Green Chemistry

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: A. Van den Bossche, E. De Witte, W. Dehaen and K. Binnemans, *Green Chem.*, 2018, DOI: 10.1039/C8GC01061G.

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [author guidelines](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the ethical guidelines, outlined in our [author and reviewer resource centre](#), still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

Manuscript for: Green Chemistry (GC-ART-04-2018-001061, revision 1)

Trihalide ionic liquids as non-volatile oxidizing solvents for metals[†]

Arne Van den Bossche^a, Elise De Witte^a, Wim Dehaen^a and Koen Binnemans^{a*}

^a KU Leuven, Department of Chemistry, Celestijnenlaan 200F bus 2404, B-3001 Heverlee (Belgium)

* Corresponding author. E-mail: Koen.Binnemans@kuleuven.be

[†] Electronic supplementary information (ESI) available: chlorine reaction setup and procedure, characterization, Raman spectra and NMR spectra (¹H, ¹³C and ³¹P).

Abstract

Various ionic liquids containing a trihalide anion $[X_3]^-$ ($X = \text{Cl, Br or I}$) were synthesized by addition of molecular chlorine, bromine or iodine (X_2) to a halide ionic liquid precursor, forming the trihalide anion *via* a Lewis acid-base reaction. All ionic liquids were characterized by ^1H NMR, ^{13}C NMR, ^{31}P NMR, and Raman spectroscopy. Phosphonium trihalide ionic liquids $[\text{PR}_4][X_3]$ ($X = \text{Cl, Br or I}$) were selected because of their low viscosity, low melting point and stability towards chlorine. The melting point, viscosity and density were measured for all ionic liquids. A series of seven trihalide ionic liquids (with anions ranging from trichloride to triiodide), containing both single trihalide and mixed trihalide anions, was prepared for the tributyldecylphosphonium cation. The effect of the trihalide anion on the physical properties of the phosphonium ionic liquids was determined using this series of ionic liquids. Trihalide anions, and polyhalides in general, are strongly oxidizing agents due to their charge deficit with respect to the number of halogen atoms. This strong oxidizing power has been applied to oxidatively dissolve several metals into tributyldecylphosphonium tribromide $[\text{P}_{44410}][\text{Br}_3]$. A broad range of metals was tested: Fe, Cu, Sb, Co, Zn, In, Ga, Bi, Ge, Sn, Pd, Au, Rh and Pt. With the exception of Pt and Rh, all the metals dissolved in the ionic liquid. The dissolution of Cu in six different trihalide ionic liquids was performed to confirm that these trihalide ionic liquids have similar oxidizing properties compared to $[\text{P}_{44410}][\text{Br}_3]$. Due to the negligible vapor pressure of ionic liquids, the entire oxidative dissolution process proceeded in a non-volatile solvent and without the formation of gases. This work can contribute to the development of safe, solvometallurgical methods for oxidative dissolution of metals.

Keywords: ionic liquids; ionometallurgy; oxidative dissolution of metals; polyhalides; solvometallurgy

Introduction

Abandoning the concept of a linear economy and shifting to a circular economy must be a goal of our modern society, for both environmental and economic reasons. This is clearly illustrated by the so-called 'critical metals'.^{1,2} These metals are essential for green and sustainable applications, but they lack a reliable supply source, either due to a limited abundance or a production monopoly by certain countries.¹ Examples of critical metals are the rare-earth elements (REEs), the platinum-group metals (PGMs), cobalt, indium and antimony. Recycling of critical metals from end-of-life products is gaining a lot of interest. The key to recycling is proper collection and sorting into different fractions that can be further processed.

A difficult step in recycling is the quantitative separation of all the metals. The separation of metals is often based on different chemical and physical properties of the metal cations or salts. This implies that in order to purify and process metals, they have to be present in their oxidized state (M^{n+}). If the metal is oxidized and dissolved in the same step, the term 'oxidative dissolution' is used. There are various ways of oxidizing and processing metals, but they are traditionally divided into two major groups: hydrometallurgy and pyrometallurgy. Additionally there is the emerging field of solvometallurgy.³ In solvometallurgy organic solvents and reagents are used to process metals. The most significant advantage compared to pyrometallurgy is the lower temperature of the processes, lowering the energy costs.^{4,5} The benefits compared to hydrometallurgy are all linked to largely eliminating water from the system: different selectivities, reducing waste water production, avoiding the formation of flammable hydrogen gas in strongly reducing media, the absence of gel phases or hydrolysis products and a broader electrochemical window for electrowinning of reactive metals. When looking at the oxidative dissolution of metals, many options for solvents exist when the metals are chemically not noble: many acids, both organic and inorganic, are sufficiently reactive to dissolve such metals. However, oxidative dissolution of

noble metals such as PGMs poses a larger challenge and requires more reactive reagents. Halogens in volatile molecular solvents, hydrofluoric acid, cyanides or *aqua regia* are examples that are currently used in oxidative dissolution of metals for extractive metallurgy or in analytical procedures.^{4,6–11} These reagents are often dangerous and/or volatile, making them difficult and costly to handle. Certain ionic liquids (ILs) can be used as safer alternatives, since they have a negligible vapor pressure.^{12,13} Functionalized ILs bearing a Brønsted acidic group have been applied for the dissolution of metals and metal oxides.^{14–17} Another promising class of ILs are polyhalide ILs, which contain a polyhalide anion in their structure. These anions are composed of covalently bound halogen atoms with a negative charge of less than one per atom, resulting in a charge deficit.¹⁸ The formation of a polyhalide anion can be considered as the adduct formation between a Lewis acidic halogen molecule and a Lewis basic halide anion. The best known example of a polyhalide anion is the triiodide (I_3^-) anion, which is commonly used as a starch indicator.¹⁹ Halogens can catenate to form large anions: polyhalides with up to 20 halogen atoms have been reported.¹⁸ The structure of polyhalides is also not limited to linear structures composed of identical halogen atoms. A large variety of three-dimensional polyhalide anions composed of different halogen combinations have been reported.^{18,20–25} Due to the above-mentioned charge deficit and the high electronegativity of the halogen atoms, these polyhalides are strong oxidizers. In non-aqueous environment (e.g. in ILs), the redox behavior of halogens can drastically change. Abbott *et al.* showed that iodine in deep-eutectic solvents showed more positive redox potentials, oxidizing a broad range of metals.²⁶ The assumption that the trihalide ILs could be used to oxidize metals in bulk is supported by the fact that these solutions, iodine in deep-eutectic solvents was used by Abbott *et al.* to oxidize gold coatings from SEM samples.²⁶ Incorporating these halogens in the anion of ILs combines the high reactivity of the halogens and the advantageous properties of ILs (nonflammable, no electrostatic buildup and negligible vapor pressure at ambient temperature).²⁷ The highly tunable character of ILs combined with the large option of polyhalide and trihalide anions results in a wide variety of

applications for these trihalide ionic liquids.^{18,28–30} Basic research has been done in using them as oxidizing solvents.^{28,31–33} Also, some very specific applications such as immersion fluids for gemstones or the use in dye sensitive solar cells have been reported.^{29,30} It should be noted that triiodide anions have been used as electrocatalyst in metal recycling, where they were used to oxidize metals.³³ The triiodide ion, present in small amounts, was used to oxidize several metals (including gold), while the metals were reduced and recovered on the cathode and the triiodide ion was regenerated at the anode. Although these experiments were performed in deep-eutectic solvents (DES) with high chloride content, it shows the potential of trihalide anions, and ILs, as oxidizing solvents for metals. However, in spite of all these recent developments, the main use of these reactive polyhalide ionic liquids still remains their use as selective halogenating reagents in organic synthesis.^{34–40}

In spite of the many fundamental studies on polyhalide anions themselves, and the use of polyhalide ionic liquids as halogenating reagents, no versatile synthetic procedures on the preparation of these ILs has been described, nor has the effect of the anions on the physical properties of the ILs been investigated. This paper describes the efficient synthesis of different trihalide ionic liquids (with anions: trichloride, bromidedichloride, chloridedibromide, tribromide, iodidedibromide, bromidediiodide and triiodide) and the effect on the physical properties of these ILs. In addition, the oxidative dissolution of a broad range of metals in these trihalide ILs is described.

Experimental

Chemicals

Tri-*n*-butylphosphine (95% with Acroseal®), 1-chlorodecane (97-99%), 1-bromodecane (98%), 1-iododecane (98%, stabilized), 1,10-dibromodecane (97%), bromine (99.6%) and iodine (99.5%, resublimed), tin powder (< 325 mesh, 99.8%) and gallium powder (99.99%) were purchased from Acros Organics (Geel, Belgium). The gallium had melted and solidified during transportation, rendering a solid chunk of metal instead of the ordered powder. Sodium hydroxide beads were purchased from Fisher Scientific (Geel, Belgium). Tri-*n*-butylamine (99%), copper powder (< 200 mesh, 99%), zinc powder (< 10 µm, > 98%), indium powder (< 100 mesh, 99.9%), cobalt powder (< 2 µm, 99.9%) platinum wire (diam. 0.5 mm, 99.9%), palladium wire (diam. 0.5 mm, 99.9%), rhodium wire (diam. 1.0 mm, 99.9%) and gold wire (diam. 1.0 mm, 99.997%) were purchased from Sigma-Aldrich (Diegem, Belgium). Cyphos® IL 101 (trihexyltetradecylphosphonium chloride) was purchased from Cytec industries Inc. (Niagara Falls, Ontario, Canada). Germanium powder (< 100 mesh, 99.9%), antimony powder (< 200 mesh, 99.5%) and bismuth powder (< 200 mesh, 99.99%) were purchased from Alfa Aesar (Geel, Belgium). Iron powder (20 mesh, 99%) was purchased from abcr (Karlsruhe, Germany). The lecture bottle of liquefied chlorine (1 kg, 4.9 bar at 15 °C, > 99.5%) and a pressure regulator (DIM 200-3-5 T purge type) to adjust the pressure of outgoing gas between 0.3 and 3 bar were purchased from Air Liquide (Belgium). The chlorine flow meter (range: 2.1 to 21 g/h at 2 bar) was ordered from Brooks Instrument (The Netherlands).³¹ All chemicals, with the exception of Cyphos IL 101, were used as received without any further purification.

Techniques

The ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance 300 spectrometer (operating at 300 MHz for ¹H and 75 MHz for ¹³C). The reference tetramethylsilane was used to determine the chemical shifts. The ³¹P NMR spectra were recorded on a Bruker Avance 400 Spectrometer, operating at

162 MHz for ^{31}P . A reference solution of 25 wt% of H_3PO_4 in water was used to determine the chemical shifts. For ^{31}P NMR measurements on phosphonium ILs, the delay time (d1) was adjusted to 5 s and 128 scans were recorded. Raman spectra were recorded on a Bruker Vertex 70 spectrometer with a RAMII Raman module (laser wavelength: 1064 nm), operating at different laser powers (specified for each IL). The data were analyzed using the OPUS software. Viscosities were measured using an Anton-Paar Lovis 2000 ME rolling-ball viscometer with capillaries of 2.5 mm in diameter. Densities were measured using an Anton-Paar DMA 4500 M density meter.

Synthesis of halide ionic liquids

Details regarding the characterization, yield, spectra and physical properties of the ILs can be found in the ESI.

Tributyldecylphosphonium halides: $[\text{P}_{44410}][\text{X}]$

The halide ionic liquids were prepared from tri-*n*-butylphosphine and the appropriate haloalkane. To prevent the oxidation of tri-*n*-butylphosphine to tri-*n*-butylphosphine oxide, the reaction was carried out in an inert nitrogen atmosphere. The glassware (condenser and three-neck flask) was dried in an oven at 110 °C for 3 hours. The setup was assembled and flushed with a nitrogen gas flow for 2 minutes. Two septa and a reflux condenser were used to seal the three-neck flask (250 mL). Dry acetonitrile was added through the septum, followed by 1.1 equivalents of the corresponding 1-halodecane. The solution was purged with nitrogen gas for 1 hour to remove traces of oxygen or water from the mixture. Afterwards, the solution was cooled to 0 °C in an ice bath and 1 equivalent of tri-*n*-butylphosphine was added dropwise. The solution was stirred and heated to 85 °C, after which the mixture was refluxed overnight. The solution was allowed to cool down and extra acetonitrile was added until the mixture was completely clear and transparent. The solution was washed with heptane (immiscible with the acetonitrile solution) until all the phosphine oxide and the excess haloalkane were removed. This was

checked using ^1H and ^{31}P NMR. The haloalkane was removed after two washing steps, the phosphine oxide after three to six washing steps. Afterwards the acetonitrile was removed using a rotary evaporator and the IL was dried on a Schlenk line. Details regarding the yield and properties of the ionic liquids can be found in the ESI.

Tributyldecylammonium bromide: $[\text{N}_{44410}]\text{Br}$

Tributylamine (50 mmol, 12.03 mL) and 1-bromodecane (1.3 eq. 65 mmol, 13.84 mL) were dissolved in acetonitrile and refluxed at 85 °C for 48 hours. In the meantime, completion of the reaction was checked with thin layer chromatography. After all the tributylamine had reacted, the solution was washed with heptane to remove the excess of 1-bromodecane. Acetonitrile was removed with a rotary evaporator and the product was dried on the Schlenk line. This resulted in 19.23 g (95 % yield) of a light brown IL with a melting point of 51 °C.

Trihexyltetradecylphosphonium chloride: $[\text{P}_{66614}]\text{Cl}$

Cyphos IL 101 (21 mmol, 10 g) was added to a 1 M NaOH solution (25 mL) and the mixture was stirred for 2 hours at room temperature in order to convert the traces of chlorotrihexylphosphonium chloride to trihexylphosphine oxide. Afterwards, the two phases were allowed to settle and the NaOH solution was separated from the IL. The Cyphos IL 101 was washed several times with water until the water phase was neutral. Heptane was added to the product and the mixture was stirred under reflux for 2 hours. The phases were then allowed to settle and the heptane was removed. The washing step was performed in order to remove the remaining impurities: trihexylphosphine oxide, 1-chlorotetradecane and 1-tetradecene. The washing steps were repeated until no impurities remained, this was checked using ^{31}P NMR and ^1H NMR. 4.18 g (42% yield) of pure $[\text{P}_{66614}]\text{Cl}$, a colorless, odorless and viscous IL, was obtained.

1,10-Decanediylbis(tributylphosphonium) dibromide: $[\text{C}_{10}(\text{P}_{444})_2][(\text{Br})_2]$

The same procedure as for the tributyldecylphosphonium halide ILs was used, except that 1,10-dibromodecane (22 mmol, 6.60 mL) instead of 1-bromodecane and a proportionally larger amount of tributylphosphine (2.3 eq. 50 mmol, 12.49 mL) were used. This was necessary since the haloalkane could not be used in excess anymore as that would result in products of 1,10-dibromodecane where only one bromine atom is replaced by a tributylphosphine group instead of both bromine atoms. After the same synthetic and purification procedures as described above, 14.14 g of a white solid with a melting point of 75.1 °C (Yield: 91%) was obtained.

Synthesis of trihalide ILs

The synthesis of the trihalide ILs is divided into three sections, each covering the addition of a particular halogen. Unless stated otherwise, all the syntheses towards trihalide ILs were carried out as described below.

Being a gas, chlorine is difficult to add in quantitative amounts. Its toxicity also necessitates manipulation in a closed environment. A sealed and controllable setup for the addition of chlorine was used and a detector for chlorine gas (with a threshold of 0.5 ppm) was present inside the fume hood monitoring the chlorine level. The chlorine bottle was connected to a flow meter to control the amount of chlorine flowing through the flask. A piece of glassware was designed to bubble the chlorine through the IL before being led through two washing bottles containing a 10% NaOH solution. A third washing bottle containing a KI solution was attached so any remaining chlorine could be detected by a color change of the solution (chlorine oxidizes iodide, forming the brown colored triiodide). This was followed by an additional washing bottle with a 10% NaOH solution. A schematic overview of the setup can be found in the ESI. The addition of bromine (Br_2) is more straightforward than that of chlorine, because bromine is a liquid. Some precautions are required, since it is a fuming liquid, especially at room

temperature. This does not only pose safety risks, but also makes it difficult to accurately add a certain amount of bromine to a flask without evaporation. Because iodine (I_2) is a solid, its addition does not require special precautions.

Addition of chlorine

The IL was dried on a Schlenk line in a round bottom flask while stirring with a stirring bar. Afterwards, the flask was attached to the chlorine setup and nitrogen (2 bar, 20 g/h) was used to purge the system for 30 minutes.³¹ The flask was covered with aluminum foil in order to block incident light that can cleave the halide bonds, forming reactive radicals. Then, the nitrogen flow was replaced by chlorine gas (2 bar, 2.1 g/h), which was fully absorbed by the IL, since no bubbles escaped the IL. After the required amount of chlorine was added, nitrogen was again used to drive all the remaining chlorine gas in the tubing into the IL. The flushing was maintained for 30 minutes (2 bar, 2.1 g/h).

Addition of bromine

First, the bromine container was placed in dry ice and allowed to cool down to reduce the volatility of the bromine. In the meantime, the targeted amount of dried ionic liquid was added to a round bottom flask together with a stirring bar. The bromine was added dropwise to the IL. The advantage of adding the IL first is that the bromine is heavier and sinks, so no vapor can escape from the flask, allowing for a more precise addition of bromine. When the flask was sealed it could be weighed on an accurate balance, and if needed, more bromine or IL was added. This was repeated until an equimolar addition of bromine and IL was achieved. The flask was closed and the mixture was stirred for 1 hour while being covered from light.

Addition of bromine to $[C_{10}(P_{444})_2][(Br)_2]$

The IL and 2 equivalents of bromine (1 for each bromide anion in the dicationic liquid) were dissolved in cold dichloromethane in separate flasks. The bromine solution was slowly added to the IL solution. The

dichloromethane was removed using a rotary evaporator and the resulting solid was quantitatively isolated.

Addition of iodine

The halide IL was dried on a Schlenk line. Afterwards an equimolar amount of iodine and the IL were added to a round bottom flask sealed from light. The solution was stirred at room temperature for two hours.

Dissolution of metals

The metal powders (Fe, Zn, Cu, Co, Bi, In, Sn, Ga, Sb and Ge) were submerged in 10 molar equivalents of IL (for Cu, Sn, Ge, Co and Zn) or 15 molar equivalents of IL (for Fe, Sb, Bi, Ga and In). The suspension was stirred at room temperature for 2 hours. After it was visually observed that the metal had dissolved completely, acetone was added as a diluent to the IL and the solution was filtered while checking for metallic particles as residue. When the metals appeared to be not completely dissolved, they were stirred for an additional 22 h, adding up to 24 h in total. If the powder had not been dissolved by then, the experiment was repeated at 50 °C for 24 h. If that still was not sufficient, the experiment was again repeated at a higher temperature, 75 °C. The clear solutions that were presumed to have fully reacted were diluted and filtered as described above in order to check for metal particles. Gallium required an additional pre-treatment step before the dissolution experiments since it had melted and solidified during transportation. The metallic gallium block was crushed into a powder with an unknown particle size and particle distribution. Afterwards, the powder was treated as the other powders.

Each metal wire (Au, Pd, Pt and Rh) was placed in a 2 mL vial. The metal wires were long enough to stick out of the vial, so they could be removed easily from the solution using tweezers. The vials were filled with tribromide IL ($[P_{44410}][Br_3]$) until half of the wire was submerged. The solutions were stirred at room temperature and at certain time intervals the wires were removed from the solution, rinsed with

acetone, dried and weighed on an analytical balance. This procedure was repeated several times during the dissolution process.

Results and Discussion

Synthesis

Phosphonium-based ionic liquids were studied into detail because of their favorable physical properties (low melting point and viscosity) compared to other cations.⁴¹ Imidazolium ILs have similar desirable properties, but these cations are not compatible with all the halogens since the aromatic ring is chlorinated when contacted with chlorine gas.³¹ For the phosphonium cation tributyldecylphosphonium ($[P_{44410}]^+$), three different halide ILs were prepared, all with a different halide anion. From these ILs a series of trihalide ILs could be prepared and since they would contain an identical cation, a comparison of the effects of the trihalide anions could be made. The phosphonium cation $[P_{44410}]^+$ was specifically chosen for its shorter alkyl chains. This results in a higher concentration of the trihalide anions per unit of volume and therefore a more profound effect of the anions in measurements and physical properties. However, the alkyl chains had to be long enough to result in a room-temperature ionic liquid (RTIL), so the tributyldecylphosphonium cation ($[P_{44410}]^+$) was the cation of choice. The ionic liquids were prepared from tributylphosphine and the appropriate alkyl halide: 1-chlorodecane, 1-bromodecane, or 1-iododecane. These products were mixed in dry acetonitrile and refluxed. The product was further purified and dried to obtain the pure ionic liquid (Scheme 1).

Green Chemistry Accepted Manuscript

Figure 1: Overview of the halide ionic liquids used in this study: a) tributyldecylphosphonium chloride, b) tributyldecylphosphonium bromide, c) tributyldecylphosphonium iodide, d) tributyldecylammonium bromide, e) trihexyltetradecylphosphonium chloride and f) 1,10-decanediylbis(tributylphosphonium) dibromide.

In this research, only trihalide ILs were considered instead of higher polyhalide anions, for various reasons. Firstly, the oxidative strength of the trihalides was expected to be comparable to higher polyhalides. Moreover, the oxidative dissolution of metals in the IL might be limited by the number of cations available as counter ions. Therefore, increasing the halide content will not benefit the dissolution process. Finally, the oxidative dissolution process itself ideally proceeds in the most safe and controllable way possible, loading the IL with more halogens might cause volatile chlorine or bromine to escape the IL when reacting with metals.

The trihalide ILs were prepared from their halide precursors. This was done only *via* the addition of chlorine, bromine or iodine (X_2 with $X = \text{Cl}, \text{Br}$ or I). When a halide IL reacted with the halogens, they

formed separate phases. Upon mixing they underwent a Lewis acid-base reaction to form the trihalide IL. In spite of the simple chemistry of these reactions some practical challenges arose, caused by the volatility and toxicity of the halogens. The addition of chlorine in particular required a specialized setup and proper safety measures.³¹

The conversion from a halide to a trihalide IL was easily observed by the change in color and viscosity. All the trihalide anions have a distinctive color, which could easily be observed visually (Figure 2). Additionally, the viscosity drop was another good indication of the conversion. This drop resulted from a decreased interaction between the anion and cation of the IL, caused by a decreased charge density of the anion, since a trihalide anion has more atoms to delocalize the single negative charge.

For the tributyldecylphosphonium cation, seven different ionic liquids with a different trihalide anion were prepared: trichloride ($[P_{44410}][Cl_3]$), bromidedichloride ($[P_{44410}][BrCl_2]$), chloridedibromide ($[P_{44410}][ClBr_2]$), tribromide ($[P_{44410}][Br_3]$), iodidedibromide ($[P_{44410}][IBr_2]$), bromidediiiodide ($[P_{44410}][BrI_2]$) and triiodide ($[P_{44410}][I_3]$).

Figure 2: Schematic overview of the synthesis of trihalide ILs and their different colors. A colorless phosphonium bromide IL is shown at the left as a reference for the color of the monohalide ILs. Displayed from left to right: $[P_{44410}][Br]$, $[P_{44410}][Cl_3]$, $[P_{44410}][BrCl_2]$, $[P_{44410}][ClBr_2]$, $[P_{44410}][Br_3]$, $[P_{44410}][IBr_2]$, $[P_{44410}][BrI_2]$, $[P_{44410}][I_3]$.

The room-temperature IL $[P_{66614}]Cl$ could be handled in the same way as $[P_{44410}]Cl$, so these experiments were carried out in an analogous way. Both $[N_{44410}]Br$ and $[C_{10}(P_{444})_2][(Br)_2]$ were solid at room temperature and the two methods of adding bromine were tested. For the former, the same synthesis procedure as for the RTILs was chosen. For the latter, a method using dichloromethane as solvent was applied. Here, the IL and two equivalents of bromine (one for each bromide anion) were dissolved in cold dichloromethane, both in different flasks. The bromine solution was slowly added to the IL solution. In contrast to the mixing of pure bromine and pure IL, the formation of the tribromide (observed by the color change) occurred instantly. The dichloromethane was removed using a rotary evaporator and the resulting solid was isolated in a 100% yield. Both methods could therefore be used to prepare tribromide ILs from a solid IL. Dilution with dichloromethane resulted in more facile addition and quicker reaction times, although this required extra follow-up steps (drying) and therefore took more time in total. Another noteworthy observation is the fact that upon removal of the dichloromethane using a rotary evaporator, no bromine escaped from the IL. Even when exposing the IL to low pressures (50 mbar) and increased temperatures (50 °C), the tribromide IL did not degrade into the volatile bromine and the bromide IL precursor. This observation confirms the non-volatile nature of the tribromide ionic liquids, even when they are loaded with volatile bromine. Thanks to the stability of the trihalide anion, halogens can be taken up by the ionic liquid, forming a non-volatile IL. An overview of the prepared ILs is given in Figure 3.

Figure 3: Structures of the synthesized trihalide ILs: a) tributyldecylphosphonium trihalides ($X = \text{Cl}_3^-, \text{BrCl}_2^-, \text{ClBr}_2^-, \text{Br}_3^-, \text{IBr}_2^-, \text{BrI}_2^-$ and I_3^-), b) trihexyltetradecylphosphonium trichloride ($Y=\text{Cl}$) and chloridedibromide ($Y=\text{Br}$), c) tributyldecylammonium tribromide and d) $[\text{C}_{10}(\text{P}_{444})_2][(\text{Br}_3)_2]$.

All the prepared trihalide ILs were liquid at room temperature, with the exception of $[\text{C}_{10}(\text{P}_{444})_2][(\text{Br}_3)_2]$, and were stored in a freezer and sealed from light to prevent degradation of the trihalide anion. The light would cleave the trihalide bonds generating radicals (homolytic cleavage), thus destroying the anion in the process and subsequently the cation as well (by the generated radicals). During storage in the freezer, none of the trihalide ILs showed degradation of the cation in the ^1H or ^{31}P NMR spectra, indicating that the investigated trihalide anions did not react with the phosphonium cations.

Raman spectroscopy

Infrared spectroscopy is based on a change in dipole moment and therefore not suited for the characterization of the trihalides. Many, and sometimes all, trihalide bonds are homonuclear and therefore do not have a dipole moment. Raman spectroscopy on the other hand, exploiting the polarizability of atoms and molecules, is ideal to study polyhalides.^{18,45–47} The large and electron-rich structures result in intense and distinctive Raman signals. Due to increased signal scattering when

measuring the heavier halogen atoms, the laser intensity had to be adjusted in order to obtain qualitative spectra. All Raman spectra can be found in the ESI. Besides the signals originating from the phosphonium cation of the IL (500-1500 cm^{-1} and around 3000 cm^{-1}), the region below 500 cm^{-1} shows several peaks in the Raman spectrum (Figure 4). When zooming in on the 100-400 cm^{-1} region, distinctive patterns for the different trihalide anions become clear (Figure 5). The different peaks of all the trihalide anions are listed in Table 1. The Raman peaks of these trihalide RTILs are in good accordance to reported Raman spectra of (in)organic trihalide salts in literature.^{46,48–51} One of the synthesized trihalide ILs, $[\text{P}_{44410}][\text{Br}_3]$, was investigated further. The tribromide anion had two distinctive peaks: 163 and 192 cm^{-1} . A series of 7 samples was made, all with a different ratio of tribromide over monobromide as anion. They are described as ‘percentage conversion’ meaning that 100% denotes pure $[\text{P}_{44410}][\text{Br}_3]$, 0% denotes $[\text{P}_{44410}]\text{Br}$, and 20% denotes 20 mol% of $[\text{P}_{44410}][\text{Br}_3]$ in $[\text{P}_{44410}]\text{Br}$. From Figure 6 it can be seen that the signal increases progressively with increasing tribromide content.

Figure 4: Raman spectrum (50-3500 cm^{-1}) of the different trihalide anions with $[\text{P}_{44410}]^+$ as the counterion in the IL.

Figure 5: Raman spectrum (50-400 cm^{-1}) of the different trihalide anions with $[\text{P}_{44410}]^+$ as the counterion in the IL.

Table 1: Distinctive Raman signals measured for different trihalide anions.

IL	Raman peaks (cm^{-1})
	experimental
$[\text{P}_{44410}][\text{Cl}_3]$	271
$[\text{P}_{44410}][\text{BrCl}_2]$	277
$[\text{P}_{44410}][\text{ClBr}_2]$	163, 196, 215, 277
$[\text{P}_{44410}][\text{Br}_3]$	163, 192
$[\text{P}_{44410}][\text{IBr}_2]$	161
$[\text{P}_{44410}][\text{BrI}_2]$	115, 136, 177
$[\text{P}_{44410}][\text{I}_3]$	113, 146

Figure 6: Raman spectra (100-350 cm^{-1}) of mixtures between $[\text{P}_{44410}][\text{Br}_3]$ and $[\text{P}_{44410}]\text{Br}$.

For both peaks, there is a linear correlation between the Raman intensity and the percentage conversion. A fit can be made by using equations (1) and (2). The R^2 values are 0.99961 for (1) and 0.99748 for (2). These formulae can be used to determine the amount of tribromide in the IL, which is useful for stability or degradation studies.

$$\text{Conversion} = \frac{\text{Raman intensity (163 cm}^{-1}\text{)}}{4.551} 100\% \quad (1)$$

$$\text{Conversion} = \frac{\text{Raman intensity (192 cm}^{-1}\text{)}}{1.223} 100\% \quad (2)$$

Viscosity and Density

The viscosities and densities of all the ILs were measured. In order to visualize the effect of the monohalide to trihalide transitions, an overview of the parameters for the tributyldecylphosphonium series are presented in Table 2. It can be seen from Table 2 that the viscosity decreases sharply when the halide ILs are transformed into the corresponding trihalide ILs. This is not surprising since the charge is now delocalized over more atoms, such that the charge density, and hence the anion-cation interactions, decreases resulting in a lower viscosity. The same reasoning holds true for the monohalide anions, which show a decrease in viscosity going from chloride to iodide. The small difference in viscosity between the ILs containing different trihalide anions was surprising. It was expected that the viscosity would decrease over the entire series ranging from Cl_3^- to I_3^- , but no clear trend was observed. The densities of the ILs, however, do follow the expected trend: the heavier the halides, the higher the densities. This was observed for both the monohalide ILs and the trihalide ILs, as can be clearly seen in the last column of Table 2.

Table 2: Viscosities and densities of the tributyldecylphosphonium halide and trihalide ionic liquids at 25 °C. *Error on the viscosity measurements, displayed by the variation coefficient of 7 consecutive measurements for each sample.

IL	Viscosity (mPa·s)	Variation coefficient (%)*	Density (g/cm ³)
[P ₄₄₄₁₀]Cl	8167	0.9	0.917(1)
[P ₄₄₄₁₀]Br	7317	2.0	1.006(1)
[P ₄₄₄₁₀]I	4298	0.5	1.091(1)
[P ₄₄₄₁₀][Cl ₃]	400	7.2	0.996(1)
[P ₄₄₄₁₀][BrCl ₂]	303	1.2	1.094(1)
[P ₄₄₄₁₀][ClBr ₂]	377	1.9	1.169(1)
[P ₄₄₄₁₀][Br ₃]	337	1.0	1.253(1)
[P ₄₄₄₁₀][IBr ₂]	381	0.4	1.325(1)

[P ₄₄₄₁₀][BrI ₂]	358	1.9	1.433(1)
[P ₄₄₄₁₀][I ₃]	371	0.9	1.469(1)

The effect of the tribromide conversion on the viscosity and density was investigated. A series of ILs with a different bromide conversion was made, similar to the samples in Figure 6. The viscosity and density of all the samples were recorded with the same instrument and under the same conditions. As is depicted in Figure 7, the viscosity decreases exponentially with increasing temperature, as is normal for ILs. The same trend was observed for the conversion of monobromide to tribromide IL (Figure 8). This is an asset for the applicability of trihalide ILs in industrial processes, since a lower viscosity results in a faster mass transfer and hence faster reaction rates.⁵² The exponential decrease implies that only a small fraction of trihalide IL in monohalide IL can already result in a significant decrease in viscosity. In Figure 9, the density is plotted as a function of the temperature and the percentage conversion. Here a linear trend was observed for both parameters. An anticipated result, since increasing the heavy bromine content in the IL increases the density. The density drop with increasing temperature was an expected consequence since heating cause the IL to expand. Figure 10 shows the density as a function of the tribromide conversion, again following a proportional trend. Also here, it is a direct consequence of loading the ionic liquid with the heavy bromine.

Figure 7: Effect of the temperature on the viscosity of $[P_{44410}]Br$ and $[P_{44410}][Br_3]$ mixtures. The amount of tribromide anion compared to the molar amount of cation is displayed as the 'tribromide conversion'.

Figure 8: Effect of the percentage of tribromide conversion on the viscosity of $[P_{44410}]Br$ and $[P_{44410}][Br_3]$ mixtures.

Figure 9: Effect of the temperature on the density of $[P_{44410}]Br$ and $[P_{44410}][Br_3]$ mixtures. The amount of tribromide anion compared to the amount of cation is displayed as the 'tribromide conversion'.

Figure 10: Effect of the percentage of tribromide conversion on the density of $[P_{44410}]Br$ and $[P_{44410}][Br_3]$ mixtures.

Oxidative dissolution of metals

When the viscosity measurements were performed overnight and the sample remained inside the viscometer, the IL reacted with the stainless steel ball used in the measurement (Figure S 2). Upon isolation and cleaning of the ball, it was clear that the IL had dissolved the gold coating (Figure S 3). The color change of the IL was a clear indication that the gold was oxidatively dissolved instead of peeled off during the recovery and cleaning of the ball. Considering the standard potentials of redox equations (3) and (4), this was no unexpected observation.⁵³ Nevertheless, it clearly indicated that the oxidizing power of the IL is strong enough to oxidatively dissolve gold, a statement that was confirmed in further experiments.

It is important to realize is that the redox reactions and the values of the reduction potentials are valid for aqueous solutions. Therefore, the electrochemistry of the trihalide ILs might vary from the values observed for the trihalide anions in aqueous solutions, but they are shown for comparability. The exact redox behavior of the trihalide ILs will be investigated and reported in a future paper. The dissolution of the gold coating shows that, despite the stability of the tribromide anion toward physical parameters (low pressure and elevated temperature), the strong oxidation power is still retained. These two properties – stability and oxidative strength – are advantageous when using the trihalide ILs as safer solvents for the oxidative dissolution of metals.

The tribromide IL $[\text{P}_{44410}][\text{Br}_3]$ was chosen to perform the dissolution experiments in order to evaluate the oxidative dissolution capabilities of the trihalide ILs. The choice for a tribromide IL is based on a consideration between price and reduction potential of the halogens on one hand, and the ease of synthesis on the other hand. Tribromide ILs can be made more efficiently compared to trichloride ILs.

The synthesis of phosphonium bromides is easier since bromide is a better leaving group than chloride. But more importantly, the addition of bromine can be achieved much faster and more precise than that of chlorine (as is described in the Experimental section). For the same reasons, triiodide ILs can be prepared even more quickly and in a more controllable manner, but the reduction potential of iodine (6) is significantly lower than those of bromine (3) and chlorine (5).⁵³ Another disadvantage of triiodide ILs is their dark color (Figure 2), rendering it difficult to visually monitor the oxidative dissolution process.

Difficulties were faced for determining the metal content in the ILs by TXRF or ICP-OES. TXRF measurements gave inaccurate metal concentrations due to the strong high scattering and absorption of the X-rays by the heavy halogen atoms. ICP-OES was not suited to determine the metal content in the viscous and apolar ILs with a very high concentration of halogens. Moreover, the solutions were too corrosive for direct injection in the ICP-OES. Therefore, it was opted to check the dissolution of the metals visually.

Several base metals and metalloids were dissolved in $[\text{P}_{44410}][\text{Br}_3]$: iron, zinc, copper, cobalt, bismuth, indium, tin, gallium, antimony and germanium. The followed procedure to dissolve the metals in $[\text{P}_{44410}][\text{Br}_3]$ is described in detail in the experimental section. An overview of the conditions required to dissolve the various metals and metalloids is given in Table 3. When a mixture was presumed to have fully reacted, the IL was diluted with acetone and filtered over a glass filter whilst checking for remaining metal pieces, to be able to confirm full oxidative dissolution of the metal.

Table 3: Overview of the metals tested for oxidative dissolution in $[P_{44410}][Br_3]$ and the different conditions in which full oxidative dissolution was observed.

Metal	Particle size	Oxidative dissolution	Temperature and duration required for complete dissolution
Fe	< 20 mesh	Yes	2 h at RT
Cu	< 200 mesh	Yes	2 h at RT
Sb	< 200 mesh	Yes	2 h at RT
Co	< 2 μm	Yes	2 h at RT
Zn	< 10 μm	Yes	24 h at 50 °C
In	< 100 mesh	Yes	24 h at 50 °C
Ga	n.a. ¹	Yes	24 h at 50 °C
Bi	< 200 mesh	Yes	24 h at 75 °C
Ge	< 100 mesh	Yes	24 h at 75 °C
Sn	< 325 mesh	Yes	n.a. ²

¹ The particle size of gallium is unknown since the metal melted and solidified during transport, the metallic block was ground into a powder of unknown particle size.

² Even though the metal was being oxidatively dissolved, the process was not complete after 24 hours.

Although the conditions for quantitative dissolution differed significantly (Table 3), the tribromide IL was able to oxidatively dissolve all the tested metals. Another observation is that, with the exception of antimony, the metals that required higher temperature (75 °C) for the oxidative dissolution are metalloids or post-transition metals. However, this does not imply that their weak metallic character is necessarily the cause for their slow dissolution, since this is a kinetic effect. Another possible cause for the more difficult dissolution of certain metals might be the presence of a metal oxide layer on the surface of the respective metal particles, reducing the active surface available for the tribromide to oxidize. Nonetheless, the fact remains that all the metals and metalloids listed in Table 3 could be

oxidatively dissolved in the tribromide IL, without the generation of any gases. This evidently shows the potential of trihalide ionic liquids as safer, non-volatile oxidizing solvents for metals and alloys.

In order to study the dissolution of noble metals (Au, Pd, Pt, Rh) in a more quantitative way, metal wires were used, instead of metal powder. The wires were placed in a vial and submerged in the tribromide IL $[P_{44410}][Br_3]$ for half of their length. In doing so the wires could be removed from the solution and weighed accurately on an analytical balance to monitor the mass loss. An overview of the metals as well as the wire diameter and the degree of dissolution is given in Table 4.

Both the gold and palladium wire showed a steady mass decrease for each weighing step, indicating the oxidation of the metals by $[P_{44410}][Br_3]$. Platinum and rhodium were not affected by the tribromide IL. After 47 hours of contact with the IL at room temperature, the mass of the rhodium wire decreased by only 0.01 mg, and the mass of the platinum wire increased by 0.02 mg over the same period of time. Both mass differences are within the standard error of the balance, so it can be concluded that rhodium neither platinum were oxidized by $[P_{44410}][Br_3]$. A possible explanation might be that a protective layer of metal salts on the surface of the metal wires limits the further oxidation. However, it is unlikely that this layer can also explain the mass increase since the wires were rinsed with acetone and rubbed with a paper tissue, which should have removed any halide salts on the surface of the wires. The followed procedure proved successful for dissolution of palladium and gold, indicating that the difference compared to platinum and rhodium can be attributed to the metals themselves rather than to the experimental procedure. The incapability of the trihalide ILs to oxidize all the PGMs limits the oxidative dissolution capability to metals less noble than platinum and rhodium, and maybe other metals as well. However, it does not limit the applicability of the trihalide ILs as oxidizing solvents and can be interesting for the selective leaching of Au and Pd from Rh and Pt, being a relevant step for the recycling of PGMs from car exhaust catalysts. The availability of metals that are not chemically attacked by the IL may be

advantageous for the processing of these metals in ILs, for instance as electrode material in electrochemical processes.

Table 4: Overview of the noble metals tested for oxidative dissolution in $[P_{44410}][Br_3]$.

Noble metal	Wire diameter (mm)	Oxidative dissolution in $[P_{44410}][Br_3]$
Au	1.0	Yes
Pd	0.5	Yes
Pt	0.5	No
Rh	1.0	No

To confirm the assumption that the behavior of the tribromide IL $[P_{44410}][Br_3]$ is a correct representation of the trihalide ILs in general, one metal (Cu) was tested for all the other 6 trihalide ionic liquids mentioned in this study. The same copper powder was added to the other trihalide ILs: $[P_{44410}][Cl_3]$, $[P_{44410}][BrCl_2]$, $[P_{44410}][ClBr_2]$, $[P_{44410}][IBr_2]$, $[P_{44410}][BrI_2]$ and $[P_{44410}][I_3]$. Due to the dark color of $[P_{44410}][BrI_2]$ and $[P_{44410}][I_3]$ the progression could not be monitored visually, the solution was stirred for 24 h at room temperature and all samples were investigated afterwards. After testing the solutions, it was found that the copper had been fully oxidized and dissolved in all 6 ionic liquids, since no metallic residues remained in any of the mixtures. This observation is no guarantee that all trihalide ILs will have similar oxidation properties, considering the different redox potentials of the halogens (Equations 3, 5 and 6). Nevertheless it does support the hypothesis that all trihalide ILs used in this study, including the mixed trihalide (YX_2^-) ILs, can be used to oxidatively dissolve metals and metalloids. An asset of this observation is that the trihalide IL with the best properties can be selected and tailored for each specific application. The trichloride ILs contain the cheapest halogen (chlorine), making them cost-effective and the best choice for processes where the halides are consumed. Triiodides can be regarded as the safest of the trihalides, since iodine itself is not volatile. Even though the trihalide ILs themselves are not

volatile, spills of the halogen precursors can never be prevented with 100% certainty. From this point of view, they can be regarded as the safest and greenest solvent of all the trihalides. The tribromide ILs form interesting intermediates between the trichloride and triiodide ILs, combining a strong oxidative strength and beneficial physical properties. The trihalide ILs are beneficial for process safety and process intensification, since these ILs are non-volatile and can contain high concentrations of trihalide anions, reducing the amount of solvent required for leaching.

Conclusions

A range of trihalide ILs was prepared from their halide IL precursors by the addition of halogen atoms. The most convenient methods for a precise addition of volatile halogens to RTILs were discussed in the experimental section. In order to study the effect of the different trihalide anions, a series of seven trihalide ILs was synthesized for one cation, $[P_{44410}]^+$, ranging from Cl_3^- to I_3^- . The physical properties of this range of seven trihalide ILs were investigated, reported and compared. One IL, $[P_{44410}][Br_3]$, was employed as a non-volatile oxidizing solvent for various base and noble metals and metalloids. These metals were chosen to represent a wide group of metals present in everyday applications. Almost all the tested metals were effectively oxidized into their respective halide salts and dissolved in the IL. A second experiment, the dissolution of copper in 7 different trihalide ILs, was performed in order to confirm the applicability of all the trihalide and mixed trihalide ILs for the dissolution of metals. These results proved that trihalide ILs can indeed be used as an effective and versatile oxidative solvents for metals. Given that the entire dissolution process proceeded without the formation of any gasses, the non-volatile trihalide ILs obviously provide a safer dissolution method for metals and metalloids.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research was funded by a PhD grant of the Research Foundation Flanders (FWO) to Arne Van den Bossche (1S04216N). The assistance of Paul Wynants and Dr. Xiaohua Li regarding the chlorine setup is greatly acknowledged.

References

- 1 K. Binnemans, P. T. Jones, B. Blanpain, T. Van Gerven, Y. Yang, A. Walton and M. Buchert, *J. Clean. Prod.*, 2013, **51**, 1–22.
- 2 K. Binnemans, P. T. Jones, B. Blanpain, T. Van Gerven and Y. Pontikes, *J. Clean. Prod.*, 2015, **99**, 17–38.
- 3 K. Binnemans and P. T. Jones, *J. Sustain. Metall.*, 2017, **3**, 570–600.
- 4 A. M. K. Gustafsson, B.-M. Steenari and C. Ekberg, *Sep. Sci. Technol.*, 2015, **50**, 1–9.
- 5 I. Gaballah, M. Djona, J. C. Mugica and R. Solozobal, *Resour. Conserv. Recycl.*, 1994, **10**, 87–96.
- 6 W. Lin, *Rare Met.*, 2012, **31**, 92–95.
- 7 A. Dadgar, *JOM*, 1989, **41**, 37–41.
- 8 K. Strubbe and W. P. Gomes, *J. Electrochem. Soc.*, 1993, **140**, 3294–3300.
- 9 S. Ubaldini, P. Fornari, R. Massidda and C. Abbruzzese, *Hydrometallurgy*, 1998, **48**, 113–124.
- 10 G. F. Brunzie, T. R. Johnson and R. K. Steunenbergh, *Anal. Chem.*, 1961, **33**, 1005–1006.
- 11 E. N. Trifonova, D. V. Drobot and V. A. Krenev, *Inorg. Mater.*, 2003, **39**, 529–531.
- 12 N. V. Plechkova and K. R. Seddon, *Chem. Soc. Rev.*, 2007, **37**, 123–150.
- 13 T. Welton, *Chem. Rev.*, 1999, **99**, 2071–2084.
- 14 A. S. Amarasekara, *Chem. Rev.*, 2016, **116**, 6133–6183.
- 15 D. Dupont and K. Binnemans, *Green Chem.*, 2015, **17**, 856–868.
- 16 P. Nockemann, B. Thijs, T. N. Parac-Vogt, K. Van Hecke, L. Van Meervelt, B. Tinant, I. Hartenbach, T. Schleid, V. T. Ngan, M. T. Nguyen and K. Binnemans, *Inorg. Chem.*, 2008, **47**, 9987–9999.
- 17 P. Nockemann, B. Thijs, S. Pittois, J. Thoen, C. Glorieux, K. Van Hecke, L. Van Meervelt, B. Kirchner and K. Binnemans, *J. Phys. Chem. B*, 2006, **110**, 20978–20992.
- 18 H. Haller and S. Riedel, *Z. Anorg. Allg. Chem.*, 2014, **640**, 1281–1291.
- 19 I. Josefsson, S. K. Eriksson, N. Ottosson, G. Öhrwall, H. Siegbahn, A. Hagfeldt, H. Rensmo, O. Björneholm and M. Odellius, *Phys. Chem. Chem. Phys.*, 2013, **15**, 20189–20196.
- 20 H. Haller, M. Hog, F. Scholz, H. Scherer, I. Krossing and S. Riedel, *Z. Naturforsch. B*, 2013, **68**, 1103–1107.
- 21 B. Burgenmeister, K. Sonnenberg, S. Riedel and I. Krossing, *Chem. – Eur. J.*, 2017, **23**, 11312–11322.
- 22 M. E. Easton, A. J. Ward, T. Hudson, P. Turner, A. F. Masters and T. Maschmeyer, *Chem. Eur. J.*, 2015, **21**, 2961–2965.
- 23 M. Wolff, J. Meyer and C. Feldmann, *Angew. Chem. Int. Ed.*, 2011, **50**, 4970–4973.
- 24 M. Wolff, A. Okrut and C. Feldmann, *Inorg. Chem.*, 2011, **50**, 11683–11694.
- 25 F. Pichierri, *Chem. Phys. Lett.*, 2011, **515**, 116–121.
- 26 A. P. Abbott, G. Frisch, S. J. Gurman, A. R. Hillman, J. Hartley, F. Holyoak and K. S. Ryder, *Chem. Commun.*, 2011, **47**, 10031–10033.
- 27 D. M. Fox, W. H. Awad, J. W. Gilman, P. H. Maupin, H. C. D. Long and P. C. Trulove, *Green Chem.*, 2003, **5**, 724–727.
- 28 Z. Barnea, T. Sachs, M. Chidambaram and Y. Sasson, *J. Hazard. Mater.*, 2013, **244–245**, 495–500.
- 29 M. Deetlefs, K. R. Seddon and M. Shara, *New J. Chem.*, 2006, **30**, 317–326.
- 30 M. Gorlov, H. Pettersson, A. Hagfeldt and L. Kloo, *Inorg. Chem.*, 2007, **46**, 3566–3575.
- 31 X. Li, A. Van den Bossche, T. Vander Hoogerstraete and K. Binnemans, *Chem. Commun.*, 2018, **54**, 475–478.
- 32 R.D. Rogers, J. Holbrey, US Patent US20120090430 A1, 2012.
- 33 A. P. Abbott, R. C. Harris, F. Holyoak, G. Frisch, J. Hartley and G. R. T. Jenkin, *Green Chem.*, 2015, **17**, 2172–2179.
- 34 S. P. Borikar, T. Daniel and V. Paul, *Tetrahedron Lett.*, 2009, **50**, 1007–1009.
- 35 O. Bortolini, M. Bottai, C. Chiappe, V. Conte and D. Pieraccini, *Green Chem.*, 2002, **4**, 621–627.

- 36 C. Chiappe and D. Pieraccini, *J. Org. Chem.*, 2004, **69**, 6059–6064.
- 37 R. Cristiano, K. Ma, G. Pottanat and R. G. Weiss, *J. Org. Chem.*, 2009, **74**, 9027–9033.
- 38 A. Deshmukh, B. Gore, H. V. Thulasiram and V. P. Swamy, *RSC Adv.*, 2015, **5**, 88311–88315.
- 39 M. P. Kaushik and V. Polshettiwar, *Indian J. Chem. B*, 2006, **45B**, 2542–2545.
- 40 V. M. Zelikman, V. S. Tyurin, V. V. Smirnov and N. V. Zyk, *Russ. Chem. Bull.*, 1998, **47**, 1541–1546.
- 41 L. K. Scarbath-Evers, P. A. Hunt, B. Kirchner, D. R. MacFarlane and S. Zahn, *Phys. Chem. Chem. Phys.*, 2015, **17**, 20205–20216.
- 42 C. Deferm, M. Van de Voorde, J. Luyten, H. Oosterhof, J. Fransaer and K. Binnemans, *Green Chem.*, 2016, **18**, 4116–4127.
- 43 C. Deferm, J. Luyten, H. Oosterhof, J. Fransaer and K. Binnemans, *Green Chem.*, 2018, **20**, 412–424.
- 44 T. Vander Hoogerstraete, S. Wellens, K. Verachtert and K. Binnemans, *Green Chem.*, 2013, **15**, 919–927.
- 45 W. C. Child and G. N. Papatheodorou, *J. Phys. Chem.*, 1983, **87**, 271–275.
- 46 G. R. Burns and R. M. Renner, *Spectrochim. Acta A*, 1991, **47**, 991–999.
- 47 R. Brückner, H. Haller, M. Ellwanger and S. Riedel, *Chem. Eur. J.*, 2012, **18**, 5741–5747.
- 48 J. C. Evans and G. Y.-S. Lo, *J. Chem. Phys.*, 1966, **44**, 3638–3639.
- 49 J. C. Evans and G. Y.-S. Lo, *J. Chem. Phys.*, 1966, **45**, 1069–1071.
- 50 J. R. Ferraro, M. A. Beno, R. J. Thorn, H. H. Wang, K. S. Webb and J. M. Williams, *J. Phys. Chem. Solids*, 1986, **47**, 301–308.
- 51 A. G. Maki and R. Forneris, *Spectrochim. Acta A*, 1967, **23**, 867–880.
- 52 S. Bornemann and S. T. Handy, *Molecules*, 2011, **16**, 5963–5974.
- 53 W. M. Haynes, *CRC Handbook of Chemistry and Physics*, 93rd Edition, CRC Press, Boca Raton (FL), 2012.

Various trihalide ionic liquids were prepared and used as non-volatile solvent to oxidatively dissolve metals.