Johanna Kärkkäinen

PREPARATION AND CHARACTERIZATION OF SOME IONIC LIQUIDS AND THEIR USE IN THE DIMERIZATION REACTION OF 2-METHYLPROPENE
JOHANNA KÄRKKÄINEN

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Faculty of Science, Department of Chemistry, University of Oulu, P.O.Box 3000, FI-90014 University of Oulu, Finland
Oulu, Finland

Abstract
This study concentrates on the preparation and characterization of some ionic liquids and their use in dimerization reaction of 2-methylpropene. Ionic liquids consist of cations and anions, and are commonly understood as green solvents. By definition their melting points should be lower than 100 °C. Prepared ionic liquids were used as catalytic solvents in dimerizations of 2-methylpropene to a high octane compound, isoctene. The monograph consists of two parts: the literature survey and the practical work. The literature survey reviews the preparation and characterization of ionic liquids as well as their environmental aspects, such as toxicity, biodegradability and recyclability. In addition, the acid catalyzed dimerization of butenes is discussed together with the dimerizations of light olefins carried out in ionic liquids. The practical work consists of three entities: The environmentally benign preparation of 1-alkyl-3-methylimidazolium-based ionic liquids under microwave activation, the characterization of ionic liquids and the use of the ionic liquids in the dimerization reaction.

Ionic liquids absorb efficiently microwave irradiation and the most beneficial aspect in the microwave-assisted preparations was the considerably shortened reaction time compared to the conventional methods. In addition to the microwave-assisted preparations, \([\text{C}_n\text{mim}]\text{[InCl}_4\text{]}\) ionic liquids were prepared successfully without microwave irradiation. A special attention was paid to the characterization of ionic liquids since impurities are known to affect on the properties of the ionic liquids. Ionic liquids were analysed with the following methods: \(^1\text{H}\) and \(^{13}\text{C}\) NMR, MS(ESI\(^+\) and ESI\(^-\)), GC and elemental analysis. Characterization of ionic liquids was done by determining the thermal stability, the melting point and the crystal structure of each solid ionic liquid. The determination of the liquid range of ionic liquid is necessary in order to know the temperature limits for each ionic liquid.

Novel InCl\(_3\) based ionic liquids revealed to be more efficient than Bronsted acidic ILs as a catalytic reaction media in the dimerization of 2-methylpropene. It was preferable to apply \([\text{C}_n\text{mim}]\text{Cl/InCl}_3\) (x(InCl\(_3\)) = 0.55) as a catalytic IL since then the conversion of 2-methylpropene and the product distribution revealed to be good. In order to maximize the production and the separation of dimers reaction should be carried out continuously at temperature high enough, such as 160 °C. Neutral InCl\(_3\)-based ionic liquid did not catalyze reaction of 2-methylpropene, but it had to be acidic x(InCl\(_3\)) > 0.5. Excess of InCl\(_3\) did not leach out from the IL and the recycling of IL was possible.

Keywords: 2-methylpropene, crystal structure, dimerization, green chemistry, ionic liquids, microwave irradiation
To my Grandmother
Acknowledgements

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Oulu, January 2007

Johanna Kärkkäinen
Abbreviations and definitions

Bu  butyl
Cy  cyclohexyl
[C\textit{n}mim]\+  1-alkyl-3-methylimidazolium cation
[C\textit{3}mim]\+  1,3-dimethylimidazolium cation
[C\textit{4}mim]\+  1-ethyl-3-methylimidazolium cation
[C\textit{4}C\textit{4} im]\+  1,3-dibutylimidazolium cation
[C\textit{6}mim]\+  1-hexyl-3-methylimidazolium cation
[C\textit{8}mim]\+  1-octyl-3-methylimidazolium cation
[C\textit{10}mim]\+  1-decyl-3-methylimidazolium cation
[C\textit{12}mim]\+  1-dodecyl-3-methylimidazolium cation
[C\textit{14}mim]\+  1-tetradecyl-3-methylimidazolium cation
[C\textit{16}mim]\+  1-hexadecyl-3-methylimidazolium cation
[C\textit{18}mim]\+  1-octadecyl-3-methylimidazolium cation
[Hmim]\+  1-hydrogen-3-methylimidazolium cation
dppp  bisdiphenylpropane
DSC  differential scanning calorimetry
Et  ethyl
ETBE  ethyl-\textit{t}ert-butyl ether
FID  flame ionization detector
GC  gas chromatography
IL  ionic liquid
i\textit{Pr}  \textit{iso}-propyl
i\textit{PTBE}  \textit{iso}-propyl-\textit{t}ert-butyl ether
MS(ESI)  mass spectrometry (electrospray ionization)
MsO  methylsulfonate
MTBE  methyl-\textit{t}ert-butyl ether
MW  microwaves
NMR  nuclear magnetic resonance spectroscopy
NTf\textsubscript{2}  bis(trifluoromethylsulfonil)imide
\textit{p}-TsO  \textit{para}-toluenesulfonate
Py  pyridinium
QUILL  Queen’s University Ionic Liquid Laboratory
TAME  tert-amylmethyl ether
TBA  tert-butyl alcohol
WHSV  weight hourly space velocity
TGA  thermal gravimetric analysis
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References
1 Introduction

Recently, the growing awareness of environmental issues has focused attention on the need for greener and more sustainable technologies in the chemical industry (1). The number of environmental laws and regulations has increased over the years, and more specific regulations have been set in order to provide a safer environment. The U.S. Environmental Protection Agency (EPA) has almost twenty different programmes for protecting the environment (2). Environmental legislation in Finland covers various sectors of environmental protection, and it originates mainly from the 1980s and 90s. The legislation was harmonized with relevant EC legislation, and pollution control legislation was revised in 2000 by passing the Environmental Protection Act (3). The current focus in legislation is mainly on waste prevention and chemical safety.

At the moment, the European Union is preparing a new chemical policy that aims to protect the environment and human health better against the harmful affects of chemicals. The policy will create a new system for the Registration, Evaluation and Authorization of Chemicals, known as REACH. A new European Chemicals Agency has been established in Helsinki and it will start operation after the REACH system has come into effect in 2007. The policy also aims to maintain the competitiveness of the European chemical industry.

The chemistry community has been mobilized to develop new chemistries that are less hazardous to human health and the environment. One of these approaches is the green chemistry movement, which is based on 12 principles developed by Anastas to prevent pollution (4). Green chemistry is not a part of the large field of chemistry, but it is a way of thinking and doing things better and more efficiently. Despite all the environmental regulations and broader knowledge about environmental issues, the traditional way of thinking still hinders the application of green chemistry principles as the standard practice in the development of new industry.

Principles of green chemistry (4):

1. It is better to prevent waste than to treat or clean up waste after it is formed.
2. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. Chemical products should be designed to preserve efficacy of function while reducing toxicity.
5. The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible, and innocuous when used.
6. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient pressure and temperature.
7. Raw material for feedstock should be renewable rather than depleting wherever technically and economically practicable.
8. Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.
9. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. Chemical products should be designed so that at the end of their function they do not persist in the environment and they break down into innocuous degradation products.
11. Analytical methodologies need to be further developed to allow for real-time in-process monitoring and control prior to formation of hazardous substances.
12. Substances and the form of substances used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

The fifth principle concerns the use of auxiliary substances in order to reduce or eliminate solvent waste in the chemical industry (2). Because solvents are often necessary in chemical reactions, alternative solvents have been developed. The ideal solvent should have very low volatility, and it should be chemically and physically stable, recyclable, reusable and easy to handle. One such candidate is an ionic liquid (IL). Unlike volatile organic compounds, ionic liquids have a low vapour pressure and they do not evaporate or burn very easily. This results in safer chemical processes, given that releases, explosions and fires will not take place so easily.

Therefore, ionic liquids, which consist of cations and anions, have become an interesting research topic in the last decade, and some books (5-8) and reviews (9-16) have been published about them. Many different ionic liquids have been prepared and they have been successfully used as solvents in diverse reactions, such as Diels-Alder (17,18), Friedel-Crafts (19,20), Heck (21), hydration (22), oxidation (23), alkylation (24), allylation (25), hydroformulation (26), esterification (27), dimerization (28) and polymerization reactions (29,30) and enzyme catalysis (31,32), often leading to better selectivity, yield and reaction rates than with volatile organic solvents. ILs have a great variety of chemical and physical properties that can be tuned with cations and anions (33). Ionic liquids are polar. Their water miscibility depends on their cation and anion composition. In addition, many catalysts are miscible into ILs and do not leach from them. Hence, ILs are ideal solvents for two-phase catalysis. When an IL contains a catalyst and a product forms its own layer above the IL phase, separation of the product is easy and recycling of the IL and the catalyst is possible. In addition, volatile products can be distilled from an IL, because ILs do not evaporate, or products can be separated by precipitation with a suitable solvent, that is miscible with the IL, but not with the product. After precipitation the applied solvent can be distilled from the IL that can be recycled for a next reaction.
Recently, ILs have been utilized in some industrial applications (34). BASF was one of the first companies that employed ILs. The process is called BASIL and it uses N-methylimidazol as a base to neutralize a formed hydrogen chloride, and as a result, 1-hydrogen-3-methylimidazolium chloride, IL is synthetized. Another company that applies ILs is IFP and the process is called Difasol.

The sixth principle of green chemistry considers a consumption of energy and its environmental and economic impacts. Nowadays, processes should use as little energy as possible, while maintaining high productability. Lately, microwave techniques have been applied in the chemical industry, especially in a pharmaceutical industry, owing to efficient heating ability of microwaves and hence a low energy consumption. Microwave irradiation is based on an absorption of energy that causes a reaction mixture to warm up. Ability to absorb energy depends on a chemical nature of a reactant, polar and ionic compounds absorb energy very efficiently. Therefore, ionic liquids have proved to be excellent solvent for microwave-assisted synthesis.

When new practices are developed it is important to have methods for measuring the “greenness” of the process. Since, an analysis based on a product life cycle is difficult to measure, the chemical industry utilizes parameters, such as E-number, atom economy, atom efficiency, reaction mass efficiency, effective mass production, in order to evaluate processes. Another more extensive approach is to measure eco-efficiency or efficiency of the process. According to the World Business Council for Sustainable Development eco-efficiency should be measured by ecological and economical parameters, such as consumption of energy, time, materials, water, amount of toxic chemicals and hazardous waste, releases to air, operating profit, earnings, turnover etc (3).

1.1 Aims of the study

The aim of this work was to study the dimerization reaction of 2-methylpropene (isobutene) to produce a high octane compound, isooctene, in an ionic liquid medium. Therefore, the literature survey consists of two parts: ionic liquids and the dimerization reaction. Until now, research has mostly focused on using ionic liquids in various chemical reactions and studying their physical properties, while their fundamental environmental aspects have been neglected. Studies have also shown that achieving high quality in ILs is very important. Therefore, the preparation and characterization of ILs, together with environmental aspects such as toxicity, biodegradability and recyclability, are highlighted. In the second part the acid-catalyzed dimerization reaction is reviewed, since most of the current technologies use acidic ion-exchange resins as a catalyst in the dimerization reaction (35,36). IFP’s Dimersol process is the only commercial process that uses a nickel catalyst (37). Recently, the process has been developed further and now ionic liquids are used in the process called Difasol (38). The use of ionic liquids has improved the separation of the products and made catalyst recycling possible. The drawback in the Difasol process is the hygroscopic nature of the chloroaluminate(III) ionic liquids utilized. Until now, most of the dimerization reactions of light olefins have been carried out with a nickel catalyst in chloroaluminate(III) ionic liquids (16,39). There are also a few patents concerning using these acidic ionic liquids in oligomerization and
polymerization reactions (40) and alkylation reactions (41). Recently, also oligomerizations in Brønsted acidic ILs were reported (42).

Based on the previously mentioned acid-catalyzed dimerizations, it was decided to study the dimerization reaction of 2-methylpropene in ionic liquids that can act both as a solvent and a catalyst. Since handling of commonly applied chloroaluminate(III) ionic liquids is difficult, novel indiumtrichloride-based Lewis acidic ILs, \([\text{C}_{n}\text{mim}][\text{InCl}_4]\), were prepared. In addition, some Brønsted acidic ILs were synthetized and utilized in the dimerization reaction. Selection of the Brønsted acidic ILs was based on an acid strength of an applied acid. It was also desirable that applied IL would have a melting point lower than 100 °C, preferably lower than 20 °C, providing a room temperature liquid IL and possess a moderate toxicity.

1.1.1 Preparation of ionic liquids

Preparation of ionic liquids, commonly understood as green solvents, is quite straightforward. The first step, and sometimes the only step, is a quaternization reaction that takes a rather long time to accomplish, even when heated with an oil bath (43). An attempt has been made to decrease the reaction time by carrying out the synthesis of the ionic liquids in an ultrasonic atmosphere (44). In the beginning of the 21st century, microwave activation made a breakthrough by shortening the reaction times considerably (45,46). Therefore, it was decided to study the preparation of ionic liquids under microwave irradiation. The preparations were done according to the principles of green chemistry whenever possible. The aim was to do the reactions atom-efficiently, without a solvent, in an energy- and time-saving manner. The quaternization reactions of a precursor ionic liquid, \([\text{C}_4\text{mim}]\text{Cl}\) 1, and sulfonate ionic liquids \([\text{C}_4\text{mim}][\text{TsO}]\) 2 and \([\text{C}_4\text{mim}][\text{MsO}]\) 3 were carried out in a single-mode microwave reactor designed for synthetic purposes (Fig. 1). Also \([\text{C}_4\text{mim}][\text{PF}_6]\) 4 was prepared with a metathesis reaction in a microwave reactor.

Fig. 1. Ionic liquids prepared under microwave irradiation.

In 2004, during my visiting period in QUILL and Professor Kenneth Seddon’s research group, indium(III)chloride-based ILs were successfully applied in Friedel-Crafts acylation reactions (47). Indium(III)chloride was selected as a Lewis acid for this study, since it resembles aluminium(III)chloride that catalyzes well dimerizations, but is not hygroscopic. The preparations of Lewis acidic ionic liquids were carried out without microwave activation, because of the reaction conducted with conventional heating is efficient enough, contrary to quaternization reactions. A set of eleven 1-alkyl-3-
methylimidazolium tetrachloroindates 5 was prepared from equivalent amounts of 1-alkyl-3-methylimidazolium chloride 6 and indium(III)chloride in order to study their properties (Fig. 2). Three of them: [C2mim]Cl/InCl3, [C4mim]Cl/InCl3 and [C6mim]Cl/InCl3 were selected for the dimerization study. The 1-ethyl-3-methylimidazolium chloride and indium(III)chloride mixture was studied in detail, since it is solid at room temperature. Its phase diagram revealed that certain ion pairs were formed with different compositions of [C2mim]Cl and InCl3, as was expected.

\[
\begin{align*}
\text{Cl}^- & \quad \text{InCl}_3 \\
\text{N} & \quad \text{N} \\
\text{C}_n\text{H}_{2n+1} & \quad \text{C}_n\text{H}_{2n+1} \\
\text{InCl}_4^- & \\
\end{align*}
\]

\(n = 0, 1, 2, 4, 6, 8, 10, 12, 14, 16, 18\)

Fig. 2. Set of 1-alkyl-3-methylimidazolium tetrachloroindates prepared with conventional heating.

### 1.1.2 Characterization of ionic liquids

The production of pure ionic liquids is very important, since impurities have a strong influence on their physical properties and stability. Hence, special attention was paid to characterization of the ionic liquids. The ionic liquids were analyzed with NMR, MS(ESI+ and ESI–) and elemental analysis. Their thermal stability was determined with TGA in order to know their upper temperature limit. Melting points were measured with DSC or a melting point apparatus. The determination of a liquid range of an ionic liquid is necessary in order to know a temperature range, where IL can be utilized. Their crystal structures were determined with a single crystal X-ray diffractometer for solid ionic liquids. The phase diagram of a 1-ethyl-3-methylimidazolium chloride and indium(III)chloride mixture was published by Yang et al. (48). We also determined it and were able to find more transitions and determine higher melting points for certain ion pairs. As Yang suggested, different ion pairs were formed with certain 1-ethyl-3-methylimidazolium chloride and indium(III)chloride compositions. We were able to recrystallize those ILs and confirm their structures with a single crystal X-ray diffractometer.
1.1.3 Dimerization reaction of 2-methylpropene

The acid-catalyzed reaction of 2-methylpropene 7 easily produces oligomers, such as tri-, tetra-, penta-, hexa-, hepta- and octamers, in addition to desired isooctenes, 2,4,4-trimethyl-1-pentene 8 and 2,4,4-trimethyl-2-pentene 9 (Fig. 3). By changing the reaction conditions, for example the ionic liquid, its composition, reaction temperature, gas flow rate and reaction setup, it was possible to control the product distribution to yield mainly dimers. The starting point for the reaction was to mix the catalytic ionic liquid with the gaseous starting material. The products were not miscible into the ionic liquid, and hence they formed their own layer above the ionic liquid. In order to get mainly dimers, once formed they should not be in contact with the ionic liquid, because then trimers are formed following the production of other oligomers. Therefore, after initial batchwise reactions in an autoclave, the reaction setup was changed to a continuous one. The catalytic ionic liquid was prepared by adding certain acid into the ionic liquid. The Brønsted acidic ionic liquids were: [C₄mim][PF₆] + HPF₆, [C₄mim][TsO] + TsOH and [C₄mim][MsO] + MsOH an the Lewis acidic ionic liquids were: [C₂mim]Cl + InCl₃, [C₄mim]Cl + InCl₃ and [C₆mim]Cl + InCl₃. The composition of the [Cₙmim]Cl/InCl₃ ILs varied from 1:1 to 1:2.

Fig. 3. Reaction of 2-methylpropene in a catalytic ionic liquid.
2 Ionic Liquids

The earliest discovery of an ionic liquid can be dated to the middle of the nineteenth century, when some “red oil” was observed in a Friedel-Crafts reaction (49). A few decades later, in 1914, the first room-temperature IL ethylammonium nitrate, \([\text{EtNH}_3][\text{NO}_3]\), was synthesized (50). In 1951 AlCl\(_3\)-based ionic liquids were developed by Hurley and Wier (51) at Rice Institute in Texas as a bath solution for electroplating aluminum. In 1963 the U.S. Air Force Academy became interested in that work and developed it further with the aim of finding new electrolytes for batteries. In the 1970s Osteryoung (52) and Wilkes (53) succeeded in preparing room-temperature liquid chloroaluminate melts. In the 1980s Hussey and Seddon (54,55,56) started to use these alkylpyridinium tetrahalidoaluminate, \([\text{Rpy}][\text{AlCl}_3\text{X}]\), ionic liquids as solvents in transition metal complex studies. The first organic reaction that was carried out in an acidic tetrachloroaluminate ionic liquid was Friedel-Crafts alkylation (57), and since then ionic liquids have been used as reaction solvents in various organic reactions. The first generation of ionic liquids that contain aluminium are very hygroscopic and air-sensitive, and therefore they are not easy to handle. A few years later this problem was solved when new air- and water-stable anions, such as halides, \([\text{PF}_6]^−\), \([\text{BF}_4]^−\) and \([\text{CF}_3\text{SO}_2]^−\), were discovered by Wilkes and Zaworotko (58). Since then, a wide selection of different ionic liquids has been synthesized. These ionic liquids are the second generation of ILs.

An ionic liquid is formed from organic cations and inorganic or organic anions, and it is possible to make even \(10^{18}\) different ILs. Commonly used cations are large and unsymmetric, e.g. derivatives of imidazolium, pyridinium, pyrrolidinium, ammonium, phosphonium and sulfonium (Fig. 4). Typical inorganic anions are e.g. halides, tetrachloroaluminate, hexafluorophosphate, tetrafluoroborate and bis(trifluoromethylsulfonyl)imide and typical organic anions are alkylsulfate, alkylsulfonate, \(p\)-toluenesulfonate (tosylate) and trifluoroacetate (Fig. 5).
The chemical and physical properties of ionic liquids can be tuned by selecting a certain anion and cation combination (33). Also, different ionic liquids can be mixed together to make binary or ternary ILs. The general definition of ionic liquids is that they have a melting point lower than 100 °C. The melting point of large, unsymmetric ions, whose charge can be distributed over a large volume, is low and hence the melting point of the IL can be far below 0 °C. Common table salt, NaCl, contains small, single-atom ions, and its melting point is therefore as high as 801 °C (59). Furthermore, ILs do not evaporate like volatile organic compounds do, but they will decompose at high temperatures. The decomposition temperature depends on the IL, and particularly on the anion. The low melting point and negligible vapour pressure lead to a wide liquid range, often more than 300-400 °C (60). For example, water has a liquid range of 100 °C.
The solubility of ILs is also tunable (12). Generally, ILs are miscible into polar solvents, but not into non-polar ones. The anion usually has a larger effect on solubility than the cation, but some fine-tuning can be done with the alkyl chains of the cation. The longer the alkyl chains are, the more non-polar the IL is. Water solubility is an important property, and it also varies according to the anion. Halides, tetrafluoroborate and triflate-containing ILs commonly are miscible with water, and hexafluorophosphate and bis(trifluoromethylsulfonyl)imide-containing ILs are immiscible. In addition to these properties, most ILs are non-flammable and recyclable.

More detailed information about the physical properties of ionic liquids can be found, e.g. in the book “Ionic Liquids in Synthesis” by Wasserscheid and Welton (7). The most important properties of ionic liquids are: thermal stability, low vapour pressure, electric conductivity, tunable solubility (possibility for biphasic systems), liquid crystal structures, high electroelasticity, high heat capacity and inflammability. These properties enable the use of ionic liquids in a wide range of applications, as shown in Fig. 6 (61).

Fig. 6. Selection of applications where ionic liquids have been used (61).

2.1 Conventional preparation of ionic liquids

Ionic liquids can be synthesized, e.g. from amines, phosphanes or sulfonates. The general synthetic paths for preparing ammonium-based ILs are shown in Fig. 7. The first step is usually a quaternization reaction, where an amine (NR₃) is alkylated with an appropriate alkylation reagent (R’X), e.g. alkyl halide or alkylsulfate, resulting in the corresponding IL. When an IL with a desired anion cannot be formed via this reaction, an anion exchange reaction is needed. A previously formed IL is used as a precursor, and the anion
is changed by a metathesis reaction or with a Lewis acid (MX1). The metathesis reaction can be performed by using a metal salt (MA), a Brønsted acid (HA) or an ion exchange resin. Nowadays, commonly used ionic liquids can be purchased from several commercial sources (Sigma-Aldrich, Fluka, Acros Organics, Merck, Solvent Innovation, Covalent Associates and Waco).

2.1.1 Quaternization reaction

Alkyl halides are widely used as alkylating agents in a quaternization reaction, since they are cheap and easily available. Quaternization is a simple reaction: the amine and the desired alkyl halide are mixed and the reaction mixture is heated. The reaction temperature and the reaction time depend on the reactivity of the alkyl halide. The reactivity decreases as a function of increasing alkyl chain length. The nature of the halide also influences the reactivity of the alkyl halide. Iodine is most reactive, followed by bromine and chlorine, as is expected for a nucleophilic substitution reaction, SN2. Preparation of [C4mim]Cl 1 from N-methylimidazole 10 and butyl chloride 11 is carried out at 80 °C for 2-3 days (Fig. 8) (43). Preparation of [C4mim]Br 12 from 10 and butyl bromide 13 is carried out under milder conditions at 50-80 °C for 12-24 hours (Fig. 9) (7, 62).

![Fig. 7. Synthetic paths for preparing ammonium-based ionic liquids (7).](image)

![Fig. 8. Preparation of 1-butyl-3-methylimidazolium chloride.](image)
The reactions are typically carried out in an inert atmosphere (N₂, argon). The formed ionic liquid is immiscible with the starting materials, and it forms a dense phase on the bottom of a reaction flask. Therefore, efficient stirring is necessary for the reaction to proceed. Sometimes solvents such as 1,1,1-trichloroethane (63), ethyl acetate (43) or toluene (64), are used in the reaction. These solvents are immiscible with the ionic liquid. ILs should be heated carefully, since excess heat during the preparation reaction generates a discoloured product indicating impurities might have been formed in the solvent. The formed ionic liquid may be dark brown. Using an excess of alkyl halide is effective for completing the reaction (43). Washing the crude IL with ethylacetate removes unreacted starting materials. The rest of the ethyl acetate is removed by heating the ionic liquid in a vacuum. Extremely pure ionic liquids can be obtained via crystallization.

Alkyl halides are used as alkylating agents, hence ILs based on halides are easily converted into ionic liquids with other anions. The problem in the following anion exchange reaction is that the complete exchange of Cl⁻ is difficult to accomplish. Therefore, other alkylating agents, such as methyltriflate 14 (63), methyl sulfate 15 (65), octyl tosylate 16 (66), and methyl tosylate 17 (67), have been used in the quaternization reaction (Fig. 10).

In addition to the quaternization reaction, the formation of an ionic liquid can also be carried out by protonating amine with an acid. The very first ionic liquid [EtNH₃][NO₃] 19 was synthesized from ethylamine 18 and nitric acid (HNO₃), see Figure 11 (68). Protonation of amine is also used, e.g. in the preparation of [Hmim][BF₄] from N-methylimidazole and tetrafluoroboric acid (69).

![Fig. 9. Preparation of 1-butyl-3-methylimidazolium bromide.](image1)

![Fig. 10. Alkylating agents used in a quaternization reaction.](image2)

![Fig. 11. Preparation of ethylammonium nitrate.](image3)
2.1.2 Anion exchange reactions

2.1.2.1 Lewis acid-based ionic liquids

In 1951 Hurley and Weir (51) reported about the preparation of a salt that was liquid at room temperature, based on the combination of 1-ethylpyridinium bromide with AlCl₃. More recently, Osteryoung (52) and Wilkes (53) developed a technology of room-temperature chloroaluminate melts based on 1-alkylpyridinium and 1-alkyl-3-methylimidazolium cations. Treatment of a quaternary halide salt \([R'RN]^+X^-\) with Lewis acid MX₃ results in the formation of more than one anion species, depending on the relative proportions of \([R'RN]^+X^-\) and MX₃.

The most studied system is a 1-ethyl-3-methylimidazolium chloride-aluminium(III)chloride mixture (70). The composition of the \([\text{C}_2\text{mim}]\text{Cl}/\text{AlCl}_3\) ionic liquid is studied with Raman (71), ²⁷Al NMR (72) and MS (73), and its phase diagram is determined with DSC analysis (69). The composition of Lewis acid-based ionic liquids is generally referred to as the mole fraction of monomeric acid present in the mixture, \(x(\text{AlCl}_3)\). When \(x(\text{AlCl}_3) < 0.5\), the mixture is basic and \([\text{C}_2\text{mim}]\text{Cl}\) is present in a molar excess over \(\text{AlCl}_3\), meaning that \(\text{Cl}^-\) is the dominant anion in the mixture (see the top equation in Fig. 12). When the mixture contains equivalent amounts of \([\text{C}_2\text{mim}]\text{Cl}\) and \(\text{AlCl}_3\), the dominant anion is \(\text{[AlCl}_4^-\) and the mixture is neutral, \(x(\text{AlCl}_3) = 0.5\). This shifts the equilibrium from the left-hand side to the right in the top equation. The acidic mixture \(x(\text{AlCl}_3) > 0.5\) contains an excess of \(\text{AlCl}_3\), and there are several anions in the mixture. The amount of \([\text{AlCl}_4^-\) decreases, and at the same time the amount of \([\text{Al}_2\text{Cl}_7^-\) increases. When \(x(\text{AlCl}_3) > 0.67\), \([\text{Al}_2\text{Cl}_10^-\) anions start to form; see the middle and bottom equations, respectively. For example, in the mixture of \([\text{C}_2\text{mim}]\text{Cl}/\text{AlCl}_3\) 1:2, the amount of \(\text{AlCl}_3\) is 0.66.

![Fig. 12. Series of equilibria in the reaction between \([\text{C}_2\text{mim}]\text{Cl}\) and \(\text{AlCl}_3\).](image)

Lewis acid-based ionic liquids are prepared by mixing appropriate amounts of a quaternary halide salt and a Lewis acid, and no solvent is needed. The reaction is exothermic, and hence the build-up of excess local heat can result in decomposition and discoloration of the ionic liquid. Therefore, the reaction mixture should be cooled with an ice bath and the Lewis acid should be added to the quaternary halide salt in small proportions. Since the reagents and the product are water-sensitive, the reaction should be carried out in a dry box. The use of \(\text{AlCl}_3\) as a Lewis acid in the preparation of an ionic liquid is mostly studied, but also other Lewis acids can be used, such as EtAlCl₂ (74), BCl₃ (75), CuCl (76), SnCl₂ and GeCl₂ (77) and InCl₃ (78).
2.1.2.2 Anion metathesis

In 1992 Wilkes and Zaworotko (58) reported the preparation of relatively air- and water-stable ionic liquids based on an 1-alkyl-3-methylimidazolium cation. They used silver salts, such as AgNO₃, AgBF₄ and Ag[CO₂CH₃], which are relatively expensive, and 1-ethyl-3-methylimidazolium iodine in their reactions that were carried out in methanol. Silver iodine was filtered after the reaction and the solvent was evaporated, yielding the pure ionic liquid. Later sodium, lithium and potassium salts have been used in metathesis reactions (63). Dichloromethane (79) or acetone (80) are usually used as solvents in metathesis reactions. Preparation of [C₄mim][PF₆] \text{4} from [C₄mim]Cl \text{1} and NaPF₆ takes 24 hours at room temperature, in either dichloromethane or acetone (Fig. 13). The organic phase is washed several times with water to extract NaCl from it. Finally, the solvent is evaporated to yield the ionic liquid, which is dried in a vacuum overnight.

![Fig. 13. Preparation of 1-butyl-3-methylimidazolium hexafluorophosphate.](image)

In addition to metal salts, Brønsted acids have also been used in metathesis reactions. [C₃mim][PF₆] is prepared from [C₃mim]Cl and HPF₆ in water (81). The reaction is exothermic, and therefore the reaction vessel has to be cooled with an ice bath. The formed [C₃mim][PF₆] precipitates and is separated by filtration.

\[
\text{Cl}^- + \text{NaPF}_6 \rightarrow \text{PF}_6^- + \text{NaCl}
\]

2.2 Microwave-assisted preparation of ionic liquids

It was the pharmaceutical industry that first started using microwave activation in drug discovery and development efforts at the end of the 20th century (45,46). Since then, the number of publications has continuously increased. In addition to many papers, also books about microwave synthesis have been published (82,83). Microwave-assisted preparation of ionic liquids has interested researchers for some years now, mostly because quaternization reactions are slow and microwaves have shown to shorten reaction times. Due to their ionic nature, ionic liquids will also heat very efficiently under microwave irradiation.

Most synthetic research has been conducted in domestic microwave ovens without any temperature, power or safety control. A serious problem with these ovens is that their energy is not dispersed evenly, and there are different levels of energy intensity detected as hot and cold spots. Hence, the demand for microwave ovens designed for laboratory use was clear. Nowadays, there are various microwave reactors on the market from several producers: CEM, Milestone and Biotage. These reactors are equipped with real-time temperature and pressure monitoring systems and automatic safety controls. Depending on the cavity design, microwave reactors can be grouped into multi-mode and
single-mode systems (84). Multi-mode reactors resemble domestic microwave ovens, but the monitoring and safety controls are more advanced in a multi-mode reactor. The applied electric field does not provide an equal distribution of energy and, to correct this, mode stirrers or turntables have to be used in multi-mode devices. The benefit of using multi-mode device is that many samples can be heated at the same time, but reactions are not very well reproducible. The total power generated in industrial multi-mode instruments can be high, typically 1000 - 1200 W, but the power density of the field is quite low due to the total volume of the cavity, typically 0.025-0.040 W/ml. Therefore, heating of small individual samples is difficult.

Single-mode systems were designed in order to obtain reproducible results. The applied electric field is more homogeneous in a single-mode than in a multi-mode system. Single-mode instruments produce one homogenous, intense pocket of energy. Due to their uniform energy distribution and higher power density, these systems typically couple more efficiently with small samples. Although single-mode systems have an output power of only 300 - 400 W, their small cavity volume and the single, focused energy pocket yield a density of 0.90 W/ml.

The trend in microwave-assisted synthesis is towards large-scale reactions. Flow-through systems based on multi-mode technology have been used in analytical applications, and now along with the single-mode technology new and more controllable flow-through reactors have been designed. These reactors emerged only a couple of years ago.

When this study was started there was one patent from Biotage AB (former Personal Chemistry) that concerned microwave-assisted preparation of ionic liquids (85) and a couple of papers about metathesis reactions carried out in a common microwave oven (86,87). Along with the necessary microwave reactor design, the first papers concerning performing a quaternization reaction in a multi-mode microwave reactor were published (88,89). At the same time this study was carried out in a single-mode microwave reactor (90).

### 2.2.1 Quaternization reactions

In 2003 Seddon et al. (88) studied the preparation of imidazolium- and pyridium-based halide-containing ionic liquids in a multi-mode microwave reactor. The reactions were controlled by power, and the power input was decreased according to the reactivity of the alkyl halides. The power was set at 300, 240 and 200 W for alkyl chlorides, alkyl bromides and alkyl iodines, respectively. The reaction conditions and yields of these reactions are shown in Table 1. Imidazole reacted faster than pyridine with the halides in the order iodine > bromine > chlorine.
Table 1. Comparison of reaction conditions in the preparation of some ionic liquids performed in a multi-mode reactor.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ionic liquid</th>
<th>Power W</th>
<th>Temperature ºC</th>
<th>Time min</th>
<th>Yield %</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[C₄mim]Cl</td>
<td>300</td>
<td>150</td>
<td>20</td>
<td>96</td>
<td>72</td>
</tr>
<tr>
<td>2</td>
<td>[C₄mim]Cl</td>
<td>300</td>
<td>150</td>
<td>24</td>
<td>91</td>
<td>73</td>
</tr>
<tr>
<td>3</td>
<td>[C₄mim]Br</td>
<td>240</td>
<td>80</td>
<td>6</td>
<td>93</td>
<td>72</td>
</tr>
<tr>
<td>4</td>
<td>[C₄mim]I</td>
<td>200</td>
<td>165</td>
<td>4</td>
<td>92</td>
<td>72</td>
</tr>
<tr>
<td>5</td>
<td>[C₄py]Cl</td>
<td>300</td>
<td>120</td>
<td>40</td>
<td>90</td>
<td>72</td>
</tr>
<tr>
<td>6</td>
<td>[C₄py]Cl</td>
<td>300</td>
<td>180 + 200</td>
<td>35 + 25</td>
<td>66</td>
<td>73</td>
</tr>
<tr>
<td>7</td>
<td>[C₄py]Br</td>
<td>240</td>
<td>130</td>
<td>30</td>
<td>95</td>
<td>72</td>
</tr>
<tr>
<td>8</td>
<td>[C₄py]Br</td>
<td>300</td>
<td>120 + 150</td>
<td>15 + 5</td>
<td>97</td>
<td>73</td>
</tr>
<tr>
<td>9</td>
<td>[C₄py]I</td>
<td>200</td>
<td>165</td>
<td>10</td>
<td>95</td>
<td>72</td>
</tr>
</tbody>
</table>

Rebeiro et al. (89) also prepared similar ionic liquids by using the same type of microwave reactor. [C₄mim]Cl was prepared under the same reaction conditions in both research groups, and the yields were 91% and 96%, see entries 1 and 2 in Table 1. Butylpyridinium chloride and bromide were prepared in different conditions. It appeared that a reaction temperature of 200 ºC was too high for butylpyridinium chloride, because the yield of the product was only 66% (entry 6) compared with a preparation made at 120 ºC (yield 90%, entry 5). On the other hand, the yields of the preparation of butylpyridinium bromide were almost the same (95% vs. 97%, entries 7 and 8), as were the reaction temperatures, as well.

1-Butyl-3-methylimidazolium bromide was prepared by Varma et al. (91) in a domestic microwave oven with a power of 240 W. After 75 seconds the reaction was finished. The yield was 86%, but the IL was brown. The reaction was faster in the domestic microwave oven than in the multi-mode microwave reactor (6 min, entry 3). Chan et al. (92) studied the preparation of 1-butyl-3-methylimidazolium bromide also in a domestic microwave oven, but they immersed the reaction vessel in a water bath, attempting to moderate the heat. The temperature of the water was 60 ºC at the beginning of the reaction and 80 ºC at the end. A 1.2 mol excess of butyl bromide was used, and the reaction was completed in 10 minutes, yielding 100% 1-butyl-3-methylimidazolium bromide.

2.2.2 Anion exchange reactions

2.2.2.1 Lewis acid-based ionic liquids

Only a few ionic liquids based on Lewis acids, such as [C₄mim][AlCl₄] (93) and [C₄mim][InCl₄] (94), have been prepared using microwave activation. The microwave-assisted reactions of the ionic liquids were performed in domestic microwave ovens. The reaction conditions in these preparations were not very accurate, since the reaction time was the only parameter that could be regulated. The temperature could not be controlled and the power level was not reliable. There was no possibility to stir during the
irradiation. So, the reaction mixtures were mixed with a vortex before irradiation and every now and then during the irradiation. This means the heating was done in several short periods. The reaction conditions are shown in Table 2. The preparation of \([\text{C}_4\text{mim}][\text{AlCl}_4]\) took 3.5 minutes to complete and the yield was 100%. The preparation of \([\text{C}_4\text{mim}][\text{InCl}_4]\) took only 30 seconds and the yield was 93%. The reaction between quaternary ammonium salt and Lewis acid is fast and exothermic, hence the use of microwave activation is not really necessary in these reactions.

Table 2. Reaction conditions in the preparation of Lewis acid-based ionic liquids performed in a domestic microwave oven.

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>Power W</th>
<th>Reaction time s</th>
<th>Yield %</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{C}_4\text{mim}][\text{AlCl}_4])</td>
<td>360</td>
<td>30 s x 7</td>
<td>100</td>
<td>97</td>
</tr>
<tr>
<td>([\text{C}_4\text{mim}][\text{InCl}_4])</td>
<td>600</td>
<td>15 s x 2</td>
<td>93</td>
<td>98</td>
</tr>
</tbody>
</table>

2.2.2.2 Anion metathesis

The microwave-assisted metathesis reactions of the ionic liquids were performed in domestic microwave ovens. Also in these preparations the reaction mixtures were mixed with a vortex before irradiation and every now and then during the heating. \([\text{C}_4\text{mim}][\text{BF}_4]\) was prepared from \([\text{NH}_4][\text{BF}_4]\) and I by Varma et al. (86) and \([\text{C}_4\text{mim}][\text{HSO}_4]\) was prepared from \(\text{NaHSO}_4\) and I by Singh et al. (87). The reaction conditions are shown in Table 3. The yields of these reactions were high and the reactions occurred fast.

Table 3. Reaction conditions for metathesis reactions performed in a domestic microwave oven.

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>Power W</th>
<th>Reaction time s</th>
<th>Yield %</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{C}_4\text{mim}][\text{BF}_4])</td>
<td>360</td>
<td>(60 s x 2) + (30 s x 3)</td>
<td>91</td>
<td>86</td>
</tr>
<tr>
<td>([\text{C}_4\text{mim}][\text{HSO}_4])</td>
<td>70</td>
<td>10 x 2</td>
<td>92</td>
<td>87</td>
</tr>
</tbody>
</table>

2.2.3 Conclusions concerning microwave-assisted reactions

The microwave-assisted preparations of ionic liquids published so far show that microwave irradiation clearly enhances the reaction rates. This is especially useful for quaternization reactions that take a rather long time to accomplish with conventional heating. Reactions carried out in domestic microwave ovens are not reproducible and therefore results are lacking a scientific value. Luckily, recent development of microwave reactors enables better reaction control, and hence more accurate results are gained. Until now, only alkyl halides have been used as alkylating reagents in the quaternization reactions of imidazole and pyridine.
2.3 Quality of ionic liquids

The purity of an ionic liquid is of paramount importance, since impurities influence its chemical and physical properties (95). Prior to use, ionic liquids should be carefully characterized with several methods, such as NMR, MS (ESI+ and ESI−) and elemental analysis. Ionic liquids have a very low vapour pressure and, therefore, cannot be purified by distillation. It is important to use purified starting materials in their preparation in order to get a pure ionic liquid. The main contaminants of ionic liquids are halides, water, organic compounds or inorganic salts. The application where an ionic liquid will be used determines the level of purity of the ionic liquid required. Solid ionic liquids can be characterized by determining their crystal structure, and the determined structures can be found in the Cambridge Crystal Database (96).

2.3.1 Halides, organic compounds and inorganic salts

Halides, organic compounds and inorganic salts present in a prepared IL are the result of unfinished reactions. In the preparation of [C₄mim]Cl (1), the possible impurities are unreacted organic starting compounds, N-methylimidazole 2 and butyl chloride 3 (Fig. 14). (43). Their presence can be detected quite easily by ¹H NMR spectroscopy. Volatile compounds, such as butyl chloride in this reaction, are easily removed by distillation. N-methylimidazole has a high boiling point (196 ºC) and, therefore, its removal by extraction with a volatile solvent (diethyl ether, dichloromethane or ethyl acetate) is preferred. The remains of extraction solvents can be removed in a high vacuum. In the case that the prepared ionic liquid is a solid at room temperature, it can be crystallized from an organic solvent.

![Fig. 14. Preparation of 1-butyl-3-methylimidazolium chloride (1).](image)

Inorganic salts result from metathesis reactions. Synthesis of [C₄mim][BF₄] (4) from [C₄mim]Cl (1) can be achieved with silver tetrafluoroborate, (AgBF₄) (63), or sodium tetrafluoroborate, (NaBF₄) (60). When NaBF₄ is used in a reaction, NaCl is formed as a by-product, as shown in Figure 15. If the metathesis reaction is not completed, the crude ionic liquid also contains unreacted halide-based IL. When the metathesis reaction is done with AgBF₄, the ionic liquid contains lesser impurities than when NaBF₄ is used, but the drawback is that silver salts are very expensive to use in a large amount.
A metathesis reaction should be carried out by using a solvent that dissolves the prepared ionic liquid, but not inorganic salts. Then, the insoluble halide by-product, such as NaCl, or the unreacted inorganic salt can be removed by filtration. When a Brønsted acid, such as HBF$_4$, is used in the metathesis reaction, HCl is formed as a by-product. If the IL is water-immiscible, the HCl and also inorganic impurities can be removed by washing with water (12).

Possible chloride impurities can be detected by titration with AgNO$_3$ (97), using a chloride-selective electrode (98), ion chromatography (99), inductively coupled plasma-mass spectrometry (ICP-MS) (100) or electrospray ionization mass spectrometry MS (ESI) (101-104). The alkali metal content can be determined by, e.g. selective electrode, atomic emission or atomic absorption spectroscopy (15).

Unfortunately, there is no general method for obtaining a halide-free ionic liquid. The best way to avoid halide impurities is to prepare a precursor ionic liquid for a metathesis reaction by using alkylation reagents other than alkyl halides e.g. alkylsulfonates (105). Halides are especially problematic if the ionic liquid prepared by metathesis is used in transition metal-catalyzed reactions, since a very small amount of chloride might be enough to deactivate the catalyst.

### 2.3.2 Water

Miscibility with water depends on the nature of the ionic liquid. Some ionic liquids are totally soluble in water, while others are not miscible at all (106). Most ionic liquids contain some water that might originate from its preparation or purification process. In addition, many ILs are hygroscopic. A large amount of water can be detected by $^1$H NMR spectroscopy, and a small amount by using a Karl-Fisher titrator (98).

Water is removed from ionic liquids by heating at 60–80 °C in a high vacuum for at least three hours, preferably overnight. Recently, it has been noticed that some ionic liquids have a tendency to decompose when heated in the presence of water. For example, ILs that contain hexafluorophosphate ions will form hydrogen fluoride when heated (107). This can be detected through pH measurement directly from the ionic liquid or from aqueous washings. Hydrogen fluoride is toxic, and consequently the use of hexafluorophosphate-based ionic liquids should be avoided (108).
2.3.3 Colour

Impurities sometimes affect the colouration of ionic liquids. The chemical nature of colouring impurities is not clear, but they are assumed to be oxidation products or thermal degradation products of starting materials (95,109). Even if the amount of the impurity is so small that it cannot be detected by $^1$H NMR or CHN microanalysis it might have significance on the application IL is used. Coloured impurities can be eliminated by using distilled reagents and a low reaction temperature. Especially amines very easily take on a yellowish colour upon standing, but distillation removes the colour. When the prepared IL is coloured, it can be purified with activated charcoal followed by filtration through activated alumina or silica (79).

2.4 Stability of ionic liquids

Considering the different applications where ionic liquids can be used, it is essential to know their stability. Stability can be evaluated in terms of thermal or chemical reactivity according to the temperatures and reaction conditions they withstand. The stability of ionic liquids also depends on their purity. Especially water and halide impurities will affect physical properties such as density, viscosity, melting point and degradation temperature. In reference to these, it can be concluded that impurities also affect chemical properties, and hence thermal stability and reactivity.

2.4.1 Thermal stability

The thermal stability of an ionic liquid is determined by the strength of the formed heteroatom-carbon or heteroatom-hydrogen bonds and the stability of the formed ion species. A N-C bond is stronger than a N-H bond and accordingly, the stability of ammonium cations decreases in the following order: quaternary > tertiary > secondary > primary (24). Quaternary ammonium or phosphonium salts are decomposed by a retro-quaternization reaction (reverse Menschutkin reaction) or a Hofmann elimination reaction (Fig. 16) (110). The retro-quaternization reaction produces amine and alkyl halide, which are used as starting materials in the preparation of an ammonium-based ionic liquid. The Hofmann elimination may be promoted by a trialkylamine formed in the retro-quaternization reaction. The Hofmann elimination produces alkene and tertiary ammonium halide from quaternary ammonium halide. At a sufficiently high temperature, decomposition occurs with complete mass loss and volatilization of component fragments.
Fig. 16. Decomposition of tetraalkylammonium salts by a retro-quaternization reaction (top) and a Hofmann elimination reaction (below) (110).

The degradation temperature is measured by using thermogravimetric analysis (TGA) or differential thermal analysis. The reported degradation temperature values of a certain ionic liquid vary largely (43,104,106,111-114). The values depend on both the measuring method and the interpretation of the data. Measurements have been done with different heating rates, ranging from 2 to 20 °C min⁻¹, in an air or dinitrogen atmosphere and by using different pan materials (aluminium, alumina, ceramic). Isothermal measurements have shown that the actual decomposition occurs at a lower temperature than fast scan TGA measurements indicate (115). More accurate measurements have been done during the last two years, and they are very welcome for providing information on the real stability of ionic liquids (116,117).

The general trend between different cations seems to be that a phosphonium cation is more stable than an imidazolium cation, and an ammonium cation is least stable in terms of thermal degradation. The stability of an imidazolium cation increases when nitrogen atoms and the carbon atom between nitrogens in the ring have alkyl substituents. Stability increases with straight alkyl chains compared with branched ones, not to mention the hydrogen atom as a substituent. TGA measurements show that quaternary ammonium chlorides decompose at around 150 °C and imidazolium-based ionic liquids at above 200 °C (33). Phosphonium-based ionic liquids decompose at above 300 °C (118).

The stability of ionic liquids depends largely on the anion (119). The more nucleophilic the anion is, the more easily it reacts via a retro-quaternization reaction, and hence the less thermally stable the IL is. This means that ionic liquids containing weakly coordinating anions are most resistant to thermal decomposition (Figure 17).

The degradation temperatures of some 1-alkyl-3-methylimidazolium-based ionic liquids are presented in Table 4. The degradation temperature increases only slightly when the alkyl chain is changed from ethyl to octadecane, but the anion has a much stronger effect on the degradation temperature. These temperatures have to be considered as indicative of resistance to thermolysis relative to other ionic liquids. The maximum operating temperature has to be lower than these degradation values indicate, since during reactions ionic liquids are kept at a high temperature for a certain time, not only a few minutes. The flashpoints of some imidazolium-based ionic liquids have also been measured. No flashpoints below 200 °C were detected (120).

\[
\text{R}_3\text{N}^+ \xrightarrow{X^-} \text{RX} + \text{R}_2\text{N}^+ \\
\left(\begin{array}{c}
\text{C} \\
\text{H} \\
\text{C} \\
\text{N}
\end{array}\right)^+ \xrightarrow{X^-} + \left(\begin{array}{c}
\text{C} \\
\text{H} \\
\text{C}
\end{array}\right)_3\text{NH}^+ \xrightarrow{X^-}
\]

Fig. 17. Coordinating ability of some common anions used in ionic liquids (119).
Table 4. Effect of an anion and the length of an alkyl substituent on degradation temperatures with some imidazolium-based ionic liquids (33).

<table>
<thead>
<tr>
<th>[C_n mim]X</th>
<th>T °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-alkyl-3-methylimidazolium chloride</td>
<td>240 – 290</td>
</tr>
<tr>
<td>1-alkyl-3-methylimidazolium hexafluorophosphate</td>
<td>330 – 420</td>
</tr>
<tr>
<td>1-alkyl-3-methylimidazolium tetrafluoroborate</td>
<td>350 – 410</td>
</tr>
<tr>
<td>1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide</td>
<td>400 – 480</td>
</tr>
</tbody>
</table>

* Chain length of alkyl substituent, C_n = C_2 - C_18.

### 2.4.2 Chemical stability

The chemical stability of ionic liquids has been studied with acids, bases and some other reagents. An ionic liquid is considered to be chemically stable when it does not react or decompose under reaction conditions. Until now, imidazolium-based ionic liquids have been the most studied and used. Research has shown that most imidazolium-based ILs withstand acidic conditions, but not basic ones (103). The reason is the acidic proton at the carbon atom between nitrogen atoms in the imidazolium ring. Even a mild base can remove it and decompose the ionic liquid. Stability towards bases slightly increases when this carbon atom is alkylated. When higher stability is needed, phosphonium-based ionic liquids are a good choice, since they are compatible even with strong bases (121).

Most ionic liquids are considered as inert solvents, but there are some studies where ILs have been reported to react with some reagents. In Heck reactions ionic liquids seem to react with metal catalysts and form an *in situ* carbene-palladium complex (122). In nucleophilic reactions some ionic liquids are not only inert solvents (123). This is the case when the ionic liquid contains a nucleophilic anion that might act as a nucleophile instead of added nucleophile. On the other hand, the added nucleophile might react with an imidazolium cation and dealkylate it. This has been reported to happen at elevated temperatures accompanied by a distinct colour change in ionic liquids (123). A similar phenomenon was observed when [C_n mim]Cl was prepared with microwave irradiation at elevated temperatures (90). New, undesired imidazolium-based cations were formed during the reaction.

### 2.5 Toxicity of ionic liquids

One of the most important aspects of designing new ionic liquids is an evaluation of the toxicological and ecotoxicological risks involved. In order to study the toxic effect of separate functionalities, Jastorff *et al.* (124,125) defined three types of sub-structures in ionic liquids: 1. A positively charged moiety, which he called a headgroup, 2. Substituents of the headgroup, called side chains and 3. A type of an anion. The toxicity of an ionic liquid has been tested on different levels of complexity in a few research laboratories (126-129). The aim was to screen a general toxicity potential by using quick and
inexpensive methods and to obtain information about the influence of structural variations of ionic liquids on their toxicity.

### 2.5.1 Acute toxicity

Acute toxicity was measured with *Vibrio fischeri* (luminescent bacterium) by Ranke *et al.* (127), and antimicrobial potential with a variety of bacteria, e.g. *Escherichia coli*, *Staphylococcus aureus*, *Bacillus subtilis*, *Pseudomonas fluorescens*, *Saccharomyces cerevisiae* by Docherty and Kulpa (126). The tests showed that a majority of the toxic effects of ionic liquids are acute and inhibit the respiration of an organism. The chemical nature of the headgroup influences its biological activity, but the influence varies, and in some cases is only marginal. The effect of an anion on toxicity is more complicated, and no general trend is found. The side chains have a much stronger influence on toxicity. The longer and more branched the side chain is, the more toxic is the ionic liquid. Most toxic ionic liquids have an alkyl chain with more than eight carbons.

Toxicity tests using *Vibrio fischeri* clearly indicate the influence of a side chain (Table 5). EC50 is the effective concentration (μM) where 50% of the cells die. The lower the EC50 value, the more toxic the ionic liquid. Concentration is usually presented as a decadic logarithm of the concentration, log EC50 (μM). For comparison, the log EC50 values of a selection of organic solvents are listed in Table 6. The least toxic solvents are methanol and acetone.
Table 5. Effect of the length of an alkyl chain and an anion on the acute toxicity of ionic liquids tested with Vibrio fischeri (126,127).

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>log EC₅₀ μM</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C₄mim]Br</td>
<td>3.07 (3.35)</td>
<td>126 (127)</td>
</tr>
<tr>
<td>[C₄mim][BF₄]</td>
<td>3.55</td>
<td>126</td>
</tr>
<tr>
<td>[C₄mim][p-TsO]</td>
<td>3.52</td>
<td>126</td>
</tr>
<tr>
<td>[C₄mim]Cl</td>
<td>2.95</td>
<td>127</td>
</tr>
<tr>
<td>[C₄mim][N(CN)₂]</td>
<td>2.99</td>
<td>127</td>
</tr>
<tr>
<td>[C₅mim][BF₄]</td>
<td>3.14</td>
<td>126</td>
</tr>
<tr>
<td>[C₆mim][BF₄]</td>
<td>2.15</td>
<td>126</td>
</tr>
<tr>
<td>[C₆mim]Br</td>
<td>0.81</td>
<td>127</td>
</tr>
<tr>
<td>[C₇mim][BF₄]</td>
<td>2.44</td>
<td>126</td>
</tr>
<tr>
<td>[C₈mim][BF₄]</td>
<td>1.41</td>
<td>126</td>
</tr>
<tr>
<td>[C₈mim]Br</td>
<td>0.07</td>
<td>127</td>
</tr>
<tr>
<td>[C₉mim][BF₄]</td>
<td>0.72</td>
<td>126</td>
</tr>
<tr>
<td>[C₁₀mim][BF₄]</td>
<td>-0.18</td>
<td>126</td>
</tr>
<tr>
<td>[C₄py]Br</td>
<td>2.73</td>
<td>127</td>
</tr>
<tr>
<td>[C₄py]Cl</td>
<td>2.64</td>
<td>127</td>
</tr>
<tr>
<td>[C₄py][N(CN)₂]</td>
<td>2.61</td>
<td>127</td>
</tr>
<tr>
<td>[C₅mpy]Br</td>
<td>2.12</td>
<td>127</td>
</tr>
<tr>
<td>[C₆mpy][N(CN)₂]</td>
<td>1.99</td>
<td>127</td>
</tr>
<tr>
<td>[C₇mpy]Br</td>
<td>1.48</td>
<td>127</td>
</tr>
<tr>
<td>[C₈mpy]Br</td>
<td>0.25</td>
<td>127</td>
</tr>
<tr>
<td>[C₉mpy]Br</td>
<td>2.08</td>
<td>127</td>
</tr>
</tbody>
</table>

N(CN)₂ = dicyanoamine

Table 6. Acute toxicity of organic solvents to Vibrio fischeri (59).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>log EC₅₀ μM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>5.00</td>
</tr>
<tr>
<td>Acetone</td>
<td>4.29</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>3.77</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>3.40</td>
</tr>
<tr>
<td>Chloromethane</td>
<td>3.08</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>2.79</td>
</tr>
<tr>
<td>Benzene</td>
<td>2.03</td>
</tr>
<tr>
<td>Methyl isobutyl ketone</td>
<td>1.90</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.50</td>
</tr>
<tr>
<td>Phenol</td>
<td>1.49</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>0.97</td>
</tr>
</tbody>
</table>
2.5.2 Cytotoxicity

The cytotoxicity of ionic liquids has been studied by using promyelocytic leukemia rat cell line ICP-81 cells (127) and acetylcholinesterase (128). Acetylcholinesterase was chosen by Stock et al. as a model enzyme because of its substrate, acetylcholine \( \text{21} \) (Fig. 18), possesses similar chemical structure than many cations used in ionic liquids. Acetylcholinesterase is an essential part of the nervous system of nearly all higher organisms, including humans. The active part of the enzyme consists of a catalytic site and an anionic site. The enzyme is inhibited by surfactants (cationic compounds) and various metals. Inhibition of this enzyme by an ionic liquid is assumed to occur via cation binding to the anionic site, which interferes with the charge-transfer interaction (128). Toxicological tests of tetrafluoroborate-based ionic liquids with ICP-81 and acetylcholinesterase also showed that the longer the alkyl chain, the more toxic the IL (Table 7).

![Fig. 18. Structure of acetylcholine.](image)

Table 7. Effect of the length of an alkyl chain in \([\text{C}_n\text{mim}]\text{[BF}_4\text{]}\) ionic liquids on cytotoxicity, tested with acetylcholinesterase (128) and an ICP-81 cell line (127).

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>Acetylcholinesterase log EC(_{50}) μM</th>
<th>ICP-81 log EC(_{50}) μM</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{C}_3\text{mim}]\text{[BF}_4\text{]})</td>
<td>2.28</td>
<td>&gt; 3</td>
</tr>
<tr>
<td>([\text{C}_4\text{mim}]\text{[BF}_4\text{]})</td>
<td>2.02</td>
<td>3.14</td>
</tr>
<tr>
<td>([\text{C}_5\text{mim}]\text{[BF}_4\text{]})</td>
<td>3.09</td>
<td></td>
</tr>
<tr>
<td>([\text{C}_6\text{mim}]\text{[BF}_4\text{]})</td>
<td>2.95</td>
<td></td>
</tr>
<tr>
<td>([\text{C}_7\text{mim}]\text{[BF}_4\text{]})</td>
<td>2.58</td>
<td></td>
</tr>
<tr>
<td>([\text{C}_8\text{mim}]\text{[BF}_4\text{]})</td>
<td>1.66</td>
<td>1.74</td>
</tr>
<tr>
<td>([\text{C}_9\text{mim}]\text{[BF}_4\text{]})</td>
<td>1.65</td>
<td></td>
</tr>
<tr>
<td>([\text{C}_{10}\text{mim}]\text{[BF}_4\text{]})</td>
<td>1.10</td>
<td>0.77</td>
</tr>
<tr>
<td>([\text{Benzylmim}]\text{[BF}_4\text{]})</td>
<td>2.10</td>
<td></td>
</tr>
<tr>
<td>([\text{Phenylethylmim}]\text{[BF}_4\text{]})</td>
<td>1.97</td>
<td></td>
</tr>
</tbody>
</table>

A comparison of pyridinium, imidazolium and phosphonium cations in toxicity tests with acetylcholinesterase showed that pyridinium as a cation inhibited enzymes more strongly than the corresponding imidazolium analog, and ILs based on a phosphonium cation were least inhibitory (128). The results are shown in Table 8. The reason for this behaviour might be that a phosphonium cation with long alkyl chains has a larger van der Waals radius and the charge is more shielded than with nitrogen analogs. The role of an anion in causing toxicity is not clear. In any case, \([\text{BF}_4\text{]}\) seemed to be more toxic in connection with imidazolium and phosphonium cations than \([\text{PF}_6\text{]}\), but with a pyridinium cation it was vice versa.
The toxicity of an anion to acetylcholinesterase was also tested by Stock et al. (128) with a 1-butyl-3-methylimidazolium cation, and the results are shown in Table 9. The effective concentrations are between 1.90 and 2.15, depending on the anion, and according to the study, halides seem to be the most toxic.

Table 8. Effect of the cationic part of an ionic liquid on cytotoxicity, tested with acetylcholinesterase (128).

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>Acetylcholinesterase log EC₅₀ μM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Butyl-3-methyl pyridinium tetrafluoroborate</td>
<td>1.53</td>
</tr>
<tr>
<td>1-Butyl-3-methyl pyridinium hexafluorophosphate</td>
<td>1.45</td>
</tr>
<tr>
<td>1-Butyl-3-methylimidazolium tetrafluoroborate</td>
<td>2.02</td>
</tr>
<tr>
<td>1-Butyl-3-methylimidazolium hexafluorophosphate</td>
<td>2.15</td>
</tr>
<tr>
<td>Tetradecyltrihexyl phosphonium tetrafluoroborate</td>
<td>3.47</td>
</tr>
<tr>
<td>Tetradecyltrihexyl phosphonium hexafluorophosphate</td>
<td>≥ 3.30</td>
</tr>
</tbody>
</table>

Table 9. Cytotoxicity of C4mim-based ionic liquids with various anions to acetylcholinesterase (128).

<table>
<thead>
<tr>
<th>Anion</th>
<th>Acetylcholinesterase log EC₅₀ μM</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF₆</td>
<td>2.15</td>
</tr>
<tr>
<td>BF₄</td>
<td>2.02</td>
</tr>
<tr>
<td>OctylSO₄</td>
<td>1.98</td>
</tr>
<tr>
<td>N(CN)₂</td>
<td>1.95</td>
</tr>
<tr>
<td>Triflate</td>
<td>1.94</td>
</tr>
<tr>
<td>Cl</td>
<td>1.92</td>
</tr>
<tr>
<td>Br</td>
<td>1.90</td>
</tr>
</tbody>
</table>

2.5.3 Toxicity to a higher organism

Release of certain ionic liquids into an aquatic environment may lead to water pollution, because of their high solubilities into the water. Acute toxicity tests on water fleas and saltwater bacteria were carried out by Jastorff et al. to assess aquatic toxicity (125). These bioassays show good sensitivity and have been used to evaluate the toxicity of many classes of chemical contaminants. The tested imidazolium-based ionic liquids were [C₄mim]⁺ cation with Br⁻, Cl⁻, [BF₄]⁻ and [PF₆]⁻ anions; [C₆mim]⁺ cation with Cl⁻, [BF₄]⁻ and [PF₆]⁻ anions and [C₈mim]⁺ cation with Cl⁻, [BF₄]⁻ and [PF₆]⁻ anions. Imidazolium cations with long alkyl chains were found more toxic than those with short alkyl chains. The data also indicate that the water flea is more sensitive to the toxic effects than bacteria. A comparison of the results with corresponding data for common organic solvents showed that ILs are more toxic than organic solvents to an aquatic environment.

Jastorff et al. carried out toxicity studies of ionic liquids by using plants [lesser duckweed (a floating aquatic organism) and garden cress (a fast-growing terrestrial
plant), which showed parallel results for the effect of the length of alkyl chains as were noticed in cell culture and enzyme tests. Both assays are more time-consuming to do than cell culture and enzyme tests. Therefore, only two ionic liquids, \([\text{C}_4\text{mim}]\)[BF_4] and \([\text{C}_8\text{mim}]\)[BF_4], were tested. Both studies showed that the toxicity of ionic liquids increases as a function of alkyl chain length (127).

*Caenorhabditis elegans* (a free-living soil roundworm) has been used to examine the toxicity and accumulation of pesticides and heavy metals. Therefore, this organism was chosen by Swatloski to study the toxicological effects of \([\text{C}_n\text{mim}]\)Cl (n = 4, 8 or 14) ionic liquids (129). The results were similar to those of the previous studies. The toxicity of ionic liquids increases as a function of alkyl chain length.

### 2.5.4 Conclusions about toxicity

The reported studies indicated that valuable information about structure-activity relations is gained from toxicological tests. Bacteria have been used in these investigations since they have short generation times. Quaternary ammonium, pyridinium and imidazolium cations were confirmed to have significant toxic effects on a variety of bacteria and fungi. Generally, the toxicity of ionic liquids increases as a function of alkyl chain length. Biological membranes are essentially non-polar interfaces, and the toxicity of chemicals is caused by the ability of the molecules to disrupt the integral membrane by hydrophobic/ionic adsorption at the cell membrane-water interface. Therefore, because hydrophobic molecules have a greater ability to accumulate at this interface, increasing toxicity would be expected with increasing hydrophobicity (130). Imidazolium-based ionic liquids have also demonstrated anti-microbial activity. Ionic liquids with a reasonably long alkoxy chain, such as OC_{10-14}, are active against cocci, rods and fungi (131).

 Principally, ionic liquids are more toxic than organic solvents when the comparison is based on effective concentrations. On the other hand, because of their low volatility and non-flammability, exposure to ionic liquids is far lower than to organic solvents. The relative risk to humans and the environment is the sum of these issues. The carcinogenicity, genotoxicity or teratological effects of ionic liquids are not yet available (129).

### 2.6 Biodegradability of ionic liquids

The chemical and physical properties of ionic liquids have been studied intensively since their discovery. Diverse modifications of cations and anions have provided ionic liquids with desired properties for many technical applications (62). Yet, the design of an ionic liquid with suitable properties for a specific application in view is not enough, and more attention needs to be paid to the total life-cycle impacts of ionic liquids. Studies on the biodegradation of ionic liquids and their potential accumulation in the environment have begun only recently (130,132). Degradation of organic compounds can be either aerobic or anaerobic. In both processes micro-organisms require a source of nitrogen and other
essential nutrients in order to decompose an organic substrate into carbon dioxide and water. A difference of the processes is that an aerobic treatment requires a source of oxygen and an anaerobic treatment requires an electron acceptor such as Fe$^{3+}$ (133).

### 2.6.1 Biodegradability tests

Biodegradation studies have been done for commonly used 1-butyl-3-methylimidazolium ILs with different anions, such as Br, BF$_4$, PF$_6$, Tf$_2$N, N(CN)$_2$ and octylOSO$_3$, using the Closed Bottle Test (OECD 301D) by Scammells (132). In the biodegradability test, the ionic liquid is added into an aerobic aqueous medium inoculated with wastewater microorganisms. The degradation ability of the compound is measured by the depletion of dissolved molecular oxygen after 28 days. A readily biodegradable compound has a degradation level higher than 60%. In the study, the reference compound was sodium dodecyl sulphate, which underwent very rapid biodegradation, $>60\%$, after 5 days. The tested ILs proved to be poorly biodegradable. The only IL that underwent a significant level of degradation, 25%, was [C$_4$mim][octylOSO$_3$].

Since C$_4$mim-based ionic liquids proved to be poorly biodegradable, some modifications were made to the alkyl chain. Scammells et al. (132) first incorporated an ester and then an amide functionality into the alkyl chain. See Figure 19 for the structures of ester and amide functional groups containing ionic liquids 22 and 23, respectively.

![Fig. 19. Structures of ionic liquids containing an ester 22 or an amide 23 functionality in the alkyl chain.](image)

Scammells reported that 3-methyl-1-(alkyloxycarbonylimidazolium)ionic liquids showed higher biodegradability than C$_4$mim-based ionic liquids they had previously tested (132). Biodegradation increased slightly with increasing alkyl chain length from methyl to octyl. The most biodegradable ionic liquid contained octylsulphate as an anion (49% biodegradation after 28 days). The biodegradation of other ionic liquids was 10-30% after 28 days. Amide analogs were found to be poorly biodegradable ($<5\%$ after 28 days). Biodegradation studies showed that incorporation of chemical bonds susceptible to enzymatic hydrolysis resulted in a significant enhancement of biodegradability. The biodegradability of ionic liquids might be low because they can be toxic to the microorganisms responsible for their degradation (133).
2.6.2 Accumulation in the environment

It is very important to develop biodegradable ionic liquids to prevent them from accumulating in the environment. Some preliminary studies on sorption of ionic liquids into soils and sediments have been carried out by Stepnowski (134). Tests were applied for a few [C\text{n}mim][BF\text{4}] (n = 1-10) that sorbed strongly into soil materials; agricultural soil, clayey soil, peaty soil and marine sediment. Desorption of ionic liquids from soil is shown to decrease with increasing alkyl chain length. Only 1.5% of initially sorbed 1-hexyl-3-methylimidazolium tetrafluoroborate is desorped.

Since certain ionic liquids are highly soluble in water, their release into an aquatic environment may lead to water pollution, but owing to their very low vapour pressure, their accumulation into the atmosphere is not expected.

2.6.3 Design of biodegradable compounds

The design of biodegradable compounds is not very advanced, but some functional groups are known to be more degradable than others. The idea of biodegradable ionic liquids started from a study on biodegradable surfactants by Boethling (135, 136). Many surfactants contain a tetraalkylammonium or dialkylimidazolium core. The studies indicated that biodegradation increased when a compound contained a functionality that might undergo enzymatic hydrolysis, or a functional group like a hydroxyl, an aldehyde, a carboxylate group, an unsubstituted linear alkyl chains or phenyl rings.

Additional factors that were found to be beneficial for designing biodegradable surfactants are structures that resemble natural products, or catechol, because they are easily degradable. On the other hand, many heterocyclic species, highly electron-withdrawing groups, ether groups or halide-containing bonds (C-Cl, C-F) are slow to biodegrade. Highly branched aliphatic chains degrade more slowly than a linear aliphatic chain, a water soluble compound is unlikely to be readily biodegradable, and increasing molecular weight decreases the rate of degradation (133).

2.7 Recycling of ionic liquids

Environmental considerations require the recovery of ionic liquids after their use. Ionic liquids are quite expensive, and hence their recycling is also necessary due to economic reasons. A review by Olivier-Bourbigou and Magna indicates that ILs have been successfully recycled in many reactions (137). Several procedures for recycling ionic liquids have been reported, and the efficiency of the recycling varies from poor to very good recovery. Examples of reactions using recyclable IL included palladium-catalyzed Heck reactions (121,138) oxidations of benzaldehyde and alkylbenzene (139), Friedel-Crafts acylations (19,20,140), copolymerization of styrene and carbon monoxide (141), and dimerization of propene (28).
Recyclability requires rates and yields to be maintained at a reasonable level after repeated reactions. In particular, reactions containing a transition metal catalyst immobilized into the ionic liquid of a biphasic reaction system have proved to be recyclable. Generally, recycling is based on the non-volatile nature of ionic liquids and the solubility differences between ionic liquids, organic compounds and water. Products can be extracted from ionic liquids with a non-polar solvent or they can be separated by distillation. A water-immiscible ionic liquid can be washed with water to get a water-soluble product or side products out of the reaction mixture.

### 2.8 Benign ionic liquids

Until now, research on ionic liquids has mainly focused on imidazolium-based ionic liquids because they have good, adjustable properties for many applications and they are easy to prepare. Growing concerns about environmental issues have led the design of ionic liquids into a direction where more attention is paid to ecotoxicology. New anion candidates have been suggested on the basis of the first toxicological and ecotoxicological studies. Imidazolium-based ionic liquids with acetate 24 and lactate 25 (142), saccharinate 26 and acesulfamate 27 (143) and amino acid-based anions (144) have been designed (Fig. 20). These anions form non-toxic, readily biodegradable and water-soluble ionic liquids. Combining these anions with non-toxic, biodegradable cations, e.g. butyryl choline 28, could result in new ionic liquids with benign properties. The need remains for poorly coordinating, hydrophobic anions that could replace commonly used fluorous anions such as [PF$_6$] and [NTf$_2$], until now, no potential candidates have been discovered.

![Figure 20. Biodegradable anions and cation.](image-url)
3 Dimerization

3.1 Introduction

Gasoline reformulation is one of the main chemical industries whose technology has to be improved (145). New legislation concerning gasoline properties was passed in the EU (146). It specifies that the evaporative emissions of gasoline have to be reduced, more complete combustion of gasoline has to be achieved and the amount of biofuel in gasoline has to be increased. Environmental regulations determine the composition of gasoline and diesel fuel. The main restrictions limit the amount of sulphur and total aromatics, especially benzene, and olefin in gasoline (147).

Gasolines are complex mixtures of hydrocarbons, and their quality is measured with three important properties that have the greatest effect on engine performance: vapour pressure, boiling range and antiknock characteristics (147). The vapour pressure of gasoline should not exceed limit values that are determined for certain temperatures, e.g. 75 kPa at 20 ºC. The typical boiling range for gasoline is 38-205 ºC. The knock resistance of gasoline is measured with octane numbers. They are determined by two laboratory tests. The motor octane number (MON) stands for engine performance on the highway and the research octane number (RON) stands for engine performance in city driving. The posted octane number (PON) is the average of the two, and it is the most well-known by the typical driver. By definition, the octane numbers for n-heptane and 2,4,4-trimethylpentane are 0 and 100, respectively.

Knocking is premature ignition of the fuel in the engine, and it can lead to engine damage. Therefore, gasoline is treated with additives that improve combustion. In 1921 the strong octane-boosting effect of tetraethyllead (Et_4Pb) was discovered. Et_4Pb was added into gasoline, until in the 1980s it was realized that it is environmentally harmful (148). Since then, tert-alkyl ethers, such as MTBE, ETBE and TAME, have been used as octane enhancers. The reason for the use of tert-alkyl ethers was the Clean Air Act (1990), which required a 2% oxygenate content in gasoline (3). MTBE is the most used of these oxygen-containing compounds, but because of its water solubility it has been found in groundwater in California. Therefore, in 2003, its use in gasoline was banned in California (149).
An important class of compounds for gasoline reformulation are branched saturated hydrocarbons, since they have a high octane number, low volatility and they do not contain sulphur or aromatics (147). Branched saturated hydrocarbons can be produced in different ways, e.g. by alkylation of olefins with isoparaffins (150) and by dimerization of light olefins followed by hydrogenation (149). An excellent substitute for MTBE is a branched hydrocarbon, 2,4,4-trimethylpentane, commonly called isooctane. Alkylation of 2-methylpropene (isobutene) with isobutane directly produces isooctane, and the dimerization reaction of 2-methylpropene produces 2,4,4-trimethyl-1-pentene 8 and 2,4,4-trimethyl-2-pentene 9 (RON= 100 and MON = 89). These pentenes can be used as such in gasoline, if the alkene limitations of gasoline are not exceeded. Or they can be converted into alkanes by hydrogenation. The hydrogenated product of 2,4,4-trimethylpentene is 2,4,4-trimethylpentane, and its octane numbers are RON = 100 and MON = 100 (151).

### 3.1.1 Sources of 2-methylpropene

2-Methylpropene is available from oil conversion processes, such as catalytic cracking, thermal cracking and steam cracking (152). These processes produce various olefins (e.g. C_3, C_4, C_5) that are separated by distillation. The amount and composition of the C_4 fraction obtained from the cracking of hydrocarbons depend on three factors: type of cracking process, severity of conditions and feed stock. The best condition for producing desired unsaturated C_4 compounds is steam cracking of crude gasoline under low severity conditions. The C_4 fraction consists of butadiene, n-butenes, isobutene, and isobutane. Butadiene is separated first from the C_4 fraction, and then it is called raffinate I. Almost half of the raffinate I is 2-methylpropene. For example, raffinate I from the steam cracking process contains 28-46% 2-methylpropene 7, 30-45% 1-butene 29, 5-15% 2-butenes (cis-2-butene 30 and trans-2-butene 31) and 4-8% isobutane 32 (Fig. 21). 2-Methylpropene is branched and more reactive than other butenes: 2-methylpropene >> 1-butene > 2-butene. Therefore, it can be separated by physical separation via selective molecular sieves or by chemical reaction that can be reversible or irreversible (153).

![Fig. 21. Composition of raffinate I.](image)

Lately, some new fluid catalytic cracking catalysts and processes have been discovered, and they have increased the production of light olefins (C_3-C_5) with respect to paraffins. In addition, the amount of branched olefins is increased with respect to linear ones. Therefore, the availability of 2-methylpropene is increasing continuously (154). A small part of 2-methylpropene is produced from isobutane dehydrogenation and tert-butyl alcohol (TBA) dehydration (155).
3.1.2 Factors that influence on dimerization reaction

The dimerization reaction can be controlled with various factors, such as catalyst, temperature, pressure, gas flow rate of olefin, additives and reactor design. Commonly applied catalyst systems for dimerization and also polymerization reactions are (156):

1. A proton catalyst that includes mineral acids, (H₃PO₄ or H₂SO₄), Lewis acids (BF₃, AlCl₃) and acidic ion-exchange resins (Amerlysts)
2. An organo-Al catalyst, such as a trialkylaluminium compound, and possibly a cocatalyst
3. Homogeneous and heterogeneous transition metal complexes

Trialkylaluminium catalysts can be used alone to produce products highly selectively. Higher activity is gained when they are used together with a transition metal cocatalyst, such as a nickel salt, but selectivity is then decreased (157).

In this study the main focus is on the acid-catalyzed reaction of 2-methylpropene, that is exothermic and proceeds very quickly even at low temperatures, and it is not limited by thermodynamic equilibrium. In addition to dimers, the reaction produces trimers and tetramers, etc. (147). Therefore, in the literature the term oligomerization is generally used for dimerization, trimerization, etc., and the products of these reactions are generally called oligomers when the number of monomers in them is between 2 and 10 (158). However, dimers are the most favoured products in the oligomerization reaction, because of their suitable properties for gasoline additives. Trimers have reasonable boiling points, but a high percentage of these is not favourable in gasoline. The boiling points of tetramers are too high, and hence they are not suitable for gasoline. The molecular mass of the product and hence the outcome of the reaction is dependent on many variables, especially temperature. Increasing the temperature generally results in products with lower molecular masses (157).

3.2 Reaction mechanism

3.2.1 Cationic mechanism for oligomerization

The acid-catalysed dimerization (or oligomerization or polymerization) reaction of 2-methylpropene proceeds with a cationic mechanism (159). The mechanism involves formation of a tertiary carbocation intermediate by transfer of a proton from the acid catalyst to the 2-methylpropene molecule, see Figure 22. Then the tertiary carbocation acts as an electrophile and reacts with the alkene to form a second tertiary carbocation produced from two 2-methylpropene monomers. Termination happens when the dimeric carbocation loses a proton, usually to water, and forms a dimer (E1).
When the carbocation is reasonably stable, this termination reaction is slower than chain elongation that produces first a trimer, then a tetramer and finally a polymer. The aim of using additives, such as water or lower alcohols, is to prevent chain elongation and to stop the elongation reaction after the dimeric carbocation has been formed (160). Instead of using a Brønsted acid catalyst, a stabilized carbocation can also be produced from 2-methylpropene with a Lewis acid, such as BF₃, and water as the proton source. This reaction easily produces a 2-methylpropene polymer (159).

### 3.2.2 Isomerization via Wagner-Meerwein rearrangement

Depending on the reaction conditions (catalyst, temperature, pressure), isomerization reactions may be observed during the oligomerization reaction. Isomerization can proceed by the migration of an alkyl group to a cationic centre, known as Wagner-Meerwein rearrangement (159). Migration of a methyl group stabilizes the cation. Usually it becomes tertiary instead of secondary and allows E1 elimination of H⁺ to take place, giving a stable alkene. Wagner-Meerwein rearrangement can also occur when the first-formed cation cannot eliminate H⁺ or the loss of the only available proton would give a very strained alkene. The reaction mechanism for the oligomerization reaction together with Wagner-Meerwein rearrangements is shown in Figure 23 (161).
Fig. 23. Oligomerization reaction of 2-methylpropene together with Wagner-Meerwein rearrangements (161).

Typically, in order to produce the highest possible substitution of the double bond, the equilibrium of alkenes favours the species with a double bond farther from the end of the carbon chain, but the opposite is observed with the 2-methylpropene dimer. The main products that form in the dimerization reaction of 7 are 2,4,4-trimethyl-1-pentene 8 and 2,4,4-trimethyl-2-pentene 9. A reaction of 2-methylpropene catalyzed with Amberlyst 15 yielded isomers 8 and 9 in a ratio of 3.5:1 (151). And a reaction catalyzed with 60% sulphuric acid produced isomers 8 and 9 in a ratio of 4:1 (160). Hence, the less-substituted alkene was the main product in both cases.

Fig. 24. Isomerization of 2,4,4-trimethyl-1-pentene 8 to 2,4,4-trimethyl-2-pentene 9.
Isomerization of 8 and 9 was studied in more detail by Karinen et al. (162), see Fig 24. Intermediate carbocation has two methyl groups, and hence six hydrogens, and one methylene group with two hydrogens, and elimination of a proton happens more readily from the methyl groups than from the methylene group. Therefore, the dimerization reaction of 2-methylpropene produces more 8 than 9. They also concluded that 8 is more stable than 9. The double bond of 9 is trisubstituted, and hence more crowded, than the disubstituted double bond of 8, and this causes more internal repulsion between the substituents. They noticed that the equilibrium constant for isomerization of 8 to 9 increased with a temperature rise, leading to a positive reaction enthalpy and meaning that isomerization is an endothermic reaction. When the reaction was carried out after equilibrium between 8 and 9 had been established, isomerization to C₈ alkenes other than 8 and 9 increased. 2,3,4-Trimethyl-1-pentene 33 and 2,3,4-trimethyl-2-pentene 34 were favoured over 8 and 9 in a gas phase. The formation of these isomers is slower because isomerization by the migration of the methyl substituent (Wagner-Meerwein rearrangement) is much slower than double bond isomerization. Below 90 ºC, the conversion to these species was only 1-3% per day, but isomerization increased rapidly as the temperature was raised. At 100-110 ºC the conversions were 20-30% per day.

Fig. 25. Structures of 2,3,4-trimethyl-1-pentene 33 and 2,3,4-trimethyl-2-pentene 34.

3.2.3 Products of codimerization of 2-methylpropene with n-butenes

Since commonly used C₄ feeds also contain 2-butene and 1-butene in addition to 2-methylpropene, they can react with 2-methylpropene, producing other C₈ isomers than 8 and 9. Codimerization of 2-methylpropene with 2-butene produces 3,4,4-trimethyl-1-pentene 35 and 3,4,4-trimethyl-2-pentene 36, 2,3,3-trimethyl-1-pentene 37, and 2,3,4-trimethyl-1-pentene 33 and 2,3,4-trimethyl-2-pentene 34 (Fig. 26).

For one, codimerization of 2-methylpropene with 1-butene produces hexenes, such as 5,5-dimethyl-2-hexene 38, 5,5-dimethyl-3-hexene 39, 2,3-dimethyl-1-hexene 40 and 2,3-dimethyl-2-hexene 41. These codimerization reactions are slower than homodimerization of 2-methylpropene, since 2-methylpropene is the most reactive of butene isomers. Codimerizations occur at a high temperature when linear butenes are present in high concentrations with respect to 2-methylpropene. Isomerization of 1-butene to 2-butene has also been observed at a high temperature. (Fig. 27) (151).
Fig. 26. Codimerization of 2-methylpropene with 2-butene (151).

Fig. 27. Codimerization of 2-methylpropene with 1-butene (151).
3.3 Common dimerization reactions

3.3.1 Acid-catalyzed dimerizations

Isooctene has been produced from 2-methylpropene with different acid catalysts, e.g. with sulphuric acid (160) and with phosphoric acid on an inert support (163). 60% sulphuric acid is known to produce mainly dimers, as was already mentioned in the reaction mechanism chapter. In the phosphoric acid-catalyzed dimerization reaction, the conversion of 2-methylpropene was 99%. The reaction was studied by Scharfe in 1973, and it produced 58% dimers, 38% trimers and 4% tetramers at 100 °C. In 1967 Haag (164) was the first to discover that Amberlyst 15, a synthetic organic ion-exchange resin (styrene-divinylbenzene copolymers with sulphonic groups as the functional structure), was highly active in the oligomerization reaction of 2-methylpropene. Ten years later O’Connor (165) studied the effect of the reaction conditions, such as the resin bead size, porosity, degree of functionalization, reaction temperature, reaction pressure and WHSV of the feed in the C4 alkene oligomerization reaction. He noticed that temperature had the largest effect on product distribution. The temperature limit was 150 °C according to the thermal stability of the Amberlyst catalyst (166). The conversion of alkenes increased, but the amount of dimers decreased when the temperature was increased from 100 to 150 °C (Table 10). The pressure was kept at 1.5 MPa in these reactions, and for the comparison the reactions were carried out at atmospheric pressure at temperatures of 90, 130 and 160 °C. These reactions gave much lower conversions than the high pressure ones. Also, the conversions increased with the temperature increase, and they were 10, 20 and 30%, respectively. The next reaction was carried out at 100 °C with the pressure as high as 2.7 MPa, but higher oligomers were produced instead of dimers. Higher oligomers poisoned the active sites of the catalyst and blocked the pores. In O’Connor’s study, the product distribution did not depend on the number of acid sites. It was concluded that acid sites with a strength greater than an equivalent sulphuric acid concentration of approximately 40% were required for the reaction to take place.

Table 10. Effect of temperature on the conversion of 2-methylpropene and product distribution in the dimerization reaction of 2-methylpropene catalyzed with Amberlyst 15 (163).

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Conversion %</th>
<th>Dimer %</th>
<th>Trimer %</th>
<th>Tetramer %</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>55</td>
<td>65</td>
<td>28</td>
<td>6</td>
</tr>
<tr>
<td>130</td>
<td>70</td>
<td>61</td>
<td>30</td>
<td>8</td>
</tr>
<tr>
<td>150</td>
<td>75</td>
<td>50</td>
<td>43</td>
<td>7</td>
</tr>
</tbody>
</table>

In 1985 Saus and Schmidl (167) studied the oligomerization of 2-methylpropene with a benzyl sulfonic acid siloxane catalyst. The catalyst is more stable than ion-exchange resins and can be used at reaction temperatures higher than 150 °C. A reaction that was carried out at 130 °C and under normal pressure yielded 52% dimers, 40% trimers, 3% tetramers and 2% odd-numbered products. The conversion of isobutene was 97%. The conversion of isobutene was even better than in O’Connor’s reaction that was carried out.
at 130 ºC under 1.5 MPa pressure and catalyzed with the Amberlyst (70%). Saus and Schmidl studied the effect of temperature on the reaction. The conversion of 2-methylpropene and the product distribution at different temperatures for each reaction is shown in Table 11.

Table 11. Effect of temperature on the conversion of 2-methylpropene and product distribution in the dimerization reaction of 2-methylpropene catalyzed with a benzyl sulfonic acid siloxane catalyst and carried out under atmospheric pressure (142).

<table>
<thead>
<tr>
<th>Temperature ºC</th>
<th>Conversion %</th>
<th>2-Methylpropene %</th>
<th>Dimers %</th>
<th>Trimers %</th>
<th>Tetramers %</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>24</td>
<td>1</td>
<td>74</td>
<td>2</td>
<td>23</td>
</tr>
<tr>
<td>100</td>
<td>54</td>
<td>7</td>
<td>44</td>
<td>33</td>
<td>16</td>
</tr>
<tr>
<td>150</td>
<td>41</td>
<td>18</td>
<td>57</td>
<td>23</td>
<td>2</td>
</tr>
<tr>
<td>200</td>
<td>43</td>
<td>37</td>
<td>56</td>
<td>7</td>
<td>-</td>
</tr>
<tr>
<td>250</td>
<td>61</td>
<td>63</td>
<td>37</td>
<td>1</td>
<td>-</td>
</tr>
</tbody>
</table>

Saus and Schmidl’s study indicated that the conversion of isobutene decreased due to pseudoequilibria between the initial oligomerization products and their splitting products at high temperatures. Above 100 ºC triisobutylene is split into diisobutylene and isobutene. Since the first formed dimers are in a liquid state, the formation of triisobutylene is favoured at temperatures up to 100 ºC. This also favours the solubility of isobutene. Beyond the boiling point of diisobutylene (110 ºC), this effect is reversed and the formation of higher oligomers is complicated, since the dimers are no longer in a liquid state. Therefore, the formation of tetramers disappeared at temperatures higher than 150 ºC in favour of a temperature-dependent equilibrium of isobutene, diisobutene and triisobutene.

After these first studies on the acid-catalyzed dimerization reaction, there has been a renewed interest in the dimerization reaction. A large number of patents have been issued on the subject during the last five years (168-173). Recently, Hauge (174) studied the oligomerization of 2-methylpropene with various zeolites and Amberlyst 15 in a liquid phase. Research indicated that zeolites deactivated rapidly, but Amberlyst showed a relatively good activity and stability, as has been seen already in Haag and O’Connor’s studies. Hauge’s results indicated that the reaction is a first-order reaction with respect to isobutene.

Dimerization of 2-methylpropene has also been studied at the Helsinki University of Technology, and as a result a doctoral dissertation was published in December 2005 (175). Honkela’s dissertation concentrates on selective production of diisobutenes via an ion-exchange resin-catalyzed dimerization reaction of isobutene in the presence of TBA and construction of a kinetic model for diisobutene dimerization (176-179). TBA was used as an additive to control reaction selectivity, since dimerization of isobutene in the absence of polar components gave a very low selectivity toward dimers. This was expected from the studies of Scharfe (163) and Di Girolamo (151). A reaction that was carried out at 90 ºC yielded 95% dimers and 5% trimers, while the conversion of 2-methylpropene was 45%. Hence, the use of TBA (2 mol%) decreased the rate of the reaction and increased the selectivity toward dimers. The conversion of isobutene increased with increasing temperature, also when TBA was used in the reaction. The
research was carried further, and dimerization of 2-methylpropene was studied in a miniplant-scale reactor in the presence of a solid macroporous ion-exchange resin catalyst and TBA (180). Also in this study, an increase in the reaction temperature increased the conversion of 2-methylpropene, while the selectivity toward dimers was decreased. The conversion of isobutene was 35% at 44 ºC and 63% at 75 ºC.

### 3.3.2 Dimerization as a side reaction in MTBE synthesis

Until the end of 1990, research in the Snamprogetti Research Laboratories had been focused on etherification technology that produces MTBE as a gasoline additive from 2-methylpropene and methanol (181). After the use of MTBE in gasoline was banned in California in 2003, they started to focus more on the dimerization reaction of 2-methylpropene, which had been a side reaction in MTBE synthesis (Figure 28).

![Fig. 28. Etherification reaction of 2-methylpropene that produces dimers as side products (181).](image)

They studied the reaction conditions and were able to find factors that favoured dimerization and factors that favoured an etherification reaction. Di Girolamo and Marchionna showed that the concentration of the acidic sites on resin had a strong effect on the dimerization reaction. The most active catalyst was found to be the most acidic, Amberlyst 35. Alcohol was used to modify the reaction rate and selectivity. Alcohol affects the reaction by being absorbed by the active sites of the catalyst and hence reducing its strength. Therefore, the conversion of 2-methylpropene was decreased and the selectivity toward dimers was increased. When methanol, ethanol or isopropanol was used as an alcohol, some MTBE, ETBE or iPTBE was formed, respectively. The thermodynamic equilibrium of the etherification reaction was less favorable for higher alcohols than for lower alcohols. When TBA was used, no ether was formed. On the other hand, during the reaction TBA can dehydrate and form isobutene and water. The formed water is absorbed very quickly by the acid sites and reduces the acidity of the catalyst, hence lowering the conversion of 2-methylpropene. It was also noticed that acidic sites located on the surface disfavoured the formation of higher oligomers. With this catalyst the conversion of isobutene was quite low, but the selectivity toward diisobutene was very good (182).

The process that produces diisobutenes and MTBE simultaneously is called the Isoether DEP (dimerization etherification process) (149). In the research, C4 streams from various sources were used, and hence the amount of 2-methylpropene varied between 28-46%. The C4 streams also contained 30-45% 1-butene, 5-15% 2-butene and 4-8% isobutane. One of the reactions was carried out at 75 ºC with a methanol/olefin ratio of 0.4, and the WHSV of the feed was 4.4/h (181). In the reaction, the C4 feed contained
38% 2-methylpropene and 89% of it was converted. Of the 2-methylpropene, 42% produced MTBE and 47% produced oligomers. The products of the oligomerization reactions were dimers (90%) and trimers (10%). The product distribution of the dimers was: 2,4,4-trimethyl-1-pentene, 2,4,4-trimethyl-2-pentene, 2,2-dimethylhexenes, 2,3-dimethylhexenes, 2,3,3-trimethylpentenes, 2,3,4-trimethylpentenes and 3,4,4-trimethylpentenes. The percentual product distribution is shown in Table 12. When the methanol/olefin ratio was decreased from 0.4 to 0.2, the conversion of 2-methylpropene did not change (88%), but now only 21% of it produced MTBE and 67% produced oligomers. The products of the oligomerization reactions were dimers (80%) and trimers (20%). Hence, the amount of dimers decreased from 90 to 80%, but the overall yield of oligomers was better.

Table 12. Product distribution of dimers produced in the dimerization reaction of a 
C₄ feed containing 38% 2-methylpropene (149).

<table>
<thead>
<tr>
<th>Dimer</th>
<th>% by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4,4-trimethyl-1-pentene 8</td>
<td>61.98</td>
</tr>
<tr>
<td>2,4,4-trimethyl-2-pentene 9</td>
<td>17.40</td>
</tr>
<tr>
<td>5,5-dimethylhexenes 38 and 39</td>
<td>7.55</td>
</tr>
<tr>
<td>2,3-dimethylhexenes 40 and 41</td>
<td>6.62</td>
</tr>
<tr>
<td>2,3,3-trimethylpentenes 37</td>
<td>0.72</td>
</tr>
<tr>
<td>2,3,4-trimethylpentenes 33 and 34</td>
<td>1.63</td>
</tr>
<tr>
<td>3,4,4-trimethylpentenes 35 and 36</td>
<td>3.80</td>
</tr>
<tr>
<td>other dimers</td>
<td>0.30</td>
</tr>
</tbody>
</table>

Similar results were also found in some other studies. Izquierdo et al. (183,184) showed that during their MTBE synthesis, high temperature and a low methanol/2-methylpropene ratio gave rise to diisobutene isomers in addition to MTBE products. When diisobutenes were present in a large proportion, trimers and higher oligomers were produced. These higher oligomers then promoted catalyst deactivation due to fouling.

Rehfinger and Hoffmann (185) noticed the same side reaction and started to study the dimerization reaction separately from MTBE synthesis. They showed that the reaction did not reach a true steady state, but the rate of activity declined and depended on the reaction conditions. In their study, production of diisobutenes was optimized with a fresh resin catalyst with a large particle size, a high reactant concentration and a low temperature.

3.3.3 Summary

In conclusion, some acid-catalyzed dimerization reactions of 2-methylpropene studied by Scharfe, Haag, Di Girolamo, Marchionna and Honkela are collected in Table 13. Trimers (5-40%) are formed in every reaction. The selectivity toward dimers is increased by using alcohol additives (entries 4 and 5). The use of methanol as an additive also produces MTBE in addition to oligomers (entry 4). The product distribution of oligomers is: 79% dimers, 20% trimers and 1% tetramers. By using TBA, the best selectivity toward dimers
is achieved (entry 5). No ether is formed, and hence the reaction produces only dimers (95%) and trimers (5%). Fortunately, the amount of tetramers is quite low in all cases, < 8%.

Table 13. Effect of the reaction conditions on conversions and product distributions in the dimerization reactions of 2-methylpropene catalyzed with different acids in a liquid phase.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Scharfe</th>
<th>Haag</th>
<th>Di Girolamo</th>
<th>Marchionna</th>
<th>Honkela</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion %</td>
<td>99</td>
<td>58</td>
<td>86</td>
<td>88-21-67</td>
<td>45</td>
</tr>
<tr>
<td>Dimers %</td>
<td>58</td>
<td>52</td>
<td>54</td>
<td>79</td>
<td>95</td>
</tr>
<tr>
<td>Trimers %</td>
<td>38</td>
<td>40</td>
<td>40</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>Tetramers %</td>
<td>4</td>
<td>8</td>
<td>6</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>MTBE %</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>21</td>
<td>-</td>
</tr>
<tr>
<td>Additive/isobutene</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>MeOH 0.2</td>
<td>TBA 2mol%</td>
</tr>
<tr>
<td>T °C</td>
<td>100</td>
<td>60</td>
<td>100</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Phosphoric acid slurry</td>
<td>Amberlyst15</td>
<td>Amberlyst15</td>
<td>Amberlyst15</td>
<td>Amberlyst15</td>
</tr>
<tr>
<td>Feed rate WHSV</td>
<td>1/h</td>
<td>5.5/h</td>
<td>5.5/h</td>
<td>36g/h</td>
<td></td>
</tr>
<tr>
<td>2-Methylpropene in the C₄ feed w%</td>
<td>45.4</td>
<td>30</td>
<td>45.4</td>
<td>53</td>
<td>100</td>
</tr>
</tbody>
</table>

3.4 Dimerizations carried out in ionic liquids

Depending on the nature of the ionic liquid, it can act as an inert solvent or as both a catalyst and a solvent. When an IL is prepared from equivalent amounts of starting materials, it is usually inert. Ionic liquids containing e.g. halides, alkylsulfonate, triflate or hexafluorophosphate as an anion are considered to be inert. Generally, ILs based on Lewis acids, such as AlCl₃, are considered as catalytic ionic liquids. The Lewis acidic properties of an ionic liquid depend on the nature of the anion and the molar ratios of the organic cation and inorganic anion. Acidic chloroaluminate ionic liquids have been used as both a solvent and a catalyst, e.g. in dimerization (28), oligomerization (40) and alkylation reactions (186).

In addition to Lewis acidic ILs, also Brønsted acids can form acidic ionic liquids (187). The Brønsted acidity of an IL can originate from both the cation and the anion. It comes from the cation when the quaternized N atom contains an acidic proton, e.g \([\text{Hmim}]^+\) and from the anion when it contains acidic protons, e.g. \([\text{HSO}_4]^-\), \([\text{H}_2\text{PO}_4]^-\). Also, an excess of Brønsted acid can be added to an inert second-generation IL to form a Brønsted acidic IL (42). Bronsted acidic ILs have been used, e.g. in oligomerization (188) and esterification reactions (189-192).
3.4.1 Dimerizations in [C₄mim]Cl/AlCl₃/EtAlCl₂ ionic liquids

Olivier-Bourbigou and Chauvin had much experience in performing the dimerization reaction in a single-phase system, on an industrial scale (IFP dimersol process), when they started to study the reaction in ionic liquids. They thought the ionic liquid would stabilize the active cationic nickel catalyst, [PR₃NiCH₂R’][AlCl₄], that was used in the Dimersol process. First, they focused on the dimerization of propene (74), and later they studied the dimerization reaction of butene (193). During the research they noticed that nickel complexes were catalytically active only in a [C₄mim]Cl/AlCl₃ ionic liquid with an acidic composition, since the basic ionic liquid contains strongly coordinating Cl⁻ anions that deactivate the catalyst. The acidic IL contains, in addition to [AlCl₄]⁻, other anions, such as [Al₂Cl₇]⁻ and [Al₃Cl₁₀]⁻, which produce higher oligomers by a cationic oligomerization mechanism. EtAlCl₂ was added to the acidic ionic liquid in order to reduce the cationic side reaction. Three acidic ILs, x(AlCl₃) > 0.5, were used in the dimerization reaction of propene: A [C₄mim]Cl/EtAlCl₂ (1:1.2), B [C₄mim]Cl/AlCl₃/EtAlCl₂ (1:0.82:0.26) and C [C₄mim]Cl/AlCl₃/EtAlCl₂ (1:1.2:0.1). These ILs contained different kinds of anions, such as [AlEtCl₃]⁻, [Al₂Et₂Cl₇]⁻, [AlCl₄]⁻, [Al₂Cl₇]⁻ and [AlEtCl₆]⁻, depending on the amount of AlCl₃ and EtAlCl₂ in it.

Fig. 29. Nickel-catalyzed dimerization reaction of propene in Lewis acidic ionic liquids (74).

The reactions were carried out under atmospheric pressure at different reaction temperatures, ranging from -15 to 15 °C, and heptane was used as a cosolvent to improve the product separation from the IL phase. The best IL proved to be C, which contained only a small amount of EtAlCl₂. The reaction was very selective, producing ca. 80-90% dimers and 10-20% trimers. The produced dimers were 2,3-dimethylbutenes 44, 2-pentenes 45, 4-pentenes 46 and n-hexenes 47 (Fig. 29). Good selectivity toward dimers can be ascribed to the lower miscibility of dimers into ionic liquids compared with monomers, hence reducing the formation of trimers. The reaction that was catalyzed with NiCl₂ without a ligand produced dimers with uncontrolled regioselectivity. In the following reactions, different phosphine ligands, such as P(Bu)₃, P(iPr)₃, P(cyclohexyl)₃, P(benzyl)₃, or pyridine, were applied to produce highly branched products. The product distribution showed to be dependent on the steric demands of the ligand in question. P(iPr)₃ and P(cyclohexyl)₃ were the most effective ligand candidates for producing 2,3-dimethylbutenes, shown in Table 14. 2,3-Dimethylbutene was then converted to methoxyether, which can be used as a fuel additive to increase octane number.
Table 14. Effect of a ligand on product distribution in the dimerization reaction of propene in a [C4mim]Cl/AlCl3/EtAlCl2 (1:1.2:0.1) ionic liquid catalyzed with a NiCl2 2L complex (74).

<table>
<thead>
<tr>
<th>L</th>
<th>T °C</th>
<th>P(iPr)3</th>
<th>P(cy)3</th>
<th>P(benzyl)3</th>
<th>P(Bu)3</th>
<th>Pyridine</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>-15</td>
<td>-15</td>
<td>-15</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>t h</td>
<td></td>
<td>1</td>
<td>1</td>
<td>4</td>
<td>4.5</td>
<td>3</td>
</tr>
<tr>
<td>Productivity kg/g Ni</td>
<td>100</td>
<td>65</td>
<td>34</td>
<td>100</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td>Dimers %</td>
<td>79</td>
<td>80</td>
<td>78</td>
<td>91</td>
<td>77</td>
<td></td>
</tr>
<tr>
<td>Trimers %</td>
<td>19</td>
<td>17</td>
<td>17</td>
<td>7</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>Oligomers %</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>2</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>

Dimer distribution:

- 2,3-Dimethylbutenes %: 83, 84, 46, 33, 7
- 2-Methylpentenes %: 7, 8, 18, 47, 47
- 4-Methylpentenes %: 8, 7, 33, 17, 28
- n-Hexenes %: 2, 1, 3, 3, 18

Oligomerization of 1-butene 29 was carried out at 10 °C under atmospheric pressure in a [C4mim]Cl/AlCl3/EtAlCl2 (1:1.2:0.1) IL with different nickel complexes (193,194). The aim was to study the effect of the different catalyst precursors on the reaction outcome. The product distribution remained the same in spite of the different catalyst precursors, but the activity of the catalyst was dependent upon the nature of the nickel catalyst. The activity of the catalysts increased in the following order: [Ni(PhCN)6][BF4]2, [Ni(MeCN)6][BF4]2, [Ni(MeCN)6][AlCl4]2, [Ni(MeCN)6][ZnCl4] and NiCl2(PBu3)2. When [Ni(MeCN)6][BF4]2 was used as a catalyst, the reaction produced 97% dimers and 3% trimers. The conversion of 1-butene was 70-80% and the product distribution of the dimers was 38% 3,4-dimethylhexenes 48, 56% 3-methylheptenes 49 and 6% n-octenes 50 (Fig. 30).

Fig. 30. Nickel-catalyzed dimerization reaction of 1-butene in a Lewis acidic ionic liquid (193).

A related system, [C4mim]Cl/AlCl3/EtAlCl2 (1:1.2:0.1), was also utilized in the oligomerization of ethene 51 (195). The behaviour of three different nickel catalysts, NiF2, NiCl2(Pcy3)2 and [Ni(MeCN)6][BF4]2, were studied in the reaction. The first two catalysts gave 1-butene 29 and 2-butene 30 and hexenes 47 as products, but the third one gave only butenes (Table 15). In the study, toluene was used as a cosolvent because heptane caused production of higher oligomers (Fig. 31).
Table 15. Effect of different Ni catalysts on product distribution in the oligomerization reaction of ethene carried out in a \([\text{C}_4\text{mim}]\text{Cl}/\text{AlCl}_3/\text{EtAlCl}_2\) (1:1.2:0.1) ionic liquid (195).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TOF h(^{-1})</th>
<th>Temperature °C</th>
<th>1-butene %</th>
<th>2-butene %</th>
<th>Hexenes %</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiF(_2)</td>
<td>326</td>
<td>25</td>
<td>18</td>
<td>49</td>
<td>33</td>
</tr>
<tr>
<td>NiCl(_2)(Pcy(_3))(_2)</td>
<td>7595</td>
<td>-10</td>
<td>10</td>
<td>53</td>
<td>37</td>
</tr>
<tr>
<td>[Ni(MeCN)(_6)]([\text{BF}_4])(_2)</td>
<td>1731</td>
<td>-10</td>
<td>83</td>
<td>17</td>
<td>-</td>
</tr>
</tbody>
</table>

TOF = Turnover frequency in mol of butene converted per mol of nickel per hour.

The nickel-catalyzed dimerization reactions of lower olefins in a \([\text{C}_4\text{mim}]\text{Cl}/\text{AlCl}_3/\text{EtAlCl}_2\) IL were carried out at low temperatures, since the alkylaluminium compound affected the temperature stability of the nickel catalyst reductively. In addition, at very high alkylaluminium concentrations a precipitation of black metallic nickel was observed, even in room temperature reactions, and with long reaction times (> 8 hours), small amounts of alkylaluminium compound leached into the organic phase.

### 3.4.2 Dimerizations in a \([\text{C}_4\text{mim}]\text{Cl}/\text{AlCl}_3/\text{base}\) ionic liquid

Wasserscheid and Keim (39,196) developed an alternative alkylaluminium-free IL for the dimerization of 1-butene 29, producing linear dimers. Since production of linear dimers was favoured, alkylaluminium dichloride, which is known to exhibit strong isomerization activity (28), was not used in their study. Instead of alkylaluminium, weak organic bases were applied to buffer all the acidic species in the ionic liquid that could catalyze the unselective, cationic oligomerization reaction. Therefore, the base should have the following properties: 1) It has to be reactive enough to eliminate all free acidic species in the IL. 2) It has to be non-coordinating with respect to the catalytic active Ni centre. 3) It has to have high solubility in the IL and it has to stay in the IL layer and not become extracted into the organic product layer. 4) It has to be inert against the butene feedstock and the oligomerization products. Hence, a possible base would be any cyclic, heterocyclic, or aliphatic, aromatic or non-aromatic base. Wasserscheid and Keim decided to use pyrrole, \(N\)-methylpyrrole and chinoline, pyridine, 2,6-lutidine, di-tert-butylpyridine, 2,6-dichloropridine and 2,6-difluoropyridine in the study. The composition of the ionic liquid they applied was \([\text{C}_4\text{mim}]\text{Cl}/\text{AlCl}_3/\text{base}\) 0.43:0.53:0.04. Dimerizations of \(n\)-butenes were carried out at 25 °C with a \((\text{Hcod})\text{Ni(hfacac)}\) nickel catalyst 52. The reaction time was varied in order to achieve comparable conversions for \(n\)-butenes, ca. 15-20%. Chinoline and \(N\)-methylpyrrole showed to be the best bases for
the reaction (Table 16). When chinoline or N-methylpyrrole was employed as a base in the IL, the reaction produced dimers, such as 3,4-dimethylhexenes 48, 3-methylheptenes 49 and n-octenes 50, with 98% selectivity (Fig. 32). The amount of favoured product, n-octenes, was 64% with chinoline and 51% with N-methylpyrrole.

Table 16. Effect of the base on product distribution in the dimerization reaction of 1-butene in a [C₄mim]Cl/AlCl₃/base ionic liquid catalyzed with 52 nickel complex (43).

<table>
<thead>
<tr>
<th>Base</th>
<th>TOF h⁻¹</th>
<th>Dimers %</th>
<th>Linear dimers %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrrole</td>
<td>1350</td>
<td>86</td>
<td>56</td>
</tr>
<tr>
<td>N-methylpyrrole</td>
<td>2100</td>
<td>98</td>
<td>51</td>
</tr>
<tr>
<td>Chinoline</td>
<td>1240</td>
<td>98</td>
<td>64</td>
</tr>
<tr>
<td>Pyridine</td>
<td>550</td>
<td>78</td>
<td>33</td>
</tr>
<tr>
<td>2,6-Lutidine</td>
<td>2480</td>
<td>55</td>
<td>68</td>
</tr>
<tr>
<td>Di-tert-butylpyridine</td>
<td>2100</td>
<td>49</td>
<td>68</td>
</tr>
<tr>
<td>2,6-Dichloropyridine</td>
<td>56</td>
<td>34</td>
<td>74</td>
</tr>
<tr>
<td>2,6-Difluoropyridine</td>
<td>730</td>
<td>29</td>
<td>72</td>
</tr>
</tbody>
</table>

TOF = Turnover frequency in mol of butene converted per mol of nickel per hour.

After the initial results, the lifetime and overall activity of the [C₄mim]Cl/AlCl₃/N-methylpyrrole ionic liquid system was studied (197). The reactions were carried out at 40 °C in a continuous flow loop reactor and samples were taken after one and three hours’ reaction time. The reaction produced 98% dimers and 2% trimers. The product distribution of the dimers stayed the same during the reaction: 2% 48, 40% 49 and 58% 50. The continuous experiment with linear dimerization of 1-butene resulted in overall activity (turnover frequency) of over 18000 for the Ni catalyst.

Later they applied nickel(II)heterocyclic carbene complexes, Ni₃₂(1-butyl-3-methylimidazolin-2-ylidine)_2 53 and NiCl₂(Pcy₃)_2 as a catalyst in the dimerization of propene and 1-butene in a [C₄mim]Cl/AlCl₃/N-methylpyrrole 0.45:0.55:0.1 ionic liquid (198), see Fig. 33. The reactions of 1-butene were carried out at room temperature for 30 minutes. Both catalysts gave a similar result. The product distributions were the following: 57% 48, 32% 49 and 12% 50 with Ni₃₂(1-butyl-3-methylimidazolin-2-ylidine)_2, and 59% 48, 27% 49 and 12% 50 with NiCl₂(Pcy₃)_2.
3.4.3 Dimerizations in Lewis acidic ILs without a nickel catalyst

In the beginning of the 1990s Seddon’s and Holbrey’s laboratories did some collaboration with British Petroleum Chemicals, and the research revealed that a wide range of acidic chloroaluminate(III) and alkylchloroaluminate(III) ionic liquids catalyzed cationic oligomerizations of alkenes (40,41). In the study, the olefinic feedstock was mixed or simply bubbled through the catalytic ionic liquid, 1-alkyl-3-methylimidazolium chloride/AlCl₃, x(AlCl₃) > 0.5, producing oligomeric products. The reaction temperature varied between -50 and 100 ºC. Even though the oligomerization reaction is exothermic, the temperature rise was not greater than 10 ºC during the reaction. The products had low solubility into the ionic liquid, and hence they separated as an organic phase above the IL. It is claimed that the catalytic activity of 1-alkyl-3-methylimidazolium chloride increased in the polymerization reaction with respect to the length of the alkyl chain, especially when the alkyl group contained more than five carbon atoms.

In 1993 Goledzinowski (199) studied the oligomerization of ethene and propene in three acidic ionic liquids, butylpyridinium chloride/AlCl₃ (1:2), hydrogenpyridinium chloride/AlCl₃ (1:2) and imidazolium chloride/AlCl₃ (2:3), without an added catalyst. The reactions were not very selective, as dimers and also odd-numbered hydrocarbons were produced. A hydrogen pyridinium chloride/AlCl₃ ionic liquid proved to have the best catalytic properties, which was thought to be related to a weakly bonded proton attached to the heterocyclic nitrogen atom.

Stenzel et al. (200) studied the oligomerizations of light olefins, ranging from ethene to octene, in a [C₄mim]Cl/AlCl₃/EtAlCl₂ (1:1:1:0.1) ionic liquid at 60 ºC. The results indicated that ethene was the most reactive of the olefins and 1-octene was the least reactive. Oligomerization of ethene produced 25% dimers, 36% trimers and 6% tetramers, with an overall yield of 67%. 1-Butene produced 30% dimers and 1% trimers, with an overall yield of 31%. In the case of 1-octene the reaction was very slow, and only 3% dimers and 1% trimers were formed with an overall yield of 4%. The reaction time was 16 hours in each case. When a TiCl₄ catalyst was used in the reactions, all the olefins produced polymers. The number of monomer units in the polymer varied between 8 and 35. Ethene was the most reactive also in the polymerization reaction.
In addition to the oligomerization of light olefins, polymerization reactions are also reported to happen in acidic chloroaluminate(III) and alkylchloroaluminate(III) ionic liquids. Ambler et al. (201) studied the polymerization reaction of isobutene and they assumed that the product distribution could be controlled with the nature of the cation. As a matter of fact, increasing the length of the alkyl group in a 1-alkyl-3-methylimidazolium cation or N-alkylpyridinium cation increased the degree of polymerization. The production of polyisobutylene in a [C_2mim][AlCl_4] ionic liquid at -40 ºC was patented by Murphy in 2002 (202). Polyisobutene is traditionally produced from raffinate I by the Cosden process, which applies a supported or liquid phase aluminium(III) chloride catalyst at temperatures between -10 and -100 ºC (152). Polyisobutenes with molecular masses between 300 and 2700 are obtained in the Cosden process. The use of an ionic liquid in the polymerization process makes product separation easy, since the polymers are not miscible into the IL. No aqueous washing is required to remove the catalyst, and hence the catalyst is not destructed at the end of the reaction, unlike in a traditional Cosden process.

### 3.4.4 Dimerizations in Brønsted acidic ionic liquids

1-Alkyl-3-methylimidazolium hexafluorophosphate [C_nmim][PF_6] ionic liquids (n = 4,6,8,10) were utilized in the oligomerization of ethene by Wasserscheid et al. (203). The reactions, catalyzed with a cationic nickel catalyst, were carried out at 25 ºC for 2 hours, and heptane was used as a co-solvent (Fig. 34). The nature of the ionic liquid did not change the product distribution. All the reactions gave mainly trimers, ca. 95%, and the selectivity toward 1-hexene was only a few percentage points lower. The rate of the oligomerization reaction was highest in the IL where the alkyl of the 1-alkyl-3-methylimidazolium cation was butyl, and it decreased when the length of the alkyl chain was increased to decyl. In spite of the catalyst’s water sensitivity, the IL including a Ni catalyst could be recycled at least three times. No leaching of the catalyst was detected.

![Fig. 34. Nickel-catalyzed trimerization of ethene in [C_nmim][PF_6] ionic liquids (203).](image)

SO_3H-functionalized imidazolium-based ionic liquids have been applied in the oligomerization reaction of 2-methylpropene (188). The reactions were carried out at 120 ºC for 6 hours, the ratio of ionic liquid to olefin was 1:4, and no added catalyst was used. The conversion of 2-methylpropene was 68% in 1-(4-sulfonic acid)butyl-3-methylimidazolium triflate and the selectivity toward dimers and trimers was 87%, but also tetramers were produced (Fig. 35). When the length of the alkyl chain in the 1-(4-sulfonic acid)butyl-3-alkylimidazolium cation was increased from...
methyl to hexyl, the conversion increased to 94% and the product distribution changed so that 61% dimers, 36% trimers and 3% tetramers were gained. The increase in the nonpolar character of the ionic liquid favoured the formation of higher oligomers because of the solubility of isobutene and because the solubility of the dimers into the ionic liquid layer was higher when its non-polar character was increased. The product formed its own layer above the ionic liquid, and this layer was decanted after the reaction. The same ionic liquid could be used at least seven times, and only a slight deactivation of the liquid was noticed.

There are also some patents that report about oligomerization reactions carried out in ionic liquids that contain Brønsted acids. For example, IFP has patented a system where dimerization of 2-methylpropene is carried out in a catalytic ionic liquid that consists of ionic liquid Q A and Brønsted acid HA (42). Typically the B of the Brønsted acid and the anion of the IL A are similar. The Brønsted acid could be selected from tetrafluoroboric acid, tetraalkylboric acid, hexafluorophosphoric acid, sulfonic acid, triflic acid, trifluoroacetic acid, etc. The molar ratio of Brønsted acid to ionic liquid should be between 0.01 and 0.7 for the dimerization reactions. If the oligomerization reaction is favoured, then the ratio of Brønsted acid to ionic liquid should be between 0.01 and 1. The patent claims that an ionic liquid combined with an excess of Brønsted acid provides a catalytic composition with improved activity compared with pure ionic liquid. Also a Lewis acid, such as AlCl₃, ZrCl₄, TiCl₃, BPh₃, BF₃ and SbF₆ (1-500 mmol), could be added to the catalytic IL.

One patent reports the oligomerization of 2-methylpropene performed in a [Hmim][BF₄] ionic liquid that acts as both a catalyst and a solvent. The reactions were carried out at temperatures between 45-110 °C for 10-50 hours in an autoclave (204). The conversion of 2-methylpropene varied between 52-95%, depending on the reaction conditions. The product distribution consists of 17-82% dimer, 16-81% trimers and 2% tetramers. The dimer selectivity toward 8 was very high, 74-78%. Yang et al. claimed that the process is simple, recyclable and environmentally friendly.
3.4.5 Summary

Most of the dimerization reactions done so far have been carried out in acidic chloroaluminate(III) ionic liquids with nickel catalysts. The patent literature, for one, includes dimerization reactions carried out in Lewis or Brønsted acidic ionic liquids without a nickel catalyst. The major benefit of using ionic liquids in the dimerization reaction is simplified separation of the products. ILs are polar, and hence non-polar products are not miscible into them. The biphasic procedure enables separation of the products by decantation. The cationic nickel catalysts used showed good activity in ILs and they do not seem to leach from the IL phase to the product phase. This makes recycling of the IL and the catalyst possible. However, the sensitivity to air and water limits the use of AlCl₃-based ILs.

3.5 Commercial dimerization processes

Nowadays, most commercial technologies use acidic ion-exchange resin catalysts in the production of isooctene. The reason for this is that heterogeneous ion-exchange resins offer advantages over homogeneous catalysts with respect to corrosion, pollution, product recovery and selectivity (149). The additives commonly used in the dimerization reactions are water and tert-butanol. They are used together with an acid resin catalyst to control the conversion and reaction selectivity. Without TBA the reaction kinetics favour the formation of larger oligomers of isobutene, such as trimers and tetramers. Reactions with acid resins have to be carried out at temperatures lower than 150 °C, because the catalyst is not thermally stable above that. On the other hand, low-temperature reactions produce more trimers and tetramers than high-temperature reactions, and the higher oligomers formed block the acidic sites of the catalyst and deactivate it.

Therefore, some commercial dimerization processes are catalyzed with a nickel catalyst together with a trialkylaluminium compound instead of an acid resin. IFP’s Dimersol process uses a cationic nickel complex, [PR₃NiCH₂R’][AlCl₄], as a catalyst. The process is homogeneous and hence it suffers from considerable catalyst consumption and waste disposal expenses. Therefore, IFP has developed the process further by using an ionic liquid in it. The new process is called Difasol, and it is biphasic. The biphasic procedure makes separation of the products simple and recycling of the catalyst possible. The commercial processes for using 2-methylpropene are introduced below.

3.5.1 NExOCTANE process of Neste Oil

Dimerization of 2-methylpropene has been studied very intensively by Neste Oil (35). In 1999 Alberta Ecofuels Inc (AEF), which is a joint venture between Chevron Texaco and Fortum Oy, started to study alternatives for its MTBE operation. Since there was no commercial process for isooctane production and it seemed to be the most economical option for them, they started to convert their MTBE unit to isooctane operation. Until
October 2002 AEF has produced isoctane in a liquid phase with an acidic ion-exchange resin catalyst in the presence of TBA and water. The process is called NExOCTANE and it generates 91-93% dimers and 7-8% trimers from fluid catalytic cracking or steam cracking C4 streams (205). The isoctene is then separated and hydrogenated to produce isoctane.

### 3.5.2 Isoether DEP of Snamprogetti

Snamprogetti Research Laboratories managed to change the reaction conditions of their Isoether DEP (dimerization/etherification process) so that mainly dimers were formed along with some MTBE production. (149). The technology was tested on an industrial scale in Ecofuel’s MTBE plant in Ravenna, Italy, in 1997 (36). In this process the reaction of 2-methylpropene was catalyzed with an acidic ion-exchange resin and methanol was applied as an additive to control the selectivity of the reaction. Later they used TBA as an additive and were able to produce dimers without MTBE production (Iso-OctEne process). Isooctene was then hydrogenated to produce isoctane (iso-OctAne process).

### 3.5.3 Other acid-catalyzed processes

One of the commercial process that produces isoctene from 2-methylpropene is the Universal Oil Products (UOP) InAlk process that uses a H3PO4/SiO2 catalyst in a fixed bed. The reaction is carried out at 170-220 °C under 40-60 bar, and the conversion of 2-methylpropene is 90%. Water is applied as an additive to control the conversion and the selectivity of the reaction (156). The Lyondell Alkylate 100 process is very similar to the NExOCTANE process used by Neste Oil. It produces isoctene and isoctane from 2-methylpropene and mixed C4 feedstocks. An acid resin is used as a catalyst and water or TBA is employed as an additive (206). ExxonMobil Chemical is the world’s largest producer of branched olefins, produced with the Bayer process. The process was also used in the oligomerization reaction of 2-methylpropene in a liquid phase. The process was carried out at 100 °C under 20 bars and catalyzed with an acidic ion-exchange catalyst, producing dimers and trimers in a ratio of 3:1. The conversion of 2-methylpropene was 99%. The advantage of the process is its simple technology. After the reaction, the catalyst is centrifuged off and and the mixture of butenes, dimers and trimers is separated by distillation (153).

### 3.5.4 Dimersol process of Institut Francaise du Petrole

Since the mid 1960s, Institut Francaise du Petrole (IFP) has studied dimerizations catalyzed with a catalyst consisting of a nickel compound and an aluminium trialkyl instead of commonly used acid resins (37). The Dimersol G process dimerizes propene and Dimersol X dimerizes butenes to the more valuable branched hexenes and octenes.
The Dimersol process is operated in the liquid phase without a solvent at temperatures between 40-60 ºC and at a pressure of 18 bars with a cationic nickel complex [PR₃NiCH₂R’][AlCl₄]. After the reaction, the catalyst is neutralized and the catalyst residue is separated from the products by aqueous washings. Unreacted olefins and inert hydrocarbons are separated from the dimeric products by distillation. Operation of the first Dimersol X plant was started by Nissan Chem. in Japan in 1980. In the Dimersol X process the conversion of butenes is 80% and the selectivity toward octenes is 85%. The reaction is second-order in monomer concentration and first-order in catalyst concentration. The advantage of the process is the low capital cost, as it is operated at low temperatures and therefore at low pressure, but separation of the products from the catalyst is a major problem. The catalyst is not recycled, and it leads to increased operational cost, since the waste has to be disposed and a new catalyst is required for the net reaction.

### 3.5.5 Difasol process of Institut Francaise du Petrole

IFP has modified its Dimersol process so that it uses a [C₄mim]Cl/AlCl₃/EtAlCl₂ (1:1:2:0.1) ionic liquid in the dimerization reaction of butene. The process is called Difasol, and it is biphasic, since the products are not miscible in the IL (38). The same cationic nickel complex, [PR₃NiCH₂R’][AlCl₄], is applied as a catalyst as in the Dimersol process. It does not leach from the IL phase to the product phase, and hence it is easily recycled with the ionic liquid, contrary to the Dimersol process. Therefore, nickel consumption is decreased by a factor of 10 in the Difasol process compared with Dimersol. The reactor volume is 40 times lower than in a homogeneous Dimersol process. Besides, the Difasol process is a first-order reaction relative to the monomer. The conversion of butene is 80-85% and dimer selectivity is 90-95%. The ratio of IL to the organic phase plays an important role. Too high a level results in a long decantation time and causes low dimer selectivity. The increase of the nickel concentration in the IL phase affects the olefin conversion by increasing it (207).

### 3.6 Conclusions

Dimerization of 2-methylpropene has been studied intensively, since iso octane has proved to be the best candidate as a gasoline octane enhancer. Another reason is the increasing availability of 2-methylpropene, since its use in MTBE production has decreased and new fluid catalytic cracking catalysts and processes have made it possible to increase its production. Currently, acid resins are the most used catalysts in the dimerization reactions, although they suffer from the catalyst deactivation to some extent. The Difasol process has revealed that using an ionic liquid in the dimerization reaction significantly improves the current Dimersol process, since the nickel catalyst is recyclable when an ionic liquid is used. However, sensitivity to air and water limits the use of chloroaluminate(III) ionic liquids. Ionic liquid research is still in its infancy, and more efforts to study the properties of ionic liquids and their behaviour under the diverse reaction conditions are needed.
4 Results and discussion

4.1 Preparation of ionic liquids

4.1.1 1-Butyl-3-methylimidazolium chloride

1-Butyl-3-methylimidazolium chloride \([\text{C}_4\text{mim}]\text{Cl}\) is a common precursor of many ionic liquids. Its preparation by the conventional method mentioned in the literature takes a rather long time, and excess heat easily produces coloured products (43). Recent studies have reported the preparation of 1 in a multi-mode microwave reactor (88,89). In this study microwave–assisted preparation of 1 was explored further with the objective of minimizing the formation of coloured side products and shortening the reaction time (90). Special attention was directed to the reaction temperature and the molar ratio of \(N\)-methylimidazole:butyl chloride in a closed single-mode microwave reactor designed for synthetic purposes. A solvent was not applied in the reaction, since both of the starting materials, \(N\)-methylimidazole 10 and butyl chloride 11, are liquids (Fig. 36).

![Fig. 36. Preparation of 1-Butyl-3-methylimidazolium chloride [C4mim]Cl.](image)

The first preparations of 1 were carried out at 150 °C, and the molar ratio of 10 and 11 varied between 1:1 and 1:1.5. The crude products were washed a few times with dry ethyl acetate. During the washings, \([\text{C}_4\text{mim}]\text{Cl}\) crystallized and the crystals were dried overnight in a vacuum. The best yield (90%) was obtained when the molar ratio was 1:1.1 and the reaction time was 10 minutes. A molar ratio higher than 1:1.1 decreased the yield. Since the ionic liquids were slightly yellow, the effect of temperature on the purity of the ionic liquid was studied. The preparation reaction of 1 was carried out at nine different temperatures ranging from 80 °C to 160 °C for 15 minutes, and the products
were analyzed with ¹H NMR and later with MS(ESI⁺ and ESI⁻). It was noticed that the reactions carried out at a high temperature (>110 °C) yielded coloured products. The ¹H NMR analysis of the reaction carried out at 160 °C revealed that something else was formed during the reaction in addition to [C₄mim]Cl. Therefore, the reaction mixture was analyzed with MS(ESI⁺ and ESI⁻). The MS(ESI⁺) spectra contained four peaks instead of the expected two, m/z 82 and 139, corresponding to [mim]⁺ and [C₄mim]⁺ cations. The extra peaks had m/z values of 97 and 181. The former peak was assumed to come from the 1,3-dimethylimidazolium, [mmim]⁺ cation, and the latter from the 1,3-dibutylimidazolium, [C₄C₄im]⁺ cation, 58 and 59, respectively (Fig. 37). This conclusion was consistent with the ¹H NMR analysis.

Fig. 37. Cations formed in the quaternization reaction of N-methylimidazole with butylchloride.

When other reaction mixtures were analyzed with MS(ESI⁺ and ESI⁻), the results revealed that [C₄C₄im]⁺ started to form when the reaction temperature was 140 °C, and the presence of [mmim]⁺ was first detected in the reaction carried out at 150 °C. The analysis showed that the optimal reaction conditions for microwave-assisted preparation of [C₄mim]Cl 1 were 130 °C for 15 min, since above this temperature (1,3-dimethylimidazolium chloride [mmim]Cl and 1,3-dibutylimidazolium chloride [C₄C₄im]Cl) side products from the transalkylation reaction started to form in addition to the ionic liquid, [C₄mim]Cl. Transalkylation reactions were not reported in quaternizations carried out in a multi-mode microwave reactor (88,89). However, this study revealed that the amount of side products depended on the reaction temperature and they could be avoided by performing the reaction at a low enough temperature.

4.1.2 Halide-free ionic liquids

Most preparations of ionic liquids have been carried out by the formation of an organic halide salt. The halide anion is then exchanged to give the desired ionic liquid by a metathesis reaction. For example, 1-butyl-3-methylimidazolium tosylate has been prepared from 1-butyl-3-methylimidazolium chloride and p-toluene sulfonic acid (208). As a consequence, the ionic liquid usually contains some halide contamination. Subsequent separation of the halide can be difficult, and impurities can change the properties of the ionic liquid (95). Therefore, halide-free ionic liquids have recently received some attention. The literature mentions conventional procedures for preparing alkylpyridinium or tetraalkylammonium tosylates and mesylates (209), tetraalkylphosphonium tosylates (210), imidazolium alkylsulfates (114), 1-hydrogen-3-methylimidazolium tosylate (211) and 1-butyl-3-methylimidazolium mesylate (212).
In this study, microwave-assisted preparation of halide-free ionic liquids was carried out by using sulfonate esters as starting materials. Since transalkylation products were formed in the preparation of 1, it was assumed that transalkylation might also happen in the preparation of 1-butyl-3-methylimidazolium p-toluenesulfonate 2 and 1-butyl-3-methylimidazolium methanesulfonate 3. The reaction conditions were optimized by using either temperature or power control. Use of a solvent was not necessary in these reactions, since the starting materials are liquids.

4.1.2.1 1-Butyl-3-methylimidazolium p-toluenesulfonate

1-Butyl-3-methylimidazolium p-toluenesulfonate, [C4mim][TsO] 2, was prepared from N-methylimidazole 10 and previously prepared butyl p-toluenesulfonate 60 (Fig. 38).

The preparations were carried out at eight different temperatures: 60, 70, 80, 90, 100, 110, 120 and 130 °C. The reaction time was 5 minutes in each reaction. It was noticed that the colour of the reaction mixture changed from pale orange to dark brown as the reaction temperature was increased. Since it seemed that a high reaction temperature yielded coloured products, the next reaction was carried out at 60 °C for 5 minutes. Simultaneous heating and cooling was applied to see how it would affect the reaction. The resulting crude product was dark brown. The amount of microwave energy was too high, and it clearly showed that, in order to avoid coloured ionic liquids, the amount of microwave irradiation should not be very high. Since the temperature-controlled reaction yielded coloured products, power regulation was used next. In the temperature-controlled reactions the temperature was kept at the set value and the power was varied accordingly. However, in these reactions the maximum power was 75 W. The following power-controlled reaction was carried out with the power at 20 W, because 75 W was assumed to be too high. The temperature stayed below 25 °C during the reaction, and no intense colour was seen. After the reaction the product started to crystallize upon cooling.

The reaction mixtures were analyzed with 1H NMR, and it showed that all the reactions were complete. The crude products were also analyzed MS(ESI) and they proved to be pure. MS(ESI+) showed the presence of only the [C4mim]+ cation, and MS(ESI−) showed only the tosylate anion. Hence, no transalkylated products were formed in these reactions. The crude products were washed three times with dry ethyl acetate and then crystallized from a 4:1 ethyl acetate/acetonitrile mixture. The crystals were dried overnight in a high vacuum. The yield of 2 was 88% in the reaction at 60 °C and 79% in the reaction at 130 °C. The products that were prepared at a lower temperature were
easier to purify and the crystals were white. Purification of the product from the high temperature reactions was labourious, and the crystalline product was brownish.

During the study it was noticed that unreacted N-methylimidazole was very hard to remove from the reaction mixture. Crystallization was the only way to remove it properly. However, ester 60 could be easily extracted from the product mixture with ethyl acetate. Therefore, the most efficient way to prepare 2 was to use an excess of ester (110 mol%) to consume all the N-methylimidazole and to make purification easy. After washing the excess of ester with ethyl acetate, the product crystallized easily.

Preparation of 2 was also attempted by using butanol as a solvent. The yield was low, only 15%, when the reaction was carried out at 130 °C for 15 minutes. As was expected, the use of butanol decreased the reaction rate owing to its ability to absorb microwave irradiation, but dibutyl ether was formed as a side product instead of producing only 2.

For comparison, 1-butyl-3-methylimidazolium p-toluenesulfonate 2 was also prepared at room temperature. Without heating, the reaction took several hours to complete. After 6 hours the yield was 78%. This result showed that microwave irradiation promoted the reaction, since under microwave activation, preparation required only 10 minutes at 25°C and the yield of the product was 85% (the power-controlled reaction).

Power-controlled conditions were a more efficient way to prepare the 1-butyl-3-methylimidazolium p-toluenesulfonate ionic liquid than was regulation by temperature. The time that sufficed to complete the reaction was short, only 10 minutes, and the resulting ionic liquid was nearly colourless. Simultaneous cooling made it possible to use stronger microwave irradiation, and hence the reaction proceeded faster than without cooling, but this kind of irradiation was too strong in this case. It was concluded from these results that the reaction temperature optimal for microwave-assisted preparation of 1-butyl-3-methylimidazolium chloride (130 °C) was too high for the preparation of tosylate ionic liquids. Tosylate is a better leaving group than chloride, and hence this reaction occurred under milder reaction conditions than the preparation of 1-butyl-3-methylimidazolium chloride, and no transalkylation products were observed to form.

**Attempt to prepare 18 as a one pot reaction**

Preparation of [C₄ mim][TsO] 2 was also attempted as a one pot reaction by using N-methylimidazole, butanol and p-toluenesulfonic acid. It was expected that the p-toluenesulfonic acid might first react with butanol to yield butyl-p-toluenesulfonate ester 61, which would further react with N-methylimidazole 10. The microwave-assisted reaction was carried out at 60 °C by using simultaneous heating and cooling for 15 min. After washings with ethyl acetate, white crystals were obtained. After ¹H NMR measurement and MS(ESI) analysis the product was verified to be 1-H-3-methylimidazolium-p-toluenesulfonate [Hmim][TsO] 62, see Figure 39.

Ionic liquid 2 could not be prepared in this way. In this reaction, butanol acted as a solvent and the only reaction that occurred was an acid-base reaction between N-methylimidazole 10 and p-toluenesulfonic acid.
4.1.2.2 1-Butyl-3-methylimidazolium methanesulfonate

The preparation of 1-butyl-3-methylimidazolium methanesulfonate, [C₄mim][OMs] 3 was based on the knowledge gained from the preparation of 1-butyl-3-methylimidazolium p-toluenesulfonate 2 and 1-butyl-3-methylimidazolium chloride 1. The starting compounds of 3 were N-methylimidazole 10 and previously prepared butyl methylsulfonate 61 (Fig. 40).

The preparations were carried out at three temperatures: 60, 100 and 130 °C. The reaction time was 5 minutes in each reaction. During these experiments it was noticed that the colour of the crude product did not change as much as in the reaction with butyl p-toluenesulfonate 60. Only the reaction at 130 °C produced a dark brown crude product. The reactions were monitored by GC, and it showed that the reactions performed at 60 and 100°C were not complete in 5 minutes. Therefore, the reaction time was increased to 10 minutes for these two reactions and, according to GC results, this was sufficient to complete the reactions. The crude products were also analyzed with ¹H NMR, and it indicated that one of the reactions was not complete. It was noticed that the FID was not sensitive enough to detect small amounts of N-methylimidazole. Therefore, the information from the GC analysis regarding the completeness of the reaction was misleading. According to the ¹H NMR spectrum, the reaction carried out at 100°C was finished in 10 minutes, but the reaction at 60 °C still contained some unreacted starting compounds. The crude products were also analyzed with MS(ESI), and no transalkylation products were formed in these reactions. MS(ESI⁺) confirmed the presence of only the [C₄mim]⁺ cation, and MS(ESI⁻) showed only the mesylate anion. The crude products from all three reactions were washed three times with dry ethyl acetate and then crystallized from a 3:1 ethyl acetate/acetonitrile mixture. The crystals were dried in a
high vacuum overnight. The yields of 3 were 67% (60 °C, 10 min), 85% (100 °C, 10 min) and 90% (130 °C, 5 min). However, the reaction should be carried out at 60 °C if colourless ionic liquids are required. Because the reaction was not complete in 10 minutes at 60 °C, it was repeated by using an excess of ester 61. Using the excess ester resulted in the completion of the reaction in 10 minutes, according to 1H NMR. When the unreacted ester 61 was washed with ethyl acetate, the product started to crystallize. Use of a slight excess of ester increased the reaction rate and made purification easy. The yield of the recrystallized 3 was 89%.

Preparation of 3 was also attempted by using butanol as a solvent. In this case the yield was better than in the preparation reaction of 2. 58% of 3 was formed in a reaction carried out at 130 °C for 30 minutes. Also now the use of butanol decreased the reaction rate, but only a small amount of dibutyl ether was formed as a side product.

As a reference, 1-butyl-3-methylimidazolium methanesulphonate 3 was also prepared at room temperature without heating. The reaction was very slow and it took four days to complete, and the yield of the purified product was 87%.

The reactions with 61 could be carried out with temperature control, no power controlled reactions were necessary. It seemed that 61 was not as reactive as 60 in a quaternization reaction, and hence mesylate was not as good a leaving group as tosylate. No transalkylation products were formed in the preparation of [C₄mim][OMs].

### 4.1.3 Anion exchange reactions

Only a few microwave-assisted anion exchange reactions have been reported until now. [C₄mim][BF₄], [C₄mim][HSO₄], [C₄mim][AlCl₄] and [C₄mim][InCl₄] have been prepared by using a household microwave oven (86,87,93,94). In this study, preparation of 1-butyl-3-methylimidazolium hexafluorophosphate 4 by means of a metathesis reaction was studied briefly in the single-mode microwave reactor (90). 1-Alkyl-3-methylimidazolium tetrachloridoindates were prepared without microwave irradiation.

#### 4.1.3.1 1-Butyl-3-methylimidazolium hexafluorophosphate

1-Butyl-3-methylimidazolium hexafluorophosphate, [C₄mim][PF₆], 4 was prepared from equimolar amounts of 1 and NaPF₆, see Figure 41. The reactions were carried out in acetone, since the starting materials were solids. The preparation reaction was done at different temperatures ranging from 80 °C to 100 °C, and the reaction time varied from 5 to 15 minutes. After cooling, a solid by-product, NaCl, was separated by filtration through Celite. Neutral alumina and Silica Gel were also appropriate filtration agents. Then the solvent was evaporated and the liquid product was dried in a high vacuum overnight. The products were analyzed with 1H NMR and MS(ESI+ and ESI-). The MS(ESI+) spectrum of 4 contained m/zs due to [C₄mim]+ (139) and [(C₄mim)₂][PF₆]+ (423), and the MS(ESI-) spectrum contained m/zs due to [PF₆]⁻ (145) and [C₄mim][PF₆]⁻ (429). The highest yield, 99%, was obtained from the metathesis reaction carried out at 80 °C in acetone with 10 minutes of reaction time. A shorter
reaction time or a higher reaction temperature seemed always to decrease yields. For comparison, the reaction was performed at room temperature without microwave heating, and it took 5 hours to complete. The yield of 4 was 83%.

![Fig. 41. Preparation of 1-butyl-3-methylimidazolium hexafluorophosphate, [C₄mim][PF₆].](image)

### 4.1.3.2 1-Alkyl-3-methylimidazolium tetrachloridoindates

Preparations of [Cₙmim][InCl₄] 5 ionic liquids were carried out without microwave heating, because the reaction conducted with conventional heating is efficient enough. The preparation reaction of [Cₙmim][InCl₄] IL is not very exothermic, and hence it could be heated with an oil bath. For comparison, preparation of chloroaluminate(III) IL is a very exothermic reaction, and hence chloroaluminate(III) has to be added to the [Cₙmim]Cl in small batches and cooled simultaneously with an ice bath in order to avoid decomposition of the product (53). [Cₙmim]AlCl₄ is also air- and water-sensitive. The chloroindate(III) ILs that were synthesized are more air- and water-stable than chloroaluminate(III) ionic liquids, and hence easier to handle.

![Fig. 42. Preparation of 1-alkyl-3-methylimidazolium tetrachloridoindates, [Cₙmim][InCl₄].](image)

Different 1-alkyl-3-methylimidazolium tetrachloridoindate salts 5 with the general formula [Cₙmim][InCl₄] (n = 0, 1, 2, 4, 6, 8, 10, 12, 14, 16 and 18) were prepared from equimolar amounts of [Cₙmim]Cl 6 and indium(III) chloride (Fig. 42). Both of the starting materials are quite hygroscopic, and for that reason the reactions were carried out in a dinitrogen atmosphere. Before use the [Cₙmim]Cl was dried in a high vacuum overnight. InCl₃ was used without purification. Solid [Cₙmim]Cl was heated with an oil bath until it melted, and after that InCl₃ was added to the melt in small portions. At the same time the reaction mixture was stirred well. The reaction mixture was stirred for a while after a homogenous mixture was formed at the temperature that was adjusted according to the melting point of [Cₙmim]Cl, and then it was allowed to cool down to room temperature. Finally, all the products were dried in a high vacuum. [Hmim][InCl₄] and [mmim][InCl₄] crystallized upon cooling. [C₄mim][InCl₄], [C₆mim][InCl₄], [C₈mim][InCl₄] and
[C₁₀mim][InCl₄] are liquids at room temperature. [C₁₆mim][InCl₄] and [C₁₈mim][InCl₄] crystallized when the product was dried in a high vacuum. [C₂mim][InCl₄], [C₁₂mim][InCl₄] and [C₁₄mim][InCl₄] crystallized upon standing in a freezer. The salts were analyzed with a combination of ¹H NMR, ¹³C NMR and elemental analyses. The ¹H and ¹³C NMR spectra are very similar for all the [Cₙmim][InCl₄] salts. The chemical shift of the C(1)-H protons did not show the large downfield shift related to hydrogen bonding that was observed with the chloride salts.

4.1.4 Summary

The quaternization reaction proceeds by an S₂N₂ mechanism. Therefore, both the nucleophile and the alkylating reagent have a strong influence on the reaction rate. The preparations were performed more efficiently without a solvent. The nucleophile in all the quaternization reactions was N-methylimidazole. The alkylating reagents applied were butyl chloride, butyl methanesulfonate and butyl p-toluenesulfonate, yielding [C₄mim]Cl ¹, [C₄mim][OTs] ² and [C₄mim][OMs] ³, respectively. The reaction rates in the preparations of ionic liquids depended on the alkylating reagent, and the rates decreased in the following order, butyl p-toluenesulfonate > butyl methanesulfonate > butyl chloride. In other words, the leaving group determined the reaction rate. Tosylate was the best of these three leaving groups, and hence preparation of ² was the fastest and preparation of ¹ was the slowest reaction. Transalkylation as a side reaction was observed only when preparing ¹ at elevated temperatures. Preparation of ² required slight activation by using very low microwave power and a short reaction time. Optimal reaction conditions were achieved by using power control: 20 W of power, a temperature of 25 °C and a reaction time of 10 min. Formation of ³ required more activation, and its preparation was carried out at 60 °C in 10 minutes. The optimal reaction conditions for the preparation of ¹ were found to be 15 min at 130 °C. Using a small excess of alkylating reagent ensured completion of the reaction and easy purification of the product. In addition, the excess alkylating reagent decreased the viscosity of the reaction mixture, making stirring more effective.

A metal salt or a Lewis acid was applied in the anion exchange reactions. Preparation of [C₄mim][PF₆] ⁴ by means of a metathesis reaction was studied with microwave activation, but the reactions with InCl₃ Lewis acid were carried out without microwaves. The optimized reaction temperature and reaction time for ⁴ were found to be 80 °C and 10 minutes. [Cₙ-mim][InCl₄] ILs ⁵ were prepared successfully with conventional heating.
4.2 Characterization of ionic liquids

4.2.1 Quality of ionic liquids

The preparations of the ionic liquids were monitored with $^1$H NMR, GC and MS(ESI$^+$ and ESI$^-$). $^1$H NMR proved to be generally the most efficient method for monitoring a quaternization reaction. Both the reagents and the resulting ionic liquid could be detected from the $^1$H NMR spectrum. Monitoring with GC or GCMS was also applied in some cases. Ionic liquids do not evaporate, and hence the only compounds expected to be detect were the starting components, $N$-methylimidazole and the alkylating reagent. When the results of the $^1$H NMR and GC analyses were compared, it was noticed that the FID was not sensitive enough to detect small amounts of $N$-methylimidazole. Hence, the completeness of the reaction could not be interpreted reliable with GC analysis.

MS(ESI) proved to be a very useful technique for following the metathesis reactions, because ions are easily detected with it. $^1$H NMR was not as reliable as MS(ESI) for monitoring metathesis reactions, because the cation remained the same and only the anion was changed. The exchange of an anion from Cl$^-$ to [PF$_6$]$^-$ caused only slight changes in the NMR spectrum. The biggest difference in the NMR spectra of [C$_4$mim]Cl and [C$_4$mim][PF$_6$] is the chemical shift of the most acidic proton H(1) of the [C$_4$mim]$^+$ cation, see Table 17.

<table>
<thead>
<tr>
<th>Anion</th>
<th>CH$_3$</th>
<th>CH$_2$</th>
<th>CH$_3$</th>
<th>NCH$_3$</th>
<th>NCH$_2$</th>
<th>C(2)H</th>
<th>C(3)H</th>
<th>C(1)H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$^-$</td>
<td>0.97</td>
<td>1.37</td>
<td>1.90</td>
<td>4.13</td>
<td>4.33</td>
<td>7.33</td>
<td>7.44</td>
<td>10.9</td>
</tr>
<tr>
<td>[PF$_6$]$^-$</td>
<td>0.99</td>
<td>1.38</td>
<td>1.86</td>
<td>3.92</td>
<td>4.20</td>
<td>7.54</td>
<td>7.61</td>
<td>8.85</td>
</tr>
</tbody>
</table>

Reliable results on the purity of the ionic liquids were obtained when both analysis methods, $^1$H NMR and MS(ESI), were used together. The presence of additional ions in the product could be detected with MS(ESI$^+$ and ESI$^-$) even when their content was small. The MS(ESI$^+$) spectrum of 1 contained m/z's due to [C$_4$mim]$^+$ (139) and [(C$_4$mim)$_2$]Cl$^+$ (313), and the MS(ESI$^-$) spectrum of 4 contained m/z's due to [C$_4$mim]$^-$ (139) and [(C$_4$mim)$_2$][PF$_6$]$^-$(423). Unfortunately, because of variation in the sensitivity of the ions, a quantitative analysis is not possible using MS(ESI).

Purified ionic liquids were also studied with $^{13}$C NMR, and an elemental analysis was carried out. The observed and calculated elemental contents of the studied compounds were consistent.

During the studies it was noticed that the colour of the crude ionic liquid correlated with the reaction temperature used: the higher the temperature was, the darker the colour of the crude product became. In the preparation of [C$_4$mim]Cl, the formed transalkylation products also seemed to cause colourization of the ionic liquid. This phenomenon was also reported in the literature (123). In order to find out the reason for the brown colour of the high-temperature preparations of [C$_4$mim][TsO] 2, the crude products were washed with ethyl acetate and the washings were studied with GCMS. The GCMS analysis
indicated that the washings contained by-products originating from ester 60: \( p \)-toluenesulfonic acid \((m/z\) 171\), bis(4-methylphenyl)sulfoxide \((m/z\) 246\) and 4-methylphenyl 4-methyl-benzenethiosulfonate \((m/z\) 278\). It was concluded that ester 60 was sensitive to high temperature, and hence it decomposed or reacted easily. The presence of water could also hydrolyze butyl-\( p \)-toluenesulfonate ester into \( p \)-toluenesulfonic acid and butanol. In accordance with this, a small amount of \([\text{Hmim}]\text{[TsO]}\) 62 was observed to form in some preparation reactions of 2. Also, ester 61 seemed to decompose at temperatures higher than 100 °C.

### 4.2.2 Melting points

The melting point of an ionic liquid depends on its cation/anion composition (33). Generally, symmetric ions with a localized charge and strong interactions between ions result in good packing efficiency and hence a high melting point. (the m.p. of NaCl is 801°C) (59). Ionic liquids based on large, unsymmetric cations with a delocalized charge often have low melting points. Packing efficiency depends on interactions between ions. Hydrogen bonding (or similar non-bonded interactions) increases the order of the system and thus raises the melting point (213).

The melting points of the solid ILs prepared with the quaternization reaction were determined with differential scanning calorimetry and a melting point apparatus. The melting points determined with DSC showed only one transition, indicating that the product was pure. The melting points measured with DSC were slightly higher than those measured with the melting point apparatus, as seen in Table 18.

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>DSC °C</th>
<th>Melting point apparatus °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>([C_4\text{mim}]\text{Cl})</td>
<td>69</td>
<td>66-68</td>
</tr>
<tr>
<td>([\text{Hmim}]\text{[TsO]})</td>
<td>92</td>
<td>90-91</td>
</tr>
<tr>
<td>([C_4\text{mim}]\text{[TsO]})</td>
<td>60</td>
<td>57-59</td>
</tr>
<tr>
<td>([C_4\text{mim}]\text{[MsO]})</td>
<td>76</td>
<td>71-73</td>
</tr>
</tbody>
</table>

The melting points of \([C_n\text{mim}]\text{[InCl}_4\text{]}\) ILs were determined with DSC, and the results are shown in Figure 43. The DSC trace showed only one transition, indicating that each product was pure. The melting point of \([C_n\text{mim}]\text{[InCl}_4\text{]}\) decreases with increasing alkyl chain length, when \(n\) is between 1 and 6. When the alkyl chain contains more than 8 carbons, the melting point of \([C_n\text{mim}]\text{[InCl}_4\text{]}\) increases again. Hence, ionic liquids that have an alkyl chain containing 4, 6, 8 or 10 carbon atoms are liquid at room temperature and the others are solids.
4.2.2.1 Phase diagram of the binary system [C2mim]Cl-InCl3

One way to study a Lewis acid-based ionic liquid is to measure its phase diagram. The aim is to see which kinds of ion pairs are present in the IL at certain compositions, since treatment of a quaternary halide salt Q’X- with a Lewis acid MXn results in the formation of more than one anion species, depending on the relative proportions of Q’X and MXn. The most studied system is 1-ethyl-3-methylimidazolium chloride-aluminium(III)chloride (69). Recently, studies on 1-alkyl-3-methylimidazolium chloride-indium(III)chloride systems have also been reported (214,215).

The phase diagram of the binary system [C2mim]Cl-InCl3 was reported by Yang et al. (214), but it was repeated in this study in order to study the system in more detail. The phase diagram measured by Yang et al. consists of quite few data points, and it was measured only while heating the sample (from -60 to 160 °C). Only one or two transitions were observed in each mixture. We measured the phase diagram in more detail (DSC was recorded after every 1 mol% addition of InCl3) and transitions were determined both while heating and cooling the sample, and the heating-cooling cycle was repeated (from -80 to 200 °C). It was noticed that the transition temperatures determined by Yang et al. appeared to be lower than ours, and they did not observe glass transitions. The results are compared in Table 19.

However, Yang et al. assumed in their study that the following ion pairs should be present in a certain composition of a [C2mim]Cl-InCl3 mixture: [C2mim]3[InCl6] when x(InCl3) = 0.25, [C2mim]2[InCl5] when x(InCl3) = 0.33, [C2mim][InCl4] when x(InCl3) = 0.5 and [C2mim][In2Cl7] when x(InCl3) > 0.5. They measured the Raman spectra of these mixtures and concluded that other anions, but not [In2Cl7]-, may exist.
Table 19. Temperatures (°C) of recorded transitions in DSC measurements of the binary system [C₂mim]Cl-InCl₃.

<table>
<thead>
<tr>
<th>x(InCl₃)</th>
<th>[InCl₄]</th>
<th>[InCl₅]</th>
<th>[InCl₆]</th>
<th>T₁</th>
<th>[InCl₄]</th>
<th>[InCl₅]</th>
<th>[InCl₆]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>97.2</td>
<td>85</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>72.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>86.4</td>
<td>75.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.15</td>
<td>106.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.20</td>
<td>114.2</td>
<td>85.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>119.8</td>
<td>105.3</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>0.30</td>
<td>113.9</td>
<td>71</td>
<td>97.7</td>
<td>58.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.33</td>
<td>116.6</td>
<td>71.2</td>
<td>39.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.35</td>
<td>116.1</td>
<td>71.7</td>
<td>37.1</td>
<td>58.8</td>
<td>23.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.40</td>
<td>41.8</td>
<td></td>
<td></td>
<td>46.5</td>
<td>20.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.45</td>
<td>50.9 (32.9)</td>
<td>43.7 (21.7)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>45.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.55</td>
<td>44.5</td>
<td>-29.6</td>
<td>35.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.60</td>
<td>42.7</td>
<td>-30.8</td>
<td>33.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.65</td>
<td>43.7</td>
<td>-28.8</td>
<td>33.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.70</td>
<td>45.9</td>
<td>-27.6</td>
<td>33.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.75</td>
<td>452</td>
<td>-28.3</td>
<td>74.3</td>
<td>33.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

We were able to detect three of the assumed ion pairs from the phase diagram and managed to crystallize the ionic liquids and confirm the structures. With an indium chloride content, x(InCl₃) = 0.5 or 0.25, only one compound was present in a mixture corresponding to [emim][InCl₄] or [emim][InCl₅], respectively. However, a pure single component phase was not observed in the case of x(InCl₃) = 0.33, but three transitions were seen in a DSC trace. In the case of InCl₃ > 0.5 mol%, two transitions were observed; the one was a glass transition and the other a melting point. These mixtures were also analyzed with ¹H NMR, MS(ESI⁺) and MS(ESI⁻) and elemental analysis. ¹H NMR and elemental analysis indicated that the products were pure. The MS(ESI⁻) spectra contained m/zs due to [C₂mim]⁺ (111) and the MS(ESI⁺) spectra contained m/zs due to [InCl₄]⁻ (257). Other anions, [InCl₅]²⁻ and [InCl₆]³⁻ were not seen in the MS(ESI⁻) analysis.

The melting points of [C₂mim]Cl-InCl₃ mixtures, where x(InCl₃) = 0.25, 0.33, 0.5, 0.55, 0.6 or 0.65, were also determined with a melting point apparatus equipped with a polarizing microscope and a camera. Only one melting point was seen with indium chloride contents of 0.25 and 0.5, but several melting points were observed with an indium chloride content of 0.33. In the case of InCl₃ > 0.5, only one melting point was observed. The analysis also indicated that an excess of InCl₃ did not dissolve into [C₂mim][InCl₄]. This might be the reason why the assumed [C₂mim][In₂Cl₇] was not detected in the phase diagrams. The melting points of the [C₂mim]Cl-InCl₃ mixtures determined with DSC and the melting point apparatus are compared in Table 20. The melting points of the mixtures determined with DSC are more reliable, since the determination was done right after the mixture was formed and the measurement with the melting point apparatus was done a few weeks later. On the other hand, the melting
points in this later measurement were similar to those of Yang et al. According to the microscope analysis, the mixtures seemed to be stable up to 250 °C, but above that they started to decompose.

Table 20. Comparison of the melting points of [C₇mim]Cl-InCl₃ mixtures measured with differential scanning calorimetry and a melting point apparatus.

<table>
<thead>
<tr>
<th>x(InCl₃)</th>
<th>DSC °C</th>
<th>Melting point apparatus °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>120</td>
<td>105-108</td>
</tr>
<tr>
<td>0.33</td>
<td>40, 71, 117</td>
<td>40, 70, 110</td>
</tr>
<tr>
<td>0.5</td>
<td>45</td>
<td>33-36</td>
</tr>
<tr>
<td>0.55</td>
<td>45</td>
<td>33-36</td>
</tr>
<tr>
<td>0.6</td>
<td>43</td>
<td>33-36</td>
</tr>
<tr>
<td>0.67</td>
<td>43</td>
<td>33-36</td>
</tr>
</tbody>
</table>

4.2.3 Thermal stability

The thermal stability of an ionic liquid seemed to depend on the cation/anion composition. Two different temperatures were recorded on the basis of a thermal gravimetric analysis. T\text{onset} is the temperature at which decomposition of the compound starts and T\text{end} is the temperature at which decomposition of the compound is finished. An ionic liquid containing [TsO]⁻ or [MsO]⁻ as an anion was more stable than an IL containing indium(III)chloride. T\text{onset} was 230-240 °C for [C₇mim][InCl₄] ILs, and 330 and 335 °C for [C₇mim][TsO] and [C₇mim][MsO], respectively (Table 21). T\text{onset} of a tosylate-based IL increased from 290 to 330 °C when the cation changed from [Hmim]⁺ to [C₄mim]⁺. However, the length of the alkyl chain did not have a strong influence on T\text{onset} in [C₇mim][InCl₄] ILs (n = 2, 4 or 6). For some reason, an IL with x(InCl₃) > 0.5 was more stable than an IL with x(InCl₃) < 0.5. It seemed that an excess of InCl₃ stabilized the ionic liquid and T\text{onset} was 100 °C higher for an IL with x(InCl₃) = 0.67. The decomposition step was noticed to be steeper for an ionic liquid containing [TsO]⁻ or [MsO]⁻ rather than [InCl₄]⁻. The melting point of InCl₃ is 586 °C, and hence it was only the cation that decomposed during heating. The residual weight corresponds quite well to the amount of InCl₃ (w%) in the IL; see last column in Table 21.
Table 21. Thermal stability of ionic liquids.

<table>
<thead>
<tr>
<th>IL</th>
<th>T onset ºC</th>
<th>T end ºC</th>
<th>Residual weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Hmim][TsO]</td>
<td>290</td>
<td>500</td>
<td>0</td>
</tr>
<tr>
<td>[C4mim][TsO]</td>
<td>330</td>
<td>500</td>
<td>0</td>
</tr>
<tr>
<td>[C4mim][MsO]</td>
<td>335</td>
<td>460</td>
<td>0</td>
</tr>
<tr>
<td>[C2mim][InCl4]</td>
<td>230</td>
<td>600</td>
<td>45</td>
</tr>
<tr>
<td>[C4mim][InCl4]</td>
<td>230</td>
<td>600</td>
<td>40</td>
</tr>
<tr>
<td>[C6mim][InCl4]</td>
<td>230</td>
<td>600</td>
<td>40</td>
</tr>
<tr>
<td>[C2mim][InCl5]</td>
<td>230</td>
<td>600</td>
<td>40</td>
</tr>
<tr>
<td>[C2mim][InCl6]</td>
<td>230</td>
<td>600</td>
<td>25</td>
</tr>
<tr>
<td>[C2mim][InCl4]+InCl3&lt;sup&gt;a&lt;/sup&gt;</td>
<td>330</td>
<td>600</td>
<td>0.67</td>
</tr>
</tbody>
</table>

<sup>a</sup>x(InCl₃) = 0.67.

### 4.2.4 Crystal structures

Structural information about 1,3-dialkylimidazolium-based ILs was rather sparse when the characterization of the solid products was decided to do with a single crystal X-ray diffractometer (216-218). The literature survey indicated that disorder is common in the packing of ionic liquids. For example, there are several alternative conformations of the \( n \)-butyl side chain of 1-butyl-3-methylimidazolium that depend on the mutual orientations of the carbon atoms in the chain (213,219,220). Two conformations of the \( n \)-butyl chain of the cation are shown in Figure 44. A more open conformation of the butyl group is shown on the left and a twisted conformation on the right. The packing effects seem to be the determining factor in deciding the actual conformation of the \( n \)-butyl chain in 1-butyl-3-methylimidazolium salts (221). The \( N,N' \)-dialkylimidazolium cations and anions are usually joined together by a hydrogen bonding network.

Fig. 44. Observed conformations of the 1-butyl-3-methylimidazolium cation, open (left) and twisted (right).
4.2.4.1 1-Butyl-3-methylimidazolium chloride

The first crystal structure I was determined in the beginning of 2003 (74), but published in 2004, and at the same time the structure was also published by Seddon (220) and Saha (222). The molecular structure and numbering of the atoms of [C₄mim]Cl I is shown in Fig. 45. Crystal data and details of the structure determinations are given in Table 22 and the selected bond lengths and angles are shown in Tables 23 and 24.

![Crystal structure of 1-butyl-3-methylimidazolium chloride I showing the numbering scheme and three short H···Cl contacts. The thermal ellipsoids have been drawn at a 50% probability level.](image)

**Table 22. Details of the crystal structure determination of [C₄mim]Cl**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>C₁₆H₃₃ClN₂</td>
</tr>
<tr>
<td><strong>M</strong></td>
<td>174.67 T (K)</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>monoclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P2(1)</td>
</tr>
<tr>
<td><strong>θ range (°)</strong></td>
<td>4.22 - 25.99</td>
</tr>
<tr>
<td><strong>Unique reflections</strong></td>
<td>1881</td>
</tr>
<tr>
<td><strong>Observed reflections</strong></td>
<td>1675</td>
</tr>
<tr>
<td><strong>Parameters/restraints</strong></td>
<td>103</td>
</tr>
<tr>
<td><strong>R_INT</strong></td>
<td>0.1465</td>
</tr>
<tr>
<td><strong>V (Å³)</strong></td>
<td>960.6(3)</td>
</tr>
<tr>
<td><strong>R₁</strong></td>
<td>0.0387</td>
</tr>
<tr>
<td><strong>wR₂ (all data)</strong></td>
<td>0.0797</td>
</tr>
<tr>
<td><strong>μ (Mo-Kα) (mm⁻¹)</strong></td>
<td>0.341</td>
</tr>
<tr>
<td><strong>GOOF</strong></td>
<td>1.112</td>
</tr>
<tr>
<td><strong>Max. and min. heights in final difference Fourier synthesis (e Å⁻³)</strong></td>
<td>1.201, -0.255</td>
</tr>
</tbody>
</table>

*a I ≥ 2σ(I) b R₁ = Σ |Fo| - |Fc| / |Σ |Fo| , wR₂ = [Σw(Fo²Fc²)²/ΣwFo⁴]¹/²
Table 23. Selected bond lengths (Å) of [C₄mim]Cl

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)-C(2)</td>
<td>1.382(2)</td>
<td>N(1)-C(5)</td>
<td>1.473(2)</td>
<td>N(1)-C(6)</td>
<td>1.473(2)</td>
</tr>
<tr>
<td>N(3)-C(10)</td>
<td>1.466(2)</td>
<td>C(4)-C(5)</td>
<td>1.354(2)</td>
<td>C(6)-C(7)</td>
<td>1.521(2)</td>
</tr>
<tr>
<td>C(8)-C(9)</td>
<td>1.524(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 24. Selected angles (°) of [C₄mim]Cl

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (°)</th>
<th>Bond</th>
<th>Angle (°)</th>
<th>Bond</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)-C(2)-N(3)</td>
<td>108.7(1)</td>
<td>N(1)-C(5)-C(4)</td>
<td>106.9(1)</td>
<td>N(1)-C(6)-C(7)</td>
<td>110.4(1)</td>
</tr>
<tr>
<td>C(2)-N(1)-C(5)</td>
<td>108.7(1)</td>
<td>C(2)-N(1)-C(6)</td>
<td>125.9(1)</td>
<td>C(5)-N(1)-C(6)</td>
<td>125.0(1)</td>
</tr>
<tr>
<td>C(6)-C(7)-C(8)</td>
<td>112.2(1)</td>
<td>C(7)-C(8)-C(9)</td>
<td>111.8(1)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It can be seen from Table 23 that all the bond lengths in the [C₄mim]⁺ cation are quite normal and agree with those of other related salts (216-218). The butyl group possesses a more open conformation. The [C₄mim]⁺ cation and the Cl⁻ anion are joined by a hydrogen bonding network, as shown in Figure 37. The shortest C-H···Cl contacts of 2.485, 2.653 and 2.688 Å involve hydrogen atoms H(1), H(11A) and H(11B), respectively. These atoms are expected to be the most acidic in the cation. The respective C-H···Cl angles are 157.9, 166.0 and 145.6 °.

4.2.4.2 Sulfonate-based ionic liquids

Crystals were obtained for the analysis from a 1:4 mixture of acetonitrile and ethyl acetate for [C₄mim][TsO] 2 and [Hmim][OTs] 62 and from a 1:3 mixture for [C₄mim][MsO] 3. The crystal structure of [Hmim][OTs] (at 293 K) can be found in the literature (223), but the data of the low-temperature measurement is reported here as well. The molecular structures and numbering of the atoms of 2, 3 and 62 are shown in Figs. 46-48, respectively. The asymmetric unit of [C₄mim][MsO] consists of one independent cation and anion. The n-butyl group of the cation has a twisted conformation. The asymmetric unit of [C₄mim][TsO] consists of two independent cations and anions and the n-butyl group possesses either an open or a twisted conformation. The asymmetric unit of [Hmim][TsO] consists of two independent cations and anions. Crystal data and details of the structure determinations are given in Table 25.
Fig. 46. Crystal structure of 1-butyl-3-methylimidazolium $p$-toluenesulfonate 2, showing the numbering scheme and disordered conformation. The thermal ellipsoids have been drawn at a 50% probability level. Both orientations of the twisted butyl chain are shown in the figure. The more abundant orientation A [s.o.f. 0.641(4)] is displayed with black bonds, while the less abundant orientation B [s.o.f. 0.359(4)] is displayed with grey bonds.

Fig. 47. Crystal structure of 1-butyl-3-methylimidazolium methylsulfonate 3, indicating the numbering of the atoms. The thermal ellipsoids have been drawn at a 50% probability level.
Fig. 48. Crystal structure of 1-methylimidazolium $p$-toluenesulfonate 62, indicating the numbering of the atoms. The thermal ellipsoids have been drawn at a 50% probability level.
Table 25. Details of the crystal structure determination of 2, 3 and 62.

<table>
<thead>
<tr>
<th></th>
<th>[C₄mim][TsO]</th>
<th>[C₄mim][MsO]</th>
<th>[Hmim][OTs]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>C₄H₁₀N₂O₃S</td>
<td>C₄H₁₀N₂O₃S</td>
<td>C₁₁H₁₄N₂O₃S</td>
</tr>
<tr>
<td><strong>M</strong></td>
<td>310.41</td>
<td>234.31</td>
<td>254.30</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>Triclinic</td>
<td>Triclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P-1</td>
<td>P-1</td>
<td>P₂₁/c</td>
</tr>
<tr>
<td><strong>a (Å)</strong></td>
<td>8.841(2)</td>
<td>7.936(2)</td>
<td>8.873(2)</td>
</tr>
<tr>
<td><strong>b (Å)</strong></td>
<td>10.293(2)</td>
<td>8.480(2)</td>
<td>9.379(2)</td>
</tr>
<tr>
<td><strong>c (Å)</strong></td>
<td>18.519(4)</td>
<td>10.264(2)</td>
<td>29.064(6)</td>
</tr>
<tr>
<td><strong>α (°)</strong></td>
<td>101.56(3)</td>
<td>103.46(3)</td>
<td>90</td>
</tr>
<tr>
<td><strong>β (°)</strong></td>
<td>103.76(3)</td>
<td>99.45(3)</td>
<td>96.97(3)</td>
</tr>
<tr>
<td><strong>γ (°)</strong></td>
<td>90.37(3)</td>
<td>111.66(3)</td>
<td>90</td>
</tr>
<tr>
<td><strong>V (Å³)</strong></td>
<td>1601.0(6)</td>
<td>599.9(2)</td>
<td>2400.8(8)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>2</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>664</td>
<td>252</td>
<td>1072</td>
</tr>
<tr>
<td><strong>Dₜ (g cm⁻³)</strong></td>
<td>1.288</td>
<td>1.297</td>
<td>1.407</td>
</tr>
<tr>
<td><strong>μ (Mo-Kα) (mm⁻¹)</strong></td>
<td>0.214</td>
<td>0.261</td>
<td>0.268</td>
</tr>
<tr>
<td><strong>Crystal size (mm)</strong></td>
<td>0.15 x 0.15 x 0.08</td>
<td>0.20 x 0.15 x 0.10</td>
<td>0.20 x 0.15 x 0.10</td>
</tr>
<tr>
<td><strong>T (K)</strong></td>
<td>150(2)</td>
<td>150(2)</td>
<td>150(2)</td>
</tr>
<tr>
<td><strong>θ range (°)</strong></td>
<td>2.88-25.00</td>
<td>2.73-25.99</td>
<td>3.03-24.99</td>
</tr>
<tr>
<td><strong>Reflections collected</strong></td>
<td>16937</td>
<td>10212</td>
<td>16518</td>
</tr>
<tr>
<td><strong>Unique reflections</strong></td>
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<td>2354</td>
<td>4054</td>
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<td><strong>Observed reflections</strong></td>
<td>3980</td>
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<td>3290</td>
</tr>
<tr>
<td><strong>Parameters/restraints</strong></td>
<td>397/8</td>
<td>1400</td>
<td>312/0</td>
</tr>
<tr>
<td><strong>R_{ déf}</strong></td>
<td>0.1016</td>
<td>0.0467</td>
<td>0.0888</td>
</tr>
<tr>
<td><strong>R₁</strong></td>
<td>0.0566</td>
<td>0.0429</td>
<td>0.0498</td>
</tr>
<tr>
<td><strong>wR₂</strong></td>
<td>0.1309</td>
<td>0.1165</td>
<td>0.1207</td>
</tr>
<tr>
<td><strong>R₁ (all data)</strong></td>
<td>0.0814</td>
<td>0.0464</td>
<td>0.0660</td>
</tr>
<tr>
<td><strong>wR₂ (all data)</strong></td>
<td>0.1447</td>
<td>0.1202</td>
<td>0.1315</td>
</tr>
<tr>
<td><strong>GOOF</strong></td>
<td>1.039</td>
<td>1.142</td>
<td>1.051</td>
</tr>
<tr>
<td><strong>Max. and min. heights in final difference Fourier synthesis (e Å⁻³)</strong></td>
<td>0.440, -0.332</td>
<td>0.514, -0.486</td>
<td>0.448, -0.333</td>
</tr>
</tbody>
</table>

All the bond lengths and angles in the compounds for [C₄mim][TsO], [C₄mim][MsO] and [Hmim][OTs] were normal (see Table 26 and 27). The bond lengths of the cations can be compared, for example, with the corresponding bond lengths in [C₄mim]Cl (174). The bond lengths of the anions are comparable with the S-O and S-C bond lengths in p-toluenesulfonate salts of 1-methylimidazolium (223), 2-ethylimidazolium (224), 1-benzylimidazolium (225), and 2-methylimidazolium (226) and in 1,3-dimethylimidazolium methyl sulphate (114).
Table 26. Selected bond lengths (Å) of 2, 3 and 62.

<table>
<thead>
<tr>
<th></th>
<th>[C4mim][TsO]</th>
<th>[C4mim][MsO]</th>
<th>[Hmim][TsO]</th>
</tr>
</thead>
<tbody>
<tr>
<td>S(1)-O(11) a</td>
<td>1.446(2)</td>
<td>1.460(1)</td>
<td>1.471(2)</td>
</tr>
<tr>
<td>S(2)-O(21) b</td>
<td>1.446(2)</td>
<td>S(2)-O(21) b</td>
<td>1.475(2)</td>
</tr>
<tr>
<td>S(1)-O(12) a</td>
<td>1.461(2)</td>
<td>S(1)-O(12)</td>
<td>1.447(2)</td>
</tr>
<tr>
<td>S(2)-O(22) b</td>
<td>1.448(2)</td>
<td>S(2)-O(22) b</td>
<td>1.448(2)</td>
</tr>
<tr>
<td>S(1)-E(13) a</td>
<td>1.445(2)</td>
<td>S(1)-E(13)</td>
<td>1.458(2)</td>
</tr>
<tr>
<td>S(2)-O(23) b</td>
<td>1.444(2)</td>
<td>S(2)-O(23) b</td>
<td>1.450(2)</td>
</tr>
<tr>
<td>S(1)-C(51) a</td>
<td>1.776(3)</td>
<td>S(1)-C(31)</td>
<td>1.769(2)</td>
</tr>
<tr>
<td>S(2)-C(61) b</td>
<td>1.779(3)</td>
<td>S(2)-C(51) b</td>
<td>1.771(3)</td>
</tr>
<tr>
<td>N(1)-C(1) a</td>
<td>1.324(4)</td>
<td>N(1)-C(1) a</td>
<td>1.331(4)</td>
</tr>
<tr>
<td>N(3)-C(4) b</td>
<td>1.329(4)</td>
<td>N(3)-C(4) b</td>
<td>1.334(4)</td>
</tr>
<tr>
<td>N(1)-C(2) a</td>
<td>1.379(4)</td>
<td>N(1)-C(2) a</td>
<td>1.380(4)</td>
</tr>
<tr>
<td>N(3)-C(5) b</td>
<td>1.370(4)</td>
<td>N(3)-C(5) a</td>
<td>1.385(4)</td>
</tr>
<tr>
<td>N(2)-C(1) a</td>
<td>1.328(4)</td>
<td>N(2)-C(1) a</td>
<td>1.305(4)</td>
</tr>
<tr>
<td>N(4)-C(4) b</td>
<td>1.330(4)</td>
<td>N(4)-C(4) a</td>
<td>1.320(4)</td>
</tr>
<tr>
<td>N(2)-C(3) a</td>
<td>1.374(4)</td>
<td>N(2)-C(3) a</td>
<td>1.354(4)</td>
</tr>
<tr>
<td>N(4)-C(6) b</td>
<td>1.369(4)</td>
<td>N(4)-C(6) a</td>
<td>1.374(4)</td>
</tr>
<tr>
<td>C(2)-C(3) a</td>
<td>1.342(4)</td>
<td>C(2)-C(3) a</td>
<td>1.359(5)</td>
</tr>
<tr>
<td>C(5)-C(6) b</td>
<td>1.352(4)</td>
<td>C(5)-C(6) a</td>
<td>1.349(4)</td>
</tr>
<tr>
<td>N(1)-C(11) a</td>
<td>1.482(4)</td>
<td>N(1)-C(11) a</td>
<td>1.465(4)</td>
</tr>
<tr>
<td>N(3)-C(31) a</td>
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<tr>
<td>N(3)-C(31) b</td>
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<td>N(2)-C(21) a</td>
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</tr>
<tr>
<td>N(2)-C(21) a</td>
<td>1.464(4)</td>
<td>N(2)-C(21) a</td>
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</table>

a,b Two independent molecules in the asymmetric unit: a molecule 1, b molecule 2.
Table 27. Selected angles (º) of 2, 3 and 62.

<table>
<thead>
<tr>
<th></th>
<th>[C4mim][TsO]</th>
<th>[C4mim][MsO]</th>
<th>[Hmim][TsO]</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)-C(1)-N(2)</td>
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<td>N(3)-C(4)-N(4)</td>
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<td>108.3(3)</td>
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<td>108.6(3)</td>
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<tr>
<td>C(2)-C(3)-N(2)</td>
<td>107.4(3)</td>
<td>107.4(3)</td>
<td>107.8(3)</td>
</tr>
<tr>
<td>C(5)-C(6)-N(4)</td>
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<tr>
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<td>107.0(3)</td>
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<tr>
<td>C(6)-C(5)-N(3)</td>
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<tr>
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<td>108.4(3)</td>
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<td>124.6(3)</td>
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<tr>
<td>C(4)-N(3)-C(31B)</td>
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<tr>
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<td>126.7(3)</td>
<td>127.4(3)</td>
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<tr>
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<td>126.0(5)</td>
<td>129.9(3)</td>
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<td>126.7(9)</td>
<td>125.3(3)</td>
</tr>
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<td>125.7(3)</td>
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</tr>
<tr>
<td>C(4)-N(4)-C(41)</td>
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<tr>
<td>C(6)-N(4)-C(41)</td>
<td>125.1(3)</td>
<td>125.1(3)</td>
<td>125.3</td>
</tr>
</tbody>
</table>

a, b Two independent molecules in the asymmetric unit: a molecule 1, b molecule 2.

The [C4mim]+ cations and sulfonate anions are joined together by a hydrogen bonding network, H•••O is shorter than the sum of the van der Waals radii of 2.6 Å (227). [C4mim][TsO] has different contacts corresponding to two independent conformations of the butyl group. The closest C-H•••O contacts involve both the ring and alkyl H atoms of the [C4mim]+ cation. In a more open conformation of the butyl group the shortest C-H•••O distances of 2.261(2) Å and 2.285(2) Å involve hydrogen atoms H(3) and H(1), respectively. The shortest C-H•••O distance of 2.237(2) Å involves a hydrogen atom H(4) in a twisted conformation of the butyl group. In [C4mim][MsO] the shortest C-H•••O distance of 2.334(2) Å involves a hydrogen atom H(21C). The closest contact in [Hmim][TsO] involves a hydrogen atom H(21) bonded to nitrogen, and it is 1.865(2) Å. The packing of ILs is shown with the shortest interactions for each ionic liquid in Figures 49-51. Cations and anions form polar and non-polar layers, so that the sulfonate group is near to the imidazolium ring, and non-polar hydrocarbon chains of the cation and the non-polar toluene ring or the methyl group of the anion are close to each other.
Fig. 49. Packing of [C₄mim][TsO], showing the shortest C-H···O contacts between anions and cations.

Fig. 50. Packing of [C₄mim][MsO], showing the shortest C-H···O contacts between anions and cations.
4.2.4.3 InCl₃-based 1-ethyl-3-methylimidazolium ionic liquids

A crystal structure analysis was done for crystals obtained from ethylacetate:acetonitrile solutions containing [C₂mim]Cl and InCl₃ in varying molar fractions. The [C₂mim]₃[InCl₆] and [C₂mim][InCl₄] were crystallized from mixtures containing 0.25 and 0.5 of InCl₃, respectively. Crystallization of [C₂mim]₃[InCl₆(H₂O)] was more demanding. It did not crystallize from the ethylacetate:acetonitrile solution containing [C₂mim]Cl and InCl₃ in a molar fraction of 0.33, but [C₂mim]₃[InCl₆] crystals were found in the mixture instead. Finally, [C₂mim]₃[InCl₆(H₂O)] crystallized in the toluene:acetonitrile solution containing 0.5 of InCl₃. Later it was also found in the mixture containing 0.5 of InCl₃, where the ethylacetate:acetonitrile solution had evaporated.

The molecular structures and numbering of the atoms of [C₂mim][InCl₄] 63, [C₂mim]₃[InCl₆(H₂O)] 64 and [C₂mim]₃[InCl₆] 65 are shown in Figures 52-54, respectively. The cation in 63 was found to be distorted. Crystal data and details of the structure determinations are given in Table 28 and selected bond lengths and angles are given in Tables 29 and 30, respectively.
Fig. 52. Crystal structure of 1-ethyl-3-methylimidazolium tetrachloridoindate, showing the numbering scheme and disordered conformation. Thermal ellipsoids have been drawn at a 30% probability level.

Fig. 53. Crystal structure of bis(1-ethyl-3-methylimidazolium) pentachloridoindate, indicating the numbering of the atoms. Thermal ellipsoids have been drawn at a 50% probability level.
Fig. 54. Crystal structure of tris(1-ethyl-3-methylimidazolium) hexachloridoindate, indicating the numbering of the atoms. Thermal ellipsoids have been drawn at a 50% probability level.
Table 28. Details of the crystal structure determination of 63-65.

<table>
<thead>
<tr>
<th></th>
<th>[C$<em>{2}$mim][InCl$</em>{4}$] 63</th>
<th>[C$<em>{2}$mim][InCl$</em>{4}$(H$_{2}$O)] 64</th>
<th>[C$<em>{2}$mim][InCl$</em>{6}$] 65</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>C$<em>{2}$H$</em>{11}$Cl$<em>{4}$InN$</em>{2}$</td>
<td>C$<em>{2}$H$</em>{23}$Cl$<em>{5}$InN$</em>{4}$O</td>
<td>C$<em>{2}$H$</em>{33}$Cl$<em>{6}$InN$</em>{6}$</td>
</tr>
<tr>
<td><strong>M</strong></td>
<td>367.79</td>
<td>532.42</td>
<td>661.02</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
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<td>monoclinic</td>
<td>orthorombic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P2(1)/c</td>
<td>P2(1)/n</td>
<td>Pna2(1)</td>
</tr>
<tr>
<td><strong>a (Å)</strong></td>
<td>7.4384(15)</td>
<td>9.2977(19)</td>
<td>19.424(4)</td>
</tr>
<tr>
<td><strong>b (Å)</strong></td>
<td>14.322(3)</td>
<td>16.858(3)</td>
<td>13.063(3)</td>
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<tr>
<td><strong>c (Å)</strong></td>
<td>12.324(3)</td>
<td>14.187(3)</td>
<td>11.063(2)</td>
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<tr>
<td><strong>β (°)</strong></td>
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<td>103.17(3)</td>
<td>90</td>
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<td><strong>V (Å$^3$)</strong></td>
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<td>2165.1(8)</td>
<td>2807.1(10)</td>
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<tr>
<td><strong>Z</strong></td>
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<td>4</td>
<td>4</td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>712</td>
<td>1064</td>
<td>1336</td>
</tr>
<tr>
<td><strong>D$_{s}$ (g cm$^{-3}$)</strong></td>
<td>1.863</td>
<td>1.633</td>
<td>1.564</td>
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<td><strong>µ (Mo-K$_{α}$) (mm$^{-1}$)</strong></td>
<td>2.580</td>
<td>1.715</td>
<td>1.431</td>
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<td><strong>Crystal size (mm)</strong></td>
<td>0.25 x 0.25 x 0.25</td>
<td>0.20 x 0.10 x 0.10</td>
<td>0.25 x 0.15 x 0.10</td>
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<tr>
<td><strong>T (K)</strong></td>
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<td>120(2)</td>
<td>120(2)</td>
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<tr>
<td><strong>θ range (°)</strong></td>
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<td>1.91 - 26.00</td>
<td>3.12 - 26.00</td>
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<td><strong>Reflections collected</strong></td>
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<td>18679</td>
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<td><strong>Unique reflections</strong></td>
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<td>4235</td>
<td>5280</td>
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<td><strong>Observed reflections</strong></td>
<td>1765</td>
<td>3659</td>
<td>4983</td>
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<td><strong>Parameters/restraints</strong></td>
<td>146</td>
<td>219</td>
<td>286</td>
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<tr>
<td><strong>R$_{e}$</strong></td>
<td>0.0912</td>
<td>0.1277</td>
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<tr>
<td><strong>R$_{1}$</strong></td>
<td>0.0717</td>
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<td>0.0337</td>
</tr>
<tr>
<td><strong>wR$_{2}$</strong></td>
<td>0.1816</td>
<td>0.1168</td>
<td>0.0851</td>
</tr>
<tr>
<td><strong>R$_{1}$ (all data)</strong></td>
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<td>0.0544</td>
<td>0.0372</td>
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<tr>
<td><strong>wR$_{2}$ (all data)</strong></td>
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<td><strong>GOOF</strong></td>
<td>1.068</td>
<td>1.118</td>
<td>1.008</td>
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<tr>
<td><strong>Max. and min. heights in final difference Fourier synthesis (e Å$^{-3}$)</strong></td>
<td>1.269, -1.090</td>
<td>1.753, -1.222</td>
<td>0.477, -0.969</td>
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</tbody>
</table>

$^a$I $\geq$ 2σ(I), $R_1 = \sum |F_o| - |F_c|/|\sum F_o|, wR$$_2 = [\sum w(F_o^2-F_c^2)^2/\sum wF_o^4]^{1/2}$

Table 29. Selected bond lengths (Å) of complexes 63-65.

<table>
<thead>
<tr>
<th></th>
<th>[C$<em>{2}$mim][InCl$</em>{4}$] 63</th>
<th>[C$<em>{2}$mim][InCl$</em>{4}$(H$_{2}$O)] 64</th>
<th>[C$<em>{2}$mim][InCl$</em>{6}$] 65</th>
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</thead>
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<tr>
<td>In(1)-Cl(1)</td>
<td>2.343(3)</td>
<td>2.522(1)</td>
<td>2.545(1)</td>
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<tr>
<td>In(1)-Cl(2)</td>
<td>2.348(3)</td>
<td>2.483(1)</td>
<td>2.546(1)</td>
</tr>
<tr>
<td>In(1)-Cl(3)</td>
<td>2.347(3)</td>
<td>2.457(1)</td>
<td>2.505(1)</td>
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<tr>
<td>In(1)-Cl(4)</td>
<td>2.354(3)</td>
<td>2.478(1)</td>
<td>2.553(1)</td>
</tr>
<tr>
<td>In(1)-Cl(5)</td>
<td>2.353(1)</td>
<td>2.535(1)</td>
<td>2.526(1)</td>
</tr>
<tr>
<td>In(1)-Cl(6)</td>
<td>2.278(3)</td>
<td>2.645(1)</td>
<td>2.495(1)</td>
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</table>

Symmetry transformations used to generate equivalent atoms: # -x+1, -y, -z+1
Table 30. Selected angles (°) of complexes 63-65.

<table>
<thead>
<tr>
<th>[C2mim][InCl4]</th>
<th>[C2mim][InCl5(H2O)]</th>
<th>[C2mim][InCl6]</th>
</tr>
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<tr>
<td>Cl(1)-In(1)-Cl(2)</td>
<td>107.6(1)</td>
<td>89.52(4)</td>
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<td>Cl(1)-In(1)-Cl(3)</td>
<td>113.7(1)</td>
<td>91.24(4)</td>
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<tr>
<td>Cl(1)-In(1)-Cl(4)</td>
<td>108.8(1)</td>
<td>170.47(3)</td>
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<td>111.6(1)</td>
<td>88.56(3)</td>
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<td>107.3(2)</td>
<td>95.26(4)</td>
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<td>107.6(2)</td>
<td>92.93(4)</td>
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<td>Cl(2)-In(1)-Cl(5)</td>
<td>168.95(3)</td>
<td>92.2(4)</td>
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<tr>
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<td>97.7(0)</td>
<td>178.2(4)</td>
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<td>95.66(3)</td>
<td>92.2(4)</td>
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<tr>
<td>Cl(4)-In(1)-Cl(5)</td>
<td>87.28(3)</td>
<td>89.73(5)</td>
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<td>85.70(8)</td>
<td>89.74(3)</td>
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<tr>
<td>O(10)-In(1)-Cl(2)</td>
<td>85.70(8)</td>
<td>89.74(3)</td>
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<tr>
<td>Symmetry transformations used to generate equivalent atoms: # -x+1, -y, -z+1</td>
<td></td>
<td></td>
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</table>

All the bond lengths and angles of the [C2mim]+ cation of the ionic liquids were normal and can be compared, for example, with those in [C2mim]Br (228), [C2mim]I (229) and [C2mim][PF6] (230). The bond lengths in a [C2mim]+ ring vary from 1.313 to 1.387 Å and the angles from 105.5 to 109.2° in all three different ILs.

The [InCl4]− anion in 63 shows a slightly distorted tetrahedral geometry with In-Cl bond lengths of 2.343(3) – 2.354(3) Å and Cl-In-Cl angles varying from 107.3(2) to 113.7(1)°. The bond lengths and angles were comparable with those found in [Bu4N][InCl4] (231), [Et4N][InCl4] (232) and [Ph4P][InCl4] (233). In [C2mim][InCl4] the shortest C-H···Cl contact of 2.664(4) Å involves H (6B1) and the lengths of the hydrogen bonds vary from 2.664 to 2.889 Å.

The [InCl5(H2O)]2− anion in 64 shows an octahedral geometry with five chlorine and one aqua ligand. The In-O bond length is 2.278(3) Å and the shortest In-Cl bond length is 2.457(1)trans to the aqua ligand. The rest of the In-Cl bond lengths varied from 2.478(1) to 2.535(1) Å. The In-Cl bond lengths were longer in the [InCl4(H2O)]2− than in the [InCl4]− anion. The bond lengths can be compared with those in [NH4]2[InCl4(H2O)], 2.466(2)-2.491(2) and 2.52-2.71(2) Å (234,235). The bond lengths were slightly longer than those found in [Et2N]2[InCl5], where [InCl5]2− possesses a tetragonal-pyramidal geometry of 2.42-2.46 Å (236,237). The In-Cl bond lengths were 2.410-2.508 and 2.409-2.515 Å in [(PPh2Cl)2][InCl5] and [PPh3]2[InCl5]·CH3CN, where the trigonal bipyramid co-ordination is found around [InCl5]2− (238,239). The shortest C-H···Cl distance of 2.658(1) Å in [emim]2[InCl5(H2O)] involves a hydrogen atom H(2). The lengths of the hydrogen bonds vary from 2.658 to 2.950 Å.

The [InCl6]3− anion in 65 possesses a slightly distorted octahedral geometry composed of six independent chlorine atoms. The In-Cl bond lengths vary between 2.495(1) – 2.553(1) Å. The bond lengths can be compared with those in [MeNH3]3[InCl6], 2.510-2.539 Å (240). The bond lengths are slightly longer than those in [MeNH3]3[InCl6]Cl.
or in tris(2-amino-5-nitro-pyridinium) hexachloroindate (242). The shortest C-H···Cl distances of 2.617(1) and 2.618(1) Å involve hydrogen atoms H(6) and H(41A) in [C$_2$ mim]$_3$[InCl$_6$]. The lengths of the hydrogen bonds vary from 2.617 to 2.983 Å.

The packing of ionic liquids is shown in Figures 55-57. The shortest C-H···Cl distances of 2.617(1) and 2.618(1) were found in [C$_2$ mim]$_3$[InCl$_6$]. That also has the highest melting point, ca. 120 ºC. The crystal structure analysis confirmed the presence of the expected three different ion pairs.

![Fig. 55. Packing of [C$_2$ mim][InCl$_4$].](image-url)
Fig. 56. Packing of \([\text{C}_2\text{mim}]_2[\text{InCl}_3(\text{H}_2\text{O})]\).

Fig. 57. Packing of \([\text{C}_2\text{mim}]_3[\text{InCl}_6]\).
4.2.5 Summary

Ionic liquids were analyzed by combing several methods of analysis. The best way to monitor both the quaternization and the metathesis reaction was to combine MS(ESI) and 1H NMR analysis. MS(ESI) was a useful method for detecting the ions (90), and together these methods gave reliable results on the outcome of the reaction. The ILs were also analyzed with 13C NMR and elemental analysis. The ILs were characterized by determining the thermal stability, melting point and crystal structure of each solid IL. Thermogravimetric analysis showed that sulfonate-based ionic liquids were stable almost up to 300 °C, and above that temperature they started to decompose gradually. InCl3-based ILs were not as stable as sulfonate ILs, and they started to decompose when the temperature reached 200 °C. Crystal structure determination indicated that the number of contacts and the strength of contacts between the ions changed according to the ions of the ionic liquid. The stronger the interaction between the ions, the higher the melting point of the IL. Recent crystal structure studies have revealed that disorder is common in ionic liquids, especially when the imidazolium cation has long alkyl side chains (221). It has been interpreted that disorder in the cation is a direct reflection of poor packing efficiency in the imidazolium ions. Hence, factors such as the size of the ions, delocalization of charge, interactions between ions and disorder in the cation will affect the packing of the ionic liquid and also the observed melting point. The prediction of the individual effect of each factor was not straightforward, but it seemed that disorder and low symmetry in a cation as well as the increasing size of ions correlated with a low melting point.

The purpose of preparing and characterizing the ILs was to produce suitable ILs for the dimerization reaction of 2-methylpropene. [C₄mim][PF₆], [C₄mim][TsO] and [C₄mim][MsO] were selected as the ionic liquids on the grounds of Olivier-Bourbigou’s patent considering Bronsted acidic ILs. Three InCl₃-based ILs were selected from the 11 [Cₙmim][InCl₄] candidates. They were [C₂mim][InCl₄], [C₄mim][InCl₄] and [C₆mim][InCl₄]. Using the [C₄mim][InCl₄] IL would also have been interesting, but it was excluded owing to its toxicity (103). Three of the selected ILs were solids, [C₄mim][TsO], [C₄mim][MsO] and [C₄mim][InCl₄], and the rest were liquids at room temperature, [C₄mim][PF₆], [C₄mim][InCl₄] and [C₄mim][InCl₄]. The liquid ranges for the solid ILs were following: 60-330 °C for [C₄mim][TsO], 70-335 °C for [C₄mim][MsO] and 40-230 °C for [C₂mim][InCl₄].

4.3 Dimerization of 2-methylpropene

4.3.1 First attempts

The very first idea was to catalyze the dimerization reaction of 2-methylpropene with a palladium complex in the second generation IL, such as [C₄mim][PF₆]. The idea originated from my Master thesis, which dealt with the dimerization of 2-methylpropene in AlCl₃-based ILs with a nickel catalyst, as did all the previous dimerization reactions of light olefins carried out in IL media (28,193-202). Owing to the hygroscopic nature of the
catalytic ionic liquid, the reaction was not the easiest to perform. Therefore, other alternatives for ILs and catalyst were considered. Pd was selected as the catalyst, since it has been applied in some dimerization reactions and it is not water-sensitive (243,244). Commonly used \([\text{C}_4\text{mim}][\text{PF}_6]\) was selected as the first IL candidate.

These very first dimerization reactions of 2-methylpropene 7 were carried out in \([\text{C}_4\text{mim}][\text{PF}_6]\) using microwave irradiation at 80 °C (Fig. 58). Hexane was used as a second phase to extract products from the IL. The reaction was catalyzed with a) HPF\(_6\), b) Pd(1,3-bisdiphenylpropane)(PF\(_6\))\(_2\), c) an \textit{in situ} Pd catalyst that consists of Pd(OAc)\(_2\) + dppp + HPF\(_6\) (1:1:2), yielding Pd(dppp)(PF\(_6\))\(_2\), or d) an \textit{in situ} Pd catalyst; Pd(OAc)\(_2\) + dppp + p-TsOH (1:1:2), yielding Pd(dppp)(p-TsO)\(_2\). Only dimers and trimers were formed in these reactions, see Table 31. The ionic liquid by itself did not catalyze the reaction.

Fig. 58. Dimerization of 2-methylpropene in \([\text{C}_4\text{mim}][\text{PF}_6]\) with four different catalysts under microwave activation.

<table>
<thead>
<tr>
<th>Products</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4,4-trimethyl-1-pentene 8</td>
<td>40</td>
<td>38</td>
<td>38</td>
<td>50</td>
</tr>
<tr>
<td>2,4,4-trimethyl-2-pentene 9</td>
<td>11</td>
<td>9</td>
<td>11</td>
<td>12</td>
</tr>
<tr>
<td>2,2,4,6,6-pentamethyl-3-heptene 56</td>
<td>22</td>
<td>29</td>
<td>26</td>
<td>18</td>
</tr>
<tr>
<td>2,2,6,6-tetramethyl-4-methyleneheptane 57</td>
<td>17</td>
<td>25</td>
<td>19</td>
<td>15</td>
</tr>
</tbody>
</table>

Reaction time was 60 min, but 180 min when b was a catalyst.

The product distribution was similar in all the reactions. The previously prepared Pd complex did not catalyze the reaction as effectively as an \textit{in situ} catalyst, therefore the reaction time had to be three times longer. A comparison between the \textit{in situ} catalysts, c and d, indicated that when the acid component was p-TsOH, ca. 10% more 8 was formed than with HPF\(_6\). HPF\(_6\) as a catalyst gave similar results as the Pd complex, hence it was assumed that Pd was not necessary for the reaction. These results led to the idea of studying dimerizations with Brønsted acids without a transition metal catalyst.

\subsection*{4.3.2 Dimerization in Bronsted acid-based ionic liquids}

According to Olivier-Bourbigou’s patent ionic liquids containing an excess of Lewis acid and/or Bronsted acid could be used in dimerization, oligomerization and alkylation...
reactions (28). In dimerization reaction the molar ratio of an acid to an IL should be in the range of 0.01-0.7.

Ionic liquids based on the 1-butyl-3-methylimidazolium cation, \([C_4\text{mim}]^+\) were selected for solvents to study the dimerization reaction of 2-methylpropene. The anion (\(A^-\)) of the ionic liquid was hexafluorophosphate, methylsulfonate, \(p\)-toluenesulfonate or formate. \([C_4\text{mim}][\text{PF}_6]\) was chosen as the IL since it is commonly used and it was also mentioned in the patent. Sulfonate-based ILs were selected since they are not as well known and the corresponding sulfonic acids are strong. The formate-based ILs were prepared in another study and owing to the easy availability \([C_4\text{mim}][\text{HCO}_2]\) was tested in a reaction. The catalytic IL was prepared prior to the reaction and it contained a slight excess of the corresponding acid. Therefore, the Brønsted acids (HA) used in the reactions were hexafluorophosphoric acid, methylsulfonic acid (\(pK_a = -2.0\)), \(p\)-toluenesulfonic acid (\(pK_a = -2.5\)), and formic acid (\(pK_a = 3.75\)), respectively (245,246). The dimerization reactions were carried out in a continuous reactor at 120 ºC for 30 minutes. The composition of the catalytic ionic liquid, \([C_4\text{mim}]A/HA\), was 1:0.05 or 1:0.1. The reaction carried out in the IL containing formic acid did not succeed, due to the weak acid nature, but other acids catalyzed the reaction. Conversion of 2-methylpropene in ILs containing methylsulfonic acid or \(p\)-toluenesulfonic acid was low. No proper product layer was formed in the reactor, and only a few drops were distilled in a cold trap. Conversion of 2-methylpropene was high when hexafluorophosphoric acid was used as a catalyst. The reaction in \(p\)-toluenesulfonic acid-containing IL produced mainly dimers and trimers in the ratio of 3:1 (Fig. 59). This result was the same as in the conventional \(H_2\text{SO}_4\)-catalyzed (\(pK_a = -3.0\)) dimerization reaction (160). The reactions carried out in ILs containing methylsulfonic acid or hexafluorophosphoric acid mainly produced trimers. Generally, the amounts of higher oligomers were low in all the reactions. Reaction with hexafluorophosphoric acid as a catalyst yielded some tetramers, and methylsulfonic acid also yielded some pentamers.

![Fig. 59. Product distributions (in the reactor) of the dimerization reaction of 2-methylpropene carried out in a catalytic IL with a 1:0.05 composition of \([C_4\text{mim}]A/HA\).](image.png)
The product distribution of the distilled products was similar for methylsulfonic acid and 
$p$-toluenesulfonic acid-catalyzed reactions (Table 32). The main dimers were 2,4,4-
trimethyl-1-pentene 8 and 2,4,4-trimethyl-2-pentene 9, and the main trimers were 
2,2,4,6,6-pentamethyl-3-heptene 56 and 2,2,6,6-tetramethyl-4-methyleneheptane 57. The 
dimer content decreased and the trimer content increased when the amount of acid was 
increased from 0.05 to 0.1. The reaction with hexafluorophosphoric acid gave different 
outcome, it yielded mainly dimers 8 (75%) and 9 (22%), while only a few percent of 
trimers 56 and 57 were produced. The higher acid content did not change the product 
distribution. None of the applied ionic liquids catalyzed the reaction without the added 
acid catalyst.

Table 32. Detailed product distributions of the distilled products of the dimerization 
reactions of 2-methylpropene carried out in a Bronsted acid-based catalytic IL at 120 °C.

<table>
<thead>
<tr>
<th>Products</th>
<th>[C₄mim][p-TsO]/p-TsOH</th>
<th>[C₄mim][MsO]/MsOH</th>
<th>[C₄mim][PF₆]/HPF₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4,4-trimethyl-1-pentene 8</td>
<td>42 27</td>
<td>36 16</td>
<td>75 77</td>
</tr>
<tr>
<td>2,4,4-trimethyl-2-pentene 9</td>
<td>14 9</td>
<td>11 5</td>
<td>22 16</td>
</tr>
<tr>
<td>2,3,4-trimethyl-2-pentene 33</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2,2,4,6,6-pentamethyl-3-heptene 56</td>
<td>20 31</td>
<td>25 38</td>
<td>2 0.5</td>
</tr>
<tr>
<td>2,2,6,6-tetramethyl-4-methyleneheptane 57</td>
<td>17 22</td>
<td>20 26</td>
<td>1 0.5</td>
</tr>
</tbody>
</table>

In addition to the acid catalyst used, the IL also affects the reaction. The solubility of 2-
methylpropene might be different in [C₄mim][PF₆] and sulfonate-based ILs, but that was 
not specifically compared. A major drawback in all these reactions was the extraction of 
acid catalyst from the ionic liquid phase into the product phase, which led to the loss of 
catalytic activity. Mass peaks of [$p$-TsO]⁻, [MsO]⁻ and [PF₆]⁻ anions, $m/z$ 171, 95 and 145, 
respectively, were detected in the MS(ESI -) analysis of the hexane phase. Therefore, the 
catalytic system was not recyclable. Hexafluorophosphoric acid worked well in 
dimerization, mainly dimers 8 and 9 were formed. It seemed that the formed dimers 
separated easily from the [C₄mim][PF₆]/HPF₆, as the amount of dimers was low in the 
reactor but high in the cold trap. Unfortunately, using hexafluorophosphate-containing 
ILs is not practical, since they are unstable and release HF (108). Owing to these 
drawbacks, these ILs were omitted in further dimerizations.

### 4.3.3 Dimerization reactions in Lewis acid-based ionic liquids

The idea of using novel InCl₃-based ILs in the dimerization reaction originated during my 
visiting period in QUILL and Seddon’s research group, where these ILs were 
successfully applied in Friedel-Crafts reactions. It was thought that InCl₃-based ILs
would catalyze the dimerization reaction, since good results have been obtained from studies using AlCl₃-based ILs. It was assumed that the solubility of the gaseous starting material in an IL was good enough for the reaction to take place, in that the dimerization reactions of light olefins in IL media had already been successfully studied. Prior to the reaction, the ionic liquid was dried in a high vacuum to maximize the solubility of 2-methylpropene and to evacuate water. The reaction mixtures were stirred at a constant speed so that mass transfer would be similar in all the reactions. After initial studies in an autoclave, the reactions were carried out continuously, and the effect of the IL, its composition, the reaction temperature and the gas flow rate of 2-methylpropene on the reaction were studied.

Due to the nature of the Lewis acid-catalyzed reaction of 2-methylpropene, it easily also produces oligomers other than the desired dimers. It was known that the reaction temperature would affect product distribution. A high reaction temperature would favour the production of dimers (157). According to the literature, the main products of the dimerization reaction of 2-methylpropene are 2,4,4-trimethyl-1-pentene 8 and 2,4,4-trimethyl-2-pentene 9 (149,181). Isomerization of dimers at high temperatures was reported by Karinen et al. (162) and formation of isomers was also detected in this study. The products were analyzed with GCMS, and identification of the C₈ isomers was based on the results obtained from the dimerization reactions reported in the literature (181), the library mass spectrum and the boiling points of the isomers (59); 2,4,4-trimethyl-1-pentene 8 (bp. 101.4 ºC), 2,4,4-trimethyl-2-pentene 9 (bp. 104.9 ºC), 2,3,4-trimethyl-1-pentene 33 (bp. 108 ºC), 2,3,4-trimethyl-2-pentene 34 (bp. 116.5 ºC), 2,3,3-trimethyl-1-pentene 37 (bp. 108.3 ºC), 3,3,4-trimethyl-1-pentene 35 (bp. 105 ºC), 3,4,4-trimethyl-2-pentene 36 (bp. 112 ºC), 3,4,4-trimethyl-1-pentene 66 (bp. 104 ºC), see Figure 60.

![Fig. 60. C₈ isomers formed in the dimerization reaction of 2-methylpropene.](image)

4.3.3.1 Batch reactions

Dimerization reactions of 2-methylpropene were carried out in a 1-butyl-3-methylimidazole chloride/indium(III)chloride ionic liquid ([C₄mim][Cl/InCl₃]) in an autoclave. First the effect of the catalytic composition of the ionic liquid on the reaction was studied. The amount of InCl₃ in the IL mixtures was x(InCl₃) = 0.5, 0.52, 0.55, 0.57,
0.58, 0.6 or 0.66. It was noticed that the reactions where x(InCl₃) was 0.58, 0.6 or 0.66 took place at room temperature without heating. The reactions where x(InCl₃) was less than 0.58 had to be heated with an oil bath, as no products were formed at room temperature within 3 hours. When x(InCl₃) was 0.57, 0.55 or 0.52, the reaction required heating up to 50 °C, 80 °C or 120 °C, respectively. As was expected, when equal amounts of [C₄mim]Cl and InCl₃ were used, whereupon x(InCl₃) = 0.50, the IL did not catalyze the reaction at all, even though it was heated up to 120 °C for several hours. This was also reported in the dimerization reactions that were carried out in ILs containing aluminium(III)chloride as a Lewis acid (37). An ionic liquid needs to have an excess of Lewis acid to catalyze the dimerization reaction of 2-methylpropene.

Finally, batchwise reactions of 2-methylpropene were carried out at an adequate temperature for one hour. The product layer could be separated by decantation, as the nonpolar products were not miscible into the ionic liquid phase. GCMS analysis revealed that products ranging from dimers (C₄H₁₀) to octamers (C₃₂H₆₄) were formed. The product distributions of the reactions where the InCl₃ content in the IL was 0.67, 0.6, 0.58, 0.57 and 0.55 are shown in Figure 61. A comparison of the room temperature reactions where x(InCl₃) was 0.67, 0.6 or 0.58 indicated that the amount of higher oligomers increased and the amount of dimers and trimers decreased with increasing InCl₃ content in a catalytic IL. Temperature also affected product distribution. The amount of dimers increased from 10% to nearly 20% when the temperature was increased from room temperature to 80 °C.

Fig. 61. Product distributions of the reactions of 2-methylpropene carried out in five different catalytic [C₄mim]Cl/InCl₃ ionic liquids, x(InCl₃) = 0.67, 0.60, 0.58, 0.57 or 0.55.

The batchwise reactions carried out in an autoclave showed that, due to the nature of the Lewis acid-catalyzed reaction, 2-methylpropene easily reacted to dimers, trimers and other oligomers. Hence, the reaction seemed to be more like an oligomerization than a dimerization reaction. The oligomerization reaction was more dominant at a low temperature and when the amount of InCl₃ was high. It was assumed that, in order to produce mainly dimers, the amount of InCl₃ in the ionic liquid has to be higher than 0.5, but not too high. Therefore, a good catalytic ionic liquid would contain ca. 0.55 mol% of InCl₃.
4.3.3.2 Continuous reactions

The batchwise reactions of 2-methylpropene indicated that ILs based on InCl$_3$ will catalyze the reaction. Unfortunately, the reaction conditions favoured oligomerization instead of the dimerization reaction of 2-methylpropene. It was thought that the amount of oligomers could be reduced by continuously adding 2-methylpropene into the reactor. Then the concentration of 2-methylpropene would not be too high all at once. Since there was no proper reaction set up for a continuous reaction, it had to be planned first. The idea was to bubble gaseous 2-methylpropene through the catalytic ionic liquid. The formed dimer would then separate from the IL and form its own layer above the IL phase. Because the 2-methylpropene would be added continuously, the reactor could be smaller than an autoclave (200 ml). The first reactor was a 25 ml glass tube equipped with a long glass tube that went down to the bottom of the reactor (gas was fed in through it), an outlet on the top of the tube (unreacted 2-methylpropene was released through it into the bubbler) and a magnetic stirring bar.

The reaction setup was tested and it seemed to work fine when the reactions were carried out at room temperature. However, a comparison of the continuous reaction and the batch reaction carried out in 1-butyl-3-methylimidazole chloride/indium(III)chloride, x(InCl$_3$) = 0.58 showed that the product distributions were similar. Therefore, it was concluded that it was not enough to change the reaction setup to a continuous one. To produce more dimers, separation of the products from the catalytic ionic liquid has to be more efficient. In the literature a co-solvent, such as heptane or toluene, is applied in the dimerization reactions (189-201). In this study use of organic solvents was avoided, and it was thought that the products could be separated by distillation. This idea was also supported by the fact that dimerization is favoured at higher temperatures. Hence, a cold trap was added to the system. The products formed from the reaction were distilled and collected in the cold trap (0 ºC), and unreacted 2-methylpropene (bp. -7 ºC) passed through it to the bubbler. After some tests with this reaction setup, it reached its final form. The reaction setup consists of a gas bottle (placed on a balance), a gas-flow regulator, a flask mounted in an oil bath, a distillation bridge, a receiver flask set in an ice bath and a bubbler (Fig. 62).

![Fig. 62. Set up of the continuous flow reactor.](image-url)
Effect of temperature on the dimerization reaction

Dimerisation of 2-methylpropene was carried out in a continuous flow reactor applying three different ionic liquids \([C_n\text{mim}]\text{Cl}/\text{InCl}_3\), where \(n = 2, 4\) or 6 and \(x(\text{InCl}_3) = 0.55\). The reaction temperatures were 80, 120, 160 and 200 °C. The reaction temperature of 80 °C proved to be too low, as the boiling points of dimers are higher, around 100 - 115 °C. Therefore, most of the products stayed in the reactor as another layer above the catalytic ionic liquid. The reactions carried out at 120 °C allowed some part of the products to be collected in the cold trap. Most of the products were collected in the cold trap when the reaction temperature was 160 or 200 °C.

A comparison of the reactions carried out at 80 °C indicated that conversion of the 2-methylpropene to the products was most efficient, 25%, in a hexyl-substituted ionic liquid. In a butyl- or ethyl-substituted IL the conversions were 10% and 5%, respectively. The conversion seemed to increase with the non-polar nature of the IL. This was also reported in a study that considered the alkylation reaction of 2-methylpropene (186). It was assumed that the solubility of 2-methylpropene increased with the increasing non-polar nature of the IL. Conversions of the reactions carried out at 80 °C were calculated according to the products collected in the reactor.

The higher the reaction temperature was, the easier it was to distillate the products in the cold trap. Hence, the amount of separated products was biggest in reactions carried out at 200 °C. Conversions of 2-methylpropene, calculated according to the products found in the cold trap, were 2, 10, 25 and 30% for the reactions carried out in the hexyl-substituted IL at 80, 120, 160 and 200 °C, respectively. The total conversion of 2-methylpropene (calculated according to the products in the reactor and the cold trap) seemed to be more or less the same in reactions carried out at 80 and 200 °C, but the product distribution was different.

Samples for the GCMS analyses were taken from both the reactor and the cold trap. The analysis of the reactor sample showed that product distribution depended on reaction temperature. The amount of desired dimers increased and the amount of higher oligomers decreased with a rise in temperature. At a higher temperature dimers were also easier to separate from the other products by distillation. However, all the reactions mainly produced trimers (bp. 200 °C). The product distributions of the reactions where 1-hexyl-3-methylimidazolium chloride/InCl\(_3\), \(x(\text{InCl}_3) = 0.55\) was employed as a catalytic IL at four different temperatures are shown in Figure 63. The amount of dimers increased from 7% to 38% with the rise in temperature (from 80 to 200 °C), and the amount of trimers varied between 74% and 46%. The amount of trimers was greatest in the reaction carried out at 120 °C. The amount of higher oligomers (tetramers, pentamers, etc.) was biggest when the reaction temperature was 80 °C.
Fig. 63. Product distributions (in the reactor) of the reactions of 2-methylpropene carried out in 1-hexyl-3-methylimidazolium chloride/InCl\textsubscript{3}, \(x(\text{InCl}_3) = 0.55\), at four different temperatures.

The product distributions of the distilled products from the reactions carried out in 1-hexyl-3-methylimidazolium chloride/InCl\textsubscript{3}, \(x(\text{InCl}_3) = 0.55\) at 80, 120, 160 and 200 °C are shown in Figure 64. The main products were dimers, and the amount of trimers was low, only 1-3%, in all cases when the reaction temperature was above 120 °C. Only a small amount of the product was separated when the reaction temperature was 80 °C. The temperature was not high enough for the dimers to be distilled, and hence it was assumed that unreacted 2-methylpropene carried products with it into the cold trap. Therefore, ca.15% of the trimers were found in the cold trap.

Fig. 64. Product distributions of the distilled products of the reaction of 2-methylpropene carried out in 1-hexyl-3-methylimidazolium chloride/InCl\textsubscript{3}, \(x(\text{InCl}_3) = 0.55\), at four different temperatures.
The distilled products were analyzed in more detail and the GCMS analysis showed that in all the reactions the main products were 2,4,4-trimethyl-1-pentene 8 and 2,4,4-trimethyl-2-pentene 9, as was expected based on the previous dimerization studies reported by Marchionna (181). In addition to these two dimers, a small amount of other C₈ isomers were formed at all temperatures (Table 33). Increasing the reaction temperature changed the product distribution so that more isomers were observed to form. (162). Karinen et al. reported that 2,3,4-trimethylpentenes 33 and 34 started to form when they studied the isomerization of 8 to 9 above 100 °C. In this study, in addition to 33 and 34, other C₈ isomers, such as 3,3,4-trimethyl-1-pentene 66, 3,4,4-trimethyl-2-pentene 36 and 2,3,3-trimethyl-1-pentene 37, were seen when the reaction temperature was increased. The amount of main dimers 8 and 9 decreased when the temperature was increased up to 160 °C. As a result, especially the amount of 2,3,4-trimethyl-2-pentene 34 and also 2,3,4-trimethyl-1-pentene 33 increased. 3,4,4-trimethyl-1-pentene 35 was not observed in the GCMS analysis, owing to the fact that its boiling point is the same as the boiling point of 9. It was assumed according the GCMS analysis that trimethylpentenes were not the only isomerization products, but also dimethylhexenes were formed at higher temperatures. The main trimers that formed in the reactions were 2,2,4,6,6-pentamethyl-3-heptene 56 and 2,2,6,6-tetramethyl-4-methylene-heptane 57.

Table 33. Detailed product distribution of the distilled products of the reaction of 2-methylpropene carried out in 1-hexyl-3-methylimidazolium chloride/InCl₃, x(InCl₃) = 0.55 at four different temperatures.

<table>
<thead>
<tr>
<th>Products %</th>
<th>Reaction temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>80</td>
</tr>
<tr>
<td>2,4,4-trimethyl-1-pentene 8</td>
<td>64</td>
</tr>
<tr>
<td>3,3,4-trimethyl-1-pentene 66</td>
<td>1</td>
</tr>
<tr>
<td>2,4,4-trimethyl-2-pentene 9</td>
<td>19</td>
</tr>
<tr>
<td>2,3,4-trimethyl-1-pentene 33</td>
<td>19</td>
</tr>
<tr>
<td>2,3,3-trimethyl-1-pentene 37</td>
<td>1</td>
</tr>
<tr>
<td>3,4,4-trimethyl-2-pentene 36</td>
<td>1</td>
</tr>
<tr>
<td>2,3,4-trimethyl-2-pentene 34</td>
<td>3</td>
</tr>
<tr>
<td>Dimethylhexenes</td>
<td>1</td>
</tr>
<tr>
<td>Trimers 56 and 57</td>
<td>12</td>
</tr>
</tbody>
</table>

The thermal stability of the ionic liquids was determined, as the colour of the catalytic ionic liquid was observed to change during the dimerization reaction of 2-methylpropene at higher temperatures. The reaction that was carried out at 160 °C yielded a slightly orange IL, and during the reaction at 200 °C the IL turned brown. The thermal gravimetric analyses showed that all three different cations, [C₂,mim]⁺, [C₄,mim]⁺ and [C₆,mim]⁺, decomposed around 200 °C. The following reactions were carried out at 120 or 160 °C, excluding 80 °C as too low and 200 °C as too high reaction temperature.
Effect of the gas flow rate on product distribution at 120 °C

The effect of the gas flow rate on product distribution was studied in three different ionic liquids \([\text{C}_n\text{mim}]\text{Cl}/\text{InCl}_3\), where \(n = 2, 4\) or 6 and \(x(\text{InCl}_3) = 0.55\), at 120 °C. The flow rate of 2-methylpropene was set to 1.5 (low), 3 (medium) or 6 mmol/min (high) in these reactions. It was noticed that increasing the concentration of 2-methylpropene in the reaction mixture slightly decreased the amount of dimers and increased the amount of other oligomers. The effect of gas flow on product distribution is shown in Fig. 65 for the ethyl-substituted IL.

Fig. 65. Product distributions (in the reactor) of the reactions of 2-methylpropene carried out in 1-ethyl-3-methylimidazolium chloride/\text{InCl}_3, x(\text{InCl}_3) = 0.55, with three different gas flow rates at 120 °C.

The effect of the gas flow rate on the product distribution of the distilled products is shown in Fig. 66 for reactions carried out in three different ILs. The results showed that the higher the gas flow rate was, the less dimers were obtained. This was seen in all three catalytic ionic liquids. The amount of dimers decreased from 98 to 64%, from 82 to 49% or from 99 to 65%, when \([\text{C}_2\text{mim}]^+\), \([\text{C}_4\text{mim}]^+\) or \([\text{C}_6\text{mim}]^+\)-containing ILs were applied, respectively. When \([\text{C}_2\text{mim}]^+\) was used as a cation, tetramers were also detected in the cold trap. The amount of products in the cold trap increased with gas flow. It seemed that the unreacted 2-methylpropene carried products with it. To get more efficient separation of the dimers, the reaction temperature should have been higher. Owing to the low temperature, the conversions of 2-methylpropene were not good, only 10% at best.
The main products were dimers 8 and 9, and the main dimer of the isomerization reaction was 34. The more 2-methylpropene was fed into the reactor, the more easily it reacted with the dimers to yield trimers. The main trimers were 56 and 57. The product distribution of the reactions of 2-methylpropene in 1-hexyl-3-methylimidazolium chloride/InCl$_3$ (x(InCl$_3$) = 0.55) with three different gas flow rates are presented in Table 34. The most efficient gas flow rate was the lowest one, 1.4 mmol/min of 2-methylpropene in [C$_6$ mim]Cl/InCl$_3$ at 120 °C.

Table 34. Detailed product distributions of the reactions of 2-methylpropene carried out in 1-hexyl-3-methylimidazolium chloride/InCl$_3$, x(InCl$_3$) = 0.55, with three different gas flow rates at 120 °C.
Effect of different gas rates at 160 °C

The effect of the gas flow rate on product distribution was studied in three different ionic liquids \([C_n\text{mim}]\text{Cl}/\text{InCl}_3\), where \(n = 2, 4\) or \(6\) and \(x(\text{InCl}_3) = 0.55\), at 160 °C. The flow rate of 2-methylpropene was set at either 1.5 (low) or 3 mmol/min (medium) in these reactions. In these reactions the temperature was high enough that most of the products were distilled and collected in the cold trap. There was no visible product layer in the reactor.

The results of this experiment are presented in Figure 67. They revealed that the faster the gas feed, the less dimers were obtained. In this sense there was no difference between the applied three ionic liquids. The amount of dimers decreased from 83 to 71%, from 82 to 67% or from 99 to 94%, when \([C_2\text{mim}]^+\), \([C_4\text{mim}]^+\) or \([C_6\text{mim}]^+\)-containing ILs were used, respectively. Mainly dimers and trimers were collected in the cold trap, but when \([C_2\text{mim}]^+\) was used as a cation tetramers were also detected with the medium gas flow rate. The conversion of 2-methylpropene was most efficient in \([C_6\text{mim}]\text{Cl}/\text{InCl}_3\), around 25%, with both gas flow rates. The slow gas flow rate, 1.4 mmol/min of 2-methylpropene, was better than the medium one, since it produced more dimers.

![Figure 67](image-url)

Fig. 67. Product distributions of the distilled products of the reaction of 2-methylpropene carried out in three different ionic liquids \([C_n\text{mim}]\text{Cl}/\text{InCl}_3\), \(x(\text{InCl}_3) = 0.55\), with two different gas flow rates at 160 °C.

Comparison of reactions carried out at 120 °C and 160 °C

The product distributions of the dimerizations of 2-methylpropene at temperatures 120 and 160 °C are compared in Table 35. Reactions were performed in three different ionic liquids \([C_n\text{mim}]\text{Cl}/\text{InCl}_3\), where \(n = 2, 4\) or \(6\) and \(x(\text{InCl}_3) = 0.55\), with the slow gas flow rate. Dimers \(8, 9\) and \(34\) were the main products in all ILs at both temperatures. The highest dimer content was attained in \([C_6\text{mim}]\text{Cl}/\text{InCl}_3\) at 120 °C. The amount of the two major dimers \(8\) and \(9\) decreased when the temperature was increased from 120 to 160 °C. At the same time the amounts of dimers \(34, 33\) and \(36\) increased. Besides, some dimethylhexenes were produced at 160 °C. In \([C_6\text{mim}]\text{Cl}/\text{InCl}_3\) the amount of trimers was
significantly lower than in ethyl- and butyl-substituted ionic liquids at both temperatures. According to these results, \([\text{C}_6\text{mim}]^+\)-containing IL seemed to be the most efficient IL.

Table 35. Comparison of the detailed product distributions of the reactions of 2-methylpropene carried out in three different ionic liquids \([\text{C}_n\text{mim}]\text{Cl}/\text{InCl}_3, x(\text{InCl}_3) = 0.55\), at 120 and 160 °C.

<table>
<thead>
<tr>
<th>Products %</th>
<th>([\text{C}_6\text{mim}]\text{Cl}/\text{InCl}_3)</th>
<th>([\text{C}_4\text{mim}]\text{Cl}/\text{InCl}_3)</th>
<th>([\text{C}_6\text{mim}]\text{Cl}/\text{InCl}_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>120 °C</td>
<td>160 °C</td>
<td>120 °C</td>
</tr>
<tr>
<td>2,4,4-trimethyl-1-pentene 8</td>
<td>57</td>
<td>36</td>
<td>47</td>
</tr>
<tr>
<td>3,3,4-trimethyl-1-pentene 66</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2,4,4-trimethyl-2-pentene 9</td>
<td>16</td>
<td>14</td>
<td>15</td>
</tr>
<tr>
<td>2,3,4-trimethyl-1-pentene 33</td>
<td>3</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>2,3,3-trimethyl-1-pentene 37</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>3,4,4-trimethyl-2-pentene 36</td>
<td>2</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>2,3,4-trimethyl-2-pentene 34</td>
<td>9</td>
<td>18</td>
<td>11</td>
</tr>
<tr>
<td>Dimethylhexenes</td>
<td>3</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Trimers 56 and 57</td>
<td>8</td>
<td>17</td>
<td>18</td>
</tr>
<tr>
<td>Tetramers</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

The residence time of the 2-methylpropene affects on the composition of the product mixture. The residence time in the previous batch reactions was far too long, and hence the product distribution favoured oligomers. In a continuous reactions the residence time of 2-methylpropene was highly dependent on the reaction temperature. The higher the temperature, the more easily the dimers were separated and the shorter the residence time was. Most of the products were collected in the cold trap when the reaction temperature was 160 °C. The cation of the IL had an effect on the reaction, dimers were produced most selectively in \([\text{C}_6\text{mim}]^+\)-containing IL. The formation of trimers and higher oligomers was favoured in ethyl- or butyl-substituted IL. The higher reaction temperature increased the isomerization reaction, but owing to the similarity of the trimethylpentene isomers, they all are equally good octane enhancers and hence isomerization did not negatively affect the reaction.

Effect of indium(III)chloride content in a catalytic ionic liquid

Further experiments were carried out to study the effect of the amount of InCl₃ in IL on product distribution. Reactions were carried out in \([\text{C}_n\text{mim}]\text{Cl}/\text{InCl}_3\) (where \(n = 2, 4 \text{ or } 6\)) with the InCl₃ content 0.55 or 0.58 mol%. The reaction temperatures were 80, 120 and 160 °C and the gas flow rate of 2-methylpropene was 1.5 mmol/min. The results showed that the ratio of dimeric and trimeric products in the cold trap was dependent on the amount of InCl₃ in the IL. Its increase led to a lower yield of dimers in every IL and at all temperatures and the formation of trimers was increased. Tetramers were not detected in these reactions. Figure 68 shows the product distribution of the reaction carried out in 1-hexyl-3-methylimidazolium chloride/InCl₃ as a function of indiumtrichloride content and the reaction temperature.
The detailed product distributions of the above-mentioned reactions of 2-methylpropene are compared in Table 36. The main products were dimers 8 and 9 with both InCl₃ contents at 80 or 120 °C. At 160 °C the isomerization reaction increased, and hence the amount of dimer 34 increased and the amount of the two major dimers, 8 and 9, decreased. The amount of oligomers increased with the increasing InCl₃ content at all temperatures along with the conversion of 2-methylpropene. Therefore, it seemed that InCl₃ catalyzed the oligomerization rather than the isomerization reaction. The same trend was also observed in the first dimerization reactions of 2-methylpropene that were carried out batchwise in the autoclave. Owing to the nature of the reaction, oligomers were generated at the lower temperature and the dimerization was favoured at the higher temperature. Hence, the amount of trimers 56 and 57 (33%) was highest at 80 °C and with a higher indium(III)chloride content, x(InCl₃) = 0.58. It was assumed that the dimer distribution depended more on the temperature than on the amount of indium in the catalytic ionic liquid.
Table 36. Detailed product distributions of the reaction of 2-methylpropene carried out in 1-hexyl-3-methylimidazolium chloride/InCl₃, where x(InCl₃) = 0.55 or 0.58, at three different temperatures: 80, 120 and 160 ºC.

<table>
<thead>
<tr>
<th>Products</th>
<th>80 ºC</th>
<th>120 ºC</th>
<th>160 ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.55</td>
<td>0.58</td>
<td>0.55</td>
</tr>
<tr>
<td>2,4,4-trimethyl-1-pentene</td>
<td>64</td>
<td>50</td>
<td>68</td>
</tr>
<tr>
<td>3,3,4-trimethyl-1-pentene</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2,4,4-trimethyl-2-pentene</td>
<td>19</td>
<td>14</td>
<td>19</td>
</tr>
<tr>
<td>2,3,4-trimethyl-1-pentene</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>2,3,3-trimethyl-1-pentene</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>3,4,4-trimethyl-2-pentene</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2,3,4-trimethyl-2-pentene</td>
<td>3</td>
<td>1</td>
<td>7</td>
</tr>
<tr>
<td>Dimethylhexenes</td>
<td>3</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Trimers 56 and 57</td>
<td>12</td>
<td>33</td>
<td>1</td>
</tr>
</tbody>
</table>

The previous experiments have shown that the gas flow rate affects product distribution. Increasing the gas flow rate increased the amount of trimers when the catalytic ionic liquid contained 0.55 mol% of InCl₃, as was shown in Fig. 57. Further experiments were carried out to study a possible correlation between the gas flow rate and the composition of the catalytic ionic liquid. The applied IL was [C₆mim]Cl/InCl₃, where the amount of InCl₃ was increased to 0.58 mol%. Two different gas flow rates of 2-methylpropene were applied, 1.5 or 3 mmol/min, and the reaction temperature was 120 ºC. When the IL contained 0.58 mol% of InCl₃, both of the gas flow rates gave similar results; see the right hand side of Figure 69. For comparison, the results from the reactions carried out in [C₆mim]Cl/InCl₃ containing 0.55 mol% of InCl₃, are shown on the left hand side in the Figure. In this case it was more efficient to use the slow gas flow rate, because the medium gas flow rate gave more trimers, ca. 15%.

![Fig. 69. Product distributions of the distilled products of the reaction of 2-methylpropene carried out in 1-hexyl-3-methylimidazolium chloride/InCl₃, where x(InCl₃) = 0.55 and 0.58, with two different gas flow rates (slow and medium).](image-url)
The InCl$_3$ content and the gas flow rate of 2-methylpropene did not affect the dimer distribution, the main dimers were 8 and 9 (Table 37). Nearly 10% of dimer 34 was formed in every reaction. The amounts of other trimethylpentenes were low, and no dimethylhexenes were detected. Most of the dimers were obtained when x(InCl$_3$) was 0.55 and a slow gas flow was used.

Table 37. Detailed product distributions of the reaction of 2-methylpropene carried out in 1-hexyl-3-methylimidazolium chloride/InCl$_3$, where x(InCl$_3$) = 0.55 or 0.58, with two different gas flow rates (low and medium) at 120 ºC.

<table>
<thead>
<tr>
<th>Products %</th>
<th>0.55 low</th>
<th>0.55 medium</th>
<th>0.58 low</th>
<th>0.58 medium</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4,4-trimethyl-1-pentene 8</td>
<td>68</td>
<td>55</td>
<td>64</td>
<td>61</td>
</tr>
<tr>
<td>3,3,4-trimethyl-1-pentene 66</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2,4,4-trimethyl-2-pentene 9</td>
<td>19</td>
<td>18</td>
<td>19</td>
<td>19</td>
</tr>
<tr>
<td>2,3,4-trimethyl-1-pentene 33</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>2,3,3-trimethyl-1-pentene 37</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3,4,4-trimethyl-2-pentene 36</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2,3,4-trimethyl-2-pentene 34</td>
<td>7</td>
<td>8</td>
<td>7</td>
<td>9</td>
</tr>
<tr>
<td>Dimethylhexenes</td>
<td></td>
<td></td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Trimers 56 and 57</td>
<td>1</td>
<td>15</td>
<td>6</td>
<td>7</td>
</tr>
</tbody>
</table>

Recycling and reproducibility

A possibility of recycling is an essential property of ionic liquids. Therefore, it was valuable to study the recyclability of an applied catalytic system. Recycling studies indicated that the catalytic properties of an ionic liquid could be maintained for several hours. The batch reaction were carried out in [C$_4$mim]Cl/InCl$_3$, with InCl$_3$ 0.58 mol%, at 120 ºC for 1 hour. In these experiments the product layer separated on the surface of IL and was decanted before a new batch of 2-methylpropene was fed in. The conversions of 2-methylpropene stayed at the same level in first three reactions, but the fourth one gave a 40% lower conversion. Oligomerized products formed in the reactions started to accumulate on the walls of the reactor and hence they were omitted from the calculations based on the products decanted from the reactor. It would have been possible to avoid the formation of higher oligomers by using a non-polar solvent in the reaction. That might also be facilitated the separation of the products from the ionic liquid layer and thus reduced the formation of secondary products. Or, instead of decanting the products, they could have been extracted with a non-polar solvent to get all the products out from the reactor, which would have avoided the accumulation of the higher oligomers in the reactor. Since the continuous reaction was in practice more useful than the batch reaction, the recycling of the IL and optimization of the conditions of batch reactions were not studied further.

The dimerization reaction with a continuous feed of 2-methylpropene (1.5 mmol/min) was carried out in [C$_6$mim]Cl/InCl$_3$, x(InCl$_3$) = 0.55 for 6 hours at 160 ºC. The colour of the IL changed during the reaction. At the beginning the solution was clear, but over 6
hours it changed \textit{via} yellow and orange to brown. The formation of the products in the cold trap was monitored by GC as a function of reaction time. The conversion of 2-methylpropene was 15%. The amounts of the main dimers as a function of reaction time are shown in Table 38. The amount of dimer 8 steadily reduced during the reaction, but the amounts of the other main dimers 9, 33 and 34 remained nearly at the same level.

\textbf{Table 38. Amount of main dimers formed as a function of reaction time in the continuous reaction of 2-methylpropene in [C\textsubscript{6}mim]Cl/InCl\textsubscript{3}, x(InCl\textsubscript{3}) = 0.55, IL at 160 °C.}

<table>
<thead>
<tr>
<th>Products %</th>
<th>Reaction time h</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>2,4,4-trimethyl-1-pentene 8</td>
<td>63</td>
</tr>
<tr>
<td>2,4,4-trimethyl-2-pentene 9</td>
<td>18</td>
</tr>
<tr>
<td>2,3,4-trimethyl-1-pentene 33</td>
<td>5</td>
</tr>
<tr>
<td>2,3,4-trimethyl-2-pentene 34</td>
<td>8</td>
</tr>
</tbody>
</table>

The accumulation of the products on the surface of the reaction mixture in the reactor increased with the reaction time. At the end of the reaction formed products were decanted and analyzed with GC. The conversion of 2-methylpropene calculated according to the products found in the reactor was ca. 15%. Compared the short reaction time (30 min) the long reaction time (360 min) increased the amount of dimers and oligomers, but decreased the amount of trimers. The results indicated that it was possible to carry out the dimerization reaction of 2-methylpropene for several hours.

The used catalytic ionic liquid was washed several times with hexane to purify it for the next reaction. After drying in a high vacuum it was analyzed with NMR. The \textsuperscript{1}H NMR spectrum indicated that the IL did not contain any products. In addition, indium content was analyzed from the hexane extract by elemental analysis and it showed the absence of InCl\textsubscript{3} indicating that it stayed in the ionic liquid and did not leach out from it. The ionic liquid was used again in a dimerization reaction and it catalyzed successfully the reaction.

The results of the dimerization reaction of 2-methylpropene seemed to be reproducible with low and medium gas flow rates. The product distribution varied more when a high gas flow rate was used, and especially the amounts of dimer 8 and trimers 56 and 57 varied considerably.

\textbf{4.3.4 Summary}

The dimerization reaction of 2-methylpropene can be carried out in ionic liquids containing an excess of Bronsted or Lewis acid as a catalyst. A neutral ionic liquid will not catalyze the reaction. The reactions carried out in Bronsted acid-based ILs did not work as well as the reactions catalyzed with InCl\textsubscript{3}. The main drawback was that the added Bronsted acid leached out from the IL to the product phase, and for the loss of its catalytic activity the ionic liquid was not recyclable. The amount of oligomers formed in
the reactions was lower than in Lewis acid-catalyzed reactions, but the reaction produced a lot of trimers.

The batch reactions catalyzed with InCl₃ favoured the production of oligomers. It was concluded that the residence time was too long, and led to the further reaction of dimers to higher oligomers. The results from the batch reactions indicated that increasing the amount of InCl₃ in the IL favoured the production of higher oligomers further. When the InCl₃ content in IL was higher than 0.58 mol% the reaction could be carried out at room temperature, otherwise it needed activation by heating.

The following reactions were carried out continuously in order to reduce residence time and the subsequent formation of side products. The experiments with this reaction set up indicated that 80 ºC as a reaction temperature was too low, as separation of the products (bp. > 100 ºC) was not possible and hence the product distribution favoured oligomers. The rise of the reaction temperature to 120 ºC and furthermore to 160 ºC led to a more efficient separation of the products but catalyzed the isomerization of dimers. The reactions carried out at 160 ºC and 200 ºC showed rather similar product distributions, but the used ionic liquid started to decompose at higher temperature.

The conversion of 2-methylpropene was highest with the ionic liquid containing [C₆mim]+ as a cation, 1-hexyl-3-methylimidazolium chloride/InCl₃. It seemed that increasing the non-polar nature of the ionic liquid was advantageous for the reaction. It was assumed that 2-methylpropene had better solubility into the more non-polar IL. Unfortunately, the conversion of 2-methylpropene was quite low at all temperatures. The reaction carried out in [C₆mim]Cl/InCl₃ at 160 ºC gave a 25% conversion, which was calculated according to the distilled products found in the cold trap.

The cation of the IL had an effect on product distribution. When [C₆mim]Cl/InCl₃ was applied as a catalytic reaction medium, mainly dimers were formed, but when the cation was ethyl- or butyl-substituted, the amount of trimers was increased. In addition to the cation, also the InCl₃ content affected product distribution. Increasing the amount of InCl₃ in the IL increased the oligomerization reaction. Furthermore, a correlation between the amount of InCl₃ in the IL and the gas feed of 2-methylpropene was detected. The high gas flow rate of 2-methylpropene added the formation of trimers at the expense of dimers. The results obtained from this study indicated that the dimerization reaction of 2-methylpropene should be carried out in [C₆mim]Cl/InCl₃, x(InCl₃) = 0.55, at 160 ºC with a slow gas flow rate.

One of the main subjects of this study was the product distribution of dimers. A summary of the main products of the dimerization reaction of 2-methylpropene carried out in [C₆mim]Cl/InCl₃, x(InCl₃) = 0.55 at 120, 160 and 200 ºC with a slow gas flow rate is shown in Table 39. The reaction temperature had the strongest effect on the product distribution of the dimers. A high reaction temperature favoured the formation of dimers, facilitated their separation and added the selection of isomeric dimers. Anyhow, isomerization is not really a disadvantage because all isomeric trimethylpentenes are good octane enhancers.
Table 39. Main dimers formed in the dimerization reaction of 2-methylpropene at different temperatures.

<table>
<thead>
<tr>
<th>Products %</th>
<th>Reaction temperature ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>120</td>
</tr>
<tr>
<td>2,4,4-trimethyl-1-pentene 8</td>
<td>68</td>
</tr>
<tr>
<td>2,4,4-trimethyl-2-pentene 9</td>
<td>19</td>
</tr>
<tr>
<td>2,3,4-trimethyl-1-pentene 33</td>
<td></td>
</tr>
<tr>
<td>2,3,4-trimethyl-2-pentene 34</td>
<td></td>
</tr>
<tr>
<td>Trimers 56 and 57</td>
<td>1</td>
</tr>
</tbody>
</table>

It was possible to carry out the continuous reaction for several hours at 160 ºC, and the product distribution of the distilled products did not change during the reaction. However, the accumulation of the products in the reactor increased the formation of oligomers. It was possible to recycle the ionic liquid after it was washed with hexane to extract the product residue from it.

The reaction of 2-methylpropene is exothermic, but in this study it did not cause any problems. The results obtained from the study indicate the variety of factors affecting in dimerization. Further optimization of the production of dimers and the scale-up of the reaction require improvements in the reaction set up in order e.g. to recycle the unreacted 2-methylpropene.
5 Conclusions

One major goal of this study was to prepare suitable ionic liquids for the dimerization reaction of 2-methylpropene. Ionic liquids were prepared by applying the principles of green chemistry whenever it was possible. The preparations were carried out in a single-mode microwave reactor and for comparison same preparations were performed by conventional methods. The sixth principle of green chemistry involves minimization of energy consumption and supports reactions conducted at ambient pressure and temperature. Microwave activation compared with conventional heating considerably shortens the reaction time, hence reducing energy consumption. Short reaction time means saving of time, which is also a valuable resource. Since side products were not formed and no additional reaction solvents were used in the quaternization reactions, atom economy was found to be good in these reactions. Derivatization or a catalyst was not required, and the yield was quantitative in almost every reaction. Therefore, principles 1, 2, 8 and 9 were also applied in this study. The last of the principles concerns the use of substances that minimize the potential for chemical hazards. Ionic liquids do not evaporate or burn easily, hence the use of ionic liquids instead of organic solvents improves safety, given that releases, explosions and fires will not take place so easily. In addition, ionic liquids possess a very important property: they are recyclable.

1-Butyl-3-methylimidazolium-based ionic liquids were successfully prepared by means of a quaternization reaction in a single-mode microwave reactor. The optimal reaction conditions were found to be different for all three ionic liquids $[\text{C}_4\text{mim}]\text{Cl}$ 1, $[\text{C}_4\text{mim}][\text{TsO}]$ 2 and $[\text{C}_4\text{mim}][\text{MsO}]$ 3 formed with the quaternization reaction. The maximum reaction temperature depended on the nature of the alkylating reagent. Reactions with butyl chloride yielded transalkylation products, $[\text{C}_4\text{C}_4\text{im}]\text{Cl}$ and $[\text{mmim}]\text{Cl}$, in addition to the desired IL 1 at elevated temperatures $>130$ °C (74). This was not reported in other preparation studies (88,89). Usually, a solvent and large excess of alkylating reagent are required when ionic liquids are prepared with conventional heating (43). In this study, quaternization reactions were performed without a solvent by using only a slight excess of alkylating agent. During the study it was noticed that temperature and the power level had a strong influence on the purity and also the colour of the ionic liquid. Side reactions and decomposition of reagents could be avoided by using low reaction temperatures and reasonably adjusted power levels. The biggest benefit of microwave irradiation compared with conventional heating was the
considerably shortened reaction time. The reaction time could be decreased from 24 hours to 20 minutes, from 6 hours to 10 minutes and from 96 hours to 10 minutes in the microwave-assisted preparation of 1, 2 and 3, respectively. Microwave-assisted preparation of [C₆mim][PF₆] 4 by means of a metathesis reaction shortened the reaction time from 5 hours to 10 minutes compared with the conventional method. [C₆mim][InCl₃] ILs 5 were prepared successfully without microwave irradiation.

ILs were characterized by combining several analysis methods, such as ¹H and ¹³C NMR, MS(ESI⁺ and ESI⁻), GC, DSC, TGA, elemental analysis and crystal structure analysis. The analytical results supported each other and gave a reliable picture of the purity and suitability of the ionic liquids for the dimerization reaction. The study concerning the microwave-assisted preparations of 1 and 4 together with the crystal structure of 1 was published in 2004 (90). A manuscript dealing with the microwave-assisted preparation and characterization of sulfonate-based IL 2 and 3, and two manuscripts of preparation and characterization of InCl₃-based ILs 5 are almost ready to be submitted.

Due to the excellent heating ability of ionic liquids under microwave irradiation their microwave-assisted preparation as well as their application as a reaction media in various microwave-assisted chemical processes might be of a great industrial importance in future. New flow-through microwave reactors will allow the large scale production of IL and the applications of ionic liquids provide environmental benefits compared to utilization of VOC’s.

The dimerization study indicated that novel InCl₃-based ILs are suitable catalytic solvents for the dimerization reaction of 2-methylpropene. Current dimerization processes apply acidic ion-exchange resins as catalysts and water and/or low alcohols as additives to control the selectivity of the reaction (e.g. Neste Oil), or a nickel catalyst with AlCl₃ as a co-catalyst (e.g. IFP). Production of octene or octane with these processes is good. However, IFP’s Dimersol process suffers from the separation of the products and the consumption of the catalyst owing to its not being recyclable. The use of AlCl₃-based ionic liquids has improved the process so that separation of the products and recycling of the catalyst (Difasol) are possible. In this study, InCl₃ catalyzed the reaction, and hence the use of a transition metal catalyst was not necessary and no catalyst waste was produced. Since InCl₃-based ILs are not as water-sensitive as AlCl₃-based ILs, they are easier to handle. The dimerization reaction of 2-methylpropene was controlled with temperature, and hence additives were not necessary as in the acid resin-catalyzed reactions. It was also possible to apply a higher reaction temperature than with the acid resin catalysts, > 120 ºC. Lewis acids are commonly used as catalysts in oligomerization and polymerization reactions. Therefore, acidic AlCl₃-based ILs have been employed to catalyze the oligomerization reactions of light olefins (40). This study indicated that InCl₃-based ILs can also be utilized to produce dimers. In order to maximize the production and separation of dimers, the reaction should be carried out continuously at a high enough temperature, such as 160 ºC. It was preferable to use [C₆mim]Cl/InCl₃ (x(InCl₃) = 0.55) as a catalytic IL, since then the conversion of 2-methylpropene and the product distribution proved to be good. Excess InCl₃ did not leach out from the IL and recycling of the IL was possible. Based on the results, a patent application considering the method itself was filed on June 2005. This method should be suitable for dimerizing other light olefins as well.
6 Experimental

6.1 Reagents

*N*-Methylimidazole (99%, Aldrich), *p*-toluenesulfonic acid chloride (98%, Aldrich), methanesulfonylchloride (98%, Aldrich), alkylchlorides (99%, Fluka), sodium hexafluorophosphate 98%, Aldrich), indium(III)chloride (98%, Aldrich and 99.99%, Alfa Aesar) and butanol (98% Riedel-de Haen) were used without further purification. Acetone (98% Labscan), ethyl acetate (99% Rathburn) and acetonitrile (98% Labscan) were dried prior to use. Pyridine was distilled from CaH₂ prior to use. The filtering agent was Celite 577.

2-Methylpropene (99%) was purchased from Aldrich and used as received. Hexane was distilled over CaH₂. Reaction temperatures refer to bath temperatures. Palladium acetate (97%, Lancaster) 1,3-propanediylbisphenylphosphite (98%, Aldrich), hexafluorophosphoric acid (0.65% water solution, Fluka), *p*-toluenesulfonic acid monohydrate (99%, Fluka), methanesulfonic acid (99%, Fluka) and formic acid (98%, Fluka) were used as obtained from the supplier.

6.2 Microwave reactor

All the microwave-assisted reactions were performed using a single-mode microwave reactor, Emrys™ Synthesizer, Biotage, designed for synthetic use. The reactor is equipped with a magnetic stirrer and pressure, temperature (IR detection) and power control. The maximum operating pressure of the reactor is 20 bar. The power and temperature range are 15 - 300 W and 60 – 250 °C, respectively. The reactor vessels were Emrys Process Vials™ for 2-5 ml reactions. The method of microwave irradiation could be programmed by controlling temperature or power. The temperature control keeps the reaction constant by modulating power. Respectively, the power control keeps the power constant and the temperature varies accordingly.

The power of the microwave reactor could be set to three levels: very high, high or normal, even if the reaction is controlled by temperature. The very high level was used
because ionic liquids absorb microwave energy very well. At this level the maximum power output is 75 W. The reaction time does not include the time used for heating and cooling. Usually the reaction temperature was reached in 15-30 seconds, and roughly the same time was required for cooling with compressed air.

6.3 Analytical methods for characterization of ionic liquids

6.3.1 \(^1\)H and \(^{13}\)C NMR analysis

The \(^1\)H and \(^{13}\)C spectra of 1-alkyl-3-methylimidazolium tetrachloridoindate ionic liquids were recorded with a Bruker DPX300 spectrometer in CD\(_3\)CN or in CDCl\(_3\). The \(^1\)H NMR and \(^{13}\)C NMR spectra of the other ionic liquids were recorded by a Bruker DBX 200 instrument (\(^1\)H 200.13 MHz, \(^{13}\)C 50.32 MHz) in CDCl\(_3\) or D\(_2\)O. Chemical shifts (\(\delta\)) are reported in ppm with respect to a scale calibrated to tetramethylsilane (TMS, \(^1\)H NMR \(\delta_H = 0.00\) ppm, \(^{13}\)C NMR \(\delta_C = 0.00\) ppm). The numbering of the [C\(_4\)mim\(]^+\) cation used to interpret the NMR spectrum is shown below.

![Fig. 70. Numering of the [C\(_4\)mim\(]^+\) cation used to interpret the NMR spectrum.](image)

6.3.2 GC and GCMS analysis

Gas chromatographs of some ionic liquids were recorded with a PerkinElmer Autosystem XL gas chromatograph equipped with an OV-1 (30 m, 0.32 mm, 0.25 \(\mu\)m) capillary column and a FID. Mass analyses were performed by the University of Oulu mass spectrometry laboratory with GCMS (EI) 70 eV ionization energies, an HP 6890 series GC System equipped with a capillary column BPX5 (25m, 0.33 mm, 0.25 \(\mu\)m), a FID and an HP5973 MSD mass spectrometer.

6.3.3 Mass and elemental analysis

The electrospray ionization mass spectra were measured by the University of Oulu mass spectrometry laboratory with a Micromass, LCT mass spectrometer. CNH elemental analyses were performed by the University of Oulu trace element laboratory with a Perkin Elmer elemental analyzer 2400 series II CHNS/O. Elemental analyses (C, H, N, Cl, In) of indiumtrichloride-based ionic liquids were performed by A.S.E.P. at the Queens University of Belfast.
6.3.4 Melting points and thermal stability analysis

Melting points were determined with a Gallenkamp melting point apparatus MFP-595 and a differential scanning calorimeter Perkin-Elmer Pyris 7 DSC. The heating rate with the melting point apparatus was 2 °C min⁻¹. The samples for DSC analysis were 10-20 mg, the heating and cooling rate was 10 °C min⁻¹ over a temperature range of 25-200 °C and the carrier gas was dinitrogen. The samples were placed in an aluminium pan, and an empty aluminium pan was used as a reference. The melting points were measured from the highest position at the peak of the heating cycle.

Thermogravimetric analyses were performed with a Mettler TG50 Thermobalance and dinitrogen was used as a carrier gas. The sample (10-20 mg) was placed in an aluminium pan and heated over a temperature range of 25-450 °C or 25-600 °C at a heating rate of 10 °C min⁻¹.

6.3.5 X-ray crystal structure analysis

Diffraction data were collected with a Nonius Kappa CCD diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). All the structures were solved using SIR-92 (247) and refined using SHELXL-97 (248). After full-matrix least-squares refinement of the non-hydrogen atoms with anisotropic thermal parameters, the hydrogen atoms were placed in calculated positions (N-H = 0.88 Å; C-H = 0.95, 0.98, and 0.99 Å in the case of aromatic hydrogen atoms, methyl hydrogen atoms, and methylene hydrogen atoms, respectively). In the final refinement, the hydrogen atoms were riding with the carbon atom they were bonded to. The isotropic thermal placement parameters were fixed at 1.2 and 1.5 times that of the corresponding aromatic and aliphatic carbon atoms, respectively. The scattering factors of the neutral atoms were those incorporated with the programmes.

6.4 Preparation of ionic liquids

6.4.1 1-Butyl-3-methylimidazolium chloride

N-Methylimidazole 10 (0.263 g, 3.2 mmol) and butylchloride 11 (0.324 g, 3.5 mmol) were placed in a microwave reactor vessel and irradiated for 15 minutes at 130 °C. The crude product was washed a few times with dry ethyl acetate and dried overnight in a vacuum at 70 °C. The yield of white [C₄mim]Cl was 77%. The product was analyzed with ¹H NMR and MS(ESI⁺). ¹H NMR (CDCl₃, 200 MHz) δ: 0.97 (t, 3H, J = 7.3 Hz, CH₃) 1.37 (m, 2H, J = 7.4 Hz, CH₂), 1.90 (m, 2H, J = 7.4 Hz, CH₂), 4.13 (s, 3H, NCH₃), 4.33 (t, 2H, J = 7.3 Hz, NCH₂), 7.33 (t, 1H, J = 1.8 Hz, C(2)H), 7.44 (t, 1H, J = 1.8 Hz, C(3)H) and 10.9 (s, 1H, C(1)H). MS(ESI⁺) [m/z (rel. int. (%)): M⁺ 83 (20, [mim]⁺) and 139 (100, [C₄mim]⁺)].
Conventional preparation of 1 was carried out from 10 (10.35 g, 0.126 mol) and 11 (14.59 g, 0.158 mol). The reaction mixture was heated under reflux under N₂ for 24 hours. The crude product was washed a few times with dry ethyl acetate and dried overnight in a vacuum at 70 °C. Product was analyzed with ¹H NMR and MS(ESI⁺) and the yield of 1 was 92%.

### 6.4.2 1-Butyl-3-methylimidazolium p-toluenesulfonate

N-Methylimidazole 10 (0.55 g, 6.6 mmol) and butyl-p-toluenesulfonate 60 (1.73 g, 7.6 mmol) were placed in a microwave reactor vessel. The reaction was controlled by microwave power, which was set at 20 W. The reaction time was 10 minutes. The reaction was monitored with ¹H NMR. The cooled reaction mixture was washed three times with ethyl acetate. [C₄mim][OTs] precipitated during the washing. The precipitate was collected and recrystallized from a 4:1 ethyl acetate:acetonitrile mixture. The crystals were dried in a high vacuum. The yield of white 1-butyl-3-methylimidazolium p-toluenesulfonate 2 was 1.76 g (85%), mp. 63-65 °C. ¹H NMR (CDCl₃, 200 MHz) δ: 0.92 (t, 3H, J = 7.30 Hz, CH₃), 1.31 (m, 2H, J = 7.45 Hz, CH₂), 1.81 (m, 2H, J = 7.45 Hz, CH₂), 2.34 (s, 3H, TsO-CH₃), 4.02 (s, 3H, NCH₃), 4.21 (t, 2H, J = 7.45 Hz, NCH₂), 7.14, 7.18, 7.22 and 7.30 (m, 4H x arom. H), 7.78 (t, 1H, J = 1.7 Hz, C(2)H), 7.82 (t, 1H, J = 1.7 Hz, C(3)H) and 9.95 (s, 1H, C(1)H). ¹³C NMR (CDCl₃, 50 MHz) δ: 13.53 (CH₃), 19.59 (CH₂), 21.45 (TsO-CH₃), 32.19 (CH₂), 36.67 (CH₂), 49.95 (CH₂), 121.60 (C2), 123.24 (C3), 126.10 (2 x arom. C), 128.81 (2 x arom. C), 139.55 (C1). MS(ESI⁺) [m/z (rel. int. (%))] M⁺ 83 (80, [mim⁺]), 139 (100, [C₄mim⁺]). MS(ESI⁻): 171 (100, [TsO⁻]).

Elemental analysis: calculated: C 58.04%, H 7.14%, N 9.02% and S 10.33%; observed: C 55.13%, H 7.11%, N 9.01% and S 10.86%. The product was stable up to 330 °C and then it decomposed at the rate of 0.24 mg/°C.

Convenational preparation of 2 was carried out from 10 (0.55 g, 6.6 mmol) and 60 (1.73 g, 7.6 mmol). The reaction mixture was stirred at room temperature for 6 hours. Purification of the crude product and the analysis was done as in the MW-assisted preparation reaction. The yield of 2 was 78%.

### 6.4.3 1-Butyl-3-methylimidazolium methanesulfonate

N-Methylimidazole 10 (0.55 g, 6.6 mmol) and butyl methylsulfonate 61 (1.15 g, 7.6 mmol) were placed in a microwave reactor. The reaction was carried out at 60 °C and the reaction time was 10 minutes and it was monitored with ¹H NMR. After cooling, the reaction mixture was washed three times with ethyl acetate. The crude [C₄mim][OMs] 3 precipitated from a 3:1 ethyl acetate:acetonitrile mixture and dried in a high vacuum. The yield of white 1-butyl-3-methylimidazolium methanesulfonate 3 was 1.41 g (89%), mp. 71-73 °C. ¹H NMR (CDCl₃, 200 MHz) δ: 0.97 (t, 3H, J = 7.30 Hz, CH₃), 1.36 (m, 2H, J = 7.50 Hz, CH₂), 1.89 (m, 2H, J = 7.45 Hz, CH₂), 2.82 (s, 3H, MsO-CH₃) 4.07 (s, 3H, NCH₃), 4.28 (t, 2H, J = 7.45 Hz, NCH₂), 7.23 (t, 1H, J = 1.7 Hz, C(2)H), 7.29 (t, 1H, J = 1.7 Hz, C(3)H), 10.10 (s, 1H, C(1)H). ¹³C NMR (CDCl₃, 50 MHz) δ: 13.54 (CH₃), 19.56
(CH₂), 32.21(CH₂), 36.65 (CH₃), 49.97 (CH₂), 121.52 (C2), 123.11 (C3), 139.00 (C1). MS(ESI⁺): [m/z (rel. int. (%))] 83 (30, [mim]⁺), 139 (100, [C₄mim]⁺). MS(ESI⁻): [m/z (rel. int. (%))] 95 (100, [MsO]⁻). Elemental analysis: calculated: C 46.13%, H 7.74%, N 11.96% and S 13.68% ; observed: C 45.13%, H 8.18%, N 11.36% and S 13.48%. The product was stable up to 335 °C and then it decomposed at the rate of 0.17 mg/°C.

Conventional preparation of 3 was carried out from 10 (0.55 g, 6.6 mmol) and 61 (1.73 g, 7.6 mmol). The reaction mixture was stirred at room temperature for 96 hours. Purification of the crude product and the analysis was done as in the MW-assisted preparation reaction. The yield of 3 was 87%.

Butyl-p-toluene sulfonate and butyl methylsulfonate

Butyl-p-toluene sulfonate 60 was prepared from butanol and p-toluene sulfonic acid chloride. First butanol (14.9 g, 0.20 mol) was weighed into a flask and cooled in an ice bath to 0 °C. p-Toluene sulfonic acid chloride (42.0 g, 0.22 mol) was added to 1-butanol. Pyridine (32.0 g, 0.40 mol) was slowly added within 1 hr with vigorous stirring. The mixture was stirred for 2 h at 0°C. Diluted HCl (2 M, 150 ml) was added and the mixture was extracted twice with 50 ml of CH₂Cl₂. The combined organic layers were washed with saturated NaHCO₃ and water and dried with MgSO₄. The solvent was evaporated in a high vacuum. The yield of 60 was 40.7 g (89%). ¹H NMR (CDCl₃, 200 MHz) δ : 0.86 (t, 3H, J = 7.3 Hz, Bu-CH₃), 1.34 (m, 2H, J = 7.33 Hz, Bu-CH₂), 1.63 (m, 2H, J = 7.33 Hz, Bu-CH₂), 2.45 (s, 3H, Tosyl-CH₃), 4.03 (t, 2H, J = 6.43 Hz, Bu-CH₂), 7.37 (m, 4H x arom. H), 7.79 (broad-d, 2H, aromatic-H). MS(ESI⁺): 251 (product + Na).

Butyl methylsulfonate 61 was prepared from butanol (14.9 g, 0.20 mol) and methanesulfonyl chloride (25.1 g, 0.22 mol) by using the above method. The yield of 61 was 16.0 g (53%). ¹H NMR (CDCl₃, 200 MHz) δ : 0.96 (t, 3H, J = 7.23 Hz, Bu-CH₃), 1.44 (m, 2H, Bu-CH₂), 1.75 (m, 2H, Bu-CH₂), 3.02 (s, 3H, -CH₃), 4.23 (t, 2H, J = 6.43 Hz, Bu-CH₂). MS [EI, m/z, rel. int. (%)]: 109(60), 79(80), 56(100), 39(35).

6.4.4 1-H-3-methylimidazolium p-toluene sulfonate

N-Methylimidazole 10 (0.54 g, 6.6 mmol), p-toluene sulfonic acid 1.14 g (6.6 mmol) and butanol (0.49 g, 6.6 mmol) were placed in a microwave reactor. The reaction was carried at 60°C for 15 min. The reaction was monitored with GC. Addition of ethyl acetate precipitated crude 62, which was recrystallized from a 4:1 ethyl acetate:acetonitrile mixture. The crystals were dried in a high vacuum. The yield of pure white 1-H-3-methylimidazolium p-toluene sulfonate 62 was 0.881 g (43%), mp. 90-91°C. ¹H NMR (CDCl₃, 200 MHz) 2.35 (s, 3H, TsO-CH₃) 3.94 (s, 3H, NCH₃), 7.08, 7.15, 7.19 and 7.35 (m, 4H x arom. H), 7.78 (t, 1H, J = 1.7 Hz, C(2)H), 7.82 (t, 1H, J = 1.7 Hz, C(3)H), 9.22 (s, 1H, C(1)H). MS(ESI⁺): [m/z (rel. int. (%))] 85 (100, [mim]⁺). MS(ESI⁻): [m/z (rel. int. (%))] 171 (100, [TsO]⁻). The product was stable up to 290 °C and then it decomposed at the rate of 0.11 mg/°C.
6.4.5 1-Butyl-3-methylimidazolium hexafluorophosphate

[C4mim][Cl] (0.18 g, 1 mmol) was placed in a microwave reactor vessel, 1 ml acetone and NaPF₆ (0.17 g, 1 mmol) was added. The reaction was carried out for 10 min at 80 ºC. The cooled reaction mixture was filtered through Celite to remove solid NaCl. After the evaporation of acetone the yield of [bmim][PF₆] was 99%. 4 was analyzed with ¹H NMR and MS(ESI⁺ and ESI⁻). ¹H NMR (MeOD, 200 MHz) δ: 0.99 (t, 3H, J = 7.3 Hz, CH₃) 1.38 (m, 2H, J = 7.4 Hz, CH₂), 1.86 (m, 2H, J = 7.4 Hz, CH₂), 3.92 (s, 3H, NCH₃), 4.20 (t, 2H, J = 7.4 Hz, NCH₂), 7.54 (t, 1H, J = 1.8 Hz, C(2)H), 7.61 (t, 1H, J = 1.8 Hz, C(3)H) and 8.85 (s, 1H, C(1)H). MS(ESI⁺) [m/z (rel. int. (%))]: 83 (45, [mim]⁺) and 139 (100, [C₄mim]⁺). MS(ESI⁻) [m/z (rel. int. (%))]: 145 (100, [PF₆]⁻).

Conventional preparation of 4 was carried out from 1 (0.35 g, 2 mmol) and NaPF₆ (0.34 g, 2 mmol). The reaction mixture was stirred at room temperature for 5 hours. Purification of the crude product and the analysis was done as in the MW-assisted preparation reaction. The yield of 4 was 83%.

6.4.6 1-Alkyl-3-methylimidazolium tetrachloroindates

Precursor 1-alkyl-3-methylimidazolium chlorides 6 were prepared, characterized and dried using procedures described in the literature (43).

1-Methylimidazolium tetrachloroindate [H₃mim][InCl₄]

Indium(III)chloride (1.597 g, 7.2 mmol) was added to a round-bottom flask containing 1-H₃methylimidazolium chloride (0.85 g, 7.2 mmol). The mixture was heated with an oil bath until a homogeneous liquid was formed. The formed [H₃mim][InCl₄] was dried in a high vacuum. ¹H NMR (300 MHz, CD₂CN, ppm): δ 2.93 (1H, s, C(1)H), 3.85 (3H, s, NCH₃) 7.35 (1H, s, C(2)H), 7.36 (1H, s, C(3)H), 8.44 (1H, s, C(1)H. ¹³C NMR (300 MHz, CD₂CN, ppm): δ 36.75 (NCH₃), 120.52 (C₂), 124.17 (C₃), 136.15 (C₁). Elemental analysis: calculated: C: 14.14% H: 2.08% N: 8.25% Cl: 41.74% In: 33.80%; observed: C: 13.42% H: 2.60% N: 7.32% Cl: 41.44% In: 33.41%.

1,3-Dimethylimidazolium tetrachloroindate [mmim][InCl₄]

Indium(III)chloride (2.051 g, 9.3 mmol) was added to a round-bottom flask containing 1,3-dimethylimidazolium chloride (1.230 g, 9.3 mmol). The mixture was heated with an oil bath until a homogeneous liquid was formed. The formed [mmim][InCl₄] was dried in a high vacuum. ¹H NMR (300 MHz, CDCl₃, ppm): δ 3.82 (6H, s, 2 x NCH₃), 7.31 (1H, s, C(2)H), 7.32 (1H, s, C(3)H), 8.34 (1H, s, C(1)H. ¹³C NMR (300 MHz, CD₃CN, ppm): δ 36.75 (NCH₃), 120.52 (C₂), 124.17 (C₃), 136.15 (C₁). Elemental analysis: calculated: C: 16.96% H: 2.56% N: 7.92% Cl: 32.46% In: 40.09%; observed: C: 17.18% H: 2.71% N: 7.95% Cl: 32.35% In: 40.18%.
1-Ethyl-3-methylimidazolium tetrachloroindate [C\textsubscript{2}mim][InCl\textsubscript{4}]

Indium(III) chloride (1.105 g, 5 mmol) was added to a round-bottom flask containing 1-ethyl-3-methylimidazolium chloride (0.733 g, 5 mmol). The mixture was heated with an oil bath until a homogeneous liquid was formed. The formed [emim][InCl\textsubscript{4}] was dried in a high vacuum. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}, ppm): \(\delta\) 1.63 (3H, t, \(J = 7.5\) Hz, CH\textsubscript{3}), 4.03 (3H, s, NCH\textsubscript{3}), 4.32 (2H, t, \(J = 7.5\) Hz, CH\textsubscript{2}), 7.30 (1H, d, \(J = 1.8\) Hz, C(2)H), 7.31 (1H, d, \(J = 1.8\) Hz, C(3)H), 8.69 (1H, s, C(1)H). \textsuperscript{13}C NMR (300 MHz, CDCl\textsubscript{3}, ppm): \(\delta\) 15.61 (CH\textsubscript{3}), 37.19 (NCH\textsubscript{3}), 45.75 (NCH\textsubscript{2}), 122.49 (C2), 124.13 (C3), 134.85 (C1). Elemental analysis: calculated: C: 19.59% H: 3.01% N: 7.52% Cl: 38.56% In: 31.22%; observed: C: 20.04% H: 3.35% N: 7.80% Cl: 38.46% In: 30.70%. The product was stable up to 230 °C and then it decomposed at the rate of 0.04 mg/°C.

1-Butyl-3-methylimidazolium tetrachloroindate [C\textsubscript{4}mim][InCl\textsubscript{4}]

Indium(III) chloride (1.105 g, 5 mmol) was added to a round-bottom flask containing 1-butyl-3-methylimidazolium chloride (0.873 g, 5 mmol). The mixture was heated with an oil bath until a homogeneous liquid was formed. The formed [bmim][InCl\textsubscript{4}] was dried in a high vacuum. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}, ppm): \(\delta\) 1.00 (3H, t, \(J = 7.5\) Hz, CH\textsubscript{3}), 1.42 (2H, m, \(J = 7.5\) Hz, NCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}), 1.91 (2H, m, \(J = 7.5\) Hz, NCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}), 4.01 (3H, s, NCH\textsubscript{3}), 4.23 (2H, t, \(J = 7.5\) Hz, NCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}), 7.31 (1H, d, \(J = 1.8\) Hz, C(2)H), 7.33 (1H, d, \(J = 1.8\) Hz, C(3)H), 8.58 (1H, s, C(1)H). \textsuperscript{13}C NMR (300 MHz, CDCl\textsubscript{3}, ppm): \(\delta\) 13.17 (CH\textsubscript{3}), 19.14 (CH\textsubscript{2}), 31.54 (CH\textsubscript{2}), 36.76 (NCH\textsubscript{3}), 49.99 (NCH\textsubscript{2}), 122.45 (C2), 123.71 (C3), 134.36 (C1). Elemental analysis: calculated: C: 24.20% H: 3.82% N: 7.18% Cl: 35.87% In: 2.50%; observed: C: 24.27% H: 3.82% N: 7.08% Cl: 35.82% In: 29.01%. The product was stable up to 230 °C and then it decomposed at the rate of 0.05 mg/°C.

1-Hexyl-3-methylimidazolium tetrachloroindate [C\textsubscript{6}mim][InCl\textsubscript{4}]

Indium(III) chloride (3.150 g, 14 mmol) was added to a round-bottom flask containing 1-hexyl-3-methylimidazolium chloride (2.900 g, 14 mmol). The mixture was heated with an oil bath until a homogeneous liquid was formed. The formed [C\textsubscript{6}-mim][InCl\textsubscript{4}] was dried in a high vacuum. \textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}, ppm): \(\delta\) 0.89 (3H, t, \(J = 7.0\) Hz, CH\textsubscript{3}), 1.33 (6H, m, CH\textsubscript{2}), 1.91 (2H, m, \(J = 7.5\) Hz, NCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}), 4.01 (3H, s, NCH\textsubscript{3}), 4.22 (2H, t, \(J = 7.5\) Hz, NCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}), 7.33 (1H, d, \(J = 1.8\) Hz, C(2)H), 7.35 (1H, d, \(J = 1.8\) Hz, C(3)H), 8.62 (1H, s, C(1)H). \textsuperscript{13}C NMR (300 MHz, CDCl\textsubscript{3}, ppm): \(\delta\) 13.97 (CH\textsubscript{3}), 22.32 (CH\textsubscript{2}), 25.84 (CH\textsubscript{3}), 29.98 (CH\textsubscript{3}), 30.95 (CH\textsubscript{3}), 37.09 (NCH\textsubscript{3}), 50.60 (NCH\textsubscript{2}), 122.64 (C2), 124.02 (C3), 134.97 (C1). Elemental analysis: calculated: C: 28.72% H: 4.57% N: 6.93% Cl: 32.69%; observed: C: 28.33% H: 4.61% N: 6.61% Cl: 33.45%. The product was stable up to 240 °C and then it decomposed at the rate of 0.05 mg/°C.

1-Octyl-3-methylimidazolium tetrachloroindate [C\textsubscript{8}mim][InCl\textsubscript{4}]

Indium(III) chloride (0.707 g, 3.2 mmol) was added to a round-bottom flask containing 1-octyl-3-methylimidazolium chloride (0.733 g, 3.2 mmol). The mixture was heated with an oil bath until a homogeneous liquid was formed. The formed [C\textsubscript{8}-mim][InCl\textsubscript{4}] was dried in a high vacuum. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}, ppm): \(\delta\) 0.87 (3H, t, \(J = 7.0\) Hz,
1-Decyl-3-methylimidazolium tetrachloroindate [C_{10}mim][InCl$_4$]

Indium(III) chloride (0.582 g, 2.6 mmol) was added to a round-bottom flask containing 1-decyl-3-methylimidazolium chloride (0.678 g, 2.6 mmol). The mixture was heated with an oil bath until a homogeneous liquid was formed. The formed [C_{10}-mim][InCl$_4$] was dried in a high vacuum. $^3$H NMR (300 MHz, CDCl$_3$, ppm): δ 0.88 (3H, t, $J$ = 7.0 Hz, CH$_3$), 1.33 (14H, m, CH$_2$), 1.91 (2H, m, $J$ = 7.2 Hz, NCH$_2$CH$_2$), 4.00 (3H, s, NCH$_3$), 4.21 (2H, t, $J$ = 7.5 Hz, NC$_2$H$_2$), 7.34 (1H, d, $J$ = 1.8 Hz, C(2)H), 7.35 (1H, d, $J$ = 1.8 Hz, C(3)H), 8.51 (1H, s, C(1)H). 13C NMR (300 MHz, CDCl$_3$, ppm): δ 14.18 (CH$_3$), 22.72 (CH$_2$), 28.85 (CH$_2$), 29.18 (CH$_2$), 29.27 (CH$_2$), 29.39 (CH$_2$), 30.01 (CH$_2$), 31.79 (CH$_2$), 37.07 (NCH$_3$), 50.61 (NCH$_2$). Elemental analysis: calculated: C: 38.03% H: 5.76% N: 5.56% Cl: 28.8% In: 22.72%; observed: C: 37.82% H: 6.15% N: 5.51% Cl: 27.94% In: 23.92%.

1-Dodecyl-3-methylimidazolium tetrachloroindate [C_{12}mim][InCl$_4$]

Indium(III) chloride (0.453 g, 2.1 mmol) was added to a round-bottom flask containing 1-dodecyl-3-methylimidazolium chloride (0.587 g, 2.1 mmol). The mixture was heated with an oil bath until a homogeneous liquid was formed. The formed [C_{12}-mim][InCl$_4$] was dried in a high vacuum. $^3$H NMR (300 MHz, CDCl$_3$, ppm): δ 0.88 (3H, t, $J$ = 7.0 Hz, CH$_3$), 1.33 (18H, m, CH$_2$), 1.91 (2H, m, $J$ = 7.2 Hz, NCH$_2$CH$_2$), 4.00 (3H, s, NCH$_3$), 4.21 (2H, t, $J$ = 7.5 Hz, NCH$_2$CH$_2$), 7.34 (1H, d, $J$ = 1.8 Hz, C(2)H), 7.35 (1H, d, $J$ = 1.8 Hz, C(3)H), 8.51 (1H, s, C(1)H). 13C NMR (300 MHz, CDCl$_3$, ppm): δ 14.18 (CH$_3$), 22.72 (CH$_2$), 28.97 (CH$_2$), 29.39 (2 x CH$_2$), 29.55 (CH$_2$), 29.64 (2 x CH$_2$), 30.12 (CH$_2$), 31.95 (CH$_2$), 37.16 (NCH$_3$), 50.70 (NCH$_2$), 50.61 (NCH$_2$), 122.64 (C2), 124.07 (C3), 135.04 (C1). Elemental analysis: calculated: C: 38.03% H: 5.76% N: 5.56% Cl: 28.8% In: 22.72%; observed: C: 37.82% H: 6.15% N: 5.51% Cl: 27.94% In: 23.92%.

1-Methyl-3-tetradecylimidazolium tetrachloroindate [C_{14}mim][InCl$_4$]

Indium(III) chloride (0.388 g, 1.8 mmol) was added to a round-bottom flask containing 1-tetradecyl-3-methylimidazolium chloride (0.553 g, 1.8 mmol). The mixture was heated with an oil bath until a homogeneous liquid was formed. The formed [C_{14}-mim][InCl$_4$] was dried in a high vacuum. $^3$H NMR (300 MHz, CDCl$_3$, ppm): δ 0.88 (3H, t, $J$ = 7.0 Hz, CH$_3$), 1.33 (22H, m, CH$_2$), 1.91 (2H, m, $J$ = 7.2 Hz, NCH$_2$CH$_2$), 4.00 (3H, s, NCH$_3$), 4.20 (2H, t, $J$ = 7.5 Hz, NCH$_2$CH$_2$), 7.33 (1H, d, $J$ = 1.8 Hz, C(2)H), 7.35 (1H, d, $J$ = 1.8 Hz, C(3)H), 8.54 (1H, s, C(1)H). 13C NMR (300 MHz, CDCl$_3$, ppm): δ 14.23 (CH$_3$), 22.78 (CH$_2$), 28.97 (CH$_2$), 29.55 (CH$_2$), 29.64 (2 x CH$_2$), 31.95 (CH$_2$), 37.16 (NCH$_3$), 50.70 (NCH$_2$), 122.65 (C2), 124.07 (C3), 135.04 (C1). Elemental analysis: calculated: C: 38.03% H: 5.76% N: 5.56% Cl: 28.8% In: 22.72%; observed: C: 37.82% H: 6.15% N: 5.51% Cl: 27.91% In: 22.60%.
1-Hexadecyl-3-methylimidazolium tetrachloroindate \([\text{C}_{16}\text{mim}][\text{InCl}_4]\)

Indium(III)chloride (0.264 g, 1.2 mmol) was added to a round-bottom flask containing 1-hexadecyl-3-methylimidazolium chloride (0.418 g, 1.2 mmol). The mixture was heated with an oil bath until a homogeneous liquid was formed. The formed \([\text{C}_{16}\text{-mim}][\text{InCl}_4]\) was dried in a high vacuum. \(^1\)H NMR (300 MHz, CDCl\(_3\), ppm): \(\delta\) 0.88 (3H, t, \(J = 7.0\) Hz, CH\(_3\)), 1.33 (26H, m, CH\(_2\)), 1.91 (2H, m, \(J = 7.2\) Hz, NCH\(_2\)CH\(_2\)), 4.00 (3H, s, NCH\(_3\)), 4.22 (2H, t, \(J = 7.5\) Hz, NCH\(_2\)), 7.32 (1H, d, \(J = 1.8\) Hz, C(2)H), 7.36 (1H, d, \(J = 1.8\) Hz, C(3)H), 8.62 (1H, s, C(1)H). \(^{13}\)C NMR (300 MHz, CDCl\(_3\), ppm): \(\delta\) 14.22 (CH\(_3\)), 22.77 (CH\(_2\)), 26.36 (CH\(_2\)), 29.03 (CH\(_2\)), 29.45 (2 x CH\(_2\)), 29.62 (CH\(_2\)), 29.76 (6 x CH\(_2\)), 30.18 (CH\(_2\)), 32.00 (CH\(_2\)), 37.21 (NCH\(_3\)), 50.72 (NCH\(_2\)), 122.62 (C2), 124.08 (C3), 135.20 (C1). Elemental analysis: calculated: C: 42.50% H: 6.62% N: 5.07% Cl: 24.81% In: 20.04%; observed: C: 42.58% H: 6.97% N: 4.97% Cl: 25.14% In: 20.35%.

1-Methyl-3-octadecylimidazolium tetrachloroindate \([\text{C}_{18}\text{mim}][\text{InCl}_4]\)

Indium(III)chloride (0.287 g, 1.3 mmol) was added to a round-bottom flask containing 1-octyl-3-methylimidazolium chloride (0.481 g, 1.3 mmol). The mixture was heated with an oil bath until a homogeneous liquid was formed. The formed \([\text{C}_{18}\text{-mim}][\text{InCl}_4]\) was dried in a high vacuum. \(^1\)H-NMR (300 MHz, CDCl\(_3\), ppm): \(\delta\) 0.88 (3H, t, \(J = 7.0\) Hz, CH\(_3\)), 1.34 (22H, m, CH\(_2\)), 1.91 (2H, m, \(J = 7.2\) Hz, NCH\(_2\)CH\(_2\)), 4.00 (3H, s, NCH\(_3\)), 4.21 (2H, t, \(J = 7.5\) Hz, NCH\(_2\)), 7.33 (1H, d, \(J = 1.8\) Hz, C(2)H), 7.35 (1H, d, \(J = 1.8\) Hz, C(3)H), 8.53 (1H, s, C(1)H). \(^{13}\)C-NMR (300 MHz, CDCl\(_3\), ppm): \(\delta\) 14.22 (CH\(_3\)), 22.78 (CH\(_2\)), 26.36 (CH\(_2\)), 29.02 (CH\(_2\)), 29.45 (2 x CH\(_2\)), 29.62 (CH\(_2\)), 29.80 (8 x CH\(_2\)), 30.15 (CH\(_2\)), 32.01 (CH\(_2\)), 37.23 (NCH\(_3\)), 50.78 (NCH\(_2\)), 122.71 (C2), 124.14 (C3), 135.00 (C1). Elemental analysis: calculated: C: 44.46% H: 6.91% N: 4.53% Cl: 23.16% In: 20.03%; observed: C: 44.62% H: 7.32% N: 4.73% Cl: 23.95% In: 19.39%.

6.4.7 1-Ethyl-3-methylimidazolium-based ionic liquids

Tris(1-ethyl-3-methylimidazolium) hexachloroindate \([\text{C}_{2}\text{mim}]_3[\text{InCl}_6]\)

Indium(III)chloride (0.445 g, 2 mmol) was added to a round-bottom flask containing 1-ethyl-3-methylimidazolium chloride (0.880 g, 6 mmol). The mixture, \(x(\text{InCl}_3) = 0.25\), was heated with an oil bath until a homogeneous liquid was formed. The formed \([\text{emim}]_3[\text{InCl}_6]\) was dried in a high vacuum. \(^1\)H NMR (200 MHz, D\(_2\)O, ppm): \(\delta\) 1.44 (3H, t, \(J = 7.3\) Hz, CH\(_3\)), 3.83 (3H, s, NCH\(_3\)), 4.17 (2H, q, \(J = 7.3\) Hz, CH\(_2\)), 7.36 (1H, s, C(2)H), 7.43 (1H, s, C(3)H), 8.65 (1H, s, C(1)H). \(^{13}\)C NMR (200 MHz, D\(_2\)O, ppm): \(\delta\) 15.61 (CH\(_3\)), 36.70 (NCH\(_3\)), 45.91 (NCH\(_3\)), 123.00 (C2), 124.55 (C3), 136.70 (C1). Elemental analysis: calculated: C: 32.71% H: 5.03% N: 12.71%; observed: C: 32.71% H: 5.05% N: 12.94%. MS(ESI\(^+\)) \([m/z\) (rel. int. (%))]: M\(^+\) 111 (100, \([\text{C}_{2}\text{mim}]^+\)) MS(ESI\(^-\)) \([m/z\) (rel. int. (%))]: M\(^-\) 62 (100), 257 (15, \([\text{InCl}_4]^-\)). The product was stable up to 230 °C and then it decomposed at the rate of 0.06 mg/°C.
Bis(1-ethyl-3-methylimidazolium) pentachloroindate \([C_{2}mim]\)[InCl\(_{5}\)(H\(_{2}O\))]  
Indium(III)chloride (0.580 g, 4 mmol) was added to a round-bottom flask containing 1-ethyl-3-methylimidazolium chloride (0.444 g, 2 mmol). The mixture, \(x(\text{InCl}_3) = 0.33\), was heated with an oil bath until a homogeneous liquid was formed. The formed \([\text{emim}][\text{InCl}_5(\text{H}_2\text{O})]\) was dried in a high vacuum. \(^1\text{H}\) NMR (200 MHz, D\(_2\)O, ppm): \(\delta\) 1.44 (3H, t, \(J = 7.3\) Hz, CH\(_3\)), 3.83 (3H, s, NCH\(_3\)), 4.17 (2H, q, \(J = 7.3\) Hz, CH\(_2\)), 7.36 (1H, s, C(2)H), 7.43 (1H, s, C(3)H), 8.65 (1H, s, C(1)H. \(^{13}\text{C}\) NMR (200 MHz, D\(_2\)O, ppm): \(\delta\) 15.61 (CH\(_3\)), 36.73 (NCH\(_3\)), 45.88 (NCH\(_2\)), 122.95 (C2), 124.53 (C3), 136.73 (C1). Elemental analysis: calculated: C: 28.02% H: 4.31% N: 10.89%; observed: C: 29.12% H: 4.42% N: 11.53%. MS(ESI\(+\)) \([m/z\) (rel. int. (%))]: M\(^+\) 111 (100, \([\text{C}_2\text{mim}]^+\)). MS(ESI\(-\)) \([m/z\) (rel. int. (%))]: M\(^-\) 62 (25 %), 257 (100 %, \([\text{InCl}_4^-\])). The product was stable up to 230 °C and then it decomposed at the rate of 0.04 mg/°C.

1-Ethyl-3-methylimidazolium tetrachloroindate \([\text{C}_2\text{mim}][\text{InCl}_4]\)
Indium(III)chloride (0.580 g, 4 mmol) was added to a round-bottom flask containing 1-ethyl-3-methylimidazolium chloride (0.895 g, 4 mmol). The mixture, \(x(\text{InCl}_3) = 0.5\), was heated with an oil bath until a homogeneous liquid was formed. The formed \([\text{emim}][\text{InCl}_4]\) was dried in a high vacuum. \(^1\text{H}\) NMR (200 MHz, D\(_2\)O, ppm): \(\delta\) 1.44 (3H, t, \(J = 7.3\) Hz, CH\(_3\)), 3.83 (3H, s, NCH\(_3\)), 4.17 (2H, q, \(J = 7.3\) Hz, CH\(_2\)), 7.36 (1H, s, C(2)H), 7.42 (1H, s, C(3)H), 8.65 (1H, s, C(1)H. \(^{13}\text{C}\) NMR (200 MHz, D\(_2\)O, ppm): \(\delta\) 15.61 (CH\(_3\)), 36.74 (NCH\(_3\)), 45.89 (NCH\(_2\)), 122.96 (C2), 124.53 (C3), 136.73 (C1). Elemental analysis: calculated: C: 19.59% H: 3.01% N: 7.62%; observed: C: 18.68% H: 3.57% N: 7.43%. MS(ESI\(+\)) \([m/z\) (rel. int. (%))]: M\(^+\) 111 (100, \([\text{C}_2\text{mim}]^+\)). MS(ESI\(-\)) \([m/z\) (rel. int. (%))]: M\(^-\) 62 (15 %), 257 (100 %, \([\text{InCl}_4^-\]). The product was stable up to 230 °C and then it decomposed at the rate of 0.04 mg/°C.

1-Ethyl-3-methylimidazolium tetrachloroindate with an excess of InCl\(_3\) \([\text{C}_2\text{mim}][\text{InCl}_4]+\text{InCl}_3\)
Indium(III)chloride (7.83 g, 0.036 mol) was added to a round-bottom flask containing 1-ethyl-3-methylimidazolium chloride (2.60 g, 0.018 mmol). The mixture, \(x(\text{InCl}_3) = 0.67\), was heated with an oil bath, but no homogeneous liquid was formed. The formed \([\text{emim}][\text{InCl}_4]+\text{InCl}_3\) was dried in a high vacuum. \(^1\text{H}\) NMR (200 MHz, D\(_2\)O, ppm): \(\delta\) 1.41 (3H, s, CH\(_3\)), 3.80 (3H, s, NCH\(_3\)), 4.13 (2H, m, CH\(_2\)), 7.33 (1H, s, C(2)H), 7.39 (1H, s, C(3)H), 8.62 (1H, s, C(1)H. \(^{13}\text{C}\) NMR (200 MHz, D\(_2\)O, ppm): \(\delta\) 15.61 (CH\(_3\)), 36.74 (NCH\(_3\)), 45.89 (NCH\(_2\)), 122.96 (C2), 124.53 (C3), 136.73 (C1). Elemental analysis: calculated: C: 12.24% H: 1.88% N: 4.76%; observed: C: 12.01% H: 2.05% N: 4.58%. MS(ESI\(+\)) \([m/z\) (rel. int. (%))]: M\(^+\) 111 (100, \([\text{emim}]^+\)). MS(ESI\(-\)) \([m/z\) (rel. int. (%))]: M\(^-\) 257 (100 %, \([\text{InCl}_4^-\]). The product was stable up to 330 °C and then it decomposed at the rate of 0.13 mg/°C.
6.5 Dimerization of 2-methylpropene

6.5.1 Batchwise reaction in Lewis acid-based ionic liquids

Reactions with 2-methylpropene were carried out in a glass reactor (200 ml, autoclave) equipped with a magnetic stirring bar and mounted in an oil bath. An ionic liquid with the desired InCl$_3$ content, x(InCl$_3$) = 0.5-0.67, was prepared prior to the reaction from [C$_4$mim]Cl and InCl$_3$. The ionic liquid was dried in a high vacuum before use and 1 g of it was weighed into the reactor. After that the reactor was flushed with a gaseous starting material, 2-methylpropene. The reaction mixture was heated with an oil bath when necessary. The reaction temperatures varied between room temperature and 120 °C according to the composition of the catalytic ionic liquid. The reaction time was 1 hour. After the reactions the products were decanted from the reactor and analyzed with GCMS.

6.5.2 Continuous reaction in Lewis acid-based ionic liquids

Continuous reactions were carried out with a reaction setup consisting of a gas bottle (placed on a balance), a gas-flow regulator, a pearl flask mounted in an oil bath, a distillation bridge, a receiver flask mounted in an ice bath and a bubbler. Catalytic ionic liquids were prepared in a reaction vessel (25 ml) by mixing 1-alkyl-3-methylimidazolium chloride (5 mmol) and indium(III)chloride (6 mmol or 7 mmol) at 80 °C to yield catalytic ionic liquids with compositions of 0.55 or 0.58. The formed [C$_r$mim]Cl/InCl$_3$ mixture was dried in a high vacuum for a couple of hours. Then the dried catalytic ionic liquid was heated with an oil bath to the reaction temperature and then 2-methylpropene was fed continuously down to the bottom of the reaction vessel so that it bubbled through the ionic liquid. The gas flow rate of the 2-methylpropene was controlled with a gas-flow regulator. The reaction time was 30 min and the reaction mixture was stirred at a constant speed of 500 rpm. The products were distilled from the reactor and collected in a cold trap (cooled with an ice bath). Unreacted 2-methylpropene passed through, carrying the formed products with it.

6.5.3 Continuous reaction in Brønsted acid-based ionic liquids

An appropriate Bronsted acid (HA) was added to an ionic liquid ([C$_4$mim]A) to form a catalytic ionic liquid. The catalytic composition of [C$_4$mim]A/HA was 1:0.05 or 1:0.1 mol, where A was hexafluorophosphate, methylsulfonate, p-toluenesulfonate or formate. The reactions were carried out with a reaction setup consisting of a gas bottle (placed on a balance), a gas-flow regulator, a pearl flask mounted in an oil bath, a distillation bridge, a receiver flask mounted in an ice bath and a bubbler. The reaction temperature was 120 °C and the reaction time was 30 min. 2-methylpropene was fed continuously into the bottom of the reaction vessel so that it bubbled through the ionic liquid. The gas flow rate of the 2-
methylpropene was controlled with a gas-flow regulator. The reaction mixture was stirred at a constant speed of 500 rpm. The products were distilled from the reactor and collected in a cold trap (cooled with an ice bath). Unreacted 2-methylpropene passed through, carrying the formed products with it.

### 6.5.4 Attempts at performing the dimerization reaction

#### 6.5.4.1 Preparation of a Pd catalyst complex

Palladium acetate (0.2247 g, 1 mmol) was dissolved in 40 ml of methanol and after that a 1,3-propanediyldiphenylphosphite ligand, dppp (0.4127 g, 1 mmol) was added. When the ligand started to dissolve, the colour of the solution turned from brown to green. Finally, HPF₆ (0.65 % water solution 0.2919 g, 2 mmol) was added drop by drop and some precipitate started to form. The precipitate was filtered and washed with cold methanol. The yield was 55 % (244).

#### 6.5.4.2 Dimerization of 2-methylpropene in [C₄mim][PF₆] with a palladium catalyst

2-Methylpropene was added to a microwave reaction vessel containing [bmim][PF₆] (1ml) and hexane (1ml). Then a catalyst was added to the vessel. The catalysts that were used were HPF₆ (0.02 mmol), Pd(1,3-bisdiphenylpropane)(PF₆)₂ (20 mg, 0.025 mmol), an in situ Pd catalyst: Pd(OAc)₂ + dppp + HPF₆ (1:1:2) (0.05 mmol of Pd) or an in situ Pd catalyst, Pd(OAc)₂ + dppp + p-TsOH (1:1:2) (0.05 mmol of Pd). The reactions were carried out in a microwave reactor at 80 °C for 1 hour. After the reaction the products were analyzed with GC.

### 6.5.5 Reaction details

#### 6.5.5.1 Analysis of the products

The products from the batch reactions were analyzed with a Perkin-Elmer Turbomass GCMS (column RTX5, 60m, 0.25mm). The products from the continuous flow reactions were analyzed with a GC-MS HP 6890 series GC System equipped with a capillary column BPX5 (25m, 0.33 mm, 0.25 μm), a FID and an HP5973 MSD mass spectrometer. A PerkinElmer Autosystem XL-GC equipped with a capillary column OV-1 (30m, 0.32 mm, 0.25 μm) and a FID was also used. Octane was used as an internal standard. The products were integrated using two different methods. One was for the reactor samples that integrated products as a product groups (dimers, trimers, tetramers, etc.), and the other was for the cold trap samples that integrated all the dimers and possible trimers individually.
6.5.5.2 Consumption of 2-methylpropene

The consumption of 2-methylpropene was controlled with a gas-flow regulator and the real consumption of 2-methylpropene was calculated according to the weight loss of the gas bottle of 2-methylpropene. Three different gas flow rates were used in one experiment and they corresponded to 2.5, 5 and 10 g of 2-methylpropene. The gas flow rate was calculated according to the total consumption of 2-methylpropene during the reaction, and it was expressed in moles of 2-methylpropene/minute: low: 1.5 mmol/min, medium: 3 mmol/min and high: 6 mmol/min.

6.5.5.3 Conversion of 2-methylpropene

The conversion of 2-methylpropene was calculated according to the products observed in the reactor and/or the cold trap. The total conversion summarizes both conversions.

Conversion of 2-methylpropene: m(products in the trap)/m(2-methylpropene) * 100 %. 
References


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175. Honkela ML (2005) The selective production of disobutenes via ion-exchange resin catalyzed dimerization reaction of isobutene in the presence of tert-butanol (TBA) and constructing kinetic model for the disisobutene dimerization. Industrial chemistry publication series, Otamedia Oy, Espoo.


469. Kekonen, Teija (2006) Environmental information from the Svalbard ice core for the past 800 years
475. Klaavuniemi, Tuula (2006) PDZ-LIM domain proteins and α-actinin at the muscle Z-disk
478. Hillukkala, Tomi (2006) Roles of DNA polymerase epsilon and TopBP1 in DNA replication and damage response

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PREPARATION AND CHARACTERIZATION OF SOME IONIC LIQUIDS AND THEIR USE IN THE DIMERIZATION REACTION OF 2-METHYLPROPENE