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Green & Sustainable Chemistry Network

GSCN was established in 2000 to promote research and development for the Environment and Human Health and Safety, through the innovation of Chemistry.

Challenges of Chemistry and the GSCN

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All of humanity shares major problems that need to be solved in relation to things such as natural resources, energy, environment, medical services and health, information and telecommunications, and natural disasters. Japan, in particular, faces the critical challenge of further strengthening and developing its scientific/technological and educational capabilities, as well as its industrial competitiveness, in order to accomplish the sustainable development of economic/industrial competitiveness and our cultural/social relevance in the wake of the Great East Japan Disaster and the Fukushima Nuclear Power Plant Accident. For more than 10 years the GSCN has been engaged in progressive activities to pursue social responsibility, such as the conservation of finite resources and protection of the environment. For this reason I expect the network to play a greater role and make a major contribution in the future.

The Chemical Society of Japan compiled the “Roadmap to Dreams of Chemistry 30 Years in the Future” for the first time in March, enumerating future goals in the general field of chemistry. Accordingly, "green and sustainable chemistry (GSC)" is one of the basic principles advocated in the overview of the roadmap. By showing what we assume are the future challenges of chemistry and their possible solutions, I believe this roadmap will prove to be an invaluable reference material from which policy makers, ordinary people and experts from other fields can seek information in contemplating the future direction of chemistry and chemical technology.

The industry, government and academia must all cooperate with one another, make their utmost efforts and share the responsibilities, with an eye toward the creation of a new chemistry and chemical technology oriented toward a sustainable society and the fostering of human resources that will consistently tackle the many challenges of chemistry and cope with unpredictable problems.

Advanced science and technology are considered to be the results of intellectual activities in which, throughout the long process of evolution, humans alone could participate. With chemistry and chemical technology as crucial elements in the foundation of human civilization, I hope the principle of GSC will be further promoted, its concept promulgated and disseminated to the public. Thus more human resources that support a sustainable society will be nurtured, and a stronger, brighter future for Japan will be ensured.

Green Chemistry and The Activation of Non-reactive Bonds and Molecules

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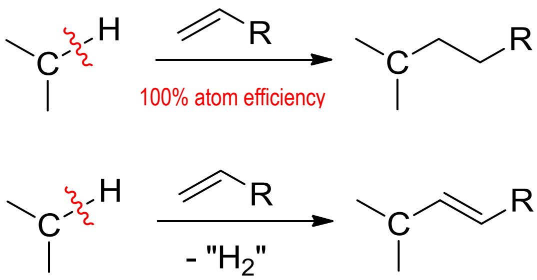
No one would question the importance of green chemistry activities. With that said, there are several different perspectives on how we should address the general issue of green chemistry. In this report I will discuss the relationship between green chemistry and synthetic organic chemistry with emphasis on the activation of non-reactive bonds and molecules.

Organic synthesis frequently entails the breaking of existing chemical bonds and the creation of new bonds. Although an organic molecule typically contains numerous chemical bonds, organic chemists do not utilize all of them. Instead, they have exploited only the highly reactive, readily available and easy-to-use bonds. If chemical bonds that have not thus far been utilized in organic chemistry could be made accessible without constraints, it will be possible to develop new, more efficient methodologies of organic synthetic chemistry. From this perspective, the direct conversion reaction of carbon-hydrogen bonds has recently drawn the attention of chemists. The carbon-hydrogen bond is the most commonly found bonding mode in organic substances, but it is not generally regarded as a functional group. Although some basic reactions, such as the Friedel-Crafts reaction and the photohalogenation of alkanes are known and are covered in textbooks on organic chemistry, the C-H bond has not been utilized in organic chemistry to the extent that other highly reactive bonds have. This is partly attributable to the fact that such bonds are difficult to break, because of the high binding energy of the C-H bond. In fact, the term "activation of carbon-hydrogen bonds" was once unknown in the field of organic synthetic chemistry, being mentioned only in connection with stoichiometric reactions in organometallic chemistry. Back then, carbon-hydrogen bonds would first be converted to other highly reactive bonds such as carbon-halogen bonds. Today, however, the direct conversion of carbon-hydrogen bonds is frequently practiced.



An oxidizing agent (hydrogen scavenger) is necessary.

Unfortunately, it is now commonly assumed that any conversion reaction of C-H bonds is acceptable. For example, a stoichiometric reaction in the presence of oxidizing agents is essentially a one-pot reaction, equivalent to the conversion of C-H bonds to halogen or other bonds. In the future it will be imperative to increase the types of new reactions with high atom efficiencies, although I cannot at present argue that high atom efficiency automatically translates to excellent reactions. In any event, the application of molecules and bonds that have previously been considered (or assumed) to be non-reactive will be a major strategic goal in synthetic organic chemistry in the future. Taking into account the importance of discussing green chemistry from the perspective of molecular activation, the 18th Green Chemistry Forum convened under the auspices of the Research Group on Green Chemistry (representative: Professor Takashi Tatsumi, Tokyo Institute of Technology) and Grants-in-Aid for Scientific Research on Innovative Areas “Molecular Activation” (area representative: Chatani). As part of the forum we invited the following four experts to present lectures: Fumitoshi Kakiuchi (Faculty of Science and Technology, Keio University) “Development of a Catalytic Introduction Method of Functional Groups Utilizing the Carbon-Hydrogen Bond,” Yoshiaki Nishibayashi (School of Engineering, University of Tokyo) “Can an Ammonia Synthesis Method Surpassing the Haber-Bosch Process Be Born? Expectations for Next-Generation Energy Sources Substituting Fossil Fuels,” Masami Murakami (Mitsui Chemicals Inc.) “Harmony with the Environment: Efforts to Reduce Carbon Dioxide,” and Takao Ikariya (Graduate School of Science and Engineering, Tokyo Institute of Technology) “Capture of Carbon Dioxide and Immobilization in Useful Organic Compounds Through the Power of Chemistry.” Each of the lecturers provided the audience with great insight into the advanced research and industrial applications pertaining to the use of the C-H bond, N_2 and CO_2. The development of reactions utilizing non-reactive bonds and molecules that are catalyzed by base metals instead of by expensive transition metals would be an important strategic subject for researchers in the field of synthetic organic chemistry and catalytic chemistry to address in the future. What is expected is the successful development of green organic synthetic reactions that have little or no impact on the environment.

Application of Ionic Liquids for Separation Processes

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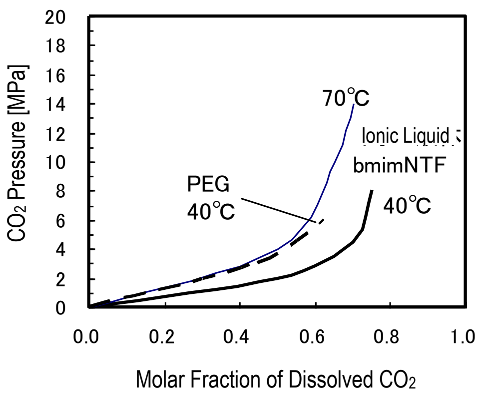
Ionic liquids have attracted attention as reaction solvents in green chemistry, and research has been actively conducted to develop new varieties and apply them to the reaction field. Accordingly, there is now a wide variety of ionic liquids whose characteristic separation-related physical properties, such as gas solubility, have come to light. Therefore, researchers have recently turned their attention to the application of ionic liquids as functional materials to industrial separation processes. Although this endeavor is still in its nascent stage, in this report I will discuss how ionic liquids can be applied to separation processes.

In September 2011, the “1st International Conference on Ionic Liquids in Separation and Purification Technology” convened in Spain. Characteristically, the conference was held under the auspices of major chemical corporations that manufacture ionic liquids, including Merck, DuPont and BASF. This shows a high level of interest and expectation in the separation processes, which may lead to the increased use of ionic liquids by developers and manufacturers. Many of the presenters, particularly those from European universities, spoke about their joint research projects with manufacturers. In this report I will introduce the trend of the application of ionic liquids in each separation process, based on some of the presentations made at the conference. (Due to the space limitation, only the titles of the presentations will be shown in the parentheses.)

The application of ionic liquids attracting the most attention is that of utilization in the gas absorption process. Particularly, the application to CO_2 separation is regarded as promising (I01: Application of Ionic Liquids for CO_2 Capture; and O24: Sour Gases (CO2 and CH4) Separation Using Ionic Liquids). As shown in the figure below, the gas solubility of ionic liquids is greater than that of a conventional physical absorbent (PEG). A possible CO_2 absorptive separation process from methane and exhaust gas is being considered, whereby CO_2 is absorbed at a few MPa of pressure and low temperature and is then collected at high temperature and low pressure. As the types of ionic liquids to be used, bmimNTF and emimAc have been proposed. Additionally, the possibility of VOC removal has been suggested (O37: Ionic Liquid as a Novel Absorbent for the Removal of Hydrophobic VOCs).



Another promising application of ionic liquids is to use them as agents for liquid-liquid extraction (K02: Separation of Aliphatic and Aromatic Hydrocarbons; and O42: Ionic Liquids in Extractive Separations and Related Processes). There have been reports of butanol being extracted from water and aromatic compounds from hydrocarbon. For ionic liquids to be applied to extraction processes, their viscosity needs to be low, and consequently the achievement of such low viscosity is a challenge for the future.

An extractive distillation process in which ionic liquids coexist in the distillation field may be put to practical use in the near future (O34: Ethylbenzene/Styrene Separation by Extractive Distillation with Ionic Liquids; and O35: Separation of Benzene and Cyclohexane by Extractive Distillation). These extractive distillation processes take advantage of the non-volatile and highly soluble properties of ionic liquids. Ionic liquids such as bminBF4 have been reported to possess higher separation capability than conventional solvents such as sulfolane.

Many ideas were presented regarding the application to gas separation using membranes impregnated with ionic liquids. The capabilities of such liquid membranes have been substantiated in propane/propylene separation (O36 and P77) and CO_2 separation (O25, O48, O53 and O55). Additionally, I have reported on the separation of vapors/gases such as CO_2 by membranes impregnated with ionic liquids (O55: Liquid Membranes Using Ionic Liquids for Air Cleaning - CO_2, Humidity, VOC). In this section I have expounded on how the separation capabilities of ionic liquids can be enhanced through the intermixture of amines and hygroscopic salts. This too was an idea intended to make full use of the highly soluble properties of ionic liquids.

Many interesting applications of ionic liquids in multitudes of circumstances are being considered in addition to the above, such as uses in pervaporation membranes and absorption refrigeration cycles. In the future, significant progress will be made in the development of ionic liquids specializing in the separation of specific substances.