$ atm L (moles K)21).
- Based on the following equation, calculate the molecular weight of Mg.
- Calculate the % error in your obtained weight (At. Wt. Mg = 24).

$$\mathrm{Mg} + 2\mathrm{H_3O^+} \rightarrow \mathrm{Mg^{2+}} + \mathrm{H_2} + 2\mathrm{H_2O} \quad (1)$$

Part B

Get the unknown mixture of Mg–MgO provided by your instructor. Using the same setup as before, refill your graduated cylinder with water and accurately weigh about 500 mg of the mixture and place it into a new tube containing 8 mL of 6 M HCl (make sure the tube is dipped in ice). Cap the tube immediately and wait for the reaction to stop. Again, remove the tube from the ice and wait for five minutes. Measure the amount of H_2 gas obtained. Calculate the number of moles of H_2 obtained and deduce the weight of pure Mg you have started with. Calculate the percentage composition by weight of Mg in the original mixture. Remember that the presence of MgO does not contribute to the generation of hydrogen gas because acid consumes MgO according to the following equation:

$$\mathrm{MgO} + 2\mathrm{H_3O^+} \rightarrow \mathrm{Mg^{2+}} + 3\mathrm{H_2O} \quad (2)$$

Conclusion

A new method for the efficient use of ‘useless’ material has been devised. This trend promises to utilize previously discarded materials and will aid in reducing the environmental stress created by improper disposal of such materials. In the process, we have offset the potential waste products of another experiment that would have been done in its place. The wastes generated in this reaction are simply magnesium salts and water. It is our hope that the experiences of all those working in this field can be pooled together to ultimately generate a handbook on methods to use expired materials rather than suggesting methods to expensively dispose of it.

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Communication

Microwave assisted phosgenation – alcoholysis using triphosgene

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Received 5th November 2002
First published as an Advance Article on the web 25th April 2003

The microwave assisted reaction engineering of the phosgenation of alcohols with triphosgene as a safe-to-handle phosgene substitute was investigated. The phosgenation of *n*-butanol was carried out in the homogeneous phase as a one-pot reaction, and in a two-chamber reactor in which freshly produced phosgene gas was bubbled through the educt solution. New catalysts such as phenanthroline, benzyltriethylammonium chloride (BTAC), and the ionic liquid 1-ethyl-2,3-dimethylimidazolium-bis-trifluoromethanesulfoneimide (PW1022) were successfully employed for the decomposition of triphosgene, alone or in combination with activated charcoal, which acted as a microwave absorber. In another experimental series, the reaction of a wide range of alcohols (isopropanol, *n*-butanol, *tert*-amyl alcohol, 2-butoxy-ethanol, cyclohexanol, benzyl alcohol, 1-phenyl alcohol, *n*-octanol) with triphosgene was investigated for two different microwave set-ups.

Introduction

Phosgene is an important and commonly used reagent in organic synthesis. However, its various applications[1] are limited due to its corrosive and toxic properties. Dosage of phosgene on the laboratory-scale (often added in excess) is difficult because the weighing of small amounts of phosgene on the gram-scale from gas-bottles requires high security precautions and precision.[2,3] Bis(trichloromethyl) carbonate (“triphosgene”) is a synthetic equivalent that has been available for some time and has advantages over phosgene gas. Triphosgene, a crystalline and thermostable solid (mp 81–83 °C, bp 203–206 °C), is a stoichiometric trimer of phosgene, which is easier to handle than phosgene gas due to its comparatively low volatility. In addition, triphosgene can be weighed and dosed precisely in order to achieve very high yields with stoichiometric amounts. It reacts in the presence of a nucleophile (mostly triethylamine, ethyldiisopropylamine and pyridine) in the same way as three equivalents of phosgene. For certain reactions, the nucleophile can be added in substoichiometric amounts, substituted by a catalyst,[4] or the nucleophile can also be the educt. Triphosgene is a versatile reactant because it can be used as a phosgenation reagent in many organic syntheses.[5] For these reasons, triphosgene is used for the *in situ* on-demand production of phosgene and is selected for direct reactions in the homogeneous phase due to its high solubility in organic solvents.

We chose to investigate the synthesis of symmetrical dialkyl carbonates, as an example reaction of the many phosgenation reactions[1,5] documented in literature. This paper describes the alcoholysis of phosgene with *n*-butanol in various reaction conditions, including alternative reaction engineering.

Results and discussion

Dialkyl carbonates have a broad application as alkylation agents, and in the production of polycarbonates.[6] The classical synthesis of alkyl carbonates involves bubbling large amounts of phosgene through alcohols at high temperatures, or the copper-catalysed reaction of alcohols with oxygen and carbon monoxide.[7] The reaction of alcohols with phosgene is a two-step reaction, detailed in the formulae below:

$$\text{R–OH} + \text{COCl}_2 \rightarrow \text{RO–COCl} + \text{HCl} \qquad (1)$$

$$\text{RO–COCl} + \text{R–OH} \rightarrow \text{RO–CO–OR} + \text{HCl} \qquad (2)$$

In order to completely substitute phosgene with triphosgene, we chose reactions in the homogeneous phase and thus had to find a suitable catalyst. Although iron oxide and activated charcoal are known to catalyse the release of phosgene gas from triphosgene,[8] they had to be ruled out as catalysts in our reaction because they are usually present in their solid state in the reaction mixture, and consequently cannot be used for a reaction in the homogeneous phase. Tertiary amines[9] and pyridine[10] are well-known nucleophilic reaction mediators but their use was not considered due to the health concerns associated with these substances. Yet another possibility to catalytically control the quantitative decomposition of triphosgene is the use of deactivated amine and imine functions. In these compounds, the deactivation of the lone electron pair is achieved through the insertion of space-filling and electron-attracting groups in the vicinity of the nitrogen atom. Another reliable method for the synthesis of deactivated amines and imines is the integration of the catalyst in a polymer matrix. Furthermore, deactivation could be achieved through the insertion of spacer molecules or metallic centers.[11] Typical members of this new catalyst generation are, for example, poly(2-vinylpyridine) and metal-

Green Context

The formation of carbonates is the subject of much work at the moment. This paper describes the combination of triphosgene and microwave irradiation, in the presence of a microwave-active catalyst, to carry out a selective formation of carbonates from alcohols and a masked phosgene equivalent. Handling of phosgene itself is avoided, and conversions and selectivities are good. The choice of catalyst is critical, since neither of the reactants are microwave-heatable. The effect of different reactor designs is investigated. *DJM*

DOI: 10.1039/b210895j

phthalocyanine. The use of a catalyst with a deactivated amine-function for the direct reaction with triphosgene is described comprehensively for the example of tetrabutylammonium chloride (5–10 wt%) in ref. 12. For the alcoholysis of triphosgene in the homogeneous phase, quaternary ammonium salts (catalyst with deactivated amine-function) proved very suitable due to their good solubility in the educts (alcohol).

In the experiments reported in this paper, benzyltriethylammonium chloride (BTAC), and to a lesser extent, phenanthroline-monohydrate (possible deactivation through hydrogen bonds) were employed as catalysts. All reactions were carried out at ambient temperature, with continuous stirring, and at approximately 120 °C in the microwave field. In a blank experiment, all reactions were carried out without the addition of a catalyst but under otherwise identical conditions. Microwave assisted reactions, even in the absence of a catalyst, resulted in high yields (> 80%), Table 1.

Table 1 Influence of the catalyst on the measured yields (GC) of the alcoholysis of triphosgene with *n*-butanol

Catalyst	RO–COCl (%)	RO–CO–OR (%)	R–Cl (%)	Conversion (%)
[a] —	33	5	—	38
[b] —	8	72	2	82
[a] phenanthroline	35	5	—	40
[b] phenanthroline	5	80	6	91
[a] BTAC	33	5	—	38
[b] BTAC	2	88	8	98
[a] PW 1022	30	4	—	34
[b] PW 1022	7	93	—	100

[a] Stirred for 2 h at room temperature. [b] Microwave batch: 30 min., 900 W, 120–130 °C. BTAC: benzyltriethylammonium chloride, PW 1022: 1-ethyl-2,3-dimethylimidazolium-bis-trifluoromethanesulfoneimide.

The results of the alcoholysis of triphosgene in the homogeneous phase with BTAC as the catalyst and for various reaction conditions are summarised in Table 2. Triphosgene was dissolved in an excess of *n*-butanol (bp 118 °C) and refluxed in the microwave field. First, phosgene released from triphosgene reacted *in situ* with *n*-butanol to butylchloroformate (eqn. 1). The reaction usually ceased at this initial stage if it was carried out at room temperature and in the presence of different catalysts, as well as in an excess of alcohol and for extended reaction times. The secondary reactions of this primarily formed chloroformate with *n*-butanol to the carbonate only started upon a significant increase in reaction temperature (eqn. 2). Thus, yields of 44% (at 60 °C) and 83% (at 120 °C) for a reaction time of 30 minutes and a preheated oil bath, and 88% for irradiation in the microwave field (30 min/900 W/120–130 °C) were found.

Table 2 Dependence of the alcoholysis of triphosgene with *n*-butanol on the reaction conditions (catalyst: BTAC, GC yields)

Time/min	RO–COCl (%)	RO–CO–OR (%)	R–Cl (%)	Conversion (%)
[a] 120	33	5	—	38
[b] 5	12	3	—	15
10	46	11	—	57
20	48	13	—	61
30	34	44	—	78
[c] 5	24	12	—	36
10	26	39	—	65
20	10	67	—	77
30	5	83	—	88
[d] 5	16	50	4	70
10	13	59	5	77
20	5	82	7	94
30	2	88	8	98

[a] Stirred for 2 h at room temperature [b] batch in oil bath at 60 °C [c] batch in oil bath at 120 °C [d] microwave batch at 120–130 °C

The performed alcoholyses resulted, besides the expected reactions (1) and (2), in the partial formation of a by-product. *N*-butyl chloride (identified by GC-MS) apparently results from the decarboxylation of the primarily formed chloroformate in the microwave field. Surprisingly, this reaction was also observed to a smaller extent in the absence of the catalyst. As apparent in Table 2, this reaction is not solely the result of thermal effects. Therefore, the question arose if phosgene would show a comparable reaction behaviour.

The alcoholysis of gaseous phosgene was performed in a specially designed glass reactor (Fig. 1). This reactor consisted of a developing chamber for the decomposition of triphosgene and a reaction chamber, which was filled with the educt. Both chambers were connected *via* a gas dispersion tube, and thus formed a closed system. The two-chamber reactor was installed in the microwave apparatus and externally connected to a dry ice cooler including a gas exhaust. During the reaction, the phosgene released was passed through the reaction mixture by applying a low nitrogen stream *via* the immersion tube. The gas stream also prevented the condensation of reaction mixture in the developing chamber after the phosgene release ceased. Since excess *n*-butanol, due to its dielectric properties, was at boiling temperature during microwave irradiation, the preferred formation of dibutyl carbonate (eqn. 2) was expected.

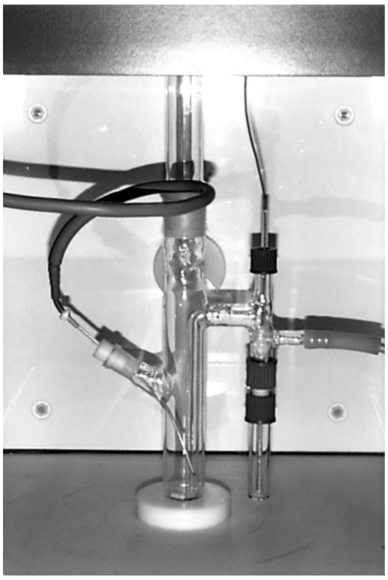
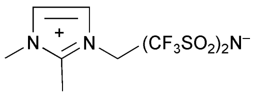


Fig. 1 Two-chamber reactor in microwave system ETHOS MR™.

The commercially available catalyst H 383™ (Dr. Eckert GmbH) was used for the release of phosgene. The catalytic action of this catalyst only starts after reaching the melting point of triphosgene. Because neither the catalyst nor triphosgene are microwave active, the developing unit had to be heated externally with an appropriate heating liquid. Diethylene glycol (bp 224 °C) was chosen for this purpose. Temperature control in the microwave system was performed with a fibre-optic sensor in the heating liquid. The reaction unit was irradiated at a temperature of 120 °C for 30 minutes with a microwave power of 500 W. After the reaction, the mixture was analysed with a gas chromatograph. At a conversion of 95%, the yield of carbonate was 86% and the yield of chloroformate was 9%. By-products could not be detected. The indirect heating of the developing chamber proved disadvantageous because the warm heat transfer fluid remained at a constant temperature over a long period of time. Therefore, in order to ensure the safety of the reaction, the possibility to stop the phosgene production at any time is necessary. As a consequence, we were looking for a substance which was both catalytically active and microwave active. It was assumed that with such a substance the release of phosgene gas could be directly and precisely controlled during the reaction *via* internal heating of the triphosgene/catalyst mixture (adaptable parameters: temperature, microwave irradiation power). Several readily available substances were tested for their suitability to catalyse the decomposition of triphosgene in the microwave field. Catalytic substances such as copper-phthalocyanine and zinc-picolinate, which are catalytically active in the triphosgene melt, as well as BTAC, which is already somewhat active at room temperature, cannot be activated by microwaves. Therefore, we tried to achieve the desired catalyst properties by using different carbon supports. The catalytic activity of activated charcoal, which is a well-established catalyst[8] with good coupling properties, was tested. It was found that triphosgene readily decomposes after little contact to activated charcoal at ambient temperature. In order to study the decomposition behaviour of triphosgene in the presence of activated charcoal, both compounds were mixed at a mass ratio of 5 : 1 in a Schlenk flask under a nitrogen atmosphere and stirred with a magnetic stirring bar. The decomposition of triphosgene was determined with difference weighing. Decomposition rates were: 12% after 5 min, 19% after 15 min, 22% after 45 min, and 31% after 90 min. As a result, we concluded that this catalyst could only be added to triphosgene immediately before the start of the microwave programme. The phosgenation reaction in the reactor was conducted in the same manner as the alcoholysis described before, using the same catalyst (H 385™) and direct temperature control in the developing chamber. After starting the microwave irradiation, complete melting of triphosgene was observed within a few seconds. The decomposition of triphosgene took place under heavy gas evolution and lasted approximately 2 minutes. According to GC analysis, the calculated amount of educt reacted to 96% (chloroformate 13%, dibutyl carbonate 83%). Thus, activated charcoal in combination with the catalyst H 385™ yielded high conversion rates after short times. After the melting of triphosgene, however, the reaction could not be controlled. The difference to the theoretically possible yield of 100% could be explained by the partial decomposition to tetrachloromethane and carbon dioxide. Other secondary products or rests of triphosgene (determined by weighing of the developing chamber) were not found. Other carbon supports, *e.g.* carbon enriched synthetic polymers (PLASBLAK™, WEFLON™), revealed only insufficient microwave activity caused by the poor geometry of those microwave absorbers. Investigated graphite powder was easily miscible with triphosgene and showed good microwave absorption. However, graphite powder was completely inactive as a catalyst.

Furthermore, ionic liquids were investigated as another possibility for the release of phosgene gas from triphosgene in the microwave field. Ionic liquids are salts with low melting points (< 100 °C), which have a low-molecular and ionic character, and are currently the subject of many investigations.[13] Our special interest focused on the family of imidazolinium salts[14] due to their deactivated amine or imine functions. Those salts are mostly liquid at room temperature and showed good miscibility with triphosgene. In addition, salt melts have good dielectric properties. We used 1-ethyl-2,3-dimethylimidazolium-bis-trifluoromethanesulfoneimide (mp 20 °C) for our experiments.

Before being used for the controlled release of phosgene, 1-ethyl-2,3-dimethylimidazolium-bis-trifluoromethanesulfoneimide was tested for its catalytic activity at room temperature in the same way that the activated charcoal was tested. Only small mass losses of triphosgene were found (1% after 15 min, 3% after 30 min, 6% after 60 min, and 11% after 120 min).



After the general suitability of the imidazolium salt as a catalyst had been tested, the phosgenation reaction could be carried out in the two-chamber reactor. The catalyst amount in the developing chamber was chosen to be 10 wt% and the microwave power was set to 900 watts. After a reaction time of 30 minutes, the calculated amount of *n*-butanol reacted quantitatively to 6% chloroformate and 94% dibutyl carbonate. The catalyst first employed was reused for the reproduction of the performed synthesis and did not show significant loss of activity. The decomposition of triphosgene and the resulting phosgenation of the alcohol were again quantitative. Extension of the reaction time could possibly result in the complete formation of dibutyl carbonate according to (eqn. 2). Hence, the employed ionic liquid fulfils all process requirements for the microwave assisted phosgenation of *n*-butanol in a two-chamber reactor. In contrast to the H 385™ catalyst, the imidazolium salt can be recycled. Under the described experimental conditions, this alcoholysis can be carried out in the reactor without any danger, and the formation of secondary products is avoided.

Finally, the reaction behaviour of different alcohols during the phosgenation with triphosgene was investigated. The choice of educts was limited to monohydric alcohols, because polyhydric alcohols tend to react to polycarbonates or cyclic carbonates of which the latter easily decarboxylate at temperatures above room temperature.[15,16] The microwave-assisted esterification of the selected alcohols was carried out *via* parallel syntheses in the homogeneous phase, and with BTAC as the catalyst. The rotor systems HPR 1000/10™ and MMR-8™ (Fig. 2), the design of which is the result of our extensive experiences with rotor systems in microwave apparatuses,[17] were used in these experiments. The rotors were especially adapted to the requirements of parallel syntheses.

Fig. 2 Reactor system MMR 8™.

Alcoholyses were performed in the closed rotor system HPR 1000/10™ (Fig. 3).

In double batches, five alcohols reacted with triphosgene in an equimolar ratio in the microwave field, Table 3. Batch size, molar ratio, and the microwave programme were identical to the conditions applied to the one-pot syntheses with *n*-butanol. Besides the formation of the respective chlorides, along with other secondary products, a conversion rate of $> 100\%$ (with respect to the theoretical conversion) was found for educt alcohols, which were used in excess. GC-MS analysis allowed the characterisation of secondary products and conclusions about possible competing reactions. Besides the expected reactions according to eqn. (1) and (2), chloroalkanes RCl (eqn.

Fig. 3 Reactor system HPR 1000/10™S and one segment with pressure reactor.

3a) were formed during the reaction of phosgene with the respective educt. Furthermore, chloroalkanes were also formed at the reaction of hydrogen chloride, resulting from the chloroformylation or carbonylation of the alcohols, through substitution of the alcoholic function according to eqn. (3b). Ether formation was also observed to a small extent and could be identified from the condensation of water (eqn. 4).

$$2R\text{–}OH + COCl_2 \rightarrow 2R\text{–}Cl + CO_2 + H_2O \qquad (3a)$$

$$R\text{–}OH \rightarrow R\text{–}Cl + H_2O \qquad (3b)$$

$$2R\text{–}OH \rightarrow R\text{–}O\text{–}R + H_2O \qquad (4)$$

Benzyl alcohol showed benzylation, and cyclohexanol showed dehydratisation to cyclohexene due to the presence of protons from hydrogen chloride.

Table 3 Microwave assisted reaction of selected alcohols with triphosgene in the rotor system HPR 1000/10™ (GC yields after irradiation for 30 min at 900 W and 130 °C)

Educt	RO–COCl (%)	RO–CO–OR (%)	R–Cl (%)	Secondary products (%)	Conversion (%)
Isopropanol	—	50	10	16[a]	76
n-Butanol	0.5	13	40	3[a]	56.5
tert-Amyl alcohol	—	—	51	0.5[a]	51.5
Cyclohexanol	—	3	25	5[a] 20[c]	53
Benzyl alcohol	3.5	—	7	21[a] 10[b]	41.5

[a] R–O–R. [b] Benzoyl chloride. [c] Cyclohexene.

Table 4 Microwave assisted reaction of selected alcohols with triphosgene in the rotor system MMR-8™ (GC yields after irradiation for 30 min at 900 W and 120 °C)

Educt	RO–COCl (%)	RO–CO–OR (%)	R–Cl (%)	Secondary products (%)	Conversion (%)
Isopropanol[a]	5.5	5	2	—	12.5
n-Butanol	5	38.5	2	—	45.5
tert-Amyl alcohol	—	—	26	—	26
2-Butoxy-ethanol	7.5	19	—	—	26.5
Cyclohexanol	—	3	37.5	3[b] 8.5[d]	52
Benzyl alcohol	0.5	2.5	37.5	11[b] 1[c]	52.5
1-Phenyl alcohol	—	17	29	17[c]	63
n-Octanol	2	37.5	4.5	—	44

[a] About 70 °C. [b] R–O–R. [c] Benzoyl chloride. [d] Cyclohexene.

Since the alcoholysis of triphosgene in the presence of a catalyst in a closed system yielded a high number of secondary reactions, more parallel syntheses were carried out in an open reactor system. Thus, eight alcohols were investigated individually in the rotor system MMR-8™ in the microwave field. Reaction conditions were comparable to those described earlier (batch size, molar ratio), however, the microwave programme was adapted to the new system. The temperature of this system was measured externally with an IR-sensor. The results of the GC analyses, which were performed after a reaction time of 30 minutes, are summarised in Table 4.

The conversion rate of *n*-butanol amounts to 91% after subtracting the excess amount of the educt (100%), which is included in Table 4. This conversion rate is comparable to the rate observed for the one-pot reactions (Table 2). Therefore, the reaction conditions of the reaction in the rotor system MMR-8™ are comparable to those of the one-pot reaction. Parallel syntheses in the microwave field therefore allow us to identify possible reactants to optimise single synthesis. According to the presented results, *n*-octanol, with a yield of 88% (subtracting the excess amounts of the educt), would be a good candidate for the optimisation of process parameters. While linear aliphatic alcohols react easily to dialkyl carbonates, the phosgenation of tertiary alcohols exclusively yields the corresponding chlorides. High conversion to chlorides was also observed for the phosgenation of benzylic and alicyclic alcohols. Since those compounds react to secondary products to a great extent, further syntheses were disregarded. The partial formation of the chloroalkane proved to be non-specific for *n*-butanol. With the exception of 2-butoxy-ethanol, the alcoholysis with triphosgene in the homogeneous phase always yielded the respective chlorides.

Experimental

Microwave experiments

Microwave assisted reactions were performed using the ETHOS 1600™ system equipped with the segment rotors HPR 1000/10™ and MMR-8 (MLS GmbH, Leutkirch). The computer controlled laboratory microwave furnace ETHOS 1600™ has a dual-magnetron unit and an adjustable moving-magnet field in order to ensure synchronic and even magnetic stirring of all reaction vessels. The operating software (easywave™, MLS GmbH, Leutkirch) allows maximum temperature settings of 300 °C for a microwave power of 1000 W. All process parameters can be adjusted during microwave operation. The HPR 1000/10™ rotor system consists of ten single reactors with a volume of 100 mL each. The reactors are made of PTFE and have a safety jacket as well as caps with a pressure relief valve (maximum pressure: 30 bar). The single reactors are arranged in a circle on the rotor rack. Temperature control is provided by a fibre-optic sensor, which is immersed in the reaction mixture. Rotation of the rotor rack ensures equal irradiation of each batch. In addition, each reactor has variable magnetic stirring. The eight-reactor rack MMR™ is an unpressurised system, which consists of circularly arranged glass reactors (150 mL) equipped with magnetic stirring and condenser coils. The latter ones are cooled by forced ventilation of the microwave apparatus. The temperature is measured with non-contact IR at the outer walls of the reactors.

Analytic equipment

Gas chromatograms of the samples, dissolved in dichloromethane, were recorded on Hewlett-Packard gas chromatographs (FID-detector: series 5890, MSD-detector: series 5972). The column was an HP 5 (30 m, ID 0.32 × 0.25 mm). The temperature programme was: 3 min isothermal at 50 °C, followed by a ramp of 8 K min^{-1} up to 320 °C. The detector temperature was set to 300 °C, and the pre-column pressure was 4.55 psi. The split was 194 : 1. Yields were calculated with respect to the minority compound (triphosgene). Because triphosgene cannot be detected with GC, peak area ratios of the respective educts (equimolar to triphosgene) over the products were determined. Yields were calculated from the resulting peak area percentages with the molar masses of the detected compounds.

Note: due to secondary reactions, the theoretically possible yield of 100% for R–OH was exceeded with respect to the formation of the respective carbonate. In order to calculate the reaction yields, the whole amount of used educts (including excess amounts) was considered. Main products and secondary products were analysed with GC-MS and compared to reference samples.

Educts, reference samples, and materials

Chemicals used in the reactions were purchased from Merck. Triphosgene and the H 385™ catalyst were provided by Dr. Eckert GmbH, Hallbergmoos, Germany. The imidazolium salt PW 1022 was donated by Dr. P. Wasserscheid, Aachen, Germany.

Alcoholyses with triphosgene

All educts were distilled before use and dried extensively. All alcohols, prepared in this way, were used in 100% excess (with respect to the quantitative reaction to dialkyl carbonate) for phosgenations. Thus, educts served as reactants and solvents. Since 1/3 mol of triphosgene equals 1 mol of phosgene, educt amounts for the different reaction batches were calculated as phosgene-equivalents. For a better comparison of the results, all batches were chosen to have the same dimensions. Hence, 4.95 g of triphosgene (50 mmol of phosgene-equivalents) reacted with 200 mmol of the respective alcohol. Catalysts were usually used in a mass ratio of 1 : 10 with respect to the amount of triphosgene.

Phosgenation of *n*-butanol

Catalyst tests in homogeneous phase. For each batch, 4.95 g triphosgene, 14.83 g *n*-butanol, and 0.5 g catalyst (BTAC or phenathroline) were weighed in a 100 mL two-neck flask equipped with a magnetic stirring bar. The flask was furthermore equipped with a temperature probe (fibre-optic sensor) and was adjusted with a glass tube in the microwave apparatus. A reflux cooler was attached to the glass tube and connected to the exhaust. The batch was irradiated at a set-temperature of 120–130 °C with a microwave power of 900 W. At the end of the microwave programme, the reaction mixture was cooled down before a sample was taken and analysed with GC. Parallel to the microwave assisted reactions, reactions with the respective catalysts were carried out at room temperature. For these experiments, the compounds were weighed in a 100 mL single-neck flask. The flask was closed with a calcium chloride drying tube and the mixture was stirred for two hours. The degree of conversion was again monitored with a gas chromatograph. In order to compare both methods, the alcoholysis reaction was also carried out without catalyst.

Reaction of *n*-butanol in homogeneous phase under different reaction conditions. 4.95 g of triphosgene, 14.83 g of *n*-butanol, and 0.5 g of BTAC were weighed in a 100 mL two-neck flask with a magnetic stirring bar and irradiated for 30 minutes at a set-temperature of 120–130 °C with 900 W. Parallel to the microwave assisted reactions, reactions were carried out in preheated oil baths at 60 and 120 °C. For this purpose, the two-neck flask was equipped with a thermometer. The reflux apparatus was then closed with a calcium chloride drying tube, and the reaction mixture was stirred for 30 minutes at the pre-set temperature. In order to follow the progress of the reaction, samples were taken after 5, 10, 20 and 30 minutes, and analysed with a GC. Sample collection from the microwave-assisted alcoholyses was done during microwave operation. The programme was shortly interrupted by pressing the pause key and then continued once again by the pause key.

Reactions in the two-chamber reactor. The reactor, which was equipped with a dry ice cooling system comprising of a double-valve and bubble gage, was adjusted with a glass tube in the microwave apparatus, and subsequently flooded with nitrogen. *N*-butanol was weighed in a Schlenk flask and transferred to the reaction chamber through a capillary tube with nitrogen. The Schlenk flask was reweighed in order to determine the exact amount of educt present in the reactor. Triphosgene and the respective amount of the catalyst H 385™ (one pellet weighs approx. 30 mg) or the imidazolinium salt PW 1022 (500 mg) were weighed directly in the developing chamber. The chamber was attached to the reactor *via* a gas-tight GL-union. Temperature-control of the phosgene release was performed either externally with a diethylene glycol bath for the H 385™, or internally with a fibre-optic sensor directly in the developing chamber for the PW 1022. The temperature in the reaction chamber was constantly measured with a second temperature probe. Prior to starting the microwave programme, a low nitrogen flow was adjusted. After these preparations, the reactor was irradiated for 15 minutes at a set-temperature of 110 °C and another 15 minutes at 130 °C with 800 W microwave power (following an optimised temperature programme). By reweighing the developing chamber, we were able to assess the completeness of the triphosgene decomposition. Conversion rates in the reaction chamber were analysed with GC.

Isolation of di-*n*-butyl carbonate. For product isolation, an equivalent amount of petroleum ether (30–60 °C) was added to a 50 mmol batch of the reaction mixture and subsequently extracted with 30 mL water, saturated sodium hydrogen carbonate solution, and two times with water, respectively. The petroleum ether was then removed at reduced pressure in a rotary evaporator. Subsequently, excess butanol was removed at 60 °C (20 mbar) along with all low-boiling secondary products. Traces of washing water were removed as azeotrope with butanol. Di-*n*-butyl carbonate was obtained in a yield of 83% with a purity of 97%.

Phosgenation of selected alcohols in combinatorial reactions

Alcoholysis with the rotor system HPR 1000/10™. 200 mmol educt alcohol, 4.95 g triphosgene, and 0.5 g BTAC were weighed in the PTFE inserts. The single reactors were then sealed gas-tight after the addition of a magnetic stirring bar. Segments with the same educts were mounted facing each other into the rotor rack and the whole system was installed in the microwave apparatus. Temperature was controlled with a fibre-optic sensor that was inserted through the cap of reactor 1. The rotor system was irradiated for 30 min at 130 °C with 900 W. After cooling down to room temperature, the slightly pressurised reactor segments were carefully opened under a hood. Samples were collected and analysed with GC and the results found were comparable for each of the used educts.

Alcoholysis in the rotor system MMR-8™. 200 mmol of the respective alcohol, 4.95 g of triphosgene, and 0.5 g BTAC were weighed in the glass vessels, which were equipped with magnetic stirrers. The appropriate cooling coils were then attached to the reaction vessels. The single reactors were mounted into the rotor rack and the rack was installed in the microwave apparatus. Because temperature control of this reactor type was performed with an IR-sensor at the outer walls of the reaction vessels, a modified microwave programme was employed, accounting for the different heating behaviour. Thus, irradiation was performed with 900 W microwave power starting from 30 °C in 10-degree-steps to a final set-temperature of 60 °C. Within 35 min, heating was done in 5-minute-intervals during which the reached temperature was held for 5 minutes. The temperature range of 50–60 °C determined with the IR-sensor in the described fashion was assumed to be approximately equivalent to 120 °C because boiling of the butanol batch was observed (bp of the educt: 118 °C). After a ventilation time of 30 min, a sample was taken from each batch and analysed with GC.

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Communication

Oxidation of styrene and cyclohexene under microwave conditions

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Received 23rd December 2002
First published as an Advance Article on the web 12th May 2003

The coupling of microwave energy with solvent-free phase-transfer catalysis was studied for the oxidation of cyclohexene and styrene. The former Noyori oxidation system (*Science*, 1998, **281**, 1646) was restudied under the aforementioned conditions and optimised. In addition, parallel oxidations were successfully employed by using a special microwave set-up.

Introduction

Oxidation processes play an important role in modern organic chemistry.[1,2] Cyclohexene, for example, is an initial product for the production of adipic acid and synthetic fibres. It is therefore a challenge for technical chemists or chemical engineers to develop new environmentally benign and hence non-polluting oxidation patterns.

Our scientific aim was to restudy and to assess the well-known hydrogen peroxide–sodium tungstate–methyltrioctylammonium salt system (first described by Noyori[3]) under microwave conditions[4–6] and by means of specially designed experimental set-ups. In order to check and widen this aforementioned system, sodium tungstate was replaced by commercially available and chemically comparable tungsten salts and molybdenum salts. The use of hydrogen peroxide as a relatively inexpensive oxidant seemed promising. The choice of our model system, *i.e.* the oxidation of cyclohexene and styrene, as already described in numerous publications,[7–9] was influenced on the one side by the interest in the manufacturing of fine chemicals, and on the other side by our engagement within the framework of sustainability. The considered oxidation system in combination with an alternative system for energy input should meet this challenge. This is demonstrated for the example of cyclohexene as a source for adipic acid, *cf.* Scheme 1.

To date, the production of adipic acid is accomplished for the most part from cyclohexanone and cyclohexanol with the use of nitric acid. This production process causes considerable environmental impacts, *e.g.* the formation of nitrous oxide (referring to the manufacturing process at Radici Ltd., Zeitz, Germany).

The catalyst system mentioned above enables the synthesis of adipic acid from cyclohexene without the use of halogens or organic solvents. The employment of microwave energy results in time-saving and energy-conserving oxidation methods.

Results and discussion

The oxidation of cyclohexene by conventional heating (thermal energy) afforded a yield of 83% adipic acid after about 9 hours (*cf.* entry 5, Table 1). Using microwave energy and 45 min reaction time, a yield of 21% adipic acid was observed (entry 1). Doubling the reaction time and the amount of catalyst further increased the yield (entry 2).

The conditions described in entry 4 afforded yields nearly comparable to those of the classical thermal energy input (entry 5). From these results, it is obvious that microwave application is advantageous for the reduction of reaction time and energy conservation. Yields of adipic acid increase with increasing catalyst amounts and/or extension of reaction time.

In order to assess the Noyori-system, sodium tungstate was substituted by various commercially available tungsten salts and molybdenum salts. The ability of the new catalysts to convert cyclohexene into adipic acid in a microwave-assisted reaction could be confirmed (Table 2).

Best yields were achieved with sodium polytungstate. Some representatives of molybdenum salts and ammonium paratungstate did not afford any adipic acid.

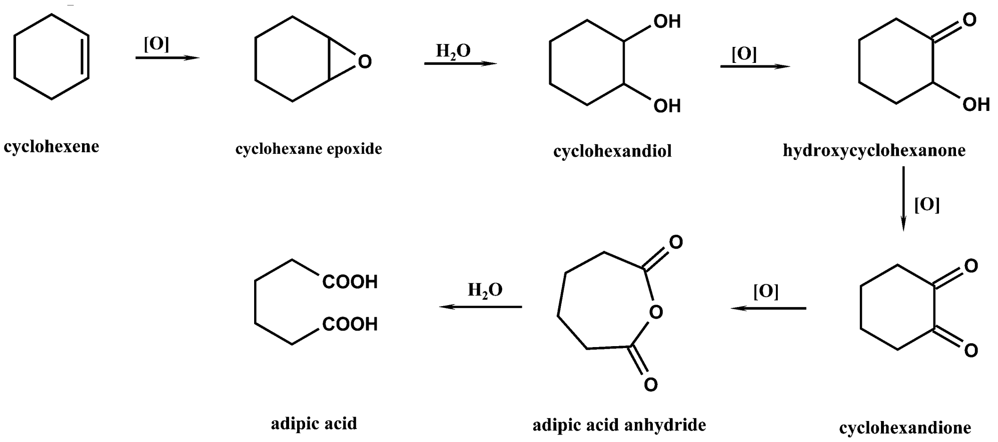
Furthermore, the system developed by Noyori was adapted to the oxidation of styrene. Doubling the catalyst amount enhanced the conversion of styrene considerably. Yields of benzoic acid increased considerably after doubling the amount of catalyst. The conditions, as described in entry 7 (Table 1), facilitated the oxidation of styrene to benzoic acid and gave a yield of 77%. Under the conditions described in entry 6, a yield of only 45% was attained. On the basis of the detected products as well as products reported in literature, reaction scheme 2 was developed.

In a first step, phenyloxirane is formed from styrene. Reaction pathways I to IV are derived from phenyloxirane. From the conversion of styrene, benzaldehyde and benzoic acid

Green Context

Adipic acid is one of the most important intermediates in the organic chemicals industry, being used in the manufacture of nylon 6,6. However, current manufacturing methods employ hazardous nitric acid as the oxidant and produce extremely large volumes of unacceptable NO_x pollutants. Here we see a new method for synthesising adipic acid using the inexpensive cyclohexene as starting material. The catalytic methodology is based on the tungstate–PTC system developed by Noyori. Hydrogen peroxide, one of the most environmentally acceptable sources of oxygen is used and the reaction is accelerated through the use of microwave energy. Under these conditions the reaction is remarkably quick. The methodology has also been extended to the oxidation of styrene with some interesting results. ***JHC***

DOI: 10.1039/b212522f



Scheme 1 Reaction steps from cyclohexene to adipic acid.

Table 1 Oxidation of cyclohexene and styrene under microwave conditions[a]

Educt	Entry	$Na_2WO_4{\cdot}2H_2O$/ $CH_3[(C_8H_{17})_3N]HSO_4$ (mmol/mmol)	Time/min	Yield (%)	
Cyclohexene (9.97 g; 0.1217 mol)	1	1.22/1.22	45	21	adipic acid
	2	1.22/1.22	90	38	adipic acid
	3	2.44/2.44	45	50	adipic acid
	4	2.44/2.44	90	68	adipic acid
	5	1.22/1.22 (classical method)	555	83	adipic acid
Styrene (12.68 g; 0.1217 mol)	6	1.22/1.22	45	45	benzoic acid
				11	benzaldehyde
				1	phenylacetaldehyde
				19	phenylglycol
	7	2.44/2.44	45	77	benzoic acid
				13	benzaldehyde
				0.5	phenylacetaldehyde
				0	phenylglycol

[a] reflux; 400 W

Table 2 Microwave-assisted oxidation of cyclohexene (*cf.* Table 1; entry 1)

Catalyst	Abbreviation	Yield of adipic acid (%)
Phosphomolybdic acid ammonium salt hydrate	PMAH	0
Phosphomolybdic acid sodium salt hydrate	PMSH	0
Ammonium molybdate tetrahydrate	AMTH	0
Ammonium paratungstate	APT	0
Ammonium metatungstate hydrate	AMT	30
Phosphotungstic acid disodium salt hydrate	PTDH	39
Phosphotungstic acid trisodium salt hydrate	PTTH	40
Sodium polytungstate	SPT	45

are identified in respectable yields. A preference of reaction path III is likely. However, it remains unresolved in how far the chemical equilibrium is responsible for the observed results.

Using several tungsten and molybdenum salts to check the Noyori system, high yields of benzoic acid are achieved with APT and AMTH. Therefore, reaction pathways I to IV are taken into account. Using AMT, only low conversion but high selectivity for benzaldehyde was observed (Table 3), which led to the conclusion that reaction pathway III is preferred.

Results varied considerably for the variation of catalysts. While APT and AMTH promote the formation of benzoic acid, benzaldehyde is formed upon the application of PMAH, AMT, and SPT. PMSH affords phenylglycol with the highest selectivity. PMSH reveals lower oxidation efficiency for styrene than any other of the applied catalysts (Table 3).

The catalysts PTTH and PTDH are very well suited for conversion with the methyltrioctylammonium hydrogensulfate–H_2O_2 system. Under microwave irradiation, however, styrene is totally oxidized. Irradiation power does not influence the variety and quantity of reaction products, the heat-up time is elongated only.

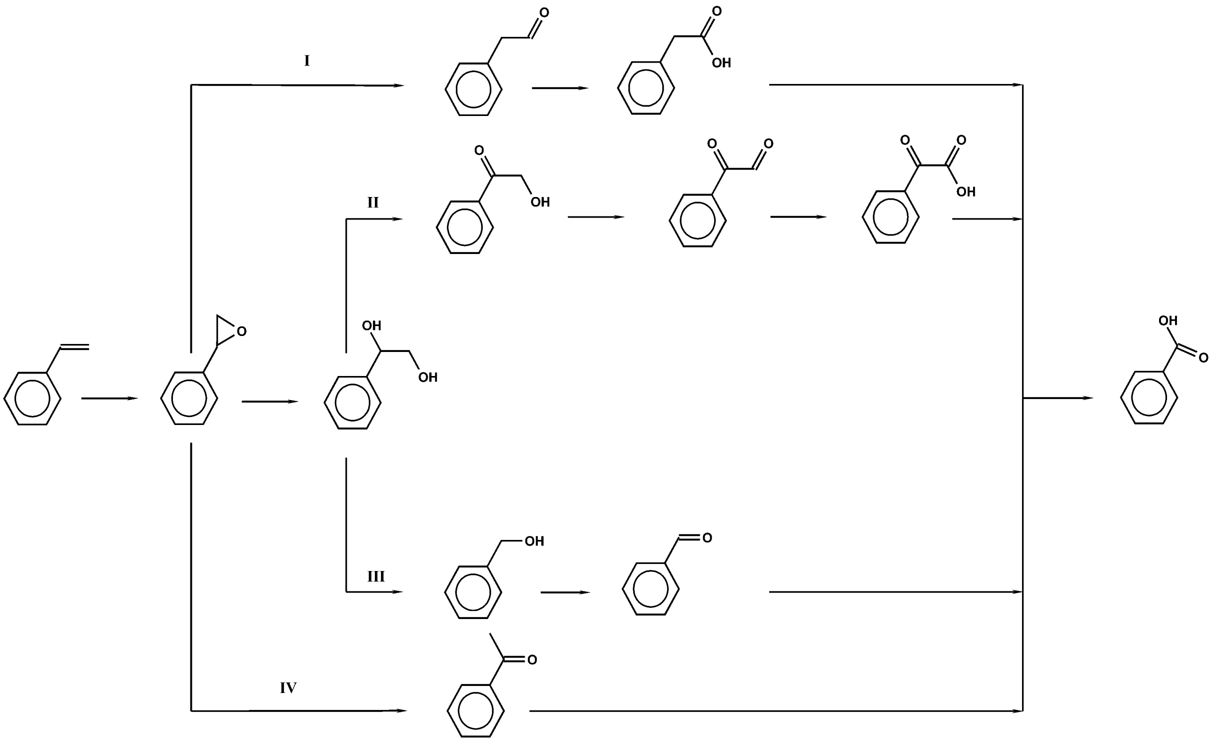
Due to this circumstance, experiments were performed at ambient temperatures (Table 4). High yields of benzoic acid are observed for both PTTH and PTDH.

In addition, we studied advantages of microwave application in parallel reactions. For these experiments, we used the rotor system MMR 8 (MLS GmbH, Leutkirch, Germany) (Fig. 1). The design of this equipment allowed control of eight reaction systems simultaneously. The temperature in the reaction system was determined by a fibre optic sensor. A glass capillary was designed to immerse the sensor into the reaction mixture (Fig. 2). In order to explore the possibilities of the rotor system MMR 8, we oxidized styrene under similar conditions to those described by Noyori. Comparable conditions could be assured for each of the eight reaction systems in order to give comparable results.

We changed the ratio of sodium tungstate : methyltrioctylammonium salt. Table 5 summarizes yields of selected products. The catalyst ratio strongly affected the reaction with respect to conversion, yield, and selectivity. Highest conversion was observed for a catalyst ratio of 1 : 1, which does not agree with Noyori's results.

Conclusion

Through optimisation of microwave-assisted syntheses, it seems possible to achieve advantages in time consumption and



Scheme 2 Reaction pathways of the styrene oxidation.

Table 3 Oxidation of styrene with microwave irradiation[a]

Catalyst	Conversion (%)	Selectivity (%) Benzoic acid	Benzaldehyde	Phenylacetaldehyde	Phenylglycol	Others
AMT	30	8	88	4	0	0
PMAH	52	5	62	19	12	2
PMSH	71	10	33	9	41	7
APT	87	92	7	0	0	1
SPT	88	27	30	13	25	5
AMTH	90	92	7	0	0	1

[a] 45 min; reflux; 400 W.

Table 4 Oxidation of styrene under adiabatic conditions without microwave irradiation[a]

Catalyst (mmol)	Yield (%) Benzoic acid	Benzaldehyde	Phenylacetaldehyde	Phenylglycol
PTDH (1.22)	17	38	6	12
PTDH (2.44)	67	27	1	1
PTTH (1.22)	71	24	1	0
PTTH (2.44)	82	10	0	0

[a] 45 min; room temperature to 100 °C

energy conservation compared to a thermal reaction regime. Microwave-driven experiments of cyclohexene were similar to thermally-driven experiments. Conversion of styrene using a sodium tungstate/phase-transfer catalyst system was successful. However, it remains unclear which of the suggested reaction pathways among I through IV is preferred (Scheme 2).

Fig. 1 Rotor system MMR 8.

The use of several tungsten salts and molybdenum salts affords yields which challenge those obtained with the Noyori system. Highest conversion of cyclohexene was achieved with NPT, and the highest conversion of styrene with APT and AMTH. The application of PTTH and PTDH shows at ambient temperatures considerable oxidation efficiency.

The experimental set-up ETHOS 1600 in combination with the rotor system MMR 8 (both MLS GmbH, Leutkirch,

Table 5 Microwave-initialised oxidation of styrene using rotor system MMR 8 (MLS GmbH, Leutkirch, Germany)

Reaction vessel	$Na_2WO_4 \cdot 2H_2O$/ $CH_3[(C_8H_{17})_3N]HSO_4$ (mmol/mmol)	Conversion (±2%)	Yield (±1%)				
			Phenyloxirane	Phenylglycol	Phenylacetaldehyde	Benzaldehyde	Benzoic acid
1–8[a]	1.22/1.22	60	0	2	1	50	0
1	1.22/1.22	60	0	3	1	49	0
2	1.22/2.44	34	0	7	2	13	0
3	2.44/1.22	34	1	7	1	11	4
4	0.61/0.61	8	0	1	0	4	0
5	0.61/1.22	12	0	3	0	5	0
6	1.22/0.61	11	2	1	0	5	0
7	0.61/2.44	17	0	2	1	9	0
8	2.44/0.61	9	3	0	0	3	0

[a] Each vessel was prepared identically.

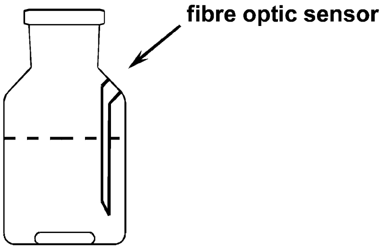


Fig. 2 Reaction vessel.

Germany) is well suited for rapid parallel studies of oxidation reactions under identical conditions.

Experimental

General

The synthesis set-up consisted of the microwave system ETHOS 1600 (MLS GmbH, Leutkirch). Gas chromatographic (GC) analyses were carried out using an HP 6890 series gas chromatograph equipped with an HP 5 column (0.32 mm x 25 m) and hydrogen as carrier gas. Gas chromatographic/mass spectroscopic (GC/MS) analyses were carried out using an HP 5890 series II gas chromatograph/HP 5972 series MS detector equipped with a HP 5 column (0.32 mm x 30 m) and helium as carrier gas.

Materials

Methyltrioctylammoniumhydrogensulfate was synthesised as described in reference 10. All other chemicals were purchased from Aldrich.

Oxidation of cyclohexene/styrene at reflux

1.137 g (1.22 mmol) methyltrioctylammoniumhydrogensulfate was added to a solution of catalyst (Table 1–3) and 60.7 g hydrogen peroxide (0.535 mol). The mixture was stirred at room temperature for 15 min. 0.1217 mol olefin (cyclohexene or styrene) were added and the reaction vessel was mounted into the microwave system ETHOS 1600 (MLS GmbH, Leutkirch). Microwave heating programmes for cyclohexene and styrene were started (Tables 6 and 7, respectively). The mixture was vigorously stirred with a magnetic stirring bar. After running the microwave programme, the reaction mixture was cooled down to room temperature. The reaction mixture was extracted with 3 × 20 ml dichloromethane, followed by the separation of the organic phase. The organic phase was washed with saturated $FeSO_4$ solution, dried over magnesium sulfate, evaporated, and analysed by GC using the internal standard method.

Table 6 Microwave heating programme (cyclohexene, 400 W)

Step	Time/min	Temperature/ °C
1	3	70
2	3	70
3	3	75
4	3	75
5	3	80
6	3	80
7	3	90
8	10	90
Total time	31	

Table 7 Microwave heating programme (styrene, 400 W)

Step	Time/min	Temperature/ °C
1	3	70
2	10	70
3	5	80
4	3	80
5	3	80
6	10	80
Total time	34	

Oxidation of styrene using the experimental set-up MMR 8

The educts were combined as previously described with catalyst in ratios of sodium tungstate : methyltrioctylammoniumhydrogensulfate as described in Table 5. Cross-shaped magnetic stirring bars were used for agitating the solution. After loading the eight reaction vessels with defined reaction mixtures, the vessels were mounted into the rotor system MMR 8. The fibre optic sensor was usually immersed into the reaction vessel with the highest ratio of educts. After running the microwave programme, the reaction mixtures were worked-up as previously described. Products were identified by comparison with standard samples and by GC/MS.

Acknowledgement

The authors would like to thank the “Fonds der Chemischen Industrie” for financial support (B. O.).

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Ionic liquids and their heating behaviour during microwave irradiation – a state of the art report and challenge to assessment†

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Received 23rd December 2002
First published as an Advance Article on the web 30th April 2003

Ionic liquids of the 1,3-dialkylimidazolium-type reveal great potential for the innovative application of microwaves for synthesis as well as for separations. Ionic liquids efficiently absorb microwave energy and thus are employed as solvents and co-solvents. In this context, microwaves assist in carrying out syntheses or unit operations.

Introduction

The application of ionic liquids as alternative reaction media was frequently reported in literature during recent years.[1–5] Properties of ionic liquids such as solubility, solvation strength, acidity, and coordination were selectively varied and in most cases successfully validated. Most chemical reactions were carried out at low temperatures (0–80 °C).[1c,4,5] Ionic liquids usually have a liquid range that significantly exceeds 300 K. The upper temperature limit of selected ionic liquids is higher than the temperatures described for their applications so far, *i.e.* $\vartheta > 200$ °C.[1a,6] It is energetically favourable if reactions are carried out at low temperatures. However, extended reaction times of some syntheses[7–9] lead to the question of whether higher temperatures and thus shorter reaction times would result in higher product yields and selectivities.

This question motivated us to investigate the efficient energy input through microwaves, as known from literature, in the case of ionic liquids. Microwave-assisted reactions are known for their short reaction times.[10–12] This advantage results from the way in which substances are heated in the microwave field. Microwaves directly excite polar molecules (dipole relaxation) and ions (ionic conduction). On the macroscopic scale, the substance or substance mixture heats up, which is induced through friction of molecules and/or ions with each other. Therefore, the presence of ions and/or polar molecules is necessary for substances to be heated in the microwave field.

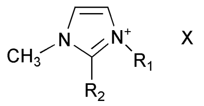
Ionic liquids fulfil both requirements and should be principally suitable for energy dissipation with microwaves. Due to their broad application spectrum, a series of 1,3-dialkylimidazolium compounds (Table 1) was synthesised and their heating behaviour was studied under multi-mode microwave conditions.

Experimental

Chemicals

The ILs **1–4** were made available by Solvent Innovation GmbH, Köln, Germany. **5** and **6** were synthesized as described in ref. 13 and 14 The basic material for **5** and **6** (1-butyl-3-methylimidazolium chloride) was synthesized by microwave-solvent-free synthesis[15] from N-methylimidazole and n-butyl chloride. The purity of the substances was examined by ^1H and ^{13}C NMR (Bruker AVANCE 200) as soon as Karl Fischer titration (Mettler DL 37 KF Coulometer). The analysis showed no organic impurities and the water content of the ILs was smaller than 0.05% w/w (after drying at 60 °C under vacuum for 12 hours). Tests with silver nitrate showed no halide in **1–6**. Cyclohexane (99.5%) and toluene (99.7%) were purchased from Fluka.

Table 1 Synthesised and studied ionic liquids



IL	1	2	3	4	5	6
R1	CH_3	C_2H_5	C_2H_5	n-C_4H_9	n-C_4H_9	n-C_4H_9
R2	H	H	CH_3	H	H	H
X	Tf_2N[a]	Tf_2N	Tf_2N	Tf_2N	$[BF_4]$	$[PF_6]$

[a] Bis(trifluoromethylsulfonyl)imide-anion.

Green Context

Ionic liquids by their very nature would seem to be ideal media for the application of microwave activation. In particular, it should be possible to gain the advantage of much shorter reaction periods for synthetic reactions through the use of ionic liquids. Here, for the first time the complex heating behaviour of commonly employed ionic liquids has been investigated under the conditions of dielectric heating. It is particularly interesting to note that the presence of only small amounts of ionic liquids are necessary in order to significantly reduce the heating time of hydrocarbon solvents under microwave conditions. Thus the door is opened for the further utilisation of these fascinating compounds through their use as co-solvents to enable fast, microwave assisted synthesis. ***JHC***

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† Some parts of this paper were presented for the first time as a poster at the 221st ACS meeting (San Diego, USA, 2001).

DOI: 10.1039/b212533a

Microwave heating experiments

The substances summarised in Table 1 were investigated in glass reflux apparatuses equipped with magnetic stirring. The temperature was recorded with a fibre optic sensor for different microwave power settings in an ETHOS® 1600 microwave furnace (MLS GmbH, Leutkirch, Germany). Furthermore, selected mixtures of aforementioned ionic liquids with toluene or cyclohexane were prepared and temperature–time-curves were registered.

Results and discussion

Heating experiments with pure ionic liquids showed curved temperature–time-dependencies, *cf.* Fig. 1.

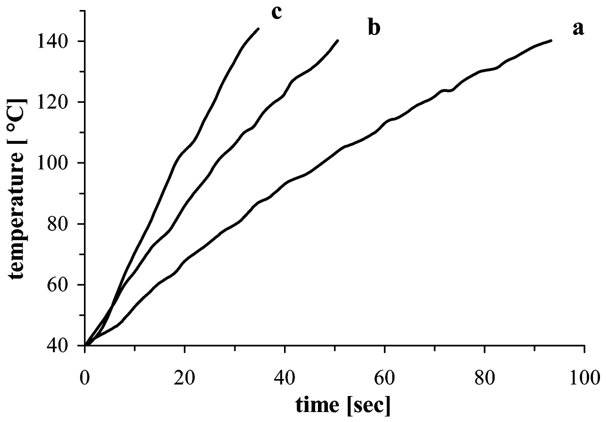

Fig. 1 Heating curves of **6** (20 g) at different microwave power P_{MW}: [a] 200 W, [b] 300 W and [c] 400 W

Depending on the set microwave power the curvature increases or decreases. This behaviour is due to the influence of the heat transfer. In addition, the specific heat capacity increases with increasing reaction temperatures. Thus, more energy is required for heating. Because energy is provided through unpulsed continuous microwave irradiation, heating time consequently increases. The mechanism of the absorption of microwaves by the substance has a further influence on the heating behaviour. Reference[16–18] refers to the temperature dependency of relevant parameters (loss factor, conductivity, density, *etc.*). The change of these parameters with temperature also suggests a curved temperature–time-function. The increase of microwave power results in a drastic decrease in heating time. In order to compare different substances, the heating times of the pure ionic liquids, which were in the temperature range between 40 and 140 °C (ΔT = 100 K), were determined (Table 2).

Heating time does not show linear behaviour for a constant increase of introduced microwave power. This results from the dependency of the absorbed microwave power on the square of the electrical field strength ($P \propto E^2$).[16–18] Quotients which relate to the increase in microwave power F_P and the decrease in heating time F_{HT} clarify this (Table 3).

Nevertheless, the derived quotients reveal deviations, which mainly result from time differences. The more time the microwave system requires for heating the ionic liquids, the more heat can be exchanged between the substances and the microwave space. The result is an extended additional heating period at low microwave power settings, which influences the quotient F_{HT}.

Table 2 Heating times of ILs (20 g) at different microwave power

	$HT_{40–140\ °C}$/s					
P_{MW}/W	**1**	**2**	**3**	**4**	**5**	**6**
200	142	129	103	85	105	93
300	32	30	25	28	55	51
400	20	23	20	22	35	33

Further analysis of Table 2 reveals even more dependencies. Thus, the heating time decreases for the same anion (Tf_2N) with increasing molar mass at low microwave powers (200 W). With increasing microwave power, this effect becomes less significant because heating rates cannot be distinguished any more within the margin of error of the measurement. This behaviour is due to the conductivity of the investigated substances, which decreases with increasing molar masses.[19] Conductivity is inversely proportional to time. According to literature values, ionic liquid **3** should heat up faster than ionic liquid **4**. However, experiments do not correspond with these conclusions. In addition, the difference in conductivity between **2** and **3** of 5 mS cm^{-1} does not greatly affect the heating behaviour. In other words, conductivity is not the only influencing factor on the microwave absorption mechanism of different substances. Dipole relaxation plays another key role. Only the superposition of those two principles explains the order in heating behaviour according to the molar masses for the same anion.

The influence of different volumes for the same mass is significant. Because the microwave power P must be understood as absorbed power per volume, significant differences in density are another contribution to differences. Investigations with the same molar amounts did not change the order. For the same molar amount the same number of molecules is exposed to microwave radiation. Therefore, it can be concluded that the found dependency of the heating behaviour on the molar mass for the same anion (Tf_2N) is characteristic for this type of ionic liquid.

It is remarkable that ionic liquids with the same cation (1-butyl-3-methylimidazolium-cation) do not show this dependency. Moreover, differences in heating time occur, which are mainly due to the character of the anion. $[PF_6]^-$ and $[BF_4]^-$ are inorganic anions with high symmetry. The negative charge is thus evenly distributed over the surface. However, the Tf_2N-anion is of organic origin and has not such high symmetry. In addition, the Tf_2N-anion shows dipole relaxation. As mentioned before, a superposition of two mechanisms, dipole relaxation and ionic conduction, prevails. Therefore, a better coupling with microwaves cannot be excluded.

For the example of **6**, the dependency of the heating behaviour on the molar amount of the ionic liquid was investigated in depth. The square dependency of the microwave power P on the electrical field strength E could be confirmed for all investigated samples. For the analysis of the so obtained data, the approximation through polynomial equations was sufficient. Thus, it was concluded that for constant molar amounts the increase of microwave power decreased the heating

Table 3 Quotients of microwave power F_P and heating time F_{HT} of IL (20 g)

IL	**1**			**2**			**3**			**4**			**5**			**6**		
$(F_P)^2$	1.8	2.3	4.0	1.8	2.3	4.0	1.8	2.3	4.0	1.8	2.3	4.0	1.8	2.3	4.0	1.8	2.3	4.0
F_{HT}	1.6	4.4	7.1	1.3	4.3	5.6	1.3	4.1	5.2	1.3	3.0	3.9	1.6	1.9	3.0	1.5	1.8	2.8

$F_P = (P_{MW1})/(P_{MW2})$; $F_{HT} = (HT_2)/(HT_1)$.

time. For further increase of microwave power, the heating time approaches a limiting value. Therefore, it becomes necessary to determine for each ionic liquid-system the optimal power input in order to reduce heating time in an energy-favourable way.

Another important conclusion is the dependency of the molar amount on heating time at the same microwave power. At this point, the advantage of microwave processing becomes evident, *i.e.* for double the amount of **6**, half the heating time is required (Fig. 2).

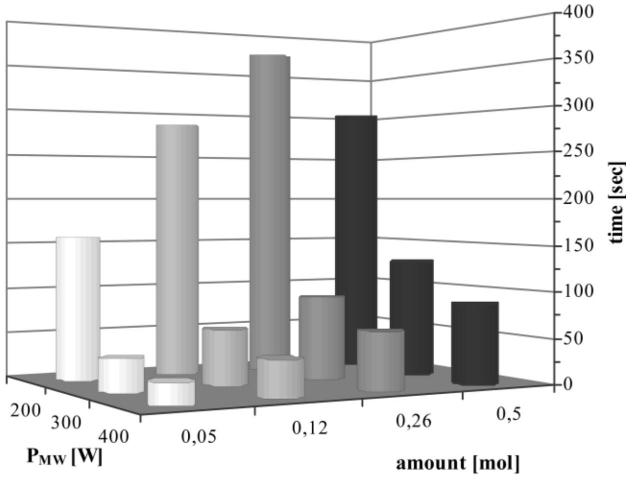

Fig. 2 Heating times of **6** at different microwave power and amounts.

Again, the examination of experimental data resulted in polynomial dependencies of variable molar amounts at the same microwave power, *i.e.* large amounts of ionic liquids can be heated in shorter time and with less energy than expected from linear extrapolation (see ref. 10). Reasons for this behaviour are mainly due to the ratio of the volume of the substance to be heated and the internal volume of the microwave apparatus (*cf.* ref. 16). Impact factors, such as surface, volume, penetration depth, *etc.* have a key role. With exception of the heating times obtained at 200 W, a polynomial dependency was found for all samples. Another phenomenon occurred for the sample investigated at 200 W and for 0.26 and 0.5 mol, which requires further investigation. It seems possible that for amounts of 0.5 mol and higher, the exploitation of microwave power in the chosen microwave space becomes very efficient. Conventional heating methods show clear disadvantages in this context.

A further investigation covered the heating behaviour of ionic liquids when mixed as additives to microwave-inactive solvents, *e.g.* toluene and cyclohexane. Ionic liquids were added in 1 mL-steps from 1 to 5 mL to 100 mL of the respective solvent. Those binary mixtures were also investigated with respect to heating behaviour in the same microwave apparatus and with the same temperature probe as used before. Toluene and cyclohexane are insufficiently heated in the microwave field. Through the addition of ionic liquids in an additive amount, the binary mixture can be heated quickly to its boiling point. Therefore, we conclude that only small amounts of ionic liquids are necessary in order to significantly reduce the heating time of toluene or cyclohexane under microwave conditions. An increase in the microwave power further amplifies this reduction in heating time (Table 4, Fig. 3).

Also in this case, heating time approaches a limiting value upon increasing the microwave power. This is also true for the addition of ionic liquids to both nonpolar solvents (toluene and cyclohexane).

Conclusion

For the first time, the complex heating behaviour of commonly employed ionic liquids was investigated under the conditions of dielectric heating. Ionic liquids of the 1,3-dialkylimidazolium-type can be advantageously employed as solvents and co-solvents in synthesis as well as separations. Application examples of synthesis protocols comprising microwave assistance and ionic liquids are under way and will soon be published elsewhere, *cf.* ref. 20.

Table 4 Heating times of toluene/IL-mixtures

IL	P_{MW}/W	$HT_{35–105\,°C}$/s, (100 mL : *x* mL)		
		100 : 1	100 : 3	100 : 5
1	300	318	90	70
	400	167	66	53
	500	112	54	39
6	300	548	168	143
	400	319	126	92
	500	229	88	86

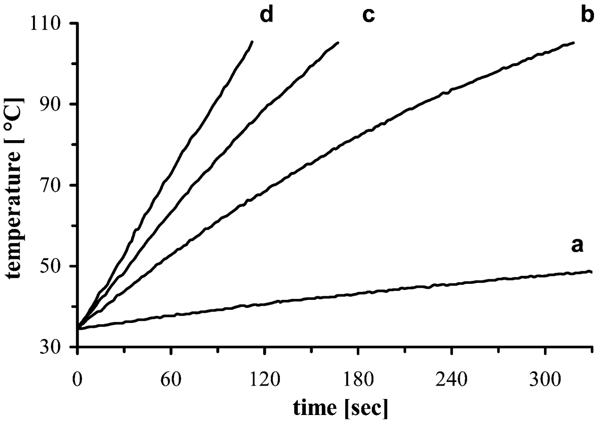

Fig. 3 Heating curves of mixtures of toluene and **1** at different microwave power ^{a} toluene : **1** (100 mL : 0 mL), P_{MW} = 500 W;^{b,c,d} toluene : **1** (100 mL : 1 mL), ^{b} P_{MW} = 300 W, ^{c} P_{MW} = 400 W, ^{d} P_{MW} = 500 W

Acknowledgements

The authors would like to thank the “Deutsche Bundesstiftung Umwelt (Osnabrück, Germany) for a research grant (J. H.) and the Fonds der Chemischen Industrie for financial support (B. O.).

Thanks to referee A for the interesting note to possible formation of polymeric supramolecules and their interactions by addition of further substances. These are not, however, the subject of our investigations, but should be considered if required in the future.

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Communication

Synthesis of *ε*-caprolactam precursors through the *N*-hydroxyphthalimide-catalyzed aerobic oxidation of K/A-oil

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Received 5th November 2002
First published as an Advance Article on the web 22nd May 2003

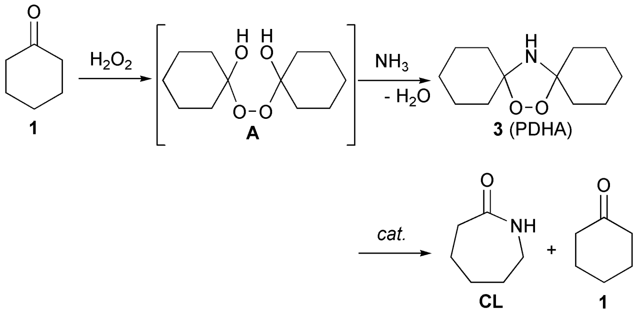
A methodology for the preparation of *ε*-caprolactam (CL) precursors like 1,1′-peroxydicyclohexylamine (PDHA) and/or cyclohexanone oxime from K/A-oil (a mixture of cyclohexanone and cyclohexanol) has been established by the use of *N*-hydroxyphthalimide (NHPI) as a key catalyst. Thus, the aerobic oxidation of K/A-oil catalyzed by NHPI followed by treatment with ammonia afforded CL precursors in high selectivities.

Introduction

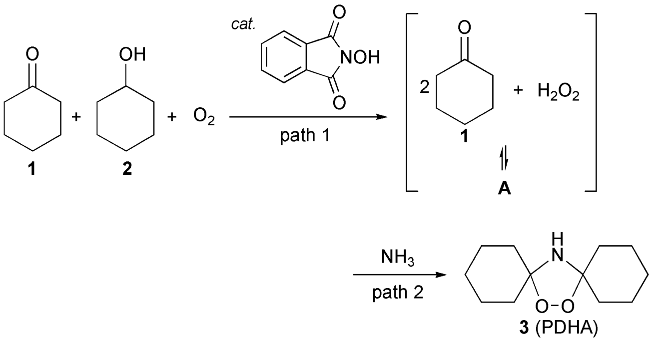
ε-Caprolactam (CL) is a very important monomer for the production of nylon-6, and about 4.2 million tons of CL were manufactured worldwide in 1998.[1] Most methods of current CL production involve the conversion of cyclohexanone with hydroxylamine sulfate into cyclohexanone oxime followed by Beckmann rearrangement by the action of oleum and then treatment with ammonia giving CL. A serious drawback of this process is the co-production of a large amount of ammonium sulfate waste.[1,2] So far, several attempts have been examined to develop a new method to minimize by-products and waste like ammonia sulfate. From an environmental aspect, in particular, the development of no-waste methods for the production of CL has been desired for a long time in industrial chemistry. Quite recently, Raja *et al.* reported a method for one-step production of cyclohexanone oxime and CL by the reaction of cyclohexanone with ammonia under pressure of air (34.5 atm) in the presence of a bifunctional molecular sieve catalyst.[3] In this reaction, 15% of cyclohexanone was converted into cyclohexanone oxime (76% selectivity) and CL (17% selectivity). It was known that titanium silicate-catalyzed ammoxidation of cyclohexanone with H_2O_2–NH_3 followed by solid acid-catalyzed rearrangement produces CL.[4] In patent work, on the other hand, the transformation of 1,1′-peroxydicyclohexylamine (PDHA, **3**) to a 1 : 1 mixture of CL and cyclohexanone by LiBr is reported.[5]

Previously, we have shown that *N*-hydroxyphthalimide (NHPI) serves as an efficient catalyst for the oxidation of various organic substrates with molecular oxygen under relatively mild conditions.[6] Our attention has been focused on development of a novel route to the CL precursor, PDHA, which has so far been prepared by hydrogen peroxide oxidation of cyclohexanone (**1**) followed by treatment with ammonia (Scheme 1).[1,5] Due to easy transformation of PDHA to a 1 : 1 mixture of CL and **1** under the influence of an appropriate catalyst such as lithium halides, the CL production *via* PDHA is considered to be a superior candidate of a next-generation waste-free process for CL. In this communication, we wish to report a new approach for the synthesis of PDHA by the use of NHPI as a key catalyst.

Our strategy is outlined in Scheme 2. The NHPI-catalyzed oxidation of K/A-oil, a mixture of cyclohexanone (**1**) and cyclohexanol (**2**), with O_2 produces 1,1′-dihydroxydicyclohexyl peroxide (**A**) which seems to exist in equilibrium with cyclohexanone and H_2O_2 (path 1). Subsequent treatment of the resulting reaction mixture with NH_3 would afford PDHA (path 2).[7] This route provides a more economical and environmen-



Scheme 1



Scheme 2

Green Context

ε*-Caprolactam is one of the most important intermediates in the polymer industry being used for the production of several MT of nylon-6 every year. The most common route to the lactam is *via* a multi-step process which has low atom efficiency and produces large volumes of salt waste (high E factor). The lactam can be easily made from 1,1′-peroxydicyclohexylamine and this paper describes a simple, atom efficient and low waste route to that intermediate using the direct reaction of the commercial cyclohexanone–cyclohexanol mixture with O_2 and NH_3 using *N*-hydroxyphthalimide as a catalyst. The method represents a salt-free route to a large scale important intermediate.** ***JHC

DOI: 10.1039/b300354j

tally friendly process than that by the current method using hydroxylamine sulfate.

Results and discussion

A 1 : 2 mixture of **1** (6 mmol) and **2** (12 mmol) was oxidized under dioxygen atmosphere (1 atm) in the presence of small amounts of NHPI (0.6 mmol) and 2,2′-azobisisobutyronitrile (AIBN) (0.3 mmol) in ethyl acetate (3 mL). After stirring the reaction mixture at 60 °C for 20 h, the mixture was treated with an atmospheric ammonia at 70 °C for 2 h to give 1.82 mmol of PDHA (**3**) together with cyclohexanone azine (**4**) (0.11 mmol) and trace amounts of cyclohexanone oxime (**5**) and some unidentified products derived from the reaction of **1** with NH_3. In this reaction, 3.76 mmol of **1** and 9.93 mmol of **2** were obtained, indicating that 24% of the K/A-oil was converted, and the selectivity of **3** based on the K/A-oil consumed was 84% (Table 1, Run 1). This is the first direct transformation of K/A-oil into PDHA using molecular oxygen and NH_3. In this reaction, a large amount of the NHPI catalyst could be recovered. After treatment of the reaction mixture with NH_3, NHPI was transformed into the corresponding ammonium salt which was separated from the reaction solution by filtration, while the desired product, PDHA, existed in the filtrate. Treatment of the ammonium salt of NHPI with 1 M HCl followed by extraction with ethyl acetate was found to regenerate 0.45 mmol of NHPI.

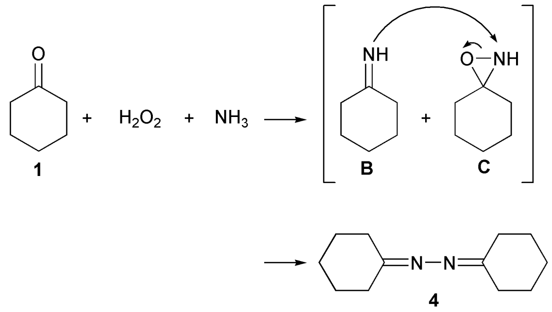
Table 1 Transformation of K/A-oil to PDHA by the NHPI–O_2 system under various reaction conditions[a]

Run	NHPI/AIBN (mmol)	**1/2** recovered (mmol)	Conv.[a] (%)	Yield (mmol)	Select.[a] (%)
1	0.6/0.3	3.76/9.93	24	1.82	84
2	0.6/0	no reaction			
3	0/0.3	11.73/5.00	7	0.35	55
4	0.6/0.12	4.11/10.34	20	1.48	83
5[b]	0.6/0.3	4.34/10.73	16	1.24	85
6[c]	0.6/0.3	4.22/10.37	19	1.57	90
7[d]	0.6/0.3	3.86/8.45	32	1.60	56
8[e]	0.6/0.3	1.57/10.66	18	1.20	87
9[f]	0.6/0	4.87/8.91	23	1.38	65
10[g]	0.6/0.3	0.14/10.47	13[h]	0.52	68[i]

[a] See experimental section. [b] Oxidation of K/A oil was carried out for 10 h. [c] Oxidation of K/A oil was carried out using AcOEt (6 mL) as a solvent. [d] Oxidation of K/A oil was carried out using CH_3CN (3 mL) as a solvent. [e] A mixture of **1** (3 mmol) and **2** (12 mmol) was oxidized. [f] Oxidation of K/A oil was carried out in the presence of $Co(acac)_3$ (0.003 mmol). [g] Reaction was carried out without **1**. [h] Based on **2** used. [i] Based on **2** consumed.

Table 1 summarizes the representative results for synthesis of PDHA from K/A-oil by NHPI-catalyzed aerobic oxidation followed by treatment with NH_3. Almost no reaction occurred using NHPI alone (Run 2). Previously, we have shown that the aerobic oxidation of cumene to cumene hydroperoxide was enhanced by the use of NHPI combined with AIBN.[8] The amount of AIBN could be reduced to 0.12 mmol (Run 4). When the reaction time was halved, the conversion of K/A-oil decreased to 16% (Run 5). The use of CH_3CN as a solvent resulted in decrease of the selectivity to **3**, and considerable amounts of by-products derived from **1** with NH_3 were formed (Run 7). By current technology, K/A-oil manufactured consists of a 1 : 2.5–4 mixture of **1** and **2**.[1] Thus, the reaction using a 1 : 3 mixture of **1** to **2** was examined under these reaction conditions and found to lead to a slight decrease of the conversion (Run 8). The oxidation of **2** was enhanced by a small addition of a Co(III) species,[6] but the yield of **3** was slightly lowered (Run 9). This is due to the fact that the Co ions promote the decomposition of the resulting hydroperoxide **A** and hydrogen peroxide during the reaction course. The reaction employing **2** alone as a substrate afforded **3** (68%) together with **4** (20%) and **1** (9%) (Run 10).

Interestingly, the product distribution was dramatically changed by treating with aqueous ammonia in place of gaseous ammonia. Treatment of a 1 : 2 mixture of **1** (6 mmol) and **2** (12 mmol) by the NHPI–O_2 system at 70 °C for 20 h, followed by exposing the reaction mixture containing water (2 mL) to NH_3 gave **4** (1.01 mmol, 60% selectivity) and **5** (0.35 mmol, 11% selectivity) as major products along with **3** (0.11 mmol, 7% selectivity) at 19% conversion of K/A-oil (eqn. (1)). Schirmann and Weiss reported that **4** was obtained by the reaction of **1** with aqueous H_2O_2 and NH_3 in benzonitrile and suggested that **4** is formed by the reaction of imine (**B**) and oxaziridine (**C**) derived from **B** with H_2O_2 (Scheme 3).[9] Recently, it was also reported that the titanium silicate-catalyzed reaction of **1** with H_2O_2 and NH_3 formed **5** along with a small amount of **4** as a by-product.[4] Although a detailed reaction pathway for the formation of **4** in the present reaction is still unclear at this stage, the reaction seems to take place through a similar pathway as that suggested by Schirmann and Weiss. In addition, it was found that when **4** (1 mmol) was allowed to react in the presence of NHPI (0.6 mmol) with aqueous NH_3 (28%) (3 mL) in AcOEt (3 mL), 0.49 mmol of **5** was obtained, and 0.68 mmol of **4** was recovered unchanged. This indicates that **4** was converted into **5** by the action of NHPI. These results provide an alternative route to cyclohexanone oxime (**5**), a precursor of CL, from K/A-oil.

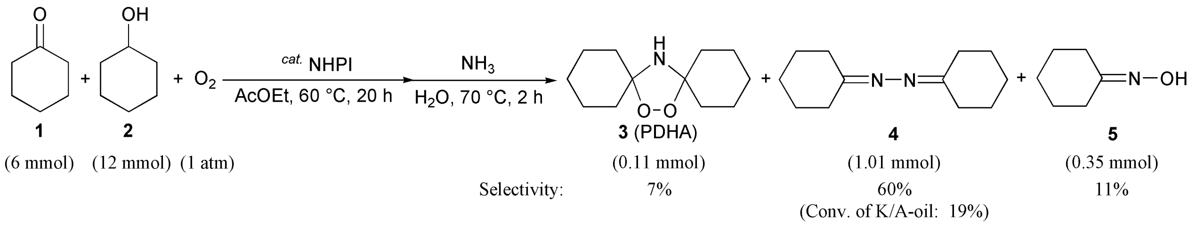


Scheme 3

In summary, we have shown a novel direct synthetic method for the production of PDHA or cyclohexanone oxime from K/A-oil with O_2 and NH_3 using NHPI as a key catalyst. This method is thought to be a sulfate-free production route to CL. Further studies for the optimization of the reaction conditions are now in progress.

Experimental

All starting materials, catalysts and initiators were purchased from commercial sources and used without further treatment.



(1)

To a solution of NHPI (0.6 mmol) and AIBN (0.3 mmol) in EtOAc (3 mL) was added a 1 : 2 mixture of **1** (6 mmol) and **2** (12 mmol), and then the flask was flushed with dioxygen and equipped with a gas-bag filled with about 2 L of O_2. *CAUTION: a balloon filled with oxygen can be hazardous, even with a small-scale reaction.* After stirring the reaction mixture at 60 °C for 20 h, the flask was flushed with gaseous NH_3 and equipped with a gas-bag filled with about 2 L of NH_3 and further stirred at 70 °C for 2 h. The yields of products were estimated from the peak areas based on the internal standard technique using GC. The conversion and selectivity (%) of **3** were calculated by the following equations.

$$\mathrm{Conv.}(\%) = \frac{\begin{bmatrix}\text{the amount (mmol)}\\ \text{of starting KA-oil}\end{bmatrix} - \begin{bmatrix}\text{the amount (mmol)}\\ \text{of KA-oil recovered}\end{bmatrix}}{\begin{bmatrix}\text{the amount (mmol)}\\ \text{of starting KA-oil}\end{bmatrix}} \times 100 \qquad (2)$$

$$\mathrm{Select.}(\%) = \frac{[\text{the amount (mmol) of } \mathbf{3} \text{ produced}] \times 2}{\begin{bmatrix}\text{the amount (mmol)}\\ \text{of starting KA-oil}\end{bmatrix} - \begin{bmatrix}\text{the amount (mmol)}\\ \text{of KA-oil recovered}\end{bmatrix}} \times 100 \qquad (3)$$

Acknowledgements

This work was partially supported by a Grant-in-Aid for Scientific Research (KAKENHI) (S) (No.13853008) from Japan Society for Promotion of Science.

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Communication

Ionic liquids as catalytic "green" reactants and solvents for nucleophilic conversion of fatty alcohols to alkyl halides

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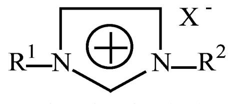
Received 7th April 2003
First published as an Advance Article on the web 13th May 2003

We show that ionic liquids such as 1-octyl-3-methylimidazolium bromide or iodide (OMIM/X) make excellent reagents and solvents for the transformation of fatty alcohols into fatty halides in the presence of paratoluene sulfonic acid (PTSA). The conversion used either direct or microwave heating with excellent yields. The ionic liquid was successfully regenerated and reused.

Introduction

The development of less-polluting neoteric solvents is a key element in an emerging programme for sustainable industrial development.[1,2] This is an important driving force in the quest for novel reaction media. Owing to their unique chemical and physical properties, ionic liquids (IL) are promising candidates as recyclable reaction media for "green" applications. This approach has been successfully applied in a wide range of catalysed processes collected recently in excellent reviews.[3] These IL provide a medium for performing clean nucleophilic substitution reactions[4] with minimum waste generation.

But, to our knowledge, only the conversion of C_4 and C_8 alcohols to alkyl halides has been reported.[5] However, reaction times are very long (24 to 48 h). In addition, while preparing this manuscript, in general work, Leadbeater *et al.*[6] proposed microwave irradiation for the synthesis of heptyl and decyl halides (Br or I) from the corresponding alcohols in the presence of 1-methyl-3-alkylimidazolium halides. The necessity to operate under pressure (sealed tube, high temperature) and the possible use of co-solvent (toluene) presents major drawbacks. In the continuation of our work into the synthesis of new surfactants,[7,8] we investigated the possibilities of obtaining long-chain alkyl halides. Even though the literature proposes numerous solutions,[9] many present disadvantages, either due to the choice of reagents (costly, toxic, *etc.*) or to the drastic operating conditions required (lengthy refluxing, difficulties in separation) and do not always provide good yields. The use of 1-butyl-3-methylimidazolium halides, BMIM/X, described by Ren and Wu,[5] to convert alcohols into halides in the presence of Brønsted acids (H_2SO_4 and CH_3SO_3H) at ambient temperature, does not appear to be applicable to fatty alcohols. Various attempts have led to low-yield mixtures of alkyl halides. This is probably due to the low solubility of the fatty alcohols in the IL used. So, we felt it would be advantageous to find a more suitable IL and to assist the elimination of the water formed and thus shift the equilibrium towards synthesis.



Ionic Liquid (IL)

BMIM/X: R^1=CH_3; R^2=C_4H_9
*i*PMIM/X: R^1=CH_3; R^2=*i*C_3H_7
OMIM/X: R^1=CH_3; R^2=C_8H_{17}
X=Br or I

Our aim was to find an improved synthetic pathway for long chain (C_8 to C_{18}) alkyl bromides and iodides from the corresponding fatty alcohols using the halide of 1-octyl-3-methylimidazolium (OMIM/X) which is more lipophilic acting as both reagent and solvent in the presence of paratoluene sulfonic acid (PTSA), a non-volatile solid that is easy to manipulate. Unfortunately, the conversion of ROH into R–X at room temperature was not obtained. Owing to the high thermal stability of the IL, we worked at moderate temperature, either by direct heating or under microwave irradiation. In this paper, we report the synthesis of fatty alkyl halides using the potential of IL.

Experimental

Reagents and solvents were commercially available and used without further purification. Microwave irradiation was conducted using a domestic oven with operator selectable power output from 0 to 300 watts and operator selectable time.

The IL: BMIM, iPMIM and OMIM bromides were synthesised from 1-methylimidazole and the corresponding alkyl bromides following described methods.[10]

The conversion of alcohols to halides was followed by thin layer chromatography (TLC) and gas chromatography (GC). The structures of various alkyl halides were confirmed by comparison with authentic standards of alkyl halides.

Green Context

Published methods of synthesising long chain alkyl halides mostly present serious disadvantages including the use of costly or toxic reagents and drastic operating conditions. Ionic liquids have been reported to be suitable reaction media for the synthesis of relatively short chain alkyl halides but the poor solubility of longer chain substrates makes their use inappropriate for the reactions of these substrates. Here more lipophilic ionic liquids are tested as reagent and solvent for the transformation of fatty alcohols into fatty acids using an acid catalyst. By using microwave irradiation reaction times can be remarkably short and product isolation is quite simple. ***JHC***

DOI: 10.1039/b303892k

Typical conversion by conventional heating procedure

For example, synthesis of octyl bromide: a mixture of 1-octanol (650 mg, 5 mmol), equivalent TPSA (950 mg, 5 mmol) and OMIM/Br (1375 mg, 5 mmol) was stirred at 90 °C (oil bath) for 1 hour. After reaction, the mixture was decanted and the IL phase was extracted by hexane (3 × 5 ml). The organic phase was evaporated; the crude 1-octyl bromide was characterised by comparison of data with that of authentic 1-octyl bromide (purity $>96\%$).

Typical conversion under microwave irradiation

The previous mixture was irradiated by microwave using cycles of 30 seconds (75 watts) followed by mechanical stirring for 10 seconds. After 4 cycles, 1-octyl bromide was isolated by hexane extraction as before.

Typical procedure for IL recycling

OMIM/Br. To a stirred IL phase (recovered from the synthesis of alkyl bromide) was added a solution of NaBr (515 mg, 5 mmol) in water (2 ml). The water was removed *in vacuo*, acetone (3 ml) was added and the mixture was stirred for 15 minutes at 50 °C. The solid Na/PTS was filtered and washed with acetone. Evaporation of acetone solution afforded the OMIM/Br characterised by NMR; it was reused for a novel conversion.

OMIM/I. NaI (750 mg, 5 mmol) in acetone (2 ml) was added to stirred recovered IL phase after conversion. The mixture was stirred at rt for 30 minutes. The solution was filtered and evaporated *in vacuo*. Acetonitrile (2 ml) was added, the solid was filtered and OMIM/I was obtained after evaporation *in vacuo* and characterised by NMR.

Results and discussion

The reactions were carried out in a homogeneous equimolar mixture of fatty alcohols (C_8–C_{18}), PTSA and OMIM/X (X: Br, I) at different temperatures using an oil-bath. As the reaction advanced, phase separation was seen to occur facilitating the isolation of the halogenated derivative. Systematic optimisation of the yields was performed.

Table 1 gathers a few results to illustrate the utility of the protocol.

Table 1 Conversion of fatty R–OH to R–X by heating with OMIM/X

Entry	X	R(OH)	*T*/°C (time)/ min	% conversion[a]
1	Br	C8	90 (60)	100
2	I	C8	90 (60)	92
3	Br	C12	120 (30)	99 (90)[b]
4	I	C12	110 (60)	97 (78)[b]
5	Br	C14	105 (60)	100
6	Br	C14	120 (30)	97
7	I	C14	100 (75)	88
8	Br	C18	100 (60)	98
9	Br	C18	100 (75)	98
10	I	C18	100 (60)	99

[a] Determined by GC and ^1H NMR. Structures confirmed by analogy with authentic standards. [b] % yield pure product isolated.

With our operating conditions, the yields of RX were quantitative irrespective of the halogen on the condition that the temperature/time parameter took into account the length of the alkyl chain. When the temperature was increased, maximum yield was reached sooner: for a 15 °C rise in temperature, the reaction time can be halved (see, for instance, entries 5 and 6). It can be seen that the initial rate of these reactions is very high as 80 to 85% conversion was obtained in the first 20 to 25 minutes. In contrast, increasing the temperature also generated by-products, particularly alkenes. Excess OMIM/X or PTSA did not notably accelerate the reaction.

The good solubility of the fatty alcohols and the insolubility of the halides formed in OMIM/Br is a clear advantage. Attempts made with 1-butyl-3-methylimidazolium bromide (BMIM/Br) and 1-isopropyl-3-methylimidazolium bromide (iPMIM/Br) led to a strong decrease in R–X conversion yields: the longer the alkyl chain, the stronger the decrease. Up to C_8, however, they seem to give results comparable to those obtained with OMIM/Br.

Comparing the results obtained in the series with those reported for 1-octyl bromide by Ren and Wu[5] clearly illustrates the advantages of the process described. Instead of 6 hours reaction time and the requirement for H_2SO_4, octyl bromide was obtained quantitatively by heating at 90 °C for 1 hour in the presence of PTSA. Under the same conditions, octyl iodide was obtained with a 92% yield while only 70% was obtained in 24 hours using CH_3SO_3H in Ren and Wu's procedure. We think the evaporation of the water (effect of the heating) and the phase separation after conversion (utility of the OMIM/X) favour the synthesis of the halide bromide justifying the originality of the process described here.

Apart from the simplicity of the process and its excellent results, the possibility to recycle the IL offers a significant advantage (see Fig. 1).

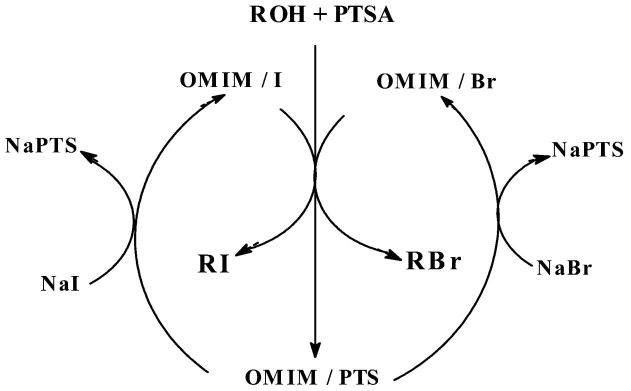


Fig. 1 Conversion of the fatty alcohols into halides with recycling procedure.

OMIM/X can be considered as a catalyst. Its imidazolium cation is not consumed and the IL is easily regenerated and put back into the reaction by exchanging the PTS anion with the bromides and iodides of inorganic salts (NaBr and NaI respectively). However, after five runs the conversion drops by only 10% under identical reaction conditions. The stability of the IL under the reaction conditions was also studied. After many cycles, we did not observe any structural modification in the NMR spectra or analytical data of the OMIM/X, in agreement with the heat stability assigned to the IL.[1,2]

Considering the remarkable properties of the IL and since we found that a strong rise in temperature over a shorter lapse of time favoured conversion, we tested the suitability of microwave heating. It is the parameter "power/exposure time" as a function of the amount of matter involved that appears to govern the conversion. Reaction mixtures of 2 to 4 grams subjected to strong irradiation (>150 watts) for several minutes led to the formation of alkene by-products. The elevated temperature of the reaction mixture can also lead to a decomposition of the IL restricting the possibilities of the microwave procedure as described by Leadbeater *et al.*[6] We therefore carefully limited the temperature of the reaction mixture. So, we carried out the conversion under low-power intermittent irradiation (75 watts) for 30 seconds followed by mechanical stirring for 10 seconds. In this way, the formation of alkenes was avoided. In general, the transformation of fatty alcohols into halides was extremely rapid and almost quantitative after 3 to 4 cycles. Table 2 reports the results obtained.

Table 2 Conversion of fatty R–OH to R–X under microwave irradiation

Entry	X	R(OH)	% conversion[a]
OMIM			
1	Br	C12	78[b]
2	Br	C12	86
3	Br	C14	95
4	I	C14	88
5	Br	C18	80
BMIM			
6	Br	C14	60
7	I	C14	56
iPMIM			
8	Br	C8	72
9	I	C8	51
10	I	C8	53
11	Br	C12	55
12	I	C12	52
13	Br	C14	57

[a] Determined by GC and ^{1}H NMR. [b] After 6 microwave irradiation cycles.

Moreover, OMIM/X appeared to be the most useful of the IL tested, especially since the release of R–X was almost quantitative in this medium. The principle of recycling was successful but deterioration by oxidation was faster than with the previous protocol especially when cycling iodides.

In conclusion, this work proposes the rapid synthesis of long-chain alkyl halides with excellent yields and in suitable conditions (a few seconds to a few minutes with microwaves or 1 hour at around 100 °C). The alkyl halides produced are easily isolated. This is due to the remarkable properties of the IL in which the nucleophilic agents bromide and iodide prove to be more active than in classic organic solvents. This is an eco-friendly method using OMIM/X, which is easily recycled with inorganic salts. The protocol described could be scaled up for “green” industrial application justified by our test (over 10 g) demonstrating clean chemistry at low cost (IL directly reused). Our strategy opens new fields of investigation for IL as “reagent-solvents”, as yet little developed. These directions are currently being explored by our group.

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Communication

Soaked *Phaseolus aureus L*: an efficient biocatalyst for asymmetric reduction of prochiral aromatic ketones

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Received 20th January 2003
First published as an Advance Article on the web 14th April 2003

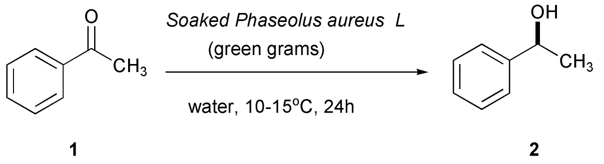
An ecofriendly and environmentally benign asymmetric reduction of various prochiral ketones employing soaked *Phaseolus aureus L* as a biocatalyst was developed. We found for the first time that the soaked *Phaseolus aureus L* (commonly called green grams in India) could be effectively used for enantioselective bioreduction. This process is more efficient and generates less waste than the conventional chemical reagents or microorganisms. This process has been successfully tested for multigram scale production of optically active alcohols and this approach is found to be the most suitable for the preparation of pharmaceutically important molecules.

Introduction

Plant cell cultures represent a unique class of potential biocatalysts for the transformation of synthetically important foreign substrates. Over the past decade, several investigations have been carried out on the biotransformation of foreign substrates.[1] These processes are more efficient and generate less waste than the conventional chemical reagents or microorganisms.[2] Biotransformation of organic xenobiotics, such as monoterpenes, aliphatic ketones and aromatic ketones using either freely suspended or immobilized cell culture have been described in the literature.[3]

Results and discussion

In our attempts to produce chiral aromatic alcohols in high enantiomeric excess, we have investigated several edible grams as potential biocatalysts for the enantioselective reduction of prochiral aromatic ketones. We began our study using acetophenone as a test substrate. After considerable experimentation, we found for the first time that soaked *Phaseolus aureus L* could be effectively used for enantioselective bioreduction of **1** to give (*S*)-1-phenylethanol **2** with good selectivity (84% ee) as shown in Scheme 1. Other potential biocatalysts screened for the above reduction were *Phaseolus mungo L* and *Cicer arietinum L* which gave only 10%, and 6% ee respectively with negligible yield of alcohol **2**. The effect of catalyst and substrate concentration on the reaction was studied. The best results were obtained using 50 g of soaked *Phaseolus aureus L* in 400 ml of deionised water for 0.5 mmol of substrate. This reaction gave aromatic alcohol **2** in 84% optical purity with 52% isolated chemical yield of the product. No significant change either in yield or in enantioselectivity of **2** was observed when 100 g of soaked *Phaseolus aureus L* were used for the reduction of **1** with 0.5 mmol substrate concentration (49% yield, 85% ee). In sharp contrast, 25 g of soaked *Phaseolus aureus L* with the same substrate concentration gave only 5% yield of **2**. When 50 g of soaked *Phaseolus aureus L* were used and the amount of water increased from 400 ml to 600 ml for the reduction, product **2** was obtained in 35% yield.[4]



Scheme 1

In another study, deionised water (400 ml) degassed with argon (20 min) was used as the reaction medium. Surprisingly, here only the starting material was recovered. When the reaction was conducted in air bubbled deionised water (400 ml, 20 min), although no formation of **2** was seen disappearance of the starting material was observed.[5] The above experiments imply that the dissolved oxygen is essential for the product formation. At present, we have no satisfactory explanation for this phenomenon. The optimum temperature for this biotransformation was found to be 10–15 °C and at subzero temperature the reaction proceeded sluggishly where as at elevated temperatures *i.e.* 25–30 °C the optical purity of the product decreased.

To test the generality and efficiency of this protocol, we subjected various aromatic keto substrates to enantioselective bioreduction and the results are shown in Table 1. An examination of the experimental results reveals that the presence of electron-donating substituents in the aromatic ring (entries 5 and 6) slows down the reaction rate[6] and in contrast cyclic alkanones were efficiently reduced (entry 7). α, β-Unsaturated ketone was reduced to corresponding secondary alcohol (entry 10) in 85% ee with a poor chemical yield.[7] Particularly noteworthy is that the unactivated phenyl-2-propanone was reduced to the corresponding alcohol with excellent levels of asymmetric induction (entry 9).

Green Context

Biocatalysis is an important component in the green chemistry toolkit. This short paper describes the first use of soaked *Phaseolus aureus L* as an efficient and environmentally friendly biocatalyst for the reduction of various aromatic ketones with high optical purity. As is typical for biocatalytic processes, reactions run in water and under mild conditions although they are somewhat slow. After reaction the spent *Phaseolus aureus* can be used as a manure. *JHC*

An attempt to oxidize racemic alcohol **2** by soaked *Phaseolus aureus L* was not successful. A small amount of oxidation product *i.e.* phenylacetic acid was observed, this was confirmed by comparison with authentic sample. These observations indicate that a stereoselective reduction pathway is responsible for this biotransformation as predicted by Naoshima *et al.*[8]

To demonstrate the viability of this bioreduction protocol, we have conducted a multigram scale reduction of acetophenone (5 g batch) and 1-tetralone (2 g batch). Although, the ee's of the product decreased by 5% (79%, and 93% ee respectively) comparable chemical yields were obtained (entry 1, and 7).[9]

In conclusion we have developed an efficient and environmentally friendly biocatalyst, soaked *Phaseolus aureus L*, which reduces various aromatic ketones with high optical purity. The green grams after the reaction can be used as manure, thus minimizing chemical waste.

Experimental

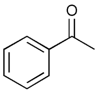
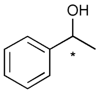
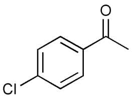
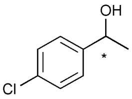
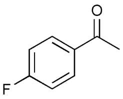
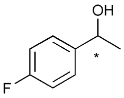
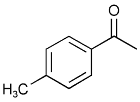
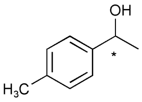
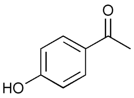
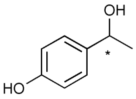
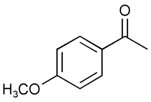
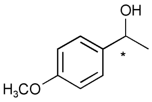
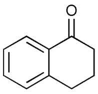
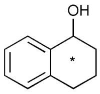
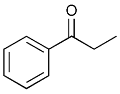
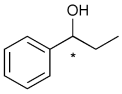
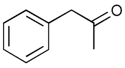
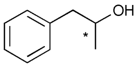
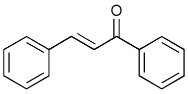
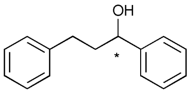
Typical procedure for the reduction

Washed *Phaseolus aureus L* 50 g (purchased from grocery store for approximately 1$ for 2 Kg) were taken into a conical flask and allowed to soak in deionised water (400 ml) for a period of 24 h. Acetophenone (600 mg; 5 mmoles) **1** was added to the soaked *Phaseolus aureus L* in the above water, covered and allowed to shake for 24 h at 15–20 °C. Then the green grams were filtered off and washed with deionised water (3 × 100 ml). The combined filtrate was extracted with chloroform (3 × 500 ml). The chloroform layer was dried and the crude product obtained. Pure 1-phenyl-(1*S*)-ethan-1-ol **2** was obtained after column chromatography with silica gel using chloroform as eluent; yield: 0.316 g, 52%; ee: 84%; ($[\alpha]_D^{25}$ = −38°, *c* = 1, methanol)

Preparative scale reduction. Washed *Phaseolus aureus L* 500 g. was taken into a conical flask and allowed to soak in deionised water (4 L) for a period of 24 h. Acetophenone (5 g; 0.0416 moles) **1** was added to the soaked *Phaseolus aureus L* in the above water, covered and allowed to shake for 24 h at room temperature (28 °C). Then the green grams were filtered off and washed with deionised water (5 × 600 ml). The combined filtrate was extracted with chloroform (30 × 500 ml). The chloroform layer was dried and the crude product obtained (3.21 g). Pure 1-phenyl-(1*S*)-ethan-1-ol **2** was obtained after column chromatography with silica gel using chloroform as eluent; yield: 2.64 g, 52%; ee: 79%.

The same procedure has been adopted for a 2 g batch of 1-tetralone entry no. 7, but the isolated product showed 5% decrease in optical purity (yield 1.12 g, 55% and ee 93%).

Table 1 Enantioselective bioreduction of various aromatic ketones with soaked *Phaseolus aureus L*

Entry	Substrate	Product[a]	Optical rotation $[\alpha_D^{25}]$	Optical purity[b] % ee & config.[c]	Time/h	% yield[d]
1			−38 (*c* = 1, MeOH)	84 (*S*)	24	52
2			−38.6 (*c* = 1, $CHCl_3$)	90 (*S*)	24	50
3			−35 (*c* = 1, $CHCl_3$)	87 (*S*)	24	45
4			−48.5 (*c* = 1, $CHCl_3$)	95 (*S*)	24	51
5			−38.6 (*c* = 1, EtOH)	72 (*S*)	72	23
6			−46.8 (*c* = 1, $CHCl_3$)	90 (*S*)	24	28
7			+31.5 (*c* = 1, $CHCl_3$)	98 (*S*)	46	55
8			−38.8 (*c* = 1, $CHCl_3$)	80 (*S*)	24	50
9			+32.6 (*c* = 1, $CHCl_3$)	98 (*S*)	24	48
10			+28 (*c* = 1, CH_2Cl)	85 (*S*)	24	28

[a] All reactions were carried out on a 0.5 mmol scale except entries 1 & 7 which were carried out on a 5 g and 2 g scale. [b] Enantiomeric excess (ee) values were determined by optical rotation and comparison of values from known literature.[3,10] [c] Absolute configurations were assigned by comparison of specific rotations with literature values.[10] [d] Isolated and unoptimized yields, products were characterized by NMR and MASS.

Acknowledgement

We thank the Director, IICT for encouragement and support and also Dr. M. Pardhasaradhi for helpful discussions.

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4 The over oxidation and water solubility of product **2** might be the probable reasons for its low yield.

5 In case of air bubbling, the reaction mixture after work-up showed on TLC polar spots including phenylacetic acid, which was identified by authentic material co-spot.

6 This phenomenon was observed by other biotransformation reactions also. See ref. 3.

7 Solid compounds were dissolved either in 1,4-dioxane or in ethanol. Best results were obtained in 1,4-dioxane.

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Critical Review

Advances in greener separation processes – case study: recovery of chlorinated aromatic compounds

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Received 3rd January 2003
First published as an Advance Article on the web 14th April 2003

Effective waste management must address waste avoidance, waste reuse, waste recovery and, as the least progressive option, waste treatment. Separation methodologies fit well within a modern green processing ethos, serving to isolate, concentrate and recover valuable material from toxic waste (notably aqueous) streams. An overview is provided of the established separation techniques that focuses on organic contaminants and the associated remediation objectives. The Case Study chosen to illustrate the role separation has to play in environmental pollution control deals with the removal of toxic chloroarenes from wastewater. This is a topic of growing concern as governmental legislation focuses on a substantial reduction in the emission of a broad range of chlorinated compounds. The sources and environmental impact associated with chloro-emissions and the existing treatment technologies are presented and discussed. Adsorption represents the most widely applicable non-destructive control technology, offering the possibility of recovery/recycle. Taking adsorption on activated carbon as a standard, the performance of novel catalytically generated structured carbon is evaluated and shown to outperform activated carbon in batch and semi-batch operation. The level of uptake is markedly higher on carbon surfaces that have been functionalised by acid washing and partial oxidation. The carbon nanofilament adsorbent bed exhibits lower back pressures when treating a continuous contaminant flow, separation of the liquid from the solid in batch operation is more facile and a chloroarene recovery/concentration is possible in polar solvents, a combination of factors that facilitates cleaner separation/recycle.

I Overview: the role of separation processes in environmental pollution control

Environmental pollution may be anthropogenic and/or geochemical in nature but the principal source of appreciable pollution by organic and inorganic species is the waste generated from an array of commercial/industrial processes.[1–5] As a direct consequence of the resultant negative environmental impact in terms of global warming, climate change and loss of biodiversity, stringent legislation has been introduced to limit those emissions from commercial operations that lead to contamination of water/land/air.[6,7] The legislation imposed by the regulatory bodies is certain to become increasingly more restrictive and the censure of defaulters is now receiving high priority in Europe and the US. This has leant an added degree of urgency to the development of effective control strategies. In addition to the legislative demands, the economic pressures faced by the commercial sector in the 21st century include loss of potentially valuable resources through waste, escalating disposal charges and increasing raw material/energy costs. The concept of "sustainable development" has now taken hold in the chemical industry where a reduction in mass/energy intensity, *i.e.* the total mass/energy required to produce a unit of product, is viewed as ultimately more profitable.[8] The study of the causes, effects and control of pollution remains a fast moving field of research, characterised by changes of emphasis and often of perception. Authoritative scientific data with a solid interpretative basis are essential to ensure significant progress in terms of environmental pollution control. It is now accepted that a progressive approach to chemical processing must embrace the "four Rs", *i.e.* reduction, reuse, recycling and (energy) recovery.[7] Separation/purification processes have a clear role to play in advancing "green" processing technology. Where a manufacturing process is energy intensive, recycle/reuse through controlled separation is an effective means of decreasing overall negative environmental impacts.[9] Established methodologies that serve to separate, concentrate and recover (potentially valuable material) include distillation, precipitation, solvent extraction, filtration, reverse osmosis, ion exchange and adsorption; each fits within the environmental remediation ethos.

It is estimated that over 90% of hazardous waste is aqueous[10] and for that reason, this Review will deal with separations from aqueous media. Water is, perhaps, the most fundamental of resources and without it, as the cliché has it, life could not exist on land. Water quality is typically assessed on the basis of three easily measured parameters:[11] pH; conductivity; colour. The fate and overall impact of any pollutant that enters the aquatic environment is difficult, if not impossible, to assess given the prevailing complex interrelated bio- processes/cycles. A study of water contamination/treatment can be, however, conveniently divided into two groups of pollutants, *i.e.* organic and inorganic. The established separation techniques for the re-

Green Context

The environmental, health and safety implications of toxic chemicals in wastewater discharges are a matter of great concern. This paper is a case study which illustrates the role separation has to play in environmental pollution control and deals with the removal of organochlorine compounds from wastewater. The most popular method for this is based on adsorption on carbon and here it is shown that novel catalytically generated carbon can out-perform conventional activated carbon in both batch and semi-batch operation. ***DJM***

DOI: 10.1039/b300062c

moval of organic and inorganic contaminants from liquid streams are listed in Table 1 with a succinct operational description that identifies the limitations of each approach. With regard to inorganic pollutants, "heavy metal" is a general collective term applied to the group of metals and metalloids with an atomic density greater than 6 g cm^{-3} (including Cu, Cd, Hg, Ni, Pb, Zn, Co, Al, and Fe) that are known to present a serious environmental threat.[12–15] The most commonly employed treatment method for heavy metal removal is chemical precipitation.[12,16] Although this approach is relatively simple and inexpensive, it has the decided drawback of generating a large volume of "sludge" for disposal. Alternative heavy metal recovery methods include electrowinning, reverse osmosis, electrodialysis, solvent extraction, evaporation, ion exchange and biological treatment.[3,12,13,17] The process of ion exchange involves the replacement of toxic metal ions in solution by the more benign counter-ions that balance the surface charge of the solid exchanger. Aluminosilicate zeolites,[18,19] clay minerals[20,21] and silica gel[22] have all been successfully applied to the removal of heavy metals from solution. Heavy metal biosorption or bioaccumulation encompasses ion exchange (and adsorption), involving uptake by whole biomass (living or dead) *via* physico-chemical mechanisms.[23–28] Low cost heavy metal bio-removal systems are particularly suited for utilisation by small industries and in developing countries.[29] The low cost materials that have been investigated include waste products from fermentations such as *Aspergillus niger*,[30] agricultural products such as rice bran,[31] waste tea leaves,[32] peanut skins,[33] sugar cane bagasse,[34] cypress leaves[35] and even waste rubber tyres.[36] Many of the biomasses that have been investigated are industrial waste products that often have no commercial value and even represent a disposal cost. In such cases (re)use of the materials is both of environmental and economic benefit.

The focus of this Review is placed firmly on the issue of organic pollution and examines the role of separation processes in treating recalcitrant organic waste as an immediate problem that faces chemical industries. In the past decade, there has been a plethora of scientific publications that address the issue of organic separations from the perspective of "green" synthesis/environmental pollution control. The number of publications is so great that any attempt at an enumeration in this short Review would be foolhardy. Instead, the author has chosen to focus on one Case Study for illustrative purposes – the role of separation in processes involving chloro-aromatic waste. The release of chlorinated organic compounds into the natural environment proceeded unabatedly until the late 1960s, as a result of the upsurge in industrial processes based on halogenated raw materials. Aromatic chlorination reactions are notoriously non-selective with limited control on the ultimate product composition. The effectiveness of distillation as a means of treating effluent stream(s) from the chlorinator is limited even when coupled with a crystallisation step.[37] The presence of these non-biodegradable compounds in effluent discharges is of increasing concern due to the mounting evidence of adverse ecologic and public health impacts.[6] Pertinent chemical and toxicity values are given in Table 2 for three representative chlorobenzenes where it can be seen that an increase in Cl content lowers volatility and soil contamination is increasingly the predominant environmental impact. Chlorophenols are significantly more soluble in water (1000 mg 2-chlorophenol dm^{-3} at 298 K[41]) with recorded[42,43] LC_{50} values spanning the range 2–20 mg dm^{-3} Haloarenes have been listed for some time by the EPA as "priority pollutants"[44,45] and targeted in terms of emission control. This Review will focus on the application of conventional and novel carbon adsorbents in the removal of toxic chloroarenes (principally chlorobenzene and monochlorophenols) from water.

II Strategies for handling/disposing of chloro-organics

Two terms/acronyms are widely used in environmental remediation parlance to categorize organic pollutants,[46,47] *i.e.* Volatile Organic Compounds (*VOC*s) and Persistent Organic Pollutants (*POP*s). *VOC*s encompass a broad range of sub-

Table 1 Established separation methods for water remediation with associated limitations

Method of remediation	Description
Air stripping	Mass transfer of volatile contaminants from water to air. Aeration methods (optimized to extend the exposed surface area of contaminated water) include packed towers, diffused aeration, tray aeration, and spray aeration. Limitations: energy demanding; high maintenance costs; ineffective for non-volatile contaminants.
Ion exchange	Removal of ions from the aqueous phase by exchange with counter ions on the exchange medium. Ion exchange materials may be synthetic organic resins that contain ionic functional groups to which exchangeable ions are attached or inorganic and natural polymeric materials. Limitations: treatment of charged species; sensitive to pH changes; fouling by particulates; susceptible to attack by oxidants.
Precipitation	Transformation of dissolved contaminants into an insoluble form with subsequent removal by sedimentation or filtration. Typically involves pH adjustment and the addition of chemical precipitants/coagulants with flocculation to increase particle size. Limitations: possible generation of toxic sludge; problematic solids settling and separation; water can be subjected to unwanted pH changes.
Distillation	Chemical separations process involving vaporization and condensation to separate components of varying vapour pressure. Limitations: multistage distillation can be prohibitively energy demanding; not suitable for compounds that decompose or polymerize at the operating temperature.
Filtration/ultrafiltration/microfiltration	Mechanical separation based on particle size whereby particles suspended in a fluid are separated by forcing the fluid through a porous medium. Ultrafiltration/microfiltration occurs when particles are separated by forcing fluid through a semipermeable membrane. Limitations: suitable only for separation of solids; can involve high back pressures.
Freeze crystallization	Removes solvent from solution as frozen crystals. Limitations: avoidance of eutectic mixture formation; high running costs.
Membrane pervaporation/reverse osmosis	Use of permeable membranes that preferentially adsorb volatile organics from preheated contaminated water where the VOCs diffuse by vacuum from the membrane/water interface through the membrane wall. In reverse osmosis water is forced through the pervaporation module under pressure and the organic vapors are extracted by vacuum, condensed and vented downstream. Limitations: low water recovery; costly maintenance; high energy loads/associated pressures.
Adsorption	Contaminated water is contacted with adsorbent (typically carbon-based) to which the dissolved contaminants adsorb. Type, pore size, and surface area of carbon adsorbent impact on performance; carbon regeneration is possible. Limitations: streams with high suspended solids will cause fouling; problematic disposal of contaminated carbon.

Table 2 Chemical properties, environmental fate and aquatic toxicity of three representative chloroarenes[38–40]

Parameter	Chlorobenzene	1,3-Dichlorobenzene	1,2,4-Trichlorobenzene
Boiling point (at 101.3 kPa)	405 K	446 K	486 K
Vapour pressure	1.2 kPa[a]	0.2 kPa[a]	0.04 kPa[b]
Solubility in water (at 293 K)	210 mg dm^{-3}	145 mg dm^{-3}	49 mg dm^{-3}
Fish LC$_{50}$[c]/mg dm^{-3}	4.1–10.5	8	2.0–6.3
Predicted environmental distribution			
Air	26%	12%	6%
Water	31%	19%	12%
Soil	43%	69%	79%

[a] 293 K. [b] 343 K. [c] Lethal concentration for 50% of organisms.

stances that are easily vaporised and that contain carbon and different proportions of other elements such as hydrogen, oxygen, fluorine, chlorine, bromine, sulfur or nitrogen. *POP*s are classified as chemical substances that persist in the environment, bioaccumulate through the food web, and pose a direct risk to human health and the environment. The *POP*s regarded as high priority pollutants include a range of halogenated aromatics and the *POP*s/*VOC*s that present an environmental hazard are of anthropogenic origin, associated with industrial processes, product use and applications, waste disposal, leaks and spills, combustion of fuels and waste incineration. With the evidence of long-range transport of these substances to regions where they have never been used or produced, it is now clear that *POP*s and *VOC*s pose a serious immediate threat to the global environment. Chemical spills may be much smaller than oil spills but they can still be devastating in their impact. Such was the case in June 2001 with a phenolic spill in Singapore’s Jahor Strait, both one of the busiest seaways in the world and home to many commercial fish farms. An Indonesian-registered ship, the Endah Lestari, capsized in the strait between Malaysia and Singapore, releasing its (630 tonnes) phenolic cargo. While salvage activities took effect immediately to pump phenol from the damaged vessel, the chemicals that had been leaked killed most marine life within 2 km of the ship.

The reduction, if not elimination of organic pollutants can be achieved through a combination of resource management, product reformulation, process modification or, at the very least, some form of end-of-pipe treatment. In selecting the optimum control strategy, many considerations must be taken into account, such as recycling potential, the phase and character of the organic compound(s), the volume of the stream to be treated and the treatment costs.[48] The established *VOC* treatment technologies are largely based on incineration/oxidation, biological treatment, absorption and adsorption processes. Incineration is a widely used, robust methodology for treating/destroying hazardous waste.[49] However, halogenated organics fall within the category of Principal Organic Hazardous Constituents, compounds that are inherently difficult to combust. As a direct consequence of the thermal stability of these compounds, complete combustion occurs at such high temperatures (> 1700 K) to be economically prohibitive while the formation of such hazardous by-products as polychlorodibenzodioxins (PCDD) and polychlorodibenzofurans (PCDF) (dioxins/furans) can result from incomplete incineration.[50–52] Catalytic oxidation represents a more progressive approach where conversion proceeds at a much lower temperature and fuel/air ratio with an associated reduction in energy costs and NO_x emissions.[53] By-products, however, include CO, Cl_2 and $COCl_2$ that are difficult to trap while complete oxidation (the ultimate goal) generates unwanted CO_2. Catalyst deactivation is also an important consideration, given the expense involved in synthesizing noble metal based catalyst systems. The application of photolysis and ozonation to the treatment of recalcitrant organic compounds falls under what is now regarded as advanced oxidation technologies.[54–56] Ultrasonic irradiation as applied to the treatment of chloroarenes is also undergoing some feasibility studies.[57,58] While these approaches show promise, especially at low contaminant concentrations,[59] each is hampered by practical considerations in terms of the high-energy demands associated with these processes.[60] Although biological oxidation can be effective when dealing with biodegradable organics, chloroarenes are used in the production of herbicides and pesticides and, as such, are very resistant to biodegradation.[61,62] Conversion of chloroarenes, where possible, is very slow, necessitating the construction of oversized and expensive bio-reactors.[63] As the biological toxicity is directly linked to the Cl content, a feasible bioprocess would require a chemical pre-treatment that served to remove some of the Cl component in a controlled fashion, rendering the waste more susceptible to biodegradation. An innovative and effective environmental remediation strategy may call on a combined or two pronged approach, employing a separation unit operation to reduce the Cl content in concentrated streams followed by a secondary (low energy) biological treatment of the diluted effluent.

Catalytic treatment under non-oxidizing conditions is now emerging as a viable non-destructive (low energy) recycle strategy.[64–66] The possibility of achieving a dechlorination by electrochemical means has been addressed in the literature.[67,68] However, high dechlorination efficiency typically necessitates the use of non-aqueous (aprotic solvent) reaction media or environmentally destructive cathode materials (Hg or Pb) that has mitigated against practical application. Catalytic steam reforming shows considerable merit and recent work by Richardson *et al.*[69] has revealed the feasibility of this progressive approach as a means of generating synthesis gas as product. Catalytic hydrodehalogenation represents an effective means of transforming halogenated waste into recyclable product(s) with selective C–X bond scission to generate the reusable hydrocarbon with H–X recovery.[70–72] In liquid phase hydrodechlorination applications the viability of coupling a semi-permeable membrane to a chemical reactor as a means of simultaneously concentrating and reacting the chloroarene solution has recently been considered.[73] The author has demonstrated[74] that, taking incineration as the principal means of “disposal”, a move to separation and/or catalytic processing represents immediate savings in terms of fuel and/or chemical recovery. Incorporation of catalytic hydroprocessing units in distillation/separation lines is envisaged with an HCl recovery unit where HCl absorption into an aqueous phase produces a dilute acid solution which can be concentrated downstream to any level desired. The excess hydrogen gas can be scrubbed and washed to remove trace contaminants and recycled to the reactor.

Adsorption, as a separation process, where certain components of a fluid phase are transferred to the surface of a solid adsorbent is an established technology in wastewater treatment.[75] Adsorption offers a means of chemical recovery and, as such, this strategy promotes an efficient use of resources, greatly reducing both direct and indirect waste/emissions costs, fostering sustainable development. Regeneration of the adsorbent, *i.e.* desorption of the organic pollutant, is usually carried out by either heating the adsorbent or by stripping with steam.[76–80] The uptake of VOCs, in general, from gas or liquid streams can call on a variety of solid adsorbents, ranging from macroporous polymeric resins,[79–85] mesoporous silica based MCM materials,[86–88] microporous zeolites[83,89,90] to carbons.[91–98]

III Application of carbonaceous adsorbents to chloroaromatic separation

Currently, carbon is by far the preferred adsorbent for chloroarene separations where the carbon is typically derived from either a selection of natural products, *e.g.* coal, wood, peanut shells and fruit stones, or can be generated from the decomposition of a range of organics. Carbon adsorbents find widespread use as they can be readily and precisely functionalised to meet various demands.[99–102] The importance of parameters such as solute concentration, solution pH, and adsorbent porosity/surface area in governing ultimate *VOC* uptake has been established.[91,95,96,98,103–107] The standard amorphous activated carbons do not perform well under "wet" conditions and when treating aqueous streams exhibit indiscriminate adsorption with an uptake of both organic contaminant and water.[106–108] The adsorption of water on the surface is mainly driven by hydrogen bonding interactions where surface functionalities (O, OH and Cl) can act as nucleation and/or adsorption sites resulting in the formation of an adsorbed water cluster.[109,110] Moreover, recovery of the "loaded" carbon from the treated water can be problematic. Activated carbon is typically supplied in the form of a powder and loss of fine particulates can only be circumvented by additional fine (membrane) filtration. The high overall uptake on activated/amorphous carbons typically overrides this drawback.[111] Activated carbon in fibrous form exhibits a greater adsorption capacity than the granulated variety for the removal of liquid pollutants.[112–114] Graphite, the highly uniform and ordered form of carbon possesses delocalised π-electrons on the basal planes which impart a weakly basic character that, in consort with its hydrophobic nature, allows selective VOC adsorption.[106,115–117] However, the characteristic low surface area/mass ratios (<20 m^2 g^{-1}) of graphite results in lower overall specific uptake values.

In batch operation, removal of activated carbon and/or graphite from the solute can be problematic, the fine carbon particles require a prolonged settling period to facilitate phase separation. Conversely, operation of a continuous flow separation process, employing a fixed bed of activated carbon, although highly effective, is hampered by the associated high back pressures. Maintenance of a constant flow is energy demanding and flow disruptions/plugging and channeling/solute bypass can impair an effective processing of contaminant streams. A significant improvement in existing *VOC* uptake operations involving carbonaceous materials would result from the development of an adsorbent that: (i) is readily separated from the solute; (ii) exhibits high mechanical strength; (iii) is resistant to crushing/attrition; (iv) delivers uptake values comparable with activated carbon. Carbon nanofilaments represent novel adsorbents that encompass the favorable aspects of both graphite (selective adsorption) and amorphous carbon (high uptake) combined with a facile separation from the treated phase. A discussion of carbon nanofilament production and an assessment of its performance in haloarene uptake from aqueous media follow.

IV (a) Production of carbon nanofilaments

Carbon is unique in that it can bond in different ways to create structures with quite dissimilar properties. Carbon nanofilaments are classified as graphitic structures, characterised by a series of ordered parallel graphene layers arranged in specific conformations[118] with an interlayer distance of *ca.* 0.34 nm. Two common forms of carbon nanofilaments ("ribbon" and "herringbone") are illustrated in Fig. 1 wherein actual transmission electron micrographs (TEM) are given as well as simple schematic renderings as a visual aid. In the "ribbon" form, the carbon platelets are oriented solely parallel to the filament axis.[119] In the alternative "herringbone" arrangement (Fig. 1b),

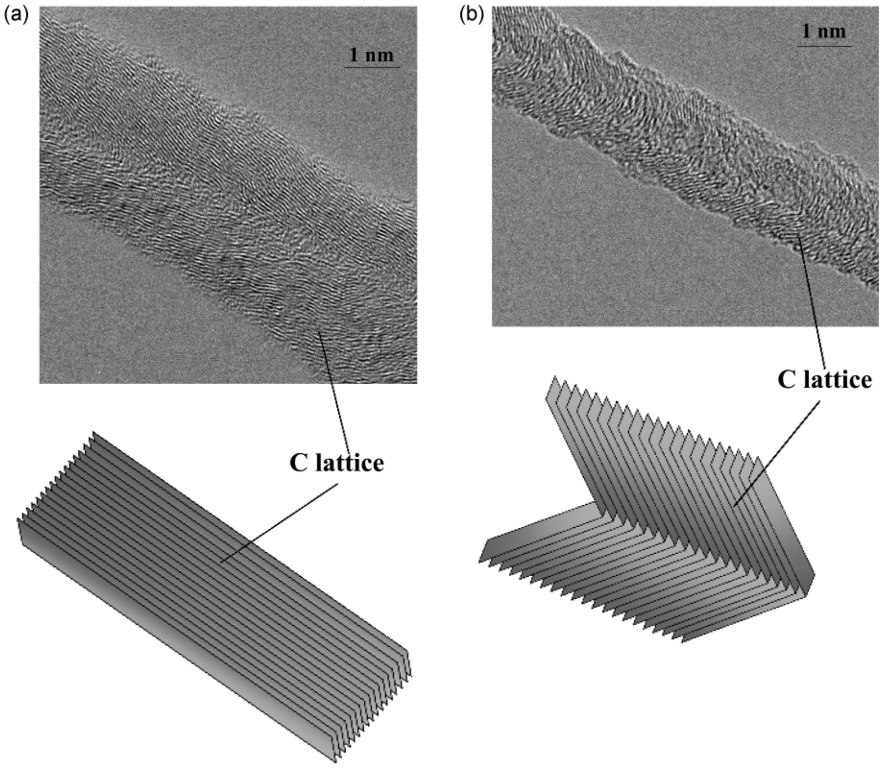

Fig. 1 HRTEM images of carbon nanofilaments that exhibit (a) "ribbon" and (b) "herringbone" lattice configuration with schematic diagrams illustrating an idealized rendering of both lattice structures.

the parallel carbon platelets are oriented at an angle to the filament axis.[120–122] The latter can lead to deviations in the interlayer spacing towards the outer edges of the graphitic platelets making this particular nanofilament a potential candidate for adsorption purposes. The distinction between nanofilaments and nanotubes, as presented in the literature, is somewhat blurred with the term "nanotube" serving as a virtual "catch-all" to describe every nano-scale structured carbon. The two classes of ordered carbon structures are, however, quite distinct and, in terms of applications, the nanofilament presents many unique properties. While a nanotube is characterised by a large exposed exterior basal plane, the nanofilament has a greater availability of edge sites that can be exploited in adsorption applications. Moreover, the nanofilament is appreciably more thermally stable than the nanotube and significantly higher temperatures are required to induce filament gasification. The C–C covalent bond that constitutes the graphite planes is one of the strongest in nature and the perfect alignment of the lattice along the filament axis endows the carbon nanofilaments with high conductivity, enhanced strength and chemical specificity.[123,124]

Ordered carbon structures have been detected in benzene, acetylene and ethylene flames[125,126] but flame synthesis is not viewed as a viable preparative strategy. The direct synthesis of graphitic carbon nanotubes/nanofilaments is now well established by arc discharge[127] and plasma decomposition[127,128] but such methodologies also yield polyhedron carbon nanoparticles (low aspect ratio) and an appreciable amorphous carbon component,[128,129] which necessitates a cumbersome and costly purification stage in order to extract the desired structured product.[130,131] The generation of ordered carbon, with different mechanical/chemical/electrical properties under milder conditions by catalytic means is emerging as a lower cost route with feasible scale up[131,132] and the application of solid metal catalysts to the growth of ordered carbon filaments is now established.[132–139] Filamentous carbon production is possible from a catalytic decomposition of CO[119,140,141] and such hydrocarbons as methane,[135] 1-butene,[142] 1,3-butadiene,[119] acetylene,[119] ethylene,[136,142–144] *n*-hexane[145] and benzene.[146] The nature of the carbon growth is dependent on the composition of the reactant feed and the process conditions; the structure of the carbon filaments is largely governed by the crystallographic orientation of the exposed catalytic metal face(s). Indeed, the commonly accepted mechanism[120,133] involves reactant (carbon source) decomposition on the top surface of a metal particle followed by a diffusion of carbon atoms into the metal with precipitation at other facets of the particle to yield the filament, which continues to grow until the metal particle becomes poisoned or completely encapsulated by carbon. The diameter of the nanofilament is governed by the dimensions of the seed metal particle while the length depends largely on the duration of reaction.[147,148] In general, nanofilament diameters range from 5 to 200 nm with lengths of up to 100 µm when grown from an unsupported catalyst.[120] Use of supported metals can facilitate the production of an appreciably narrower carbon product with diameters in the range 2–50 nm.[130,131,149] The degree of crystalline order of the carbon product is controlled by various factors including the wetting properties of the metal with graphite and the crystallographic orientation of the metal faces that are in contact with the carbon deposit, features that are ultimately reliant upon the choice of catalyst.[120,132,133]

IV (b) Application of carbon nanofilaments to chloroaromatic recovery

The applicability of these novel carbon materials as *VOC* adsorbents has yet to be established; a performance evaluation for the removal of chlorobenzenes and chlorophenols from water is provided herein. The uptake measurements on commercially available activated carbon and graphite serve as a basis against which to assess the adequacy of the various forms of catalytically generated carbon nanofilaments. The decomposition of ethylene over supported nickel catalysts was employed as the synthesis route to generate carbon nanofilaments of varying overall dimension and lattice orientations: the catalytic procedure/analysis has been described in some detail elsewhere[137–139,143,144] The filament morphology/lattice orientation can be controlled through the judicious choice of catalyst – the catalysts used to generate three distinct filamentous carbons are identified in Table 3. Straight carbon filaments with limited curvature were generated from Ni/SiO$_2$ and Ni–Cu/SiO$_2$ with a preponderance of "ribbon" and "herringbone" lattice orientations (see Fig. 1) associated with the mono- and bi-metallic systems, respectively. In marked contrast, carbon grown from Ni/Ta$_2$O$_5$ (Fig. 2) is helical in nature, exhibiting a greater degree of curvature than was observed for the other catalysts. The growth of spiral (or helical) carbon filaments can be attributed to an unequal diffusion of carbon through the metal particle, leading to anisotropic growth. The filamentous nature of the carbon (high aspect ratio) is immediately evident from the representative scanning electron micrograph (SEM) given in Fig. 3. The average filament diameter (and range of diameters) generated from each catalyst system is similar where the herringbone configuration exhibits the lowest density but possesses the highest surface areas due to the large number of accessible edge sites in this more open structure. By comparison, the ribbon and helical filaments are significantly denser with a lower BET surface area. Temperature programmed oxidation (TPO) is a technique that has been put to good effect in probing the degree of order in carbon structures where a move from amorphous to graphitic carbon is accompanied by an elevation of the temperature at which gasification is induced.[150,151] The T_{max} values associated with the gasification of filamentous and conventional carbon materials are given in Table 3. On the basis of the TPO response, the catalytically generated filaments exhibits a higher overall degree of order compared with the standard activated carbon. The occurrence of multiple T_{max} values is indicative of a

Table 3 Physical characteristics of conventional activated carbon and graphite and catalytically produced nanofilaments with (in the latter case) the parent catalyst and associated nanofilament lattice structure/diameter

	Nanofilament			Activated carbon	Graphite
	Ribbon	Herringbone	Helical		
Catalyst	Ni/SiO$_2$	Ni–Cu/SiO$_2$	Ni/Ta$_2$O$_5$	—	—
Filament diameter size range/nm	< 5 to 65	< 5 to 50	< 5 to 80	—	—
Average filament diameter/nm	16	13	23	—	—
BET surface area/m^2 g^{-1}	110	140	80	625	10
Density/g cm^{-3}	0.38	0.09	0.39	0.42	0.35
TPO T_{max}/K	1040, 1233	889, 1048	838, 920, 1078, 1233	848	1233

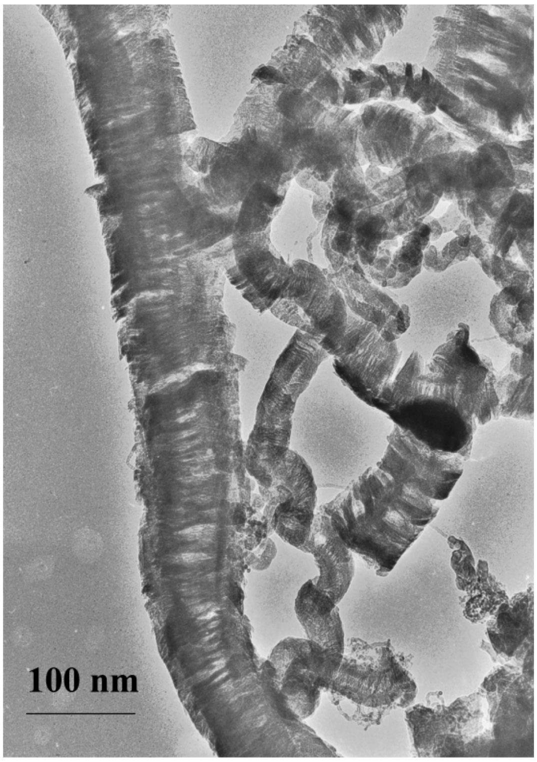

Fig. 2 TEM images of coiled/helical nanofilaments.

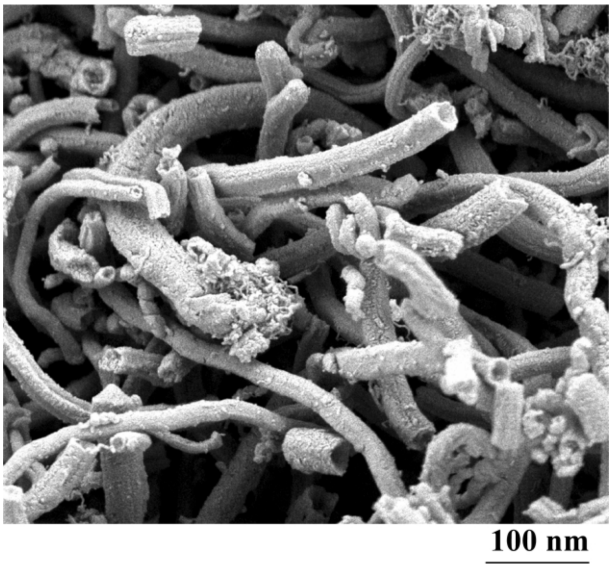

Fig. 3 SEM images showing structural features associated with "ribbon" nanofilaments.

diversity of structural order that approaches that of graphitic carbon.

The uptake of chlorobenzene and 4-chlorophenol exhibited by the five carbon adsorbents under identical conditions in batch operation is given in Table 4. The highest uptake (per gram of adsorbent) was achieved using the model activated carbon, the lowest (by a factor of over two) with the model graphite while the catalytically generated nanofilaments delivered roughly equivalent values that fall within these two extremes. Chlorobenzene uptake was consistently higher, regardless of the nature of the adsorbent. The adsorption capacity of activated carbon for aromatic compounds has been related to the solute solubility in water where the lower the solubility, the greater is the uptake.[152,153] The lower solubility of chlorobenzene[154] can account, at least in part, for the higher uptakes recorded in Table 4. Moreno-Castilla *et al.*[152] have proposed that the relative affinity of substituted aromatics for attachment to a carbonaceous surface is governed by the electronegativity of the ring substituent in that electron withdrawing functions favour the formation of electron donor–acceptor complexes between the aromatic ring and basic groups on the surface. On this basis, the lower chlorophenol uptake may also be due to electron donation by the hydroxyl substituent that weakens the sorbate/sorbent interaction(s). An acid washing of carbon adsorbents has been shown elsewhere to impact on uptake characteristics[84,112,155] through a functionalisation of the surface. The latter can also be achieved through partial oxidation by heat treatment in an oxidizing gas stream. A controlled oxidation can also serve to remove any amorphous carbon residue (visible in Fig. 3) from the nanofilaments. The effect of a combined acid (HNO_3) treatment and partial oxidation on 4-chlorophenol removal efficiency (in batch operation) is shown in Table 5. The treated carbons all exhibited higher uptakes, an effect that can be ascribed to an increase in the surface concentration of oxygenated functional groups/electron rich regions that can participate in the formation of electron donor–acceptor complexes with the aromatic sorbate. The enhancement of removal efficiency was particularly marked in the case of the carbon nanofilaments where the acid/oxidation treatment raised the level of uptake to such an extent that each nanofilament outperformed the standard activated carbon (on a per weight basis). The presence of delocalised π electrons situated between adjacent graphite layers is known to impart weakly basic character to the material in its pristine state and, in conjunction with the uniformly ordered small diameter carbon filaments, contributes to a high directional conductivity.[132,156] The high conductivity and greater availability of delocalized π-electrons, relative to conventional graphite, must be the source of stronger sorbate/filament interaction(s) that results in the observed uptake. The highest recorded 4-chlorophenol uptake was delivered by the herringbone nanofilament, suggesting that a variability of the interlayer spacings (at the edge regions) is beneficial in raising the total adsorption capacity.

Table 4 Chlorobenzene and 4-chlorophenol uptake (in batch operation) from aqueous solution by the standard activated carbon/graphite adsorbents and by carbon nanofilaments: T = 298 K; initial Cl/adsorbent = 4.2 mmol g^{-1}

	Uptake/mmol g^{-1}	
Adsorbent	Chlorobenzene	4-Chlorophenol
Activated carbon	2.7	2.3
Graphite	0.9	0.8
Ribbon nanofilaments	2.3	1.9
Herringbone nanofilaments	2.1	1.8
Helical nanofilaments	2.0	1.9

Table 5 4-Chlorophenol removal efficiencies exhibited by the carbon adsorbents (in batch operation) pre- and post-acid/oxidation treatment: T = 298 K; initial [Cl] = 6 mmol dm^{-3}

	Removal efficiency (%)	
Adsorbent	Without treatment	After treatment
Activated carbon	48	78
Graphite	15	17
Ribbon nanofilaments	40	82
Herringbone nanofilaments	37	87
Helical nanofilaments	37	79

One important aspect of a separation process based on adsorption is the ease with which the solid can be removed from the treated solution. The recovery of the carbon nanofilaments from aqueous media was observed to be far more facile than phase separation involving the activated carbon powder. The nanofilaments are extremely robust in nature and did not disintegrate or exhibit any significant damage during vigorous agitation unlike the activated carbon that showed signs of appreciable attrition with prolonged use. Indeed, the time taken for the separation of roughly the same mass of activated carbon from the treated solution was greater by a factor of up to 10. The intrinsic hydrophobicity of the carbon nanofilaments can also serve to aid filtration by repelling water molecules. Moreover, unlike the activated carbon, separation of the filaments from solution was not accompanied by any significant loss of fine carbon particulates and adsorbent reuse is greatly facilitated. The performance of the two model carbons and the herringbone nanofilament in continuous semi-batch operation is considered in Fig. 4. This mode of operation (closed loop with a continuous flow from a reservoir of contaminated water) represents a more effective means of water treatment, extending the batch testing to conditions wherein any intrinsic improvement in performance should be more pronounced. Each of the adsorbents had been subjected to the acid washing/oxidation treatment that enhanced batch uptake performance. The adsorbent bed volume was the same in each case with a constant contact time (*ca.* 10 s). Chloroaromatic uptake under transient conditions was significantly higher for the herringbone nanofilament. It is instructive to note that the pressure required to maintain a constant flow (10 cm^3 min^{-1}) of feed through the bed of activated carbon and graphite (3800–3900 psig) was substantially higher than that recorded for the same nanofilament bed volume (2400–2700 psig). This pressure difference has significant ramifications in terms of energy usage/costs in that operation of an activated carbon bed (to deliver equivalent levels of clean up) would necessitate the design and operation of equipment rated for higher pressures. While these tests represent a preliminary screening, they do demonstrate the potential of the catalytically generated carbon nanofilaments as adsorbents for a less energy intensive continuous extraction of toxic chloroarenes from aqueous media.

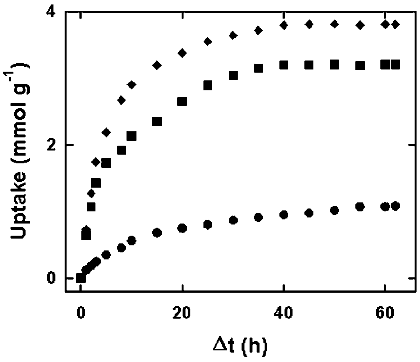

Fig. 4 Time dependence of the 4-chlorophenol uptake on activated carbon (■) graphite (●) and the herringbone nanofilament (◆) under semi-batch operation: T = 293 K; $[Cl]_{initial}$ = 12 mmol dm^{-3}; feed flow rate = 10 cm^3 min^{-1}.

Regeneration of activated carbon saturated with chloroorganics typically involves thermal treatment.[157–160] Heating the spent carbon to elevated temperatures (> 1000 K) first releases the physically held fraction but some physisorbed species can be transformed into a chemisorbed component while the latter is degraded into light gases and heavy products and a significant residue can remain on the adsorbent surface.[157] Such a thermal regeneration does not represent the best practicable environmental option and can result in the uncontrolled release of hazardous byproducts. Wet oxidation is a more progressive approach where an optimum treatment temperature of *ca.* 443 K has been established[161,162] and the oxidative methodology has been found to modify surface area and hydrophobicity.[163] A chemical treatment that does not involve degradation of the chlorinated adsorbate and serves to concentrate the chlorocompound (in solution) represents a more environmentally sound approach. The efficiency of chemical regeneration has been shown[157,164] to depend on the strength of the adsorbate–carbon interactions and the solubility of the adsorbate in the organic regenerant. A controlled *in situ* elution of the adsorbed chloroarene from the herringbone filament was assessed by contacting the loaded carbon bed with a constant flow of two eluents, *i.e.* acetone and hexane; the effectiveness of each is recorded in Table 6 in terms of the ultimate concentration factor. A chemical elution and concentration was viable in the case of acetone treatment and the ultimate level of concentration was higher in the case of the chlorophenols. Hexane proved inefficient as an elution medium, an effect that can be can be attributed to a poorer solvation by the less polar organic. The use of a polar chemical regenerant does not however represent an entirely "green" solution – this is an issue that must be resolved.

Table 6 Concentration factor associated with a hexane and acetone elution of a range of chloroarenes from a loaded herringbone carbon nanofilament bed operated in semi-batch mode: T = 298 K

	Concentration factor	
Adsorbate	In hexane	In acetone
Chlorobenzene	1.0	2.7
2-Chlorophenol	1.4	3.8
4-Chlorophenol	1.5	4.0
1,2-Dichlorobenzene	0.7	1.6
1,4-Dichlorobenzene	0.7	1.8
2,6-Dichlorophenol	1.2	2.9
2,5-Dichlorophenol	1.3	2.8

V Concluding remarks

The environmental, health and safety implications of toxic organic and inorganic residues in municipal and industrial wastewater discharges are now causes for grave concern. Separation processes have a progressive role to play in not only minimizing such toxic releases but also in facilitating sustainable development through chemical recycle/reuse. Taking chloroaromatic emissions as an established environmental hazard, separation represents immediate benefits over disposal by incineration. Adsorption on carbon based materials, while well established as an effective means of separation is still far from optimised. It has been demonstrated in this report that catalytically generated highly ordered carbon nanofilaments are viable materials for application in chloroarene removal from aqueous solution. The nanofilaments when functionalised through acid washing/partial oxidation outperform standard activated carbon in both batch and semi-batch operation. Moreover, the filamentous adsorbent exhibits a greater ease of separation from solution and lower operating pressures under semi-batch operation. A regeneration of the loaded carbon nanofilament bed is possible by chemical treatment (with a polar solvent) that serves to concentrate the original chloroarene contaminant. The emergence of a novel carbon that displays high and reversible chloroarene uptake at room temperature represents a tangible development that can form the basis for cleaner/more effective separations. Further developments can be directed at reactive separation, the use of carbon filaments as catalyst support, *i.e.* a coupling of adsorption and catalytic transformation (possibly hydroprocessing) to convert the toxic chloro-waste directly into reusable raw material.

Acknowledgements

The author is grateful to Dr. Colin Park, Dr. Patricia Patterson, Brando Okolo and Ling Zhang for assistance with the uptake and adsorbent characterization measurements.

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Green and selective epoxidation of alkenes catalysed by new TiO_2–SiO_2 SBA mesoporous solids

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Received 8th January 2003
First published as an Advance Article on the web 30th April 2003

New catalysts TiO_2–SiO_2 (Ti–SBA) with pore sizes of 37 and 65 Å have been synthesized by grafting titanium on a structured mesoporous SBA15 (SBA for Santa BArbara and 15 for hexagonal structure) by means of titanium tetrachloride in the gas phase. These catalysts have been tested in the selective epoxidation of cyclooctene, cyclohexene, (*R*)-limonene and α-pinene. Whatever the oxidant, hydrogen peroxide (H_2O_2), *tert*-butyl hydroperoxide (TBHP) or cumyl hydroperoxide (CHP), the selectivity is 100%. However, the yield is low with H_2O_2 and the catalyst is partially leached out. In the case of TBHP and CHP the epoxide yields can reach practically 100% and no leaching of titanium is observed after four successive reaction cycles. An effect of pore size on the epoxidation kinetics of α-pinene and cyclooctene has been found.

I. Introduction

Since the discovery of the titanosilicalite-1 (TS-1) by researchers at ENICHEM,[1] the catalysis of low-temperature heterogeneous oxidation in the liquid phase has undergone continuous development. This zeolite proves to be an efficient oxidation catalyst, under very mild conditions, for a certain number of organic molecules.[2,3] In the presence of H_2O_2, primary and secondary alcohols are oxidized to aldehydes and ketones, respectively.[3,4] It also catalyses the ammoxidation of cyclohexanone in the presence of NH_3,[3] the hydroxylation of aromatic compounds, in particular of phenol[2,5,6,7] as well as the epoxidation of alkenes. This last reaction is important because of the use of epoxides as intermediates both in fine chemistry and in the synthesis of high-tonnage products such as propylene epoxide.[8] However, it rapidly became apparent that the use of TS-1 is limited to reactants and products able to diffuse in the channels, that is, with a kinetic diameter less than 6 Å. Thus, a simple reaction like the epoxidation of cyclohexene is impossible: while this alkene can enter the zeolite channels, for steric reasons the epoxide cannot be formed.[9] It is therefore reasonable to research the elaboration of new titanium-based catalysts with a greater porosity and able to host larger reactants. In 1993, Camblor *et al.*[10] perfected the synthesis of a zeolite isomorphous with beta-zeolite, a system of three-dimensional channels of which one has a diameter of 7 Å. This new Ti-beta zeolite proves to be more interesting than the TS-1 zeolite in the oxidation reactions of olefins like cyclohexene. The last decade has seen the discovery and the development of new titanium-based structured mesoporous materials such as Ti–MCM[11–14] and Ti–SBA.[15–18] These have the advantage of presenting a narrow size distribution of cylindrical pores whose diameter can be tailored to between 20 and 200 Å. We have therefore undertaken to synthesize mesoporous Ti–SBA solids with pore diameters of 35 to 65 Å in which the titanium has been deposited by reaction of SBA with $TiCl_4$ in the gas phase.[19] This method was chosen for its relative simplicity and the low cost of $TiCl_4$ which lends hope of practical development. Apart from cyclooctene, a molecule commonly used to test epoxidation catalysts, we have studied the reactivity of (*R*)-limonene, α-pinene and cyclohexene. The epoxide of the latter is of particular interest since it could replace cyclohexanone, the key intermediate in the synthesis of adipic acid, the precursor of Nylon-6,6.[20] The peroxides tested for epoxidation were H_2O_2, *tert*-butyl hydroperoxide (TBHP) and cumyl hydroperoxide (CHP) for their interest from the point of view of ″green″ chemistry: H_2O_2 for its degradation into H_2O; TBHP and CHP for the possibility of recycling the *tert*-butanol and cumyl alcohol. In this study, we have paid particular attention to the stability of our mesoporous materials in successive catalysis tests, and to the effect of the pore size on the selectivity of the reactions.

II. Results and discussion

Initial catalyst characterization

The specific surface areas, the pore volumes and pore sizes of the samples are presented in Table 1. The materials will be denoted Ti–SBA(ϕ)-573 where ϕ represents the mean diameter of the pores of the support and 573 (in K) the temperature of titanium deposition. The two samples prepared Ti–SBA(65)-573 and Ti–SBA(37)-573 present very similar specific surface areas and titanium contents; only the pore diameters and the pore volumes differ significantly. They should therefore be very

Green Context

Epoxidation is one of the most important synthetic methodologies for converting hydrocarbons into useful organic intermediates. There are numerous epoxidation methods as reported in the literature but their limitations are reflected in the fact that for all but the very small alkenes, commercial epoxidation methods are still largely based on the use of hazardous peracids which leave acid waste. Here we see described a new catalytic methodology for the epoxidation of several larger alkenes including the preparation of the valuable α-pinene and (*R*)-limonene oxides. Unfortunately, reactions using the most desirable peroxide sources, hydrogen peroxides, are quite poor, but the efficient use of organic hydroperoxides still represents a useful process. *JHC*

DOI: 10.1039/b300244f

Table 1 Specific surface area, pore volume and pore size of Ti–SBA(65)-573 and Ti–SBA(37)-573

Sample	S_{BET}/ m^2 g^{-1}	Pore volume/ cm^3 g^{-1}	Pore size/Å	Ti/Si molar
Ti–SBA(65)-573	773	0.98	61	0.0440
Ti–SBA(37)-573	712	0.57	29	0.0455

suitable for comparison in the context of shape-selective reactions.[21–24]

Catalysis tests

The following definitions will be used, where n_{init} and n_{final} are the initial and final amounts of the substrate or the oxidant:

- The conversion of the substrate (alkene) is then defined as:

$$\text{Conv}(\%) = \frac{n_{init}(\text{alkene}) - n_{final}(\text{alkene})}{n_{init}(\text{alkene})} \times 100 \qquad (1)$$

n_{final} (alkene) is determined by gas phase chromatography. The conversion of TBHP is defined in the same way. n_{final} of TBHP is obtained by iodometric titration of the reaction medium.

In the absence of solvent, [for example, in the case of cyclohexene (Table 2, last line)] the conversion is defined as the ratio of the effective conversion to the maximum conversion and is noted in italics.

- The epoxide selectivity is defined as:

$$\text{Sel}(\%) = \frac{n_{final}(\text{epoxide})}{n_{init}(\text{alkene}) - n_{final}(\text{alkene})} \times 100 \qquad (2)$$

and the efficiency of the oxidant:

$$\text{Oxidant efficiency}(\%) = \frac{n_{final}(\text{epoxide})}{n_{init}(\text{Oxidant}) - n_{final}(\text{Oxidant})} \times 100 \qquad (3)$$

The results obtained in the presence of Ti–SBA(65)-573, (conversion, selectivity and efficiency of the oxidant) are listed in Table 2. Reactions carried out in the absence of Ti–SBA or in the presence of pure silica materials do not work. Oxidants are slightly decomposed at 343–353 K and their oxidizing power is not used efficiently.

Oxidation by H_2O_2

Ti–SBA(65)-573 was tested in the epoxidation of cyclooctene, (*R*)-limonene and α-pinene by H_2O_2. At ambient temperature (298 K) there is no product. At 343 K, the corresponding epoxides are obtained with conversions of between 35 and 50% of the alkene but with 100% selectivity. There is therefore no activation of the allylic C–H bond.

During the reaction, the colour of the catalyst changes from white to yellow. This coloration is attributed to the formation of hydroperoxy complexes of pentacooordinate titanium.[24] In the case of mesoporous materials, interaction between the OH groups and H_2O_2 occurs readily, because of the high hydrophilicity of the titanium environment. The catalyst was studied by DRUV-Vis. (Fig. 1A): (i) after immersion in CH_3CN and drying by filtration, the spectrum (Fig. 1A-b) is the same as that of the initial catalyst (Fig. 1A-a); (ii) after treatment with H_2O_2 in CH_3CN and drying, a weak shoulder appears at about 380 nm (Fig. 1A-c). This band is identical with that observed by Baiker;[25] (iii) after the same treatment followed by desorption under vacuum at 353 K, the spectrum presents two shoulders at 260 and 380 nm (Fig 1A-d). The first is attributed to

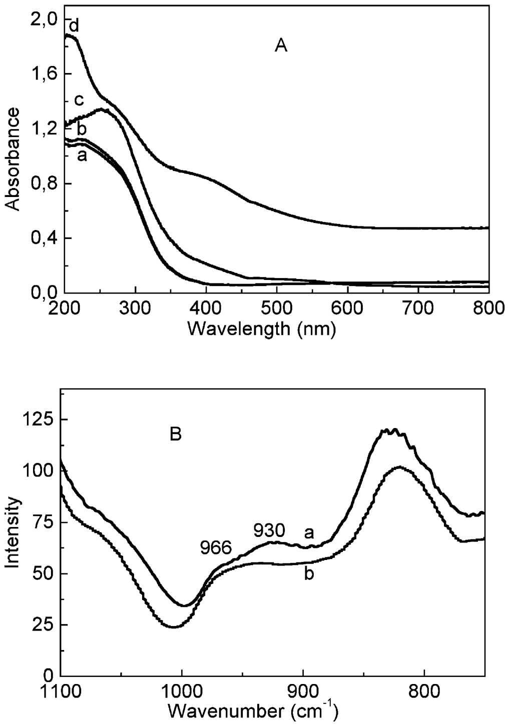

Fig. 1 A. DRUV-Vis. spectra of a: Ti–SBA(65)-573; b: Ti–SBA(65)-573 + CH_3CN; c: Ti–SBA(65)-573 after reaction in the presence of H_2O_2 without substrate for 24 h; d: c + desorption under vacuum at 353 K. B. DRIFT spectra of a: Ti–SBA(65)-573; b: Ti–SBA(65)-573 after reaction of cyclooctene with H_2O_2 for 24 h (see conditions in Table 2).

Table 2 Oxidation of various alkenes catalysed by Ti-modified SBA: Ti–SBA(65)-573, in the presence of H_2O_2[a], TBHP[b], and CHP[c,d]

Oxidant	Substrate	Alkene/Ti (molar ratio)	Substrate conv. (%)	Oxidant conv. (%)	eff.	Epoxide sel. (%)
H_2O_2[a]	cyclooctene	127	50	70	24	100
	(*R*)-limonene	42	40	50	18	100
	α-pinene	127	35	32	19	100
	cyclohexene	127	7	80	20	100
TBHP[b]	cyclooctene	88	98	69	90	100
	(*R*)-limonene	30	97	69	89	100
	α-pinene	88	91	62	93	100
	cyclohexene	88	15	10	96	100
CHP[c]	cyclohexene	88	60	46	97	100
CHP[d]	*cyclohexene*	*1266*	*63*	*46*	*97*	*100*

Reaction conditions: catalyst, 0.1 g (8.10^{-5} mol of Ti) except (*R*)-limonene: 0.3 g; solvent acetonitrile, 10 ml.[a] Substrate, 10 mmol; H_2O_2 (30 wt.% in aqueous solution), 30 mmol; temperature, 343 K; time, 24 h. [b] substrate, 7 mmol; TBHP (5 M in decane), 11 mmol; temperature, 353 K; time, 24 h (except cyclohexene, 2 h).[18] [c] Cyclohexene, 7 mmol; CHP (88% in cumene), 11 mmol; temperature, 353 K; time, 2 h. [d] Cyclohexene, 100 mmol without acetonitrile; CHP (88% in cumene), 11 mmol; temperature, 353 K; time, 2 h.

hexacoordinate Ti and the second to the Ti–OOH group.[26] According to Baiker these groups disappear after thermal treatment (at about 333 K) and the spectrum becomes identical to the original spectrum.[25] We have attempted to detect Ti–OOH groups by reacting cyclooctene on the catalyst peroxidized by H_2O_2 then rinsed with CH_3CN. No epoxide formation was observed. The attribution of the band at 380 nm to TiOOH groups therefore seems somewhat doubtful. Everything seems rather to indicate that the anchoring of the Ti is strongly affected by contact with H_2O_2. This could be because the Ti–O–Si bonds are weaker in our catalysts than with other supports, such as aerogels.[25]

The IR spectra (Fig. 1B-b) recorded after the catalysis tests with cyclooctene show that the intensity of the band at 930 cm^{-1}, attributed to the Si–O–Ti bonds, decreases relative to that at 966 cm^{-1} associated with SiOH.[11,27] This decrease can be attributed to leaching of the surface titanium. Whatever the interpretation in terms of the reaction mechanism, the reaction is inefficient in the use of H_2O_2 and shows low substrate conversion. The dismutation of H_2O_2 on the catalyst with or without alkene has been monitored by measuring the amount of dioxygen released and the outcome of H_2O_2 (epoxide, remaining H_2O_2) is given in Fig. 2. About 2/3 of the H_2O_2 is transformed into oxygen. Previous work[28] suggests that the silanol groups Si–OH present at high concentration in certain mesoporous materials could catalyse this dismutation. Moreover, the water supplied as solvent with the H_2O_2 or produced by its dismutation reduces the performance of these catalysts and leads to leaching of the titanium. It did not appear worthwhile to study the recycling of our catalysts after reaction with H_2O_2 in aqueous media. In order to overcome these problems, it is preferable to work in anhydrous conditions.[29]

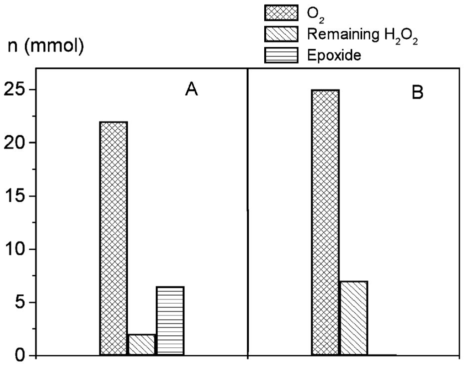

Fig. 2 Outcome of hydrogen peroxide (30 mmol) H_2O_2 in the presence of 0.1 g of Ti–SBA(65)-573 with (A) or without (B) the substrate (cyclooctene, 10 mmol in CH_3CN). (According to the equation for dismutation of H_2O_2, 2 moles of H_2O_2 are required to produce 1 mole of oxygen.)

Oxidation by TBHP

When epoxidation is carried out in acetonitrile in the presence of *tert*-butyl hydroperoxide TBHP (5 M in decane), the conversion of all the alkenes is roughly twice that obtained with H_2O_2 (Table 2). The selectivity for epoxide formation is still 100% but with much more efficient use of the oxidant, since its efficiency as defined above is between 90 and 96%. These results confirm our first observations.[19] The DRUV-Vis. spectra of the Ti–SBA(65)-573 catalysts before and after reaction with cyclooctene are practically identical (Fig. 3A); the band at about 220 nm characteristic of Ti in a tetrahedral environment is unchanged. The IR spectra in the 1100–700 cm^{-1} range are also very similar (Fig. 3B). Thus the band at 930 cm^{-1} characteristic of Si–O–Ti bonds is unchanged. These results show that the catalyst is little altered by the reaction when the oxidant is TBHP. The stability of these catalysts with time (recycling) when TBHP is the oxidant is discussed in what follows.

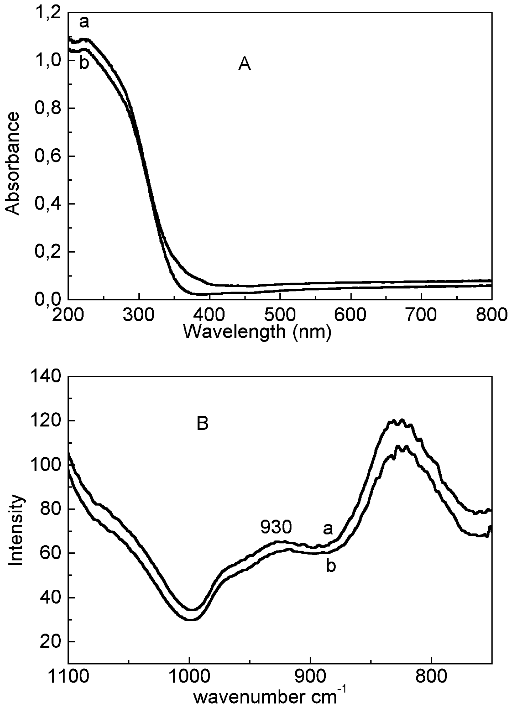

Fig. 3 A. DRUV-Vis. spectra of a: Ti–SBA(65)-573; b: Ti–SBA(65)-573 after reaction with TBHP and cyclooctene for 24 h (see conditions in Table 2). B. DRIFT spectra of a: Ti–SBA(65)-573; b: Ti–SBA(65)-573 after reaction with TBHP and cyclooctene for 24 h.

(a) Catalyst recycling. In order to study the stability of the catalytic performance of the mesoporous materials Ti–SBA(65)-573 and Ti–SBA(37)-573, they were subjected to four successive reaction cycles. Fig. 4A and B present the conversions, epoxide yields and the efficiencies of the oxidant in four

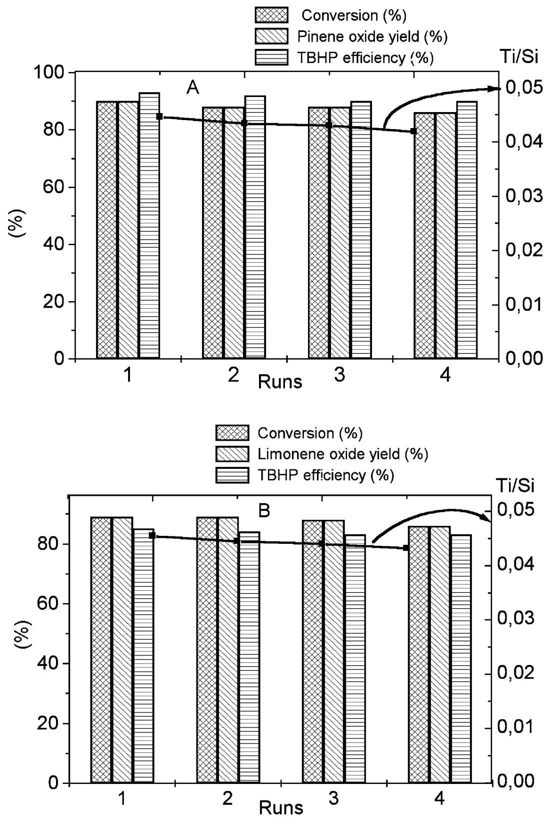

Fig. 4 Catalytic performance of A: Ti–SBA(65)-573 in α-pinene epoxidation; B: Ti–SBA(37)-573 in (*R*)-limonene epoxidation (conditions are similar to those reported in Table 2).

24 h runs. It is seen that the values obtained are practically constant, the Ti/Si ratio decreasing by only 5% between the first and fourth runs. Leaching of titanium in anhydrous media, in the presence of TBHP as oxidant, is therefore minimal, which means that the metal is strongly anchored to the surface and that it must be relatively well dispersed. Aggregates of TiO_2 would favour the decomposition of TBHP, which is not observed (TBHP efficiency 90–95%). The N_2 adsorption and desorption isotherms, and the pore size distribution before and after use show that these samples are stable (Fig. 5A and B). The specific surface areas and the porosities vary by at the most 10% (Table 3). Under these conditions the particle size stays the same. These results are in agreement with the studies of Wu *et al.* on the stability of TiSBA15 catalysts prepared by impregnation.[16]

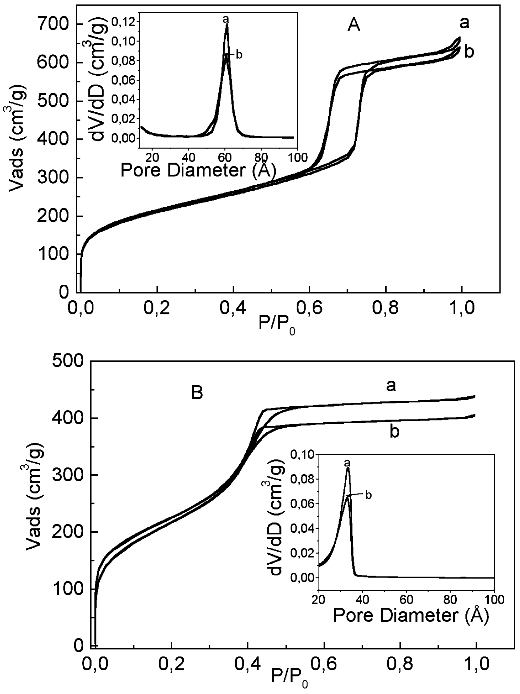

Fig. 5 N_2 adsorption isotherms on A: Ti–SBA(65)-573; B: Ti–SBA(37)-573, before and after 4 catalysis tests (respectively epoxidation of α-pinene and (*R*)-limonene).

Table 3 Specific surface area, pore volume and pore size of the samples before and after 4 catalysis tests (see Fig. 4)

Sample	S_{BET}/ $m^2 g^{-1}$	Pore volume/ $cm^3 g^{-1}$	Pore size/Å	Ti/Si molar
Ti–SBA(65)-573 Fresh catalyst	773	0.98	61	0.044
Ti–SBA(65)-573 Third re-use	750	0.90	61	0.042
Ti–SBA(37)-573 Fresh catalyst	712	0.57	29	0.045
Ti–SBA(37)-573 Third re-use	695	0.48	29	0.043

(b) Effect of pore size. Fig. 6 presents the curves for the kinetics of the epoxidation by TBHP of an equimolar mixture of two substrates (TBHP/total alkene molar ratio = 1.6): cyclooctene and α-pinene in the presence of Ti–SBA(65)-573 and Ti–SBA(37)-573. The two substrates have different intrinsic reactivities and one expects to obtain higher yields of cyclooctene oxide. This is what was found in both cases. The cyclooctene oxide is produced at roughly the same yield in the presence of Ti–SBA(65)-573 and Ti–SBA(37)-573 (Fig. 6). However our results show that the kinetics of α-pinene are slower with the mesoporous support having the smaller pore size. All other reaction conditions being the same, these results show that the relative reactivities of the two substrates are strongly affected by the pore size of the catalysts.

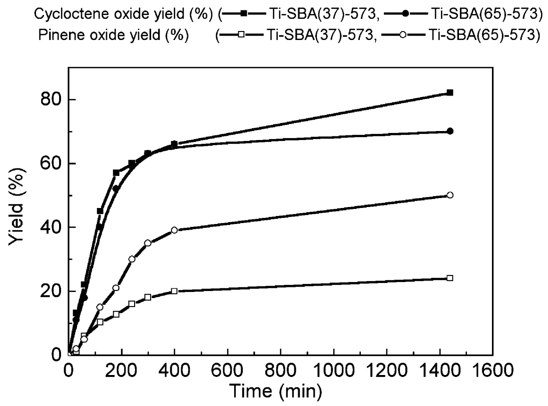

Fig. 6 Curve of the kinetics in the presence of Ti–SBA(65)-573 and Ti–SBA(37)-573. Reaction conditions: catalyst, 0.2 g; substrate (cyclooctene 7 mmol, α-pinene 7 mmol); TBHP (5 M in decane), 22 mmol; acetonitrile, 20 ml; temperature, 353 K.

Oxidation of cyclohexene by CHP

Unlike other cyclic substrates which we have tested, cyclohexene is known for its low reactivity with peroxides. It is therefore not surprising to find with H_2O_2 an epoxide yield as low as 7% (Table 2).

The use of TBHP, as for the other substrates, results in an increase in the conversion but this remains very mediocre (15%) (Table 2). In contrast, cumyl hydroperoxide (CHP) leads to a marked improvement (60%). The reaction run without solvent also gives good results (63% conversion). Under these conditions it is more interesting both from an industrial viewpoint and in the context of "green" chemistry, which seeks precisely to limit the use of solvents. Comparison of the results obtained for epoxidations by the hydroperoxides TBHP and CHP (Table 2) shows that the choice of the oxidant is very important, in that it strongly affects the activity of the catalyst. Electron-withdrawing substituents in the hydroperoxide increase the activity since they make the [Ti–OOR] complexes more electrophilic and therefore more reactive with alkenes.[30,31] Moreover, CHP has recently been applied to the Sumitomo process for the synthesis of propylene epoxide, and the epoxidation of cyclohexene could follow this pattern. The alcohol by-product, in this case cumyl alcohol, could easily be converted to cumene (isopropylbenzene), the precursor of CHP.[32] Recycling of the catalyst in epoxidation by CHP leads to results analogous to those obtained for TBHP.

III Conclusion

The new Ti–SBA catalysts which we have synthesized have been tested in the epoxidation. Despite its outstanding interest in green chemistry, hydrogen peroxide H_2O_2 gives poorer results, partly because its dismutation is strongly catalysed by Ti–SBA and competes with epoxidation, and also because of serious deterioration of the catalyst by dissolution of the titanium. On the other hand, the use of organic hydroperoxides such as TBHP and CHP leads to the epoxides with high yield and selectivity.

The effect of pore size on the kinetics of the epoxidation of alkenes of different sizes opens up the possibility of performing on a substrate mixture reactions made selective by adjusting the catalyst geometry. The activity of our catalysts and their stability with time in the epoxidation of cyclohexene by CHP hints that it might be possible to create a cleaner nylon chemistry.

IV Experimental section

(1) Synthesis

The parent supports are prepared following the method proposed by Zhao *et al.*[33] by means of neutral triblock copolymer surfactants. Two types of support were prepared: for the first, 4 g of Pluronic copolymer 123 ($EO_{20}PO_{70}EO_{20}$, Aldrich) are dissolved in 20 ml of 37 wt% HCl and 120 ml of distilled water and the mixture stirred for 3 h at 313 K. Then 9 ml of tetraethylorthosilicate (TEOS) are added and the final solution is stirred at this temperature for 24 h, then finally raised to 373 K and held at this temperature for 24 h without stirring. After filtration and washing, the solid is dried at 373 K and calcined in a stream of air at 823 K. This sample is denoted SBA15(65), the number in brackets indicating the mean pore diameter in Ångstrom. For the second, the procedure is the same, the surfactant being Brij56 ($C_{16}EO_{10}$, Aldrich); the corresponding sample is denoted SBA15(37).

The parent solid is placed in a fixed-bed reactor and is pretreated in flowing nitrogen at 673 K for 3 h then brought back to the deposition temperature (573 K). Then nitrogen (7.2 l h^{-1}) saturated with $TiCl_4$ at room temperature (1.3% in volume) is passed over the sample for 1 h. The sample is then purged under pure nitrogen at the deposition temperature, and finally hydrolysed in moist air at room temperature. It is dried for 12 h at 353 K, then calcined in air at 673 K for 4 h. The samples will be denoted Ti–SBA(ϕ)-573 where ϕ represents the mean diameter of the pores of the support and 573 (in K) the temperature of titanium deposition. The Ti/Si ratios of the samples are listed in Table 1.

(2) Apparatus

The UV-Vis. spectra were recorded on a Varian Cary 5E spectrometer, in the diffuse reflectance mode with a teflon-coated integration sphere.

The IR spectra were also obtained, in the diffuse reflectance mode, on a IRFT Bruker Vector-22 apparatus at 473 K (2000 scans).

The sample composition (Si/Ti ratio) was determined by atomic absorption spectroscopy at the CNRS analysis centre at Vernouillet, France.

The specific area and the porosity were measured on an automatic Micromeritics ASAP-2010 apparatus.

(3) Catalysis tests

Epoxidation reactions were generally performed in acetonitrile at 343 or 353 K and, in one case, in the absence of solvent at 353 K. The oxidants tested are H_2O_2 (30 wt% in H_2O, Prolabo), *tert*-butyl hydroperoxide (TBHP, Aldrich, 5 M in decane), and CHP (88% in cumene, Aldrich). The molar ratio of oxidant to substrate is fixed at 3.0 (H_2O_2) and at 1.6 (TBHP and CHP), and the amount of catalyst is 0.1 g (0.3 g for the epoxidation of (*R*)-limonene). After 24 h, the reaction medium is centrifuged and the catalyst washed with CH_3CN for possible further use (recycling) in a new catalysis test. Products are analysed by gas phase chromatography on a SPB™-5 capillary column (length 30 m, internal diameter 0.25 mm, thickness of the phase 0.25 μm) with temperature programming (T_1 = 343 K, T_2 = 523 K, temperature gradient 5 K min^{-1}). The products were identified by comparison with commercial samples and by mass spectrometry. The composition of the sample is determined by using mesitylene as internal standard. In the test for the recovery of the catalyst, the solid was reused as described above.

The decomposition of H_2O_2 on the Ti–SBA catalyst with or without alkene was followed by measuring the volume of oxygen released.

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Predicting melting points of quaternary ammonium ionic liquids†

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Received 3rd February 2003
First published as an Advance Article on the web 29th April 2003

A melting point at or below ambient temperature is an essential property of ionic liquids being considered as non-volatile replacement solvents. Here we use the Quantitative Structure-Property Relationship (QSPR) method to correlate and predict the melting points of organic salts based on the quaternary ammonium cation. For a set of 75 tetraalkyl-ammonium bromides, a correlation with $R^2 = 0.790$ is created, and for a set of 34 (n-hydroxyalkyl)-trialkyl-ammonium bromides, two correlations are created with $R^2 = 0.716$ and $R^2 = 0.766$. Descriptors used in the correlations are analyzed to determine structural features that lower melting point, and melting points are predicted for salts that incorporate these features.

Introduction

Recently, much interest has been shown in ionic liquids (ILs) for their unique properties. ILs are salts that melt at or near room temperature. Since they are salts, ILs exhibit negligible vapor pressure,[1] which eliminates the potential for air pollution problems. Other unique and important properties including large liquidus range, high thermal stability and ability to solvate compounds of widely varying polarity make ILs good candidates to replace current volatile organic solvents. Another unique property of ILs is that their physical properties are tunable.[2] This means that physical properties depend strongly on the nature of the cation and anion, which can be changed wilfully. This ability to select physical properties is very appealing, but it is not necessarily known beforehand what structures yield desirable properties. The large number of possible compounds makes it impractical to search for ILs with specific properties using trial-and-error methods. Instead, techniques for predicting physical properties from structure should be used to guide synthesis efforts.

Since the defining feature of an IL is its low melting point (T_m), it is important to determine how structural features affect melting point. Most research has focused on the familiar dialkyl-imidazolium cation (shown in Fig. 1), so information on how melting point relates to structure is known for this group. For example, data have been gathered for the dialkyl-imidazolium cation in which R_1 is a methyl group and R_2 is varied from a methyl to an octadecyl group.[2] When this cation is paired with the BF_4^- anion, a wide range of melting behavior is observed. Melting point drops as the R_2 chain length increases beyond a methyl group, with the lowest melting point occurring when R_2 is a pentyl group. The melting point changes very little as R_2 is increased from a pentyl to a nonyl group, but then gradually rises as R_2 lengthens beyond C9. Formation of liquid crystals is possible for longer alkyl chain lengths. Similar behavior is seen when the anion is PF_6^-. The melting point decreases to a minimum when R_2 is a pentyl group, and increases as the length of R_2 is further increased. These and other experimental observations have led to heuristics as to why an IL is low melting. For example, it is generally accepted that the more asymmetric and bulky a cation is, the lower the melting point will be. Unfortunately, this provides only qualitative guidelines and not quantitative predictions of melting point. In addition, these heuristics have only been examined for a small number of cation types. We cannot confidently predict how different cation structural motifs will impact melting point.

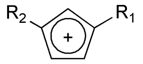

Fig. 1 Structure of the dialkyl-imidazolium cation.

To explore different classes of ILs, more concrete relations between structure and property are needed. Recent data suggest that ILs based on the dialkyl-imidazolium cation may have a moderate aquatic toxicity,[3,4] indicating that other classes of ILs need to be analyzed more closely. One IL class that might be expected to be less toxic is based on the quaternary ammonium cation. In particular, we are interested in ILs based on the (n-hydroxyalkyl)-trialkyl-ammonium cation. One compound from this class is (2-hydroxyethyl)-trimethyl-ammonium chloride, also known as choline chloride or vitamin B4. This compound is used among other things as a supplement in animal feed. For this reason, this cation is expected to have low toxicity. One problem with these types of salts, though, is that they tend to be high melting. In fact, many of the compounds analyzed in the present work have melting points much higher than room

Green Context

The flexibility of ionic liquid design is both a benefit and a difficulty. It can allow the tailoring of the solvent to the reaction in question, but this introduces several additional variables which need to be investigated. Therefore, the availability of data which allow a rapid and fairly accurate method of zooming in on the most likely candidates is invaluable in situations where timescales are tight. This paper provides such a set of data, and allows the prediction, with a reasonable degree of success, of the melting points of combinations of cations and anions. The data also indicate which structural features are likely to influence melting points the most. ***DJM***

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† Electronic supplementary information (ESI) available: training sets B and C. See http://www.rsc.org/suppdata/gc/b3/b301217d/

DOI: 10.1039/b301217d

temperature. This is due in part to the fact that most of the data available are for salts based on halide anions, which typically have higher melting points than salts with larger, more complex anions. Since the number of potential anions is relatively small compared to the large number of possible cations, we have chosen to analyze how changes in the cation structure can lower melting point. Low melting cations could then be paired with more complex anions to further lower T_m. Therefore, we believe that a firm relationship between cation structure and melting point is needed to create low melting ILs based on these cations.

The objective of this work is to use the Quantitative Structure–Property Relationship (QSPR) method to relate melting point to cation structure in order to determine what structural features could lead to low melting ILs. The QSPR method is based on the idea that all physical properties of a compound are directly related to its chemical structure. It is an empirical method that attempts to correlate some property with molecular descriptors. These descriptors attempt to encode various aspects of molecular structure. Topological descriptors, for example, describe branching, connectivity, and overall topology of a molecule. Electronic descriptors analyze the charge distribution around a molecule. Quantum descriptors include values from quantum calculations, such as HOMO and LUMO energies. Descriptors are calculated for a base set of compounds for which a property of interest is known. Then regression methods are used to select the descriptors that best correlate the property. From these descriptors, a predictive correlation is created. A more detailed description of the algorithms, history and uses of QSPR is given in a review by Katritzky *et al.*[5]

The QSPR method has been used previously to relate melting points of imidazolium and pyridinium-based salts.[6,7] For both data sets, melting point was successfully correlated with structure. Correlations were created with R^2 values ranging from 0.7 to 0.9. In both of these previous works, data were gathered from the Beilstein database[8] and the CODESSA software[9] was used to create correlations. In the present work, the pyridinium bromide training set taken from ref. 6 is used to validate our QSPR method.

This work begins with a discussion of the methods used to gather data and create QSPR correlations. Next, results are presented for the validation of our method followed by results for two new training sets, consisting of tetraalkyl-ammonium bromides and (n-hydroxyalkyl)-trialkyl-ammonium bromides. Following this is a discussion of these results. This discussion includes an analysis of the predictive abilities of the correlations created and the potential uses of these correlations. Finally, some conclusions based on this work are given.

Methodology

Three data sets were used for this study. The first set, set A, was the N-pyridinium bromide set taken from ref. 6 and used for validation. The next two data sets were both collected from the Beilstein database. The second data set, set B, consisted of quaternary ammonium bromides where the side chains on the cations were acyclic, saturated alkyl chains. The third set, set C, contained similar structures, but one side chain of each cation was either a 2-hydroxyethyl or 3-hydroxypropyl group. These cations were chosen for their structural similarity to choline. Set B consisted of 75 compounds while set C contained 34 compounds. Fig. 2 shows the base cations of the three training sets.

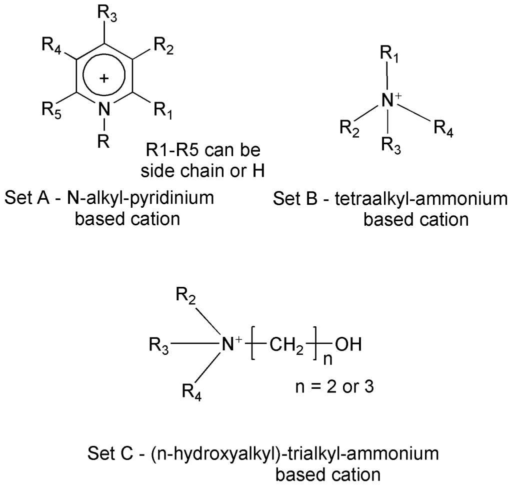

Fig. 2 Cations used for each training set.

It is important to mention briefly how data were selected from the Beilstein database. One problem with ammonium salts is that they are hygroscopic, and even small water impurities can affect melting point. Also, some entries in the Beilstein database listed several melting points for the same compound. All entries that explicitly indicated water impurities were thrown out. In addition, compounds prepared with solvents that are commonly contaminated with water, such as alcohols, were rejected unless more reliable entries were present. Finally, compounds with multiple melting points that differed widely were typically disregarded.

Data sets B and C were exported from the Beilstein database into the ISIS/Base database software.[10] From there, they were loaded into the Cerius2 software[11] and the anion was removed. Data set A was directly entered into Cerius2 without the anion. The geometry of the cation was optimized using molecular mechanics-based energy minimization methods. Following this, MOPAC[12] was used with the PM3 semiempirical Hamiltonian[13,14] to further optimize geometry and assign partial charges.

Descriptors were calculated using the QSAR module available in Cerius2. The descriptor pool available includes topological, electronic, quantum mechanical and 3-dimensional descriptors. For set A, all available descriptors were used. For sets B and C, though, correlations were initially created based only on topological descriptors because the ammonium-based cations differ from one another mostly topologically (*i.e.* branching and connectivity). For set C, an additional correlation was created using topological and electronic descriptors. Electronic descriptors were added to determine if topology-based correlations could be improved. Descriptors used in the correlations given below are described briefly, and more detailed information on the various molecular descriptors in common use may be found in recent reference books.[15,16] Correlations were created from calculated descriptors using the genetic function approximation (GFA).[17] Since the GFA produces several correlations, the highest scoring correlation was picked as the best. This approach was chosen since the top few correlations typically only varied by one descriptor, exchanging one descriptor for another very similar descriptor. Validation was performed automatically by the software using a leave-one-out approach.

Results

N-Pyridinium bromides (set A)

To validate our approach, the first set analyzed, set A, was the training set obtained from ref. 6 consisting of 126 N-pyridinium bromides. The correlation obtained for set A is shown below.

$$T_m/°\mathrm{C} = 125.846 + 0.5773446[\mathrm{PNSA}_2] - 2273.22\,[\mathrm{FNSA}_3] - 104.034\,[\mathrm{BIC}] + 254.703[\mathrm{RNCG}] - 74.3734\,[\mathrm{RPCS}] \quad (1)$$

An R^2 value of 0.790 was obtained using a five-descriptor correlation, which compares very favorably with the previous work's value of $R^2 = 0.788$ for a six-descriptor correlation. A plot of predicted *vs.* experimental melting point for each compound in set A is shown in Fig. 3, where eqn. 1 is used to predict melting point. Using additional descriptors did not significantly improve the correlation. The descriptors used in the previous work[6] indicate the importance of electronic and symmetry effects. The descriptors used in eqn. 1 indicate a similar trend. Four of the descriptors, [$PNSA_2$], [$FNSA_3$], [RNCG] and [RPCS], are charged partial surface area descriptors. The total charge weighted negative surface area, [$PNSA_2$], indicates that a larger accessible surface area with a negative partial charge lowers melting point. The atomic charge weighted fractional negative surface area, [$FNSA_3$], along with the relative negative charge, [RNCG], and relative positive charge surface area, [RPCS], indicate that the partial negative charge should be spread across the accessible molecular surface area. Finally the bonding information content, [BIC], weakly indicates that a more complex (asymmetric) molecule should be lower melting.

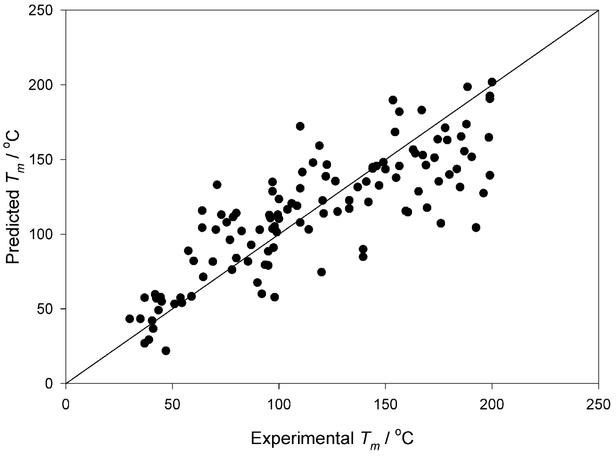

Fig. 3 Predicted *vs.* experimental melting point for the N-pyridinium bromide training set, set A. $R^2 = 0.790$.

The fact that eqn. 1 correlates the training set data with accuracy comparable to that obtained in the previous work indicates that our method is valid. It is important to note that the correlation given in eqn. 1 uses different descriptors than those used in the previous work. This is to be expected, since the software used in the present study does not have available exactly the same descriptors as the software employed in ref. 6. However, the fact that the descriptors used in eqn. 1 describe the same structural features as the descriptors in the previous work and yield a similar correlation coefficient indicates that a similar correlation was obtained.

Tetraalkyl-ammonium bromides (set B)

After validating our method with set A, the first new set was analyzed. This set, set B, consisted of 75 quaternary ammonium salts with acyclic, saturated alkyl side chains. The correlation found for set B is given as:

$$T_m/°C = 119.32 + 1841.668[{}^3\chi_c - {}^3\chi_c^v] + 6.598[{}^VI_{adj}^M] + 120.51[CIC] - 124.9688[{}^2\chi^v] - 65.08[\Phi] \quad (2)$$

with $R^2 = 0.775$. Note that only topological descriptors were used in the initial descriptor pool. A comparison of melting point predicted using eqn. 2 with the experimental melting point for each compound in the training set is shown in Fig. 4. The first descriptor, [${}^3\chi_c - {}^3\chi_c^v$], is the difference between the standard third order connectivity index, [${}^3\chi_c$], and the valence modified third order connectivity index, [${}^3\chi_c^v$], both for a cluster of three bonds connected to a central atom. This descriptor describes the degree of branching around the central nitrogen and indicates that more branch points adjacent to the central nitrogen lower melting point. This first descriptor and the [${}^2\chi^v$] descriptor are part of the Kier–Hall connectivity index family, which attempts to encode connectivity information. The [${}^2\chi^v$] descriptor is the valence-modified connectivity for two bond paths, or three atoms in a row. It indicates that more than one branch point on one atom and increasing alkyl chain length decreases melting point. Care must be taken, though, to account for the relatively high degree of collinearity when analyzing descriptors. For instance, [${}^2\chi^v$] favors multiple branch points on one atom, but the Kier flexibility index, [Φ], penalizes 'compactness' or 'clustering.' In addition, the two remaining descriptors, [${}^VI_{adj}^M$] and [CIC], are affected by this clustering as well, making it virtually impossible to analyze descriptors individually. Still, some information can be gleaned from descriptor analysis in order to develop general guidelines. For instance, more can be said about the Kier flexibility index, [Φ]. This descriptor has to do with the presence of cycles and compactness, or in more physical terms, molecular flexibility. It makes intuitive sense that a more flexible molecule should melt more easily, and this is reflected in the [Φ] index. The two remaining descriptors are the total information content on the adjacency magnitude, [${}^VI_{adj}^M$], and the complementary information content, [CIC]. These two indices are both information theory indices indicating that more complex molecules (or roughly, more asymmetric molecules) will be lower melting.

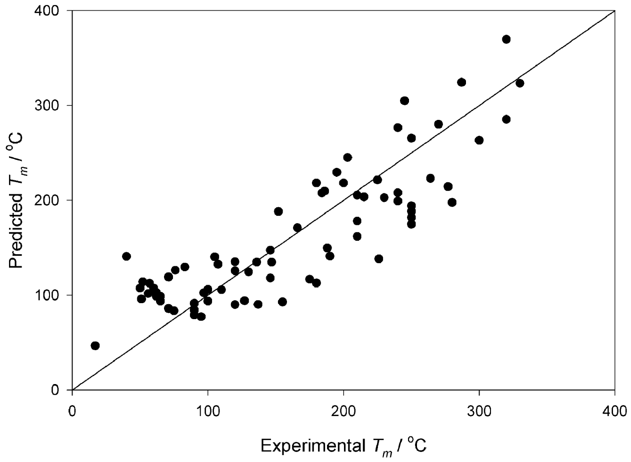

Fig. 4 Predicted *vs.* experimental melting point for the tetraalkyl-ammonium bromide training set, set B. $R^2 = 0.775$.

(n-Hydroxyalkyl)-trialkyl-ammonium bromides (set C)

The next new set analyzed was set C, consisting of 34 compounds similar to those in set B except one of the four alkyl chains was either a 2-hydroxyethyl or 3-hydroxypropyl chain (see Fig. 2). The melting point correlation obtained was:

$$T_m/°C = 5072.73 + 1239.11[{}^3\chi_p^v] - 240.719[IC] + 10457.4[{}^1\chi^v] + 3499.28[{}^2\chi^v] - 6783.74[SC_1] \quad (3)$$

with $R^2 = 0.716$. Again, only topological descriptors were used in the initial descriptor pool. However, this correlation was not quite as good as found for set B. To try to improve this, electronic descriptors were added to the initial descriptor pool. The correlation created from this expanded descriptor pool is shown below.

$$T_m/°C = -1280.59 + 21414.5[FPSA_3] + 0.87634[PPSA_1] + 1.4254[TPSA] - 19.0349[^2\kappa] - 3491.21[RNCG] \quad (4)$$

An improved value of $R^2 = 0.766$ was obtained, and it can be seen that electronic descriptors were chosen preferentially over topological descriptors. However, it turns out that these electronic descriptors end up describing topology indirectly. Fig. 5 and 6 are plots of predicted *vs.* experimental melting point for the training set C compounds, using eqn. 3 and 4, respectively.

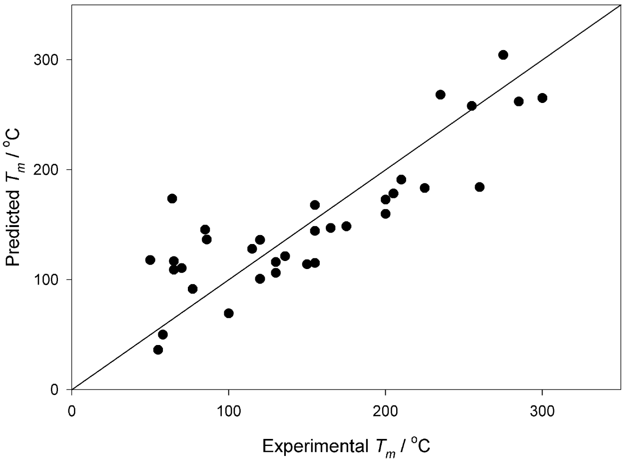

Fig. 5 Predicted *vs.* experimental melting point for the (n-hydroxyalkyl)-trialkyl-ammonium bromide training set, set C. Predicted melting points based on eqn. 3, which uses only topological descriptors. $R^2 = 0.716$.

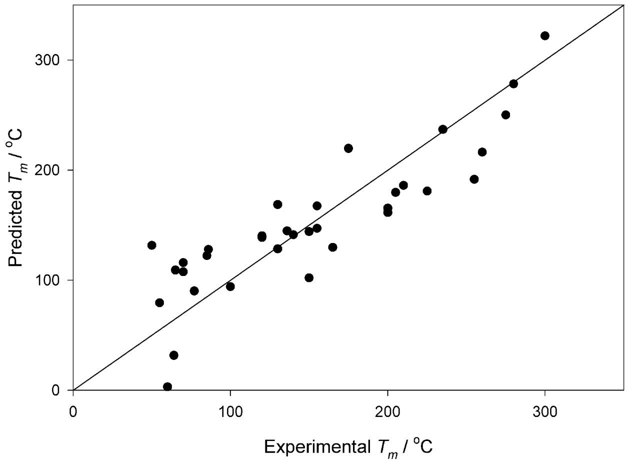

Fig. 6 Predicted *vs.* experimental melting point for the (n-hydroxyalkyl)-trialkyl-ammonium bromide training set, set C. Predicted melting points based on eqn. 4, which uses topological and electronic descriptors. $R^2 = 0.766$.

For the correlation shown in eqn. 3, three descriptors are Kier–Hall valence modified path connectivity indices. The first order index, [$^1\chi^v$], indicates that the presence of branch points lower melting point. The second and third order indices [$^2\chi^v$] and [$^3\chi_p^v$] collectively indicate that branch points should be separated by at least two bond lengths. All three of these indices also indicate that increasing alkyl chain lengths will increase melting point. However, this effect of increasing chain length is offset by the descriptor [SC_1], which simply counts the number of bonds present in a molecule. This descriptor encourages increasing alkyl chain length. Finally, the information content descriptor [IC] encourages complexity of the molecule, which roughly relates to increased asymmetry. Taken together, the descriptors indicate that lower melting compounds of this class should contain one or two moderately long alkyl chains along with two or three shorter ones. This would provide asymmetry. In addition, on the longer chains, branching should be present so long as branch points are separated by at least two bond lengths.

A similar analysis can be done for the correlation in eqn. 4. The [$FPSA_3$] descriptor is the fractional charge-weighted positive partial surface area descriptor. Since hydrogens on long alkyl chains are less positively charged than those close to the nitrogen, cations with long chains have a lower value for the [$FPSA_3$] descriptor. From this descriptor alone, it appears that increasing chain length indefinitely would always be beneficial. However, two other descriptors, [$PPSA_1$] and [RNCG], indicate otherwise. The [$PPSA_1$] descriptor is simply the sum of the positive surface area contributions, and increases as the length of an alkyl chain increases. The [RNCG] descriptor is the value of the most negative partial charge divided by the total negative charge. The largest negative partial charge is located on the oxygen of the hydroxyl group for all these compounds and stays relatively constant. The total negative charge increases as the size of the molecule increase, thus reducing the value of the [RNCG] descriptor. The competition between these two descriptors and [$FPSA_3$] leads to the conclusion reached above that intermediate chain length is most favorable. As for branching, the [$^2\kappa$] descriptor, one of the Kier shape descriptors, increases as the 'compactness' or degree of branching in the graph increases. Finally, the [TPSA] descriptor, or the total polar surface area descriptor, is increased when the chains around the nitrogen are very short (methyl or ethyl). This is because the [TPSA] descriptor is the sum of all surface areas contributed by atoms whose absolute charge is greater than 0.2. Methyl group carbons bonded to the positive nitrogen are more negative than longer chain carbons since the electron withdrawing effect cannot be spread over several carbons. As can be seen, even though charged partial surface area descriptors were chosen preferentially, in this correlation they effectively describe topology. Conclusions as to what characteristics lower melting point based on eqn. 4 are consistent with those reached by examining eqn. 2 and 3.

Discussion

The analysis of what lowers the T_m of quaternary ammonium salts yields similar results for both sets B and C, using different descriptors in three different correlations. To determine if a consistent set of descriptors could describe the melting behavior, six descriptors were chosen in an attempt to correlate each of sets B and C separately, as well as a combined set composed of both sets B and C. The six descriptors were chosen from the three correlations for sets B and C given previously (eqn. 2–4). The descriptors selected manually were the ones that appeared to be able to best describe the features that are most important in lowering the T_m of quaternary ammonium salts. The descriptors chosen were [Φ], [SC_1], [$^2\chi^v$], [$^3\chi_p^v$], [$PPSA_1$], and [$FPSA_3$]. The results were reasonably good. For the combined set, an R^2 of 0.6 was obtained using the consistent six-descriptor set. Allowing the GFA to select six descriptors from all available ones yielded a value of $R^2 = 0.65$, a modest increase. For set B alone, an R^2 value of 0.640 was obtained with the consistent descriptor set, as compared to the previous value of 0.775. In this case, the quality of the correlation was lowered quite a bit. For set C, an R^2 value of 0.703 was obtained with the consistent descriptor set, as compared to 0.716 and 0.776 for the topological descriptors alone and full descriptor pool, respectively. These results indicate that the structural factors that most influence melting point can be described by a fixed set of descriptors, but best results can be obtained from searching through the full descriptor pool.

Overall, these results show that the QSPR method can correlate with some accuracy the melting points of quaternary ammonium salts. There is some error in the correlation, but not all of this is necessarily due to poor correlative ability. One possible source of error is the Beilstein database, since there are often conflicting data entries. As mentioned earlier, care was taken to reduce this source of error, but it could not be eliminated entirely. Despite the error present in the above correlations, they still have many possible uses. The descriptors give physical insight into structural characteristics that tend to lower melting point, which can help guide synthetic efforts. In addition, the correlations can serve in a predictive capacity.

To examine predictive ability, five compounds similar in structure to set B but not included in the original training set were taken from the Beilstein database. Descriptors were calculated for the compounds, and eqn. 2 was used to predict their melting points. Also, six new compounds that the correlations indicate should be low melting but for which no experimental melting point data were available were generated and melting points predicted. Two of these compounds were similar to set B, and eqn. 2 was used to predict their melting points. The remaining four were similar to set C, and eqn. 3 and 4 were used to predict their melting points. In Table 1, predicted melting points are listed and compared to the values given in the Beilstein database, if available.

For the first two compounds, predicted melting points deviate significantly from what was reported experimentally. For the next three compounds, deviations are smaller, but still significant. However, it is important to note that while the predicted melting points do not agree quantitatively with the experimental values, the *qualitative* agreement is excellent. That is, the correlation successfully identified the compounds having the lowest and highest melting points. Such information is valuable in helping focus synthetic efforts.

The last six entries in Table 1 are for the compounds whose melting points are unknown. The first two of these compounds are structurally similar to those used in training set B. The correlation predicts relatively low melting points that are not significantly different from those of the lowest melting compounds available in Beilstein and used in the training set. The correlation is expected to perform well for these compounds, since the training set contained several compounds in this melting point range. The last four compounds are similar to those used in training set C. Note that training set C contained only 34 compounds, and very few of these compounds had the low-melting features that the four new compounds have. The four compounds are organized in the table such that the first is the most similar to the training set compounds and the last shows the most deviation from the training set compounds. As can be seen, the predictions from eqn. 3 appear most reasonable for the compound most similar to the training set compounds, while the predictions for the more dissimilar compounds appear to be unreasonably low. This is perhaps not surprising, as the correlation in eqn. 3 must "extrapolate" to obtain melting point estimates for the more dissimilar compounds. Interestingly, the melting points predicted by eqn. 4 appear much more reasonable than those obtained from eqn. 3. This probably indicates that the correlation shown in eqn. 4 does a better job at extrapolating, which is to be expected since its correlation coefficient is higher due to the use of an expanded descriptor pool. Although the melting points for the unknown compounds may not be quantitatively correct, the results are intriguing, and suggest that synthetic efforts directed at these lowest melting cations may prove fruitful.

One problem with these correlations is that almost all of the compounds used in the training sets melt quite a bit above room temperature. As mentioned before, this is to be expected since the anion, bromide, is so small. However, it is expected that when anions such as PF_6^-, BF_4^-, $(CF_3SO_2)_2N^-$, or any other complex anion are substituted, the melting point should drop significantly. In fact, there is good evidence that certain anions can have a substantial lowering effect on melting point. For example, Matsumoto and coworkers have reported data for symmetric ammonium salts with the cation varying from tetraethyl-ammonium up to tetradodecyl-ammonium. Their data shows that when the bromide anion is replaced by the $(CF_3SO_2)_2N^-$ anion, melting points for all species drop by roughly 100 °C.[18] What the correlations above capture is the effect the cation plays. Therefore, one suggestion for making even lower melting quaternary ammonium salts is to select the lower melting bromide salts and then exchange the bromide ion for another anion that is likely to further lower the melting point.

Conclusions

The results obtained from a QSPR study of quaternary ammonium salts are able to correlate melting points with some success. These correlations can be used to rank structures and determine which cation structures should be lower melting along with giving a fair estimate of the actual melting point temperature. They are also useful in determining which structural features lower melting point. The QSPR correlations indicate asymmetry due to one or two moderately long chains (*e.g.* octyl chains) with two or three shorter chains (*e.g.* butyl) should be beneficial. In addition, branching on the longer chains is predicted to be beneficial as long as two or more bonds separate branch points. Finally, substituting a more complex anion for the bromide anion should further lower melting point.

Table 1 Experimental and predicted melting points for compounds not included in the training sets

Compound name	$T_{m, exp}$/°C	$T_{m, pred}$/°C
Docosyl-dimethyl-octadecyl-ammonium bromide	150	108.7
Triethyl-(2-methylbutyl)-ammonium bromide	100	171.8
Tridodecyl-methyl-ammonium bromide	75	68.5
Trioctyl-propyl-ammonium bromide	74	61.7
Tetradecyl-tripentyl-ammonium bromide	63	57.3
Tributyl-(4-ethyloctyl)-ammonium bromide	—	69.2
Tributyl-(3,5-dimethyloctyl)-ammonium bromide	—	53.3
Dibutyl-(2-hydroxyethyl)-octyl-ammonium bromide	—	32.9 (from eqn. 3) 29.8 (from eqn. 4)
(7-Ethyldodecyl)-ethyl-(2-hydroxyethyl)-methyl-ammonium bromide	—	−80.3 (from eqn. 3) 17.4 (from eqn. 4)
Dibutyl-(2-hydroxyethyl)-(3-methylheptyl)-ammonium bromide	—	−94 (from eqn. 3) 30.4 (from eqn. 4)
Dibutyl-(7-ethyl-3-methyldecyl)-(3-hydroxypropyl)-ammonium bromide	—	−310.7 (from eqn. 3) 36.2 (from eqn. 4)

Acknowledgement

Funding through a grant from the National Science Foundation and a fellowship from the Arthur J. Schmitt foundation is gratefully acknowledged.

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Total chlorine free laser bleaching of cellulosic fabrics using sodium peroxocarbonate aqueous solutions

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Received 7th January 2003
First published as an Advance Article on the web 14th April 2003

Natural colored compounds adsorbed or chemically bound on cellulosic fabrics were bleached effectively by a selective photolysis of the colored compounds using KrF, XeCl, and XeF excimer lasers in the presence of sodium peroxocarbonate aqueous solutions at room temperature. The efficiency of the bleaching was found to be KrF < XeCl ≈ XeF and the decrease of the tensile strength was completely suppressed by the use of the XeF laser.

Introduction

The use of conventional halogenated oxidizing reagents in textile[1] and paper[2] industries is known to form harmful compounds known as adsorbable organically bound halogens[3,4] so that the development of total chlorine free (TCF) processes for the bleaching of natural cellulosic fibers to prevent the formation of these halogenated compounds is of great importance.

As a TCF process, hydrogen peroxide is partly used in the conventional bleaching processes but they are generally operated at high temperature for a long time so that a significant amount of carbon dioxide and other gasses that are not preferable for the environment are generated by the combustion of a large amount of fuels. Therefore, the development of more environmentally friendly and energy conserving TCF processes is necessary.

Recently, we have reported an efficient TCF bleaching method by a combination of sodium borohydride aqueous solution and laser irradiation.[5,6] However, due to some toxicity of boron compounds[7] and the need for oxidative processes, we have conducted further investigations on the development of more environmentally friendly oxidative bleaching processes.

We report here a more environmentally benign TCF bleaching process of cellulosic fabrics, a UV laser irradiation in the presence of sodium peroxocarbonate ($2Na_2CO_3{\cdot}3H_2O_2$) aqueous solutions at room temperature.

Results and discussion

The sample used was a scoured cotton fabric (**SF**) [G poplin (J6220), scoured by Awazu Rensen Kogyo]. A sheet of the fabric was padded in sodium peroxocarbonate aqueous solution. The uptake of the solutions[8] by 1 g **SF** was *ca.* 2.5 g. The sheet was then irradiated with an excimer laser [KrF (248 nm) and XeF (351 nm): Lambda Physik LPX210i, XeCl (308 nm): Lambda Physik COMPex102] at room temperature, washed with water, and dried. Reflectance and absorption spectra of the laser bleached cotton fabrics (**LF**) were measured by a UV spectrophotometer (Shimadzu UV-2400PC) and their whiteness[9] and yellow index[9] were measured by the same spectrophotometer equipped with an integration sphere (Shimadzu ISR-2200) using $BaSO_4$ (Merck, for white standard DIN 5033) as a reference. The tensile strength of the cotton fabrics was measured by breaking strength method A.[10] Whiteness, yellow index, and the tensile strength of a sheet of **SF** were 32, 10.1, and 32.7 kg, respectively, and those of the conventionally bleached cotton fabric (**CF**) were 57, 1.1, and 34.4 kg. **CF** was bleached by using $NaClO_2$ from the same batch of **SF** used in the laser experiments [G poplin (J6220), bleached by Awazu Rensen Kogyo].

Fig. 1 shows the laser wavelength dependence on the whiteness and yellow index of **LF** as a function of laser irradiation time. In the case of KrF laser irradiation, whiteness reached its maximum (56) at 2 min but gradually decreased after prolonged irradiation. Similarly, the yellow index gave its minimum (1.2) at 2 min and then increased with further irradiation. The maximum whiteness and the minimum yellow index were almost the same as those of **CF**.

On the other hand, XeCl and XeF laser irradiations showed no decrease of whiteness by prolonged laser irradiations after reaching their maximum. The maximum whiteness was 57 ~ 58 for both lasers, which was almost the same as that of **CF**. In the case of the XeCl laser bleaching, the yellow index showed its minimum (−0.1) at 4 min with a slight recovery of the color with further irradiation. On the other hand, the yellow index of the XeF laser bleaching (0 ~ 0.4) stayed constant under prolonged irradiation. The minimum yellow index of both XeCl and XeF laser irradiation was better than that of **CF**, even after prolonged irradiation with the XeCl laser.

The whiteness, yellow index, and tensile strength of **LF** obtained by the KrF, XeCl, and XeF lasers are summarized in Table 1 together with those of **CF** and **SF**. The result indicates that the damage of **LF** decreased with the increase of the laser wavelength and no damage was observed with the XeF laser

Green Context

The bleaching of cellulosic fibres is a very important industrial process which suffers from a poor environmental record due to the use of very large quantities of chlorinated oxidizing reagents which tend to lead to the production of hazardous organochlorine compounds. While some progress has been made with halogen-free systems such as those based on hydrogen peroxide, these tend to suffer from other problems – notably the need for heating and hence energy consumption. Here we see an ingenious method based on the photochemical activation of the coloured components in the fibres which become stronger reducing agents enabling quite facile reactions with the benign oxidant sodium peroxocarbonate. ***JHC***

DOI: 10.1039/b300183k

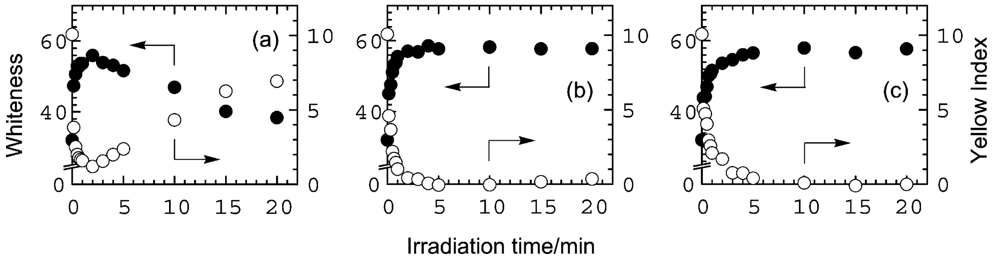

Fig. 1 Whiteness and yellow index of excimer laser bleached cotton fabrics (**LF**) as a function of irradiation time. Utilized lasers, (a) KrF, (b) XeCl, and (c) XeF excimer lasers. Whiteness: black symbols, yellow index: white symbols. Laser bleaching condition: 40 mJ cm^{-2} pulse^{-1}, 5 Hz, 6 wt% sodium peroxocarbonate (aq), room temperature. Number of cotton cloths: 1 sheet.

Table 1 Whiteness, yellow index, and tensile strength of the fabric obtained by different bleaching methods

Bleaching method	Whiteness[b]	Yellow index[b]	Tensile strength/kg
KrF laser (**LF**)[a]	56	1.2	13.7
XeCl laser (**LF**)[a]	57	0.4	23.6
XeF laser (**LF**)[a]	54 (57[c])	1.7 (0.4[c])	33.7 (33.3[c])
Conventional (**CF**)	57	1.1	34.4
None (**SF**)	32	10.1	32.7

[a] Laser bleaching condition: 40 mJ cm^{-2} pulse^{-1}, 5 Hz, 2 min, 6 wt% sodium peroxocarbonate (aq), room temperature. [b] Number of cotton cloths: 1 sheet. [c] Irradiation time: 5 min.

bleaching. This is a big advantage over the reported photochemical bleaching of cellulosic fabrics in the presence of aqueous H_2O_2 which showed strong degradation of the fabric despite the acceleration of the bleaching.[11]

It should be noted that the laser bleaching required only 2 ~ 5 min and was operated at room temperature, in contrast to the standard thermal processes using sodium peroxocarbonate and other peroxides such as H_2O_2 that are used in production sites (*ca.* 1 h at 93 ~ 99 °C or 8 ~ 16 h at room temperature).[1]

Fig. 2 shows the whiteness and yellow index of thermally bleached **SF** at room temperature. As seen in the figure, whiteness and yellow index leveled off after 3 ~ 4 min and did not show considerable change with further treatment. However, after 8 h treatment at room temperature, the whiteness and yellow index reached 52 and 2.5, respectively. These results indicate that the irradiation of the lasers was essential for fast bleaching.

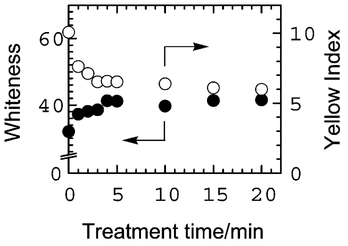

Fig. 2 Whiteness and yellow index of thermally bleached cotton fabrics as a function of treatment time. Whiteness: black symbols, yellow index: white symbols. Bleaching condition: 6 wt% sodium peroxocarbonate (aq), room temperature. Number of cotton cloths: 1 sheet.

Fig. 3a shows the whiteness and yellow index of **LF** as a function of the XeCl laser frequency. Similarly, Fig. 3b shows the whiteness and yellow index of **LF** as a function of the XeCl laser pulse energy; in this experiment, total energy irradiated at a unit area was kept constant so that the number of laser pulses decreased with the increase of the laser pulse energy. The increase of the laser frequency and the pulse energy did not show considerable change in both whiteness and yellow index. These results indicate that the necessary time for the bleaching can be shortened by increasing the laser frequency and/or the pulse energy. Fig. 3c shows the whiteness and yellow index of **LF** as a function of sodium peroxocarbonate concentration. Considerable improvement on the whiteness and yellow index was observed by increasing the concentration up to 4 ~ 6% but they leveled off after reaching their maximum and minimum, respectively.

Fig. 4a shows the absorbance of five sheets of **SF**, **CF**, and **LF**.[12] The figure shows a significant decrease of the absorption in **CF** and **LF** compared with that of **SF**, especially in the visible region. Although the structures of the natural colored compounds remaining on the scoured cotton fabrics are still not clarified, this decrease indicates the decomposition or the shortening of the extended π-electron systems of the colored compounds.

Fig. 4b shows the absorption differences between **SF**, **CF**, and **LF**, namely, **SF** − **LF**, **SF** − **CF**, and **CF** − **LF**. The absorption differences **SF** − **LF** and **SF** − **CF** show the decrease of the colored compounds by the laser and conventional bleachings, respectively. They also show that the colored compounds have broad absorption in the UV to visible region. Difference absorption **CF** − **LF** shows that the extent of the laser and conventional bleachings was almost the same at > 400 nm but the laser bleaching was more effective at 220 ~ 400 nm and the conventional bleaching was more effective at < 220 nm.

The conventional thermal bleaching of cellulosic fabrics using alkaline H_2O_2 is initiated by an electron transfer to

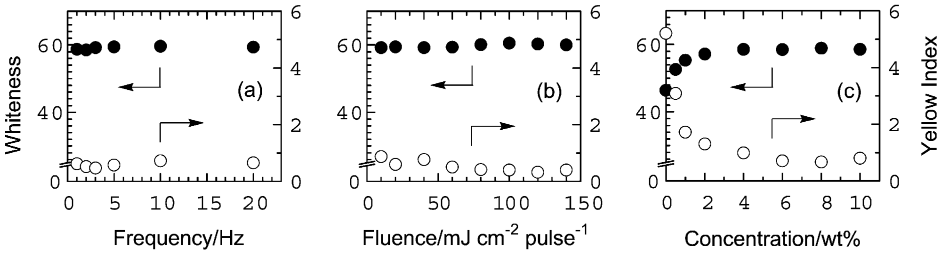

Fig. 3 Whiteness and yellow index of XeCl excimer laser bleached cotton fabrics (**LF**) as a function of (a) laser frequency [bleaching condition: 40 mJ cm^{-2} pulse^{-1}, 600 pulses, 6 wt% sodium peroxocarbonate (aq)], (b) laser pulse energy [bleaching condition: 24 J cm^{-2}, 5 Hz, 6 wt% sodium peroxocarbonate (aq)], and (c) sodium peroxocarbonate (aq) concentration (bleaching condition: 40 mJ cm^{-2} pulse^{-1}, 5 Hz, 2 min). Whiteness: black symbols, yellow index: white symbols. Treatment temperature: room temperature. Number of cotton cloths: 1 sheet.

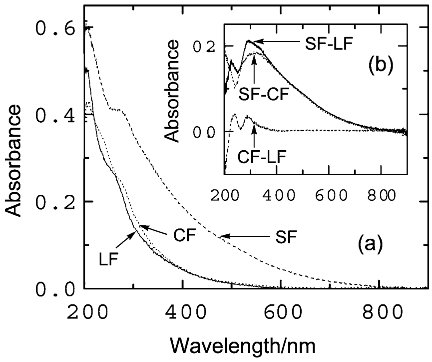

Fig. 4 Absorption (**a**) and absorption difference (**b**) spectra of cotton fabrics. (**a**) ---: scoured fabric (**SF**), . .: conventionally bleached fabric (**CF**), —: laser bleached fabric (**LF**). (**b**) . .: (**SF** − **CF**), —: (**SF** − **LF**), ---: (**CF** − **LF**). Laser bleaching condition: XeCl laser, 40 mJ cm^{-2} pulse^{-1}, 5 Hz, 2 min, 6 wt% sodium peroxocarbonate (aq), room temperature. Number of cotton cloths: 5 sheets.

hydroperoxy ions and the damage of the fabric is attributed to the action of hydroxy radicals.[1]

Fig. 5 shows the UV absorption spectra of sodium peroxocarbonate. As seen in the figure, the absorbance of sodium peroxocarbonate at each laser emission was KrF >> XeCl > XeF ≈ 0. Therefore, the concentration of hydroxy radicals in the laser bleachings is expected to be in the order KrF > XeCl > XeF because the photochemical generation of hydroxy radicals from H_2O_2 have been reported.[13] The wavelength dependence on the decrease of the tensile strength (KrF > XeCl > XeF ≈ none) can be explained by the concentration of the hydroxy radical generated by each laser.

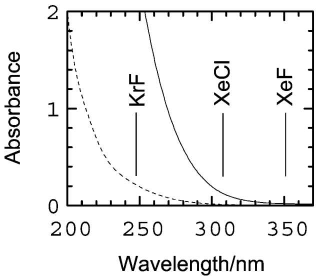

Fig. 5 Absorption spectrum of sodium peroxocarbonate (aq). Concentration: 10^{-2} M (—) and 10^{-3} M (---). Optical path: 10 mm. The wavelengths of the KrF, XeCl, and XeF lasers are marked in the figure.

The acceleration of the bleaching by the laser irradiation can be explained by the increase of the reducing power of the natural colored compounds through photochemical excitation. In the thermal bleaching, one of the electrons in the HOMO is responsible for the oxidation of the natural colored compounds; the electron is transferred to the hydroperoxy ions. However, in the excited states, an excited electron of the colored compounds that has higher energy than the HOMO electron of the ground state is involved in the oxidation, which increases the reducing power of the colored compounds and facilitates the electron transfer to the hydroperoxy ions.

Acknowledgement

We thank Mr. Jun Ito, Nisshinbo Industries, Inc., for the measurement of tensile strength.

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Production of H_2O_2 in CO_2 and its use in the direct synthesis of propylene oxide†

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Received 10th January 2003
First published as an Advance Article on the web 21st May 2003

Hydrogen peroxide is generally considered to be a green oxidant, as it is relatively non-toxic and breaks down in the environment to non-toxic by-products. However, the current method for production, the sequential hydrogenation and oxidation of an alkyl anthraquinone, is capital-intensive, produces significant volumes of waste, and consumes sizeable quantities of energy during the purification and concentration of the product. We have designed CO_2-soluble catalysts, and have successfully generated H_2O_2 from H_2 and O_2 in carbon dioxide–water mixtures. The use of CO_2 as solvent allows for use of reasonable concentrations of H_2 and O_2 without danger of explosion, and homogeneous catalysis eliminates diffusional limitations to reaction. Although aqueous hydrogen peroxide is an important product in its own right, H_2O_2 is also a benign intermediate for a variety of oxidation reactions. We have shown that H_2O_2 generated *in situ* from H_2 and O_2 in CO_2 cleanly epoxidizes propylene to propylene oxide (PO). PO is currently produced either *via* the chlorohydrin route, which produces two pounds of waste per pound of PO, or *via* one of several “peroxidation” processes, where a co-product must be produced with the desired PO and hence waste volumes and energy requirements are much higher than desired. Because those factors that render the current AQ process for H_2O_2 less than green also contribute to its relatively high cost, generation of H_2O_2 from H_2 and O_2 in CO_2 not only permits green synthesis of an important commodity, but also opens other applications for use of this green oxidant.

Introduction

The sequential hydrogenation and oxidation of an alkyl anthraquinone produces 95% of the world’s hydrogen peroxide.[1] The anthraquinone (AQ) is dissolved in an organic solvent and hydrogenated over a supported catalyst to the hydroquinone (H_2AQ). The H_2AQ is subsequently air-oxidized back to the anthraquinone plus hydrogen peroxide. The H_2O_2 is stripped into water in a liquid–liquid extraction column, and the anthraquinone solution is recycled to the hydrogenation reactor. Typical H_2O_2 plants include a sizeable distillation train to both concentrate the product and remove organic impurities “acquired” during extraction. The anthraquinone process for generating H_2O_2 is commercially successful because it continuously produces H_2O_2 at moderate temperature while preventing the direct contact between oxygen and hydrogen. However, the AQ/H_2AQ process produces several significant waste streams that derive from the use of an organic solvent and from the phase behavior in each of the reactors. First, the aqueous product becomes contaminated by the organic solvent in the extraction column, requiring distillation of the product prior to its commercial use. Consequently, although the reactions used to generate H_2O_2 are exothermic, its production requires 2.4 lbs of steam per pound of product for distillation. Utilities make up approximately 24% of the per pound cost of H_2O_2 with steam comprising 30% of the utility total. Given worldwide H_2O_2 production of 2 million tons, nearly 10 trillion BTU’s are consumed annually to deal with contamination introduced during the synthesis.

Second, a portion of the solvent mixture is either hydrogenated or oxidized during each AQ cycle; the degraded material must be removed because it acts as a non-solvent. Approximately 0.006 lbs of solvent per pound of H_2O_2 are needed; hence approximately 24 million pounds of solvent must be synthesized annually simply to make up for losses in H_2O_2 processes. Third, because commercial hydrogenation reactors operate in a 3-phase mode, the AQ exhibits a spectrum of residence times within the reactor. Side reactions, where the aromatic rings of the AQ are hydrogenated or where hydrogenolysis degrades carbonyl groups, occur during each cycle. It is estimated that 0.0006 pounds of AQ are consumed per pound of H_2O_2 produced, or $2\,\frac{1}{2}$ million pounds per year worldwide. The cost of the make-up AQ and solvent, plus the wasted hydrogen, adds over 12% to the production cost of H_2O_2.

The direct reaction of $H_2 + O_2 \rightarrow H_2O_2$ is clearly the most atom-efficient method by which to form hydrogen peroxide, yet is also potentially the most dangerous. Several chemical companies have investigated the direct route over the past 25 years,[2] and the number of patents in this field continues to grow. However, none of the available processes has solved the productivity *vs.* safety dilemma; either the process is safe but cannot produce H_2O_2 economically, or the process is economic yet exhibits too many potential liabilities.

Green Context

While hydrogen peroxide is often cited as one of the key reagents in the green chemistry laboratory due to the relatively good by-product potential in use in oxidations, it is itself prepared by a less than environmentally acceptable method. Here we see how the direct combination of H_2 and O_2 can be efficiently achieved in carbon dioxide solvent by using a CO_2-soluble catalyst. By using H_2O_2 generated *in situ* we can gain further advantage for example, in the important epoxidation of propylene to form propylene oxide. *JHC*

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† This work was presented at the Green Solvents for Catalysis Meeting held in Bruchsal, Germany, 13–16th October, 2002.

DOI: 10.1039/b300387f

Synthesis of H_2O_2 in CO_2: homogeneous catalysis for synthesis of aqueous H_2O_2

Carbon dioxide is generally considered to be an environmentally benign solvent, in that it is naturally abundant, relatively non-toxic, and non-flammable. The use of CO_2 as the "organic" solvent in the direct synthesis of hydrogen peroxide from H_2 and O_2 can solve the safety *vs.* productivity dilemma, provided that one redesigns the catalyst for express use in the new process.

Both hydrogen and oxygen are miscible in all proportions with CO_2 at temperatures above 304 K. Consequently, one can prepare mixtures of H_2–O_2–CO_2 at whatever concentrations are desired, quite unlike the situation when using either water or organic solvents. Our catalyst dissolves in CO_2, and hence the reaction between O_2 and H_2 is conducted homogeneously. The reaction in our case will thus be kinetically rather than diffusionally controlled, and we can employ higher concentrations of H_2 and O_2 than in aqueous reactions, meaning that the rate of production of H_2O_2 will be higher in CO_2 than in water or organic solvent. Hydrogen peroxide is less soluble in CO_2 than in organic solvents, and the H_2O_2 produced will therefore partition preferentially to the aqueous phase. This rapid separation of product and catalyst will minimize the product degradation that plagues the analogous reaction conducted using a heterogeneous catalyst in water. Because the pH of a CO_2–water mixture is approximately 2.8, there will be no need to add acidic stabilizers to the aqueous product, as is the case in conventional H_2O_2 production. The lack of contamination from additives or organic solvent, plus the ability to generate high concentration H_2O_2 solutions means that distillation of the product is not necessary, eliminating an energy intensive unit operation from the process.

Catalyst design and reaction results

To render the process feasible, we designed and synthesized a series of highly CO_2-soluble tri-aryl phosphine Pd^{2+} catalysts.[3] We found that use of the appropriate "CO_2-philic" ligand permits 1–3 mM solubility at pressures of only 10 MPa.

In general, we found that all of the Pd(+2) catalysts were active in the generation of H_2O_2 (yield of 30–40% after 3 hours[3]), and that the nature of the CO_2-philic portion of the ligand did not significantly affect the yield of H_2O_2. Recently[4] we have evaluated the use of a Pd(0) catalyst (dibenzylidene acetone ligands) in the H_2–O_2–CO_2 system, and found the activity to be approximately twice that of the Pd(+2) catalyst. Future work will continue to focus on catalyst optimization, including the use of Pd–Pt mixtures.

In summary, we have shown that one can conduct the synthesis of H_2O_2 directly from H_2 and O_2 in liquid or supercritical carbon dioxide. Use of CO_2 and a soluble catalyst allows us to reap a variety of process benefits (kinetic control, no solvent waste, no need for distillation, minimal catalyst-induced product degradation) that directly impact both sustainability and cost.

Direct synthesis of propylene oxide from propylene in CO_2

Over 4 million tons of propylene oxide (PO) are produced each year[5] using either the chlorohydrin or co-product processes. In the chlorohydrin route (see Fig. 1), propylene is reacted with water and Cl_2 to produce 1-chloro-2-propanol (plus HCl), which is then reacted with base to generate PO plus salt. Over 2 lbs of salt waste are produced per pound of PO, which leads to production of wastewater at volumes roughly 40 times that of the PO produced.

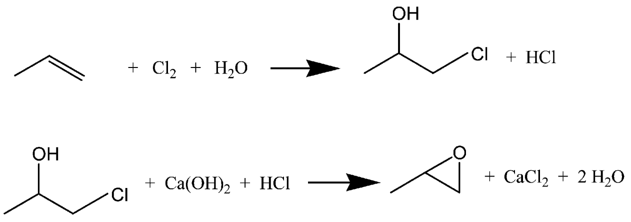

Fig. 1 Chlorohydrin process for generation of PO.

Peroxidation processes (see Fig. 2) generate PO and a co-product, either styrene (2.4 moles per mole of PO) or MTBE (3–4 moles per mole of PO). In the styrene process (which predominates), ethyl benzene is first oxidized with O_2, where the peroxy compound is used to generate PO from propylene. The residual aromatic alcohol is then dehydrated to styrene. Here 20% waste is produced during the oxidation of ethyl benzene alone. Consequently, current processes that generate PO produce sizeable waste streams and are far more complex and energy-intensive than desired, owing to the need to generate and purify the co-product.

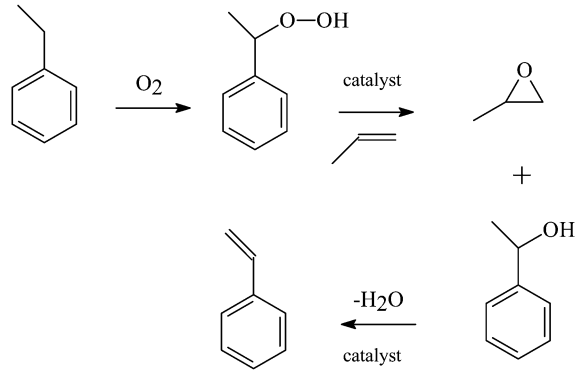

Fig. 2 Hydroperoxide process for generation of PO, styrene variant.

Direct oxidation of propylene to PO with O_2 would be highly desirable,[6] but the presence of propylene's highly combustible allylic hydrogens renders this quite difficult;[7] catalysts reported in the literature have yet to be able to support both high conversion of propylene and high selectivity to PO, based on converted propylene.

Oxidation of propylene using percarbonate formed *via* reaction of CO_2, H_2O, and H_2O_2

Previous work by Richardson and colleagues[8] showed that one can generate an epoxide from an alkene using the percarbonate ion under basic conditions; in Richardson's work the percarbonate is formed from hydrogen peroxide and sodium carbonate. We postulated that one could form percarbonate *via* the reaction of aqueous CO_2 (H_2CO_3) and hydrogen peroxide, where the carbonic acid is formed *via* simple contact between water and liquid CO_2. Our results,[3*b*,4] as well as those of Eckert's group,[9] showed that one could indeed efficiently form an epoxide from the alkene in the CO_2–H_2O_2–H_2O biphasic system if (a) an appropriate base (NaOH) at the appropriate concentration were employed, and (b) transport between the phases was optimized, through either use of a surfactant, a phase transfer catalyst, or a cosolvent. Although this percarbonate system proved very effective at generating cyclohexene oxide from cyclohexene (over 50% yield at 100% selectivity in 1 hour), for the case of propylene the selectivity was high although conversion was very low (see Table 1).

Table 1 Epoxidation of propylene using biphasic CO_2–H_2O_2–H_2O mixture with NaOH used as base catalyst and ethanol as cosolvent. Propylene oxide was the only product detected

C_3H_6 EXPOXIDATION BY H_2O_2–NaOH–CO_2

Exp.	C_{NAOH}/ mol kg^{-1}	C_{EtOH}/ mol kg^{-1}	$C_{H_2O_2}$/ mol kg^{-1}	C_{H_2O}/ mol kg^{-1}	$C_{C_3H_6}$/ mol kg^{-1}	Yield PO (%)
1	0.18	0	2.11	25.96	0.13	1.51
2	0.24	0	2.09	25.8	0.13	1.95
3	0.3	0	2.11	25.96	0.13	3.03
4	0.2	7.26	2.3	10.4	0.13	1.20
5	0.2	3.25	2.11	17.6	0.13	1.23
6	0.2	0	2.3	27.8	0.13	1.42

One-pot synthesis of PO from H_2, O_2, and propylene in CO_2

A number of researchers have shown that H_2O_2 will produce PO directly from propylene over the appropriate catalyst, with water as the co-product. Laufer *et al.*, Thiele and Roland, and others[10] showed that a titanium silicalite (TS-1) catalyst would promote the formation of PO from propylene and hydrogen peroxide at selectivities approaching 100%. Because H_2O_2 is an environmentally benign oxidant, this route would seem to combine both green and economic advantages. Unfortunately, pre-manufactured hydrogen peroxide is currently too expensive to allow an economically viable process.[5]

The use of hydrogen peroxide as a gentle but effective oxidant could be rendered economically viable if it could be generated *in situ* from hydrogen and oxygen. Holderich and colleagues[11] have examined the liquid phase generation of PO from hydrogen, oxygen, and propylene in a methanol–water solvent over Pd (alone and with Pt) on TS-1 (the Pt–Pd combination has been shown[12] to be particularly effective in the generation of H_2O_2 from H_2 and O_2). Early work showed yields less than 5%, while later inclusion of promoters (such as NaBr) boosted the conversion and selectivity to near 40% in batch experiments. Runs in semi-continuous equipment increased the selectivity to over 60% while dropping the conversion substantially. The use of TS-1 to generate propylene oxide from propylene using hydrogen peroxide (either pre-manufactured or generated *in situ*) has been investigated extensively over the past decade; in general researchers have concluded that an alcohol (preferably methanol) is needed as part of the solvent mixture to perform the reaction efficiently. Clerici and colleagues, for example, propose that the methanol interacts with the catalyst surface at the active site.[13] Other researchers[10*b*,11*a*,14] confirm Clerici's contention that the highest activities in traditional solvent systems can be found using methanol as the sole solvent or as the co-solvent with water.

Jenzer *et al.* have recently investigated the generation of PO from H_2, O_2, and propylene over a Pt–Pd–TS-1 catalyst in a continuous fixed bed reactor[15] using a mixture of methanol and water as the solvent. By-product generation was extensive, where the primary by-product was methyl formate (acetone, acrolein, acrylic acid, and PO ring-opening products were also observed). The formates were created *via* the oxidation of methanol, a known reaction that takes place under mild conditions. Hydrolysis followed by further oxidation creates formic acid, which then reacts with methanol to generate the formate. Although methanol was clearly the primary source of by-products, the literature[13] maintains that methanol interacts with the active site of the catalyst, stabilizing the intermediate, and is hence vital to successful PO synthesis. The presence of the MeOH–H_2O also creates process problems; it is likely that the rate of the reaction is limited by the slow diffusion of the gaseous reactants across the vapor–liquid interface and the poor solubility of the gases in MeOH–H_2O.

Formation of H_2O_2 in CO_2: results

Given this background, we have investigated the use of carbon dioxide as the sole solvent for the generation of PO from hydrogen, oxygen, and propylene over a Pd–TS-1 catalyst in order to determine whether we can reap the safety and transport benefits from use of CO_2 while avoiding the by-product problems deriving from use of methanol. Given Clerici's results,[13] a key question was whether the reaction would proceed effectively without the presence of methanol. CO_2 provides a unique combination of advantages to this process – CO_2 can solubilize large quantities of gases, is immune to oxidative degradation, provides a non-flammable environment in which to mix H_2 and O_2, and is miscible with both propylene and PO.

The effect of solvent system (CO_2 *versus* water–MeOH) was compared *via* three sets of experiments:

(a) use of CO_2 as the sole solvent (a single phase mixture),

(b) use of methanol–water and nitrogen to produce the same operating pressure as in (a) (either 2 or 3 phases), and

(c) Use of methanol–water and CO_2 to produce the same operating pressure as in (a) (a 2-phase mixture)

The results are reported as conversion of propylene and selectivity to PO (total PO divided by total amount of propylene contained in products detected) at the conclusion of the 4.5-hour runs. In the case where CO_2 is used as the sole solvent, the by-product is propane, whereas a number of ring opening products (products owing to reaction between PO and either water or methanol) and oxidation products are found when MeOH is employed.

As shown in Table 2, the use of CO_2 as the sole solvent in the reaction allows for high selectivity to PO at reasonable conversions, whereas selectivity drops when methanol–water is added. The latter results are consistent with Jenzer's observations that methanol is a major contributor to by-product formation (both through reaction with PO and oxidation), and that use of CO_2 in place of nitrogen leads to improvements. Additional by-products observed when methanol was present included methyl formate, 1-methoxypropan-2-ol and 2-methoxypropan-1-ol. Typically, the molar ratio of these three was 12 to 1.7 to 1, in agreement with previous observations that methyl formate is the major by-product when methanol is present.

From entries 1–3 in Table 2, it would appear that simply increasing the amount of catalyst in the reactor increases the selectivity of the reaction, but this is somewhat deceiving. We strongly suspect that, despite having pretreated the catalyst with hydrogen before use, the first step in the process in the reactor is additional reduction of the catalyst by available hydrogen, which then changes the hydrogen : oxygen ratio (from a molar perspective, the amounts of palladium and hydrogen are indeed comparable at higher levels of catalyst). It is known that lowering the hydrogen : oxygen ratio favors the formation of H_2O_2 *versus* water over palladium; further, the reduction in the amount of available hydrogen lessens the chances for simple hydrogenation of propylene to propane.

The presence of the gas–liquid interface (entries 3–6) also contributes to decreasing selectivity, as any splashing of the powder catalyst onto the walls of the reactor would lead to the gas-phase hydrogenation of propylene. The last two entries in Table 1 show that use of nitrogen as the pressure transmitting medium leads to enhanced conversion but low selectivity as the significant gas–liquid interface promotes propane formation (it

Table 2 Comparative results for batch epoxidation in three different systems.[16] Total pressure = 13.1 MPa, temperature = 318 K, 4.5 h reaction time. In all cases the absolute concentrations were 4 mM for propylene, 1.26 mM for H_2, and 8.3 mM for O_2, in 3.84×10^{-5} m^3 of CO_2. Conversion continued to change up to 4.5 hours, so we believe that the hydrogen had not yet been completely consumed at that point. The data are averages of 4 runs

Solvent system	Catalyst mass/g	Propylene conversion (%)	Propylene selectivity to PO (%)	Propylene selectivity to C_3H_8 (%)	Propylene selectivity to ring opened by-products
CO_2	0.1502	9.5	77.1	22.9	N.D.[a]
CO_2	0.1952	6.5	91.2	8.8	N.D.
CO_2	0.2998	7.5	94.3	5.7	N.D.
MeOH + H_2O + CO_2	0.1565	3.5	17.4	75.0	7.6
MeOH + H_2O + CO_2	0.2063	4.7	41.1	46.5	12.4
MeOH + H_2O + N_2	0.1993	16	3.5	95.2	1.4

[a] N.D. indicates that no PO ring opening by-products (propylene glycols, methoxypropanols, or propylene carbonate) were detected by online GC analysis.

is also possible that methanol can further reduce the palladium to the point where propane hydrogenation is favored over hydrogen peroxide production). The fact that the presence of CO_2 *versus* N_2 improves conversion and selectivity to PO when used with MeOH–water likely derives from phase behavior effects. CO_2 will swell a mixture of methanol–water (75/25), and hence improvements owing to the replacement of nitrogen by CO_2 may derive from increased solubility of the gaseous reactants (O_2, H_2 and propylene) in the liquid phase due to the presence of CO_2. Also, a mixture of N_2, propylene, O_2, H_2 and MeOH–water will likely create a 3-phase mixture, while use of CO_2 (in place of N_2) will likely create a two-phase mixture, thus reducing the number of interfaces and enhancing transport. When CO_2 is employed as the sole solvent, the gas–liquid interface (a prime source for formation of propane) is eliminated entirely, further enhancing selectivity.

Process safety

Use of H_2 and O_2 in CO_2 provides clear productivity and waste minimization advantages, but is the process safe enough to operate? Dupont[17] scaled a $H_2 + O_2 \rightarrow H_2O_2$ process (not CO_2-based) to the pilot stage in the early 1990's, and only experienced safety problems when an inappropriate material was used in the oxygen handling system. Recent literature[18] shows that CO_2 produces a significantly larger non-explosive concentration range than N_2 when used with O_2–H_2 mixtures, and hence scaling a CO_2-based process would present fewer problems than an N_2-based system. Subramaniam's group has recently[19] shown that CO_2 at temperatures near the critical is an ideal medium for absorbing the excess heat that would be created during an uncontrolled $H_2 + O_2 \rightarrow H_2O$ reaction, owing to the maximum exhibit by CO_2's heat capacity (a 42 K rise compared to 270 K in N_2). Further, contact between O_2 and CO_2 does not create a safety hazard (CO_2 cannot be oxidized), unlike organic solvents. Hence, CO_2 appears to be the ideal solvent for achieving both productivity and safety in the direct route to H_2O_2, but it must be made clear that the extent of the non-explosive regime must actually be measured at some point.

In summary, we have found that carbon dioxide is an excellent solvent for conducting the epoxidation of propylene, where the *in situ* reaction of H_2 and O_2 creates the oxidant. Unlike organic solvents, CO_2 can solubilize large quantities of gases, is immune to oxidative degradation, provides a non-flammable environment in which to mix H_2 and O_2, is miscible with both propylene and PO, and is chemically inert to the PO product. Significantly, we have found that methanol is not required to efficiently produce PO from propylene *via* the *in situ* H_2O_2 route, contrary to suggestions from previous reports.

Experimental

The catalyst was prepared by suspending TS-1 (1.6% Ti, 20 g) in deionized water (8.0×10^{-5} m^3) in the presence of tetraamine palladium nitrate (5% Pd, 2.542 g) at 353 K for 24 hours. The solid was recovered by filtration under pressurized N_2, washed with deionized water, dried under vacuum at 323 K, then calcined at 423 K for 4 hours in a 5% O_2–95% N_2 mixture. The resulting catalyst has 0.47% Pd by weight. Pd–TS-1 catalyst prepared in this way was then suspended in a 75/25 mixture methanol–water (2 grams catalyst in 100 cm^3 solvent) and preactivated in a 1×10^{-4} m^3 min^{-1} gas flow (10% propylene, 4% O_2, and 4% H_2) at 318 K and 0.02 MPa for 22 hours.

Reactions were carried out in a 4×10^{-5} m^3 stainless steel batch reactor capable of operating pressures to 40.0 MPa at temperatures up to 373 K, where the contents were mixed using a multi-blade stirrer (Parr Instrument Co) that had been mated to the reactor lid. Gases were introduced using a calibrated high-pressure syringe pump (High Pressure Equipment Co, Erie, PA). The temperature of the reactor was monitored *via* a thermocouple fitted through one of the five reactor ports, while the pressure was monitored using a transducer and readout. Samples could be withdrawn from either liquid or gas phases through an additional pair of ports, each fitted with a frit filter to retain catalyst. Material was injected *via* the final two ports. Samples were analyzed using one of two gas chromatographs (Hewlett Packard 5890 Series 2, featuring both TCD and FID detectors). Where CO_2 alone was the solvent, the reactor was charged with a known amount of catalyst, and then evacuated. The reactor was heated to 318 K and known amounts of CO_2, hydrogen, O_2–N_2 mix, and propylene were added in that order. Additional CO_2 was charged using the compressor (Haskell Equipment Co, Houston) to achieve a final pressure of 13.1 MPa. The mixture was vigorously mixed, then sampled at intervals for GC analysis, then slowly depressurized to one atmosphere. Any side products that precipitate on the catalyst were extracted in methanol and analyzed separately by GC. When methanol–water was employed as the solvent, 1.0×10^{-5} m^3 of a 75/25 methanol–water mixture was charged to the reactor with the catalyst before conducting the experiment. Both the gas and liquid phases were sampled and analyzed for PO and other products. For some of the two phase (gas–liquid) experiments, N_2 was substituted for CO_2.

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Infrared-assisted eco-friendly selective synthesis of diindolylmethanes

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Received 8th November 2002
First published as an Advance Article on the web 8th May 2003

An alternative and environmentally benign pathway for selective synthesis of aryl-3,3′-diindolylmethanes from indole and several aromatic aldehydes is described. The electrophilic aromatic substitution (EAS) reactions are achieved with good yield and short reaction time employing infrared irradiation as energy source and a bentonitic clay as catalyst and reaction medium, in solvent-free reaction conditions.

Introduction

Actually, diindolymethanes are very important chemical compounds with potential pharmaceutical activity. One of these compounds, diindolymethane (DIM), has been the subject of much research and it is proposed that DIM has potential uses in promoting healthier estrogen metabolism, breast cancer prevention, control of cervical dysplasia,[1] a strong anti-proliferative effect in human endometrial cancer cells[2] and many others.

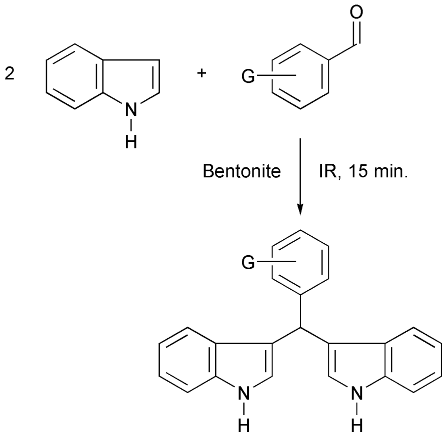
Several methods are available for the preparation of 3,3′-diindolylmethanes. Kamal and Qureshi[3] obtained it from the reaction of either indole or 2-methylindole with aldehydes under controlled pH with a 10 day reaction time, but in some reactions the desired compound was not obtained. In the same way, Bergman and coworkers[4] reported the synthesis of the title compounds under acidic reaction conditions with the formation of cyclooligomeric compounds in moderate yields, and Jackson and coworkers[5] reported the synthesis of DIM in moderate to good yields under acidic reaction conditions.

In recent years we have been engaged in designing alternative synthetic strategies with an environmentally benign approach, utilising a bentonitic clay as catalyst or reaction medium and alternative energy sources, such as microwaves, infrared or ultrasound, in solvent-free reaction conditions applied to several organic reactions.[6] With this synergetic methodology we have found in many cases that the reactions are cleaner, with high selectivity, an easy experimental work-up and with very important economic advantages.

Our continuing interest in the Green Chemistry postulates prompted us to develop a convenient alternative synthesis of several aryl-3,3′-diindolylmethanes from indole and aromatic aldehydes in the presence of a bentonitic clay, using infrared energy in the absence of solvent, outlined in Scheme 1.

Results and discussion

Firstly, we looked at the effectiveness of the proposed strategy by the reaction of benzaldehyde with indole. At 15 minutes reaction time the highest yield of a single reaction product was detected and after this time no significant changes were observed by thin layer chromatography.



Scheme 1

After the recrystallization purification process, spectroscopic identification revealed the 3,3′-diindolylmethane structure of the reaction product. Then, we took this reaction time as a reference for the other substituted benzaldehyde reactions.

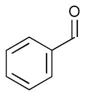
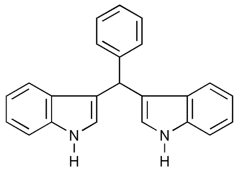
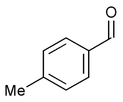
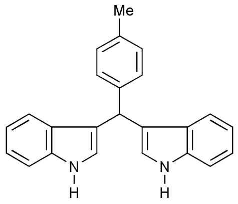
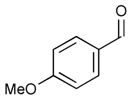
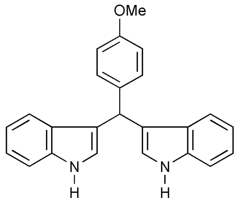
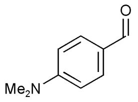
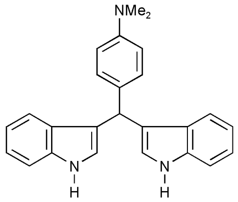
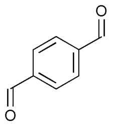
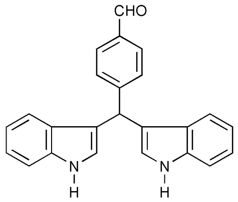
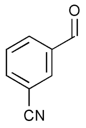
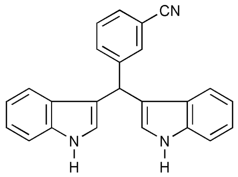
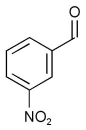
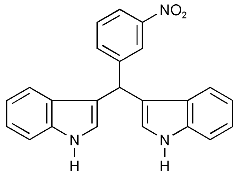
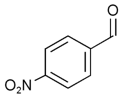
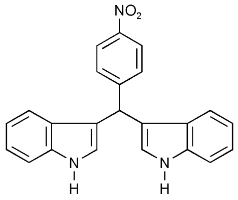
The obtained yield for each used benzaldehyde is given in Table 1.

Green Context

Diindolylmethanes are an important class of organic compounds with numerous pharmaceutical applications. Several synthetic strategies are available but these suffer from drawbacks including long reaction periods and hazardous conditions. Here a new, more environmentally benign pathway to aryl-3,3′-diindolylmethanes is described. This involves the avoidance of solvents, short reaction times through the use of infrared irradiation as the energy source and the use of an inexpensive and natural clay catalyst. Thus through the combination of several items in the clean technology toolkits a much improved, reduced environmental impact synthesis to an important class of compounds is achieved. ***JHC***

DOI: 10.1039/b211011c

Table 1 Condensation of aromatic aldehydes with indole, formation of diindolylmethanes

Entry	Aldehyde	Product	Melting point/°C	Isolated yield (%)
1			125–127	75
2			83–85	70
3			191–193	70
4			166–168	55
5			203–204	85
6			102–104	82
7			265–266	93
8			221–223 (Dec.)	96

These results show a regular chemical behavior according to the substituent on the phenyl group; that is, with electron-releasing groups (Me, OMe, Me_2N, Me) in the *para* position the electrophilic character of the carbonylic carbon is expected to be smaller for the EAS reaction, while with electron-withdrawing groups (CHO, CN, NO_2) although they are in the *meta* position the electrophilic character of the same carbonylic carbon is increased and this effect is clearly more enhanced with the nitro group in the *para* position

Finally, as another purpose of the present work it is important to point out the reaction with the terephthalaldehyde (entry 5), since under both the reaction conditions and stoichiometric quantities used only a single aldehyde function was reacted and with the mild experimental work-up it was not altered.

In conclusion, we found an alternative and selective method to diindolylmethanes synthesis in good yields which is achieved under solvent-free reaction conditions and short reaction times with the use of a cheap bentonitic clay and infrared energy.

Experimental

A typical experimental procedure is as follows. To a mixture of indole (1.0 g, 8.54 mmol) and benzaldehyde (0.45 g, 4.27 mmol) was added the bentonitic clay (4 g). The reaction mixture was IR irradiated with a commercial IR lamp (250 W), according to the methodology reported by Pool and Teuben,[7] for 15 minutes (after this reaction time no changes were detected by thin layer chromatography), and the temperature reached during the reaction was 180 °C.[8] Then, to the produced reaction mixture a 1 : 1 water–methanol mixture was added for recrystallization purposes. The pure product was identified by both nuclear magnetic resonance (^{1}H, ^{13}C) and mass spectrometry. Selected data for phenyl-3,3′-diindolylmethane (**1**): HR-MS M 322.1464 g mol^{-1} observed (322.1470 g mol^{-1} estimated) for a molecular formula $C_{23}H_{18}N_2$. Pink solid; yield: 75%; mp 125–127 °C (methanol–water 1 : 1); EIMS (r.a.): m/z 322 (M$^+$, 100), 321 (34), 245 (52); ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 9.98 (s, 2H), 7.82 (s, 2H), 7.35–6.95 (m, 13H), 5.87 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 144.0, 136.7, 129.1, 128.7, 128.2, 126.1, 123.5, 121.9, 119.9, 119.6, 119.2, 111.0, 40.1.

Acknowledgements

The authors wish to thank Rocío Patiño, Luis Velasco and Francisco J. Pérez for their technical assistance. G. Penieres wishes to acknowledge support from CONACYT Project 35593E.

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8 The same reaction was also performed using an oil bath at the same temperature and reaction time. After the recrystallization process the obtained yield was similar to the infrared method, but with great amounts of pollution vapors produced from the hot oil.

Synthesis of cyclic ureas and urethanes from alkylene diamines and amino alcohols with pressurized carbon dioxide in the absence of catalysts

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Received 20th January 2003
First published as an Advance Article on the web 9th May 2003

Clean synthesis to imidazolidone and oxazolidone compounds using direct reaction of carbon dioxide with diamine or amino alcohols can be achieved at 6 MPa CO_2 and 150 °C without use of any catalyst.

Introduction

The development of environmentally benign processes based on a greenhouse gas such as carbon dioxide as a building block has gained considerable attention.[1] The quest for certain molecules that can effectively act as carbon dioxide fixation agents is required from an environmental viewpoint. Epoxides,[2] dienes,[3] alkynes,[4] formic acid synthesis,[5] and dimethylformamide syntheses[6] have been studied well in this regard. Other molecules such as diamines and amino alcohols are also worth investigating as effective agents for the fixation of carbon dioxide into valuable chemicals. Cyclic ureas can find extensive applications as intermediates for the synthesis of medicines,[7] chemotherapeutic agents,[8] dislignification reagents,[9] and cosmetics[10] and cyclic urethanes can also find similar useful applications.[11] The cyclic ureas or urethanes can be synthesized by reactions of alkylene diamines or amino alcohols with several different reagents such as phosgene,[12] urea,[13] dialkyl carbonates,[14] or a mixture of carbon monoxide and oxygen *via* oxidative carbonylation.[11,15] The use of urea has the major drawback of formation of large quantities of polyurea and high reaction temperatures are also required.[16] Dialkyl carbonates and oxidative carbonylation are currently in use and there are several works using these two methods.[14,15] The use of phosgene and oxidative carbonylation is not eco-friendly due to risks associated with explosion hazards and poisonous phosgene or carbon monoxide. It should be noted that dialkyl carbonates are also produced *via* such hazardous routes. With respect to cyclic urethane, this compound can be produced from aziridine (ethyleneimine) and CO_2; however, this route requires high reaction temperatures[17] or has the drawback of polymer formation.[18]

In view of these, the direct reaction of carbon dioxide and diamines or amino alcohols to produce cyclic ureas or urethanes has been most desired. Okuno and coworkers reported the reactions of carbon dioxide and ethanolamines to cyclic urethanes in the presence of triphenylphosphine, a thiol/Fe_4S_4 cluster, and amines[19] or in the presence of triphenylphosphine, carbon tetrachloride, and amine.[20] In these reaction systems, a stoichiometric amount of triphenylphosphine molecules are oxidized to their oxides. Cyclic urethanes can also be produced from carbon dioxide and amino alcohols in the presence of dehydration reagents;[21] however, dehydration reagents are expensive and may generate wasteful byproducts. Preparations of cyclic ureas from carbon dioxide and diamines and of cyclic urethanes from carbon dioxide and amino alcohols using triphenylstibine oxide as a catalyst have also been reported.[22,23] Dibutyltin oxide can also be used for the latter reaction.[24]

Although these catalytic reactions are significant, it is preferable to avoid the use of catalysts to eliminate the catalyst–product separation and catalyst recycling procedures. Mulvaney and Evans previously reported the synthesis of 2-imidazolidone from carbon dioxide and ethylenediamine without any catalysts,[25] and lately a few examples of the direct condensation of carbon dioxide with diamines and amino alcohols were reported.[23,24] These methods are an extension of the Fichter and Becker method,[26] in which carbon dioxide and ammonia or amine are heated together, and these are very attractive under the circumstances described above. However, the detailed study for other substituted diamines or amino alcohols has not been made so far. This has initiated us into a systematic study of the preparation of cyclic ureas and urethanes from diamines and amino alcohols with carbon dioxide in the absence of catalysts.

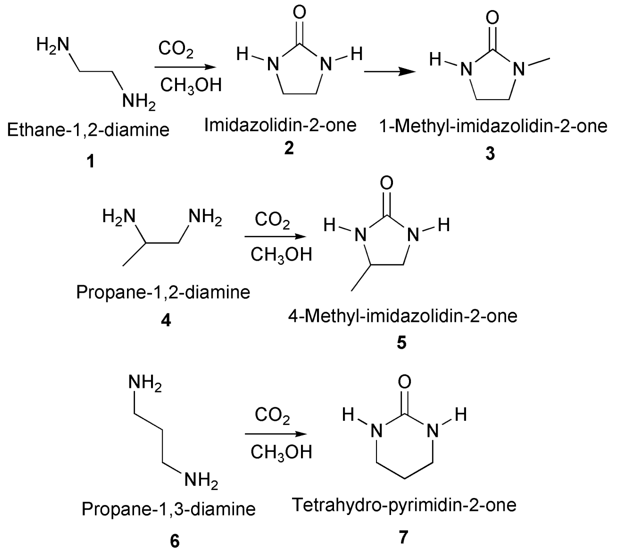
Results and discussion

In this work, several diamines (Scheme 1) and amino alcohols (Scheme 2) have been used. The results obtained are given in Table 1. The reaction of ethane-1,2-diamine **1** gives imidazoli-

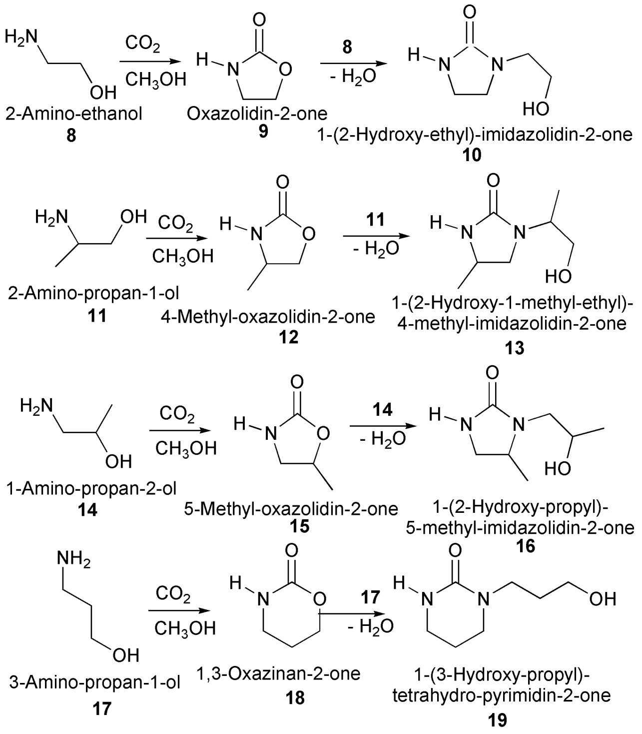
Green Context

The synthesis of ureas is of great importance in many areas, although current methods, such as phosgenation of amines and diamines, are very unattractive processes, and oxidative carbonylation, although avoiding phosgene and the salt waste associated with its use, requires the use of CO and catalysts. The process described here indicates that a direct reaction of diamines with carbon dioxide at high pressure will lead directly to the desired ureas, often in very good yields and with excellent selectivity. No catalysis is required for these transformations, making the process simple and very direct. ***DJM***

DOI: 10.1039/b300778b



Scheme 1 Reactions of diamines with CO_2 in methanol.



Scheme 2 Reactions of amino alcohols with CO_2 in methanol.

din-2-one **2** with more than 80% conversion and 97% selectivity (entry 1). The side product is 1-methyl-immidazolidin-2-one **3** which is produced *via* the reaction of methanol with the product **2**. The yield of **2** increases with an increase in CO_2 pressure from 3 to 6 MPa and then remains unchanged up to 10 MPa (entries 1–3). The increase in the yield in the low-pressure region can be attributed to the increase in the concentration of CO_2 absorbed in the methanol. When the reaction temperature is raised from 150 to 200 °C, the conversion increases from 81 to 97% but the formation of side product **3** increases up to 24% (entry 4). Various solvents such as acetonitrile, ethyl acetate, *N*-methylpyrrolidone have also been tested instead of methanol. However, these solvents give several side products due to the high reactivity of the solvents. Ethanol has also been found to be a good solvent (entry 5), in which the product **2** is insoluble and quantitatively precipitates from the reaction mixture. When water was used as a solvent, the formation of carbamate salt, $^{+}H_3NCH_2CH_2NHCO_2^{-}$, has been observed with high conversion of **1**. Probably, further transformation of the carbamate to the cyclic urea should be inhibited by the presence of water.

When propane-1,2-diamine **4** is used, the conversion decreases from 81 to 53% but it selectively gives 4-methyl-immidazolidin-2-one **5** (entry 6). The steric hindrance due to the bulky methyl group may be responsible for the decrease in the conversion and the increase in the selectivity. Propane-1,3-diamine **6** has been found to give six-membered tetrahydro-pyrimidin-2-one **7** with a conversion similar to that of **1** (entry 7). In this case as well, the product has quantitatively precipitated from methanol after reaction. For 1,2-phenylenediamine only a trace amount of 2-benzimidazolone was formed and aryldiamine was inactive under the present reaction conditions.

For 2-amino-ethanol **8**, the conversion is 23% and the selectivity for oxazolidin-2-one **9** is only 17% (entry 8). Side products are 1-(2-hydroxy-ethyl)-imidazolidin-2-one **10** and unidentified compounds. The selectivity for **10** reaches 49% and this compound would be produced from the reaction of **8** and **9**. The reaction of **8** and **9** to form **10** is also confirmed by additional experiments, *e.g.* **8** and **9** (standard procured from Aldrich) were mixed together in methanol and heated at 150 °C for 4 h. This reaction also forms compound **10**. It is suggested from GC-MAS analysis that the unidentified side products have

Table 1 Results of the reactions of diamines or amino alcohols with CO_2 in methanol in the absence of catalysts

Entry	Substrate	Temperature/° C	CO_2 pressure/ MPa	Conversion[a] (%)	Selectivity [b] (%)		
					Product I	Product II	Others [c]
1	**1**	150	6	81	**2**, 97	**3**, 3	
2	**1**	150	3	63	**2**, 93	**3**, 5	
3	**1**	150	10	82	**2**, 97	**3**, 3	
4	**1**	200	6	97	**2**, 74	**3**, 24	
5 [d]	**1**	200	6	93	**2**, 94	**3**, 0	6
6	**4**	150	6	53	**5**, 99		
7	**6**	150	6	80	**7**, 95		
8	**8**	150	6	23	**9**, 17	**10**, 49	34
9 [d]	**8**	150	6	13	**9**, 51	**10**, 31	18
10	**8**	200	6	76	**9**, trace	**10**, 89	11
11	**11**	150	6	11	**12**, 72	**13**, 17	11
12	**14**	150	6	10	**15**, 87	**16**, 1	12
13	**14**	200	6	24	**15**, 41	**16**, 51	8
14	**17**	150	6	21	**18**, 86	**19**, 10	4

Reaction conditions: reactor volume, 50 cm^3; substrate, 60 mmol; solvent, methanol 4 cm^3; time, 6 h.[a] Total conversion of substrates of **1**, **4**, **6**, **8**, **11**, **14**, and **17**. [b] Selectivity (%) = (moles of product formed/moles of substrate consumed) × 100. [c] Other products contain substrate dimers, oligomers and ring opening products of cylic ureas and urethanes. The selectivity is 100 − the sum of the selectivities of Products I and II. [d] Ethanol (4 cm^3) was used instead of methanol.

structures similar to that of the dimer of the substrate **8**. When ethanol is used as the solvent, the selectivity for **9** can be increased to 51% (entry 9). The product **10** can also be obtained in a high selectivity of 89% at 76% conversion of **8** at a higher temperature of 200 °C (entry 10). 2-Amino-propan-1-ol **11** gives 11% conversion (entry 11) and the selectivity for 4-methyl-oxazolidine-2-one **12** is higher than the selectivity for **9** using substrate **8** (entry 8). Steric hindrance of the methyl group is probably responsible for further reaction of **11** and **12** to produce 1-(2-hydroxy-1-methyl-ethyl)-4-methyl-imidazolidin-2-one **13** (17% selectivity). This steric hindrance is more pronounced when the methyl group is attached to the carbon atom adjacent to the OH group (entry 12). In this case, the selectivity towards 1-(2-hydroxy-propyl)-5-methyl-imidazolidin-2-one **16** is merely 1% whereas 5-methyl-oxazolidin-2one **15** can be obtained in 87% selectivity. However, when the temperature is raised, the selectivity for **15** decreases from 87% at 150 °C to 41% at 200 °C, whereas that for **16** increases from 1 to 51%. Finally, 3-amino-propan-1-ol **17** gives 21% conversion and 86% selectivity for 1,3-oxazinan-2-one **18** and 10% selectivity for 1-(3-hydroxy-propyl)-tetrahydro-pyrimidin-2-one **19**. The selectivity for unidentified products is lowest among the amino alcohols used.

In conclusion, cyclic ureas can be obtained in high yields from direct interaction of diamines and CO_2 without any catalysts, which gives a simple, convenient, and eco-friendly process. Amino alcohols also interact with CO_2, producing cyclic urethanes and substituted cyclic ureas depending on the reaction conditions and the substrates used. The reaction procedures are very simple and the solvent (methanol) can be easily separated by evaporation to obtain solid products.

Experimental

All experiments were carried out in a 50 ml stainless steel autoclave with mechanical agitator. In a typical experiment, substrate (60 mmol) and methanol (4 cm^3) were charged into the reactor. The reactor was flushed with CO_2 three times and then CO_2 was injected up to around 0.5 MPa. The reactor was heated up to 150 °C and then CO_2 was further injected up to 6 MPa under stirring. The reaction mixture was stirred for 6 h. After the reaction, the reactor was cooled to 0 °C by ice water and depressurized. The liquid reaction mixture was analyzed by a gas chromatograph with a flame ionization detector and retention time is compared with available authentic standards in most of the cases. The results were also confirmed using a gas chromatograph coupled with a mass spectrometer (GC-MAS), which also confirms several structures. Quantitative precipitation produced a white solid in some cases, which also confirms the analytical method.

Acknowledgement

The authors are thankful for financial support for this work from Japan Science and Technology Corporation (JST) under CREST Program.

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Synthesis of dimethyl carbonate by transesterification over CaO/carbon composites

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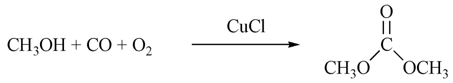
Received 30th October 2002
First published as an Advance Article on the web 29th April 2003

A CaO/C composite, a new solid base catalyst, was prepared and served as a convenient and efficient heterogeneous catalyst for synthesis of DMC from methanol and propylene carbonate. Compared with pure CaO, the CaO/C shows the same basic properties and a high performance. In addition, the CaO/C catalyst, which is easily recovered, can be reused with little deactivation, if a suitable particle size is chosen.

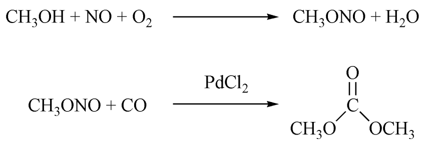
Introduction

Dimethyl carbonate (DMC) is very attractive due to its versatile chemical reactivity and unique physical properties.[1,2] DMC is an important intermediate for polycarbonate resins as well as a useful carbonylation and methylation agent.[3] Because of the negligible toxicity of DMC, it is promising as a safe substitute for toxic and corrosive phosgene, dimethyl sulfate or methyl iodide in organic synthesis, and is a so called environmentally benign building block.[4] In addition, DMC has been mentioned as a potential gasoline octane enhancer due to its very high oxgen content (53 weight percent), good octane ($(R + M)/2 = 105$), freedom from phase separation, good gasoline/water distribution coefficient, low toxicity, and rapid biodegradability.[5] Furthermore, DMC has also been widely used as an electrolyte in lithium batteries due to its high dielectric constant.

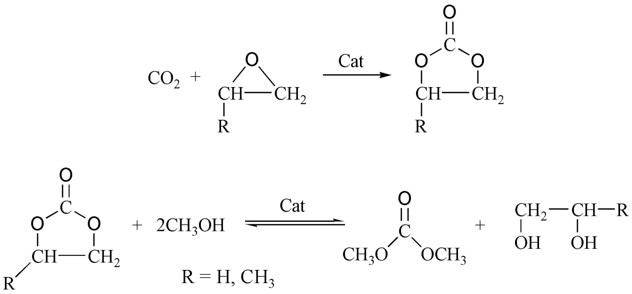
Since DMC was manufactured from methanol and phosgene for the first time in the 1910s,[6] which was eliminated in recent years due to the use of virulent phosgene, there have mainly been three environmentally compatible routes for the production of DMC. For instance, it can be prepared by oxidative carbonylation of methanol using CuCl as catalyst (Scheme 1), yet the main drawback of this method is the production of corrosive hydrogen chloride.[7] Carbonylation of methyl nitrite over Pd/carbon is also used to produce DMC with high yield (Scheme 2),[8] where the use of toxic NO is the main problem. In addition, both routes bear a potential explosion hazard. The third route is the transesterification method (Scheme 3),[9] in which a cyclic carbonate is formed from oxirane and carbon dioxide and subsequently *trans*-esterified to form DMC and coproduce alkylene glycol, very useful agents for synthesis of polyester. In this route, there is no waste or corrosion to equipment, and the naturally abundant carbon dioxide is used as a starting material; all of these make it more attractive from an environmental aspect.



Scheme 1 Synthesis of DMC by oxidative carbonylation of methanol.



Scheme 2 Synthesis of DMC by carbonylation of methyl nitrite.



Scheme 3 Synthesis of DMC by the transesterification method.

For transesterification of cyclic carbonate with methanol, various acid and base catalysts have been reported as being effective.[9–15] Knifton and Duranleau found that bases were generally more effective than acids for this reaction.[9] Bayer and Dow companies patented the use of inorganic base, such as alkali metal alkoxide, carbonates and hydroxide *etc.* as catalyst.[10,11] Bayer company also patented the use of organic base, usually tertiary amine, as catalyst.[12] Some of these catalysts had pretty high activity. For instance, when KOH was used as catalyst, DMC yield was 45% at 353 K under a continuous process with ethylene carbonate as a starting material.[10] However the homogeneous nature of these catalysts made it difficult for them to be separated from products and

Green Context

The production of dimethyl carbonate by transesterification of propylene carbonate with methanol is a potentially clean route to this valuable chemical. Generally reactions are run at relatively elevated temperatures, which is undesirable from the point of view of energy and equilibrium position. The CaO/carbon composites described here prove to be very good and reusable catalysts for this conversion, and operate at lower temperatures than most other catalysts. The CaO/carbon composites appear to be slightly better in some respects than bulk CaO. *DJM*

DOI: 10.1039/b210716n

reused, and consequently paved the way for solid base catalysts. There were some reports on the synthesis of DMC from alkylene carbonate and methanol over solid bases.[9,13–15] In these studies, basic resin, basic zeolite, metal oxide, hydrotalcite *etc.* are used for this reaction. However, all these catalysts require either a high temperature or a long reaction time. Bhanage *et al.* reported that DMC yield was 32.4% in 4 h at 423 K with the methanol and propylene carbonate ratio being 8.[14] To our knowledge, there are few reports on solid base catalysts being effective for this reaction near room temperature. In our previous work, CaO prepared from the dissociation of $CaCO_3$ at elevated temperature was found to be very effective for synthesis of DMC from methanol and propylene carbonate (PC).[16,17] The reaction even reached equilibrium in 30 min at 293 K. The mechanism of synthesis of DMC from methanol and PC was also investigated in detail in our other published paper.[17] However, ultra fine CaO prepared from $CaCO_3$ is difficult to filter from the products and reuse. Therefore, CaO/carbon composites (CaO/C) were prepared in the present paper; the structure, basicity and the catalytic performance of such a catalyst were also investigated compared with those of pure CaO.

Results and discussion

The XRD shows that the structure of CaO in the CaO/C composite hardly changes (see Fig. 1). As a result, the basic properties of CaO/C almost remain as that of pure CaO, which is illustrated by CO_2-TPD of CaO and CaO/C (see Fig. 2 and Table 1). Both CaO and CaO/C CO_2 desorption appear at 923 K. These indicate that no chemical interaction takes place between carbon and CaO, and carbon mainly acts as the inert supporter. The pore distributions of CaO/C and carbon prepared from linear phenolic resin and hexamethylenetetramine only are illustrated in Fig. 3. It can be seen that there are only micropores in carbon, while both micropores and mesopores are formed in CaO/C samples, which means that the mesopores in the CaO/C composite may result from the addition of $CaCO_3$ in the starting materials. This is reasonable since $CaCO_3$ will dissociate into CaO and CO_2 at 1173 K, and then the effluent of CO_2 will result in the formation of mesopores. Therefore, it can be suggested that only mesopores are effective for the catalysis of CaO loaded on carbon.

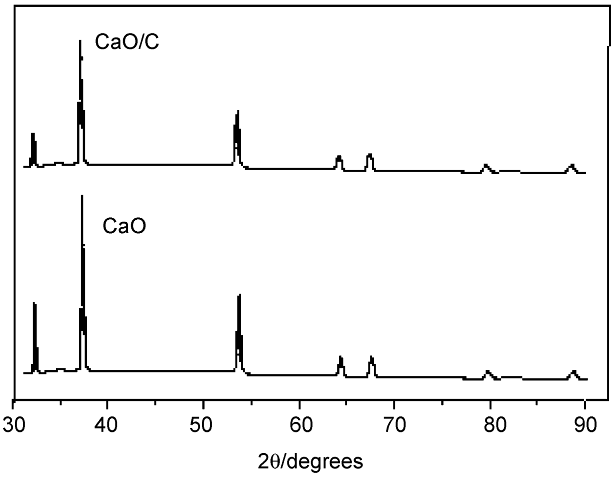


Fig. 1 XRD pattern of CaO and CaO/C.

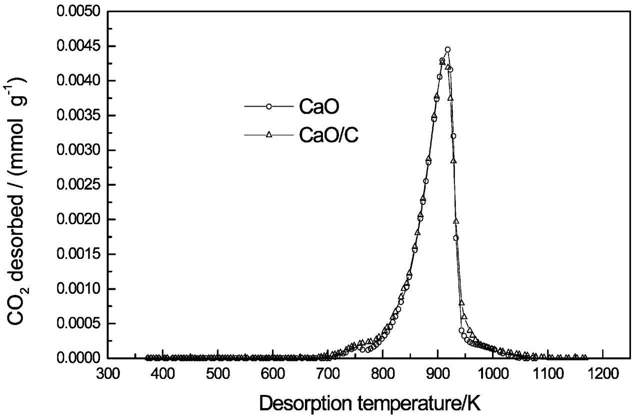


Fig. 2 CO_2 TPD of CaO and CaO/C.

Table 1 CO_2 uptake of CaO and CaO/C

Catalyst	CO_2 uptake mmol/CaO
CaO	0.32
CaO/C	0.34

*Experimental error = ±5%.

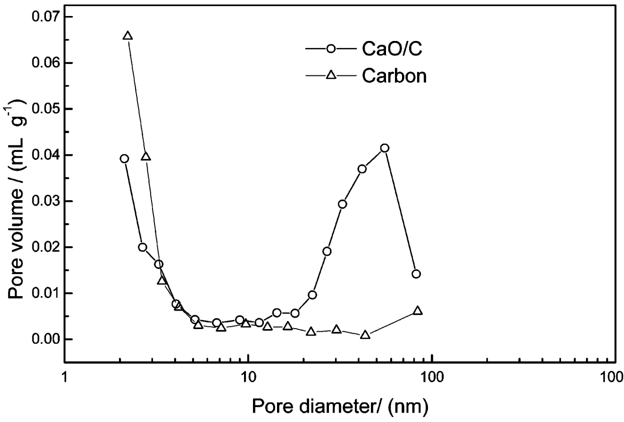


Fig. 3 Pore distributions of CaO/C and carbon.

As we reported in our previous work,[16] CaO could catalyze the transesterification of PC and methanol effectively at a temperature lower than other reported solid base catalysts needed, and the reaction even reached equilibrium in 30 min at 293 K. When CaO is loaded on carbon, the reaction rate decreases, DMC yield is only 13% after 120 min at 293 K (see Fig. 4). Because the crystal structure, base strength and basicity of CaO/C are similar to that of pure CaO, the catalytic performance difference between CaO and CaO/C may come

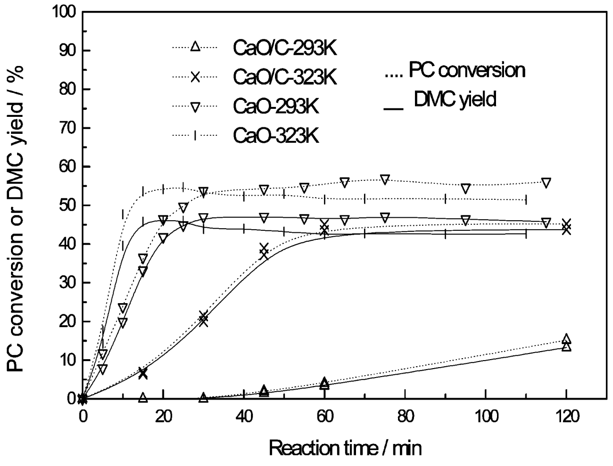


Fig. 4 Catalytic performance of pure CaO and CaO/C. CaO: 0.90 wt%; CaO/C: 1.80 wt%.

from the mass transfer variance of them. The CaO used in this paper are ultra fine particles with a diameter of about 10–20 nm (see Fig. 5) and the reaction mainly proceeds on the surface of the particles under strong mixing (1000 ± 50 r min^{-1}). Thus the reaction rate is intrinsic. In contrast, the CaO/C catalyst used is composed of particles of 0.18–0.28 mm; the reaction, therefore, proceeds on the outer surface and especially on the inner surface of the catalyst. Furthermore, this reaction proceeds in the liquid phase and the viscosities of the reactants and products, especially that of propylene glycol, are very high under low temperature (see Table 2), which make the reactant and product molecules, particularly propylene glycol, move very slowly in the pores of the CaO/C catalyst. Hence the reaction rate decreases greatly at 273 K when CaO/C is used as catalyst compared with that of pure CaO as catalyst. With the rise of temperature, the reaction rate over CaO/C increases, though the reaction still proceeds slower than that over pure CaO. The viscosities of the reactants and products decrease greatly with the rise of temperature (see Table 2), which makes the molecule movement speed increase remarkably, because viscosity (μ) and the self-diffusion coefficient (D), which reflect the molecule movement speed, are interrelated through the Stokes–Einstein equation $RT/D\mu = 6\pi r$ (T: temperature, r: molecule diameter). Therefore the reaction reaches equilibrium (DMC yield: 45%) only after 45 min over CaO/C at 323 K. On the other hand, from Fig. 4 we can see that the selectivity of DMC also increases when CaO is loaded on carbon. Since we reported that the mean side reaction of this reaction over CaO might be the slow polymerization of PC after equilibrium,[17] the mesopores in CaO/C would inhibit this polymerization, and consequently increase DMC selectivity.

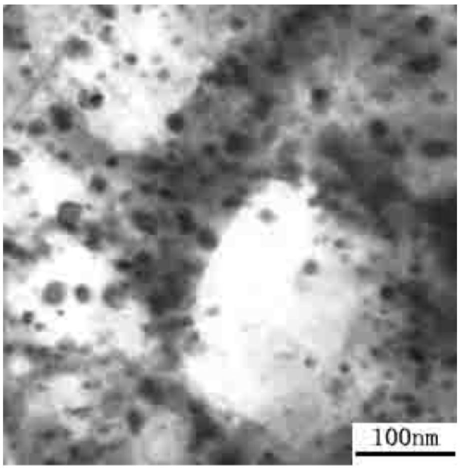


Fig. 5 TEM of the CaO catalyst.

Table 2 Viscosity of reactants and products at 293 and 373 K[18–20]

	Viscosity/mPa s			
Temperature/K	MeOH	DMC	PG	PC
293	0.677	0.630	56.0	2.78
323	0.387	0.445	8.71	1.63

In order to further understand the effect of inner mass transfer on the reaction rate, the catalytic performance of the CaO/C catalyst with different particle sizes was investigated as shown in Fig. 6. It can be seen that with the increase of the particle size, the reaction rate decreases gradually, which further indicates that inner diffusion is the main factor that decreases the reaction rate. What is interesting is that when CaO/C catalysts of different particle size are reused, the second time and third time reaction rate decreases greatly with the increase of the particle size (see Fig. 7). Table 3 lists DMC yield with CaO/C of different particle size with the catalyst being reused twice. For catalyst of 0.18–0.28 mm, the catalytic activity hardly changes when the CaO/C catalyst is used three times. Whereas, for catalysts of 0.28–0.45 mm and 0.45–0.90 mm, the catalytic activity decreases greatly when the catalyst is reused twice, and the larger the particle size is, the more the reaction rate decreases. Since, as mentioned above, this reaction proceeds in the liquid phase, the viscosity of molecules, especially that of propylene glycol, has a great effect on the mass transfer of this reaction. With the proceeding of the reaction and the reuse of the catalyst, the propylene glycol concentration in pores becomes higher and higher due to its high viscosity and low molecule movement speed. Consequently, the movement speed of the reactants, methanol and PC, in pores becomes slower and the reaction rate decreases.

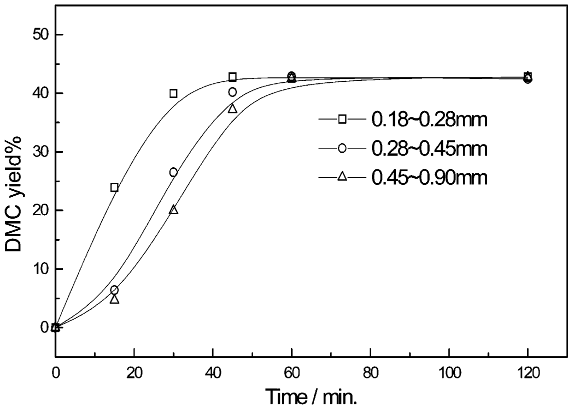


Fig. 6 Effect of catalyst particle size on DMC yield. Temperature: 323 K.

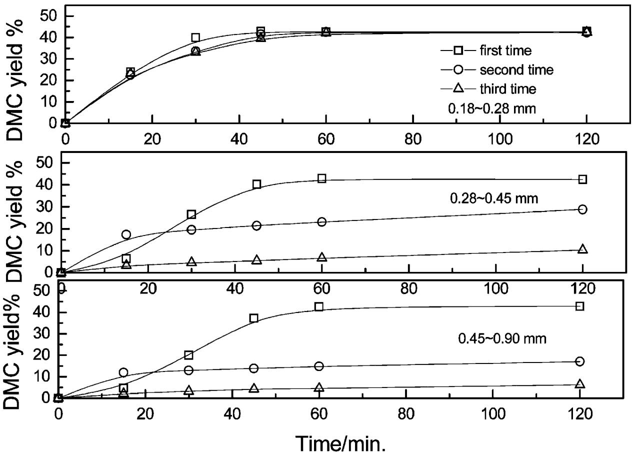


Fig. 7 DMC yield with CaO/C catalyst of different particle size being reused twice. Temperature: 323 K.

Conclusion

In conclusion, CaO/carbon composite serves as an efficient and convenient heterogeneous catalyst for synthesis of dimethyl carbonate from methanol and propylene carbonate. Compared with pure CaO, the CaO/C shows the same basic properties and a high performance. Inner diffusion is the main factor that decreases the reaction rate over the CaO/C catalyst, and propylene glycol in pores makes the reaction rate decrease when the catalyst is reused. In addition, the CaO/C catalyst can be

Table 3 DMC yield with CaO/C catalyst of different particle size being used three times

Particle size	DMC yield %		
	First time	Second time	Third time
0.18–0.28 mm	42.89	42.55	42.07
0.28–0.45 mm	42.65	23.10	6.60
0.45–0.90 mm	42.54	14.84	4.52

*Time 60 min.

reused with little deactivation, if a suitable particle size is chosen.

Experimental

CaO was prepared by heating $CaCO_3$ at 1173 K for 1 h in a N_2 atmosphere. CaO/C composite was prepared from linear phenolic resin 217 (provided by Tianjin Resin Company), hexamethylenetetramine and $CaCO_3$ (weight ratio = 5:1:5), which were ground and mixed homogeneously. The mixture then was pumped at 20 MPa and solidified at 473 K for 10 h in a N_2 atmosphere. After being broken into small particles ranging from 0.18 to 0.28 mm (unless otherwise stated), the solidified mixture was activated at 1173 K for 1 h in a N_2 atmosphere to prepare the final catalyst: CaO/C composite. The CaO content of the CaO/C composites, which was calculated from the Ca content (determined by ICP), was 50 wt%. For comparison, carbon was prepared from linear phenolic resin and hexamethylenetetramine only, with the ratio and procedure the same as that of CaO/C. XRD of the catalysts were measured in Rigaku D/max-γA using Cu target with Ni filtration. Pore distribution and surface area of the samples were determined with the BET method through Micromeritics ASAP-2000, and the BET surface area for CaO/C and carbon were 288.8 $m^2 g^{-1}$ and 207.6917 $m^2 g^{-1}$ respectively. CO_2-TPD measurement was performed at a heat rate of 12 K min^{-1} under He flow (50 mL min^{-1}), and CO_2 desorbed was detected by a BALZA Q-Mass spectrometer. The reaction was carried out in a 250 mL flask equipped with reflux condenser, water bath and strong magnetic stirring. The mole ratio of MeOH to PC for all evaluation reactions was 4:1, the catalyst used was 0.90 wt% (CaO) or 1.80 wt% (CaO/C), the stirring speed was 1000 ± 50 r min^{-1}, and the temperature was controlled to a range of ±0.1 K. The product was analyzed on a gas chromatograph with a TCD after centrifugal separation from the catalyst.

Acknowledgement

The financial support from PetroChina Co. Ltd is highly acknowledged.

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Synthesis and properties of tetra-alkyl-dimethylguanidinium salts as a potential new generation of ionic liquids†

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Received 26th March 2003
First published as an Advance Article on the web 16th May 2003

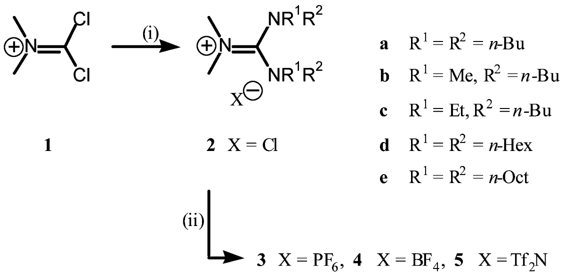
New room temperature ionic liquids based on the tetra-alkyl-dimethylguanidinium cation present high stability under thermal, basic, acid, nucleophilic and oxidative conditions, low temperature glass transition phases and peculiar solubility properties in common solvents.

Introduction

Room temperature ionic liquids (RTILs) have been recognised as a possible environmentally benign alternative to classic organic solvents, mainly due to their negligible vapour pressure, thermal stability, high ionic conductivity, large electrochemical window, insolubility in supercritical CO_2 (*sc* CO_2) and ease of solubilization of a large range of organic molecules and transition metal complexes.[1] Applications of RTILs include their use as a recyclable media for chemical processes, including bio- and chemical catalysis,[2] CO_2 capture,[3] biphasic extraction, gas chromatography,[1c,d] selective transport using supported liquid membranes,[4a,b] pervaporation,[5] dissolution of cellulose,[6] in fuel cells,[1d] and their potential use as matrix for mass spectrometry[7] or as a solvent in nuclear electricity powerplants.[8] The properties of the RTILs are generally dependent on both ion structures. For the anion, a broad range of examples have been reported from air-sensitive Lewis acids[1,9a] to more stable anions such as ClO_4^-, NO_3^-, BF_4^-, PF_6^-,[1] alkyl[9b] and aryl sulfonates,[9c] phosphates,[9d] carboxylates[1] and even more inert carboranes.[9e] Regarding the cation, in spite of several reported examples consisting of alkyl phosphonium,[9c] ammonium[9a,b,10a] (including chiral ones[10b]), sulfonium,[10c] pyridinium[1] and 8-alkyl-1,8-diazabicyclo[5,4,0]-7-undecenium [alkyl-DBU],[10d] the 1,3-dialkyl-imidazolium [im] unit is the most commonly used cation.[1] Further extension of the properties of the RTILs based on the [im] unit has been achieved by introducing other functional groups in the alkyl chain.[3,11] In spite of the considerable stability and lower viscosity of the RTILs based on the [im] unit, the presence of the more labile proton H–C(2) can be useful in some cases, due to the formation of strong hydrogen bonds,[1,4] but, depending on the anion used, can also react with electrophiles under basic conditions.[12]‡ Here we report a new type of RTILs based on the very stable tetra-alkyl-dimethylguanidinium cation [dmg] **2**.

Results and discussion

The guanidinium chlorides **2a–e** were prepared in a one pot procedure starting from commercially available N,N-dimethylphosgeniminium chloride **1** using a general reported method[13] followed by chloride exchange (Scheme 1) (see ESI†). The remaining chloride content for **4d** was 1.6% and for the other salts tested (**3d**, **3e**, **5c** and **5d**) were in the lower limit of the method used (≤0.3 %).



Scheme 1 General method used for the preparation of the guanidinium salts **2–5**; (i) HNR^1R^2 (2.1 equiv.), triethylamine (2.2 equiv.), CH_2Cl_2, 70–86%; (ii) MX (M = Na, K or Li), CH_2Cl_2.

In Table 1 we present some of the guanidinium salts prepared and several observed properties. It seems that the salt's physical state at room temperature is dependent on the length of the alkyl chain (*e.g.* **3a** *vs.* **3d**) but also changes according to the difference between the alkyl chains in the molecules (*e.g.* **3a** *vs.* **3b**).

The examples presented here allow us to anticipate the possibility of having many more RTILs just by introducing the

Green Context

While variations in the anion are commonly encountered in ionic liquids, changes to the structure of the cation are less frequent. Here, alkyl guanidinium cations are used, allowing variations in any one of 6 groups to tune properties. The physical and solubility properties of the guanidinium series do not parallel those of the imidazolium series, opening up potential for a wider range of properties. ***DJM***

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† Electronic supplementary information (ESI) available: ^{13}C NMR spectral data of guanidinium salts **2–4**. See http://www.rsc.org/suppdata/gc/b3/b303408a/

‡ For example, the Baylis–Hillman (BH) reaction (PhCHO, methyl acrylate, DABCO) is faster in the ionic liquid [bmim][PF_6] allowing the isolation of the BH product in moderate yields,[12a] but some side reaction (< 20%) occurs between the [bmim] and the aldehyde.[12b] However, we observed that this side reaction is strongly dependent on the anion used (Cl^- > BF_4^- > PF_6^-), which is in line with recent detailed studies for nucleophilic substitution.[16]

DOI: 10.1039/b303408a

six different alkyl groups or by using a mixture of amines in their preparation.§ It should be mentioned here that prior to the growing interest in the subject of ionic liquids, Kantlehner *et al.* in 1984 reported the preparation of a large number of hexa-alkylguanidinium salts, which in two cases were described as oils.[14a] Similarly, several room temperature ionic liquids based on di-alkylimidazolium halides (1977)[14b] and tetra-alkylammonium tetra-alkylborides (1973)[14c] have been previously reported. In our work, some peculiar solubility properties were observed: all the salts prepared were miscible in dichloromethane and in absolute ethanol, and in the case of examples containing more hydrophobic alkyl chain (*n*-hexyl, **3d–5d**; *n*-octyl, **2e–4e**) and less polar anions (PF_6^-, **3a–3e** and Tf_2N^-, **5c** and **5d**) were immiscible in water. To our surprise, the chlorides **2d** and **2e** containing the long alkyl chains *n*-hexyl and *n*-octyl were miscible in *n*-hexane while all the others were immiscible. Some of these solubility properties are quite different from the reported [im] series.[11d,15] The measured density of the [dmg] series are in general slightly lower than the ones observed for the [im] series.[11d,15] The viscosity observed for the [(di-h)$_2$dmg][Tf_2N] **5d** is higher than in the case of [bmim][Tf_2N].[15b] It is also noteworthy that all the salts tested are good glass-formers with glass transition temperatures in the range of −55 °C to −78 °C which is very similar to the observed properties for some [im] series.[11d,15b] The remaining water content is in the same order as the imidazolium series[11d,15] and follows the anion order $Cl^- > BF_4^- > PF_6^-$.

The stability of the RTILs under reaction conditions and in other processes is another important issue for their use. In order to address the possibility of the present dimethylguanidinium [dmg] series being good candidates, we selected the chlorides **2c** and **2d** and compared by ^{1}H and ^{13}C NMR their stability with the *n*-butylimidazolium chloride [bmim][Cl] under several representative conditions (Table 2): thermal (160 °C), basic (KOH), acid (HCl), nucleophilic (NH_3), reductive ($NaBH_4$) and oxidative ($NaIO_4$ and O_2) in the absence and in the presence of solvent (D_2O). It is interesting to note that for all the conditions tested the new [dmg] salts **2c** and **2d** presented similar stability to [bmim][Cl] under thermal, acid (HCl), nucleophilic (NH_3, [bmim][Cl] is unstable in solution) and in the presence of oxidative conditions (O_2 or $NaIO_4$). Additionally, while **2c** and **2d** were stable under basic conditions (KOH), the neat imidazolium salt [bmim][Cl] was unstable. However, in the presence of $NaBH_4$ at 60 °C, the neat guanidinium salt was unstable while the [bmim][Cl] was stable.

In conclusion, the studies presented here give strong support that the guanidinium unit is a good candidate for a new potential generation of diverse RTILs. These new [dmg] series are easily prepared, robust, stable and they have useful solubility and thermal properties. It should also be mentioned that the presence of six alkyl groups allows the opportunity to prepare a diverse range of more specific RTILs, including chiral ones, by using the amine containing the desired functionality.

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§ By using a 1 : 1 mixture of di-*n*-butylamine and ethyl-*n*-butylamine or di-*n*-butylamine and methyl-*n*-butylamine in step (i) gave the salts **3** and **4** as liquids at room temperature.

Table 1 Representative properties of the guanidinium [dmg] salts **2–5**

Salt	Physical state[a]	Miscible[b]	Immiscible[b]	Density[c]	T_g/°C[d]	Water content[e]
2a	solid	dcm, H_2O, EtOH	Et_2O, hex		−55.3	
3a	solid	dcm, EtOH	Et_2O, H_2O, hex			
4a	solid	dcm, EtOH	Et_2O, H_2O, hex		−57.7	
2b	solid	dcm, H_2O, EtOH,	Et_2O, hex			
3b	liquid	dcm, EtOH	Et_2O, H_2O, hex			9.4
4b	solid	dcm, H_2O, EtOH	Et_2O, hex			
2c	solid	dcm, H_2O, EtOH	Et_2O, hex		−79.0	
3c	solid[f]	dcm, EtOH	Et_2O, H_2O, hex		−67.8	
4c	liquid	dcm, H_2O, EtOH	Et_2O, hex	1.05		
5c	liquid	dcm, EtOH	Et_2O, H_2O, hex	1.36	−75.1	2.7
2d	liquid	dcm, H_2O, EtOH, hex	Et_2O	0.90	−63.0	37.2
3d	liquid	Et_2O, dcm, EtOH	H_2O, hex		−60.5	2.9
4d	liquid	Et_2O, dcm, EtOH	H_2O, hex	0.97	−75.6	15.6
5d[g]	liquid	dcm, EtOH	Et_2O, H_2O, hex	1.20	−71.4	4.5
2e	liquid	Et_2O, dcm, EtOH, hex	H_2O	0.96	−76.0	47.8
3e	liquid	Et_2O, dcm, EtOH	H_2O, hex	0.91	−78.0	3.9
4e	liquid	Et_2O, dcm, EtOH	H_2O, hex	0.97	−75.3	7.6

[a] Physical state of the salt at room temperature. [b] Visual observed miscibility or immiscibility in water and in common organic solvents: hex = *n*-hexane, dcm = dichloromethane. [c] Observed density (g mL^{-1}). [d] T_g = glass transition temperature. [e] Water content in µL (H_2O) mL^{-1} (RTIL). [f] Liquid at 35 °C. [g] Viscosity (cP): 346 (25 °C), 335 (30 °C), 296 (35 °C), 269 (40 °C), 182 (50 °C), 124 (60 °C).

Table 2 Comparative stability by ^{1}H and ^{13}C NMR between the chlorides [bmim][Cl] and the guanidinium salts [dmg] **2d**[a] and **2c** (in brackets)[b]

Conditions	Temp./°C		Time/h		[bmim][Cl][a] neat	**2d**[a] neat	[bmim][Cl][b] in D_2O	**2c**[b] in D_2O
HCl (1 equiv.), neat[a] or (in D_2O)[b]	60[a]	(80)[b]	24[a]	(48)[b]	stable[c]	stable[d]	stable[d]	stable[d]
KOH (1 equiv.), neat[a], or (in D_2O)[b]	60[a]	(80)[b]	24[a]	(48)[b]	unstable[e,f]	stable[c]	stable[c,g,j]	stable[c]
NH_3 (2 equiv.), neat[a], or (in D_2O)[b]	60[a]	(80)[b]	24[a]	(48)[b]	stable[c]	stable[d]	unstable[e,g]	stable[d]
$NaBH_4$ (3 mol equiv.), neat[a], or (in D_2O)[b]	60[a]	(rt)[b]	24[a]	(48)[b]	stable[d]	unstable[h]	stable[c,g]	stable[d]
$NaIO_4$ (1 equiv.), neat[a], or (in D_2O)[b]	60[a]	(80)[b]	24[a]	(48)[b]	stable[d]	stable[d]	stable[d,j]	stable[d]
O_2 (saturated) neat[a] or (in D_2O)[b]	(80)[b]		(48)		—	—	stable[c,g,j]	stable[d]
neat[a], or (in d_6-DMSO)[b]	150[a]	(160)[b]	24[a]	(48)[b]	stable[d,i]	stable[d,j]	stable[d,i]	stable[c,j]

[a] 500 mg of **2d** or of [bmim][Cl] were used. [b] 40 mg of **2c** or of [bmim][Cl] were used in 0.4 mL of D_2O or of d_6-DMSO. [c] No change in the basic skeleton was observed. [d] No change in the ^{1}H and ^{13}C NMR was observed. [e] Major changes in the basic skeleton were observed. [f] The solution became vivid yellow. [g] Partial disappearance of the H–C(2) proton was observed. [h] Complete decomposition of the guanidinium unit was observed. [i] The solution became brown. [j] The solution became dark.

Experimental

General remarks

All glassware was oven-dried. Commercially supplied reagents were used as supplied, except for CH_2Cl_2, which was dried over P_2O_5. All aqueous solutions were prepared using distilled water.

^{1}H (400.13 MHz), ^{13}C (100.61 MHz), ^{19}F (376.47 MHz) and ^{31}P (161.98 MHz) NMR spectra were recorded on a Bruker AMX 400 Spectrometer. Chemical shifts are reported downfield in parts per million (ppm) from tetramethylsilane reference. IR spectra were recorded on a Mattson Instruments model Satellite FTIR as thinly dispersed films. Melting points (uncorrected) were determined on a Electrothermal Mod. IA 6304 capillary melting point apparatus. Microanalyses were carried out at the *Laboratório de Análises do CQFB/FCT/UNL*. High and low resolution mass spectra (EI) were carried out by the mass spectrometry (MS) service of the University of Santiago de Compostela (Spain). The differential scanning calorimetry (DSC) experiments were performed using a 2920 MDSC system from TA Instruments Inc. The water content of each dimethylguanidinium [dmg] salt was determined by a volumetric Aquastar Karl–Fischer titration. Each [dmg] sample (2 mL scale) used for MS, DSC and for the determination of water content experiments was further purified by flash column chromatography (eluent: dichloromethane) followed by removal of the volatile components under high vacuum (6×10^{-6} mbar) at room temperature for 12 hours.

Viscosity

The viscosity was measured with a Brookfield, Model RVTDV-II viscosimeter. For each analysis, an 8 mL sample was used and the measurements were performed in duplicate. The temperature of the samples was maintained to ±0.1 °C by means of an external temperature controller.

Density

The density of each dimethylguanidinium [dmg] salt was determined with a picnometer. For each analysis a 1 mL sample was used and the mass of that volume of liquid was determined. The measurements were repeated three times and the average value is reported. All measurements were taken at room temperature (25 ± 1 °C).

Potentiometry

The potentiometric measurements were performed on a Radiometer PHM 250 potentiometer, with a Radiometer REF 251 reference electrode and a Radiometer ISE 25 Cl, chloride ion selective electrode. The chloride measurements were accomplished by using ethanol solutions of the dimethylguanidinium salts **3d**, **3e**, **4d**, **5c** and **5d** by comparision with a calibration using the chloride salt **2g** as a standard.

Solid–liquid phase transition analysis

The calorimetric measurements were performed with a 2920 MSDSC system from TA Instruments Inc. Dry high-purity He gas with a flow rate of 30 cm^3 min^{-1} was purged through the sample. Cooling was accomplished with the liquid nitrogen cooling accessory (LNCA) which provides automatic and continuous programmed sample cooling down to −150 °C. The Baseline was calibrated by scanning the temperature domain of the experiments with an empty pan.

General procedure for the preparation of guanidinium chlorides (Method A)

To a suspension of phosgene iminium chloride **1** (2.0 g; 12 mmol) in anhydrous dichloromethane (20 ml) at 0 °C (ice bath) was added dropwise a mixture of secondary amine (2.1 equiv.) and triethylamine (2.2 equiv.) in dichloromethane (30 ml). After 30 min at 0 °C (complete solubilization of the phosgeniminium salt), the reaction was stirred at room temperature for 4 h. The solvent was removed under vacuum and an aqueous solution of NaOH (2 M ;20 ml) was added. The mixture was washed with diethyl ether (2×25 ml) and the pH adjusted to 7 by dropwise addition of hydrochloric acid (37%). The water was removed under vacuum, the residue extracted with dichloromethane (50 ml), dried ($MgSO_4$), the solvent evaporated and the residue left under vacuum (<1 mm Hg) overnight. The guanidinium salt was obtained as a solid.

2a [(di-b)$_2$dmg][Cl]. This compound was prepared following method A using phosgene iminium chloride **1** (2.1 g; 13 mmol), dibutylamine (4.7 ml; 27 mmol) and triethylamine (4.0 ml; 28 mmol). The salt [(di-b)$_2$dmg][Cl] (3.7 g; 81%) was obtained as a yellow coloured hygroscopic solid. IR ν_{max} (film): 3358, 2959, 2934, 2873, 1580, 1537, 1460, 1417, 1266, 1110, 1061, 891, 728 cm^{-1}. ^{1}H-NMR δ ($CDCl_3$, 400 MHz): 3.31−3.19 (8H, m, N–CH_2–CH_2–CH_2CH_3); 3.15 (6H, s, N–CH_3); 1.41–1.30 (16H, m, N–CH_2–CH_2–CH_2–CH_3); 0.98 (12H, t, J = 7.2 Hz, N–CH_2–CH_2–CH_2–CH_3). ^{13}C-NMR δ (100 MHz, $CDCl_3$): 163.22; 49.56 and 48.96 (rotamers); 40.72; 29.66 and 29.33 (rotamers); 19.86 and 19.70 (rotamers); 13.46. MS (EI) (m/z): 312; 140; 85; 71. HMRS (EI) (m/z) calc (M^+) 312.337874, found (M^+) 312.337171. Analysis: Calc. for [(di-b)$_2$dmg][Cl]·3H_2O ($C_{19}H_{48}ClN_3O_3$): N 10.45, C 56.76, H 12.03. Found: N 9.82, C 56.14, H 11.64%.

2b [(bm)$_2$dmg][Cl]. This compound was prepared following method A using phosgene iminium chloride **1** (3.72 g; 23 mmol), *n*-butyl-methylamine (5.7 ml; 48 mmol) and triethylamine (7.0 ml; 50 mmol). The salt [(bm)$_2$dmg][Cl] (5.0 g; 85%) was obtained as a yellow coloured hygroscopic solid. IR ν_{max} (film): 3411, 2960, 2934, 2874, 1567, 1463, 1407, 1313, 1250, 1130, 912, 727 cm^{-1}. ^{1}H-NMR δ (400 MHz, $CDCl_3$): 3.10 (4H, m, N–CH_2–CH_2–); 2.93–2.86 (12H, m, N–CH_3); 1.47–1.13 (8H, m, N–CH_2–CH_2–CH_2–CH_3); 0.76 (6H, t, J = 7.2 Hz, N–CH_2–CH_2–CH_2–CH_3). ^{13}C-NMR δ (100 MHz, $CDCl_3$): 163.26; 52.17; 40.62; 38.01; 29.21; 19.56; 13.28. MS (EI) (m/z): 228; 101; 85; 71. HMRS (EI) (m/z) calc (M^+) 228.243973, found (M^+) 228.244689.

2c [(be)$_2$dmg][Cl]. This compound was prepared following method A using phosgene iminium chloride **1** (3.8 g; 23 mmol), *n*-butyl-ethylamine (6.8 ml; 49 mmol) and triethylamine (7.3 ml; 52 mmol). The salt [(be)$_2$dmg][Cl] (5.82 g; 84%) was obtained as a yellow coloured hygroscopic solid. IR ν_{max} (film): 3390, 2961, 2874, 1580, 1543, 1455, 1422, 1381, 1276, 1184, 1064, 977, 878, 802, 728 cm^{-1}. ^{1}H-NMR δ (400 MHz, $CDCl_3$): 3.45–3.23 (8H, m, N–CH_2–); 3.12 (6H, s, N–CH_3); 1.49–1.23 (14H, m, N–CH_2–$(CH_2)_2$–CH_3 and N–CH_2–CH_3); 0.95 (6H, t, J = 7.2 Hz, N–CH_2–CH_2–CH_2–CH_3). ^{13}C-NMR δ (100 MHz, $CDCl_3$): 162.11; 48.07 and 47.33 (rotamers); 43.66 and 43.15 (rotamers); 39.57; 28.53 and 28.21 (rotamers); 18.85 and 18.72 (rotamers); 12.47; 11.93. MS (EI) (m/z): 256; 112; 85; 71.

HMRS (EI) (*m*/*z*) calc (M$^+$) 256.275273, found (M$^+$) 256.275212.

General procedure for the preparation of guanidinium chlorides insoluble in water (Method B)

To a suspension of phosgene iminium chloride **1** (2.0 g; 12 mmol) in anhydrous dichloromethane (20 ml) at 0 °C (ice bath) was added dropwise a mixture of secondary amine (2.1 equiv.) and triethylamine (2.2 equiv.) in dichloromethane (30 ml). After 30 min at 0 °C (complete solubilization of the phosgeniminium salt), the reaction was stirred at room temperature for 4 h. The solvent was removed under vacuum and water was added (30 ml). The aqueous phase was extracted twice with diethyl ether (25 ml). The combined organic layers were washed with hydrochloric acid (1 M) aqueous solution. The solvent was removed under vacuum, the residue extracted with dichloromethane, dried (MgSO$_4$), the solvent evaporated and left under vacuum (< 1 mmHg) overnight. The guanidinium salt was obtained as an oil.

2d [(di-h)$_2$dmg][Cl]. This compound was prepared following method B using phosgene iminium chloride **1** (4.8 g; 29 mmol), di-*n*-hexylamine (14.7 ml; 62 mmol) and triethylamine (9.1 ml; 65 mmol). The salt [(di-h)$_2$dmg][Cl] (11.7 g; 86%) was obtained as an orange coloured liquid. IR $\nu_{\max}$ (film): 3381, 2955, 2929, 2870, 1582, 1537, 1466, 1418, 1315, 1273, 1197, 1062, 970, 907, 879, 796, 728 cm^{-1}. ^{1}H-NMR δ (CDCl$_3$, 400 MHz): 3.29–3.20 (8H, m, N–CH_2–(CH$_2$)$_4$CH$_3$); 3.14 (6H, s, N–CH_3); 1.76–1.30 (32H, m, N–CH$_2$–$(CH_2)_4$–CH$_3$); 0.89 (12H, m, N–CH$_2$–(CH$_2$)$_4$–CH_3). ^{13}C-NMR δ (100 MHz, CDCl$_3$): 162.75; 49.41 and 49.20 (rotamers); 40.28; 31.92 and 31.09 (rotamers); 27.23 and 26.87 (rotamers); 25.86 and 25.81 (rotamers); 21.83; 13.31. MS (EI) (*m*/*z*): 424; 196; 181; 112; 85; 71. HMRS (EI) (*m*/*z*) calc. (M$^+$) 424.463074, found (M$^+$) 424.462637. Analysis: Calc. for [(di-h)$_2$dmg][Cl]·H$_2$O ($C_{27}H_{60}ClN_3O$): N 8.79 C 67.81 H 12.65. Found: N 8.71 C 67.49 H 12.59%.

2e[(di-o)$_2$dmg][Cl]. This compound was prepared following method B using phosgene iminium chloride **1** (5.0 g; 30 mmol), di-*n*-octylamine (19.5 ml; 64 mmol) and triethylamine (9.4 ml; 67 mmol). The salt [(di-o)$_2$dmg][Cl] (12.3 g; 70%) was obtained as a dark orange coloured liquid. IR $\nu_{\max}$ (film): 3375, 3044, 2928, 2857, 1579, 1537, 1466, 1420, 1378, 1311, 1265, 1181, 1144, 1108, 1059, 895, 845, 737, 701 cm^{-1}. ^{1}H-NMR δ (CDCl$_3$, 400 MHz): 3.28–3.19 (8H, m, N–CH_2–(CH$_2$)$_6$CH$_3$); 3.15 (6H, s, N–CH_3); 1.73–1.27 (48H, m, N–CH$_2$–$(CH_2)_6$–CH$_3$); 0.88 (12H, t, J = 6.4Hz, N–CH$_2$–(CH$_2$)$_6$$CH_3$). ^{13}C-NMR δ (100 MHz, CDCl$_3$): 163.44; 50.01 and 49.52 (rotamers); 41.02; 31.74; 29.34; 29.18; 27.96 and 27.60 (rotamers); 26.95 and 26.84 (rotamers); 22.60; 14.06. MS (EI) (*m*/*z*): 536; 252; 240; 183; 85; 71; 57. HMRS (EI) (*m*/*z*) calc. (M$^+$) 536.588275, found (M$^+$) 536.589958. Analysis: Calc. for [(di-o)$_2$dmg][Cl]·3H$_2$O ($C_{35}H_{80}ClN_3O_3$): N 6.71, C 67.10, H 12.87. Found: N 7.04, C 67.57, H 12.68%.

General procedure for the substitution of chloride with PF$_6^-$

The [dmg] chloride was transferred to a plastic erlenmeyer followed by the addition of dichloromethane. KPF$_6$ (1.4 equiv.) was added and the mixture stirred at room temperature for 24 hours. The resulting solid was collected by filtration and washed with dichloromethane. The combined organic layers were collected, dried (MgSO$_4$) and filtered. The salt was then recovered after passing through a column with silica and activated carbon, and the solvent removed under vacuum. The residue was stirred under vacuum (< 1 mmHg) overnight.

3a [(di-b)$_2$dmg][PF$_6$]. This compound was obtained as a yellow solid; mp 55–57 °C. IR $\nu_{\max}$ (film): 2960, 2875, 1578, 1544, 1460, 1423, 1381, 1316, 1220, 1110, 1061, 941, 739 cm^{-1}.^{1}H-NMR δ (400 MHz, CDCl$_3$): 3.21–3.04 (8H, m, N–CH_2–); 2.97 (6H, s, N–CH_3); 1.41–1.31 (16H, m, N–CH$_2$–$(CH_2)_2$–CH$_3$); 0.94 (12H, t, J = 7.2 Hz, N–CH$_2$–CH$_2$–CH$_2$–CH_3). ^{13}C-NMR δ (100 MHz, CDCl$_3$): 163.33; 49.59 and 48.79 (rotamers); 40.01; 29.51 and 29.15 (rotamers); 19.80 and 19.59 (rotamers); 13.40.^{31}P-NMR δ (160 MHz, CDCl$_3$): −143.9 (hept, J = 713 Hz). Analysis: Calc. for $C_{19}H_{42}F_6N_3P$: N 9.18, C 49.88, H 9.25. Found: N 9.25, C 50.24, H 9.44%.

3b [(bm)$_2$dmg][PF$_6$]. This compound was obtained as a slightly yellow viscous liquid. IR $\nu_{\max}$ (film): 2961, 2936, 2875, 1573, 1468, 1409, 1315, 1269, 1039, 839, 735 cm^{-1}. ^{1}H-NMR δ (400 MHz, CDCl$_3$): 3.15 (4H, m, N–CH_2–CH$_2$–); 2.95–2.92 (12H, m, N–CH_3); 1.62–1.29 (8H, m, N–CH$_2$–CH_2–CH_2–CH$_3$); 0.92 (6H, t, J = 7.3 Hz, N–CH$_2$–CH$_2$–CH$_2$–CH_3). ^{13}C-NMR δ (100 MHz, CDCl$_3$): 163.62; 52.48; 40.09; 37.86; 29.46; 19.85; 13.57. ^{31}P-NMR δ (160 MHz, CDCl$_3$): −144.0 (hept, J = 713 Hz). Analysis: Calc. for $C_{13}H_{30}F_6N_3P$: N 11.25, C 41.82, H 8.10. Found: N 11.25, C 41.88, H 8.11%.

3c [(be)$_2$dmg][PF$_6$]. This compound was obtained as an orange solid (liquid at 35 °C). IR $\nu_{\max}$ (film): 3667, 3607, 3394, 3212, 2963, 2876, 1462, 1383, 1306, 1185, 1101, 1064, 979, 739 cm^{-1}.^{1}H-NMR δ (400 MHz, CDCl$_3$): 3.29–3.14 (8H, m, N–CH_2–); 2.93 (6H, s, N–CH_3); 1.41–1.16 (14H, m, N–CH$_2$–$(CH_2)_2$–CH$_3$ and N–CH$_2$–CH_3); 0.92 (6H, t, J = 7.3 Hz, N–CH$_2$–CH$_2$–CH$_2$–CH_3). ^{13}C-NMR δ (100 MHz, CDCl$_3$): 163.41; 49.02 and 48.27 (rotamers); 44.59 and 43.96 (rotamers); 40.10; 29.47 and 29.16 (rotamers); 19.97 and 19.78 (rotamers); 13.53; 12.98 and 12.66 (rotamers). ^{31}P-NMR δ (160 MHz, CDCl$_3$): −143.9 (hept, J = 713 Hz). Analysis: Calc. for [(be)$_2$dmg][PF$_6$]·2H$_2$O ($C_{15}H_{38}F_6N_3O_2P$): N 9.61, C 41.18, H 8.76. Found: N 9.27, C 40.81, H 9.05%.

3d [(di-h)$_2$dmg][PF$_6$]. This compound was obtained as a yellow viscous liquid; chloride content: < 0.1 % (w/w). IR $\nu_{\max}$ (film): 2957, 2931, 2860, 1574, 1538, 1455, 1422, 1379, 1311, 1266, 1117, 1060, 844, 738 cm^{-1}. ^{1}H-NMR δ (CDCl$_3$, 400 MHz): 3.19–2.98 (8H, m, N–CH_2–(CH$_2$)$_4$CH$_3$); 2.95 (6H, s, N–CH_3); 1.68–1.26 (32H, m, N–CH$_2$–$(CH_2)_4$–CH$_3$); 0.87 (12H, t, J = 6.7 Hz, N–CH$_2$–(CH$_2$)$_4$–CH_3). ^{13}C-NMR δ (100 MHz, CDCl$_3$): 163.43; 49.97 and 49.28 (rotamers); 40.24; 31.34 and 31.23 (rotamers); 27.66 and 27.31 (rotamers); 25.85 and 25.63 (rotamers); 22.41; 13.84.^{31}P-NMR δ (160 MHz, CDCl$_3$): −143.9 (hept, J = 713 Hz). Analysis: Calc. for $C_{27}H_{58}F_6N_3P$: N 7.38, C 56.92, H 10.26. Found: N 7.56, C 57.62, H 10.71%.

3e [(do)$_2$dmg][PF$_6$]. This compound was obtained as a dark orange liquid; chloride content: 0.3% (w/w). IR $\nu_{\max}$ (film): 3054, 2956, 2929, 2857, 1579, 1538, 1463, 1422, 1265, 1054, 895, 846, 739 cm^{-1}.^{1}H-NMR δ (CDCl$_3$, 400 MHz): 3.26–3.08 (8H, m, N–CH_2–(CH$_2$)$_6$CH$_3$); 2.98 (6H, s, N–CH_3); 1.80–1.24 (48H, m, N–CH$_2$–$(CH_2)_6$–CH$_3$); 0.85 (12H, t, J = 6.8 Hz, N–CH$_2$–(CH$_2$)$_6$$CH_3$). ^{13}C-NMR δ (100 MHz, CDCl$_3$): 163.40; 49.87 and 49.29 (rotamers); 40.54; 31.65; 29.22; 29.08; 27.75 and 27.40 (rotamers); 26.84 and 26.68 (rotamers); 22.50; 13.96.^{31}P-NMR δ (160 MHz, CDCl$_3$): −143.9 (hept, J = 713 Hz).

General procedure for the substitution of chloride with BF_4^-

The [dmg] chloride was transferred to a plastic erlenmeyer followed by the addition of dichloromethane. $NaBF_4$ (1.4 equiv.) was added and the mixture stirred at room temperature for 24 hours. The resulting solid was collected by filtration and washed with dichloromethane. The combined organic layers were collected, dried ($MgSO_4$) and filtered. The salt was then recovered after passing through a column with silica and activated carbon, and the solvent removed under vacuum. The residue was stirred under vacuum (< 1 mmHg) overnight.

4a [(di-b)$_2$dmg][BF$_4$]. This compound was obtained as a yellow solid. IR ν_{max} (film): 3391, 2958, 2934, 2873, 1580, 1537, 1460, 1418, 1379, 1315, 1272, 1220, 1177, 1146, 1110, 1055, 939, 892, 729 cm^{-1}.^{1}H-NMR δ (400 MHz, $CDCl_3$): 3.41–3.26 (8H, m, N–CH_2–); 3.14 (6H, s, N–CH_3); 1.74–1.31 (16H, m, N–CH_2–$(CH_2)_2$–CH_3); 0.96 (12H, t, J = 6.8 Hz, N–CH_2–CH_2–CH_2–CH_3). ^{13}C-NMR δ (100 MHz, $CDCl_3$): 163.15; 49.56 and 48.90 (rotamers); 40.65; 29.61 and 29.26 (rotamers); 19.80 and 19.66 (rotamers); 13.42. ^{19}F-NMR δ (376 MHz, $CDCl_3$): −170.1.

4b [(bm)$_2$dmg][BF$_4$]. This compound was obtained as a yellow solid, mp 50–52 °C. IR ν_{max} (film): 2961, 2935, 2874, 1572, 1467, 1409, 1315, 1271, 1054, 893, 732 cm^{-1}.^{1}H-NMR δ (400 MHz, $CDCl_3$): 3.18 (4H, s, N–CH_2–CH_2–); 2.97–2.94 (12H, m, N–CH_3); 1.64–1.31 (8H, m, N–CH_2–CH_2–CH_2–CH_3); 0.94 (6H, J = 7.2 Hz, N–CH_2–CH_2–CH_2–CH_3). ^{13}C-NMR δ (100 MHz, $CDCl_3$): 163.45; 52.18; 39.93; 37.66; 29.27; 19.67; 13.47.^{19}F-NMR δ (376 MHz, $CDCl_3$): −176.6. Analysis: Calc. for $C_{13}H_{30}BF_4N_3$: N 13.33, C 49.54, H 9.59. Found: N 13.22, C 49.80, H 9.68%.

4c [(be)$_2$dmg][BF$_4$]. This compound was obtained as an orange liquid. IR ν_{max} (film): 3636, 3559, 3347, 3154, 2962, 2875, 1580, 1547, 1462, 1423, 1382, 1306, 1184, 1053, 876, 803, 737 cm^{-1}.^{1}H-NMR δ (400 MHz, $CDCl_3$): 3.24–3.08 (8H, m, N–CH_2–); 2.94 (6H, s, N–CH_3); 1.73–1.15 (14H, m, N–CH_2–$(CH_2)_2$–CH_3 and N–CH_2–CH_3); 0.90 (6H, t, J = 6.0 Hz, N–CH_2–CH_2–CH_2–CH_3). ^{13}C-NMR δ (100 MHz, $CDCl_3$): 163.41; 48.98 and 48.18 (rotamers); 44.55 and 43.94 (rotamers); 40.14; 29.47 and 29.17 (rotamers); 19.95 and 19.78 (rotamers); 13.52; 13.00 and 12.58 (rotamers).^{19}F-NMR δ (376 MHz, $CDCl_3$): −169.7.

4d [(di-h)$_2$dmg][BF$_4$]. This compound was obtained as a slightly orange viscous liquid; chloride content: 1.6 % (w/w). IR ν_{max} (film): 3183, 3065, 2956, 2930, 2859, 1579, 1542, 1466, 1422, 1379, 1270, 1197, 1060, 907, 878, 734 cm^{-1}.^{1}H-NMR δ ($CDCl_3$, 400 MHz): 3.23–3.10 (8H, m, N–CH_2–$(CH_2)_4CH_3$); 3.00 (6H, s, N–CH_3); 1.77–1.29 (32H, m, N–CH_2–$(CH_2)_4$–CH_3); 0.89 (12H, m, N–CH_2–$(CH_2)_4$–CH_3). ^{13}C-NMR δ (100 MHz, $CDCl_3$): 163.40; 49.77 and 49.25 (rotamers); 40.70; 31.18 and 31.04 (rotamers); 27.62 and 27.27 (rotamers); 26.26; 22.21; 13.65. ^{19}F-NMR δ (376 MHz, $CDCl_3$): −183.2. Analysis: Calc. for $C_{27}H_{58}BF_4N_3$: N 8.21, C 63.38, H 11.43. Found: N 8.35, C 62.67, H 12.14%.

4e[(di-o)$_2$dmg][BF$_4$]. This compound was obtained as a dark orange viscous liquid. IR ν_{max} (film): 3063, 2956, 2928, 2856, 1579, 1538, 1467, 1422, 1378, 1265, 1062, 894, 736 cm^{-1}.^{1}H-NMR δ ($CDCl_3$, 400 MHz): 3.20 (8H, m, N–CH_2–$(CH_2)_6CH_3$) ; 3.00 (6H, s, N–CH_3); 1.81–1.27 (48H, m, N–CH_2–$(CH_2)_6$–CH_3); 0.86 (12H, t, J = 6.9 Hz, N–CH_2–$(CH_2)_6CH_3$). ^{13}C-NMR δ (100 MHz, $CDCl_3$): 163.48; 49.87 and 49.25 (rotamers); 40.39; 31.68; 29.25; 29.12; 27.73 and 27.39 (rotamers); 26.87 and 26.68 (rotamers); 22.54; 14.00. ^{19}F-NMR δ (376 MHz, $CDCl_3$): −176.3. Analysis: Calc. for $C_{35}H_{74}BF_4N_3$: N 6.79, C 67.39, H 11.96. Found: N 7.14, C 67.53, H 12.27%.

General procedure for the substitution of chloride with Tf_2N^-

The [dmg] chloride was transferred to a plastic erlenmeyer followed by the addition of dichloromethane. Lithium bistrifluoromethanesulfonimidate (Tf_2NLi) (1.4 equiv.) was added and the mixture stirred at room temperature for 24 hours. The resulting solid was collected by filtration and washed with dichloromethane. The combined organic layers were collected, dried ($MgSO_4$) and filtered. The salt was then recovered after passing through a column with silica and activated carbon, and the solvent removed under vacuum. The residue was stirred under vacuum (< 1 mmHg) overnight.

5c [(be)$_2$dmg][Tf$_2$N]. This compound was obtained as an orange viscous liquid; chloride content < 0.1% (w/w). IR ν_{max} (film): 3582, 3162, 2967, 2940, 2879, 1579, 1547, 1463, 1424, 1348, 1195, 1139, 1060, 978, 876, 791, 741 cm^{-1}.^{1}H-NMR δ (400 MHz, $CDCl_3$): 3.26–3.01 (8H, m, N–CH_2–); 2.95 (6H, s, N–CH_3); 1.33–1.18 (14H, m, N–CH_2–$(CH_2)_2$–CH_3 and N–CH_2–CH_3); 0.96–0.91 (6H, m, N–CH_2–CH_2–CH_2–CH_3). ^{13}C-NMR δ (100 MHz, $CDCl_3$): 163.35; 119.52 (q, J = 321 Hz); 49.14 and 48.35 (rotamers); 44.69 and 44.01 (rotamers); 40.09; 29.48 and 29.15 (rotamers); 19.91 and 19.75 (rotamers); 13.36; 12.99 and 12.56 (rotamers).^{19}F-NMR δ (376 MHz, $CDCl_3$): −170.1.

5d [(di-h)$_2$dmg][Tf$_2$N]. This compound was obtained as a yellow viscous liquid; chloride content: 0.1% (w/w). IR ν_{max} (film): 3421, 2958, 2934, 2862, 1574, 1542, 1467, 1350, 1195, 1136, 1060, 739 cm^{-1}. ^{1}H-NMR δ ($CDCl_3$, 400 MHz): 3.24–2.98 (8H, m, N–CH_2–$(CH_2)_4CH_3$); 2.95 (6H, s, N–CH_3); 1.70–1.27 (32H, m, N–CH_2–$(CH_2)_4$–CH_3); 0.89–0.86 (12H, t, J = 6.7 Hz, N–CH_2–$(CH_2)_4$–CH_3). ^{13}C-NMR δ (100 MHz, $CDCl_3$): 163.38; 119.69 (q, J = 321 Hz); 50.09 and 49.36 (rotamers); 40.30; 31.27 and 31.18 (rotamers); 27.71 and 27.33 (rotamers); 26.39 and 26.29 (rotamers); 22.37; 13.75. ^{19}F-NMR δ (376 MHz, $CDCl_3$): −171.4. Analysis: Calc. for $C_{29}H_{58}F_6N_4O_4S_2$: N 7.95, C 49.43, H 8.24. Found: N 8.71, C 48.05, H 8.72.

Comparative stability between 1-*n*-butyl-3-methylimidazolium chloride [bmim][Cl] and guanidinium chlorides [(be)$_2$dmg][Cl] 2c and [(di-h)$_2$dmg][Cl] 2d

Standard procedure for the stability test using neat salt. The chloride [(di-h)$_2$dmg][Cl] **2d**(500 mg, 1.1 mmol) or [bmim][Cl] (500 mg, 2.8 mmol) was added to a flask with a magnetic stirrer. Several conditions were tested, namely thermal (160 °C), heating at 60 °C in the presence of hydrochloric acid 37% (1 equiv.), ammonia (aqueous solution 25%, 2 equiv.), $NaIO_4$ (1 equiv.), $NaBH_4$ (3 mol equiv.) and KOH (1 equiv.). The resulting effects were evaluated using ^{1}H and ^{13}C NMR spectroscopy, by taking an aliquot followed by dissolution in $CDCl_3$.

Standard procedure for the stability test using a solution of the salt. The chloride [(be)$_2$dmg][Cl] **2c**(40 mg, 0.14 mmol) or [bmim][Cl] (40 mg, 0.23 mmol) were dissolved in 0.4 ml of D_2O or of d_6-DMSO in an NMR tube. Several conditions were tested, namely thermal (160 °C in d_6-DMSO), heating at 80 °C (except for $NaBH_4$ which was performed at rt) in the presence of hydrochloric acid 37% (1 equiv.), ammonia (aqueous solution 25%, 2 equiv.), $NaIO_4$ (1 equiv.), $NaBH_4$ (3 mol equiv.) and KOH (1 equiv.). The resulting effects were evaluated by ^1H and ^{13}C NMR spectroscopy.

Acknowledgments

We are grateful to REQUIMTE/CQFB and FCT (Ref. POCTI/EQU/35437/1999) for financial support and Professor Joaquim J. Moura Ramos for helpful discussions.

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Preparative and mechanistic studies of solvent-free Rap–Stoermer reactions

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Received 4th April 2003
First published as an Advance Article on the web 16th May 2003

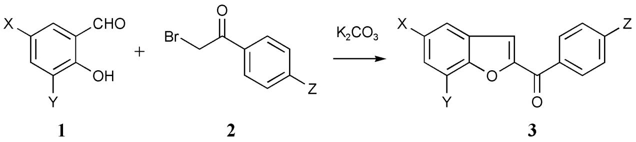
Solvent-free Rap–Stoermer reactions were found to very efficiently give products in almost quantitative yield by just washing the reaction mixture with water. The reaction mechanism has been clarified completely by continuous IR spectral monitoring and by isolation of two reaction intermediates.

Introduction

From the viewpoint of green and sustainable chemistry, solid-state[1] and solvent-free reactions[2] are becoming more and more attractive and popular, although some reactions are accelerated in the presence of a small amount of solvent.[3] We have recently found solid-state, solvent-free reactions to be very useful for mechanistic study, since they can easily be monitored by spectral measurement. For example, formation of an imine intermediate, 1-cyano-2-imino-indan in the solid-state Thorpe reaction of 1,2-bis(cyanomethyl)benzene to 2-amino-1-cyanoindene has been detected by IR spectral monitoring of Nujol mulls.[4] Here, we report that Rap–Stoermer reactions proceed very efficiently under solvent-free conditions, and we have also clarified the reaction mechanism.

Results and discussion

Rap–Stoermer reactions are useful for preparation of 2-benzoylbenzofuran derivatives (**3**) by a base-assisted condensation of salicylaldehydes (**1**) with phenacyl bromides (**2**) (Scheme 1).



a: X=Y=H
b: X=Cl; Y=H
c: X=Br; Y=H
d: X=Y=Br

a: Z=H
b: Z=Br
c: Z=OMe

a: X=Y=Z=H
b: X=Y=H; Z=Br
c: X=Y=H; Z=OMe
d: X=Cl; Y=Z=H
e: X=Cl; Y=H; Z=Br
f: X=Cl; Y=H; Z=OMe
g: X=Br; Y=H; Z=H
h: X=Z=Br; Y=H
i: X=Y=Br; Z=H

Scheme 1

However, these reactions are not very efficient in solution, and the yield of products is not very high. For example, heating a solution of **1a**, **2a** and K_2CO_3 in EtOH under reflux for 1.5 h gave **3a** in 77–90% yield.[5] In the reaction between substituted derivatives of **1** and **2** in solution, the yield of the product is much lower. Thus, reaction of **1b** and **2b** in EtOH under reflux for 3 h gave **3h** in 70% yield.[6] In these cases, the solvent must be removed from the reaction mixture by evaporation and the residue worked up for isolation of the product.

By contrast, solvent-free reactions proceed efficiently under much simpler conditions to give products in almost quantitative yield. For example, a mixture of **1a** (0.61 g, 5 mmol), **2a** (0.99 g, 5 mmol) and K_2CO_3 (1.38 g, 10 mmol) was heated at 80 °C for 1 h, and the reaction mixture was washed with water to give **3a** in 98% yield (1.09 g).

Similar solvent-free reactions of various salicylaldehydes (**1a–d**) and phenacyl bromides (**2a–c**) at 80–100 °C for 1 h gave the corresponding 2-benzoylbenzofuran derivatives (**3a–i**) in almost quantitative yields (Table 1).

Table 1 K_2CO_3-assisted solvent-free Rap–Stoermer reactions

Aldehyde (1)	Ketone (2)	Reaction temperature/°C	Benzofuran (3)	Yield (%)	mp/°C
1a	**2a**	80	**3a**	98	90–91[a]
1a	**2b**	80	**3b**	95	226–228
1a	**2c**	80	**3c**	98	99–100
1b	**2a**	80	**3d**	99	143–144
1b	**2b**	100	**3e**	93	194–195[b]
1b	**2c**	100	**3f**	97	147–148
1c	**2a**	80	**3g**	98	138–139
1c	**2b**	100	**3h**	94	196–197
1d	**2a**	100	**3i**	93	171–172

[a] Lit. 89–91 °C. [b] Lit. 202 °C

In order to clarify the reason why the Rap–Stoermer reaction proceeds so efficiently under solvent-free conditions, the

Green Context

Solventless reactions have become an important component of the green chemistry toolkit but they are generally not that well understood. Here we see a good example of the method applied to the synthesis of benzofurans *via* the Rap–Stoermer reaction. Reactions proceed in high yield and products can be easily extracted by treatment with water only. To help understand the solvent free process, the authors describe a very revealing infrared spectroscopic study of the reaction as it progresses. This reveals the formation of key reaction intermediates, one of which was subsequently isolated and characterised by X-ray analysis.
JHC

DOI: 10.1039/b303802p

K_2CO_3-assisted reaction of **1a** and **2a** was studied by IR spectral monitoring in Nujol mulls.

Firstly, the potassium salt formation of **1a** was studied. One min after mixing **1a** with twice the molar amount of K_2CO_3, a C=O absorption band (B) appeared at 1692 cm^{-1} (spectrum II in Fig. 1), although **1a** itself shows C=O absorption (A) at 1664 cm^{-1} (spectrum I in Fig. 1). After 10 min, B disappeared and a new C=O absorption band (C) appeared at 1670 cm^{-1} (spectrum III in Fig. 1). The absorption (C) was assigned to *ν*(C=O) in the potassium salt (**5a**) by comparison of spectrum III with that of an authentic sample. Absorption B was assigned to *ν*(C=O) in a 1 : 1 complex (**4a**) of **1a** with **5a**, by comparison of spectrum II with that of an authentic sample (colourless needles, which did not show clear melting point) prepared by mixing **1a** with half the molar amount of K_2CO_3. Unfortunately, the structure of **4a** could not be determined, since **4a** did not form suitable crystals for X-ray analysis. Treatment of **4a** with K_2CO_3 gave **5a** (Scheme 2).

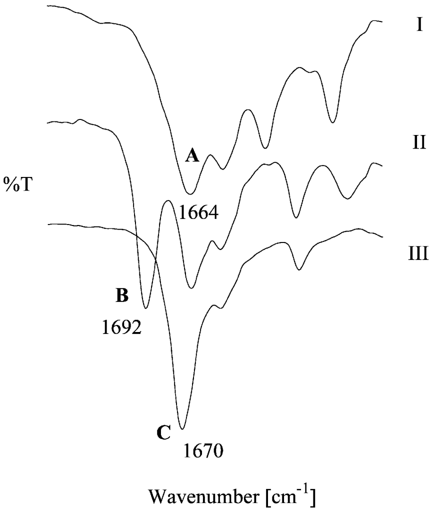
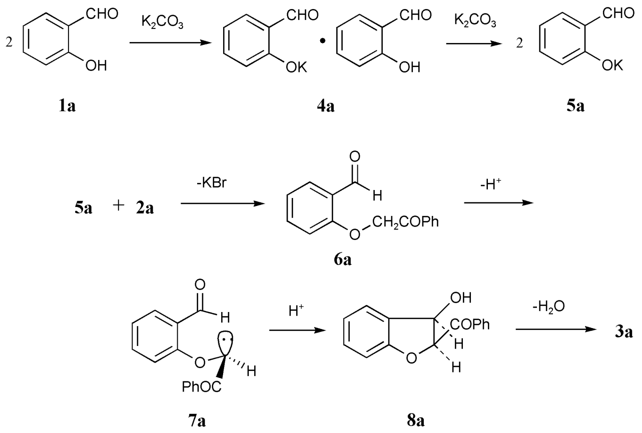


Fig. 1 IR spectra of a mixture of **1a** and twice the molar amount of K_2CO_3 in Nujol mulls. I: Pure **1a** for reference, II: 1 min after mixing, III: 10 min after mixing.



Scheme 2

Secondly, the reaction of **1a, 2a** and K_2CO_3 under solvent-free conditions was monitored by IR spectral measurement.

A mixture of **1a**, an equimolar amount of **2a** and twice the molar amount of K_2CO_3 initially showed C=O absorption (C) at 1670 cm^{-1}, assigned to formation of **5a**; this absorption decreased gradually and new C=O absorptions appeared at 1696 (D) and 1641 cm^{-1} (E) (Fig. 2). After 60 min, the C absorption band disappeared and the D and E absorptions increased. After further reaction at 80 °C for 10 min, the D absorption disappeared and only the E absorption remained in the spectrum (VI in Fig. 2). Spectrum VI is identical to that of the final product **3a**. The appearance of the D absorption band together with a strong OH absorption band at 3465 cm^{-1} suggests production of a ketoalcohol intermediate.

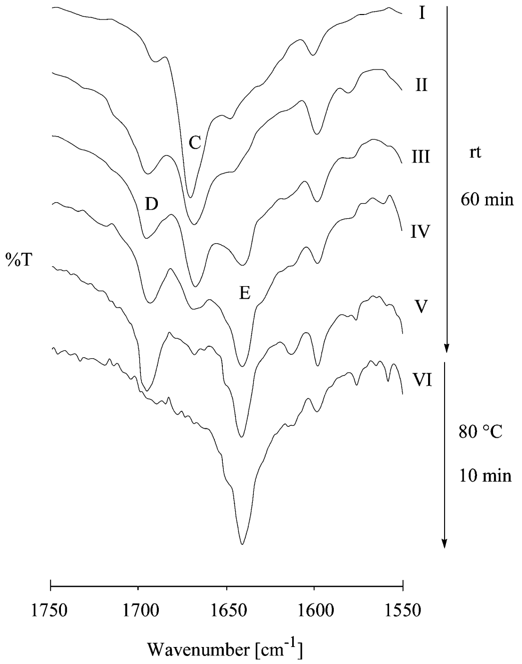


Fig. 2 IR monitoring of the K_2CO_3-assisted solvent-free reaction of **1a** with **2a** by spectroscopic measurements in Nujol mulls. I–V: measured every 15 min.

In order to isolate the ketoalcohol intermediate, the following experiment was carried out. A mixture of **1a** (1.0 g, 8.2 mmol), **2a** (0.77 g, 5 mmol) and K_2CO_3 (1.38 g, 10 mmol) was stored at room temperature for 3 h, and the crude reaction product was added to a 1 : 1 mixture of ether and water. From the ether solution, *cis*-2-benzoyl-3-hydroxy-2,3-dihydrobenzofuran (**8a**) was obtained, after recrystallisation from ether, as colourless prisms [0.18 g, 15% yield, mp 157–158 °C, *ν*(C=O) = 1696, *ν*(OH) = 3465 cm^{-1}]. Heating **8a** under solvent-free Rap–Stoermer reaction conditions easily gave **3a**.

The *cis*-configuration of **8a** was established by X-ray structure analysis (Fig. 3).

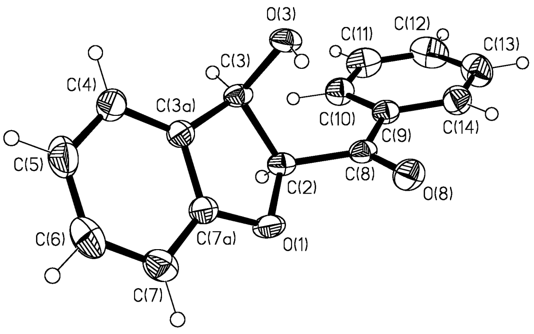


Fig. 3 Perspective view of compound **8a**. The C and O atoms are represented by their atomic displacement ellipsoids drawn at the 30% probability level.

The 2,3-dihydrobenzofuran moiety is flat to within 0.29 Å, and the non-hydrogen atoms of the C(O)Ph substituent are also coplanar to within 0.08 Å. The least-squares (LS) planes through these two flat moieties form a dihedral angle of 58.09(4)° in the solid state. The OH group at C(3) is 1.372(2) Å out of the benzofuran LS plane, whereas the C(8)=O carbonyl

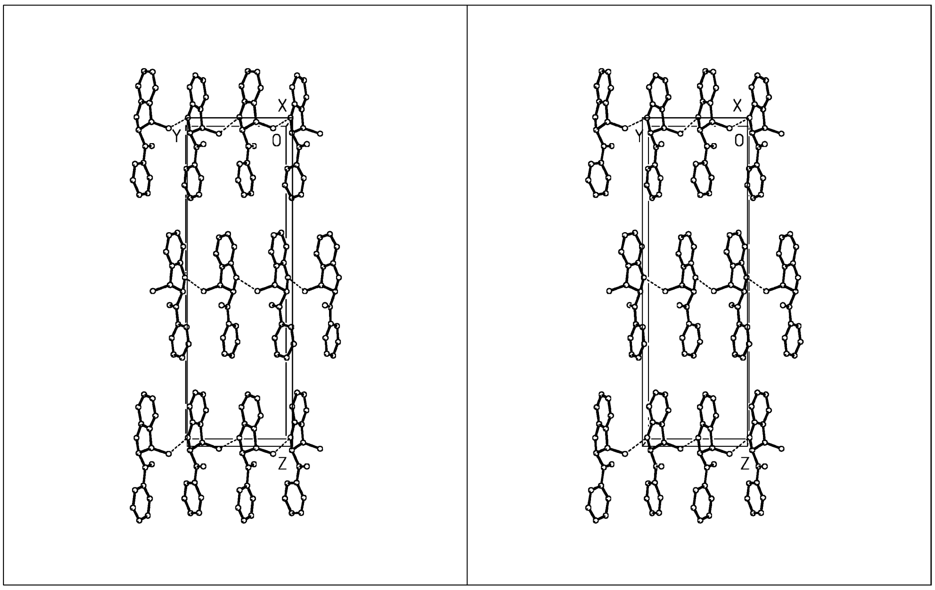
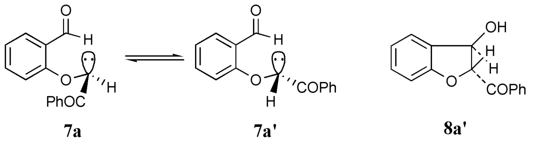


Fig. 4 Stereoscopic packing illustration of compound **8a**. The H atoms are omitted for clarity. Solid and dashed lines represent covalent and H-bond interactions, respectively.

group is coplanar with the phenyl ring it is linked to [τ{C(14)–C(9)–C(8)–O(8)} = −0.8(2)°]. The two substituents of the dihydrobenzofuran moiety, namely the C(O)Ph group at C(2) and the OH function at C(3), are *cis* oriented [τ{C(8)–C(2)–C(3)–O(3)} = −18.5(2)°].

In the crystal, the **8a** molecules are linked *via* hydrogen bonds [O(3)···O(1)$_{(1-x,\ 0.5+y,\ z)}$ = 2.855(1), H(3O)···O(1) = 2.00 Å, O(3)–H(3O)···O(1) = 161°] into endless *zigzag* chains, which run parallel to each other in the crystallographic *b* direction (Fig. 4).

The *cis* conformation of **8a** suggests the following steric course of the reaction. In an attack of the carbanion (**7a**) on the formyl carbonyl carbon from below, the carbanion should have the configuration depicted in **7a** (Scheme 3).



Scheme 3

This course is sterically favourable, since the repulsion between the formyl hydrogen and the hydrogen binding to the carbanion is not serious. In contrast, cyclisation of the carbanion **7a′** would be unfavourable due to serious steric repulsion between the formyl hydrogen and the benzoyl group. This would be a reason that the *trans* isomer (**8a′**) of **8a** is not isolated. When **8a′** is produced in the reaction, more stable **8a′** should be isolated, since its *cis*-dehydration reaction to **3a** is more difficult than the *trans*-dehydration of **8a**. However, it is not clear whether the more favourable **7a** is formed from **6a** for kinetic or thermodynamic reasons (Scheme 3).

Experimental

General procedure

Solvent-free Rap–Stoermer reactions proceed efficiently under simple conditions to give products in almost quantitative yield. For example, a mixture of **1a** (0.61 g, 5 mmol), **2a** (0.99 g, 5 mmol) and K_2CO_3 (1.38 g, 10 mmol) was heated at 80 °C for 1 h, and the reaction mixture was washed with water to give **3a** in 98% yield (1.09 g).

The progress of the reactions has been followed by continuous IR spectroscopic measurement of the reaction mixture of salicylaldehyde (**1**), 2-bromoacetophenone (**2**) and K_2CO_3, using a JASCO FT/IR-450plus instrument in Nujol mulls at room temperature.

Analytical data for the isolated intermediates **4a** and **8a** (Scheme 2):

4a: Analysis (%): Found, C 59.55, H 3.68; Calc. for $C_{14}H_{11}O_4$, C 59.56, H 3.93.

8a: Analysis (%): Found, C 74.88, H 5.06; Calc. for $C_{15}H_{12}O_3$, C 74.99, H 5.06.

Crystallography

X-Ray intensity data were collected at room temperature from a colourless single crystal with the approximate dimensions 0.19 × 0.23 × 0.35 mm, using a STOE Imaging Plate Detection System.[7] The net intensities were corrected for Lorentz and polarization effects. Application of direct methods[8] yielded reliable position for all non-hydrogen atoms of the **8a** molecule. The preliminary structure model was then refined and completed with hydrogen atoms using the programs of the SHELXL system.[9] Crystal data of **8a**: $C_{15}H_{12}O_3$, M = 240.25, orthorhombic, a = 5.912(1), b = 8.043(1), c = 25.070(2) Å, V_c = 1192.1(3) Å^3, T = 293 K, space group $Pbc2_1$ (no. 29), Z = 4, D_c = 1.339 Mg m^{-3}, μ(Mo–Kα) = 0.093 mm^{-1}, F(000) = 504, 8084 reflections measured, 2204 unique (R_{int} = 0.085), $wR(F^2)$ = 0.104 (2196 reflections, 172 variables), R = 0.041 [for 1994 reflections with $F > 4\sigma(F)$], S(goodness-of-fit on F^2) = 1.060, final $\Delta\rho$ = +0.19/−0.18 e$^-$ Å^{-3}. CCDC reference number 200218. See http://www.rsc.org/suppdata/gc/b3/b303802p/ for crystallographic data in .cif or other electronic format.

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Environment-friendly method of high alkaline bauxite's Red Mud and Ferrous Slag utilization as an example of green chemistry

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Received 13th January 2003
First published as an Advance Article on the web 22nd May 2003

This paper focuses on the development of new environment-friendly construction materials based on Red Mud – the mineral processing waste from bauxite. This type of waste is commonly produced by Al-plants during the Bayer process. The new materials consist only of industrial wastes. However, their strength can be accelerated by adding small amounts (2%) of CaO or Portland cement. Only amorphous new formations have been found to grow during the materials' strengthening process. The high strength of these new materials renders them applicable in the construction of roads and airfield runways, levee cores, industrial and municipal dumps, building foundations, in tile and brick production, *etc.* In addition to the economic advantages of these materials, they are extremely easy to use and do not create new residues.

1 Introduction

Red Mud is the main by-product of aluminium production in Bayer plants. The storage of large amounts of Red Mud in landfills generally creates not only serious environmental problems for the local population because of its high level of alkalinity (usually near pH 12–13), but also economic problems for its producer.

Enormous amounts of Red Mud have been accumulating for many decades in large dumps near Al-plants. To cite just one example, one of the Kaiser Aluminium & Chemical Co. plants, located in Louisiana (USA), has about 20,000,000 tons of Red Mud deposited in three lakes, and annually produces additional amounts of over 1,000,000 tons.[1] The use of these mineral deposits as a secondary raw material for a variety of applications would produce economic benefits and solve a grave environmental problem.

Red Mud can be used as a raw material for the production of tiles or red bricks, based on a mixture of Red Mud and fly ash from power stations burning powdered coal.[2] Some products containing Red Mud can be used as levee core, road base, and in the production of mineral coagulants for thermal sulfurization.[3] Other investigations focus on the calcination of Red Mud up to 1200 °C,[4] although this method leads to great losses of thermal energy. Red Mud can also be used to produce fertiliser filters and synthetic soils.[1]

The use of dumped ferrous slag (DFS) is a much more crucial concern for many countries, due to the large amounts of DFS they produce, the large areas needed to store these slags and the length of time over which they have accumulated. In the territory of the states of the former USSR, for instance, there is an accumulation of more than 450×10^6 tons of DFS. To illustrate the magnitude of the problem, one has but to see the case of a single metallurgical plant in Russia (Magnitogorsk), which has accumulated over 180×10^6 tons of DFS in its nearby dump.

This paper presents laboratory results that confirm the viability of using Red Mud and DFS as basic construction material components consisting exclusively of industrial wastes with small additions of Portland cement or lime. These new materials can be used as bases of roads and airfield runways, levee cores, industrial and municipal waste dumps, in the foundations of buildings, in the production of tiles, bricks, *etc.* In addition to the economic benefits accruing from its use, Red Mud is easy to apply, adapting to local industrial waste dumps without creating new residues. The results of investigations in Spain are currently being adapted for future development in Brazil.

2 Research objectives

The main goals of this research work were to propose new solutions for the environmental problem, *i.e.*,

1. To utilise as much industrial waste (Red Mud and Dump Ferrous Slag) as possible;
2. To study the possibilities of heavy metal binding in waste processing;

Green Context

The utilization of large volume wastes from established industrial processes is of prime importance to the global environment and to clean technology. It can not only provide an outlet for material that is otherwise accumulating in dumps but can also reduce the consumption of primary raw materials. Red Mud and Ferrous Slag are two very large volume waste materials that are accumulating at a staggering rate. The scale of these wastes far outweighs those from the organic chemical processes that are often discussed in the Green Chemistry community. Here it is shown that simple addition of a small amount of calcium oxide can give these wastes real value as large-scale construction materials. The properties and stability of these materials are shown to be very good. ***JHC***

DOI: 10.1039/b300495n

3. To obtain new environment-friendly construction materials with suitable mechanical properties;

4. To study the structural formation processes of new materials in order to increase their positive properties.

3 Industrial wastes as basic materials

The Red Mud sludge used in this work was kindly donated by the administration of Aluminio Español S.A.'s plant in San Ciprian (Lugo), Spain. The main components of Red Mud are: Fe-oxides – 35.5, TiO_2 – 15.2, Al_2O_3 – 12.2, CaO – 7.9, SiO_2 – 5.7, Na_2O – 4.6%. Except, it also contains V_2O_5 – 1.0 and Cr – 1.0%.

Dump Ferrous Slag (DFS) of an open-hearth (steel) mill was obtained from the Azma Plant near Madrid. The chemical composition of DFS consists of Fe-oxides – 36.2, CaO – 24.0, CaO_{free} – 0, SiO_2 – 17.8, Al_2O_3 – 9.3, MnO – 3.9, MgO – 3.5%. It has the following mineralogical composition (approximately): Larnite β-C_2S – 25, Olivine $(Mg, Fe)_2SiO_2$ – 15, Periclase MgO – 25, Pyroxene Rhombic – 10, RO-phase (MgO, MnO, FeO) – 1, Melilite $Ca_2(Al,Mg,Si)Si_2O_7$ – 5, Glass – 5%. DFS was ground in a ball mill till the BET surface area was equal to 0.858 sq.m g^{-1}.

4 Experimental procedure

Samples of the material were produced by mixing the initial components with optimal humidity and then subjecting the mixture to a pressure of 10 MPa. The samples were allowed to harden at a humidity of 98%.

The sample hardening process was monitored by X-ray diffraction analysis (XRD), using the powder method with λ-Cu K_α and by scanning electron microscopy (SEM) at the National Center of Metallurgical Investigations, Madrid, and was controlled by defining the limit of uniaxial compression and the temporal changes in linear deformation.

5 Results

In line with the primary objective of this research, the new materials include a maximal (close to 70%) amount of Red Mud. All the materials show rather high strength values (Fig. 1), most of them of over 3 MPa at 7 days and up to 5 MPa at 90 days.

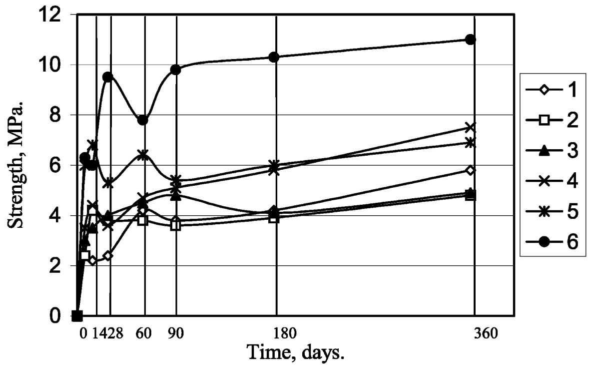

Fig. 1 Dynamic of the materials strengthening.

Further increases of the DFS content, which is the only binding material in compositions 2–4, to up to 50% led to greater strengthening of the samples, reaching almost 7.5 MPa on the 360th day (sample 4) in comparison to 5.8 MPa in the composition containing only 30% of slag (sample 1).

The introduction of a small amount (2%) of traditional binding materials – CaO or Portland cement (compositions 5, 6) – increased the samples' strength by 1.5 to 4 times, particularly in the early stages (up to the 60th day of hydration) in comparison with the similar composition 1. After 90 days, the advantage offered by the use of CaO decreased significantly. The best results were obtained with Portland Cement (sample 6, Fig. 1) during all the material's hardening stages. The material's strength was 6.3 MPa on the 7th day, 9.8 MPa on the 90th day and up to 11.0 MPa at one year of age.

The materials are highly water resistant:

$$C_w = \frac{R_w}{R_a}$$

where: C_w – coefficient of water resistance,

R_w – strength of 90-day-old samples kept under air-humidity conditions (94–96% humidity) after saturation in water for 24 hours,

R_a – strength of 90-day-old samples kept in air-humidity conditions (94–96% humidity).

The C_w coefficient exceeded the value of 0.94–0.96.

An analysis of the strength curves (Fig. 1) and the linear deformation coefficient (Fig. 2) show that the samples' main structural formation took place within 28 days. This is characteristic of many materials with binding properties, and is followed by a gradual expansion. However, the samples prepared for this experiment displayed a strong linear expansion of up to 2.35% by the 28th day, and especially up to the 60th day of the hardening process. Prior to (samples 4, 5) and following (samples 6, 5, and 1) that time interval, reductions in strength usually occurred. Such temporary strength losses have been observed in most slag-containing materials during these periods.[5,6] In a one-year period of strengthening, all the materials show a coefficient of linear deformation of close to 2.0% (Fig. 2).

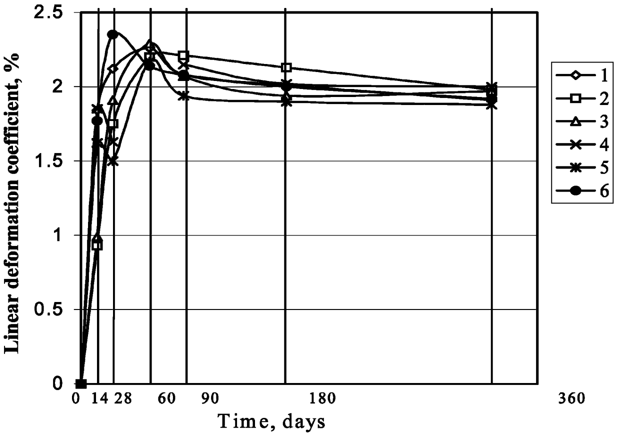

Fig. 2 Changing of the samples' linear deformation coefficient during the strengthening.

The results of the XRD analysis of the initial and one-year-old samples did not reveal the small changes shown in the diffractograms (Fig. 3) during the samples' hardening. The initially amorphous structure (Fig. 3(A)) of the sample composed of the bauxite waste-slag mixture can be explained by the complete destruction of the original crystal structure of bauxite during the Bayer process. The crystal components of the slag were invisible in the diffractogram because of the absorption of their reflexes (peaks) by the mixture's amorphous components.

The strength of the samples after one year showed no alterations in the diffractogram (Fig. 3(B)), *i.e.*, no new peaks appeared on the diffractogram, indicating that they remained amorphous.

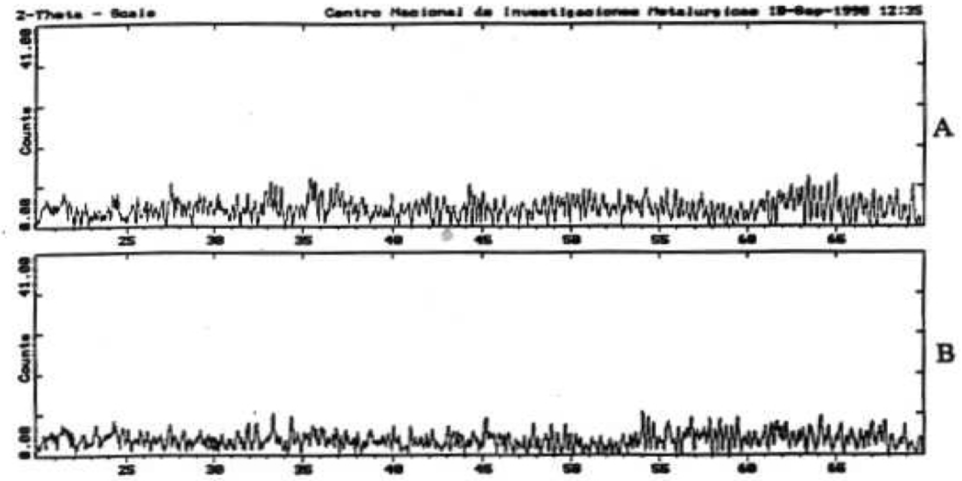

Fig. 3 The XRD of initial (A) and 360-days hydration (B) mixtures of Red Mud, Dump Ferrous Slag and activator.

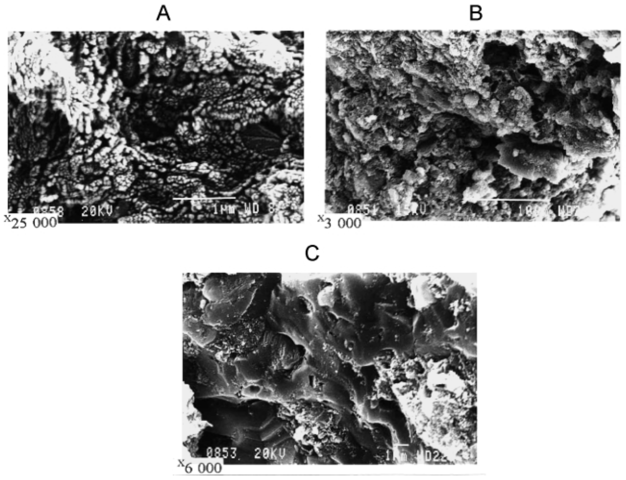

Fig. 4 The sample of the mixture of Red Mud, Dump Ferrous Slag and activator: (A) initial, (B) and (C) after 60 days of hydration.

The structural changes are more readily visible in the SEM micrographs (Fig. 4(A), (B) and (C)). Sample A initially displayed a kidney-shaped surface, which became more amorphous at 60 days of aging, its surface appearing swollen or resembling melting ice, as shown in (Fig. 4(B)) and (Fig. 4(C)), respectively. Possibly, these new structures were the main reason for the samples' increased bulk strength over time.

All the new formations had amorphous structures (Fig. 4(B), (C)). This phenomenon has been well explained and is corroborated by Groth–Fedorow's law of the chemistry of crystals regarding the growth of crystal structures from solutions. This law states that crystals with the least syngony (crystal systems) can be grown from the most chemically complex solutions. According to the Groth–Fedorow law, a solution as complex as the mixture of Red Mud and Dump Ferrous Slag cannot be synthesized into crystalline structures, but only into amorphous formations. Our previous research work on these materials had already produced similar results.[5–8]

The way in which the newly developed materials gained strength is suggestive of Michaels and Khul's almost forgotten theory of colloidal hardening of Portland cement. Their theory of amorphous hardening is applicable to our systems, in which the gel of new formations strengthens the sample's bulk.

These amorphous formations, which can be highly stable, are very similar to amorphous minerals (*e.g.*, hisingerite, limonite, *etc.*) or to sedimentary rocks such as flint, opoka, tripolite, *etc.* that have existed over geologic eons in amorphous form.

6 Applications

The results of the present study prove that Red Mud deriving from the industrial waste of aluminium production in Bayer processing plants during bauxite digestion can be used as the main component of construction materials for roads and airfield runways, levee cores, industrial and municipal waste dumps, multistory building foundations, tile and brick production, *etc.* Red Mud can be used in mixtures with other industrial wastes such as Dump Ferrous Slag or in combination with other similar wastes, with the addition of several alkaline activators that interact chemically with Red Mud and DFS. Small additions of CaO or Portland cement to the mixtures can accelerate the materials' strengthening process.

7 Environmental and economic factors

The large-scale use of this method is environmentally beneficial. Its greatest advantage is that it neutralizes the high alkalinity of Red Mud, which is used extensively in mixtures with other industrial wastes that would otherwise contaminate the environment.

Powders of the samples were mixed with HCl solution (with pH = 3.5) and alkaline (with pH = 11.0) solutions, for 48 hours.

The solutions were filtered and analysed with atomic-adsorption Spectrometers AA-30 (Cd and Cr) and Quantum AFA (Cu, As and Pb).

Leaching tests performed on samples have demonstrated (Table 1) their very low level of leachability in acid and alkaline solutions, far below the demands of the national environmental standards of Spain, Russia and Brazil. This fact is attributed to the strong chemical binding of heavy metals in practically insoluble chemical compositions. Furthermore, the use of these industrial wastes would reduce the open-quarry extraction of natural construction materials.

Table 1 Results of leachability of new materials on the base of Red Mud

Element-contaminator	Containing (ppm)	
Cu	< 0.5	< 0.5
Cr	< 0.5	< 0.5
As	< 2	< 2
Pb	4	5
Cd	1.3	1.6

This fact was ascertained by two independent competent medical and sanitary expert groups from Russia and Spain.

From the economical standpoint, the use of these newly developed materials can be very attractive in many of the aforementioned applications because they are composed only of cheap (or free) industrial wastes.

Considerable production cost reductions are further decreased by:

1. The low price of binding materials (industrial wastes such as Dump Ferrous Slag);

2. The small consumption of these binding materials and the reduction of transported materials.

Additional benefits are expected to be much higher due to the financial benefits accruing from the use of industrial wastes in these processes.

In addition to economic factors, the materials are very easy to apply and do not create new residues.

Dump Ferrous Slag can be replaced by other industrial wastes, which may be more readily available locally. However, the proportions of initial mixtures require refining since the chemical and mineralogical compositions of industrial wastes may vary from one plant to another.

8 Conclusions

1. The new materials resulting from mixtures of Red Mud and Dump Ferrous Slag, with or without small additions of CaO or Portland cement, possess significant strength and water resistance. These characteristics make them highly recommendable for use as construction materials for roads and airfield runways, levee cores, industrial and municipal dumps, multistory building foundations, in tile and brick production, *etc.* The materials are extremely easy to apply, creating no new residues.

2. The strength of these materials increases during hydration due to the solution of solid particle surfaces and the growth of amorphous gel compounds, their syneresis and transition to a stone-like condition.

3. The development of Red Mud-based materials can be very attractive economically. The substantial drop in production costs is further reduced by the low cost of binding and activating materials (industrial wastes), by the small consumption of binding material (Dump Ferrous Slag) and by the reduction of transported materials.

4. The large-scale use of the method is environmentally beneficial, since leaching tests have revealed the materials' very low leachability in acid and alkaline solutions, which is far below the demands of Spain's and Russia's environmental standards. This low leachability results from the chemical binding of heavy metals. The most important advantage is the use of Dump Red Mud, Dump Ferrous Slag and other industrial wastes that would otherwise contaminate the environment; thus, these materials offer a potential alternative to the open-quarry extraction of natural construction materials.

9. Acknowledgements

V. A. Mymrin is highly indebted to the administration of Aluminio Español S.A.'s plant in San Ciprian (Lugo), Spain for kindly donating samples of Red Mud and to the Azma plant (Madrid) for the samples of Dump Ferrous Slag (DFS) used in this work.

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